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## NOTES

# Pore-Size Distributions from Nitrogen Adsorption by an Abbreviated Method

The determination of pore-size distributions of catalysts from nitrogen sorption isotherms is a well-established technique and is done extensively in most large industrial laboratories. However, the time consumed (up to 40 hr) in the experimental procedure and laborious calculations has limited its use, particularly among academic workers and in smaller installations.

By making some small sacrifices in accuracy, we have reduced the experimental time by about one-third and programmed the calculations. In our method only 12–15 experimental points are taken (in place of the usual 40 or more) and the regions between data points are synthesized by use of a modified form of the Halsey (*1*) equation, $\log p/p_0 = -A/v^n$; $A$ and $n$ are determined by the two adjacent real data points. The latter procedure is justified by agreement of computed and actual points within experimental error for a series of catalysts and adsorbents. The complete calculation (including interpolation) is performed by the IBM 7070 computer.

The calculation of the pore volume size distribution after this point follows the method of Cranston and Inkley (*2*). On the assumption of cylindrical pores, the surface area and pore length for each diameter are also computed but these are of less interest generally and are, of course, more sensitive to deviations from the model.

All experimental points up to $p/p_0 = 0.25$ are used to calculate the least-squares straight line fits to the Brunauer-Emmett-Teller (BET) (*3*) and Langmuir (*4*) equations. If there are more than two such points, the fit of the two equations is compared and the equation giving the smaller standard deviation is used to compute the surface area. The BET equation is used if there are only two such points.

In addition to the distributions and surface area, other useful data are generated. The micropore volume (MPV) is the total volume adsorbed at the $p/p_0$ (0.931) corresponding to pores smaller than 300 Å, and the pore volume (PV) is the total volume adsorbed at the $p/p_0$ (0.967) corresponding to 600 Å pores; the average micropore diameter (AMPD) and average pore diameter (PD) are the corresponding average diameters generated by the usual method from the proper pore volume and surface area; i.e., $PD = PV \times 4 \times 10^4/S$ ml/g. The differential pore volumes and surface areas to 300 Å are summed to give a calculated MPVC and calculated surface area (SC) which are then compared in ratios to MPV and BET surface area (S), respectively. These ratios afford a check on the theoretical model since the denominators are obtained independently of the cylindrical pore assumptions.

Figure 1 shows the pore-size distributions of two gamma alumina samples formed by calcination of two different alumina hydrates: boehmite (Sample A) and bayerite (Sample B). Only 12 experimental adsorption points were used in these determinations but the differences in pore structure are obvious. The values of pore diameters corresponding to actual experimental pres-

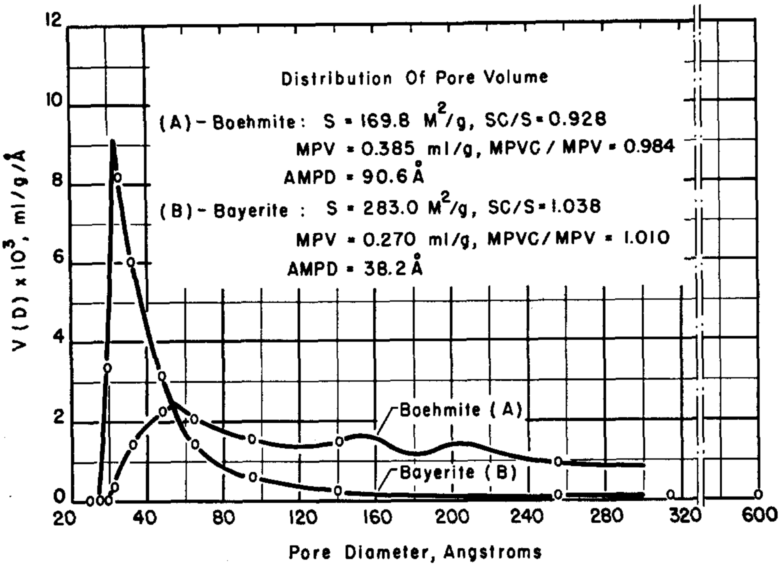

FIG. 1. Distribution of pore volume for two γ-alumina samples.

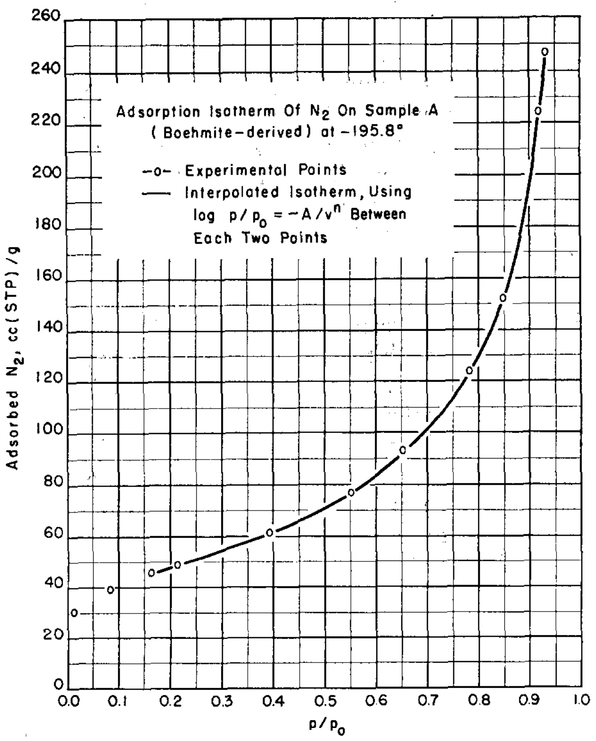

FIG. 2. Experimental points and interpolated curve for adsorption isotherm of $N_2$ on sample A.

sures are shown by circles on the curves or on the abscissa. Apparently, the interpolation has produced the two minor peaks between 140 and 255 Å for Sample A; the simple addition of an extra experimental point in that region (at $p/p_0 = 0.880$, for example) would clarify any doubts.

The experimental points are shown along with the interpolated curve for Sample A in Fig. 2. The final point (at $p/p_0 = 0.966$) is off the scale of this plot, but the complete interpolated region is shown. The smoothness of the interpolation indicates that little accuracy is lost, considering the time and effort saved by this method.

The input data are shown in Table 1 and computed volume distribution in Table 2 for Sample A.

TABLE 1
INPUT DATA FOR SAMPLE A (BOEHMITE-DERIVED)

| $p_{N_2}$ Pressure (mm Hg) | $p_{0,N_2}$, Saturation pressure (mm Hg) | $V_{N_2}$ Adsorbed [(cc) (STP)] | Pore diameter for $p/p_0$ |
|---|---|---|---|
| 10.0 | 753.0 | 30.38 | 9.0 |
| 61.0 | 752.0 | 39.14 | 15.0 |
| 122.0 | 751.0 | 45.44 | 19.0 |
| 160.0 | 751.0 | 48.69 | 22.5 |
| 296.0 | 751.0 | 61.19 | 32.5 |
| 415.0 | 751.0 | 76.24 | 47.5 |
| 492.0 | 751.0 | 92.63 | 65.0 |
| 590.0 | 751.0 | 123.81 | 95.0 |
| 639.0 | 751.0 | 152.16 | 140.0 |
| 690.0 | 750.0 | 224.24 | 255.0 |
| 698.0 | 748.0 | 246.88 | 315.0 |
| 721.0 | 748.0 | 307.26 | 600.0 |

TABLE 2
PORE-VOLUME DISTRIBUTION

| Diameter for interpolated $p/p_0$ (Å) | Volume adsorbed for interpolated $p/p_0$ $V$[cc(STP)] | Average diameter $D$ (Å) | Volume of pores of diamerer, $D$ $V(D)$ = ml/g-Å |
|---|---|---|---|
| 300 | 242.7 | 295.0 | 0.000706 |
| 290 | 239.0 | 285.0 | 0.001010 |
| 280 | 233.8 | 275.0 | 0.000640 |
| 270 | 230.5 | 265.0 | 0.000920 |
| 260 | 225.8 | 255.0 | 0.000953 |
| 250 | 220.9 | 245.0 | 0.000941 |
| 240 | 216.1 | 235.0 | 0.001186 |
| 230 | 210.0 | 225.0 | 0.001108 |
| 220 | 204.4 | 215.0 | 0.001295 |
| 210 | 197.9 | 205.0 | 0.001199 |
| 200 | 191.9 | 195.0 | 0.001334 |
| 190 | 185.3 | 185.0 | 0.001228 |
| 180 | 179.2 | 175.0 | 0.001131 |
| 170 | 173.6 | 165.0 | 0.001401 |
| 160 | 166.8 | 155.0 | 0.001588 |
| 150 | 159.1 | 145.0 | 0.001546 |
| 140 | 151.7 | 135.0 | 0.001319 |
| 130 | 145.3 | 125.0 | 0.001379 |
| 120 | 138.6 | 115.0 | 0.001398 |
| 110 | 131.9 | 105.0 | 0.001541 |
| 100 | 124.6 | 95.0 | 0.001610 |
| 90 | 117.0 | 85.0 | 0.001726 |
| 80 | 108.9 | 75.0 | 0.001834 |
| 70 | 100.3 | 65.0 | 0.002029 |
| 60 | 90.9 | 55.0 | 0.002434 |
| 50 | 79.8 | 47.5 | 0.002237 |
| 45 | 74.2 | 42.5 | 0.001856 |
| 40 | 69.0 | 37.5 | 0.001825 |
| 35 | 63.6 | 32.5 | 0.001515 |
| 30 | 58.0 | 27.5 | 0.001018 |
| 25 | 52.1 | 22.5 | 0.000316 |
| 20 | 45.8 | 19.0 | 0.000000 |

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