

Uncertainties in the realisation of ITS-90 metal freezing points using sealed cells

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Abstract

Sealed cells are an attractive means for realising the indium, tin, zinc, aluminium, and silver ITS-90 fixed points. The cells, which typically have borosilicate glass or fused silica envelopes, are less prone to contamination, easier to maintain, and easier to use than open cells. However, anecdotal evidence suggests that the cells are prone to defects causing the internal pressure of the cells to depart from that specified by ITS-90 (101.325 kPa) when the fixed point is realised. This report discusses mechanisms by which the pressure errors may be introduced into the cells, summarises the experimental evidence for the effects, and recommends values for the uncertainties to be applied to fixed-point-realizations made using sealed cells. Amongst the 223 sealed cells assessed, 10 cells clearly exhibited errors of sufficient magnitude to suggest that the cells had leaks or operated at an incorrect pressure. Approximately one in six of the aluminium and silver cells appeared faulty with errors as large as 11 mK. All sealed cells should be checked regularly against either open cells or other certified sealed cells to ensure the cells' integrity.

1. Introduction and Scope

The fixed points defined by ITS-90 [1] for the calibration of standard platinum resistance thermometers are not only the backbone of the temperature scale, they are also commonly used for the calibration of secondary thermometers such as industrial platinum resistance thermometers, noble-metal thermocouples, and thermistors. Ideally, for the realisation of ITS-90 at the lowest levels of uncertainty, the fixed points should be realised in cells where the pressure can be measured directly and the measurements corrected to the standard pressure specified by ITS-90 (101.325 kPa). In recent years, sealed fixed-point cells have been developed, and are now manufactured for sale by perhaps a dozen or more manufacturers. Because these cells are sealed, typically in borosilicate glass or fused silica, they are less prone to contamination, easier to maintain, and easier to use. They are particularly attractive for laboratories with limited resources, such as small National Measurement Institutes (NMIs) and industrial laboratories. The majority of fixed-point cells now sold commercially are sealed cells.

In 2008, Working Group 3 of the CCT (Uncertainties) prepared a working document summarising all known sources of uncertainty associated with the realisation of the SPRT subranges of ITS-90, including effects associated with fixed points [2]. Because the focus of the report was on the realisation of ITS-90 in accordance with the ITS-90 and the Supplementary Information [3] at the lowest levels of uncertainty, it did not discuss in detail the calculation of uncertainties for the sealed cells commonly used for the metal fixed points. Although the working document provided a simple model for the additional contribution due to the uncertainty of the pressure in the sealed cell, the model was applicable only under near ideal conditions. It became clear, from the anecdotal experiences of several large NMIs, that many sealed cells developed a leak either during or sometime after manufacture, or were sealed with the incorrect pressure, leading to operation at an incorrect pressure and resulting in significant errors in the realised temperature. A more realistic uncertainty estimation procedure was required.

In December of 2014, the CCT agreed to the establishment of a new task group, the Task Group for Sealed Metal Freezing-Point Cells (TG-SMFPC), charged with the responsibility of preparing a report

- 1) advising on the definition of SMFPCs, and
- 2) providing guidance on estimating the uncertainty in temperatures realized by SMFPCs.

Accordingly, this report provides guidance on the assessment of the uncertainties due to pressure in sealed metal freezing-point cells, specifically, cells for the freezing-points of indium, tin, zinc, aluminium, and silver. Miniature and slim fixed-point cells are not considered in this evaluation. Because of the poor thermometer-immersion conditions, miniature and slim cells exhibit much larger measurement uncertainties due to their susceptibility to variations in furnace temperature, ambient temperature and furnace temperature non-uniformity, and their performance falls well short of that necessary as defining standards for ITS-90.

The first of the following sections discusses mechanisms by which the pressure errors may be introduced into the cells, Section 3 summarises the experimental evidence for the effects, and Section 4 provides conclusions and recommendations. This report should be read and used in conjunction with the most recent Guide to the Realisation of ITS-90 [4, 5] and the SPRT Uncertainty Guide [2].

2. Pressure Effects in Sealed Freezing-Point Cells

2.1 Overview

Fixed-point cells may be sealed or open. Sealed cells are sealed at the time of manufacture with the result that the internal pressure cannot subsequently be measured or controlled when the cell is in use. Open cells may be operated open to the atmosphere or, more usually, under control of a system controlling the gas pressure and composition (often argon, occasionally helium).

During all realisations of all ITS-90 freezing points, the pressure above the surface of the substance in the cell should be the standard atmosphere, $p_0 = 101.325$ kPa. Measurements made in cells at a different pressure, p_{meas} , should be corrected for the pressure difference:

$$\Delta T_p = -\frac{dT}{dp}(p_{\text{meas}} - p_0), \quad (1)$$

where dT/dp is the pressure coefficient for the fixed point, the values of which are tabulated by ITS-90 (See Table 1). For melting and freezing points in open cells without any pressure control or measurement, the pressure is determined principally by the weather and altitude at the location of the measurement. The pressure variations with weather are typically about 1 kPa (standard uncertainty) with extremes of about +3 kPa and –5 kPa. The decrease of pressure with altitude is about 11 kPa/km leading to pressure errors of up to 20 kPa or more at some locations, and to temperature errors of up to 1.4 mK, depending on the pressure sensitivity of the fixed point.

The uncertainty in the pressure correction is given by

$$u^2(\Delta T_p) = \left(\frac{dT}{dp}\right)^2 u^2(p_{\text{meas}}) + u^2\left(\frac{dT}{dp}\right)(p_{\text{meas}} - p_0)^2, \quad (2)$$

where $u(p_{\text{meas}})$ is the uncertainty in the pressure inside the cell and $u(dT/dp)$ is the uncertainty in the pressure coefficient, which is practically negligible. The current values of the pressure coefficients tabulated by ITS-90 for the fixed points are consistent with values calculated from the Clausius-Clapeyron equation:

$$\frac{dT}{dp} = \frac{T_{\text{fp}} \Delta V}{\Delta H_f}, \quad (3)$$

where ΔH_f is the molar heat of fusion, T_{fp} is the fixed-point temperature, and ΔV is the molar volume change on freezing. In open cells, the pressure coefficient can be confirmed by monitoring the fixed-point temperature while changing the gas pressure.

2.2 The pressure in sealed cells

Typically, during the manufacture of sealed cells, the filled graphite crucible is placed in the furnace within the glass or fused-silica envelope with a long capillary attached to the gas filling system. Once the cell has been raised to the fixed-point temperature and the pressure of the inert filling gas has been adjusted to the standard atmosphere, the capillary is sealed at a point close to the top of the furnace. Then, once the cell has been cooled to room temperature, the excess capillary is removed by resealing the cell close to the crucible.

An estimate of the final pressure of the cell can be made by using the ideal gas law, as follows. At the time the cell is filled with gas at the fixed-point temperature, the gas in that part of the container around the fixed-point crucible (i.e., excluding the capillary) is described by

$$p_0 V_{\text{fp}} = n_{\text{fp}} R T_{\text{fp}}, \quad (4)$$

where n_{fp} is the number of moles of gas in the space in the fixed-point cell, of volume V_{fp} . The gas in the capillary obeys a similar relationship

$$p_0 V_c = n_c R T_c, \quad (5)$$

where the subscript, c, refers to the capillary, and T_c is the average temperature of the gas in the capillary. When the cell is later returned to room temperature and the capillary is removed, a large fraction, $V_{fp}/(V_c+V_{fp})$, of the total quantity of the gas is retained in the cell envelope, and this leads to a cell with an internal pressure at the fixed-point temperature of

$$p = p_0 \left(1 + \left(\frac{V_c}{V_c + V_{fp}} \right) \left(\frac{T_{fp} - T_c}{T_c} \right) \right). \quad (6)$$

According to this equation, the pressure error is minimised by ensuring the capillary has a small volume, and, at the time when the capillary is sealed outside the furnace, ensuring that the average temperature of the gas in the capillary is as close as practical to the fixed-point temperature. The capillary temperature is, unfortunately, not single valued and parts of the capillary may range between room temperature, approx. 300 K, through the fixed point temperature, to 1900 K (the melting point of silica), depending on the details of the manufacturing process. The capillary volume is also dependent on local manufacturing processes, but can be made as low as 2% of the total volume, though it may be very much greater than 2% if capillary tubing is not used.

With a capillary volume of 2% of V_{fp} , and an average temperature, T_c , ranging from 300 K to near the fixed-point temperature, the pressure errors range from 2% to perhaps as much as 10% (2 kPa to 10 kPa). It is not known how closely the ideal is approached by the different manufacturers, but it is a guide to the best uncertainties that can be achieved in practice.

For some manufacturers, a practical complication arises from the difficulty of sealing glass tubes when there is significant pressure difference between the fill gas and the local atmosphere. This means that cells manufactured at sites well above sea level are nearly always sealed at the local ambient pressure, and not at the standard pressure specified by ITS-90. For these cells, the pressure is low due to the decreasing pressure that occurs with increasing altitude (about 11.3% low for cells sealed at 1000 m, and 21.5% low at 2000 m)). There are three practical solutions. Firstly, a pressure correction can be applied using Equation (1) whenever the cell is used. Secondly, the cell can be treated as a secondary reference and calibrated against another certified cell. Alternatively, the loss in pressure due to altitude can be compensated by sealing the cells at a temperature lower than the fixed-point temperature, but the choice of temperature requires some care and is specific to the manufacturer's site, equipment and procedures. It is not known if any manufacturer makes such an adjustment.

There is also a compromise in the choice of glass for the cell envelope. Borosilicate glass (similar to Pyrex®), which is commonly used for laboratory glassware, is very easily worked but must be annealed to give the best immunity to thermally induced stresses. Unfortunately, annealing a completed and sealed fixed-point cell is not practical, and unannealed borosilicate glass is prone to developing fine cracks. Fused-silica glass is much more difficult to work, but has a near-zero temperature coefficient so has a very good immunity to thermal stress. Most cells are apparently manufactured using fused silica. The softening point for borosilicate glass is too low for it to be used in the aluminium and silver point cells, so fused silica is essential for these points.

2.3 Primary effects of leaks

The most significant source of uncertainty associated with sealed freezing-point cells is pressure effects due to leaks in the glass where the cell was sealed, which may occur during manufacture or afterwards when the cell is in use. The effect of a leak is complicated by the nature of the leak. In principle, but not in practice, three different situations can be distinguished.

2.3.1 Major leak

A major leak allows the gas pressure within the cell to equilibrate rapidly with the ambient pressure at the location where the cell is used. In this case, the cell behaves the same as an open cell operated at

atmospheric pressure without any control of the pressure or composition of the gas. This leads to the previously described pressure variations with weather and altitude, and temperature errors of up to 1.4 mK.

2.3.2 Slow leak

A slow leak is one where the cell pressure equilibrates with the ambient pressure over very long periods of time, but not over the relatively short period of a fixed-point realisation (hours). In this case, the cell behaves as a cell sealed at ambient temperature and pressure (the cell storage conditions). Thus, when the cell is operated at the fixed-point temperature, the internal pressure is elevated by, approximately, the ratio of the fixed-point temperature to the ambient temperature, T_{amb} :

$$p = \frac{T_{\text{fp}}}{T_{\text{amb}}} p_0, \quad (7)$$

which leads to a fixed-point temperature error of

$$\Delta T \approx \left(\frac{T_{\text{fp}}}{T_{\text{amb}}} - 1 \right) \frac{dT_{\text{fp}}}{dP}. \quad (8)$$

As Table 1 shows, the potential errors for cells with slow leaks range from about approximately 2 mK for indium cells to approximately 19 mK for silver cells.

2.3.3 Intermittent leak

In the event of an intermittent leak, the internal cell pressure never equilibrates with the ambient pressure while the cell is in storage. The temperature realised by the cell will be in error, but the error may or may not change with time and will range between zero (i.e., the cell is at the standard pressure) and the worst case given by Equation (8).

Note that both slow and intermittent leaks (as defined here) lead to an increased pressure at the fixed-point temperature, while cells sealed at altitude typically have a low pressure, so the signs of the errors are different.

Table 1 summarises the relevant properties of the five fixed points considered here, and the magnitude of the pressure effects under different circumstances.

Table 1: Properties of the fixed-point substances and estimates of pressure effects

Fixed point	In	Sn	Zn	Al	Ag
Fixed-point temperature (K)	429.7485	505.078	692.677	933.473	1234.93
dT/dP (mK/atmosphere)	4.9	3.3	4.3	7.0	6.0
Error for $\Delta P = 10$ kPa (mK)	0.48	0.33	0.42	0.69	0.59
Error for 1000 m elevation, $\Delta P \approx 11.3$ kPa (mK)	0.55	0.37	0.48	0.78	0.67
Maximum error, Eq. 8 (mK)	2.12	2.26	5.63	14.78	18.70
Maximum error, Eq. 8 but with no O ₂ (mK)	-	-	-	-	14.77

2.4 Secondary effects of leaks

Ideally, fixed-point cells should be operated with an inert atmosphere to prevent oxidation of the fixed-point substance, to prevent the dissolution of unwanted gases in the fixed-point substance, and to prevent the oxidation of the graphite crucible. These concerns are especially relevant for aluminium and silver cells.

With aluminium cells, the fixed-point temperature is sufficiently high for oxidation of the graphite crucible to occur. Note that the oxidation reaction $\text{O}_2 + \text{C} \rightarrow \text{CO}_2$ preserves the number of moles of gas, so there is no major pressure change accompanying the oxidation of graphite in the event of a slow leak.

With silver-point cells, a more serious problem occurs because oxygen is soluble in silver, and is an impurity that depresses the freezing-point temperature [6]. This means that cells with a slow or intermittent

leak may initially show an elevated temperature due to the elevated pressure as modelled by Equation (8), but quite rapidly, the oxygen reacts with the silver and dissolves. Since the oxygen is about 21% of the atmosphere, the pressure in a cell with a slow leak may drop to 79% of the values suggested by Equation (8). With time and repeated use, the temperature realised by a cell may become increasingly depressed as air diffuses into the cell and more oxygen reacts with the silver and dissolves.

3. Experimental Evidence

To confirm both the high frequency of faulty cells reported anecdotally and the features and magnitudes of the effects suggested by the models described above, calibration data on sealed cells from some of the laboratories represented on the Task Group were collated. Where the manufacturers reported the internal cell pressure, pressure corrections were made to make the analysis consistent with expected use. (Note: when sealed cells are calibrated, it is better to report the realisation temperature without the pressure correction to eliminate uncertainties associated with the manufacturers' pressure measurements.) In all cases, errors in realisations made with the sealed cells were determined by comparison with reference open cells maintained under inert gas at a controlled pressure. The results are summarised in Table 2 and Figure 1. In total, 223 cells from 7 different manufacturers are represented in the data. Not all known manufacturers have cells represented in the sample.

In total, 10 of the 223 cells have large errors suggesting the presence of slow or intermittent leaks. Perhaps the most conspicuous feature of the figure is the number of aluminium and silver cells exhibiting large errors. Note that cells with major leaks will not be apparent in the plots unless they are also contaminated. Several of the silver cells exhibit large negative errors, which are characteristic of the effects of dissolved oxygen, and some of these cells may have major leaks. Also, as expected, there are no silver cells with errors exceeding 79% of the value predicted by Equation (8).

Table 2: Summary of the experimental results

Fixed point	In	Sn	Zn	Al	Ag
Number of cells evaluated (total = 223)	28	49	58	57	31
Number of conspicuous outliers (total = 10)	0	0	0	3	7
Maximum error (mK)	0.50	0.9	1.59	11.1	11.4
Minimum error (mK)	-0.84	-0.87	-1.80	-3.3	-9.09
Root-mean-square error (mK)	0.33	0.38	0.69	2.17	4.30
Equation (9) , see text	0.32	0.34	0.84	2.22	2.22
Number of cells outside $k = 2$ interval (total = 16)	3	3	5	2	3

It is notable that there are no cells exhibiting more than about 75% of the maximum error predicted by Equation (8), which suggests that the slow-leak scenario described in Section 2.3.2, does not occur in practice, and that all the anomalous cells exhibiting positive errors must have intermittent leaks. Note too, that there are no obvious outliers amongst the indium, tin, and zinc cells, and the distribution of errors for these points is not obviously skewed, suggesting that there are no indium, tin, or zinc cells amongst the sample of 135 cells with slow or intermittent leaks. This may be because none of the cells have leaks, or it may be that because the glass envelopes (borosilicate or fused silica) are not conducive to the formation of slow leaks at these temperatures.

It is not possible to determine how many of the 223 cells have major leaks. For the indium, tin, zinc and aluminium cells, major leaks cause errors smaller than the observed cell-to-cell variations, so are practically indistinguishable. With silver cells, the large freezing point depression observed in four of the cells is indicative of a major leak, but there may be other silver cells with major leaks that cannot be recognised.

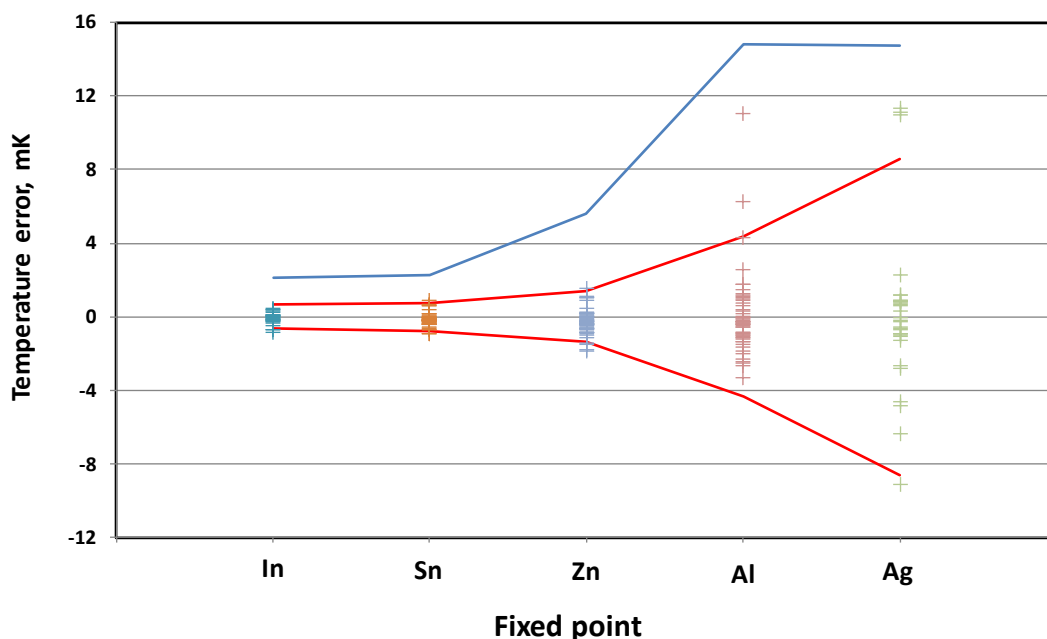


Figure 1: Summary of the measurements of the temperature errors in the 223 sealed fixed-point cells. The blue line shows the maximum error estimated according to Equation (8), except for the silver cell, which is additionally assumed to have no gaseous oxygen present. The red line shows the recommended $k = 2$ uncertainty envelope (see text).

Although it is possible, in principle, to distinguish some types of leak (as described in Sec. 2), we found no way in practice to detect a leaky cell or distinguish different types of leak other than by direct comparison with a known reference, either an open cell or a certified sealed cell. This means that in the absence of such evidence, every sealed cell must be treated as though it has a leak, and the only means to guarantee the performance of the cell at the lowest levels of uncertainty is by comparison with another certified cell, preferably an open cell at known pressure.

For the indium, tin, zinc and aluminium cells, the root-mean-square (rms) measured temperature errors were found to be in direct proportion to the maximum temperature error predicted by Equation (8). Indeed, the equation

$$u(\Delta T) \approx 0.15 \left(\frac{T_{\text{fp}}}{T_{\text{amb}}} - 1 \right) \frac{dT_{\text{fp}}}{dP} \quad (9)$$

is a good guide to the uncertainty in temperatures realised by most of the sealed metal-fixed-point cells, as shown in rows 6 and 7 of Table 2. However, for silver cells, the observed standard deviation of temperature errors is almost exactly twice that given by Equation (9). The increased uncertainty in silver cell realisations is almost certainly due to the additional effects of dissolved oxygen in silver cells with major leaks. With the indium, tin, zinc and aluminium fixed points, cells with major leaks have relatively small temperature errors, and, in most situations, will be indistinguishable from properly sealed cells. The red lines in Figure 1 indicate the $k = 2$ uncertainty envelope using the measured rms error (Table 2 Row 6, shaded) as the standard uncertainties in the realised temperatures. There are 16 of the 223 cells (7%) outside the $k = 2$ envelope.

4. Conclusions and recommendations

In total, 223 sealed cells were compared against open cells in four different laboratories. Amongst the 135 indium, tin and zinc cells, there were no errors consistent with slow or intermittent leaks, although the existence of major leaks that would cause the cells to operate at local ambient pressure could not be ruled out. For the 88 aluminium and silver cells, there was clear evidence of leaks in at least 10 of the cells (about

1:9). It is possible that there were other aluminium and silver cells with major leaks and not be immediately distinguishable from intact cells.

We found no way to identify cells with leaks other than by direct comparison with open cells operated at known pressures, and no means for conclusively identifying all cells with leaks. No cells exhibited the maximum temperature error predicted by Equation (8), which suggests that cells with slow leaks are rare, and most cells either have intermittent or major leaks. For silver cells, contamination by dissolved oxygen is a complicating factor.

The first general recommendation is that sealed cells should be calibrated after manufacture by comparison with another, preferably an open reference cell, before they are used as fixed points for the calibration of thermometers. Subsequently they should be recalibrated at intervals sufficient to ensure that users can be confident that the realised temperature remains within the desired uncertainty. The chosen intervals should depend on the intensity of use, the specified uncertainty, and the performance of the cell in use (quality of melts and freezes, immersion tests, etc). The use of a check SPRT each time a cell is used is a useful quality control measure.

For cells calibrated directly against open cells operated at a known pressure, the calculated uncertainty should be as for a normal fixed-point calibration considering all the relevant sources of uncertainty (see [4, 5]). In that case the uncertainties in temperatures realised with sealed cells can approach the calibration and measurement capabilities (CMC) of the calibrating laboratory.

For sealed cells that have been manufactured in every other respect in accordance with the best practice recommended by the ITS-90 guides (i.e., excluding miniature and slim cells), it is recommended that temperature realised by the cells be assigned standard uncertainties as indicated by Row 6 of Table 2 (shaded), i.e. In: 0.33 mK, Sn: 0.38 mK, Zn:0.69 mK, Al: 2.17 mK, and Ag: 4.3 mK.

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