Hydrostatic Pressure Correction Coefficient of the Triple Point Cell of Water

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The hydrostatic pressure correction coefficient of the traditional triple point cell of water is determined from the measurements of temperature distribution along the thermometer well. The hydrostatic pressure coefficient obtained from these measurements is $-0.855(30)$ mK/m, which is slightly different from the recommended value, -0.73 mK/m, of the International Temperature Scale of 1990. The latter is the value calculated from the liquidus curve of ice. This discrepancy is estimated to be caused by the difference between free-floating ice and the ice mantle in the cell which is compulsorily immersed around the thermometer well. The temperatures near the bottom of the thermometer well are also confirmed to be cooler than the other part of the thermometer well. It is recommended that these new uncertainty sources must be included in calibrating thermometers at the triple point of water.

This article is the summary of the next two papers concerning the hydrostatic pressure correction coefficient on the triple point cell of water.

- Precise Measurement of Hydrostatic Pressure Correction Coefficient of Triple Pint Cell of Water,

  Trans. Soc. Instrum. Contr. Eng. **38**(2002) 590

  by H. Sakurai

- Precise Determination of Hydrostatic Pressure Correction Coefficient of the Triple Point Cell of Water Using Cryogenic Current Comparator bridge,

  Jpn J. Applied Physics **44**(2005)

  to be published in May 2005.

  by M. Nakanishi and H. Sakurai

1. Introduction

The triple point cell of water is one of the most important equipment for the temperature standards, i.e. the International Temperature Scale of 1990 (ITS-90)[1)].

A typical triple point cell of water has the structure of a cylindrical glass container containing about 1 L of pure water, at the center of which is a glass thermometer well of more than 25 cm depth. The ice mantle is formed around the thermometer well. To calibrate a thermometer precisely at the triple point of water, the hydrostatic pressure correction is needed as the sensing element of the thermometer is placed near the bottom of the thermometer well, which is not the triple point but the equilibrium of liquid and solid under the hydrostatic pressure.

The hydrostatic pressure correction coefficient of the triple point cell of water has been thought to be consistent with the slope of the liquidus curve of ice, but it should be determined experimentally from the temperature distribution along the thermometer well. To avoid the confusion of these two values in this article, the slope of the liquidus curve, which is equivalent to the recommended value of the ITS-90, will be called as '**recommended value**' hereafter and the value determined by the measurement of the temperature distribution will be called as '**experimental value**'.

Both values have been expected to agree with each other within the experimental uncertainties. However, the experimental value has not been confirmed to be consistent with the recommended value. In any way the coefficient obtained from the temperature distribution along the thermometer well, the experimental value, is practically preferable to use as a correction coefficient in calibrating thermometers.

McAllan pointed out first this disagreement[2)]. He thought that the main reason of this discrepancy is caused by the cylindrical crystals of ice in the cell. But the difference of two values seems to be too large to be explained only by the *shapes* of the ice crystals.

The difficulties in measuring the temperature distribution along the thermometer well of the triple point cell are in the reasons as follows.

1. Thermal conduction through thermometer sheath will disturb thermal conditions of the liquid/solid surface along the thermometer well.

2. The self-heating in measuring the resistance of a thermometer disturbs thermal conditions.

3. The measuring precision should be better than 30 μK.

Considering these, we measured the temperature distribution along the thermometer well of the triple point cell of water and determined the hydrostatic pressure correction coefficient using

- three different cells including two different types,
- two different measuring systems, i.e. a traditional direct current comparator bridge and a new designed cryogenic current comparator bridge,

  and

- three kinds of thermometers with different thermal conduction.

The results show that the recommended value of the ITS-90, −0.73 mK/m, differs slightly from the experimental values by about 15 %.

Another minor problem of the triple point cell is the temperature anomaly at the bottom of the thermometer well. This phenomenon will also give some uncertainty in calibrating thermometers. However, any caution is not mentioned in the Supplementary Information of the ITS-90 and also of the IPTS-68. Some results will be demonstrated in this article.

2. Experimental equipment

2.1 Thermometers

In measuring the temperature distribution of the triple point cell, one of the reasons of the discrepancy between the recommended value of the TS-90 and the experimental value has been thought to be the thermal conduction through the sheath and the leads of a thermometer.

To eliminate such thermal disturbance, three different thermometers with different thermal conduction were used, i.e. *a standard long-stem platinum resistance thermometer*, *a standard capsule type platinum resistance thermometer* and *a thermistor thermometer*. The long stem thermometer is a typical single coil type thermometer and was used without any modification. The capsule type thermometer was covered with a cooper block and a stainless steel tube as shown in **Fig. 1, B**.

The sensor of the thermistor thermometer was mounted at the top of the thin glass tube as shown in **Fig. 1, A**. The both ends of the glass tube with four leads were sealed. The thermistor thermometer shows initially some drift of about 0.1 mK/h, but after the thermistor was kept for about a month in the triple point cell, the drift became 5 μK/h. So the thermistor was always kept in the cell's bath and before using thermistor thermometer, the thermometer was kept for about 12 h in the cell measuring the drift rate. In measuring the temperature distribution of the thermometer well of the cell, the data were corrected by this drift rate.

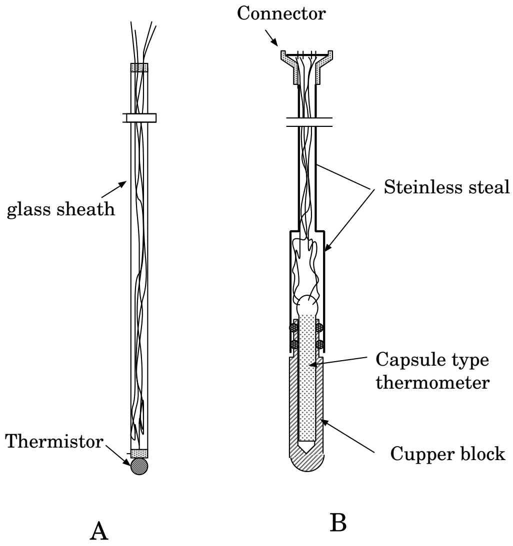

Fig. 1: Schematic side view of the sheath assemblies of a thermistor thermometer (A) and a capsule type thermometer (B). The outer diameter of the copper block is 11 mm and its length is about 50 mm. The outer diameter of the glass tube is about 4 mm.

2.2 Resistance measuring instruments

The precise resistance measurement with the low self-heating is compulsorily needed for the precise measurement of the temperature distribution along the thermometer well. For such purposes, two measuring instruments are used, i.e. a direct current comparator bridge (**DCC bridge**, sw6010/TTI3, Measurement Insternational) and a cryogenic current comparator bridge with a SQUID-flux detector (**CCC bridge**, designed and fabricated at MIJ/AIST[4)]).

The DCC bridge was operated with the measuring currents of 0.3 mA for the SPRT's and of 15 μA for the thermistor. The self-heating temperature rise by these currents was less than 0.1 mK.

The CCC bridge is basically the same structure as those used for the resistance standard[5, 6)] except the current comparator transformer. The transformer was specially designed for the measurement of a SPRT; the resistance ratio between 25.5 Ω and 1 Ω is measurable with low measuring currents, such as 100 μA or less[4)] within the uncertainty of the order of 10^{-8}.

Table 1: Specification of the triple point cells of water used in those experiments.

Cell	serial number	manufacture	structure*)	well depth**) cm
H-1	1102	Hart	NBS-type	26.7
T-1	1325	Toa	Toa-type	31.1
T-2	1968	Toa	Toa-type	31.0

*) NBS-type means the thermometer well has not a extended guide pipe above the cell and Toa-type has a long glass guide.
**) The well depth is the length between the liquid level and the inner bottom of the thermometer well.

The CCC bridge was used only for the measurement of the *capsule type SPRT* with the operating current of 100 μA. The long-stem thermometer and the thermistor may not be measurable. It is because the CCC bridge is so sensitive against electric noises.

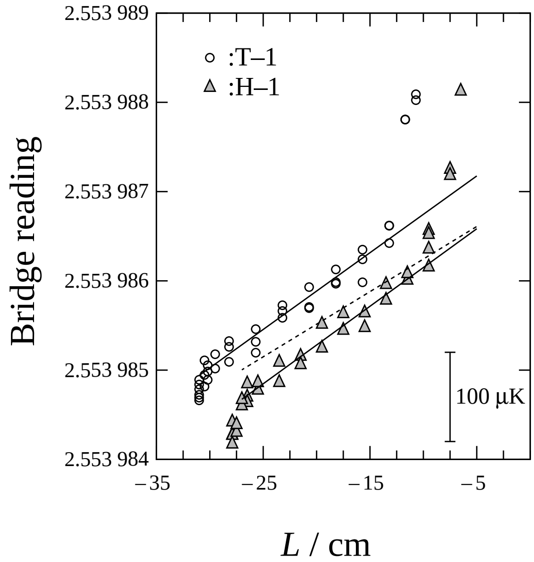

Fig. 2: Hydrostatic pressure effects of two different types of cells measured by the capsule type platinum resistance thermometer. The solid lines are determined by the method of least squares using the data from 1.5 cm above the bottom of the thermometer well to 10 cm (H-1) or 13 cm (T-1) below the water level. The dotted line is the recommended value of the ITS-90[3)].

2.3 Triple point cells

Three cells, with two different types, were used in those experiments as listed in **Table 1**. For the direct current comparator measurements, two cells, H-1 and T-1, were used. For the cryogenic current comparator measurements, two cells, H-1 and T-2, were used.

The ice mantle was formed by a heat-pipe cooled by liquid nitrogen. After forming the ice mantle, the cells were kept in a liquid bath controlled at about 0.01 ℃ for more than a week to eliminate the initial drift of the cell temperatures.

3. Experimental procedure

The temperature distribution along the thermometer well was measured by changing the position of the thermometer sensor from the bottom of the thermometer well up to about 10 cm below the water level of the cell. The temperature distribution near the bottom of the well was precisely measured by the thermistor thermometer.

One of the uncertainties in measuring the temperature distribution along the thermometer well is the disturbance of the liquid/solid surface caused by the self-heating. To reduce this disturbance, *the measuring currents were reduced so that the self-heating temperature rise became within 0.1 mK or less.*

Another is whether the thermometer shows precisely the average temperature of the thermometer well at the position of the sensing element. To measure the average temperature precisely, the sensing element of the long-stem thermometer, or of the thermistor, was adjusted *to be always moving at the cylindrical center of the thermometer well* using a guide pipe at the top of the thermometer well. For the capsule type thermometer, as the sensing part was covered with the copper block with nearly the same diameter of the thermometer well, the copper block is expected to show the average temperature and no guide pipe was used.

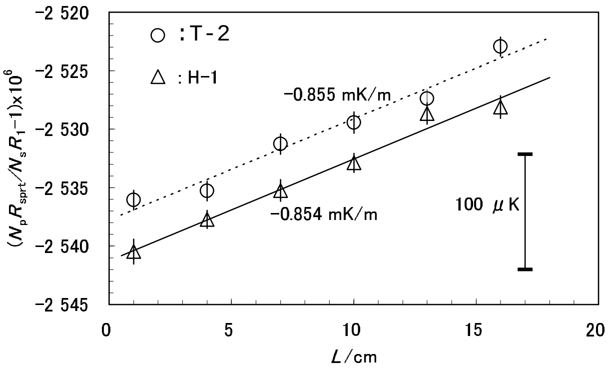

Fig. 3: Temperature distribution along the thermometer wells of two triple point cells of water. The horizontal axis is the position of the sensing element of the SPRT measured from the bottom of the thermometer well. The vertical axis is the deviation from the balanced value of the CCC bridge, which is approximately proportional to the deviation of temperature. R_{SPRT} is the resistance of the thermometer and the bars indicate twice of the standard measurement uncertainty[4].

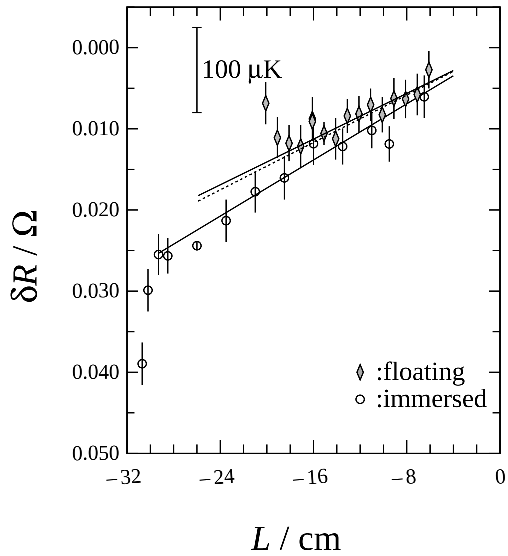

Fig. 4: Difference of temperature distribution between the floating ice mantle (upper solid line) and an immersed one(lower solid line) measured by the thermistor thermometer using the Cell T-1. The vertical scale, δR, is the difference of the thermistor resistance from the value at the water level of the cell. The dotted line is the value of the ITS-90.

4. Results and discussion

4.1 Hydrostatic pressure coefficient of the triple point cell of water

The results of the temperature distribution along the thermometer well of three cells are shown in **Fig. 2** for the measurements by the DCC bridge and in **Fig. 3** by the CCC bridge. Both figures are the results obtained by the capsule type thermometers. The results obtained by the long-stem thermometer and the thermistor thermometer are nearly the same as Fig. 2.

The horizontal axis of Fig 2 is the depth of the thermometer measured from the water level. On the other hand, the horizontal axis of Fig. 3 is the height of the thermometer measured from the bottom of the well. The solid lines of Fig. 2 and the solid and dotted lines of Fig. 3 are calculated by the method of least squares using the data from about 1.5 cm above the bottom of the thermometer well to about 10 cm below the water level of the cell. As the thermal condition near the bottom of the well differs from the other part, the data near the bottom were eliminated from the estimation.

The slopes of these lines correspond to the hydrostatic pressure correction coefficient of the triple point cell of water. The vertical values of the data depend on the total depth of the thermometer well, the impurities in the water of the cell, the isotope content of water and so on.

The dotted line in Fig. 2 is the recommended value of the ITS-90. Two slopes of the solid lines obtained from the temperature distribution measurements agree well. However, systematic differences can be seen between the slopes of the solid lines and the recommended value of the ITS-90.

The results are summarized in **Table 2**. The scatters of the DCC bridge are larger than those of the CCC bridge, but the average values agree well. The recommended value of the ITS-90 differs from the average value of the experimental values by about 15 %. In practical calibration of thermometers, the difference between these is not so important but should be included in one of the the uncertainty sources. Further more, the experimental value may be superior to the recommended value of the liquidus curve of ice, if the hydrostatic pressure correction is needed.

4.2 Temperature distribution of floating ice mantle

The next problem is why the difference happens between the value of the liquidus curve of ice and these obtained from the temperature distribution. There may be two possibilities.

1. One possibility is that the slope of the liquidus curve of ice is not correct in such low pressures as hydrostatic pressure.

Table 2: Summary of the hydrostatic pressure coefficient measured by DCC bridge and CCC bridge

source	thermometer	measurement current	Hydrostatic pressure coefficient H-1	T-1	T-2	average
		mA	mK/m			
ITS-90						−0.73
Sakurai[3)]	capsule SPRT	0.3	−0.860(10)	−0.868(18)		
	long stem SPRT	0.3	−0.887(13)	−0.843(7)		
	thermistor	0.015	−0.865(47)	−0.847(12)		
	average					−0.856(15)
Nakanishi et.al.[4)]	capsule SPRT	0.1	−8.854(46)		−0.855(30)	
						−0.854(39)
average						−0.855(30)

To confirm the slope of the liquidus curve in the low pressure range below 100 kPa, the pressure dependency of the ice/liquid equilibrium was measured by fabricating a new triple point cell with a glass pipe, through which the ice/liquid equilibrium is pressurized by helium. The result[3)] was −73.9 mK/MPa, which is equivalent to −0.724 mK/m. This value is close to the recommended value of the ITS-90, −0.73 mK/m.

The pressure dependency of the liquidus curve of ice may be applicable to such hydrostatic pressure range.

2. Another possibility of the discrepancy is that *the ice in the triple point of water is not the same as the free-floating ice.*

   To confirm this possibility, the temperature distribution along the thermometer well was measured using the floating ice mantle around the thermometer well. For this experiment, the ice mantle was formed along the thermometer well of T-1 from 2 cm above the bottom of the well in the same way as mentioned. There is no ice near the bottom of the thermometer well. The cell was kept for about a day in the water bath. Then the thin layer of the ice was melted along the thermometer well and the ice mantle is floating around the thermometer well.

   In this condition, the temperature distribution along the thermometer well was measured by the thermistor thermometer. The results are shown in **Fig.4** (the upper solid line). The hydrostatic pressure coefficient calculated from the data 9 cm to 16 cm is −0.704(75) mK/m. The dotted line in this figure is the recommended value of −0.73 mK/m. The result of the immersed ice mantle is the lower solid line in this figure. The temperature distribution along the thermometer well of the floating ice mantle differs clearly from that of the immersed ice mantle.

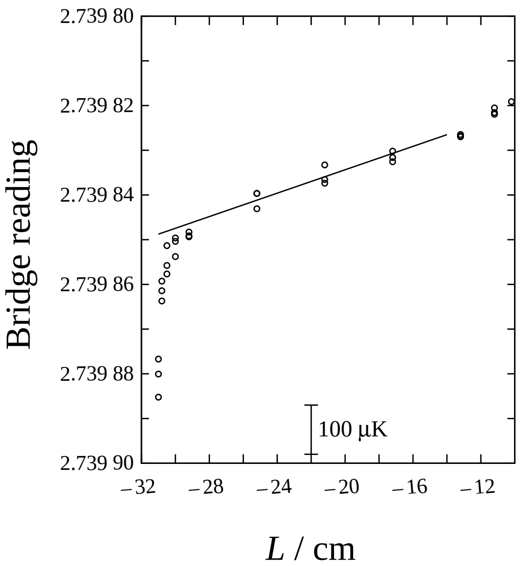

Fig. 5: Precise temperature distribution near the bottom of the thermometer well measured by the thermistor thermometer using the Cell T-1.

By the compulsory immersion of the cylindrical ice mantle, the ice may be tensioned by buoyance. It may be reasonable to think that by this force the virtual hydrostatic pressure becomes large and that the hydrostatic pressure coefficient is changed.

The temperature distribution of the floating ice mantle could not be measured so precisely as that of the immersed ice mantle in this experiment, but the results obtained here are indicating that the expansion tension of ice mantle in the triple point cell has an important role in solving the inconsistency between the pressure dependency of the ice/liquid equilibrium and the hydrostatic pressure coefficient of the triple point cell. Further theoretical calculation and the more precise measurements are needed, which will clarify the inconsistency.

4.3 Temperature distribution at the bottom of the well

As shown in Fig. 2 and in Fig. 4, the temperatures near the bottom of the thermometer well were cooler than the other part of the well. It is because the ice mantle was immersed by the thermometer well and the ice crystals near the bottom of the well are pressurized. The precise temperature distribution was measured using the thermistor thermometer. The results are shown in **Fig.5**. The results tell that the bottom temperature is cooler than that of other parts of the well by about 0.2 mK.

This temperature dip might depend on the size of the ice mantle, i.e. the diameter and the length of the ice mantle. In this experiment the outer diameter of the ice mantle is about 30 mm and the lenth is about 300 mm. The total volume of the ice mantle is about 400 cm^3. The ice mantle in the cell is immersed against the buoyance of the density difference between ice and water. If we assume that the bottom surface of the thermometer well (15 mm in outer diameter) is keeping this ice mantle homogeneously, the pressure of the ice at the bottom is about 0.19 kPa. By this pressure, the temperature of ice is cooled by about 0.14 mK compared with that of the vertical part of the well. The results shown in Fig.5 agree well with this calculation result.

From these results, it is recommendable to put some insulator spacer with about 1 cm length at the bottom of the thermometer well.

5. Conclusion

In using a typical triple point cell of water, some caution must be needed.

1. The hydrostatic pressure correction coefficient obtained from the temperature distribution of the thermometer well is -0.855 mK/m, which slightly differ from the value of -0.73 mK/m. The latter value includes about 15 % uncertainty.

2. The temperatures near the bottom of the thermometer well are cooler than the other part of the well. It is recommended to use some insulator spacer in the bottom of the thermometer well.

References

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