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The melting point of gallium under calorimetric conditions

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Abstract

The International Temperature Scale of 1990 (ITS-90) is the latest of six temperature scales adopted by the Commité International des Poids et Mesures (CIPM) and the only one recommended for current use. It is defined by assigning a precise temperature value to 17 fixed points and the election of the interpolating instruments and equations.

One of these fixed points is the gallium melting point (302.4196 K). This point, if used correctly, could help to elucidate problems associated with the reproduction of other fixed points.

In this paper we describe an apparatus used for the reproduction of this point under calorimetric conditions. The plateaus obtained in the result are compared with those obtained using a traditional method. The reproducibility and repeatibility of this fixed point using this apparatus are also discussed.

Keywords: Calibration; Gallium fixed point; International temperature scale of 1990; Thermometric fixed points; Thermometry

1. Introduction

The International Temperature Scale of 1990 (ITS-90) is the international agreement by means of which temperature measurements are carried out. It is defined in terms of the precise assignment of temperature values to 17 equilibrium states (fixed point) of 15 very pure substances, and the election of the defining thermometers and interpolating equations [1].

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One of the fixed points is the gallium melting point whose assigned temperature is 302.9146 K, and it has been shown [2] that it is very reproducible. Therefore, this point is very useful for ensuring precise pharmaceutical, biological and medical temperature measurements. Likewise, it can be used as a check point for establishing the accuracy of another fixed point (the mercury triple point) [3].

The standard practice for reproducing this fixed point in National Laboratories requires rather expensive equipment which, in most of cases, is too sophisticated for mere calibration purposes. Since we are interested in spreading the use of this fixed point in industry, we have developed a non-expensive, self-contained oven-and-cell unity, able to function as a reference point either for users or secondary laboratories.

There have been some suggestions concerning this [4], but they rely on commercial instruments (which make them expensive), and they do not satisfy the requirements imposed by the ITS-90 over this fixed point.

2. Apparatus design

2.1. Gallium melting-point cell design

The cell was designed originally for use in the triple-point mode, combining the National Institute of Standards and Technology (EU) and the National Research Laboratory of Metrology (Japan) designs [5,6]; it was later modified for use in both triple-point and melting-point modes. The gallium sample obtained from Johnson Matthey (79 grade shot, lot number L22C25, 99.999 99_5% pure) was placed inside a teflon and nylon crucible. This crucible was protected with a quartz glass envelope provided with a valve for gas interchange. Fig. 1 shows a diagram of the gallium cell and its glass envelope.

2.2. Calorimeter

The cell was inserted in an airtight, closed, 3-mm walled, copper tube within a vacuum PVC chamber. The tube was surrounded by a manganin heating coil. The cap of this tube is provided with a vacuum valve in order to control the heating rate of the gallium sample. Fig. 2 shows the calorimeter and the cell within it.

2.3. Temperature controller

A temperature controller, shown in Fig. 3, was designed in order to maintain the temperature of the copper tube constant. It is possible to increase manually the current delivered by this circuit to the heating coil and, therefore, to control the heating rate of the copper tube.

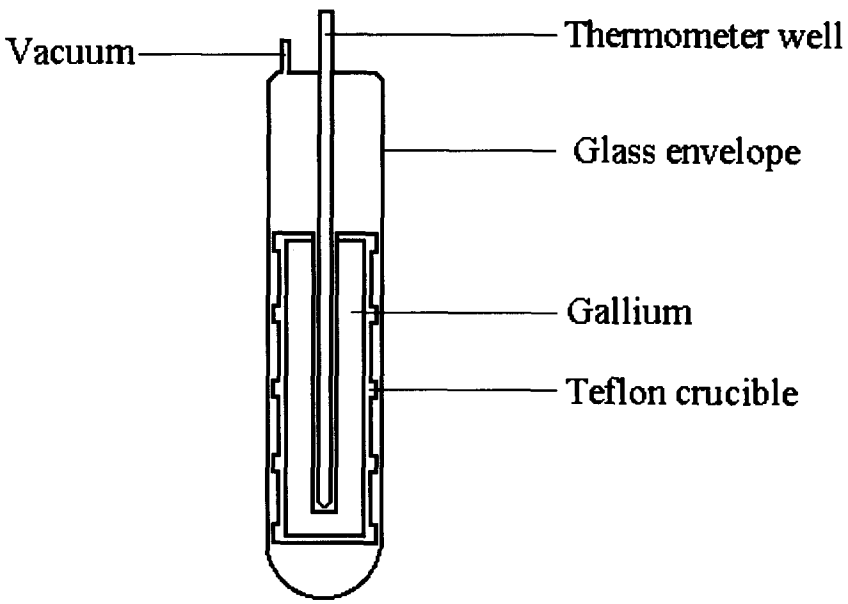

Fig. 1. Gallium melting point cell. The very pure gallium sample is contained in a teflon and nylon crucible. A glass envelope allows gas interchange and provides the possibility of melting-point and triple-point experiments.

3. Experimental

A series of 10 melting-point temperature measurements was obtained using the traditional method which is as follows. The cell, with the sample at room temperature, was inserted in a furnace at 40°C for 30 min in order to produce an outer solid–liquid interface. At the same time, a heater, whose temperature was also 40°C, was inserted in the thermometer well in order to form an inner interface. The measurement started at least one hour after both interfaces were established [7]. Once the melting plateau was reached, the furnace temperature was set 0.5–0.75 K above the melting point temperature. This procedure allowed us to have a plateau duration of 16 h.

The experimental procedure used with this calorimeter was as follows. The cell was evacuated and filled with argon at a pressure of 1 atm. In the first set of experiments neither the PVC vacuum chamber nor the cooper shield were evacuated. In this case, the copper shield temperature was fixed at different values in order to obtain the melting plateau.

In the second set of experiments the copper shield temperature was fixed at 0.3 K above the gallium melting point once the melting temperature was reached. This temperature was choosen because it allowed us to obtain the longest plateaus. Some experiments regarding the reproducibility of the melting plateau and its stability, and the differences between the melting and freezing points were made. Neither the vacuum chamber nor the copper shield were evacuated.

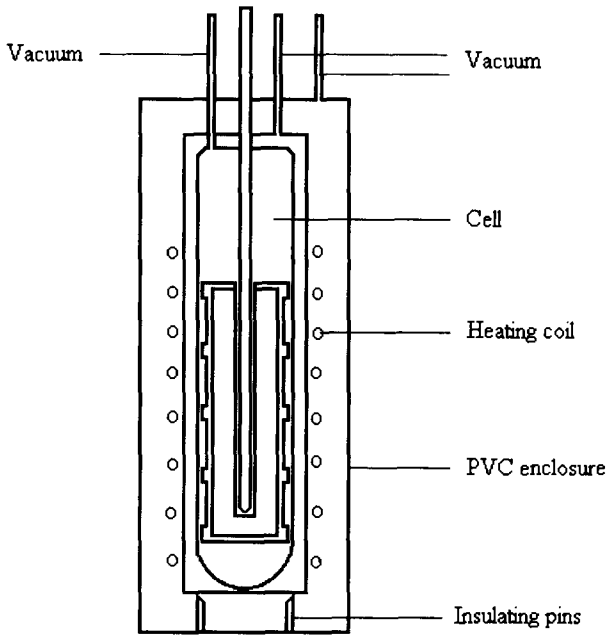

Fig. 2. Calorimeter. The gallium cell is placed inside an airtight, electrically heated, copper shield provided with a vacuum valve. An external PVC vacuum chamber ensures thermal insulation.

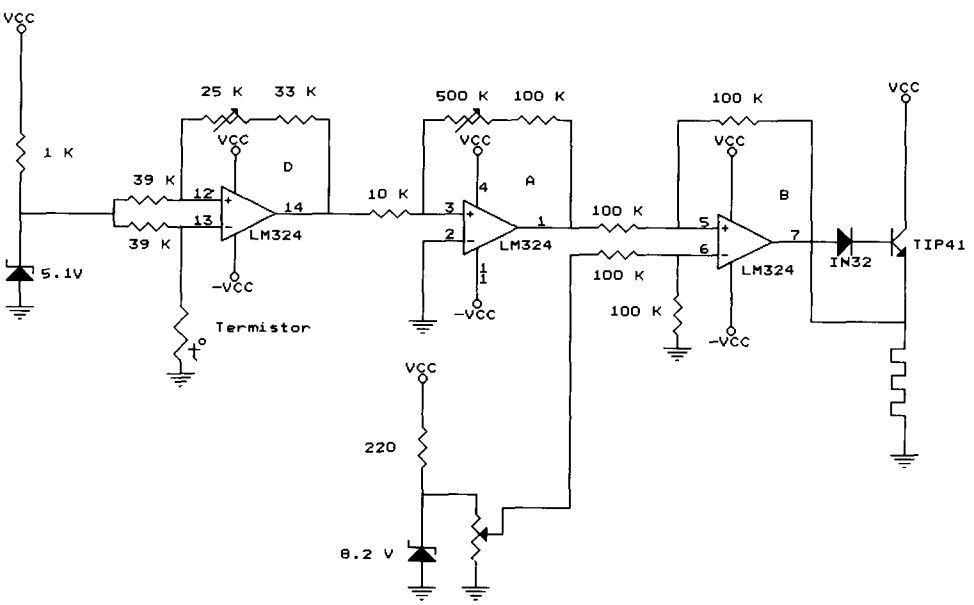

Fig. 3. Temperature controller.

During all the experiments the temperature was measured using a Standard Platinum Resistance Thermometer (SPRT) (Yunan, serial number 92195), and the plateau was recorded using a plotter.

4. Results

4.1. First set of experiments

In order to determine the plateau duration under the worst conditions, the temperature of the copper tube was adjusted at 5, 2 and 0.3 K above the gallium melting point, and the sample was allowed to melt. The minimum durations of the melting plateaus under these conditions were 10, 14.5 and 48 h for 5, 2 and 0.3 K, respectively.

4.2. Second set of experiments

A reproducibility better than 0.2 mK was observed. During the melting, a brass rod whose temperature was 21°C was inserted in the thermometer well, and left there for 10 min in order to investigate the stability of the process. The sample temperature decreased more than 0.1 K and, once the rod was extracted, the new temperature of equilibrium was lower by 0.1 mK and was reached in 30 min.

The difference in temperature between the melting and freezing experiments was 0.6 mK, the freezing temperature being higher.

During the freezing, a cold SPRT (21°C) was inserted in the thermometer well and was left there in order to observe the stability of the process. The sample temperature decreased less than 0.1 mK and recovered after 10 min.

5. Discussion

Although it is necesary to perform many more experiments evacuating both chambers, we think that the results obtained so far indicate that the calorimeter design is good enough for calibration purposes. It is important to note that the cost of this calorimeter is several orders of magnitude less than a calibration furnace, and that the plateaus thus obtained are as long and as flat as those obtained using a calibration furnace.

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