FUNDAMENTALS OF THERMOMETRY
PART II
FIXED POINTS OF THE ITS-90

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CONFIDENCE IN THE METAL FREEZING POINTS OF ITS-90

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ABSTRACT

As Part II of the ongoing series generally entitled "Fundamentals of Thermometry", Sostmann discusses the fixed points of the International Temperature Scale of 1990 (ITS-90) which encompass the long stem platinum resistance thermometer range.

A cogent question is: "How does the user know that the equipment he uses to realize these fixed points indeed reproduce the definitions of the Scale?" and because the definitions are superior to any measurement which can be made upon them, there is no direct answer to that question. However there are indirect answers, and this discussion is interspersed with Tavener's description of his own adventures in pursuit of them.

INTRODUCTION (Sostmann)

We saw in the previous article in this series[1] that the International Temperature Scale of 1990[2] defines a temperature scale in terms of fixed points; states in nature in which pure materials exhibit equilibrium between two or three phases, during which equilibrium states temperature is invariant. It has become popular to refer to these equilibrium conditions as 'intrinsic standards'.

In the dictionary definition of intrinsic, we have

> Intrinsic, (adjective): belonging to the inmost constitution or essential nature of a thing, essential or inherent and not merely relative ... as the very essence of the thing in virtue of the metaphysical structure of the universe ... [3]

from which we infer that the intrinsic property derives from its fundamental nature and not from an applied attribute, such as the result of a

calibration. A committee of the National Conference of Standards Laboratories has achieved this definition of an intrinsic standard, applicable, for example, to the Josephson Volt, the Von Klitzing Ohm, and the equilibrium fixed points of the Temperature Scale:

> Intrinsic standard (noun): Designated measurement standard derived from the innate value of natural physical constants whose value can be accurately reproduced under carefully controlled conditions.

I believe that this definition is insufficiently pure because of its reference to "accurate reproduction" - the Committee definition includes within its scope the artifact and the experiment with which the value is realized - and I offer the following definition in its place:

> Intrinsic standard (noun): a standard of measurement having the property that is the ideal value of the natural physical constant which defines it. The assignment of a numerical value on a Scale may be arbitrary.

My definition differs essentially in that the "standard" is the ideal physical state, approachable only as a limit, and requires that the value which is obtained from the artifact and the experiment must be shown to approach the natural value, preferably within some assignable degree of uncertainty.

The fixed points of the Scale are intrinsic standards; indeed, it would be difficult to build a working temperature scale on any other foundation. The freezing, melting and triple-point temperatures of pure metals and the three-phase equilibria of pure gases, in the ideal case, are constants of nature. As such, they can be approached by measurement, but we recognize that they are superior to any measurement which can be made of them.

Artifact embodiments of intrinsic principles may deviate from ideal from a number of causes. Among them are these:

> (1) Although made from material as pure as obtainable, they are not ideally pure. For example, pure metals used in metal freezing point artifacts are generally impure by less than 1 ppm, but they must still be regarded as very dilute alloys.

> (2) They may be contaminated in manufacture, or in use, perhaps over long periods of time.

(3) They generally require correction for such things as ambient pressure, hydrostatic head, etc., which are in themselves the results of measurement and subject to measurement error.

(4) In use, the measuring system may not be in ideal thermal equilibrium with the phase equilibrium temperature.

These, and other effects, lend great importance to the establishment of confidence in the reproducibility and uncertainty assignable to fixed point standards as they are represented by the artifacts we use to calibrate thermometers. The fixed points which are used to define the Scale over the range of the long-stem platinum resistance thermometer and their associated pressure coefficients are shown in Table 1.

We will look first at the temperatures provided by the freezing points of high purity metals, and following that, the triple points of, mercury, argon and water. In this discussion I will relate some of my own experiences as a manufacturer of cells at YSI, and Tavener will describe his further experiences after Isotech acquired this product line in 1987.

THE FREEZING POINTS OF HIGH PURITY METALS (Sostmann)

It is usual practice to confine the metals in cells which contain them during the process of melting and freezing, provide an axial well into which a thermometer may be inserted, include some means (either by gas purging or by a totally sealed enclosure) for ensuring that the metal is not contaminated in use, and which are made of materials which themselves are not sources of contamination. Most impurities (although not all) depress the freezing point of a metal. As a generality, impurities at the level of 1 ppm will depress the freezing point between 0.3 and 1 mK.

Figs. 1(a) and 1(b) show two common designs of cell, used for indium, tin, zinc, aluminum and silver, and the less-often used metals such as bismuth, lead and cadmium. The cell shown in 1(a) contains the metal in a crucible of purified graphite. The well for the thermometer is also sheathed in graphite. The system is surrounded by an envelope of fused quartz, which is continuous and extends to the bottom of the thermometer well. This total enclosure permits the manufacturer to purge the cell with vacuum and inert gas, and finally to seal the cell with a gas content of pure argon at a pressure of 1 standard atmosphere at the freezing point of the metal. Thus the interior of the cell becomes a world in itself, and, unless broken, is not in danger of contamination from outside sources, and does not require correction for the effects of ambient pressure.

I recommend sealed cells for all users. I have used some cells for as much as 20 years without experiencing shifts in the temperature realized. However there is a theoretical objection that the internal pressure cannot be, measured in use, and the realized temperature would vary with pressure, if for some reason the built-in pressure of a sealed cell should change. Fig 1(b) shows a cell which is identical except that it is not sealed. Instead, provision is made for gas purging during the heating and cooling of the cell. Some (but by no means all) National Laboratories feel it their legal responsibility to use open cells, and I cannot disagree; they must seek for the ultimate assurance. But the required pressure measurement is a possible source of uncertainty. Also, the blanking gas must be absolutely oxygen-free, since some metal freezing temperatures (silver, for example) are depressed by the presence of oxygen. (This is usually done by passing the gas through a getter, such as copper wool held at about 500°C).

A general discussion of how a metal freeze point is realized, and the equipment and technique necessary for doing so, is given in a previous issue of The Isotech Journal of Thermometry[4]. While some metals require detail variations of technique, the general procedure is as follows:

A cell is assured to be in the solid state, as it will be if it has been stored at ambient temperature. The cold cell is inserted into the furnace and the furnace controller is set a few degrees (e.g., 5°C) above the melt temperature.[5] A monitoring thermometer is placed in the well of the cell. At the onset of melting, the temperature rise will cease (this is called the "melt arrest") because the heat supplied is absorbed in phase change rather than temperature change. When the metal is completely molten, the monitoring thermometer will indicate a rise to the temperature of the controller setting. The controller is then set slightly (e.g. 1°C) below the freeze temperature. As the temperature drops, the monitoring thermometer will indicate a decrease in cell temperature. The metal will remain liquid, briefly, below the temperature at which it will freeze ("supercool", and then, as the first crystal nucleation occurs, will rise to the freeze plateau as the latent heat is released. The slow release of latent heat will maintain the metal on the freeze plateau for some period of time, following which the metal is completely solidified, and the temperature will drop to that of the controller setting. Fig. 2 illustrates this cycle.

More information is given in Tavener's comments in this article. In addition, Isotech furnishes most comprehensive operating instructions with its furnaces and cells.

CONFIDENCE IN THE FREEZING POINTS OF HIGH-PURITY METALS
(Tavener)

Isothermal Technology is in the unusual position of being both a Nation-
ally accredited laboratory and a producer of commercially-distributed
metal equilibrium fixed-point cells and ITS-90 thermometers. We must
therefore satisfy ourselves, our customers, and the National Physical
Laboratory of England, which supervises us, that the cells we use for
our own calibrations, and the cells we sell to others, are acceptable em-
bodiments of the intrinsic standards which define ITS-90.

There are several indirect approaches to the verification of a cell. As
part of our application to our National Accreditation and Assessment
Authority (NAMAS) to assess our capability, establish evaluation proce-
dures and designate our uncertainty of measurement, our Certificate of
Accreditation includes the following text:

> In order to evaluate the performance of your fixed-point cells, the
> following procedure should be carried out:
>
> (1) Total melt, followed by fast freeze to segregate any impurities
>
> (2) Slow melt, to be fully plotted from initial undercool to final
> rise
>
> (3) Freezing curves, for all cells except the gallium cell, followed
> by determination of plateau temperature using NPL calibrated
> Standard Platinum Resistance Thermometers.

The metals used in freezing-point cells are the purest we can obtain;
99.9999% (or in the parlance of the trade, "6 nines) or better. "Better"
must be taken qualitatively, since at 6N purity we approach the limit of
spectrographic analysis. Nevertheless, these metals must be regarded as
having minute fractions of impurity which usually (but not always) de-
press the freezing point. Ideally pure materials have unique melting and
freezing temperatures, whilst alloys exhibit a melting or freezing range.
Examination of the melting range, (2) in our qualification requirements,
provides an estimate of the purity of the metal. Fig. 3 shows the typical
phase diagram of a dilute binary alloy. Table 2 shows the effects upon
melting and freezing range of a selection of possible impurities, taken
one at a time in small amounts, and makes clear the sensitivity of the
melt plateau slope as opposed to the freeze plateau slope in the de-
tection of impurities and the qualification of cells.

When we use freeze point cells to calibrate thermometers, we first hold the metal molten at about 5°C above the melt temperature overnight, to thoroughly mix the metal by convective stirring, and to distribute any previously segregated pockets of impurity. We then freeze the metal slowly, by setting the surrounding temperature slightly below the metal's freezing temperature and by introducing a cold rod or cold thermometer into the re-entrant well of the cell. (Tin, because of its large supercool, requires a somewhat different technique). We obtain a very flat freeze plateau, with a thin layer of solid material formed on the outer and inner walls, and the liquid-solid interface progressing away from the thermometer. This is a form of zone-refining, sweeping the minute quantity of impurity ahead of the interface. This method forms the most constant and reproducible plateau for calibration. A brief discussion of freeze and melt curves, and their dependance upon recent history, is given in Annex 2.

However to assess the purity of the metal, we consult the melting curves. Fig. 4 shows that three cells with various levels of impurity all give rather flat freezes. Inspection of the melting curves tells us, immediately, which cell contains the most pure metal.

In melting studies, the metal is held molten at 5°C above the melt temperature for 12 hours, to distribute the impurities homogeneously throughout the ingot, and then frozen rapidly by removing the cell from the furnace into ambient temperature. It is then slowly melted, with a monitoring thermometer connected to a recorder. Informed inspection of the melting curve indicates to what extent the cell is an acceptable embodiment of an intrinsic standard.

Thus, a comparison of the melting curve obtained after a fast freeze with the freezing curve as the metal is frozen slowly (as it is during a thermometer calibration) is one necessarily oblique but useful means of qualifying the purity of the metal in a freeze-point cell[6]. Other methods are described by other authors.

THEORY INTO PRACTICE (Tavener)

I will now discuss our own experience in performing just such analyses upon cells which we have manufactured. I begin with silver and aluminium, because these are new points of the ITS-90, and only now can be studied adequately, with the high-temperature platinum resistance thermometers recently made available.

THE FREEZING POINT OF ALUMINIUM * 660.323°C (Tavener)

To realize the plateau, we allow the molten ingot to cool slowly (≈0.1 K/min) until it is below the freezing point and at the temperature of supercool. Aluminium usually supercools 0.4 to 0.6 K. At first, concerned about shocking thermometers, we did not withdraw the thermometer from the hot cell as one does with tin and zinc. This led us to very long recalescent curves. We now believe, at least with our own 0.25Ω thermometers, that a thermometer is restored very nearly to its original state within 30 minutes after it is reinserted into the cell. Also, at first, we tried for long plateaux, and because of the excellent isothermal properties of the sodium heat pipe which is the core of our high-temperature furnace, we obtained 24 hour plateaux. We expected to see flatter plateaux on long freezes and were surprised to find that short ones were flatter. This seems to be not a function of the cell, but of slow changes in the resistance thermometer over 20-plus hours.

This leads us to the following recommendations:

(1) Do initiate a freeze by cold-quenching with cold quartz rods after withdrawing the thermometer. Then, after reinserting the thermometer, allow half an hour for it to anneal before believing the measurement.

(2) Control the plateau length to 4 to 6 hours to minimize drift of the thermometer.

Using these techniques, we expect cells to show slopes flatter than 2 to 4 mK during 50% melt and flatter than 1 to 2 mK during 50% freeze. We have now made measurements on 8 cells, during which time we developed these techniques. Cells 4, 7, 7 and 9 of the table below were done without withdrawing the thermometer. Cell 10 used the new technique I have just described.

CELL NO	FREEZE PLATEAUX TIME	%	SLOPE	MELT PLATEAUX TIME	%	SLOPE	%	SLOPE
4	10h	50	0.9 mK					
7	13h	70	1.0 mK					
8	24h	50	1.0 mK					
9	16h	50	0.9 mK					
10	10h	50	0.3 mK	18h	50	0.6 mK	90	3 mK

THE FREEZING POINT OF SILVER * 961.78°C (Tavener)

The freezing point of silver is the most difficult to evaluate, because analysis may be complicated by changes in the characteristics of the monitoring thermometer due to the high temperature. We began by looking for long plateaux, and in our isothermal furnace we can produce plateaux of 24 and longer. However these long plateaux appeared to be inferior in stability to plateaux lasting only 4 to 6 hours. We finally understood that we were seeing thermometer changes rather than plateau temperature changes.

The specification on a respected competitive high-temperature platinum resistance thermometer indicates that a drift of about 43 mK per 100 hours at temperature may be expected, or, if it is linear, about 10 mK for one of our 24 hour plateaux. However it is also accepted that withdrawing a thermometer from 961°C to ambient alters its characteristics. We tried quenching 4 of our Model 961 thermometers from the silver point to ambient, and averaged changes, at the water triple point, of +35 mK equivalent resistance and, at the gallium point, -0.00035 resistance-ratio. It required 24 hours at 650°C followed by slow cooling to 450°C to restore these thermometers to close to their initial values. We now use the following procedure:

(1) Plateaux should be restricted to 4 to 6 hours.

(2) In nucleating the melt, remove the thermometer from the silver cell and place it immediately in the preheat tube which is built into the Isotech high-temperature furnace. Cold-rod the cell with quartz tubes rather than quartz-rods, to avoid cold shocks which are too large.

(3) Place the thermometer in the cell again, and wait 1/2 hour for the thermometer to reanneal before making measurements.

If this procedure is followed, 50% melt should occur over 4 to 6 mK, and 50% freeze over 1 to 2 mK, including thermometer stability over the measured time.

At Isotech, we have evaluated 8 cells during this learning phase, and the following is a representative selection of results:

CELL NO	TIME HRS	FREEZE %	PLATEAUX mK SLOPE	TIME HRS	MELT %	PLATEAUX mK SLOPE
4	2	50	0.2	4.5	50	1.0
9	24	50	5.0	2.5	50	0.5
10	3.5	50	0.5	6	50	1.0

THE FREEZING POINT OF INDIUM (Sostmann)

Indium is a new defining point of the Scale, although IPTS-68 included it as a secondary reference point. My own production experience includes only 6 indium cells. It is a most satisfactory point to realize, and occupies a position of great utility. The statistics of my 6 indium cells is shown in Fig. 5.

THE FREEZING POINT OF INDIUM * 156.5985 (Tavener)

For evaluation, the metal is melted overnight at 5°C above the melt temperature, removed from the furnace for 30 minutes to fast-freeze the ingot; meanwhile the furnace is set to 5°C above the melt temperature. The cell is placed in the furnace again, and the temperature monitored. We experience a melting range of less than 0.5 mK with a plateau duration of more than 4 hours.

When the metal is completely molten, the furnace is reset 0.5°C below the melt temperature. When the monitoring thermometer indicates that the slight supercool (0.5°C) of indium is achieved, the thermometer is removed, and two cold quartz rods are inserted, in succession, for 2 to 3 minutes each. The thermometer is then returned to the cell. The effect of inserting the quartz rods is to quickly freeze a thin mantle of metal on the thermometer well, releasing sufficient latent heat to raise the melt to the equilibrium temperature. We have now built 5 indium cells from 2 batches of metal, and have found plateaux longer than 6 hours, melting slopes between 0.2 and 0.3 mK, and freeze plateaux between 0.1 and 0.2 mK. The absolute value has been 156.5985°C within our measurement uncertainty of 1 mK, and repeatability better than 0.1 mK.

THE FREEZING POINT OF TIN (Sostmann)

My experience includes the production of 21 tin cells. Statistics of these are shown in Fig. 6. While I believe these to be very good results, I

think that the lack of a strong central tendency is the result of thermometer oxidation effects and measurement uncertainty.

THE FREEZING POINT OF TIN * 231.928°C (Tavener)

The cell is taken through an overnight melt and a quick freeze outside the furnace, like indium. When the metal is frozen, the cell is returned to the furnace, which is set 5°C above the melt temperature, and the temperature is monitored.

Achieving the freeze plateau requires a different technique than other metals, because tin supercools as much as 10° to 15°C. If the furnace were set low enough to allow supercoolin the furnace, it would not recover in time to allow a reasonably long plateau. Therefore the cell of molten metal is lifted free of the furnace until nucleation is observed, and then quickly returned to the furnace, which is controlled 0.5°C below the freeze temperature. Two cold quartz rods are inserted in succession, to cause nucleation around the thermometer well, and the thermometer replaced to track the tin freeze plateau.

We find long melt and freeze plateaux which correspond closely. The 6 cells produced to date have exhibited melt and freeze plateau slopes of 0.1 to 0.2 mK, with reproducibility of 0.1 mK. There is some difficulty which relates to the measuring thermometer, of minor order, because platinum tends to show an oxidation shift at this temperature[7]. The effect is made negligible by using the ratio W of the resistance at temperature to the resistance of a measurement at the triple point of water immediately following.

THE FREEZING POINT OF ZINC (Sostmann)

I show, in Fig. 7, statistics on 23 zinc cells made before 1987.

THE FREEZING POINT OF ZINC * 419.527°C (Tavener)

Zinc is manipulated in a manner similar to indium. However, for melting curves taken after freezes, zinc seems to show a "memory" of the freeze plateau. In general the melt plateaux are not as constant as the freeze plateaux, but differ by a few tenths of a mK for highest-purity metal to as much as 3 mK for metal less pure. Of the 7 zinc cells we have made to date, from 2 batches of material, we have measured melt slopes from 2 to 3 mK, and freeze slopes from 0.1 to 0.2 mK. Within our measurement uncertainty, all cells have reproduced the ITS-90 value of 419.527°C. If a procedure for freezing is set and rigorously followed, reproducibility

is 0.1 to 0.2 mK. Oxidation may here also be a factor, and use of the W ratios is essential for highest precision.

THE MELTING POINT OF GALLIUM (Sostmann)

The melting point of gallium[8] is also a new defining point on the ITS-90; so new that it was not mentioned even as a secondary point on the IPTS-68. The melt temperature is 29.7646°C. It is an important point, at a temperature useful in many disciplines requiring measurements in the near-ambient or biological range. It was first developed for calibrating the small thermistor sensors used in biomedical studies, because of the proximity to body temperature.

Indium, tin, zinc, aluminum and silver are operated as freezing points, for reasons which were described above. Gallium is used on the melt instead, because, unlike most other metals, it expands when it freezes, and the pressure effects of the metal as it does so interfere with the realization of the equilibrium temperature. Because of the solidus expansion, the cell must be made of a relatively elastic material; Teflon is a common choice. A typical gallium cell is shown in Fig. 9. The interface free energy distribution in Teflon also inhibits the long supercool of gallium (≈ 75°C) which would be intolerable in practice.

Over the years, I have supervised the manufacture of 141 gallium cells. Measurements were made of these using SPRTs calibrated by the NBS and also by the Physikalisch-Technische Bundesanstalt of West Germany. The statistics of these cells are summarized on the bar chart of Fig. 8.

An anecdote. I once made a gallium cell for the National Instiute of Metrology (Beijing). Of course I made a number of measurements of the plateau temperature before it was delivered, and Dr. Ling Shan Kang made a number of measurements after he received it. The two realizations of the Scale, as transferred to thermometers, were entirely independant; nothing was common except the gallium cell. The difference between our measured mean values was 120 μK!

THE MELTING POINT OF GALLIUM * 29.7646°C (Tavener)

We cycle the gallium cell in an essentially automatic apparatus, our Model 17402, which has a two-position switch for MELT and FREEZE. The apparatus is set for MELT and the internal temperature of the thermometer is monitored with a thermometer in its well. Just before the melt point is reached, 17 cm^3 of water at about 50°C is introduced into the well in order to start an inner melt and to provide a thermal transfer medium for the thermometer. We have to date produced more

than 30 gallium cells, with 0.1 to 0.2 mK stability over 50% of the melt, plateaux of 8 to 20 hours duration with a range of 0.1 to 0.2 mK, and reproducibility of temperature better than 0.1 mK. Absolute values are 29.7646°C within our Laboratory uncertainty of 1 mK.

THE TRIPLE POINT OF MERCURY (Sostmann)

The triple point of mercury, -38.8344°C, appears first as a defining fixed point in ITS-90. (The freezing point, not the triple point, of mercury was a secondary reference point of IPTS-68). It is the only defining point between 0.01°C and the triple point of argon, -189.3442°C. It is therefore a point of great value to users whose range of interest extends below 0°C but not into the very cold regions.

The general design of the mercury cell is similar to that of the sealed cell of Fig. 1(a) except that a graphite crucible is not necessary (and cannot be used, since it would outgas). Mercury triple point cells have been made in envelopes of borosilicate glass and of stainless steel. Since mercury is considered to be a hazard in the workplace, glass envelopes are distinctly contraindicated. The stainless cell, fusion welded at its few joints, evacuated and fusion sealed, reduces the atmospheric contamination probability to nearly zero. The mercury is purified to approximately 10 parts per billion impurities. A typical cell contains about 4 kg of metal.

THE TRIPLE POINT OF MERCURY * -38.8344 (Tavener)

The mercury we use contains impurities of less than 15 parts per billion. It is prepared by chemical washing and triple distillation, and analysis to that level is made possible by boiling off 90% of a sample and analyzing the residue. The mercury is contained in a welded stainless steel cell, which sealed containing only mercury and mercury vapor.

The cell is fast-frozen overnight at about -42°C. It is then placed in our own Model 17724 Mercury Triple Point Apparatus, which allows close control of the refrigeration temperature around the cell. The control setpoint is 0.1°C above the melting point. When the monitoring thermometer indicates that the cell temperature is very close to the melting point, the thermometer is removed, and warm quartz rods are inserted to create an inner melt. The thermometer is then replaced. Melts of 12 hours duration are typical.

When the metal is completely molten, the control temperature is set 0.1°C below the freeze point. The monitoring thermometer is removed, and quartz rods chilled in liquid nitrogen are inserted to form a thin frozen

sheath around the thermometer well. The thermometer is replaced, and the plateau tracked. Typical freezes and melts are shown in Fig 10. It should be noted that the triple point can be approached either from the warm or the cold side. I have described the approach from the warm side.

UNCERTAINTIES IN USE (Tavener)

Although Isotech has been making and testing cells since only June, 1989, enough cells have been made to allow us to make some estimates of what can be expected of them.

Of course, as a British Laboratory supervised for our accreditation by NPL, we cannot claim uncertainties smaller than those of our supervising Laboratory. (The same would be true for a manufacturer or a National Calibration Service in any other country.) It is considered appropriate for a NAMAS Laboratory to claim uncertainties no smaller than 1.5 to 2 times those of the National Laboratory. In the United Kingdom, this re-sults in the following table:

Temperature	NPL thermometer calibration uncertainty ±mK	Isotech cell calibration uncertainty ±mK	Isotech thermometer calibration uncertainty ±mK
Hg triple	0.5	1	2
Water triple	0.5	1	1
Ga melt	0.5	1	2
In freeze	1	2	3
Sn freeze	1	2	3.5
Zn freeze	1	2	3.5
Al freeze	4	6	10
Ag freeze	20	30	40

If these appropriately conservative values are compared with reported uncertainties during melt-freeze experiments, it will be realized that the freeze points, melt points or triple points discussed can operate well within the limits of the above Table. The estimates for aluminium and silver given below are based on the techniques described in this paper for 50% melt or freeze, and include the stability of the Isotech Model 962 (Hotspot) High Temperature Platinum Resistance Thermometer over a 4 to 6 hour plateau.

Metal	Melt range mK	Freeze range mK	Reference
Mercury	.2	0.2	(9)
Gallium	0.2	Not applic.	(8)
Indium	2	0.2	(6)
Tin	2	0.2	(6)
Zinc	3	0.3	(6)
Aluminium	2-4	1-2	This paper
Silver	4-6	1-2	This paper

ANOTHER USE FOR MELTING POINTS (Sostmann)

There may be a totally different reason to be interested in melting points, rather than freezing points, with the uncertainties Tavener has just described.

We have seen that, to achieve a proper freeze plateau, a good deal of hands-on manipulation is required. Melting points, on the other hand, require only that the furnace controller be set, and the furnace turned on (which can be done by a timer, before the laboratory day begins). Some laboratories, whose charter is for production of calibrations, with a heavy work load and a high throughput, and which do not require the ultimate in accuracy, may choose to operate on the melt plateau instead of at the freeze equilibrium. The equipment is the same, the uncertainty will be higher, and the time consumed in establishing the calibration point is substantially reduced.[11]

THE TRIPLE POINT OF ARGON (Sostmann)

There exist in the literature many descriptions of the realization of the triple point of argon[10]. The argon triple point requires highly special equipment and a source of a liquid gas which is expensive and not readily available.

Most laboratories will choose to calibrate thermometers at this end of the range by a comparison method, where the thermometer under test is compared to a thermometer of known calibration, usually a valid calibration from a National Laboratory. Indeed, the National Laboratories will most often calibrate thermometers submitted to them by comparison, realizing the argon triple point only for infrequent periodic calibrations of their own standard thermometers. In its publication "Adoption of the

ITS-90", the National Physical Laboratory of England makes this statement:

> Most thermometers submitted (for calibration) will involve measurements at the tin and zinc freezing points, plus a comparison with NPL standards in a bath of liquid nitrogen (about -195°C)

Fig. 11 shows a bath intended specifically for the comparison calibration of long-stem thermometers, against a reference standard thermometer, in liquid nitrogen; Isotech Model 18205. The apparatus comprises a stainless steel dewar, an inner equalizing block, three wells for thermometers, top connections for filling and monitoring the height of liquid refrigerant, and a manifold by means of which the thermometers may (optionally) be thermally tied down. Using this comparator, calibration uncertainties not larger than 0.002°C can be achieved at about 1/10 the cost of an absolute calibration.

With regard to electrical measurements, using a resistance bridge which employs a single reference resistor, a useful technique is to connect the reference thermometer in place of the reference resistor, and the test thermometer in place of the unknown, and thus read the ratio of the unknown thermometer to the reference thermometer. Since the slopes of standard platinum resistance thermometers are so similar, at least over limited temperature intervals, the ratio of the resistances is representative of the resistance of the unknown, and the resistance of the unknown can be calculated quickly from the calibration table of the calibrated thermometer. The calibration temperature need not be exactly established, nor even need be known precisely.

THE TRIPLE POINT OF WATER * 0.01°C (Sostmann)

Of the defining fixed points of the ITS-90, the triple point of water is the first among equals. It is the sole realizable fixed point common to the Kelvin Thermodynamic Temperature Scale and the ITS-90. Its assigned value on these Scales is 273.16 K and 0.01°C, respectively. It is one of the most accurately realizable of the defining points. Properly used, the triple point temperature can be realized with an accuracy of +0.0°, -0.00015°C. (For comparison, it is difficult to set up and use an water and ice bath with accuracy better than 0.002°C). The triple point of water can be maintained easily in a replenished bath of ice and water for a number of days, and in an apparatus dedicated to the purpose, Isotech Model 18233, for weeks or months, making this fundamental point continuously available in the Laboratory.

Also, the triple point of water is the temperature to which the resistance-ratios of SPRT calibration tables are referred:

$$W = R(t_2)/R(t_1)$$

where on IPTS-68 t_1 was 0°C, and on ITS-90, t_1 is 0.01°C.

Furthermore, the triple point of water provides a useful quality-assurance check in verifying the condition of thermometers. A measurement at the triple point of water immediately upon a thermometer's return from a calibration journey will reveal any shift which has occurred in transportation. Valuable continuing history of a thermometer's stability is preserved if measurement results are placed on a control chart each time the thermometer is measured at the triple point of water.

One design of water triple point cell is shown in Fig. 12. There is a glass flask nearly filled with pure water, and sealed containing only water vapor in the headspace. A coaxial well is provided for the thermometer.

In use, the cell is chilled to about 0°C in an ice and water bath, and then a mantle of ice is frozen onto the thermometer well by, for example, filling the well with crushed Dry Ice. When a good mantle has been formed, the well is cleared of any remaining ice and water, and a warm rod inserted to melt a thin film between the ice mantle and the well. (This can be detected by holding the cell upright and giving it a short sharp twist. The mantle should spin freely about the thermometer well). When freshly frozen, the mantle will be under some strain which will tend to elevate its temperature. It will relax in about 24 hours. Specific instructions and precautions are given in manufacturer's literature, and the use and preparation of water triple point cells is the subject of a draft ASTM standard which is expected to be published in 1991.

The problem of verifying the temperature of a water triple point cell to date is intractable. Some manufacturers certify cells by comparing a new cell with a bank of as many as 20 old cells, kept for that purpose; others do not certify their cells. Assuming that a cell contains properly pure water, it is possible to determine that the cell contains only water vapor in the headspace, and that it has not leaked air.

> 1: Holding the cell upright, turn it over slowly. A bubble of water vapor will collect in the upper tubulation or handle, which will compress to the size of a small pea, or even disappear. This effect is more sensitive when the cell is at room temperature.

2: Again turning the cell over slowly, a sharp click will be heard, similar to water hammer in a pipe, as the gas bubble collapses. The click is more pronounced when the cell is cold.

These two tests are the only verification which a user can perform on the cell.

Laboratories which have space or budget for only one fundamental temperature standard should consider the water triple point favorably.

FINAL WORD

In our next issue, Vol. 2 No. 1, this series will discuss in detail platinum resistance thermometry.

USEFUL REFERENCES

Instruction manuals furnished with Isotech furnaces, fixed point cells and platinum resistance thermometers. These may be purchased separately from a product, if desired. Isothermal Technology Ltd., Southport, England, or Durham, North Carolina.

Mangum, B.W., Platinum Resistance Thermometer Calibrations, NBS Special Publication No. 250-22. Superintendant of Documents, Washington. (IPTS-68 Scale, but still useful).

Mangum, B.W., Furukawa, G.T., Guidelines for realizing the International Temperature Scale of 1990, NIST Technical Note 1265, Superintendant of Documents, Washington. (This is a new publication which will be reviewed in the Isotech Journal, Vol 2. No. 1.)

Riddle, J.L., Furukawa, G.T., Plumb, H.H., Platinum Resistance Thermometry, Superintendant of Documents, Washington. (IPTS-68 Scale, a classic.)

FOOTNOTES

(1) Sostmann, H.E., *Fundamentals of Thermometry, Part I*, Isotech Journal of Thermometry, Vol. 1 No. 1 (Spring 1990)

(2) Preston-Thomas, H., *The International Temperature Scale of 1990 (ITS-90)*, Metrologia 27, No. 1 (1990); also *Errata*, Metrologia 27, No. 2 (1990).

(3) Webster's Third New International Dictionary

(4) Sostmann, H.E., *Practical calibration of thermometers on the International Temperature Scale of 1990*, Isotech Journal of Thermometry, Vol. 1 No. 1, pp. 25-27 (Spring 1990)

(5) Please see Annex 1 for a discussion of how a furnace controller can be calibrated using the fixed point as a reference.

(6) McLaren, E.H., *The freezing points of high-purity metals as precision temperature standards*, Temperature, its measurement and control in science and industry, Vol. 3, pp 185-198, Reinhold, 1962

(7) Berry, R.J., *Effect of oxidation on Pt resistance thermometry*, Metrologia 16, p 117 (1980); also *Evaluation and control of platinum oxidation errors in standard platinum resistance thermometers*, Temperature, Its Measurement and Control in Science and Industry, Vol 5, Schooley ed., Am Inst Physics (1982)

(8) Sostmann, H.E., *Melting point of gallium as a temperature calibration standard*, Rev. Sci. Instr. 48, No 2, pp 118-121 (1977); also Borovicka, M, Sostmann, H.E., *Melting and triple points of gallium as fixed points of the International Practical Temperature Scale*, Rev. Sci. Instr., 55, pp 1639-1642 (1984)

(9) Furukawa, G.T., et al, *Application of some metal SRMs as thermometric fixed points*, NBS Special Publication 260-77, Superintendant of Documents, Washington (1982)

(10) Furukawa, G.T., *Reproducibility of the triple point of argon in sealed transportable cells*, Temperature, Its Measurement and Control in Science and Industry, Vol 5., pp 239-248 (Schooley ed) Am. Inst. Physics (1982); also Pavese, F., *The triple points of argon and oxygen*, Metrologia 14, pp 93-103 (1978)

(11) McAllan, J. V., *Sensitive temperature measurements on pure metals during melting and freezing*, J. Crystal Growth, 12, North Holland (1972); also *Practical reference temperatures using melting point techniques*, J. Phys. E., The Institute of Physics, London (1982)

TABLE 1

FIXED POINTS OF THE ITS-90 AND THEIR PRESSURE COEFFICIENTS

Substance	Equilib. Temperat. T_{90}	Pressure effects-	
		Atmosph. mK per std. atmos	Hydrostat. Mk per M liquid head
Argon (tp)	13.8033	*	3.3
Mercury (tp)	234.3156	*	7.1
Water (tp)	273.16	*	-0.73
Gallium (mp)	302.9146	-2.0	-1.2
Indium (fp)	429.7485	4.9	3.3
Tin (fp)	505.078	3.3	2.2
Zinc (fp)	692.677	4.3	2.7
Aluminum (fp)	933.473	7.0	1.6
Silver (fp)	1234.93	6.0	5.4

* indicates that a triple point is independant of atmospheric pressure, since it is defined as an equilibrium under its own vapor pressure.

TABLE 2

PHASE DIAGRAM PARAMETERS

SOLVENT	SOLUTE	m_L 10^{-4} °C / ppm	m_S 10^{-4} °C / ppm	k_o	R 10^{-4} °C / ppm	D_L
Zn	Cd	-1.9	-77	0.02	75	<0.1
	Cu	2.5	1.7	1.5	1	1
	Fe	-4.1	-33	0.12	27	0.1
	Pb	-1.9	large		large	<0.1
	Sn	-2.4	large		large	<0.1
	Tl	-1.9	large	0.1	large	<0.1
Sn	Bi	-1.6	-4.4	0.36	3	1
	Ca	-20	large		large	<0.1
	Cu	-7.1	large		large	<0.1
	Fe	-33	large		large	<0.1
	In	-2.3	-3.5	0.66	1	1
	Ni	-5	large		large	<0.1
	Pb	-1.3	-20	0.06	19	0.1
	Sb	1.6	1.3	1.2	<1	1
In	Ag	-5	large		large	0.1
	Bi	-2.5	-4.1	0.61	2	<0.1
	Cd	-1	-2	0.5	1	2
	Cu	-10	large		large	0.1
	Pb	<-1	<-1	1.0	<1	2
	Zn	-70	-120	0.6	50	<0.1

Key: m_L = liquidus slope, m_S = solidus slope, k_o = equilibrium distribution coefficient, R = equilibrium alloy melting range, D_L = detection limit (wt ppm) of platinum resistance thermometer.

This table shows the depressing or elevating effects of 1ppm of various solutes on solvents used in ITS-90. It is after McLaren (see Footnote 6). The authors whould be pleased to receive information which would extend the table to include mercury, gallium, aluminium and silver.
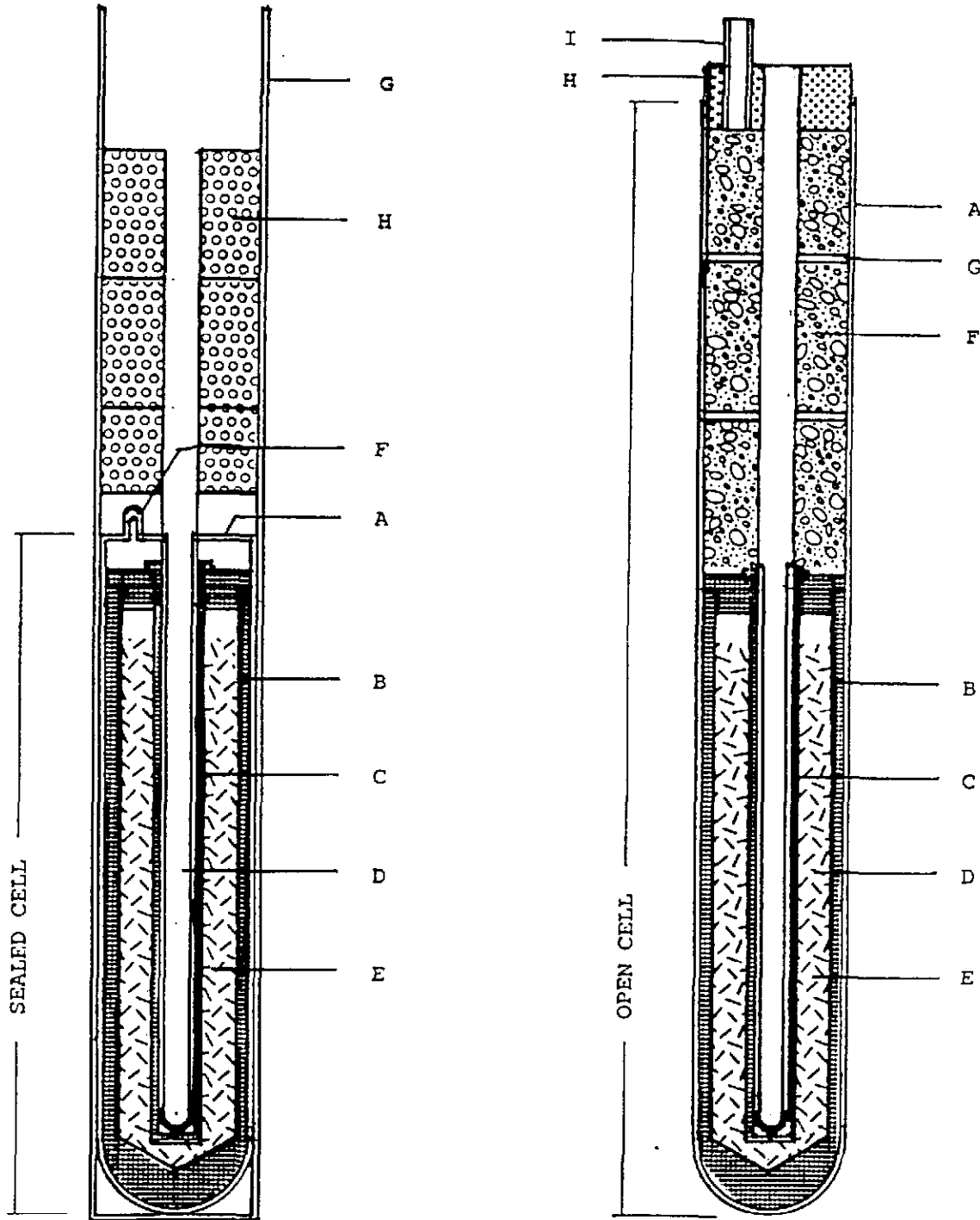
FIG. 1(A)   FIG. 1(B)

FIG 1(a): A, quartz envelope; B, graphite crucible; C, graphite sheath over thermometer well; D, thermometer well; E, pure metal; F, fill gas seal-off; G, inconel can for removal of cell; H, insulating bricks. FIG 1(b): A, quartz envelope; B, graphite crucible; (C), graphite sheath over thermometer well; D, thermometer well; E, pure metal; F, thermal insulation; G, graphite heat shunt; H, stopper; I, port for evacuation and fill with blanking gas. (Be careful evacuating over zinc; vapor pressure is $\approx 10^{-4}$ atmosphere at the melt temperature).
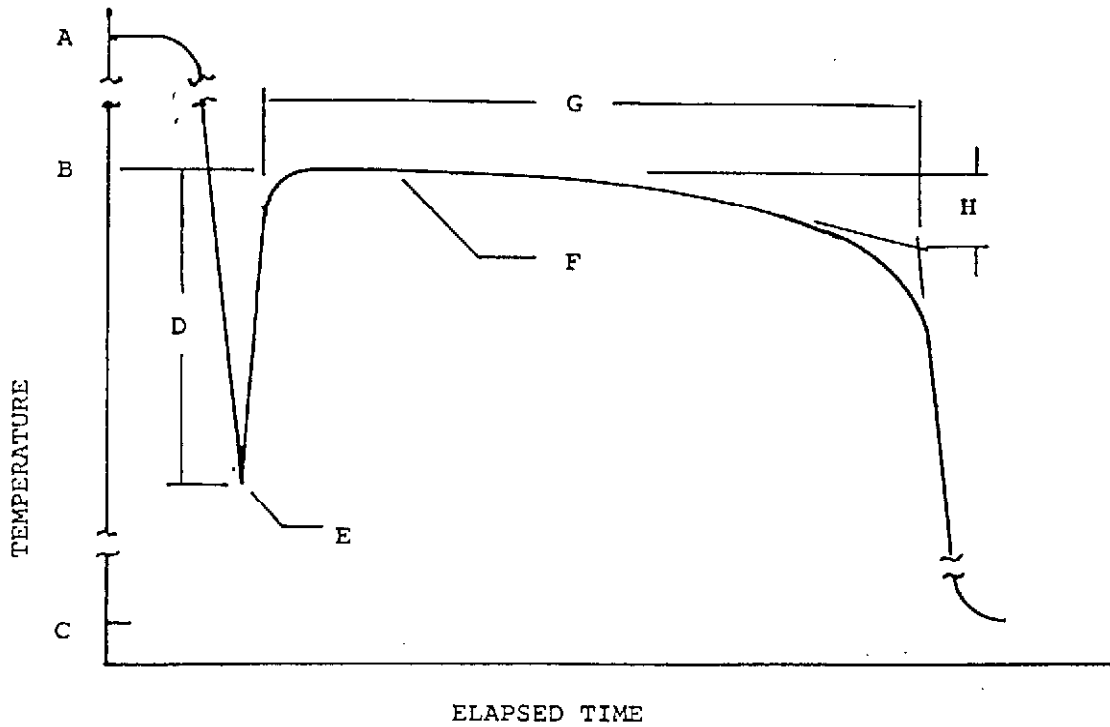
FIG. 2 - A TYPICAL FREEZE CURVE

A: Stabilized temperature of the cell, in liquid phase, under furnace control before freezing.

B: The freezing temperature of the cell.

C: Thetemperature of the furnace environment around the cell, under control of the furnace set below the freezing temperature.

D: The maximum supercool.

E: The onset of recalescence (nucleation).

F: The freezing plateau.

G: The total freezing time.

H: The freezing range.
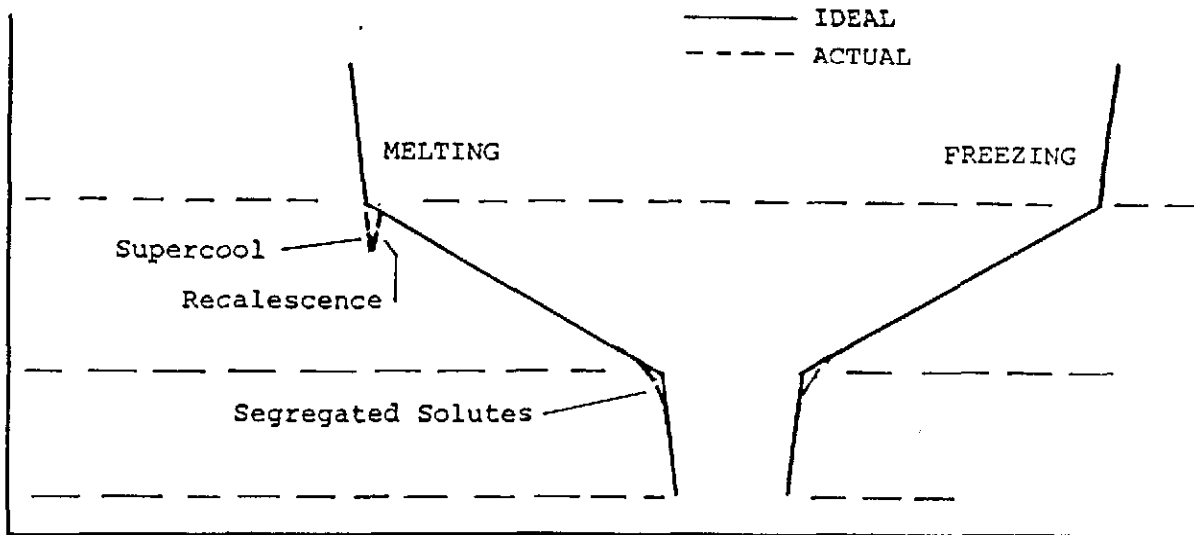
FIG. 3: TYPICAL MELTING AND FREEZING BEHAVIOR OF A DILUTE BINARY ALLOY (after McLaren).
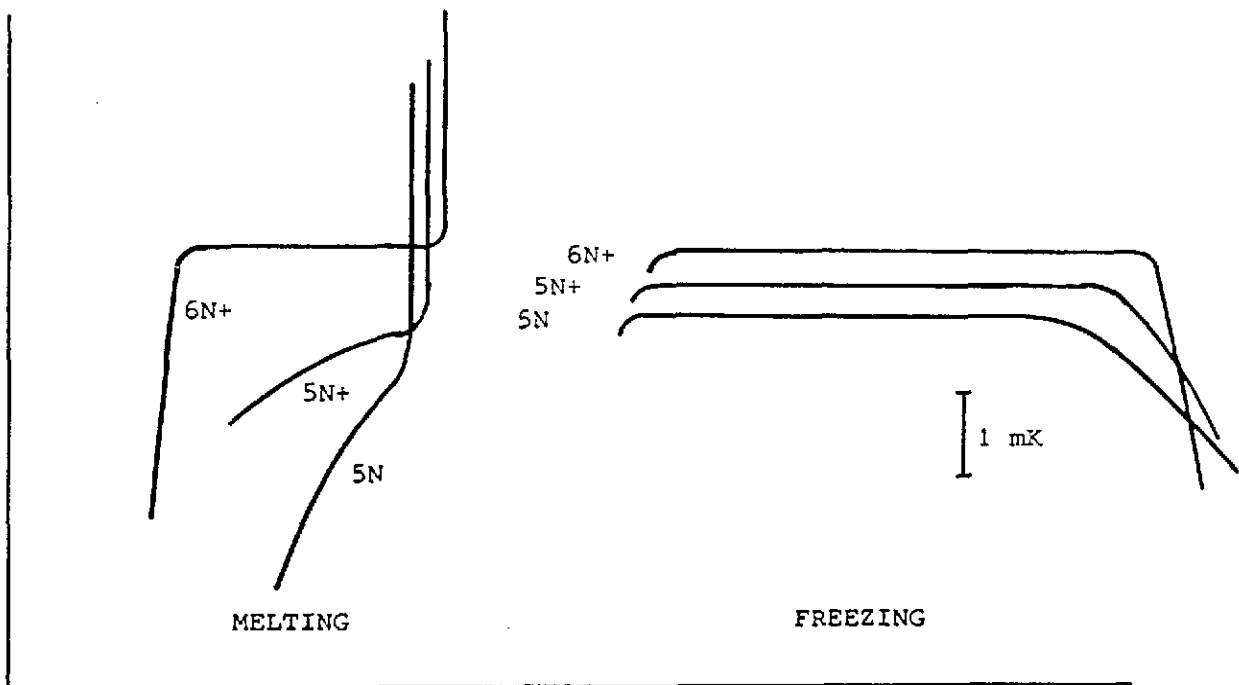
FIG 4: TYPICAL MELTING AND FREEZING CURVES OF METALS OF THREE LEVELS OF PURITY

FIG 5-INDIUM FREEZING POINT
6 CELLS
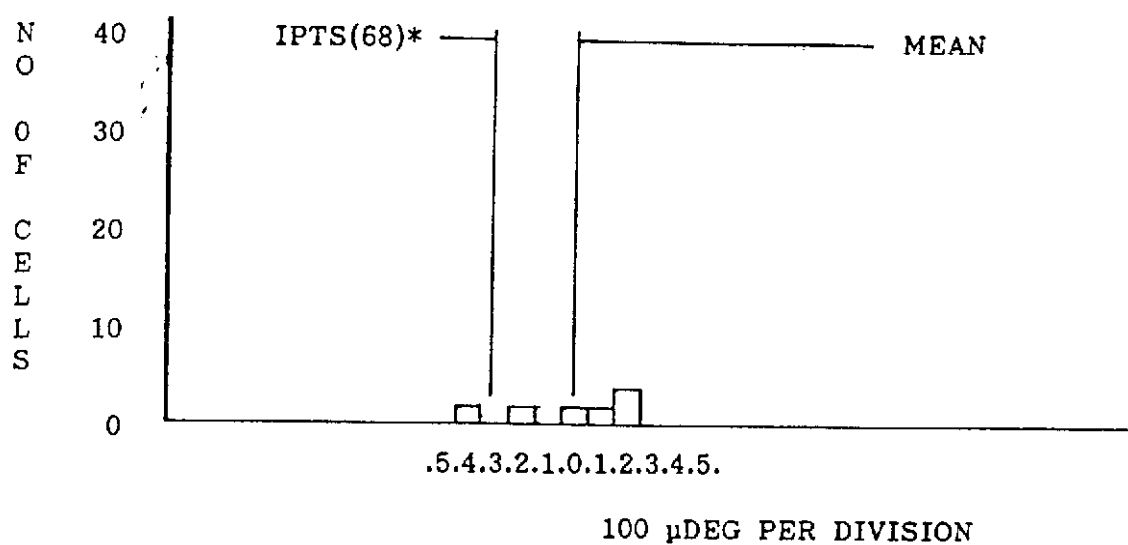
MEAN OF 6 CELLS 156.6348°C   1 STD DEVIATION 0.0002
MAXIMUM CELL 156.6350°C   MINIMUM CELL 156.6344°C
IPTS(68) TEMP 156.6345°C   BIAS VS IPTS +.0003°C
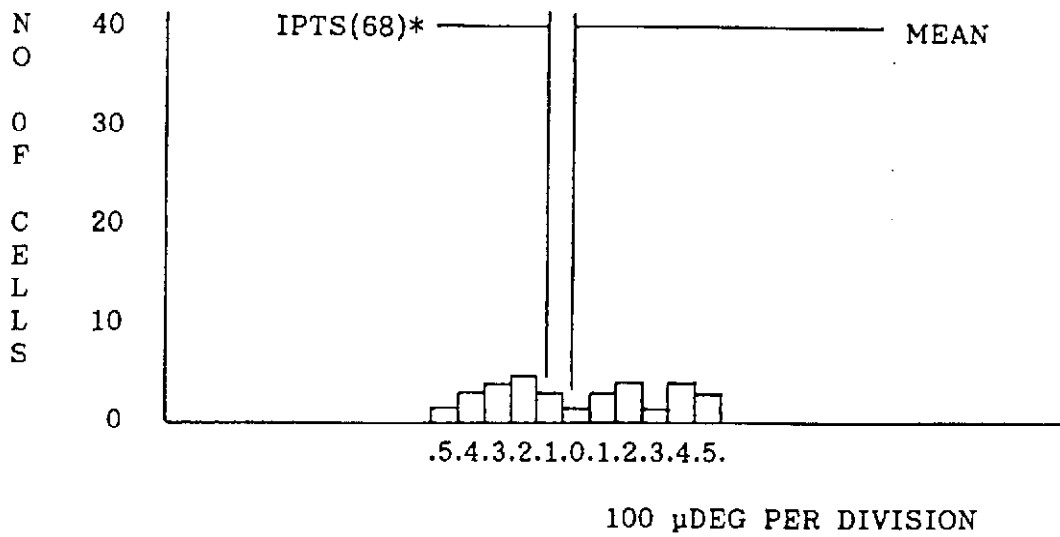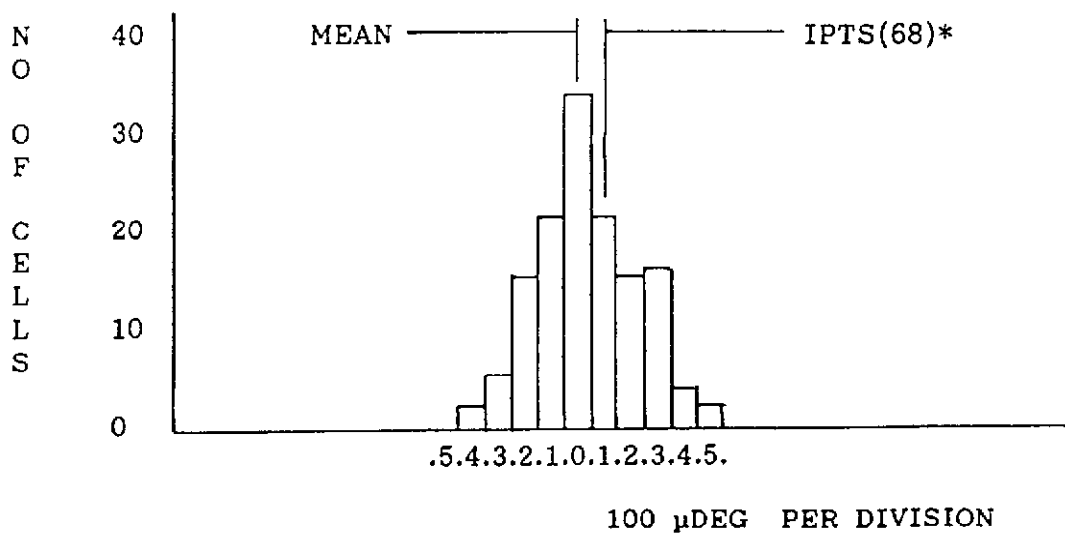*IPTS(68) TEMP IS CORRECTED FOR HYDROSTATIC HEAD

FIG 6-TIN FREEZING POINT
21 CELLS
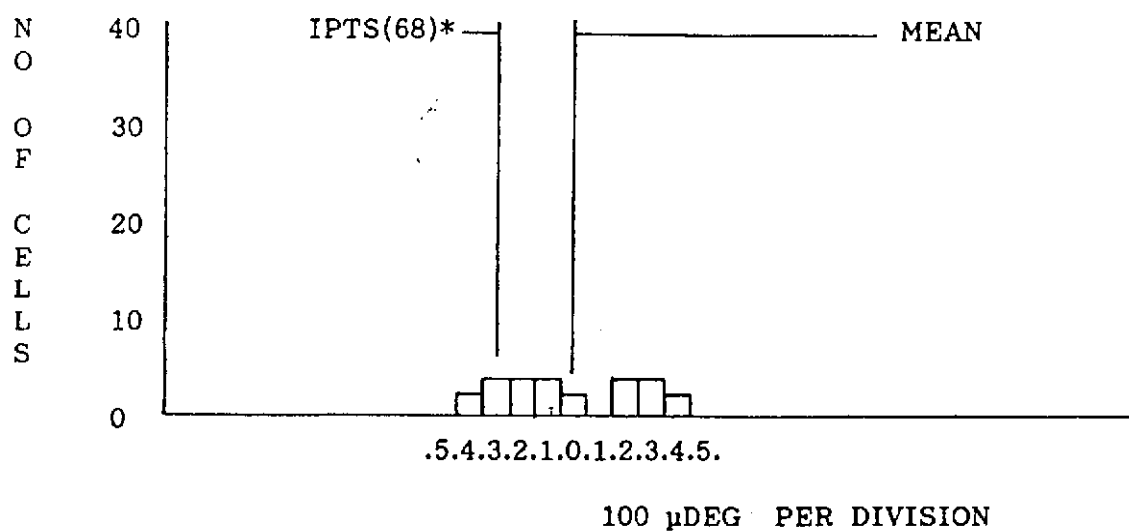
MEAN OF 21 CELLS 231.9688°C   1 STD DEVIATION 0.0003
MAXIMUM CELL 231.9692   MINIMUM CELL 231.9681°C
IPST(68) TEMP 231.9685   BIAS VS IPTS 0.0003°C
*IPTS(68) TEMP IS CORRECTED FOR HYDROSTATIC HEAD

FIG.7-ZINC FREEZING POINT
23 CELLS

N   40   IPTS(68)* ──────┐ ┌──────────── MEAN
O
O   30
F
C   20
E
L
L   10
S
     0

.5.4.3.2.1.0.1.2.3.4.5.

100 µDEG PER DIVISION

MEAN OF 23 CELLS 419.5805°C   1 STD DEVIATION 0.0003
MAXIMUM CELL 419.5810°C   MINIMUM CELL 419.5800°C
IPTS(68) TEMP 419.5804°C   BIAS VS IPTS 0.0001
*IPTS(68) TEMP IS CORRECTED FOR HYDROSTATIC HEAD

FIG. 8-GALLIUM FREEZING POINT
141 CELLS

N   40   MEAN ──────┐ ┌──────── IPTS(68)*
O
O   30
F
C   20
E
L
L   10
S
     0

.5.4.3.2.1.0.1.2.3.4.5.

100 µDEG   PER DIVISION

MEAN OF 141 CELLS 29.7715°c   1 STD DEVIATION 0.0002
MAXIMUM CELL 29.7720°C   MINIMUM CELL 29.7710°C
IPTS(68) TEMP 29.7716°C   BIAS VS IPTS -.0001°C
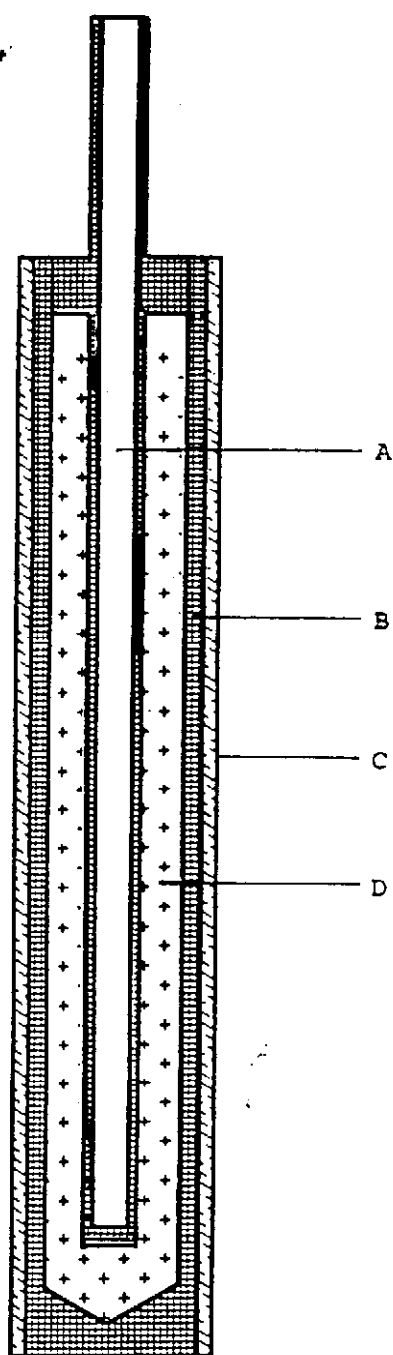*IPTS (68) TEMP IS CORRECTED FOR HYDROSTATIC HEAD
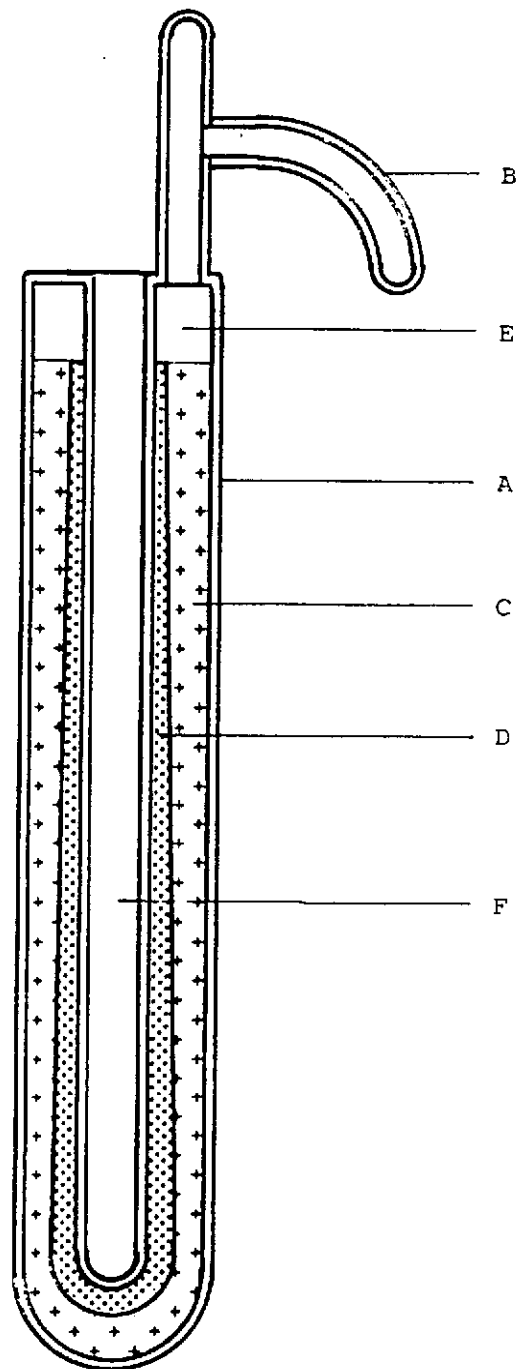
FIG. 9   FIG. 10

FIG. 9: A type of gallium cell. A, thermometer well; B, cell wall; C: aluminum sleeve; D, high-purity gallium. A and B are Teflon.

FIG 10: A type of water triple point cell. A, borosilicate glass cell; B, handle; C, liquid water; D, solid water (ice); E, water vapor; F, thermometer well.
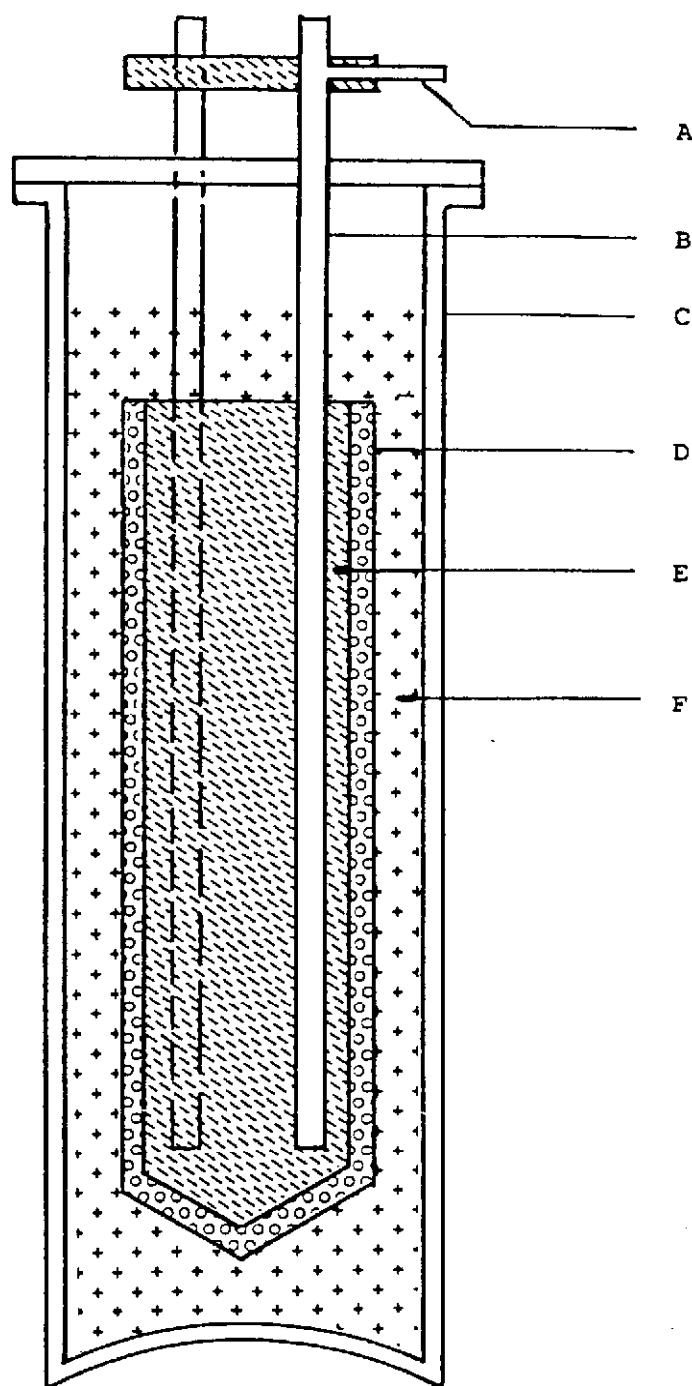
FIG. 11: Comparator for the argon point. A, manifold to surround the thermometers with helium gas (optional); B, thermometer well (three provided); C, stainless steel dewar; D, porous blanket; E, tellurium copper equalizing block; F, liquid nitrogen cryogen. Not shown: fill port, level control, pressure reliefs.

ANNEX 1

CONTROLLER ABSOLUTE CALIBRATION

The freezing-point furnace is usually equipped with an electronic control system, which obtains its signal from a temperature sensor built into the furnace core. In the Isotech low temperature furnace Model 17701 the sensor is an industrial platinum resistance thermometer. In the Isotech High Temperature Furnace Model 17702, it is a Platinel thermocouple.

Proper realization of the freeze point may depend upon controller set-point accuracy of 0.1 mK or better. It is provident, therefore, to calibrate the controller against the freeze point cell itself, and this can be done as follows:

1: With a cell in the furnace and a monitoring thermometer in the well, set the controller at a setting which is a few degrees below the nominal freeze temperature of the metal. Turn on the furnace. (It is helpful to record the output of the thermometer on a strip chart recorder.)

2: Allow the furnace to come to equilibrium, as indicated by the thermometer or the recorder chart. Observe any cycling for an adequate period of time. Note (a) the controller setting and (b) the mean temperature indicated by the thermometer.

3: Reset the controller for a temperature several degrees higher than the nominal freeze temperature of the metal. Allow the furnace temperature to rise through the melt arrest to the new furnace control temperature. Observe any cycling for an adequate period of time. Note (a) the controller setting and (b) the mean temperature indicated by the thermometer.

4: Reset the controller to the lower temperature used in (2). Follow the drop in temperature until the freeze plateau is observed. (Follow instructions for the specific metal on the technique of initiating the freeze plateau.) Note the temperture indicated by the thermometer.

5: Using the following notation:

C_1 and t_1 = the controller setting and the temperature, respectively, at the furnace setting below the freeze temperature.

C_2 and t_2 = the controller setting and the temperature, respectively, at the furnace setting above the freeze temperature.

t_3 = the temperature measured on the freeze plateau.

6: Calculate the furnace controller setting equivalent to the freeze plateau:

$$CS = C_1 + \{[(c_2 - c_1)/(t_2 - t_1)] \; (t_3 - t_1)\}$$

This is the furnace controller setting which corresponds to the furnace temperature at the freezing point of the metal. For subsequent freezes, set the controller slightly below this setting, or at a setting which assures that the peak furnace cycling temperature (if cycling is present) will be less than t_3.

ANNEX 2

The freezing and melting curves of freeze point cells are largely dependant upon their recent history. The charts below illustrate this, and indicate how the best method of working with a cell may be derived and developed.

"Normal freezing" refers to undisturbed natural solidification, whilst "induced freezing" refers to a technique that is used to shorten the recalescent period. The latter is effected by freezing a thin mantle of metal onto the axial thermometer well after nucleation has commenced; this releases sufficient latent heat to raise the metal temperature to the liquidus temperature. The graphs are after McLaren (Footnote 6).
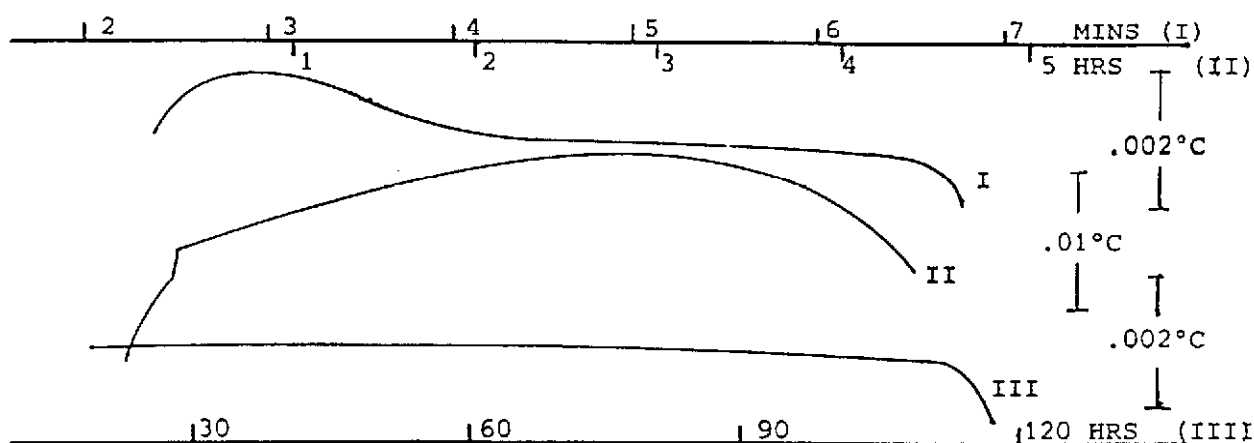

FIG. A: Typical freezing curves of high-puity indium: I, very fast normal; II, very slow normal; III, slow induced
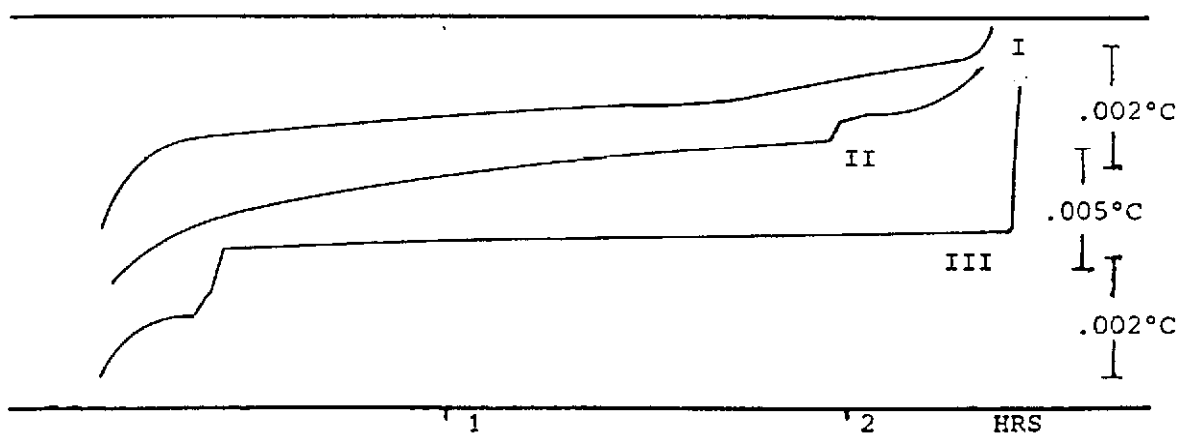

FIG B: Typical melting curves of high-purity indium following: I, very fast normal freeze; II, very slow normal freeze; III, slow induced freeze.