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Standard Test Method for Surface Area of Catalysts and Catalyst Carriers¹

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 (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 line.

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.

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

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2. Referenced Documents

2.1 *ASTM Standards:*

~~D3766 Terminology Relating to Catalysts and Catalysis³~~

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:* Definitions:

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

⁴ This test method is under the jurisdiction of ASTM Committee D-32 on Catalysts and is the direct responsibility of Subcommittee D32.01 on Physical-Chemical Properties.

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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*, Vol 05.03, volume information, refer to the standard's Document Summary page on the ASTM website.

- 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 = weight/mass of sample, g
- W_1 = tare weight/mass of sample tube, g
- W_2 = sample + tare weight/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, $^{\circ}\text{C}$
- T_{2x} = extra-volume bulb temperature after equilibrium, K
- $T_{2x}'(i)$ = extra-volume bulb temperature after equilibrium, $^{\circ}\text{C}$

4. Summary of Test 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. Apparatus⁴

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^3 , (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.

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).

NOTE1—See, for example, the article by Joy, A. S., *Vacuum*, Vol 3, 1953, p. 254, for a description of a constant-volume manometer. 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 cm^3 , known to the nearest 0.05 cm^3 . V_x includes the volume of the stopcock bore in the glass apparatus.

5.2 *Sample Tubes*, with volumes from 5 to 25100 cm^3 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.

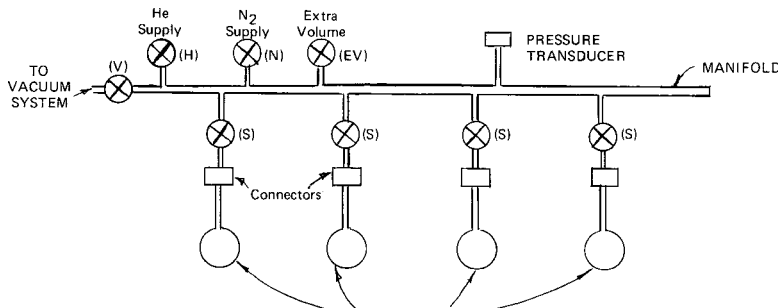


FIG. 1 Schematic Diagram of Surface Area Apparatus

⁴ Annual Book of ASTM Standards, Vol 14.02.

⁴ Automated equipment is commercially available.

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

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~~ *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 from which~~] *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 99.9 % 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-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.

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

7.4 Place the catalyst sample, whose weightmass 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. 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 weightmass 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

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*,²² BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*,²³ U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.