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Standard Guide for Use of Freezing-Point Cells for Reference Temperatures[1]

This standard is issued under the fixed designation E 1502; 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.

ε[1] NOTE—Updated caution note in Section 7.2.2 in November 2003.

INTRODUCTION

During freezing, pure material transforms from the liquid state to the solid state at a constant temperature known as the freezing point. The freezing points of highly purified materials can serve as reference temperatures, and in fact, the International Temperature Scale of 1990 (ITS-90)[2] relies on the freezing points of some highly purified metals as defining fixed points. Freezing points can be realized in commercially available systems incorporating freezing-point cells. When the cells are properly made and used, they establish useful reference temperatures for the calibration of thermometers and for other industrial and laboratory purposes; with care, the freezing points of highly purified materials can be realized with an uncertainty of a few millikelvins[3] or less.

1. Scope

1.1 This guide describes the essential features of freezing-point cells and auxiliary apparatus, and the techniques required to realize freezing points in the temperature range from 29 to 1085 °C.[3]

1.2 Detailed design and construction are not addressed in this guide.

1.3 This guide is intended to describe good practice and establish uniform procedures for the realization of freezing points.

1.4 This guide emphasizes principles. The emphasis on principles is intended to aid the user in evaluating cells, in improving technique for using cells, and in establishing procedures for specific applications.

1.5 For the purposes of this guide, the use of freezing-point cells for the accurate calibration of thermometers is restricted to immersion-type thermometers that, when inserted into the reentrant well of the cell, (*1*) indicate the temperature only of the isothermal region of the well, and (*2*) do not significantly alter the temperature of the isothermal region of the well by heat transfer.

1.6 This guide does not address all of the details of thermometer calibration.

1.7 This guide is intended to complement special operating instructions supplied by manufacturers of freezing-point apparatus.

1.8 The following hazard caveat pertains only to the test method portion, Section 7, of this guide. *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:* [4]

E 344 Terminology Relating to Thermometry and Hydrometry

E 644 Test Methods for Testing Industrial Resistance Thermometers

3. Terminology

3.1 *Definitions:*

3.1.1 *reference temperature, n*—a fixed, reproducible temperature, to which a value is assigned, that can be used for the calibration of thermometers or other purposes.

[1] This guide is under the jurisdiction of ASTM Committee E20 on Temperature Measurement and is the direct responsibility of Subcommittee E20.07 on Fundamentals in Thermometry.

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[2] Preston-Thomas, H., "The International Temperature Scale of 1990 (ITS-90)," *Metrologia*, Vol 27, No. 1, 1990, pp. 3–10. For errata see *ibid*, Vol 27, No. 2, 1990, p. 107.

[3] In this guide temperature intervals are expressed in kelvins (K) and millikelvins (mK). Values of temperature are expressed in degrees Celsius (°C), ITS-90.

[4] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.1.2 Additional terms used in this guide are defined in Terminology E 344.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *first cryoscopic constant, A, n*—a constant of proportionality between the freezing point depression of, and concentration of impurities in, a sample of reference material, given by the ratio of the molar heat of fusion of the pure material, *L*, to the product of the molar gas constant, *R*, and the square of the thermodynamic temperature of fusion, *T*, of the pure material (freezing point):

$$A = \frac{L}{RT^2} \tag{1}$$

3.2.2 *freeze, n*—an experiment or test run conducted with a freezing-point cell while the reference material in the cell solidifies.

3.2.3 *freezing curve, n*—the entire time-temperature relation of the reference material in a freezing-point cell during freezing, including initial cooling, undercool, recalescence, freezing plateau, and final cooling to complete solidification.

3.2.3.1 *Discussion*—Graphic representations of freezing curves are shown in Fig. 1 and Fig. 2.

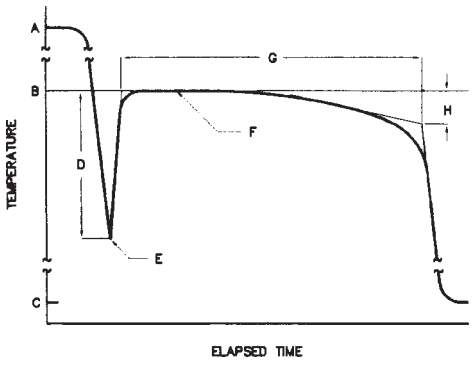
3.2.4 *freezing plateau, n*—the period during freezing in which the temperature does not change significantly.

3.2.5 *freezing-point cell, n*—a device that contains and protects a sample of reference material in such a manner that the freezing point of the material can establish a reference temperature.

3.2.6 *freezing range, n*—the range of temperature over which most of the reference material in a freezing-point cell solidifies.

3.2.6.1 *Discussion*—The freezing range is indicated graphically in Fig. 1.

3.2.7 *nucleation, n*—the formation of crystal nuclei in liquid in the supercooled state.



A = Stabilized temperature of cell before freezing, typically about 1 K above freezing point.
B = Freezing point of cell.
C = Temperature of cell surroundings during freezing, typically about 1 K below freezing point.
D = Maximum undercool.
E = Onset of recalescence.
F = Freezing plateau.
G = Total freezing time.
H = Freezing range.

FIG. 1 Structure of a Typical Freezing Curve

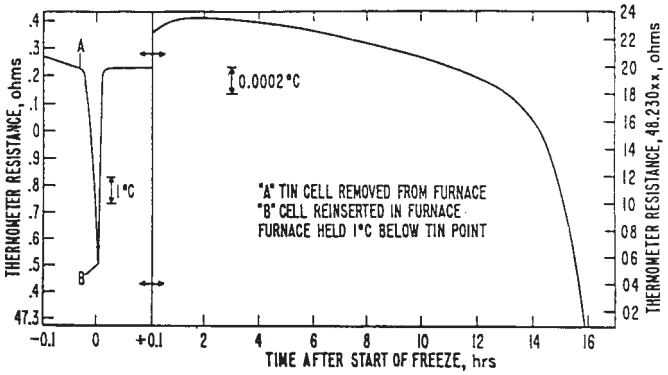


FIG. 2 Freezing Curve of a Sample of Highly Purified Tin

3.2.8 *recalescence, n*—the sudden increase in temperature of reference material in the supercooled state upon nucleation and crystal growth, due to the release of latent heat of fusion of the reference material.

3.2.9 *reference material, n*—the material in a freezing-point cell that melts and freezes during use, the freezing point of which can establish a reference temperature.

3.2.10 *supercooled state, n*—the meta-stable state of reference material in which the temperature of the liquid phase is below the freezing point.

3.2.11 *undercool, n*—the temperature depression below the freezing point of reference material in the supercooled state.

4. Summary of Guide

4.1 A freezing-point cell is used for thermometer calibration by establishing and sustaining a reference material at the freezing point, to which a value of temperature has been assigned. The thermometer to be calibrated is inserted into a reentrant well in the cell; the well itself is surrounded by the freezing reference material.

4.2 The cell is heated to melt the reference material. The temperature of the surrounding environment is then reduced to about 1 K below the freezing point so that the reference material cools. Following the undercool, nucleation, and recalescence, the well temperature becomes constant during the freezing plateau. After a time, depending on the rate of heat loss from the cell, the amount of reference material, and the purity of the reference material, the temperature starts to decrease and eventually all of the material becomes solidified.

4.3 Since the temperature in the reentrant well remains constant during the freezing plateau, one or more test thermometers may be calibrated by inserting them singly into the well. In some cases the plateau can be sustained for many hours, and even under routine industrial conditions, the plateau may be readily sustained long enough to test several thermometers. The duration of the plateau may be lengthened by preheating the test thermometers.

4.4 Measurements are made also during each freeze with a dedicated monitoring thermometer. These measurements, together with other special test measurements, provide qualification test data (see 6.4 and 7.5).

5. Significance and Use

5.1 A pure material has a well-defined freezing behavior, and its freezing point, a characteristic of the material, can serve

as a reproducible reference temperature for the calibration of thermometers. The freezing points of some highly purified metals have been designated as defining fixed points on ITS-90. The freezing points of other materials have been determined carefully enough that they can serve as secondary reference points (see Table 1 and Table 2). This guide presents information on the freezing process as it relates to establishing a reference temperature.

5.2 Freezing-point cells provide users with a means of realizing freezing points. If the cells are appropriately designed and constructed, if they contain material of adequate purity, and if they are properly used, they can establish reference temperatures with uncertainties of a few millikelvins or less. This guide describes some of the design and use considerations.

5.3 Freezing-point cells can be constructed and operated less stringently than required for millikelvin uncertainty, yet still provide reliable, durable, easy-to-use fixed points for a variety of industrial calibration and heat treatment purposes. For example, any freezing-point cell can be operated, often advantageously, as a *melting-point cell*. Such use may result in reduced accuracy, but under special conditions, the accuracy may be commensurate with that of freezing points (see 6.2.10).

5.4 The test procedure described in this guide produces qualification test data as an essential part of the procedure. These data furnish the basis for quality control of the freezing-point procedure; they provide for evaluation of results, they assure continuing reliability of the method, and they yield insight into the cause of test result discrepancies. The test procedure is applicable to the most demanding uses of freezing-point cells for precise thermometer calibration; it may not be appropriate or cost-effective for all applications. It is expected that the user of this guide will adapt the procedure to specific needs.

6. Principles

6.1 *Freezing Process*:

6.1.1 Ideally pure material at a given pressure has a unique temperature when its solid and liquid phases are in perfect thermal equilibrium. In contrast, the phase transition of a real material from liquid to solid, as heat is released in semi-equilibrium freezing, exhibits a complex time-temperature relation (freezing curve) as shown in Figs. 1 and 2.

TABLE 2 Estimated Achievable Uncertainties in Freezing-Point Cells[A]

Materials	Laboratory	
	Primary, mK	Industrial, mK
Gallium[B]	0.1	1
Indium	1	10
Tin	1	10
Cadmium	2	10
Lead	2	10
Zinc	1	10
Antimony	10	50
Aluminum	2	20
Silver	2	40
Gold	. . .	. . .
Copper	10	50

[A] Values for cells of good design, construction, and material purity used with careful technique. Cells of lesser quality may not approach these values.
[B] Realized as melting point.

6.1.2 The deposition of the solid phase from the liquid phase requires the presence of liquid in the supercooled state, nucleation, and crystal growth. Nucleation may begin spontaneously in the meta-stable supercooled liquid, or it may be induced artificially. As crystals nucleate and grow, the liberated latent heat of fusion produces recalescence.

6.1.3 The undercool of materials may range from as little as 0.05 K, for some materials such as zinc, to more than 20 K for tin and other materials (see Table 1). The magnitude of the undercool can depend on the initial temperature, the cooling rate, and the purity of the material.

6.1.4 Following recalescence, the temperature remains relatively constant for a while during the freezing plateau. The temperature associated with the freezing plateau is the temperature to which a value is assigned as the freezing point of the material.

6.1.5 As freezing progresses, some trace impurities in the freezing material tend to be swept in front of the advancing liquid-solid interface and concentrated in the remaining liquid. Since impurities usually depress the freezing point of the reference material, the temperature of the material decreases ever more rapidly until all of the material is solid.

6.1.6 The effect of small concentrations of impurities may be estimated from an approximation rule: the temperature difference between the start of freezing and midpoint of freezing (when half the material is solid) equals the temperature difference between the freezing point of the ideally pure

TABLE 1 Characteristics of Pure Freezing-Point Reference Materials

Material	Freezing Point, ITS-90, °C	Typical Undercool, K	Pressure Coefficient at Freezing Point		First Cryoscopic Constant, K^{-1}
			mK/Pa	mK/m (of liquid)	
Gallium[A,B]	29.7646	76	− 20	−1.2	0.0073
Indium[A]	156.5985	0.1	+ 49	+ 3.3	0.0021
Tin[A]	231.928	25	+ 33	+ 2.2	0.0033
Bismuth	271.403	0.19	− 34	− 3.4	. . .
Cadmium	321.069	0.05–0.5	+ 61	+ 4.8	0.0021
Lead	327.462	0.15	+ 79	+ 8.2	0.0016
Zinc[A]	419.527	0.05–0.1	+ 43	+ 2.7	0.0018
Antimony	630.630	20	+ 8	+ 0.5	0.0029
Aluminum[A]	660.323	0.4–1.5	+ 70	+ 1.6	0.0015
Silver[A]	961.78	1–3	+ 60	+ 5.4	0.00089
Gold[A]	1064.18	1–3	+ 61	+ 10.0	0.00083
Copper[A]	1084.62	1–2	+ 33	+ 2.6	0.00086

[A] Defining fixed point for ITS-90.
[B] Realized as melting point.

material and the freezing point (at the start of freezing) of the real reference material (see 8.6.2). The product of this temperature difference and the *first cryoscopic constant* gives an estimate of the mole fraction impurity concentration in the reference material. Conversely, if the impurity concentration is known, then the temperature difference can be estimated.

6.1.7 The change in temperature during the freezing plateau due to a change in pressure is generally less than 0.1 μK/Pa (Table 1). Thus, normal changes in atmospheric pressure have little effect on the freezing point, but the effect of the pressure of a *head* of dense liquid reference material may be significant. The freezing point is usually taken to be the temperature during the freezing plateau at a pressure of 101 325 Pa.

6.2 *Freezing-Point Cells*:

6.2.1 The usual freezing-point apparatus consists of a freezing-point cell containing the reference material, a means to melt the reference material and allow the material to freeze slowly and uniformly, with provision for exposing one or more test thermometers to the freezing point. A typical cell and auxiliary furnace are shown in Figs. 3 and 4. Control equipment is not shown.

6.2.2 The freezing-point apparatus must be able to maintain a freezing plateau of useful duration and must include enough reference material to establish an isothermal region and depth of immersion suitable for the intended use. Typically, a mass of reference material of 1 to 1.5 kg (or a sufficient mass of material to supply 50 to 100 kJ of heat from the latent heat of fusion) is used. However, carefully designed systems using half the above mass of some reference materials can produce freezing plateaus longer than 24 h (see 6.2.6, 6.4.3, and 6.5).

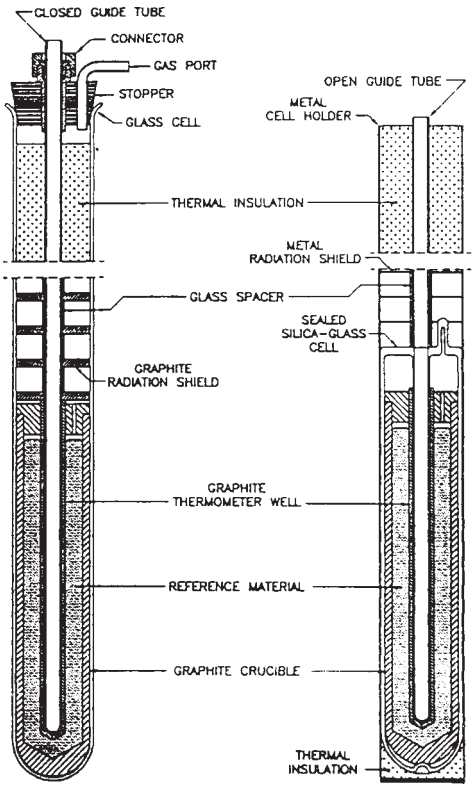
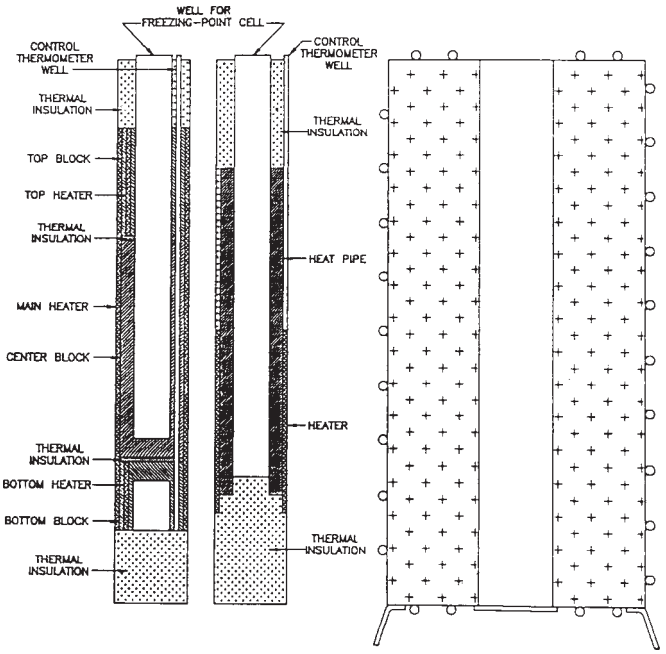


FIG. 3 Examples of Freezing-Point Cells



NOTE 1—This example shows an insulated furnace body and two alternative types of furnace cores. The core on the left is a three-zone shielded type. The core on the right employs a heat pipe to reduce temperature gradients.

FIG. 4 Example of Freezing-Point Furnace

6.2.3 The freezing point and its repeatability, as well as the duration of the freezing plateau for a given rate of heat loss, depend on the purity of the reference material (6.1.5); material purity must therefore be adequate for the intended purpose. Typically, the freezing point of the reference material in a cell will be within 10 mK of the freezing point of pure material, if the impurity content of the reference material is of the order of 10 ppm (6.1.6).

6.2.4 The freezing-point cell must be fabricated to prevent contamination of the reference material during construction and during prolonged use of the cell. A container (crucible), made of a material (such as high purity graphite) that is chemically compatible with the reference material and will not contaminate it, holds the freezing point reference material. This container is usually placed inside another vessel, or cell, that further protects the reference material from contamination and the container from air. The container and cell must accommodate expansion and contraction of the reference material from ambient to about 10 K above the freezing point.

6.2.5 Cells often have provision for sealing and evacuation in order to protect the reference materials from contaminants in the gaseous or vapor phase. For example, oxygen can significantly affect the freezing points of some materials by dissolving in them or by oxidizing them, or both. Some cells have a close-fitting glass envelope completely surrounding the graphite crucible and well that can be hermetically sealed after the cell has been purged and filled with an inert gas (usually argon). The value assigned to the cell freezing point must take into account the gas pressure inside the cell during freezing.

6.2.6 Under preferred freezing conditions, uniform heat loss from the container of reference material produces an advancing

uniform shell of solid on the walls of the container. The liquid-solid interface, thus formed, establishes an isothermal shield around the reentrant well. The freezing-point cell must be designed so that the isothermal region of the well is long enough to accommodate the type of thermometer to be calibrated (see 6.4.3 and 6.5).

6.2.7 For many materials, the duration and repeatability of the freezing plateau can be enhanced by *inducing* freezing, a procedure by which a portion of the liquid metal is rapidly solidified by cooling.

6.2.7.1 For reference materials that exhibit a relatively small undercool (a few kelvins), freezing is induced, after recalescence is observed on a monitoring thermometer, by removing the thermometer and inserting a cool object into the well. The object may be a rod or tube at room temperature, or even the cooled monitoring thermometer itself. This procedure, sometimes referred to as *inside nucleation*, results in a thin mantle of solid frozen onto the well, forming a liquid-solid interface close to the measuring well.

6.2.7.2 For reference materials such as tin and antimony, which exhibit a deep undercool of many kelvins, it is essential that freezing be induced to avoid the unwanted excessive lowering of the cell heating device temperature. An *outside-nucleated* freeze is conveniently induced by removing the cell briefly from the heating device and exposing it to room temperature, or by cooling only the cell while it is in the heating device with a controlled flow of air or suitable gas. Upon recalescence, observed by a monitoring thermometer in the measuring well, the cell is placed in the heating device, or the gas flow is interrupted.

6.2.8 A value of temperature must be assigned to the freezing point of a cell; specifically, a value must be assigned to the reference temperature realized in the isothermal region of the well. This value may be assigned by one of two means:

6.2.8.1 If the purity of the original reference material warrants, if assembly of the cell has maintained the purity, and if subsequent qualification tests so verify, the cell may be assigned the value of the freezing point of the pure material, as promulgated by appropriate authority (for example, ITS-90). In this case, there is associated with the assigned value an uncertainty that must be evaluated from knowledge of impurity content of the reference material, augmented by results of qualification tests. See 6.1.6 and 6.4.

6.2.8.2 The value of the freezing point may be determined by measurement with several calibrated thermometers. All of these thermometers must be capable of measurement with smaller uncertainty than is required of the freezing-point cell in its intended application. In this case, the assigned value of temperature and its components of uncertainty are derived from the measurements and from an analysis of errors in the complete measurement process.

6.2.9 Important considerations in the design of a freezing-point cell include:

6.2.9.1 The use of a reference material of the highest practicable purity is cost effective and justified. High material purity minimizes variability in the observed freezing point caused by variations in operating conditions and procedures, and it reduces the uncertainty in the value to assign to the freezing point of the cell. The cell must be designed to maintain the purity of the reference material with repeated use.

6.2.9.2 A major source of error in the use of freezing-point cells is the failure of an object under test to attain the reference temperature because of unwanted heat flow to or from the object. The heat flow depends in part on the characteristics of the object itself. This source of error is minimized by designing the cell to (*1*) provide adequate immersion for the test object in the region of the reference material (see 6.4.3 and 6.5.2), and (*2*) provide adequate immersion of the cell in the heating device.

6.2.10 Users of freezing-point cells interested in using the cells to realize melting points should consider 6.2.10.1-6.2.10.3. A detailed description of melting-point techniques is beyond the scope of this guide. For more information, see Footnote 5.[5]

6.2.10.1 Plateaus obtained during melting may have practical advantages. First, since heat is added to the system during melting, the insertion of a cold test object into the cell tends to slow down the phase transition rather than to hasten it. Thus it is easier to prolong the melting curve than a freezing curve upon multiple insertions. Second, for reference materials such as tin that exhibit a large undercool, it is necessary to use special techniques in order to initiate freezing in a useful manner, whereas melting initiation is usually simple.

6.2.10.2 Impurity segregation upon freezing helps to promote reproducibility of the plateau temperature from freeze to freeze. The melting process does not have this advantage, and in fact, the melting curve shape and plateau temperature may depend upon impurity distribution in the solid. Nonetheless, melting points may still be useful at reduced accuracy for less demanding applications.

6.2.10.3 A freezing-point cell that contains very pure metal (impurity concentration less than 1 part in 10^7) will produce melting points that are as reproducible as freezing points and that are indistinguishable from them.[6] Special techniques are required to achieve this as described in Footnote 5.[5] For freezing-point cells containing an impurity concentration of more than 1 part in 10^7, the freezing-point method may give more reproducible and accurate values than the melting-point method, since the melting range is very dependent on the method of solidification of the metal prior to the melt.

6.3 *Auxiliary Apparatus*:

6.3.1 Heating devices, such as furnaces (ovens) or baths, are used to heat the freezing-point cells. An important requirement for such devices is temperature uniformity in the region of the cell, so that the reference material will melt and freeze uniformly. To minimize temperature gradients, furnaces may be equipped with high-conductivity temperature moderator blocks or heat pipes, or they may employ multiple zone heaters.

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[5] Mangum, B. W., Bloembergen, P., Chattle, M. V., Marcarino, P., and Pokhodun, A. I., Comité Consultatif de Thermométrie, 19th Session, 1996, Document CCT/96–8, entitled "Recommended Techniques for Improved Realization and Intercomparisons of Defining Fixed Points: Report to the CCT by Working Group 1."

[6] Working Group 1 of the Comité Consultatif de Thermométrie (Mangum, B. W., Bloembergen, P., Chattle, M. V., Fellmuth, B., Marcarino, P., and Pokhodun, A. I.), "On the International Temperature Scale of 1990 (ITS-90) Part I: Some Definitions," *Metrologia*, Vol 34, 1997, pp. 427–429.

6.3.2 Another important requirement is the ability to control the heating device during melting and slow freezing. Control may be achieved manually or with automatic controllers that are suitable for the task. In either case, the heating device must not be operated in a manner that could obscure the normal freezing plateau, for example, by establishing a period of constant temperature near the freezing point that could be mistaken for the freezing plateau, or by inadvertent remelting after the initiation of freezing.

6.3.3 Auxiliary heating devices are useful for heating thermometers to a temperature near the freezing point before they are inserted into the well (see 6.5.4).

6.3.4 A monitoring thermometer is recommended for each freezing point. The thermometer is used for monitoring and qualification testing at the specific freezing point, and for no other purpose. The thermometer must be of a quality suitable for the purpose (see 6.4.4); in general, the monitoring thermometer should be more sensitive and stable than the thermometers to be calibrated in the freezing-point cell. Cells of the highest quality should be monitored and qualified with calibrated standard platinum resistance thermometers.

6.3.5 A reference temperature such as the ice point or the triple point of water may be required for some monitoring thermometers. If the monitoring thermometer is a standard platinum resistance thermometer, the reference temperature should be the triple point of water.

6.4 *Qualification Testing*:

6.4.1 *Complete Qualification Test*:

6.4.1.1 A complete qualification test should be performed each time the equipment is set up, or if the equipment, operator, or procedure is changed in a significant way, or at any time when an anomalous result is observed during use of the cell. The purpose of this test is to observe whether or not any changes have occurred in the characteristic features of the freezing curve that imply a change in the freezing point of the reference material in the cell.

6.4.1.2 In a complete qualification test, the entire freezing curve is observed using the monitoring thermometer. Observations are started while the reference material is completely liquid and continued until all of the material is frozen. Observations are made of the magnitude of the undercool, the shape and flatness of the freezing plateau, the freezing point, and the range of temperature over which the material freezes.

6.4.1.3 If no significant change from the freezing curve of the previous qualification test is observed, the freezing-point cell is qualified for use, and the entire system is under statistical control.

6.4.2 *Incidental Qualification Test*:

6.4.2.1 An incidental qualification test is conducted with the dedicated monitoring thermometer each time the freezing-point cell is used for thermometer calibration. The purpose of the test is to ensure that the reference material starts in the liquid state, that all calibration measurements are at the freezing point, and that the freezing point has not changed significantly since the previous freeze.

6.4.2.2 Observations with the monitoring thermometer are started while the reference material is liquid and are continued through the undercool to the first part of the freezing plateau. The monitoring thermometer is then removed from the cell well, and it is replaced after the last test thermometer has been calibrated.

6.4.2.3 If the monitoring thermometer indicates that the reference material was initially in the liquid state, that the undercool was not significantly different from previous undercools, that the first part of the freezing plateau was not significantly different from previous freezing points, and that the final observation on the freezing plateau was not significantly different from the initial observation on the plateau, then the calibration run is qualified as being valid.

6.4.3 *Immersion Qualification Test*:

6.4.3.1 The immersion qualification test is performed with the dedicated monitoring thermometer to determine the uniform temperature region in the freezing-point cell. The test is made when a system is first put into service, and, thereafter, when substantial changes are made in the cell heating device and control system.

6.4.3.2 A freezing plateau is established in the freezing-point cell, and the temperature profile of the portion of the well surrounded by the reference material is determined with the monitoring thermometer while the plateau is maintained. The uniform temperature region is that region where temperature differences are not significant for the intended application.

6.4.3.3 The freezing-point cell is qualified for the calibration of thermometers that can be accommodated within the uniform temperature region (see 6.5).

6.4.4 *Dedicated Monitoring Thermometers*:

6.4.4.1 A monitoring thermometer suitable for evaluating features of the freezing curve (for example, the undercool, the shape and duration of the freezing plateau, freezing range of a single freeze) must be sensitive enough to show the features distinctly, and it must be stable enough to avoid degrading the observations with thermometer drift. Past performance history of the thermometer can aid in assessing its suitability.

6.4.4.2 Repeatability of the freezing point from one freeze to the next can be determined with a monitoring thermometer only if it is known that the thermometer does not change significantly with use. If the monitoring thermometer is a precision platinum resistance thermometer, measurements made at a reference temperature (for example, the triple point of water or the ice point) before and after the freezing-point measurements are useful in assessing thermometer stability. If the monitoring thermometer is a standard platinum resistance thermometer, the assessment should be based on the ratio of the thermometer resistance at the freezing point to the resistance at the triple point of water.

6.4.4.3 The thermometer used for determining the temperature profile in a freezing-point cell must be sensitive enough for the task, and it must not permit a significant transfer of heat along the length of the well axis. In determining the uniform temperature region of the measuring well, the length of the temperature sensitive region of the thermometer must be accounted for.

6.4.5 *Interpretation of Qualification Test Observations*:

6.4.5.1 A distinct decrease from previous observations in the magnitude of the maximum undercool may indicate contamination of the reference material. However, recent past

temperature history of the cell can also influence the maximum. An unusually shallow undercool, or the complete absence of an undercool, indicates that the reference material was probably not completely molten before the freezing cycle was started.

6.4.5.2 A distinct increase in the range of temperature over which the entire quantity of reference material freezes probably indicates that contamination of the material has occurred. It is useful to verify an increase in freezing range by observing a corresponding increase in melting range. The amount of contamination, and the resulting depression of the freezing point, may be estimated roughly using the method in 6.1.6.

6.4.5.3 A decrease in the duration of the freezing plateau, without a corresponding decrease in the total freezing time, also indicates that possible contamination has occurred. A decrease in both plateau duration and total freezing time may indicate that the reference material is losing heat more rapidly because of a change in the heating device or its control.

6.4.5.4 For the incidental qualification test, two measurements on the freezing plateau are made with the monitoring thermometer, one before test thermometer calibration and one after. If the second measurement is significantly lower than the first, this indicates that the plateau duration is not long enough for the calibration load. If the second measurement is significantly higher than the first, this indicates that some of the reference material may be remelting, instead of freezing.

6.4.5.5 Failure to observe a uniform temperature region in the immersion qualification test indicates that the freezing-point cell does not provide adequate immersion into the freezing reference material for the monitoring thermometer, or that the heating device is not establishing an adequately uniform freezing environment for the cell.

6.4.5.6 If measurements at the freezing point with a stable monitoring thermometer (see 6.4.4.2) indicate a significant decrease in the freezing point from one freeze to the next, contamination of the reference material is the probable cause. When a freezing-point cell is used at the highest level of accuracy, small changes (1 or 2 mK) may be significant, and it becomes a difficult matter to determine whether an observed change should be attributed to the thermometer or the cell, or both. The recorded trend of complete qualification tests helps to reveal any significant changes in the cell.

6.4.5.7 If repeated measurements at the freezing point with the monitoring thermometer indicate no significant change from one freeze to the next, then the measurements may be used to derive a value for the precision component of uncertainty of the combined thermometer-cell system. The resulting value can be considered an upper bound to the precision component of the freezing point itself.

6.4.5.8 If, upon evaluation of all qualification tests, it is concluded that a significant change has occurred in the freezing-point cell, then the value of temperature assigned to the cell or the uncertainty associated with the value, or both, must be redetermined.

6.5 *Thermometer Calibration*:

6.5.1 The freezing-point cell can be used to realize a prolonged and repeatable fixed temperature environment for the calibration of a variety of immersion-type thermometers such as resistance thermometers (see Test Methods E 644), thermocouples, and others.

6.5.2 Thermometers suitable for calibration in a freezing-point cell are characterized in 1.5. A thermometer must be long enough to extend fully into the well, and all of the temperature-sensing portion of the thermometer must be contained in the isothermal region of the well, as determined in 6.4.3. There should be no difference in the indication of a thermometer under test, attributable to unwanted heat transfer by the thermometer, when its temperature sensing portion is moved between extremes in the uniform temperature region of the well, that is significant in the intended application or use of the thermometer.

6.5.3 Heat is transferred between the cell and a thermometer in the measuring well mainly by radiation and by conduction through the gas-filled annulus between the well and the thermometer. Conduction can be enhanced by use of a close-fitting metal or graphite bushing in the annulus, but then oxygen must be eliminated from the annulus in order to prevent false readings due to oxidation.

6.5.4 It is usually advantageous to heat thermometers to near the freezing point before they are inserted into the freezing-point cell. This reduces the heat load on the cell; it helps to prolong the freezing plateau, and it reduces demand on temperature control systems. A thermometer is conveniently heated in an auxiliary device held at a temperature above the freezing point. With a little practice, the thermometer can be transferred to the cell without excessive cooling.

6.5.5 The thermometer temperature must become steady at the freezing point before the thermometer is calibrated. The temperature is steady when the thermometer indication no longer changes significantly with time.

7. Test Procedure

7.1 Prepare the test equipment.

7.1.1 Check and adjust all measuring, recording, and controlling equipment for correct operation.

7.1.2 Prepare the monitoring thermometer and make reference-temperature measurements. If the monitoring thermometer is a standard platinum resistance thermometer, determine its resistance at the triple point of water (see 6.4.4.2).

7.1.3 With the freezing-point cell installed, supply power to the heating device and stabilize the temperature several kelvins below the freezing point, as indicated by the control system. Record control parameters.

7.1.4 Establish the temperature of the auxiliary heating device about 20 K above the freezing point (see 6.5.4). Record control parameters.

7.1.5 Time each significant event and datum in each procedure. Record times as real time, or as elapsed time from the time of a reference event.

7.2 Allow the reference material to melt.

7.2.1 Insert the monitoring thermometer into the cell well.

7.2.2 Adjust the controls to stabilize the heating device at a temperature approximately 5 K above the freezing point. Record control parameters. (**Warning—**Overheating may damage the cell.)

7.2.3 Note the indications of the monitoring thermometer at the onset, during, and at completion of melting.

7.2.4 Continue to observe the indication of the monitoring thermometer until all the reference material is molten and the cell is at the steady temperature of the heating device. Evaluate the setting of the heating device control, based on the indication of the monitoring thermometer, and note any adjustments to the control parameters implied by the evaluation.

7.3 Establish the freezing point.

7.3.1 Adjust the controls to stabilize the temperature of the heating device approximately 1 K below the freezing point of the reference material. Record the control parameters.

7.3.2 Observe the indications of the thermometer in the well as the temperature decreases into the undercool. If the freeze is for a complete qualification test (see 6.4.1), record the indications continuously or at frequent intervals to establish the shape of the freezing curve.

7.3.3 If freezing is to be induced by inside nucleation (see 6.2.7.1), continue to observe or record thermometer indications until recalescence is detected. Note and record the maximum undercool. Remove the thermometer from the well and insert a room-temperature rod or tube (ceramic or silica glass for temperatures greater than 420 °C) for at least 60 s, then replace the rod or tube with the monitoring thermometer.

7.3.4 If freezing is to be induced by outside nucleation (see 6.2.7.2), remove the freezing-point cell from the heating device when the thermometer in the well indicates that the temperature is below the freezing point. Keep the thermometer in the well and continue recording or observing its indications as the cell is held at room temperature. As soon as the thermometer indicates recalescence, replace the cell in its heating device. Note and record the maximum undercool.

7.4 Observe the indication of the monitoring thermometer as its temperature approaches the freezing point. When the temperature is steady (see 6.5.5), record the thermometer indication, and then proceed to 7.5, 7.6, or 7.7, as appropriate.

7.5 *Qualification Testing*:

7.5.1 For the complete qualification test (see 6.4.1), record the indication of the monitoring thermometer continuously or at frequent intervals to establish the freezing curve. Continue recording until all of the reference material is frozen and the temperature in the cell approaches the temperature of the heating device. Evaluate the setting of the heating device control, based on the indication of the monitoring thermometer, and note any adjustments to the control parameters implied by the evaluation.

7.5.2 For the immersion qualification test (see 6.4.3), proceed as in 7.5.1 until the monitoring thermometer indicates that the freezing plateau has been reached. Raise and hold the monitoring thermometer so that its temperature sensing portion is near the top of the reentrant well. When the thermometer indication becomes steady, record the indication. Lower the monitoring thermometer a predetermined distance, wait for a steady indication, and record the indication as before. Repeat this process at five to ten uniformly spaced stations in the reentrant well until the monitoring thermometer is again fully immersed. Then continue recording as in 7.5.1.

7.6 *Thermometer Calibration*:

7.6.1 Remove the monitoring thermometer from the cell and insert a heated test thermometer. When the test thermometer indicates a steady temperature, record its indication. If it has been determined previously that the test thermometer meets the requirements of 6.5.2, then remove it from the cell. Otherwise, raise and hold the test thermometer so that its temperature-sensing region is near the top of, but inside, the uniform temperature region determined in 7.5.2 (see also 6.4.3). When the indication of the test thermometer becomes steady, record the indication. If the temperature equivalent of the difference between the two indications is not significant, the test thermometer meets the requirements of 6.5.2.

7.6.2 Repeat the procedure for the next test thermometer, if any. See 6.5 for details. After calibration of the last test thermometer, replace the monitoring thermometer in the cell well and proceed as in 7.4 or 7.5.

7.7 Remove the monitoring thermometer from the cell and make any appropriate low-temperature reference measurements (see 6.4.4.2).

8. Documentation

8.1 *Purpose and Scope*:

8.1.1 Thorough documentation provides a permanent, comprehensive historical record of the freezing-point cell and its auxiliary apparatus sufficient to support an estimate of the quality of the cell, and an evaluation of the procedure for using the cell. The documentation system should be designed to meet these purposes.

8.1.2 The documentation should include experimental data; histories of the cell, monitoring thermometer, and auxiliary equipment; and calculations required for evaluating results.

8.2 *Experimental Data*:

8.2.1 Configuration data should include identification of the freezing-point cell and all other apparatus by unique serial number, instrument and control settings, relevant ambient conditions, narrative description of setup (or departure from normal setup), date, and name of operator.

8.2.2 Measurement data should be recorded in the natural units (for example, volts, ohms) of the thermometric property whenever possible. The time of each determination should be recorded. Corrections to the data (for example, measuring instrument calibration corrections) should be shown explicitly.

8.2.3 Procedural and incidental data should be recorded as appropriate. These should include the time of all procedural actions, and the time and a brief description of any observed experimental anomalies.

8.3 *Freezing-Point Cell Records*:

8.3.1 *Initial Description and Characteristics*:

8.3.1.1 Source of the cell,

8.3.1.2 Date acquired and placed into service,

8.3.1.3 Mass and chemical composition of reference material,

8.3.1.4 Critical dimensions, including depth of immersion, and

8.3.1.5 Assigned value of freezing point and associated uncertainty.

8.3.2 *History of Cell Use*:

8.3.2.1 The cumulative time above room temperature,

8.3.2.2 The cumulative time at or near the freezing point,

8.3.2.3 A description of accidents, abuse, and unusual use, and

8.3.2.4 A complete description of any cell modification and its purpose.

8.3.3 *History of Cell Performance*:

8.3.3.1 The maximum undercool,

8.3.3.2 The indication of the dedicated monitoring thermometer at the freezing point,

8.3.3.3 For a calibration test, the difference between the first and final indications of the monitoring thermometer, and

8.3.3.4 For a complete qualification test, the duration of the freezing plateau, the time required for complete freezing, and the freezing range.

8.4 *Dedicated Monitoring Thermometer Records*:

8.4.1 The thermometer records should include initial description, characteristics, and history of use comparable to those for the freezing-point cell in 8.3.1 and 8.3.2.

8.4.2 The records should include the results of all calibrations of the thermometer and all available information dealing with thermometer contributions to uncertainty.

8.4.3 In addition to the data in 8.3.3.2 and 8.3.3.3, thermometer performance records should include the results of any measurements at low-temperature reference points. If the monitoring thermometer is a platinum resistance thermometer, performance records should be tabulated in terms of resistance ratios, for example, *R(T)/R(0)* or *R(T)/R(TP)*, where *R(T)* is the resistance of the thermometer at temperature *T*, *R(0)* is the resistance at 0 °C, and *R(TP)* is the resistance at the triple point of water.

8.5 *Other Auxiliary Equipment*:

8.5.1 The equipment records should include initial description, characteristics, and history of use comparable to those for the freezing-point cell in 8.3.1 and 8.3.2.

8.5.2 The records should include the results of all calibrations of measuring instruments, tabulations of current and past instrumental corrections, and all available information dealing with measuring instrument contributions to uncertainty.

8.5.3 The records should include tabulations of current and past control settings.

8.5.4 The records should include a schedule for periodic maintenance and calibration of equipment.

8.6 *Calculations*:

8.6.1 *Temperature and Temperature Difference*:

8.6.1.1 Thermometer indications in terms of the thermometric property, *X*, are converted to values of temperature, *T*, on a particular temperature scale, through the relationship between *X* and *T* determined when the thermometer is calibrated. The relationship may be expressed by a formula or by a calibration table, or the conversion may be made automatically by recording instrumentation. Note that in the case of a platinum resistance thermometer serving as a monitoring thermometer, resistance ratio (see 8.4.3) is the usual quantity related to temperature.

8.6.1.2 Small temperature differences or increments, ΔT, may be estimated from small differences or increments in X, ΔX, by the approximation

$$\Delta T = \frac{\Delta X}{dX/dT} \tag{2}$$

where the quantity dX/dT is the first derivative of X as a function of T, evaluated at the midpoint of the temperature increment. The value of dX/dT may be obtained from the thermometer calibration or from reference tables.

8.6.2 *Freezing Point Depression*:

8.6.2.1 If the concentration of impurities in the reference material is known, and the impurities are known to depress the freezing point, the depression of the freezing point, ΔT, from that of the ideally pure material may be estimated by the approximation

$$\Delta T = \frac{C}{A} \tag{3}$$

where C is the mole fraction of impurities, and A is the first cryoscopic constant of the reference material (see Table 1).

8.6.2.2 If the freezing point depression, ΔT, caused by impurities is small, it may be estimated from measurements on the freezing curve using the approximation in Eq 2:

$$\Delta T = \frac{X_b - X_h}{dX/dT} \tag{4}$$

where X_b is the indication of the monitoring thermometer at the beginning of the freezing plateau, and X_h is the indication when half the reference material is frozen. For a constant cooling rate, it may be assumed that half the material is frozen when half the total freezing time has elapsed (see Fig. 1).

8.6.3 *Variability*:

8.6.3.1 If a set of observations, covering many qualification tests, shows no significant change or drift in the indications of the dedicated monitoring thermometer at the freezing point, then the variability of the combined thermometer-freezing point system may be expressed by:

$$S = \sqrt{\frac{\Sigma(\bar{X} - X_i)^2}{(n-1)(dX/dT)^2}} \tag{5}$$

where $\bar{X}$ is the mean of the set of indications, X_i is the i-th indication of the set, n is the number of determinations in the set, and S is the estimate of the standard deviation of one determination in terms of temperature.

8.6.3.2 If a set of indications, covering many qualification tests, of the dedicated monitoring thermometer at the freezing point displays a uniform drift with time that the thermometer is at elevated temperature, then a linear regression analysis can yield both a drift rate and standard deviation of the combined thermometer-freezing point system.

9. Precision and Bias

9.1 A freezing-point cell contributes to the uncertainty of a thermometer calibration because of variability in the cell and its use, and because of uncertainty in the value assigned to the freezing point of the cell.

9.2 The precision component due to cell variability and use must be evaluated from an analysis of measurement variability of the combined system, consisting of the monitoring thermometer and the freezing-point cell. Separating thermometer variability from cell variability is usually not possible. If the system is very stable, the evaluation of 8.6.3.1 yields an upper

bound on the standard deviation of the freezing point of the cell. The best of such systems have standard deviations of less than 1 mK.

9.3 The uncertainty in the value assigned to the cell freezing point contributes a component to thermometer calibration uncertainty. If the value assigned is that attributed to the freezing point of pure material, then the contribution to uncertainty caused by impurities in the cell reference material may be estimated by the methods of 8.6.2. If a freezing-point value is determined by measurement, then the uncertainty in the value must come from analysis of the measurement process upon which the determined value is based. See 6.2.8.

10. Keywords

10.1 calibration; cryoscopic constant; fixed point; freeze; freezing curve; freezing plateau; freezing point; freezing-point cell; freezing range; ITS-90; precision; qualification; recalescence; reference material; reference temperature; resistance thermometer; thermocouple; thermometer; uncertainty; undercool