Designation: E 476 – 87 (Reapproved 2001)

Standard Test Method for
Thermal Instability of Confined Condensed Phase Systems (Confinement Test)[1]

This standard is issued under the fixed designation E 476; 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.

INTRODUCTION

This test method is one of several methods developed by Committee E-27 for determining the hazards of chemicals. This test method is to be used in conjunction with other tests to characterize the hazard potential of chemicals.

1. Scope

1.1 This test method[2] is designed to determine the temperature at which a chemical or mixture of chemicals, confined initially as a solid or liquid in air or other controlled atmosphere under normal laboratory conditions, will start a reaction, generating appreciable heat when subjected to a programmed temperature increase. This test method is also designed to measure the magnitude and rate of heat generation.

1.2 This test method is for use with condensed phases.

1.3 This test method can be used over a temperature range from 0 to 500°C, and a pressure range of 0 to 5000 psi.

1.4 As with any thermal stability test, proper safety precautions should be instituted to protect personnel. See also Section 6.

1.5 *Limitations*:

1.5.1 The threshold temperature determined by this method may be higher than one determined by heating at a lesser rate.

1.5.2 Samples of the same material having different thermal histories may have different threshold temperatures.

1.6 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems 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. Terminology

2.1 *threshold temperature*—temperature on the ΔT versus T curve (see Fig. 2) where the slope changes in the direction indicating an exothermic reaction, that is, the sample is beginning to self-heat.

3. Summary of Method

3.1 The sample is confined in a specially designed vessel equipped with a shielded thermocouple. The test assembly is put into a bath and equilibrated, usually at room temperature. The bath is then heated at a constant temperature rise rate. The differential temperature (sample temperature minus bath temperature) in the vessel is recorded versus bath temperature. Heating is continued until the diaphragm bursts or the upper temperature limit is reached. The differential temperature curve is then analyzed to determine the threshold temperature for initiation of measurable reaction as indicated by an exothermic temperature rise.

4. Significance and Use

4.1 The threshold temperature measured by this test method is an indication of the thermal instability of a chemical or mixture of chemicals, qualitatively expressed by the temperature rise. There is a potential hazard whenever the temperature of the chemical exceeds the threshold temperature unless proper design safeguards are utilized. This does not imply that temperatures lower than the threshold temperature are safe. Since this test is not an adiabatic type and does not indicate the effect of mass or time, other testing would be needed to characterize the use or storage of the chemical at lower temperatures.

4.2 Because of rate and mass dependent factors, failure to find evidence of an exothermic reaction does not ensure thermal stability unless substantiated by other test methods.

5. Apparatus

5.1 *Sample Container*—A diagram of a suggested test cell assembly is shown in Fig. 3 and an engineering drawing is shown in Fig. 4. The assembly shall consist of the following parts: basic test cell, sample thermocouple, compression fitting,

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[1] This test method is under the jurisdiction of CommitteeE27 onHazard Potential of Chemicals and is the direct responsibility of Subcommittee E 27.02 on Thermal Stability.

Current edition approved Sept. 25, 1987. Published November 1987. Originally published as E 476 – 73. Last previous edition E 476 – 73 (1979)$^{\epsilon 2}$.

[2] This test method is a modification of the Thermal Stability Test recommended by the Interagency Chemical Rocket Propulsion Group, published by the Chemical Propulsion Information Agency in May, 1964, and is the responsibility of E 27.02 on Thermal Stability.

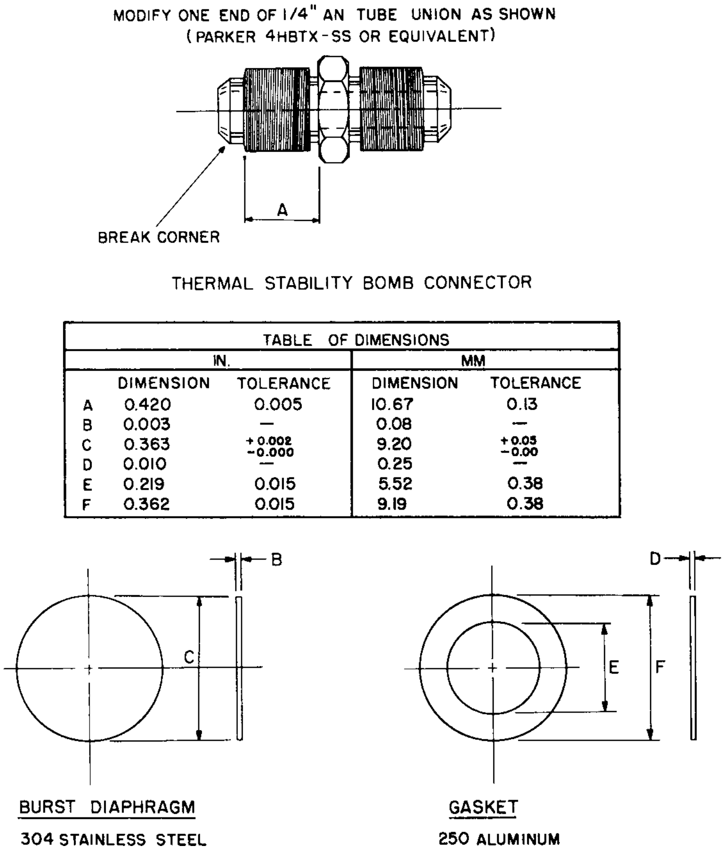

TABLE OF DIMENSIONS

	IN.		MM	
	DIMENSION	TOLERANCE	DIMENSION	TOLERANCE
A	0.420	0.005	10.67	0.13
B	0.003	—	0.08	—
C	0.363	+0.002 −0.000	9.20	+0.05 −0.00
D	0.010	—	0.25	—
E	0.219	0.015	5.52	0.38
F	0.362	0.015	9.19	0.38

FIG. 1 Connector, Gasket, and Burst Diaphragm

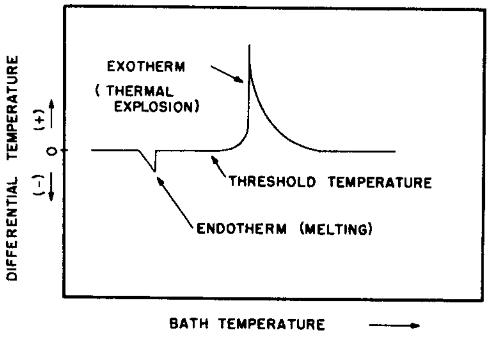

FIG. 2 Idealized Thermogram

sealing ring, burst diaphragm, modified Army-Navy specification union (AN union), vent tube and flare fitting. Detailed dimensions of all parts are given in Fig. 4 with the exception of those parts readily available from manufacturers. The parts are listed in Table 1. The internal volume ofthe assembled test cell is approximately 1.1 mL.[3,4]

5.2 *Instrumentation*:

5.2.1 One recorder is used for recording the difference between the sample temperature and the bath temperature as a function of bath temperature. A suitable recorder for this test is a standard 8.5 by 11 in. *X-Y* plotter. Two recorders are required if pressure versus bath temperature is monitored. Dual-pen plotters are suitable, provided the temperature pens do not interact at any critical junction of the reaction.

5.2.2 The maximum reaction rates that can be followed using the recommended instrumentation are limited by the writing speeds of the mechanical writing recorders. When these are calibrated as described in Section 8, rates of reaction producing temperature changes of 5°C per s can be determined. Certain reactions may cause temperature changes in excess of these. If more exact resolution for rapid reactions is desired, it is necessary to use a recording oscillograph in place of the: *X-Y* recorder.

5.3 *Low-Range Heating Bath*—For temperatures from 0 to 370°C the bath may be a conventional 2-L silicon oil[5] unit with heaters (1800 W), stirring motor, and temperature programmer. The bath container shall be metal with strip heaters on the outside. The bath shall be well insulated. A cooling coil shall be wrapped around the container to reduce the time lost between tests (optional). The coolant shall be tap water. The nominal heating rate for the bath shall be 8 to 10°C per min.

5.4 *High-Range Heating Bath*—For temperatures between 100 and 500°C a bath of a low-melting alloy may be employed. The bath medium may be cerrobend/Alloys or Woods' metal (**Caution.** Woods' metal may contain cadmium and should be used with adequate ventilation to remove toxic fumes). A

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[3] Apparatus of similar designs with a total volume of 1 to 10 mL can be used.

[4] This revised test method, when used with its provision for optional pressure measurement, is essentially similar to earlier versions of this in which pressure measurement was an integral part.

[5] Dow Corning 710 has been found satisfactory for this purpose.

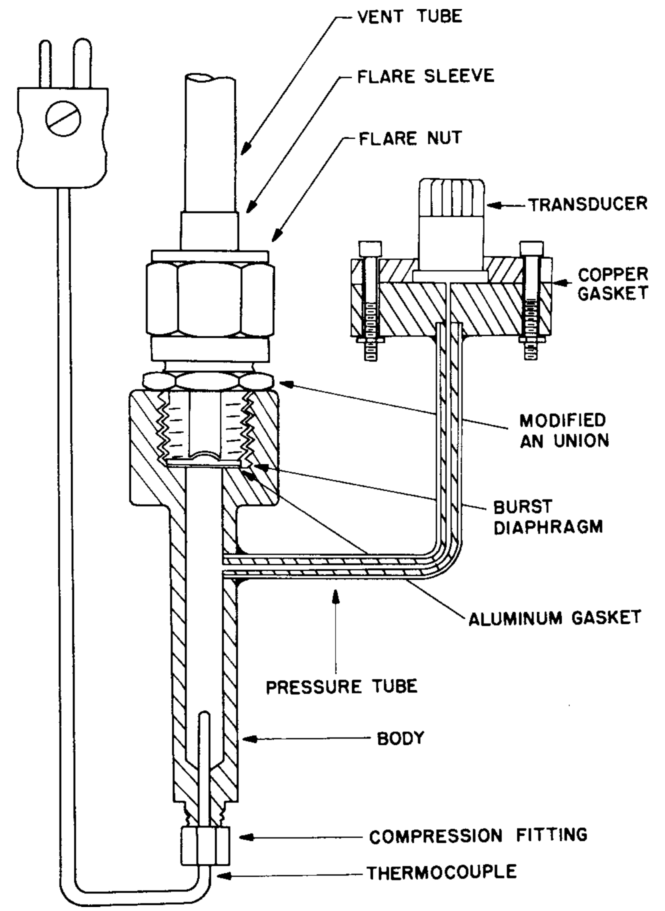

FIG. 3 Thermal Stability Bomb Assembly

temperature programmer is also employed with the metal bath. The nominal heating rate for the metal bath is 8 to 10°C per min. This heating rate may prove difficult to maintain above 400°C unless the bath is well protected from air currents.

5.5 *Full-Range Heating Bath*—A fluidized sand bath equipped with vacuum dust ring may be conveniently used for the full range of temperatures. However, without additional heaters, it appears that commercial units are designed for a heatup rate of about 5°C per min.

5.6 **Warning**—Coiled electric heaters may cause electrical interference with electronic measuring equipment. *X-Y* recorders can pick up stray currents unless shielded thermocouple leads are used and shielding, bath and recorders are grounded to a common ground potential.

6. Safety Precautions

6.1 After placing the sample in the test cell, exercise caution to ensure that the threaded parts of the apparatus are clean before final assembly. For some sensitive materials, sample material caught in the threads may detonate and may set off the bulk of the sample in the test vessel. Serious injury to personnel may result.

6.2 It may be necessary to powder the sample (see 7.2) or, since the packing density of solids varies over a wide range, to compact the sample in the cell. These operations may be hazardous and should not be performed unless a determination of impact sensitivity[6] has previously been made and has shown sufficient insensitivity to permit powdering or compaction.

6.3 Upon rupture of the diaphragm, noxious fumes may be released into the laboratory. To prevent escape of the reaction products into the laboratory atmosphere, conduct tests either in a fume hood or pipe the vent line to a suitable exhaust system.

6.4 The bath of hot oil or molten metal may inadvertently be spilled or ruptured and cause personnel burns or laboratory fires. To prevent such accidents, the test unit should be located in a separate fume hood constructed of non-combustible materials. The use of a fluidized sand bath minimizes this particular hazard.

6.5 During the test, certain sensitive chemicals may detonate resulting in destruction of the basic test cell assembly and possible destruction of the bath. Such violent reactions frequently hurl fragments through the surroundings at high velocity with great danger to personnel. To prevent injury from possible shrapnel, conduct tests in a barricaded enclosure or behind a blast shield contained within a fume hood.

6.6 All controls and switches should be on the operator side of the blast shield or enclosure so that during emergencies, steps can be taken to turn off heaters and shut down the system without exposing personnel to danger.

6.7 A loud report accompanies the rupture of a burst diaphragm; this may cause accidents by startling personnel engaged in other tasks. Although the use of fume hoods and blast shields muffles the sound, all nearby personnel should be warned that the test is in progress prior to running the test.

6.8 Give thought to procedures for cooling. If water is to be used for cooling, care is needed since in most instances, the temperatures of the bath will be much higher than the boiling point of water.

6.9 In some cases the pressure may not be sufficient to burst the pressure diaphragm. On cooling to room temperature, there may still be a high residual pressure in the test cell. Take care in relieving pressure from the cell. The operator should be protected by a shield and have protective covering for eyes, arms and hands.

NOTE 1—It would be judicious to insert a suitably pressure-rated valve on the cell to allow a controlled venting of pressure. Cracking of the union nut may allow gas-saturated liquid contents to rapidly leave the cell.

7. Test Sample

7.1 It is recommended that a sample weight of 0.3 g be used. The sample size has been chosen so that the thermal expansion of most substances will not cause the sample volume to exceed the volume of the cell. In cases where thermal expansion is a problem, lower weights of sample may be used and reported.

7.2 Solid samples should be powdered. A particle size of 50 mesh or smaller is preferred.

8. Procedure

8.1 Review Section 6 carefully before proceeding.

8.2 Calibrate the *X-Y* recorder with a potentiometer from 0 to 500°C on the *X*-axis. Calibrate the differential temperature trace to 10°C per 25 mm or 10°C per in. on the *Y*-axis. Offset the base line for a 20°C endothermic deflection.

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[6] An ASTM Standard for determining impact sensitivity is under development.

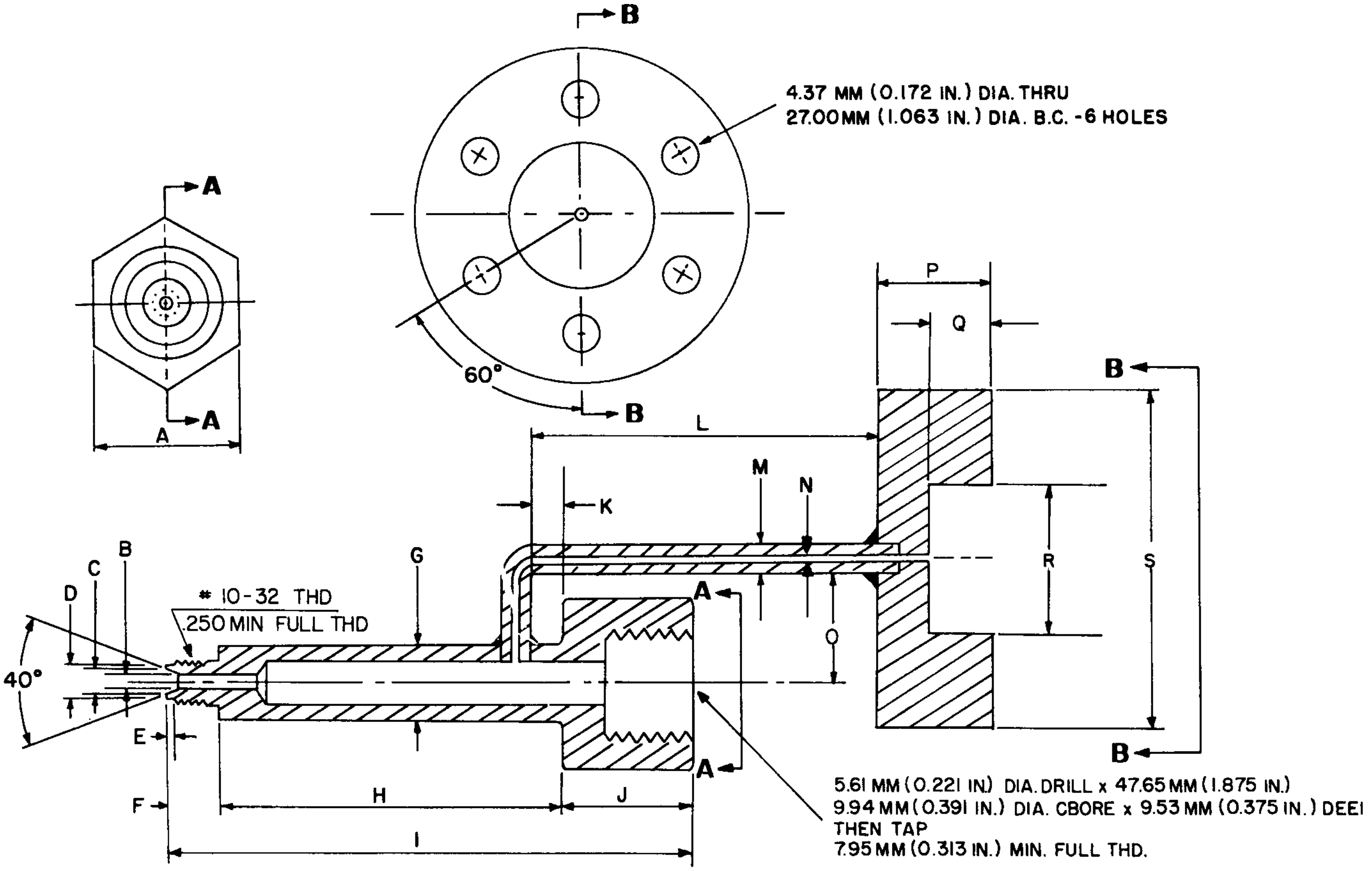

FIG. 4 Bomb Body Structural Diagram

TABLE 1 Parts List

	Item	Required	Possible Vendor
1	Bomb body, 316 SS	1	none (see Fig. 3 and Fig. 4)
2	Thermocouple, 1⁄16 in. IC ungrounded, SS sheath, min. sheath length 6 in. MLP plug	2	Thermoelectric Co.; Omega Engineering, Inc.
3	Compression fitting, 1⁄16-in. (nut, 2 ferrules)	1	Crawford Fitting Co.
4	Gasket, 1100-0 aluminum, 7⁄32-in. by 0.362 in.	1	
5	Burst diaphragm, 0.003-in. 304SS, 0.363 in.	1	
6	Modified AN 815-4 Union	1	AN 815-4 Union can be purchased from various companies. Modification can be performed in-house.
7	Vent tube, 1⁄4-in. copper, SS, etc., 36 in. long	1	varied
8	Flare nut, sleeve, 1⁄4-in. (AN 818, AN 819-4)	1	varied
9	Stainless steel bristle 1⁄4-in. size cleaning brush	1	Schaefer Brush Manufacturing Co., 117 W. Walker St., Milwaukee, WI 53204

8.3 Seal the clean, basic test cell at the bottom with the 1.61-mm (1⁄16-in.) thermocouple and compression fitting. Extend the thermocouple tip about 10 mm (0.4 in.) into the test cell interior. Clamp the unit upright in a vise or other support and charge with 0.3 g sample (see Section 7). Keep threads clean and remove any material that may be on them before proceeding (see 6.1 and 6.2). Put into place the sealing ring, burst diaphragm, and modified AN union, and tighten to complete the initial assembly.

8.4 Place the heating bath in a blast enclosure or behind a blast shield contained within a fume hood (see 6.3 to 6.6). Support the test assembly in the heating bath so that the body is completely below the surface of the heating medium. Support the vent tube with a clamp. Position the blast shield. Warn nearby personnel (see 6.7). Turn on the stirrer if an oil bath is being used. Review all safety precautions. Equilibrate the test cell for 10 min. at the desired starting temperature. Turn on the recorder. Start the programmer to maintain a heating rate of 8 to 10°C per min. Continue the test until the diaphragm bursts or the upper temperature limit is reached (for most organic chemicals an upper limit of 350 to 400°C will suffice). Stop heating.

8.5 Start the cooling units (see 5.3 and 6.8). Monitor the temperature during the cooling cycle. Cool the test cell to room temperature if the diaphragm has not burst (see 6.9). Put on eye protection and protective gloves and clothing for hands and arms. Remove the cell from the bath but not from the blast enclosure. Relieve residual pressure from the cell by loosening the AN union slowly (see 6.9). Disassemble the cell when pressure has equalized.

8.6 Some residue will remain in the test cell after a run. This can be cleaned from the main body of the cell by means of a 6 mm (¼ in.) stainless steel bristle brush.

9. Interpretation of Results

9.1 An idealized curve is illustrated in Fig. 2. The thermal curve shows endothermic reactions as negative peaks and exothermic reactions as positive peaks in a manner analogous to DTA (differential thermal analysis) curves. Exothermic reactions arise from a variety of sources. Frequently, successive or simultaneous reactions will yield overlapping peaks.

9.2 The lowest temperature at which an exothermic deflection is observed is the threshold temperature as defined by this test method. Other testing should be done before storage or processing at this temperature is considered.

9.3 Always give consideration to the potential catalytic effect of materials of construction. These can be evaluated by simple equipment modifications. Impurities in the sample may also have a large effect on the test results and should be considered.

9.4 The recommended heating rate is 8 to 10°C/min. and the recommended sample size is 0.3 g. A higher heating rate will result in higher threshold temperatures.

10. Report

10.1 The report shall include the following:

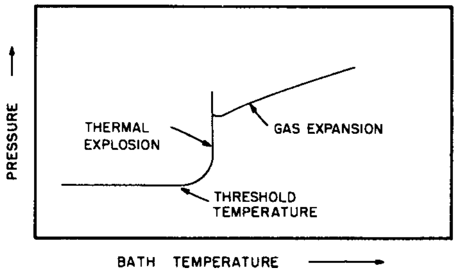

FIG. 5 Idealized Pressure Response

10.1.1 Sample identification and description that includes name, structure, history, weight used, purity, known additives, etc.,

10.1.2 Composition and pressure of the starting atmosphere within the test chamber,

10.1.3 Instrument parameters including heating rate, temperature range, calibration factors of differential temperature sensitivity, and maximum reliable rate sensitivity of the recorder, and

10.1.4 Threshold temperature as obtained from the ΔT versus T curve as the temperature of departure from the baseline. Peak ΔT and rating of pressure disk (if burst).

ANNEX

(Mandatory Information)

A1.

A1.1 A variation of this test method has been used to measure decomposition pressures associated with thermal decomposition reactions. For this purpose, the basic cell is modified as shown in Fig. 3 and Fig. 4. An idealized pressure trace is shown in Fig. 5.

A1.2 Performance of this variation requires the use of a second recorder to monitor pressure as a function of bath temperature; alternatively, dual-pen *X Y Y* recording equipment may be used.

The pressure curve is used to confirm the interpretation of the thermal curve and to yield information as to the nature of the reaction and the relative severity of the hazard. The instantaneous rate of pressure rise (*dp/dt*), neglecting lags, may be obtained from the pressure curve at any given bath temperature since the heating rate is known. The corresponding sample temperatures may be obtained from the thermal curve. Materials that show high rates of pressure rise are generally more hazardous than those with lower rates having comparable threshold temperatures. Comparative test information with materials of known hazardous properties can be helpful in establishing qualitative classifications. Recording of pressure of mixtures of solutions is especially advantageous since highly exothermic materials, which do not generate high pressures by themselves, can create high pressures by vaporizing associated materials such as solvents. The temperature curve alone might be misinterpreted to mean that dilution reduces the hazard since the differential temperature peak is reduced relative to that for undiluted material. This misinterpretation can lead to dangerous practices. The situation may arise when there will be a large increase in pressure with very little change in temperature because thermal expansion of the liquid phase of the sample exceeds the volume of the cell. The result will be a sudden hydrostatic pressure rise which may burst the diaphragm. In this case the test should be repeated with a lesser weight of sample.

NOTE A1.1—Samples having a low density or high coefficient of thermal expansion may produce a significant pressure change with little change in temperature.

NOTE A1.2—This procedure is not designed to determine the actual pressure rise as a function of temperature. Pressure generation frequently occurs under prolonged exposures at lower temperatures than that at which pressure is first detected in this experimental method.

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