

A TECHNICAL GUIDE AND STANDARD FOR THE USE OF GALLIUM MELT-POINT CELLS

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RATIONALE

In the last issue of the Isotech Journal of Thermometry (Vol. 3 No. 2, 1992) we published a Technical Guide to the qualification and use of water triple point cells. Reader response to that article indicated that it was popular and useful, and suggested that similar guides to other calibration points would be welcomed from time to time. Since there are several references to the gallium point in the present edition, we have chosen to provide such a Guide to the gallium melting point here.

INTRODUCTION

The development of the gallium melting point as a thermometric standard occurred between the promulgation of the International Practical Temperature Scale of 1968 (IPTS-68) and the International Temperature Scale of 1990 (ITS-90). It appears not at all in the text of the IPTS-68, even as a secondary reference point, and then achieves full prominence in the ITS-90 as a defining fixed point [1]. The major impetus for its development in the early 1970s by Sostmann at YSI, Sostmann and Borovicka at CSMU, Lau and Schlott at ASMW, Oleinik at the Mendeleev, and Mangum and Thornton at the NBS, was the perceived need for a thermometric point in the biological- medical- ecological range to be used for the calibration of thermistor sensors and quartz sensors. Indeed, its first commercial use was in the calibration of thermistor sensors used in spectrophotometer cuvettes for enzyme analysis. As things proceeded, and as the idea occurred in the development of the text of ITS-90 with its numerous stipulated ranges, the melting point of gallium was recognized as having great importance.

The gallium point (29.7646 C) is the only pure-metal fixed point between the triple point of water (0.01 C) and the freezing point of indium (156.5985 C), with the exception of rubidium, a difficult and hazardous material. Confidence in and reproducibility of the gallium melt point is 0.00015 C.

The gallium point occupies an important position on the Scale relative to normal body temperature, normal environmental temperature, standard temperatures for measurement and reaction laboratories (e.g., the prescribed temperature for quantifying enzyme reactions, once 30 C, is now specified as the gallium melt temperature).

The gallium melt temperature is used in the ITS-90 to qualify individual standard platinum resistance thermometers (SPRTs) as suitable for Scale interpolation devices. An SPRT must exhibit the relationship:

W_{ga}/W_{wtp} greater than or equal to 1.118 07 Eq. 1 in order to be considered as an acceptable instrument of the ITS-90.

The gallium melt point is a required calibration point in four ranges of the ITS-90:

0 C to 29.7646 C (requires also the triple point of water)

0 C to 156.5985 C (requires also the triple point of water and the freezing point of indium)

-38.8344 C to +29.7646 C (requires also the triple points of mercury and water)

Other fixed points between 0 C and 156 C include the triple points of ethylene carbonate (36.315 C, confidence 0.002 C), succinonitrile (58.064 C, confidence 0.0015 C, and benzoic acid (122.330 C, confidence 0.005 C) and the boiling point of water. It is generally recognized that fixed points involving big organic molecules are not as satisfactory as pure metals, because they are difficult to purify adequately, and their heat capacity and heat transfer characteristics are relatively poor. Also, the continuing availability of succinonitrile triple point cells is doubtful. The boiling point of water, as a fixed point, includes a difficult pressure measurement. These difficulties reinforce the importance of the gallium melt point as a thermometric reference.

1. Scope

1.1 This guide describes the nature of a representative commercial cell for realizing the melting point of gallium, and a method for realizing the liquid-solid equilibrium, in a generalized situation (a controlled fluid bath), and in an apparatus intended for this use, preparatory to the cell's use in calibrating thermometers. Precautions are given for solidifying the gallium prior to the next melt realization.

1.2 This guide presents a procedure for placing the gallium melting point cell into service, and using it as a thermometer calibration standard.

1.3 The reference temperature obtained is that of a fundamental state of pure gallium, the equilibrium between the solid and the liquid state at 1 standard atmosphere of external pressure. The gallium cell is not subject to calibration.

1.4 The cell may be qualified as representing the solid-liquid phase equilibrium of pure gallium at 1 standard atmosphere by comparison with a bank of similar cells of known history, and is usually so qualified by its manufacturer. A certificate of verification is usually available from the manufacturer.

2. Apparatus

2.1 The essential features of a gallium melt-point cell are shown in Fig. 1. A Teflon flask is nearly filled with gallium having impurities less than 1 ppm. A coaxial re-entrant well is provided to receive the device that is to be exposed to the reference temperature. A cylindrical shell of aluminum is pressed onto the outside diameter of the Teflon flask to (a) stabilize the diameter of the Teflon under conditions of internal pressure (b) provide a temperature equilibration path longitudinally along the cell. The aluminum shell is typically covered with plastic tubing, shrunk into place, to prevent electrical conduction between the shell and any metallic parts of other apparatus under moist conditions.

Note: Details of the construction of the cell are dictated by the fact that gallium, like water, expands as it freezes; the solid is lower in density and occupies more space than the same mass of liquid. This requires a cell whose walls are somewhat flexible.

In addition, the solidus expansion of gallium requires that it be used on the melt equilibrium, the only two-phase metal fixed point which is not used on the freezing equilibrium. When the metal solidifies it becomes and remains under some pressure, which is relieved as it melts. If used on the freeze equilibrium the increase in pressure due to solidus expansion would distort the equilibrium temperature.

2.2 In use, a portion of the solid gallium is melted into a layer of liquid surrounding the thermometer well. For that time during which the gallium in the cell exists in both the liquid and the solid phases, the temperature is invariant and may be used as a calibration reference for thermometers.

2.3 The temperature of the melting point equilibrium of pure gallium depends upon the ambient pressure of the surrounding environment, and varies with atmospheric pressure expressed upon the surface of the gallium column as follows:

$$t \text{ C} = 29.7646 \pm (-0.002 \text{ C per std. atmos.}) \text{ Eq. 2}$$

(The negative sign of the coefficient is a result of the solidus expansion (liquidus contraction).

2.4 The gallium in the cell is melted by allowing its temperature to rise above 29.7646 C. The rate of rise will not affect the temperature at which the gallium melts, but will affect the duration of the melt plateau. To prolong the plateau for a useful length of time the cell may be immersed in a closely-controlled liquid bath, or use in an essentially automated apparatus, Isotech Model 17402A Gallium Temperature Standard. In this apparatus the cell may be brought to its equilibrium condition automatically and maintained at the equilibrium temperature for 8 to 12 hours under normal ambient temperature conditions.

2.5 When the gallium has passed through its melt equilibrium and the entire mass of gallium is liquid, it is necessary to return it to the solid state before using it again. This requires that the cell be exposed to a temperature of about 5 C or less for a period of time. During the solidification process, the gallium will expand. Experience has shown that, if the gallium is allowed to freeze first at the top surface and the freeze progresses downward, the closed bottom of the Teflon flask will be distorted downward and in extreme cases has been known to cause hairline fractures of the flask bottom. Caution should be taken to freeze the gallium column upward so that the bottom freezes first and the surface freezes last. A method for assuring this in the generalized case is given in 3.2.1.

(The Isotech Model 17402A Gallium Temperature Standard is so constructed that the cell, left in the throat of the apparatus, will freeze in the correct direction, even if the apparatus has been disconnected from any source of power. Earlier YSI apparatus labelled 17402 (not followed by A) does not include this safety precaution.)

2.6 The true gallium melt point temperature occurs at the upper surface of the gallium in the cell. For ultimate accuracy a correction must be made for the pressure effect of the hydrostatic head of gallium above the thermodynamic vertical center of the temperature sensor which is in the thermometer well. This correction is -1.2 mK per meter of liquid head; with a typical cell and thermometer, this may amount to -0.0003 C and in some cases may be ignored.

The surface of the gallium in the Isotech Model 17401 Gallium Cell is 11.5cm below the top of the handle, as shown in Fig. 1. The thermal vertical center of the sensor is then (L - 11.5)cm below the surface of the gallium, and the temperature at this point is

$$C = 29.7646 + (L - 11.5 \text{ cm})(-0.012 \text{ mk} \cdot \text{cm}^{-1}) \text{ Eq. 3}$$

3. Realizing the melting point of gallium.

3.1 Determine that the gallium cell meets the requirements of 1.4.

3.2 Empty the thermometer well of any objects or fluids.

3.3 When the gallium cell is first put into service, it is necessary to assure that (a) the column of gallium is in the solid phase (b) it has been frozen with the cell axis vertical and the thermometer opening at the top. This assurance can be obtained by putting the cell through one complete melt-freeze cycle, as follows:

3.3.1, in a bath: Set the temperature of the bath at 35 C. Place the cell in the bath with the cylindrical axis vertical and the thermometer opening at the top. Place a thermometer in the thermometer well. If the thermometer indication rises steadily and smoothly to approximately 35 C, the cell is in the liquid phase. If the thermometer indication rises to approximately 29.8 C, pauses for a time, and then continues its rise to approximately 35 C, the gallium was in the solid phase and is now in the liquid phase. Maintain the cell at 35 C for about 4 hours to permit all the gallium to liquify. Remove the cell from the bath and, holding the cell upright in some convenient manner, place the lower 2 to 3 inches in a container of water and water ice to assure that solidification proceeds upward.

3.3.2, in the Isotech Model 17402A Gallium Temperature Standard: Place the cell in the well of the Standard. *Note: Do not use any fluid transfer medium (e.g. water) between the OD of the cell and the ID of the well.* Supply the unit with mains power as indicated on the nameplate. Switch the unit on. The WARMUP indicator light will light and remain lit for 25 to 60 minutes, depending upon the initial temperature of the cell. Leave the control unit in the MELT mode for about 24 hours after the WARMUP light goes off, to assure that all the gallium in the cell is in the liquid phase; then switch the MODE switch to FREEZE. The FREEZE mode indicator and the FREEZING indicator should be lit. The FREEZING indicator will go off when all the gallium is in the solid phase; about 3 hours. If the Standard is turned off or disconnected from mains power during this period, the freeze will take substantially longer (e.g., 15 to 20 hours), although the freeze will proceed in the correct direction.

When either 3.3.1 or 3.3.2 has been completed, the cell is ready for use as a defining fixed point for thermometer calibration, per ITS-90.

3.4 The following steps are used to realize the melting point of gallium for the calibration of thermometers.

3.4.1, in a bath: Set the bath temperature control to 31 - 32 C. Place the cell, whose gallium contents are known to be in the solid phase, in the bath with the axis vertical and the thermometer well upward, so that the handle extends above the bath fluid approximately 2.5 cm (1 inch). Do not allow bath fluid to enter the thermometer well. Place a thermometer in the thermometer well and monitor the temperature rise. At some time the temperature will cease rising as the melt equilibrium plateau is reached. At this time, reset the bath control to 30.2 - 30.4 . The bath control setting will not affect the temperature of the melt plateau but will affect its duration. When the monitoring thermometer indicates that the temperature has stabilized (when there is no further temperature rise for 15 to 30 minutes) place 17 cc of water at about 55 C in the thermometer well around the monitoring thermometer, to melt a film of gallium on the OD of the thermometer well. The water may remain in the cell during thermometer calibration as a thermal transfer medium. The cell is ready to use in calibrating thermometers.

3.4.2, in the Isotech Model 17402A Gallium Temperature Standard: If there is any condensed moisture on the outside surface of the gallium cell, wipe it off with a dry cloth or paper towel. If there is any condensed moisture in the well of the Standard, dry it with a wad of cloth or paper.

Place the cell in the well of the Standard. Switch the mode switch to MELT to initiate a melt sequence. The WARMUP indicator will light and remain lit for 30 to 35 minutes. Please note that the ambient temperature must be limited to not higher than 28 C.

When the WARMUP light goes out, the gallium in the cell is in equilibrium between the solid and liquid phases; it is on the "melt plateau". However the inside of the thermometer well may not be yet in equilibrium with the gallium, and it is advisable to wait for 15 minutes or so after the WARMUP light goes out before calibrating a thermometer. Then place 17cc of water at about 55 C in the thermometer well around the monitoring thermometer, to melt a film of gallium on the OD of the thermometer well. The water may remain in the cell during thermometer calibration as a thermal transfer medium. The cell is then ready to use in calibrating thermometers.

The Model 17402A Standard is designed to maintain the cell on the melt plateau for more than 8 hours at ambient temperatures between 15 C and 28 C, with most thermometers. Thermometers having high heat transfer rates to ambient, plateau duration times may be longer, or in the extreme case melting may not occur. For purposes of estimating stem errors, the terminal conductance from the thermometer well to the surrounding gallium may be taken as 0.5W/ C per 2.5 cm of depth. A typical plateau with a quartz-sheathed Standard Platinum Resistance Thermometer is about 12 hours long.

3.5 The calibration operation is the same with the gallium cell used in a bath or in the Isotech Model 17402A Gallium Temperature Standard, and is a matter for appropriate good practice. It is advisable to monitor the thermometer being calibrated to assure (a) that it has reached equilibrium with the gallium plateau temperature (b) that the temperature is not rising, indicating that the liquid-solid equilibrium has been lost. As a general observation, the time required to reach equilibrium is longer than the time constant in a water triple point cell, a mercury triple point cell or a metal freezing-point cell because of the poor heat transfer characteristics of the Teflon thermometer well.

If a number of thermometers are to be calibrated, the quantity of heat transferred from the cell can be reduced, and the equilibrium plateau duration extended, by bringing each thermometer to a few degrees below the plateau temperature (for example by tempering it in a water bath before transferring it to the gallium cell). This will have the effect of retarding the melt and adding to its duration. For a long series of thermometers, monitoring the later thermometers to assure that the temperature is not rising is a necessary precaution.

3.6 Concluding the melt cycle: when all the thermometers have been calibrated or when the bath equilibrium is lost and the cell temperature had risen from the plateau, indicating that the gallium is now liquid, it is convenient to place the cell in condition for re-use.

3.6.1, for a cell used in a bath, remove the cell from the bath and, holding the cell upright in some convenient manner, place the lower 2 or 3 inches in a container of water and ice. Monitor the temperature with a thermometer in the well until it is seen to be about 5 C. The cell may then be left in this position, or may be placed in a refrigerator for more rapid freezing.

3.6.2, for a cell used in Model 17402A Standard, switch the MODE switch to FREEZE. The cell should be left in the well of the STANDARD at least until the FREEZE light goes out, to assure that the gallium in the cell is frozen from bottom to top. (The Standard is designed to provide a proper freezing environment and direction without power, but recycle time for passive freezing is about 15 hours compared to 3 hours for freezing under power).

3.7 Material Safety Information

Gallium is a silvery-white elemental metal with the longest molten range of any metal; from the melting point at 29.7646 C to the boiling point at 2347 C. (The vapor pressure is 1 atmosphere at the boiling point). The metal is enclosed within the cell and is normally not free in the Laboratory.

The material is not flammable and poses no explosion hazard.

Dermal exposure to the metal has been reported to cause dermatitis. Upon contact, the skin area should be washed thoroughly with soap and water. In the unlikely event of inhalation or ingestion, seek medical attention.

Gallium reacts with alkalis to produce hydrogen, and with halogens to cause embrittlement of aluminum. Because of its effect on aluminum, international air cargo rules forbid its shipment by air except when packaged (e.g. in dry ice) to assure that the metal is in the solid state during transportation.

If gallium is spilled it may be collected in a container (using rubber gloves and eye protection) and returned to the supplier or disposed of according to local codes.

FOOTNOTE:

[1] H. Preston-Thomas, The International Temperature Scale of 1990, (ITS-90), Metrologia 27, 3-10 (1990)

About the Author

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