

Standard Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting¹

This standard is issued under the fixed designation D1434; 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.

ε¹ NOTE—Editorial corrections were made in September 2015.

1. Scope

- 1.1 This test method covers the estimation of the steady-state rate of transmission of a gas through plastics in the form of film, sheeting, laminates, and plastic-coated papers or fabrics. This test method provides for the determination of (1) gas transmission rate (GTR), (2) permeance, and, in the case of homogeneous materials, (3) permeability.
 - 1.2 Two procedures are provided:
 - 1.2.1 *Procedure M*—Manometric.
 - 1.2.2 Procedure V—Volumetric.
- 1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.
- 1.4 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:²

D618 Practice for Conditioning Plastics for Testing
D1898 Practice for Sampling of Plastics (Withdrawn 1998)³

3. Terminology

- 3.1 Definitions of Terms Specific to This Standard:
- 3.1.1 gas transmission rate, GTR—the quantity of a given gas passing through a unit of the parallel surfaces of a plastic

film in unit time under the conditions of test. The SI unit of GTR is 1 $\text{mol/}(\text{m}^2 \cdot \text{s})$. The test conditions, including temperature and partial pressure of the gas on both sides of the film, must be stated. Other factors, such as relative humidity and hydrostatic pressure, that influence the transport of the gas must also be stated. The inch-pound unit of GTR, a commonly used unit of GTR, is 1 mL (STP)/($\text{m}^2 \cdot \text{d}$) at a pressure differential of one atmosphere.

- 3.1.2 *permeance*, *P*—the ratio of the gas transmission rate to the difference in partial pressure of the gas on the two sides of the film. The SI unit of permeance is 1 mol/ (m²·s·Pa). The test conditions (see 5.1) must be stated.
- 3.1.3 permeability, \underline{P} —the product of the permeance and the thickness of a film. The permeability is meaningful only for homogeneous materials, in which it is a property characteristic of the bulk material. This quantity should not be used unless the constancy of the permeability has been verified using several different thicknesses of the material. The SI unit of \underline{P} is 1 mol/(m·s·Pa). The test conditions (see 3.1) must be stated.

Note 1—One millilitre (STP) is $44.62 \, \mu \text{mol}$, one atmosphere is $0.1013 \, \text{MPa}$, and one day is $86.4 \times 10^3 \, \text{s}$. GTR in SI units is obtained by multiplying the value in inch-pound units by 5.160×10^{-10} . Additional units and conversions are shown in Appendix X1.

3.1.4 *steady state*—the state attained when the amount of gas absorbed in the film is in equilibrium with the flux of gas through the film. For Method V, this is obtained when the GTR is constant.

4. Summary of Test Method

- 4.1 The sample is mounted in a gas transmission cell so as to form a sealed semibarrier between two chambers. One chamber contains the test gas at a specific high pressure, and the other chamber, at a lower pressure, receives the permeating gas. Either of the following procedures is used:
- 4.1.1 *Procedure M*—In Procedure M the lower pressure chamber is initially evacuated and the transmission of the gas through the test specimen is indicated by an increase in pressure.
- 4.1.2 *Procedure V*—In Procedure V the lower pressure chamber is maintained near atmospheric pressure and the

¹ This test method is under the jurisdiction of ASTM Committee F02 on Flexible Barrier Packaging and is the direct responsibility of Subcommittee F02.10 on Permeation.

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² 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 The last approved version of this historical standard is referenced on www.astm.org.

transmission of the gas through the test specimen is indicated by a change in volume.

5. Significance and Use

5.1 These measurements give semiquantitative estimates for the gas transmission of single pure gases through film and sheeting. Correlation of measured values with any given use, such as packaged contents protection, must be determined by experience. The gas transmission rate is affected by conditions not specifically provided for in these tests, such as moisture content (Note 2), plasticizer content, and nonhomogeneities. These tests do not include any provision for testing seals that may be involved in packaging applications.

Note 2—The tests are run using gas with 0 % moisture changes.

- 5.2 Interlaboratory testing has revealed that permeances measured by these procedures exhibit a strong dependence on the procedure being used, as well as on the laboratory performing the testing. Agreement with other methods is sometimes poor and may be material-dependent. The materials being tested often affect the between-laboratory precision. The causes of these variations are not known at this time. It is suggested that this method not be used for referee purposes unless purchaser and seller can both establish that they are measuring the same quantity to a mutually agreed upon level of precision.
- 5.3 Use of the permeability coefficient (involving conversion of the gas transmission rate to a unit thickness basis) is not recommended unless the thickness-to-transmission rate relationship is known from previous studies. Even in essentially homogeneous structures, variations in morphology (as indicated, for example, by density) and thermal history may influence permeability.

6. Test Specimen

- 6.1 The test specimen shall be representative of the material, free of wrinkles, creases, pinholes, and other imperfections, and shall be of uniform thickness. The test specimen shall be cut to an appropriate size (generally circular) to fit the test cell.
- 6.2 The thickness of the specimen shall be measured to the nearest $2.5~\mu m$ with a calibrated dial gage (or equivalent) at a minimum of five points distributed over the entire test area. Maximum, minimum, and average values should be recorded. An alternative measure of thickness involving the weighing of a known area of specimens having a known density is also suitable for homogeneous materials.

7. Conditioning

- 7.1 Standard Conditioning—Condition all test specimens at $23 \pm 2^{\circ}$ C in a desiccator over calcium chloride or other suitable desiccant for not less than 48 h prior to test in accordance with Practice D618, for those tests where conditioning is required. In cases of disagreement, the tolerances shall be $\pm 1^{\circ}$ C.
- 7.2 Alternative Conditioning—Alternatives to 7.1 may be used for conditioning the specimens provided that these conditions are described in the report.



FIG. 1 Manometric Gas Transmission Cell

8. Sampling

8.1 The techniques used in sampling a batch of material to be tested by these procedures must depend upon the kind of information that is sought. Care should be taken to ensure that samples represent conditions across the width and along the length of rolls of film. Practice D1898 provides guidelines for deciding what procedures to use in sampling a batch of material. Enough specimens must be tested to ensure that the information obtained is representative of the batch or other lot size being tested.

PROCEDURE M

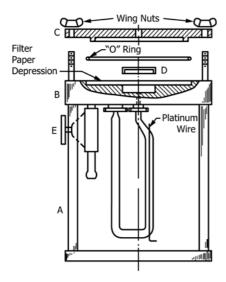
(Pressure changes in the manometric cell may be determined by either visual or automatic recording.)

MANOMETRIC VISUAL DETERMINATION

9. Apparatus

- 9.1 The apparatus shown in Fig. 1 and Fig. 2 consists of the following items:⁴
- 9.1.1 *Cell Manometer System*—The calibrated cell manometer leg, which indicates the pressure of transmitted gas, shall consist of precision-bore glass capillary tubing at least 65 mm long with an inside diameter of 1.5 mm.
- 9.1.2 *Cell Reservoir System*, consisting of a glass reservoir of sufficient size to contain all the mercury required in the cell.
- 9.1.3 Adapters—Solid and hollow adapters for measurement of widely varying gas transmission rates. The solid adapter provides a minimum void volume for slow transmission rates. The hollow adapter increases the void volume by about a factor of eight for faster transmission rates.

⁴ The sole source of supply of the apparatus (Dow gas transmission cell) known to the committee at this time is Custom Scientific Instruments, Inc., Whippany, NJ. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, ¹ which you may attend.



- A-Supporting Legs
- B—Lower Plate
- C-Upper Plate
- D—Adapter
- E-Vacuum Valve

FIG. 2 Schematic View of Gas Transmission Cell

- 9.1.4 *Cell Vacuum Valve*, capable of maintaining a vacuumtight seal.⁵
- 9.1.5 *Plate Surfaces*, that contact the specimen and filter paper shall be smooth and flat.
 - 9.1.6 O-Ring, for sealing the upper and lower plates.
- 9.1.7 *Pressure Gage*, mechanical or electrical type with a range from 0 to 333 kPa absolute. Used for measuring upstream gas pressure.
- 9.1.8 *Barometer*, suitable for measuring the pressure of the atmosphere to the nearest 133 Pa.
- 9.1.9 *Vacuum Gage*, to register the pressure during evacuation of the system to the nearest 13 Pa.
- 9.1.10 *Vacuum Pump*, capable of reducing the pressure in the system to 26 Pa or less.
- 9.1.11 *Needle Valve*, for slowly admitting and adjusting the pressure of the test gas.
- 9.1.12 *Cathetometer*, to measure the height of mercury in the cell manometer leg accurately. This instrument should be capable of measuring changes to the nearest 0.5 mm.
- 9.1.13 *Micrometer*, to measure specimen thickness, graduated to 2.5 μ m (0.1 mil) or better.
- 9.1.14 *Elevated-Temperature Fittings*—Special cell fittings are required for high-temperature testing.

10. Materials

10.1 *Test Gas*—The test gas shall be dry and pure. The ratio of the volume of gas available for transmission to the volume of gas transmitted at the completion of the test shall be at least 100:1.

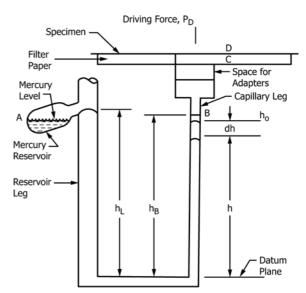


FIG. 3 Cell Manometer with Test Specimen in Place

- 10.2 *Mercury*—Mercury used in the cell shall be triple distilled, checked regularly for purity, and replaced with clean mercury when necessary.
- 10.2.1 Warning—Very low concentrations of mercury vapor in the air are known to be hazardous. Guidelines for using mercury in the laboratory have been published by Steere. Be sure to collect all spilled mercury in a closed container. Transfers of mercury should be made over a large plastic tray. Under normal daily laboratory-use conditions, the cells should be cleaned about every 3 months. Dirty mercury is indicated when the drop of the capillary becomes erratic or when mercury clings to the side of the capillary, or both. Whenever such discontinuities occur, the mercury should be removed and the cell cleaned as follows:
 - (1) Wash with toluene (to remove greases and oils).
 - (2) Wash with acetone (to remove toluene).
 - (3) Wash with distilled water (to remove acetone).
- (4) Wash with a 1 + 1 mixture of nitric acid and distilled water (to remove any mercury salts that may be present). This operation may be repeated if necessary in order to ensure complete cleaning of glassware.
 - (5) Wash with distilled water (to remove nitric acid).
 - (6) Wash with acetone (to remove water).
- (7) Dry the cell at room temperature or by blowing a small amount of clean dry air through it.

11. Calibration

- 11.1 Each cell should be calibrated at the test temperature as follows (Fig. 3):
- 11.1.1 Determine the void volume of the filter paper from the absolute density of its fiber content (Note 3), the weight of the filter paper, and its apparent volume (Note 4). Express the void volume determined in this way in microlitres and designate as V_{CD} .

⁵ The sole source of supply of the apparatus (Demi-G Valve (¼-in. IPS)) known to the committee at this time is G. W. Dahl Co., Inc., Bristol, RI. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, ¹ which you may attend.

⁶ Steere, N. E. "Mercury Vapor Hazards and Control Measures" in *Handbook of Laboratory Safety*, N. V. Steere, Ed., CRC Press Inc., Boca Raton, FL, 1979.

Note 3—Any high-grade, medium-retention qualitative nonashing cellulosic filter paper, 90 mm in diameter will be satisfactory for this purpose. Cellulose fiber has an approximate density of 1.45 g/mL.

Note 4—The apparent volume may be calculated from the thickness and diameter of the filter paper.

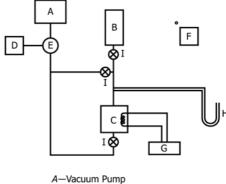
11.1.2 Determine the volume of the cell manometer leg from B to C,Fig. 3, by mercury displacement. (Since the void volume of the adapters is included in this part of the calibration, the volume from B to C should be determined twice, once with the solid adapter in place, and once with the hollow.) This volume is obtained by dividing the weight of the mercury displaced by its density (Note 5). Determine this volume to nearest 1 μ L and designate as V_{BC} .

Note 5—The density of mercury at 23°C is 13.54 g/mL.

- 11.1.3 Determine the volume, in microlitres, of the cell manometer leg from A to B, Fig. 3, by mercury displacement. Determine the average cross-sectional area of the capillary by dividing this volume by the length (expressed to the nearest 0.1 mm) from A to B.Determine this area to the nearest 0.01 mm² and designate as a_c .
- 11.1.4 Determine the area of the filter paper cavity to the nearest 1 mm^2 . Designate this area as A, the area of transmission.
- 11.1.5 Pour the mercury from the reservoir into the manometer of the cell by carefully tipping the cell. Record the distance from the datum plane to the upper calibration line B in the capillary leg as h_B . Record the distance from the datum plane to the top of the mercury meniscus in the reservoir leg as h_L . Determine h_B and h_L to the nearest 0.5 mm.
- 11.2 NBS Standard Reference Material 1470⁷ is a polyester film whose permeance to oxygen gas has been certified for a range of experimental conditions. The calibration steps in 11.1 can be verified by comparing measurements obtained using this method of test in the user's laboratory with the values provided on the certificate accompanying the SRM.

12. Procedure

- 12.1 Transfer all the mercury into the reservoir of the cell manometer system by carefully tipping the cell in such a way that the mercury pours into the reservoir.
 - 12.2 Insert the appropriate adapter in the cell body.
 - 12.3 Center a filter paper in the lower plate cavity.
- 12.4 Apply a light coating of vacuum grease on the flat metal that the surface of the specimen will contact. Avoid excessive grease.
- 12.5 Place the conditioned specimen smoothly on the lower lightly greased plate so that it covers the filter paper and the entire exposed face of the lower plate.



B—Test Gas Cylinders

C-Gas Transmission Cell

D-Vacuum Gage

E—Trap

F—Barometer

G-Automatic Recorder (Optional)

H-Mercury Manometer

I-Needle Valve

FIG. 4 Component Arrangement of Gas Transmission Equipment

- 12.6 Locate the O-ring on the upper plate; then carefully position this plate over the specimen and fix the plate with uniform pressure to ensure a vacuum-tight seal.
- 12.7 Connect the line in which the test gas will be subsequently admitted to the upper plate. (The entire cell is now directly connected to the test gas line.)
- 12.8 Connect the vacuum source to the nipple attached to the cell vacuum valve. Evacuate the bottom of the cell; then, with the bottom still being evacuated, evacuate the top of the cell. Close off the vacuum line to the top of the cell; then close the line to the bottom (Fig. 4).
- 12.9 Flush the connecting line and the top of the chamber with test gas.
- 12.10 Reevacuate the system in the same manner as 12.8. The cell manometer system should be evacuated to a pressure of 26 Pa or less, as indicated on the vacuum gage.
- 12.11 Pour mercury from the reservoir into the manometer system of the cell by carefully tipping the cell. The height of the mercury in the capillary leg should be at approximately the same level as line *B*(Fig. 3) and stationary.

Note 6—A leak is indicated if the height of the mercury does not remain stationary. If such a leak occurs, discontinue the test and repeat the entire procedure. (If a leak occurs on a second trial, this may indicate a mechanical failure of the equipment.)

- 12.12 Record the height of the mercury in the capillary leg, h_o , at the start of each test, that is, immediately before the test gas has been admitted to the top of the cell.
- 12.13 After a suitable estimated time for attaining steady-state conditions, record the height of the mercury in the capillary leg, h_o , to the nearest 0.5 mm and the elapsed time, t_o , to the nearest 1 min.
- 12.14 Record the height of the mercury, h, in the capillary leg to the nearest 0.5 mm versus time, t, in hours, to the nearest 1 min. Take several readings (at least six are recommended) during the test. Calculate the function g(h) for each t as defined

⁷ The sole source of supply of the apparatus known to the committee at this time is Office of Standard Reference Materials, National Bureau of Standards, Washington, DC 20234. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

in 13.1. Plot these values versus time, $(t-t_o)$, and construct the best straight line through these points. Use any observed values of h and t for h_o and t_o , respectively, if these values are within the steady-state region. A nonlinear plot of g(h) versus $(t-t_o)$ that does not pass through the origin could indicate an improper selection of h_o and t_o ; a new selection should then be made by using a larger mercury depression for the initial conditions.

Note 7—If, after all the mercury has been displaced from the capillary, any doubt exists as to the attainment of steady state, perform a check as

- (1) Return the mercury to the reservoir.
- (2) Reevacuate the bottom of the cell only, leaving the top pressurized with test gas.
- (3) Repeat 12.11, 12.13, and 12.14.
- 12.15 Return the mercury in the capillary leg to the reservoir by tipping the cell upon completion of the test and prior to opening the cell vacuum valve.
- 12.16 Remove the specimen from the cell and measure the thickness with a micrometer (Note 8). Record the average of five determinations made uniformly throughout the specimen to the nearest 2.5 µm.

Note 8-If there is reason to believe that the specimen will expand or contract during transmission, the thickness should be measured prior to 12.5, as well as after transmission. If any change in thickness occurs, a note to this effect shall be included with the results.

- 12.17 Test three specimens with each gas.
- 12.18 If the requirements of 12.14 are not met in the normal atmospheric pressure test, repeat the procedure at a higher (up to 304 kPa) or lower (not less than 50 kPa) test pressure.

13. Calculation

13.1 Calculate the permeance, P, in SI units from the following relationship (Note 9):

$$P = g(h)/(t - t_o)$$
 (1)

where:

$$g(h) = -\frac{1}{ART} \left[\left[V_f + a \left(p_u + h_B - h_L \right) \right] \right]$$

$$\cdot 1 n \left\{ 1 - \frac{\left(h_o - h \right)}{P_u - \left(h_L - h_o \right)} \right\} + 2 a \left(h_o - h \right) \right]$$
(2)

= area of capillary \overline{AB} , mm², a_c

= area of transmission, cm², A

= height of mercury in the capillary leg at the start of the actual transmission run, after steady-state conditions have been attained, mm,

= height of mercury in cell capillary leg at any given

= maximum height of mercury in the cell manometer h_{R} leg from the datum plane to upper calibration line B,

= height of mercury in cell reservoir leg from datum plane to top of mercury meniscus, mm,

= upstream pressure of gas to be transmitted,

= universal gas constant 8.3143×10^3 L·Pa/(mol·K),

time at the start of the actual transmission run, h, after steady-state conditions have been attained,

= time, h,

= absolute temperature, K, V_{BC} = volume from B to C, μ L,

 V_{CD} = void volume of depression, μ L, and V_f = $(V_{BC} + V_{CD})$, μ L.

Note 9—The derivation of this equation is given in Appendix X2. Refer to Fig. 3 for location of symbols used in this equation.

13.2 A test result is defined as a single determination of the permeance of an individual sheet of material.

MANOMETRIC RECORDING DETERMINATION

14. Apparatus

- 14.1 The description of the apparatus is identical to that in Section 9, with the omission of 9.1.12, which does not apply in this procedure, and the addition of the following apparatus:
- 14.2 Resistance-Recording Instrument—A resistancerecording instrument suitably connected to a uniform-diameter platinum wire (Note 10) that runs the calibrated length of the cell manometer leg shall be employed to measure changes in height of the mercury in the cell manometer leg versus time. This instrument shall be capable of measuring such changes to the nearest 0.5 mm.

Note 10—A recommended automatic recording device (Fig. 4 shows a simplified schematic of a setup utilizing an automatic recorder) consists of No. 44 platinum wire (with a resistance of 0.8 Ω /cm) with No. 30 tungsten leads to the glass. These are connected by means of No. 16 gage three-conductor copper wire to a suitable ten-turn potentiometer in series with a resistance recorder whose full-scale range is 10 to 15Ω .

15. Materials

15.1 Same as Section 10.

16. Calibration

- 16.1 Same as Section 11, but should also include the following:
- 16.2 The recording instrument with the cell, lead wires, and external resistance (Note 11) in series as used in the test shall be calibrated at test temperature initially and every time after a cell has been cleaned or repaired.

Note 11-The external resistance should be so chosen to permit complete traverse of the chart by the pen when a change in the height of mercury equal to the height of A to B occurs (Fig. 3).

- 16.3 The recording system shall be calibrated as follows:
- 16.3.1 Allow the cell to come to constant temperature at test temperature.
- 16.3.2 With the top of the cell removed and the vacuum valve open, pour the mercury into the cell manometer leg such that the mercury is approximately at the same level as line B(Fig. 3) and relatively stationary. Adjust the external resistance of the recorder so that the pen indicates a chart position of zero.

⁸ The sole source of supply of the apparatus (Minneapolis-Honeywell Regulator Co. 60V Model 153X64W8-X-41 resistance recorder) known to the committee at this time is Insco Co., Division of Barry Controls, Inc., Groton, MA. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. It is recommended that a quick-change variable speed chart drive be installed in the recorder.

- 16.3.3 Vary the height of the mercury column and note the position indicated by the chart pen so that a plot of chart position as ordinate versus mercury height as abscissa is obtained. A straight line should result.
- 16.3.4 Determine the rate of chart paper travel to the nearest 2.54 mm (0.1 in.)/h.
- 16.4 See 11.2 for the use of NBS Standard Reference Material 1470 in checking the calibration of the permeance measuring apparatus.

17. Procedure

- 17.1 Same as Section 12, with the following exceptions:
- 17.2 Adjust the pen of the resistance recording instrument by means of the external resistance so that the pen position corresponds with the height of mercury in the capillary leg as determined in Section 16.
- 17.3 For best results, set the chart to run at a speed that will plot the gas transmission curve at a slope of about 45° (Note 12). Once experience is gained, the proper chart speed is easily selected.

Note 12—This applies only to charts that have a variable-speed drive.

18. Calculation

- 18.1 For several values of t (at least six are recommended), read h from the recorder chart and plot the function g(h) versus t as defined in 12.14.
- 18.2 Calculate the permeance from the equations given in 13.1.
- 18.3 A test result is defined as the value of a single individual determination of permeance of a film.

PROCEDURE V

(Volumetric determinations may be made with several similar type apparatus.)

19. Apparatus

- 19.1 Volumetric Gas Transmission Cell⁹, shown in Fig. 5.
- 19.2 *Precision Glass Capillaries* or manometers with various diameters (0.25, 0.50, and 1.0 mm are recommended). The glass capillaries should have a suitable U-bend to trap the manometer liquid and a standard-taper joint to fit into the cell.
- 19.3 *Cathetometer* or suitable scale for measuring changes in meniscus position to the nearest 0.5 mm.
 - 19.4 Temperature Control:
- 19.4.1 A temperature-control liquid bath is recommended for controlling the temperature of the cell body to ± 0.1 °C.
- 19.4.2 The apparatus should be shielded to restrict the temperature variations of the capillary to ± 0.1 °C during the test.
- ⁹ The sole source of supply of suitable cells known to the committee at this time is Custom Scientific Instruments, Whippany, NJ. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, ¹ which you may attend.

- 19.5~Micrometer, to measure specimen thickness, to the nearest $2.5~\mu m$ at a minimum of five points distributed over the entire test area. Maximum, minimum, and average values shall be recorded.
- 19.6 *Barometer*, suitable for measuring the pressure of the atmosphere to the nearest 133 Pa.
- 19.7 *Pressure Gage*, precision mechanical or electrical type for measuring absolute pressure over the range from 0 to 333 kPa.

20. Materials

- 20.1 Cylinder of Compressed Gas, of high purity equipped with pressure reducing valves.
- 20.2 Capillary Liquid—4-Methyl-2-pentanone (methyl isobutyl ketone) (Note 13) or other appropriate liquid colored with a suitable dye (Note 14).

Note 13—4-Methyl-2-pentanone has a vapor pressure of 933 Pa at 23°C. Erroneous results may be obtained in some cases, if the attainment of this equilibrium causes slug movement in the capillary. This may take an appreciable time, especially in small capillaries, and thereby lead to an erroneous answer. Also, the vapor of 4-methyl-2-pentanone may cause swelling of some materials, which will result in a change in the permeation rate.

Note 14—Mercury is not recommended for the capillary liquid except for use in calibrating cross-sectional areas because of contact angle hysteresis and resulting pressure errors (about 3 cm Hg in a 0.5-mm capillary), plus the much smaller readings resulting from the greater density of mercury as compared to 4-methyl-2-pentanone.

20.3 *Filter Paper*—Any high grade, medium-retention, non-ashing cellulosic filter paper.

Note 15—Other porous filters such as sintered metal have been found to be satisfactory.

21. Calibration

- 21.1 **Warning**—Very low concentrations of mercury vapor in the air are known to be hazardous. Be sure to collect all spilled mercury in a closed container. Transfers of mercury should be made over a large plastic tray.
- 21.2 Place a column of clean mercury, approximately 70 mm long, in the capillary and measure its length with a cathetometer.
- 21.3 Transfer all of the mercury to a tared beaker and obtain the weight of the mercury on an analytical balance. Discard the mercury to be cleaned.
- 21.4 Since the density and weight of the column of mercury are known, its volume, V_M , in microlitres at room temperature (23°C), is given by the equation:

$$V_M = 10^3 \times W/13.54 \tag{3}$$

where:

W = weight of the mercury, g, and 13.54 g/mL = density of mercury at 23°C.

Since for a cylinder:

$$V_{M} = a_{c}l \tag{4}$$

where:

 $a_c = \text{cross-sectional area, mm}^2$, and

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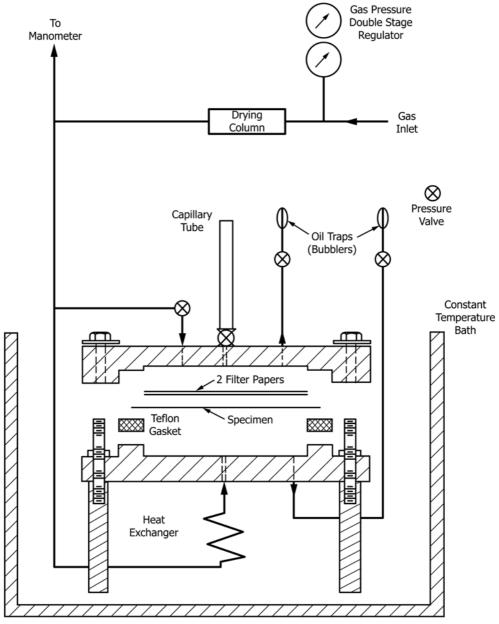


FIG. 5 Volumetric Gas Transmission Cell

l = length of mercury column, mm, then:

$$a_c = V_M / l \tag{5}$$

- 21.5 Calibrations shall be made at 23°C.
- 21.6 See 11.2 for the use of NBS Standard Reference Material 1470 in checking the calibration of permeance-measuring apparatus.

22. Procedure

- 22.1 Center a piece of filter paper in the upper portion of the test cell.
- 22.2 Place the conditioned specimen smoothly on the upper portion of the test cell.

- 22.3 Lightly grease the rubber gasket, O-ring, or flat metal that the surface of the specimen will contact. Avoid excessive grease.
- 22.4 Place the upper half of the cell on the base and clamp it firmly to achieve a tight seal.
- 22.5 Apply positive test gas pressure to both sides of the cell, flushing out all air before closing the outlet vent. A recommended flushing time is at least 10 min at a flow rate of about 100 mL/min.

Note 16—The pressure differential is obtained by monitoring and adjusting the gage pressure on the high-pressure side of the cell so that it is the desired amount above the observed barometric pressure on the open (downstream) side.

22.6 Introduce an approximately 20-mm liquid slug (keep it intact) at the top of the capillary (Note 17) and close the upper outlet vent after the slug rests on the bottom of the capillary (Note 18). The capillary shall be clean and free of obstructions.

Note 17—It is convenient to add the liquid slug to the capillary with a syringe fitted with a long thin needle to aid proper insertion.

Note 18—After lowering the liquid slug into the capillary, sufficient time must be allowed for drainage down the inner wall of the capillary before beginning to take a series of readings.

- 22.7 Adjust the pressure across the specimen to maintain the exact pressure differential desired.
- 22.8 Small leaks around connections and joints can often be detected with soap solutions, but in some cases it may be necessary to immerse the cell in water while applying gas pressure, in order to observe bubbles at leak sites. Small leaks occurring on the high-pressure side of the cell should not be considered significant.
- 22.9 After a time interval estimated to be sufficient for attaining steady-state, begin measuring the displacement of the slug, using a stop watch (or clock) and distance scale maintained on the capillary or cathetometer. Take measurements at the top of the meniscus.
- 22.10 On completion of the run, return the slug to its starting position by slightly opening the low-pressure vent.
- 22.11 Repeat the measurement as necessary to assure the attainment of a steady-state condition.

Note 19—The time required to reach steady state will depend upon the nature of the specimen, its thickness, and the applied pressure differential. For specimens of low permeability, changes in ambient pressure may interfere, particularly if long periods of test and repeated measurements are required to obtain reliable results.

23. Calculation

- 23.1 Plot the capillary slug position versus elapsed time and draw the best straight line through the points so obtained.
- 23.2 Calculate the volume-flow rate, V_r , in microlitres per second of transmitted gas from the slope of this line as follows:

$$V_r = \text{slope} \times a_c$$
 (6)

where:

slope = rate of rise of capillary slug, mm/s, and a_c = cross-sectional area of capillary, mm².

23.3 Calculate the gas transmission rate (GTR) in SI units as follows:

$$GTR = p_o \times V_r / (ART)$$
 (7)

where:

 $A = \text{transmitting area of specimen, mm}^2$,

 p_o = ambient pressure, Pa,

 $R = \text{universal gas constant } (R = 8.3143 \times 10^3 \text{ L} \cdot \text{Pa/} (\text{mol} \cdot \text{K})), \text{ and}$

T = ambient temperature, K.

23.4 Calculate the permeance, *P*, in SI units as follows:

$$P = \text{GTR}/(p - p_o) \tag{8}$$

where p is the upstream pressure in pascals.

23.5 A test result is defined as the value obtained from an individual determination of the permeance of a specimen.

Note 20—The reliability of the measurements can be assessed to some extent by making measurements on SRM 1470 (see 11.2).

24. Report

- 24.1 The report shall include the following:
- 24.1.1 Procedure used,
- 24.1.2 Description of the sample, including identification of composition, presence of wrinkles, bubbles, or other imperfections, and manufacturer, if known.
- 24.1.3 Test gas used, and test gas composition, including purity,
- 24.1.4 Test temperature in degrees Celsius, and the pressure difference used,
- 24.1.5 Each thickness measurement made plus the average for each specimen. When five or more thickness measurements are made per specimen, the average, standard deviation and number of measurements made may be reported instead of each measurement, and
- 24.1.6 Each measurement obtained plus the appropriate averages in the units of choice. When five or more replicates are obtained the average, standard deviation, and number of replicates may be substituted for the above.

25. Precision

- 25.1 General—An interlaboratory evaluation of this method has been conducted.¹⁰ Ten laboratories participated in determining the permeability, *P*, of four materials to oxygen and carbon dioxide. The results from the round robin are summarized in Table 1. The results demonstrate clearly that the precision of the results obtained depends strongly, but in an unpredictable manner, on the combination of material and gas being tested. Potential users of this method must, therefore, use their own experience in assessing the precision of the results being obtained.
- 25.1.1 The contribution arising from the between-laboratory component of the variance is larger than that from the within-laboratory component for all materials. This indicates that there are systematic differences between the procedures used in different laboratories. The magnitudes of these differences must be determined whenever two laboratories are comparing results for referee purposes.
- 25.2 Repeatability—Approximately 95 % of all test results will lie within $2(CV_r)$ % of the mean of all test results obtained within a given laboratory on a given material. Typical values of (CV_r) are given in Table 1.
- 25.3 Reproducibility—Approximately 95 % of all test results obtained in different laboratories will lie within $2(CV_R)$ % of the population mean of such values. Typical values of (CV_R) for the material examined in the round robin are shown in Table 1.
- 25.4 Users who wish to test materials other than those considered in the round robin must make their own assessment

 $^{^{\}rm 10}$ Supporting data are available from ASTM Headquarters. Request RR:D20-0049.

TABLE 1 Results of Round-Robin Evaluation

Material	Gas	P (barrers) ^A	<u>P</u> (Inch- pound units) ^B	(<i>S_r</i>) (barrers)	(S_L) (barrers)	(CV _r) (%)	(CV _R) (%)
Polyester film (100 A Mylar®)	02	0.028	72.4	0.006	0.012	21	48
Polyester film (65 HS Mylar®)	02	0.048	124	0.003	0.019	6	40
Polyester film (100 A Mylar®)	CO ₂	0.094	243	0.007	0.014	7	16
Polyester film (65 HS Mylar®)	CO2	0.18	466	0.009	0.028	5	16
Poly(propylene) film	0,	1.29	3340	0.15	0.28	12	25
Poly(ethylene) film	02	1.94	5020	0.08	0.23	4	13
Poly(propylene) film	CŌ ₂	4.85	12550	0.45	0.69	9	17
Poly(ethylene) film	CO ₂	7.62	19710	0.40	0.94	5	13

 $(S_r)_i$ = the within-laboratory standard deviation of a single laboratory result for material *i*.

 $(S_I)_i$ = the square root of the between-laboratory component, of variance.

 $(CV_r)_i = 100 (S_r)_i / P_i$

 $(CV_R)_r = 100[(S_r)_i^2 + (S_L)_i^2]1/2/P_i$

of the precision of their results. Variability between specimens is likely to be a dominant factor in such measurements.

APPENDIXES

(Nonmandatory Information)

X1. UNITS IN GAS TRANSMISSION MEASUREMENTS

- X1.1 SI units for various quantities related to transmission of gases can be derived by recalling that the present standard defines the transmission rate, *G*, as the quantity of gas crossing a unit area of a barrier in unit time. Since the SI base unit for quantity of matter is the mole, the SI base unit for length is the metre, and the SI base unit for time is the second, the derived SI unit of transmission rate should be the mol/m²·s. Similarly, since the permeance, *P*, is defined as the ratio between the transmission rate and the partial pressure differential across the barrier, and since the SI unit of pressure is the pascal, appropriate SI units for permeances are mol/m²·s·Pa. Finally, for a homogeneous material, the permeability, *P*, is defined as the product of the permeance and the thickness of the film, which leads to the mol/m·s·Pa as the appropriate SI units.
- X1.1.1 Appropriate unit prefixes must be attached to the SI units in order to bring the values that are actually observed onto a convenient scale for reporting or further manipulation. The following example will help to clarify this point: Consider a homogeneous film with a permeability of 1 amol/m·s·Pa (1 amol = 10^{-18} mol) and a thickness of 25.4 m. The permeance of this film would be 39.37 fmol/m²·s·Pa (1 fmol = 10^{-15} mol). If a pressure differential of one standard atmosphere (1 atm = 0.10132 MPa) were imposed across the barrier, the gas transmission rate would be 3.989 nmol/m²·s (1 nmol = 10^{-9} mol). Using the ideal gas law to convert this to inch-pound units yields a value of 7.725 mL(STP)/m²·d, which is a reasonable value for a good barrier.

- X1.1.2 In these units the permeability of NBS Standard Reference Material to oxygen gas is approximately 7.8 amol/m·s·Pa.
- X1.2 Table X1.1, Table X1.2, and Table X1.3 give conversion factors for converting measured permeabilities, permeances, and transmission rates between various unit systems. Considerable care must be taken in dealing with powers of 10 because transport coefficients can vary by as much as a factor of 10⁵ from one polymer to another.
- X1.3 The major advantage of this proposed system of units over existing ones is that it essentially eliminates opportunities for incorrect dimensional calculations. It also affords a good basis for making comparisons when permeating substances are liquids or do not obey the ideal gas law. Modern coulometric and chromatographic detection systems are most readily calibrated in molar terms.
- X1.4 In order to use the tables, proceed as follows: (1) label the measured quantity (G, P, or P) by X_i , where i is the number of the row in the table corresponding to the system of units in which X was measured, (2) extract Y_i from the appropriate table as the value at the intersection of the ith row and the jth column where jlabels the column corresponding to the units in which X is to be expressed after conversion, and (3) obtain X_j from $X_j = X_i Y_j$.

^A One barrer equals 3.349 × fmol/m²·s·Pa (see Table X1.1)

^B Inch-pound units are mL (STP) mil/m²·d·atm. See X1.1, X1.2, X1.3, and Appendix X2 for conversion factors.

[®] Registered trademark, E.I. duPont, Inc. for its polyester film.

TABLE X1.1 Factors for Converting Permeabilities from One System of Units to Another

Note 1—For instructions on using the table see X1.4.

Unit System Dimensions of <u>P</u>

To Obtain Multiply↓	→ SI amol/m·s·Pa	Barrers 10 ⁻¹⁰ mL (STP) cm·s·cm Hg	Metric mL (STP) mil m²·d·atm	Inch-pound mL (STP) mil 100 in. ² ·d·atm
SI amol/m·s·Pa	1	2.986×10^{-3}	7.725	0.4984
Barrers 10 ⁻¹⁰ mL (STP) cm·s·cm Hg	0.3349 × 10 ³	1	2.587 × 10 ³	0.16691 × 10 ³
Metric mL (STP) mil m ² ·d·atm	0.12945	0.3865 × 10 ⁻³	1	64.52 × 10 ⁻³
Inch-pound mL (STP) mil 100 in. ² ·d·atm	2.0064	5.991 × 10 ⁻³	15.50	1

TABLE X1.2 Factors for Converting Permeances from One System of Units to Another

Note 1—See X1.4 for instructions on using this table.

Unit System Dimensions of \underline{P}

	To Obtain →	SI fmol/m²·s·Pa	Barrer-type 10^{-10} mL (STP) cm ² ·s·cm Hg	Metric <u>mL (STP)</u> m²·d·atm	Inch-pound mL (STP) 100 in. 2 · d · atm
SI fmol/m²·s·P	a	1	29.86 × 10 ⁻³	0.19621	12.659 × 10 ⁻³
Barrer-type 10 ⁻¹⁰ mL (ST cm ² ·s·cm Hg	<u>P)</u>	33.49	1	6.571	0.4240
Metric <u>mL (STP)</u> m ² ·d·atm		5.097	0.15218	1	64.52 × 10 ⁻³
Inch-pound _mL (STP) 100 in. ²·d·at	_	79.00	2.359	15.50	1



TABLE X1.3 Factors for Converting Gas Transmission Rates from One System of Units to Another

Note 1—See X1.4 for instructions on using this table.

Unit System
Dimensions of G

To Obtain →	SI nmol/m²·s	Barrer-type 10 ⁻¹⁰ mL (STP)	Metric mL (STP)	Inch-pound mL (STP)
Multiply ↓ \	nmoi/m²·s	cm²∙s	m²∙d	100 in. ² · d
SI nmol/m²·s	1	22.414	1.9366	0.12494
Barrer-type 10 ⁻¹⁰ mL (STP) cm ² ·s	44.62 × 10 ⁻³	1	86.40 × 10 ⁻³	5.574 × 10 ⁻³
Metric <u>mL (STP)</u> m²∙d	0.5164	11.574	1	64.52 × 10 ⁻³
Inch-pound mL (STP) 100 in. ² · d	8.004	179.40	15.50	1
·				

X2. ADDITIONAL CONVERSION FACTORS FOR VARIOUS PERMEABILITY UNITS

Note X2.1—To obtain unit in left-hand vertical column multiply unit in top horizontal column by figure opposite both units.

To Obtain	Multiply	cm³·cm_ cm²·s·cm Hg	$\frac{\text{cm}^3 \cdot \text{mil}}{\text{m}^2 \cdot 24 \text{ h} \cdot \text{atm}}$	cm³·mil 100 in.²·24 h·atm	$\frac{\text{cm}^3 \cdot \text{mm}}{\text{m}^2 \cdot 24 \text{ h} \cdot \text{atm}}$
cm³·cm cm²·s·cm F	_ lg	1.00	3.87×10^{-14}	6.00×10^{-13}	1.52×10^{-12}
cm³·mil m²·24 h∙at	_ m	2.58×10^{13}	1.00	15.5	39.4
cm ³ · mil 100 in. ² · 24 h	atm	1.67 × 10 ¹²	6.45×10^{-2}	1.00	2.54
cm³·mm m²·24 h·at	_	6.57 × 10 ¹¹	2.54 × 10 ⁻²	0.394	1.00

X3. DERIVATION OF EQUATION FOR PERMEANCE USING THE MANOMETRIC GAS CELL

X3.1 The following symbols are used in the derivations of the equation used in Section 13 to calculate the permeance.

a = area of capillary \overline{AB} , mm², A = area of transmission, mm²,

dP = dh = differential pressure change of transmitted gas,

 $dV = adh = differential volume change of transmitted gas, <math>\mu L$,

 h_o = initial height of mercury in the capillary leg at the start of the actual transmission run with steady-state conditions attained, mm,

h = height of mercury in cell capillary leg at any given time, mm, h_B = maximum height of mercury in the cell manometer leg from the datum plane to upper calibration line B, mm,

 h_L = height of mercury in cell reservoir leg from datum plane to top of mercury meniscus, mm,

 n_o = quantity of gas transmitted at the start of the actual transmission run after steady-state conditions have been attained, mol,

n = quantity of gas transmitted, at any given time, mol,

P = permeance of the film, the SI unit of permeance is 1 mol (m²·s·Pa),

 $p_t = (h_L - h)$ = pressure of transmitted gas at time t, mm Hg,

= pressure of gas to be transmitted, mm Hg, p_u

R = universal gas constant, 8.314×10^3 , L·Pa/(mol·K),

= time, h.

= time at start of the actual transmission run after steady-state conditions have been attained, h,

= absolute temperature, K. = volume from B to C, μ L,

= void volume of depression, μ L,

= $(V_{BC} + V_{CD})$, μ L, and = $[V_f + a(h_B - h)]$ = volume of transmitted gas, μ L at

X3.2 The number of mols of gas transmitted, n, may be determined from the ideal gas law (which is valid at the low pressure involved) as follows:

$$n = p_{*}V_{*}/RT \tag{X3.1}$$

For differential changes in p_t and V_t Eq X3.1 can be differentiated as follows:

$$nRT = p_{t}V_{t}$$

$$RTdn = d(p_{t}V_{t})$$

$$RTdn = p_{t}dV + V_{t}dp$$
(X3.2)

(Note X3.1)

Note X3.1—This differentiation is the form d(uv) = udv + vdu. Substitute into Eq X3.2 the values for dV and dPgiven in the definition of symbols.

$$RTdn = -p_{t}adh - V_{t}dh$$
, or (X3.3)
 $dn = (-ap_{t}dh - V_{t}dh)/RT$

By definition,

$$p_t = (h_L - h)$$
, and $V_t = [V_t + a(=h_B - h)]$

Therefore, substituting into Eq X3.3 and collecting terms,

$$dn = \{-a(h_L - h)dh - [V_f + a(h_B - h)]dh\}/RT \quad (X3.4)$$

$$dn = [(-ah_L + ah)dh - (V_f + ah_B - ah)dh]/RT$$

$$dn = [dh(-ah_L + ah - V_f - ah_B + ah)]/RT$$

$$dn = \{dh[2ah - a(h_I + h_B) - V_f]\}/RT$$

X3.3 The permeance (P) expressed in cm³/m $^{2}\cdot$ 24 h·atm can be obtained by integrating Eq X3.4 and using the following conversion factors:

$$\int_{t_o}^{t} P \, dt = \int_{n_o}^{n} dn \, \text{mol} \times \frac{24}{24 \, h}$$

$$\times 22 \, 415 \, \frac{\text{cm}^3}{\text{mol}} \times \frac{760 \, \frac{\text{mm}}{\text{atm}} \times 10000 \, \frac{\text{cm}^2}{\text{m}^2}}{P_d(\text{mm}) \times A \, (\text{mm}^2)}$$

The term P_d , which is the driving force, and A, the area of transmission, must be included in this equation in order to obtain the permeance in the desired units. Collecting terms and substituting for the following:

$$P_{d} = (p_{u} - p_{t})$$

$$\int_{t_{u}}^{t} dt = \int_{t_{u}}^{t} \frac{dn}{(p_{u} - p_{t})A} (24 \times 22415 \times 760 \times 10000)$$

or substituting for dn from Eq X3.4 and $p_t = (h_L - h)$:

$$\int_{t_0}^{t} P \, dt = \frac{1}{ART} \int_{h_0}^{h} \frac{\left[2ah - a(h_L + h_B) - V_f\right] dh}{p_u - \left(h_L - h\right)}$$
 (X3.5)

X3.4 To find an expression that applies over an extended period of time, Eq X3.5 must be integrated as described by Evans. 11

$$\int_{t_0}^{t} P \, dt = \frac{1}{ART} \left[2a \int_{h_0}^{h} \frac{h dh}{p_u u - (h_L - h)} - a(h_L + h_B) \right]$$

$$\cdot \int_{h_0}^{h} \frac{dh}{p_u (h_L - h)} - V_f \int_{h_0}^{h} \frac{dh}{p_u - (h_L - h)}$$

The first term can be integrated by parts or found in standard integration tables. The remaining terms are straightforward. The following result is obtained for steady-state gas transmission:

$$P(t - t_o) = \frac{-1}{ART} \left\{ 2a(ho - h) + \left[V_f + a(2p_u - h + h_B) \ln \left[\frac{p_u - (h_L - h)}{p_u - (h_L - h_o)} \right] \right\}$$

This can be written in the form:

$$P(t - t_o) = \tag{X3.6}$$

$$\frac{-1}{ART} \left\{ 2a(ho-h) + \left[V_f + a(2p_u - h_L + h_B) \right] \ln \left[1 - \frac{(h_o - h)}{S} \right] \right\}$$
where:

$$S = p_u - (h_I - h_o).$$

 $S = p_u - (h_L - h_o).$ Eq X3.6 is the exact relationship for calculating steady-state permeance over an extended period of time.

X3.5 If we assume that time-lag effects are not important, Eq X3.6 takes proper account of the fact that the driving force for permeation is decreasing continuously during a manometric permeation experiment. If one assumes that the rate of pressure rise is constant with time in the downstream cell volume, thereby failing to correct for the decrease in driving force, the resulting permeance values are too low. If we denote the permeance value obtained from uncorrected data by P', we can say that the true permeance, P, is given by

$$P = \frac{P'}{1 - \varepsilon}$$

X3.6 It can be demonstrated, by computer simulation or by series expansion methods, that

$$\varepsilon \simeq (h_L - h_f) \left[\frac{a}{V_{f+ac}(h_B - h_L)} + \frac{1}{2p_u} \right] \text{ for } \varepsilon < 0.3$$

where h_f is the depression of the mercury column at the end of the experiment. Evans has demonstrated 11 that ε can become as large as 0.2 in realistic situations.

X3.7 If the function g(h), as given by the right-hand side of Eq X3.6, exhibits curvature when plotted as a function of time one or more of the assumptions used in deriving Eq X3.6 is not being met, and further studies are needed to establish the causes of this behavior.

¹¹ Evans, R. E. "The Calculation of Gas Transmission Rates Using Manometric Methods," Journal of Testing and Evaluation, Vol 2, No. 6, pp. 529-532.



X3.7.1 Possible sources of error include (1) failure to achieve steady-state conditions, (2) the presence of time-lag effects, and (3) viscoelastic processes.

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