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.

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[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

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

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The small angle X-ray scattering technique has been described[6] previously.

The gels were obtained from several sources and the methods of preparation for some gels were not reported. The emphasis here, however, is placed on physical properties rather than on methods of preparation. It may be mentioned that the gels were heated in a furnace at about 540° prior to all physical measurements so that the residual water content must have been quite small. No correction for this was made.

Experimental Results

A list of the silica–alumina gels which have been studied is given in Table I. The alumina content of these gels is seen to vary between 0 and 28 weight per cent. with most of the samples at the ends of this range. The variety of physical properties obtained are believed for the most part to reflect the various physical and chemical conditions of preparation rather than the alumina content.

TABLE I

SUMMARIZED GAS ADSORPTION AND DENSITY DATA

Gel	Weight per cent. Al_2O_3	Specific surface, sq. m./g.	V_p micropore volume (cc./g.)	Density (g./cc.) by displacement of Helium ρ	Mercury ρ_a	Percentage porosity	Total pore volume, cc./g.
I	25	453	0.563	2.53	1.031	59	0.575
II	23	425	.733	2.45	0.854	65	.774
III	24	475	.681	2.46	.750	69	.927
IV	26	321	.855	2.49	.787	68	.868
V	28	267	.994	2.31	.719	69	.958
VI	13	568	.863	2.30	.755	67	.890
VII	..	344	.870	2.32	.786	66	.840
VIII	0	657	.384	2.39	1.168	51	.436
IX	0	248	.612	2.32	0.911	61	.667
X	0	478	.575	2.19	0.982	55	.562

The nitrogen adsorption–desorption isotherms are shown in Fig. 1. The desorption curves are the upper ones in each case. All except that for sample VIII have similar shapes, but differ in the magnitude and position of the steepest part of the curves. The isotherm for sample VIII, in which the adsorption and desorption data fell on the same curve, is the Langmuir type.

From the adsorption data, the values shown in Table I for the specific surface S and the specific micropore volume V_p (expressed as cc. of void per gram of gel) have been calculated. The solid density ρ obtained by helium displacement, the apparent density ρ_a obtained by mercury displacement and the percentage porosity and total pore volume calculated from the density values are also listed. The specific micropore volume has been obtained from the volume of gas adsorbed at saturation pressure and presumably is indicative of the pore volume in pores of diameter less than about 1000 Å. On the other hand, the percentage porosity and total pore volume given in the last two columns include all pores up to the size which is penetrated by mercury at atmospheric pressure, namely, about 50,000 Å. It is seen that practically all of the pore volume (with the exception of that for gel III) exists in the micropore region. The total pore volume is listed as being slightly smaller than the micropore volume (obviously an impossibility) for three of the gels and this must be due to the presence of small errors in one or more of the measurements.

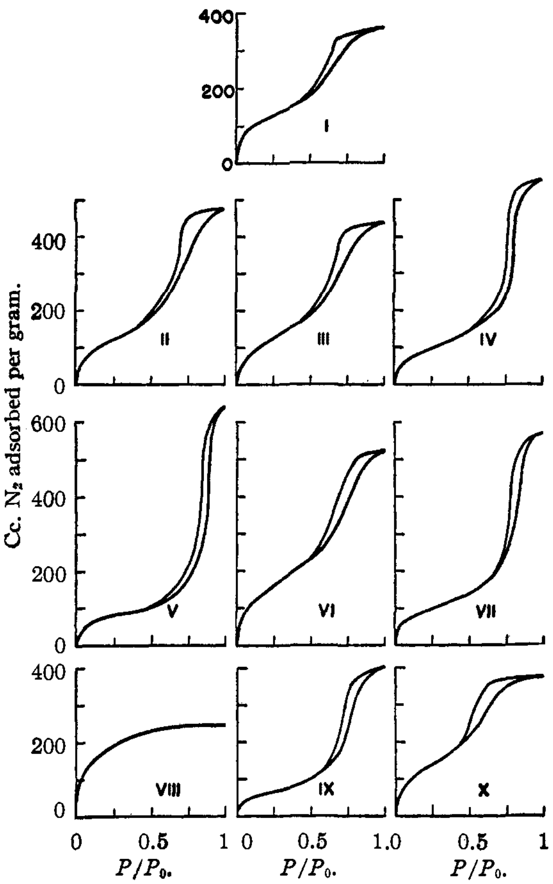

Fig. 1.—Nitrogen adsorption–desorption isotherms (−195°) for gels I to X.

Both the specific surface and the micropore volume are seen to vary over a wide range of values. As is expected, the solid density shows little variation from gel to gel with some indication that the gels with higher alumina content possess somewhat higher solid density values.

Table II summarizes the results of pore size analysis as obtained from both adsorption and desorption isotherms on the assumption that the pores are cylindrical. In this table the mean pore diameter D_0 is defined by

$$D_0 = 4V_p/S \tag{2}$$

the median pore diameter $\bar{D}$ is defined by

$$\frac{V_p}{2} = \int_0^{\bar{D}} V(D)\,dD \tag{3}$$

where $V(D)$ is the pore volume distribution function. $\bar{D}$ is thus defined as the pore diameter such that one half of the pore volume is contained in pores smaller than $\bar{D}$. The mean pore diameter $\bar{D}_0$ is defined as

$$\bar{D}_0 = \frac{\int_0^\infty V(D)\,\mathrm{d}D}{\int^\infty \frac{V(D)}{D}\,\mathrm{d}D} \qquad (4)$$

Since in equation (4) the numerator is the pore volume per gram and the denominator is one-fourth the specific surface, it follows that D_0 and $\bar{D}_0$ represent equivalent mean values. They are designated differently to emphasize that they have been calculated in an independent manner. It is not expected that the median and mean values should agree in magnitude since they represent differently weighted quantities. Also given in Table II is the ratio of the two mean values for the pore diameter.

TABLE II

PORE DIAMETER VALUES CALCULATED FROM ADSORPTION AND DESORPTION DATA (ALL VALUES EXPRESSED IN ÅNGSTRÖMS)

D_0 is mean pore diameter calculated from $4Vp/S$. $\bar{D}$ is median pore diameter calculated from pore size distribution. $\bar{D}_0$ is mean pore diameter calculated from pore size distribution.

		From desorption data			From adsorption data		
Gel	D_0	$\bar{D}$	$\bar{D}_0$	$D_0/\bar{D}_0$	$\bar{D}$	$\bar{D}_0$	$D_0/\bar{D}_0$
I	50	52	48	1.04	59	48	1.04
II	69	65	60	1.15	73	60	1.15
III	57	57	53	1.08	70	57	1.00
IV	107	90	89	1.20	114	105	1.02
V	149	136	126	1.18	170	157	0.95
VI	61	61	56	1.09	74	58	1.05
VII	101	95	94	1.07	131	121	0.84
VIII	23	21	18	1.31	21	18	1.31
IX	99	73	72	1.37	92	85	1.17
X	48	41	41	1.17	46	37	1.30
			Average	1.17			1.08

Figure 2 illustrates the agreement found between values for D_0 and $\bar{D}_0$ using both adsorption and desorption data. The general sequence of the points indicates that D_0 is about 10% larger than $\bar{D}_0$ and, considering the assumptions which are necessary in evaluating the pore size distributions, this can be considered quite satisfactory. Although it is seen that slightly better agreement is obtained when adsorption data are used, it is not felt that this is conclusive of a general criterion on the basis of the present data.

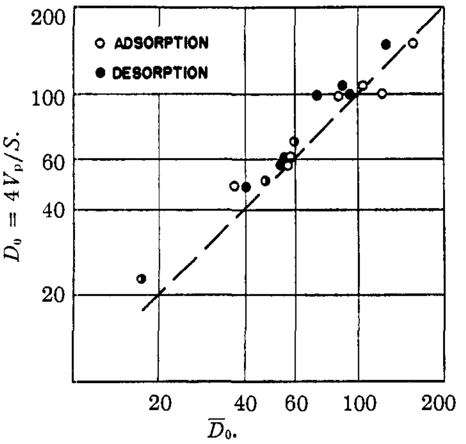

Fig. 2.—Comparison of mean pore diameters (ångströms) calculated from $V_p(D_0)$ and from pore size distribution curves ($\bar{D}_0$).

The results of the small angle X-ray scattering analysis and their correlation with adsorption data for these gels are given in Table III. The scattering analysis has been carried through in terms of a particle size distribution for spherical particles and from this the median particle diameter $\bar{L}$ is evaluated as defined by

$$\int_0^\infty M(L)\,\mathrm{d}L = 2\int_0^{\bar{L}} M(L)\,\mathrm{d}L \qquad (5)$$

where $M(L)$ is the mass distribution function in terms of the particle diameter L. Values of $\bar{L}$ ranging from 29 to 88 Å. are to be noted in the second column of Table III.

TABLE III

COMPARISON OF PARTICLE SIZE VALUES WITH PORE SIZE AND POROSITY RESULTS

Values of L and D are in ångströms and S_ρ in 10^4 cm.$^{-1}$

Gel	$\bar{L}$	S_ρ	$\bar{D}/\bar{L}$	$V_{p\rho}$
I	48	1147	1.08	1.42
II	47	1041	1.38	1.80
III	45	1170	1.27	1.68
IV	65	799	1.38	2.13
V	88	617	1.55	2.30
VI	48	1308	1.27	1.99
VII	75	798	1.27	2.02
VIII	29	1570	0.72	0.92
IX	81	576	0.90	1.42
X	48	1048	0.85	1.26

In view of the dependence of the X-ray intensity scattered at small angles on differences in electron density, independent evidence is required to establish whether the scattering is characteristic of the particles or of the pores. With crystalline materials, good agreement[6] is found between the crystal size and the average particle size calculated on the assumption that the scattering is characteristic of the particles, and this can be considered as good evidence that the small angle scattering is indeed characterized by the particles. With amorphous materials such evidence is not available, and hence it is particularly interesting to compare the particle size data and the pore size data for the ten amorphous gels being discussed.

It can be shown that the specific surface of an assemblage of particles is given by an expression of the type

$$S = \frac{K}{\rho}\,\frac{\int_0^\infty \frac{M(L)}{L}\,\mathrm{d}L}{\int^\infty M(L)\,\mathrm{d}L} = K_0/\rho\bar{L} \qquad (6)$$

where K_0 is a constant whose value depends insensitively on the geometrical shape of the particle and the shape of the particle size distribution curve. Values for the product $S\rho$ are given in the third column of Table III and these are plotted versus $\bar{L}$ in the log-log graph of Fig. 3. The inverse relationship between these variables is clearly indicated by the sequence of the points. The line drawn on the figure is the theoretical line to be expected for spherical particles and appears to be shifted from the median correlation line by about 10%. In view of the uncertainties in the interpretation of small angle scattering analysis, this discrepancy of the particle size values by 10% on an absolute basis is certainly not outside of possible error. It should be mentioned that correlation of the type given in Fig. 3 is by no means restricted to one class of materials (*viz.*, silica-alumina gels) but can be obtained with a whole variety of substances whose solid density, specific surface and particle size cover much wider ranges than are indicated in the present data.

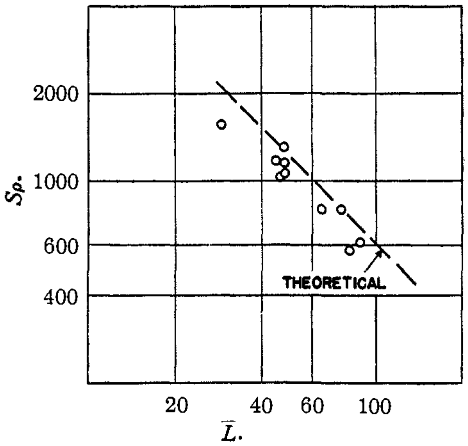

Fig. 3.—Correlation between specific surface times density $S\rho$ and median particle diameter $\bar{L}$. The dashed line is that calculated for spheres. $S\rho$ is given in units of 10^4 cm.$^{-1}$ and $\bar{L}$ in ångströms.

Of particular interest is the comparison of pore and particle size. The ratio of these variables is given in the fourth column of Table III. This ratio is seen to include values between 0.72 and 1.55. Since the surface area of the pores must equal that of the particles, it follows from Equations (2) and (6) that

$$\bar{D}/\bar{L} = k(V_p\rho) \qquad (7)$$

since $\bar{D}$ is proportional to D_0 for a given distribution. The product $(V_p\rho)$ is called the *porosity factor* and is merely the ratio of total micropore volume to total solid volume in the gel. The constant k depends insensitively on the pore and particle size distributions. Figure 4 illustrates the agreement of the experimental data with the correlation predicted by Equation (7). Values for the pore diameter are those obtained from the desorption analysis and the line is the theoretical correlation using a value of 2/3 for the constant k which is the average for the size distributions encountered experimentally. A consistent trend in the values of the pore to particle size ratio with the porosity factor is to be noted and this can be considered evidence that the small angle X-ray scattering is characteristic of the particle size rather than the pore size. If the X-ray scattering were indicative of the pore size, values of $\bar{D}/\bar{L}$ should have remained constant independent of the porosity factor.

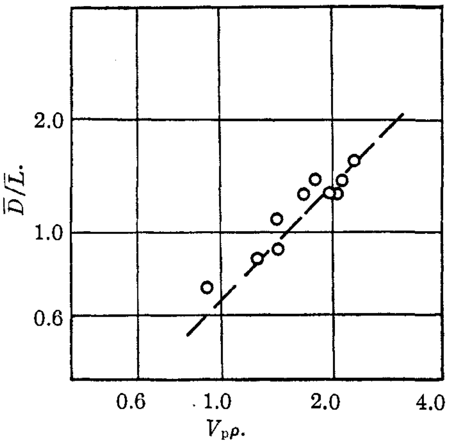

Fig. 4.—Correlation between pore to particle size ratio $\bar{D}/\bar{L}$ and porosity factor $V_p\rho$. The line is the theoretical correlation according to Equation (7).

The over-all agreement of the independently determined variables above appears very satisfactory and is even somewhat surprising in view of the several assumptions which are necessary in interpreting the data. It is recognized immediately that the assignment of a spherical shape to the particles and a cylindrical shape to the pores is inconsistent in a strict sense. The pores and particles are very probably irregular in both shape and size, but it would appear from the data that as far as the determination of average dimensions is concerned, they can be represented by these simple geometrical shapes. Once these discontinuity shapes are decided upon, further assumptions specific to the technique are required. Principal among these are the assumption of incoherence in the X-ray scattering from adjacent particles and the assumption that vapor condensation in a capillary of colloidal size is exactly similar to that in macroscopic capillaries. Neither of these has been the subject of direct experimental test, but as the evidence presented above would indicate indirectly, they appear not far from being correct.

Acknowledgments.—Several of the gel preparations were kindly supplied by the Shell Development Company and the Standard Oil Development Corporation and the remaining ones were prepared by M. M. Stewart of these laboratories. Grateful acknowledgment is also accorded to Dorothy Diener, Bernice Good and Sybil Cumming for assistance in the accumulation of experimental data.

Summary

Physical data on the microstructure of a series of ten amorphous silica and silica–alumina gels have been obtained from studies of low temperature gas adsorption, porosity and small angle X-ray scattering. Good correlations are obtained between (1) the mean pore diameter calculated from the specific micropore volume and the specific surface and the mean pore diameter calculated according to a capillary condensation theory of isotherm analysis, (2) the average particle size and the specific surface and (3) the pore to particle size ratio and the porosity factor. It is concluded that the over-all correlations which are found indicate the validity of the assumptions necessary in the data interpretation at least for the materials which have been studied.

BEACON, NEW YORK RECEIVED OCTOBER 16, 1947

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NAVAL RESEARCH LABORATORY]

The Preparation of Nitrite Salts of Alkyl Amines[1]

BY JOHN K. WOLFE[2] AND KENNETH L. TEMPLE[3]

Alkyl ammonium nitrite salts have been prepared by the reaction of the amine hydrochloride with sodium nitrite[4] or silver nitrite,[5] the amine sulfate with barium nitrite, or the amine with nitrogen sesquioxide,[6] all of these reactions being carried out in aqueous solution. The present study outlines a new method of preparation, employing the amine, sodium nitrite, solid carbon dioxide, methanol and a small amount of water. Sodium carbonate precipitates as the reaction proceeds, leaving a methanol solution of the nitrite. The general reaction, using a primary amine as the example, can be represented by the equation

$$2RNH_2 + CO_2 + H_2O + 2NaNO_2 \longrightarrow 2RNH_2{\cdot}HNO_2 + Na_2CO_3$$

The reaction between the amine and carbon dioxide in methanol in the absence of water formed a white powder which precipitated at about $-20°$ and corresponded to the formula $(RNH_2)_2{\cdot}CO_2$. These substances could be filtered and isolated at room temperature but they sublimed readily. Compounds of this type have been previously observed and identified.[7]

This white powder reacted with sodium nitrite and water in the presence of methanol to produce the ammonium nitrite.

This method has been applied successfully to isopropylamine, diisopropylamine, diisobutylamine and triethylamine, with a yield of about 75% of the nitrite in each case.

The use of methanol instead of water as the solvent permits the use of a lower temperature, thus decreasing the formation of nitrosamines and the decomposition of unstable nitrites. The evolution of carbon dioxide gas during the preparation excludes oxygen and thus tends to prevent the formation of nitrates.

Table I summarizes the various reaction conditions studied. Sodium nitrite is superior to potassium nitrite since potassium carbonate separates in a flocculent condition and is much harder to filter. Absolute ethanol, acetone and isopropanol are inferior to methanol as a solvent, undoubtedly due to the higher solubility of sodium nitrite in methanol. The yield of sodium carbonate is fairly constant in all of the cases in which methanol was used. The yield of sodium carbonate is probably a better measure of the extent of the nitrite reaction than is the yield of the nitrite, since in many cases the nitrites are difficult to isolate.

This new method of synthesis was tried for higher molecular weight amines, whose nitrite salts are not water soluble, and quite low yields were obtained. It was found that some of these nitrites had been described in the literature and were prepared in aqueous solution but the yields reported were often quite low and the methods were poorly described. Dicyclohexylammonium nitrite, a compound not previously described, was prepared in this study in 98% yield and the experimental method used in its preparation is described as an example. Dicyclohexylaminenitrite is easily converted to the N-nitrosamine by warming in dilute acid solution. A comparison of these two materials shows the expected chemical behavior.

A study of the alkyl ammonium nitrite salts which have been investigated indicates that, in general, the salts of primary amines of low molecular weight and the salts of tertiary amines are

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[1] The opinions or assertions contained in this paper are the authors' and are not to be construed as official or reflecting the views of the Navy Department.

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