



Designation: D3663 – 20

Standard Test Method for Surface Area of Catalysts and Catalyst Carriers¹

This standard is issued under the fixed designation D3663; 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 surface areas of catalyst and catalyst carriers that have Type II or IV nitrogen adsorption isotherms, and at least 1 m²/g of area. A volumetric measuring system is used to obtain at least four data points which fit on the linear BET² equation line.

1.2 *Units*—The values stated in SI units are to be regarded as standard. The values given in parentheses 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 appropriate safety, health, and 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

[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 Consult Terminology [D3766](#) for definitions of other terms used.

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

Current edition approved Oct. 1, 2020. Published November 2020. Originally approved in 1978. Last previous edition approved in 2015 as D3663 – 03(2015). DOI: 10.1520/D3663-20.

² Brunauer, Emmett, Teller, *Journal of American Chemical Society, JACS*, No. 60, 1938, p. 309.

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.2 Definitions:

3.2.1 *surface area of a catalyst, n*—the total probe accessible surface of the catalyst; it is expressed in square metres per gram.

3.3 Symbols:

P_{H_1}	=	initial helium pressure, torr
P_{H_2}	=	helium pressure after equilibration, torr
T_{H_1}	=	temperature of manifold at initial helium pressure, °C
T_{H_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
P_0	=	liquid nitrogen vapor pressure, torr
T_s	=	liquid nitrogen temperature, K
X	=	relative pressure, P_2/P_0
V_d	=	volume of manifold, cm ³
V_x	=	extra volume bulb, cm ³
V_s	=	dead-space volume, cm ³
W_s	=	mass of sample, g
W_1	=	tare mass of sample tube, g
W_2	=	sample + tare mass of tube, g
V_{ds}	=	volume of nitrogen in the dead-space, cm ³
V_1	=	see 10.4.4
V_2	=	see 10.4.6
V_t	=	see 10.4.7
V_a	=	see 10.4.9
V_m	=	see 10.8
T_{1x}	=	initial extra-volume bulb temperature, K
$T_{1x}(i)$	=	initial extra-volume bulb temperature, °C
T_{2x}	=	extra-volume bulb temperature after equilibrium, K
$T_{2x}(i)$	=	extra-volume bulb temperature after equilibrium, °C

4. Summary of Test Method

4.1 The surface area of a catalyst or catalyst carrier is determined by measuring the amount of nitrogen gas adsorbed at various low-pressure levels by the catalyst sample. Pressure differentials caused by introducing the catalyst surface area to a fixed volume of nitrogen in the test apparatus are measured and used to calculate BET surface area.

5. Apparatus⁴

5.1 A schematic diagram of a suitable apparatus is shown in Fig. 1. It may be constructed of glass or of metal. Commercial metal instruments are available. It has the following features:

5.1.1 *Distribution Manifold*, having a volume between 20 and 35 cm³, (V_d), known to the nearest 0.05 cm³. This volume is defined as the volume between the stopcocks or valves and includes the pressure gauge.

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

5.1.3 *Pressure-Measuring Device*, that operates at constant volume and is capable of measurements to the nearest 0.1 torr, in the range from 0 to 1000 torr (1 torr = 133.3 Pa).

NOTE 1—See, for example, the article by Joy⁵ for a description of a constant-volume manometer.

5.1.4 *Valve (H)*, from the helium supply to the distribution manifold.

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

5.1.6 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.

5.1.7 *Extra Volume Bulb*, (V_x), should be 100 to 150 cm³, known to the nearest 0.05 cm³. V_x includes the volume of the stopcock bore in the glass apparatus.

5.2 *Sample Tubes*, with volumes from 5 to 100 cm³ depending on the application. Use sample tubes recommended by the instrument manufacturer. If necessary, markings should be placed on the sample tube about 30 to 50 mm below the connectors to indicate the desired liquid nitrogen level.

5.3 *Heating Mantles or Small Furnaces*.

5.4 *Dewar Flasks*.

5.5 *Laboratory Balance*, with 0.1 mg (10⁻⁷ kg) sensitivity.

5.6 *Thermometer or Thermocouple*, for measuring the temperature of the distribution manifold [$T_1'(i)$ or $T_2'(i)$] in degrees Celsius or kelvins.

5.6.1 It is preferred that the manifold be thermostated at a particular temperature, a few degrees above ambient, to obviate the necessity of recording this temperature at each reading.

5.7 *Thermometer*, for measuring the temperature of the liquid nitrogen bath [$T_s(i)$] in kelvins. This will preferably be a nitrogen vapor-pressure thermometer, often referred to in a commercial instrument as a pressure saturation tube, from which P_0 values may be derived.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁶ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Helium Gas*—A cylinder of helium gas at least 99.999 % pure.

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

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

7. Procedure—Sample Preparation and Degassing

7.1 Select a sample tube of the desired size. A 5 cm³ sample tube is preferred for samples not exceeding about 1 g, to minimize the dead-space. However, a 25 cm³ sample tube may be preferred for finely powdered catalysts, to avoid “boiling” when degassing is started.

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

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

⁴ Automated equipment is commercially available.

⁵ Joy, A. S., *Vacuum*, Vol 3, 1953, p. 254.

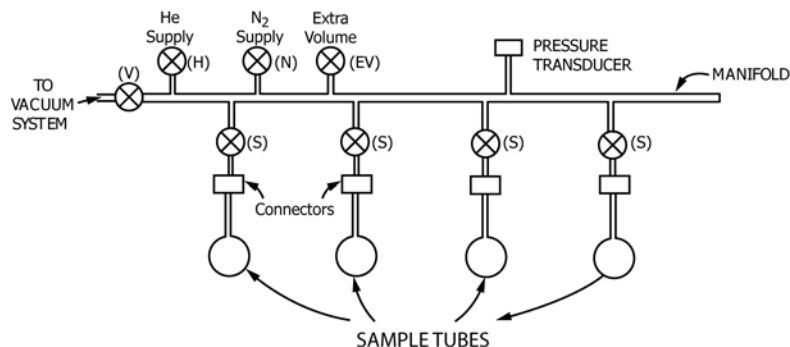


FIG. 1 Schematic Diagram of Surface Area Apparatus

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

7.4 Place the catalyst sample, whose mass is known approximately, into the sample tube. Choose the sample size to provide an estimated total sample surface area of 20 to 100 m².

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

7.6 Open the *S* valves where there are samples.

7.7 It may be necessary to close the *V* valve system periodically to protect the diffusion pump fluid from exposure to pressures above 0.1 torr for periods of more than 30 s. Close the valve off for 2 min.

7.8 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. A stepped or pressure-controlled heating routine is recommended under these circumstances.

NOTE 3—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.

7.9 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.

7.10 Remove the heating mantles, and allow the samples to cool.

7.11 Close the *EV* valve, if open.

7.12 Close the *S* valve.

7.13 It is permissible to exercise the option of preliminary degassing on an external unit. In such a case, follow the procedures of 7.4 – 7.11 and then repeat on the surface area unit, except that the degassing time in 7.9 should not exceed 1 h.

7.14 If it is desired to weigh the sample after preliminary degassing on an external unit, backfill with the same gas used in 7.2 to above atmospheric pressure. Close the *S* valve.

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

7.16 Remove the backfilled gas by evacuation to less than 10⁻⁴ torr at room temperature.

8. Procedure—Dead-Space Determination

8.1 From this point on, each sample being tested for surface area must be run on an individual basis. Thus each Step (8.2 – 9.17) must be carried out separately for each tube in test.

8.2 The “dead-space” is the void volume of the charged sample tube, including the *S* valve, when the tube is immersed in liquid nitrogen to the proper depth (see 5.2).

NOTE 4—The dead-space may be determined after the nitrogen adsorption, if more convenient, as long as adequate degassing precedes it. In that case, replace the liquid nitrogen bath after Step 9.14 before proceeding with Steps 8.3 – 8.9.

NOTE 5—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 dead-space by helium and can be used if helium is not available. Follow the recommendations of the instrument manufacturer for these measurements.

8.3 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.

8.4 Zero the pressure gauge.

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

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

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

8.8 Repeat 8.5 – 8.7 for each sample on the manifold.

8.9 Open all *S* valves; then slowly open the *V* valve to remove the helium gas.

8.10 When a pressure less than 0.01 torr has been attained, close the *S* valve. This operation should take 5 to 10 min.

9. Procedure—Nitrogen Adsorption

9.1 Close the *V* valve and open the *EV* valve if the extra-volume bulb is to be used, when the surface area is known to be high.

9.2 Recheck the zero setting of the pressure gauge.

9.3 Admit nitrogen gas, and record the pressure as $P_1(1)$ (torr) and the temperature as $T_1'(1)$ (degrees Celsius) and read the temperature of the extra-volume bulb and record it as $T_{1x}(1)$. 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. If the surface area is small, it may be desirable to eliminate use of the extra-volume bulb by closing the *EV* valve.

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

9.5 Allow sufficient time for equilibration, readjusting the liquid nitrogen level when necessary. Equilibrium shall be considered as attained when the pressure change is no more than 0.02 torr/min.

9.6 Record the equilibrium pressure as $P_2(1)$, manifold temperature $T_2'(1)$, and the extra volume bulb temperature $T_{2x}(1)$.

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

9.8 Close the *S* valve and close the *EV* valve; then admit nitrogen gas to increase the pressure by 100 to 200 torr, depending upon surface area. Record the pressure as $P_1(2)$, the manifold temperature as $T_1'(2)$, and the extra-volume bulb temperature as $T_{1x}'(2)$.

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

9.10 Allow sufficient time for equilibration, readjusting the liquid nitrogen level as necessary. The criterion for equilibrium is defined in 9.5.