

Determination of the Triple-Point Temperature of Gallium

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Abstract

We have determined the triple-point temperature of high-purity gallium to be 29.77406°C using three standard platinum resistance thermometers (SPRTs) calibrated on the IPTS-68 and using samples of gallium from three commercial sources. All data obtained on the highest purity sample have a standard deviation of $\pm 0.00011^\circ\text{C}$. The overall systematic uncertainty is estimated to be $^{+0.6}_{-1.1} \text{ m}^\circ\text{C}$. The day-to-day irreproducibility of a single melt of each gallium cell was found to be $< \pm 15 \mu^\circ\text{C}$, while over a period of 7 months the irreproducibility among melts of each gallium cell was $\leq \pm 0.00011^\circ\text{C}$. These limits on the reproducibility appear to be largely instrumental since every time an SPRT was left in a gallium cell for several days there was no change in the indicated temperature of the triple-point to within the instrumental resolution of $\pm 1.5 \mu^\circ\text{C}$. The pressure dependence was measured and determined to be $dT/dP = -2.011 \pm 0.001 \text{ m}^\circ\text{C/atm}$.

1. Introduction

Apart from the boiling-point of water at 100°C and the melting-point of phenoxybenzene at 26.86°C , both of which are extremely difficult to realize at the milli-degree level, there are no internationally-accepted fixed points on the International Practical Temperature Scale of 1968 (IPTS-68) [1, 2] between the triple-point of water at 0.01°C and the melting-point of benzoic acid at 122.37°C . Phenoxybenzene is an organic compound rather than a metallic element and, as such, is relatively difficult to purify and has a low thermal conductivity. Consequently, its usefulness as a temperature fixed point is severely limited. Practically speaking, then, there are no accurately-realizable and convenient

Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose

temperature fixed points in the very important range between 0.01°C and 122°C , a range of crucial importance to the biomedical, oceanographic and industrial communities.

We report here an investigation of the suitability of the triple-point and melting-point of pure gallium as secondary temperature fixed points or, in the case of the triple-point, as a defining temperature fixed point of the International Practical Temperature Scale. Because of its widespread use by the semiconductor industry, gallium is now commercially available in very pure form and is relatively inexpensive, making it readily available to anyone to use as a fixed point.

The abundance of gallium in the earth's crust is about 5 to 15 parts per million but, unlike the more common metals such as lead and tin, it is widely dispersed. It was first isolated [3] in 1875 and the first determination of its melting temperature [4] was made by Lecoq de Boisbaudran in 1876. Several other melting-point temperature determinations were subsequently made [5, 6] but the first really accurate determination was made in 1934 by Roeser and Hoffman [7]. The samples used by Roeser and Hoffman [7] were purified by Hoffman [8], and according to tests made by him, the gallium was 99.999% pure. The temperature obtained by Roeser and Hoffman for the melting-point was $29.780 \pm 0.005^\circ\text{C}$ on the ITS-27. In terms of the IPTS-68 this becomes $29.771 \pm 0.005^\circ\text{C}$.

Since the metal has become commercially available in large quantities at high purity, it has been used in many studies of melting behaviour [9-14]. Also there have been several recent reports of determinations of melting-point or freezing-point temperatures [13, 15-18], but none of those adequately documented all of the variables affecting the melting temperature, i.e., purity, pressure, methodology, etc.

On the basis of our own work and in consideration of earlier work, it was thought that the liquid-solid equilibrium of gallium should constitute an excellent fixed point. The study reported here was undertaken (a) to determine both the day-to-day and the sample-to-

Table 1. Specifications of gallium samples

Source	Lot number	Nominal purity	Comments
Alusuisse	F17/220	99.9999+% (microwave grade)	Recrystallized six times from semiconductor-grade material which had been analysed by mass spectroscopy as 6Ns.
Alcoa	3809B	99.9999+%	Recrystallization. Details unavailable
Eagle-Picher	J-57-76	99.99999%	Recrystallized until no impurities are detected by emission spectroscopy or until the level of detected impurities is below 0.1 ppm. Manufacturer certified that no impurities were detected in this lot

sample reproducibilities, and (b) to measure the equilibrium temperature to the highest possible accuracy. Samples from three commercial sources were investigated. The temperatures were measured with long-stem standard platinum resistance thermometers (SPRTs) [19], three such thermometers being used in the investigation.

In Section II, we give a description of the samples, the apparatus and the measurement procedures. In Section III, we discuss the results and their analysis. A summary is given in Section IV.

II. Experimental

A. Gallium Samples

Gallium is available from a number of commercial sources at a nominal purity of 99.9999% (6Ns) or better. Such purities are difficult, if not impossible, to verify. The limits of detection of most of the heavy metals expected to affect the melting-point temperature of gallium are about 0.1 ppm for emission spectroscopy and about 0.01 to 0.05 ppm for mass spectroscopy; neutron activation analysis is not feasible because of the large neutron absorption cross-section of gallium. Thus, we can only be reasonably certain that if any metals were present in our samples, their concentrations were less than 0.1 ppm. The sources, lot numbers, and nominal purity of the three samples are listed in Table 1 along with comments regarding methods of purification, etc.

B. Gallium and Water Triple-Point Cells

i. Gallium Triple-Point Cells: A drawing of the gallium triple-point cells which were used in this study is shown in Figure 1. The all-plastic construction of these cells was meant to circumvent potential problems associated with the 3.1% expansion of the metal upon freezing, as well as to avoid direct contact with free metal. The cell was made to be used in a constant-temperature oil bath. The outer case of the cells was made of nylon whereas the inner container, the container actually holding the gallium, was Teflon. Teflon was selected because it is relatively soft. The design of the inner container, incorporating several ridges for mechanical strength and a loose fit, leaves an excess volume inside the nylon

outer case to relieve stresses induced by the volume increase incurred upon the freezing of the gallium sample. The re-entrant thermometer well was constructed of nylon. This choice was made because we had found in some preliminary studies that machined

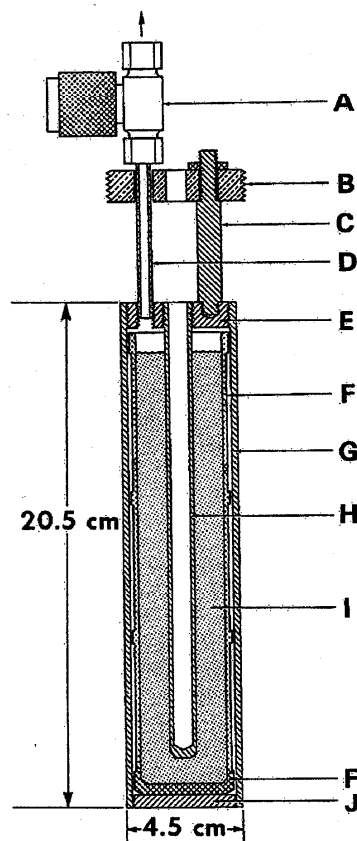


Fig. 1. Cross-section of gallium triple-point cell. A — Valve (Zytel), B — bath lid (plexiglass), C — support (nylon), D — pumping tube (polyethylene), E — cap (nylon), F — container (TFE), G — case (nylon), H — re-entrant well (nylon), I — gallium, J — base (nylon)

nylon provided a surface that readily nucleated crystallization of the gallium, which is notorious for its ability to supercool.

After the components of the triple-point cells were machined, they were cleaned in the following manner. The Teflon components were soaked overnight in aqua regia, thoroughly rinsed in distilled water, and air dried. The nylon parts were washed in a gentle detergent solution, rinsed thoroughly with distilled water, and air dried. Then they were partially assembled, with epoxy being liberally applied to the threaded sections. The cap assembly was not joined to the base assembly until after the cells had been filled with gallium.

The gallium samples were received in polyethylene squeeze bottles sealed under argon. All handling of the gallium, including the filling and final assembly of the cells, was conducted in a glove box under a dry argon atmosphere. The gallium was liquefied by raising the temperature inside the glove box above 30°C. Each cell was filled with approximately 900 grams of gallium poured directly from the shipping bottles into the Teflon container. The cap assembly, which included the thermometer well, the pumping tube and valve, and the support assembly, was joined to the base by a threaded section liberally doped with epoxy. The epoxy was allowed to set and the gallium was solidified before the valve of each cell was sealed and the cell removed from the glove box.

In all cases, the gallium was solidified by lowering the glove box temperature below 29°C and inserting a liquid-nitrogen-chilled copper rod into the nylon well.

The containers were sufficiently translucent that it was possible to determine when the gallium was completely solidified by observing its top surface through the cell wall.

ii. Water Triple-Point Cells: Four water triple-point cells were used in this investigation. All were obtained from Jarrett, Inc. (USA). One of them was a type B and the other three were type A. The types of cells, their serial numbers, the dates they were used, and the SPRTs with which they were used are given in Table 2.

C. Apparatus

i. Constant Temperature Bath: The constant temperature bath used in this investigation was a Rosemount Engineering Company Variable Temperature Oil Bath, Model 913A, with a capacity of 10 litres. The fluid was clear mineral oil for which the viscosity was 17 centistokes¹ at 40°C and 3.6 centistokes at 100°C. A lower viscosity fluid would have been preferable from the point of view of temperature stability, but this oil was known to have very little, if any, effect on the gallium cell components. Temperature control was not a problem. Cooling was obtained with pressurized air which had been chilled by passage through a copper coil immersed in an ice bath before it was passed through the oil bath cooling coils. The heater was controlled by a Tronac Temperature Controller, Model No. PTC-40, which used a thermistor as the sensing element. Through the use of this system, we were able to maintain temperatures uniform and constant to ± 1 m°C, or better.

ii. Resistance Bridges: Two resistance-ratio bridges were used in making SPRT resistance measurements in this investigation. One employed ac and the other dc techniques. The ac bridge, designed by Cutkosky [20] and built by R.S. Kaeser at NBS, is a resistance-ratio bridge operating at 400 Hz and is stated to be in error by no more than $3 \mu\Omega$ when used with a 100 Ω standard resistor. It was used in making measurements of the temperature reproducibility of each of the gallium cells and for the comparison of the three samples, but not for determinations of the triple-point temperature. The alignment of the bridge was checked prior to the measurements reported here. Its resolution when used with a 100 Ω standard resistor and at measuring currents of 0.71, 1, and 1.4 mA was $\pm 0.15 \mu\Omega$. Since the measured current ratios were found to vary a few percent from the nominal factor of $\sqrt{2}$, we used current values of 0.71, 1 and 1.41 mA in obtaining the extrapolated zero-current value of resistance bridge ratio. The uncertainty resulting from this procedure was estimated to be $\pm 0.5 \mu\Omega$.

In making SPRT resistance measurements, it is desirable to duplicate calibration conditions as closely as possible. Since the SPRTs were calibrated using a dc Mueller bridge, the instrument used in making SPRT

Table 2. Water triple-point cells used in measurements, dates of measurements, and SPRTs involved

Date of measurement	Water triple-point cell	SPRT
12 February 1977	B-11-536	374, 375
13 February 1977	B-11-536	089, 374, 375
17, 18, 19 March 1977	B-11-536	089, 374, 375
16 May 1977	A-13-587	375
17 May 1977	A-13-587	089, 374, 375
18 May 1977	A-13-587	089, 374
19 May 1977	B-11-536	089, 374, 375
20 May 1977	B-11-536	089, 374, 375
23 May 1977	A-13-587	089, 374
23 May 1977	B-11-536	375
24 May 1977	B-11-536	089, 374, 375
16 August 1977	A-13-506	089, 374, 375
17 August 1977	A-13-506	089, 375
17 August 1977	B-11-536	089, 374
18, 19, 23, 24, 25, 26 August 1977	B-11-536	089, 374, 375
10, 31 August 1977	A-13-723	089, 374, 375
1, 2 September 1977		
12, 13, 15, 16 September 1977	A-13-723	375

¹ 1 stokes = 10^{-4} m²/s (unit of kinematic viscosity)

resistance measurements for the determination of the triple-point temperature was the Guideline Current Comparator, Model 9975. This is a dc instrument with automatic current reversal, the period of which was adjustable to either 4, 8, or 16 seconds. Unless otherwise stated, all measurements were made with a 4 second reversal period. The inaccuracy of the current comparator was stated by the manufacturer to be ≤ 2 parts in 10^7 plus 1 digit in the last dial (8th). Since we did not have a temperature-controlled $10\ \Omega$ standard resistor to use with the bridge, we used a nominal $100\ \Omega$ standard resistor which was kept in a temperature-controlled environment. This meant that the last (8th) dial represented $10\ \mu\Omega$ steps. Using a 3 second time constant and averaging the strip-chart recorder tracing of the bridge output for 5 to 10 minutes permitted a resolution, at measuring currents of 1 and $\sqrt{2}$ mA, of $\pm 1.5\ \mu\Omega$ ($\pm 15\ \mu^\circ\text{C}$).

iii. *Thermometers:* Three SPRTs purchased from Leeds and Northrup were used in this investigation. One of them had a platinum element that consisted of a coiled helix mounted on a mica cross (L&N 8163 Series), while the other two had elements that consisted of a single layer helix of bifilarly wound fine platinum wire on a mica cross (N&N 8167-25 Series). In Table 3, we have listed the serial numbers of the three thermometers used, the NBS identification number (I.D.#), the type of thermometer, and the dates they were calibrated.

The SPRTs were supplied by the manufacturer with standard external copper leads designed for dc measurements. The four leads from the helical element were platinum wires brought straight up the stem in a square array and through a hermetic seal at the head. Although the current leads and the potential leads were normally formed from the diagonal pairs, one SPRT was connected such that the current leads were adjacent, as were the potential leads. To correct this situation and in order to reduce coupling to stray electromagnetic fields and to reduce capacitive coupling between the leads, the SPRTs were modified for ac measurements by removing the external cables supplied by the manufacturer and installing BNC connectors mounted in bakelite caps such that one coaxial cable would serve as the current leads and the other would serve as the potential leads. Using this arrangement of leads, the SPRTs were insensitive to lead positions.

The SPRT of the 8163 Series was obtained in 1973, and the two SPRTs of the 8167-25 Series were

obtained in 1976. They were calibrated by the NBS Platinum Resistance Thermometer Calibration Laboratory at measuring currents of 1 and 2 mA, with extrapolations to zero current. The calibrations for zero current were then used in all calculations of temperature, thereby eliminating self-heating effects in all of the measurements.

iv. *Standard Resistors:* The standard resistor used with each of the above bridges was a nominal $100\ \Omega$ precision resistor, Model No. HA518 (which we have designated as H17) manufactured by Vishay. It was enclosed by and thermally shielded from a large copper enclosure whose temperature was regulated at $27.3 \pm 0.1^\circ\text{C}$ using a mercury thermostat. On the basis of measurements on similar enclosures, it is estimated that the temperature variation of the resistor was $\sim \pm 3\ \text{mK}$ over a period of a few days. Based on the manufacturer's specifications, the temperature coefficient of resistance is estimated to be about 0.1 to 0.3 ppm/ $^\circ\text{C}$ at the control temperature, which means that the resistance would vary by no more than $\pm 0.1\ \mu\Omega$. The resistor was calibrated at both 400 Hz and at dc by the Absolute Electrical Measurements Section of the NBS on 9 February 1977, and the results of that calibration are given in Table 4.

v. *Chart Recorder:* A Leeds and Northrup Speedomax XL, Model 602, strip-chart recorder with an adjustable zero balance was used with each bridge in making resistance-ratio measurements. The true zero was determined for the complete measurement system by setting the measuring current flowing through the SPRT to zero and, in the case of the Guideline Current Comparator, also setting the sensitivity to the minimum position. The same zero was obtained for other sensitivity settings of the current comparator but the noise was much smaller at the minimum sensitivity setting, making the zero easier to determine.

vi. *Vacuum System:* The vacuum system contained a mechanical rotary pump, a mercury manometer, an oil manometer, two alcohol-solid-carbon dioxide mixture cold traps, manometer bypasses, and some valves, as shown schematically in Figure 2. With this pumping system, we were able to obtain pressures of the order of a few tenths of a pascal. Although the vapour pressure of gallium is very low, even at elevated temperatures ($< 10\ \text{mPa}$ at $T \sim 1000^\circ\text{C}$), this was adequate since the pressure dependence of the melting-point is relatively small. The manometer system was used only during the measure-

Table 3. SPRTs used in the study

SPRT S/N	NBS I.D.#	SPRT type	Date calibrated
1808364	089	8163	January 1977
1846617	374	8167-25	January 1977
1846729	375	8167-25	January 1977

Table 4. Calibration data of standard resistor H17

Manufacturer	Resistor type	Date calibrated	dc resistance value	400 Hz resistance value
Vishay	HA518	9 February 1977	99.99346	99.993592

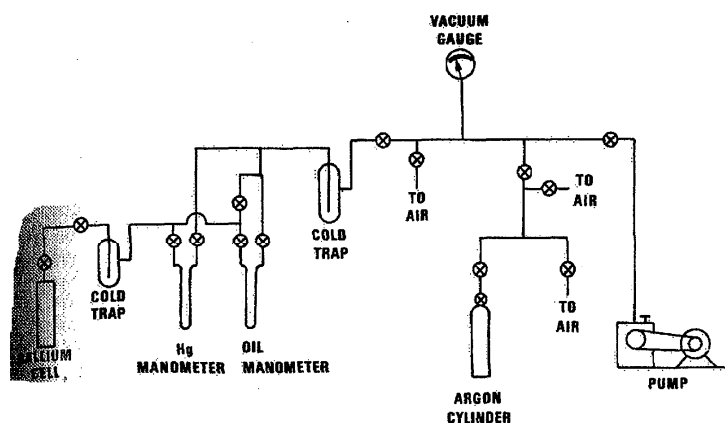


Fig. 2. Schematic of vacuum and gas-handling system

ments of the pressure dependence of the melting-point of gallium and during the filling of the cells with an atmosphere of argon at the conclusion of the experiments on a given cell. At all other times the manometers were closed off from the system and bypassed. A cold trap was located between the gallium cell and the remainder of the system so that even when the manometers were open to the pumping system the gallium cells were protected from contamination. All of the argon gas that entered the gallium cells passed through the cold trap.

Measurements and Procedures

In this section we shall describe the preparation and maintenance of the gallium and water triple-points, the procedure for determining the gallium triple-point temperature and its stability, the technique used for establishing thermal contact between the SPRTs and triple-points, the power dependences of the SPRTs, the pressure dependence of the gallium melting-point, and the effects of immersion of the SPRTs in the gallium triple-point cell.

Preparation and Maintenance of Water Triple-Point

Four water triple-point cells were used in this investigation. They were prepared for triple-point measurements in the following way. First, the cell was placed in an ice bath for 3 to 4 hours. Then, by means of a liquid-nitrogen-cooled copper tube being alternately repeatedly dipped into liquid nitrogen and then into a beaker of ethyl alcohol in the bottom of the thermometer well, a spherically-shaped mantle of ice was formed around the bottom end of the well. After approximately 30 minutes, the mantle appeared to be about 1 cm thick. Then a heat pipe, cooled by a solid carbon dioxide and ethyl alcohol mixture, was placed in the thermometer well and the well slowly filled to within approximately 1 cm of the top of the water column in the annular space of the cell with cold ethyl alcohol. After approximately 60 minutes, the ice mantle was 1 cm or more thick. As experience was gained in

this stage of the preparation, it appeared that the best practice was to avoid overcharging the heat pipe with dry ice. This appeared to regulate the heat removal rate, permitting a slow, steady growth of the mantle. Cracking of the mantle could be avoided by terminating the freeze after the mantle reached about 1 cm in thickness as viewed through the water. The heat pipe and the alcohol were then removed from the well and the triple-point cell packed in ice. In the early stages of this work, the ice mantle was permitted to grow overnight under these conditions. The thermometer well was then filled with water, the initial temperature of which was approximately 20°C. This would melt a little of the ice mantle in contact with the thermometer well, producing a liquid-solid interface near the well. This is essential to obtain an equilibrium temperature. A small piece of foam rubber was placed in the bottom of the thermometer well to cushion the SPRT from shock when it was being inserted into the well. An aluminium bushing, 5 cm long, fitted snugly in the thermometer well and was also a relatively snug fit to the SPRT. Usually the bushing was prechilled in ice water before inserting it into the thermometer well. Thermal contact between the inner liquid-solid interface and the SPRT was thus provided by the thin layer of water and the bushing, the latter playing the major role. Without a bushing present, self-heating effects of the SPRTs were much more pronounced.

Once the water triple-point cells had been prepared as described above, they were kept packed in ice in either a dewar or a home-made Styrofoam container. With the use of either of these, a water triple-point cell could be kept in good working condition for several weeks, even though it was being used more or less continuously every day. During the measurement period, the water triple-point cell was checked at least every morning, and normally several times a day, to ensure that the ice mantle was free to rotate, that is, that there was no freezing either to the outer wall or to the thermometer well. If there were ice needles or an ice crust extending from the mantle to the outer wall of the cell, these were melted either by the heat from one's hands or by placing the cell in a container of water at ambient

temperature. In any event, the mantle itself was tested in a container of water such that one could clearly see the outer boundary of the ice and see that it was not touching the outer wall of the cell.

ii. Preparation and Maintenance of Gallium Triple-Point Cells: The filling of the gallium cells and the subsequent solidification of the gallium were described in Section II.B.i. In preparation for each series of measurements, e.g., May or August–September, each cell containing solid gallium was placed in an auxiliary oil bath at $\sim 60^\circ\text{C}$. Hot oil was more or less continuously pumped into the thermometer well, maintaining an average temperature of approximately 40°C , to ensure that there was always an inner and outer liquid–solid interface the full length of the column of gallium. After 15 to 20 minutes, during which time 25 to 50% of the sample was melted, the cell was placed in the Rosemount bath, the temperature of which was normally kept approximately 10°C above the gallium triple-point temperature. During this operation, the cell contained argon gas at a pressure of ~ 1 atmosphere. The cell was then connected to the vacuum system and evacuated. For the pressure dependence experiments, the cell was pressurized with argon gas, but during the triple-point measurements, the cell was pumped continuously.

Upon completion of each series of measurements, the samples were solidified. Whenever the sample had been completely melted, it was cooled to $\sim 29^\circ\text{C}$ and then a freeze was initiated by repeated insertions into the thermometer well of a liquid-nitrogen-cooled copper tube. The cell was then put into a dewar containing a small quantity of ice at the bottom and then covered. Following those experiments when the sample was not completely melted, the cell was placed in a dewar as just described and the sample permitted to freeze.

Thermal contact to the SPRTs was provided by the oil in the thermometer wells. Since the SPRTs fitted snugly into the wells, no bushings were required.

iii. Temperature Measurements: The gallium triple-point temperature was determined by making resistance measurements of the three SPRTs in the gallium triple-point cells and in a water triple-point cell. The SPRTs were normally cycled through the gallium and water triple-point cells in the following measurement sequence each day: the SPRT was preheated in the oil bath containing the gallium cell for at least 30 minutes, then placed in the gallium cell. After being there for at least 30 minutes, measurement of its resistance was begun with the Guildline Current Comparator. The SPRT was then removed from the cell, stored temporarily at room temperature, and then precooled in an ice bath for at least 30 minutes. The resistance of the SPRT in the water triple-point cell was then measured in the same way as outlined above for the gallium cell.

The power dependence of each SPRT was determined each time its resistance was measured either in the gallium cell or in the water triple-point cell. Until the

end of May, we obtained readings at three currents, $0.3\sqrt{2}$, 1, and $\sqrt{2}$ mA, using a 1 second time constant and a 5 minute integration time. From these, we estimated an uncertainty of $\pm 5\ \mu\Omega$ in the extrapolated zero-current value of resistance. In August and September we used only 1 and $\sqrt{2}$ mA (a check had shown that the current values reproduced precisely) but, as stated earlier, a time constant of 3 seconds and an integration time of 10 minutes resulted in a reduction of the estimated uncertainty to $\pm 1.5\ \mu\Omega$ in the extrapolated zero-current value.

iv. Stability of Gallium Triple-Point Temperature: The stability of the gallium triple-point temperature of a given melt of a given cell was determined by continuously monitoring the resistance of an SPRT in the gallium cell for several days at a time using the Cutkosky ac bridge. For this procedure, the cell was prepared and maintained as described in Section II.D.ii. At least three melts of each cell were investigated by this procedure. Only changes of resistance were of interest for this study and the bridge resolution of $\pm 0.15\ \mu\Omega$ ($\pm 1.5\ \mu^\circ\text{C}$) at 1 mA measuring current enabled us to make an accurate study of this.

v. Repeatability of Gallium Triple-Point Temperature Measurements and Intercomparison of Gallium Cells: After preparation of the gallium cells as described in Section II.D.ii, the repeatability of the triple-point temperature for a given mantle in each cell was determined using the Cutkosky ac bridge. At the same time, a comparison of the three cells was made using two gallium cells at a time and SPRTs 374 and 375. Before the SPRTs were put into the gallium triple-point cells, they were preheated in the oil bath for a minimum of 30 minutes. After being in the cells for at least 30 minutes, their power dependence was measured. The SPRTs were then interchanged in the two gallium cells and after 30 minutes had elapsed, their resistances were measured again. Several interchanges were made per day.

vi. Gallium Melting Experiments: In order to obtain melting curves, each cell containing solid gallium at room temperature was placed in the Rosemount bath maintained at $\sim 40^\circ\text{C}$. An SPRT was placed in the well while the cell was at room temperature and then monitored continuously until the sample was totally melted and in equilibrium with the bath. From a consideration of the cell as shown in Figure 1, it is clear that the principal point of thermal contact between the bath and the gallium would be at the bottom of the cell. In order to reduce heat flow at that point and prevent the premature melting of the gallium at the bottom, we fitted a Styrofoam jacket to the bottom half of the cell.

vii. Pressure Dependence of Gallium Melting-Point Temperature: The measurements of the pressure dependence began with the SPRT in the gallium cell under a vacuum. The sample used was that obtained

from Alusuisse. The variation in the gallium melting temperature as a function of argon gas pressure over the melt was then determined from measurements made with the Cutkosky bridge. Although phase diagrams indicate that mercury and gallium are completely insoluble in both liquid and solid phases [21], we took care to have no mercury vapour from the manometers backstreaming into the gallium cell during these measurements.

viii. Thermometer Immersion and Hydrostatic Head Effects: The immersion characteristics of the cells were studied using SPRT 375, the resistance of which was measured with the Cutkosky bridge at 1 mA measuring current. The cell was prepared as described in Section II.D.ii. At the start of the experiment, the tip of the SPRT was placed at the bottom of the thermometer well. At that position the centre of the platinum sensing element was approximately 13 cm below the top of the gallium. In order to determine the effect of the bath temperature on the SPRT resistance, it was cycled by $\sim 0.1^\circ\text{C}$ about the triple-point temperature with a period of 4 hours. Measurements were made as the thermometer was withdrawn in increments of approximately 1 centimetre. With the thermometer tip about 7 cm above the bottom of the well, the effect of cycling the bath temperature was pronounced. Consequently, the cycling was discontinued and the bath temperature was set $10\text{ m}^\circ\text{C}$ above the triple-point temperature.

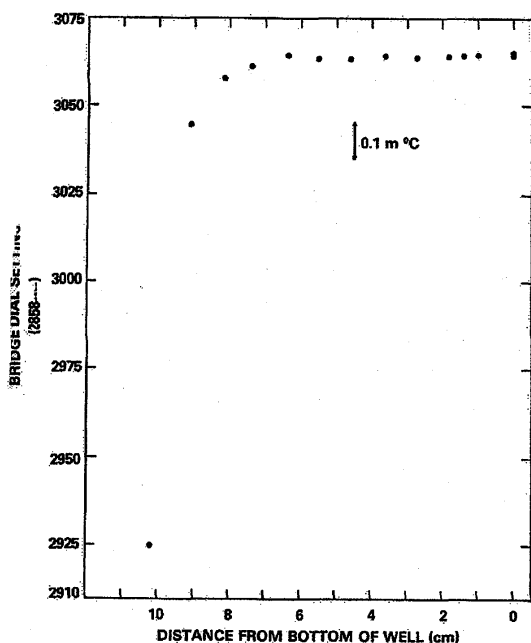


Fig. 3. Immersion characteristics of SPRT 375 in the triple-point cell containing Alusuisse gallium. The data have been corrected for hydrostatic head effects

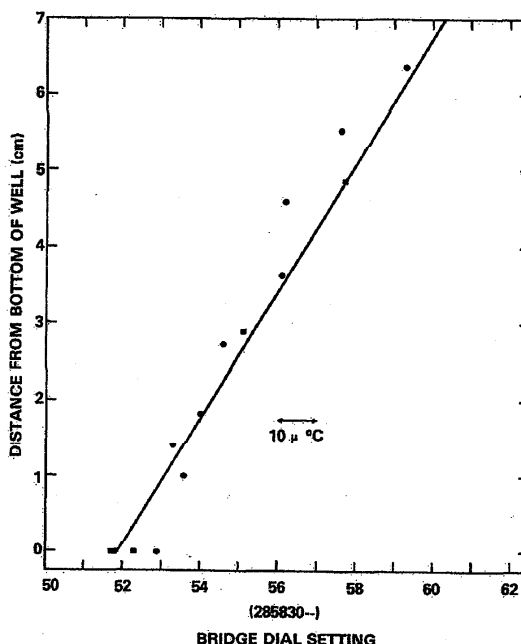


Fig. 4. Measurements of the hydrostatic head effect using SPRT 375 and the Alusuisse gallium sample, ● and ■ represent data obtained on two different runs. The straight line represents the hydrostatic head effect calculated from the density and the results of the experiment on the pressure vs. melting temperature of gallium

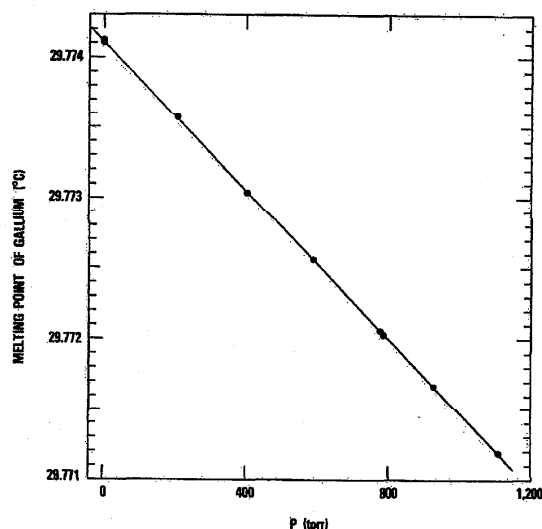


Fig. 5. Pressure dependence of the gallium melting-point temperature. The straight line through the data has a slope of -19.85 nK/Pa ($-2.011\text{ m}^\circ\text{C/atm.}$)

Results of these measurements are shown in Figures 3 and 4. These results show that under the conditions of our experiments the effects of the temperature outside the cell are no longer discernible when the tip of the thermometer is within about 6 cm of the bottom of the well. As shown in Figure 4, the change of the melting temperature with the distance of the SPRT from the bottom of the well (hydrostatic head effect) is in agreement with the results of the melting temperature vs. pressure experiments presented in Section III.A. Both the results shown in Figure 3 and the few points obtained when the effects of cycling the bath temperature were observable indicate that the relative temperature difference decreases by about a decade for every 2 centimetres of immersion. These results are further supported by the observation that varying the room temperature by as much as 10°C had no effect on the SPRT reading when its tip was at the bottom of the well.

III. Results and Analysis

A. Pressure Dependence

The results of the pressure dependence of the melting-point temperature of gallium as determined by an

SPRT in the Alusuisse gallium cell is shown in Figure 5. The uncertainty in the pressure measurement was about ± 100 Pa (~ 1 mmHg) and, hence, does not show on this scale. The ± 15 $\mu^{\circ}\text{C}$ uncertainty in the temperature measurement is indicated by the size of the circle representing the data. The straight line fitted through the data points has a slope of $dT/dP = -2.011 \pm 0.001$ $\text{m}^{\circ}\text{C}/\text{atm}$ (or -19.85 nK/Pa). Using thermodynamic data [22], the Clausius-Clapeyron equation ($dT/dP = T \Delta V/L$, where T = temperature, P = pressure, ΔV = volume change during phase change, and L = latent heat of fusion) yields the value $dT/dP = -2.032$ $\text{m}^{\circ}\text{C}/\text{atm}$ (or -20.06 nK/Pa). In Table 5, we list these values as well as those determined by other investigations [17, 23, 24].

B. Water Triple-Point Results

As stated in Section II.B.ii, we used four water triple-point cells during the course of this work. The ice mantles of the triple-point cells were annealed for several days [19, 25] before they were used for actual measurements. With the exception of A-13-506, the SPRT resistances in the cells agreed to within the scatter observed for a given cell (i.e., ± 0.07 m°C). The

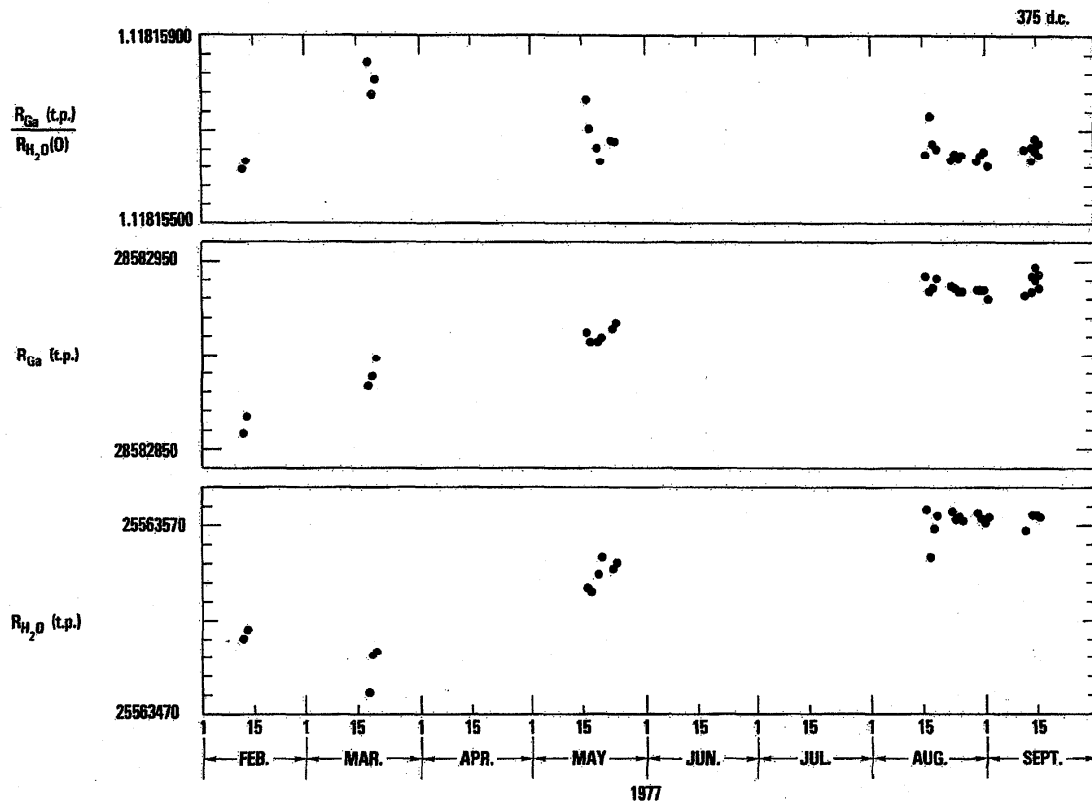


Fig. 6. Resistance ratio data for gallium triple-point temperatures taken with SPRT 375. Values of R_{Ga} and $R_{\text{H}_2\text{O}}$ are Guildline bridge ratios (times 10^8) of the resistance of SPRT 375 to that of standard resistor H17

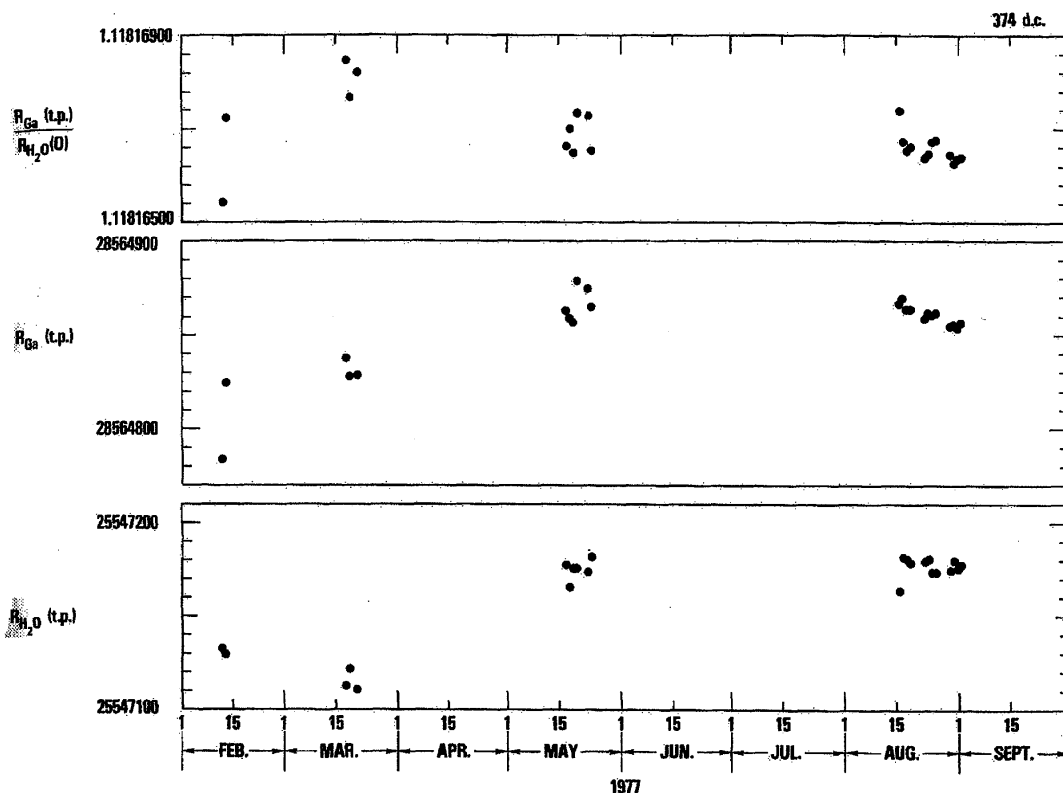


Fig. 7. Resistance ratio data for gallium triple-point temperatures taken with SPRT 374. Values of R_{Ga} and R_{H_2O} are Guildline bridge ratios (times 10^8) of the resistances of SPRT 374 to that of standard resistor H17

triple-point temperature of A-13-506, however, was consistently about $0.2\text{ m}^\circ\text{C}$ below that of the other cells. It is unlikely that the isotopic composition of the water of the various triple-point cells would have been sufficiently different to account for the $0.2\text{ m}^\circ\text{C}$ lower temperature observed for A-13-506 since the manufacturer obtained the water for the cells from the same source. Since cell A-13-506 was an old cell, it apparently had become contaminated, and consequently, it was not used in the determination of the gallium triple-point or melting-point temperatures.

Table 5. Experimentally determined values of the pressure dependence of the melting-point temperature of pure gallium

dT/dP value	Reference
-2.011 mK/atm.	This work
-2.12 mK/atm.	Bridgman [23]
-2.0 mK/atm.	Jayaraman et al. [24]
-1.5 mK/atm.	Sostman [17]
-2.032 mK/atm.	Calculated

The resistances of each of the three SPRTs obtained from measurements in one or the other of the three water triple-point cells are shown in Figures 6–8. The water triple-point cell used for measurements on any of the various days shown in the figures is given in Table 2.

The data obtained in March 1977 were not used in calculating the gallium triple-point temperature since there were problems associated with the ice mantle of the water triple-point cell and with the values realized for the water triple-point (but apparently not for the gallium triple-point). Some of the effects of the problems can be seen in the bottom portions of Figures 6, 7, and 8. Some of the problems arose because the ice mantle was permitted to freeze to the outside wall. Although the mantle was melted so that it was free to rotate, the ice would grow back and stick to the wall after several hours. This was detected during attempted measurements by a pronounced drift in SPRT resistance. By melting the mantle substantially away from the wall, the refreezing problem and the drift in SPRT resistance were solved although for some reason, perhaps stresses still present in the ice mantle, the resistance values of the SPRTs were still low.

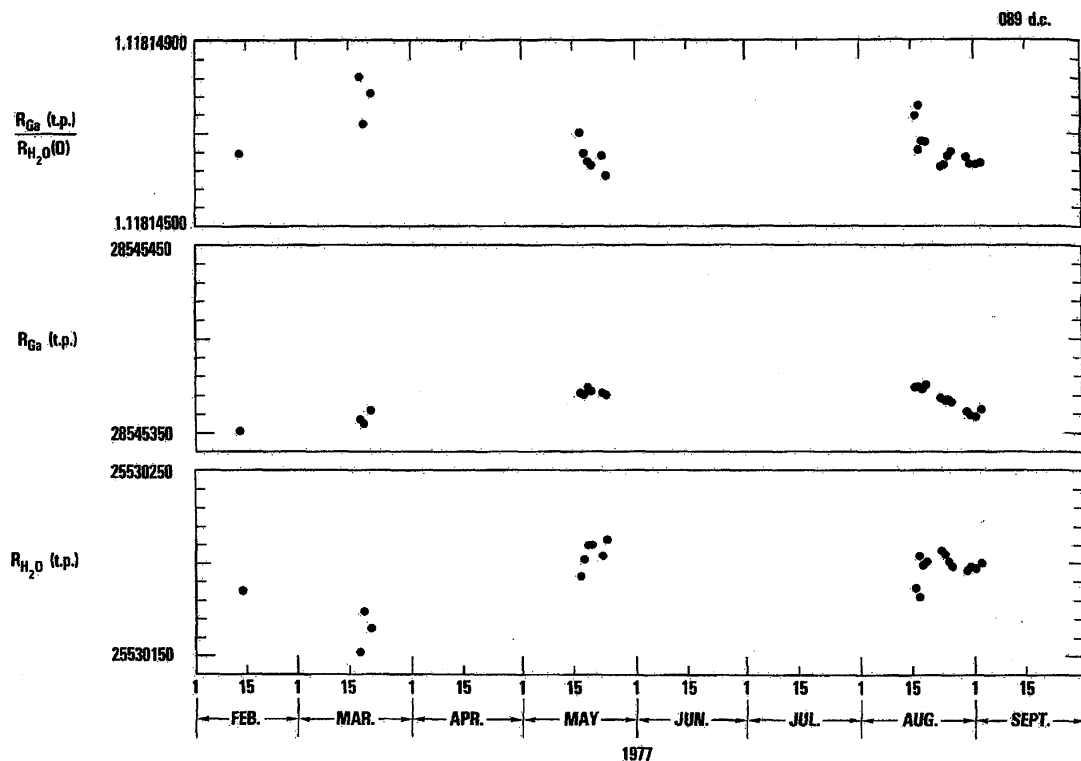


Fig. 8. Resistance ratio data for gallium triple-point temperatures taken with SPRT 089. Values of R_{Ga} and R_{H_2O} are Guildline bridge ratios (times 10^8) of the resistances of SPRT 089 to that of standard resistor H17

C. Results of Gallium Melting Experiments

Melting curves shown in Figures 9 through 11 were obtained, as described in Section II.D.vi, for each cell after the gallium had been frozen in the usual way. The melting curve shown in Figure 12 was obtained for the Eagle-Picher sample after it had been rapidly frozen from a totally liquid state. The data shown in Figure 13 were obtained for the Eagle-Picher sample when it had been prepared according to Section II.D.ii for a triple-point temperature determination before being placed in a bath at 40°C . Although data points are shown on the curves, the thermometer was monitored continuously using a strip chart recorder. The points indicated in the figures were used for transferring the data from the strip charts to the graphs. Each set of melting data is presented at three levels of resolution to display the main features of the melting behaviour. There are three salient features in the lowest resolution curve for each sample. The temperature rapidly attains a constant value at which it remains for about 7 hours. It then gradually increases by one to two degrees over the next 2 to 3 hours before increasing rapidly and then approaching the bath temperature.

Approximately 7 hours after melting began and when the temperature begins to show a gradual

increase on the uppermost curve, the other curves show a very abrupt increase in temperature. We attribute this behaviour to penetration of the mantle by liquid in the vicinity of the thermometer sensor. Subsequent melting of the remaining solid accounts for the gentle increase in temperature over the next 2 to 3 hours, as shown by the uppermost curve. Upon complete melting, the sample temperature approaches the bath temperature exponentially.

The details of the melting curves at the highest resolution are strongly characteristic of each sample, reflecting the influence of at least two factors. Firstly, the distribution of impurities in a sample, as determined by its prior thermal treatment, plays a major role in determining the shape of the melting curve. Secondly, the establishment of the hydrostatic head, which varies from cell to cell, will affect the initial portion of the melting curve. Although it would be difficult to account for the details of the highest resolution curve for each sample, the curves do show that the samples, when prepared in the same way, have different melting ranges.

The effect of different freezing methods on the shape of the melting curve can be seen by comparing Figures 11 and 12. The results of Figure 13 are

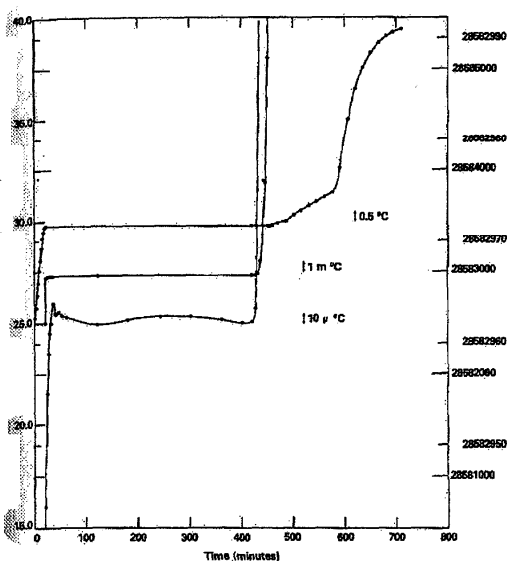


Fig. 9. Melting curve at three levels of resolution obtained with SPRT 375 for the Alusuisse gallium sample in a 40°C bath following a standard freeze. The temperature scale on the left-hand side of the figure is associated with the upper curve; the scale running from 28581000 to 28585000 on the right-hand side of the figure is associated with the middle curve; the other scale on the right-hand side is associated with the lowest curve

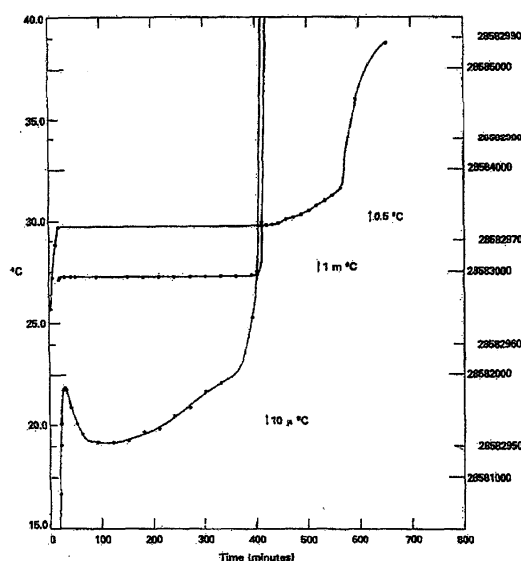


Fig. 11. Melting curve at three levels of resolution obtained with SPRT 375 for the Eagle-Picher sample in a 40°C bath following a standard freeze. The scales are the same as in Figure 9

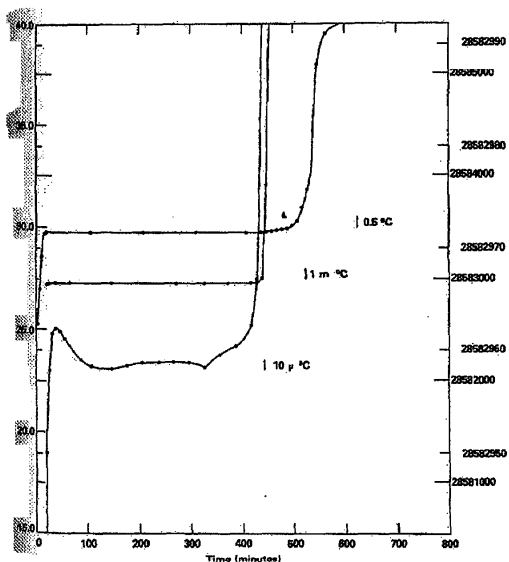


Fig. 10. Melting curve at three levels of resolution obtained with SPRT 375 for the Alcoa gallium sample in a 40°C bath following a standard freeze. The scales are the same as in Figure 9

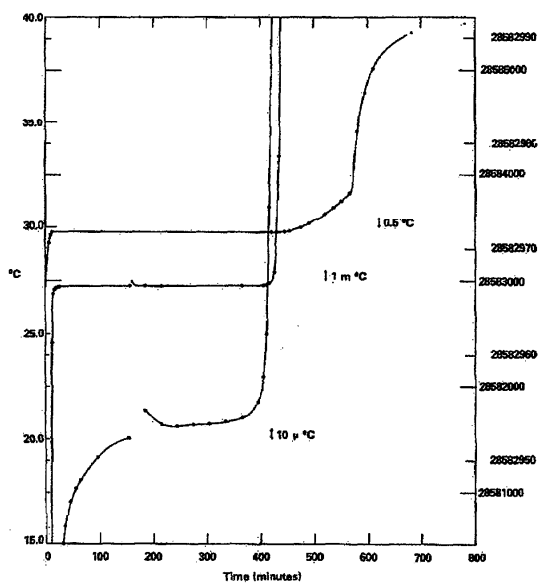


Fig. 12. Melting curve at three levels of resolution obtained with SPRT 375 for the Eagle-Picher sample in a 40°C bath following a fast freeze. The scales are the same as in Figure 9. At 160 minutes the SPRT was removed briefly from the cell and reinserted

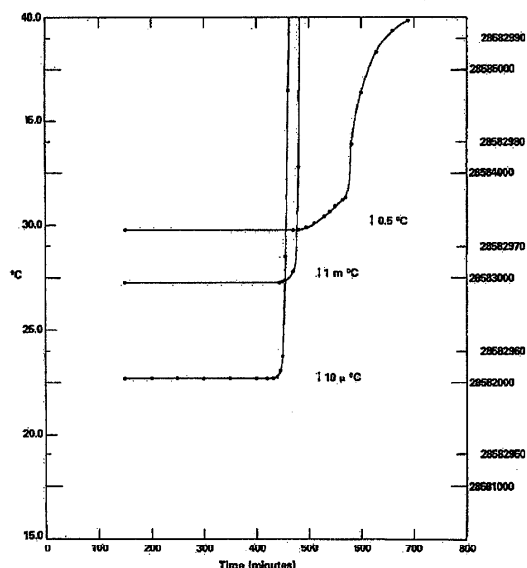


Fig. 13. Melting curve for the Eagle-Picher sample which had been prepared for the determination of the triple-point temperature and then placed in a 40°C bath. The scales are the same as in Figure 9

significant in that when the cell is prepared according to Section II.D.ii, the temperature, as indicated by the highest resolution curve, is independent of time and is independent of the fraction of gallium melted.

D. Gallium Triple-Point Results

The gallium triple-point temperatures, tabulated in Table 6, were calculated from the zero-power resistance ratios shown in Figures 6–8, using the standard interpolating formula specified by the IPTS-68, the SPRT calibration constants provided by the NBS Platinum Resistance Thermometer Calibration Laboratory, and the appropriate corrections described below. In Figures 6–8, $R_{H_2O}(0)$ represents the ice-point resistance of an SPRT calculated from the value, $R_{H_2O}(t.p.)$, obtained at the triple-point. The resistances of the SPRTs in the gallium and water triple-point cells were corrected for the depression of the true triple-point temperatures due to the hydrostatic pressures exerted by the columns of liquid. The size of the depression in the water triple-point cell is $7 \mu^\circ\text{C}$ per cm of water above the point of measurement [19]. For B-11-536, the approximate height of the water column was 25 cm and for A-13-587 and A-13-723, the heights of the water columns were approximately 28 cm. The variations in the amount of ice comprising the mantle could cause an uncertainty of ± 0.5 cm in these numbers. The depression of the water triple-point temperature was calculated for the appropriate water triple-point cell used in the measurements, i.e., $175 \mu^\circ\text{C}$ for cell B-11-536 or $196 \mu^\circ\text{C}$ for cells A-13-587 and A-13-723. The zero-power resistance of the SPRT determined in the triple-point of water cell and experiencing a temperature of 0.009825°C for cell B-11-536 or 0.009804°C for cells A-13-587 and A-13-723 was then corrected to 0°C by dividing that resistance by the appropriate resistance ratio (either 1.00003916 or 1.00003908, respectively).

The depression of the temperature due to the

Table 6. Gallium triple-point temperature as determined for each sample by each of the SPRTs used in the investigation

SPRT I.D.#	Alusuisse		Alcoa		Eagle-Picher		
	May 1977	Aug–Sept 1977	May 1977	Aug–Sept 1977	February 1977	May 1977	Aug–Sept 1977
375	29.77403	29.77402	29.77420	29.77393	29.77388	29.77400	29.77392
	29.77406	29.77399	29.77410	29.77396	29.77392	29.77392	29.77395
		29.77400		29.77393			29.77397
		29.77405		29.77395			29.77389
		29.77402					29.77399
							29.77392
							29.77398
374	29.77409	29.77395	29.77393	29.77386	29.77363	29.77389	29.77388
	29.77390	29.77390	29.77402	29.77395	29.77409	29.77411	29.77384
		29.77393		29.77396			29.77386
							29.77387
089	29.77420	29.77427	29.77432	29.77413	29.77421	29.77416	29.77419
	29.77409	29.77427	29.77421	29.77415		29.77414	29.77414
				29.77419			29.77415
				29.77421			29.77415

column of liquid gallium was calculated from the results of the pressure dependence of the melting-point temperature, which was shown to be $-2.001 \text{ m}^\circ\text{C}/\text{atm}$, and is $12 \mu^\circ\text{C}$ per cm of gallium (at the triple-point temperature). Since the height of the liquid gallium columns was approximately 13 cm, this results in a depression of $156 \mu^\circ\text{C}$. This was added to the temperature actually measured in the gallium triple-point cell as calculated above for the appropriate resistance ratio.

In addition to the hydrostatic head corrections, it was also necessary to make corrections for the effects of the measuring current reversal frequency. Most of the SPRT resistance values were obtained for a 4 second reversal period for the measuring current but changes in resistance of each SPRT in both gallium and water triple-point cells were measured when the current reversal period was changed from 4 to 16 seconds. Small effects were observed only at the triple-point of water and for all SPRTs except 375. This effect was probably due to the presence of moisture on the thermometer insulation since it was not observed at the gallium point. Wet insulation is known [26] to give rise to polarization effects. Assuming that the 16 second period of current reversal of the Guildline bridge more nearly reproduces the situation regarding measurements with the Mueller bridge in the Calibration Laboratory [27], we have corrected the 4 second period current reversal data to those at a 16 second period. These corrections also have been included in the values given in Table 6.

In order to get some indication of the long-term reproducibility of the three gallium triple-point cells, we have averaged the temperatures of each set of measurements made in February, May and August–September. These are given in Table 7. It is difficult to draw any definite conclusions regarding a possible change with time of the gallium triple-point temperature for each cell, since only two temperatures per cell were measured with each SPRT in May. We observe that the differences between the May and August–September averages are of the order of the differences in the May values and are consistent with the $\pm 5 \mu\Omega$ instrumental uncertainty estimated in II.D.iii. Moreover, the differences are not particularly systematic from SPRT to SPRT. Thus, about all that can be concluded from the results in Table 7 is that over the long term the triple-point temperature of a given gallium cell reproduces to within $\pm 0.11 \text{ m}^\circ\text{C}$ and that this limit largely reflects the measurement errors.

The average temperature and its standard deviation derived for each SPRT in each gallium triple-point cell are given in Table 8. The systematic differences among the thermometers, as shown there, may arise from three sources. For measurements of a given SPRT, the uncertainty arising from calibration errors (calibrated against fixed points of the IPTS-68 as maintained at NBS) may be as large as $\pm 0.21 \text{ m}^\circ\text{C}$ [19]. The presence of moisture on the thermometer insulation is another source of error and this, of course, varies from thermometer to thermometer. It has been shown [26] that shunting of an SPRT resistor with moisture can cause an error at the triple-point temperature of water equivalent to $\pm 0.9 \text{ m}^\circ\text{C}$ without the thermometer exhibiting a detectable "wet kick". Apart from any calibration errors, different SPRTs may indicate discrepant temperatures at fixed points intermediate to the calibration points due to an inherent source of error resulting from the use of real materials. Although we have no documentation, we would expect the error from this source to be small compared to $0.1 \text{ m}^\circ\text{C}$ near 30°C . Overall then, different SPRTs may indicate temperatures of a given intermediate fixed point near 30°C which differ by approximately $0.9 \text{ m}^\circ\text{C}$. Consequently, the differences in the temperatures calculated for the different SPRTs for a given gallium triple-point cell are not inconsistent with these error estimates.

The results in Table 8 indicate that there is a systematic difference in the temperatures of the different gallium cells. The Alusuisse sample has the highest triple-point temperature, the Alcoa sample is lower by $0.01 \text{ m}^\circ\text{C}$ and the Eagle–Picher sample is lowest, being $0.06 \text{ m}^\circ\text{C}$ below the Alusuisse sample. Since these temperature differences are of the same order of magnitude as the experimental uncertainty, it was decided to compare the three gallium cells more precisely. The results of this comparison (using SPRTs 374 and 375 and the ac bridge), shown in Figure 14, clearly confirm the dc results and demonstrate that the Alusuisse sample triple-point temperature is indeed $0.02 \text{ m}^\circ\text{C}$ higher than that of the Alcoa sample and approximately $0.07 \text{ m}^\circ\text{C}$ higher than that of the Eagle–Picher sample. It is equally clear that the day-to-day reproducibility of the triple-point temperature of each cell is at least as good as the instrumental uncertainty.

In accounting for the differences among the cells, it should be recalled that the hydrostatic pressure correction for a centimetre of gallium is $12 \mu^\circ\text{C}$. Since the height of the column of liquid gallium above the sensor varied less than a centimetre, both as a result of

Table 7. Average gallium triple-point temperature determined as a function of time

SPRT	Alusuisse		Alcoa		Eagle–Picher		
	May	Aug–Sept	May	Aug–Sept	February	May	Aug–Sept
375	29.77404	29.77402	29.77415	29.77394	29.77390	29.77396	29.77395
374	29.77400	29.77393	29.77398	29.77392	29.77386	29.77400	29.77386
089	29.77414	29.77427	29.77426	29.77417	29.77421	29.77415	29.77416

Table 8. Average temperature and standard deviation for each SPRT in each gallium triple-point cell

SPRT	Alusuisse	Alcoa	Eagle-Picher
375	29.77402 ± 0.000025	29.77401 ± 0.000112	29.77394 ± 0.000039
374	29.77395 ± 0.000079	29.77394 ± 0.000058	29.77390 ± 0.000151
089	29.77421 ± 0.000085	29.77420 ± 0.000066	29.77416 ± 0.000027
Average	29.77406 ± 0.00011	29.77405 ± 0.00013	29.77400 ± 0.00014

the volume change on freezing and from cell to cell, the largest possible effect on the equilibrium temperature is of order $0.01 \text{ m}^\circ\text{C}$, and hence, is at or below our level of detection. Possible differences in isotopic composition of the starting material and isotopic fractionation during purification and freezing could conceivably be factors in the sample-to-sample differences, since the Alusuisse sample is refined from European bauxite, while the other samples are from North or South American bauxite. The differences observed among the triple-point temperatures of the three gallium samples, however, most likely arise primarily from differences in purity. This is supported by the differences in melting range as shown in Figures 9–11. (See Sections II.D.vi and III.C.) A 0.1 ppm difference in concentration of alloying impurity, such as lead, silver, copper, indium, etc., would cause a change of about 0.01 to $0.05 \text{ m}^\circ\text{C}$ in the melting temperature [21]. Estimates of the purity of the Alusuisse sample put concentrations of each such impurity at less than 0.01 ppm, perhaps as low as 0.001 ppm, whereas the Eagle-Picher sample seems more likely to have concentrations of 0.01 to 0.05 ppm of each. These estimates are based on information provided by the manufacturers. Thus, the total concentration of alloying impurities in the Eagle-Picher

sample could have been as high as 0.1 to 0.5 ppm, depressing the melting temperature by as much as 0.01 to $0.25 \text{ m}^\circ\text{C}$. The effect of impurities in the Alusuisse sample would be to depress the melting temperature by less than $0.01 \text{ m}^\circ\text{C}$. It follows, then, that the triple-point temperature of the Alusuisse sample most closely represents the triple-point temperature of *pure* gallium. That value is 29.77406 with a standard deviation of all data points of $\pm 0.00011^\circ\text{C}$. The standard deviation of the data for individual SPRTs, however, range from ± 0.000025 to $\pm 0.000085^\circ\text{C}$.

Potential sources of systematic errors which contribute to the overall uncertainty of the measured triple-point temperature of gallium on the IPTS-68 arise from calibration, "wet" insulation, bridge inaccuracy, variations in isotopic composition, and impurities, as indicated above in the discussion of differences among the thermometers and among the gallium cells. The uncertainties in realizing the fixed points of the IPTS-68 used in the calibration of the thermometers are $\pm 0.1 \text{ m}^\circ\text{C}$ for the triple-point of water [1, 19] and $\pm 1 \text{ m}^\circ\text{C}$ for the freezing points of both tin and zinc [19]. These result in an uncertainty from calibration of $\pm 0.4 \text{ m}^\circ\text{C}$. The three thermometers used in the determination of the gallium triple-point temperature showed no "wet kick", but, even so, we attribute an uncertainty of $\pm 0.5 \text{ m}^\circ\text{C}$ to the realization of the triple-point temperature of water to allow for the possibility of moisture on the insulation [26]. The uncertainty at the triple-point temperature of gallium due to such "wet" insulation would be negligible. The estimated inaccuracy of the bridge, as discussed in Section II.C.ii, corresponds to an uncertainty in the temperature measurements of $\pm 0.16 \text{ m}^\circ\text{C}$. As stated above, the uncertainty resulting from impurities in the Alusuisse sample is estimated to be less than $\pm 0.01 \text{ m}^\circ\text{C}$. Variations in isotopic composition of the gallium samples would affect the gallium triple-point temperature but we have no information regarding the magnitude of such an effect. Therefore, it is not possible for us to make a realistic estimate of the uncertainty arising from this source. The triple-point temperature of water is known to vary with the isotopic composition [1] and this, in fact, is the source of the uncertainty in that temperature discussed above under systematic errors due to calibrations. One could normally include this uncertainty again in temperature measurements involving calibrated SPRTs, but since the triple-point of water cells used in our measurements came from the same source as those used in the calibration of our thermometers, it is inappropriate to include this

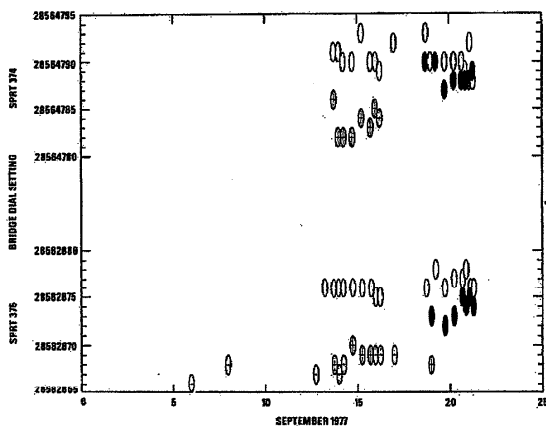


Fig. 14. Direct comparison of gallium triple-point cells using SPRTs 374 and 375. Bridge dial settings represent Cutkosky bridge ratios (times 10^8) of the resistances of the SPRTs to that of standard resistor H17. \circ represent data for Alusuisse sample; \bullet represent data for Alcoa sample; \circ represent data for Eagle-Picher sample

uncertainty a second time. Thus, the total uncertainty from all of the sources from which we can form estimates is approximately $\pm 0.6 \text{ m}^\circ\text{C}$.

The total uncertainty is the sum of both systematic and random uncertainties and for our measurements is $\pm 0.7 \text{ m}^\circ\text{C}$.

V. Summary

We have determined the triple-point temperature of high-purity gallium to be 29.77406°C using three standard platinum resistance thermometers calibrated on the IPTS-68 and using samples from three commercial sources. An assessment of the relative purity of our samples was confirmed by the results of an inter-comparison of the triple-point temperatures of the samples and by their melting curves. All data obtained with the three SPRTs on the highest-purity sample have a standard deviation of $\pm 0.00011^\circ\text{C}$, although the standard deviations of the data for individual SPRTs range from ± 0.000025 to $\pm 0.000085^\circ\text{C}$. The overall systematic uncertainty is estimated to be $\pm 0.6 \text{ m}^\circ\text{C}$. We have established that over a 7 month period the irreproducibility was $\leq \pm 0.00011^\circ\text{C}$ while the day-to-day irreproducibility of a single melt of each gallium cell was found to be $< \pm 15 \mu^\circ\text{C}$. These limits on the reproducibility appear to be largely instrumental since every time an SPRT was left in a gallium cell for several days, there was no change in the indicated temperature of the triple-point to within the instrumental resolution of $\pm 1.5 \mu^\circ\text{C}$. The pressure dependence was measured and determined to be $dT/dP = -2.011 \pm 0.001 \text{ m}^\circ\text{C/atm}$ (or -19.85 nK/Pa). This results in a value of the normal melting-point temperature of 29.77205°C .

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