



Standard Guide for Use of Water Triple Point Cells¹

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INTRODUCTION

The triple point of water is an important thermometric fixed point common to the definition of two temperature scales of science and technology, the Kelvin Thermodynamic Temperature Scale (KTTS) and the International Temperature Scale of 1990 (ITS-90). The ITS-90 was designed to be as close to the KTTS as the experimental data available at the time of the adoption of the ITS-90 would permit. The temperatures (T) on the KTTS are defined by assigning the value 273.16 K to the triple point of water, thus defining the thermodynamic unit of temperature, kelvin (K), as $1/273.16$ of the thermodynamic temperature of the triple point of water (**1**, **2**).² The triple point of water, one of the fixed points used to define the ITS-90, is the temperature to which the resistance ratios $W(T) = R(T)/R(273.16 \text{ K})$ of the standard platinum resistance thermometer (SPRT) calibrations are referred.

The triple points of various materials (where three distinct phases, for example, their solid, liquid, and vapor phases, coexist in a state of thermal equilibrium) have fixed pressures and temperatures and are highly reproducible. Of the ITS-90 fixed points, six are triple points. The water triple point is one of the most accurately realizable of the defining fixed points of the ITS-90; under the best of conditions, it can be realized with an expanded uncertainty ($k=2$) of less than $\pm 0.00005 \text{ K}$. In comparison, it is difficult to prepare and use an ice bath with an expanded uncertainty ($k=2$) of less than $\pm 0.002 \text{ K}$ (**3**).

1. Scope

1.1 This guide covers the nature of two commercial water triple-point cells (types A and B, see Fig. 1) and provides a method for preparing the cell to realize the water triple-point and calibrate thermometers. Tests for assuring the integrity of a qualified cell and of cells yet to be qualified are given. Precautions for handling the cell to avoid breakage are also described.

1.2 The effect of hydrostatic pressure on the temperature of a water triple-point cell is discussed.

1.3 Procedures for adjusting the observed SPRT resistance readings for the effects of self-heating and hydrostatic pressure are described in Appendix X1 and Appendix X2.

1.4 *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 appro-*

priate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 *ASTM Standards*:³

E344 Terminology Relating to Thermometry and Hydrometry

E1594 Guide for Expression of Temperature

3. Terminology

3.1 *Definitions*—The definitions given in Terminology E344 apply to terms used in this guide.

3.2 *Definitions of Terms Specific to This Standard*:

3.2.1 *inner melt, n*—a thin continuous layer of water between the thermometer well and the ice mantle of a water triple-point cell.

3.2.2 *reference temperature, n*—the temperature of a phase equilibrium state of a pure substance at a specified pressure, for example, the assigned temperature of a fixed point.

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² The boldface numbers in parentheses refer to the list of references at the end of this standard.

³ 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.

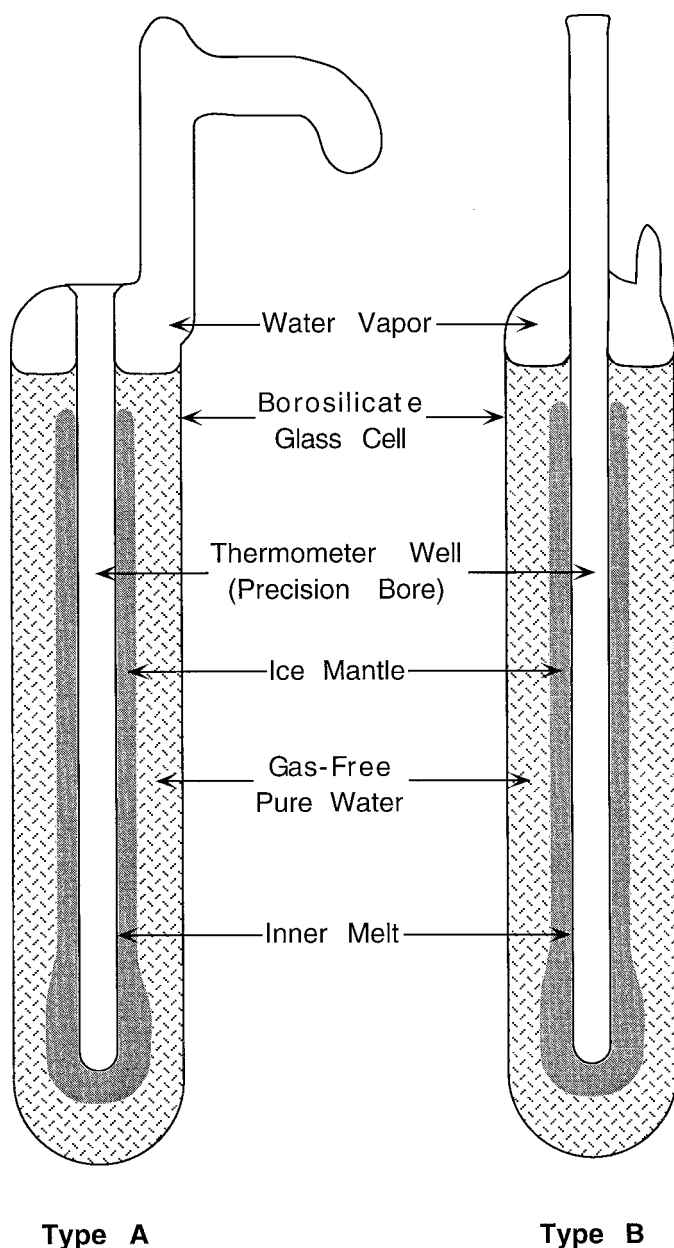


FIG. 1 Configurations of two commonly used triple point of water cells, Type A and Type B, with ice mantle prepared for measurement at the ice/water equilibrium temperature. The cells are used immersed in an ice bath or water bath controlled close to 0.01°C (see 5.4)

3.2.2.1 *Discussion*—At an equilibrium state of three phases of a substance, that is, at the triple point, both the temperature and pressure are fixed.

4. Significance and Use

4.1 This guide describes a procedure for placing a water triple-point cell in service and for using it as a reference temperature in thermometer calibration.

4.2 The reference temperature attained is that of a fundamental state of pure water, the equilibrium between coexisting solid, liquid, and vapor phases.

4.3 The cell is subject to qualification but not to calibration. The cell may be qualified as capable of representing the

fundamental state (see 4.2) by comparison with a bank of similar qualified cells of known history, and it may be so qualified and the qualification documented by its manufacturer.

4.4 The temperature to be attributed to a qualified water triple-point cell is exactly 273.16 K on the ITS-90, unless corrected for isotopic composition (refer to Appendix X3).

4.5 Continued accuracy of a qualified cell depends upon sustained physical integrity. This may be verified by techniques described in Section 6.

4.6 The commercially available triple point of water cells described in this standard are capable of achieving an expanded uncertainty ($k=2$) of between ± 0.1 mK and ± 0.05 mK, depending upon the method of preparation. Specified measurement procedures shall be followed to achieve these levels of uncertainty.

4.7 Commercially-available triple point of water cells of unknown isotopic composition should be capable of achieving an expanded uncertainty ($k=2$) of no greater than 0.25 mK, depending upon the actual isotopic composition (3). These types of cells are acceptable for use at this larger value of uncertainty.

5. Apparatus

5.1 The essential features of type A and type B water triple-point cells are shown in Fig. 1. A transparent glass flask free of soluble material is filled with pure, air-free water and then is permanently sealed, air-free, at the vapor pressure of the water. A reentrant well on the axis of the flask receives thermometers that are to be exposed to the reference temperature.

5.2 For the lowest level of uncertainty, the water used as the reference medium shall be very pure and of known isotopic composition. Often it is distilled directly into the cell. The isotopic composition of cells filled with “rain water” is expected not to vary enough to cause more than 0.05 mK difference in their triple points. Extreme variations in isotopic composition, such as between ocean water and water from old polar ice, can affect the realized temperature by as much as 0.25 mK (7). In cases where the isotopic composition is unknown, or if the cell has not been qualified by comparison with a cell of known isotopic composition, the larger value of uncertainty (± 0.25 mK) should be assumed.

5.3 For use, a portion of the water is frozen within the cell to form a mantle of ice that surrounds the well and controls its temperature.

5.4 The temperature of the triple point of water realized in a cell is independent of the environment outside the cell; however, to reduce heat transfer and keep the ice mantle from melting quickly, it is necessary to minimize heat flow between the cell and its immediate environment. This may be done by immersing the cell in an ice bath that maintains the full length of the outer cell wall at or near the melting point of ice. Alternatively, commercial automatic maintenance baths, built specifically for this purpose, are available. In such baths, the triple point of water equilibrium of the cell, once established, can be maintained for many months of continual use. To avoid radiation heat transfer to the cell and to the thermometer, the outer surface of the maintenance bath is made opaque to radiation.

6. Assurance of Integrity

6.1 The temperature attained within a water triple-point cell is an intrinsic property of the solid and liquid phases of water under its own vapor pressure. If the water triple-point conditions are satisfied, the temperature attained within the cell is more reproducible than any measurements that can be made of it.

6.2 The accuracy of realization of the water triple-point temperature with a qualified cell depends on the physical integrity of the seal and of the walls of the glass cell and on their ability to exclude environmental air and contaminants.

6.3 Initial and continued physical integrity is confirmed by the following procedures:

6.3.1 *Test for the Presence of Air:*

6.3.1.1 Remove all objects from the thermometer well.

6.3.1.2 The solubility and the pressure of air at 101 325 Pa lower the ice/water equilibrium temperature 0.01°C below the triple-point temperature. Since air is more soluble in water at lower temperatures, the test for air shall be done at room temperature. The test is less definitive when performed on a chilled cell. At room temperature, with the cell initially upright and the well opening upward, slowly invert the cell. As the axis of the cell passes through horizontal and as the water within the cell strikes the end of the cell, a sharp “glassy clink” sound should be heard. The distinctive sound results from the sudden collapse of water vapor and the “water hammer” striking the glass cell. The smaller the amount of air, the sharper the clink sound; a large amount of air cushions the water-hammer action and the sound is duller.

6.3.1.3 With a type A cell, continue to tilt the cell to make a McLeod-gauge type test until the vapor (water saturated air) bubble is entirely captured in the space provided in the handle. The vapor bubble should be compressed to a volume no larger than about 0.03 cm³ (4 mm diameter). It may even vanish as it is compressed by the weight of the water column. As in the tilt test, the bubble test is more definitive when the cell is at room temperature (see 6.3.1.2). Since type B cells do not have a space to capture the vapor, the amount of air in the cell is estimated by comparing the sharpness of the clink sound with that of a type A cell.

6.3.2 *Test for the Presence of Water Soluble Impurities:*

6.3.2.1 When ice is slowly formed around the thermometer well, impurities are rejected into the remaining unfrozen water. Therefore, the impurity concentration of the unfrozen water increases as the ice mantle thickens. The ice is purer than the unfrozen water. Consequently, the inner melt (see section 7.1.3) that is formed from the ice mantle is purer than the unfrozen water outside of the mantle.

6.3.2.2 Prepare a relatively thick ice mantle, according to Section 7, by maintaining the dry ice level full for about 20 minutes. Make certain that the ice does not bridge to the cell wall (see 7.1.9).

6.3.2.3 Prepare an inner melt according to 7.1.13. Using an SPRT, make measurements on the cell and determine the zero-power resistance according to Section 8 and Appendix X1.

6.3.2.4 After 6.3.2.3, remove the SPRT. Gently invert the water triple-point cell and then return it to the upright position

several times to exchange the unfrozen water on the outside of the ice mantle with the inner melt water. (**Warning**—When inverting the cell, do not allow the floating ice mantle to severely strike the bottom of the water triple-point cell.)

6.3.2.5 Reinsert the pre-chilled SPRT used in 6.3.2.3 into the well. Make measurements on the cell and determine the zero-power resistance, according to Section 8 and Appendix X1.

6.3.2.6 Typically, for high quality water triple-point cells, the results of 6.3.2.3 and 6.3.2.5 will not differ by more than ±0.03 mK.

6.4 Any cell that had previously been qualified by comparison with cells of known integrity (as in 4.3), that has not thereafter been modified, and which currently passes the tests of 6.3.1 and 6.3.2, is qualified as a water triple-point cell.

6.5 Any cell that fails to pass the tests of 6.3.1 and 6.3.2, even though previously qualified, is no longer qualified for use as a water triple-point cell.

7. Realization of the Water Triple-Point Temperature

7.1 The ice mantle that is required to realize the triple-point temperature of water can be prepared in a number of ways. They produce essentially the same result. A common procedure is as follows:

7.1.1 Empty the well of any solids or liquids. Wipe the well clean and dry, and seal the well opening with a rubber stopper.

7.1.2 If the triple point of water cell has not already been tested for the presence of air, perform the tests indicated in 6.3.1 for presence of air.

7.1.3 To obtain an ice mantle of fairly uniform thickness that extends to the top, immerse the cell completely in an ice bath, and chill the cell to near 0°C.

7.1.4 Remove the cell from the bath and mount it upright on a plastic foam cushion. Wipe the cell dry around the rubber stopper before removing the rubber stopper.

7.1.5 Remove the rubber stopper and place about 1 cm³ of dry alcohol in the well to serve as a heat-transfer medium while forming an ice mantle around the well within the sealed cell.

7.1.6 Place a small amount of crushed dry ice at the bottom of the well, maintaining the height of the dry ice at about 1 cm for a period of 2 to 3 min. In repeated use of the cell, the ice mantle melts mostly at the bottom; hence, it is desirable that the ice mantle be thicker at the bottom. Crushed dry ice may be prepared from a block or by expansion from a siphon-tube tank of liquid CO₂.

7.1.7 At the interface of the well, the water is initially supercooled, and the well becomes abruptly coated with fine needles of ice frozen from the supercooled water.

7.1.8 After a layer of ice forms around the bottom of the well, fill the well with crushed dry ice up to the vapor/liquid interface.

7.1.9 Replenish the dry ice as it sublimates, maintaining the well filled to the liquid surface, until a continuous ice mantle as thick as desired forms on the surface of the well within the water (usually 4 to 8 mm thick). The mantle will appear thicker than its actual thickness because of the lenticular shape of the cell and the refractive index of water. The actual thickness may be best estimated by viewing from the bottom of the cell while it is inverted or by immersing the cell in a large glass container

of water. (**Warning**—During preparation, the mantle should never be allowed to grow at any place to completely bridge the space between the well and the inner wall of the cell, as the expansion of the ice may break the cell. In particular, if bridging occurs at the surface of the water at the top of the cell under the vapor space, melt the ice bridge by warming the cell locally with heat from the hand, while gently shaking the cell.)

7.1.10 When the mantle attains nearly the desired thickness or after maintaining the dry ice level in the well at the water surface for about 20 min, return the cell to the ice bath with the entrance to the thermometer well slightly above the ice bath surface and allow the dry ice to sublime completely. By allowing the dry ice to sublime completely, the bottom of the well stays cold longer and the mantle grows thicker there.

7.1.11 After the thermometer well becomes free of dry ice, immerse the cell deeper into the ice bath and fill the well with ice bath water.

7.1.12 Allow the cell to remain packed in ice or in the ice bath for two days to stabilize its temperature. Because of the strains in the ice mantle prepared using dry ice, a freshly prepared mantle can give a temperature that is as much as 0.2 mK low.

7.1.13 When initially prepared, the mantle will be fixed to the wall of the well. Before the cell can be used, a thin layer of ice next to the thermometer well shall be melted. To prepare this “inner melt,” briefly and gently insert a metal or glass rod, initially at room temperature, into the well to heat the well slightly. The rod should have a smooth rounded end to avoid scratching or possibly breaking the cell. Upon removal of the rod, tilt the cell to an angle of about 45° from the vertical axis and observe for the rotation of the mantle. If the mantle is properly detached, it will spin freely about the well. The liquid water film should be thin to minimize the thermal resistance between the thermometer well and the ice/water interface. The liquid water film between the mantle and the well surface is essential to the proper realization of the triple-point temperature. The freedom of the mantle should always be checked by tilting the cell prior to and after calibrating thermometers.

7.1.14 When the cell is stored completely immersed at the ice point, ice will grow between the mantle and the cell wall. If the cell is exposed to the ice point temperature, the cell will not be harmed by the growth of ice. Before using the cell, melt any ice that bridges the mantle and the cell wall by momentarily immersing the cell in a large container of water, by running water from the faucet over the cell, or by warming with your hands. (**Warning**—Do not warm the water triple point cell any more than necessary. Since the density of water is the greatest at approximately 4°C, this warm water will drift downward and melt more ice than desirable.)

8. Use of the Triple Point of Water Cell

8.1 Ensure that the ice mantle is well-formed over most of the vertical wall of the well and over the bottom of the well and that it can spin freely about the well.

8.2 Soak a small piece of plastic foam in ice-cold water that is free of ice and push it to the bottom of the thermometer well. If any ice is adhering to the foam, the thermometer readings will be unstable. The foam cushions the thermometer at the bottom of the well.

8.3 Cool an aluminum bushing in ice-cold water and lower it onto the top of the foam. The aluminum bushing should “slide-fit” inside the thermometer well and over the thermometer, and it should be long enough to extend about 1 cm beyond the top of the temperature sensing part of the thermometer. The upper end of the bushing should have an internal taper so that the thermometer can be guided easily into the bushing. The aluminum bushing enhances the thermal contact and also centers the thermometer in the thermometer well.

8.4 Chill the thermometer to near 0°C in a tube of water immersed in the ice bath before inserting it into the well. This cooling will keep the thickness of the inner melt about the same for different thermometers to be calibrated and also will prolong the duration of the ice mantle. The thermometer is chilled in a tube of water cooled in the ice bath, instead of being chilled directly in the ice bath, to avoid introducing ice particles into the thermometer well.

8.5 Except while inspecting it, keep the cell immersed to such a depth that bath water flows into the well. Avoid the presence in the well of ice particles. These particles would cause an unwanted depression of the well temperature. The bath should be designed to prevent ambient radiation from reaching the water triple-point cell.

8.6 Insert the chilled thermometer into the well, allow the thermometer to come into equilibrium with the cell, and make “steady-state” resistance readings at the chosen continuous current (see [Appendix X1](#)). (**Warning**—As in all calibration and temperature measurements, care shall be taken so that the stem of the thermometer does not conduct significant heat to or from the sensing element in the well. Test objects of high thermal conductivity, such as some metal-sheathed industrial thermometers, might conduct significant ambient heat to the sensing element along their sheaths. For these thermometers, it is advisable to insert them fully into the well and to immerse the cell deeper into the ice bath so that the emergent portion of the thermometer outside the well would be cooled in the ice bath to approximately 0°C. Transparent test objects, such as silica-glass-sheathed thermometers, may transmit heat by “light piping” to the sensor from heat radiating sources, such as lights, in the laboratory environment. For these, it is advisable to cover the emergent portion of the thermometer with an opaque cover, such as a black felt cloth.)

9. Keywords

9.1 calibration; defining fixed point; fixed point; hydrostatic head pressure; International Temperature Scale of 1990 (ITS-90); intrinsic property; Kelvin Thermodynamic Temperature Scale (KTTs); qualification; self-heating; standard platinum resistance thermometer (SPRT); triple point; triple point of water; water triple point cell

X1. SELF-HEATING OF RESISTANCE THERMOMETERS IN THE TRIPLE POINT OF WATER CELL

X1.1 In resistance thermometry, the applied electric current results in Joule heating, which raises the temperature of the resistor above that of the measurement medium (reference temperature) and, correspondingly, increases its resistance. This temperature increase or the self-heating depends upon the electric power being dissipated and the thermal resistance between the sensor wire and the measurement medium (that is, water/ice interface of the inner melt of the water triple-point cell). For accurate measurements, it is necessary to account for any variation in the self-heating of the thermometer under the conditions of calibration and under the conditions of temperature measurement. Self-heating will be expressed interchangeably in the following analysis as either the temperature increase (difference) or the corresponding resistance increase under conditions of steady-state Joule heating of the thermometer. The temperature difference ΔT is related to the product of the measured resistance difference ΔR and the reciprocal of the temperature derivative of resistance (dR/dT) of the thermometer at the temperature of measurement, that is, in **X1.2-X1.13**, at the water triple-point temperature.

X1.2 The self-heating can be separated into two components. The first is the internal self-heating (ISH), which is the temperature difference between the thermometer sensor and the external surface of the thermometer sheath. At a given measurement temperature, this difference depends only upon the thermometer construction and the electric power; hence, at the same electric power, the internal self-heating is the same at the time of calibration and when the thermometer is being used to determine temperature. The second is the external self-heating (ESH), which is the temperature difference between the thermometer sheath and the measurement medium; this difference depends upon the thermal resistance between the two and on the electric power.

X1.3 The total self-heating (TSH), the sum of internal and external self-heating, can be determined simply by making steady-state resistance measurements at two currents.

X1.4 At low thermometer currents, the TSH is directly proportional to the electric power dissipated in the thermometer resistor. The thermometer resistance R_0 at zero current or no self-heating is, therefore,

$$R_0 = R_1 - i_1^2 \times (R_2 - R_1)/(i_2^2 - i_1^2) \quad (\text{X1.1})$$

where:

R_1 = the steady-state resistance at i_1 mA, and

R_2 = the steady-state resistance at i_2 mA.

The TSH at i_1 mA is given by:

$$\begin{aligned} \text{TSH} &= [R_1 - R_0] \times [1/(dR/dT)] \\ &= i_1^2 \times [(R_2 - R_1)/(i_2^2 - i_1^2)] \times [1/(dR/dT)] \quad (\text{X1.2}) \end{aligned}$$

X1.5 Insert the chilled thermometer into the thermometer

well of the water triple-point cell and record steady-state resistance readings at a continuous current, for example, of 1 mA and then at 2 or 1.414 mA according to Section 8. Calculate the resistance at zero current from the observations according to Eq X1.1.

X1.6 When $i_1 = 1$ mA and $i_2 = 2$ mA, Eq X1.1 reduces to:

$$R_0 = R_1 - (R_2 - R_1)/3 = (4R_1 - R_2)/3 \quad (\text{X1.3})$$

At 1 mA,

$$\text{TSH} = [(R_2 - R_1)/3] \times [1/(dR/dT)] \quad (\text{X1.4})$$

X1.7 Calculate TSH at 1 mA from the observations in **X1.5**.

X1.8 The ISH can be determined by conducting the measurements under conditions of negligible external self-heating, with the thermometer making nearly perfect thermal contact with the temperature medium. An ice bath, prepared using finely shaved ice and a minimum of water so that the small ice particles and water would be in intimate contact with the thermometer sheath, closely approximates the conditions of nearly perfect thermal contact. The observed TSH becomes, therefore, the ISH, since $\text{ESH} = 0$ (see **X1.3**, Eq X1.2, and Eq X1.4).

X1.9 Prepare an ice bath of at least 50 cm depth using finely shaved ice with a minimum of water. Prepare a close-fitting well for the thermometer in the ice bath by inserting into the bath a chilled glass rod or tube of the same outside diameter as the thermometer. First chill the thermometer according to **8.4 and 8.5**, carefully insert the thermometer into the ice-bath well, and then make steady-state resistance measurements at 1 mA and at 2 mA, according to **X1.5**.

X1.10 Calculate the ISH at 1 mA, according to **X1.6** and **X1.8** and the data from **X1.9**. At the triple point of water, the range of ISH of SPRTs at 1 mA can range from 0.3 mK to 4 or 5 mK, depending upon the thermometer design.

X1.11 The ISH determined in the ice bath can be used to calculate the ESH in the measurements with the triple point of water cell according to:

$$\text{ESH} = \text{TSH} - \text{ISH} \quad (\text{X1.5})$$

where: TSH is from measurements in the triple point of water cell (see **X1.6**, Eq X1.4, and **X1.9**). With a water triple point cell of 13 mm inside diameter well and a thin inner melt, the ESH at 1 mA corresponds to about 0.1 mK using a close-fitting aluminum bushing with a thermometer of 7.5 mm outside diameter sheath.

X1.12 Thermometer calibrations are usually expressed in terms of steady-state readings with continuous 1 mA current with the thermometer making perfect thermal contact with the temperature medium. To express the calibrations at 1 mA for

the measurements of the thermometer in the triple point of water cell, the steady-state resistance reading R_1 (see X1.4, Eq X1.1) is adjusted to zero ESH (0ESH) (see X1.11, Eq X1.5).

$$R_1(0ESH) = R_1 - ESH \times (dR/dT) \quad (X1.6)$$

X2. EFFECT OF HYDROSTATIC HEAD ON RESISTANCE THERMOMETERS IN THE TRIPLE POINT OF WATER CELL

X2.1 The triple-point temperature within the cell is independent of the atmospheric pressure and temperature surrounding the cell. However, the triple-point temperature is realized only at the solid-liquid-vapor interface near the top of the cell. At the location of the temperature-sensing element of a thermometer, the temperature is influenced by the hydrostatic-head pressure of the internal water column (-0.73 mK/m). For accurate measurements, it is necessary to apply a correction to the observed resistance for the temperature effect of water height above the thermal center (middle) of the sensing element of the thermometer.

X2.2 For example, when a resistance thermometer is inserted in a water triple-point cell with its thermal center 265 mm below the upper surface of the water, the observed resistance would correspond to that at a temperature 0.193 mK (-0.73 mK/m $\times$ 0.265 m) below the water triple-point temperature, that is, 0.009807°C. (**Warning**—The example given in X2.2.1 and X2.2.2 are based upon the depth of 265 mm as described herein.)

X2.2.1 To adjust this observed thermometer resistance, for example, at zero current (see X1.4, Eq X1.1), to that of the water triple-point temperature, use the relation:

X1.13 Compare the results of X1.12 with those of X1.4, X1.5, and X1.6.

$$R_0(273.16 \text{ K}) = R_0 + 0.000193 \times dR/dT \quad (X2.1)$$

where: dR/dT corresponds to that value at 273.16 K.

$$dR/dT = R(273.16 \text{ K}) \times dW/dT \approx R_0 \times dW/dT \quad (X2.2)$$

For SPRTs:

$$dW/dT = 0.0039880/\text{K at } 273.16 \text{ K} \quad (X2.3)$$

Hence, the thermometer resistance at 273.16 K and zero current becomes:

$$\begin{aligned} R_0(273.16 \text{ K}) &= R_0 + R_0 \times 0.000193 \times 0.0039880 \\ &= 1.000000770 \times R_0 \end{aligned} \quad (X2.4)$$

For thermometer calibrations at zero-current, use the value from Eq X2.4 to calculate resistance ratios.

X2.2.2 For thermometer calibrations at 1 mA, adjust R_1 (0ESH) for the hydrostatic head effect (0.193 mK), according to Eq X2.1-X2.4, see also X1.12, Eq X1.6. The thermometer resistance at 273.16 K and 1 mA current becomes:

$$R_1(0ESH, 273.16 \text{ K}) = 1.000000770 \times R_1(0ESH) \quad (X2.5)$$

For 1-mA thermometer calibrations, use the value from Eq X2.5 to calculate resistance ratios (1, 2).

X3. ADDITIONAL INFORMATION PERTAINING TO ISOTOPIC EFFECTS, V-SMOW, AND THE TRIPLE POINT OF WATER (7)

X3.1 Variations in the isotopic content of naturally occurring water can cause detectable differences in the TPW temperature. A difference as large as 0.25 mK in TPW temperatures has been found between ocean water and water obtained from melted polar ice. Neither the SI definition of kelvin (the unit of the thermodynamic temperature as 1/273.16 of the thermodynamic temperature of the triple point of water) nor the official ITS texts (ITS-90 and IPTS-68) specify the isotopic composition of water for the TPW. Some suggest that documents published by BIPM, such as “Supplementary Information for the International Temperature Scale of 1990” (7) and “Supplementary Information for the IPTS and EPT-76” specify that the isotopic composition of water for TPW should be substantially the same as ocean water.

X3.2 The following excerpts are taken directly from “Supplementary Information for the International Temperature Scale of 1990”:

“An operating triple-point cell contains ice, water, and water vapor, all of high purity and of substantially the isotopic composition of ocean water.”

“Variations in the isotopic content of naturally occurring water can give rise to detectable differences in the triple-point temperature. Ocean water contains about 0.16 mmol of ^2H per mole of ^1H , 0.4 mmol of ^{17}O , and 2 mmol of ^{18}O per mole of ^{16}O ; this proportion of heavy isotopes is almost never exceeded in naturally-occurring water. Continental surface water normally contains about 0.15 mmol of ^2H per mole of ^1H ; water coming from polar snow or glacial ice may occasionally contain as little as 0.1 mmol of ^2H per mole of ^1H .

X3.3 The purifying of water may slightly modify its isotopic composition (distillation normally entails a decrease in the ^2H content), and the isotopic composition at an ice-water interface is very slightly dependent on the freezing technique.

X3.3.1 A decrease of 10 μmol of ^2H per mole of ^1H corresponds to a decrease of temperature of the triple point of about 40 μK ; this is the difference between the triple points of ocean water and the normally occurring continental surface water. An extreme, and quite atypical, difference in the

triple-point temperatures of naturally-occurring water is about 0.25mK and is that between sea water and water obtained from melted polar ice.”

X3.4 The international science community, through the International Atomic Energy Agency, uses a defined Standard Mean Ocean Water (SMOW) as a point of reference for studies in the isotopic composition of waters. Measurements of isotopic composition are made with respect to V-SMOW (Vienna-SMOW) and SLAP (Stand Light Antarctic Precipitation), two standard reference materials (waters) that span the isotopic range of naturally occurring waters. Absolute measurements of the isotope ratios for V-SMOW give:

$$(D/H)_{V-SMOW} = 0.00015576(5), \quad (X3.1)$$

$$(^{18}O/^{16}O)_{V-SMOW} = 0.00200520(45) \quad (X3.2)$$

$$(^{17}O/^{18}O)_{V-SMOW} = 0.0003799(8). \quad (X3.3)$$

Variations in isotope ratios are conventionally reported as deviations from V-SMOW:

$\delta^{18}O = [(^{18}O/^{16}O)_{\text{sample}} - (^{18}O/^{16}O)_{V-SMOW}] / (^{18}O/^{16}O)_{V-SMOW}$, and similarly for δD and $\delta^{17}O$. Usually the results are in the parts-per-thousand range so are expressed as permil (per thousand, ‰).

For isotopic compositions near V-SMOW, the effect of the isotopes can be approximated by a liner function of the delta values:

$$T_{\text{meas}} = T_{V-SMOW} + A_D \delta D + A_{17O} \delta^{17}O + A_{18O} \delta^{18}O \quad (X3.4)$$

The most precise isotopic depression constants are believed to be: $A_D = 628 \pm 6 \mu K$ and $A_{180} = 641 \pm 23 \mu K$. The value of A_{170} is inferred as 57 μK .

The delta values δD , $\delta^{17}O$, and $\delta^{18}O$ for precipitation (meteoric waters) are highly correlated. Approximate relationships are $\delta D = 8 * \delta^{18}O + 0.01$, and $1 + \delta^{17}O = (1 + \delta^{18}O)^{0.528}$. Therefore, the temperature correction can be predicted from measurements of δD only according to:

$$(T_{\text{meas}} - T_{V-SMOW}) \cong (712 \times \delta D - 0.8) \mu K \quad (X3.5)$$

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