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StandardGuide 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 Fig. 1 and Fig. 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.

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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.

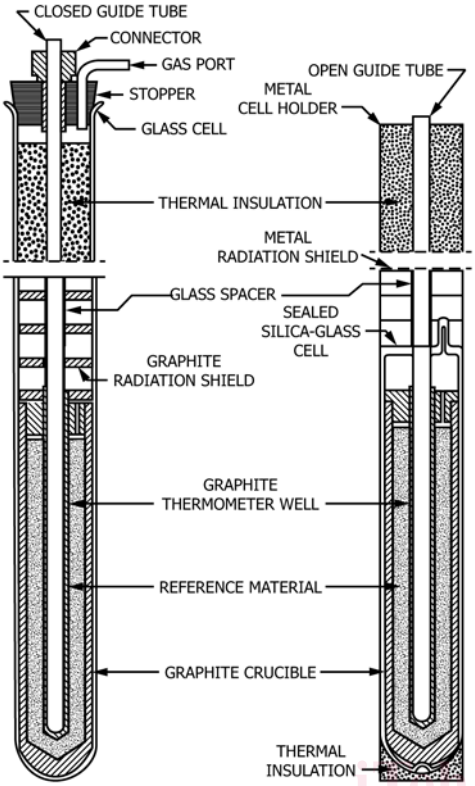


FIG. 1 Examples of Fixed-Point Cells

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):

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

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 Fig. 3 and Fig. 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 Fig. 5 and Fig. 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.

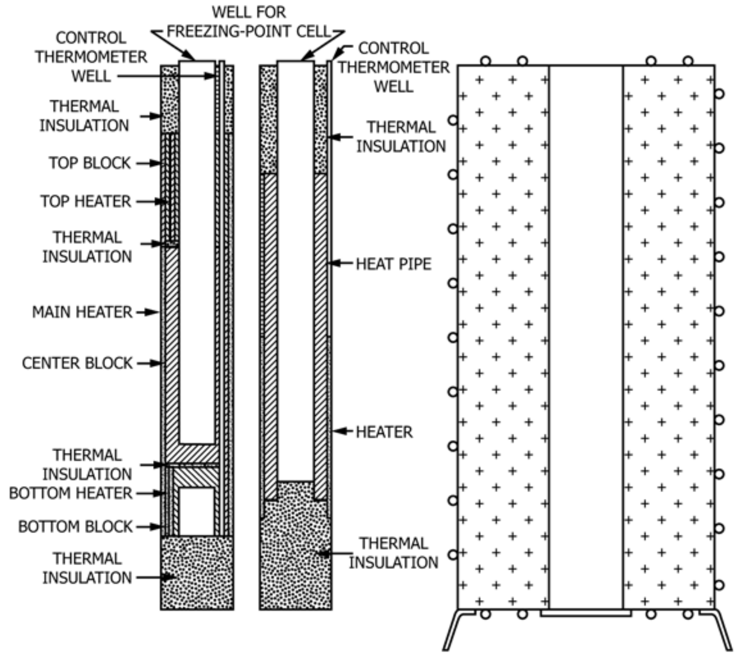
3.2.14 *supercooled state, n*—the meta-stable state of reference material in which the temperature of the liquid phase is below the freezing point.

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

4. Summary of Guide

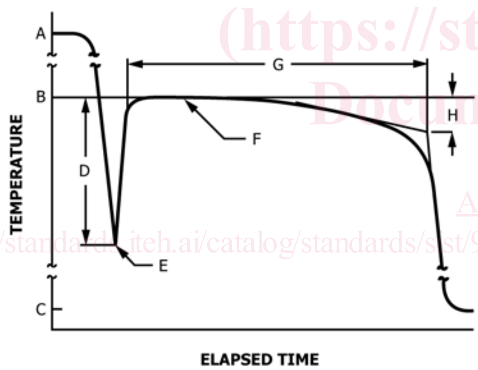
4.1 A fixed-point cell is used for thermometer calibration by establishing and sustaining a reference material at either the melting or freezing point, to which a value of temperature has been assigned. The thermometer to be calibrated is inserted into a reentrant well in the cell; the well itself is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

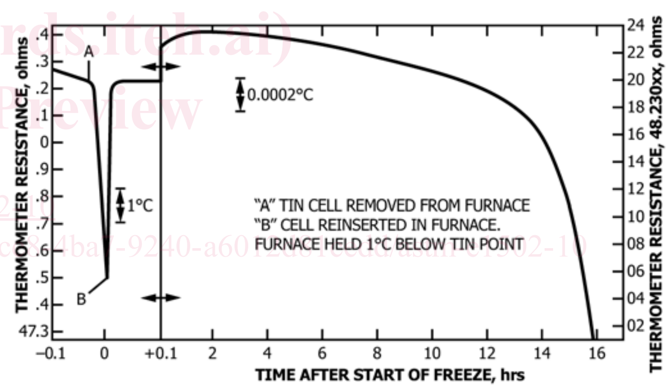
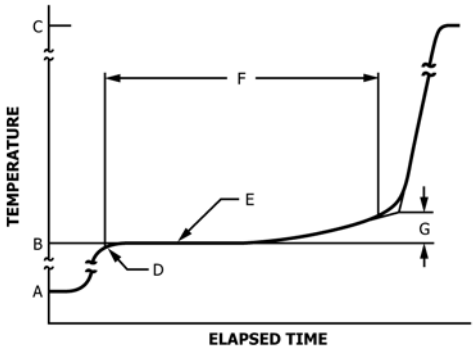


FIG. 4 Freezing Curve of a Sample of Highly Purified Tin

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 a Typical Melting Curve

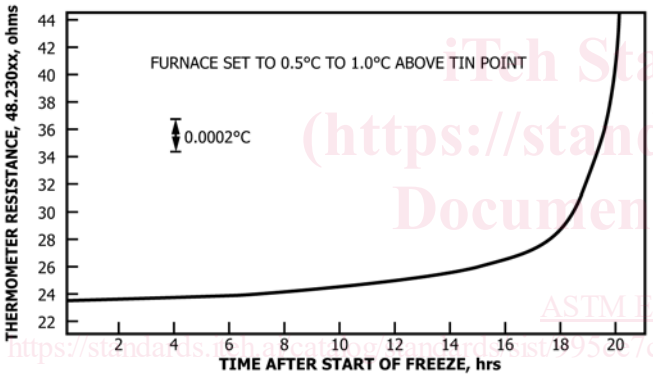


FIG. 6 Melting Curve of a Sample of Highly Purified Tin

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 Table 1 and Table 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.

TABLE 1 Characteristics of Pure Fixed Point Reference Materials

Material	Freezing point, ITS-90, °C	Typical Undercool, K	Pressure Coefficient at fixed 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.

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
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 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 and antimony, 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

[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."