[CONTRIBUTION FROM THE BEACON LABORATORIES, THE TEXAS COMPANY]

The Determination of Pore Size Distribution from Gas Adsorption Data

BY C. G. SHULL*

Introduction

There has been widespread application in the past of gas adsorption data in determining quantitatively the physical structure of finely divided and porous materials. Most notable among the theories of adsorption which have been advanced are those of Brunauer, Emmett and Teller[1] and Harkins and Jura,[2] both of which have proved very successful in evaluating the specific surface of such materials. There are, however, frequent isotherm phenomena which cannot be treated by these theories and, in order to explain some of these, the presence of capillary condensation in the porous structure has been suggested. Excellent summaries of some of the early quantitative or semi-quantitative attempts in this direction have been given by Brunauer[3] and by Cohan.[4] These attempts have all been recognized as merely approximations for one reason or another.

Recently, Wheeler[5] has introduced a composite theory which combines the BET multilayer adsorption and capillary condensation viewpoints. Upon suitable application of this theory to the experimental isotherm, the pore size distribution which would account for the experimental data may be evaluated. It is the purpose of the present paper to point out a simple method by which the Wheeler theory can be applied to isotherm data thereby obtaining the pore size distribution.

The Wheeler theory can be summarized in one simplified equation

$$V_s - V = \pi \int_R^\infty (r - t)^2 L(r) \mathrm{d}r \qquad (1)$$

In this equation, V_s is the volume of gas adsorbed at saturation pressure, V is the volume of gas adsorbed at intermediate pressure p, $L(r)\mathrm{d}r$ is the total length of pores whose radii fall between r and $r + \mathrm{d}r$, R is the corrected Kelvin radius which is obtained as a function of the pressure, and t is the multilayer thickness which is normally built up at pressure p. This equation merely states that the volume of gas $V_s - V$ not yet adsorbed at a pressure p is equal to the total volume of pores which have not been filled.

The left hand side of Equation (1) is known from experimental data and it is desired to determine the pore size distribution function $L(r)$ which when integrated will show agreement with these experimental data. Before this can be done, it is necessary to evaluate R and t as functions of the pressure.

Evaluation of Critical Kelvin Radius and Multilayer Thickness.—Wheeler has introduced a modified Kelvin equation in evaluating the corrected Kelvin radius R. In this equation, the corrected or critical pore radius (critical in the sense that all pores having smaller radii than R have already been filled by multilayer adsorption and capillary condensation) is placed equal to the sum of the multilayer thickness and the radius normally calculated from the simple Kelvin equation. In other words

$$R = t - \frac{2\sigma v}{R_g T \ln p/p_0} \qquad (2)$$

σ being the surface tension, v the molar volume of the condensed liquid, and R_g the gas constant per mole, and T the temperature. This equation states, very reasonably, that the radius determining the presence or absence of capillary condensation is that of the open section (the part not occupied due to multilayer adsorption) in the pore and not that of the entire pore.

An approximate expression from the BET theory of multilayer adsorption has been used by Wheeler for calculating multilayer thickness values. It is known, however, that the BET thicknesses become much larger than experimental thicknesses *for flat surfaces* in the high pressure region. Figure 1 shows a comparison of these thickness values. In the upper part of this figure are shown experimental data taken from nine published isotherms[6] (nitrogen gas) for crystalline materials of large crystal size (1100 to 16,000 ångströms). These data are plotted on a V/V_m basis where V_m is the adsorbed volume corresponding to monomolecular coverage of the surface. Deviations of the experimental points from the average isotherm are seen, but the general trend of the data is well established. The average isotherm is next transferred to a multilayer thickness curve (t values) by assuming the monomolecular thickness to be 4.3 ångströms for nitrogen. This is shown in the lower part of Fig. 1 with the curve corresponding to the BET theory. Pronounced differences between the BET and experimental curves are to be noted in the higher pressure region.

Figure 2 shows curves for the corrected Kelvin radius R as a function of pressure, calculated from Equation (2) by use of the above experi-

---

* Present address: Oak Ridge National Laboratory, Oak Ridge, Tenn.

[1] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

[2] W. D. Harkins and G. Jura, *J. Chem. Phys.*, **11**, 431 (1943).

[3] S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, U. S. A., 1943, Chapter XI.

[4] L. A. Cohan, THIS JOURNAL, **60**, 433 (1938).

[5] A. Wheeler, Presentations at Catalysis Symposia, Gibson Island A. A. A. S. Conferences, June, 1945, and June, 1946.

[6] P. H. Emmett and T. DeWitt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 28 (1941); W. D. Harkins and G. Jura, THIS JOURNAL, **66**, 1362 (1944).

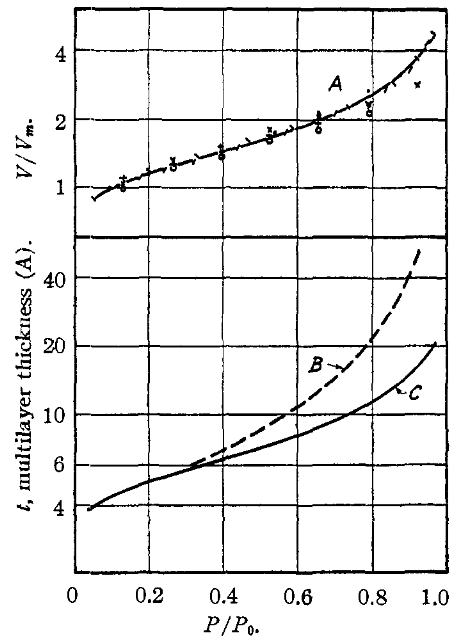


Fig. 1.—Multilayer thickness as obtained for large crystals and as calculated from the BET theory: Curve A, experimental values of the number of adsorbed layers (V/V_m) for crystalline materials of large crystal size; curve B, multilayer thickness for N_2 calculated from BET theory; curve C, multilayer thickness curve derived from curve A.

mental and BET values for multilayer thickness. As expected, the differences between the two curves show up in the high pressure region. Obviously it is necessary to make a decision as to which curve should be used in interpreting experimental isotherms.

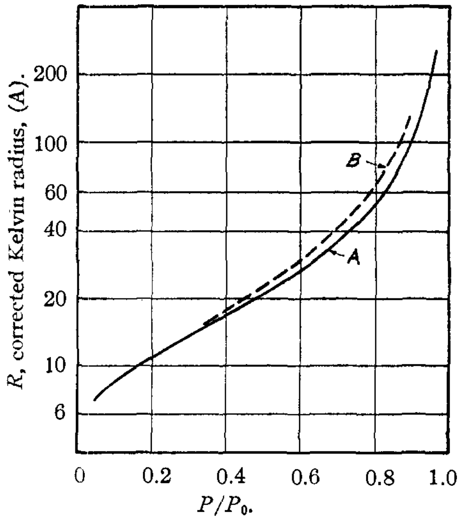
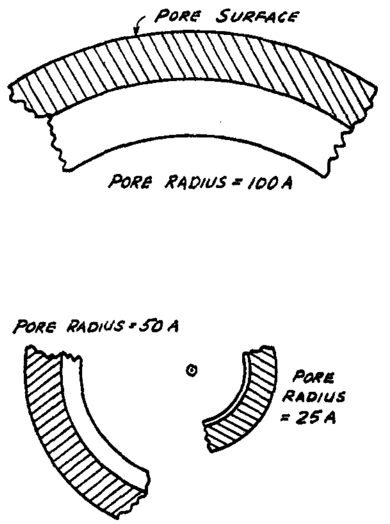


Fig. 2.—Variation of the critical Kelvin radius as a function of the adsorption pressure: curve A, calculated using experimental multilayer thickness values; curve B, calculated using BET thickness values (Wheeler).

Wheeler has argued that since adsorption occurs on the curved surface of a pore, larger thicknesses would be expected than on a flat surface, and hence the use of the BET theory is justified. Notwithstanding this, there are arguments which seem to indicate that the use of BET values is an over-correction for the effect and that it is probably better to use the flat surface experimental data.

Some insight into this can be gained by considering the adsorption process on systems having hypothetical pore structure. Consider first a system where all of the pores are 100 ångströms in radius. According to the curve derived from experimental data, which is shown in Fig. 2, capillary condensation should occur at a partial pressure of 0.895 after a multilayer thickness of 14.8 ångströms had been reached. On the other hand, the BET curve predicts capillary condensation as occurring at a partial pressure of 0.865 with a multilayer thickness of 31 ångströms. Wheeler's argument that the pore curvature would increase the adsorption to BET values seems to be an overcorrection for the effect. It appears very unlikely that the curvature in a pore of radius 100 ångströms would place in effect additional adsorptive forces sufficient to more than double the adsorbed film thickness.

A simple scale drawing with the pertinent relative dimensions indicates a much smaller effect than that given by the BET theory. Figure 3 illustrates the predicted multilayer thicknesses at the time of capillary condensation for pores of radii 100, 50 and 25 ångströms. For a radius of 100 ångströms the BET thickness seems much too large, for a 50 ångström radius it is still larger than would be expected but perhaps not unreason-



Shaded area is multilayer thickness from experimental data for large crystals. Unshaded area is extra thickness predicted by BET theory.

Fig. 3.—Diagram showing multilayer thickness at pressure of capillary condensation for pores of various sizes.

ably so, and for a 25 ångström radius the two multilayer thicknesses are close together. Since the curvature effect becomes more pronounced as the radius is reduced and has little or no effect with large radii pores, it is seen that the BET values are inherently incorrect in their dependence upon the pore radius. If anything, the true curvature values of the thickness should differ from flat surface values most drastically in the small pore region, and this is just the opposite of the result obtained by use of the BET multilayer thickness values. Until a more satisfactory theory accounting for curvature effects is available, the use of flat surface data would appear to be preferable. Accordingly, the curves on Figs. 1 and 2 corresponding to experimental data will be used in the isotherm analysis given below. It should be mentioned that the procedure of isotherm analysis to be discussed in the following section is a general one applicable to whatever multilayer thickness values are selected.

Evaluation of Pore Size Integral.—There does not appear to be a simple method of inversion applicable to the pore size integral, Equation (1), by which the pore size distribution $L(r)$ can be obtained from numerical values of $V_s - V$. Indirect methods are available, however, which permit an easy and convenient solution of the equation. The present method is one of comparison of the experimental isotherm with standard or calculated isotherms.

Wheeler has suggested that pore size distributions may be represented by simple analytical forms of Maxwellian or Gaussian type. Thus for a Maxwellian distribution of pore sizes

$$L(r) = Are^{-r/r_0} \qquad (3)$$

with A and r_0 constants, and when this is substituted into Equation (1) and the integration performed we obtain

$$V_s - V = Ar_0^4 M(R, r_0) \qquad (4)$$

where

$$M(R,r_0) = \frac{\pi}{r_0^3} e^{-R/r_0}\{R(R-t)^2 + 6r_0^3 + 2r_0^2(3R-2t) + r_0(3R-t)(R-t)\} \qquad (5)$$

The function $M(R, r_0)$ has been evaluated for various values of R and r_0, and a family of such curves is shown in Fig. 4. These curves will be referred to as standard inverted isotherms.[7]

Likewise for a Gaussian distribution of pore sizes

$$L(r) = Ae^{-[\beta/r_0(r-r_0)]^2} \qquad (6)$$

with A, β, and r_0 constants, and this integrates into

$$V_s - V = 2A(r_0^3/\beta)G_\beta(R, r_0) \qquad (7)$$

where

$$G_\beta(R, r_0) = \frac{\pi}{4r_0^2}\left\{\frac{r_0}{\beta} e^{-\rho^2}(R - 2t + r_0) + \sqrt{\pi}[1 - H(\rho)][(r_0 - t)]^2 + \frac{1}{2}\left(\frac{r_0}{\beta}\right)^2\right\} \qquad (8)$$

$$\rho = \frac{\beta}{r_0}(R - r_0), \text{ and } H(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-y^2}dy$$

$G_\beta(R, r_0)$ has been evaluated for $\beta = 2$, 5 and 10 and various values of R and r_0, and some of these standard isotherms are shown on Figs. 5 and 6. It may be mentioned that the parameter β determines the width of the pore size distribution while r_0 controls the average pore size.

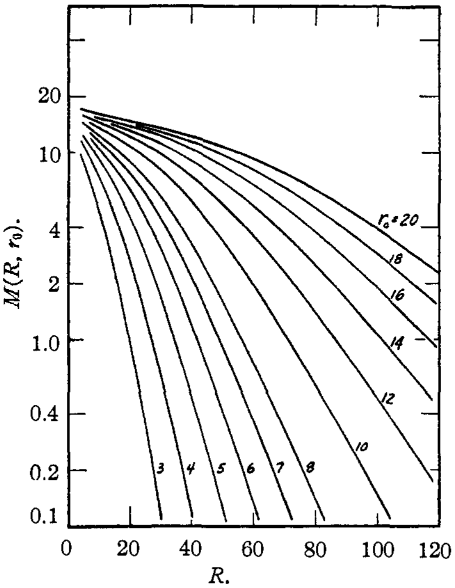


Fig. 4.—Standard inverted isotherms: calculated for a Maxwellian distribution of pore sizes.

The procedure in interpreting experimental data is then the following. The experimental isotherm is replotted as $V_s - V$ (log scale) *versus* the Kelvin radius R. This is conveniently known as an *inverted isotherm*. This inverted isotherm is next matched with one of the standard isotherms of Figs. 4–6. If a satisfactory match is obtained, the pore size distribution is known immediately from the parameters of the standard isotherm.

Sometimes the experimental inverted isotherm cannot be fitted to one of the standard isotherms and it is necessary then to resolve the experimental isotherm into two or more standard isotherms. For instance if an experimental isotherm can be resolved into the sum of a Maxwellian and a Gaussian standard isotherm, then

$$V_s - V = A_0 r_0^4 M(R, r_0) + 2A_1 \frac{r_1^3}{\beta_1} G_{\beta_1}(R, r_1) \qquad (9)$$

and hence

$$L(r) = A_0 re^{-r/r_0} + A_1 e^{-\left[\frac{\beta_1}{r_1}(r-r_1)\right]^2} \qquad (10)$$

In all cases, the coefficients A_n can be evaluated from the relative amplitudes of the component isotherms. Needless to say, as many component isotherms can be used as is necessary to fit the data to the desired accuracy. For all practical cases to date, two terms have been found suf-

---

(7) Numerical values for the standard inverted isotherms of Figs. 4 to 6 have been tabulated and are available from the author.

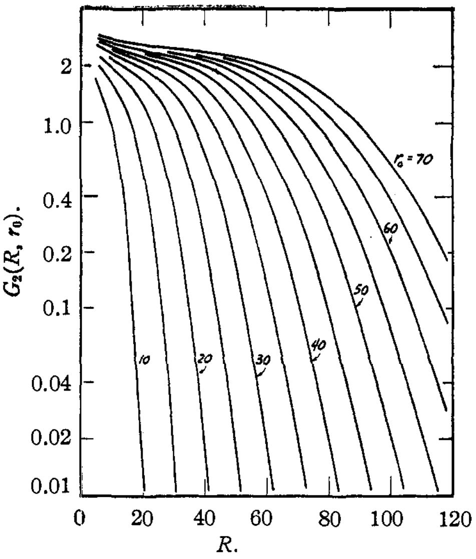


Fig. 5.—Standard inverted isotherms calculated for a Gaussian distribution ($\beta = 2$) of pore sizes.

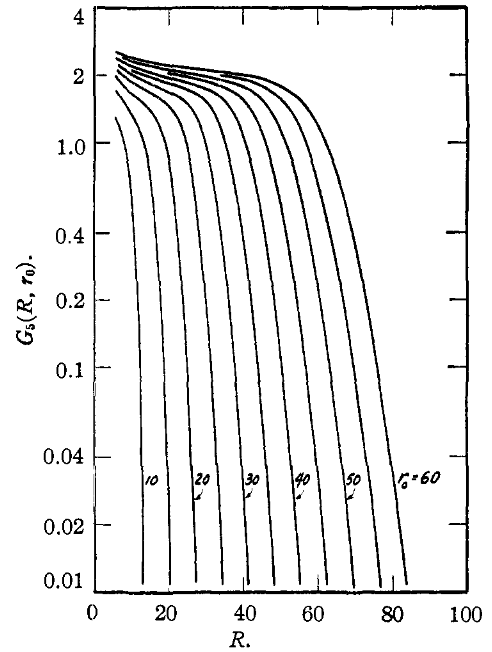


Fig. 6.—Standard inverted isotherms calculated for a Gaussian distribution ($\beta = 5$) of pore sizes.

ficient. The whole procedure can be carried out in fifteen or twenty minutes.

It is obvious that the specific surface may be calculated from the distribution $L(r)$, using the equation

$$S = 2\pi \int_0^\infty rL(r)\,dr \qquad (11)$$

This method of calculation is, of course, independent of the usual BET method[8] of determining the specific surface from adsorption isotherm data, but is more laborious and time-consuming. In particular instances, in which a variety of adsorbates have been adsorbed on the same adsorbent, more consistent values of specific surface have been obtained by this calculation than by the BET method. It should also be pointed out that the Wheeler procedure[5] of isotherm analysis does not permit a wholly independent calculation of the specific surface since the BET surface has entered directly in the pore size evaluation.

The above procedure of matching the experimental data to a calculated curve is, of course, an indirect one in that the mathematical inversion required in Equation (1) is not accomplished in a straightforward fashion. This raises the question of uniqueness in the derived pore size distribution. It has been found that the selection of the matched standard curve is, in general, a well-defined one showing that one type of distribution is in considerably better agreement with the data than any other. In cases where ambiguity in the choice of matching exists (for instance where the matching is equally good with a single curve or with the sum of two other curves), experience has shown that it makes little difference in the final distribution. It would seem that uncertainties in the basic assumptions necessary to the application of the inversion procedure are much more troublesome than the problem of uniqueness in the inversion.

Examples of Isotherm Interpretation.—As examples of the above procedure of analysis, the two isotherms given in Fig. 7 will be considered. These were obtained[9] with samples of silica gel possessing widely different physical properties. Both adsorption and desorption data are presented, there being no hysteresis loop in the case of gel I. The solid line for gel II represents the adsorption data while the broken line corresponds to desorption data. Selected isotherm points from the desorption curves have been replotted as inverted isotherm points (open and shaded circles) in Fig. 8. The isotherm points for gel I are seen to agree closely with the standard isotherm $M(R, 3)$, which has been drawn in from Fig. 4. Therefore the pore size distribution $L(r)$ for this gel can be represented by a Maxwellian distribution with the parameter r_0 having the value 3Å. On the other hand, the isotherm points for gel II cannot be matched to one of the standard curves but they can be matched to the sum of two standard isotherms, $G_5(R, 43)$ and $M(R, 18)$.

---

(8) It will be recognized that this independence is not strictly true since the BET theory has been used to obtain values of V_m used in the determination of the multilayer thickness t as shown in Fig. 1. However, this procedure has drawn on the validity of the BET determination of specific surface only in the case of materials of large crystal size and this has been shown by many studies to be quite correct. No assumptions regarding the validity of the BET theory for the material being studied have been made. It follows that the specific surface calculated from the pore size distribution is not necessarily the same as that generally calculated from the BET theory since the presence of the pore size distribution may have made questionable the application of the simple BET theory.

(9) I am indebted to Dr. P. B. Elkin for supplying the isotherm data on these materials.

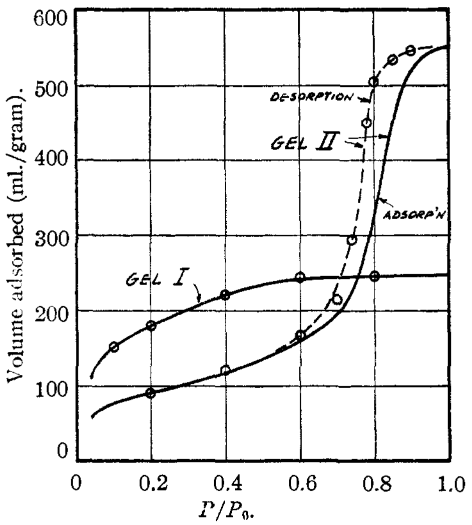


Fig. 7.—Nitrogen isotherms for two samples of silica gel. The solid and broken lines are the experimental isotherms. The circled points are taken from the matched standard isotherms of Figure 8.

The triangular points on Fig. 8 are matched with the standard isotherm $G_5(R, 43)$ and have been obtained by subtracting the standard isotherm $M(R, 18)$ from the experimental data (the open circles) for gel II. Thus the pore size distribution for gel II can be represented by an expression of the type given by Equation (10) with $r_0 = 18$, $r_1 = 43$, $\beta_1 = 5$ and relative values of A_1 and A_0 obtained ($A_1/A_0 = 222$) from the amplitudes of the two standard isotherms.

The differences between the experimental points and the standard isotherms in Fig. 8 have been transferred to the original isotherms given in Fig. 7, since here the fluctuations can be more easily visualized in terms of experimental error. The circled points on the isotherms of Fig. 7 are taken directly from the standard inverted isotherms of Fig. 8. The agreement shown by the matching process is within the experimental error of the adsorption measurements.

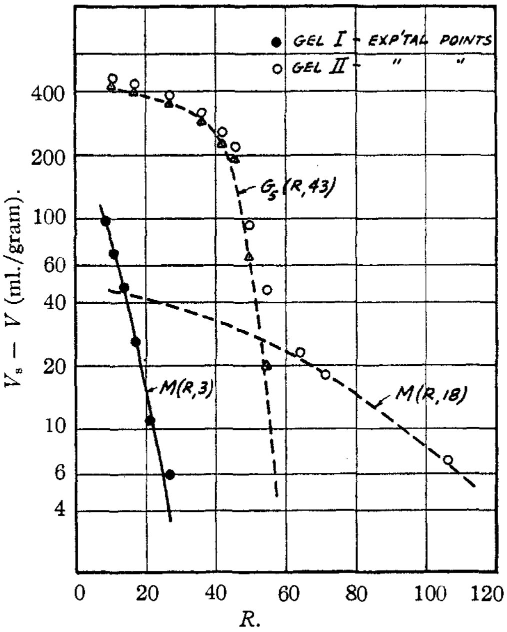


Fig. 8.—Comparison of silica gel isotherm data with selected standard inverted isotherms.

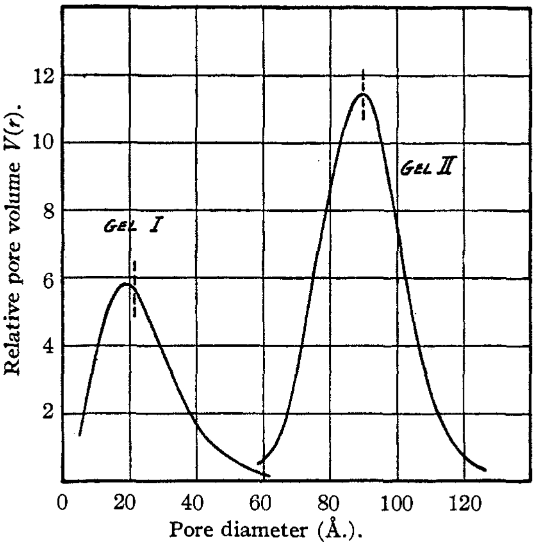


Fig. 9.—Pore volume distributions calculated for silica gel samples.

Pore size distributions for these two gels have been calculated and are shown in Fig. 9. These have been plotted as volume distributions $V(r)$, rather than length distributions, since the former seem to have greater physical significance. This transformation is easily performed since

$$V(r) = \pi r^2 L(r) \qquad (12)$$

Values of the average pore diameter (defined as that size which divides the pore volume distribution into two equal parts) have been marked on the distribution curves. These values are 21 and 90 Å. for gels I and II, respectively. It is interesting to compare these with values of the mean pore diameter calculated from the expression[10] $4V_s/S$ where S is the specific surface determined by the standard BET method. Calculation shows the latter to be 23 and 107 Å., respectively. Comparisons of the pore size distributions obtained by the above procedure with other independent data have been made for a variety of materials and these will be the subject of an accompanying publication.[11]

Summary

The theory of the interpretation of gas adsorp-

---

[10] If all pore volume is contained in one long cylindrical pore L units long, the diameter of this pore can be written

$$D = 4\,\frac{\frac{\pi D^2}{4}L}{\pi D L} = \frac{4V_s}{S}$$

[11] C. G. Shull, P. B. Elkin and L. C. Roess, THIS JOURNAL, **70**, 1410 (1948).

tion data in terms of capillary condensation as advanced by Wheeler is discussed. It is suggested that the empirical use of experimental adsorption data for materials of large crystal size is preferable to the employment of the BET theory at the higher relative pressures (0.35 to 0.99) in evaluating the multilayer thickness of the adsorbed layers. A simplified procedure for applying the theory of capillary condensation to experimental data, thereby obtaining the pore size distribution, is presented. Examples of this procedure are given in the treatment of data for two silica gels.

BEACON, N. Y. RECEIVED APRIL 3, 1947

[CONTRIBUTION FROM THE BEACON LABORATORIES, THE TEXAS COMPANY]

Physical Studies of Gel Microstructure

BY C. G. SHULL,[1] P. B. ELKIN[2] AND L. C. ROESS

Introduction

During the past few years a number of new techniques have become available for studying the physical microstructure of porous and finely divided materials. Low temperature gas adsorption has found widespread application in the determination of the specific surface available to gases.[3] More recently, attempts have been made to interpret the adsorption isotherm in terms of pore dimensions in addition to specific surface.[4] X-Ray scattering at small angles has been used in obtaining information on the solid discontinuities present in colloidal materials, and these data have been correlated to a certain extent with crystal size data from the broadening of X-ray diffraction lines and with specific surface results.[5,6]

In the application of either of these techniques certain simplifying assumptions must be made with consequent uncertainty or ambiguity in the results of the analysis. One procedure for testing the validity of these assumptions for any particular material presents itself in the correlation of independent data to form a consistent over-all picture of the physical microstructure. Thus, as will be shown later in this paper, the specific surface should show a dependence on the particle size distribution; and the pore size and the particle size distributions should be related through the porosity factor. If the various physical data can be shown to be consistent, then confidence in the validity of the analysis is gained. It is to be emphasized that conclusions of this sort drawn for one material are not sufficient to justify the validity of the assumptions for all cases.

The present paper is concerned with a series of observations of the type outlined above obtained for a series of ten silica and silica–alumina gels. These particular gels were selected because they possessed a wide range of physical properties and hence should serve as good illustrative examples of the correlative procedure.

Experimental Techniques

Nitrogen adsorption–desorption isotherms were obtained in a conventional volumetric apparatus at liquid nitrogen temperature and over a pressure range from a few millimeters of mercury up to near saturation pressure. Measurements in the high pressure region were continued to high enough pressures to determine the plateau of adsorbed volume characteristic of complete filling of the micropore volume. The saturation pressure p_0 was measured continuously throughout the runs by means of a tube containing condensed nitrogen and connected to a manometer. From the data specific surface values were calculated by the Brunauer–Emmett–Teller equation.[3] The data fit the linear plot of this method over the usual range of pressure values.

The micropore size distributions were obtained by analyzing the adsorption and desorption isotherms in terms of a composite multilayer adsorption and capillary condensation theory introduced by Wheeler.[4] A modification in the procedure of applying the Wheeler theory to the experimental data was used in the present study and details of this are given in an accompanying paper.[7] Essentially, the method consists in matching the experimental isotherm with one of a series of standard isotherms which have been calculated for various pore size distributions. Values of median and mean pore diameters (defined in the following section) have been calculated from the size distribution.

Values for the solid density ρ were obtained by displacement in helium gas in an apparatus similar to the one described by Schumb and Rittner.[8] The apparent density ρ_a was determined in a mercury pycnometer. From these values the percentage porosity was calculated by the equation

$$\%\ \text{porosity} = 100(\rho - \rho_a)/\rho \qquad (1)$$

---

[1] Present address: Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[2] Present address: Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

[3] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938); W. D. Harkins and G. Jura, *J. Chem. Phys.*, **11**, 431 (1943).

[4] A. Wheeler, Presentations at Catalysis Symposia, Gibson Island Conferences, June, 1945, and June, 1946.

[5] P. B. Elkin, C. G. Shull and L. C. Roess, *Ind. Eng. Chem.*, **37**, 327 (1945).

[6] C. G. Shull and L. C. Roess, *J. Appl. Phys.*, **18**, 295 (1947).

[7] C. G. Shull, THIS JOURNAL, **70**, 1405 (1948).

[8] W. C. Schumb and E. S. Rittner, *ibid.*, **65**, 1692 (1943).