Effects of different methods of preparation of ice mantles of triple point of water cells on the temporal behaviour of the triple-point temperatures

G. T. Furukawa, B. W. Mangum and G. F. Strouse

Abstract. We report results of an investigation of the temporal variation of the temperature of triple point of water (TPW) cells, in which the ice mantles were prepared by four different techniques using: (i) solid CO_2, (ii) an immersion cooler, (iii) liquid-nitrogen-cooled rods, and (iv) liquid nitrogen (LN), first passing cold nitrogen vapours and then LN directly into the wells of the cells. The temperature of the TPW cell water was either approximately 274 K or 295 K when the freezing of the ice mantle was started. No visible cracks formed during the preparation of any of the mantles using the crushed solid-CO_2 or the immersion-cooler method, but all of the ice mantles cracked when prepared using the LN-cooled-rod and LN techniques. The cracked mantles, however, soon healed. Initially, the temperatures of the mantles prepared by the four methods varied, but after about three or four days they agreed to within 0,1 mK; after one week they agreed to within 0,03 mK, except for mantles prepared by the LN technique, for which nine days were once required for one of the mantles; after eleven days, the results were practically the same. It appears that the temperature variations observed during the first few days following the preparation of mantles could be caused by a combination of (i) temperature decrease due to introduction of strains in the ice and to formation of fine ice crystals during the preparation of the mantle and (ii) temperature increase due to the relief of strains and the gradual conversion of fine ice crystals to larger ice crystals. Mantles that underwent severe cracking thereby released most of the energy associated with the large strains introduced during preparation of the mantle.

1. Introduction

Bonhoure and Pello [1] reported large variations (maximum exceeding 1 mK) in the observations taken over a period of about one year on triple point of water (TPW) cells, prepared for use by freezing the ice mantle within about 1 h, using liquid-nitrogen-cooled rods. Their measurements started about 48 h after the mantles were prepared. Usually, the temperature of a cell decreased from initial "high" values over the measurement period of about thirty days. When the initial values were "low", they remained relatively stable at the low values. Later, the same cells exhibited much smaller variations (0,2 mK) when they were prepared by "slow freezing in steps" using LN-cooled rods over four days, or by using solid CO_2 to freeze the ice mantle, probably within about 30 min. Measurements on each of the mantles were usually made over a period of about one month. The wide variations were attributed to large strains introduced through rapid cooling with the LN-cooled rods, with numerous cracks often being introduced in the mantle. Also, it was suggested that variations in the segregation of impurities in rapid and slow freezes may have contributed to the differences in observations. Their data also show that one TPW cell (produced in the United States of America) yielded ice mantles that were somewhat more stable, irrespective of the method of preparation.

To check for temporal variations in the triple-point temperature, as observed by Bonhoure and Pello [1] and by Berry [2], and to determine how long a newly prepared mantle in a TPW cell should be aged before use in an optimal realization, we conducted experiments on four TPW cells of the same design and manufacture (see Table 1), using four cooling methods to prepare the ice mantles: (i) solid CO_2, (ii) an immersion cooler, (iii) liquid-nitrogen-cooled rods, and (iv) liquid nitrogen (LN), first passing cold nitrogen vapours and then LN directly into the wells of the cells. Three of the TPW cells contained freshly prepared ice mantles and the fourth contained a thermally stabilized (aged) ice mantle. A comparison was then made between

G. T. Furukawa,* B. W. Mangum and G. F. Strouse: National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, USA.

* Guest researcher at the NIST.

the temperatures at the inner melt/ice interface of ice mantles formed around the central thermometer wells. A preliminary report on some aspects of this work was presented previously [3].

Earlier, Berry [2] observed that when ice mantles were frozen using solid CO_2, the TPW-cell temperatures increased by 0,2 mK to 0,5 mK during the first two days after preparation, before stabilizing to equilibrium values. These initial changes in temperature were attributed to relief of strains and crystal growth in freshly prepared ice mantles. Berry suggested that to reproduce measurements to 0,1 mK, an ice mantle should be aged for about three days, and for comparison of cells, about five days. Out of fifty mantles that were prepared, Berry found that the temperatures of four of them peaked by about 0,1 mK even as long as two days after preparation. (The term "peaking", as used by Berry, is interpreted to mean that the values are higher during the initial two or three days of ageing, following the preparation of the mantle, than the final equilibrium value). Although no explicit statement is given in Berry's paper, it is assumed that the peaking was observed with cells prepared using solid CO_2. Berry also prepared ice mantles by (i) using LN-cooled rods and (ii) forcing LN into the thermometer well for even faster (8 min) freezing. He did not mention any large variations in the temperatures of these cells, other than the initial temperature increase immediately following the preparation of the ice mantle and its stabilization after several days. No statement is made in Berry's paper about mantles cracking during preparation. Of the ten new and old TPW cells that were investigated, Berry found their equilibrium temperatures to agree to within 0,1 mK. He felt that the amount of impurities in the cells was extremely small.

All ice mantles cracked when they were prepared by the LN-cooled-rod and LN-cooling techniques. No visible cracks formed using the crushed solid-CO_2 or the immersion-cooler method. Efforts were made to determine the effects of the cracking, and of the subsequent healing of the cracks and annealing of the ice, on the triple-point temperature during the first few days following the preparation of a mantle. At the beginning of our experiments, it was thought that observing the mantle with polarized light might reveal strains resulting from different methods of preparation. Although there were some distinct variations in the appearance of the initial thin layer of ice mantle, such as opaqueness or milkiness (fine ice crystals), we were unable to record the difference photographically. Consequently, the process was abandoned in subsequent experiments.

The effects of isotopic separation during freezing by the four methods used have not been considered. Also, no attempt was made to separate the temperature effects caused by the relief of strains from those caused by the growth of larger crystals from fine ice crystals.

In this paper, we first describe the four methods used to prepare the ice mantles, then the TPW cells used in the investigation, the equipment used in the measurements, the measurement procedure, and finally the treatment of the data.

2. Preparation of ice mantles

2.1 Background

The preparation of an ice mantle around the thermometer well of a TPW cell requires crystal nucleation points on the well. Since water tends to supercool, these nucleation points are formed by rapidly cooling the well far below the triple-point temperature, using solid CO_2, LN-cooled rods, LN, or other coolants. Usually, the use of a particular coolant is continued until a mantle of adequate thickness is obtained. After the formation of crystallites or an initial layer of ice on the well, however, another method of cooling that extracts heat more slowly may be used.

The temperature at which the initial solid is formed on the thermometer well is expected to depend on the initial temperature of the TPW cell water, on the coolant, on the heat-flow conditions, and on conditions that would influence nucleation such as thermometer well surface, purity and, unlikely but possible, suspended particles. As the preparation of an ice mantle proceeds, the layer of ice next to the thermometer well cools further and becomes colder than the temperature at which it was first formed. Strains caused by cooling the ice may develop and, also, when the ice mantle is later warmed to the TPW equilibrium temperature, strains caused by warming may develop.

When the ice mantle is prepared by rapid cooling methods, the ice of the mantle is at first strained and contains fine crystals. The relief of strains and the growth of ice crystals evolve heat and the two processes are interdependent. Newly prepared ice mantles appear glass clear, but in a few days ice crystal boundaries appear. The rapidly prepared clear ice mantle may be visualized as strained, finely divided ice. If the formation of ice at the thermometer well is rapid enough that no segregation of impurities occurs, the impurity composition of the ice near the thermometer well will be the same as that of the initial bulk liquid. As the ice layer becomes thicker, the ice formation becomes slower and some impurity segregation may occur. The ice mantle would then have impurity concentration gradients. These all result in non-equilibrium liquid/solid phase conditions which can contribute to the temperature change as the system gradually shifts to equilibrium phase conditions.

At the ice/water interface, there is a continuous interchange of water molecules leaving the solid water and becoming liquid water and water molecules leaving the liquid water and becoming solid water. The net process (melting or freezing, respectively) depends on the temperature, pressure, curvature of the interface, and purity. The ice/water temperature equilibrium is established when the rates of the two processes are the same. The net freezing process requires the latent heat of fusion to be extracted from the ice/water interface and to be conducted to colder parts of the ice, i.e. towards the thermometer well. Heat flows in the direction of the temperature gradient from hotter to colder; heat is not conducted through the liquid. During the preparation of an ice mantle in a TPW cell, the rate of ice formation depends on the rate at which heat is extracted from the interface and this depends on the temperature gradient created by the coolant in the thermometer well. During freezing, the temperature of the ice adjacent to the interface must, therefore, be lower than the equilibrium temperature.

During the preparation of an ice mantle there is, in addition to the thermal gradient, a density gradient in the mantle. The differences in density between ice at the temperatures of the TPW and LN and between ice at the temperatures of the TPW and solid CO_2 are 2 % and 1 %, respectively [4]. In preparing the ice mantle by the solid-CO_2 method, the ice that is initially formed around the thermometer well is later cooled close to the solid-CO_2 temperature. Since no visible cracking of ice occurred with this method, it seems that any strains that developed on cooling from the initial temperature of formation to the temperature of solid CO_2 and then on warming to the temperature of the TPW are within the elastic limits of ice. [A milky layer (microscopic cracks or fine ice crystals?) that quickly disappears had been observed next to the thermometer well during the early stages of mantle preparation.] In preparing an ice mantle by the LN-cooling method, strains were apparently developed at or near the elastic limits, for any small mechanical disturbance or warming initiated a cascade of cracking, with strains still remaining in some of the ice or new strains being formed in the ice by the cracking process itself. In the LN-cooled-rod method, the ice mantle warmed slightly while the cooling rod was not present in the thermometer well. Cracking occurred when a LN-cooled rod was reinserted into the well. It is possible that the strains already present in the ice were amplified when the ice was warmed and then cooled, resulting in the cracking. (Note that we did not check to see whether the mantle cracks on warming.) Also, strains of different magnitude are expected to be produced at different rates of cooling or warming. It is expected that cracking would occur at the higher rates of temperature change. Although cracking manifests strains beyond the elastic limits, strains within the elastic limits seem to require more time to be relieved. In the solid-CO_2 method, no cracking occurred but it took several days for the temperature to stabilize as the strains were relieved and the ice crystals grew larger.

Many phases of ice are known to exist at pressures above about 200 MPa [4]. Under ordinary pressure conditions, ice 1 (or the hexagonal phase) exists. Ice in the vitreous and the diamond cubic phases has been produced at low pressures and temperatures by slowly condensing water vapour onto a surface held below 115 K [5, 6]. When the "vitreous ice" is warmed slowly, a glass transition occurs at around 135 K, followed by an exothermic transformation to cubic ice, which in turn transforms exothermally and irreversibly to the ordinary hexagonal ice in the range 160 K to 210 K [6, 7]. Vitreous ice has not been produced by simply cooling liquid water [4]. It is expected that to form vitreous ice, the liquid-water sample must be cooled rapidly far below the glass transition temperature before any exothermic transformation of vitreous ice occurs to convert the vitreous ice to the ordinary form of ice. In the experiments presented here, the cooling with liquid nitrogen was apparently not rapid enough to form noticeable amounts of vitreous ice. It is very unlikely that freezing the mantles by any of our four methods would lead to formation of ice other than in the hexagonal form, and the peaking that has been observed is, therefore, not due to the exothermic effects of transformation from the vitreous state to the ordinary form of ice.

The TPW cells were operated near thermodynamic equilibrium conditions of the ice/water interface at the inner melt. In order for a TPW cell to indicate a temperature lower than the ice/water equilibrium temperature, (a) the water phase or the ice phase, or both, must contain soluble impurities which, during the freezing of the water, form a non-equilibrium impurity distribution, (b) the ice phase must be finely polycrystalline, to the extent that the curvature of the ice results in sufficient ice/water interfacial tension [2], and/or (c) the ice phase must be strained. Considering the manner in which the mantles of the cells were frozen, all three conditions are expected to have existed in a freshly prepared cell. The conditions are metastable, however, and there will be a gradual shift toward the thermodynamic equilibrium conditions on ageing near the triple-point temperature.

2.2 The four methods used to prepare the ice mantles

2.2.1 Crushed solid-CO_2 method

When the solid-CO_2 cooling method was used to prepare an ice mantle, the level of solid CO_2 in the thermometer well was maintained full until a mantle of desired thickness was formed. If the solid-CO_2 level in the well is allowed to become low, cracks are likely to form when more solid CO_2 is added. Cracking occurs because the ice along the thermometer well warms when solid CO_2 is no longer in contact with it and then, when the well is refilled with solid CO_2, the extra stresses caused by the sudden cooling of the ice result in cracking. In this case, cracks appear at the upper parts of the mantle.

Since during the use of a TPW cell the ice mantle melts mostly at the bottom, mantles were made thicker at that position by starting the freezing of ice at the bottom of the thermometer well. First, for enhanced heat transfer, about 1 cm^3 of ethanol was placed in the bottom of the well and then several cm^3 of crushed solid CO_2 were added. The level of crushed solid CO_2 was maintained, by replenishing, for about 3 min. After this time, the well was filled with crushed solid CO_2 to the same level as that of the water in the TPW cell and maintained at that level for about 17 min, by replenishing as needed. During this time, any solid bridging of ice across the top surface, and the possible rupture of the cell, was prevented by gently shaking the cell and warming it at the top. After maintaining the crushed solid-CO_2 level for about 17 min, the crushed solid CO_2 was allowed to sublime completely. The complete sublimation required about 5 min to 10 min. Since the bottom of the thermometer well remained cold longer than the other parts of the well, the mantle became thickest around that part of the well. Approximately 5 min after all of the solid CO_2 had sublimed, the TPW cell was completely immersed in the water of the maintenance bath. (For convenience, in this paper the term "completely immersed" is used to mean that the TPW cell was immersed sufficiently that the water level of the maintenance bath was above the opening of the thermometer well and the well was completely filled with bath water.) In one case (experiment set VI), the thermometer well of the TPW cell was stoppered soon after the solid CO_2 had completely sublimed, and the cell was immersed for 60 min in the maintenance bath for thermal equilibration of the mantle before the complete immersion in the bath. (The term "experiment set" as used in this paper refers to a series of measurements of freshly frozen ice mantles of cells A, B and C and an aged mantle of cell D. See Table 1.)

2.2.2 Heat-pipe immersion-cooler method

The heat-pipe immersion-cooler technique [8] extracts heat from the TPW cell more slowly than the crushed solid-CO_2, the LN-cooled-rod, or the LN methods; hence the preparation of a suitable ice mantle took longer with this method. Also, because of the long freezing times, in cases where the initial TPW cell was 295 K, it is probable that the bulk of the water was cooled close to 274 K in the freezing process.

As with the solid-CO_2 method, it is desirable to prepare mantles that are thicker at the bottom of the thermometer well. Also, for efficient use of the immersion cooler, a small amount of ice is required around the bottom of the thermometer well before starting the preparation of the remainder of the mantle. Consequently, about 1 cm^3 of ethanol and several cm^3 of crushed solid CO_2 were first placed at the bottom of the well. After about 3 min, when a knob of ice had formed around the bottom of the thermometer well and all of the solid CO_2 had sublimed, the immersion cooler was inserted into the thermometer well and the well was filled with ethanol by slowly pouring it along the tube of the immersion cooler. The ethanol was used to enhance the heat transfer between the heat pipe and the thermometer well. With ice already present on the bottom of the thermometer well, the ice mantle grows up the thermometer well. As the mantle becomes thicker, the ice next to the thermometer well should become colder until quasi-steady-state cooling by the heat pipe is reached. Although solid CO_2 in ethanol was the coolant used for the operation of our heat pipe (which uses difluorodichloromethane as the working fluid), the thermometer well never cooled to the temperature of solid CO_2.

The time required for a suitable mantle to form (using a 7,9 mm O.D. heat pipe in the 13 mm I.D. well of the TPW cell) was about three times that required for the solid-CO_2 method. (A larger heat pipe, about 13 mm O.D., should be able to maintain the thermometer well at a lower temperature and thereby reduce the time required to obtain an ice mantle of the desired thickness.) When this method was used to prepare the ice mantle with the TPW cell exposed to ambient conditions and initially at 295 K, an interval of approximately 135 min was required to form a mantle of suitable thickness. Therefore, only the mantle of one cell (cell C) of experiment set I was prepared under these conditions. In subsequent preparations of mantles using this method, the TPW cell was placed inside an empty Dewar to provide thermal insulation, reducing the required time for the formation of a suitable mantle to about 80 min. When a suitable mantle was frozen, the ethanol was poured out of the thermometer well, the well was stoppered, and the cell was immersed in the maintenance bath for thermal equilibration of the mantle. (For brevity, the term "immersed in the maintenance bath" is used to mean that the TPW cell was immersed in the maintenance bath with the opening of the thermometer well stoppered and the bath water level above the stopper.) After approximately 5 min (60 min in experiment set VI), the stopper was removed and the cell was completely immersed in the bath (see Section 2.2.1).

2.2.3 LN-cooled-copper-rod method

With the LN-cooled-rod technique, cooling is interrupted for short intervals during the exchange of the cooling rods. If the diameter of the LN-cooled rods is small and the rods are exchanged frequently enough, the temperature excursion and change in the level of the heat-transfer liquid (in our case, ethanol) in the thermometer well, can be minimized. In our method, however, at some point during the exchange of the cooling rods, the ice mantle became thick enough and warmed enough (because of the drop in the ethanol level whenever the rod was removed) to cause cracking when a newly-cooled rod was inserted into the thermometer well to cool and raise the ethanol level again.

In our setup, the thermometer well was filled with enough ethanol that on insertion of one of the two copper rods used for freezing the mantle, the ethanol level was the same as that of the water in the TPW cell. Throughout the preparation of a mantle, the ethanol level was maintained at that level while the copper rod was in the thermometer well. To form an ice mantle, each copper rod (9,5 mm O.D. × 25,5 cm long) was cooled in a Dewar of liquid nitrogen before being inserted into the well. The rods were changed at 2 min intervals, except for three cases described below in which the intervals were 1 min or 3 min. Except for these three cases, between twelve and fourteen LN-cooled-rod insertions over a period of about 30 min were required to form an ice mantle of suitable thickness.

On the first or second rod insertion, a bulb of ice started to form at the bottom of the thermometer well. The mantle grew with each insertion of the cooling rod, but cracks began to form in the mantle starting from about the fourth rod insertion. Cracks grew and increased in number with each additional insertion of the cooling rod. Later some of the cracks that had formed began to heal, i.e. became smaller. To thermally equilibrate the mantle after it had become sufficiently thick, the ethanol was poured out of the thermometer well, a stopper was placed in the opening of the well, and the cell was immersed in the maintenance bath. After the cell had been in the bath for approximately 5 min (60 min in experiment set VI), the stopper was removed and the cell was completely immersed. The cracks continued to heal while the TPW cell was in the maintenance bath. Generally, cracks appeared with fewer rod insertions when the initial cell temperature was 274 K instead of 295 K.

2.2.4 LN-cooling method

With LN cooling, mantles were prepared by counter-flowing cold nitrogen vapours and liquid through a multi-tube cooler, comprising two concentric vacuum-jacketed tubes (a total of four thin-wall stainless-steel tubes). The inner tube, through which LN was introduced, extended down to the bottom of the thermometer well. The outer, vacuum-jacketed shorter tube extended down to about 1 cm below the water surface in the TPW cell. The nitrogen vapours exited between the two tubes at the top. Initially, only cold nitrogen vapours entered the well. LN began to enter the well when ice formed on it. Generally, the ice mantle began to form in 15 s when the initial cell temperature was 274 K and in 60 s when the initial temperature was 295 K. A mantle of desired thickness formed in about 6 min to 9 min. Warm air from a hot-air gun was directed at the top of the cell to prevent the ice formed on top of the water in the cell from bridging across the cell. Cracks appeared in the lower third of the mantle during preparation. After forming the mantle, the cooler was removed from the thermometer well. Noticeable cracking of the mantle continued after removal of the LN transfer tube and while the LN remaining in the well was boiling away. There were occasions when no cracks formed in the mantles during preparation. When the flow of LN was stopped, however, a sufficiently rapid change occurred in the temperature of the mantle, or removing the cooler caused enough vibration of the cell, to suddenly initiate numerous cracks, the cracking being readily audible and in some cases sufficiently violent to cause visible movement of the cell.

When all of the LN had evaporated from the thermometer well, a stopper was placed in the opening of the well, and the cell was immersed in the maintenance bath to thermally equilibrate the mantle. After the cell had been in the bath for 5 min in experiment set V, 60 min in experiment set VI, or 30 min in experiment set VII, the stopper was removed and the cell was completely immersed.

3. Equipment and experimental techniques

3.1 Triple point of water cells

Four Jarrett Instrument Company Type A TPW cells, identified in Table 1, were used for this investigation. They were selected from a bank of cells as the best (containing the smallest amount of air) for investigating different methods of preparing the TPW cells for use. Since the solubility of air in water increases with decrease in temperature, all four cells were maintained at room temperature for 48 h before testing for the amount of air in the cell. In the first test, the cells were gently inverted to listen for the sharp, water-hammer "click" as the water vapour collapses with little or no non-condensable gas present. The smaller the amount of air, the sharper the click sound; a large amount of air cushions the water hammer and the sound is duller. All four cells gave a very sharp water-hammer click. Then, a McLeod-gauge type test was performed by inverting the cell and entrapping in its side arm any air in the vapour space. The size of the air bubble trapped in the side arm of each of the four cells did not exceed 2 mm in diameter, which indicates that the effect of the amount of air present would be smaller than 0,001 mK [9].

According to the supplier, the TPW cells were filled using a procedure which purifies and produces minimal isotopic separation of continental (rain) water obtained from the tap.

3.2 TPW cell maintenance bath for the measurement

A commercially available, thermoelectrically cooled water bath, which accommodates four TPW cells, was

Table 1. Triple point of water cells and the method used to prepare their ice mantles for experiment sets I through VIII.

Experiment set	Method of mantle preparation			
	Cell A J-13-1556	Cell B J-13-994	Cell C J-13-1287	Cell D J-13-1289
I	LN-cooled rods	Crushed solid CO_2	Immersion cooler	Crushed solid CO_2
II	LN-cooled rods	Immersion cooler	Crushed solid CO_2	Crushed solid CO_2
III	LN-cooled rods	Crushed solid CO_2	Immersion cooler	Crushed solid CO_2
IV	LN-cooled rods	LN-cooled rods	LN-cooled rods	Crushed solid CO_2
V_a	Liquid nitrogen	Liquid nitrogen	Liquid nitrogen	Immersion cooler
V_b	Liquid nitrogen	Liquid nitrogen	Liquid nitrogen	Immersion cooler
V_c	Liquid nitrogen	Liquid nitrogen	Liquid nitrogen	Immersion cooler
V_d	Liquid nitrogen	Liquid nitrogen	Liquid nitrogen	Immersion cooler
VI	LN-cooled rods	Crushed solid CO_2	Immersion cooler	Immersion cooler
VII	Liquid nitrogen	Liquid nitrogen	Liquid nitrogen	Immersion cooler
VIII	Immersion cooler/ Water-ice rods	Liquid nitrogen	-	Immersion cooler

used to maintain the ice mantles of the cells during stabilization of the mantles and during measurements. The temperature of the maintenance bath was held near 0,007 °C.

3.3 Measurement instrumentation

The relative temperature of the TPW cells was measured by means of five standard platinum resistance thermometers (SPRTs) [Leeds and Northrup (L&N) Model 8163, serial number (S/N) 1803100 and L&N Model 8167, S/Ns 1888056, 1868894, 1888060 and 1881990]. The S/N 1803100 SPRT was used in the "comparison measurements" of experiment sets I through V; the S/N 1881990 SPRT was used in the comparison measurements of experiment sets VI through VIII. The other three SPRTs were included in "continual measurements" when four TPW cells were continually monitored (see experiment sets IV and V).

The measurements were carried out automatically under programmed computer control. The thermometer resistance ratio was determined by means of an Automatic Systems Laboratories, Inc. (ASL) F18 bridge operating at 30 Hz (with detector gain $\times\ 10^4$, bandwidth 0,1 Hz and quadrature detector gain $\times$ 10), with a temperature-controlled 100 Ω Tinsley Model 5685A resistor used as a reference for the resistance values. The reference resistor, which is calibrated every six months by the Electricity Division of NIST, has been changing at a relative rate of about $0{,}11 \times 10^{-6}$/yr. Thus, its short-term stability is excellent.

3.4 Measurement values

Each bridge reading for a given current was the ratio of the SPRT resistance to that of the reference resistor. The "bridge value", obtained after discarding the first two readings, was an average of thirty-six such readings taken at intervals of 7 s to 12 s. To avoid the effect of variations in the self-heating of the SPRT in a TPW cell, the SPRT resistance ratio data presented in this paper refer to the zero-power dissipation values. To calculate the zero-power resistance ratio value, bridge values were obtained at two currents, 1 mA and $\sqrt{2}$ mA. A period of about 30 min was required to make measurements of the SPRT at both currents. Whenever any reference is made to the R(SPRT) in a TPW cell or the R(TPW) of an SPRT, we are referring to the SPRT zero-power resistance value converted from the zero-power resistance ratio using the resistance value of the reference resistor. Since the TPW cells were compared in terms of the ratios of the observations relative to a reference TPW cell, and the reference resistor is highly stable, the zero-power resistance ratio values were used in the comparisons (see Section 3.6).

The data also include corrections for differences in the hydrostatic heads of the different cells. After a mantle was prepared, the depth of immersion was measured to within 1 mm as the vertical distance from the TPW cell water surface to the middle of the temperature-sensing resistor of the SPRT, using a depth-measuring scale placed in the normal position of a SPRT inside the thermometer well. The SPRT was tempered additionally by the maintenance-bath water, since during measurements the TPW cell was always completely immersed in the bath with the opening of the thermometer well about 4 cm below the water-bath surface.

3.5 Measurement procedure

The procedures used to prepare the TPW cells for measurements in the maintenance bath were the same for all of the cells after suitable mantles had been frozen using the four methods. Soon after a TPW cell was completely immersed in the maintenance bath (see Sections 2 and 3.2), a 6 mm diameter aluminium rod, initially at room temperature, was inserted into the thermometer well for 1 min to form the inner melt. For any SPRT measurements in the cell subsequent to the first comparison measurement, the aluminium rod was again inserted for 15 s to ensure free rotation of the mantle. Before starting, and again after the conclusion of measurements on an ice mantle, the TPW cell was tilted slightly to ensure that the mantle was free to rotate and, hence, was in the proper state for measurements of the triple-point temperature. It is considered that the use of a rotational impulse to ascertain if a mantle is "free" would free a "stuck" mantle but that it would soon become stuck again [9].

After the inner melt was prepared, a plastic-foam pad cooled in the maintenance-bath water was placed in the opening of the thermometer well. Then, an aluminium bushing, also cooled in the maintenance-bath water, was placed on top of the foam pad and both were inserted into the bottom of the thermometer well. The foam pad served to cushion the SPRT when it was inserted into the well. The aluminium bushing was used to centralize the SPRT in the thermometer well and to enhance the thermal contact of the SPRT with the inner melt of the ice mantle.* Finally, the SPRT, first chilled in the maintenance bath, was inserted into the well. After allowing 30 min for equilibration of the SPRT with the TPW cell, measurements were started. Measurements on a new mantle were always begun within about one hour of its preparation. The bushing and foam pad were removed from each cell at the end of the day on which measurements were made and then re-inserted prior to the next use of the cell, in accordance with the procedure just described.

3.6 Results displayed

In all experiment sets, a TPW cell previously found to be highly stable [10], designated D in Table 1, was used as measurement reference, using one SPRT in the measurement process. The SPRT zero-power resistance ratios measured in cells A, B and C were compared as ratios with that obtained in reference cell D, i.e. as ratios of R(TPW)s. As long as the temperature of the reference cell is stable, this procedure eliminates the effects of slow drifts and other changes in the measurement equipment (e.g. in the reference resistor, drift in the SPRT, accidental bumping of the SPRT at times other than during the experiment on a given day, and even the substitution of other SPRTs (see experiment set IV), making the results independent of the reference resistor and SPRT used). On any given day, a "measurement cycle" consisted of measurements first on cell D, then on the three test cells in a random sequence, and again (the second reading) on cell D. (For brevity, unless reference to an individual TPW cell is required, the three cells A, B and C are referred to as the "test cells" and the reference cell D, simply as cell D. As the data show, all four cells are essentially equivalent).

In comparison measurements, the SPRT must be moved from one TPW cell to another. Using this comparison method, two complete cycles (sets) of measurements on the four cells could readily be obtained daily. (Usually one cycle of measurements was carried out per day.) To monitor continually the behaviour of the temperature of a mantle, i.e. to avoid the transfer of the SPRT among the TPW cells and to avoid unknowingly bumping the SPRT and erroneously interpreting the effect as a property of the TPW mantle, a "continual measurement" method was also used in three experiment sets. A SPRT was installed in each of the four TPW cells and readings were taken sequentially and automatically, without disturbing the SPRTs or the TPW cells. Using this method, however, there is the possibility of the ice mantle sticking to the thermometer well, giving low values. In order to refer the results of continual measurements to cell D, each SPRT was also measured in cell D.

The results of comparison measurements are displayed in the figures. The results of continual measurements are shown in some of the figures. ***In the comparison measurements***, the ratios of zero-power resistance ratios for the test cells and cell D are relative to the first observation on cell D of the measurement cycle. The *continual measurement graphs* represent ratios of individual SPRT zero-power resistance ratios for the test cells and cell D to the mean of that observed with cell D with a free mantle at the beginning and at the end of the continual measurements. The ratio of R(TPW) of a given cell to that of cell D is identical to the resistance ratio W. The ordinates of the graphs are the ratio minus one, which is equivalent to δW, converted to the mK equivalent. The dates of observation are indicated on the abscissa of the figures. The figure captions give details of the method used, the initial temperature, the date on which each of the mantles of the test cells and cell D was prepared, and whether the mantle cracked or not. When values of temperature are stated to be low or high, they are in terms relative to the equilibrium temperature values.

3.7 Reference cell D

For experiment sets I through IV, the mantle of cell D had been prepared using the crushed solid-CO_2 method and then the cell had been stored in the maintenance bath for six months before starting the measurements of experiment set I. This "old" mantle had fairly large crystals. For experiment V_a of experiment set V, a new mantle in cell D had been prepared two weeks earlier, using the immersion-cooler technique. This mantle, however, melted over the weekend at the end of experiment V_a, due to a power loss in the laboratory. For experiments V_b through V_d, another mantle was prepared in cell D, again using the immersion-cooler

* Actually, in steady-state measurements with a continuous current flowing through the SPRT, a temperature gradient necessarily exists between the SPRT and the heat sink, i.e. the water/ice interface, to which temperature the SPRT is referenced by calculation, using results of two-current measurements. For this reason, to avoid excessive temperature gradients through the inner melt, we made the inner-melt layer as thin as practical.

method. Another ice mantle was prepared for cell D in experiment sets VI through VIII. At the beginning of experiment set VI, this new mantle of cell D was about ten weeks old. The use of this "new" mantle was continued until the conclusion of the experiment. The dates of preparation of the ice mantle for cell D used in the experiment sets are indicated in the figure captions.

4. Preparation and results of measurements on each of the ice mantles of the experiment sets

Eight sets of experiments were conducted, using the crushed solid-CO_2, the heat-pipe immersion-cooler, the LN-cooled-copper-rod, and the LN methods to prepare the ice mantles (see Section 2 for detailed descriptions of these methods). The methods used to prepare the ice mantles for each of the TPW cells in experiment sets I through VIII are summarized in Table 1. During the freezing of the mantles, the cells were held upright on a plastic-foam cushion by means of a laboratory stand and were exposed to the laboratory conditions. As described in Section 2.2.2, it was found during experiment set I that the freezing of a mantle using the heat-pipe immersion-cooler method with the TPW cell exposed to the laboratory conditions required a long time. Therefore, for experiment sets II through VIII, the cell was placed inside a Dewar to provide thermal insulation whenever the heat-pipe immersion cooler was used to freeze the ice mantle.

The methods used to freeze each of the ice mantles for the experiment sets are summarized, as mentioned above, in Table 1 and are given in the following sections, which deal specifically with each of the experiment sets and the results obtained. More details are given for the LN-cooled-copper-rod method and for the LN-cooling method in which the mantles cracked. Descriptions of special preparation of the cells for measurements are given for experiment sets VII and VIII.

4.1 Experiment set I

In experiment set I, the initial temperature of the test cells was approximately 295 K. Cell D contained a mantle that had been prepared six months earlier using the crushed solid-CO_2 method.

The ice mantle for cell A was prepared using the LN-cooled-copper-rod method. Twelve LN-cooled-copper-rod insertions were made at 2 min intervals. On the second rod insertion, a bulb of ice started to form at the bottom of the thermometer well. On the eighth rod insertion, large cracks perpendicular to the well appeared in about three-quarters of the mantle. During cooling with the ninth and tenth rod insertions, the cracks continued to grow and increase in number. During the time of the cooling with the eleventh and twelfth rod insertions, some of the cracks had begun to heal.

The ice mantle for cell B was grown using the crushed solid-CO_2 method and the ice mantle for cell C was grown using the heat-pipe immersion cooler. In using the heat-pipe cooler, an interval of about 135 min was required to freeze a suitable mantle with the TPW cell exposed to the ambient conditions.

Following the preparation of the ice mantles, measurements on the test cells and cell D were obtained using SPRT 1803100 over approximately the next four months. The results of the measurements are displayed in Figure 1. The range of values of the first set of measurements on the test cells was 0,22 mK; the values did not differ from that of cell D by more than 0,15 mK. Large changes occurred between the first and second set of measurements, i.e. from the first to the second day, especially for cells A and B.

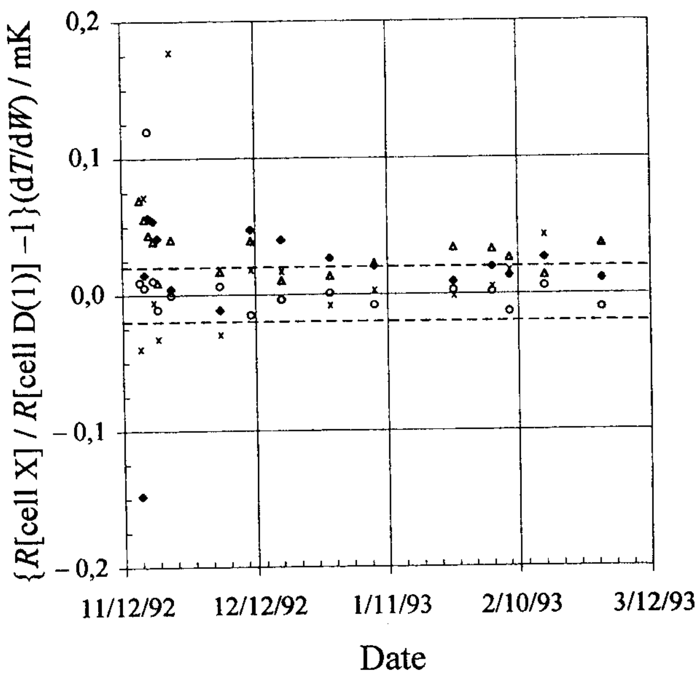

Figure 1. Results from experiment set I of the comparison of TPW cells A, B and C with cell D over a period of about four months. The mantle of cell D was prepared on 6/1/92 using crushed solid CO_2 (no cracks formed). The mantles of cells A, B and C were prepared on 11/16/92; that of cell A using liquid-N_2-cooled rods (cracks formed), that of cell B using crushed solid CO_2 (no cracks formed), and that of cell C using an immersion cooler (no cracks formed). The initial temperature of cells A, B and C, before mantle preparation, was 295 K and that of cell D was 274 K. Symbols denote the following: × cell A, ◆ cell B, △ cell C, ○ cell D (2nd reading), and dashed lines represent + 0,02 mK and − 0,02 mK. See text for details. The results are expressed in terms of the resistance R of the cells, the resistance ratio W, and the temperature T.

During days three through nine of the measurements, the temperatures of cells B and C changed by about 0,05 mK relative to cell D; they agreed with each other to within 0,04 mK and with cell D to within 0,07 mK. Cell A, for which the mantle was prepared by using LN-cooled copper rods and which had the most severe, clearly visible, cracking of the ice mantle, exhibited changes of 0,23 mK over this period. In measurements made after nine days, the temperatures of the test cells did not deviate from that of reference cell D by more than 0,04 mK and variations in the values of the three cells appear to be random in nature. During the first few days of measurements, the test cells show a number of values higher than the equilibrium values. The one high value shown for cell D and the one very high value for cell A are due to measurement errors, but the remaining high values for cell A are considered to be due to peaking. Some peaking is exhibited by cells B and C also.

4.2 Experiment set II

In experiment set II, the initial temperature of the test cells was approximately 274 K. Cell D contained the same mantle as in experiment set I, and by the beginning of experiment set II it was eleven months old.

The mantle of cell A was frozen by inserting LN-cooled rods into the thermometer well fourteen times at 2 min intervals. On insertion of the fourth LN-cooled copper rod, a small number of cracks appeared in the upper quarter, and to a lesser extent in the lower third of the mantle. Numerous additional cracks were formed and existing cracks grew with each insertion of the cooling rods. By the time of the twelfth insertion of the cooling rod, the cracks in the lower third of the mantle were observed to be healing. The thirteenth and fourteenth rod insertions caused additional cracks and caused some of the existing cracks to grow. Some of the cracks began to heal.

The ice mantle of cell B was frozen using the heat-pipe immersion cooler. For efficiency in forming the mantle, the cell was placed in a Dewar to provide thermal insulation. The immersion cooler was removed after 108 min. The ice mantle for cell C was prepared using the crushed solid-CO_2 method.

Measurements on the ice mantles of the test cells and cell D were made over a period of about one month using SPRT 1803100. Figure 2 shows the results of the measurements. The range of values of the first set of measurements on the three cells was 0,15 mK, but none of these values differed from that of the reference cell by more than 0,09 mK. During the first seven days of measurements, the maximum temperature change of any cell was about 0,11 mK. During days two through seven, the temperatures of the test cells agreed with each other to within 0,06 mK. After the first eight days of measurements, the temperatures of the test cells did not deviate from that of cell D by more than 0,04 mK and the variations of the values appear to be random in nature.

It is interesting to note that the temperatures of the test cells, including those measured during the first few days, were always within 0,1 mK of that of cell D. Comparing the results of experiment set II with those of experiment set I, fewer high values, but more low values, were observed during the first few days.

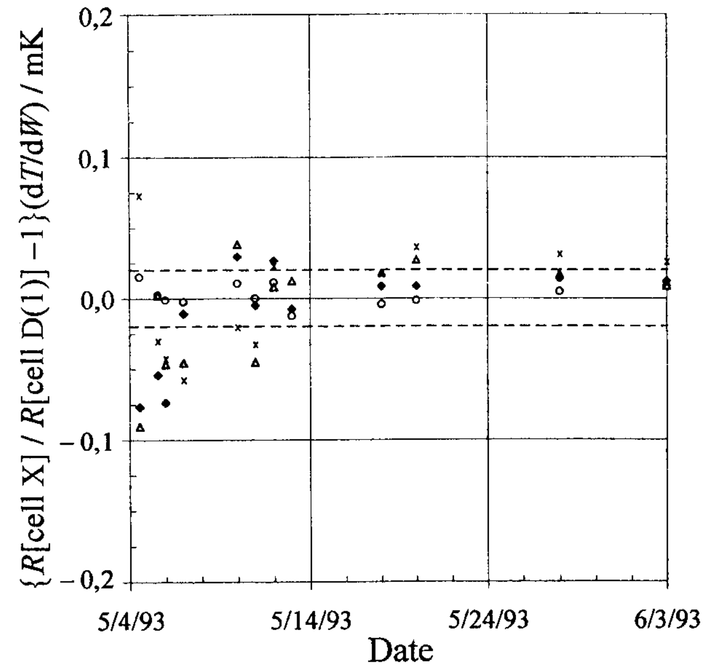

Figure 2. Results from experiment set II of the comparison of TPW cells A, B and C with cell D over a one-month period. The mantle of cell D was prepared on 6/1/92 using crushed solid CO_2 (no cracks formed). The mantles of cells A, B and C were prepared on 5/3/93; that of cell A using liquid-N_2-cooled rods (cracks formed), that of cell B using an immersion cooler (no cracks formed), and that of cell C using crushed solid CO_2 (no cracks formed). The initial temperature of all four cells, before mantle preparation, was 274 K. Symbols denote the following: × cell A, ◆ cell B, △ cell C, ○ cell D (2nd reading), and dashed lines represent + 0,02 mK and − 0,02 mK. See text for details. The ordinate is defined as in Figure 1.

The mantle of cell A, which was prepared by the LN-cooled-rod method, had a value on the first day of measurements that was about 0,05 mK higher than its equilibrium value. Since the first measurements made soon after the ice mantles are prepared are usually low, this high value was probably caused by a measurement error.

4.3 Experiment set III

In experiment set III, as in experiment set I, the initial temperature of the test cells was approximately 295 K and the techniques used in preparing the mantles of the test cells were the same as in experiment set I. Cell D contained the same mantle as that of experiment sets I and II and was twelve months old at the beginning of experiment set III.

The ice mantle of cell A was frozen using LN-cooled copper rods. Cooling rods were inserted fourteen times at 2 min intervals. On the seventh rod insertion, one small crack perpendicular to the thermometer well appeared about 2 cm above the bottom of the well. During cooling with the eighth rod insertion, one additional crack appeared in the lower third of the mantle. The twelfth rod insertion caused small cracks to appear in the upper two-thirds of the mantle. The fourteenth rod insertion caused additional cracking.

The ice mantle of cell B was frozen using the crushed solid-CO_2 method and that of cell C was frozen using an immersion cooler. The immersion cooler was removed from the TPW cell after about 80 min of cooling.

After the ice mantles were prepared, measurements on the test cells and on cell D were made for eighteen days using SPRT 1803100. Figure 3 shows the results of the measurements. Over the first three days of measurements, the maximum range of values for the test cells was approximately 0,13 mK, and none of the values differed from that of cell D by more than 0,13 mK. During the first eight days, the temperature of cell C changed by about 0,03 mK relative to that of cell D and the values were always within 0,03 mK of that of cell D. During the first eight days of measurements, the temperature of cell B changed by about 0,15 mK relative to that of cell D, and except for the value obtained on the day its mantle was prepared, the values were always within 0,04 mK of that of cell D. Cell B exhibited slightly high values on the third and fourth days. Cell A, which was prepared using LN-cooled rods and had clearly visible cracking of the ice mantle, exhibited changes of 0,18 mK during these same eight days as well as a number of high values. During the last ten days of measurements, the variations of the values for the test cells appear to be random in nature.

In comparing the measurements of only the first few days of experiment sets I, II and III, there were more high values when the ice mantles of the cells were frozen starting at 295 K rather than at 274 K. The LN-cooled-rod method of freezing the ice mantles tended to yield, during the first few days of measurements, more high values than the crushed solid-CO_2 method or the immersion-cooler method.

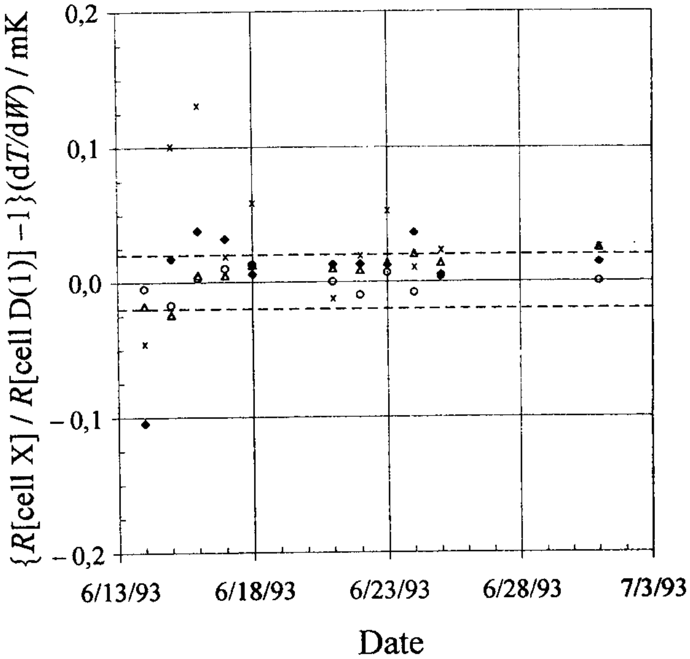

Figure 3. Results from experiment set III of the comparison of TPW cells A, B and C with cell D over an eighteen-day period. Compare with Figures 1 and 2. The mantle of cell D was prepared on 6/1/92 using crushed solid CO_2 (no cracks formed). The mantles of cells A, B and C were prepared on 6/14/93; that of cell A using liquid-N_2-cooled rods (cracks formed), that of cell B using crushed solid CO_2 (no cracks formed), and that of cell C using an immersion cooler (no cracks formed). The initial temperature of cells A, B and C, before mantle preparation, was 295 K and that of cell D was 274 K. Symbols denote the following: × cell A, ♦ cell B, △ cell C, ○ cell D (2nd reading), and dashed lines represent + 0,02 mK and − 0,02 mK. See text for details. The ordinate is defined as in Figure 1.

4.4 Experiment set IV

In experiment set IV, the ice mantles for all three test cells were prepared using LN-cooled copper rods inserted at different intervals of time. The initial temperature of cell A was 274 K and that of cells B and C was 295 K. Cell D contained the same mantle as that of experiment sets I, II and III and was about fourteen months old at the beginning of experiment set IV.

The ice mantle of cell A was frozen by inserting LN-cooled copper rods into the thermometer well thirteen times at 2 min intervals. On the third and fourth rod insertions, cracks appeared in the upper one-fifth of the ice mantle. By the time of the seventh rod insertion, cracks appeared in the upper half of the mantle. On the twelfth rod insertion, large cracks appeared in the upper two-thirds of the mantle and one small crack appeared in the lower one-fifth of the mantle. The thirteenth cooling rod caused additional cracking in the upper two-thirds of the mantle.

The ice mantle of cell B was frozen by inserting LN-cooled copper rods into the thermometer well seventeen times at 3 min intervals. After the second rod insertion, a crack appeared as a white streak down half of the mantle and then disappeared in about 3 s. On the fourth rod insertion, a small crack occurred in the ice mantle at the very bottom of the thermometer well. Small cracks appeared in the lower tenth of the mantle during the eighth and tenth rod insertions. By the time of the fourteenth rod insertion, cracks appeared in the upper half of the mantle on one side of the cell. On the seventeenth and final rod insertion, cracks appeared throughout the upper half of the mantle. In general, less cracking occurred in cell B than in cell A.

The ice mantle of cell C was prepared by inserting LN-cooled copper rods into the thermometer well twenty-one times at 1 min intervals. On the third rod insertion, the mantle began to form along the entire length of the re-entrant well. Cracking in the upper half of the mantle appeared during the eighth through the fifteenth rod insertions. By the time of the sixteenth rod insertion, healing of the cracks had begun. The continued insertion of the seventeenth through the twenty-first cooling rods caused further growth of the mantle, additional cracking, and growth, as well as healing, of the existing cracks. Cracking occurred only in the upper half of the mantle.

After the mantles were prepared, measurements were made on the cells for about a week. During this period, comparison measurements were made during the first four days, followed by continual measurements for 64 h, then finally a set of comparison measurements. Figure 4 shows the results of the comparison measurements using SPRT 1803100. The range of values of temperature of the first set of measurements on the test cells was 0,18 mK and the values did not differ from that of cell D by more than 0,18 mK. During the next three days (following the day of preparation), the temperatures of cells B and C were within 0,13 mK of that of cell D, and they were within 0,05 mK of each other. The temperature of cell A, which had been prepared starting at a lower initial temperature (274 K), was always within 0,07 mK of that of cell D. During the first three days, the temperature of cell A exhibited changes of approximately 0,06 mK. At least two, and possibly all three, test cells exhibited peaking; cell A on the second day of measurements, and cells B and C on the third. The comparison measurements at the end of the week (i.e. after 64 h of continual measurements) showed that the temperatures

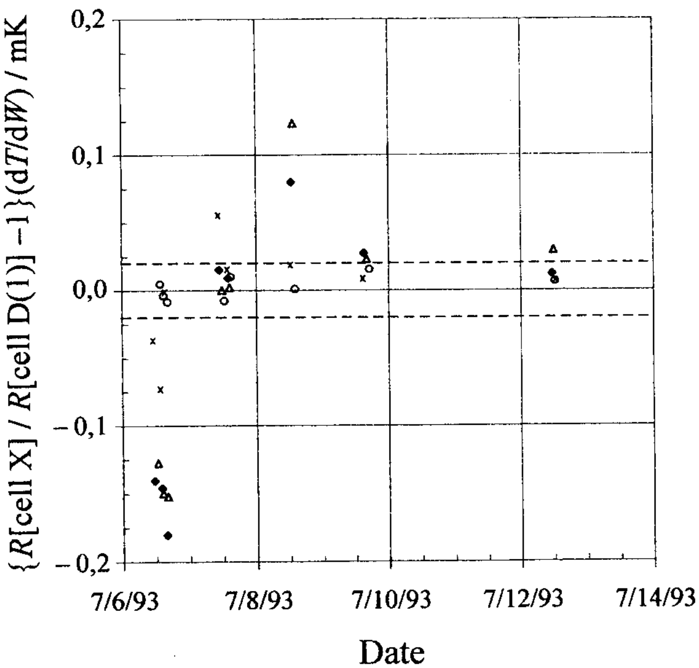

Figure 4. Results from experiment set IV of the comparison of TPW cells A, B and C with cell D over a seven-day period. The mantle of cell D was prepared on 6/1/92 using crushed solid CO_2 (no cracks formed). The mantles of cells A, B and C were prepared on 7/6/93 using liquid-N_2-cooled rods (cracks formed), in which the rods were inserted at 2 min intervals in cell A, 3 min intervals in cell B, and 1 min intervals in cell C. The initial temperature of cells A and D, before mantle preparation, was 274 K and that of cells B and C was 295 K. Symbols denote the following: × cell A, ◆ cell B, △ cell C, ○ cell D (2nd reading), and dashed lines represent + 0,02 mK and − 0,02 mK. See text for details. The ordinate is defined as in Figure 1.

of the three test cells differed from that of cell D by no more than 0,03 mK.

The results of the continual measurements are shown in Figure 5. The range of the values for cells A, B, C and D were $0{,}04_4$ mK, $0{,}07_3$ mK (due to the downward trend of the data), $0{,}03_8$ mK and $0{,}02_9$ mK, respectively. The standard deviations for the sixty-nine measurements on each of cells A, B, C and D were $0{,}00_8$ mK, $0{,}01_9$ mK, $0{,}01_1$ mK and $0{,}00_8$ mK, respectively. The downward trend (approximately 0,06 mK in total during 64 h) in measurements made with SPRT S/N 1868894 in cell B shows what happens to the SPRT temperature when an ice mantle begins to adhere to the thermometer well. As mentioned in the previous paragraph, with the mantles free, the comparison measurements on the seventh day with SPRT S/N 1803100 show that the temperatures of the three test cells differed from that of cell D by no more than 0,03 mK.

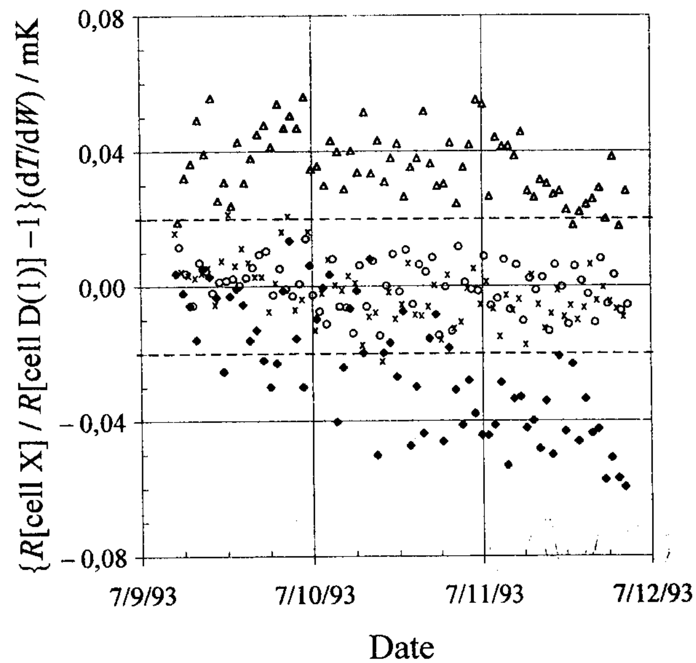

Figure 5. Results from experiment set IV, of continual measurements of SPRTs in cells A, B, C and D for 64 h, immediately following the four days of comparison measurements of cells A, B and C with cell D (for information concerning the preparation of the mantles, cf. Figure 4). Symbols denote the following: × cell A, ◆ cell B, △ cell C, ○ cell D (2nd reading), and dashed lines represent + 0,02 mK and − 0,02 mK. See text for details. The ordinate is defined as in Figure 1.

4.5 Experiment set V

Experiment set V comprised four separate "experiments" V_a, V_b, V_c and V_d, in which the ice mantles for the test cells were prepared using the LN-cooling technique. The initial temperature of the test cells for experiments V_a and V_d was approximately 274 K, and for experiments V_b and V_c it was approximately 295 K. Cell D contained a mantle that was approximately two weeks old for experiment V_a; it had been prepared by the immersion-cooler technique. As previously mentioned, after completion of experiment V_a, the mantle for cell D melted over the weekend because of the warming of the maintenance bath due to power failure in the laboratory. A new mantle was grown using the immersion-cooler technique approximately three weeks before starting experiment V_b. This second mantle for cell D was used over a six-week period for experiments V_b through V_d.

Using the LN-cooling technique, approximately 6 min to 9 min were required to freeze a mantle of desired thickness. This LN-cooling technique caused cracking, especially in the lower third of the mantle where the cracking was such that it made the ice appear opaque. Noticeable cracking of the mantles continued after removal of the LN transfer tube and while the LN remaining in the thermometer well was boiling away.

In experiment V_a, the ice mantles for the test cells were prepared one cell at a time with the initial temperature of the cells at approximately 274 K. The ice mantles began to form within 15 s after beginning the transfer of LN into the thermometer wells. Large cracks appeared in the lower third of each ice mantle within the first minute. Over the next 5 min, new cracks continued to form and some of the original cracks showed signs of annealing. After approximately 6 min, the LN transfer tube was removed and the remaining LN was allowed to boil away.

In experiment V_b, the ice mantles for each of the test cells began to form within 60 s after beginning the transfer of LN into the thermometer well. For cells A and B, large cracks appeared in the lower third of the ice mantles within the next minute. Over the next 5 min, new cracks continued to form in cells A and B, and some of the original cracks showed signs of annealing. For cell C, no cracking of the mantle occurred during the transfer of the LN. After approximately 9 min, the LN transfer tube was removed and the remaining LN was allowed to boil away. On removal of the transfer tube from the thermometer well, however, severe spiral cracking occurred in the lower third of the ice mantle.

In experiment V_c, as in experiment V_b, the ice mantle for each of the test cells began to form within 60 s after beginning the transfer of LN into the thermometer well. For cells A and C, no cracking of the mantles occurred during transfer of the LN. On removal of the transfer tube from the thermometer wells, however, severe spiral cracking occurred in the lower third of the mantles. For cell B, one small crack appeared in the lower third of the ice mantle during the transfer of LN. After approximately 9 min, the LN transfer tube was removed from cell B and the remaining LN was allowed to boil away. On removal of the transfer tube, severe spiral cracking occurred in the lower third of the ice mantle.

In experiment V_d, as in experiment V_a, the ice mantle for each of the test cells began to form within 15 s after beginning the transfer of LN into the thermometer well. For the test cells, large cracks appeared in the lower third of the ice mantle within the first minute. Over the next 5 min, new cracks continued to form and some of the original cracks showed signs of annealing. After approximately 6 min, the LN transfer tube was removed and the remaining LN was allowed to boil away.

Following the preparation of the ice mantles, measurements of SPRT 1803100 in the test cells and in cell D were made over a period of about two weeks each for experiments V_a, V_b, V_c and V_d. (Note that the gaps in the plotted data that correspond to two or three days represent the weekends in which no measurements were made.) Figures 6a and 6b show the results of experiments V_a and V_b, respectively. The initial temperature of the test cells in experiment V_a was 274 K and that in experiment V_b was 295 K. Figure 6a shows that during the first five days or so the initial values of temperatures were generally low and that the cells required a week or more to reach the equilibrium temperature. In the measurements of Figure 6b, there are fewer low values compared with those of Figure 6a, but there are more high values and the equilibrium temperature was reached in about five days. In Figure 6b, there is an apparent peaking on the second day in cell A, and also on the second through the fourth days in cell C, but with a steady decline over those days. Towards the end of the two-week period, the results of the two experiments are essentially the same.

Figures 7a and 7b show the results of experiments V_c and V_d, respectively. The initial temperatures of the test cells of experiments V_c and V_d were 295 K and 274 K, respectively. In these two experiments, continual measurements were initiated for the weekend, soon after the cells were prepared on Friday. The two figures show the results of continual measurements during the first four days, followed by comparison measurements for about four days, a weekend of no measurements, and then another set of comparison measurements for four or five days. In the comparison measurements over a period of about twelve days that followed the continual measurements, the results show that the test cells had reached their equilibrium temperatures on the fourth day (beginning of the comparison measurements). In Figures 7a and 7b, as in Figure 6b, the peaking effect in cell A is shown.

In approximately the same period of continual measurements, the results of experiment V_d show that all the ice mantles became stuck, even in cell D in which the mantle had not become stuck in previous continual measurements. In experiment V_c, only the results from cell C exhibited any definite downward trend. Also, in experiment V_d, the continual readings reached lower values than in experiment V_c. The peaking effect of cell C in Figure 6b is probably obscured in Figure 7a because the ice mantle became stuck to the thermometer well and the observations became low. Some of the relatively large scatter in the results shown in Figures 7a and 7b and in other figures

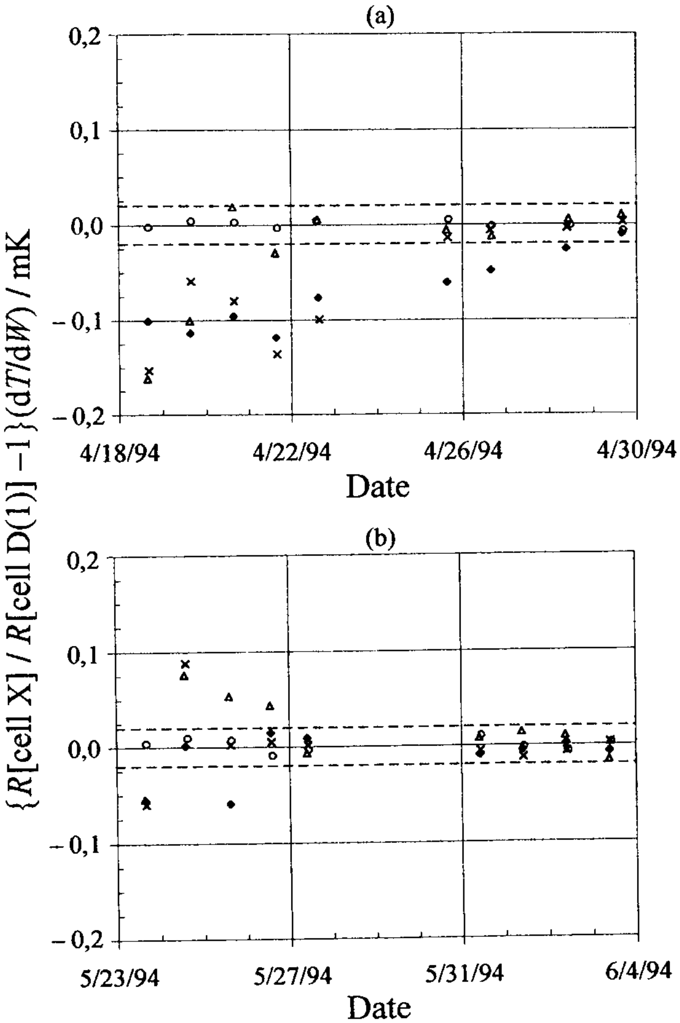

Figure 6. Results from experiment set V of the comparison of TPW cells A, B and C with cell D over a twelve-day period. The effect of the initial temperature of the cells before mantle preparation is compared. Symbols denote the following: × cell A, ◆ cell B, △ cell C, ○ cell D (2nd reading), and dashed lines represent + 0,02 mK and – 0,02 mK. See text for details. The ordinate is defined as in Figure 1.

(a) Experiment V_a. The mantle of cell D was prepared on 4/1/94 using an immersion cooler (no cracks formed). The mantles of cells A, B and C were prepared on 4/18/94 using liquid N_2 (cracks formed). The initial temperature of all four cells, before mantle preparation, was 274 K.

(b) Experiment V_b. The mantle of cell D was prepared on 5/2/94 using an immersion cooler (no cracks formed). The mantles of cells A, B and C were prepared on 5/23/94 using liquid N_2 (cracks formed). The initial temperature of cells A, B and C, before mantle preparation, was 295 K and that of cell D was 274 K.

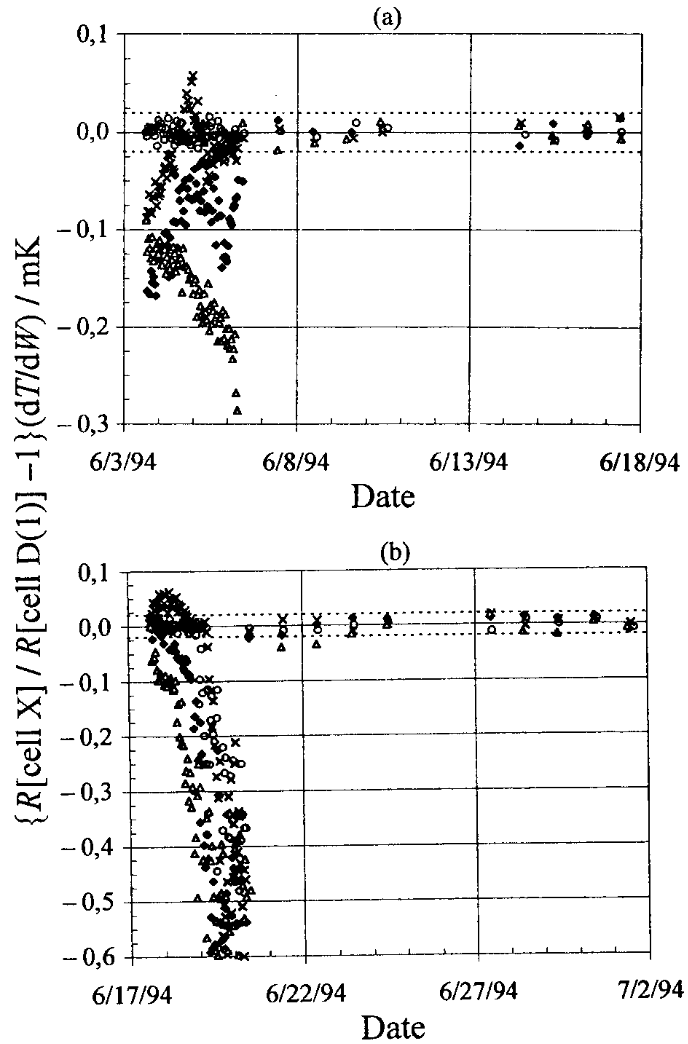

Figure 7. Results from experiment set V of measurements of TPW cells A, B, C and D over a fifteen-day period, during which continual measurements were made for three days and then comparison measurements followed immediately for a twelve-day period. The effect of the initial temperature of the cells before mantle preparation is investigated. Symbols denote the following: × cell A, ◆ cell B, △ cell C, ○ cell D (2nd reading), and dashed lines represent + 0,02 mK and – 0,02 mK. See text for details. The ordinate is defined as in Figure 1.

(a) Experiment V_c. The mantle of cell D was prepared on 5/2/94 using an immersion cooler (no cracks formed). The mantles of cells A, B and C were prepared on 6/3/94 using liquid N_2 (cracks formed). The initial temperature of cells A, B and C, before mantle preparation, was 295 K and that of cell D was 274 K.

(b) Experiment V_d. The mantle of cell D was prepared on 5/2/94 using an immersion cooler (no cracks formed). The mantles of cells A, B and C were prepared on 6/17/94 using liquid N_2 (cracks formed). The initial temperature of all four cells, before mantle preparation, was 274 K.

that show continual measurements may be due to the varying degree by which the mantles became stuck to the thermometer well.

The mantles of experiment set V, prepared using the LN-cooling technique, experienced far greater cracking than those prepared by the other techniques. The cracking of the mantles is interpreted to indicate the release of excess strains caused by large density gradients or sudden changes in the density gradient. The peaking observed with cells A and C and with some of the mantles prepared by the other techniques may be associated with the release of energy from strains that are relieved slowly without cracking of the mantle and from growth of fine ice crystals to larger ice crystals. The final results of comparison measurements of experiment V (Figures 6a through 7b) show, with the ice mantles of the cells free, that the equilibrium temperatures of the test cells and cell D were essentially the same.

4.6 Experiment set VI

In this experiment set, the mantles of the test cells were frozen by the methods used in experiment sets I and III (see Table 1). The details of the preparation of the mantles and their treatment prior to measurements are somewhat different, however. The initial temperature of the three test cells was approximately 274 K. An attempt was made to make the thickness of the mantles of the three cells the same, as determined visually. The thermometer well opening of each cell was stoppered after the mantle was made and the cell immersed in the maintenance bath for approximately 60 min to equilibrate the mantle, in contrast to the 5 min allotted in other experiment sets. After the equilibration period, the cell was completely immersed in preparation for measurements. The mantle of cell D had been prepared by the immersion-cooler technique approximately twelve weeks prior to the use of the cell in these experiments.

The ice mantle of cell A was made by inserting LN-cooled copper rods into the thermometer well twenty-five times at 1 min intervals. On the seventh rod insertion, cracks appeared on one side of the lower third of the mantle. The tenth rod insertion caused cracks to occur in the middle third of the mantle. The nineteenth rod insertion caused cracks to occur in the upper two-thirds of the mantle. By the twentieth rod insertion, the first set of cracks was beginning to heal. The twenty-fifth rod insertion caused additional cracking.

The ice mantle of cell B was prepared using crushed solid CO_2. The crushed solid CO_2 was maintained at approximately the water level of the cell for 19 min before allowing the solid CO_2 to sublime completely. The ice mantle of cell C was prepared using an immersion cooler for a period of 58 min.

After the ice mantles were prepared, measurements of SPRT 1881990 (L&N Model 8167) were made in the test cells and in cell D over a period of eleven days. The results are displayed in Figure 8. Except for interchanging the methods of preparation of the ice mantles of test cells B and C, experiment set VI duplicates experiment set II. The range of values determined from the first measurements on the test cells was 0,08 mK; the values differed from that of cell D by no more than 0,17 mK. Comparing the results of experiment set II with experiment set VI (Figure 2 with Figure 8), the initial low values extend over a longer period in experiment set II than in set VI. This difference may be due to the ice mantles of experiment set VI having been thermally equilibrated in the maintenance bath for 60 min (cf. only 5 min for experiment set II) before completely immersing in the bath for measurements. The results shown in Figure 8 do not exhibit the peaking observed in experiment set I (Figure 1). Only cell A shows any evidence of peaking. Peaking seems to have occurred more often when the ice mantle was prepared starting at 295 K than at 274 K.

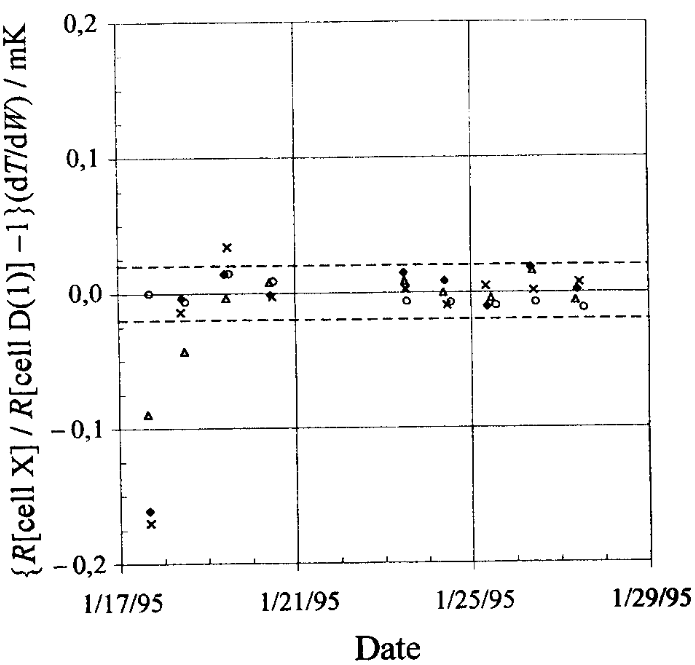

Figure 8. Results from experiment set VI of the comparison of TPW cells A, B and C with cell D over an eleven-day period. The mantle of cell D was prepared on 11/1/94 using an immersion cooler (no cracks formed). The mantles of cells A, B and C were prepared on 1/17/95: that of cell A using liquid-N_2-cooled rods, inserted at 1 min intervals (cracks formed); that of cell B using crushed solid CO_2 (no cracks formed); and that of cell C using an immersion cooler (no cracks formed). The initial temperature of all four cells, before mantle preparation, was 274 K. Symbols denote the following: × cell A, ◆ cell B, △ cell C, ○ cell D (2nd reading), and dashed lines represent + 0,02 mK and – 0,02 mK. See text for details. The ordinate is defined as in Figure 1.

4.7 Experiment set VII

In experiment set VII, the ice mantles for the test cells were prepared using the LN-cooling technique in the same manner as in experiment set V. The initial temperature of the test cells was 274 K. In this experiment set, as in experiments V_a and V_d, when the initial temperature was 274 K, the ice mantles for the cells began to form within 15 s after beginning the transfer of LN into the thermometer well. Large cracks appeared in the lower third of the ice mantles within the first minute. The cracking was so severe that the ice appeared opaque. Over the next 5 min, new cracks continued to form and some of the original cracks showed signs of healing. After approximately 6 min of cooling, the LN transfer tube was removed and the remaining LN was allowed to boil away. Noticeable cracking of the mantles continued after removal of the LN transfer tube and while the liquid nitrogen was boiling away. After all of the LN had boiled away, the thermometer well was stoppered and the cell was immersed in the maintenance bath. After an interval of 30 min, the stopper was removed and the cell was completely immersed in the bath.

The ice mantle of cell D had been prepared by the immersion-cooler technique approximately three months prior to the use of the cell in these experiments. The mantle was the same as that used in experiment set VI.

The details of the measurement procedure on the cells are somewhat different from those of the previous experiments. The first set of measurements on the cells (in the sequence D, C, B, A, D) was begun within an hour after the mantles were made. When these measurements were complete, each of the three test cells was removed from the maintenance bath, inverted six times to mix the water of the *inner* and *outer* liquid layers, and then returned to the bath. A second set of measurements (again, in the sequence D, C, B, A, D) followed the first set within about 1 h. After the first day, measurements of SPRT 1881990 (L&N Model 8167) in the test cells and in cell D were repeated over a period of about one week, using the same measurement procedure as that for experiment sets I through VI in which the TPW cells were not inverted. The results of the measurements (Figure 9a) show that the mixing caused the temperatures of the cells to increase to nearly the equilibrium values and to reach the equilibrium values within the next two days. This indicates that the water in the cells is sufficiently pure that the more impure water on the outside of the mantle did not depress the temperature at the *inner* interface by a measurable amount. (This assumes that, even with the LN-cooling technique, impurity segregation can occur and depress the equilibrium temperature.) Also, unless the process of interchanging the water of the *inner* and *outer* layers affected the nature of the ice mantle, the low values observed during the first few days and the peaking values and slow equilibration observed in experiment V_a may not be due to a property of the ice mantle.

4.8 Experiment set VIII

In experiment set VIII, the details of the preparation of the mantles and their treatment prior to, and during, measurements on them were different from those of previous experiment sets. The ice mantle of cell A was prepared using *initially* an immersion cooler and then water ice over a three-week period. Cell B contained the same mantle that had been prepared in experiment set VII; that mantle was approximately ten weeks old at the beginning of measurements of experiment set VIII. Cell C was not used during this experiment. The mantle of cell D was the same as that used in experiment sets VI and VII and had been made by the immersion-cooler technique approximately three months prior to the use of the cell in these experiments.

The initial temperature of cell A was approximately 274 K. A small amount of ethanol was placed in the bottom of the well and the immersion cooler was inserted to grow a bulb of ice at the bottom of the thermometer well. After approximately 15 min, when an ice bulb of suitable size had been formed, the immersion cooler was removed, the ethanol was removed from the well, the well was stoppered, and the cell was immersed in the maintenance bath to thermally equilibrate the ice bulb that had formed. After 30 min, the stopper was removed, a rod of ice 12 mm in diameter and 29 cm in length placed in the thermometer well, the stopper replaced, and the cell immersed in the bath. (The I.D. of the thermometer well of each of the TPW cells was 13 mm.) The rod of ice was replaced daily to promote a slow growth of the ice mantle over a three-week period. During this growing of the mantle, no *inner* liquid layer was formed.

The details of the measurements on the cells were similar to those of experiment set VII. After growing the ice mantle of cell A for three weeks, the first set of measurements on the cells (in the sequence D, A, B, D) was begun. After completion of the first set of measurements, cell A was removed from the maintenance bath, inverted ten times to mix the water of the *inner* and *outer* liquid layers, and then returned to the bath. A second set of measurements was made (again, in the sequence D, A, B, D) on the three cells that day. SPRT 1881990 (L&N Model 8167) was used in the measurements. The results (Figure 9b) show that mixing the *inner* and *outer* layers of water of cell A, following very slow growth of the ice mantle to segregate any impurities into the *outer* water layer, has no measurable effect on the temperature of the *inner* interface of the cell. Thus, the water in the cell is very pure. Figure 9b also shows that the first reading of the ice mantle of cell A, immediately after the mantle was prepared, is essentially the equilibrium value.

5. Uncertainty of measurements

The expanded uncertainty U assigned to the measurements was calculated from the equation

$$U = k\sqrt{s^2 + \sum u(i)^2}, \tag{1}$$

where k is the coverage factor, s is the Type A standard uncertainty based on the calculated standard deviation of the mean of the measurements and $u(i)$ is the estimated Type B standard uncertainty for each known component in the measurement process that cannot be directly measured [11].

Since the experiments reported here are direct *comparisons* of triple-point cells (which have the same dimensions and geometry), all systematic effects are expected to be the same and are incorporated in the Type A standard uncertainties. The Type A standard uncertainty for these experiments was estimated to be the standard deviation of the mean of the temperature

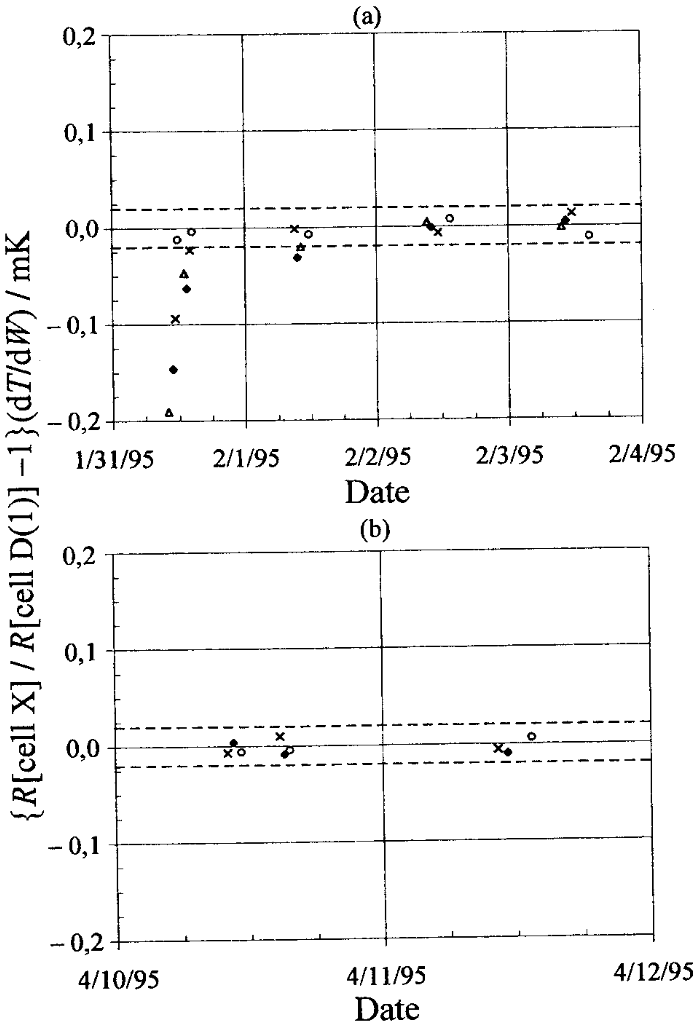

Figure 9. Results on the TPW cell purity. Symbols denote the following: × cell A, ◆ cell B, △ cell C, ○ cell D (2nd reading), and dashed lines represent + 0,02 mK and – 0,02 mK. The ordinate is defined as in Figure 1.

(a) Results from experiment set VII of the comparison of cells A, B and C with cell D over a four-day period. The mantles of cells A, B and C were prepared on 1/31/95 using liquid N_2 (all mantles developed cracks), and that of cell D on 11/1/94 using an immersion cooler (no cracks formed). The initial temperature of all four cells, before mantle preparation, was 274 K. Immediately after the first measurement cycle, each of the three test cells was inverted and then uprighted six times to mix the water in the inner melt with that outside the mantle for the remaining series of measurements. See text for details.

(b) Results from experiment set VIII of the comparison of cells A and B with cell D, after slowly growing the mantle of cell A, beginning on 3/17/95, for three weeks. See text for details of the preparation of the mantle. The mantle of cell B was that which had been prepared for experiment set VII; it was about three weeks old (cf. caption of Figure 9a). The mantle of cell D had been prepared on 11/1/94 using an immersion cooler. The initial temperature of all three cells, before mantle preparation, was 274 K. See text for the treatment of the cells before measurements.

differences of the two cells being compared, as determined from the values obtained from the SPRT readings in each of the two cells. The value of the Type A standard uncertainty for the measurements was at most 8,6 μK, and had a mean of 5,6 μK. The Type A standard uncertainty is attributed to two contributions; one from the instrumental measurements themselves and the second from handling of the SPRT (transferring the thermometer from cell to cell). The contribution from instrumentation was equivalent to at most 4,2 μK, and had a mean of 3,4 μK. The remainder, and somewhat larger contribution, to the Type A standard uncertainty came from handling of the SPRT, with a maximum contribution of the equivalent of 8,1 μK, and a mean of 4,6 μK.

Apart from the systematic effects that, because of the nature of the experiments, were incorporated in the Type A standard uncertainties, there were two known sources of Type B standard uncertainties. These were the uncertainty in the exact immersion depth of the SPRT due to the uncertainty in the position of the thermometer sensor during the measurements, and the uncertainty in the adequacy of immersion of the thermometer to eliminate thermometer stem conduction during comparisons of the TPW cells. The uncertainty in the immersion depth due to the uncertainty in the position of the SPRT sensor was estimated to be ± 1 mm. This uncertainty is equivalent to about 0,42 μK. Since the thermometer was sufficiently immersed to track the ITS-90 specified hydrostatic-head effect in the cells to within the scatter of the measurements (see Figure 10), the uncertainty in the adequacy of immersion of the thermometer to eliminate thermometer stem conduction was estimated from the residuals of a least-squares fit of the immersion data to the predicted curve. These were calculated to be equivalent to 3,6 μK (u = 0,2 μK). The combination of these two sources of uncertainties gives a Type B standard uncertainty of 3,6 μK for each cell, and a total Type B standard uncertainty of 5,1 μK for the two cells for the measurements of the differences of any two cells being compared.

The expanded uncertainty (k = 2) calculated from these Type A and Type B standard uncertainties is 15 μK for the measurements of the differences of any two cells being compared.

6. Conclusions

6.1 Time dependence of temperature stabilization

Our results show that, generally, newly prepared mantles of TPW cells may require several days of storage in a maintenance bath before they become stable to within 0,1 mK. Also, the results show that within about one week from preparation of the mantles, the triple-point temperatures of the cells had stabilized to within 0,03 mK or better (except for mantles prepared by the LN-cooling technique, for which nine days were required for one of the mantles). Further, they show, for all practical purposes, that after eleven days the temperatures of the four cells were the same.

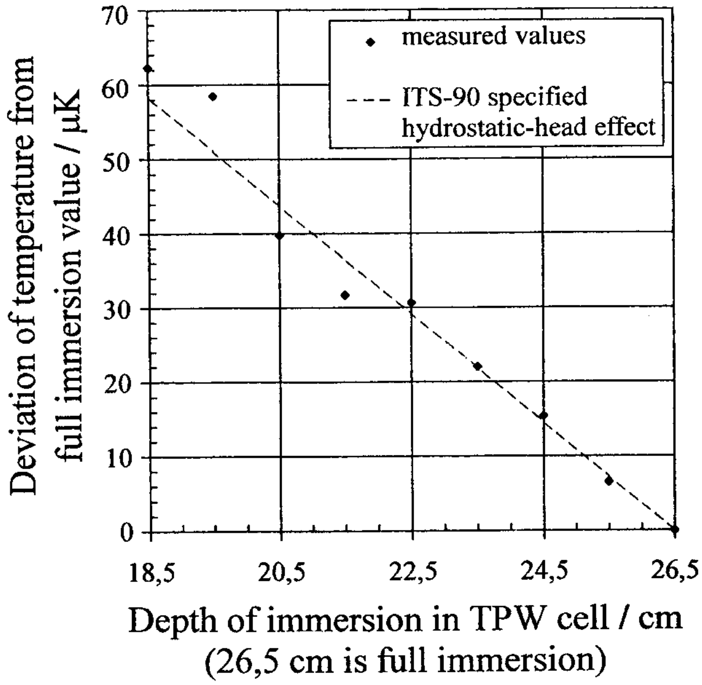

Figure 10. Immersion plot showing the effect of the variation in the hydrostatic head of liquid water in the TPW cell on the SPRT reading. The readings are relative to the maximum immersion in the thermometer well of the TPW cell. The cell was located in a maintenance bath held at 0,007 °C. The ITS-90 specified hydrostatic-head effect is shown as a dashed line.

If the requirement of several days for temperature stabilization is because of the mantle, we have no explanation at the present time for the relatively rapid temperature stabilization in experiment set VII in which the cells were inverted six times immediately after the first set of readings.

6.2 Possible effect of long-term storage of TPW cells

In experiment sets I through IV, after about one week of equilibration of the mantles, the equilibrium temperatures of the test cells were found to be consistently higher (on average about 0,02 mK) than those found with reference cell D which contained an old mantle. The mantle of cell D had been prepared on 1 June 1992, using the crushed solid-CO_2 method. The difference is negligible for all practical purposes, but it was measurable. For experiment sets V_a through VIII, however, the temperature of cell D, with a new mantle that had been prepared using the immersion-cooler method, was not lower than that of the test cells. The results of experiment set VIII demonstrated that the water of cell D was not measurably less pure than that of cell A, for which we could not determine the presence of any impurity. Since the mantle of cell D was already six months old and the ice crystals were large when our comparisons started in experiment set I, and since we did not prepare a new mantle for the cell throughout the experiments of sets I through IV, the results suggest that its mantle had some slight defect, perhaps a small channel between the crystals, that allowed the SPRT, to some extent, to "see" the bath, which was maintained 3 mK colder than the TPW temperature. On the other hand, in experiment set VIII, in which cells A and D are shown to be equivalent, the ice mantle of cell D was over five months old. The difference is that the ice mantle of cell D at the beginning of this investigation (experiment set I) was prepared using the solid-CO_2 method, while the later ice mantle was prepared using the immersion-cooler method. Whatever the cause, the difference found in experiment sets I through IV was constant over eight months of experiments. (Note that cell D, unlike cell A, was not checked for water-soluble impurities.)

6.3 Sticking of ice mantles to the thermometer well

The continual-measurement data of Figure 5 demonstrate the stability of the TPW cells and the precision of the measurement instrumentation. Each datum point involved an average of thirty-six readings taken at 7 s to 12 s intervals. The test cells and cell D, with their own individual SPRTs, were measured in sequence continually over a weekend under computer control. The time interval between the data points for any cell was about 60 min. The standard deviation of the data was 0,01 mK for cells A, C and D and 0,02 mK for cell B. The larger deviation for cell B is attributed to progressive "sticking" of the mantle to the thermometer well. Since neither the SPRTs nor the cells were moved during the measurements, these results show the capability of the measurement system. Since the datum points are approximately 60 min apart, some of the scatter in Figure 5 may have been caused by partial sticking of the mantle when the SPRT did not have a measuring current flowing through it.

The data of experiment set V, depicted in Figures 5, 7a and 7b, show the effect of the ice mantle when it is allowed to stick to the thermometer well. When the mantle was "unstuck", the readings on the cells returned to accurate TPW equilibrium values. Hence, it is important to check the mantle frequently to ensure that it is free (see Section 3.5).

6.4 Cracking of ice mantles

It is thought that all four techniques used for preparing the ice mantles initially created small ice crystals, some strains, and where strains were extreme when the ice coating had become fairly thick, visible cracking of the mantle. On storage near the TPW temperature, the strains were relieved and the small ice crystals became larger. When the LN-cooled-rod method was used to prepare a mantle, the mantle cracked before it was of the desired thickness. Such cracking occurred whether the initial temperature of the TPW cell was 274 K or 295 K. Although the amount of cracking seemed to be less in experiment sets I through IV when the initial temperature of a cell was approximately 274 K, the cracking was most likely to be related to the magnitude of the temperature excursions during the preparation of the ice mantles. The cracking seemed to start after fewer insertions of the LN-cooled rod when the starting temperature was 274 K rather than 295 K. Cracks that formed in the ice during the initial stages of the preparation of a mantle began to heal before completion of the mantle. Although no effort was made to determine how long the visible cracks remained, it is expected that the cracks disappeared during the first day of storage in the maintenance bath.

When using the LN technique, extensive cracking of the mantle occurred when the cooling assembly was withdrawn from the well. It is expected that in the 6 min to 9 min that were required to freeze a suitable mantle, a large strain gradient was produced and, when the rate of cooling was interrupted with added vibration, a change in the strain gradient was introduced, causing the cracking in the ice mantle. The cracking was audible in all cases, but in the case of LN cooling the cracking was sufficiently violent to cause the TPW cell to move and the ice to appear opaque.

We have not considered the possible effects on the strain and cracking of the mantles of differential thermal expansion between ice and borosilicate glass. Note, however, that with the LN-cooled-rod method, cracking occurred on cooling a mantle that was already frozen, but in the LN-cooling method cracking occurred in most cases either when the ice mantle was disturbed or when it was warmed.

6.5 Possible cause of the initial temperature change

The increase in the triple-point temperature of a cell for several days after preparation of its mantle, and the subsequent stabilization to an equilibrium value, has been attributed by Berry [2], and later by McAllan [12], to strains (which would reduce the temperature) that become relieved with time, and to the greater interfacial energy of the initial small ice crystals (which would also reduce the temperature) that become larger with time. The interfacial energy would decrease with the increase in crystal size. The temperature at which the ice mantles are aged may affect the rate at which the cells become stable. An ice bath at 0 °C, being slightly colder than the 0,007 °C of our TPW maintenance bath, may somewhat prolong the stabilization of newly prepared cells to the equilibrium triple-point temperature.

In our measurements, large temperature variations (0,05 mK to 0,1 mK, or larger) in the mantles occurred mostly during the first 48 h or so after their preparation. Except in a few cases, we observed very small variations (less than 0,05 mK) in the temperatures of the cells at times beyond 48 h. This is in contrast to the variations observed by Bonhoure and Pello [1], who began measurements on their cells only 48 h after preparation of their mantles (prepared by the LN-cooled-rod method). Although in some cases our investigations seem to show that larger and prolonged changes in the temperatures occurred when the cracking of the mantle was fairly severe, such as when the mantles were prepared by LN cooling, we did not observe the high or low values that Bonhoure and Pello [1] observed over an extended period of time. Except for two mantles prepared by the LN method that required four days to stabilize to within 0,1 mK of the final value, all of the mantles in our eight experiment sets, with seven mantles frozen using LN-cooled rods, stabilized to within 0,1 mK within three days.

Rapid freezing of water can result in non-equilibrium phase separation of the impurity components between the solid and liquid phases. Any migration of the impurities to equilibrium conditions is expected to have heat effects, but the diffusion of impurities through ice is slow, so heat effects from this source will not be detectable.

6.6 Peaking during the initial stabilization period of the TPW cell

The mantles prepared using the four methods showed some peaking on the second to the fourth days after preparation (see Figures 1 through 4 and 6b through 8), with most of the peaking occurring for those cases in which the mantles were prepared using the LN-cooled-rod method or the LN-cooling method. The results show that peaking most frequently occurred when an ice mantle was prepared by starting at 295 K rather than at 274 K. This was found to be quite consistent in the results of the LN-cooling method. In almost all cases, the LN-cooled-rod method resulted in some degree of peaking. The results of the immersion-cooler method suggest that peaking occurs less often when using this method. Berry [2] reported peaking in several cells prepared using solid CO_2. The peaking of values has been observed often enough in our experiments to consider the effect to be real and not instrumental "excursions". We have no solid scientific explanation for the peaking that was observed. A guess is that the release of the strain and the change in the surface energy with crystal growth may have been sufficient to warm the *inner* liquid layer slightly above the final stable temperature or above the expected trend of values. These strains were introduced during the preparation of the mantle but were not relieved by cracking of the mantle. Mantles that underwent severe cracking appeared thereby to have quickly released most of the energy associated with large strains introduced during preparation of the mantle, and the energy from any remaining less severe strains was released more slowly. Also, the nature of the fine ice crystals that were produced may depend on how and when the mantle was last made. The TPW cell A, the newest of the four cells investigated (see Table 1), seemed to exhibit peaking more frequently than the other cells. (Note that, during measurement, the SPRT is being powered and is in a steady thermal state with the inner melt and the ice/water interface.)

The four TPW cells used in these experiments at NIST and cell 758 used by Bonhoure and Pello [1] were manufactured by the same company in the United States. As indicated by the data, cell 758 was more stable than the other cells investigated by Bonhoure and Pello. The data of cell 758, however, showed a peaking similar to that observed in the first set of measurements at NIST on the ice mantle frozen with LN-cooled rods. The difference in behaviour of cell 758 from that of other cells investigated by Bonhoure and Pello [1] may be due to differences in impurity concentration and in the types of impurities that are present, or it may be due to unaccounted changes in the measurement equipment.

6.7 Procedure for preparing TPW cell ice mantles for use

The use of the TPW cell is basic to platinum resistance thermometry. The results of our measurements strongly indicate that regular measurements on a minimum of two, and preferably three, TPW cells serve as a check on the measurement process.

Sometimes it is preferable or practical to prepare ice mantles by only one of the techniques described here. Our results show that, regardless of which technique is used, the temperature of the mantle produced will, after a period of three days (maybe four days for those prepared by the LN method), agree to within 0,1 mK with those prepared by the other techniques. After about one week (maybe nine days for those prepared by the LN method), the agreement will be to within 0,03 mK or better. After eleven days, the temperature of a mantle prepared by any of the four methods will be the same as that of a mantle prepared by any other technique. For the most accurate realization of the triple-point temperature of water, and hence of the ITS-90, we recommend that mantles should not be prepared by the LN technique and that they should be prepared at least one week before they are to be used.

Acknowledgement. The authors thank the referee for many helpful comments.

References

1. Bonhoure J., Pello R., In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 6 (Edited by J. F. Schooley), New York, American Institute of Physics, 1992, 299-303.
2. Berry R. J., *Can J. Phys.*, 1959, **37**, 1230-1248.
3. Strouse G. F., Furukawa G. T., Mangum B. W., Document CCT/93-24, submitted to the 18th Meeting of the CCT, 1993.
4. Eisenberg D., Kauzmann W., *The Structure and Properties of Water*, New York, Oxford University Press, 1969, 296 p.
5. Dowell L. G., Rinfret A. P., *Nature*, 1960, **188**, 1144-1148.
6. Burton E. F., Oliver W. F., *Proc. R. Soc. London*, 1935, **A153**, 166-172.
7. Sugisaki M., Suga M., Seki S., *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2591-2599.
8. Evans J. P., Sweger D. M., *Rev. Sci. Instrum.*, **1969**, **40**, 376-377.
9. Furukawa G. T., Bigge W. R., In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 5 (Edited by J. F. Schooley), New York, American Institute of Physics, 1982, 291-297).
10. Strouse G. F., Mangum B. W., *Proc. 1993 Measurement Science Conference*, 20-24 January 1993.
11. Taylor B. N., Kuyatt C. E., *NIST Technical Note 1297*, Washington, DC, US Govt. Printing Office, 1993, 17 p.
12. McAllan J. V., In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 5 (Edited by J. F. Schooley), New York, American Institute of Physics, 1982, 285-290.

Received on 12 September 1996 and in revised form on 2 April 1997.