ASTM INTERNATIONAL

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Standard Practice for
Calculation of Pore Size Distributions of Catalysts and Catalyst Carriers from Nitrogen Desorption Isotherms[1]

1. Scope

1.1 This practice covers the calculation of pore size distributions for catalysts and catalyst carriers from nitrogen desorption isotherms. The computational procedure is particularly useful for determining how the pore volume is distributed in catalyst samples containing pores whose sizes range from approximately 1.5 to 100 nm (15 to 1000 Å) in radius. It should be used with caution when applied to isotherms for samples containing pores both within this size range and pores larger than 100 nm (1000 Å) in radius. In such instances the isotherms rise steeply near $P/P_o = 1$ and the total pore volume cannot be well defined. The calculations should begin at a point on the isotherm near saturation preferably in a region near $P/P_o = 0.99$, establishing an upper limit on the pore size distribution range to be studied. Simplifications are necessary regarding pore shape. A cylindrical pore model is assumed, and the method treats the pores as non-intersecting, open-ended capillaries which are assumed to function independently of each other during the adsorption or desorption of nitrogen.

NOTE 1—This practice is designed primarily for manual computation and a few simplifications have been made for this purpose. For computer computation, the simplified expressions may be replaced by exact expressions.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3766 Terminology Relating to Catalysts and Catalysis

D4222 Test Method for Determination of Nitrogen Adsorption and Desorption Isotherms of Catalysts and Catalyst Carriers by Static Volumetric Measurements

3. Terminology

3.1 *Definitions*—Consult Terminology D3766.

3.2 *Symbols:*

i = numerical index representing each successive data point, with $i = 1, 2… n$.

$P_4(i)$ = pressure after equilibration during desorption, torr.

$P_0(i)$ = liquid nitrogen vapor pressure, torr.

V_{de} = Quantity of gas desorbed (cm3 STP/g); see 12.4.10 and 12.5 in Test Method D4222.

$r_k(i)$ = radius of inner core calculated from Kelvin equation, Å.

T = boiling point of nitrogen, K.

V_L = liquid nitrogen molar volume at T, cm^3/mole.

$γ$ = liquid nitrogen surface tension at T, mN/m.

$t(i)$ = average thickness of the nitrogen film adsorbed on the pore walls, Å.

$r_p(i)$ = radius of cylindrical pore given by $r_k(i) + t(i)$, Å.

Q = volume correction factor defined as $(\bar{r}_p/\bar{r}_k)^2$.

$ΔV_T(i)$ = decrease in the amount of nitrogen adsorbed caused by a lowering in relative pressure, mm^3/g.

$ΔV_f(i)$ = volume of liquid nitrogen desorbed from pore walls during thinning of the film, mm^3/g.

$ΔV_k(i)$ = liquid volume of the inner core in which capillary condensation of the nitrogen occurs, mm^3/g.

$\Delta V_p (i)$ = liquid volume contained in a group of pores having mean radius $\bar{r}_p$, mm^3/g.

$\sum \Delta v_p$ = cumulative pore volume, mm^3/g.

$\Delta S_p(i)$ = area of the pore walls of a cylinder having volume ΔV_p, m^2/g.

4. Summary of Practice

4.1 The pore size distribution is determined by analyzing the desorption data of the nitrogen isotherm. The nitrogen uptake is caused by the multilayer adsorption of a film of nitrogen on the pore walls and by capillary condensation of the nitrogen in the "inner core" regions of the pores. The relative pressure at which filling of the core occurs for a given pore size by capillary condensation is predicted from the Kelvin equation (1).[3] During desorption, thinning of the multilayer film adsorbed on the pore walls occurs in pores which have previously lost their capillary condensate. Corrections for film thinning are determined by a procedure involving the surface area and radius of the film which becomes exposed as desorption proceeds. In principle, the computational procedure can be applied to either the adsorption branch or desorption branch of the nitrogen isotherm. Unless the presence of ink-bottle shaped pores is suggested by an abrupt closure of the desorption branch on the adsorption branch, the distribution curve derived from the desorption data is preferred, and is described in this procedure. The computational method is essentially the procedure developed by Barrett, Joyner, and Halenda (2), except for the incorporation of a few simplifications.

Note 2—In cases where it has been established that the adsorption branch of the nitrogen isotherm is to be analyzed, the procedure proposed by Cranston and Inkley (3) can be employed.

Note 3—Thanks to major advances in adsorption science and technology over the past two decades, it is now widely recognized (see recent IUPAC recommendations (4)) that modern statistical mechanics methods based on Density Functional Theory or Monte Carlo simulations provide significantly more accurate pore size distributions than classical procedures based on the Kelvin equation, such as the Barrett–Joyner–Halenda (BJH) or Cranston-Inkley methods (2, 3). Moreover, the choice of desorption (equilibrium) vs. adsorption (metastable) branches for reliable pore size analysis must take into consideration the potential influence of pore connectivity, tensile strength and cavitation effects. In addition, although nitrogen sorption at 77 K is widely used, its quadrupole interactions with polar surfaces can influence isotherm shapes and their interpretation; therefore, argon adsorption at 87 K is considered to be more reliable and is now recommended, particularly for samples containing micropores (4). In spite of these advances, the traditional Kelvin-based approaches described in this Standard Practice are still deemed to be useful for routine work (such as industrial process control).

5. Significance and Use

5.1 Pore volume distribution curves obtained from nitrogen sorption isotherms provide one of the best means of characterizing the pore structure in porous catalysts, provided that the limitations of the method are kept in mind. Used in conjunction with the BET treatment for surface area determination (5), these methods provide an indispensable means for studying the structure associated with pores usually important in catalysts.

This practice is particularly useful in studying changes in a series of closely related samples caused by treatments, such as heat, compression, or extrusion often used in catalyst manufacturing. Pore volume distribution curves can often provide valuable information during mechanistic studies dealing with catalyst deactivation.

6. Computational Procedure

6.1 This procedure requires the use of a series of experimentally measured relative pressures $[P_4(i)/P_0(i)]$ and the corresponding quantities of nitrogen gas adsorbed $[V_{de}]$ expressed in units of cm^3 STP/g. The experimental data required in the use of this procedure can be measured by following the steps outlined in Test Method D4222. Inspect the nitrogen sorption isotherm in the region above $P/P_o = 0.95$. If the solid contains no pores larger than 100 nm (1000 Å) radius, the isotherm remains nearly horizontal over a range of P/P_o approaching unity and it is a simple matter to select a starting relative pressure within this region, establishing an upper limit on the pore size range to be studied. If pores larger than 100 nm (1000 Å) are present, however, the isotherm rises rapidly near $P/P_O = 1$ and the total pore volume cannot be well defined. This limiting adsorption can then be identified reliably only if the temperature is very carefully controlled and there are no "cold spots" in the apparatus (which lead to bulk condensation of the gas and a false measure of the adsorption in the volumetric method). Selecting the starting relative pressure for the computational procedure is then made more difficult. In most cases a starting relative pressure of 0.99 will be suitable, which corresponds to an upper limit on pore size of 100 nm (1000 Å) in radius. If necessary, interpolate the values of V_{de} to determine the quantity of nitrogen gas adsorbed at the chosen starting relative pressure.

6.2 The procedure requires numerous arithmetical steps which can best be carried out with the aid of a work sheet. An example (5) of a form found useful in the calculations is provided in Table 1. List in descending order the experimentally determined relative pressures $[P_4(i)/P_0(I)]$ in Column 1, beginning with the value chosen as the starting relative pressure. Generally, values below a relative pressure of 0.25 will not be required in the calculations. Convert the uptake values into a liquid volume (mm^3/g) by multiplying the value of V_{de} in cm^3 STP/g with the conversion factor 1.5468 derived from $V_L = 34.67$ cm^3/mole. List in Column 9 the corresponding quantities of nitrogen adsorbed.

6.3 For each relative pressure, calculate a value for the radius of the core, r_k, by means of the Kelvin equation,

$$RT\ln(P_4/P_0) = -\frac{2\gamma V_L}{r_k} \tag{1}$$

given in the form

$$r_k(\mathring{A}) = -\frac{9.574}{\ln(P_4/P_0)} \tag{2}$$

with $T = 77.35$ K; $\gamma = 8.88$ mN/m; and $V_L = 34.67$ cm^3/mole. List the values in Column 2. For each successive decrement in relative pressure, calculate $\bar{r}_k$, the mean of the values of r_k for the present and previous pressures, and list these mean values in Column 3.

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[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

TABLE 1 Pore Distribution Computational Work Sheet

Sample Identification _____   Date_____

1 P_4/P_0	2 r_k Å	3 $\bar{r}_k$ Å	4 t Å	5 Δt Å	6 r_p Å	7 $\bar{r}_p$ Å	8 Q	9 V_{de} mm³/g	10 ΔV_T mm³/g	11 ΔV_f mm³/g	12 ΔV_k mm³/g	13 ΔV_p mm³/g	14 ΔS_p m²/g	15 $\sum \Delta S_p$ m²/g	16 $\sum \Delta V_p$ mm³/g
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Column 2: $r_k = \dfrac{-9.574}{\ln(P_4/P_0)}$

Column 4: $t = \left[\dfrac{13.99}{0.034 - \log(P_4/P_0)} \right]^{1/2}$

Column 11: $\Delta V_f = 0.085 \cdot \Delta t \cdot \sum \Delta S_p$ (preceding line)

Column 12: $\Delta V_k = \Delta V_T - \Delta V_f$

Column 13: $\Delta V_p = \Delta V_k \times Q$

Column 14: $\Delta S_p = 20 \times (\Delta V_p / \bar{r}_p)$

6.4 The average thickness, t, of the multilayer film of nitrogen adsorbed on the walls of the pores at each relative pressure is used to calculate the amount of nitrogen desorbed from the film in pores which have lost their capillary condensate. For each relative pressure, calculate a value for the film thickness from the expression (6)

$$ t\,(\overset{\circ}{A}) = \left[\frac{13.99}{0.034 - \log(P_4/P_0)} \right]^{\frac{1}{2}} \qquad (3) $$

and list the values in Column 4. For each successive decrement in relative pressure, calculate the differences in the values of t, and list these differences as Δt in Column 5.

6.5 Since a cylindrical pore model is assumed, the radius of the pore, r_p, is given by addition of the core radius, r_k, and the film thickness value, t. Add the values in Column 2 to the corresponding values in Column 4 and record the results in Column 6 as r_p. For each successive decrement in relative pressure, calculate $\bar{r}_p$, the mean of the pore radii, r_p, for the present and previous pressures, and record these values in Column 7.

6.6 Compute the quantity $(\bar{r}_p/\bar{r}_k)^2$ from the values listed in Columns 7 and 3. This quantity will be used later to correct the core volume to the volume for each group of pores. The core volume is the region within the pore that fills by capillary condensation of the nitrogen. List the computed values in Column 8 as the volume correction factor, Q.

Note 4—For a cylindrical pore $\bar{r}_p$ and $\bar{r}_k$ are related to Q by the exact expression:

$$ Q = \left[\bar{r}_p / (\bar{r}_k + \Delta t) \right]^2 \qquad (4) $$

For $\bar{r}_k > 30$ Å, $\Delta t < 1\%$ $\bar{r}_k$. Simplifying Q by eliminating Δt gives $(\bar{r}_p/\bar{r}_k)^2$.

6.7 The amounts of nitrogen desorbed for each successive decrement in relative pressure are calculated by progressive subtraction of the values of the amounts of nitrogen adsorbed, V_{de}, listed in Column 9 from the succeeding one. Compute these differences and list the values in Column 10 as, ΔV_T. Each value of ΔV_T except for the initial one in line 2 contains contributions from the amounts of nitrogen given up by loss of capillary condensate and by thinning of the nitrogen film adsorbed on the walls of pores which have previously released their capillary condensate. The initial value of ΔV_T is due solely to the amount of nitrogen contributed from loss of capillary condensate, since it is assumed that at the highest relative pressure all of the pores are completely filled with nitrogen, and that no thinning of the nitrogen film occurs for the first decrement in relative pressure.

6.8 In completing the calculation to obtain a value for the pore volume, ΔV_p, corresponding to each mean pore size, $\bar{r}_p$,

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