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Realisation and study of a CO_2 triple point thermometric cell

Réalisation et étude d'une cellule thermométrique au point triple du CO_2

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Abstract

In the 83 K – 273 K temperature range, the International Temperature Scale of 1990 (ITS-90) is realised by interpolation between the triple point of water (T_{90} = 273,16 K), mercury (T_{90} = 234,315 6 K) and argon (T_{90} = 83,805 8 K). The calibration of thermometers below -38 °C therefore requires the realisation of the argon triple point realisation with the associated "cryogenic techniques". Numbers of calibration laboratories are using comparison baths and are asking for references down to –60 °C. So, it appears pertinent to give the possibility to use a more convenient standard. A CO_2 triple point cell can be an answer to this issue.

KEY WORDS: TEMPERATURE FIXED POINT, CO_2, STANDARD.

Résumé

Dans le domaine 83 K – 273 K, l'Échelle Internationale de Température de 1990 (EIT-90) est réalisée par interpolation entre les points fixes de l'eau (T_{90} = 273,16 K), du mercure (T_{90} = 234,315 6 K) et de l'argon (T_{90} = 83,805 8 K). Un étalonnage de thermomètres à des températures inférieures à –38 °C nécessite donc la mise en œuvre du point triple de l'argon et des techniques « cryogéniques » correspondantes. Or de nombreux laboratoires d'étalonnages utilisent des bains de comparaisons et expriment des besoins de références jusqu'à –60 °C. Il apparaît donc pertinent de pouvoir disposer d'une référence mieux adaptée à ces besoins. Une cellule au point triple du CO_2 (T_{90} = 216,592 K) peut répondre à cette problématique.

MOTS CLÉS : POINT FIXE DE TEMPÉRATURE, CO_2, ÉTALON.

1. Introduction

In the ITS-90 scale, from 83,805 8 K up to 273,16 K, the Standard Platinum Resistance Thermometer (SPRT) is the interpolating instrument between three temperature fixed points: the triple points of water (T_{90} = 273,16 K), mercury (T_{90} = 234,315 6 K) and argon (T_{90} = 83,805 8 K). The associated thermal enclosures are of different types. Generally the ones associated with the water cells are melting ice baths. For mercury cells, electronically temperature regulated liquid baths are often used. However, the liquid baths cannot reach the temperature needed to realise the argon point and liquid nitrogen baths are needed.

Many calibration laboratories require references below –38 °C but not necessarily down to the argon point temperature. In this case, the standard can be a calibrated SPRT. But in case the laboratory is using fixed points as transfer standards, this situation is not satisfactory. A fixed point whose temperature is between the argon and mercury triple point temperatures can be an answer to this issue. Then the study of a CO_2 triple point cell (T_{90} = 216,592 K) is proposed.

A few years ago [1, 2], the Institut National de Métrologie (LNE-INM/CNAM) developed and studied CO_2 triple point cells intended to accommodate capsule type thermometers and associated to adiabatic calorimeters (fig. 1). The study on the first version of these cells contributed to fixing the temperature value of the CO_2 triple point in the list of the secondary fixed points (for first quality), as recommended by the Consultative Committee of Thermometry (CCT).

But calibration laboratories for temperatures in that range usually use long stem thermometers, that are much bigger that the capsule ones. Consequently, to calibrate these long stem thermometers at the CO_2 point, specific dedicated cells are to be developed.

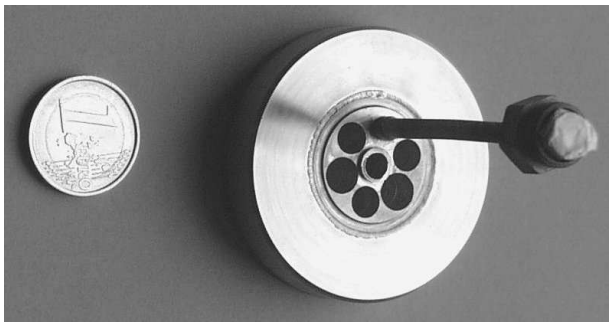

Fig. 1. – Thermometric cell for CO_2 triple point (last generation), dedicated to capsule type thermometers. This cell is a module intended to be associated to other modules containing other substances, the whole constituting a multi- fixed points device (multicell). On the element, a central hole allows the cells to be assembled by using a threaded rod. Some of the other holes are intended to receive several capsule type thermometers. The output tube is the filling tube allowing the connection to the gas handling system for filling the cell with pure gas.

The aim of this study is then to design and to metrologicaly study a new generation of CO_2 triple point cells for long stem thermometers. These cells may need to be individually calibrated because of the lack of purity of commercial CO_2 samples. But prior to this calibration, the reproducibility of a given cell and the influence of the thermal conditions when realising the transition plateau have to be studied. This last part is presented in this article.

This joint project was partly supported by a *PAI* programme (*Programme d'Action Intégrée)*, PAI-IMHOTEP, partnership France-Egypt.

2. Thermometric cell design

The geometry of the cell (fig. 2) has to meet several requirements. First of all and as mentioned previously, it must fit the long stem thermometers. The cell is therefore cylindrical with a central thermometer well so that the CO_2, whether liquid or solid, is around the thermometer-sensing element.

Fig. 2. – Carbon dioxide cell for long stem thermometers.

Secondly, a cell with a dimension compatible with the water or mercury cells is required in order to adjust the cell to the already existing enclosures.

Finally, the cell has to be used in association with cryostat allowing the CO_2 transition, either by a "constant flux method" or by a "quasi-adiabatic method".

2.1. Constant flux and quasi-adiabatic methods

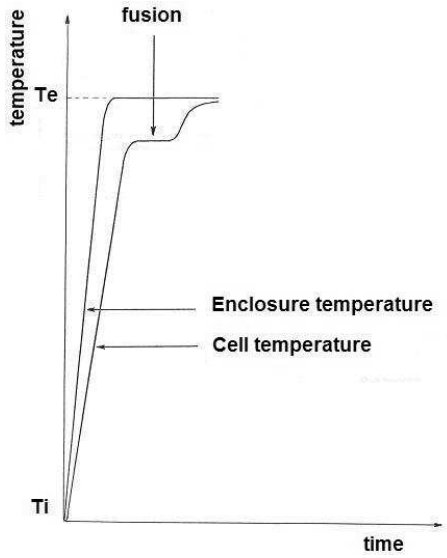

Fig. 3. – Constant flux method; the enclosure temperature is set at a value slightly higher than the transition one. In this way, the transition is not realised in thermal equilibrium conditions;
*T*i: initial temperature of the enclosure,
*T*e: enclosure temperature set .

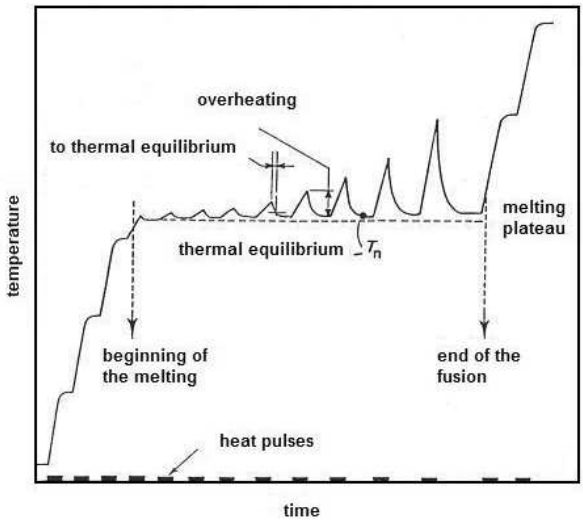

Fig. 4. – "Quasi-adiabatic" method; With this method, the thermometer is in thermal equilibrium with the thermometric substance. The solid melting is controlled by sending electrical heating pulses.

In the constant flux method (fig. 3), the bath temperature is set at a value slightly higher than the CO_2 transition. The energy from the bath reaching the thermometric substance makes the enthalpy of the solid increase, then makes the substance melt by latent heat absorption. During the triple point transition, the thermometer sensing element (measuring only its own temperature) is thermally influenced on one part by the

transition temperature and on the other part by the surroundings that is necessarily in this method at higher temperature. Strictly, the thermometer indicates an intermediate temperature.

In the "quasi-adiabatic" method, the temperature of the cell surroundings temperature is as close to the phase transition temperature as possible (fig. 4). Controlled electrical heating brings the energy necessary to melt the solid. During the transition, after stopping the heating and waiting for thermal equilibrium within the cell, the measurements are much more representative of the true transition temperature, from a thermal point of view.

Using the two techniques (constant flux and quasi-adiabatic methods) is one way to estimate the uncertainties coming from the thermal conditions and a way to optimize the design of the cell.

2.2. Cell preparation and CO_2 filling

After chemical cleaning, the mechanical pieces are hard soldered. The cell is then connected to the gas filling system. The purity of CO_2 is 4N8 and the impurity composition is given in table 1.

Table 1
CO_2 nominal impurity analysis.

Impurities (molar concentration $\times 10^{-6}$)	
H_2O	3
O_2	2
C_nH_m	2
H_2	0,5
N_2	8

The cell is flushed five times with the filling gas, and then placed in liquid nitrogen. The CO_2 liquid level is adjusted in order to fill the cell to a height of 12 cm. So the liquid entirely surrounds the thermometer well on a height twice the height of the sensing element. This is the best compromise to ensure both the thermal immersion of the thermometer, to fit the dimension of the thermometer and the associated thermal enclosures at our disposal. Copper tubes, placed inside the cell around the thermometer pit improve the heat exchanges within the CO_2 sample. After filling, the cell is sealed by pinching the filling tube that is then mechanically protected by a brass cap.

3. Setting the temperature

The cell was first placed in a temperature controlled liquid bath for constant flux method measurements at LNE-INM. This cell was then studied by an adiabatic method at NIS using a device that was previously developed in the frame of a cooperation between the two laboratories. All the experiments were jointly conducted by the teams of the two institutes.

3.1. Measurements by adopting the constant flux method

At LNE-INM, the cell was placed in a 7381 Hart Scientific bath, immersed in alcohol, the top of the cell 5 cm below the surface. The temperature set point was then adjusted to reach roughly 5 K below the CO_2 triple point value, in order to observe and go pass the super-cooling process (fig. 5).

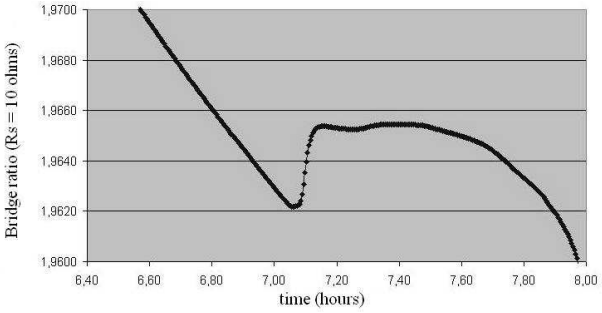

Fig. 5. – The freezing of CO_2. The bath temperature is adjusted at a value, which is 5 K below the CO_2 triple point. The super-cooling is then observed and stopped for a temperature value of 350 mK below the plateau (thermometer YSIB91265).

The thermometer signal is measured by a MI6010T bridge and sent to a computer using a homemade Labview software. After complete freezing of the substance and after waiting for the thermal equilibrium between the cell and the bath, the difference in temperature between the minimum temperature reached and the temperature plateau, ΔT, is estimated. Then the bath set point is adjusted in order to be roughly 100 mK below the transition

After thermal stabilisations, the set points are incremented step by step, 10 mK per 10 mK (which is the regulator resolution). The temperature changes are recorded and the temperature steps, δT_i, displayed on the PC screen. The best set point value is obtained when $\delta T_i < \delta T_{i-1}$ for increment i. This corresponds to the fact that the energy reaching the cell is no longer used for increasing the enthalpy but to liquefy some amount of the solid. The plateau is then recorded as a function of time.

The plateau durations for the melting were significantly increased after wrapping the cell body in a layer of stainless steal grid. The reason is that the grid modifies the convection conditions around the cell and then the thermal resistance is increased. The grid behaves as a temperature integrator for the bath temperature fluctuations.

3.2. Measurements by adopting the "quasi-adiabatic" method.

A "quasi-adiabatic" calorimeter was developed in the frame of a PhD thesis completed in the thermometry group of LNE-INM by Mohamed Gamal AHMED [3, 4]. This calorimeter was devoted to the argon point. Then the

CO_2 cell developed here was designed in order to be adapted to this calorimeter.

The cell was placed in the experimental space of the calorimeter (fig. 6). This space was first evacuated, at room temperature, and then introduced within the thermal enclosure. For this study, two different enclosures were used. The first of them is the one already used for realising the argon point and is a Dewar filled with liquid nitrogen. The second enclosure is a temperature controlled ethanol bath, based on the same principle as the one used at LNE-INM for realising the CO_2 by a constant flux method.

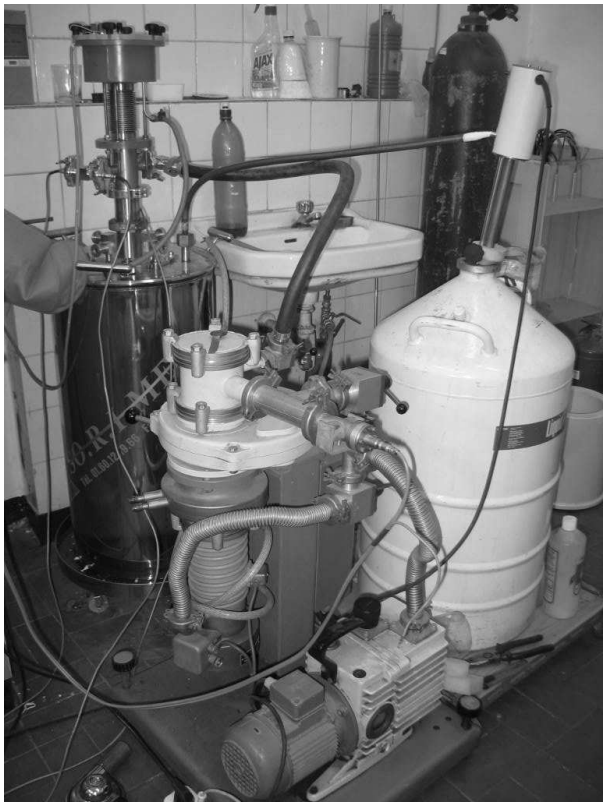

Fig. 6. – "Quasi-adiabatic" calorimeter developed in the frame of a collaboration between NIS and LNE-INM. In the foreground, the pumping system and the liquid nitrogen tank. In the background, the protection box for the thermometer head and the device allowing the moving under vacuum of the cell inside the experimental space can be seen above the main liquid nitrogen bath.

The cooling of the cell is realised by mechanical contact (under vacuum), between the bottom part of the cell and the cold part of the calorimeter. After the sample freezing, the mechanical contact is removed. The upper part of the cell is electronically temperature controlled with a thermal link to the cold part of the cryostat (sliding mechanical contact along the internal wall of the experimental space). A heater is wound around the bottom part of the cell and allows the supply of heat pulses.

The thermometer is connected to a F18 bridge and the data is recorded by using homemade software in Visual Basic.

4. Results

4.1. Constant flux method

The transition is realised and observed by the method described in paragraph 3.1. When the set point has been adjusted, the temperature variation is then recorded (fig. 7).

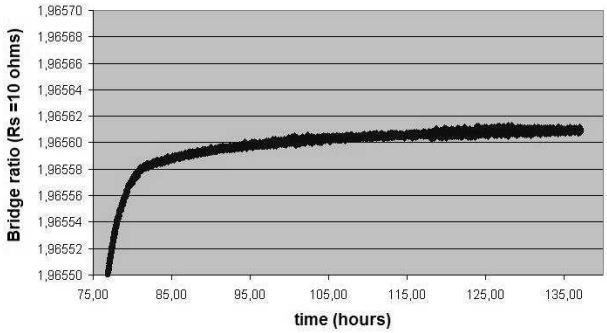

Fig. 7. – Experimental plateau realised by the constant flux method. The melting is not finished. The plateau was deliberately stopped after two days within the transition. The temperature difference between the "end" and the beginning of the plateau is less than 2 mK (thermometer: YSIB91265).

4.2. Quasi-adiabatic method

4.2.1. In the liquid nitrogen Dewar

This instrumentation is of course not the "ideal" one for realising this point. The temperature difference between the phase transition and the nitrogen bath is roughly 150 °C and drives to huge temperature gradients and spurious heat fluxes. But the experiment was nevertheless carried out to study the possibility of associating several cells in the same device as it was made for multicells [5].

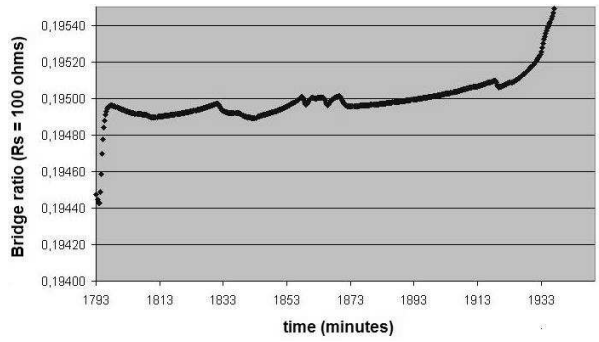

Fig. 8. – Experimental plateau realised in the liquid nitrogen bath by the quasi-adiabatic method. The expected adiabaticity conditions were not reached. The thermometer in the cell detects the temperature variation due to the thermal screen regulation (Thermometer H274242).

The results (fig. 8) showed it is possible to observe the melting plateau but the plateau duration is paradoxically smaller than the one observed by the constant flux method (two hours in this example). During the transition, temperature instabilities of roughly 0,1 °C were observed.

The effect of the heat pulses is not observed and the plateau, in the configuration of the NIS, is very sensitive to the electronic temperature regulation that has to be improved. The end of the plateau corresponds to a lack of liquid nitrogen in the main bath and consequently to a change in the thermal immersion conditions.

Consequently, the temperature difference between the transition and the main bath has to be reduced and thus a temperature-controlled bath is needed.

4.2.2. In a temperature controlled bath

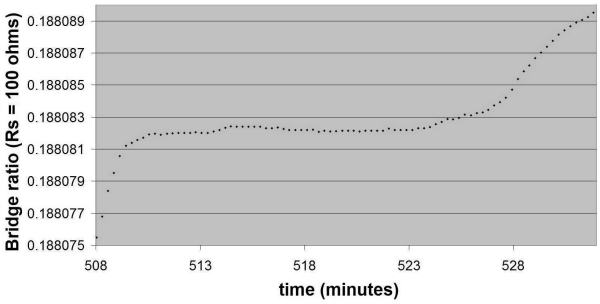

Fig. 9. – Experimental plateau realised in the NIS home-made temperature controlled bath. The width of the transition is about 1 mK. The plateau duration is only 20 min, due to "difficulties" in controlling the temperature of the liquid bath (H228855).

The same device was put in the NIS homemade temperature-controlled bath for measurements by the "quasi-adiabatic" method (fig. 9). The figure shows that the heat pulses supply has no effect, because of the long thermal path between the heating element and the thermometer-sensing element. The plateau is quite short (20 min) due to problems with the thermal regulation of the main bath. This bath needs evidently to be replaced. Nevertheless these results confirm the capabibility of the cell to reach our first goal, which was to develop a transfer standard for SPRTs calibration.

5. Conclusions

This first approach demonstrates the feasibility of the realisation of the CO_2 triple point by a constant flux method in temperature controlled bath with an uncertainty compatible with the routine calibration uncertainties for long stem thermometers in this temperature range (calibration by comparison, typical uncertainty: 10 mK). The adiabatic method has to be used again with appropriate instrumentation to confirm the possibility and perhaps improve the capability of the cell in terms of uncertainty. The study must also be completed in order to set the periodicity of the calibration.

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