



# Standard Test Method for Surface Area of Catalysts and Catalyst Carriers<sup>1</sup>

This standard is issued under the fixed designation D 3663; 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 ( $\epsilon$ ) 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 m<sup>2</sup>/g of area. A volumetric measuring system is used to obtain at least four data points which fit on the linear BET<sup>2</sup> line.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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:<sup>3</sup>

D 3766 Terminology Relating to Catalysts and Catalysis

E 177 Practice for Use of the Terms Precisions and Bias in ASTM Test Methods

E 456 Terminology Relating to Quality and Statistics

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

## 3. Terminology

3.1 Consult Terminology D 3766 for definitions of other terms used.

### 3.2 Definition:

3.2.1 *surface area of a catalyst*—the total 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 <sup>3</sup>
$V_x$	= extra volume bulb, cm <sup>3</sup>
$V_s$	= dead-space volume, cm <sup>3</sup>
$W_s$	= 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 <sup>3</sup>
$V_1$	= 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 Method

4.1 The surface area of a catalyst or catalyst carrier is determined by measuring the volume 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. Apparatus<sup>4</sup>

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

5.1.1 *Distribution Manifold*, having a volume between 20 and 35 cm<sup>3</sup>, ( $V_d$ ), known to the nearest 0.05 cm<sup>3</sup>. This volume

<sup>4</sup> Automated equipment is commercially available.

<sup>1</sup> 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.

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

<sup>3</sup> 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.

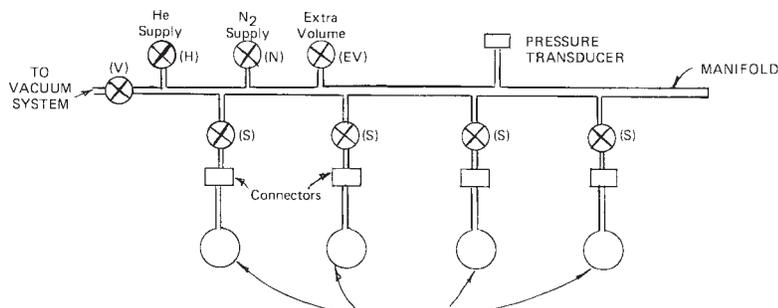


FIG. 1 Schematic Diagram of Surface Area Apparatus

is defined as the volume between the stopcocks or valves and includes the pressure gage.

5.1.2 *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.

5.1.3 *Constant-Volume Gage or Mercury Manometer*, 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 Joy<sup>5</sup> 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<sub>x</sub>)*, should be 100 to 150 cm<sup>3</sup>, known to the nearest 0.05 cm<sup>3</sup>. V<sub>x</sub> includes the volume of the stopcock bore in the glass apparatus.

5.2 *Sample Tubes*, with volumes from 5 to 100 cm<sup>3</sup> depending on the application. Markings should be placed on the sample tubes 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.

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.<sup>6</sup> 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 99.9 % 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-cm<sup>3</sup> sample tube is preferred for samples not exceeding about 1 g, to minimize the dead-space. However, a 25-cm<sup>3</sup> 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.

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 m<sup>2</sup>.

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

<sup>5</sup> Joy, A. S., *Vacuum*, Vol 3, 1953, p. 254.

<sup>6</sup> *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 *Annual 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.

approximately 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 under these circumstances.

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.

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.

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.

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 gage.

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 gage.

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.

9.11 Record the equilibrium pressure as  $P_2(2)$ , and record  $T_2'(2)$  and  $T_{2x}'(2)$ .

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

9.13 Repeat Steps 9.8-9.12 until there are at least four points in the linear BET range. This will normally be from  $P/P_0 = 0.04$  to 0.20 or 0.25. Designate the pressures as  $P_1(i)$  and  $P_2(i)$ , manifold temperature as  $T'(i)$ , and the extra-volume temperatures as  $T_{1x}(i)$  and  $T_{2x}(i)$ . ( $i = 3$  to  $n$ , where  $n$  is total number of points.)

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

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

9.16 Backfill the sample tube with the same gas used in 7.2 to about atmospheric pressure. Close the *S* valve.

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

## 10. Calculations

10.1 Calculate the mass of sample  $W_s$ , as follows:

$$W_s = W_2 - W_1 \quad (1)$$

10.2 Calculate the dead-space,  $V_s$  as follows:

$$V_s = \left( \frac{T_s V_d}{P_{H_2}} \right) \left( \frac{P_{H_1}}{(T_{H_1} + 273.2)} - \frac{P_{H_2}}{(T_{H_2} + 273.2)} \right) \quad (2)$$

NOTE 5—The user should consult IUPAC<sup>7</sup> for the latest value of

<sup>7</sup> IUPAC Secretariat, PO Box 13757, Research Triangle Park, NC 27709-3757.

absolute zero to use in these calculations, as 273.2 was current for this revision.

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

10.3.1 For pressures  $P_1(i)$  and  $P_2(i)$ , see 5.1.3, 9.3, 9.6, 9.8, 9.11, and 9.13.

10.3.2 For vapor pressures  $P_o(i)$ , or liquid nitrogen temperatures,  $T_s(i)$ , see 5.7, 9.7, and 9.12.

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

$$P_o(i) = -107293 + 4269.71[T_s(i)] - 57.3616[T_s(i)]^2 + 0.261431[T_s(i)]^3 \quad (3)$$

10.3.3 For manifold temperatures  $T_1'(i)$  and  $T_2'(i)$ , see 5.6, 9.3, 9.6, 9.8, 9.11, and 9.13.

10.3.4 Determine whether valve  $EV$  is open. If not,  $V_x = 0$ , see 5.1.7.

10.3.5 For extra-volume bulb temperatures  $T_{1x}'(i)$  and  $T_{2x}'(i)$ ; see 9.3, 9.6, 9.8, and 9.11.

10.4 For each point,  $i = 1, 2 \dots n$ , calculate the following:

10.4.1  $X(i)$  = relative pressure =  $P_2(i)/P_o(i)$

10.4.2 Manifold and extra-volume bulb temperatures in kelvins:

$$T_1(i) = T_1'(i) + 273.2 \quad (4)$$

$$T_2(i) = T_2'(i) + 273.2$$

$$T_{1x}(i) = T_{1x}'(i) + 273.2$$

$$T_{2x}(i) = T_{2x}'(i) + 273.2$$

10.4.3 Extra-volume bulb volume at manifold temperature  $T_1(i)$ :

$$V_{1x} = T_1(i) \times V_x/T_{1x}(i) \quad (5)$$

10.4.4 Volume of  $N_2$  in manifold + extra volume,  $S$  valve, closed to catalyst ( $\text{cm}^3$  STP):

$$V_1(i) = (V_d + V_x) \left( \frac{P_1(i)}{T_1(i)} \right) \left( \frac{273.2}{760} \right) \quad (6)$$

10.4.5 Extra-Volume bulb volume at manifold temperature  $T_2(i)$ :

$$V_{2x} = T_2(i) \times V_x/T_{2x}(i) \quad (7)$$

10.4.6 Volume of  $N_2$  in manifold + extra volume,  $S$  valve, open to catalyst ( $\text{cm}^3$  STP):

$$V_2(i) = (V_d + V_x) \left( \frac{P_2(i)}{T_2(i)} \right) \left( \frac{273.2}{760} \right) \quad (8)$$

See 5.1.1 and 5.1.7 for  $V_d$  and  $V_x$ .

10.4.7 Total inventory of nitrogen in the system ( $\text{cm}^3$  STP):

$$V_r(i) = V_r(i-1) + V_1(i) - V_2(i-1) \quad (9)$$

$$V_r(0) = 0$$

$$V_2(0) = 0$$

10.4.8 Volume of nitrogen in the dead-space ( $\text{cm}^3$  STP):

$$V_{ds}(i) = \left( \frac{273.2 V_s \times P_2(i)}{760 T_s} \right) \left( 1 + \frac{0.05 P_2(i)}{760} \right) \quad (10)$$

See 10.2 for  $V_s$ .

10.4.8.1 The deviation from the ideal gas law of nitrogen at liquid nitrogen temperature is 5 % at one atmosphere, proportional to pressure. Although the non-ideality constant should be applied *only* to the volume of nitrogen within the section of the sample cell that is immersed in the liquid nitrogen, the added complexity to the experimental procedure needed to determine the fraction of the volume at liquid nitrogen temperature is not justified by the increased accuracy.

10.4.9 The quantity of gas adsorbed ( $\text{cm}^3$  STP/g):

$$V_a(i) = \frac{V_1(i) - V_2(i) - V_{ds}(i)}{W_s} \quad (11)$$

See 10.1 for  $W_s$ .

10.4.10 The BET function, when  $X(i) \geq 0.04$ :

$$BET(i) = \left( \frac{X(i)}{V_a(i)} \right) \left( \frac{1}{[1 - X(i)]} \right) \quad (12)$$

10.5 Construct the BET plot, by plotting  $X(i)$  as the abscissa,  $BET(i)$  as the ordinates.

10.6 Using a straightedge, draw a line through the linear region. Deviations from the straight line, if any, should be below the line at low  $X(i)$ , above the line at high  $X(i)$ , but not apparent within the linear region.

10.7 Determine the slope ( $S$ ) and intercept ( $I$ ) of the straight line.

10.7.1 This is preferably done by a least squares calculation, choosing only those points which fall on the straight line. If a point in the linear region is not on the straight line, discard the run. It will generally be clear by inspection of the BET plot which points to choose to define the straight line. When the proper choice has been made, deviations of individual points from the straight line should not exceed about 0.6 % of the value of the ordinate. A deviation as large as 1 % is excessive.

10.8 Calculate  $V_m$ , the volume of adsorbate required to complete one statistical monolayer ( $\text{cm}^3$  STP/g)

$$V_m = 1/(S + I) \quad (13)$$

10.9 Surface area =  $4.353 \times V_m$ . This assumes a value of  $16.2 \text{ \AA}^2$  ( $1 \text{ \AA} = 0.1 \text{ nm}$ ) for the cross-sectional area of a nitrogen molecule.

## 11. Report

11.1 Report the surface area to three significant figures.

11.2 The report shall include pretreatment, and outgassing temperatures.

## 12. Precision and Bias <sup>8</sup>

12.1 *Test Program*—An interlaboratory study was conducted in which the surface area was measured on three different materials in seven different laboratories on nine different instruments. Each laboratory performed three replicate analysis on each of the samples over a period of time. All samples were degassed at  $300^\circ\text{C}$  under vacuum and evaluated at nominal  $P/P_o$  values of 0.08, 0.11, 0.14, 0.17, and 0.20. Practice E 691 was followed for the analysis of the data. Analysis details are in the research report.

<sup>8</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D32-1031.

12.2 *Precision*—Pairs of tests results obtained by a procedure similar to that described in the study are expected to differ in absolute value by less than 2.772 S, where 2.772 S is the 95% probability limit on the difference between two test results, and S is the appropriate estimate of standard deviation. Definitions and usage are given in Terminology E 456 and Practice E 177, respectively.

12.3 *Bias*—This test method is without known bias.

### 13. Keywords

13.1 catalyst; nitrogen adsorption; surface area

Sample	Test Results (consensus mean) m <sup>2</sup> /g	95% Repeatability Interval m <sup>2</sup> /g (%)	95% Reproducibility Interval m <sup>2</sup> (%)
RM8570	10.7	1.1 (10.4)	2.5 (23.0)
RM8571	160	8.9 (5.6)	9.8 (6.1)
RM8572	289	7.0 (2.4)	11.9 (4.1)

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