



# Standard Test Method for Solidification Point of Industrial Organic Chemicals<sup>1</sup>

This standard is issued under the fixed designation D 1493; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers a general procedure for determining the solidification point of most organic chemicals having appreciable heats of fusion and solidification points between  $-20$  and  $+150^{\circ}\text{C}$ .

1.2 This test method is applicable only to relatively pure compounds. Values obtained for grossly impure compounds can be low because of the freezing out of one component during the determination.

1.3 In order that the test method may be used on many materials, a choice of certain alternatives and a selection of apparatus are permitted. The report (Section 12) requires that the selected alternatives must be stated. Materials to which the test method is applicable in particular detail include phenol, naphthalene, phthalic anhydride, and maleic anhydride.

1.4 The following applies to all specified limits in this test method: for purposes of determining conformance with this test method, an observed value or a calculated value shall be rounded off "to the nearest unit" in the right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29.

NOTE 1—A companion test method is Test Method D 852.

1.5 *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.* For specific hazard statements, see Section 8.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 850 Test Method for Distillation of Industrial Aromatic Hydrocarbons and Related Materials<sup>2</sup>

D 852 Test Method for Solidification Point of Benzene<sup>2</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 06.04.

D 1015 Test Method for Freezing Points of High Purity Hydrocarbons<sup>3</sup>

D 1016 Test Method for Purity of Hydrocarbons from Freezing Points<sup>3</sup>

D 3437 Practice for Sampling and Handling Liquid Cyclic Products<sup>2</sup>

D 3438 Practice for Sampling and Handling Naphthalene, Maleic Anhydride, and Phthalic Anhydride<sup>2</sup>

D 3852 Practice for Sampling and Handling Phenol and Cresyl Acid<sup>2</sup>

E 1 Specification for ASTM Thermometers<sup>4</sup>

E 29 Practice for Using Significant Digit in Test Data to Determine Conformance with Specifications<sup>5</sup>

E 77 Test Method for Inspection and Verification of Thermometers<sup>4</sup>

### 2.2 Other Document:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200<sup>6</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 *solidification point*—an empirical constant defined as the temperature at which the liquid phase of a substance is in approximate equilibrium with a relatively small amount of the same substance in its solid phase.

3.1.1.1 *Discussion*—Solidification point is distinguished from freezing point, which is described in Test Method D 1015. An interpretation of mole percent purity in terms of freezing point is given in Test Method D 1016.

## 4. Summary of Test Method

4.1 Solidification point is measured by noting the maximum temperature reached during a controlled cooling cycle after the appearance of a solid phase in a liquid sample.

## 5. Significance and Use

5.1 This test method is suitable for setting specifications on

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.03.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>6</sup> Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

compounds of the type described in Section 1. It is also suitable for use as an intense quality-control tool and in development and research work involving these compounds.

6. Apparatus

6.1 *Thermometer*—An etched-stem liquid-in-glass thermometer having a range of no more than 30°C shall be used. It shall be graduated in subdivisions no greater than 0.1°C. Unless otherwise specified, it shall be calibrated, for 76-mm immersion, at no fewer than three points. These shall include the approximate solidification point of the material being tested and two other points, respectively, about 5°C above and below the solidification point. A total immersion thermometer can be used if it is specified for testing a particular material, as, for example, benzene. (See Test Method D 852.) The thermometer shall conform to Specification E 1. It should be so chosen that the graduation at which the solidification point is to be observed is not hidden from view when the thermometer is inserted in the sample container. Suitable thermometers are ASTM Thermometers 89C to 96C, inclusive. Table 1 lists several of these thermometers and the materials for which, respectively, they are useful in particular in accordance with this test method. A thermometer, for example ASTM Thermometer 17C, 18C, or 91C, is needed when the average temperature of the emergent mercury column of the solidification-point thermometer is measured.

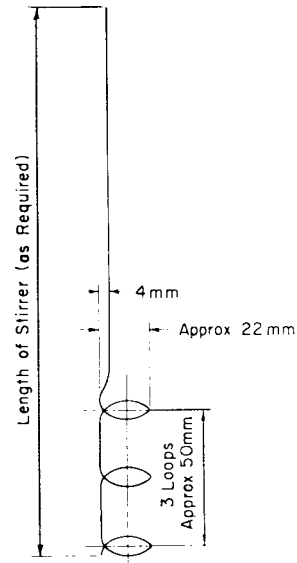


FIG. 1 Stirrer

6.5.2 An electric heater that is fully adjustable as described in Test Method D 850, or a bunsen or similar gas burner (see Section 9.2), or both.

6.6 *Insulation Board*—A sheet of hard insulation board 3 to

TABLE 1 ASTM Thermometers for Solidification Point

ASTM Number	Range of Temperature, °C	Selected Standardization Temperature, °C	Average Temperature of Emergent Mercury Column, °C	Material for Test
91C	20 to 50	40	25	phenol
92C	40 to 70	52	25	maleic anhydride
93C	60 to 90	80	30	naphthalene
96C	120 to 150	130	35	phthalic anhydride

6.2 *Specimen Container*—A standard heat-resistant glass test tube with lip shall be used. The test tube shall measure 25 mm in outside diameter and 150 mm in length.

6.3 *Stirrer* (see Fig. 1)—The stirrer shall consist of a 1-mm diameter (B&S gage 18), corrosion-resistant wire bent into a series of three circular loops about 25 mm apart at right angles to the shaft, the circle of each loop being about 20 mm in diameter, so that the stirrer can move freely in the annular space between the inner wall of the specimen container and the thermometer stem when the latter is inserted in the container. The shaft of the stirrer may be of any convenient length not less than 150 mm, and shall pass through an off-center hole in a two-hole cork stopper, the center hole of which holds the thermometer. The upper end of the shaft may be attached to a reciprocating device for mechanical stirring, or may be formed into a loop to facilitate lifting it for stirring by hand.

6.4 *Flasks*:

6.4.1 A 200-mL, side-tube, heat-resistant glass distillation flask as described in Test Method D 850 and

6.4.2 Two narrow-neck, heat-resistant glass Erlenmeyer flasks, 400-mL capacity each.

6.5 *Heaters*:

6.5.1 A hot plate, and

6-mm thick and 15 cm square, with a circular hole 50 mm in diameter in the center of it, is needed if the drying procedure given in 9.2 is used.

NOTE 2—Items described in 6.7, 6.8, and 6.9, are not essential for routinely testing materials that have solidification points substantially above room temperature, for example above 30°C; but, for referee testing, these items shall be used always, regardless of the solidification points of the materials being tested.

6.7 *Air Jacket*—A standard heat-resistant glass tube with lip, 38 mm in outside diameter and 200 mm in length, shall be fitted with a cork stopper bored with a hole of 25 to 26-mm diameter and into which the specimen container is to be inserted up to its lip.

6.8 *Cooling Bath*—A 2-L beaker or similar suitable container having an effective depth of at least 175 mm shall be filled with a cooling medium, which shall be glycerin for operating at temperatures between 145 and 25°C, water and ice between 25 and 0°C, and alcohol and dry ice between 0 and -25°C. A thermostatically controlled agitated bath may be used optionally. (See Fig. 2 for assembly of apparatus.)

6.9 *Clamp and Ring Stand*—A clamp, attached to a stand, holds the air jacket rigidly just below its lip when it is immersed in the cooling bath to a depth between 160 and 200 mm.

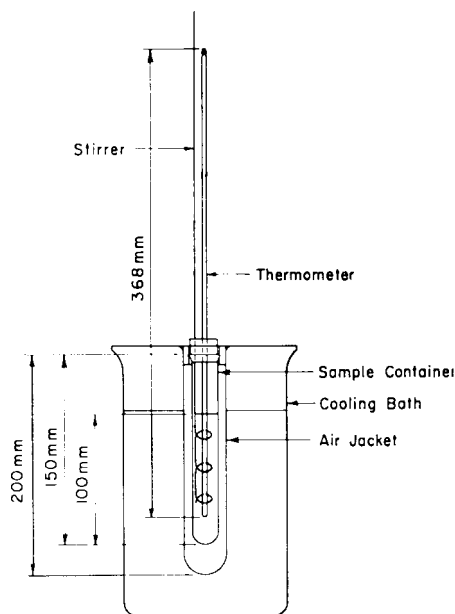


FIG. 2 Apparatus for Determining Solidification Point

NOTE 3—Items listed in 6.10-6.15 inclusive, are required only for checking the accuracy of the thermometer at the solidification point of the material being tested. This check is desirable to detect changes that occur in a thermometer with time and use and to minimize errors generally.<sup>7</sup>

6.10 *Thermometric Cell*—A sealed glass cell made from standard-wall glass tubing, 38 mm in outside diameter, and about 140 mm in length, has a thermometer well, 120-mm deep, formed as an integral part lengthwise in it. The cell contains a relatively pure crystallizable compound of known freezing point that fills it to a level about 10 mm above the height of the 76-mm immersion mark of a partial immersion thermometer when the latter is inserted in the well down to the bottom. The well shall be made from 10-mm tubing, about 8 mm in inside diameter. (See Fig. 3.) For a total immersion thermometer, the lengths of the cell and the well shall be increased to fit. The cell shall have a calibration temperature,  $T_c$ , determined with a platinum resistance thermometer and assigned to it for use as a thermometric standard. (See Section 10.)

6.11 *Vacuum Flask*—An open-mouthed Dewar-type of vacuum-jacketed flask is needed. Its capacity shall be nominally 500-mL in size. It shall be provided with a base to hold it upright. (See Fig. 4.)

6.12 *Oven*—An electrically heated oven, preferably with internal circulation of air, shall be used if the crystallizable compound described in 6.9 is solid at room temperature. The oven must be thermostatically controlled over the temperature range of 60 to 200°C with tolerance of  $\pm 10^\circ\text{C}$  at any setting in this range. Its chamber must be large enough to hold the items described in 6.10, 6.11, 6.12 and 6.13 at the same time. A chamber of satisfactory size shall be cubic, 500 mm to a side. A thermometer shall be inserted at the top with its bulb about 125 mm below the ceiling of the chamber.

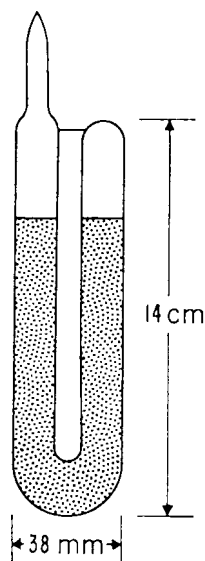


FIG. 3 Thermometric Reference Cell

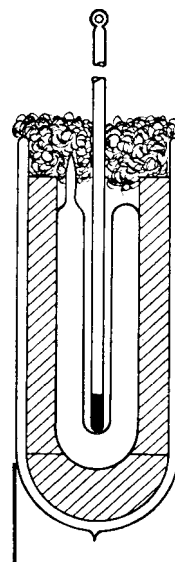


FIG. 4 Reference Cell in Vacuum Flask

6.13 *Cradle*—Two pieces of fireproof, 6.4-mm board are needed to support the thermometric cell in the oven. The dimensions of each piece shall be about 120 mm in length, 70 mm in width, and between 6 and 12 mm in thickness.

6.14 *Safety Items*—For personal protection when handling fragile cells with contents of a molten compound that is a skin-irritant or that has a melting point above 60°C, the operator will need a pair of heat-resistant gloves, a long rubber apron, and a transparent visor.

6.15 *Magnifying Glass*—For accurately reading the temperature indicated by the thermometer, it is advantageous to use a magnifying glass, provided with an eyepiece and a cross-hair, and mounted on a friction-slide that fits over the thermometer stem.

## 7. Reagents and Materials

7.1 *Cork Stoppers*—Suitable corks to be used as described in 6.2, 6.3, and 6.4.

<sup>7</sup> Enagonio, D. P., Pearson, E. G., and Saylor, C. P. *Temperature—Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, NY, Vol 3, Part 1, 1962, pp. 219-230.

7.2 *Cooling Medium*—Technical grade glycerin, technical grade methanol or denatured alcohol, water, ice, and dry ice for use with the cooling bath.

7.3 *Drying Agents*—A molecular sieve zeolite with 4A size of pores shall be used for drying liquid hydrocarbons and phenol. The zeolite may be in the form of a powder or of cylindrical granules about 3 mm in diameter. The granules are preferred. The pore size is critical, because pores larger than 4A will absorb some hydrocarbons preferentially. Sodium hydroxide pellets can be used for drying liquid hydrocarbons and other nonacidic compounds. Anhydrous calcium sulfate granules, free of dust, can also be used.

7.4 *Packing Materials*—Cotton wadding, cloth wipers, and glass wool for packing around glass cells of hot, molten compounds. Thin aluminum foil, light duty wrap, will also be needed as described in 10.10.

## 8. Hazards

8.1 Consult current OSHA regulations, supplier's Material Safety Data Sheets, and local regulations for all materials used in this test method.

## 9. Sampling and Handling

9.1 Sample the material in accordance with Practices D 3432, D 3438, and D 3852.

## 10. Preparation of Sample

10.1 If a sample is a solid mass at room temperature, melt the entire sample by heating it at about 10°C above its solidification point and swirl it for homogeneity before pouring the portion, as specified below, for drying and analysis, or both.

10.2 If the sample is to be dried before being tested, place about 100 g of the material in a 400-mL Erlenmeyer flask and add about 50 g of drying agent, for example, anhydrous calcium sulfate or sodium hydroxide pellets. Liquids shall be dried at room temperature and solids on a hot plate at about 10°C above their solidification point. If the sample is hygroscopic, place a very loosely fitting stopper in the flask. After 15 min, decant the sample to another flask and repeat the drying step with occasional stirring. Pour sufficient sample into the sample container to fill it to a depth of approximately 100 mm. Then proceed as described in 10.1.

10.3 Highly hygroscopic materials, or materials like refined phenol of which the solidification point is very sensitive to moisture, shall be dried as follows: Add 15 g of 4A molecular sieve to 100 g of the molten material in a 400-mL Erlenmeyer flask; stopper the flask very loosely and place it on a hot plate at a temperature at least 10°C above the solidification point of the sample, but not hot enough to cause the sample to boil or to decompose. For example, a sample of phenol shall be heated at 60°C. Heat the sample for 20 min with agitation by swirling at 5-min intervals. This method of drying is satisfactory for phenol containing as much as 2 % water. Quickly transfer the dried sample, including any entrained drying agent, to the specimen container to a depth of about 100 mm. The layer of entrained drying agent, after it has settled in the specimen container, must not exceed a depth of 15 mm. If there is any doubt as to the completeness of drying, decant the molten sample from the drying agent and repeat the procedure with

fresh drying agent on the same sample. After drying the sample, proceed as described in 10.1.

10.4 In an alternative method, when specified, dry the sample by heating it to its initial boiling point. Support the distillation flask on the asbestos board over the bunsen burner or the electric heater by means of the ring stand. Attach the clamp to the lower part of the neck of the flask. Transfer about 100 g of the sample to the flask and place a solid cork stopper in the neck. Heat the flask slowly and allow the sample to melt and then to boil gently. Any water present in the sample will condense in the neck of the flask. If considerable water is present, it will distill out of the side tube of the flask and it should be collected in a receiver and then discarded. This method shall not be used for materials that have initial boiling points below 80°C or above 260°C. Allow the dry condensed liquid to rise in the neck of the flask by further heating, for not more than 1 min, until the liquid just reaches the side tube. Remove the source of heat and the stopper. Let the sample cool for 1 min. Then warm the neck of the flask above the side tube with a very small flame of the bunsen burner to drive off any condensed moisture. Then stopper the flask with a dry cork. Let the sample cool until it can be poured conveniently and safely; while its temperature is still at least 10°C above its solidification point, swirl it in the flask to ensure homogeneity, and pour enough of it into the specimen container to reach a depth of about 100 mm. Then proceed as described in 11.1.

10.5 If the sample is not to be fired but is to be tested as received, pour it in liquid form into the specimen container to a depth of about 100 mm. If it is not liquid at room temperature, heat about 100 g of it in a 400-mL Erlenmeyer flask to a temperature about 10°C above its melting point and swirl it for homogeneity before pouring it into the specimen container. Use this procedure in the testing of refined naphthalene. Then proceed as described in 11.1.

10.6 If the sample is a water-immiscible substance, for example a liquid hydrocarbon, and is specified to be tested after saturation with water, proceed as described in 10.6 to introduce the sample into the sample container. Then add one drop, about 0.06 g, of water; stopper the specimen container, and shake it vigorously. Then proceed as described in 11.1.

## 11. Procedure

11.1 The cooling bath temperature shall be 5 to 10°C below the expected solidification point. When the solidification point of the material under test is sensitive to cooling conditions, it is desirable to keep the bath at the 5°C differential. Refined naphthalene and phenol are two such materials. For naphthalene the cooling bath shall be held at 70 to 75°C, and for phenol at 30 to 35°C, the higher temperature being preferable in each range. Fit the sample container up to its lip into the cork stopper of the air-jacket. Fit the thermometer and the stirrer into the two-hole stopper of the specimen container. Adjust the partial-immersion thermometer so that it is immersed up to its 76-mm calibration mark in the specimen. The bottom of the thermometer bulb will then be about 24 mm above the bottom of the specimen container. Use this procedure exactly when naphthalene, phenol, phthalic anhydride, or maleic anhydride is being tested.

11.2 Clamp the assembly, described in 10.1 and illustrated

in Fig. 2, to the ring stand and place it so that the air jacket is immersed vertically in the cooling bath to a depth at which at least 100 mm of length of the specimen container is below the surface of the cooling medium.

11.3 Allow the specimen to cool while stirring it at the rate of about 60 strokes per minute. A mechanical reciprocating device that will simulate hand stirring is permissible. The stirrer should not touch the thermometer or the wall of the sample container. Discontinue stirring after an appreciable amount of crystals has formed but while the specimen is still mainly liquid.

11.4 Observe and record the thermometer readings at regular intervals, estimating degrees to the nearest  $0.01^{\circ}\text{C}$  until the temperature rises from minimum, due to supercooling, to a maximum and finally begins to drop. The true maximum temperature is the solidification point. As the temperature approaches this point on the rise, thermometer readings should be taken at 10-s intervals in order to make sure that the temperature has reached its maximum, and at least three more readings should therefore then be taken at the maximum level, until the first drop in temperature is noted. This will ensure against mistaking a temporary plateau of temperature level for the true maximum temperature. If there is any doubt about the trend of the readings, plotting a graph of temperature versus time on linear graph paper will help in interpreting the data clearly. Note the experimental maximum temperature,  $t_e$ . (See Section 12 for temperature corrections to be added to  $t_e$ .)

NOTE 4—The accuracy of the thermometer readings can be increased by using a magnifying glass that assures a reading on a line of sight perpendicular to the stem of the thermometer. This should be done in the testing of refined naphthalene and phthalic anhydride. Also, for the record, the average temperature,  $t_0$ , of the emergent mercury column should be taken. (See 11.1-11.4.)

NOTE 5—If the temperature rise after initial crystallization exceeds  $0.5^{\circ}\text{C}$ , remelt the specimen by warming it gently in the specimen container and repeat the test. Seed with two or three small crystals of the sample when the temperature is  $0.2$  to  $0.3^{\circ}\text{C}$  below the expected solidification point. When the sample is a liquid, these crystals may be obtained by freezing a small quantity of the liquid in a test tube immersed directly in the cooling bath. Some compounds have more than one solidification point due to the occurrence of metastable phases. Therefore it is essential to select, for the seeding, crystals known to be of the desired stable phase as found by a previous determination of solidification point. As an alternative to induce crystallization, a chilled wire may be substituted in place of small crystals of the sample.

NOTE 6—The procedure described in 10.5 to 10.10 inclusive, is required only for checking the accuracy of the thermometer at the solidification point of the material being tested.

11.5 When the accuracy of the thermometer is to be checked, as indicated in Note 3 and Note 6, make the check by means of a thermometric cell. Check immediately before determining the solidification point of the sample. To make sure that the temperature of the emergent mercury column in the stem of the thermometer is the same during the check as during the determination of solidification point, carry out both operations at the same spot.

11.6 The thermometric cell contains a crystallizable compound. This shall be preferably a pure sample of the same compound as the sample of which the solidification point is to be determined with the thermometer that is being checked. The

solidification point of the material in the cell shall be certified by a referee from the measurement made with an accurate platinum-resistant thermometer in the well of the cell. Repeat the measurement under comparable conditions with the thermometer of unknown accuracy. The difference between the two measurements is a correction for the test thermometer at the temperature of the solidification point of the test sample. (See 12.4-12.8.)

11.7 Inspect the thermometer very closely, preferably with a magnifying glass, to make sure that there are no minute cracks in the bulb and no air bubbles in the thread or column of mercury. If air bubbles are noted, remove them by cooling the thermometer in dry ice and tapping it gently. Place the thermometer down to its immersion mark in the cooling bath at the temperature at which the bath will be held for determining the solidification point of a sample of the compound in the thermometric cell, and hold the thermometer there for at least  $\frac{1}{2}$  h. For example, Thermometer 96C shall be conditioned thus at about  $126^{\circ}\text{C}$  for use in testing phthalic anhydride.

11.8 If the compound in the thermometric cell is solid, it must be melted in the oven under controlled conditions at a temperature above its melting point by  $40$  to  $60^{\circ}\text{C}$ . An increment of  $60^{\circ}\text{C}$  is preferred. For example, phthalic anhydride is melted at  $190^{\circ}\text{C}$ , oven temperature. First, prepare a cradle to hold the cell, by placing the two pieces of fireproof board about  $20$  mm apart on the oven shelf, laying them flat with their long sides parallel. Place the thermometric cell lying down lengthwise in the groove thus formed by the boards and with the nipple, where the glass was sealed in the manufacture of the cell, facing upward. Place the vacuum flask on the oven floor at the same time for conditioning. If the vacuum flask is one that is set in its base with untaite cement, do not heat it above  $120^{\circ}\text{C}$ . If the compound in the thermometric cell is normally liquid or if its solidification point is below  $45^{\circ}\text{C}$ , the conditioning of the cell and the vacuum flask shall be carried out at an appropriate temperature in the cooling bath instead of the oven, in a way similar to that used for the thermometer described in 11.7. For example, a cell containing benzene shall be conditioned in cold water at  $4.5$  to  $5.0^{\circ}\text{C}$ , and a cell containing phenol shall be conditioned in hot water at  $70$  to  $80^{\circ}\text{C}$ . An alternative way to condition the vacuum flask is to store within it, for  $\frac{1}{2}$ h, a thermometric cell, for example a duplicate or a dummy, which itself has been conditioned at the appropriate temperature.

11.9 Close the oven door and leave it closed for  $10$  min. Then open the door and rotate the cell one complete turn in the groove of the cradle before reclosing the door. Repeat this turning every  $2$  min until the crystals in the cell have melted completely. For phthalic anhydride, repeat this turning four or five times; the crystals will be completely molten in about  $20$  min. This melting procedure is fairly critical in order to avoid breakage of cells containing crystals that melt at about  $80^{\circ}\text{C}$  or higher and that are fused together in a lump in the cell. Using heat-insulating gloves, take the vacuum flask out and set it on its stand. Then wrap the hot cell in cotton wadding or in several layers of cloth wipers, with both ends of the cell exposed. With due precaution against burns, grasp the bundled cell and shake it vigorously, end to end in the direction of its long axis, until

a slurry or mush of fine crystals appears in it. This fairly dense mush should appear practically all at once. Its occurrence can be promoted by directing a gentle jet of air at the top of the cell or by touching the top with a lump of dry ice. Then continue the shaking for 5.0 s longer and, with a layer of cloth wipers or cotton wadding about the cell to provide a snug fit in the vacuum flask, insert the cell right side up in the conditioned vacuum flask; lay additional wadding or glass wool over it, as shown in Fig. 4, sufficiently loose to allow the thermometer later to be inserted in the well of the cell.

11.10 Insert the thermometer, which has been conditioned in accordance with 10.7, into the well of the cell. The fit must be snug, to ensure good heat transfer through the wall of the well to the bulb of the thermometer. If the fit is loose, either wrap a turn of aluminum foil around the bulb only, or pour into the well about 0.5 mL of glycerin preheated to just slightly below the solidification point of the material in the cell, in order to improve heat transfer. Adjust the top wadding about the stem of the thermometer so as not to obscure the mercury thread from sight. After 5 min read the temperature to the nearest 0.01°C, using a magnifying glass to aid in visual estimation of hundredths of a degree. Read the temperature at regular, frequent intervals and note its maximum value, the uncorrected temperature,  $T_u$ . The time to attain the maximum, and then to reveal a distinct drop in temperature, varies for different materials. It must be not less than 10 min. The intervals at which temperature readings are taken shall be every 2 min after the first reading until the sixth reading; if the maximum reading is not attained after 15 min total elapsed time, readings shall then be made at 5-min intervals. After the first 15 min, take the average temperature,  $T_o$ , of the emergent stem of the thermometer with another thermometer placed alongside with its bulb at a level about half way along the length of the emergent mercury column. Do not hold the thermometer that is being checked, because the warmth of one's fingers can affect the value  $T_u$  as much as 0.03°C.

11.11 Platinum resistance or quartz thermometers may be used to calibrate the liquid in glass thermometers used in this test method.

## 12. Temperature Corrections

12.1 If a thermometer other than one of those listed in Table 1 was used in this test method, calculate and report a temperature correction to be added to  $t_e$ . This correction is called the emergent stem correction. In a partial immersion thermometer, this correction compensates for the difference,  $(t_s - t_o)$ , between  $t_s$ , the stem temperature at which the scale of the thermometer was standardized, and  $t_o$ , the observed average temperature of the emergent column of mercury. (See Test Method E 77.) See Note 6 for reference to  $t_o$ . For  $t_s$ , see the Selected Standardization Temperature in Table 1 or see Table 2 of Specification E 1. The correction is algebraically additive. Its value is calculated by the formula  $Kn(t_s - t_o)$ , where  $K$  is the differential coefficient of expansion between the liquid in the thermometer and the glass of which the thermometer is made. For mercury-in-glass thermometers graduated in degrees Celsius,  $K = 0.00016$ ; and  $n$  is the number of degrees Celsius between the start of the scale on a partial immersion thermometer and  $t_e$ , the experimental maximum temperature.

12.2 In a total immersion thermometer, the emergent stem correction is calculated differently and is needed only when the thermometer is used at partial immersion. This correction compensates for the difference,  $(t_b - t_o)$ , between  $t_b$ , the temperature of the bulk of the thermometer, and  $t_o$ , the observed average temperature of the emergent column of mercury. One way to assign a numerical value to  $t_b$  is to measure  $t_e$  with a thermometer of which the scale is certified to be accurate within 0.02°C and to take  $t_b = t_e$ . Another way is to repeat the procedure without using the air jacket; then, after observing  $t_e$ , let the specimen remain in the apparatus for 20 min more, measure  $t_o$  again, and take the temperature of the cooling bath for the value of  $t_b$  in the term  $(t_b - t_o)$ .

12.3 The emergent stem correction is algebraically additive. Its value for a mercury-in-glass thermometer graduated in degrees Celsius is calculated by the formula  $0.00016 N(t_b - t_o)$ , where  $N$  is the number of degrees emergent from the bath.

12.4 Report the corrected temperature as follows:

$$t_n = t_s + 0.00016 n (t_s - t_o) \text{ for a partial immersion thermometer} \quad (1)$$

or

$$t'_n = t_s + 0.00016 N (t_b - t_o) \text{ for a total immersion thermometer} \quad (2)$$

If the thermometer scale was certified to be accurate within 0.02°C when the test was made, report  $t_n$  or  $t'_n$  as the solidification point.

12.5 For referee tests, either the thermometer shall be stipulated to be accurate within 0.02°C of scale at the level of  $t_s$ , or the thermometer shall be checked for accuracy, immediately prior to the measurement of  $t_s$ . (See Section 10.6 and 10.10.) In this check the apparent scalar error is measured. It is the difference,  $(T_e - T_u)$ , between  $T_e$ , the certified calibration temperature assigned to the thermometric cell, and  $T_u$ , the uncorrected temperature observed with the test thermometer at the solidification point of the reference compound in the cell. If this difference is a number between +0.02 and -0.02°C, it shall be disregarded as being indistinguishable from zero by this measurement. If the difference is either a positive or a negative number outside of the range from +0.02 to -0.02°C, inclusive, it shall be applied as an algebraically additive scalar correction.

12.6 If the thermometer was selected in accordance with Table 1 and used in accordance with 10.10, and in general whenever the emergent stem temperature is the same in the checking procedure for accuracy as in the testing procedure for solidification point, that is, whenever  $T_o = t_o$ , report solidification point as follows:

$$t_p = t_s + Kn(t_s - t_o) + (T_c - T_u) = t_n + (T_c - T_u) \quad (3)$$

12.7 If a partial immersion thermometer other than one listed in Table 1 is used, and whenever  $T_o = t_o$ , report solidification point as follows:

$$t_q = t_m + (T_c - T_u) - Km(T_e - T_o) \quad (4)$$

where  $m$  is the number of degrees on the scale between  $T_u$

and the start of the scale.

12.8 If a total immersion thermometer is used, report solidification point as follows:

$$t'_q t'_n + (T_c - T_u) - KM(T_c - T_c) \quad (5)$$

where  $M$  is the number of degrees on the scale between  $T_u$  and the level of the surface of the molten reference compound in the cell.

### 13. Report

13.1 For completeness of record and for referee tests, report the following information:

13.1.1 Whether the sample was tested dry or water-saturated or as received,

13.1.2 Which method of drying, if any, was used,

13.1.3 Which drying agent, if any, was used,

13.1.4 Whether the air-jacket and cooling bath were used,

13.1.5 Temperature of the cooling-bath, if it was used,

13.1.6 ASTM thermometer that was used,

13.1.7  $t_e$ , the experimental maximum temperature, as the average of at least three readings of the maximum value, to the nearest 0.01°C (see 10.4), and

13.1.8 If one of the thermometers listed in Table 1 was used and if its scale was stipulated to be accurate within 0.02°C when the test was made, report  $t_e$  as the solidification point.

NOTE 7—See Section 11 for calculations to be made if a thermometer other than one of those listed in Table 1 was used or if a temperature correction must be added to  $t_e$ .

13.2 For referee tests of refined phenol, the report shall confirm that the following requirements have been met:

13.2.1 The sample was tested dry,

13.2.2 The drying method described in 13.1 was used,

13.2.3 The drying agent used was molecular sieve 4A in granular form,

13.2.4 The air jacket and cooling bath were used,

13.2.5 The temperature of the cooling bath was between 30 and 35°C, and

13.2.6 ASTM Thermometer 91C was used. The report shall also include the following:

13.2.7 The value of  $t_e$ ,

13.2.8 That scale error was stipulated to be negligible if it is neglected, and

13.2.9 The value of  $t_p$ , if, under 13.2.8, the report does not state that scale error was stipulated to be negligible.

13.3 For referee tests of refined naphthalene, the report shall conform that the following requirements have been met:

13.3.1 The sample was tested as received,

13.3.2 The air jacket and cooling bath were used,

13.3.3 The temperature of the cooling bath was between 70 and 75°C, and

13.3.4 ASTM Thermometer 93C was used. The report shall also include the following:

13.3.5 The value of  $t_e$ ,

13.3.6 That scale error was stipulated to be negligible if it is neglected, and

13.3.7 The value of  $t_p$ , if, under 13.3.6, the report does not state that scale error was stipulated to be negligible.

13.4 For referee tests of phthalic anhydride, the report shall

confirm that the following requirements have been met:

13.4.1 The sample was tested as received,

13.4.2 The air jacket and cooling bath were used,

13.4.3 The temperature of the cooling bath was between 121 and 126°C, and

13.4.4 ASTM Thermometer 96C was used. The report shall also include the following:

13.4.5 The value of  $t_e$ ,

13.4.6 That scale error was stipulated to be negligible if it is neglected, and

13.4.7 The value of  $t_p$ , if, under 13.4.6, the report does not state that scale error was stipulated to be negligible.

13.5 When the sample is tested water-saturated and a standard correction for the effect of the moisture is specified, as for benzene as described in Test Method D 852, add the correction and report the corrected solidification point.

### 14. Precision and Bias

14.1 For the materials reported respectively in accordance with 13.2, 13.3, and 13.4, the precision of the solidification point at the level of 95 % confidence is as follows:

Refined Material	Repeatability, °C	Reproducibility, °C
Phenol	0.03	0.07
Naphthalene	0.05	0.10
Phthalic anhydride	0.05	0.11

14.2 For a measure of precision in the checking procedure described in 10.10, the standard deviation of  $T_u$  has been found to be no greater than 0.005°C in repeatability.  $T_u$  is the uncorrected temperature observed with a partial immersion thermometer at the solidification point of the reference compound in a thermometric cell.

14.3 For a measure of the accuracy that is attainable in the checking procedure described in 10.10, the difference ( $T_c - T'_u$ ) has been taken.  $T_c$  is the certified temperature assigned to a thermometric cell for the solidification point of the reference compound in it.  $T'_u$  is a special value of  $T_u$ : in the special case in which  $T_u$  is observed with an accurate thermometer requiring no scalar correction,  $T_u = T'_u$ . The following limits have been found for the value of ( $T_c - T'_u$ ):

Reference Compound in Thermometric Cell	Numerical Limits of the Value of ( $T_c - T'_u$ )	
	Minimum Value, deg°C	Maximum Value, deg°C
Phenol	-0.012	-0.022
Naphthalene	+0.020	-0.031
Phthalic anhydride	-0.095	-0.112

14.4 The following criteria should be used for judging the acceptability of results for maleic anhydride:

14.4.1 *Intermediate Precision (formerly called Repeatability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.012°C at 10 dP. Two such values should be considered suspect (95 % confidence level) if they differ by more than 0.05°C.

14.4.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysis in different laboratories, has been estimated to be 0.077°C at 9 dP. Two such values should be considered suspect (95 % confidence level) if they differ by more than 0.25°C.

## 15. Keywords

15.1 heat of fusion; heat of solidification; solidification point

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