Designation: ~~E1502 – 16~~ E1502 – 22

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~~29 °C to ~~1085°C.~~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.

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[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~~June 1, 2022. Published ~~September 2016~~July 2022. Originally approved in 1992. Last previous edition approved in ~~2010~~2016 as ~~E1502 – 10.~~E1502 – 16. DOI: ~~10.1520/E1502-16.~~ 10.1520/E1502-22.

[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.

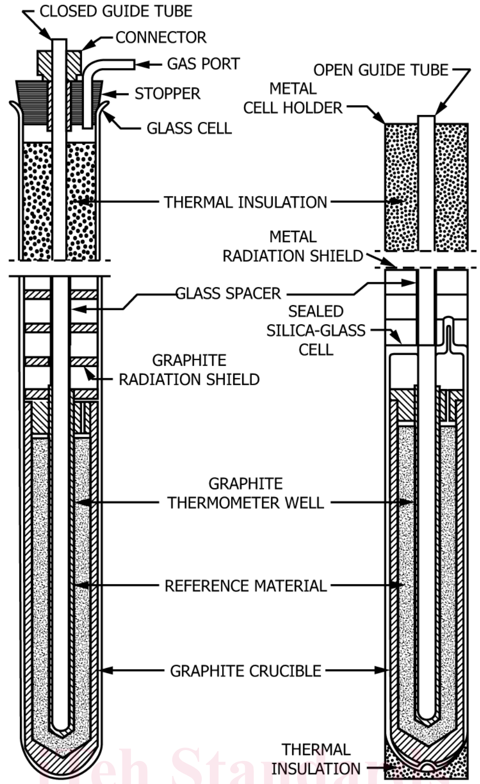


FIG. 1 Examples of Fixed-Point Cells

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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

1.10 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

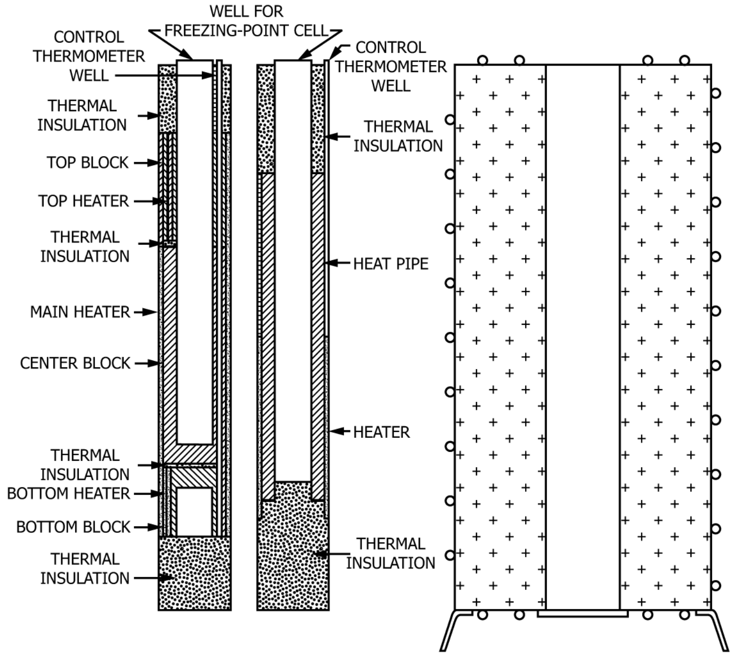
2.1 *ASTM Standards:*[4]
E344 Terminology Relating to Thermometry and Hydrometry
E644 Test Methods for Testing Industrial Resistance Thermometers

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.

[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.



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

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.

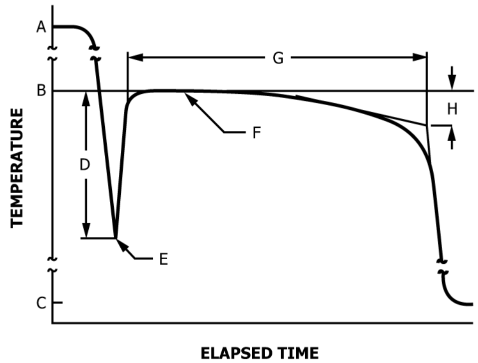
3.2.4.1 *Discussion*—
Graphic representations of freezing curves are shown in Figs. 3 and 4.

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.



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

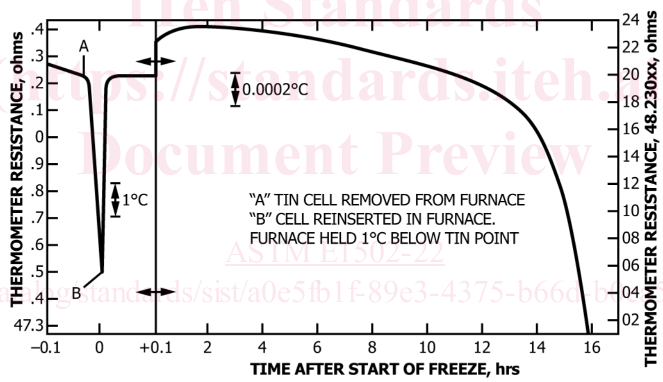


FIG. 4 Freezing Curve of Sample of Highly Purified Tin

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.

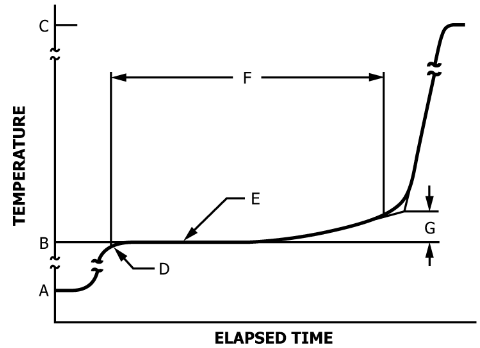
3.2.9 *melting plateau, n*—the period during melting in which the temperature does not change significantly.

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.



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

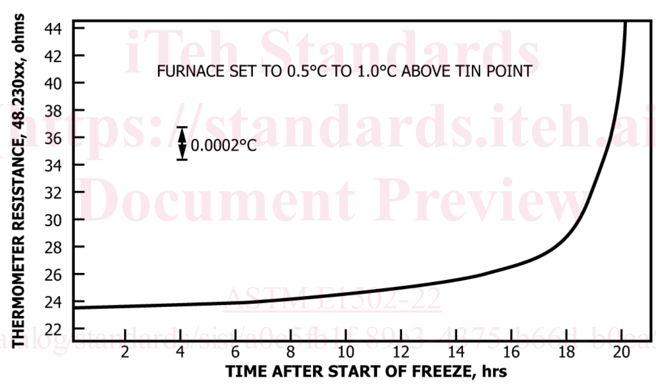


FIG. 6 Melting Curve of Sample of Highly Purified Tin

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 or more below the freezing point so that the reference material cools. In some cases, the undercool must be done to a much lower than 1 K. 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 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).

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.

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~~	~~. . .~~
Bismuth[C]	271.402	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.
[C] Based on recommendation of International Bureau of Weights and Measures (BIPM) Working Group 2 of the Comité Consultatif de Thermométrie (CCT-WG2); published as: Bedford, R. E., Bonnier, G., Maas, H., and Pavese, F., ″Recommended Values of Temperature on the International Temperature Scale of 1990 for a Selected Set of Secondary Reference Points″, *Metrologia*, Vol 33, 1996, pp. 133. DOI: 10.1088/0026-1394/33/2/3.

TABLE 2 Estimated Achievable Standard Uncertainties ($k = 1$) 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.

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 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.