tide. They represent a new class of silicon compounds.

4. Dichlorodifluorosilane reacts with *n*-propylmagnesium bromide to yield mainly dipropyldifluorosilane and some dipropylchlorofluorosilane.

WILMINGTON, DELAWARE RECEIVED JUNE 23, 1950

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

The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms

BY ELLIOTT P. BARRETT, LESLIE G. JOYNER AND PAUL P. HALENDA

Introduction

This paper describes a technique for estimating the volume and area of porous adsorbents available to molecules of various sizes. This technique was developed to deal with relatively coarsely porous adsorbents exhibiting a wide range of pore sizes, but the procedure to be described appears to be applicable to porous solids of any nature.

Wheeler[1] proposed a theory which is a composite of BET multilayer adsorption and capillary condensation viewpoints. This theory can be summarized by the equation

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

where V_s is the volume of gas adsorbed at saturation pressure, V is the volume of gas adsorbed at pressure p, $L(r)\mathrm{d}r$ is the total length of pores whose radii fall between r and $r + \mathrm{d}r$. r_{p_n} is the critical radius, that is, the radius of the largest pore still completely filled with liquid adsorbate at any particular pressure and t is the multilayer thickness which is normally built up at pressure p.

Wheeler considered the radius of the pore to be equal to the sum of the multilayer thickness as calculated from the BET theory and the radius normally calculated from the simple Kelvin equation. He also suggested that the pore size distribution, $L(r)$, may be approximated by a simple Maxwellian or Gaussian distribution.

Shull[2] pointed out that the BET thicknesses become much larger than experimental thicknesses for flat surfaces in the high pressure region. Shull proposes the use of experimental data[3,4] taken from nitrogen isotherms for crystalline materials, for the determination of the multilayer thickness, t, in the Wheeler theory. He then developed a simplified method for fitting the experimental data to Maxwellian or Gaussian distribution functions.

Almost simultaneously Oulton[5] proposed a method for determining the pore distribution from the isotherm without the necessity of assuming a definite form for the distribution. He corrects for physical adsorption on the walls of pores empty of capillary condensed adsorbate, hereafter termed capillary condensate, by assuming that the thickness of the physically adsorbed layer is constant and equal to that of the statistical number of monolayers at the relative pressure of the hysteresis point.

This paper will show that the assumption of a simple Gaussian or Maxwellian distribution of pore sizes is inadequate for many adsorbents. It will also show that Oulton's assumption of constant thickness for the physically adsorbed layer, while adequate for a finely porous material such as that to which he applied it (a cracking catalyst with a pore area maximum at radius 26.5 Å.), is inadequate to deal with more coarsely porous adsorbents. A formal analysis of the relationship between nitrogen desorption isotherms at liquid nitrogen temperatures and the distribution of pore volume and area with respect to pore radius will be made on the assumption that equilibrium between the gas phase and the adsorbed phase during desorption is determined by two mechanisms: (1) physical adsorption *on* the pore walls (which would occur to the same extent whether the area involved constituted walls of pores or a flat surface impenetrable to nitrogen), and (2) capillary condensation *in* what Oulton[5] has called the "inner capillary volume." Results of the analysis will be applied to several adsorbents utilizing the experimental data used by Shull[2] to provide a functional relationship between thickness of physically adsorbed layer and relative pressure, and utilizing the classical Kelvin equation, relating vapor pressure depression to capillary radius, to define the relationship between volume of capillary condensate and relative pressure.

Analysis of Desorption

Consider a system of open ended, cylindrical pores (Fig. 1) such that all pores of equal radius can be regarded as responding in the same way with respect to changes of relative pressure of the adsorbate. Assume that the relative pressure $(P/P_0)_1$, differs infinitesimally from unity so that substantially all pores are filled with liquid. The largest pore[6] has a radius r_{p_1}. Upon its surface is a physically adsorbed layer of molecules of statistical thickness t_1. Within this physically adsorbed layer is the inner capillary with radius r_k, from which evaporation occurs as P/P_0 is lowered.

Under the equilibrium conditions specified, the relationship between the pore volume, V_{p_1}, and the inner capillary volume, V_{k_1}, is

$$V_{p1} = V_{k1} \, r_{p1}^2 / r_{k1}^2 \qquad (2)$$

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

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

[3] P. H. Emmett and T. DeWitt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 28 (1941).

[4] W. D. Harkins and G. Jura, THIS JOURNAL, **66**, 1362 (1944).

[5] T. D. Oulton, *J. Phys. Colloid Chem.*, **52**, 1296 (1948).

[6] For simplicity all pores of equal radius, or whose radii fall within chosen limits, will be referred to as if they were one pore.

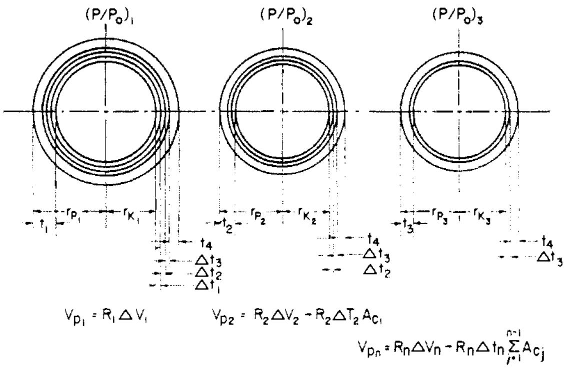

Fig. 1.—Schematic representation of assumed desorption mechanism showing three different pores and demonstrating the thinning of the physically adsorbed layer over the first three pressure decrements.

However, this relationship is not useful since V_{k_1} is unknown.

To obtain useful data it is necessary to lower $(P/P_0)_1$ to a smaller value $(P/P_0)_2$. This will result in the desorption of a measurable volume of adsorbed gas, ΔV_1. The reduction in relative pressure will result not only in emptying the largest pore of its capillary condensate, but also in a reduction in thickness of the physically adsorbed layer by the amount Δt_1. As a consequence of the reduction in relative pressure and the attendant desorption, (2) may be rewritten as

$$V_{p1} = R_1 \Delta V_1 \qquad (3)$$

where $R_1 = r_{p1}^2/(r_{k_1} + \Delta t_1)^2$ and ΔV_1 is the observed volume of gas desorbed.

A complication enters when one attempts to apply similar reasoning to the obtaining of the volume of the second pore by lowering $(P/P_0)_2$ to $(P/P_0)_3$. When this is done, the volume of liquid desorbed is not only that which comes from the second pore but also includes that from a second thinning of the physically adsorbed layer left behind in the first pore. If the volume which is released by this thinning is designated as $V_{\Delta t_2}$ then

$$V_{p2} = R_2\,(\Delta V_2 - V_{\Delta t_2}) \qquad (4)$$

where $R_2 = r_{p2}^2/(r_{k_2} + \Delta t_2)^2$.

Inspection of Fig. 1 shows that

$$V_{\Delta t_2} = \pi L_1 (r_{k_1} + \Delta t_1 + \Delta t_2)^2 - \pi L_1 (r_{k_1} + \Delta t_1)^2 \qquad (5)$$

where L_1 is the length of pore one.

Although it would not be too laborious to evaluate $V_{\Delta t_2}$ from (5) where the thinning occurs from the walls of only one pore, it is obvious that as a greater number of pores become involved such a calculation would soon become impractical.

An alternative expression for $V_{\Delta t_2}$ is

$$V_{\Delta t_2} = \Delta t_2 A c_1 \qquad (6)$$

where Ac_1 is the average area from which the physically adsorbed gas is desorbed.

Equation (6) may be generalized so as to represent any one of the steps of a stepwise desorption by writing it in the form

$$V_{\Delta t_n} = \Delta t_n \sum_{j=1}^{n-1} A c_j \qquad (6a)$$

It should be noted that the summation is simply the sum of the average area in unfilled pores down to, but not including, the pore that was emptied of capillary condensate in the *n*th desorption.

Generalizing equation (4) and substituting (6a) for $V_{\Delta t_n}$ yields

$$V_{p_n} = R_n \,\Delta V_n - R_n \,\Delta t_n \sum_{j=1}^{n-1} A c_j \qquad (7)$$

Equation (7) is an exact expression for the porous model under consideration.

Equation (7) is still unsatisfactory as a computing device because the quantity Ac for any one size of empty pore is not a constant but varies stepwise with each successive decrease in P/P_0. On the other hand A_p, the area of each pore, is a constant which can be calculated from its volume by the relationship $A_p = 2V_p/r_p$ and the successively computed A_p's can be cumulatively summed so that at any step in the desorption ΣA_p is a known quantity. Therefore, if some facile means for computing ΣAc from ΣA_p can be found, equation (7) will become a practical device for computation.

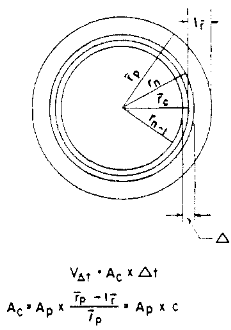

Fig. 2.—Relation of $V\Delta t$ to r_p at *n*th step.

The procedure which has been devised for obtaining a practicable means for computing ΣAc from ΣA_p is exemplified by Fig. 2. It is assumed that all capillaries emptied of their condensate during a relative pressure decrement have an average radius, $\bar r_p$, between the radii corresponding to the upper and lower values of P/P_0. Figure 2 represents the change in thickness (Δt_n) of the physically adsorbed layer of a previously emptied pore of radius $\bar r_p$ during the *n*th desorption step. The capillary radius before desorption is r_{n-1} and after desorption it is r_n. Its average value is $\bar r_c$. Since the capillary is concentric with the pore, the average area of the "capillary" during the desorption which produces Δt_n is equal to $A_p \times (\bar r_c/\bar r_p)$. Also $\bar r_c = \bar r_p - t_{\bar r}$ where $t_{\bar r}$ is the thickness of the physically adsorbed layer at the corresponding value of P/P_0. For convenient reference the ratio $\bar r_c/\bar r_p = (\bar r_p - t_{\bar r})/\bar r_p$ has been designated by "*c*." Thus equation (7) can be expressed as

$$V_{p_n} = R_n \,\Delta V_n - R_n \,\Delta t_n \sum_{j=1}^{n-1} c_j A_{p_j} \qquad (8)$$

where $c = (\bar r_p - t_{\bar r})/\bar r_p$.

Equation (8) provides a practical basis for the computation of pore volume distributions with respect to pore radii. It depends only on the two fundamental assumptions that: (1) the pores are cylindrical (more precisely that pore volume and capillary volume are related to each other as the square of some adequate measure of their cross sections), and (2) that the amount of adsorbate in equilibrium with the gas phase is retained by the adsorbent by two mechanisms: (a) physical adsorption *on* the pore walls, and (b) capillary condensation *in* the inner capillary volume.

To make (8) useful it is necessary to obtain a functional relationship between P/P_0 and r_k and between P/P_0 and Δt. Values of r_k were computed from the classical Kelvin equation

$$\log (P/P_0) = \frac{-2\sigma V}{8.316 \times 10^7 \times 2.303 T r_k} = \frac{-4.14}{r_k} \quad (9)$$

in which

σ = surface tension of liquid nitrogen
V = liquid molar volume of nitrogen
r_k = radius of capillary in cm. (later converted to ångström units for practical purposes)
T = absolute temperature (°K.)
8.316×10^7 is the gas constant in ergs per degree

Values of t as a function of the relative pressure were obtained from a plot of the experimental data used by Shull.[2] Inasmuch as $r_p = r_k + t$ the addition of the two curves yields the relationship between r_p and the relative pressure.

In equation (8) it should be noted that $\bar{r}_p$ and the $\bar{r}_k$ corresponding to it, are used whereas the Δt and the ΔV are the actual increments corresponding to the decrease in the relative pressure. To simplify and accelerate computation, values of $R = \bar{r}_p^2/(\bar{r}_k + \Delta t)^2$ were calculated as functions of $\bar{r}_p$ for pore radius increments of 10 Å. from 10 to 300 Å., of 5 Å. from 10 to 200 Å., and of 1 Å. from 7 to 25 Å. The results of these calculations are given in Table I, which constitute the actual working data of the procedure.[8]

Determination of c.—As an example of the computation of the value of c for one size of pore at one P/P_0 change, consider the pore of radius $\bar{r}_p$ = 155 Å. (this is the hypothetical pore which includes all the actual pores with radii between 150 and 160 Å.), when the value of P/P_0 is lowered from that which is in equilibrium with the capillary condensate in a pore of radius 150 Å. to that in equilibrium with the condensate in a pore of radius 140 Å., *i. e.*, a relative pressure change such as to empty the hypothetical pore of $\bar{r}_p$ = 145 Å. of its capillary condensate. In this case $\bar{r}_p$ = 155 Å. and $t_{\bar{r}}$ is the thickness of the physically adsorbed layer midway between r_{n-1} and r_n, *i. e.*, midway between 150 and 140 Å., and so from Table I we find for r = 145, t = 16.79 Å., or, effectively, 17 Å. Hence c = (155–17)/155 = 0.890. It will be seen that for any pore larger than 155 Å. radius the c value for this P/P_0 change will be larger than 0.890 and that for all smaller pores it will have no significance because, except for the 145 Å. pore, which is dealt with by the factor R, they all still contain their capillary condensate and so do not enter into the computation. Also, it is clear that, with succeeding decrements in P/P_0, the value of c for $\bar{r}_p$ = 155 will become larger since, as P/P_0 approaches zero, $\bar{r}_c/\bar{r}_p$ approaches 1.

TABLE I[a]

NUMERICAL VALUES OF REQUIRED FUNCTIONS OF P/P_0 WHEN Δr = 5 A.

P/P_0	r_p	t	$\bar{r}_p$	Δt	$\bar{r}_k$	R
0.165	10	4.74	12.5	1.21	7.1	2.318
.332	15	5.95	17.5	1.02	11.0	2.120
.488	20	6.97	22.5	0.89	15.1	1.980
.927	140	16.61	142.5	0.18	125.7	1.281
.930	145	16.79	147.5	0.175	130.5	1.274
.932	150	16.97	152.5	0.17	135.4	1.265
.947	190	18.25	192.5	0.14	174.2	1.219
.949	195	18.39	197.5	0.14	179.0	1.215
.950	200	18.52				

[a] To make the table more compact numerical values of $\bar{r}_p$ and its associated quantities are listed on the same line as the lower limit of the Δr_p to which they refer.

To investigate the limits within which c would vary in practice, several computations similar to that of the example just given were made and the data so obtained were plotted as Fig. 3. In the figure the c values for pores of various radii are plotted against the $\bar{r}_p$ values to which the appropriate P/P_0 values correspond instead of the P/P_0 values themselves. The horn-shaped area enclosed by the boundary curves of Fig. 3 contains all the possible values of c for pores of all radii from 25 to 280 Å., as P/P_0 decreases from the value corresponding to 280 Å. (P/P_0 = 0.965) to that corresponding to 25 Å. (P/P_0 = 0.580). Within these limits the c value for pores of all sizes varies between the limits of 0.72 and 0.97.

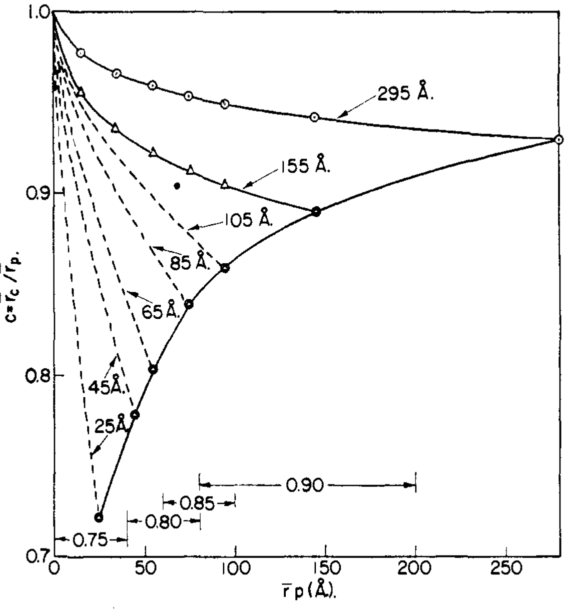

Fig. 3.—Variation of c with r_p for pores of various radii. Also shown are the ranges of pore radius maxima over which a constant approximate value of c has been found to be satisfactory.

The wide variation in possible c values for pores of different sizes at any one P/P_0 value suggests that it would not be possible to choose an average value for c at each P/P_0 value which would approximate closely enough to the correct one for all sizes of pores empty at each particular P/P_0 value. However, experience with this type of computation

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(7) Values of σ and V of 8.85 dynes per cm. and 34.65 cc. per mole at 77.3°K. were used for these calculations. It would probably have been better to use the values corresponding to 78.3°K. which is closer to the actual temperature at which the isotherms were determined. This would be a factor of 4.02 instead of 4.14. It was not considered worthwhile to recalculate all the tables on this basis.

(8) Because of space limitations only fragments of the actual tables referred to in the text are shown. For complete tables order Document 2936 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$0.50 for photocopies (6 × 8 inches) readable without optical aid.

has shown that an adequate approximation is possible. For example it is known that the whole correction term $R_n \Delta t_n \Sigma A c_j$ is negligibly small for all pores above 165 Å. radius. Also the correction does not, in general, amount to as much as 50% of the $R_n \Delta V_n$ term of equation (7) for pores of all radii down to about 35 or 40 Å. and if the error in the correction term is 10%, the resulting error in V_{p_n} will, therefore, not amount to as much as 5% until pores of 35 or 40 Å. radius are reached in the course of the stepwise computation. Moreover, it is to be noted that the most important factor in the correction term of equation (7) is $\Sigma A c_j$. This factor is principally affected by the smaller pores.

Taking all these factors into account it seemed probable that a very close approximation to the correct pore size distribution could be obtained by using a constant c value for any one adsorbent, the value being selected on the basis of the pore radius at which the pore volume maximum occurs. The lower boundary curve of Fig. 3 has been found, after several average values had been tried, to give the best c value. Moreover, since it was found that small changes in c had little effect on the distribution it was decided to use the indicated c value only to the nearest five hundredths.

If it be accepted that a constant c value may be used for any one adsorbent, then the $\Sigma A c$ factor in the correction term of equation (7) may be replaced by $c \times \Sigma A_p$ and the equation becomes

$$V_{p_n} = R_n \, \Delta V_n - R_n c \, \Delta t \sum_{j=1}^{n-1} A_{p_j} \qquad (10)$$

which is the working equation. The advantage of using values of c restricted to even multiples of 0.05 is apparent, because this makes it possible to construct a limited number of tables of values of $R \times \Delta t \times c$ as functions of the mean pore radius, $\bar{r}_p$, from which values of the correction term of equation (10) can be read directly. This makes computation much less arduous and time consuming.

Table II lists values of $R \times \Delta t \times c$ (the product for convenient reference has been designated as C) for c values of 0.75, 0.80, 0.85 and 0.90 and for P/P_0 increments corresponding to various mean pore radius ($\bar{r}_p$) increments over the ranges of $\bar{r}_p$ that have been found useful. The 1 Å. increment tables (not shown in this paper) are, in general, only necessary for materials which have pore volume maxima below 25 Å.

TABLE II

NUMERICAL VALUES OF C AS A FUNCTION OF $\bar{r}_p$ WHEN Δr_p = 5 Å. AND c = 0.75, 0.80, 0.85 or 0.90

	$C = (R)(\Delta t)(c)$			
$\bar{r}_p$	c = 0.75	0.80	0.85	0.90
12.5	2.10	2.24	2.38	2.52
17.5	1.62	1.73	1.84	1.95
22.5	1.32	1.41	1.50	1.58
47.5	0.67	0.71	0.76	0.80
52.5	.59	.63	.67	.71
57.5	.55	.58	.62	.66

Figure 3 indicates the ranges of pore volume maximum radii to which the four values of c have been found applicable. It will be seen that these ranges overlap in the case of the three higher values. This is inevitable since the best value for c depends on the character of the distribution as a whole and not on the location of the pore volume maximum alone. In general it is possible to use the c value corresponding to the pore volume maximum. Because, at this stage in the computation only the uncorrected distribution (column 7, Table III) is known, it is necessary to obtain an approximate c value from this uncorrected distribution. If, however, the distribution curve is skewed it may be necessary to use a higher or lower c value than that which applies to the particular pore volume maximum under consideration when the distribution is symmetrical.

It must be remembered that the c in equation (10) is only an *average* value used to reduce the enormous amount of computation involved in a rigid application of equation 8, which is an exact equation. If one had available a large analog or digital computing machine, it would be entirely practical to use equation (8) instead of equation (10), and compute a value of c for each pore, at each change in relative pressure during the stepwise desorption. Under such circumstances, the procedure described in this paper would constitute an independent method, but an unduly arduous one, for estimating the surface area of porous solids. Even when using the average c of equation (10) one experienced in making these computations will obtain results in reasonable agreement with the BET area,[9] simply by selecting a c based on the apparent pore volume maximum of the uncorrected distribution unless the distribution is badly skewed or the application of the correction terms shifts the location of the apparent pore volume maximum.

However, the procedure described in this paper was devised, not for the purpose of computing areas, but for the determination of the distribution of areas and volumes among pores of varying radii. Consequently, if a questionable c chosen by the computer yields a cumulative pore area larger than the measured (BET) area, it is reasonable to repeat the computation using a c 0.05 smaller so as to bring the results into concordance. Since the BET area is computed from the low pressure part of the isotherm, while estimation from the distribution curves involves, primarily, the high pressure portion, bringing the distribution area into accord with the BET area constitutes the establishment of an internal consistency for the pore volume distribution so computed.

Inspection of Fig. 6 shows that the effect of variations in c, of the order of ±0.05, on the computed pore volume distribution are almost negligible. The effect of such variations on the cumulative area are somewhat larger. For the sample to which Fig. 6 applies the cumulative pore areas corresponding to c's of 0.80, 0.85 and 0.90 are 62.2, 64.6 and 67.9 m.^{2}/g., respectively, while the BET area is 66.4 m.^{2}/g. These are typical results and the authors, therefore, feel that, although the procedure described in this paper was not devised as a method for estimating areas, it is, nevertheless,

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(9) S. Brunauer, P. H. Emmett and E. Teller, This Journal, **60**, 309 (1938).

TABLE III

COMPUTATION OF PORE VOLUME AND AREA DISTRIBUTIONS FOR BONE CHAR AFTER 32 CYCLES

P/P_0	r_p	V at S.T.P.	V_{liquid}	ΔV	$\bar{r}_p$	$\Delta V \times R$	$C^a \times \Sigma A_p \times 10^{-4}$	V_p	ΣV_p	A_p	ΣA_p
0.165	10	18.1	0.0282	0.0079	12.5	0.0183		0.0014	0.2252	2.24	64.57
352	15	23.2	361	71	17.5	150	0.01060	44	2238	5.03	62.33
488	20	27.7	432	63	22.5	125	809	44	2194	3.91	57.30
580	25	31.8	495	61	27.5	115	637	51	2150	3.71	53.39
642	30	35.7	556	55	32.5	99	504	49	2099	3.02	49.68
963	260	143.5	2227	9	265	11		11	29	0.13	0.26
964	270	144.1	2236	8	275	9		9	18	0.07	0.13
965	280	144.7	2244	5	285	6		6	9	0.04	0.06
966	290	145.0	2249	3	295	3		3	3	0.02	0.02
967	300	145.2	2252								

[a] $C = (R)(\Delta t)(c)$. For this computation the c value used was 0.85.

capable of yielding area values which are in no way grossly misleading. However, we believe that, since the BET method is much superior from the standpoint of speed and facility, it is desirable to make the very minor adjustments necessary to bring the distribution area into concordance with the BET area in any instances (and they are few) in which the selected c gives a somewhat inconcordant result.

The authors recognize that there exists a not too obvious connection between their correction terms and the BET method of computing areas. Shull[2] computed his relationship between relative pressure and t, the thickness of the physically adsorbed layer, by assuming the correctness of the BET areas calculated from experimental isotherms. This does not invalidate the theory of our method. If, in future, a demonstrably more reliable method for estimating t is devised, the more trustworthy values of t can be used to construct a revised set of tables in accordance with the theory herein described.

Method of Computation

Adsorption–desorption isotherms at liquid nitrogen temperatures were obtained with a conventional gas adsorption apparatus. Typical isotherms for four bone chars, chosen to disclose the effects of repeated use and reactivation are shown in Fig. 4. The isotherms for a natural clay cracking catalyst, an activated carbon and a silica gel[10] are shown in Fig. 5. These were chosen to show the types of isotherms to which the method has thus far been found to apply.

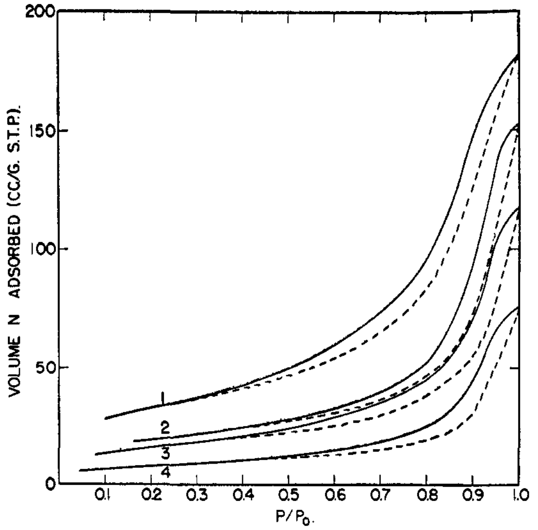

Fig. 4.—Nitrogen isotherms at −195°, for bone char of various lengths of service: desorption, —; adsorption, -------; 1, new char; 2, char after 32 cycles; 3, "A" service char; 4, "B" service char.

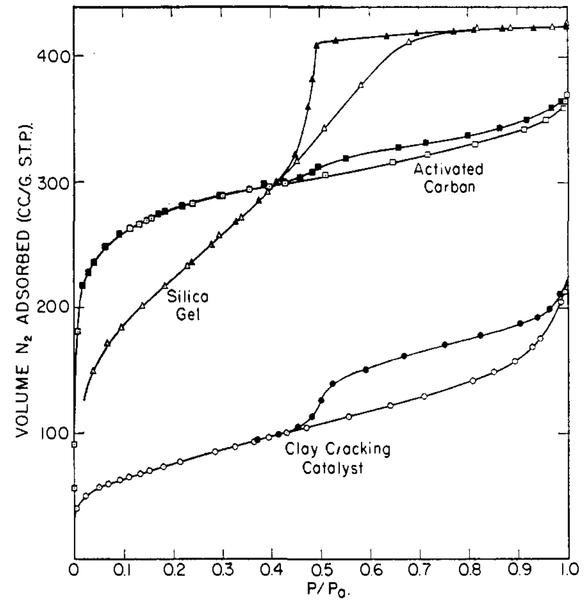

Fig. 5.—Nitrogen isotherms at −195° for a natural clay cracking catalyst, an activated carbon and a silica gel; solid points are desorption.

Although equation (10) is theoretically applicable up to a relative pressure infinitely close to unity, for practical computation it is necessary to place some arbitrary upper limit on the pore radius. Due to the logarithmic relationship between the pore radius and the relative pressure it would become necessary, as saturation is approached, to use increasingly larger increments of radius in order to detect any change in the volume desorbed. To circumvent this difficulty the pores larger than 300 Å. radius are ignored and the computations are started at a relative pressure of 0.967. This does not deny the existence of larger pores. Even though such large pores may contain

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[10] Data for this isotherm was obtained through the courtesy of Herman Ries and M. F. L. Johnson of the Sinclair Refining Company.

as much as 10% of the total volume of condensate, their number is generally small compared to the number of smaller pores and hence they do not contribute appreciably to the pore volume distribution curve. Moreover, the area of such large pores is generally less than 1% of the total area of the adsorbent and thus contributes little to any surface phenomena being investigated. The close agreement obtained between the standard BET area and the area computed by this method is further evidence that the pores with radii above 300 Å are unimportant in the over-all area distribution.

A sample computation is shown in Table III. Details of the method of computation of the various columns are:

Column 1, (P/P_0).—The relative pressure corresponding to the selected radii, r_p.

Column 2 (r_p).—The values of the selected radii. In general 5 Å. increments of r_p should be used up to a pore radius of about 60 Å., above which 10 Å. increments are suitable. However, if the desorption isotherm is very steep in the region below that corresponding to pore radii of 60 Å. as in the clay cracking catalyst of Fig. 5, it may be necessary to use even smaller increments. Similarly if the isotherm is particularly steep in the higher region, increments smaller than 10 Å. may become necessary.

Column 3, (V at S.T.P.).—The experimental volumes of nitrogen adsorbed at the relative pressures of column 1, read from the desorption isotherm.

Column 4, (V_{liquid}).—The liquid volumes, computed by multiplying the data of column 3 by the conversion factor for cc. at S.T.P. to cc. of liquid nitrogen at its boiling point, 0.001555 (P_0 = 850 mm.).

Column 5, (ΔV).—This is the volume of liquid desorbed between two consecutive relative pressures of column 1. It is obtained by progressive subtraction of each volume listed in column 4 from the succeeding one. This column represents the distribution uncorrected for physical adsorption, and the remainder of the computation is concerned with making this correction. This uncorrected distribution is utilized to select an approximate value of the correction constant c.

Column 6, ($\bar{r}_p$).—The radius which is the average of the radii of the largest and smallest pore represented by the P/P_0 increment corresponding to the ΔV of column 5.

Column 7, ($\Delta V \times R$).—Column 5 multiplied by the appropriate value of R taken from the working tables (*e.g.*, Table I), depending on the size of the Δr increments being used.

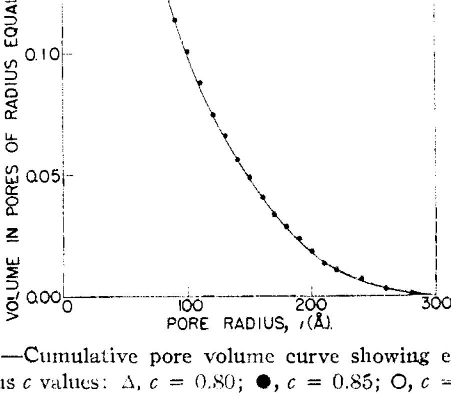

Fig. 6.—Cumulative pore volume curve showing effect of various c values: Δ, c = 0.80; ●, c = 0.85; O, c = 0.90.

Computation of the remaining five columns must be made from the bottom to the top. Column 8, ($C \times \Sigma A_p$ ($C = R \times \Delta t \times c$)).—Usually this correction term may be neglected above $\bar{r}_p$ values of 165 Å. but it is necessary to begin the remaining four columns at $\bar{r}_p$ values of 295 Å. The values of C are selected from Table II according to the c decided upon and the Δr utilized. ΣA_p values are taken from column 12. Before subtracting the values of $C \times \Sigma A_p$ from those of column 7, which are in cc./g., $C \times \Sigma A_p$ must be multiplied by 10^{-4}.

Column 9, (V_p).—This is simply column 8 subtracted from column 7 giving the corrected volume in pores between the radius limits indicated in column 2. This column will of course be identical to column 7 at $\bar{r}_p$ values for which the correction term is negligible.

Column 10, (ΣV_p).—The cumulative pore volume obtained by the progressive summing of column 9.

Column 11, (A_p).—The area of pores of indicated average radius computed from the relationship

$$A_p = 2V_p/\bar{r}_p \times 10^4 \qquad (11)$$

where V_p and $\bar{r}_p$ are from columns 9 and 6, respectively.

Column 12, (ΣA_p).—The cumulative pore area obtained by progressively summing the A_p values of column 11. This is used to calculate the next correction term in column 8.

The above-described operations are continued until ΣV_p equals the measured volume of the pores up to 300 Å. This quantity appears on the bottom line of column 4. It is generally possible to anticipate, from the trend of the V_p values, the step at which the measured pore volume will be exhausted. At this point in order to obtain the V_p for the next pore, *i.e.*, the smallest, the preceding value of ΣV_p is subtracted from the measured value of the pores up to 300 Å. thus assigning the remaining volume to the smallest pore. This may appear to be rather arbitrary but in general it has been found to be satisfactory. The only alternative procedure would be to repeat the latter part of the computation using smaller increments of Δr.

In general, if the right value for c has been chosen, the measured pore volume will be exhausted at, or before, $\bar{r}_p$ reaches 12.5 Å. If it is not, and ΣA_p does not exceed the measured (BET) area, it then becomes necessary to repeat the latter part of the computation, starting with the values at 20–25 Å., and using the C values for 1 Å. increments of r_p, but this situation arises only with very fine pored materials.

If the proper c value has been chosen the value for ΣA_p, when ΣV_p equals the measured pore volume should check the BET area within experimental error, *ca.* 5%.

Having completed the computations shown in Table III it would be possible to divide all the V_p's by the Δr's over which they were determined, and to plot the resulting $V_p/\Delta r$'s against the corresponding $\bar{r}_p$'s to obtain the pore volume distribution curves. To keep the symbols consistent with more common usage $V_p/\Delta r$ may now be designated as $\Delta V/\Delta r$. In practice it has been found that the errors in reading the values of V at S.T.P. (column 3, Table III) result in variations in the final values of V_p which frequently make the drawing of a smooth distribution curve problematical. To obviate this difficulty the values of ΣV_p, column 9, are plotted against r_p to obtain a cumulative pore volume curve as shown in Fig. 6.

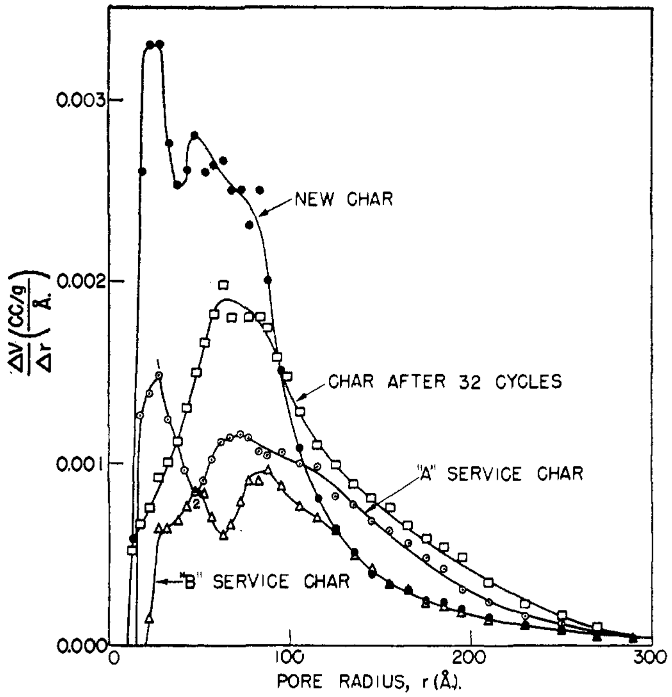

Fig. 7.—Pore volume distribution curves for bone chars of various lengths of service. The isotherms of these bone chars are shown in Fig. 4.

(Note that in this instance ΣV_p is plotted against the appropriate value of r_p *not* $\bar{r}_p$ because this is a *cumulative* plot and includes all the volume down to the lower limit of each Δr.)

When the cumulative plot has been made it is generally possible to tell by inspection whether there is more than one point of inflection and to draw a smooth curve through the points which seems reasonably to represent the character of the distribution. From the curve of Fig. 6, smoothed values for the pore volume distribution, $\Delta V/\Delta r$ as a function of $\bar{r}$ may be determined. It will be noted that this smoothing of the values of ΣV_p as a function of r_p has the additional advantage, over the immediate computation of $\Delta V/\Delta r$ as a function of $\bar{r}_p$ from column 9 of Table III, that one can see from the smooth curve where the pore volume is changing most rapidly and can locate the pore volume maximum approximately. Therefore, it is possible to choose the pore radius intervals (Δr's) advisedly, making them small when the pore volume is changing rapidly and larger when it is changing more slowly. Whatever interval is used, however, the $\bar{r}_p$ is simply the midpoint of that interval.

Discussion

In Fig. 7 are shown the distribution curves determined in the foregoing manner from the desorption isotherms of Fig. 4 for the four samples of bone chars in various stages of use. In Fig. 8 are shown the distribution curves for the three adsorbents, the isotherms of which are given in Fig. 5.

The significance of the distribution curves from the standpoint of performance of the four bone chars in sugar refining is beyond the scope of this paper which is intended to include only a description of the procedure and a preliminary estimate of its adequacy as an indication of the surface available within the particles of a granular solid, to molecules of various sizes.

Obviously there could be no rigidly "correct" distribution curve constructed because the pores are not cylinders but spaces of irregular shape between crystallites, and, consequently, the term "pore radius" has no physical significance except, possibly, a statistical one as r in an equation $r = \sqrt{A/\pi}$ where A is the cross sectional area of some irregular shape. However, the empirical test of internal consistency provided by comparing the total areas computed as above, with areas computed by the BET method[9] has been applied to the seven distributions illustrated in the figures and to sixteen additional distributions. Of the 23 distributions, 7 exhibit cumulative pore areas within 1% of the corresponding BET area, 15 are within 2%, 19 within 3%, 20 within 4% and 23 within 5%.

That this method is applicable to finely porous adsorbents, is illustrated by the curves in Fig. 8. Almost all the pores in the adsorbents of Fig. 8 have radii below 40 Å. Comparison of the cracking catalyst isotherm of Fig. 5 with the isotherm for the cracking catalyst examined by Oulton[5] indicates that the two adsorbents are very similar. Oulton found for his adsorbent a pore volume maximum at 26.5 Å. radius whereas this method indicates a maximum

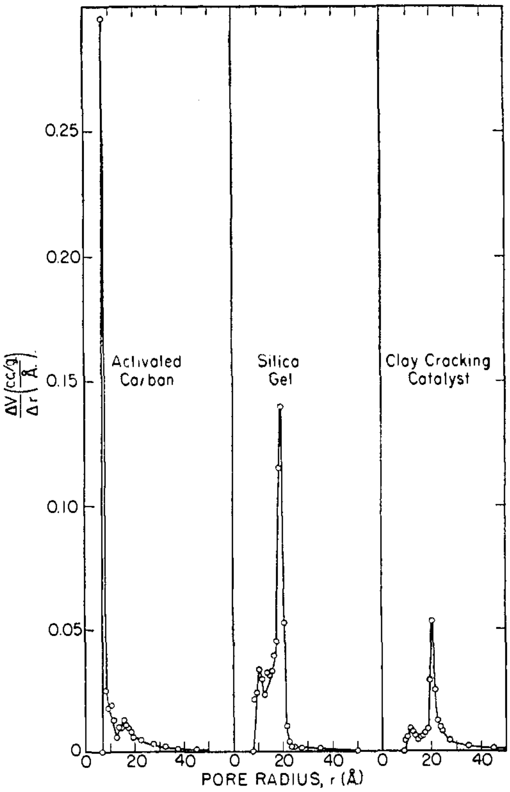

Fig. 8.—Pore volume distribution curves for a natural clay cracking catalyst, an activated carbon and a silica gel. The isotherms of these adsorbents are shown in Fig. 5.

at 22 Å. It is evident that there is no serious disagreement between the two methods when applied to finely porous substances.

It is recognized that the concept of a meniscus in equilibrium with a vapor ceases to have precise meaning as the capillary radius approaches the diameter of the adsorbate molecules. Consequently extension of the use of the Kelvin equation to pores of very small radius constitutes a sort of extrapolation which cannot be rigorously justified. However, it will be noted that, in general, only a small fraction of the total volume is contained in pores of such small radius as to cast doubt on the applicability of the Kelvin relationship. For example, it seems gratuitous to assume the likelihood of a sudden break in a smooth curve such as that of Fig. 6, occurring due to a sudden failure of the Kelvin equation to apply, at 15 or 10 Å. radius.

Further confirmation of the accuracy of both this method and that of Oulton is given by the high pressure mercury porosimeter work of Drake[11] in which he finds by a more direct approach that a silica–alumina gel of the cracking catalyst type has a sharp pore volume maximum in the neighborhood of 20 Å. radius. An exact comparison between the results of Drake, Oulton and this paper is, of course, impossible since there is no certainty that the same kind of catalyst was used in each case. However, the catalysts were of the same general type and the similarity of the results are to that extent confirmatory. High pressure mercury porosimeter measurements are being made on a selection of the adsorbents discussed in this paper so as to obtain such a direct comparison. These data will be published in the second paper of this series.

Acknowledgment.—The authors wish to acknowledge their indebtedness to Dr. A. Wheeler for his helpful suggestions on the theoretical aspects of the work. They are grateful to Baugh and Sons Company for permission to publish this paper.

Summary

An analysis of the nitrogen desorption isotherms based upon the Wheeler theory of combined physical adsorption and capillary condensation has been developed.

A method for computing the pore volume and area distribution directly from the desorption isotherm of porous substances is presented. The method has been successfully applied to adsorbents covering a wide range of pore volume maxima.

PITTSBURGH, PA. RECEIVED MAY 1, 1950

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Limiting Degrees of Supersaturation of the Sparingly Soluble Sulfates

BY VICTOR K. LA MER AND ROBERT H. DINEGAR

Introduction

Von Weimarn[1] observed that the form of the precipitate of BaSO$_4$ produced by mixing solutions of Ba(CNS)$_2$ and MnSO$_4$[2,3] depended on whether the initial concentrations of reagents were relatively low (crystals) or relatively high (jellies). He formulated these results in terms of a set of Precipitation laws, and concluded that the velocity of precipitation was a direct function of supersaturation; also that the higher the velocity of precipitation the larger the number of particles formed. He concluded that not only was the degree of supersaturation important in determining the form of the precipitate, but, in addition, so was the absolute magnitude of this concentration; for example, whether it arose from a large total concentration or from a small solubility. In the first case, a large amount of the dispersed phase will be produced and in the second very little.

Von Weimarn's results, however, are not precise since his technique may have produced local supersaturations. In any case, his interpretation neglected the important role of the ionic environment on ionic equilibria. Thus his data for the supersaturation ratio needed for the spontaneous formation of crystalline BaSO$_4$ particles may be interpreted as lying anywhere between the limits of 8 and 48.

On the other hand, A. M. Belousov and A. B. Terenteeva[4] report that by direct mixing of soluble barium and sulfate compounds, the equilibrium value for the solubility of BaSO$_4$ could be exceeded approximately 100-fold before a precipitate appeared. Their measurements, however, were very rough.

Recent advances[5] in the theory of phase transitions invite a reinvestigation of Von Weimarn's methods and conclusions from new points of view and their extension to other systems. To obtain reproducible values of the maximum concentrations of metal ion and SO$_4^=$ that can coexist in solution before the rapid spontaneous formation of particles takes place, we have substituted the production of sulfate ion by a slow chemical process for the usual techniques of direct mixing of reagents.

Although methods for producing colloidal lead and strontium sulfates have been reported, no quantitative data are available on the critical degree of supersaturation tolerated by solutions of these salts.

Theoretical Discussion

Dilute solutions of sodium persulfate in the presence of sodium thiosulfate decompose slowly

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[3] H. B. Weiser, *Inorg. Colloid Chem.*, **11**, 11 (1938).

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