



Standard Test Method for Determination of Nitrogen Adsorption and Desorption Isotherms of Catalysts By Static Volumetric Measurements¹

This standard is issued under the fixed designation D 4222; 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.

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. 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 *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:

- D 3663 Test Method for Surface Area of Catalysts²
- D 3766 Terminology Relating to Catalysts and Catalysis²
- E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods³
- E 456 Terminology Relating to Quality and Statistics³
- E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method^{3 4}

3. Terminology

3.1 *Definitions*—Consult Terminology D 3766.

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 equilibrium, 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 = weight of sample, g.
- W_1 = tare weight of sample tube, g.
- W'_2 = sample + tare weight of tube after degassing, g.
- W_2 = sample + tare weight of tube after adsorption, g.
- V_{ds} = volume of nitrogen in the dead-space, cm^3 (STP).
- V_1 = see 12.4.5.
- V_2 = see 12.4.7.
- V_t = see 12.4.8.
- $V_{ad(de)}$ = see 12.4.10.

4. Summary of Test Method

4.1 The sample is heater 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 min interval. The

¹ This test is under the jurisdiction of ASTM Committee D-32 on Catalysts and is the direct responsibility of Subcommittee D32.01 on Physical-Chemical Properties.

Current edition approved March 10, 1998. Published November 1998. Originally published as D 4222 - 83. Last previous edition D 4222 - 91.

² *Annual Book of ASTM Standards*, Vol 05.03.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ Adamson, A. W., *Physical Chemistry of Surfaces*, 3rd ed, John Wiley & Sons, New York, NY, 1976, p. 532.

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 shape and 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 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 gage.

6.1.2 *Vacuum System*, capable of attaining pressures below 10^{-4} torr (1 torr = 133.3 Pa). This will include a vacuum gage (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 25 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*, for measuring the temperature of the distribution manifold [$T'_1 (i)$ or $T'_2 (i)$] in $^{\circ}\text{C}$.

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 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 % pure.

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 % 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^3 sample tube is preferred for samples not exceeding about 1 g. However, to avoid boiling when degassing is started, a 25-cm^3 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 weight as W_1 .

8.4 Place the catalyst sample, whose approximate weight is known, into the sample tube. Choose the sample size to provide an estimated total sample surface area of approximately 20 m^2 or greater.

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).

NOTE 2—Take special precautions if the moisture content exceeds approximately 5 % to avoid bumping of powdered catalyst and to avoid surface area loss by self-steaming. It is recommended that the heating rate

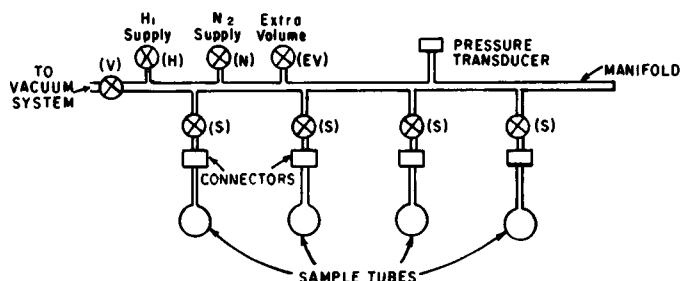


FIG. 1 Schematic Diagram of Adsorption Apparatus

not exceed 100 K/h under these circumstances.

8.9 Continue degassing at about 300°C (573 K) for a minimum of 3 h, at a pressure not to exceed 10^{-3} torr. Overnight degassing is permissible.

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 weight 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 4—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.

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 5—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 gage.

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_0 (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, (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 the equation 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 weight as W_2 .