FLUKE®

Calibration

5924/5925/5926
5927/5928/5929

Metal Freeze Point Cell

Users Guide

2004, Rev. 1, 12/11

© 2004 - 2011 Fluke Corporation. All rights reserved. Specifications subject to change without notice.
All product names are trademarks of their respective companies.

Limited Warranty & Limitation of Liability

Each Fluke product is warranted to be free from defects in material and workmanship under normal use and service. The warranty period is one year and begins on the date of shipment. Parts, product repairs, and services are warranted for 90 days. This warranty extends only to the original buyer or end-user customer of a Fluke authorized reseller, and does not apply to fuses, disposable batteries, or to any product which, in Fluke's opinion, has been misused, altered, neglected, contaminated, or damaged by accident or abnormal conditions of operation or handling. Fluke warrants that software will operate substantially in accordance with its functional specifications for 90 days and that it has been properly recorded on non-defective media. Fluke does not warrant that software will be error free or operate without interruption.

Fluke authorized resellers shall extend this warranty on new and unused products to end-user customers only but have no authority to extend a greater or different warranty on behalf of Fluke. Warranty support is available only if product is purchased through a Fluke authorized sales outlet or Buyer has paid the applicable international price. Fluke reserves the right to invoice Buyer for importation costs of repair/replacement parts when product purchased in one country is submitted for repair in another country.

Fluke's warranty obligation is limited, at Fluke's option, to refund of the purchase price, free of charge repair, or replacement of a defective product which is returned to a Fluke authorized service center within the warranty period.

To obtain warranty service, contact your nearest Fluke authorized service center to obtain return authorization information, then send the product to that service center, with a description of the difficulty, postage and insurance prepaid (FOB Destination). Fluke assumes no risk for damage in transit. Following warranty repair, the product will be returned to Buyer, transportation prepaid (FOB Destination). If Fluke determines that failure was caused by neglect, misuse, contamination, alteration, accident, or abnormal condition of operation or handling, including overvoltage failures caused by use outside the product's specified rating, or normal wear and tear of mechanical components, Fluke will provide an estimate of repair costs and obtain authorization before commencing the work. Following repair, the product will be returned to the Buyer transportation prepaid and the Buyer will be billed for the repair and return transportation charges (FOB Shipping Point).

THIS WARRANTY IS BUYER'S SOLE AND EXCLUSIVE REMEDY AND IS IN LIEU OF ALL OTHER WARRANTIES, EXPRESS OR IMPLIED, INCLUDING BUT NOT LIMITED TO ANY IMPLIED WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. FLUKE SHALL NOT BE LIABLE FOR ANY SPECIAL, INDIRECT, INCIDENTAL, OR CONSEQUENTIAL DAMAGES OR LOSSES, INCLUDING LOSS OF DATA, ARISING FROM ANY CAUSE OR THEORY.

Since some countries or states do not allow limitation of the term of an implied warranty, or exclusion or limitation of incidental or consequential damages, the limitations and exclusions of this warranty may not apply to every buyer. If any provision of this Warranty is held invalid or unenforceable by a court or other decision-maker of competent jurisdiction, such holding will not affect the validity or enforceability of any other provision.

Fluke Corporation
P.O. Box 9090
Everett, WA 98206-9090
U.S.A.

Fluke Europe B.V.
P.O. Box 1186
5602 BD Eindhoven
The Netherlands

11/99

Table of Contents

Title	Page
Introduction	1
Before You Start	3
Symbols Used	3
Safety Information	4
How to Contact Fluke	4
Specifications	5
Calibration Process Overview	5
Care of Your Metal Freezing Point Cell	6
General Information	6
Devitrification of Quartz Glass	6
Unpacking	7
Assembly Guide	7
Background Information	9
Maintaining the Cell with Argon	15
Vertical Temperature Gradient Adjustment	15
Controller Display Accuracy Adjustment	16
Procedure for Realizing the Freeze (In, Zn, Al, Ag, and Cu Fixed Points)	17
Realization of the Freezing Point of In	17
Realization of the Freezing Point of Sn	18
Realization of the Freezing Point of Zn	19
Realization of the Freezing Point of Al	20
Realization of the Freezing Point of Ag	21
Realization of the Freezing Point of Cu	22
SPRT Care At High Temperatures	23
The Correction for the Pressure Difference	23

List of Tables

Table	Title	Page
1.	The Defining Metal Freezing Points of the ITS-90, Pressure Constants, and Resistance Ratios	1
2.	Subranges of the ITS-90 and Freezing Points Required for Calibration	2
3.	International Electrical Symbols	3
4.	The Specification of Metal Freezing Point Cells.	5
5.	Summary of the First Cryoscopic Constants and the Estimated Effects of Impurities	9
6.	The Furnaces for Fixed Points and their Temperature Uniformity	15
7.	Hydrostatic Head Correction Coefficients	23

List of Figures

Figure	Title	Page
1.	The Metal Freezing Point Cell	2
2.	The Fluke Open Metal Freezing Point Cell	8
3.	Freezing Curve Comparison of One Cell	10
4.	9114 Furnace Interior with Freeze Point Cell, Cross Sectional View	11
5.	9115A/9116A Furnace Interior with Freeze Point Cell, Cross Sectional View	12
6.	The Metal Freezing Point Cell in the Cell Containment Vessel (Basket)	13
7.	Two Liquid-solid Interfaces in the Cell	14
8.	A Typical Freezing Curve for the Zinc Cell	20

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 kPa). 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 are assigned by the ITS-90. The pressure effect constants and the resistance ratios of the ITS-90 are listed in Table 1.

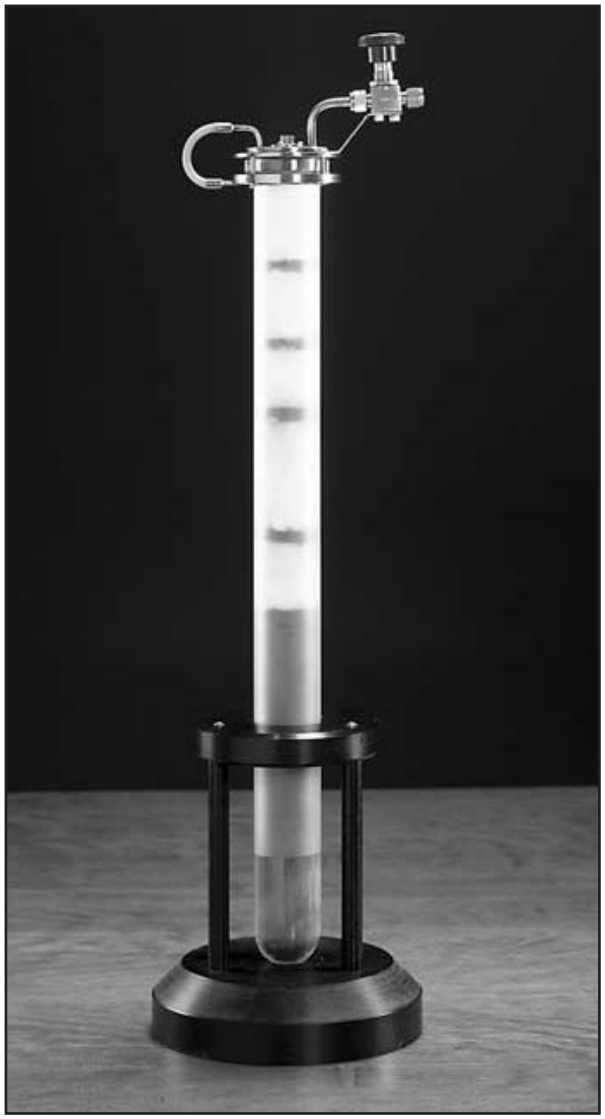
Table 1. The Defining Metal Freezing Points of the ITS-90, Pressure Constants, and Resistance Ratios

Pressure Effect of Fixed Points						
Fixed Point	Assigned Temperature T_{90} (K)	Assigned Temperature t_{90} (°C)	dt/dP (10^{-8} K/Pa) [1]	dt/dh (10^{-3} K/m)	W_r (T_{90})	dW_r/dt (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	--	--
[1] Equivalent to millikelvins per standard atmosphere.						

The fixed points in Table 1 are intrinsic temperature standards according to the definition of the ITS-90. In certain conditions, these freezing points are highly reproducible, obtaining almost the same temperature where and when a freezing point is realized. The difference among realizations of a freezing point of indium, tin and zinc might be well within 1.0 mK. For aluminum and silver, the difference among realizations of a freezing point might be within a few millikelven.

The 5900 series and 5910 Series Fixed-point Cells are fully sealed cells that simplify the realization process. The 5920 series of open fixed-point cells include stainless steel caps and ports for use with argon gas.

Fluke has open fixed-point cells for those who require traditional fixed-point cells. Contact Fluke for more information.



gpv001.jpg

Figure 1. The Metal Freezing Point Cell

To calibrate a Standard Platinum Resistance Thermometer (SPRT), you must be able to reach the fixed-point temperatures in Table 1. When working with subranges, the freezing points change depending on the metal. Refer to Table 2 for subrange freezing points.

Table 2. Subranges of the ITS-90 and Freezing Points Required for Calibration

Subrange	Freezing Points Required
0 °C to 961.78 °C	FP Sn, FP Zn, FP Al, and FP Ag
0 °C to 660.323 °C	FP Sn, FP Zn, and FP Al
0 °C to 419.527 °C	FP Sn and FP Zn
0 °C to 231.928 °C	FP In and FP Sn
0 °C to 156.5985 °C	FP In

Before You Start

Symbols Used

Table 3 lists the International Electrical Symbols. Some or all of these symbols may be used on the instrument or in this manual.

Table 3. International Electrical Symbols

Symbol	Description	Symbol	Description
	Hazardous Voltage	O	Off
	Hot Surface (Burn Hazard)	I	On
	Risk of Danger. Important information. See manual.		Fuse
	AC (Alternating Current)		Battery
	AC-DC	 N10140	Conforms to Relevant Australian EMC Requirements.
	DC		Conforms to Relevant North American Safety Standards.
	Double Insulated	CE	Conforms to European Union Directives.
	PE Ground		Do Not Dispose of this Product as Unsorted Municipal Waste. Go to Fluke's Website for Recycling Information.
CAT II	CAT II equipment is designed to protect against transients from energy-consuming equipment supplied from the fixed installation, such as TVs, PCs, portable tools, and other household appliances.		

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.

⚠Warning

To avoid 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 Users Guide.**
- **Follow all safety guidelines listed in the Users Guide.**
- **Avoid leaving a PRT installed for an extended period of time which can cause the PRT handle to become hot.**
- **Calibration Equipment should only be used by trained personnel.**
- **Use the Product only as specified, or the protection supplied by the Product can be compromised.**
- **Do not use and disable the Product if it is damaged.**
- **Use this Product indoors only.**
- **Have an approved technician repair the Product.**

⚠Caution

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

- **Keep the cell clean and avoid contact with bare hands, tap water, or contaminated PRTs. If there is any chance that the cell has been contaminated, clean the quartz with reagent grade alcohol before inserting it into a furnace.**
- **Use the product in the vertical orientation only.**

How to Contact Fluke

To contact Fluke, call one of the following telephone numbers:

- Technical Support USA: 1-877-355-3225
- Calibration/Repair USA: 1-877-355-3225
- Canada: 1-800-36-FLUKE (1-800-363-5853)
- Europe: +31-40-2675-200
- Japan: +81-3-6714-3114
- Singapore: +65-6799-5566
- China: +86-400-810-3435
- Brazil: +55-11-3759-7600
- Anywhere in the world: +1-425-446-6110

To see product information and download the latest manual supplements, visit Fluke Calibration’s website at www.flukecal.com.

To register your product, visit http://flukecal.com/register-product.

Specifications

Table 4. The Specification of Metal Freezing Point Cells

Model Number	5924	5925	5926	5927	5928	Contact Fluke	5929
Fixed Point	FP In	FP Sn	FP Zn	FP Al	FP Ag	FP Au	FP Cu
Reproducibility (mK)	0.15 to 0.30	0.2 to 0.4	0.2 to 0.4	0.6 to 1.0	1.0 to 2.0	--	2.0 to 4.0
Expanded Uncertainty (mK), k = 2	0.7	0.5	0.9	1.3	2.4	--	10.0
Metal Purity	99.9999 %	99.9999 %	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)	50	50	50	50	50	50	50
Overall Height of the Cell (mm)	596	596	596	596/696	696	696	696
Inner Diameter of the Well (mm)	8	8	8	8	8	8	8
Total Immersion Depth [1] (mm)	195	195	195	195	195	195	195
[1] The distance from the bottom of the re-entrant well to the upper surface of the metal							

Calibration Process Overview

A typical 592X Fluke Metal Fixed-Point Cell is shown in Figure 1. To calibrate a Metal Fixed-Point Cell, a proper quantity of metal with a purity of 99.9999 % is melted into a graphite crucible with a graphite lid and re-entrant well. The impurity in the graphite must be less than 5 ppm. All of the graphite parts are then subjected to a high-temperature, high-vacuum treatment before loading the metal sample. A graphite disk is put on top of the crucible. The assembled graphite crucible, with the high-purity metal, is then enclosed in a long quartz cell. Pure silica wool insulation is interspersed between graphite disks to act as a thermal barrier.

Next, the cell is sealed with a specially designed stainless steel cap with a port and vacuum valve. The cell is connected to a pumping and filling system and then 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 absorption gas on the surface of all parts in the cell. Finally, the cell is filled with 99.999 % pure argon at a pressure close to 101.325 kPa at room temperature and the vacuum valve closed.

Care of Your Metal Freezing Point Cell

General Information

The metal freezing point cell is an extremely delicate device. Great care must be taken when working with or transporting the cell. The quartz glass outer shell is fragile and can be easily broken. Fluke suggests that the cell be kept in the vertical position for safety.

Note

Putting a cool cell in the horizontal orientation for a short period of time is not a typical cause of cell damage.

Transporting the cell on a general freight carrier will damage the cell beyond repair. To prevent damage, hand carry the cell from location to location. It is extremely important to keep the outer surface of the cell clean to prevent devitrification of the quartz glass. Never touch the cell with bare hands. When you have to handle the cell, always wear clean cotton gloves and use clean ash-less paper. If there is a 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.

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.

⚠Caution

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. Be aware of the causes and signs of contamination which will help you 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.

Unpacking

Since it is difficult to hand carry or deliver an assembled 592X fixed point cell, the 592X fixed point cell must be delivered as a kit. The kit is comprised of the following parts:

1. Crucible assembly (sealed in a Pyrex vessel in dry pure argon atmosphere)
2. High-purity graphite disks, 6 pieces, sealed in a Pyrex vessel in dry pure argon atmosphere, same Pyrex vessel as for crucible assembly
3. Pure fused silica (quartz glass) wool disks (in a Pyrex tube)
4. Fused silica (quartz glass) outer shell, 1 piece
5. Fused silica (quartz glass) reentrant well, 1 piece
6. A clean Pyrex tube or rod (used as tool, and will not be assembled into the cell)
7. Extra-clean ash less filter papers (used during assembling)
8. Stainless steel (SS) cap assembly, 1 set, including the following parts:
   - SS top cover, 1 piece
   - SS well clamp, 1 piece
   - SS cover clamp ring, 1 piece
   - Silicone O-ring 1.862 ID x 0.103 w, 1 piece
   - Silicone O-ring 0.424 ID x 0.103 w, 1 piece
   - Silicone seal washer (64.0 mm/50.6 mm x 5.0 mm), 1 piece
   - High vacuum bellow valve, NUPRO SS-4H, 1 piece
   - SS valve support bracket, 1 piece
   - Screw, 8-32 x 1 SKTHD CAP, 4 pieces
   - Screw, 4-40 x ¼ SKTHD CAP SST, 3 pieces
   - Screw, 8-32 x 5⁄16 PPHD, 2 pieces

Assembly Guide

1. Assembly should be performed in a clean and suitable work area. Wear new clean gloves during assembling and only place the crucible assembly on clean ash-less paper (provided).

⚠Caution

To prevent contamination of the crucible, do not break open the Pyrex vessel until you are ready to work with it.

2. Carefully break the top of the Pyrex vessel containing the crucible assembly and graphite disks with a clean metal tool. Remove the graphite disks from the Pyrex vessel and put them on a piece of ash-less filter paper. Complete the entire assembly process without interruption in order to avoid contamination and oxidation to pure metal.
3. Keep the fused silica outer shell (outer shell) at an angle of 10 degrees relative to the horizontal direction. Let the crucible assembly slide slowly and gently to the bottom of the outer shell. Use a piece of ash-less filter paper to hold the crucible assembly during the process. Put one piece of graphite disk on the top of the crucible assembly.
4. Carefully take pure fused silica wool disks from the Pyrex tube and put them into the outer shell using the Pyrex tube as a guide. Put more pure fused silica wool disks into the outer shell until their height is approximately 80 mm.
5. Put a graphite disk into the outer shell on the top of the pure fused silica wool disks. Push down the graphite disk until the height of pure fused silica wool disks decreases to approximately 40 mm using the Pyrex tube and fused silica well as guides (keep the surface of fused silica well clean during the entire assembling process). Insert the fused silica well through the holes of graphite disks and pure fused silica wool disks into the well of the crucible assembly to check the assembly. Next, take the fused silica well out of the outer shell.
6. Repeat steps 4 and 5 until five graphite disks and enough pure fused silica wool disks are assembled into the outer shell as shown in Figure 2.

7. Carefully assemble the stainless steel (SS) cap onto the top of the Purge Gas Connection Assembly as shown in Figure 2.
8. Keep the outer surface of the fused silica cell clean to prevent devitrification. Clean the outer surface of the cell and the cell support container (basket) before assembling the cell into the container. Use only clean tissue and Reagent Grade alcohol for the cleaning. Put pure fused silica (quartz glass) wool felt with a thickness about 1 inch on the inner bottom of the container as cushion.
9. Insert the cell into the cell basket in the furnace.

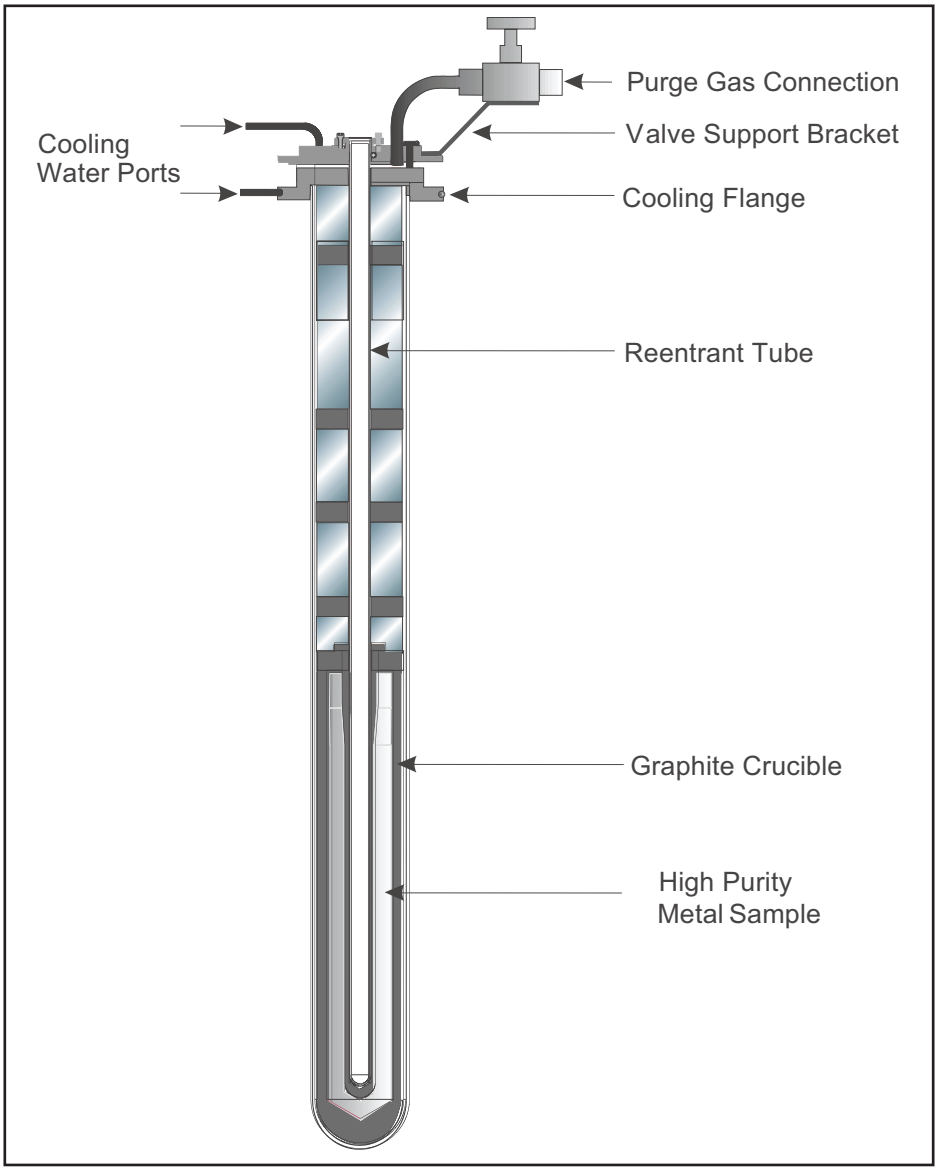


Figure 2. The Fluke Open Metal Freezing Point Cell

10. Connect the outlet of the vacuum valve to the pumping and filling system according to the attached Swagelok tube fitting instructions.
11. Open the vacuum valve and pump the cell using a mechanical vacuum pump. The vacuum pressure will decrease to about 0.01 Torr. If the pressure does not decrease, check and tighten all of the screws.

Background Information

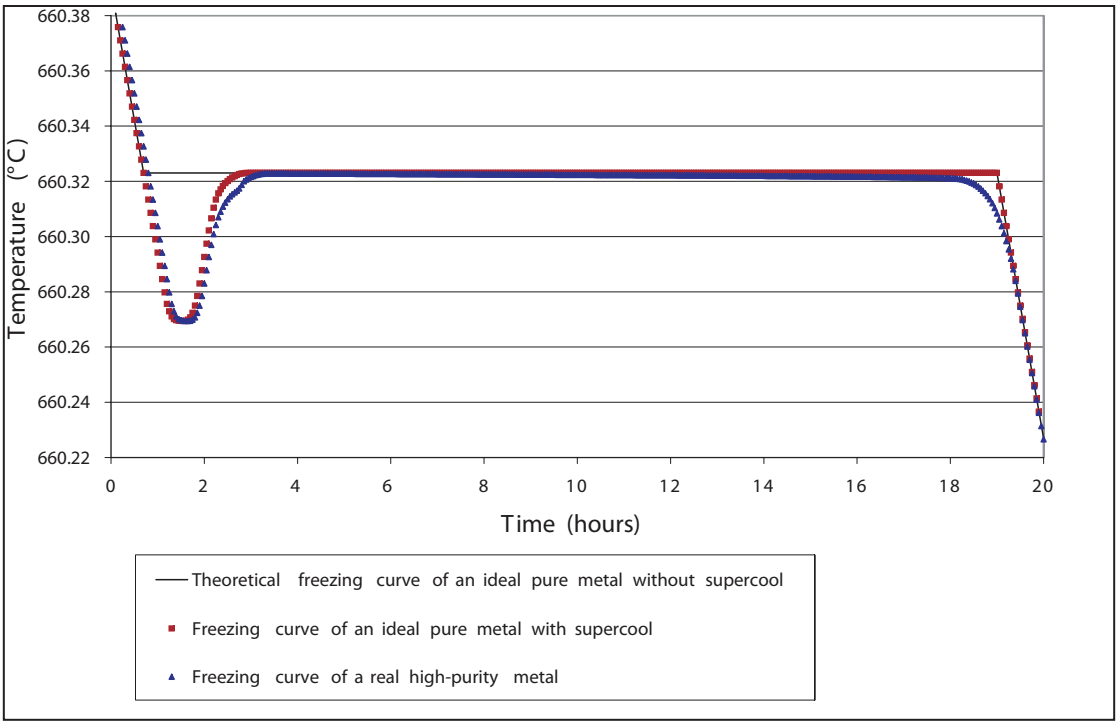
Theoretically the melting and freezing temperatures for an ideal pure metal are identical. However, with the introduction of impurities in the metal, the melting and freezing equilibrium points are usually slightly lower. The freezing plateau of an ideal pure metal is conceptually flat. The only exception is 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. For example, gallium impurities in tin will cause a drop in the freezing plateau.

Different types of impurities can cause an increase in the plateau. For example, 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 Table 5. 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 slow induced freezing technique was found to fit the purpose best (the details of the technique are described in the section Procedure for Realizing the Freeze). A very slow freeze allows enough time to calibrate a number of SPRTs at the initial portion of a single freeze.

Table 5. Summary of the First Cryoscopic Constants and the Estimated Effects of Impurities

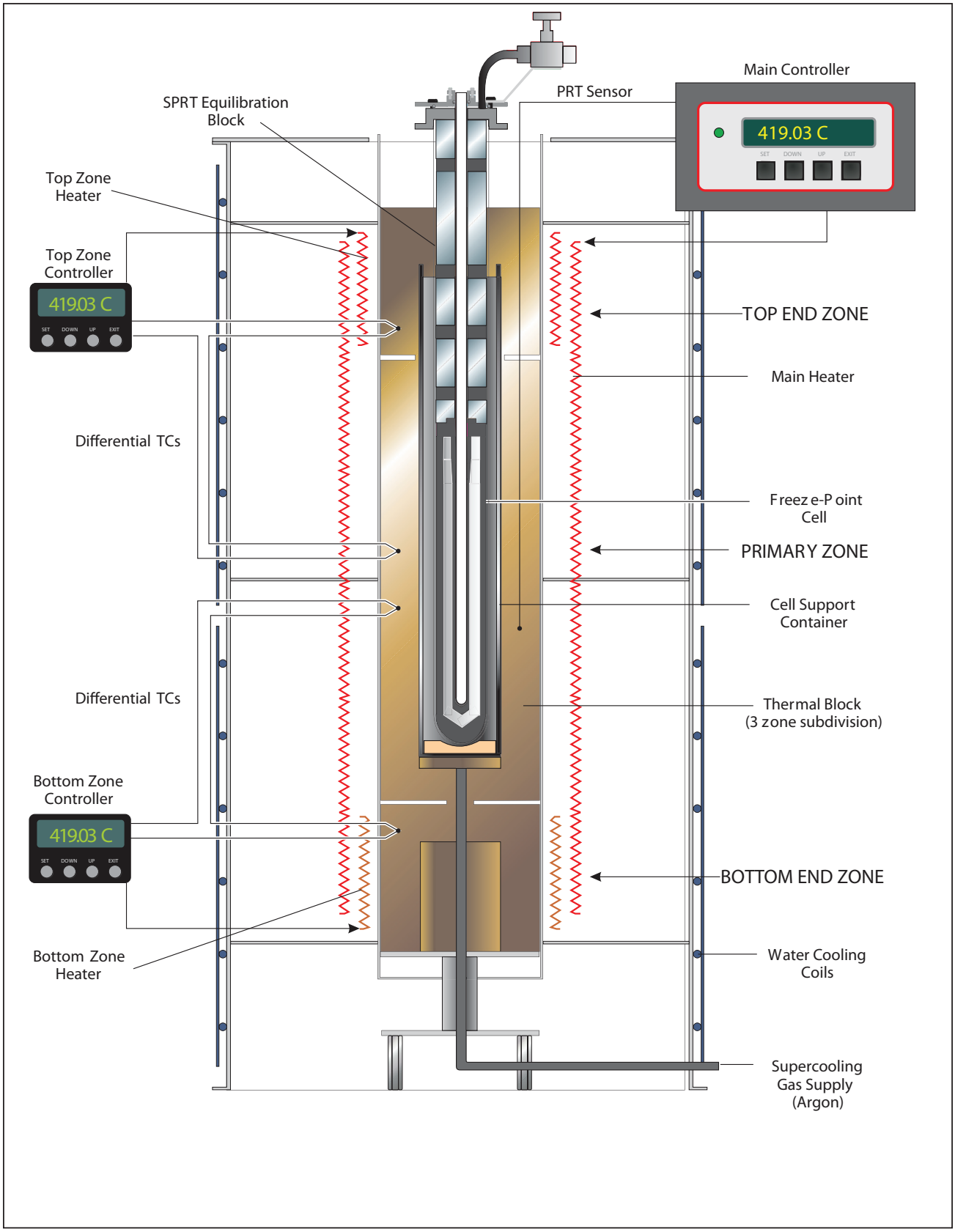
Substance	1st Cryoscopic Constant	Impurity Level	Deviation from Pure Liquidus Point
Indium	0.00732/K	99.99999 %	-0.01 mK
Tin	0.00329/K	99.9999 %	-0.3 mK
Zinc	0.00185/K	99.9999 %	-0.5 mK
Aluminum	0.00149/K	99.9999 %	-0.7 mK
Silver	0.000891/K	99.9999 %	-1.1 mK
Gold	0.000831/K	99.9999 %	-1.2 mK
Copper	0.000857/K	99.9999 %	-1.2 mK



gpv003.eps

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. For example, 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.



gpv005.eps

Figure 4. 9114 Furnace Interior with Freeze Point Cell, Cross Sectional View

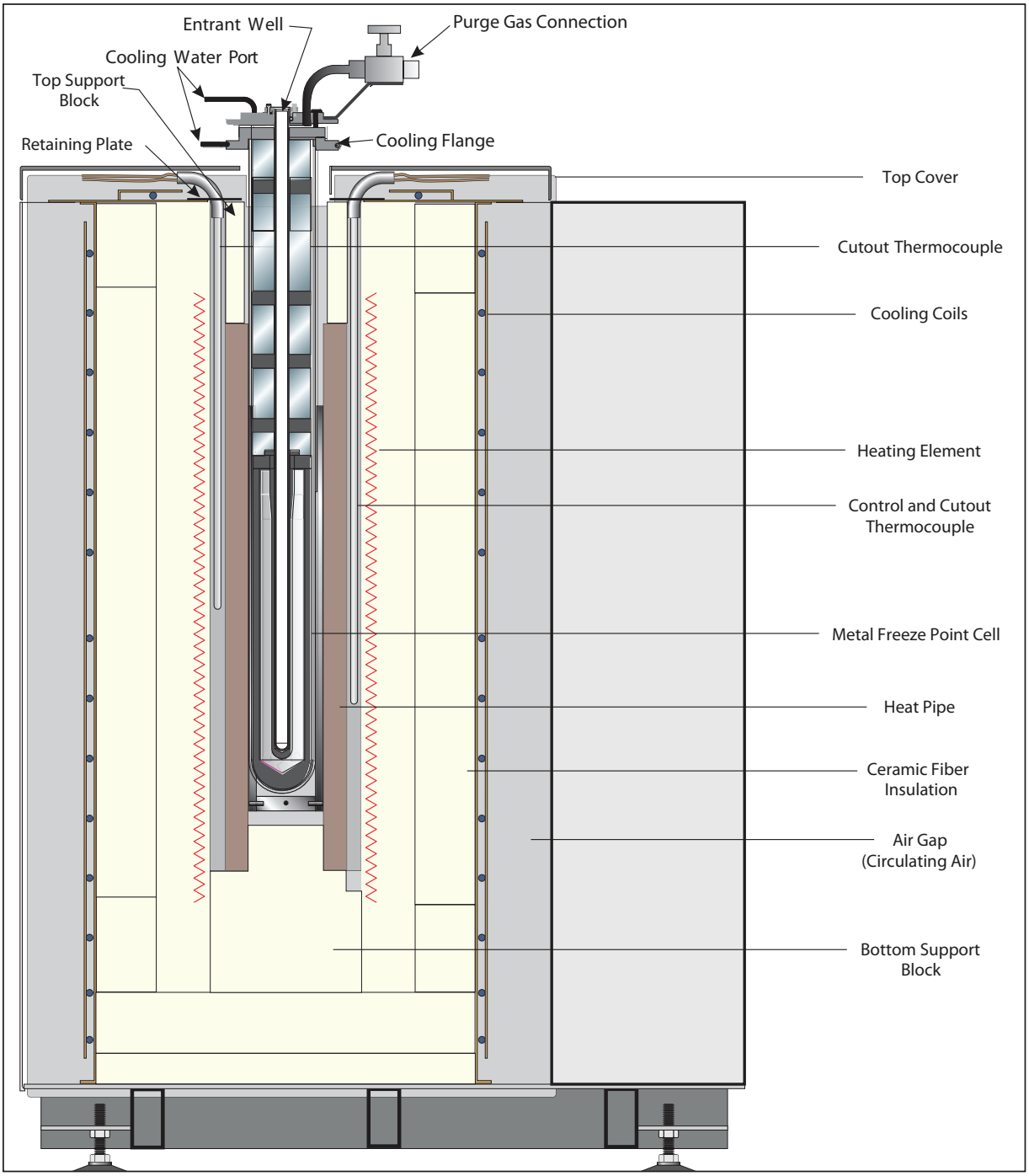
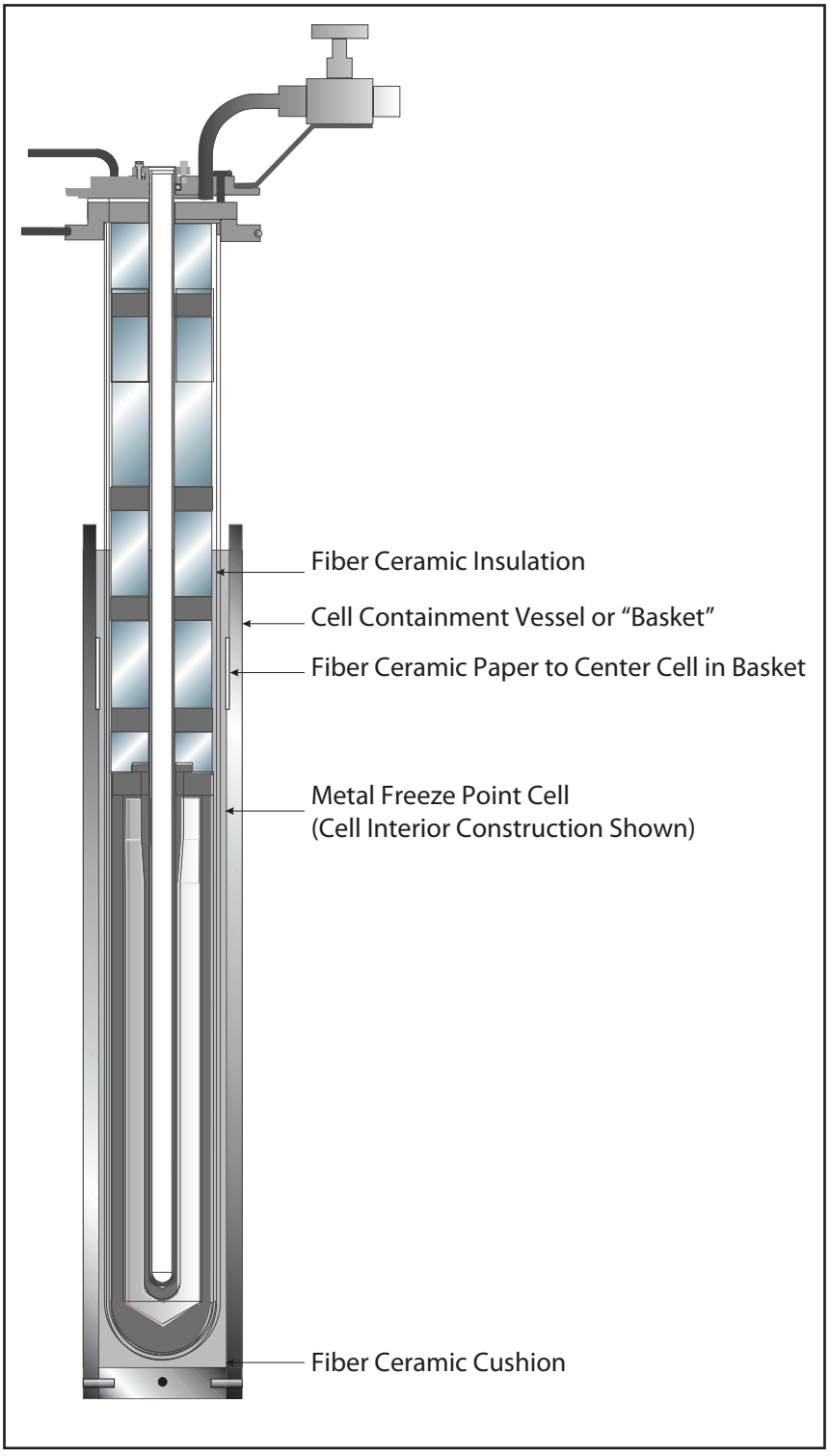


Figure 5. 9115A/9116A Furnace Interior with Freeze Point Cell, Cross Sectional View



gpv010.eps

Figure 6. The Metal Freezing Point Cell in the Cell Containment Vessel (Basket)

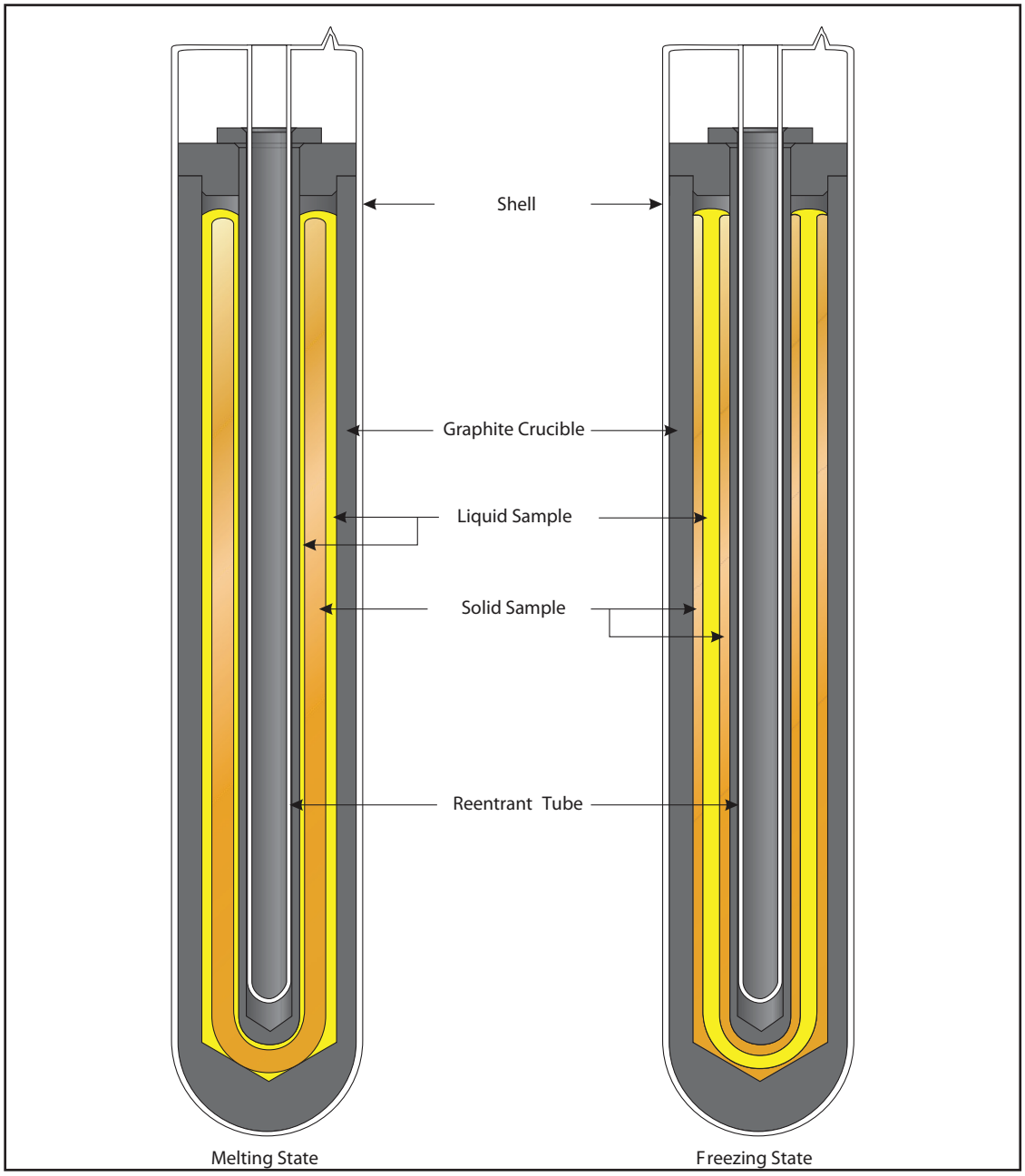


Figure 7. Two Liquid-solid Interfaces in the Cell

It is extremely important to follow the instructions in this manual to ensure that there is a uniform, stable, and controlled temperature environment when you enclose the fixed point cell. Fluke has developed three designs of fixed point furnaces to help you create this stable controlled environment. 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 4.

The Model 9115A Furnace with a sodium-in-inconel heat-pipe is designed for a temperature range from 500 °C through 1000 °C. Although the 9115A furnace can be used up to 1100 °C, the longevity of the heat pipe may be shortened if used above 1000 °C for an extended period of time.

The Model 9116A furnace (Figure 5) has a higher temperature range and is designed for extended use above 1000 °C, or more specifically, the freezing point of copper (1084.62 °C).

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 placed into the cell containment vessel before insertion into any furnace. The ideal configuration is to keep the cell in its own unique vessel. The cell containment vessel (basket) for the Model 9114 furnace is shown in Figure 6. The 9115A and 9116A furnaces use a fused silica glass (quartz) cell basket to support and enclose the freezing point cell. A minimum of 50 mm (2 in) fiber ceramic insulation is placed in the bottom of the cell basket to protect the cell.

Maintaining the Cell with Argon

It is recommended to maintain the cell in argon which will increase the life span of the cell. To maintain the cell with argon:

1. Connect the cell to a pumping and filling system.
2. Check all of the connections to make sure they are in good condition.
3. Check the seven screws on the cap to see if they are tight enough and tighten a little, if necessary.
4. Start pumping by using a mechanical vacuum pump. When the pressure reaches approximately $1e^{-2}$ Torr, open the vacuum valve slowly. If the pressure reaches approximately $1e^{-2}$ Torr again (it might take about 30 minutes), it indicates that all the connections and seals are in good condition. If not, check all connections and sealing one-by-one.
5. Pump the cell using a diffusion pump or molecular pump for at least 4 hours. Rinse the cell with 99.999 % pure argon three or four times and fill the cell with pure argon to a pressure that is slight higher than local atmosphere pressure.
6. Close all valves.

Vertical Temperature Gradient Adjustment

The vertical temperature gradient has to meet the requirement before the sample is to be melted. Otherwise, the cell may be broken. Therefore, the vertical temperature gradient should always be measured after the cell is installed and checked at least every six months. The 9114 furnace is a three-zone furnace whose gradient can be adjusted through the top and bottom zone heaters. The 9115A/9116A furnaces incorporate sodium heat pipes that distribute heat sufficient and uniform enough that temperature a gradient adjustment is not required.

Vertical temperature gradient test method (9114 only):

1. Set the furnace temperature 5 °C below the melting point of the sample. For example, the melting point temperature of Zinc is 419.527 °C; the furnace temperature should be set to 414.5 °C. After the display temperature reaches the set point temperature, allow the furnace and cell to stabilize for 4-hours before proceeding.
2. Starting with the SPRT fully immersed at the bottom of the cell, record temperature measurements along the vertical axis of the cell in increments of 50 mm, up to 180 mm from the bottom of the cell. Allow a stabilization time of 2-minutes at each point before recording a measurement.

The vertical temperature requirements are listed in Table 6. If the furnace does not meet the requirement, the vertical temperature gradient should be adjusted through the top and bottom

heater, see the sections named “End Zone Controllers” and “Nulling the Zone Controllers” in the 9114 Users Guide.

For installation of the 592X fixed point cells, you must combine the process of vertical temperature gradient measurement and the process of pressure adjustment in the cell (see “Maintaining the Cell with Argon” in this manual).

Controller Display Accuracy Adjustment

The Controller Display does not have to be verified for accuracy when maintaining a cell with an external temperature display instead of the Controller Display. If you are not using an external temperature display, there are instances where display accuracy is important and needs to be verified for accuracy. Those instances are:

- The controller accuracy should be checked to know the offset using a calibrated SPRT (for 9114 and 9115) or a thermocouple (for 9116). The offset should be considered or corrected during the realization of fixed points.
- The controller accuracy should be corrected after the vertical temperature gradient is adjusted. The accuracy can change after temperature gradient is adjusted.
- The controller accuracy should be checked after the sample fully melted in every realization of fixed point. Please refer to the 9114/9115/9116 Furnace Users Manual for the accuracy adjustment method.

To check the accuracy of the Controller Display, A calibrated SPRT or thermocouple should be used. Thermocouple accuracy is not sufficient for the realization of the copper cell.

Use the this procedure to get the realization of the copper cell:

1. Raise the furnace to a temperature of 5 °C to 6 °C above the melting point with a ramp of 0.5 °C/min. Record the emf E(Cu) of the thermocouple during the melting plateau.
2. After the copper is melted, decrease the furnace to 2 °C above the freezing point. Maintain the furnace at this temperature for at least 4 hours or longer.
3. Check the accuracy of the furnace at the set temperature. When the temperature stabilizes at this temperature, record the emf E1. The actual temperature t can be calculated using the following equation:

   $t = 1084.62\ °C + (E1 - E(Cu)) / dE/dt$

   dE/dt is 13.6 µV/°C for a Type R thermocouple, and 11.8 µV/°C for a Type S thermocouple.
4. Compare the calculated actual temperature and the furnace set temperature.

   Example: The furnace set temperature is 1085.6 °C and the calculated actual temperature is 1086.0 °C, the correction is 0.4 °C. Fluke recommends that this be performed each time.

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

⚠Warning

Due to different vapor pressure at the freezing points, the pumping and filling procedures are different for different fixed-points.

This is the recommended procedure to realize the freezing point of 592X fixed point cells. Other procedures are sometimes employed in industry. These procedures provide 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 mK to ±0.3 mK. A typical freezing curve is shown in Figure 8.

Realization of the Freezing Point of In

1. Connect a mechanical vacuum pump and start pumping. When the pressure reaches approximately $1e^{-2}$ Torr, open the vacuum valve slowly. If the pressure reaches approximately $1e^{-2}$ Torr, again (it might take about 30 minutes), it indicates that all the connections and seals are in good condition. If not, check all connections and sealing one-by-one.
2. Turn-on the high vacuum system (diffusion pump or molecular pump), and open high vacuum valve to pump cell. The vacuum should be at $1e^{-5}$ Torr or lower.
3. Insert an SPRT into the reentrant well of the cell to monitor the temperature of the cell.
4. Make sure the vertical temperature gradient of the furnace with the cell is good enough. The furnace vertical temperature gradient should be checked and adjusted if necessary at first operation and therefore every 6 months, refer to the 9114 Users Manual.
5. Turn-on the power to the furnace, and raise the temperature to 162 °C with a rate of 3 °C/min, while pumping continually. During this period, rinse the cell with pure argon (99.999 %) two or three times.
6. As soon as the indium is melted, change furnace temperature down to 2 °C higher than freezing point temperature of indium (158.6 °C). Rinse the cell with pure argon (99.999 %) two or three times. Fill the argon to the cell. Adjust the pressure close to the standard atmosphere and record the actual pressure in order to make the correction for the pressure differences as shown in the section “The Correction for Pressure Difference”.
7. Stabilize the temperature for two hours.
8. Set the furnace temperature to 3 °C below the freezing point temperature (153.6 °C) decreasing at a rate of 0.1 °C/min.
9. When recalescence is observed, remove the SPRT. Insert a room temperature quartz rod for 1 minute or quartz tube for 2 minutes (creates “double freeze”).
10. Set the furnace to 1 °C below the freezing point temperature (155.6 °C)
11. The first SPRT (check SPRT) to be calibrated is inserted into reentrant well and measurements are made after the cell and SPRT are in the equilibrium. The first SPRT is at room temperature at the time of insertion. The furnace temperature is kept at a stable temperature of 1°C below the freezing point.
12. After all SPRTs are measured, set the furnace temperature at 20 °C with a rate of 2 °C/min.
13. The cell should be pumped for 10 minutes in the second day. At that time, the furnace temperature should close to room temperature. Fill pure argon to a pressure that is slightly higher than local atmosphere pressure.
14. Close all valves and turn-off the furnace.

Realization of the Freezing Point of Sn

1. Connect a mechanical vacuum pump and start pumping. When the pressure reaches approximately $1e^{-2}$ Torr, open the vacuum valve slowly. If the pressure reaches approximately $1e^{-2}$ Torr again (it might take about 30 minutes), it indicates that all the connections and seals are in good condition. If not, check all connections and sealing one-by-one.
2. Turn-on the high vacuum system (diffusion pump or molecular pump), and open the high vacuum valve to pump cell. The vacuum should decrease to $1e^{-5}$ Torr or lower.
3. Insert an SPRT into the reentrant well of the cell to monitor the temperature of the cell.
4. Make sure the vertical temperature gradient of the furnace with the cell is good enough. The furnace vertical temperature gradient should be checked and adjusted if necessary at first operation and every 6 months after, refer to the 9114 manual.
5. Turn-on the power to the furnace, and raise the temperature to 238 °C with a rate of 3 °C/min, while pumping continually. During this period, rinse the cell with pure argon (99.999 %) two or three times.
6. As soon as the tin is melted, decrease the furnace temperature to 2 °C higher than freezing point temperature of tin (233 °C). Rinse the cell with pure argon (99.999 %) two or three times. Fill the cell with argon. Adjust the pressure close to the standard atmosphere and record the actual pressure in order to make the correction for the pressure differences as shown in Chapter 7.
7. Stabilize the temperature for two hours.
8. Set the furnace temperature to 3 °C below freezing point temperature (228 °C) with a decrease rate of 0.1 °C/min.
9. 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 CFM to 0.7 CFM) and roughly 200 kPa (29 psia).
10. When recalescence is observed, turn-off the cold gas flow. Remove the SPRT and insert two room temperature quartz rods one-by-one for 2 minutes each (creates “double freeze”).
11. Set the furnace to 1 °C below freezing point temperature (230.9 °C)
12. The first SPRT (check SPRT) to be calibrated is inserted into reentrant well and measurements are made after the cell and SPRT are in the equilibrium. The first SPRT is at room temperature at the time of insertion. The furnace temperature is kept at a stable temperature of 1 °C below the freezing point.
13. After all SPRTs are measured, set the furnace temperature at 20 °C with a rate of 2 °C/min.
14. The cell should be pumped for 10 minutes in the second day. At that time, the furnace temperature should close to room temperature. Fill the cell with pure argon to a pressure that is slightly higher than local atmosphere pressure.
15. Close all valves and turn-off the furnace.

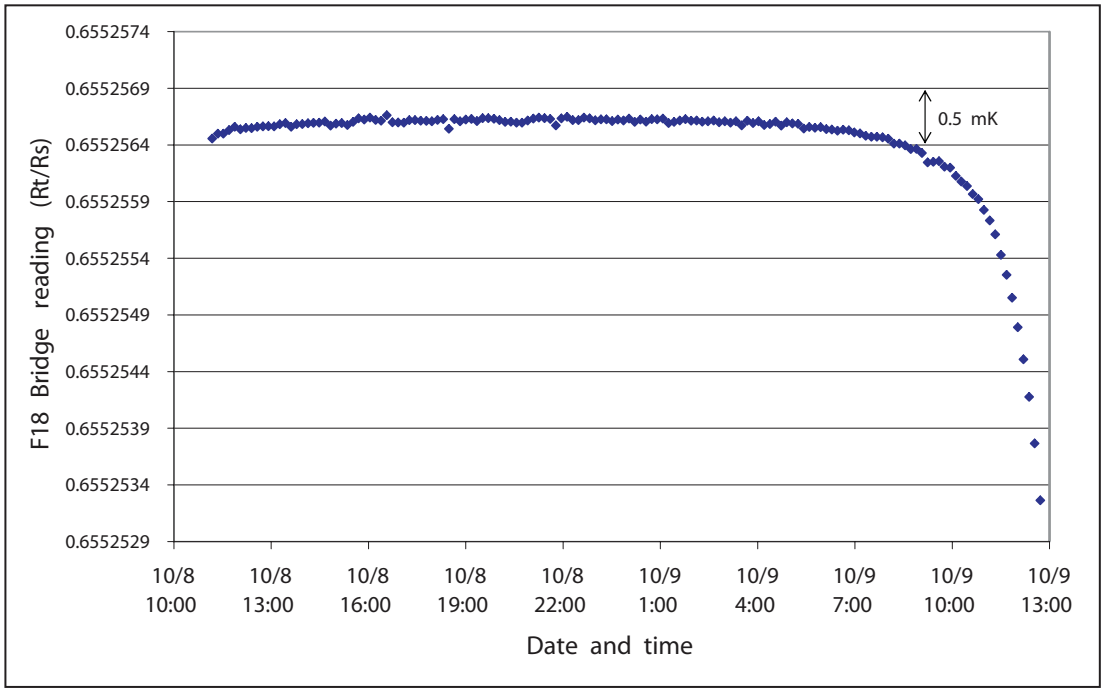
Realization of the Freezing Point of Zn

1. Connect a mechanical vacuum pump and start pumping. When the pressure reaches approximately $1e^{-2}$ Torr, open the vacuum valve slowly. If the pressure reaches approximately $1e^{-2}$ Torr again (it might take about 30 minutes), it indicates that all the connections and seals are in good condition. If not, check all connections and sealing one-by-one.
2. Turn-on the high vacuum system (diffusion pump or molecular pump), and open the high vacuum valve to pump cell. The vacuum pressure should decrease to $1e^{-5}$ Torr or lower.
3. Insert an SPRT into the reentrant well of the cell and monitor the temperature of the cell.
4. Make sure the vertical temperature gradient of the furnace with the cell meets the criteria described in Table 6. The furnace vertical temperature gradient should be checked and adjusted if necessary at first operation and every 6 months after, refer to the 9114 Users Manual.
5. Turn-on the power to the furnace, and increase the temperature to 250 °C with a rate of 3 °C/min, while pumping continually.
6. The furnace should be maintained at 250 °C for 2 hours, while pumping continually.
7. Rinse the cell with pure argon (99.999 %) two or three times. Fill the cell with argon to a pressure of 80 kPa.
8. Increase the furnace temperature to 425 °C with a rate of 3 °C.

⚠Warning

DO NOT pump the cell for more than 10 seconds.

9. As soon as the temperature of the monitor SPRT reach 419.527 °C (melting point), pump the cell for 10 seconds using a mechanical pump. Fill the cell with pure argon. Adjust the pressure close to the standard atmosphere and record the actual pressure in order to make the correction for the pressure differences as shown in the section “The Correction for Pressure Difference”.
10. As soon as the zinc is melted, decrease the furnace temperature to 2 °C higher than the freezing point temperature of zinc (421.5 °C).
11. Stabilize the temperature for two hours.
12. Set furnace temperature 2 °C below freezing point temperature (417.5 °C) with a decrease rate of 0.1 °C/min.
13. When recalescence is observed, remove the SPRT and insert a quartz rod at room temperature for 1 minute or quartz tube for 2 minutes (creates “double freeze”).
14. Set the furnace 1 °C below freezing point temperature (418.5 °C).
15. Insert the first SPRT (check SPRT) to be calibrated into the reentrant well measure after the cell and SPRT are in equilibrium. The first SPRT is at room temperature at the time of insertion. Keep the furnace temperature at a stable temperature of 1 °C below the freezing point.
16. After all SPRTs are measured, set the furnace temperature at 20 °C with a rate of 2 °C/min.
17. Pump the cell for 10 minutes in the second day. At that time, the furnace temperature should close to room temperature. Fill the cell with pure argon to a pressure that is slightly higher than local atmosphere pressure.
18. Close all valves and turn-off the furnace.



gpt009.eps

Figure 8. A Typical Freezing Curve for the Zinc Cell

Realization of the Freezing Point of Al

1. Connect a mechanical vacuum pump and start pumping. When the pressure reaches approximately $1e^{-2}$ Torr, open the vacuum valve slowly. If the pressure reaches approximately $1e^{-2}$ Torr again (it might take about 30 minutes), it indicates that all the connections and seals are in good condition. If not, check all connections and sealing one-by-one.
2. Turn-on the high vacuum system (diffusion pump or molecular pump), and open high vacuum valve to pump cell. The vacuum should be at $1e^{-5}$ Torr or lower.
3. Insert an SPRT into the reentrant well of the cell and monitor the temperature of the cell.
4. Make sure the vertical temperature gradient of the furnace with the cell meets the criteria described in Table 6. The furnace vertical temperature gradient should be checked and adjusted if necessary at first operation and every 6 months after, refer to the 9114 Users Manual.
5. Turn-on the power to the furnace, and increase the temperature to 600 °C with a rate of 3 °C/min, while pumping continually.
6. The furnace should be maintained at 600 °C for 2 hours, while pumping continually.
7. Rinse the cell with pure argon (99.999 %) two or three times. Fill the cell with argon to a pressure of 94 kPa.
8. Increase the furnace temperature to 665.5 °C with a rate of 3 °C.

⚠ Warning

DO NOT pump the cell for more than 10 seconds.

9. As soon as the temperature of the monitor SPRT reach 660.323 °C (melting point), pump the cell for 10 seconds using mechanical pump. Fill the cell with pure argon. Adjust the pressure close to the standard atmosphere and record the actual pressure in order to make the correction for the pressure differences as shown in the section “The Correction for Pressure Difference.”
10. As soon as the aluminum is melted, decrease the furnace temperature to 2 °C higher than freezing point temperature of aluminum (662.5 °C).
11. Let the temperature to stabilize for two hours.

12. Set the furnace temperature to 2 °C below freezing point temperature (658 °C) with a decrease rate of 0.1 °C/min.
13. When recalescence is observed, remove the SPRT and insert a quartz rod at room temperature for 1 minute or quartz tube for 2 minutes (creates "double freeze").
14. Set the furnace to 1 °C below freezing point temperature (659.4 °C)
15. Insert the first SPRT (check SPRT) to be calibrated into the reentrant well measure after the cell and SPRT are in equilibrium. The first SPRT is at room temperature at the time of insertion. Keep the furnace temperature at a stable temperature of 1 °C below the freezing point.
16. After all SPRTs are measured, set the furnace temperature at 20 °C with a rate of 2 °C/min.
17. Pump the cell for 10 minutes in the second day. At that time, the furnace temperature should close to room temperature. Fill the cell with pure argon to a pressure that is slightly higher than local atmosphere pressure.
18. Close all valves and turn-off the furnace.

Realization of the Freezing Point of Ag

Note

Since the silver cell is maintained in either the 9115A or 9116A, which incorporate a sodium heat pipe, adjustment for vertical temperature gradient is not necessary.

1. Connect a mechanical vacuum pump and start pumping. When the pressure reaches approximately $1e^{-2}$ Torr, open the vacuum valve slowly. If the pressure reaches approximately $1e^{-2}$ Torr again (it might take about 30 minutes), it indicates that all the connections and seals are in good condition. If not, check all connections and sealing one-by-one.
2. Turn-on the high vacuum system (diffusion pump or molecular pump), and open high vacuum valve to pump cell. The vacuum should be at $1e^{-5}$ Torr or lower.
3. Turn-on the power to the furnace, and increase the temperature to 800 °C with a rate of 3 °C/min, while pumping continually.
4. The furnace should be maintained at 800 °C for 2 hours, while pumping continually.
5. Rinse the cell with pure argon (99.999 %) two or three times. Fill the cell with argon to a pressure of 90 kPa.
6. Increase the furnace temperature to 966 °C with a rate of 3 °C.

⚠ Warning

DO NOT pump the cell for more than 10 seconds.

7. As soon as the temperature of the monitor SPRT reach 961.78 °C (melting point), pump the cell for 10 seconds using a mechanical pump. Fill the cell with pure argon. Adjust the pressure close to the standard atmosphere and record the actual pressure in order to make the correction for the pressure differences as shown in the section "The Correction for Pressure Difference."
8. As soon as the silver is melted, decrease the furnace temperature to 2 °C higher than the freezing point temperature of silver (963.8 °C).
9. Let the temperature to stabilize for two hours.
10. Set the furnace temperature to 2 °C below freezing point temperature (959.8 °C) with a decrease rate of 0.1 °C/min.
11. When recalescence is observed, remove the SPRT and insert a quartz rod at room temperature for 1 minute or quartz tube for 2 minutes (creates "double freeze").
12. Set the furnace to 1 °C below freezing point temperature (960.8 °C)
13. Insert the first SPRT (check SPRT) to be calibrated into the reentrant well measure after the cell and SPRT are in equilibrium. The first SPRT is at room temperature at the time of insertion. Keep the furnace temperature at a stable temperature of 1 °C below the freezing point.

14. After all SPRTs are measured, set the furnace temperature at 20 °C with a rate of 2 °C/min.
15. Pump the cell for 10 minutes in the second day. At that time, the furnace temperature should close to room temperature. Fill pure argon to a pressure that is slightly higher than local atmosphere pressure. Close all valves. Turn the furnace power off.

Realization of the Freezing Point of Cu

Note

Since the copper cell is maintained in the 9116A, which incorporates a sodium heat pipe, adjustment for vertical temperature gradient is not necessary.

1. Connect a mechanical vacuum pump and start pumping. When the pressure reaches approximately $1e^{-2}$ Torr, open the vacuum valve slowly. If the pressure reaches approximately $1e^{-2}$ Torr again (it might take about 30 minutes), it indicates that all the connections and seals are in good condition. If not, check all connections and sealing one-by-one.
2. Turn-on the high vacuum system (diffusion pump or molecular pump), and open the high vacuum valve to pump cell. The vacuum should down to $1e^{-5}$ Torr or lower.
3. Turn-on the power to the furnace, and increase the temperature to 850 °C with a rate of 3 °C/min, while pumping continually.
4. The furnace should be maintained at 850 °C for 2 hours, while pumping continually.
5. Rinse the cell with pure argon (99.999 %) two or three times. Fill the cell with argon to a pressure of 84 kPa.
6. Increase the temperature of the furnace to 1091 °C with ramp rates as the follows: =3 °C/min below 1000 °C, =2 °C/min below 1070 °C, and =1 °C/min below 1091 °C.

⚠ Warning

DO NOT pump the cell for more than 10 seconds.

7. As soon as the temperature of the monitor TC reach 1084.62 °C (melting point), pump the cell for 10 seconds using a mechanical pump. Fill the cell with pure argon. Adjust the pressure close to the standard atmosphere and record the actual pressure in order to make the correction for the pressure differences as shown in the section “The Correction for Pressure Difference.”
8. As soon as the copper is melted, decrease the furnace temperature down to 2 °C higher than freezing point temperature of copper (1086.6 °C).
9. Let the temperature to stabilize for two hours.
10. Set furnace temperature 2 °C below freezing point temperature (1082.6 °C) with a decrease rate of 0.1 °C/min.
11. When recalescence is observed, remove the TC and insert a quartz rod at room temperature for 1 minute or quartz tube for 2 minutes (creates “double freeze”).
12. Set the furnace to 1 °C below freezing point temperature (1083.6 °C)
13. Insert the first TC to be calibrated into the reentrant well measure after the cell and SPRT are in equilibrium. The first TC is at room temperature at the time of insertion. Keep the furnace temperature at a stable temperature of 1 °C below the freezing point.
14. After all thermocouples are measured, set the furnace temperature at 20 °C with a rate of 2 °C/min.
15. Pump the cell for 10 minutes in the second day. At that time, the furnace temperature should close to room temperature. Fill pure argon to a pressure that is slightly higher than local atmosphere pressure. Close all valves. Turn the furnace power off.

SPRT Care At High Temperatures

Each SPRT calibrated at temperatures above 500 °C is subjected to "quenched in lattice vacancy defect" when the SPRT is removed from the furnace. This quenched in lattice vacancy defect must be removed before calibration at the triple point of water. Therefore, when the SPRT is removed from the cell, place SPRT 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.

The Correction for the Pressure Difference

This is the procedure used in the Fluke lab with the Fluke Sealed Fixed-point Cells. Other procedures are sometimes employed in industry.

With few exceptions, the temperature values assigned to the defining ITS-90 fixed-points correspond to temperatures at standard atmospheric pressure (101.325 kPa). The actual pressure in a cell may not be the standard value. For example, it is more practical during the manufacturing process to seal the cell while cell pressure is slightly lower than ambient pressure. The actual pressure in the cell at the fixed-point temperature is provided on the Report of Test, making the correction calculation for the pressure difference possible.

A metal fixed-point cell will exhibit a temperature gradient relative to immersion depth due to the hydrostatic pressure of the metal. Corrections for hydrostatic pressure can be applied using the ITS-90 pressure coefficients listed in Table 7.

Table 7. Hydrostatic Head Correction Coefficients

Substance	Assigned Value of Equilibrium Temperature T Kelvin (K)	Temperature with Pressure, p K1; dT/dp (10^{-5} mK/Pa)	Variation with Depth K2 : dT/dh (mK/m)	Approximate dW/dt
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
rin0Indium (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	—
(T) – Triple Point (M) – Melting Point (F) – Freezing Point				

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

Equation 1: 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 at the fixed point temperature

P_0 = the standard atmospheric pressure. For example, 101.325 kPa

$$k_1 = \frac{dT}{dP}$$

$k_2 = \frac{dT}{dh}$

and

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

The immersion depth of the midpoint of a SPRT sensor in Fluke metal freezing point cell is approximately 0.18 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. k_1 and k_2 for the freezing point of aluminum can be found in Table 5, k1 = 7.0 * 10^{-5} mK / Pa and k2 = 1.6 mK/m. The average immersion depth is 0.17 m for most of the standard platinum resistance thermometers. Thus, use Equation 1 to calculate Δt.

Substituting values into Equation 1:

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

Consequently:

$\Delta t = -1.164\ mK$

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

$t_1 = t + \Delta t$

Thus:

t_1 = 660.323 °C − 0.001164 °C = 660.32183 °C

Where t is the defining fixed point temperature. For example, 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) x (3.204971×10^{-3})

Thus the W_{Al} for the cell is:

W_{Al} = 3.37601233