Standard Test Method for
Freezing Points of High-Purity Hydrocarbons

1. Scope

1.1 This test method covers a procedure for the precise measurement of the freezing points of high-purity hydrocarbons.

1.2 The values stated in SI units are to be regarded as the standard. The values in parentheses are for information only.

1.3 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see 5.1, 6.1 and 6.2.

Note 1—For the calculation of the molal purity of essentially pure compounds from measured freezing points and for procedures to be used for the sampling and determination of purity of certain specific compounds, see Test Method D 1016.

2. Referenced Documents

2.1 ASTM Standards:

D 1016 Test Method for Purity of Hydrocarbons from Freezing Points
D 1265 Practice for Sampling Liquefied Petroleum (LP) Gases (Manual Method)
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

3. Summary of Test Method

3.1 The precise experimental measurement of the freezing point is made from interpretation of time-temperature freezing or melting curves.3

4. Significance and Use

4.1 The freezing point measured by this test method, when used in conjunction with the physical constants for the hydrocarbons listed in Test Method D 1016, allows the determination of the purity of the material under test. A knowledge of the purity of these hydrocarbons is often needed to help control their manufacture and to determine their suitability for use as reagent chemicals or for conversion to other chemical intermediates or finished products.

5. Apparatus

5.1 Freezing-Point Apparatus,4,5 as shown in Figs. 1-3 comprising a freezing tube, a metal sheath for the freezing tube, a Dewar flask for the cooling bath, a Dewar flask for the warming bath, a stirring mechanism, suitable clamps and holders for the parts, and the absorption tubes. The outer walls of all Dewar flasks can be covered with adhesive tape to minimize danger from glass in case of breakage. (Warning—When using liquid nitrogen as a refrigerant, provide a means to prevent condensation of oxygen in the space between the freezing tube and the metal sheath and subsequent sealing of the space by ice forming on the asbestos collar. Provide the metal sheath with suitable openings in the sides and bottom. Failure to do this may result in breakage of the freezing tube when the liquefied oxygen evaporates within the sealed space.)

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3 This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Physical and Chemical Methods.

4 The sole source of supply of the apparatus known to the committee at this time is Reliance Glass Works, Inc., Bensenville, IL.

5 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.

Copyright © ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States.
A—Bracket for motor, with rubber pad.
B—Motor, with reduction gears, to give 120 r/min.
C—Coupling. (See Fig. 3).
D—Wheel. (See Fig. 3).
E—Steel rod. (See Fig. 3).
F—Bearing. (See Fig. 3).
G—Support for bearing. (See Fig. 3).
H—Support for freezing tube.
I—Adjustable clamp holder.
J—Clamp for freezing tube.
K—Stirrer. (See Fig. 3).
L—Thermometer.
M—Tube for inlet of dry air, with 12/5 spherical joint.
M—12/5 spherical joint connection to rotameter.
N—Cork stopper, with holes as shown, plus a small hole for the “seed” wire.
O—Freezing tube, with silvered jacket. (See Fig. 2)
P—Stopcock on freezing tube.
P—Stopcock (high vacuum) to drying tube.
P—Stopcock (high vacuum) to vacuum line.
Q—Asbestos collar.
R—Brass cylinder, 317.5 mm (12 1/2 in.) in length and 54 mm (2 1/8 in.) in inside diameter, with bakelite collar; when liquid nitrogen is used, the metal shield must be provided with suitable openings in sides and bottom (see 5.1). If liquid air is used, the metal shield should be constructed so as to keep hydrocarbon from contact with liquid air (see 6.2).
S—Dewar flask, for cooling or warming bath; approximate inside diameter, 101 mm (4 in.); approximate inside depth, 330 mm (13 in.).
T—Asbestos pad at bottom of cylinder R.
U—Wood block support.
V—Table top.
W—Wall.
X—Spherical joint, 18/7.
Y—Standard metal (copper or brass) to glass taper connections soldered.
Z—Connection to vacuum pump.
a—Anhydrous calcium sulfate, with indicator.
b—Anhydrous magnesium perchlorate, granular.
d—Separating layer of glass wool.
e—Ascarite.
f—Anhydrous calcium sulfate.
g—To air.
h—To source of compressed air.
i—Flow meter, for rates of 10 to 20 mL/min.

FIG. 1 Assembly of the Freezing-Point Apparatus
5.2 Resistance Bridge,\(^6\) Mueller type, reading from 0.0001 to 50 \(\Omega\), in steps of 0.001 \(\Omega\).

5.3 Platinum Resistance Thermometer,\(^6\) precision grade, with a resistance near 25.5 \(\Omega\) at 0°C, calibrated by the National Institute of Standards and Technology for the range from −190 to 500°C.

5.4 Null Point Indicator, may be either a galvanometer or a microvolt ammeter.

5.4.1 Galvanometer,\(^6\) having a sensitivity of 0.1 mV/m at 1 m for highest precision or a sensitivity of 0.5 mV/m at 1 m for routine precision.

5.4.2 Microvolt Ammeter,\(^5,7\)

5.5 Lamp and Scale,\(^6\) any suitable type.

5.6 Stopwatch or Clock, preferably having graduations in minutes and hundredths of minutes.

5.7 High-Vacuum Oil Pump,\(^5,8\) capable of evacuating the jacket of the freezing tube to a pressure of 0.133 Pa in 10 min or less.

5.8 Seeding Apparatus, as shown in Fig. 4, for inducing crystallization.

5.9 Silica Gel Funnel, as shown in Fig. 5, for filtering compounds through silica gel to remove water. To be used only when specified in Test Method D 1016.

6. Materials

6.1 Carbon Dioxide Refrigerant—Solid carbon dioxide in a suitable liquid. (Warning—Extremely cold (−78.5°C). Liberates heavy gas which can cause suffocation. Contact with skin causes burns or freezing, or both. Vapors can react violently with hot magnesium or aluminum alloys.) Acetone is recommended. (Warning—Extremely flammable. Harmful if inhaled. High concentrations can cause unconsciousness or death. Contact can cause skin irritation and dermatitis. Use refrigerant bath only with adequate ventilation.)

6.2 Liquid Nitrogen or Liquid Air—(Warning—Extremely cold. Liberates gas which can cause suffocation. Contact with skin causes burns or freezing, or both. Vapors can react violently with hot magnesium or aluminum alloys.) For use as a refrigerant. If obtainable, liquid nitrogen is preferable because of its safety.

6.2.1 Use liquid nitrogen refrigerant only with adequate ventilation. If liquid air is used as a refrigerant, it is imperative that any glass vessel containing hydrocarbon or other combustible compound and immersed in liquid air be protected with a suitable metal shield. The mixing of a hydrocarbon or other combustible compound with liquid air due to the breaking of a glass container would almost certainly result in a violent explosion. If liquid nitrogen is used as a refrigerant, no hydrocarbon sample should ever be permitted to cool below the condensation temperature of oxygen (−183°C at 1 atm). This would not be likely to occur in normal operation, but might occur if the apparatus were left unattended for some time.

6.3 Silica Gel, for use in silica gel funnel.\(^5,9\) If the gel has been exposed to the atmosphere because of punctured or loosely sealed containers, before use, dry the gel in a shallow vessel at 150 to 205°C for 3 h, then transfer while hot to an air-tight container.
A—Stainless steel rod, round.
B—German-silver tube.
C—Pins.
D—Holes, 3.2 mm (1/8 in.) in diameter.
E—Brass wheel, with three holes; tapped for machine screws, spaced 12.7 mm (1/2 in.), 19.05 mm (3/4 in.), and 25.4 mm (1 in.) from center; normal position is 19.05 mm (3/4 in.) from center.
F—Steel rod.
G—Set screws.
H—Brass coupling.
I—Steel shaft.
J—Steel rod, square.
K—Connecting pin.
L—Brass sleeve bearing.
M—Steel pipe, 12.7 mm (1/2 in.) nominal size.
N—Brass coupling.
O—Brass tee.
P—Aluminum.
Q—Double helical stirrer, made by winding 1.6 mm (1/16 in.) diameter nichrome wire downwards on a cylinder 14.3 mm (9/16 in.) in outside diameter to form the inner helix, and then upwards over a cylinder 20.7 mm (3/4 in.) in outside diameter to form the outer helix, with the two ends silver soldered together.
R—Place where shaft of the double helical stirrer is joined to the stirrer shaft.

Metric Equivalents

<table>
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<th>mm</th>
<th>0.794</th>
<th>11.91</th>
<th>4.763</th>
<th>24</th>
<th>74.612</th>
<th>77.8</th>
<th>9.53</th>
<th>22.23</th>
<th>28.6</th>
<th>60.33</th>
<th>117.5</th>
<th>6.4</th>
<th>57.15</th>
<th>108</th>
<th>63.5</th>
<th>114.3</th>
<th>215.98</th>
</tr>
</thead>
</table>

FIG. 3 Details of the Stirring Assembly and Supports
7. Sampling

7.1 Sampling from Bulk Storage:

7.1.1 Cylinder—Refer to Practice D 1265 for instructions on introducing samples into a cylinder from bulk storage.

7.1.2 Open Containers—Refer to Practice D 4057 for instructions on introducing samples into open-type containers from bulk storage.

8. Calibration of Thermometric System and Conversion of Resistance Readings to Temperature

8.1 Calibration of Resistance Bridge—The Mueller-type resistance bridge should have its calibration checked at appropriate intervals by measurement of a suitable external certified resistance, with intercomparison of the resistances of the bridge.

8.2 Calibration of Resistance Thermometer—The platinum-resistance thermometer is provided with four calibration constants certified by the National Institute of Standards and Technology for use in converting the resistance of the thermometer into temperature according to the International Temperature Scale, for use in the range from −190 to 500°C, namely, \( R_0 \), \( C \), \( d \), and \( b \). If the thermometer has been properly constructed and annealed, the certified constants \( C \), \( d \), and \( b \) will not change significantly with time, but the value of \( R_0 \) may change slightly.

**NOTE 2—**International Practical Temperature Scale (IPTS)—In 1968, a new IPTS was adopted, replacing the previous scale in use since 1948. The 1948 IPTS was based on the boiling point of oxygen, the sulfur point, ice point, and steam point. The 1968 IPTS is based on the triple point of water, tin point, zinc point, and boiling point of oxygen. The differences in the two temperature scales \( T_{68} - T_{48} \) vary. Above 100°C the differences are plus; below 100°C they may be either plus or minus.

If the measured freezing point is to be used for the determination of purity according to Test Method D 1016, the measured freezing point \( t_f \) and the freezing point of the pure material \( t_{fo} \) should be on the same temperature scale. The values of \( t_{fo} \) given in Test Method D 1016 are on the 1968 IPTS. Therefore, values of \( t_f \) determined using thermometers calibrated on the 1948 scale should be converted to their 1968 IPTS equivalent. This conversion can be made by applying the appropriate correction from Table 1.

8.3 Checking of the Ice Point—Frequent measurements (at least once every month) should be made of the resistance of the given platinum thermometer at the ice point, 0°C, as measured on the given resistance bridge.\(^{10}\) This value should differ only slightly from the certified value of \( R_0 \). If the difference becomes appreciable (approaching 0.001 Ω), the calibration of the bridge should be checked. If the bridge has not changed, the change has occurred in the thermometer, and a recalibration of it is recommended.

8.4 Conversion of Resistance Readings to Temperature—When determinations are made on a number of substances having freezing points at different temperatures, time will be saved by making up a table giving values of the resistance, \( R \), for each unit degree of temperature in the given range. Values of resistance for unit degrees, for the ranges from −190 to +50°C and +50 to 290°C, with differences between successive unit degrees tabulated for linear interpolation (which is permissible), may be easily placed on a single 300 by 400-mm (14

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\(^{10}\) The ice point may be measured according to the procedure described by J. Busse, "Temperature, Its Measurement and Control in Science and Industry," Section VIII, Reinhold Publishing Corp., 1941, p. 241. See also "Notes to Supplement Resistance Thermometer Certificates," National Institute of Standards and Technology, 1949.
by 16-in.) sheet for each range. Calculate values for the resistance, \( R \), from unit values of temperature, \( t \), by means of one of the following equations:

For temperatures below 0°C:

\[
R = R_0 [1 + C t (1 + 0.01 \delta - 10^{-4} \delta t - 10^{-3} \beta (t - 100) \mu^2)]
\]

For temperatures above 0°C:

\[
R = R_0 [1 + C t (1 + 0.01 \delta - 10^{-4} \delta t)]
\]

where:

\( t \) = given temperature, °C, on the International Temperature Scale (see Note 2),

\( R \) = resistance of the thermometer in ohms at the temperature \( t \),

\( R_0 \) = resistance of the thermometer in ohms at 0°C, and

\( C \), \( \delta \), and \( \beta \) = constants certified for the given platinum thermometer by the National Institute of Standards and Technology.

9. General Procedure for Determining a Freezing Curve

9.1 Assemble the apparatus, with no refrigerant and no sample yet in place, but with a stream of air, freed of carbon dioxide and water, flowing at a rate of 10 to 20 mL/min. Fill the jacket of the freezing tube with air freed of carbon dioxide and water. For samples whose temperature is below the freezing point of the sample. A slurry or mush of liquid and crystals is produced. The rod (ABC in Fig. 4), with wet crystals adhering to the helical coil C, is raised above the liquid level in the tube E and held in position with a cork stopper until required for seeding.

9.3 Fill the Dewar flask surrounding the freezing tube with the appropriate refrigerant. Temporarily remove the thermometer and stopper and then introduce the sample (usually 50 mL of liquid in amount) through a pipet if the material is normally liquid, or by pouring the refrigerated liquid sample through the tapered male outlet of the reservoir trap (E in Fig. 1 of Test Method D 1016) if the material is normally gaseous. When specified in Test Method D 1016, filter the sample directly into a freezing tube (\( O \) in Fig. 1) through silica gel to remove water. A detailed drawing of a funnel used for this purpose is shown in Fig. 5. Each time a freezing or melting curve is determined after the sample is melted, it is necessary to remove the sample from the freezing tube and refilter it through silica gel into a dry freezing tube to remove water. When the sample is volatile or normally gaseous at room temperature, cool the freezing tube before introduction of the sample in order to minimize loss by evaporation. Continue the flow of air (freed of carbon dioxide and water) into the freezing tube in order to keep out water vapor. Start the stirrer and allow the sample to cool down to within about 15°C of the freezing point, then begin evacuation of the jacket of the freezing tube.

9.4 Observe the time and the resistance of the thermometer at even intervals of 0.02 to 0.05 Ω (about 0.2 to 0.5°C) to determine the rate of cooling, which is continually changing as the pressure in the jacket of the freezing tube is reduced. Care must be taken to close the stopcock to the freezing tube when the desired cooling rate is obtained. In case the cooling rate is allowed to become too slow, the pressure and likewise the cooling rate can be increased by bleeding in air (freed of carbon dioxide and water) through stopcocks \( P \) and \( P \) (Fig. 1). When a cooling rate is obtained that will give a change of 1°C in about 1 to 3 min in the range of about 5 to 10°C above the freezing point, close the stopcock controlling the jacket of the freezing tube. (The optimum rate of cooling will vary with the material being examined.)
9.5 When the temperature reaches a point about 5°C above the expected freezing point, record the time \( t \) to 1 s (or 0.01 min) at which the resistance of the thermometer equals 0.1 or 0.05 \( \Omega \). At the appropriate time (see 9.2) induce crystallization. The beginning of crystallization will be accompanied by a halt in the cooling of the liquid. After recovery from undercooling is substantially complete, record the resistances at intervals of about 1 min. If a galvanometer is being used, also record the galvanometer scale at full sensitivity and with no current through the galvanometer. These observations, together with the sensitivity of the galvanometer system in terms of ohms per millimetre of scale reading, yield a sensitivity of nearly 0.0001°C. Approximately equal sensitivity is obtained when using a microvolt ammeter. Continue observations until the stirrer begins to labor, then stop the stirrer. After several minutes (when a steady rate is obtained) make alternate \( N \) and \( R \) readings through the commutator at fixed intervals of about 1 min. Determine the difference between the two at any given time from a plot of the values against time.

10. General Procedure for Determining a Melting Curve

10.1 For determining a melting curve, proceed exactly as described in Section 9 for a freezing curve, up to the point where the stirrer begins laboring. When the stirrer shows signs of laboring, make a comparison of \( N \) and \( R \) readings through the commutator, as in 9.5 except that the stirrer is still operating. When the laboring of the stirrer becomes quite pronounced, the freezing curve (with the stirrer still operating) is changed to a melting curve. The energy for melting is supplied in either of the two following ways: (1) the cooling bath is replaced by a warming bath and simultaneously the jacket is evacuated for an appropriate length of time (3 to 10 min). The stopcock on the freezing tube is closed; or (2) the cooling bath is left in position or replaced by a warming bath and the jacket evacuated as much as possible, leaving the stopcock to the freezing tube open to the vacuum system during the entire melting curve. In this case, the thermal conductivity across the jacket is so small that the energy introduced by the stirrer provides the energy for melting. Continue the observations of time and resistance along the equilibrium portion of the melting curve as along the equilibrium portion of the freezing curve. When melting is substantially complete, as evidenced by a marked change in the rate of change of resistance, make observations of time at even intervals of 0.05 \( \Omega \) (0.5°C). The experiment is concluded when the temperature has gone about 5 to 10°C above the freezing point.

11. Evaluation of the Freezing Point from a Freezing Curve

11.1 To locate zero time (the time at which crystallization would have begun in the absence of undercooling), make a preliminary plot of the time-resistance observations covering the liquid cooling line and the equilibrium portion of the freezing curve. For this plot, as shown in Fig. 6, the time scale is taken so that 10 mm is equivalent to 1 min and the resistance
scale (for a 25-Ω thermometer) is taken so that 10 mm is equivalent to 0.02 Ω (0.2°C). Zero time is determined by a visual extrapolation, on this plot, of the equilibrium portion of the freezing curve back to its intersection with the liquid cooling line.

11.2 In order to locate accurately the resistance corresponding to the freezing point, plot the time-resistance observations as shown in with the time scale as before but with the scale of temperature magnified 10 to 200 times. The equilibrium portion of the curve, \( GHI \), is extended back to its intersection at \( F \) with the liquid line by the simple geometrical construction shown in Fig. 8, selecting for this purpose three points (near the ends and the middle) of the equilibrium portion of the curve (Note 3). The point \( F \) gives the resistance corresponding to the freezing point.

**Note 3**—The location of the resistance corresponding to the freezing point can be made using algebraic expressions derived from the geometrical construction. These are as follows:

\[
R_f = R_g + \frac{(R_f - R_h)(uvw - 1)}{(3)
\]

where:

\[
u = \frac{(R_f - R_g)(R_f - R_h)}{(4)}
\]

\[
v = \frac{(Z_f - Z_g)(Z_f - Z_h)}{(5)}
\]

and

\[
v = \frac{(Z_f - Z_g)(Z_f - Z_h)}{(6)}
\]

12. Evaluation of the Freezing Point from a Melting Curve

12.1 Determine zero time from a preliminary plot (as for the freezing curve (Section 11)) of the time-resistance observations covering the equilibrium portion of the melting curve and the liquid warming line, as shown in Fig. 9. Zero time can usually be determined by visual extrapolation, on this plot, of the equilibrium portion of the melting curve to its intersection with the liquid warming line extended down in temperature to its intersection with the extension of the equilibrium portion of the curve.

12.2 The location of the freezing point at \( F \) is done exactly as in the case of the freezing curve, except that the geometrical extrapolation is made to the right as shown in Fig. 10. (See Fig. 8 and the reference in Footnote 10 for details.)
12.3 Make the conversion of resistance to temperature as described in Section 11.

13. Precision and Bias

NOTE 4—The precision of this test method was not obtained in accordance with RR: D02–1007.¹²

13.1 Results should not differ from the mean by more than the following amounts:

<table>
<thead>
<tr>
<th></th>
<th>Repeatability One Operator and Apparatus</th>
<th>Reproducibility Different Operators and Apparatus</th>
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<tbody>
<tr>
<td>Freezing point, °C</td>
<td>±0.005</td>
<td>±0.015</td>
</tr>
</tbody>
</table>

¹² This research report may be obtained from ASTM International Headquarters by requesting Research Report RR: D02–1007.

NOTE 5—The precision data were obtained using a galvanometer. Equivalent results would be expected when using a microvolt ammeter. Deviations will be greater than those shown for very impure samples, for compounds in which the liquid-solid equilibrium is established sluggishly, and for compounds having small values of the cryoscopic constant A.

13.2 Bias:

13.2.1 The procedure in this test method for measuring freezing point has no bias because the freezing point value can be defined only in terms of this test method, which is a function of the purity of the reference materials.

14. Keywords

14.1 crystallization; freeze point; LPG; pure hydrocarbons; purity
Note—The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer, and the scale of abscissas gives the time in minutes. IHG represents the equilibrium portion of the warming curve. The freezing point $F$ is determined as described in the text and Fig. 8. These data are the same as those plotted in Fig. 9.

**FIG. 10 Time-Temperature Warming Curve for Determining the Freezing Point of a Sample of Ethylbenzene**