



Designation: F 1770 – 97^{e1}

Standard Test Method for Evaluation of Solubility, Diffusivity, and Permeability of Flexible Barrier Materials to Water Vapor¹

This standard is issued under the fixed designation F 1770; 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 reappraisal. A superscript epsilon (ε) indicates an editorial change since the last revision or reappraisal.

^{e1} NOTE—Figure 2 was replaced with a corrected version in March 1998.

1. Scope

1.1 This test method covers the evaluation of mass transfer properties of water vapor in films, plastic sheeting, coated papers and laminates. Barrier properties reviewed and specified within this method include solubility, diffusivity and permeability coefficients. This method also includes the means to determine the temperature dependence of these parameters.

1.2 Diffusion and solubility coefficients are particularly important in the evaluation of heavier gage plastic sheeting as well as paper substrates. These materials tend to absorb substantial amounts of moisture and to equilibrate over substantial periods of time. Predicting the field performance of these materials therefore requires the means to estimate the rate of approach to equilibrium and the degree of moisture absorbance in addition to permeability.

1.3 This test method assumes that the material being measured exhibits Fickian behavior. Measurement values are derived by a regression on the solution to Fick's first and second laws for a planar medium. These solutions are outlined in Annex A1 and are also addressed in Crank.²

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:

E 96 Test Methods for Water Vapor Transmission of Materials³

F 1249 Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor⁴

¹ This test method is under the jurisdiction of ASTM Committee F-2 on Flexible Barrier Materials and is the direct responsibility of Subcommittee F02.30 on Test Methods.

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² Crank, J., *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1975.

³ *Annual Book of ASTM Standards*, Vol 04.06.

⁴ *Annual Book of ASTM Standards*, Vol 15.09.

3. Terminology

3.1 Definitions:

3.1.1 *activation energy*—a thermodynamic property that describes the relationship of P , D or S to temperature. The relationship is Arrhenius and the parameters may be obtained by a linear fit of the natural log of the measurement value versus inverse temperature in degrees Kelvin. Arrhenius parameters of a material are dependent on the glass transition point of the material and measurements spanning a glass transition point will require two solutions (Fig. 1). The parameters of the fit are defined by the relationship:

$$P = P_0 \exp(-E_P/RT) \quad (1)$$

$$D = D_0 \exp(-E_D/RT) \quad (2)$$

$$S = S_0 \exp(-E_S/RT) \quad (3)$$

where:

P , D , and S = permeability, diffusion, and solubility coefficients,

P_0 , D_0 , and S_0 = Arrhenius fit intercepts,

E_P , E_D , and E_S = activation energy values,

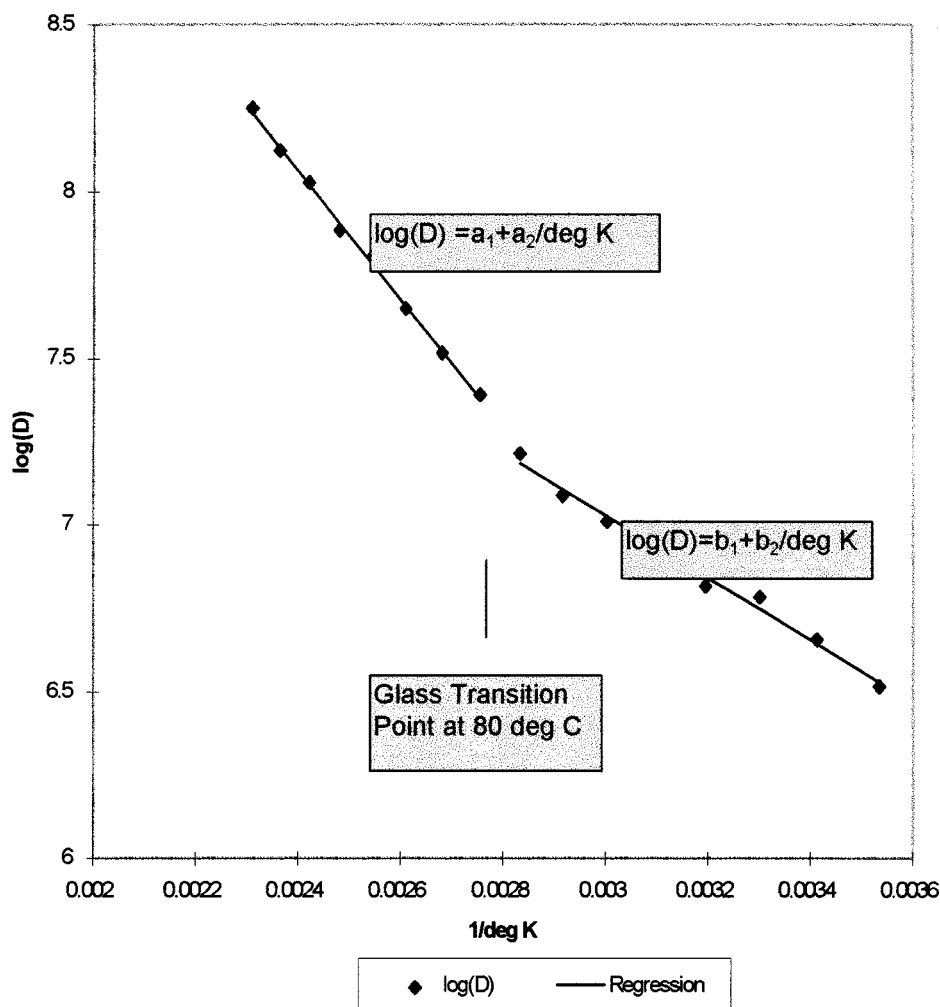
R = gas constant, and

T = temperature, K.

3.1.1.1 The Arrhenius fit intercept and activation energy values are essential to an understanding of a material's temperature dependence, and may be used to estimate a material's diffusion, solubility, and permeability values at any given temperature within the region of measurement. They may also be employed to estimate extrapolated values outside of the region of measurement if the fit is sufficiently precise and a glass transition point is not crossed in the extrapolation. Methods of estimating the extrapolation error are available in current software packages and may be obtained from standard references on statistics.

3.1.2 *diffusion coefficient*—a kinetic coefficient that describes the relationship between vapor flux and vapor concentration change within the substrate. D is defined by the following equation:

$$F = -D \, dC/dx \quad (4)$$



NOTE 1—The log of a mass transfer parameter such as diffusion, solubility, or permeability is expected to be linear with inverse temperature. At the glass transition point, the slope of the fit will change.

FIG. 1 Arrhenius Parameters of Hypothetical Experiment

where:

F = vapor flux,

D = diffusion coefficient, and

dC/dx = change in concentration in the direction of x . The SI units for D are m^2/s .

3.1.3 *permeability coefficient*—an empirical coefficient that describes the relationship of steady state vapor flux to the partial pressure difference across a planar medium. P is defined by the relation $F_e = P(p_1 - p_2)/L$, where F_e is vapor flux at steady state, p_1 and p_2 are the water vapor partial pressures on each side of the medium, and L is the barrier thickness. The SI units for P are $\text{kg}/\text{s} \cdot \text{m} \cdot \text{Pa}$.

3.1.4 *sample diffusion coefficient*, D_s —the diffusion coefficient for a specific sample structure. The material diffusion coefficient may be calculated from the sample diffusion coefficient by the following:

$$D = L^2 D_s \quad (5)$$

where L = thickness of the barrier layer.

The SI units for D_s are $1/\text{s}$. D_s is, therefore, a frequency value related to the time of flux travel for a unitary thickness.

3.1.5 *sample permeability flux*, F_e —a value describing the steady state permeation flux for the sample structure and test gas partial pressure. The permeation coefficient, P , may be calculated from F_e by the following:

$$P = F_e L / (p_1 - p_2) \quad (6)$$

where:

L = barrier thickness, and

p_1 and p_2 = opposing water vapor pressure values. The SI units for F_e are $\text{kg}/\text{m}^2 \cdot \text{s}$.

3.1.6 *sample solubility coefficient*, S_s —the solubility coefficient for a specific sample structure and test vapor pressure. S_s is equal to F_e/D_s and has the SI units kg/m^2 .

3.1.7 *solubility coefficient*—thermodynamic coefficient that describes the relationship of concentration to vapor partial pressure. S is defined by Henry's Law:

$$C = S p \quad (7)$$

where:

C = concentration within the medium,

S = solubility coefficient, and
 p = vapor pressure of water.
 The SI units for S are $\text{kg/m}^3 \cdot \text{Pa}$.

4. Summary of Test Method

4.1 One side of a planar sample is exposed to a specific water vapor pressure by means of a constant gas flow within a controlled temperature cell. Water vapor molecules which diffuse across the sample are swept by a carrier gas to a concentration dependent detector such as a capacitance or infrared detector. The resulting voltage or capacitance is then tabulated according to the time of exposure.

4.2 The diffusion and permeability coefficients of the sample material are determined by a nonlinear regression on the transient solution to Fick's laws for a planar surface. (See Annex A1.)

4.3 The solubility coefficient is determined from the relationship $P = DS$ (Annex A1).

4.4 The permeability, diffusion, and solubility coefficients are evaluated at a number of temperatures to yield activation energy values. These values provide a measure temperature dependence of the material.

5. Significance and Use

5.1 The transport values obtained may be used to estimate the mass transfer rate of water vapor through and into materials intended for use as a barrier to moisture. These values are applicable to shelf life estimation, evaluation of expected equilibrium rates, drying rates, and the evaluation of moisture solubility or absorbance levels.

5.2 Activation energy values may be employed to estimate the dependence of the measured mass transfer parameters on temperature. Since product end use conditions often vary, the effect of temperature on a material's performance can be critical to determining the ability of a material to meet the required function. These values also allow construction of a database by which materials may be compared for a range of end use temperature conditions.

6. Apparatus

6.1 *Means to Control a Continuous Stream of Water Vapor* at a partial pressure of ± 0.2 mmHg at a flow of ± 0.1 mL/min. A controlled temperature bubbler and the means to precisely mix the resulting vapor with a dry nitrogen stream is one method of generating such a vapor.

6.2 *Means to Control Temperature of the Transfer Lines from the Water Vapor Generator to the Test Cell*—These transfer lines need to be at a temperature above the dew point of the test water vapor stream.

6.3 *Means to Precisely Control Flow of Dry Carrier Gas through a Test Cell Chamber and Detector Combination*—As gas flow is critical to the precision of the measurement, a flow rate precision of at least ± 0.1 mL/min is required.

6.4 *Temperature-Controlled Test Cell*, as diagrammed in Fig. 2 consisting of two chambers diametrically opposed and with the means of supporting the measurement sample so as to separate the two chambers without leakage. Test cell parameters critical to the measurement process include the following:

6.4.1 *O-Ring*, constructed of Viton (or another known inert material) for sealing the film is mounted within the cell to prevent leakage. The O ring is to be mounted on the high vapor side of the cell so as to eliminate its effect on the detection of moisture diffusing across the test sample.

6.4.2 *Chamber Volumes* in the range of 3 to 5 cc. Larger volumes are known to interfere with the measurement process as they incorporate a significant delay time in test vapor concentration changes.

6.4.3 *Film Sample Area* as defined by the O-ring diameter in the range of 20 to 100 cm^2 .

6.4.4 *Means to Control Temperature of the Cell* with a precision of $\pm 0.05^\circ$ Centigrade.

6.5 *Valving and Stainless Steel Plumbing*, allowing operator selection of the permeant chamber gas (either the controlled moisture vapor stream or the dry carrier gas) and transport of the selected vapor into the permeant chamber.

6.6 *Concentration Dependent Detector*, such as an infrared detector or a capacitance detector which is capable of detecting moisture concentration differences to at least 1 ppm by volume, and the means to record the resulting detector signal with respect to time.

6.7 *Flow Controls and Stainless Steel Plumbing*, allowing the maintenance of a constant flow of dry carrier gas into the detector chamber and then out to the detector. As the measurement signal is proportional to flow rate changes, a flow rate precision of at least ± 0.1 mL/min is required.

6.8 *An Injection Port* located prior to detector for injections of known amounts of moisture.

6.9 *Syringes*, of varying size (10 to 1000 μL) for injection of moisture calibration samples. Syringe needles will need to be of a side port type in order to prevent plugging of the syringe and to assure consistent calibration values.

6.10 *Septum Vials*, with a volume capacity of 50 to 100 mL for preparation of calibration standards.

7. Reagents and Materials

7.1 *Nitrogen Gas Supply*—A high pressure cylinder of a low moisture grade is preferable.

7.2 *Means to Dry Nitrogen Carrier Stream*—A filter cylinder of calcium sulfate has been determined to be acceptable.

7.3 *Distilled Water*.

8. Detector Linearization

8.1 Concentration dependent detectors are not linear over the full range of gas concentrations possible in a permeation experiment. Evaluation of these nonlinearities is critical to an accurate evaluation, particularly for extremely low or high transmitting materials.

8.2 Place in the sample cell a stable material which is representative of the transmission rates to be detected and allow the system to stabilize at a constant temperature.

8.3 Expose the sample to a known moisture vapor pressure within the range of partial pressures to be evaluated and allow the detector value to achieve a steady state. Note the rate of flow through the detector and the detector signal value.