FLUKE ®

Hart Scientific ®

5904–5909

Metal Freeze Point Cell User's Guide

Rev. 5A2501

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Rev. 5A2501

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1 Before You Start

1.1 Symbols Used

Table 1 lists the International Electrical Symbols. Some or all of these symbols may be used on the instrument or in this manual.

Table 1 *International Electrical Symbols*

Symbol	Description
	AC (Alternating Current)
	AC-DC
	Battery
	CE Complies with European Union Directives
	DC
	Double Insulated
	Electric Shock
	Fuse
	PE Ground
	Hot Surface (Burn Hazard)
	Read the User’s Manual (Important Information)
	Off
	On

Symbol	Description
	Canadian Standards Association
CAT II	OVERVOLTAGE (Installation) CATEGORY II, Pollution Degree 2 per IEC1010-1 refers to the level of Impulse Withstand Voltage protection provided. Equipment of OVERVOLTAGE CATEGORY II is energy-consuming equipment to be supplied from the fixed installation. Examples include household, office, and laboratory appliances.
	C-TIC Australian EMC Mark
	The European Waste Electrical and Electronic Equipment (WEEE) Directive (2002/96/EC) mark.

1.2 Safety Information

Use this instrument only as specified in this manual. Otherwise, the protection provided by the instrument may be impaired.

The following definitions apply to the terms "Warning" and "Caution".

- "Warning" identifies conditions and actions that may pose hazards to the user.
- "Caution" identifies conditions and actions that may damage the instrument being used.

1.2.1 ⚠ Warnings

To avoid possible personal injury, follow these guidelines.

- **DO NOT** use this instrument for any application other than calibration work.
- **DO NOT** use this instrument in environments other than those listed in the user's guide.
- Follow all safety guidelines listed in the user's guide
- Calibration Equipment should only be used by Trained Personnel.

1.2.2 ⚠ Cautions

To avoid possible damage to the instrument, follow these guidelines.

- READ SECTION 5 ENTITLED CARE OF YOUR METAL FREEZING POINT CELL before removing the cell from the case.
- Incorrect handling can damage the cell.
- The fixed point cell must be kept in a vertical position. Placing the cell in a horizontal position can damage the cell and void the warranty.
- **DO NOT** place the fixed point cell upside down

1.3 Authorized Service Centers

Please contact one of the following authorized Service Centers to coordinate service on your Hart product:

Fluke Corporation, Hart Scientific Division

799 E. Utah Valley Drive
American Fork, UT 84003-9775
USA

Phone: +1.801.763.1600
Telefax: +1.801.763.1010
E-mail: support@hartscientific.com

Fluke Nederland B.V.

Customer Support Services
Science Park Eindhoven 5108
5692 EC Son
NETHERLANDS

Phone: +31-402-675300
Telefax: +31-402-675321
E-mail: ServiceDesk@fluke.nl

Fluke Int'l Corporation

Service Center - Instrimpex
Room 2301 Sciteck Tower
22 Jianguomenwai Dajie
Chao Yang District
Beijing 100004, PRC
CHINA

Phone: +86-10-6-512-3436
Telefax: +86-10-6-512-3437
E-mail: xingye.han@fluke.com.cn

Fluke South East Asia Pte Ltd.

Fluke ASEAN Regional Office
Service Center

60 Alexandra Terrace #03-16
The Comtech (Lobby D)
118502
SINGAPORE

Phone: +65 6799-5588
Telefax: +65 6799-5588
E-mail: antng@singa.fluke.com

When contacting these Service Centers for support, please have the following information available:

- Model Number
- Serial Number
- Complete description of the problem

2 Introduction

The International Temperature Scale of 1990 (ITS-90) is based on a series of defining fixed points. At temperatures above 273.16 K, most of the fixed points are the freezing points of specified pure metals. Pure metals melt and freeze at a unique temperature through a process involving the absorption or liberation of the latent heat of fusion. A metal freezing point is the phase equilibrium between the liquid phase and solid phase of a pure metal at a pressure of one standard atmospheric pressure (101,325 Pa). The freezing points of indium, tin, zinc, aluminum, silver, gold, and copper are the defining fixed points of the ITS-90. The temperature values of these freezing points assigned by the ITS-90, the pressure effect constants and the resistance ratios of the ITS-90 reference function (10a) are listed in Table 2.

Table 2 *The defining metal freezing points of the ITS-90, pressure constants, and resistance ratios.*

	Pressure Effect of Fixed Points					
	ASSIGNED TEMPERATURE		dt/dP	dt/dh		dW_r/dt
FIXED POINT	T_{90} (K)	t_{90} (°C)	(10^{-8}K/Pa)†	(10^{-3}K/m)	$W_r(T_{90})$	(x 0.001)
FP In	429.7485	156.5985	4.9	3.3	1.60980185	3.801024
FP Sn	505.078	231.928	3.3	2.2	1.89279768	3.712721
FP Zn	692.677	419.527	4.3	2.7	2.56891730	3.495367
FP Al	933.473	660.323	7.0	1.6	3.37600860	3.204971
FP Ag	1234.93	961.78	6.0	5.4	4.28642053	2.840862
FP Au	1337.33	1064.18	6.1	10	--	--
FP Cu	1357.77	1084.62	3.3	2.6	--	--

†Equivalent to millikelvins per standard atmosphere.

All of these fixed points are intrinsic temperature standards according to the definition of the ITS-90. Under controlled conditions these freezing points are highly reproducible. The variance among different realizations of a freezing point should be well within 1.0 mK for the freezing points of indium, tin and zinc; and within a few millikelven for the freezing points of aluminum, silver, gold, and copper. For your convenience Hart has developed a sealed cell design and new technique for the realization of the freezing points, which has made it easy to realize these fixed points.

Figure 1 *The metal freezing point cell.*

These freezing points are indispensable for the calibration of a standard platinum resistance thermometer (SPRT). Different subranges require different sets of freezing points, as summarized in Table 3.

Table 3 *Some subranges of the ITS-90 and freezing points required for calibration.*

SUBRANGE	FREEZING POINTS REQUIRED
0°C–961.78°C	FP Sn, FP Zn, FP Al, and FP Ag
0°C–660.323°C	FP Sn, FP Zn, and FP Al
0°C–419.527°C	FP Sn and FP Zn
0°C–231.928°C	FP In and FP Sn
0°C–156.5985°C	FP In

3 Specifications

Table 4 The specification of metal freezing point cells.

Model Number	5904	5905	5906	5907	5908	Contact Hart	5909
Fixed Point	FP In	FP Sn	FP Zn	FP Al	FP Ag	FP Au	FP Cu
Reproducibility (mK)	0.15–0.3	0.2–0.4	0.2–0.4	0.6–1.0	1.0–2.0		2.0–4.0
Expanded uncertainty (mK), k = 2	0.07	0.5	0.9	1.3	2.4		10.1
Metal Purity	99.99995%	99.99995%	99.9999%	99.9999%	99.9999%	99.9999%	99.9999%
Quantity of metal (kg)	0.97	0.96	0.95	0.35	1.35		1.13
Outer diameter of the cell (mm)	48	48	48	48	48	48	48
Overall height of the cell (mm)	282	282	282	282	282	282	282
Inner diameter of the well (mm)	8	8	8	8	8	8	8
Total immersion depth† (mm)	195	195	195	195	195	195	195

†The distance from the bottom of the re-entrant well to the upper surface of the metal

Other sizes of cells are available according to the customer's special requirement.

4 Description

A typical Hart Scientific metal freezing point cell is shown in Figure 2. An appropriate quantity of metal (See Table 4 for detail) with a purity of 99.9999% is melted into a graphite crucible with a graphite lid and re-entrant well. Industry sometimes refers to the 99.9999% purity as “a purity of 6N”. The impurity in the graphite is less than 3 PPM. All of the graphite parts are subjected to a high-temperature, high-vacuum treatment before loading the metal sample. It is important to avoid any possible contamination to the surface of the graphite parts during the manufacturing process. The assembled graphite crucible, with the high-purity metal, is then enclosed in a quartz cell and connected to a high vacuum system. The cell is drawn down to a proper pressure at a temperature near the freezing point for several days. During this period the cell is purged with high purity argon repeatedly to remove any contaminants. Finally, the cell is filled with 99.999% pure argon and permanently sealed at the freezing point. The pressure of the argon in the cell at the freezing point is closely adjusted to 101,325 Pa and the actual value of the pressure recorded. A small temperature correction for the pressure difference can be made using the information in Section 7, The Correction for the Pressure Difference. In providing the highest quality sealed cells on the market, Hart’s experts carefully eliminate possible sources of error. For example, sand-blasting the outer surface of the central re-entrant quartz well of the sealed cell decreases the radiation losses along the well to a minimum. A long immersion depth of the thermometer into the liquid metal makes any error due to the thermal conductivity along the thermometer sheath and leads negligible.

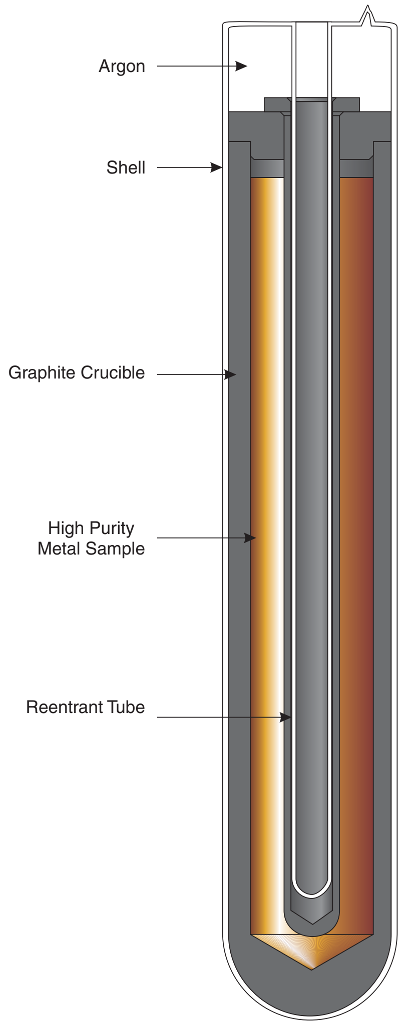

Figure 2 *The Hart sealed metal freezing point cell.*

5 Care of Your Metal Freezing Point Cell

5.1 General Information

The metal freezing point cell is an extremely delicate device. Great care must be taken in handling, using and transporting the cell. The quartz glass outer shell is easily broken. It is suggested that the cell be kept in the vertical position for safety, although putting a cool cell in the horizontal orientation for a short time period will not cause any damage. It is dangerous to transport the cell by general carrier, therefore, the cell should be hand-carried from one place to another place.

It is extremely important to keep the outer surface of the cell clean to avoid devitrification of the quartz glass. Never touch the cell with bare hands. Whenever you have to handle the cell, always wear clean cotton gloves or use clean paper. If there is any chance that the outside of the cell has been touched with bare hands, clean the quartz glass with alcohol before inserting it into a furnace.

5.2 Devitrification of Quartz Glass

Devitrification is a natural process with quartz glass. The quartz glass is utilized in a glass state. The most stable state for quartz is crystalline. Therefore, devitrification is the tendency of the quartz to return to its most stable state. If the quartz is kept extremely clean and free of contamination, devitrification will occur only at high temperatures. The process occurs more rapidly and at lower temperatures when the glass has become contaminated by alkaline metals (Na, K, Mg, and Ca). The alkalis found in normal tap water can cause the process to start. There is conflicting opinion among the experts as to whether the process can be stopped. Some say that once the process starts it does not stop. Others indicate that once the alkali is removed, the process will stop.

Removal of the devitrification is not practical as it requires drastic measures and is potentially dangerous to the instrument and/or the user.

Devitrification starts with a dulling or opacity of the quartz. It develops into a rough and crumbling surface. Devitrification ultimately weakens the glass/quartz until it breaks or is otherwise no longer useful.

The best cure for contamination and devitrification is prevention. Being aware of the causes and signs of contamination can help the user take the steps necessary to control contamination of the cell. *Keep your cell clean and avoid contact with bare hands, tap water, or contaminated SPRTs.*

6 Realization of the Freezing Point

As was mentioned in Section 2, Introduction, it is not difficult to realize a freezing point by using the Hart completely sealed metal freezing point cell. In order to get the highest possible accuracy, a general understanding of the freezing process of an ideal pure metal is helpful.

6.1 Background Information

Theoretically the melting and freezing temperatures for an ideal pure metal are identical. However, with the introduction of impurities in the metal, the melting and freezing equilibrium points are usually slightly lower. The freezing plateau of an ideal pure metal is conceptually flat, except during the supercool. Impurities in the metal generally introduce a slightly negative slope to the plateau. Most of the different types of impurities will cause a drop in the freezing plateau e.g., gallium impurities in tin will cause a drop in the freezing plateau. A few of the types of impurities can cause an increase in the plateau e.g., gold impurities in silver will cause the freezing plateau to increase. An extremely high purity metal, 99.9999% or higher, behaves very closely to an ideal pure metal. Figure 3 shows the difference between a freeze of an ideal pure metal and a high-purity metal. The approximate effect of the impurity on the equilibrium point can be calculated using the first cryoscopic constant. This calculation is discussed in the *Guidelines for Realizing the International Temperature Scale of 1990 (ITS-90)*. For general uncertainty comparisons, the first cryoscopic constant, the metal purity requirement, and the difference in the liquidus point are outlined in Table5 . In a modern temperature standard laboratory using a SPRT, a temperature change as low as 0.01 mK (0.00001 °C) can be detected. Therefore, the best technique for realizing the freezing point with a real sample is one that measures a temperature nearest to the freezing point of the ideal pure metal. The beginning of the freezing curve of a high purity metal is the closest temperature to the ideal freezing point which can be obtained in a modern temperature standard laboratory. A so-called slow induced freezing technique was found to fit the purpose best (The detail of the technique will be described a little later). A very slow freeze allows enough time to calibrate a number of SPRTs in the beginning of a single freeze.

Table 5 *Summary of the 1st Cryoscopic Constants and the Estimated Effects of Impurities*

Substance	1st Cryoscopic Constant	Impurity Level	Deviation from Pure Liquidus Point
Indium	0.00732/K	99.99999%	–0.05 mK
Tin	0.00329/K	99.9999%	–0.3 mK
Zinc	0.00185/K	99.9999%	–0.5 mK
Aluminum	0.00149/K	99.9999%	–0.7 mK

Substance	1st Cryoscopic Constant	Impurity Level	Deviation from Pure Liquidus Point
Silver	0.000891/K	99.9999%	–1.1 mK
Gold	0.000831/K	99.9999%	–1.2 mK
Copper	0.000857/K	99.9999%	–1.2 mK

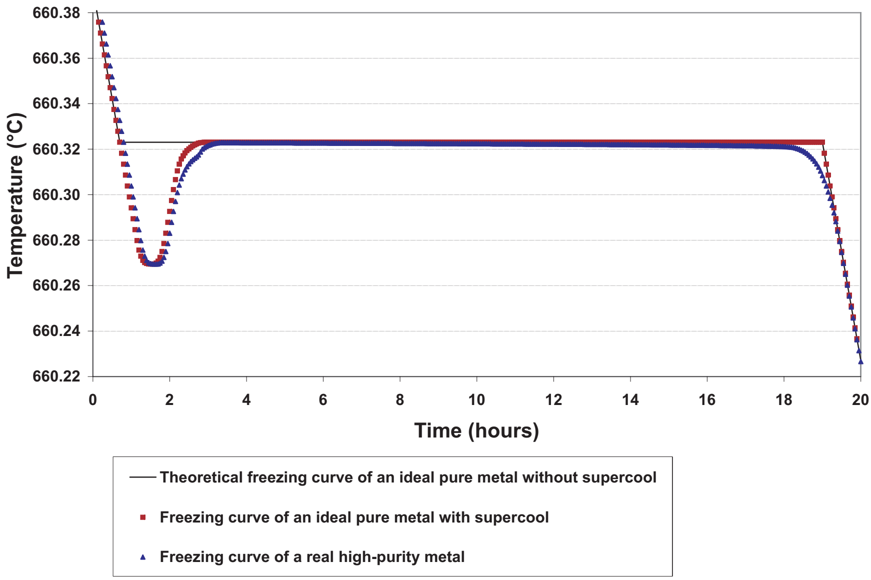

Figure 3 *Freezing curve comparison of one cell.*

The induced technique generates two liquid-solid interfaces in the cell. A continuous liquid-solid interface that, as nearly as is practical, encloses the sensor of the SPRT being calibrated. Another liquid-solid interface is formed on the wall of the graphite crucible. In such a situation, the outer interface advances slowly as the liquid continues to solidify. Ideally this generates a shell that continues to be of uniform thickness completely surrounding the liquid, which itself surrounds the inner liquid-solid interface that is adjacent to the thermometer well (Figure 4). The inner interface is essentially static except when a specific heat-extraction process takes place; e.g. the insertion of a cool replacement thermometer. It is the temperature of the inner liquid-solid interface that is measured by the thermometer. Sometimes the inner liquid-solid interface is called the defining temperature interface.

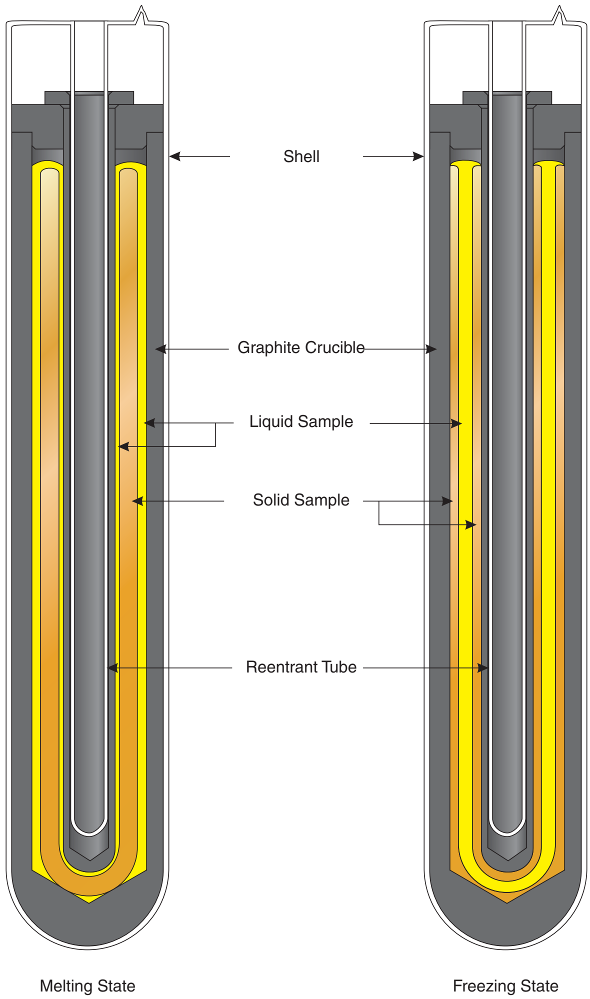

Figure 4 *Two liquid-solid interfaces in the cell.*

It is extremely important for the process described here that there is a very uniform, stable and controlled temperature environment enclosing the fixed point cell. We have developed three designs of fixed point furnaces to satisfy these requirements. The Model 9114 furnace has three independent heaters and controllers designed to be used for a temperature range up to 680 °C as shown in Figure 5.

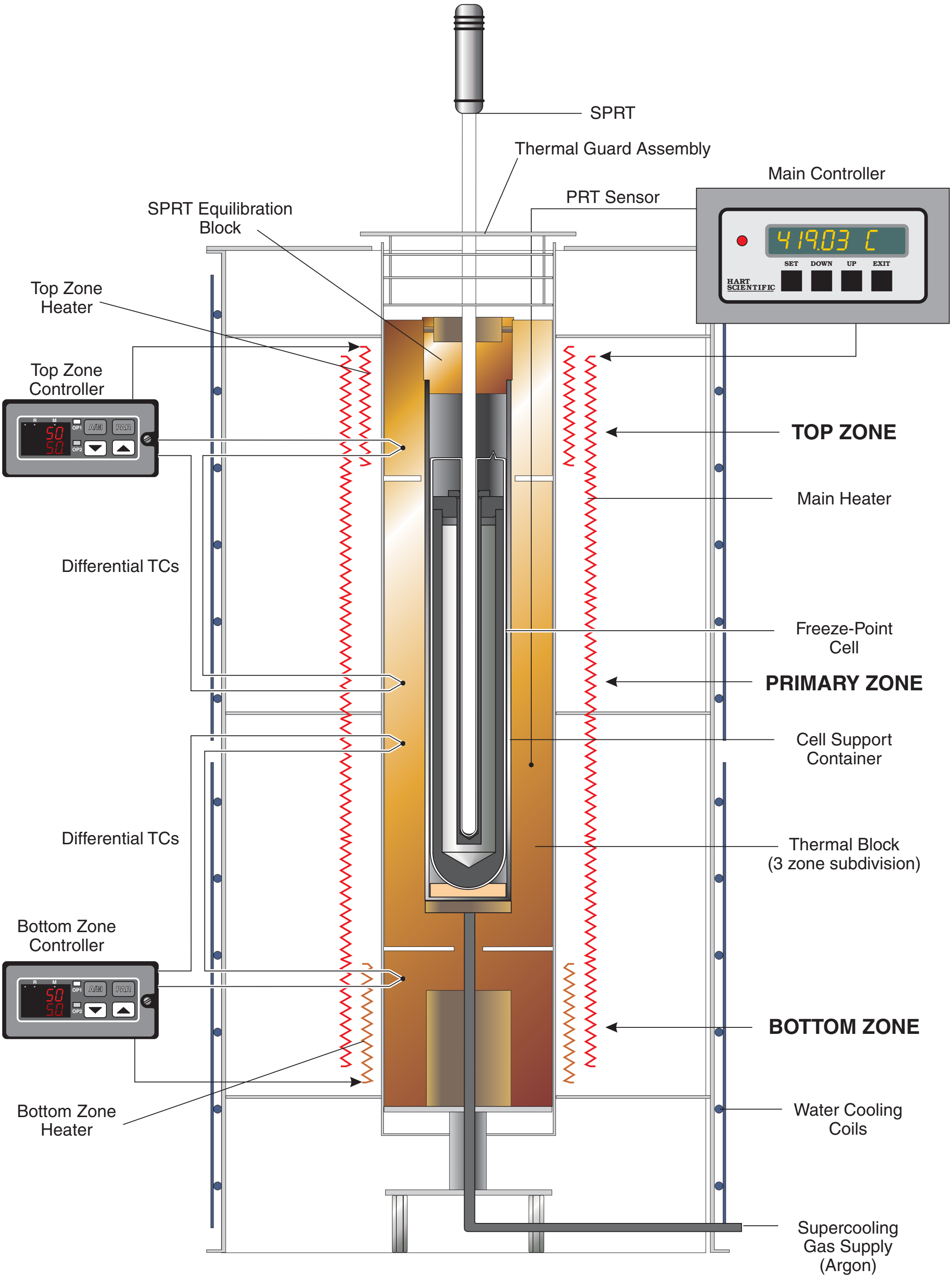

Figure 5 *9114 Furnace Interior with Freeze Point Cell, Cross Sectional View.*

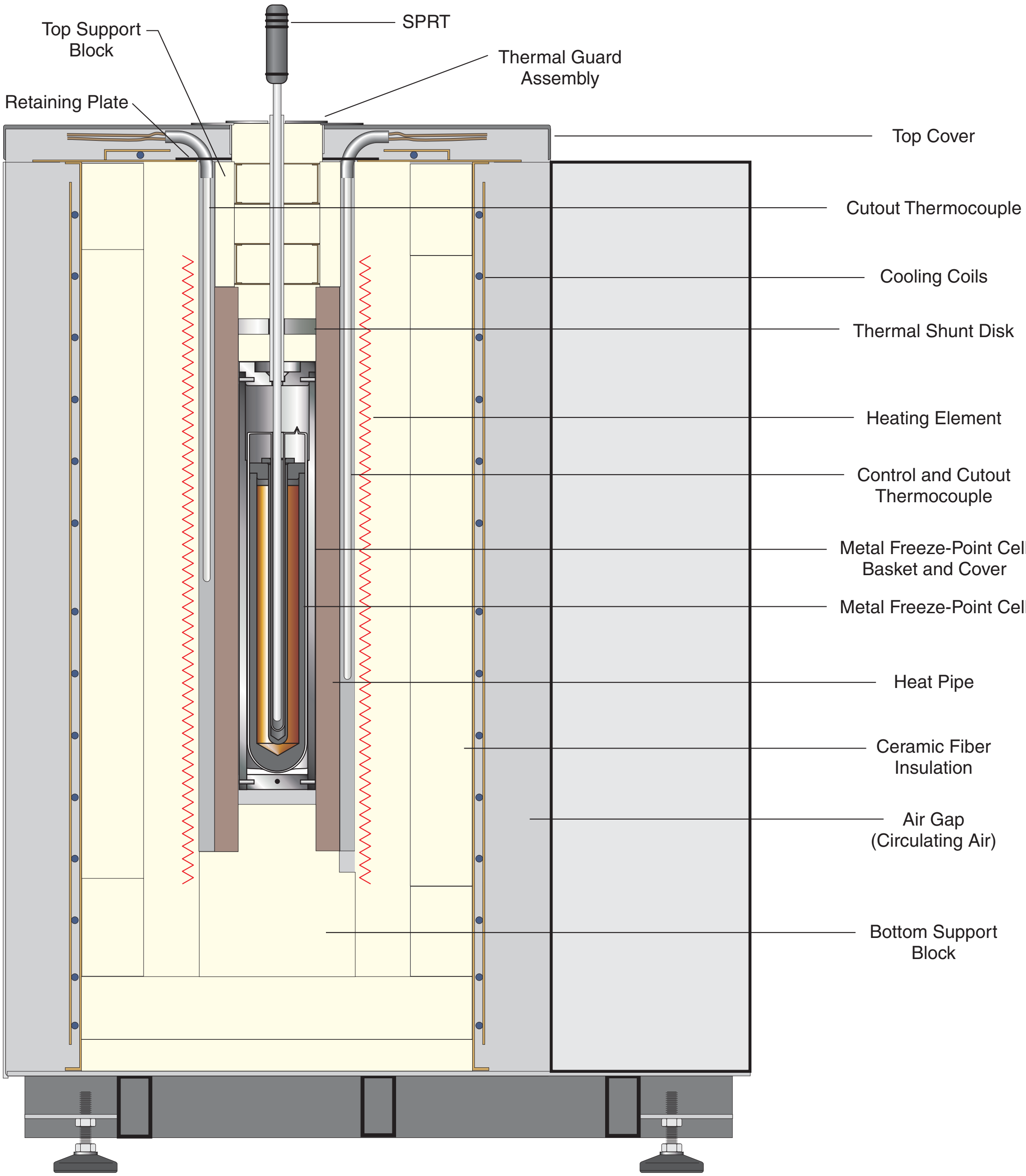

Figure 6 *9115 Furnace Interior with Freeze Point Cell, Cross Sectional View.*

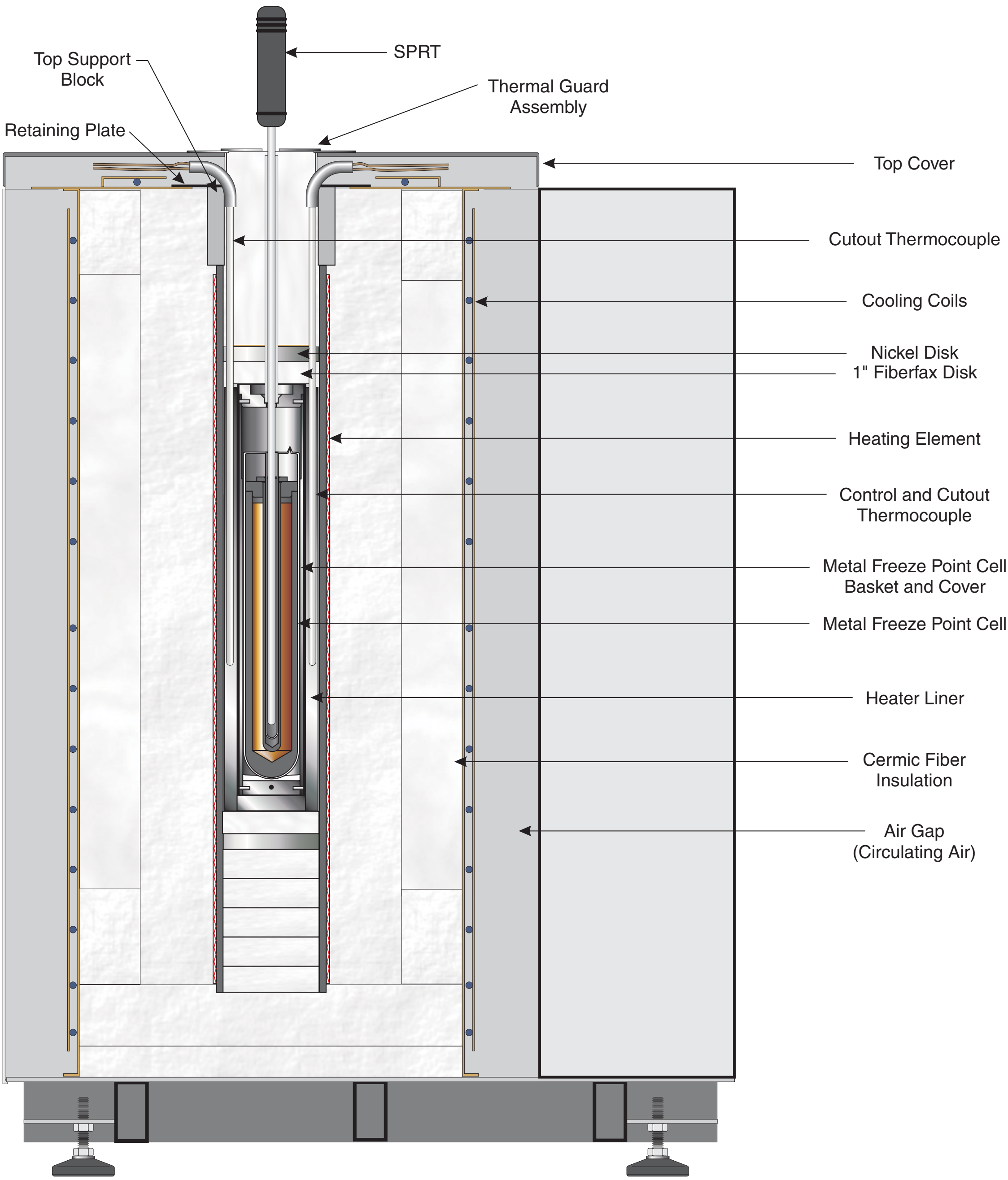

Figure 7 *9116 Furnace Interior View*

The Model 9115 furnace with a sodium-in-inconel heat pipe is designed for a temperature range from 500 °C through 1000 °C. Although the heat-pipe can be used up to 1100 °C, as a safety precaution, it is suggested not to use the 9115 furnace above 1000 °C for a long period of time. See Figure 6.

The Model 9116 furnace (Figure 7) is designed with a special single zone heater for the freezing point of copper (1084.62 °C). The furnaces and their temperature uniformities are listed in Table 6.

Table 6 *The furnaces for fixed points and their temperature uniformity*

Fixed Point	The Equipment Used	Temperature Uniformity
The freezing point of indium	Model 9114 furnace, three zones	± 0.02°C
The freezing point of tin	Model 9114 furnace, three zones	± 0.02°C
The freezing point of zinc	Model 9114 furnace, three zones	± 0.02°C
The freezing point of aluminum	Model 9114 furnace, three zones	± 0.03°C
The freezing point of aluminum	Model 9115 furnace, heat pipe	± 0.03°C
The freezing point of silver	Model 9115 furnace, heat pipe	± 0.05°C
The freezing point of copper	Model 9116 furnace, single zone	± 0.2 °C

The cell should be put into the cell containment vessel before insertion into any furnace. Ideally each cell would be kept in its own unique vessel. The cell containment vessel (basket) for the Model 9114 furnace is shown in Figure 8 on page 20. A nickel container is used to support and enclose the freezing point cell for Model 9115 (Figure 8) and an inconel container is used for the Model 9116 furnace. Fiber ceramic insulation is placed in the bottom of the cell basket to protect the cell. Insulation is also placed on top of the cell for protection and to reduce heat loss.

6.2 Procedure for Realizing the Freeze (In, Zn, Al, and Ag Fixed Points)

This is the procedure used in the Hart metrology lab with the Hart sealed fixed point cells. Other procedures are sometimes employed in industry.

All of the freezing points except tin are realized in a similar way.

1. Insert the cell with the cell containment vessel carefully into the furnace.
2. Set the temperature of the furnace about 10 °C higher than the freezing point. Allow all of the metal to melt completely.
3. After all metal is completely melted, the furnace is set at a stable temperature 1 °C or 1.5 °C higher than the freezing point over night.

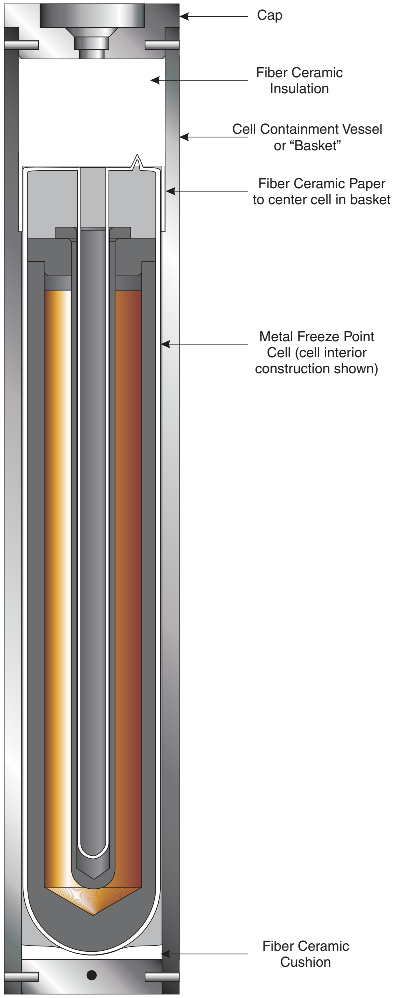

Figure 8 *The metal freezing point cell in the cell containment vessel (basket).*

4. The next morning, the furnace temperature is decreased slowly (0.1 °C –0.15 °C). In order to monitor the metal sample temperature, a SPRT is inserted into the cell. The temperature of the metal sample decreases to less than the freezing point before recalescence. The amounts of supercool are different from metal-to-metal.
5. After recalescence the thermometer is removed from the furnace immediately and two cold (room temperature) quartz glass rods are inserted into the fixed point cell one by one, each for about five minutes.

6. The preheated SPRT to be calibrated is introduced into the cell, while the furnace is kept at a stable temperature of 0.5°C below the freezing point.

This procedure provides a very stable, long freezing plateau that typically lasts for more than ten hours. The changes in temperature in the first half of the plateau are usually within ± 0.2 - 0.3 mK. A typical freezing curve is shown in Figure 9.

A number of SPRTs can be calibrated in a single freezing plateau. When multiple SPRTs are to be calibrated from a single freeze, we suggest that the SPRTs be preheated to a temperature slightly higher than the freezing point before inserting the SPRT into the furnace. As was mentioned earlier, the cold quartz glass rods inserted into the cell will generate a liquid-solid interface adjacent to the thermometer well (see Figure 4).

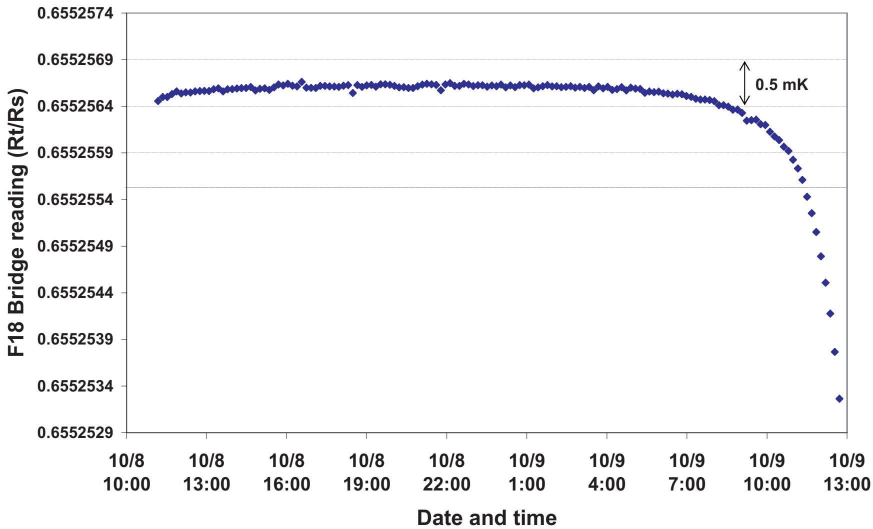

Figure 9 *A typical freezing curve for the Zinc Cell*

6.2.1 Realization of the Freezing Point of Tin (Sn)

Since tin requires a 25°C or more drop in temperature to achieve supercool, nucleation is achieved by additional cooling supplied by a cold gas flow. The procedure for the freezing point of tin is similar to that of the other fixed points, except the need to compensate for the large temperature difference required for supercool.

Follow Steps 1 - 4 listed above.

When the temperature indicated by a thermometer immersed in the tin sample reaches the freezing point, using the Model 9114 furnace introduce a cold gas flow upward around the outer surface of the cell until recalescence. "Cold gas flow" means compressed air at an approximate rate of 5-20 liter/min. (0.2-0.7 CFM) and roughly 200 kPa (29 psia). After recalescence, shut off the cold gas flow. The furnace is kept at a stable temperature of 0.5°C below the freezing point as with other metals. The Model 9114 furnace as shown in Figure 5 has a specially designed core for the realization of the freezing point of tin.

6.2.2 SPRT Care At High Temperatures

Each SPRT calibrated at temperatures above 500°C is subjected to quenched-in vacancy defect effect when the SPRT is removed from the furnace. This quenched in lattice vacancy defect effect must be removed before calibration at the triple point of water. Therefore, when the SPRT is removed from the cell, place it in an auxiliary furnace set at the same temperature as the fixed point. Slowly cool the SPRT at a rate of roughly 100°C/hour above 500°C. Once the SPRT has reached 500°C, it may be removed directly to room temperature.

7 The Correction for the Pressure Difference

This is the procedure used in the Hart metrology lab with the Hart sealed fixed point cells. Other procedures are sometimes employed in industry.

Except for a few triple points, the values of temperature assigned to the defining fixed points by ITS-90 correspond to the temperatures at the standard atmospheric pressure — 101.325 kPa. The actual pressure in a cell may be not exactly the standard value. During the course of manufacture of a fixed-point cell, it is easier for a glassblower to seal the cell if the pressure in the cell is slightly lower than the room pressure. The actual pressure in the cell exactly at the fixed point was measured at Hart. This information is provided on the Report of Test enabling the used to correct for the difference in pressure. During measurement at a fixed point, the sensor of a SPRT is usually placed at a height which is “h” meters lower than the surface of the matter used for the fixed point and where the pressure is higher than that at the surface due to the static head. ITS-90 gives all of the necessary coefficients for the calculation of the correction caused by the pressure difference, which are summarized in following table:

Table 7 *Coefficients for the Pressure Difference of Some Defining Fixed Points.*

Substance	Assigned Value of Equilibrium Temperature T Kelvin (K)	Temperature with Pressure, p k_1 ; dT/dp (10^{-5} mK/Pa)	Variation with depth k_2 : dT/dh (mK/m)	Approximate dW/dt (1/K)
Argon (T)	83.8058	25	3.3	0.004342
Mercury (T)	234.3156	5.4	7.1	0.004037
Water (T)	273.16	–7.5	–0.73	0.003989
Gallium (M)	302.9146	–2.0	–1.2	0.003952
Indium (F)	429.7485	4.9	3.3	0.003801
Tin (F)	505.078	3.3	2.2	0.003713
Zinc (F)	692.677	4.3	2.7	0.003495
Aluminum (F)	933.473	7.0	1.6	0.003205
Silver (F)	1234.93	6.0	5.4	0.002841
Gold (F)	1337.33	6.1	10	--
Copper (F)	1357.77	3.3	2.6	--

The correction of temperature caused by the difference in pressure can be calculated by using the following equation:

Equation1: Pressure Dependent Temperature Correction

$$\Delta t = (P - P_0) \times k_1 + h \times k_2$$

Where:

P = the actual pressure of argon in the cell exactly at the fixed point temperature

P_0 = the standard atmospheric pressure, i.e. 101,325 Pa

k_1 = dT / dp

k_2 = dT / dh

and

h = the immersion depth of the midpoint of the sensor of a SPRT into the matter used for the fixed point

The immersion depth of the midpoint of a SPRT sensor in Hart metal freezing point cell is approximately 0.17 m (the distance from the bottom of the central well to the surface of liquid metal is about 0.195 m). The actual pressure of the argon at the freezing point in the cell, p, is provided in the *Report of Test.* The temperature correction, Δt, can be calculated using Equation 1 .

Example

The pressure of argon at the freezing point in the aluminum freezing point cell S/N 5907-5AL004 is 80,817 Pa as given in the Report of Test. k1 and k2 for the freezing point of aluminum can be found in Table 5, $k_1 = 7.0 * 10^{-5}$ mK / Pa and k_2 = 1.6 mK / m. The average immersion depth is 0.17 m for most of standard platinum resistance thermometers. Therefore, use Equation 1 to calculate Δt.

Substituting values into Equation 1:

$$(80{,}817Pa - 101{,}325Pa)\frac{7.0 \times 10^{-5}mK}{Pa} + (0.17m)\frac{1.6mK}{m} = -1.44mK + 0.27mK$$

Consequently:

$$\Delta t = -1.164mK$$

Hence, the actual temperature of a sensor of a SPRT at the point of total immersion during a freezing plateau in the cell is calculated using Equation 2.

Equation 2: Calculation of the Actual Temperature, t_1

$$t_1 = t + \Delta t$$

Therefore:

$$t_1 = 660.323°\mathrm{C} - 0.00117°\mathrm{C} = 660.32184°\mathrm{C}$$

where t is the defining fixed point temperature, i.e. 660.323°C for the freezing point of aluminum.

The resistance ratio, W_{Al}, for the particular cell exactly at the freezing point of aluminum can be calculated using the following equation. The value for dW/dt is taken from Table 7.

Equation : Calculation of W_{Al} for the exact defining fixed point temperature.

$$W_{Al} = W(t_1) - [\Delta t]\frac{dW}{dt}$$

Substituting values:

$$3.37600860 - (-0.001164)3.204971 \times 10^{-3}$$

Thus the W_{Al} for the cell is:

$$W_{Al} = 3.37601233$$