



Designation: ~~D4222-98~~ Designation: D 4222 – 03 (Reapproved 2008)

Standard Test Method for Determination of Nitrogen Adsorption and Desorption Isotherms of Catalysts ~~By~~and Catalyst Carriers 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.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 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:*³

D 3663 Test Method for Surface Area of Catalysts and Catalyst Carriers

D 3766 Terminology Relating to Catalysts and Catalysis

E 177 Practice for Use of the Terms Precision 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 *Definitions*—Consult Terminology ~~D 3766~~— See Terminology D 3766.

3.2 *Symbols:*

ASTM D4222-03(2008)
<https://standards.iteh.ai/catalog/standards/sist/2955803a-3506-4170-b2f3-6251946a4647/astm-d4222-032008>

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.

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 This test 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 April 1, 2008. Published April 2008. Originally approved in 1983. Last previous edition approved in 2003 as D 4222-03.

³ Annual Book of ASTM Standards, Vol 05.03.

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

⁵ 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 14.02, volume information, refer to the standard's Document Summary page on the ASTM website.

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 mass of sample, g.
W_1	= tare weight of sample tube, g.
W'_2	= sample mass + tare weight of tube after degassing, g.
W_2	= sample mass + 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 see 12.4.3.
V_2	= see 12.4.7 see 12.4.4.
V_t	= see 12.4.8. see 12.4.5.
$V_{ad(de)}$	= see 12.4.10. 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 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 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).

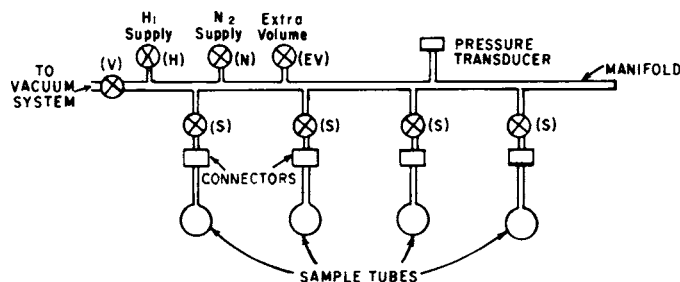


FIG. 1 Schematic Diagram of Adsorption Apparatus

- 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 cm³ to 25100 cm³ depending on the application.
- 6.3 *Heating Mantles or Small Furnaces*.
- 6.4 *Dewar Flasks*.
- 6.5 *Laboratory Balance*, with 0.1-mg (10⁻⁷kg) sensitivity.
- 6.6 ~~*Thermometer*~~ 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 that gives (*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 % 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-cm³ sample tube is preferred for samples not exceeding about 1 g. However, to avoid boiling when degassing is started, a 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 weightmass as *W*₁.

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