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Standard Test Method for
Determination of Nitrogen Adsorption and Desorption Isotherms of Catalysts and Catalyst Carriers by Static Volumetric Measurements[1]

This standard is issued under the fixed designation D4222; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

~~ε^1 NOTE—Eq 10 in subsection 12.4.7 was corrected editorially in August 2015.~~

1. Scope

1.1 This test method covers the determination of nitrogen adsorption and desorption isotherms of catalysts and catalyst carriers at the boiling point of liquid nitrogen.[2] A static volumetric measuring system is used to obtain sufficient equilibrium adsorption points on each branch of the isotherm to adequately define the adsorption and desorption branches of the isotherm. Thirty points evenly spread over the isotherm is considered to be the minimum number of points that will adequately define the isotherm.

1.2 *Units*—The values stated in SI units are to be ~~the~~ regarded as standard. The values given in parentheses ~~are for information only.~~after SI units are provided for information only and are not considered 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* ~~safety~~ *safety, health, and* ~~health~~*environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]
D3663 Test Method for Surface Area of Catalysts and Catalyst Carriers
D3766 Terminology Relating to Catalysts and Catalysis
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E456 Terminology Relating to Quality and Statistics
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—See Terminology D3766.

3.2 *Symbols:*

PH_1 = initial helium pressure, torr.
PH_2 = helium pressure after equilibration, torr.
TH_1 = temperature of manifold at initial helium pressure, °C.
TH_2 = temperature of manifold after equilibration, °C.
P_1 = initial N_2 pressure, torr.
T_1 = manifold temperature at initial N_2 pressure, K.
T'_1 = manifold temperature at initial N_2 pressure, °C.
P_2 = pressure after equilibration, torr.
T_2 = manifold temperature after equilibrrium, K.
T'_2 = manifold temperature after equilibrium, °C.
P_3 = initial N_2 pressure during desorption, torr.
T_3 = manifold temperature at initial N_2 pressure, K.
T'_3 = manifold temperature at initial N_2 pressure, °C.
P_4 = pressure after equilibration during desorption, torr.
T_4 = manifold temperature after equilibration, K.
T'_4 = manifold temperature after equilibration, °C.
P_0 = liquid nitrogen vapor pressure, torr.
T_s = liquid nitrogen temperature, K.
X = relative pressure, $P_{2(4)}/P_0$.
V_d = volume of manifold, cm^3.
V_s = the dead-space volume factor, cm^3 (STP)/torr.
W_s = mass of sample, g.
W_1 = tare of sample tube, g.
W'_2 = sample mass + tare of tube after degassing, g.
W_2 = sample mass + tare of tube after adsorption, g.
V_{ds} = volume of nitrogen in the dead-space, cm^3 (STP).
V_1 = see 12.4.3.
V_2 = see 12.4.4.
V_t = see 12.4.5.
V_{ad} = see 12.4.7.
V_{de} = see 12.5.

4. Summary of Test Method

4.1 The sample is heated and evacuated to remove adsorbed vapors from the surface. The nitrogen adsorption branch of the isotherm is determined by evacuating the sample, cooling the sample to the boiling point of liquid nitrogen (~77.3 K), and subsequently adding stepwise, known amounts of nitrogen gas to the sample in such amounts that the form of the adsorption isotherm is adequately defined and the saturation pressure of nitrogen is reached. Each additional dose of nitrogen is introduced to the sample only after the foregoing dose of nitrogen has reached adsorption equilibrium with the sample. By definition, equilibrium is reached if the change in gas pressure is no greater than 0.1 ~~torr/5~~ torr over a 5 min interval. The desorption isotherm is determined by desorbing nitrogen from the saturated sample in a stepwise mode with the same precautions taken to ensure desorption equilibration as applied under adsorption conditions. It is essential that the experimental points be distributed over the isotherm in such a manner as to correctly identify and define the isotherm. If the additions or withdrawals of nitrogen are too large, the temporarily too-high nitrogen gas pressure during adsorption or too-low gas pressure during desorption, may result in so-called scanning effects within the hysteresis loop of the adsorption-desorption branches of the isotherm. The occurrence of scanning may result in too-high equilibrium values for the adsorption isotherm and too-low values for the desorption isotherm.

5. Significance and Use

5.1 The test method has two main functions: first, it provides data useful for establishing the pore size distribution of catalyst materials, which in turn may influence their performance; and second, it serves as a laboratory test which may be used to study porosity changes that may occur during the manufacture and evaluation of catalysts.

6. Apparatus

6.1 A generic schematic diagram of the minimum apparatus requirement is shown in Fig. 1. A commercial instrument may be used
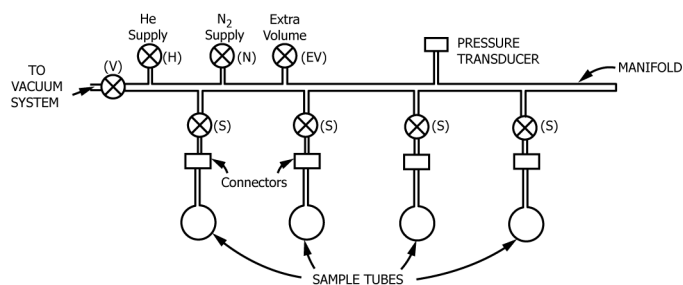
FIG. 1 Schematic Diagram of Adsorption Apparatus

and may be constructed of glass or of metal. The specific commercial apparatus chosen may have a different configuration than that shown in Fig. 1 and may require modification of the sequence of valve operation and of the calculations and equations used. It should have the following features as a minimum:

6.1.1 *Distribution Manifold,* having a (V_d), known to the nearest 0.05 cm^3. This volume is defined as the volume between the stopcocks or valves and includes the pressure gauge.

6.1.2 *Vacuum System,* capable of attaining pressures below 10^{-4} torr (1 torr = 133.3 Pa). This will include a vacuum gauge (not shown in Fig. 1). Access to the distribution manifold is through the valve *V*.

6.1.3 *Pressure Sensing Devices or Pressure Transducers,* capable of measurements with a sensitivity of at least 0.1 torr, in the range from 0 to 1000 torr (1 torr = 133.3 Pa).

6.1.4 *Value (H),* from the helium supply to the distribution manifold.

6.1.5 *Valve (N),* from the nitrogen supply to the distribution manifold.

6.1.6 The connection between the sample tube and the *S* valve can be a standard-taper glass joint, a glass-to-glass seal, or a compression fitting.

6.2 *Sample Tubes,* with volumes from 5 cm^3 to 100 cm^3 depending on the application.

6.3 *Heating Mantles or Small Furnaces.*

6.4 *Dewar Flasks.*

6.5 *Laboratory Balance,* with 0.1-mg (10^{-7}kg) sensitivity.

6.6 *Thermometer or Thermocouple,* for measuring the temperature of the distribution manifold [$T_1(i)$ or $T_2(i)$] in °C.

6.6.1 The manifold may be thermostated at a particular temperature, a few degrees above ambient, to obviate the necessity of recording this temperature at each reading.

6.7 *Thermometer,* for measuring the temperature of the liquid nitrogen bath ($T_s(i)$) in Kelvin. Preferably, this thermometer will be a nitrogen vapor-pressure-thermometer, often referred to in a commercial instrument as a pressure saturation tube, that gives P_0 directly and has greater precision, or a resistance thermometer from which P_0 values may be derived.

NOTE 1—A pressure transducer may be placed between the sample tube and the manifold to monitor equilibrium pressure, but this is not a requirement of the system.

7. Reagents

7.1 *Helium Gas*—A cylinder of helium gas at least ~~99 %~~ 99.999 % pure.

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7.2 *Liquid Nitrogen, ,* of such purity that P_0 is not more than 20 torr above barometric pressure. A fresh daily supply is recommended.

7.3 *Nitrogen Gas*—A cylinder of nitrogen gas at least ~~99.999 %~~ 99.999 % pure.

8. Procedure-Sample Preparation and Degassing

8.1 Select a sample tube of the desired size. To minimize the dead-space, a ~~5-cm~~5 cm³ sample tube is preferred for samples not exceeding about 1 g. However, to avoid boiling when degassing is started, a ~~25-cm~~25 cm³ sample tube may be preferred for finely powdered catalysts. A small glass-wool plug or fritted disk placed in the neck of the sample tube above the liquid nitrogen level, will eliminate the possibility of any small catalyst particles entering the vacuum system.

8.2 Fill the sample tube with nitrogen or helium at atmospheric pressure, after removing air by evacuation. This may be done on the adsorption unit or on a separate piece of equipment.

8.3 Remove the sample tube from the system, cap, and weigh. Record the mass as W_1.

8.4 Place the catalyst sample, whose approximate mass is known, into the sample tube. Choose the sample size to provide an estimated total sample surface area of approximately ~~20 m~~20 m² or greater.

Note 2—Follow instrument manufacturer's recommendations for sample amounts when using commercial instruments.

8.5 Attach the sample tube to the apparatus. If other samples are to be run, attach them at this time to the other ports.

8.6 Open the *S* valve.

8.7 Slowly open the *V* valve, monitoring the rate of pressure decrease to avoid too high a rate, which might lead to excessive fluidization of powdered samples.

8.8 Install a heating mantle or furnace around each sample and raise the temperature to about ~~300°C (573 K).~~300 °C (573 K).

Note 3—Take special precautions if the moisture content exceeds approximately ~~5 %~~5 % to avoid bumping of powdered catalyst and to avoid surface area loss by self-steaming. ~~It is recommended that the heating rate not exceed 100 K/h~~A stepped or pressure-controlled heating routine is recommended under these circumstances.

Note 4—Not all catalysts or their supports are stable to 300 °C. This should be noted and the appropriate temperature should be used based on thermal properties of the material.

8.9 Continue degassing at about ~~300°C~~300 °C (573 K) for a minimum of ~~3 h,~~3 h, at a pressure not to exceed 10⁻³ torr. Overnight degassing is permissible. It is recommended that a rate of rise test be performed to determine the current readiness of the sample. For such tests, isolate the sample from vacuum and monitor the cell for pressure change associated with a vapor pressure from the sample. If the pressure is nearly constant over a prolonged period (15 to 30 min), degassing is complete.

~~Note 3—Certain materials will decompose at 300°C (for example, alumina hydrates) or will sinter (for example, platinum black). Lower degassing temperatures are permissible for such materials; however, the degassing temperature should be specified when reporting the results.~~

8.10 Remove the heating mantle, and allow the sample to cool.

8.11 Close the *S* valve.

8.12 It is permissible to exercise the option of preliminary degassing on an external unit. In such a case, follow the procedures of 8.4 – 8.10 and then repeat on the adsorption unit, except that the degassing time in 8.9 should not exceed 1 h.

8.13 If it is desired to weigh the sample after preliminary degassing on an external unit, back-fill with the same gas used in 8.2 to above atmospheric pressure. Close the *S* valve.

8.14 Detach the sample tube from the apparatus, recap with the stopper used previously, and weigh. Record the mass as W_2.

8.15 Remove the backfilled gas by evacuation to less than 10^{-3} torr at room temperature.

9. Procedure-Dead-Space Determination

9.1 From this point on, each sample being tested for nitrogen adsorption must be run on an individual basis. Thus, 9.2 through 11.4 must be carried out separately for each tube in test.

9.2 The dead-space is the quantity of gas within the charged sample tube, including the *S* valve, when the tube is immersed in liquid nitrogen to the proper depth.

Note 5—The dead-space may be determined after the nitrogen adsorption and desorption, if more convenient, as long as adequate degassing precedes it. In that case, replace the liquid nitrogen bath after 10.14 before proceeding with 9.3 – 9.9. Then, remove the Dewar flask before carrying out 10.15 and 10.16.

Note 6—Some commercial equipment allows for helium-free determination of the dead-space by calibration of a blank cell and accounting for the skeletal volume of the sample when the cell is charged. This can be considered equivalent to determination of deadspace by helium and can be used if helium is not available. Follow the recommendations of the instrument manufacturer for these measurements.

9.3 Place a Dewar flask of liquid nitrogen around the sample and adjust the liquid level to a fixed point on the sample tube. Maintain this level throughout the test.

Note 7—Some modern commercial instruments do not require manual maintenance or readjusting of the level of liquid nitrogen during the analysis. Follow the manufacturer's recommendations for operating the particular instrument used.

9.4 Zero the pressure gauge.

9.5 Admit the helium gas into the system to a pressure of 600 to 900 torr by carefully opening the *H* valve. Record this pressure as P_{H1}, and the manifold temperature as T_{H1}.

9.6 Open the *S* valve to admit helium to the sample.

9.7 After about 5 min of equilibration, readjust the liquid nitrogen level, and record the pressure as P_{H2} and the manifold temperature as T_{H2} .

9.8 Repeat 9.5 – 9.7 for each sample on the manifold.

9.9 Open the *S* valve; then slowly open the *V* valve to remove the helium gas.

9.10 Close the *S* valve when a pressure below 10^{-3} torr has been attained.

10. Procedure-Nitrogen Adsorption

10.1 Admit nitrogen gas, and record the pressure as $P_1(1)$ (torr) and the temperature as $T_1(1)$ (°C). It is desirable, but not necessary, to choose $P_1(1)$ such that the first equilibrium adsorption pressure, $P_2(1)$, will be about 40 torr equivalent to $P_2(1)/P_o(1)$ of about 0.05.

10.2 Open the *S* valve to admit nitrogen to the catalyst.

10.3 Allow sufficient time for equilibration, readjusting the liquid nitrogen level to the marking on the sample tube as necessary. Equilibrium shall be considered as attained when the pressure change is no more than 0.1 torr in 5 min. If the pressure becomes less than the value which gives the desired relative pressure P_2/P_0, admit more nitrogen gas and allow the system to reequilibrate.

10.4 Record the equilibrium pressure as $P_2(1)$ and the manifold temperature as T_2.

10.5 Record the liquid nitrogen temperature [$T_s(1)$] or the nitrogen vapor pressure [$P_0(1)$].

10.6 Close the S valve and then admit nitrogen gas to increase the pressure by a suitable amount, depending upon the sample's adsorptive capacity. Record the pressure as $P_1(2)$, and the manifold temperature as $T_1(2)$.

10.7 Open the S valve to admit the new increment of nitrogen to the catalyst.

10.8 Allow sufficient time for equilibration, readjusting the liquid nitrogen level as necessary. The criterion for equilibrium is defined in 10.3. If the pressure becomes less than the value that gives the desired relative pressure P_2/P_0, an additional known amount of gas should be admitted to the manifold and the system allowed to come to equilibrium.

10.9 Record the equilibrium pressure as $P_2(2)$, and record $T_2(2)$.

10.10 Again record $T_s(2)$ or $P_0(2)$.

10.11 Repeat 10.6 – 10.10, increasing the pressure P_1 by a suitable amount above the previous pressure each time until there are sufficient data points,points (30 points as a minimum) to properly define the isotherm up to a pressure that is at least 0.995 of the determined P_0 value. As a guide, increasing P_2 by about 25 torr for each equilibration point will usually provide the required number of points necessary to adequately define the adsorption isotherm. If the amount of nitrogen adsorbed increases rapidly, which may occur for highly porous catalysts when approaching the saturation pressure, it will be desirable to use an increment in P_2 smaller than the suggested value of 25 torr. If $P_0(i)$ is not measured directly, use Eq 3 in 12.3.2.1 to determine a value from a recorded liquid nitrogen temperature.

10.12 If the desorption isotherm is to be measured, proceed to 11.1.

10.13 Slowly open the V valve, remove the Dewar flask, and allow the sample flask to come to room temperature.

10.14 When frost has disappeared from the sample tube, wipe it dry.

10.15 Back-fill the sample tube with the same gas used in 8.2 to about atmospheric pressure. Close the S valve.

10.16 Detach the sample tube from the apparatus, recap with the stopper used previously, and weigh. Record the mass as W_2.

11. Procedure-Nitrogen Desorption

11.1 Measurement of the true desorption isotherm requires first saturating the sample with nitrogen at a pressure that is at least 0.995 of the measured value of P_0. If the adsorption branch of the isotherm is not required, use the preceding procedure to reach the saturation point. Much larger increments in pressure may now be used but it is still necessary to determine the P_1 values and the final P_2 value when close to the value of P_0 so that the total amount of nitrogen added to the system and the volume of nitrogen adsorbed at saturation can be calculated. It is not necessary to wait for equilibration after dose if the adsorption isotherm is not desired. In this case, equilibration of the gas with the sample is only required at the final P_2 pressure. Record the liquid nitrogen temperature [$T_s(1)$] or the nitrogen vapor pressure [$P_0(1)$].

11.2 After the sample has been saturated, close the S valve. Open the V valve very slowly, and evacuate the manifold down to a suitable pressure. Close the V valve and record the pressure as $P_3(1)$ and the temperature as $T_3(1)$.

11.3 Open the S valve connecting the manifold and sample, allowing time necessary for the gas to equilibrate at constant pressure using the criterion in 10.3 to determine when equilibrium has been attained. Adjust the liquid nitrogen level to the marking on the sample tube as necessary. Record the pressure as $P_4(1)$ and the temperature as $T'_4(1)$.

11.4 Repeat 11.2 and 11.3 without resaturating the sample until at least thirty data points have been determined. The decrease in pressure for each step can, in general, be expected to approach 25 torr. Designate the pressures as $P_3(i)$ and $P_4(i)$ and the temperatures as $T'_4(i)$. If the amount of nitrogen desorbed begins to rapidly increase, it will be desirable to use an increment in P_4 smaller than the suggested value of 25 torr. Record $T_s(i)$ or $P_o(i)$ at each equilibrium point. It should be noted that long equilibration times may be experienced at pressures where the quantity of nitrogen desorbed is large.

11.5 Proceed to 10.13 and follow 10.14 – 10.16 to obtain the final mass on the sample and sample tube.

12. Calculations

12.1 Calculate the mass of sample W_s, as follows:

$$W_s = W_2 - W_1 \tag{1}$$

12.2 Calculate the volume factor of the dead-space, V_s as follows:

$$V_s = [(273.2 \, V_d)/(760 \, P_{H2})][P_{H1}/(T_{H1}+273.2) - P_{H2}/(T_{H2}+273.2)] \tag{2}$$

$$V_s = \left(\frac{273.15 \, V_d}{760 \, P_{H2}}\right)\left(\frac{P_{H1}}{T_{H1}+273.15} - \frac{P_{H2}}{T_{H2}+273.15}\right) \tag{2}$$

Note 6—The user should consult IUPAC for the latest value of absolute zero to use in these calculations as 273.2 was current for this revision.

12.3 For each point, $i = 1,2 \ldots n$, the following measurements will have been recorded:

12.3.1 For pressure $P_1(i)$ and $P_2(i)$, see 6.1.3, 10.1, 10.4 10.6, 10.9, and 10.11.

12.3.2 For vapor pressures $P_0(i)$, or liquid nitrogen temperatures, $T_s(i)$, see 6.7, 10.5, and 10.10.

12.3.2.1 If $P_0(i)$ is not measured directly, the values of $T_s(i)$ can be converted to $P_0(i)$ by the following equation for $76 \leq T_s(i) \leq 80$:

$$P_0(i) = -107\,293 + 4\,269.71\,[T_s(i)] \tag{3}$$

- 57.3616 $[T_s(i)]^2$ + 0.261431 $[T_s(i)]^3$ T

12.3.3 For manifold temperatures $T_1(i)$ and $T_2(i)$, see 6.6, 10.1, 10.4, 10.6, 10.9, and 10.11.

12.4 For each point, $i = 1, 2 \ldots n$, calculate the following:

12.4.1 $X(i)$ = relative pressure = $P_2(i)/P_0(i)$.

12.4.2 Manifold temperature in Kelvin:

$$T_1(i) = T'_1(i) + 273.2 \tag{4}$$

$$T_2(i) = T'_2(i) + 273.2$$

$$T_1(i) = T'_1(i) + 273.15 \tag{4}$$

$$T_2(i) = T'_2(i) + 273.15$$

12.4.3 Volume of N_2 in manifold valve S closed to catalyst (cm^3 STP):

$$V_1(i) = (V_d) \cdot [P_1(i)/T_1(i)] \cdot [273.2/760] \tag{5}$$

$$V_1(i) = (V_d)\left(\frac{P_1(i)}{T_1(i)}\right)\left(\frac{273.15}{760}\right) \tag{5}$$

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