Designation: E1502 – 16

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

This standard is issued under the fixed designation E1502; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

During melting and freezing, pure material transforms from the solid state to the liquid state or from the liquid state to the solid state at a constant temperature. That constant temperature is referred to as a fixed point. Fixed points approached in the melting direction are referred to as melting points and fixed points approached in the freezing direction are referred to as freezing points. Fixed 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 melting and freezing points of some highly purified metals as defining fixed points. Fixed points can be realized in commercially available systems incorporating fixed-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, these fixed points can be realized with an uncertainty of a few millikelvins[3] or less.

1. Scope

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

1.2 Design and construction requirements of fixed-point cells are not addressed in this guide. Typical examples are given in Figs. 1 and 2.

1.3 This guide is intended to describe good practice and establish uniform procedures for the realization of fixed 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 fixed-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 fixed-point apparatus.

1.8 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.9 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]

E344 Terminology Relating to Thermometry and Hydrometry

[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.

Current edition approved May 1, 2016. Published September 2016. Originally approved in 1992. Last previous edition approved in 2010 as E1502 – 10. DOI: 10.1520/E1502-16.

[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.

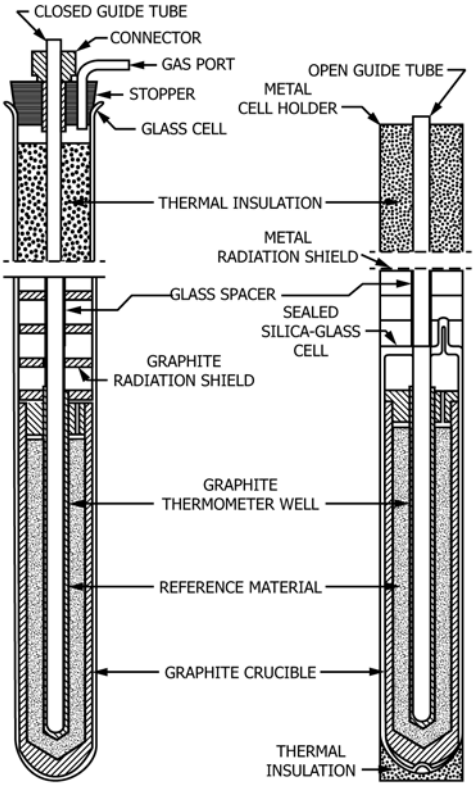


FIG. 1 Examples of Fixed-Point Cells

E644 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.

3.1.2 Additional terms used in this guide are defined in Terminology E344.

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):

$$A = \frac{L}{RT^2} \quad (1)$$

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

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

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

3.2.4.1 *Discussion*—Graphic representations of freezing curves are shown in Figs. 3 and 4.

3.2.5 *freezing plateau, n*—the time period during freezing when the temperature does not change significantly.

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

3.2.6.1 *Discussion*—The freezing range is indicated graphically in Fig. 3.

3.2.7 *melt, n*—an experiment or test run conducted with a fixed-point cell while the reference material in the cell liquifies.

3.2.8 *melting curve, n*—the entire time-temperature relation of the reference material in a fixed-point cell during melting, including initial heating, melting plateau, and final heating to complete liquification.

3.2.8.1 *Discussion*—Graphic representations of melting curves are shown in Figs. 5 and 6.

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

3.2.10 *melting range, n*—the range of temperature over which most of the reference material in a fixed-point cell melts.

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

3.2.12 *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.

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

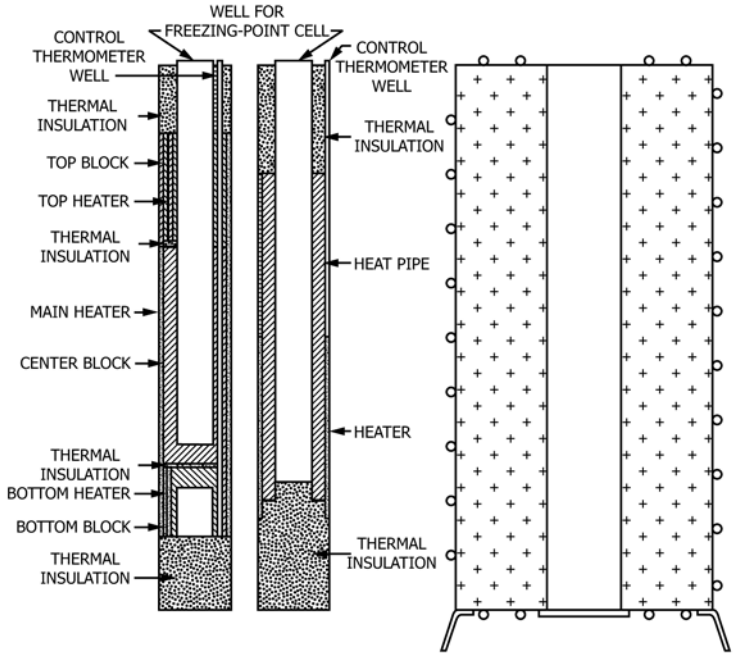
3.2.14 *supercooled state, n*—the meta-stable state of reference material in which the temperature of the liquid phase is below the freezing point.

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

4. Summary of Guide

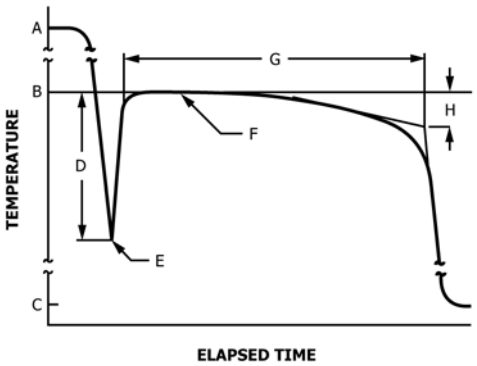
4.1 A fixed-point cell is used for thermometer calibration by establishing and sustaining a reference material at either the melting or freezing point, to which a value of temperature has been assigned. The thermometer to be calibrated is inserted into a reentrant well in the cell; the well itself is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

4.2 For freezing point realizations, 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.



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. 2 Example of Fixed-Point Furnace



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. 3 Structure of a Typical Freezing Curve

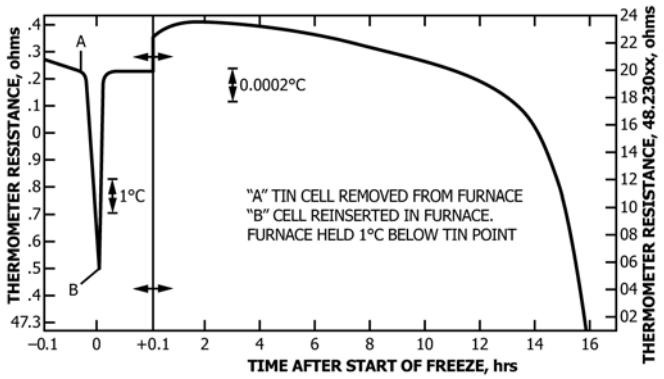
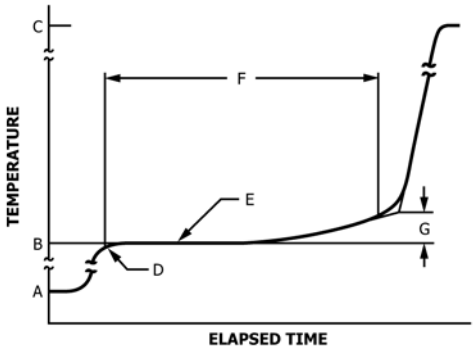


FIG. 4 Freezing Curve of Sample of Highly Purified Tin

4.3 For melting point realizations, the cell is heated to approximately 1 K below the melting point. The temperature of the surrounding environment is then increased to about 1 K above the melting point so that the reference material begins melting. Following stabilization, the well temperature becomes constant during the melting plateau. After a time, depending on the rate of heat gain by the cell, the amount of reference material, and the purity of the reference material, the temperature starts to increase and eventually all of the material becomes molten.

4.4 Since the temperature in the reentrant well remains constant during the phase transition 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.

4.5 Measurements are also made during each plateau with a dedicated monitoring thermometer. These measurements, together with other special test measurements, provide qualification test data (see 6.5 and 7.5).



A = Stabilized temperature of cell before melting, typically about 1 K below melting point.
B = Melting point of cell.
C = Temperature of cell surroundings during melting, typically about 1 K above melting point.
D = Onset of melting.
E = Melting plateau.
F = Total melting time.
G = Melting range.

FIG. 5 Structure of Typical Melting Curve

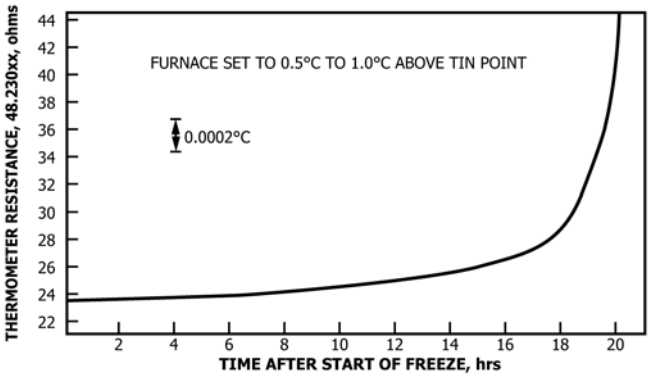


FIG. 6 Melting Curve of Sample of Highly Purified Tin

5. Significance and Use

5.1 A pure material has a well defined phase transition behavior, and the phase transition plateau, a characteristic of the material, can serve as a reproducible reference temperature for the calibration of thermometers. The melting or freezing points of some highly purified metals have been designated as defining fixed points on ITS-90. The fixed points of other materials have been determined carefully enough that they can serve as secondary reference points (see Tables 1 and 2). This guide presents information on the phase transition process as it relates to establishing a reference temperature.

5.2 Fixed-point cells provide users with a means of realizing melting and 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 Fixed-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 6.3.10).

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 fixed-point procedure. They provide for evaluation of results, assure continuing reliability of the method, and yield insight into the cause of test result discrepancies. The test procedure is applicable to the most demanding uses of fixed-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 Point Realization:*

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. 3 and 4.

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

TABLE 1 Characteristics of Pure Fixed-Point Reference Materials

Material	Fixed point, ITS-90, °C	Typical Undercool, K	Pressure Coefficient at fixed point		First Cryoscopic Constant, K^{-1}
			nK/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	. . .
Zinc[A]	419.527	0.05–0.1	+ 43	+ 2.7	0.0018
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.

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

Materials	Laboratory	
	Primary, mK	Industrial, mK
Gallium[B]	0.1	1
Indium	1	10
Tin	1	10
Zinc	1	10
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.

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 freezing point of the material.

6.1.5 As freezing progresses, 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 low 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 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 *Melting Point Realization:*

6.2.1 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 solid to liquid, as heat is absorbed in semi-equilibrium melting, exhibits a complex time-temperature relation (melting curve) as shown in Figs. 5 and 6.

6.2.2 The evolution of the liquid phase from that of the solid phase occurs spontaneously and requires no intervention to initiate the melting process.

6.2.3 As the sample is melting, the temperature remains relatively constant for a while during the melting plateau. The temperature associated with the melting plateau is the temperature to which a value is assigned as the melting point of the material.

6.2.4 As melting progresses, trace impurities in the frozen material are liberated in place and tend to alter the melting plateau. Since impurities usually widen the melting range of the reference material, the temperature of the material increases ever more rapidly until all of the material is molten.

6.2.5 The effect of low concentrations of impurities may be estimated from an approximation rule: the temperature difference between the start of melting and midpoint of melting (when half the material is molten) equals the temperature difference between the melting point of the ideally pure material and the melting point (at the start of melting) of the real reference material (see 9.6.2). 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.

6.2.6 The change in temperature during the melting 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 melting point, but the effect of the pressure of a head of dense liquid reference material may be significant. The melting point is usually taken to be the temperature during the melting plateau at a pressure of 101 325 Pa.

6.3 *Fixed-point Cells:*

6.3.1 The usual fixed-point apparatus consists of a fixed-point cell containing the reference material and a means to melt and freeze the reference material slowly and uniformly, with provision for exposing one or more test thermometers to the fixed point. A typical cell and auxiliary furnace are shown in Figs. 1 and 2. Control equipment is not shown.

6.3.2 The fixed-point apparatus shall be able to maintain a freezing plateau of useful duration and shall 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 6.3.6, 6.5.3, and 6.6).

6.3.3 The freezing or melting point, its repeatability, and the duration of the plateau for a given rate of heat loss or gain depends on the purity of the reference material (6.1.5); material purity shall therefore be adequate for the intended purpose. Typically, the actual phase transition temperature of the reference material in a cell will be within 10 mK of the assigned phase transition temperature of pure material, if the impurity content of the reference material is of the order of 10 ppm (6.1.6).

6.3.4 The fixed-point cell shall 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 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 shall accommodate expansion and contraction of the reference material from ambient to about 10 K above the phase transition temperature.

6.3.5 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 phase transition temperature 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 phase transition temperature shall take into account the gas pressure inside the cell during phase change experiments.

6.3.6 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 cell shall be designed so that the isothermal region of the well is long enough to accommodate the type of thermometer to be calibrated (see 6.5.3 and 6.6).

6.3.7 Under preferred melting conditions, uniform heat gain from the container of reference material produces an advancing uniform shell of molten material on the walls of the container. The liquid-solid interface, thus formed, establishes an isothermal shield around the reentrant well. The cell shall 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).

6.3.8 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.

6.3.8.1 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.

6.3.8.2 For reference materials such as tin or another suitable gas, which exhibit a deep undercool of many kelvins, it is essential that freezing be induced to avoid 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.

6.3.9 A value of temperature shall be assigned to the fixed point of a cell; specifically, a value shall be assigned to the reference temperature realized in the isothermal region of the well. This value may be assigned by one of two methods:

6.3.9.1 If the purity of the original reference material warrants it, 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 fixed 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 shall be evaluated from knowledge of impurity content of the reference material, augmented by results of qualification tests. See 6.1.6 and 6.5.

6.3.9.2 The value of the freezing/melting point may be determined by measurement with several calibrated thermometers. All of these thermometers shall be capable of measurement with smaller uncertainty than is required of the fixed-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.

6.3.10 Important considerations in the design of a fixed-point cell include:

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

6.3.10.2 A major source of error in the use of fixed-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 6.5.3 and 6.6.2), and (*2*) provide adequate immersion of the cell in the heating device.

6.3.11 Users of fixed-point cells interested in using the cells to realize melting points should consider 6.3.11.1 – 6.3.11.3. A detailed description of melting-point techniques is beyond the scope of this guide. For more information, see Footnote 5.[5]

6.3.11.1 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 a 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

[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."

techniques in order to initiate freezing in a useful manner, whereas melting initiation is usually simple.

6.3.11.2 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 with reduced accuracy may still be useful for less demanding applications.

6.3.11.3 A fixed-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 fixed points and that are indistinguishable from them.[6] Special techniques are required to achieve this as described in Footnote 5.[5] For fixed-point cells containing an impurity concentration of more than 1 part in 10^7, the fixed-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.

6.4 *Auxiliary Apparatus:*

6.4.1 Heating devices, such as furnaces (ovens) or baths, are used to heat the fixed-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.

6.4.2 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 shall not be operated in a manner that could obscure the normal freezing plateau (for example, by establishing a period of constant temperature near the phase transition temperature that could be mistaken for the plateau, by inadvertent remelting after the initiation of freezing, or refreezing after the initiation of melting).

6.4.3 Auxiliary heating devices are useful for heating thermometers to a temperature near the fixed point before they are inserted into the well (see 6.6.4).

6.4.4 A monitoring thermometer is recommended for each fixed point. The thermometer is used for monitoring and qualification testing at the specific fixed point, and for no other purpose. The thermometer shall be of a quality suitable for the purpose (see 6.5.4); in general, the monitoring thermometer should be more sensitive and stable than the thermometers to be calibrated in the fixed-point cell. Cells of the highest quality should be monitored and qualified with calibrated standard platinum resistance thermometers.

6.4.5 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.

6.5 *Qualification Testing:*

6.5.1 *Complete Qualification Test:*

6.5.1.1 A complete qualification test should be performed each time the equipment is set up; 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. Although the plateau can be utilized in either direction (melting or freezing), the qualification test is best carried out on a freezing plateau. 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 fixed point of the reference material in the cell.

6.5.1.2 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 fixed point, and the range of temperature over which the material freezes.

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

6.5.2 *Incidental Qualification Test:*

6.5.2.1 An incidental qualification test is conducted with the dedicated monitoring thermometer each time the fixed-point cell is used for thermometer calibration. The purpose of the test is to ensure that the reference material starts in the proper state, either solid for melting plateau or liquid for freezing plateau, that all calibration measurements are performed on a plateau, and that the phase transition temperature has not changed significantly since the previous use.

6.5.2.2 Observations with the monitoring thermometer are started while the reference material is in its pre-phase transition state and are continued through the undercool (for a freeze) to the first part of the plateau. The monitoring thermometer is then removed from the cell well, and it is replaced after the last test thermometer has been calibrated.

6.5.2.3 If the monitoring thermometer indicates that the reference material was initially in the pre-phase transition state state, that the undercool was not significantly different from previous undercools, that the first part of the plateau was not significantly different from previous freezing plateau, and that the final observation on the plateau was not significantly different from the initial observation on the plateau, then the calibration run shall be considered to be valid.

6.5.3 *Immersion Qualification Test:*

6.5.3.1 The immersion qualification test is performed with the dedicated monitoring thermometer to determine the uniform temperature region in the fixed-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.

6.5.3.2 A freezing plateau is established in the fixed-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

[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.

uniform temperature region is that region where temperature differences are not significant for the intended application.

6.5.3.3 The fixed-point cell shall be acceptable for the calibration of thermometers that can be accommodated within the uniform temperature region (see 6.6).

6.5.4 *Dedicated Monitoring Thermometers:*

6.5.4.1 A monitoring thermometer suitable for evaluating features of the curve (for example, the undercool, the shape and duration of the plateau, the temperature range of a single-phase transition) shall be sensitive enough to show the features distinctly and it shall be stable enough to avoid degrading the observations with thermometer drift. The past performance history of the thermometer can aid in assessing its suitability.

6.5.4.2 Repeatability of the fixed 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 fixed-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 fixed point to the resistance at the triple point of water.

6.5.4.3 The thermometer used for determining the temperature profile in a fixed-point cell shall be sensitive enough for the task, and it shall 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 shall be accounted for.

6.5.5 *Interpretation of Qualification Test Observations:*

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

6.5.5.2 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 fixed point, may be estimated roughly using the method in 6.1.6.

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

6.5.5.4 For the incidental qualification test, two measurements on the freezing plateau are made with the monitoring thermometer, one before the 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.

6.5.5.5 Failure to observe a uniform temperature region in the immersion qualification test indicates that the fixed-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.

6.5.5.6 If measurements at the freezing/melting point with a stable monitoring thermometer (see 6.5.4.2) indicate a significant difference in the phase transition temperature from one realization to the next, contamination of the reference material is the probable cause. When a fixed-point cell is used at the highest level of accuracy, small changes (1 or 2 mK) may be significant, and it becomes difficult 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.

6.5.5.7 If repeated measurements at the fixed 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 limit to the precision component of the fixed point itself.

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

6.6 *Thermometer Calibration:*

6.6.1 The fixed-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 E644), thermocouples, and others.

6.6.2 Thermometers suitable for calibration in a fixed-point cell are characterized in 1.5. A thermometer shall be long enough to extend fully into the well and all of the temperature-sensing portion of the thermometer shall be contained in the isothermal region of the well, as determined in 6.5.3. 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 the upper and lower limits of the uniform temperature region of the well, that is significant in the intended application or use of the thermometer.

6.6.3 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.

6.6.4 It is usually advantageous to heat thermometers to near the fixed point before they are inserted into the fixed-point cell. This reduces the heat load on the cell, helps to prolong the freezing plateau, and reduces demand on temperature-control

systems. A thermometer is conveniently heated in an auxiliary device held at a temperature slightly above or below the fixed-point temperature. With a little practice, the thermometer can be transferred to the cell without excessive cooling.

6.6.5 The thermometer temperature shall become steady at the fixed point before the thermometer is calibrated. The temperature is steady when the thermometer indication no longer changes significantly with time.

7. Test Procedure—Freezing

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 6.5.4.2).

7.1.3 With the fixed-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 6.6.4). 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 Allow the monitoring thermometer to stabilize, indicating thermal equilibrium.

7.2.3 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.

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

7.2.5 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 6.5.1), 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 6.3.8.1), 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 fused-silica glass for temperatures greater than 150°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 6.3.8.2), remove the fixed-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 6.6.5), 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 6.5.1), 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 6.5.3), 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 test thermometer which has been heated to within approximately 1 K of the fixed point. 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 6.6.2, 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 6.5.3). 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 6.6.2.

7.6.2 Repeat the procedure for the next test thermometer, if any. See 6.6 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 6.5.4.2).

8. Test Procedure—Melting

8.1 Prepare the test equipment.

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

8.1.2 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 6.5.4.2).

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

8.1.4 Establish the temperature of the auxiliary heating device about 5 K above the melting point (see 6.6.4). Record the control parameters.

8.1.5 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.

8.2 Prepare the reference material for the melting plateau.

8.2.1 Insert the monitoring thermometer into the cell well.

8.2.2 Allow the monitoring thermometer indication to stabilize, indicating thermal equilibrium.

8.2.3 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.

8.3 Establish the melting point.

8.3.1 Adjust the controls to stabilize the temperature of the heating device approximately 1 K above the melting point of the reference material. Record the control parameters.

8.3.2 Observe the indications of the thermometer in the well as the temperature increases into the melting plateau. If the realization is for a complete qualification test (see 6.5.1), record the indications continuously or at frequent intervals to establish the shape of the melting curve.

8.3.3 Observe the indication of the monitoring thermometer as its temperature approaches the melting point. When the temperature is steady (see 6.6.5), record the thermometer indication, and then proceed to 8.4, 8.5, or 8.6, as appropriate.

8.4 *Qualification Testing:*

8.4.1 For the complete qualification test (see 6.5.1), record the indication of the monitoring thermometer continuously or at frequent intervals to establish the melting curve. Continue recording until all of the reference material is molten 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.

8.4.2 For the immersion qualification test (see 6.5.3), proceed as in 8.5.1 until the monitoring thermometer indicates that the melting 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 8.5.1.

8.5 *Thermometer Calibration:*

8.5.1 Remove the monitoring thermometer from the cell and insert a test thermometer which has been heated to within approximately 1 K of the fixed point. 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 6.6.2, 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 8.5.2 (see also 6.5.3). 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 6.6.2.

8.5.2 Repeat the procedure for the next test thermometer, if any. See 6.6 for details. After calibration of the last test thermometer, replace the monitoring thermometer in the cell well and proceed as in 8.4 or 8.5.

8.6 Remove the monitoring thermometer from the cell and make any appropriate low-temperature reference measurements (see 6.5.4.2).

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

8.6.2 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.

9. Documentation

9.1 *Purpose and Scope:*

9.1.1 Thorough documentation provides a permanent, comprehensive historical record of the fixed-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.

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

9.2 *Experimental Data:*

9.2.1 Configuration data should include identification of the fixed-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 the name of the operator.

9.2.2 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.

9.2.3 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.

9.3 *Fixed-Point Cell Records:*

9.3.1 *Initial Description and Characteristics:*

9.3.1.1 Source of the cell;

9.3.1.2 Date acquired and placed into service;

9.3.1.3 Mass and chemical composition of the reference material;

9.3.1.4 Critical dimensions, including depth of immersion; and

9.3.1.5 Assigned value of the fixed point and associated uncertainty.

9.3.2 *History of Cell Use:*

9.3.2.1 The cumulative time above room temperature;

9.3.2.2 The cumulative time at or near the fixed point;

9.3.2.3 A description of accidents, abuse, and unusual use; and

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

9.3.3 *History of Cell Performance:*

9.3.3.1 The maximum undercool;

9.3.3.2 The indication of the dedicated monitoring thermometer at the fixed point;

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

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

9.4 *Dedicated Monitoring Thermometer Records:*

9.4.1 The thermometer records should include the initial description, characteristics, and history of use comparable to those for the fixed-point cell in 9.3.1 and 9.3.2.

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

9.4.3 In addition to the data in 9.3.3.2 and 9.3.3.3, 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.

9.5 *Other Auxiliary Equipment:*

9.5.1 The equipment records should include initial description, characteristics, and history of use comparable to those for the fixed-point cell in 9.3.1 and 9.3.2.

9.5.2 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.

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

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

9.6 *Calculations:*

9.6.1 *Temperature and Temperature Difference:*

9.6.1.1 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 the recording instrumentation. Note that in the case of a platinum resistance thermometer serving as a monitoring thermometer, the resistance ratio (see 9.4.3) is the usual quantity related to temperature.

9.6.1.2 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.

9.6.2 *Fixed Point Depression:*

9.6.2.1 If the concentration of impurities in the reference material is known, and the impurities are known to depress the fixed point, the depression of the fixed 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).

9.6.2.2 If the fixed 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. 3).

9.6.3 *Variability:*

9.6.3.1 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 fixed point, then the variability of the combined thermometer-fixed point system may be expressed by:

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

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.

9.6.3.2 If a set of indications, covering many qualification tests, of the dedicated monitoring thermometer at the fixed

point displays a uniform drift with time when the thermometer is at elevated temperature, then a linear regression analysis can yield both a drift rate and standard deviation of the combined thermometer-fixed point system.

10. Precision and Bias

10.1 A fixed-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 fixed point of the cell.

10.2 The precision component due to cell variability and use shall be evaluated from an analysis of the measurement variability of the combined system, consisting of the monitoring thermometer and the fixed-point cell. Separating thermometer variability from cell variability is usually not possible. If the system is very stable, the evaluation of 9.6.3.1 yields an upper limit on the standard deviation of the fixed point of the cell. The best of such systems have standard deviations of less than 1 mK.

10.3 The uncertainty in the value assigned to the cell fixed point contributes a component to thermometer calibration uncertainty. If the value assigned is that attributed to the fixed point of pure material, then the contribution to uncertainty caused by impurities in the cell reference material may be estimated by the methods of 9.6.2. If a fixed-point value is determined by measurement, then the uncertainty in the value shall come from analysis of the measurement process upon which the determined value is based. See 6.3.9.

11. Keywords

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