Model 5903
Gallium Melting Point Cell
User Manual

HART
SCIENTIFIC

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CAUTION

READ SECTION ENTITLED

CARE OF YOUR GALLIUM MELTING POINT CELL

before removing the gallium melting point cell from the case.
Incorrect handling can damage the cell and void the warranty.

CAUTION

THE RE-ENTRANT WELL IS EASILY DAMAGED.

BE CAREFUL WHEN INSERTING THE SPRT INTO THE CELL

A small piece of soft material in the bottom of the re-entrant well.
Incorrect handling can damage the cell and void the warranty.

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1 Introduction

The melting point of gallium (MPGa) at 29.7646 °C is one of the defining fixed points of the International Temperature Scale of 1990 (the ITS-90). The MPGa is the phase equilibrium between the liquid phase and solid phase of pure gallium at a pressure of one standard atmospheric pressure, i.e., 101,325 Pa. The temperature of the MPGa is defined to be 29.7646 °C by the ITS-90 making it an intrinsic temperature standard. The MPGa is highly reproducible. You can get almost the same temperature wherever and whenever you realize the MPGa. The differences among the different realizations might be well within a few tenths of millikelvin if you carefully follow the instructions given in *Supplementary Information for the ITS-90*, Comite Consultatif de Thermometrie (CCT), Bureau International des Poids et Mesures (BIPM) 1990. For your convenience Hart has developed a sealed cell and new technique for the MPGa, which has made it much easier to realize the MPGa. We believe the Hart sealed cell will assist you immensely in realizing the MPGa in your laboratory.

The MPGa is an important fixed point for the calibration of a standard platinum resistance thermometer (SPRT). The ITS-90 specifies two subranges, i.e. from 0 °C to 29.7646 °C and from - 38.8344 °C to 29.7646 °C, in which SPRTs must be calibrated at the MPGa. It is very convenient to check the stability of a temperature probe used mainly near room temperature at the MPGa. It will find widespread application in biologic, environmental, oceanographic, geological and energy research.

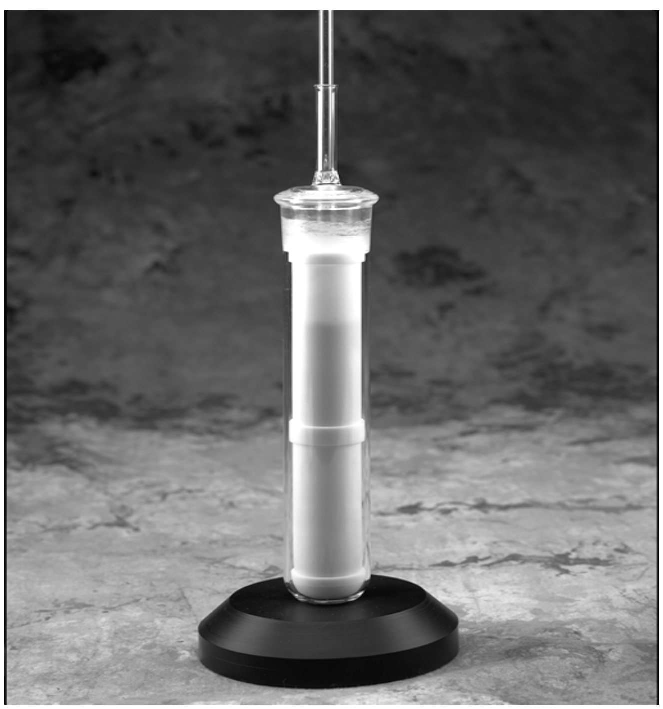

Figure 1: Model 5903 Gallium Fixed Point Cell

2 Specifications

Reproducibility:	0.06 mK -- 0.1 mK (0.00006 °C -- 0.0001 °C)
Expanded Uncertainty (k:=2)**:**	0.2 mK -- 0.4 mK (0.0002 °C -- 0.0004 °C)
The Purity of gallium:	99.99999%
Outer Diameter of the Cell:	40 mm ± 0.5 mm
Overall Height of the Cell:	240 mm
Inner Dia. of the re-entrant Well:	8.0 mm ± 0.5 mm
The Total Immersion Depth: (From the bottom of re-entrant well to the upper surface of gallium)	165 mm

Other sizes of cells are available according to the customer's special requirement.

3 Description

The Hart Scientific gallium melting point cell (Figure 2) consists of a Pyrex® (or quartz glass) outer shell, a Pyrex® cap with a re-entrant well, a Teflon® cell body containing the high-purity gallium and a Teflon® lid. Gallium expands on freezing by 3.1 % requiring the cell to have flexible walls. Teflon® is a suitable material from this point of view, but Teflon® is gas-permeable over time. It has been found that over a four-year period completely sealed Teflon® cells will drift about 0.5 mK under normal use. However, the new technique developed at Hart Scientific has successfully extended the maintenance time. The Model 5903 gallium melting point cells maintain their uncertainty for at least 5 years, possibly longer.

All parts and materials used to construct the cell were carefully cleaned to avoid any contamination to the high-purity gallium. The cell was connected to a high-vacuum system after assembling. It was then evacuated to a pressure lower than 2×10^{-5} Pa for more than a hundred hours. During this period, the cell was repeatedly purged with pure argon. Finally, the cell was sealed by fire at a known pressure during a melting curve. The pressure value of argon in the cell at the MPGa will be used to make the correction for the pressure (see **Section 7 The correction for the pressure difference**).

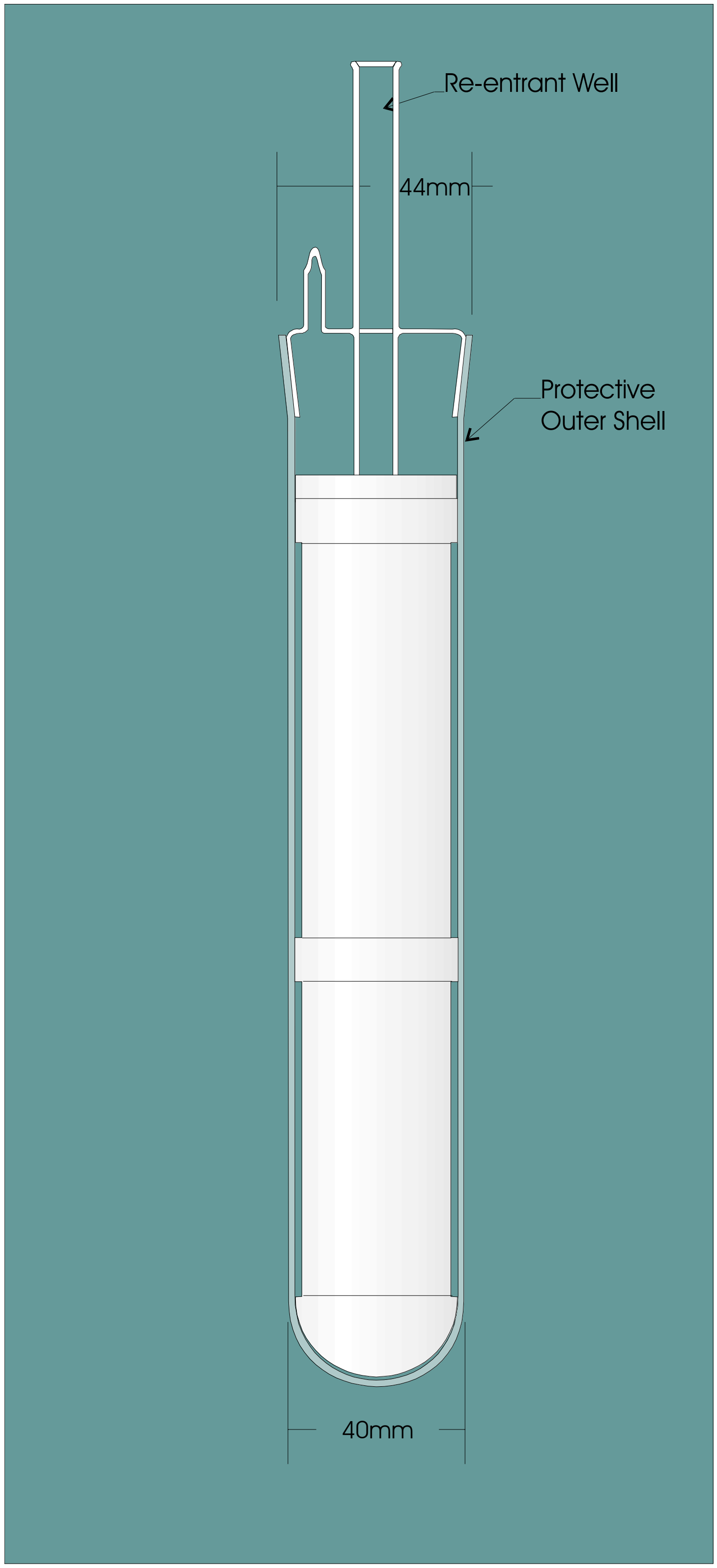

Figure 2: The Gallium Melting Point Cell

4 Care of Your Gallium Melting Point Cell

The Model 5903 gallium melting point cell is an extremely delicate device. Great care must be taken in handling, using and transporting the cell. The Pyrex® outer shell and the re-entrant well are prone to breakage. When inserting a probe into the re-entrant well, careful operation is required, especially with a metal-sheathed probe. Dropping a probe onto the bottom of the re-entrant well might break the cell. Placing a small piece of soft material in the bottom of the re-entrant well is suggested to cushion the probe.

If the gallium in the cell is in the liquid state and the cell is tilted, the gallium might flow out of the Teflon® cell body and remain in the gap between the Pyrex® outer shell and the Teflon® cell body. It is impossible to return the gallium to the Teflon® cell body. Thereafter repeated freezing and melting might break the Pyrex® outer shell. It is suggested to keep the gallium in the cell in solid state whenever possible. Store the cell in the vertical position and in a safe place. The surrounding temperature should be at least 4°C below the melting point (e.g. 25 °C or lower). Special care must be taken during transportation of the cell: keep the gallium in the solid state, the cell in vertical position and the surrounding temperature lower than 25 °C. If you carefully follow the instructions in this manual, the Model 5903 Gallium melting point cell will provide years of accurate use.

Incorrect handling which leads to the breakage of the outer shell or the re-entrant well or the flow of the Gallium from the Teflon® cell body will void the warranty.

5 Freezing the Gallium

5.1 Slow Freeze Method

In order to freeze all the gallium in the cell, immerse the cell in an ice bath (or a bath, with a temperature lower than the ice point). First, immerse only one-third of the cell in the bath, thirty minutes later immerse two thirds of the cell in the bath and another thirty minutes later immerse the whole cell in the bath. Because of the large supercool of gallium, even though the temperature of the gallium in the cell declines to a temperature near 0 °C, all gallium might still remain in the liquid state for a period of time. Therefore, it is helpful to monitor the temperature in the cell by using a SPRT. When the cell is placed in an ice bath, the temperature indicated by a SPRT in the cell will decrease fast at first and then decrease slowly, at last the temperature will stop decreasing. After a period of time the temperature will rise, a signal that the gallium starts freezing. Finally, the temperature decreases again and all of the gallium is frozen. Once frozen, the cell may be transferred to a maintenance bath such as the Hart Model 7011. (See Figure 4)

5.2 Fast Freeze Method -- Based on NIST Technical Note 1265

Start with the fixed-point cell at room temperature. Use liquid nitrogen to supercool two or three solid copper rods for insertion in the re-entrant well. The copper rods should be only slightly smaller than the inside diameter of the re-entrant well. For example, the Hart Model 5903 gallium cell has a re-entrant well with an inside diameter of 8.0 mm ± 0.5 mm. The solid copper rods should have a diameter of approximately 7.0 mm. Insert the two or three supercooled copper rods into the re-entrant well successively to induce nucleation. As soon as the rods have been used to induce nucleation, place the cell in an ice bath for at least one hour or longer. Monitor the freeze with a SPRT. Once the freeze has been achieved, place the cell in a maintenance bath.

A stable and long (a few days) melting plateau, during which ten or more thermometers can be calibrated, is easy to obtain if you follow the procedures described below.
Put the cell into the maintenance bath at a temperature of 1 °C higher than the melting point. Hart manufactures a Model 7011 with a special cell support and SPRT preheat holder for the purpose of maintaining the gallium cell. (See Figure 4) To provide adequate heat transfer to the thermometer, distilled water or light oil should be placed in the well to bring its surface to approximately the same level as that of the gallium in the cell when the thermometer is in place in the well. Put a small electric heater with a power of 10 W in the re-entrant well for twenty minutes in order to create a liquid-solid interface adjacent to the re-entrant well. Maintain the bath at a temperature of 0.15 °C higher than the melting point and take the small heater out of the well.

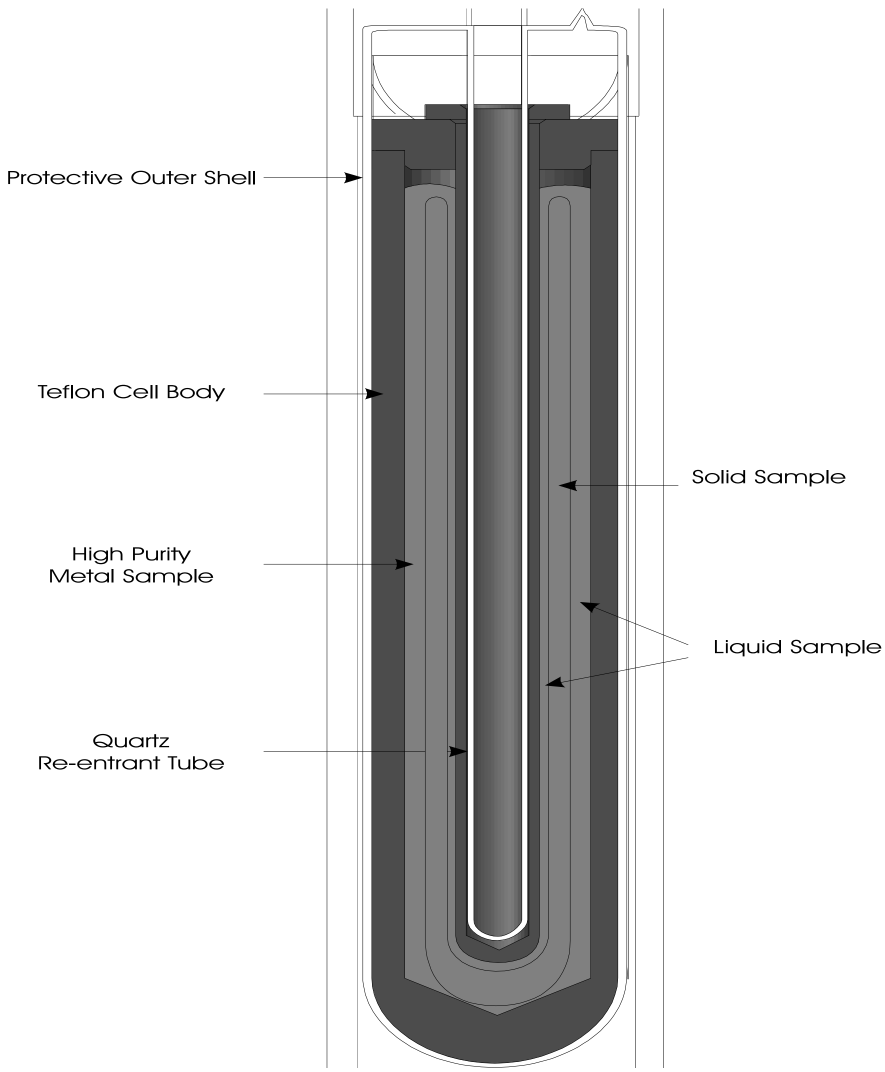

Figure 3: Idealized liquid/solid equilibrium state inside a gallium cell at the start of melt.

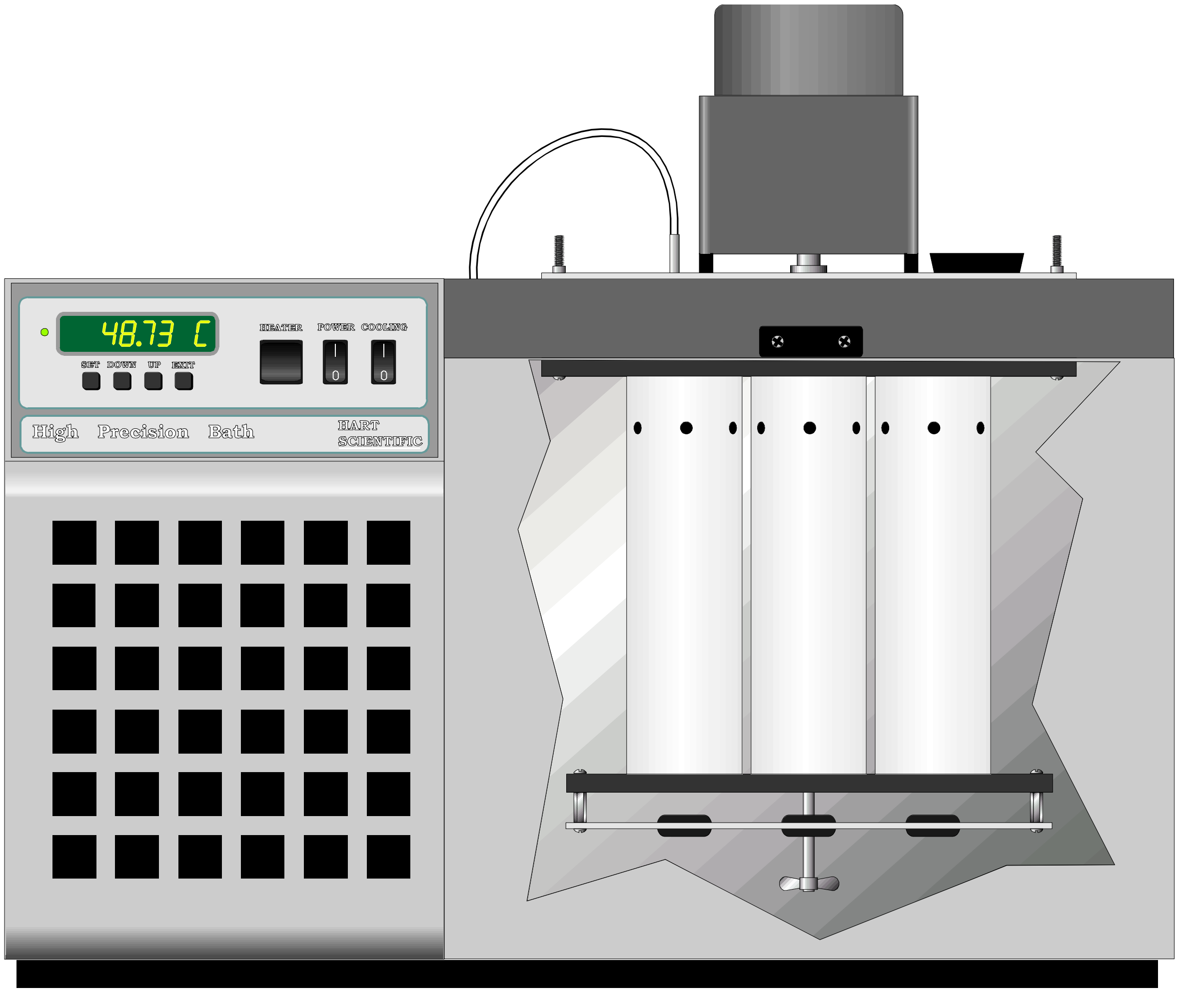

Figure 4: Hart Gallium Maintenance Bath Model 7011 with Gallium Cell Insert.

Preheat the monitoring SPRT and the SPRTs to be calibrated in the maintenance bath for at least ten minutes. Insert the preheated monitoring SPRT into the re-entrant well. When the thermal equilibrium between the SPRT and gallium is reached (approximately 20 minutes), start the measurements. Replace the monitoring SPRT with a preheated SPRT to be calibrated. Start taking measurements after thermal equilibrium (approximately 20 minutes). A typical melting curve is shown in Figure 5. The plateau can last for more than seven days. Therefore, you can calibrate as many thermometers as you want in a single melting plateau. If you have any concerns about the melting plateau, take a measurement with the monitoring SPRT. This measurement should generally agree with the initial reading within the limits of your monitoring equipment.

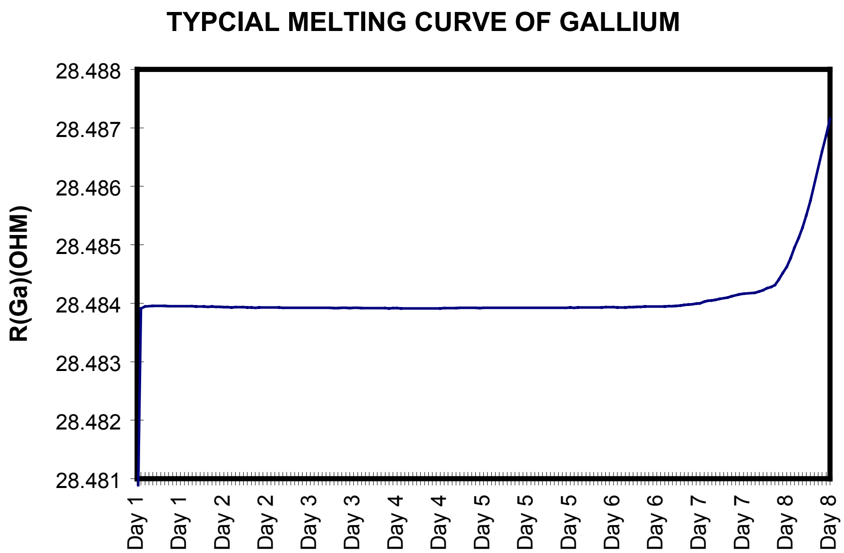

Figure 5: A Typical Melting Curve of Gallium.

7 The Correction for the pressure difference

The melting point of gallium, as mentioned earlier, is defined as the phase equilibrium between the liquid phase and solid phase of pure gallium at a pressure of 101,325 Pa (P_0). The actual pressure, P, in a gallium cell may not be exactly the standard value. During the course of manufacture of a fixed-point cell, it will be easier for a glassblower to seal the cell if the pressure in the cell is a little lower than the room pressure. The actual pressure value in the cell just at the melting point was measured at Hart so that the correction for the difference of the pressure can be made later. Table 2 of the ITS-90 gives the data of dT/dP for all the defining fixed points. For the melting point of gallium dT/dP = -2.0 x 10^{-8} °C / Pa. Therefore, the actual equilibrium temperature t' can be calculated using the following equation:

Equation 1: Actual Equilibrium Temperature

$$t' = 29.7646°C - 2.0 \times 10^{-8}(P - P0)°C / Pa$$

Furthermore, during the measurement at the melting point, the sensor of a SPRT is usually placed at an average height which is 0.15 meters lower than the surface of the gallium and where the pressure is higher than that at the surface due to the static head. The correction, calculated according to the data given in Table 2 of ITS-90, is - 0.00018 °C. Therefore, the average temperature of a sensor at an average height of 0.15 m lower than the surface of the gallium in the cell can be calculated using the following equation:

Equation 2: Average Temperature of Sensor at Average Height

$$t = 29.76442°C - 2.0 \times 10^{-8}(P - P_0)°C / Pa$$

In some cases people may want to know the exact resistance at the melting point of gallium. R(29.7646 °C) can be calculated by using the following equation:

Equation 3: Exact Resistance of a SPRT at R(29.7646°C)

$$R(29.7646°C) = R' + 0.0039524 R_{tp}[0.00018 + 2.0 \times 10^{-8}(P - P_0) / Pa]$$

where R' is the measured resistance.

[Example] The pressure of argon, P, at the melting point in the gallium point cell is 91,325 Pa as given in the Report of Test. The measured resistance R'= 28.5140532 Ω and R_{tp} = 25.5013425 Ω. Substituting these values into Equation (3) we have:

$$R(29.7646°C) = 28.5140532\Omega + 0.0039524 \times 25.5013425 \times [0.00018 + 2 \times 10^{-8}(91{,}325 - 101{,}325)]\Omega$$

$$R(29.7646°C) = 28.5140532\Omega - 2.0 \times 10^{-6}\Omega$$

Thus: $R(29.7646°C) = 28.5140512\Omega$