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Triple point and melting point of mercury[1]

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Abstract

The triple point and melting point of mercury were studied by continuous melting and adiabatic calorimetry techniques. Two geometrical configurations of the sample are compared and the effect of impurities considered.

Keywords: Cyrogenic fixed point; Hg triple point; ITS-90; Standard platinum resistance thermometer; Temperature scale

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1. Introduction

All national standards laboratories maintain units of measurements of very high accuracy. Temperature standards are based on the International Temperature Scale of 1990 (ITS-90) [1], which specifies the experiments, instruments and procedures to obtain the most reliable temperature references. These experiments define fixed points, most of them solid–liquid phase transformations (triple points, melting points or freezing points). The standard interpolation instrument in the temperature range from 13.8 K (triple point of equilibrium hydrogen) to 962°C (freezing point of silver) is the platinum resistance thermometer (PRT).

The accepted triple point temperature for Hg is – 38.8344°C. However impurities alter all phase transformation temperatures. In addition, other factors such as experimental method, and the shape and size of the sample can also change the observed

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temperatures. Thus the integrity of the temperature scale itself depends upon the quality of the samples used, and on the quality of the experiments. Therefore, some standards laboratories spend much time studying the impurity dependence of phase transitions and testing different experimental techniques. As part of such activities we studied the melting point and triple point behavior of mercury.

2. Experimental

We used two experimental techniques to measure the Hg triple point: continuous melting and adiabatic calorimetry. The continuous melting technique consists of heating a solid sample to its melting point by supplying heat at a certain constant rate. The sample temperature increases with time, and the heating rate depends on the sample size, its heat capacity and the heat losses. When the sample reaches its melting point the temperature tends to a steady value, the fixed point temperature. The melting curve in this technique is the record of temperature against time.

By contrast, the adiabatic calorimetry technique consists of reducing the heat exchange between the solid sample and its surroundings and balancing the remaining heat leaks. Then the sample is heated by heat pulses alternated with relaxation periods, to let it reach an equilibrium temperature. The melting point is eventually reached and the melting curve can then be obtained by plotting the equilibrium temperature values against the sample's liquid fractions.

Because the temperature of a phase transformation does not depend on the experimental arrangement, we expect to measure the same value using both techniques, within the experimental uncertainty, for samples taken from the same batch.

When designing an Hg phase transformation experiment, one has to consider the consequences of its low thermal conductivity: Hg is a heat insulator with a thermal conductivity about half that of stainless steel. The relaxation time (the time to reach thermal equilibrium once the thermal state of the sample is disturbed) depends on a variety of factors such as the sample size, heat capacity, thermal conductivity, geometry, etc. The size of the samples must be relatively large to accommodate long-stem thermometers. So considerable temperature gradients can occur within the sample and the PRT would read an average of those gradients.

We measured both the melting and the triple point of mercury using, in a first set of experiments, an adiabatic calorimeter with small samples (approx. 200 g) and a cylindrical shell shape. In a second set of experiments we used another adiabatic calorimeter with large samples (approx. 2 kg) in a cylindrical container, and in a third set of experiments, we used a continuous melting apparatus with fairly large samples (approx. 800 g) in a cylindrical container.

We used long-stem PRTs (25.5 Ω at ice point), and an AC resistance bridge (ASL F-18). All readings were relative to a 100-Ω standard resistor, using a bridge gain setting of 10^5 and a bandwidth of 0.5 Hz. The PRTs require immersion of 10–20 cm to minimize the longitudinal heat leak along the stem [2].

3. Procedure using the adiabatic calorimeter and small samples

The experimental arrangement uses a sample of 200 g with a cylindrical shell form of 5 cm diameter, 5 cm long and 2 mm thick [3]. An electrical heater is wound around the sample container. The shell encloses the bottom of a solid copper cylinder, 15 cm high. The copper cylinder has four thermometer wells to accommodate 4 long-stem PRTs simultaneously.

There is a copper shield surrounding the sample and the copper block. A differential thermocouple (TC) (copper–constantan) measures the temperature difference between the sample and the shield. The micro-voltmeter which picks up the thermocouple signal has an analog output (± 1 V) used to control the power of the shield heater. The shield and the sample are in a vacuum chamber. The calorimeter is in a Styrofoam box with 15 cm thick walls, filled with crushed carbon dioxide (dry ice).

To begin the experiment, the sample is frozen. During the cooling process, helium is in the vacuum chamber and crushed dry ice is in the thermometer wells. Starting from room temperature, the sample freezes in about 40 min. Once the sample is solid, the vacuum chamber is evacuated and the shield's temperature control starts; the remaining heat leaks are reduced by biasing the TC reading using a DC power supply.

Several preliminary experiments help to find the melting point and the heat of fusion value. With this information the sample is prepared with different solid-to-liquid ratios and the equilibrium temperature is measured for each of them. Finally, the melting curve is obtained by plotting the temperature against the liquid fraction.

We obtained the melting curves of two mercury samples, one sample with an unknown impurity concentration and the other with a known 1 ppm impurity concentration. The pressure dependence of the melting point of the high purity sample was also determined. A final experiment using the continuous heating technique was performed and its result is compared with results of the previous experiments.

4. Results A

The "melting range" of a sample is defined as the relatively small range of temperature increase during which most of the sample material changes state. The purer the sample, the smaller the melting range.

The melting range of our sample of unknown impurity was 3 mK between 10% and 70% liquid fraction, and 0.25 mK between 20% and 70% liquid fraction. The relaxation time, i.e. the time necessary to reach stable temperature, varied from 15 min for 5% liquid fraction to 3 h for 70% liquid fraction. The total heat of fusion was 2.30 kJ, thus giving a molar heat of fusion of 2.31 kJ mol^{-1}.

For the high-purity sample, the melting range, between 5% and 90% liquid fraction, was 0.4 mK (Fig. 1). The relaxation time was 20 min for 5% liquid fraction and 40 min for 80% liquid fraction. The triple point temperature was 5 mK higher than the previous sample. Repeatability for 30 measurements, performed over 50 days, was 0.3 mK. In this case the molar heat of fusion was 2.31 ± 0.01 kJ mol^{-1}.

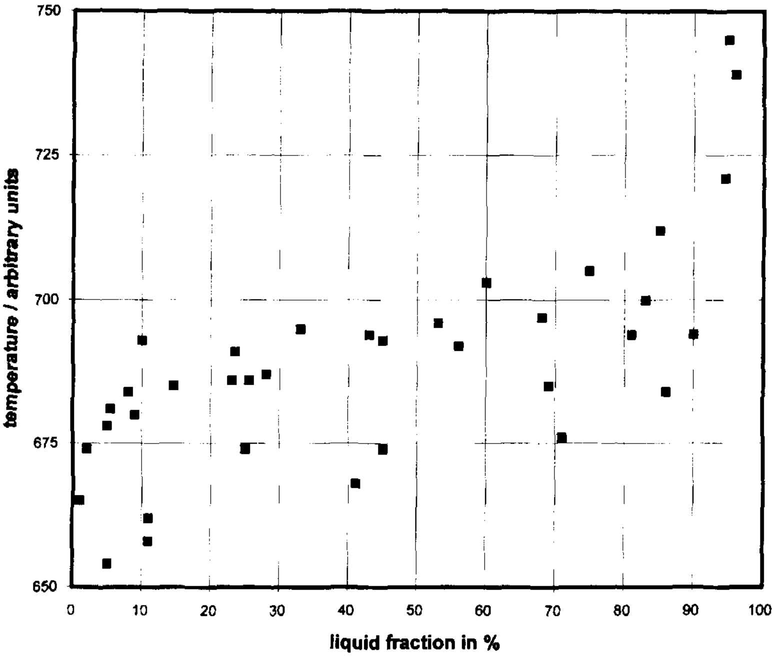

Fig. 1. Melting range of a high purity Hg sample measured with adiabatic calorimetry and a cylindrical shell sample. The temperature full scale axis is 1 mK.

The pressure dependence of the melting point, from the triple point to ambient pressure, was measured as follows: the melting point was determined at 30% liquid fraction. Helium was used to pressurize the vacuum chamber to 1 bar; a Bourdon gauge manometer measured the pressure. The equilibrium temperature was measured for six pressure values, between vacuum and 1 bar. The results were interpolated to a straight line yielding a slope of 4.8 ± 0.2 mK bar^{-1}.

When the sample was melted by continuous heating, a melting range of 8 mK and a temperature 15 mK higher than the value observed adiabatically was obtained. This demonstrates the inappropriateness of the constant heating technique in the apparatus used for our adiabatic experiment with small samples.

5. Procedure using adiabatic calorimeter and large cell

A cylindrical glass cell of 3.5 cm diameter, 20 cm long, was filled with 2 kg of Hg. The cell was filled and sealed under vacuum. The Hg sample was taken from a triple-distilled Hg or "dental grade" batch without further purity specifications and it was poured directly into the cell.

To determine its triple point under adiabatic conditions, we used a cryostat (described elsewhere [4]) designed to run with sealed glass cells. We filled the gap

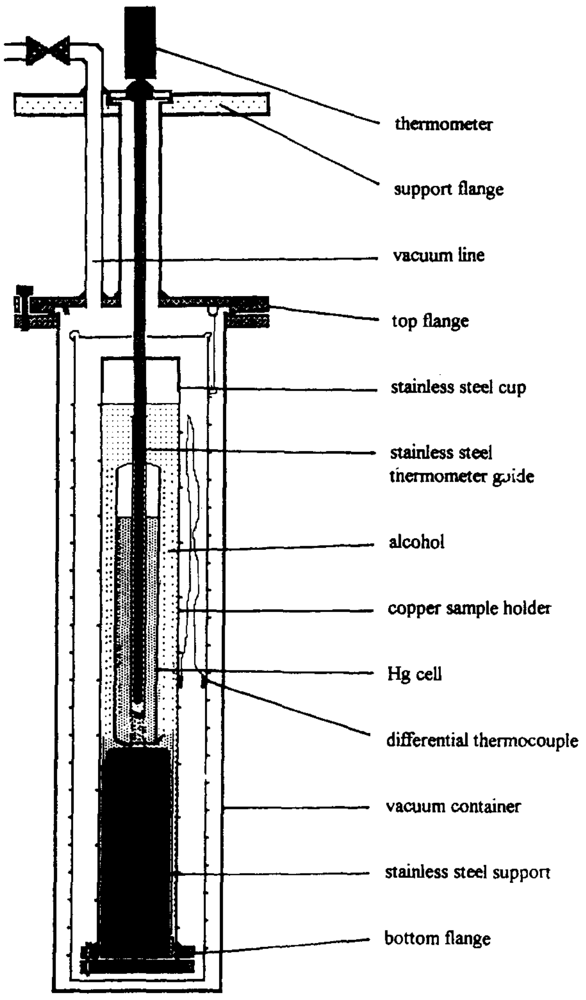

Fig. 2. Experimental arrangement of the adiabatic cryostat using the glass cell.

between the cell and the cell container with alcohol (Fig. 2). This liquid improves the thermal contact between the heater, wound on the cell container, and the cell.

The calorimeter is placed in a cylindrical Styrofoam container of 30 cm inner diameter, 70 cm high with 10-cm-thick walls, filled with dry ice. During the cooling process the vacuum chamber was filled with helium. After in 4–5 h, the sample reached the freezing point, starting from room temperature, and it took 30–40 min to freeze completely.

Once the sample is solid, the vacuum chamber is evacuated and the temperature control of the shield starts. We used a differential thermocouple to measure the temperature difference of the shield, taking the cell container temperature as reference.

The heat of fusion and points on the melting curve were measured as described previously. In this case the melting point is the triple point because the cell was sealed under vacuum.

6. Results B

The relaxation times was about 30 min while 100% of the samples remained in the solid state. Once the triple point was reached heat was supplied in units of about 5%–10% of the sample's total heat of fusion. Along the melting curve, the relaxation time was about 10 min. Temperature readings were taken when the temperature had stabilized within 0.1 mK. The total heat of fusion for the sample was found to be 22.5 ± 1 kJ, or 2.3 ± 0.1 kJ mol^{-1}.

Once about 90% of the sample was melted, sufficient heat was applied to melt the remaining 10% and to raise the liquid sample to about 4°C above the melting point. It took 20 min after the last heating cycle before the temperature, detected by the PRT, began to rise. This is because during heating cycles the liquid can become up to several degrees warmer than the temperature at the liquid/solid interface.

To simulate a calibration procedure, and estimate how accurately PRTs can be calibrated, a PRT was repeatedly inserted (6 times) into the thermometer well, with the sample 90% solidus 10% liquid 5 min after each insertion, readings were taken. The scatter was 0.1 mK and the average was indistinguishable from the final equilibrium value.

7. Continuous melting apparatus

A melting point apparatus was built using two thin-walled concentric quartz tubes (Fig. 3), of 0.7 cm and 2 cm inner diameter, respectively, each 25 cm long. The outer tube contained the Hg sample of 800 g and the inner one served as the thermometer well. A stainless steel spacer kept the well concentric with the outer tube and prevented its floating. The sample was open to ambient pressure. These tubes were then inserted into a copper jacket that could be cooled by circulating liquid nitrogen through a copper coil wound around the jacket, or else it could be heated by a heater also wound around the jacket. The entire apparatus was housed in a Styrofoam box with 4 cm thick walls. Alcohol was used in the thermometer well to enhance the heat transfer between the PRT and the sample.

The sample could be cooled from room temperature to its freezing point in 10 min by circulating liquid nitrogen through the cooling coil and frozen in a further 5 min. When the sample temperature fell about 4 K below its freezing point, the liquid nitrogen was shut off and the sample heater was turned on. It took 15–20 min to reach 1 K within the melting point. The sample heater was then turned off and only natural heat leaks through the walls of the Styrofoam box heated the sample. Within 30 min the sample temperature stabilized at its melting point and remained quite stable for about 20–40 min.

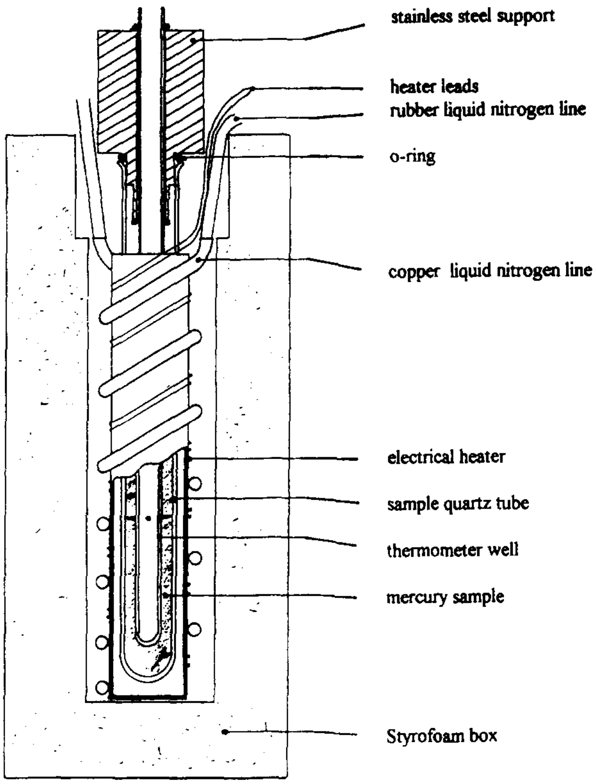

Fig. 3. Mercury melting point apparatus used with the continuous melting technique.

The total melting range was about 0.25 mK. The overall reproducibility of the melting point was better than 0.5 mK. The melting point observed was 4.5 ± 0.5 mK higher than the triple point.

8. Conclusions

Even though some impure Hg samples could yield quite a small melting range, the melting temperature in these cases proved to be several mK different from the triple point of high purity samples. It follows that a narrow melting range is not a sufficient criterion for considering an Hg melting point as an ITS-90 fixed point.

The overall adiabatically estimated uncertainty for the high purity sample and for the dental grade sample is less than 1 mK. The melting temperature of the dental grade sample was found to be the same as that of the high purity sample, used at CENAM as the defining fixed point of the ITS-90 [5]. Thus, triply distilled Hg is pure enough to be used as a fixed point material for the temperature scale.

The pressure dependence of the melting point, using small samples, was found to be 4.8 ± 0.2 mK bar^{-1}, corresponding to a difference of 4.8 mK between the normal melting and triple points. For the dental grade Hg sample, a difference of 4.5 mK was measured, while 5.4 mK is the value adopted on the ITS-90. These discrepancies may be due to some residual air pressure sealed in the triple point cells.

With appropriate experimental design and experimental apparatus, continuous melting can give nearly as accurate results as the adiabatic techniques. The critical point is to take care not to measure the temperature of an "overheated" liquid i.e. liquid whose temperature is higher than the temperature of the liquid–solid interface. In our apparatus we located the PRT along the center of symmetry in a cylindrical sample, with heat applied radially from the outside. With the PRT in contact with the solid which will be the last to melt, its temperature cannot rise above the melting point so long as the solid shell lasts. The liquid phase can "overheat", the solid phase cannot.

The melting apparatus, in spite of its simplicity, gives sufficiently accurate and reproducible results to that it can be used by standard laboratories for routine calibrations.

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