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Guidelines for Realizing the International Temperature Scale of 1990 (ITS-90)

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Table of Contents

	page
List of Tables	ix
List of Figures	x
Abstract	xiii
Scope	xiii
1. Introduction	1
2. Definition of the ITS-90	3
2.1 Between 0.65 K and 5.0 K, ³ He and ⁴ He vapor-pressure thermometry	6
2.2 Between 3.0 K and 24.5561 K (the triple point of Ne), ³ He and ⁴ He constant volume gas thermometry	10
2.3 Between 13.8033 K (the triple point of equilibrium hydrogen) and 1234.93 K (the freezing point of silver), platinum resistance thermometry	11
2.3.1 General relation between resistance ratios and T_{90}	11
2.3.2 SPRT specifications	12
2.3.3 Range 13.8033 K to 273.16 K	14
2.3.3.1 Subrange 24.5561 K to 273.16 K	16
2.3.3.2 Subrange 54.3584 K to 273.16 K	16
2.3.3.3 Subrange 83.8058 K to 273.16 K	16
2.3.4 Range 273.15 K (0 °C) to 1234.93 K (961.78 °C)	17
2.3.4.1 Subrange 273.15 K (0 °C) to 933.473 K (660.323 °C, freezing point of aluminum)	18
2.3.4.2 Subrange 273.15 K (0 °C) to 692.677 K (419.527 °C, freezing point of zinc)	18
2.3.4.3 Subrange 273.15 K (0 °C) to 505.078 K (231.928 °C, freezing point of tin)	18
2.3.4.4 Subrange 273.15 K (0 °C) to 429.7485 K (156.5985 °C, freezing point of indium)	18
2.3.4.5 Subrange 273.15 K (0 °C) to 302.9146 K (29.7646 °C, melting point of gallium)	19
2.3.5 Subrange 234.3156 K (-38.8344 °C, triple point of mercury) to 302.9146 K (29.7646 °C, the melting point of gallium)	19
2.4 Above 1234.93 K (961.78 °C, freezing point of silver); radiation thermometry based on Planck's Law of Radiation	19
3. Realization of the ITS-90	20
3.1 Vapor pressure thermometry and gas thermometry	20
3.1.1 Realization of the ITS-90 below 273.16 K	20
3.1.2 Vapor pressure thermometry and the CVGT range	20
3.1.3 Realization of the vapor-pressure and CVGT scales at temperatures below the neon triple point	22
3.1.3.1 ³ He vapor pressure measurements	23
3.1.3.2 ⁴ He vapor pressure measurements	24

Table of Contents (continued)

	page
3.1.3.3	e-H ₂ vapor pressure measurements 24
3.1.3.4	Constant volume gas thermometry 24
3.1.3.5	Pressure measurements 26
3.2	Realization of the fixed points of the ITS-90 28
3.2.1	Effect of impurities 28
3.2.2	Triple points of e-H ₂ , Ne, O ₂ , and Ar 29
3.2.2.1	General consideration of apparatus design 29
3.2.2.2	Realizations of the triple points and their application to calibration 33
3.2.3	Triple point of water, 273.16 K (0.01 °C) 36
3.2.3.1	Realization and application of the triple point of water 37
3.2.4	Freezing, melting, or triple points of metals: Hg, Ga, In, Sn, Zn, Al, Ag, Au, or Cu 39
3.2.4.1	Container material 42
3.2.4.2	Metal fixed point devices for calibrating SPRTs 42
3.2.5	Control charts of check thermometers 59
3.3	Radiation thermometry 60
4.	Calibration of thermometers on the ITS-90 at various levels of uncertainty and some approximations of the scale 61
4.1	Rhodium-iron resistance thermometers 63
4.2	Germanium resistance thermometers 64
4.3	Standard platinum resistance thermometers 64
4.3.1	Capsule SPRTs [13.8033 K to 429.7485 K or 505.078 K] 64
4.3.2	Long-stem type SPRTs (83.8058 K to 1234.93 K) 64
4.3.3	Conversion of the IPTS-68 constants and $W(T_{68})$ tables to approximate ITS-90 constants and $W(T_{90})$ tables 65
4.3.4	Uncertainties of calibrations and their propagation 69
4.3.5	Estimates of possible errors introduced by extrapolations beyond the range of calibration 70
4.4	Thermocouples (77 K to 2400 K) 78
4.5	Liquid-in-glass thermometers 78
4.6	Industrial platinum resistance thermometers 78
4.7	Thermistor thermometers, digital thermometers, and other types of thermometers 79
4.8	The logo of the National Conference of Standards Laboratories for the ITS-90 80
5	References 82

Table of Contents (continued)

	page
6. Appendices	90
6.1 Copies of, or excerpts from, some papers related to the work of the international bodies concerned with the ITS-90	90
6.1.1 Reproduction of the article by H. Preston-Thomas, entitled, "The International Temperature Scale of 1990," published in <i>Metrologia</i> 27, 3-10 (1990), with corrections	90
6.1.2 Reproduction of the article by T. J. Quinn, entitled "News from the BIPM", published in <i>Metrologia</i> 26, 69-74 (1989)	99
6.1.3 Recommendations adopted by the CCT at its 17th Session	106
6.1.3.1 Recommendation T1 (1989), The International Temperature Scale of 1990	106
6.1.3.2 Recommendation T2 (1989), Reference tables for thermocouples and industrial platinum resistance thermometers	107
6.1.3.3 Recommendation T3 (1989), The uncertainty inherent in the realization of the International Temperature Scale of 1990	107
6.1.4 Reproduction of article by B. W. Mangum, entitled "Special Report on the International Temperature Scale of 1990; Report on the 17th Session of the Consultative Committee on Thermometry," published in <i>J. Res. Natl. Inst. Stand. Technol.</i> 95, 69-77 (1990)	108
6.2 Excerpts from proceedings of some meetings of the CIPM and of the CGPM that are related to the designation of the size of the kelvin and to the ITS-90	118
6.2.1 Recommendation of the CIPM that the numerical value of 273.16 °K, exactly, be assigned to the triple point of water on the thermodynamic scale, excerpted from <i>Procès-Verbaux des Séances, Deuxième Series, Tome XXIV, Session de 1954 du Comité International des Poids et Mesures</i> , published by Gauthier Villars, Editeur-Imprimeur-Libraire, Paris, 1955	118
6.2.2 Definition of the thermodynamic scale of temperature. This entails the assignment of the value 273.16 °K, exactly, to the triple point of water as a fundamental fixed point, excerpted from <i>Comptes Rendus des Séances, Dixième Conférence Générale des Poids et Mesures, Reunie à Paris en 1954</i> , published by Gauthier Villars, Editeur-Imprimeur-Libraire, Editeur du Bureau International des Poids et Mesures, Paris, 1955	118

Table of Contents (continued)

	page	
6.2.3	Recommendations of the CCT, concerning the development of the ITS-90 and simplified methods of its realization, that were presented to the CIPM on 9 July 1987, excerpted from Procès-Verbaux des Sèances du Comité International des Poids et Mesures, Procès-Verbaux de la 76 ^e session - 1987, Tome 55, Édité par le BIPM, Pavillon de Breteuil, F-92312 Sèvres Cedex, France	119
6.2.4	The resolution, instructing the CIPM to develop the ITS-90, adopted by the 18th CGPM in 1987, and excerpted from Comptes Rendus, 18 ^e Conférence Générale des Poids et Mesures (1987), Édité par le BIPM, Pavillon de Breteuil, F-92312 Sèvres Cedex, France	121
6.3	Examples of some typical Report of Calibration documents from the NIST Calibration Laboratories for thermometers calibrated over various ranges	122
6.3.1	Example of a Report of Calibration for an SPRT calibrated over the range from 13.8033 K to 302.9146 K	122
6.3.2	Example of a Report of Calibration for an SPRT calibrated over the range from 83.8058 K to 933.473 K	126
6.3.3	Example of a Report of Calibration for an SPRT calibrated over the range from 273.15 K to 1234.93 K	129
6.3.4	Example of a Report giving the T_{68} to T_{90} conversion for a long-stem type SPRT calibrated on the IPTS-68(75) from the oxygen condensation point to the freezing point of zinc	132
6.3.5	Example of a Report giving the T_{68} to T_{90} conversion for a capsule-type SPRT calibrated on the IPTS-68(75) from the triple point of equilibrium hydrogen to the freezing point of tin	135
6.3.6	Example of a Report of Calibration for an RIRT calibrated over the range from 0.50 K to 30 K on the EPT-76	138
6.3.7	Example of a Report of Calibration for an RIRT (the RIRT of sec. 6.3.6) calibrated over the range from 0.65 K to 25 K on the ITS-90	147
6.3.8	Example of a Report of Calibration for a thermocouple calibrated over the range from 0 °C to 1450 °C	154
6.3.9	Example of a Report of Calibration for a liquid-in-glass thermometer calibrated over the range from 0 °C to 100 °C on the IPTS-68(75)	162

Table of Contents (continued)

	page
6.3.10 Example of a Report of Calibration for the liquid-in-glass thermometer of section 6.3.9 calibrated over the range from 0 °C to 100 °C on the IPTS-68(75) but converted to the ITS-90	164
6.4 The National Conference of Standard Laboratories (NCSL) Ad Hoc Committee (91.3) on the Change in the International Temperature Scale that was formed to publicize the ITS-90 and its implementation and to minimize the confusion and inconvenience of the change from the IPTS-68(75)	166
7. NIST Calibration Services, Thermometers	167
7.1 Laboratory Thermometers	167
7.2 Thermocouples, Thermocouple Materials, and Pyrometer Indicators	169
7.3 Resistance Thermometers	173

List of Tables

	page
Table 1. Differences between T_{90} and T_{68} (and t_{90} and t_{68}), and between T_{90} and T_{76}	5
Table 2. Defining fixed points of the ITS-90	8
Table 3. Comparison of temperatures of fixed points assigned on various scales.	9
Table 4. Values of the coefficients A_i and of the constants B and C for the ^3He and ^4He vapor pressure equations and the temperature range for which each equation is valid	10
Table 5. Values of the coefficients A_i , B_i , C_i and D_i and of the constants A_0 , B_0 , C_0 , and D_0 in the reference functions, equations (14) and (22), and in the functions approximating them, given by equations (15) and (23)	15
Table 6. The effect of pressure on the temperatures of the defining fixed points. The reference pressure for the equilibrium states of freezing and melting points is one standard atmosphere (101,325 Pa). Triple points have the vapor pressure of the material when the solid, liquid and vapor phases are present in equilibrium	25
Table 7. Latent heats of fusion and first cryoscopic constants of defining fixed-point materials	29
Table 8. Example of conversion of calibrations of SPRTs on the IPTS-68 to approximate calibrations on the ITS-90	66
Table 9. Values of $W(T_{68})$ and $W(T_{90})$ for various fixed-point temperatures T_{68} and T_{90} , respectively	67
Table 10. Example of a conversion of calibration values of a type K thermocouple on the IPTS-68 to an approximate calibration on the ITS-90	79

List of Figures

	Page
Figure 1. The temperature difference ($t_{90} - t_{68}$)/°C in the range between the triple point of equilibrium hydrogen (-259.3467 °C) and the freezing point of gold (1337.33 °C)	4
Figure 2. A schematic representation of the ITS-90 showing the temperatures of the defining fixed points (or phase equilibrium states) on the scale and temperature ranges defined by interpolation instruments and equations ...	7
Figure 3. A schematic representation of the ITS-90 in the range specified for the platinum resistance thermometer, showing the various defined subranges and the temperatures of the defining fixed points on the scale required for calibration	13
Figure 4. A schematic drawing of the NIST argon triple-point apparatus for calibrating seven long-stem SPRTs and six capsule SPRTs	30
Figure 5. A sealed cell suitable for containing cryogenic gases at high pressures	31
Figure 6. Two types of triple point of water cells with wells for platinum resistance thermometers	35
Figure 7. An SPRT in a Type A triple point of water cell immersed in an ice bath	38
Figure 8. Idealized liquid/solid equilibrium conditions inside fixed point cells used in freezing and melting experiments	40
Figure 9. An SPRT in a metal freezing-point cell	41
Figure 10. Two mercury triple-point cells, one constructed of borosilicate glass and one of Type 304 stainless steel	43
Figure 11. A borosilicate glass, mercury triple-point cell in a stainless steel container	45
Figure 12. Photograph of an all-plastic indium cell and its stainless steel container	46
Figure 13. An all-plastic gallium melting/triple-point cell	48

List of Figures (continued)

	Page
Figure 14. An all-plastic indium freezing-point cell to be used in a stainless steel container, such as that shown in figure 12	50
Figure 15. A graphite freezing point cell enclosed inside a fused silica tube with tube connection to high vacuum, purified argon gas source, and pressure gauge	53
Figure 16. A method for filling a graphite freezing-point cell by melting the metal sample in the graphite crucible	55
Figure 17. An apparatus for installing a graphite thermometer well and lid in a graphite crucible containing a molten metal sample	56
Figure 18. Differences between T_{90} and $(T_{90})_{as}$ calculated from IPTS-68 calibration for the long-stem SPRT, S/N RS8YA-5, of table 8	68
Figure 19. Propagation of errors from errors of calibration of SPRTs between 13.8033 K and 273.16 K	71
Figure 20. Propagation of errors from errors of calibration of SPRTs between 273.15 K and 1234.93 K. Also included in this figure are error curves for errors made by the user at the triple point of water	72
Figure 21. Curve for a NIST SPRT that shows the error introduced by extrapolating the deviation function, determined from calibration over the range from the triple point of argon to the triple point of water, downward from the triple point of argon to 54 K	73
Figure 22. Curve for a NIST SPRT that shows the error introduced by extrapolating its deviation function, determined from calibration over the range from the triple point of mercury to the melting point of gallium, downward from the triple point of mercury to 84 K	74
Figure 23. Curve for the NIST SPRT of figure 22 that shows the error introduced by extrapolating its deviation function, determined from calibration over the range from the triple point of mercury to the melting point of gallium, downward from the triple point of mercury to only 200 K	75

List of Figures (continued)

	Page
Figure 24. Curves for several NIST SPRTs that show the errors introduced by extrapolating their deviation functions, determined from calibration over the range from the triple point of water to the freezing point of zinc, downward from the triple point of water to -50 °C	76
Figure 25. Curves for several NIST SPRTs that show the errors introduced by extrapolating their deviation functions, determined from calibration over the range from the triple point of water to the freezing point of zinc, upward from the freezing point of zinc to 934 K (660 °C). Also shown are subrange inconsistencies for the subrange triple point of water to zinc, relative to the subrange triple point of water to aluminum	77
Figure 26. The NCSL ITS-90 logo	81

ABSTRACT

This Technical Note describes the International Temperature Scale of 1990 (ITS-90) that became the official international temperature scale on 1 January 1990, superseding the previous scales, and provides information on how the scale may be realized at different levels of accuracy. The ITS-90 extends upward from 0.65 K, is in close agreement with the Kelvin Thermodynamic Temperature Scale, has much improved continuity, precision and reproducibility throughout its ranges over that of previous scales, and has subranges and alternative definitions in certain ranges that greatly facilitate its use. In addition to a description of the ITS-90 and how it can be realized, there are included in this document reproductions of some articles and excerpts from documents concerned with the ITS-90. The composition of the Comité Consultatif de Thermométrie (CCT) of the Comité International des Poids et Mesures (CIPM) at the time of the adoption of the ITS-90 is given. The differences between the temperatures on the ITS-90 and those on the International Practical Temperature Scale of 1968, Amended Edition of 1975, [IPTS-68(75)] and those on the 1976 Provisional 0.5 K to 30 K Temperature Scale (EPT-76) are tabulated. Measurement procedures for realizing the ITS-90 throughout the various ranges of the scale are given. Also, for the most important temperature region, the region of the platinum resistance thermometer (PRT), computational examples are given for determining the coefficients of the relevant deviation equations for PRTs calibrated at various sets of fixed points. The effects of the introduction of the ITS-90 on electrical reference standards are addressed also.

SCOPE

The ITS-90 and, consequently, the topics discussed in this document affect all aspects of thermometry at temperatures from 0.65 K upward. This change of scale will affect principally those making high precision temperature measurements. Thus, all standards and calibration laboratories will be affected and they should implement the ITS-90 as soon as possible.

If the required minimum uncertainty of measurements over a given range of temperature is at least three times as large as the differences between the new and old scales in that range, as given in table 1 and shown in figure 1 of this document, then the effect of the change in scales will be negligible and the user will, for all practical purposes, be unaffected.

DISCLAIMER

Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

**Guidelines for Realizing the
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1. INTRODUCTION

The Comité Consultatif de Thermométrie (CCT) is one of eight specialized technical subcommittees of the Comité International des Poids et Mesures (CIPM). The CIPM is a committee of the Conférence Générale des Poids et Mesures (CGPM). These eight subcommittees are:

1. The Comité Consultatif d'Électricité (CCE), established in 1927,
2. The Comité Consultatif de Photométrie et Radiométrie (CCPR), assigned this name in 1971; the previous name was the Comité Consultatif de Photométrie, established in 1933,
3. The Comité Consultatif de Thermométrie (CCT), established in 1937,
4. The Comité Consultatif pour la Définition du Mètre (CCDM), established in 1952,
5. The Comité Consultatif pour la Définition de la Seconde (CCDS), established in 1956,
6. The Comité Consultatif pour les Étalons de Mesure des Rayonnements Ionisants (CCEMRI), established in 1958,
7. The Comité Consultatif des Unités (CCU), established in 1964, and
8. The Comité Consultatif pour la Masse et les grandeurs apparentées (CCM), established in 1980.

The CCT is composed presently of members from the following laboratories:

1. Amt für Standardisierung, Messwesen und Warenprüfung [ASMW], Berlin, DDR,
2. Bureau National de Métrologie, Paris, France : Institut National de Métrologie [INM], du Conservatoire National des Arts et Métiers,
3. Ceskoslovensky Metrologicky Ustav [CSMU], Bratislava, Czechoslovakia,
4. National Research Council [NRC], Ottawa, Canada,
5. CSIRO, Division of Applied Physics [CSIRO], Lindfield, Australia,
6. D.I. Mendeleev Institute for Metrology [VNIIM], Leningrad, USSR; Physico-Technical and Radio-Technical Measurements Institute [PRMI], Moscow, USSR,
7. National Institute of Metrology [NIM], Beijing, PRC,
8. Istituto di Metrologia G. Colonnetti [IMGC], Turin, Italy,
9. Kamerlingh Onnes Laboratorium [KOL], Leiden, The Netherlands,
10. Korea Standards Research Institute [KSRI], Seoul, Korea,

11. National Institute of Standards and Technology [NIST], Gaithersburg, MD, USA,
12. National Physical Laboratory [NPL], Teddington, UK,
13. National Research Laboratory of Metrology [NRLM], Ibaraki, Japan,
14. Physikalisch-Technische Bundesanstalt [PTB], Braunschweig, FRG,
15. Van Swinden Laboratorium [VSL], Delft, The Netherlands,
16. Iowa State University, Ames, Iowa, USA, and
17. Bureau International des Poids et Mesures [BIPM], Sèvres, France.

Shortly after the adoption of the International Practical Temperature Scale of 1968 (IPTS-68) [100], it was realized that the scale had many deficiencies and limitations. These included its lower limit of 13.81 K, its inaccuracy relative to thermodynamic temperatures, and its non-uniqueness and irreproducibility, especially in the temperature region from $T_{68} = 903.89$ K (630.74 °C) to $T_{68} = 1337.58$ K (1064.43 °C), the region in which the Pt-10%Rh/Pt thermocouple was the standard interpolating instrument. Consequently, the CCT undertook the development of a new scale, and completed it in accordance with Resolution 7 of the 18th Conférence Générale des Poids et Mesures [29], which met in October 1987 (see appendices).

The CCT met 12-14 September 1989 at the Bureau International des Poids et Mesures (BIPM) in its 17th Session [14] and completed the final details of the new temperature scale, the International Temperature Scale of 1990 (ITS-90) [66,83]. The CCT then recommended to the CIPM, which met [84] on 26-28 September 1989 at the BIPM, that the ITS-90 be adopted and made the official scale (see appendices). Upon considering this recommendation, the CIPM adopted the new temperature scale (see appendices), and the ITS-90 became the official international temperature scale on 1 January 1990, the same date on which changes affecting certain electrical reference standards were implemented [12]. The ITS-90 supersedes the IPTS-68, the International Practical Temperature Scale of 1968, Amended Edition of 1975 [IPTS-68(75)] [101], and the 1976 Provisional 0.5 K to 30 K Temperature Scale (EPT-76) [99].

The ITS-90 was implemented at the NIST on 1 January 1990. The purpose of this document is to describe the new scale, to give some guidelines for its realization and use, to facilitate its implementation, to give the differences between temperatures on it and those on the IPTS-68(75) and on the EPT-76, and to describe how the NIST realizes the scale.

The ITS-90 extends upward from 0.65 K and temperatures on this scale are in much better agreement with thermodynamic values than are those on the IPTS-68(75) and the EPT-76. The new scale has subranges and alternative definitions in certain ranges that greatly facilitate its use. Furthermore, its continuity, non-uniqueness and reproducibility throughout its ranges are much improved over the corresponding characteristics of the previous scales. The biggest improvement in reproducibility results from the replacement of thermocouple thermometry with platinum resistance thermometry in the range 630 °C to the freezing-point temperature of silver, and with radiation thermometry in the range from the freezing-point temperature of silver to that of gold.

The change in the temperature scale affects not only technical interests involved directly in thermometry but also those involved with other reference standards,

such as electrical standards, that are sensitive to temperature. As examples, standard resistors and standard cells are sensitive to temperature and generally are maintained in constant-temperature environments, at least in national standards laboratories. At the present time, the temperatures of those environments are normally determined with thermometers that were calibrated on the IPTS-68(75). A given thermodynamic temperature expressed on the ITS-90, however, has a value that is different from that expressed on the IPTS-68(75), except at absolute zero (0 K), at the triple-point temperature of water (273.16 K), and at a few other points at which the temperatures on the two scales are fortuitously the same. This difference is shown in figure 1 [83]. A table of differences between temperatures on the ITS-90, i.e., T_{90} or t_{90} , and those on the IPTS-68(75), i.e., T_{68} or t_{68} , and those on the EPT-76, T_{76} , is given in the text of the ITS-90 and is presented here in table 1. Although temperature values expressed on the two scales are different, the change is only in the expression of the value of temperature and not in the temperature itself. That is to say, the Kelvin thermodynamic temperature (the hotness) of a material at any given point is independent of the use of any of the 'practical' temperature scales. The better the 'practical' scale is, the closer the values of temperature on that scale are to the thermodynamic temperature values. Needless to say, the Kelvin thermodynamic temperature values are experimentally determined, and they may have significant error. Since temperature values expressed on the thermodynamic and 'practical' scales are different, if the temperature of the environment of a reference standard is adjusted so that its value when expressed on the ITS-90 has the same value as had been used on the IPTS-68(75), there will have been a change of the thermodynamic temperature and the value of the reference standard will usually change. Of course, one may not want to change the thermodynamic temperature of the reference standard. In that case, the thermodynamic temperature, as expressed on the IPTS-68(75), can simply be expressed on the ITS-90 (a numerical value different from that on the IPTS-68(75)) and the reference standards will be unaffected. For more details on the effects of the change of the temperature scale on electrical standards, see National Institute of Standards and Technology (NIST) Technical Note 1263 [12].

In addition to the effect on reference standards for measurements, all temperature-sensitive properties, e.g., tables of thermodynamic properties, that are presently expressed on the IPTS-68(75) may require changes in values.

2. DEFINITION OF THE ITS-90

The ITS-90 was designed by the CCT in such a manner that temperature values obtained on it do not deviate from the Kelvin thermodynamic temperature values by more than the uncertainties of the latter values at the time the ITS-90 was adopted. Thermodynamic temperature is indicated by the symbol T and has the unit known as the kelvin, symbol K. The size of the kelvin is defined to be $1/273.16$ of the thermodynamic temperature of the triple point of water. This definition of the Kelvin Thermodynamic Temperature Scale (KTTS) that is based on the value of a single finite temperature is not new; the CCT proposed it in 1954, the CIPM recommended it, and the Tenth CGPM adopted it that same year [30].

Because temperatures on previous temperature scales were expressed relative to the ice point (273.15 K), temperature, symbol t , on the Celsius Temperature Scale is defined by:

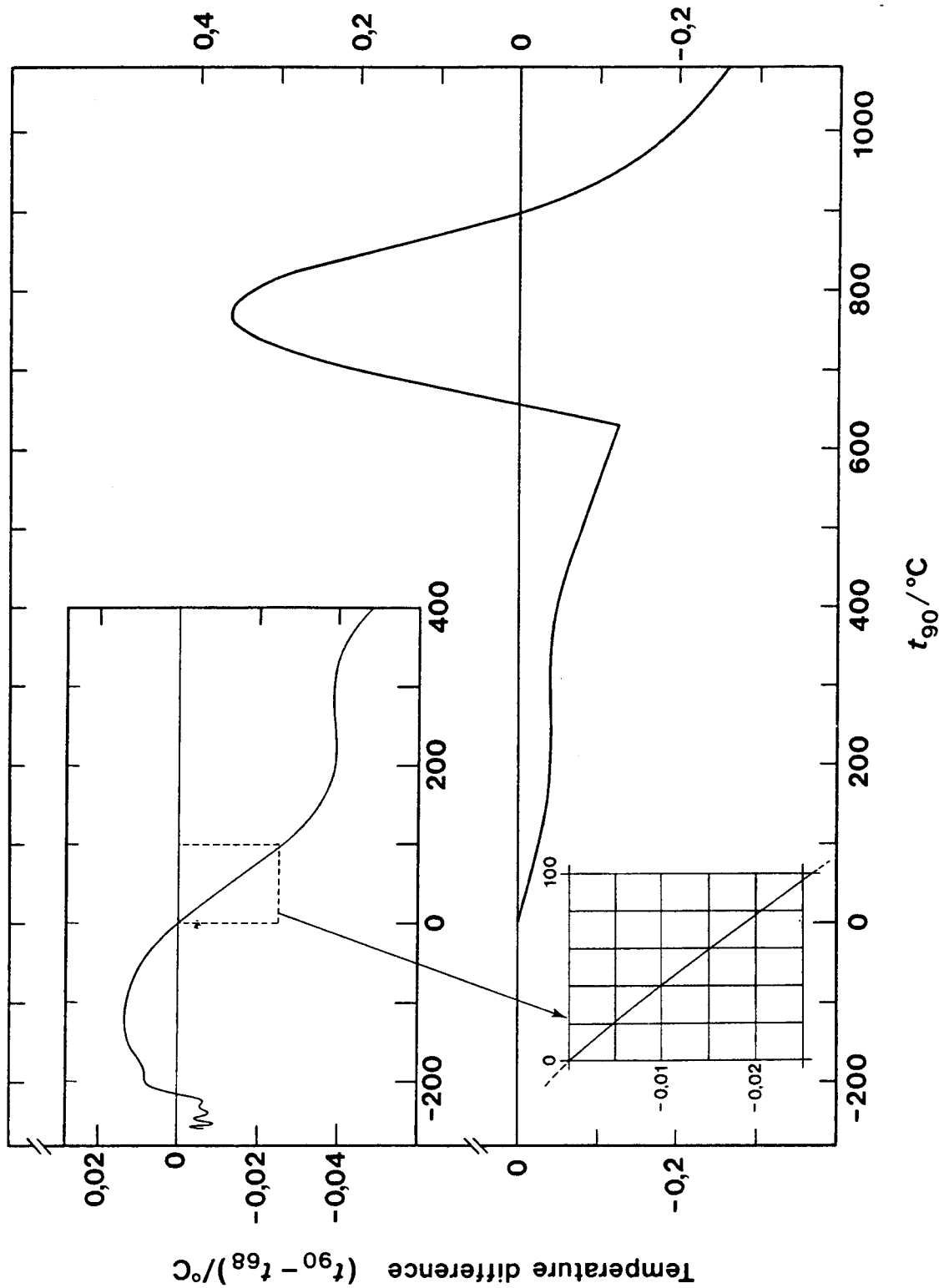


Figure 1. The temperature difference $(t_{90} - t_{68})/^{\circ}\text{C}$ in the range between the triple point of equilibrium hydrogen $(-259.3467^{\circ}\text{C})$ and the freezing point of gold $(1064.18^{\circ}\text{C})$ [83,85].

Table 1. Differences between T_{90} and T_{68} (and t_{90} and t_{68}), and between T_{90} and T_{76}

$(T_{90} - T_{76})/\text{mK}$										
T_{90}/K	0	1	2	3	4	5	6	7	8	9
0						-0.1	-0.2	-0.3	-0.4	-0.5
10	-0.6	-0.7	-0.8	-1.0	-1.1	-1.3	-1.4	-1.6	-1.8	-2.0
20	-2.2	-2.5	-2.7	-3.0	-3.2	-3.5	-3.8	-4.1		
$(T_{90} - T_{68})/\text{K}$										
T_{90}/K	0	1	2	3	4	5	6	7	8	9
10					-0.006	-0.003	-0.004	-0.006	-0.008	-0.009
20	-0.009	-0.008	-0.007	-0.007	-0.006	-0.005	-0.004	-0.004	-0.005	-0.006
30	-0.006	-0.007	-0.008	-0.008	-0.008	-0.007	-0.007	-0.007	-0.006	-0.006
40	-0.006	-0.006	-0.006	-0.006	-0.006	-0.007	-0.007	-0.007	-0.006	-0.006
50	-0.006	-0.005	-0.005	-0.004	-0.003	-0.002	-0.001	0.000	0.001	0.002
60	0.003	0.003	0.004	0.004	0.005	0.005	0.006	0.006	0.007	0.007
70	0.007	0.007	0.007	0.007	0.007	0.008	0.008	0.008	0.008	0.008
80	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008
90	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.009	0.009	0.009
T_{90}/K	0	10	20	30	40	50	60	70	80	90
100	0.009	0.011	0.013	0.014	0.014	0.014	0.014	0.013	0.012	0.012
200	0.011	0.010	0.009	0.008	0.007	0.005	0.003	0.001		
$(t_{90} - t_{68})/^{\circ}\text{C}$										
$t_{90}/^{\circ}\text{C}$	0	-10	-20	-30	-40	-50	-60	-70	-80	-90
-100	0.013	0.013	0.014	0.014	0.014	0.013	0.012	0.010	0.008	0.008
0	0.000	0.002	0.004	0.006	0.008	0.009	0.010	0.011	0.012	0.012
$t_{90}/^{\circ}\text{C}$	0	10	20	30	40	50	60	70	80	90
0	0.000	-0.002	-0.005	-0.007	-0.010	-0.013	-0.016	-0.018	-0.021	-0.024
100	-0.026	-0.028	-0.030	-0.032	-0.034	-0.036	-0.037	-0.038	-0.039	-0.039
200	-0.040	-0.040	-0.040	-0.040	-0.040	-0.040	-0.040	-0.039	-0.039	-0.039
300	-0.039	-0.039	-0.039	-0.040	-0.040	-0.041	-0.042	-0.043	-0.045	-0.046
400	-0.048	-0.051	-0.053	-0.056	-0.059	-0.062	-0.065	-0.068	-0.072	-0.075
500	-0.079	-0.083	-0.087	-0.090	-0.094	-0.098	-0.101	-0.105	-0.108	-0.112
600	-0.115	-0.118	-0.122	-0.125	-0.08	-0.03	0.02	0.06	0.11	0.16
700	0.20	0.24	0.28	0.31	0.33	0.35	0.36	0.36	0.36	0.35
800	0.34	0.32	0.29	0.25	0.22	0.18	0.14	0.10	0.06	0.03
900	-0.01	-0.03	-0.06	-0.08	-0.10	-0.12	-0.14	-0.16	-0.17	-0.18
1000	-0.19	-0.20	-0.21	-0.22	-0.23	-0.24	-0.25	-0.25	-0.26	-0.26
$t_{90}/^{\circ}\text{C}$	0	100	200	300	400	500	600	700	800	900
1000		-0.26	-0.30	-0.35	-0.39	-0.44	-0.49	-0.54	-0.60	-0.66
2000	-0.72	-0.79	-0.85	-0.93	-1.00	-1.07	-1.15	-1.24	-1.32	-1.41
3000	-1.50	-1.59	-1.69	-1.78	-1.89	-1.99	-2.10	-2.21	-2.32	-2.43

$$t/^{\circ}\text{C} = T/\text{K} - 273.15. \quad (1)$$

The unit of temperature t is the degree Celsius, symbol $^{\circ}\text{C}$, and it is by definition the same size as the kelvin. A difference of temperature may be expressed either in kelvins or in degrees Celsius.

Temperatures on the ITS-90 are expressed, in terms of the International Kelvin Temperatures, with the symbol T_{90} , or, in terms of the International Celsius Temperatures, with the symbol t_{90} . The unit of the temperature T_{90} is the kelvin, symbol K, and the unit of the temperature t_{90} is the degree Celsius, symbol $^{\circ}\text{C}$. The relation between T_{90} and t_{90} is:

$$t_{90}/^{\circ}\text{C} = T_{90}/\text{K} - 273.15. \quad (2)$$

The ITS-90 extends upward from 0.65 K. There are alternative definitions of T_{90} in certain temperature ranges and they have equal status. In measurements of the highest precision made at the same temperature, the alternative definitions will yield detectable temperature differences. Also, at any given temperature between defining fixed points, different interpolating thermometers that meet the specifications of the ITS-90 will indicate different temperature values. These latter differences are referred to as the non-uniqueness in the definition of the ITS-90. The magnitude of the differences that result from these two sources is sufficiently small to be negligible for all practical purposes.

Temperatures on the ITS-90 are defined in terms of equilibrium phase states of pure substances (defining fixed points), interpolating instruments, and equations that relate the measured property of the instruments to T_{90} . The equilibrium phase states of the pure substances and the assigned temperatures used as defining fixed points of the ITS-90 are listed in table 2. Figure 2 shows schematically the defining phase states and temperature ranges defined by the various interpolating instruments and equations. For comparison purposes, we give in table 3 the defining fixed points, and their assigned temperatures, of the ITS-90 and of all the previous internationally agreed-upon scales.

2.1 BETWEEN 0.65 K AND 5.0 K: ^3He and ^4He VAPOR PRESSURE THERMOMETRY

The ITS-90 is defined between 0.65 K and 3.2 K by the vapor-pressure-temperature relation of ^3He , and between 1.25 K and 2.1768 K (the λ point) and between 2.1768 K and 5.0 K by the vapor-pressure-temperature relations of ^4He . T_{90} is defined by the vapor-pressure equations of the form:

$$T_{90}/\text{K} = A_0 + \sum_{i=1}^9 A_i \{ [\ln(p/\text{Pa}) - B]/C \}^i. \quad (3)$$

The values of the coefficients A_i and of the constants A_0 , B and C of the vapor-pressure equations for ^3He and ^4He are given in table 4.

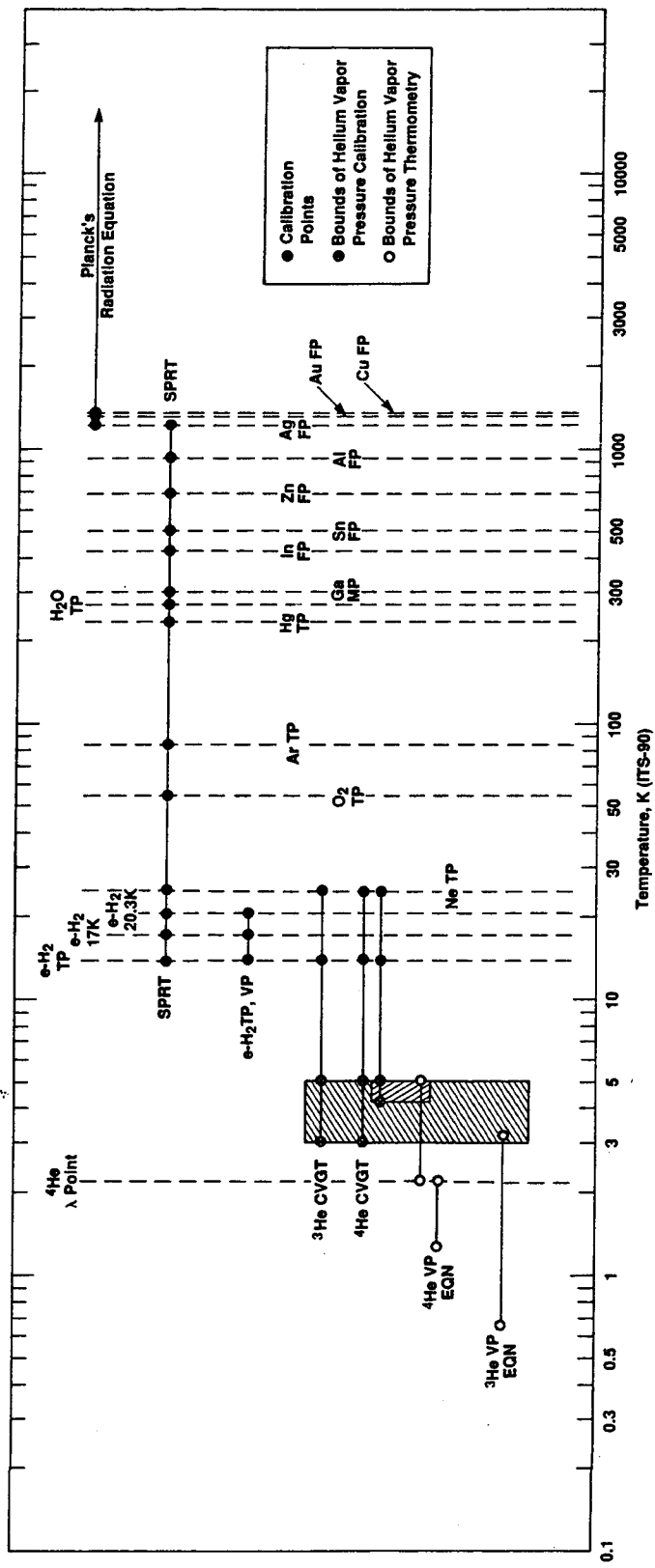


Figure 2. A schematic representation of the ITS-90 showing the temperatures of the defining fixed points (or phase equilibrium states) on the scale and temperature ranges defined by interpolation instruments and equations.

Table 2. Defining fixed points of the ITS-90

Material ^a Equilibrium State ^b		Temperature		$W_r(T_{90})^e$
		T_{90} (K)	t_{90} (°C)	
He	VP	3 to 5	- 270.15 to - 268.15	
e-H ₂	TP	13.8033	- 259.3467	0.00119007
e-H ₂ (or He)	VP (or CVGT)	≈ 17	≈ - 256.15	
e-H ₂ (or He)	VP (or CVGT)	≈ 20.3	≈ - 252.85	
Ne ^c	TP	24.5561	- 248.5939	0.00844974
O ₂	TP	54.3584	- 218.7916	0.09171804
Ar ^d	TP	83.8058	- 189.3442	0.21585975
Hg ^c	TP	234.3156	- 38.8344	0.84414211
H ₂ O	TP	273.16	0.01	1.00000000
Ga ^c	MP	302.9146	29.7646	1.11813889
In ^c	FP	429.7485	156.5985	1.60980185
Sn ^d	FP	505.078	231.928	1.89279768
Zn	FP	692.677	419.527	2.56891730
Al ^c	FP	933.473	660.323	3.37600860
Ag	FP	1234.93	961.78	4.28642053
Au	FP	1337.33	1064.18	
Cu ^c	FP	1357.77	1084.62	

^a e-H₂ indicates equilibrium hydrogen, that is, hydrogen with the equilibrium distribution of its ortho and para states at the corresponding temperatures. Normal hydrogen at room temperature contains 25% para and 75% ortho hydrogen.

^b VP indicates vapor pressure point or equation; CVGT indicates constant volume gas thermometer point; TP indicates triple point (equilibrium temperature at which the solid, liquid and vapor phases coexist); FP indicates freezing point and MP indicates melting point (the equilibrium temperatures at which the solid and liquid phases coexist under a pressure of 101,325 Pa, one standard atmosphere). The isotopic composition is that naturally occurring.

^c Previously, these were secondary fixed points.

^d Previously, these were alternative fixed points.

^e From reference functions, eqs (14) and (22).

Table 3. Comparison of temperatures of fixed points assigned on various scales. Temperatures are expressed in kelvins on the KTTS or equivalent scales

Point	NHS ^a	ITS-27 ^b	ITS-48 ^b	IPTS-48 ^b	IPTS-68	IPTS-68(75)	EPT-76	ITS-90
Au FP ^c	-	1336.15	1336.15	1336.15	1337.58	1337.58	-	1337.33
Ag FP	-	1233.65	1233.95	1233.95	1235.08	1235.08	-	1234.93
Al FP	-	-	-	-	-	-	-	933.473
S BP ^d	-	717.75	717.75	717.75	-	-	-	-
Zn FP	-	-	-	(692.655)	692.73	692.73	-	692.677
Sn FP	-	-	-	-	(505.1181)	(505.1181)	-	505.078
In FP	-	-	-	-	-	-	-	429.7485
H ₂ O BP	373	373.15	373.15	373.15	373.15	373.15	-	-
Ga TP	-	-	-	-	-	-	-	302.9146
H ₂ O TP ^e	-	-	-	(273.16)	273.16	273.16	-	273.16
H ₂ O FP	273	273.15	273.15	-	-	-	-	-
Hg TP	-	-	-	-	-	-	-	234.3156
O ₂ BP ^f	-	90.18	90.18	90.18	90.188	90.188	-	-
Ar TP	-	-	-	-	-	(83.798)	-	83.8058
O ₂ TP	-	-	-	-	54.361	54.361	-	54.3584
Ne BP	-	-	-	-	27.102	27.102	21.102	-
Ne TP	-	-	-	-	-	-	24.5591	24.5561
H ₂ BP	-	-	-	-	20.28	20.28	20.2734	20.3
H ₂ BP ^g	-	-	-	-	17.042	17.042	17.0373	17.0
H ₂ TP	-	-	-	-	13.81	13.81	13.8044	13.8033
Pb SP ^h	-	-	-	-	-	-	7.1999	-
⁴ He BP	-	-	-	-	-	-	4.2221	4.2
In SP	-	-	-	-	-	-	3.4145	-
³ He BP	-	-	-	-	-	-	-	3.2
Al SP	-	-	-	-	-	-	1.1796	-
Zn SP	-	-	-	-	-	-	0.851	-
Cd SP	-	-	-	-	-	-	0.519	-

^a NHS = Normal hydrogen scale [25].

^b For a time, the ice point was taken to be 273.16 °K. Here, the value 273.15 K was used to convert temperature values in degrees Centigrade or Celsius to kelvins in order to be as consistent as possible throughout the table.

^c FP = Freezing point.

^d BP = Boiling point at 101,325 Pa.

^e TP = Triple point.

^f Changed in 1975 to the condensation point.

^g Reduced-pressure boiling point, at P = 33,330.6 Pa.

^h SP = Superconductive transition point.

Table 4. Values of the coefficients A_i and of the constants B and C for the ^3He and ^4He vapor-pressure equations and the temperature range for which each equation is valid

Coef. or Constant	^3He	^4He	^4He
	0.65 K to 3.2 K	1.25 K to 2.1768 K	2.1768 K to 5.0 K
A_0	1.053 447	1.392 408	3.146 631
A_1	0.980 106	0.527 153	1.357 655
A_2	0.676 380	0.166 756	0.413 923
A_3	0.372 692	0.050 988	0.091 159
A_4	0.151 656	0.026 514	0.016 349
A_5	-0.002 263	0.001 975	0.001 826
A_6	0.006 596	-0.017 976	-0.004 325
A_7	0.088 966	0.005 409	-0.004 973
A_8	-0.004 770	0.013 259	0
A_9	-0.054 943	0	0
B	7.3	5.6	10.3
C	4.3	2.9	1.9

2.2 BETWEEN 3.0 K AND 24.5561 K (THE TRIPLE POINT OF Ne): ^3He and ^4He CONSTANT VOLUME GAS THERMOMETRY

Between 3.0 K and 24.5561 K, the ITS-90 is defined in terms of the ^3He or ^4He constant volume gas thermometer (CVGT). The thermometer is calibrated at three temperatures – at the triple point of neon (24.5561 K), at the triple point of equilibrium hydrogen (13.8033 K), and at a temperature between 3.0 K and 5.0 K, the value of which is determined by using either a ^3He or a ^4He vapor-pressure thermometer as described in section 2.1.

For a ^4He CVGT that is used between 4.2 K and the triple point of neon (24.5561 K), T_{90} is defined by the equation:

$$T_{90} = a + bp + cp^2, \quad (4)$$

where p is the CVGT pressure and a , b , and c are coefficients that are determined from calibrations at the three specified temperatures, but with the additional requirement that the calibration with the vapor-pressure thermometer be made at a temperature between 4.2 K and 5.0 K.

For a ^4He CVGT that is used between 3.0 K and 4.2 K, and for a ^3He CVGT that is used between 3.0 K and 24.5561 K, the non-ideality of the gas must be accounted for, using the respective second virial coefficients, $B_4(T_{90})$ or $B_3(T_{90})$. T_{90} is defined in this range by the equation:

$$T_{90} = \frac{a + bp + cp^2}{1 + B_x(T_{90})N/V}, \quad (5)$$

where p is the CVGT pressure; a , b , and c are coefficients that are determined from calibration at the three defining temperatures; $B_x(T_{90})$ refers to $B_3(T_{90})$ or $B_4(T_{90})$; and N/V is the gas density, in moles per cubic meter, in the CVGT bulb. The values of the second virial coefficients are given by the following equations:

for ^3He ,

$$B_3(T_{90})/\text{m}^3\text{mol}^{-1} = [16.69 - 336.98 (T_{90}/\text{K})^{-1} + 91.04 (T_{90}/\text{K})^{-2} - 13.82 (T_{90}/\text{K})^{-3}] 10^{-6}, \quad (6)$$

and for ^4He ,

$$B_4(T_{90})/\text{m}^3\text{mol}^{-1} = [16.708 - 374.05 (T_{90}/\text{K})^{-1} - 383.53 (T_{90}/\text{K})^{-2} + 1799.2 (T_{90}/\text{K})^{-3} - 4033.2 (T_{90}/\text{K})^{-4} + 3252.8 (T_{90}/\text{K})^{-5}] 10^{-6}. \quad (7)$$

The accuracy of realization of T_{90} by using a CVGT is dependent upon the CVGT design and the gas density used.

2.3 BETWEEN 13.8033 K (THE TRIPLE POINT OF EQUILIBRIUM HYDROGEN) AND 1234.93 K (THE FREEZING POINT OF SILVER): PLATINUM RESISTANCE THERMOMETRY

Between 13.8033 K (-259.3467 °C) and 1234.93 K (961.78 °C), the ITS-90 is defined in terms of specified fixed points to which temperature values have been assigned, by resistance ratios of platinum resistance thermometers obtained by calibration at specified sets of the fixed points, and by reference functions and deviation functions of resistance ratios which relate to T_{90} between the fixed points. (Henceforth, for convenience, the standards type platinum resistance thermometers will be referred to by the acronym SPRT.)

2.3.1 GENERAL RELATION BETWEEN RESISTANCE RATIOS AND T_{90}

Temperatures on the ITS-90 in the above-indicated range are expressed in terms of the ratio of the resistance $R(T_{90})$ at temperature T_{90} and the resistance $R(273.16 \text{ K})$ at the triple-point temperature of water. (Hereinafter, for convenience, the terms triple-point temperature, freezing-point temperature and melting-point temperature will be expressed as triple point, freezing point and melting point, respectively.) The resistance ratio $W(T_{90})$ is:

$$W(T_{90}) = R(T_{90})/R(273.16 \text{ K}). \quad (8)$$

The temperature T_{90} is calculated from the resistance ratio relation:

$$W(T_{90}) - W_r(T_{90}) = \Delta W(T_{90}), \quad (9)$$

where $W(T_{90})$ is the observed value, $W_r(T_{90})$ is the value calculated from the reference functions, and $\Delta W(T_{90})$ is the deviation of the observed $W(T_{90})$ value of the particular SPRT from the reference function value. The official version of the ITS-90 [83] does not indicate the difference $[W(T_{90}) - W_r(T_{90})]$ by $\Delta W(T_{90})$.

Note that in the earlier international scales, $W(T)$ was defined with reference to the SPRT resistance at 273.15 K, not 273.16 K.

There are two reference functions $W_x(T_{90})$, one for the range 13.8033 K to 273.16 K and another for the range 273.15 K to 1234.93 K. These reference functions will be described in the discussion of the two ranges (secs. 2.3.3 and 2.3.4).

The deviation $\Delta W(T_{90})$ is obtained as a function of T_{90} for various ranges and subranges by calibration at specified fixed points. The form of the deviation function depends upon the temperature range of calibration.

A schematic representation of the ITS-90 in the range of temperature specified for SPRTs is given in figure 3. Shown in figure 3 are the temperatures of the defining fixed points in this region of the scale and the various subranges specified by the scale.

2.3.2 SPRT SPECIFICATIONS

The SPRT sensing element must be made from pure platinum and be strain-free. The finished SPRT must meet one of the following criteria:

$$W(302.9146 \text{ K}) \geq 1.118 \text{ 07}, \quad \text{or} \quad (10)$$

$$W(234.3156 \text{ K}) \leq 0.844 \text{ 235}. \quad (11)$$

These criteria are equivalent to a requirement on the slope, namely,

$$[dW(T_{90})/dT_{90}] \geq 3.986 \times 10^{-3} \text{ K}^{-1} \text{ at } 273.16 \text{ K}. \quad (12)$$

An SPRT that is acceptable for use to the freezing point of silver must meet the following additional criterion:

$$W(1234.93 \text{ K}) \geq 4.2844. \quad (13)$$

The temperature range over which an SPRT can be used depends upon the thermometer design, but no single design of SPRT can be used over the whole temperature range with high accuracy. For measurements at temperatures from 13.8033 K (-259.3467 °C) to 429.7485 K (156.5985 °C), or perhaps to as high as 505.078 K (231.928 °C), capsule-type SPRTs that have a nominal resistance of 25.5 Ω at 273.16 K may be used. Long-stem type SPRTs of the same nominal resistance may be used in the range from about 77 K to 933.473 K (660.323 °C). For temperatures above about 660 °C and to as high as 1234.93 K (961.78 °C), long-stem type SPRTs having a nominal resistance of 0.25 Ω (or possibly 2.5 Ω) at 273.16 K should be used. When SPRTs are used at the highest temperatures, leakage currents through the insulation supports of the platinum wire become significant and these result in shunting of the resistor. The effect of this shunting is reduced by using low voltages with low resistance SPRTs.

If the sheath of the long-stem type SPRT is borosilicate glass or stainless steel, the SPRT should not be used above the upper calibration temperature limit of 420 °C. If the sheath is Inconel, the upper temperature limit becomes about

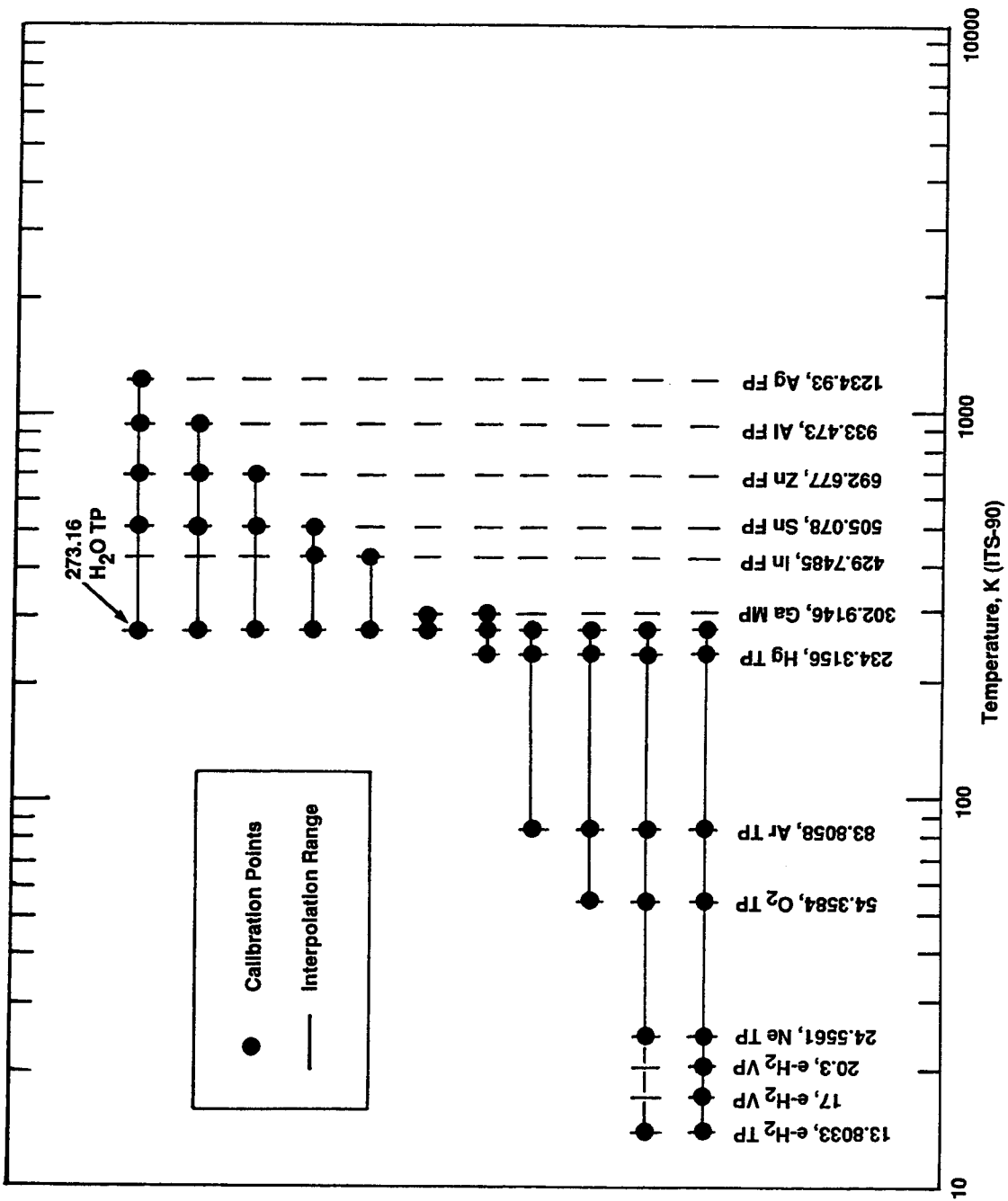


Figure 3. A schematic representation of the ITS-90 in the range specified for the platinum resistance thermometer, showing the various defined subranges and the temperatures of the defining fixed points on the scale required for calibration.

660 °C. If the sheath is fused silica, temperature measurements can be made up to 962 °C.

For measurements up to about 630 °C, mica is just barely adequate as an electrical insulator for the temperature sensing element and leads of SPRTs. Starting at about 500 °C, muscovite mica begins to decompose, evolving water that electrically shunts the thermometer resistor. Phlogopite mica is adequately stable to 630 °C. For measurements up to 962 °C, refractory materials such as fused silica and sapphire are used for electrical insulation.

2.3.3 RANGE 13.8033 K TO 273.16 K

In the range 13.8033 K to 273.16 K, the reference function $W_r(T_{90})$ is given by:

$$\ln[W_r(T_{90})] = A_0 + \sum_{i=1}^{12} A_i \{ [\ln(T_{90}/273.16 \text{ K}) + 1.5] / 1.5 \}^i. \quad (14)$$

A specified, approximate inverse [83] of this equation, equivalent to within ± 0.0001 K, is:

$$T_{90}/273.16 \text{ K} = B_0 + \sum_{i=1}^{15} B_i \{ ([W_r(T_{90})]^{1/6} - 0.65) / 0.35 \}^i. \quad (15)$$

The values of the constants A_0 and B_0 , and of the coefficients A_i and B_i of equations (14) and (15) are listed in table 5.

If an SPRT is to be used throughout the range from 13.8033 K to 273.16 K, it must be calibrated at the triple points of equilibrium hydrogen (13.8033 K), neon (24.5561 K), oxygen (54.3584 K), argon (83.8058 K), mercury (234.3156 K), and water (273.16 K), and at two additional temperatures close to 17.0 K and 20.3 K. The temperatures of calibration near 17.0 K and 20.3 K may be determined by using either a CVGT as defined in section 2.2 or the specified vapor-pressure-temperature relation of equilibrium hydrogen.

When the CVGT is used, the two temperatures must be within the ranges 16.9 K to 17.1 K and 20.2 K to 20.4 K, respectively. When the equilibrium hydrogen vapor-pressure thermometer is used, the two temperatures must be within the ranges 17.025 K to 17.045 K and 20.26 K to 20.28 K, respectively. The temperatures of the equilibrium hydrogen vapor-pressure thermometer are determined from the values of the hydrogen vapor pressure, p , and the equations:

$$T_{90}/\text{K} - 17.035 = (p/\text{kPa} - 33.3213)/13.32 \quad (16)$$

$$T_{90}/\text{K} - 20.27 = (p/\text{kPa} - 101.292)/30, \quad (17)$$

where 13.32 and 30 are values of $(dp/dT_{90})/(\text{kPa}/\text{K})$ at 17.035 K and 20.27 K, respectively.

Depending upon the temperature range of use, the SPRT may be calibrated from 273.16 K down to 13.8033 K (the triple point of equilibrium hydrogen), down to

Table 5. Values of the coefficients A_i , B_i , C_i and D_i and of the constants A_0 , B_0 , C_0 , and D_0 in the reference functions, eqs (14) and (22), and in the functions approximating them, given by eqs (15) and (23)

Constant or Coefficient	Value	Constant or Coefficient	Value
A_0	-2.135 347 29	B_0	0.183 324 722
A_1	3.183 247 20	B_1	0.240 975 303
A_2	-1.801 435 97	B_2	0.209 108 771
A_3	0.717 272 04	B_3	0.190 439 972
A_4	0.503 440 27	B_4	0.142 648 498
A_5	-0.618 993 95	B_5	0.077 993 465
A_6	-0.053 323 22	B_6	0.012 475 611
A_7	0.280 213 62	B_7	-0.032 267 127
A_8	0.107 152 24	B_8	-0.075 291 522
A_9	-0.293 028 65	B_9	-0.056 470 670
A_{10}	0.044 598 72	B_{10}	0.076 201 285
A_{11}	0.118 686 32	B_{11}	0.123 893 204
A_{12}	-0.052 481 34	B_{12}	-0.029 201 193
		B_{13}	-0.091 173 542
		B_{14}	0.001 317 696
		B_{15}	0.026 025 526
C_0	2.781 572 54	D_0	439.932 854
C_1	1.646 509 16	D_1	472.418 020
C_2	-0.137 143 90	D_2	37.684 494
C_3	-0.006 497 67	D_3	7.472 018
C_4	-0.002 344 44	D_4	2.920 828
C_5	0.005 118 68	D_5	0.005 184
C_6	0.001 879 82	D_6	-0.963 864
C_7	-0.002 044 72	D_7	-0.188 732
C_8	-0.000 461 22	D_8	0.191 203
C_9	0.000 457 24	D_9	0.049 025

24.5561 K (the triple point of neon), down to 54.3584 K (the triple point of oxygen), or down to 83.8058 K (the triple point of argon).

The deviation function for calibration over the range 13.8033 K to 273.16 K is given by the relation:

$$\Delta W_1(T_{90}) = a_1[W(T_{90}) - 1] + b_1[W(T_{90}) - 1]^2 + \sum_{i=1}^5 c_i [\ln W(T_{90})]^{i+n}, \quad (18)$$

with $n = 2$. The coefficients a_1 , b_1 , and the five c_i 's are obtained by calibration at all eight of the above temperatures, including that at the triple point of water. The values of $W_r(T_{90})$ are obtained from the reference function [eq (14)].

The official version of the ITS-90 [83] does not indicate the difference $[W(T_{90}) - W_r(T_{90})]$ by $\Delta W_m(T_{90})$, does not use the subscript m , where in eq (18), $m = 1$, nor does it label the coefficients a and b with subscript m . However, we adopt this subscript notation to identify the subranges. Additionally, this notation is useful when reporting calibration results.

If an SPRT is not to be used over the entire 13.8033 K to 273.16 K range, but its use restricted to one of the subranges, the deviation functions and the calibration points are as follows.

2.3.3.1 SUBRANGE 24.5561 K TO 273.16 K

The deviation function for calibration in the subrange 24.5561 K to 273.16 K is given by the relation:

$$\Delta W_2(T_{90}) = a_2[W(T_{90}) - 1] + b_2[W(T_{90}) - 1]^2 + \sum_{i=1}^3 c_i[\ln W(T_{90})]^{i+n}, \quad (19)$$

with $n = 0$. The coefficients a_2 , b_2 , and the three c_i 's are obtained by calibrating the SPRT at the triple points of equilibrium hydrogen (13.8033 K), neon (24.5561 K), oxygen (54.3584 K), argon (83.8058 K), mercury (234.3156 K) and water (273.16 K). The values of $W_r(T_{90})$ are obtained from the reference function [eq (14)]. Note that for this subrange, temperatures are measured only down to the triple point of neon, although the thermometer must be calibrated at the triple point of equilibrium hydrogen.

2.3.3.2 SUBRANGE 54.3584 K TO 273.16 K

The deviation function for calibration in the subrange 54.3584 K to 273.16 K is given by the relation:

$$\Delta W_3(T_{90}) = a_3[W(T_{90}) - 1] + b_3[W(T_{90}) - 1]^2 + c_1[\ln W(T_{90})]^{1+n}, \quad (20)$$

with $n = 1$. The coefficients a_3 , b_3 , and c_1 are obtained by calibrating the SPRT at the triple points of oxygen (54.3584 K), argon (83.8058 K), mercury (234.3156 K), and water (273.16 K). The values of $W_r(T_{90})$ are obtained from the reference function [eq (14)].

2.3.3.3 SUBRANGE 83.8058 K TO 273.16 K

The deviation function for calibration in the subrange 83.8058 K to 273.16 K is given by the relation:

$$\Delta W_4(T_{90}) = a_4[W(T_{90}) - 1] + b_4[W(T_{90}) - 1]\ln W(T_{90}). \quad (21)$$

The coefficients a_4 and b_4 are obtained by calibrating the SPRT at the triple

points of argon (83.8058 K), mercury (234.3156 K), and water (273.16 K). The values of $W_r(T_{90})$ are obtained from the reference function [eq (14)].

2.3.4 RANGE 273.15 K (0 °C) TO 1234.93 K (961.78 °C)

In the range 273.15 K to 1234.93 K, the equation for the reference function $W_r(T_{90})$ is given by:

$$W_r(T_{90}) = C_0 + \sum_{i=1}^9 C_i [(T_{90}/K - 754.15)/481]^i. \quad (22)$$

A specified, approximate inverse [83] of this equation, equivalent to within ± 0.000 13 K, is:

$$T_{90}/K - 273.15 = D_0 + \sum_{i=1}^9 D_i \{ [W_r(T_{90}) - 2.64]/1.64 \}^i. \quad (23)$$

The values of the constants C_0 and D_0 and of the coefficients C_i and D_i of eqs (22) and (23) are listed in table 5.

If the SPRT is to be used over the entire range 273.15 K to 1234.93 K, it must be calibrated at the triple point of water (273.16 K) and at the freezing points of tin (505.078 K), zinc (692.677 K), aluminum (933.473 K), and silver (1234.93 K).

The deviation function is given by the relation:

$$\begin{aligned} \Delta W_6(T_{90}) = & a_6 [W(T_{90}) - 1] + b_6 [W(T_{90}) - 1]^2 \\ & + c_6 [W(T_{90}) - 1]^3 + d [W(T_{90}) - W(933.473 \text{ K})]^2. \end{aligned} \quad (24)$$

The values of a_6 , b_6 , and c_6 are determined from the measured deviations $\Delta W(T_{90})$ of $W(T_{90})$ from the reference values $W_r(T_{90})$ [obtained from eq (22)] at the freezing points of tin (505.078 K), zinc (692.677 K), and aluminum (933.473 K), ignoring the term involving d . Then, d is determined from these values of a_6 , b_6 , and c_6 and the deviation $\Delta W(T_{90})$ of $W(T_{90})$ from the reference value $W_r(T_{90})$ at the freezing point of silver (1234.93 K). The coefficient d is used only for temperature measurements in the range from the freezing point of aluminum to the freezing point of silver. For temperature measurements below the freezing point of aluminum, $d = 0$.

SPRTs may be calibrated for use throughout the whole range 273.15 K to 1234.93 K or for shorter subranges by calibrations at fixed points between 273.15 K and the upper limit of 933.473 K (freezing point of aluminum, 660.323 °C), of 692.677 K (freezing point of zinc, 419.527 °C), of 505.078 K (freezing point of tin, 231.928 °C), of 429.7485 K (freezing point of indium, 156.5985 °C), or of 302.9146 K (melting point of gallium, 29.7646 °C).

The deviation function $\Delta W_5(T_{90})$ will be discussed later in the text.

If an SPRT is not to be used over the entire 273.15 K to 1234.93 K range, but its use restricted to one of the subranges, the deviation functions and the calibration points are as follows.

2.3.4.1 SUBRANGE 273.15 K (0 °C) TO 933.473 K (660.323 °C, FREEZING POINT OF ALUMINUM)

For an SPRT used throughout the subrange 273.15 K to 933.473 K, the thermometer is calibrated at the triple point of water (273.16 K), and at the freezing points of tin (505.078 K), zinc (692.677 K), and aluminum (933.473 K). The deviation function is given by the relation:

$$\Delta W_7(T_{90}) = a_7[W(T_{90}) - 1] + b_7[W(T_{90}) - 1]^2 + c_7[W(T_{90}) - 1]^3. \quad (25)$$

The coefficients a_7 , b_7 , and c_7 , identical to a_6 , b_6 and c_6 , respectively, are determined from the deviations $\Delta W(T_{90})$ of $W(T_{90})$ from the reference values $W_r(T_{90})$ [eq (22)] at the freezing points of tin (505.078 K), zinc (692.677 K), and aluminum (933.473 K).

2.3.4.2 SUBRANGE 273.15 K (0 °C) TO 692.677 K (419.527 °C, FREEZING POINT OF ZINC)

For an SPRT used throughout the subrange 273.15 K to 692.677 K, the thermometer is calibrated at the triple point of water (273.16 K), and at the freezing points of tin (505.078 K) and zinc (692.677 K). The deviation function is given by the relation:

$$\Delta W_8(T_{90}) = a_8[W(T_{90}) - 1] + b_8[W(T_{90}) - 1]^2. \quad (26)$$

The coefficients a_8 and b_8 are determined from the deviations $\Delta W(T_{90})$ of $W(T_{90})$ from the reference values $W_r(T_{90})$ [eq (22)] at the freezing points of tin (505.078 K) and zinc (692.677 K).

2.3.4.3 SUBRANGE 273.15 K (0 °C) TO 505.078 K (231.928 °C, FREEZING POINT OF TIN)

For an SPRT used throughout the subrange 273.15 K to 505.078 K, the thermometer is calibrated at the triple point of water (273.16 K), and at the freezing points of indium (429.7485 K) and tin (505.078 K). The form of the deviation function is the same as that for the subrange 273.15 K to 692.677 K, i.e.,

$$\Delta W_9(T_{90}) = a_9[W(T_{90}) - 1] + b_9[W(T_{90}) - 1]^2. \quad (27)$$

The coefficients a_9 and b_9 are determined from the deviations $\Delta W(T_{90})$ of $W(T_{90})$ from the reference values $W_r(T_{90})$ [eq (22)] at the freezing points of indium (429.7485 K) and tin (505.078 K).

2.3.4.4 SUBRANGE 273.15 K (0 °C) TO 429.7485 K (156.5985 °C, FREEZING POINT OF INDIUM)

For an SPRT used throughout the subrange 273.15 K to 429.7485 K, the thermometer is calibrated at the triple point of water (273.16 K) and at the freezing point

of indium (429.7485 K). The deviation function is:

$$\Delta W_{10}(T_{90}) = a_{10}[W(T_{90}) - 1]. \quad (28)$$

The coefficient a_{10} is determined from the deviation $\Delta W(T_{90})$ of $W(T_{90})$ from the reference value $W_r(T_{90})$ [eq (22)] at the freezing point of indium (429.7485 K).

2.3.4.5 SUBRANGE 273.15 K (0 °C) TO 302.9146 K (29.7646 °C, MELTING POINT OF GALLIUM)

For an SPRT used throughout the subrange 273.15 K to 302.9146 K, the thermometer is calibrated at the triple point of water (273.16 K) and at the melting point of gallium (302.9146 K). The deviation function is:

$$\Delta W_{11}(T_{90}) = a_{11}[W(T_{90}) - 1]. \quad (29)$$

The coefficient a_{11} is determined from the deviation $\Delta W(T_{90})$ of $W(T_{90})$ from the reference value $W_r(T_{90})$ [eq (22)] at the melting point of gallium (302.9146 K).

2.3.5 SUBRANGE 234.3156 K (-38.8344 °C, TRIPLE POINT OF MERCURY) TO 302.9146 K (29.7646 °C, THE MELTING POINT OF GALLIUM)

For an SPRT used throughout the subrange 234.3156 K to 302.9146 K, the thermometer is calibrated at the triple points of mercury (234.3156 K) and water (273.16 K), and at the melting point of gallium (302.9146 K). The form of the deviation function is the same as that for the subrange 273.15 K to 692.677 K, i.e.,

$$\Delta W_5(T_{90}) = a_5[W(T_{90}) - 1] + b_5[W(T_{90}) - 1]^2. \quad (30)$$

The coefficients a_5 and b_5 are determined from the deviations $\Delta W(T_{90})$ of $W(T_{90})$ from the reference values $W_r(T_{90})$ at the triple point of mercury (234.3156 K) and at the melting point of gallium (302.9146 K). The reference values $W_r(T_{90})$ must be calculated from the appropriate reference function [either eq (14) or eq (22)], both reference functions being required to cover this range.

2.4 ABOVE 1234.93 K (961.78 °C, FREEZING POINT OF SILVER); RADIATION THERMOMETRY BASED ON PLANCK'S LAW OF RADIATION

At temperatures above 1234.93 K, T_{90} is defined by the relation:

$$\frac{L_\lambda(T_{90})}{L_\lambda[T_{90}(X)]} = \frac{\exp[c_2/\lambda T_{90}(X)] - 1}{\exp[c_2/\lambda T_{90}] - 1}, \quad (31)$$

in which $L_\lambda(T_{90})$ and $L_\lambda[T_{90}(X)]$ are the spectral concentrations of the radiance of a blackbody at wavelength λ (in vacuum) at T_{90} and at $T_{90}(X)$, respectively. $T_{90}(X)$ refers to either the silver freezing point [$T_{90}(\text{Ag}) = 1234.93$ K], the gold freezing point [$T_{90}(\text{Au}) = 1337.33$ K] or the copper freezing point [$T_{90}(\text{Cu}) = 1357.77$ K]. The second radiation constant, $c_2 (= hc/k)$, of Planck's radiation formula has the value $c_2 = 0.014388$ m·K. Although the freezing-point

temperature of silver is the junction point of platinum resistance thermometry and radiation thermometry, it is believed that the T_{90} values of the freezing points of silver, gold and copper are sufficiently self-consistent that the use of any one of them as the reference temperature $T_{90}(X)$ will not result in any significant difference in the measured values of T_{90} from what would be obtained if only the silver freezing point were used.

3. REALIZATION OF THE ITS-90

3.1 VAPOR PRESSURE THERMOMETRY AND GAS THERMOMETRY

3.1.1 REALIZATION OF THE ITS-90 BELOW 273.16 K

The calibration of thermometers below the triple point of argon on the ITS-90, as defined, is relatively complex. It is expected that capsule-type SPRTs, rhodium-iron resistance thermometers (RIRTs), and other stable encapsulated resistance thermometers will be calibrated in terms of the defined ITS-90 and then used as reference thermometers to maintain the ITS-90 below about 84 K and used to calibrate other resistance thermometers by the comparison method. The reference thermometers will be calibrated periodically in terms of the defined ITS-90.

By use of the term "realization of the ITS-90," reference is made to obtaining the equilibrium states as defined by the scale, to having thermometers in thermal equilibrium with those equilibrium states, and to making accurate measurements and interpretations of the requisite properties of those thermometers in terms of the ITS-90.

Considerable effort has been expended to develop and realize the EPT-76, a scale which covered the range 0.5 K to 30 K. This scale has been widely disseminated among low temperature scientists. At NIST, the EPT-76 has been maintained on reference-standard RIRTs for use in calibrating customer thermometers. Upon introduction of the ITS-90, NIST converted the EPT-76 on the reference-standard RIRTs to the ITS-90 using the specified differences [83] between T_{90} and T_{76} . This converted scale is being used to calibrate other thermometers until such time that NIST realizes the ITS-90 in this temperature region directly as defined. It is recommended that those laboratories that have thermometers with calibrations on the EPT-76 adjust their T_{76} values to conform to T_{90} values. When NIST realizes the ITS-90 as defined in this range, the difference between the converted scale on the reference-standard RIRTs (and where appropriate, on capsule SPRTs) and the realized scale will be determined.

3.1.2 VAPOR PRESSURE THERMOMETRY AND THE CVGT RANGE

For most measurements below about 100 K, better precision can be obtained with capsule-type SPRTs than with the long-stem type. In the calibration of SPRTs, however, long-stem type SPRTs (immersion-type SPRTs) can be calibrated easily by a direct immersion process down to the triple point of argon (83.8058 K) by moving the SPRTs from one fixed-point device to another. Unless capsule-type SPRTs and other capsule-type thermometers are installed inside long stem-like holders, however, they will require re-installation and re-wiring whenever different fixed-point apparatuses are used. (In this document, the phrase

"capsule-type thermometers" means encapsulated resistance thermometers of small overall dimensions.) It is desirable, therefore, to be able to calibrate capsule-type SPRTs and other capsule-type thermometers at the argon triple point and below (or, if possible, even at the triple point of water and below since calibrations of SPRTs require measurements at the triple point of water) in an integrated "multi-task" (multi-fixed-point) apparatus. Such a multi-task apparatus requires, in addition to wells for capsule thermometers (in thermal equilibrium in a "single cryostat block"), means for calibration using ^3He , ^4He , and e- H_2 vapor pressure thermometry, ^3He and ^4He CVGTs, and triple points of e- H_2 , Ne, O_2 , Ar, Hg, and H_2O . A total of 11 chambers is required if all of the overlapping definitions of the ITS-90 are to be evaluated and if a "continuous calibration," without re-installation and re-wiring of the SPRTs, is desired from 0.65 K to 273.16 K. In addition, unless high pressure sealed cells of the reference gases are used, tubes to each of the chambers, except those for Hg and H_2O , are required.

Since ^3He and ^4He vapor-pressure and CVGT ranges overlap to a large extent, chambers for ^4He vapor-pressure measurements and for ^4He CVGT measurements could be eliminated and the ITS-90 could still be realized. Also, chambers for e- H_2 vapor-pressure and the e- H_2 triple-point realizations could be combined. The number of chambers could be reduced further if the cryostat block could be allowed to warm to ambient temperature or higher for exchanging certain of the fixed-point substances, or if it were permissible to perform the calibrations of the capsule thermometers at the triple points of argon, mercury, and water in other apparatuses, using a long-stem type holder. This procedure, however, would require a longer time for calibration.

The number of chambers can also be reduced if suitable, highly stable capsule thermometers are available for correlating the scales; for this purpose, the capsule SPRTs would be calibrated in another, simpler, fixed-point apparatus. It is expected that such a set of reference-standard resistance thermometers would be calibrated, and that routine calibrations of customer thermometers on the ITS-90 would be by comparison with these reference thermometers. The reference thermometers would be checked occasionally against the defined ITS-90. It is hoped that resistance thermometer devices will be more reproducible than the ability to realize the defined ITS-90. Depending upon the design of the cryostat, the defined ITS-90 may lack the desired reproducibility when realized in a multi-task apparatus of high complexity. In order to achieve the best realization of the ITS-90, it may be more practical to limit the number of defining fixed points in a single cryostat block.

The greatest problem in realization of the fixed points and in calibrations of capsule thermometers is ensuring that the multi-task or a "single-task" cryostat block is isothermal. Depending upon the design, a thermal gradient can persist. The presence of ^3He , ^4He , e- H_2 , Ne, O_2 , and/or Ar gases in their respective chambers are expected to be beneficial in making the apparatus isothermal, but, the gases may be a source of thermal oscillation. (In designing an apparatus for low temperature gases, provisions should be made to avoid thermal oscillations in the gas.) The vapor pressures of Ne and Ar are high at their respective triple-point temperatures so that thermal equilibrium should be easily attained at their triple points.

For a practical cryostat block, the ^3He and ^4He CVGTs must connect thermally the ^3He and ^4He vapor-pressure scales and the fixed points of e- H_2 and Ne. Such a cryostat block will require six chambers (separate ^3He and ^4He vapor-pressure chambers, separate ^3He and ^4He CVGT chambers, e- H_2 vapor-pressure and e- H_2 triple-point chamber, and a Ne chamber) to realize the ITS-90 in the most satisfactory manner at and below the Ne triple point. This arrangement will permit a direct comparison of the different parts of the scale and/or calibration of thermometers. Since the combination of ^4He vapor-pressure thermometry and ^4He constant volume gas thermometry are redundant with ^3He vapor-pressure thermometry and ^3He constant volume gas thermometry, the ^4He systems are not required. Hence, the number of chambers required could be reduced to four and the ITS-90 could still be realized. It should be noted, however, that, depending upon the CVGT filling pressure, the dp/dT of a ^3He CVGT may be less sensitive than ^4He vapor-pressure thermometry. Since SPRTs can be calibrated only down to the argon triple-point temperature using the long-stem SPRT apparatus, it would be most practical and useful to include an oxygen triple-point chamber in the low-temperature system, thereby increasing the number of chambers to five. Also, since it is highly desirable to overlap calibrations obtained in a long-stem type SPRT apparatus with those obtained in a low-temperature apparatus, an argon triple-point chamber should be included. This increases the number of chambers for the low-temperature apparatus to six.

Although it is desirable to have as few tubes as possible going to the cryostat block in order to minimize temperature gradients in the block, one must build into the system enough redundant components to be able to check the system for proper and accurate operation. For example, although the CVGT is calibrated at only the triple-point temperatures of neon and hydrogen and at one point in the ^3He or ^4He vapor pressure range between 3.0 K and 5.0 K, the system should have the capability for the measurement of hydrogen vapor pressures at about 17 K and 20.3 K so that temperatures measured by means of vapor pressures and by the CVGT may be compared. Of course, if the system is operating properly, the temperatures measured by the two techniques should agree. Similarly, there should be the capability to measure the vapor pressures of both ^3He and ^4He so that temperatures measured with the CVGT in the range from 3 K to 5 K and by means of ^3He and ^4He vapor pressures may be compared for agreement. Also, it is desirable to design the CVGT for absolute gas thermometry measurements; the CVGT can check the consistency of the ITS-90 from about 3 K to 90 K.

3.1.3 REALIZATION OF THE VAPOR PRESSURE AND CVGT SCALES AT TEMPERATURES BELOW THE NEON TRIPLE POINT

Since measurement of pressure is common to both vapor pressure and CVGT measurements, it will be discussed later in this section (see sec. 3.1.3.5).

In vapor pressure measurements, it is important that cold spots be absent along the gas-pressure transmitting tube. If cold spots are present, the observed vapor pressure will reflect the temperature of the condensation at the cold spot instead of that of the bulk bath. A separate vacuum jacket around the tube will maintain a continuous heat flux to the sample bulb or bath and should free the tube of any condensation [24]. The vacuum jacket should also reduce the occurrence of thermal oscillation in the gas-pressure sensing tube. If thermal oscillations do occur, they may be suppressed by either one or a combination of

the following: increasing the volume of the external gas-pressure space at the ambient temperature, or by inserting a wad of wool or glass fiber or a piece of yarn in the gas-pressure sensing tube. The thermal oscillations may be suppressed also by "tuning" a variable volume device [36]. Thermocouples should be placed along the gas-pressure sensing tube in order to determine temperatures along that tube, the distribution of those temperatures being required to determine the aerostatic head correction.

The vapor pressure may be determined over the bath of bulk liquid ^3He , ^4He , or $e\text{-H}_2$ with which the thermometer to be calibrated is in thermal equilibrium. The measurement can be made also by using a separate, small sample bulb with which the thermometer is in good thermal contact. The latter method is preferred with the rather expensive ^3He and with $e\text{-H}_2$, which requires a catalyst for the equilibrium ortho-para conversion of the sample [2,58,91].

3.1.3.1 ^3He Vapor-Pressure Measurements

Because of the relatively high cost of the sample, vapor-pressure measurements are made with ^3He contained in a small volume of about 5 cm^3 . Likewise, the gas-pressure volume to the manometer should be kept relatively small, but large enough to avoid large thermomolecular pressure effects and thermal oscillations. Thermomolecular-pressure-effect corrections depend on the sensing tube diameter, surface condition of the tube, temperature difference, and pressure [49,71,102]. As mentioned above, thermal oscillations can be reduced by varying the gas-pressure volume at the ambient temperature or by introducing a wad of fiber or yarn (cotton, wool, or glass) in the gas-pressure tube.

In the past, ^3He contained significant amounts of ^4He and the observed vapor pressures of ^3He required corrections for its presence. In recent years, however, ^3He samples of 99.9995% purity have become available, eliminating the requirement for such corrections. At 0.65 K, the vapor pressure and the temperature derivative of the vapor pressure are 115.9 Pa and 1.08 Pa/mK, respectively. At the upper limit of 3.2 K, the vapor pressure and the temperature derivative of the vapor pressure are 101,662.1 Pa and 106.83 Pa/mK, respectively. The required pressure resolution that corresponds to 0.1 mK of vapor-pressure measurements varies from 0.108 Pa at 0.65 K to 10.7 Pa at 3.2 K.

Since the amount of ^3He in the cryostat is small, and since the amount of ^4He used in cooling is relatively large, every effort should be made to avoid contamination of the sample of ^3He by the ^4He through diffusion, particularly through any glass parts of the apparatus.

The sample bulb should contain enough ^3He that the liquid surface temperature and the cryostat block temperature can be correlated with the observed vapor pressure. The temperature of the cryostat block must be checked for consistency with the observed dp/dT of the vapor pressure at the temperature of measurement.

Aerostatic-head corrections depend upon the density of the gas in the pressure-transmitting gas tube. Thermocouples must be distributed along the tube in order to measure the temperatures required for calculation of these corrections.

3.1.3.2 ⁴He Vapor-Pressure Measurements

Since liquid ⁴He can be obtained easily, the vapor pressure can be determined above a bath of the liquid in which an apparatus containing the thermometer is immersed. Or, a technique using a small bulb of ⁴He sample, with the thermometer in good thermal contact, can be employed. The lower end of the gas-pressure tube should have a small orifice in order to reduce superfluid ⁴He film flow at temperatures below 2.1768 K [61,91]. The ⁴He sample bulb must be in thermal equilibrium with the cryostat block. The cryostat block temperature should be checked for consistency with the observed dp/dT of the vapor pressure at the temperature of measurement.

At the lower temperature limit of 1.25 K, the vapor pressure of ⁴He is 114.7 Pa and the temperature derivative of the vapor pressure is 0.76 Pa/mK. At the upper limit of 5 K, the vapor pressure and the temperature derivative of the vapor pressure of ⁴He are 194629.7 Pa and 146.53 Pa/mK, respectively. The required pressure resolutions of the vapor pressure that corresponds to 0.1 mK are 0.076 Pa at 1.25 K and 14.7 Pa at 5.0 K [37,38].

3.1.3.3 e-H₂ Vapor Pressure Measurements

The equilibrium composition of the two molecular states of hydrogen (ortho and para) is temperature dependent. The room temperature composition, about 75% ortho and 25% para, is referred to as normal hydrogen (n-H₂). On liquefaction, the composition slowly changes toward the equilibrium composition corresponding to its temperature. In the process, the heat of transition is released, resulting in the evaporation of some hydrogen. A catalyst, such as activated ferric hydroxide, hastens the equilibration. The catalyst must be placed in the sample chamber in order to ensure that the hydrogen has the appropriate equilibrium composition. Most of the conversion must be made before collecting the liquid in the sample chamber since the heat of conversion (1064 J/mol) from the ortho to the para molecular state is larger than the heat of vaporization (900 J/mol) of normal hydrogen. The normal boiling point of e-H₂ (equilibrium composition: 0.21% ortho and 99.79% para) is about 0.12 K lower than that of n-H₂. The temperatures near 17.035 K and 20.27 K are determined from vapor-pressure measurements near 33,321.3 Pa and 101,292 Pa, respectively [2,31,58].

3.1.3.4 Constant Volume Gas Thermometry

Some of the following precautions and corrections that are applicable to absolute constant-volume gas thermometry should be included in the calibration of the CVGT at the three specified temperatures of calibration:

1. The volume of the gas bulb should be sufficiently large relative to the gas-pressure-line volume to minimize the error in correcting for the "dead space." On the other hand, the diameter of the gas-pressure line should not be so small as to cause large thermomolecular pressure corrections.
2. The temperature coefficient of volume expansion and the pressure expansion of the gas bulb should be known accurately. (It is desirable to check the calibration by using the CVGT in the absolute mode.)

Table 6. The effect of pressure on the temperatures of the defining fixed points. The reference pressure for the equilibrium states of freezing and melting points is one standard atmosphere (101,325 Pa). Triple points have the vapor pressure of the material when the solid, liquid and vapor phases are present in equilibrium

Material	T_{90}	<u>Pressure Effect of Fixed Point</u>	
		K Pa ⁻¹ x10 ⁸ *	mK/(meter of liquid)
e-H ₂ TP	13.8033	34	0.25
Ne TP	24.5561	16	1.9
O ₂ TP	54.3584	12	1.5
Ar TP	83.8058	25	3.3
Hg TP	234.3156	5.4	7.1
H ₂ O TP	273.16	-7.5	-0.73
Ga MP	302.9146	-2.0	-1.2
In FP	429.7485	4.9	3.3
Sn FP	505.078	3.3	2.2
Zn FP	692.677	4.3	2.7
Al FP	933.473	7.0	1.6
Ag FP	1234.93	6.0	5.4
Au FP	1337.33	6.1	10.
Cu FP	1357.77	3.3	2.6

* Equivalent to millikelvins per standard atmosphere.

3. In order to be able to calculate the aerostatic head correction, the temperature distribution along the connecting gas-pressure transmitting tube (capillary) must be known. That temperature distribution may be determined by placing thermocouples along the tube.

4. The gas-bulb filling pressure should be sufficiently high to give an adequate dp/dT for measurement, but not so high as to require large corrections for non-ideality of the gas.

5. Higher pressures reduce the thermomolecular pressure gradients in the connecting gas-pressure tube.

6. The effect of adsorption can be reduced by designing the gas bulb so that the volume is large relative to the surface and by polishing the inside surface of the bulb.

For optimizing the CVGT design, the ideal gas law may be applied. Differentiating the ideal gas relation,

$$pV = nRT, \quad (32)$$

yields

$$dp/dT = Rn/V, \quad (33)$$

where p is the pressure of n moles of gas contained in a volume of V m³.

Equation (33) shows that the dp/dT sensitivity of the CVGT is directly related to the gas density n/V . Expressing the gas constant R as 8.31441 Nm/mol·K or 8.31441 Nm³/(m²·mol·K), the sensitivity dp/dT can be expressed in the units Pa/K. Thus,

$$dp/dT = 8.31441(n/V) \text{ Pa/K}, \quad (34)$$

where n/V is given in mol/m³. If a gas bulb of 1000 cm³ is filled to four atmospheres at 273.16 K, n/V would be approximately 178 mol/m³, and dp/dT becomes 1484 Pa/K. Since the resolution of many high quality mercury-manometer systems is about 0.03 Pa to 0.2 Pa, the temperature resolution is about 0.03 mK to 0.1 mK. It is to be noted that since

$$p/T = Rn/V, \quad (35)$$

the sensitivity dp/dT is "constant," independent of the gas bulb volume, as long as the gas density at the filling temperature is constant. Hence, the gas-bulb volume and the gas filling pressure should be chosen so that errors from the effect of dead space, gas non-ideality effects, and other effects are negligibly small. See references [6,13,49,60].

3.1.3.5 Pressure Measurements

Efforts have been made to minimize the requirement of highly-precise and accurate pressure measurements in the realization of the defining fixed points of the ITS-90. The fixed points involving freezing and melting require knowledge of the pressure only within the significance of the relatively small pressure effect (cf. table 6). Accurate pressure measurements are required, however, to realize the vapor-pressure-temperature scales of ³He and ⁴He in the range 0.65 K to 5.0 K, and to realize the vapor-pressure-temperature scale of e-H₂ close to 17.035 K and 20.27 K. To realize the CVGT scale using ³He or ⁴He gas in the range 3.0 K to the triple point of neon (24.5561 K), only accurate pressure-ratio measurements are required.

3.1.3.5.1 Mercury Manometry

Mercury manometry requires precise determination of the difference in height of the two mercury surfaces in a U-tube manometer. Traditionally, cathetometers have been used with a smallest imprecision of about 2 Pa. In recent years, the levels have been sensed, in conjunction with length standards, by capacitive and interferometric methods. The resolution of such mercury manometry systems is about 0.05 Pa [19,50,52,81]. (Note: the NIST manometry resolution has been reported [50] to be about 0.0013 Pa.) For accurate pressure measurements, it is necessary to know the density of mercury (which is pressure and temperature

dependent), the capillary depression at the mercury meniscus, the vapor pressure of mercury, the aerostatic head difference of the pressure transmitting gas or gases, and the local acceleration due to gravity. At one standard atmosphere, uncertainties of absolute pressure measurements of about 3 ppm and pressure ratios of about 1 ppm have been reported. See references [19,50,52,81].

3.1.3.5.2 Oil Manometry

The techniques and the requirements of oil manometry are similar to those of mercury manometry.

3.1.3.5.3 Piston Gauges (Pressure Balances)

The pressure balanced by a dead-weight piston gauge is obtained from the mass of the piston and the applied weights, and the effective area of the freely rotating piston inside a closely-fitting cylinder. For determination of the absolute pressure, the gauge must be enclosed and evacuated by a high capacity pumping system to minimize the back pressure from the gas leaking between the piston and the cylinder [13,60,81,96]. The local acceleration due to gravity must be known accurately. Corrections must be applied for the effect of the streaming gas and for any back pressure. It is advisable to check the readings of the piston gauge against a primary mercury manometer. Also, the variation of the effective area with pressure must be determined with a mercury manometer. The aerostatic head of the manometry system will change as gas leaks between the piston and the cylinder causing the piston to sink deeper into the cylinder. The position of the piston may be maintained by automatically pumping more gas into the system. A resolution of 1 ppm [13] and an uncertainty of about 15 ppm have been reported in the pressure range 2 kPa to 200 kPa [63,81].

3.1.3.5.4 Diaphragm Pressure Detector

The diaphragm pressure detector consists of a thin metal disk clamped under tension between two flat electrodes which form two capacitors, with the disk common to both capacitors. Any pressure differential across the metal disk causes the disk to deflect, increasing the capacitance on one side while decreasing the capacitance on the other side. This change is detected by capacitance bridge techniques. Instruments for absolute pressure measurements are available; however, they require periodic recalibrations to achieve uncertainties of 1 to 5 parts in 10^4 of the readings.

The diaphragm pressure detector is used in high precision manometry as pressure balance detectors, i.e., with the pressures equal on both sides of the diaphragm. The diaphragm pressure balance detector separates the gas of the apparatus (vapor pressure apparatus or GVGT) from the counter-balancing gas of which the pressure is determined.

The resolution of diaphragm gauges has been reported [13] to be about 0.002 Pa. Instability due to different pressures, hysteresis, temperature effects, and other causes may decrease the resolution to 0.02 Pa in actual pressure measurements [13].

3.1.3.5.5 Thermomolecular Pressure Difference

Thermomolecular pressure differences occur at low gas pressures in tubes with temperature gradients when the tube diameter is not much larger than the mean free path of the gas. The pressure difference depends upon the gas, the temperature of the gas, the diameter of the tube, the tube material, and the surface condition of the tube. The best procedure is either to use a sufficiently large tube to minimize the thermomolecular pressure difference or to experimentally determine the difference by comparing the pressures between the small diameter tube being used in the cryostat and a large diameter tube [49,71,102].

3.2 REALIZATION OF THE FIXED POINTS OF THE ITS-90

3.2.1 EFFECT OF IMPURITIES

Except for the vapor-pressure-temperature points of helium and equilibrium hydrogen, the fixed points of the ITS-90 are freezing points, melting points, or triple points. The vapor-pressure measurements with ^3He , ^4He , and e- H_2 must be performed with sufficiently pure samples to minimize the effects of impurities. The principal components of air impurity would be frozen. Neon in hydrogen, however, causes positive deviations from ideal behavior [93,97]. In the vapor pressure measurements of ^4He , it is very likely that the ^4He will be pure but ^3He may contain some ^4He . For such a circumstance, Roberts, Sherman and Sydoriak described a procedure for correcting for the presence of ^4He in ^3He [90].

The temperatures of freezing points (liquid-solid or liquid-solid-vapor equilibrium points) of substances are usually lowered by the presence of an impurity. This sometimes, however, is not the case when that impurity is soluble in both the liquid and the solid phases of the major component. If a given impurity is known to be present or is suspected, one must consult the literature on the heterogeneous phase data of metal and non-metal systems to estimate the possible effect of that impurity on the freezing point [39,51,88]. (Note: often in the analysis of the effect of impurities on freezing points, the impurity is assumed to be nonvolatile.)

Assuming that the ideal solution law holds and that the impurities remain in liquid solution, with no concentration gradients, then as the major component slowly freezes, the depression in the freezing point, relative to the freezing point of the 100% pure material, is directly proportional to the overall impurity concentration divided by the "first cryoscopic constant." This is expressed as:

$$T(\text{pure}) - T(\text{obs}) = x_2/A. \quad (36)$$

In eq (36), $T(\text{obs})$ is the observed freezing point of the particular sample being investigated, $T(\text{pure})$ is the freezing point of the 100% pure material, x_2 is the mole fraction impurity concentration, and A is the first cryoscopic constant. A is given by the relation:

$$A = L/R[T(\text{pure})]^2, \quad (37)$$

Table 7. Latent heats of fusion and first cryoscopic constants of defining fixed-point materials

Substance	Fixed Point Temperature	Latent Heat of Fusion	First Cryoscopic Constant
	T/K	kJ/mole	K ⁻¹
e-H ₂	13.8033	0.117	0.0739
Ne	24.5561	0.335	0.0668
O ₂	54.3584	0.444	0.0181
Ar	83.8058	1.188	0.0203
Hg	234.3156	2.292	0.00502
H ₂ O	273.16	6.008	0.00968
Ga	302.9146	5.585	0.00732
In	429.7485	3.264	0.00213
Sn	505.078	6.987	0.00329
Zn	692.677	7.385	0.00185
Al	933.473	10.79	0.00149
Ag	1234.93	11.30	0.000891
Au	1337.33	12.364	0.000831
Cu	1357.77	13.14	0.000857

where L is the molar heat of fusion and R is the molar gas constant. (Note: eq (36) is an approximation. A more complete expression includes secondary cryoscopic constants. The term "first cryoscopic constant" is used here for distinction. Also, in some cases, the term "cryoscopic constant" refers to the reciprocal of eq (37) and in other cases, to the effect of impurities per liter or kilogram of solvent.) The first cryoscopic constants of metals are relatively smaller than those of molecular substances and of the "cryogenic" gases (³He, ⁴He, e-H₂, Ne, O₂, and Ar). Referring to eq (36), zinc, which has a first cryoscopic constant of 0.0018/K, requires an overall impurity concentration of approximately 2 parts in 10⁷ for the temperature of the half-frozen sample to be depressed by 0.0001 K, relative to the liquidus point. On the other hand, argon, with a first cryoscopic constant of 0.0203/K, requires an impurity concentration close to 2 part in 10⁶ for the same temperature depression. Table 7 lists the heats of fusion and the first cryoscopic constants of substances specified for the defining fixed points. It is the usual practice at NIST to calibrate SPRTs during the first 50% of the freeze.

3.2.2 TRIPLE POINTS OF e-H₂, Ne, O₂, AND Ar

3.2.2.1 GENERAL CONSIDERATION OF APPARATUS DESIGN

The cryogenic fixed points (triple-points of pure gases: equilibrium hydrogen, natural neon, oxygen, and argon) are best realized in a calorimetric type apparatus designed for calibrating capsule-type thermometers (SPRTs, RIRTs, germanium resistance thermometers (GRTs), and others) [1,2,17,18,20,21,41,47,58,59,78,79,80]. During calibration of the thermometers,

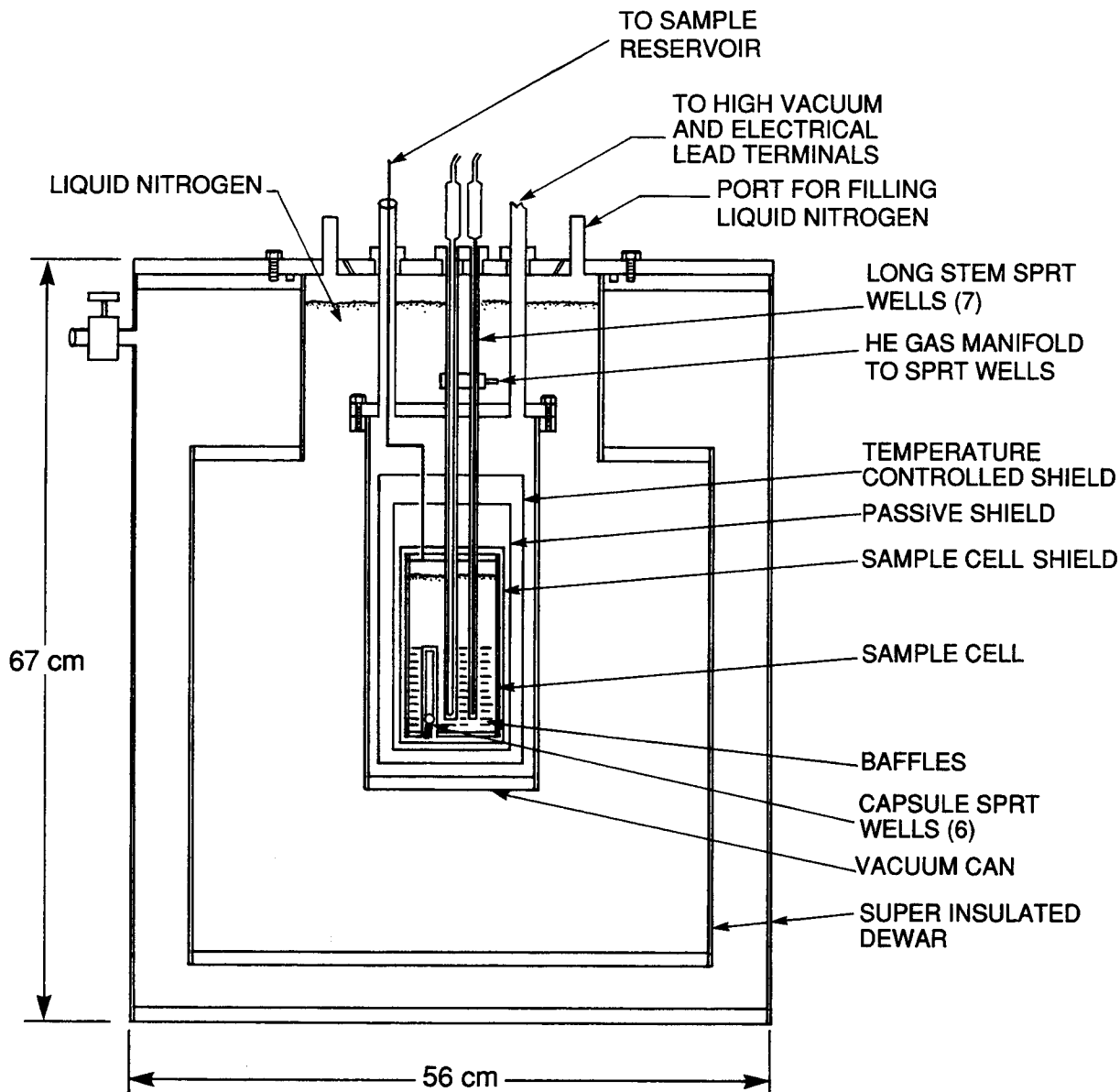


Figure 4. A schematic drawing of the NIST argon triple-point apparatus for calibrating seven long-stem SPRTs and six capsule SPRTs. Six long-stem SPRT wells surround a central SPRT well, which is large enough to accommodate a holder for calibrating a capsule SPRT. At the bottom of the sample cell, six capsule SPRT wells are circularly arranged between the long-stem SPRT wells.

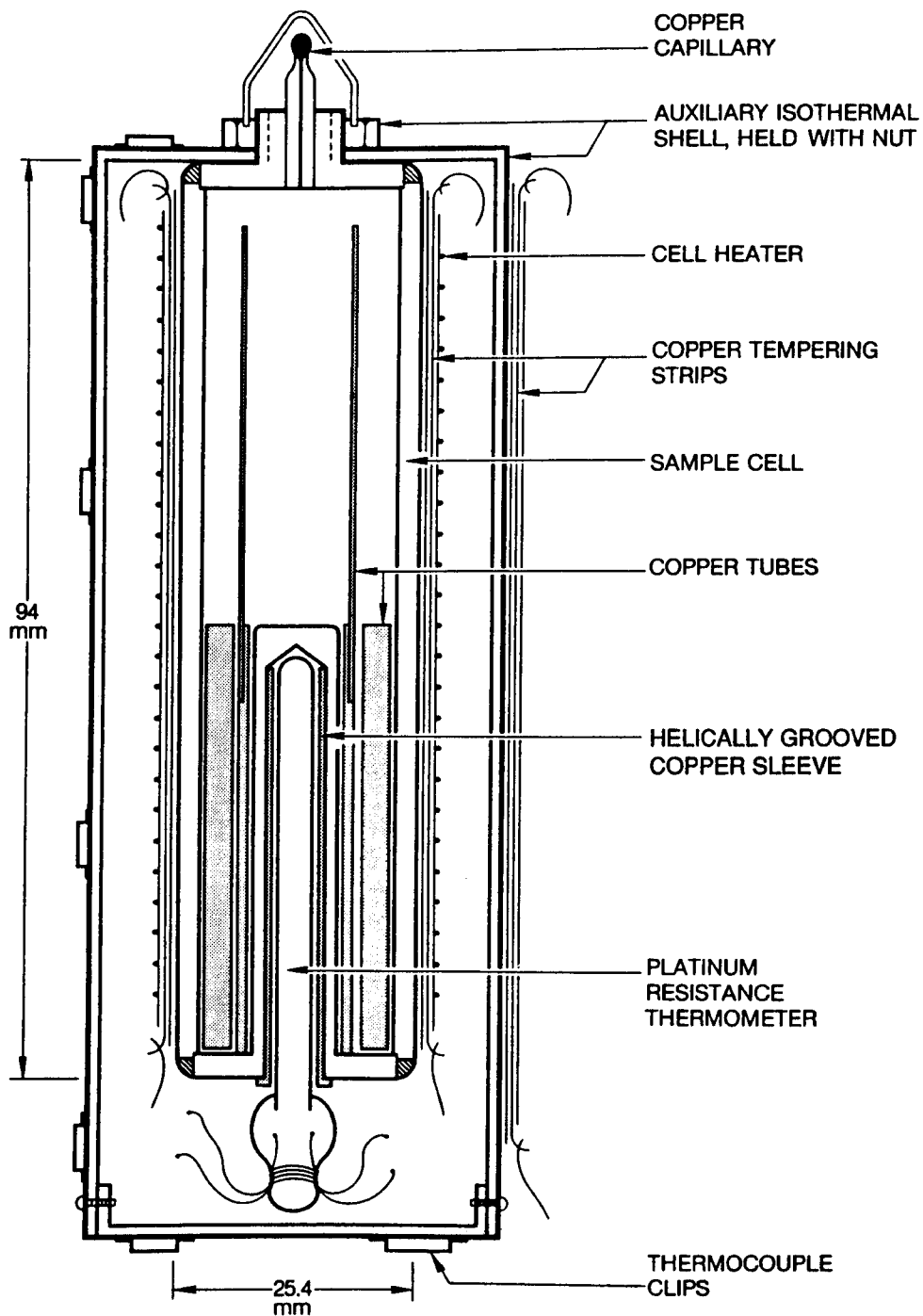


Figure 5. A sealed cell suitable for containing cryogenic gases at high pressures. This cell of 20 cm^3 volume was filled to 100 atmospheres with pure oxygen and used to realize the triple point of oxygen. Another cell of the same outer dimensions, but of 16 cm^3 volume and with wells for three capsule SPRTs, was filled to 163 atmospheres with oxygen and also used to realize the triple point of oxygen [47].

the calorimeter system thermally isolates the vessel containing the pure gas sample and the thermometers. The capsule thermometers should be installed in close-fitting wells of the sample vessel, using stopcock grease to enhance the thermal contact. The wells should be vented for easy installation and subsequent removal of the thermometers since such thermometers are sensitive to shock. The wells can be vented by designing the well tubes to extend completely through the sample cell or by machining a small groove along the length of the well wall. The number of wells in the vessel is limited only by the practical size of the vessel and of the calorimeter system. On the other hand, for large vessels, larger temperature gradients should be expected. The leads to the thermometers should be tempered on the sample vessel. (Note: the term "temper" refers to a process whereby sections of the leads or of the protective sheaths of long-stem SPRTs are placed in "steady-state thermal equilibrium" with selected parts of the apparatus.)

Since the triple point of argon is about 6 K above the normal boiling point (NBP) of nitrogen and since liquid nitrogen is readily available in large quantities, long-stem type SPRTs can be calibrated at the argon triple point in an apparatus cooled by liquid nitrogen. The apparatus should be designed to cool the upper part of the protective sheath of the long-stem SPRTs to liquid nitrogen temperatures, and then to heat the intermediate section of the sheath above the sensing element to the argon triple point so that the sensing coil will be in thermal equilibrium with the argon at its triple point [42]. See figure 4 for a schematic of such an apparatus presently in use at the NIST.

Sample vessels for the cryogenic fixed points could be ruggedly constructed for high pressures and sealed with a suitable amount of the pure gas [41,79]. These "sealed-sample vessels" can be easily installed and removed from the calorimeter for replacement of thermometers and also to be transported to other laboratories for comparison (see fig. 5). The amount of gas that can be sealed in such vessels, however, is rather limited and, hence, the calorimetric system must be operated with sufficient adiabatic control that the small amount of heat of fusion of the sample is adequate to realize the triple point and then calibrate the thermometers. Also, since the amount of sample gas is small, extra care must be taken to clean the vessel thoroughly before filling. The recommended procedure is to bake the vessel at high vacuum and then purge many times with the sample gas before finally filling and sealing the cell [41,47,79].

The vessel for a cryogenic fixed point can be installed in the calorimeter and connected by a small diameter tube to a source of pure gas [1,2,31,32,44,58,59]. In this design, enough condensed liquid could be used to nearly fill the vessel and, thus, to provide an abundant supply of heat of fusion for calibration of thermometers. The tube from the vessel must be connected to an "external expansion volume" of appropriate size so that when the system is at ambient temperature the pressure is not excessive. The vessel could also be connected to an external rugged container into which all or nearly all of the sample can be transferred by cooling, and then contained by a high-pressure valve. Since under these conditions the sample vessel would not be subjected to high pressures, it can be constructed of thin copper parts. With appropriate gas handling and cleaning provisions, the same vessel could be used with all of the reference gases, stored in separate external rugged containers, and the thermometers calibrated at the fixed points of the gases without the necessity

of having to remove the thermometers from the vessel between fixed-point determinations. On the other hand, the "sample vessel" can have separate chambers for each of the gases. In the latter design, separate tubes for the gases must enter the calorimeter system. Although each of the chambers of a "multi-chamber sample vessel" would be relatively small, the amount of sample that could be condensed inside each chamber would still be more than that which is normally used with the high pressure "sealed-sample vessel." Similar to the procedure used in filling sealed-sample vessels, a thorough baking, pumping, and purging procedure before filling should be followed with permanently installed vessels.

3.2.2.2 REALIZATIONS OF THE TRIPLE POINTS AND THEIR APPLICATION TO CALIBRATION

The procedure for realizing a triple point of the cryogenic gases is to first completely freeze the sample. If the triple point is being realized for the first time with the apparatus, the sample should be cooled sufficiently below the triple point to determine the heat capacity of the system (sample, vessel, and thermometers) from about 5 K to 20 K below (depending on the gas) to about 20 K above the triple point, and to determine the heat of fusion of the sample during the same series of measurements [41,47]. (Note: check thermometers must be calibrated along with the test thermometers. The measurements on the check thermometers will serve to guide the heating process during the calibration, as well as to provide measurement statistics.)

After cooling to the required low temperature, the vessel should be thermally isolated by placing it under continuous adiabatic control. Then the following series of measurements should be performed:

1. the equilibrium temperature should be observed with the check thermometer,
2. a measured amount of electrical energy should be added to the system,
3. a new equilibrium temperature should be established and measured,
4. steps 2 and 3 should be repeated until three heat capacity points are obtained below the triple point,
5. then, the sample should be completely melted by introducing a measured amount of heat,
6. next, the equilibrium temperature just above the triple point should be measured,
7. then, three additional heat capacity points should be obtained above the triple point in accordance with steps 2 and 3.

From the knowledge of the eight equilibrium temperatures (four below the triple point and four above the triple point) and the measured amounts of electrical energies added, the heat capacities of the system below and above the triple point, and the heat of fusion, are calculated. If Q joules are added to the system from an initial equilibrium temperature T_i just below the triple point to heat the system to a final equilibrium temperature T_f just above the triple point, the heat of fusion L is:

$$L = Q - C_s(T_o - T_i) - C_l(T_f - T_o), \quad (38)$$

where C_s and C_l are the mean heat capacities in the temperature intervals in the solid and liquid phases, respectively, and T_0 is the triple-point temperature.

For calibration of SPRTs, the sample should be completely frozen for the second time and the temperature set at about 1 K below the triple point, the sample thermally isolated, and the equilibrium temperature measured. From the knowledge of the previously determined heat capacity of the system below the triple point and of the heat of fusion, add enough electrical energy to melt about 10% of the sample. If T_1 is the initial equilibrium temperature just below the triple point, the required amount of electrical energy Q_1 to melt 10% of the sample is:

$$Q_1 = 0.1L + C_s(T_0 - T_1). \quad (39)$$

Once the system comes to equilibrium, measure the resistances of all of the thermometers. Repeat the measurements at 20%, 40%, 60%, 70%, and 80% melted. If the sample is about 99.9999% pure, all measurements on each thermometer throughout this melted range should agree to within 0.1 mK to 0.2 mK.

In using a temperature fixed point, one must make corrections for the hydrostatic head of the liquid and for the gas pressure on the defined equilibrium state. Table 6 gives the dT/dp for the defining fixed points of the ITS-90, both in terms of the external gas pressure to which the fixed-point material is exposed and in terms of the column of liquid.

3.2.2.2.1 TRIPLE POINT OF EQUILIBRIUM HYDROGEN, 13.8033 K (-259.3467 °C)

Hydrogen gas samples of 99.9999% and higher purity are readily available. [The first cryoscopic constant of hydrogen is relatively high (0.0740/K). Consequently, the liquidus point of an ideal hydrogen solution of 99.9999% purity would be approximately 0.01 mK lower than that of 100% pure hydrogen. Except for helium and deuterium, all other impurities would be either frozen or in solution in very small amounts.] The commonly used catalyst for converting ortho hydrogen to para hydrogen is hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{FeO} \cdot \text{OH}$). Other oxides of magnetic elements, either pure or mixed-metal, such as those of chromium, nickel, cobalt, and neodymium, also have been used as catalysts for ortho to para hydrogen conversion. The hydrated ferric oxide catalyst is prepared by mixing at about 30 °C relatively dilute solutions (about 2 molal) of ferric chloride and sodium hydroxide, with only a slight excess of sodium hydroxide, washing the resulting gelatinous $\text{Fe}(\text{OH})_3$ precipitate thoroughly with distilled water, air drying at 140 °C for 24 hours, vacuum baking at 110 °C for 16 to 20 hours, and back-filling with hydrogen while the catalyst is still hot [7,104]. The catalyst is activated by flowing hydrogen through it for about 4 hours while the catalyst is maintained at a temperature of about 150 °C. The sample vessel and ancillary components should be designed to permit the whole of the hydrogen sample to come into contact with the catalyst at the equilibrium temperature. See references [2,31,58].

3.2.2.2.2 TRIPLE POINT OF NATURAL NEON, 24.5561 K (-248.5939 °C)

Neon gas samples of 99.999% purity are commercially available. Samples of higher purity may be obtained by special arrangement with the supplier. The

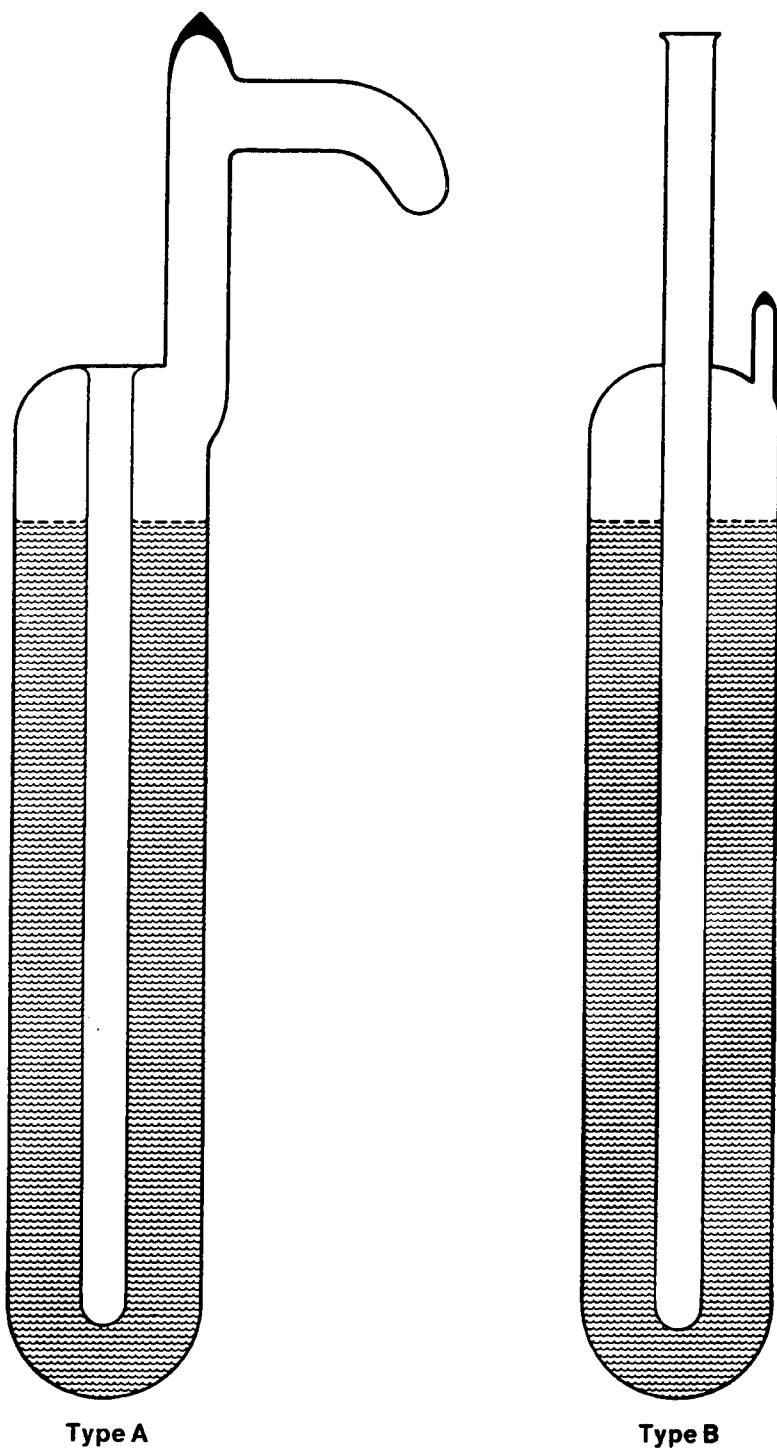


Figure 6. Two types of triple point of water cells with wells for platinum resistance thermometers. The cells contain pure air-free water. The thermometer wells are made of precision-bore tubing.

principal impurities are CO, H₂, He, and N₂. The CO and the N₂ impurities can be frozen out by slowly flowing the sample through a coiled tube immersed in liquid neon; the H₂ and the He impurities can be removed by freezing the neon sample in liquid hydrogen and pumping, with care so that the lighter isotopes of neon are not preferentially removed. [The first cryoscopic constant of neon is 0.0668/K. Consequently, the liquidus point of an ideal neon solution of 99.999% purity would be approximately 0.1 mK lower than that of 100% pure neon.] The purified sample should be collected in a clean stainless-steel cylinder by cooling the cylinder in liquid hydrogen (or cooled with liquid helium). If desired, the purified sample can be collected directly in the cooled sample vessel. See references [1,79].

3.2.2.2.3 TRIPLE POINT OF OXYGEN, 54.3584 K (-218.7916 °C)

Oxygen gas samples of 99.999% purity are commercially available. Accurate chemical analysis of oxygen is difficult and, therefore, the claimed purity may not be correct. Unknown or undetected impurities are chemically less reactive than oxygen, e.g, the noble gases, and, in particular, argon, which forms a peritectic with oxygen. Samples of purity greater than 99.999% may be obtained by special arrangement with the supplier. [The first cryoscopic constant of oxygen is 0.0181/K. Consequently, the liquidus point of an ideal oxygen solution of 99.999% purity would be approximately 0.6 mK lower than that of 100% pure oxygen.] Careful preparation by thermal decomposition of potassium permanganate can yield samples of 99.9999% purity or better [47]. The oxygen sample should be stored in clean stainless-steel cylinders. See references [32,47,59,79,80].

3.2.2.2.4 TRIPLE POINT OF ARGON, 83.8058 K (-189.3442 °C)

Argon gas samples of 99.9999% purity or better are readily available. The usual impurities are the components of air, moisture, and hydrocarbons. [The first cryoscopic constant of argon is 0.0203/K. Consequently, the liquidus point of an ideal argon solution of 99.9999% purity would be approximately 0.05 mK lower than that of 100% pure argon.] To fill the sample vessel, the gas may be used directly or it may be dried first by slowly passing it through a coiled tube immersed in either liquid oxygen or a Dry Ice/ethyl alcohol mixture. See references [17,41,42,59,79,80].

3.2.3 TRIPLE POINT OF WATER, 273.16 K (0.01 °C)

The triple-point temperature of water is assigned the value 273.16 K on the Kelvin Thermodynamic Temperature Scale and also on the ITS-90. It is the reference temperature for resistance ratios in platinum resistance thermometry. The water used in preparing triple point of water cells is pure water of naturally-occurring isotopic composition. Figure 6 shows two commonly used types of triple point of water cells.

Triple point of water cells are usually prepared from river water that has been purified by chemical treatment and distillation. River water is expected to have concentrations of deuterium and the heavier isotopes of oxygen that are lower than that of ocean water. The extreme difference in the triple points of naturally-occurring water, including polar water, is given as 0.25 mK [100].

It is expected that differences among water triple-point cells of river water would be much smaller than 0.25 mK. (The isotopic composition difference between river water and ocean water [100] has been estimated to cause no more than a 0.050 mK difference in the triple-point temperature.) While the basic material is plentifully available, preparation of water triple-point cells requires a special effort [5,40]. Although the effect on the triple-point temperature is negligible, a trace of air always remains in most sealed triple point of water cells. When a cell at room temperature is gently inverted from one end to the other and a sharp "click" is produced through the water hammer action, the amount of gas in the cell will have negligible influence on the triple-point temperature.

3.2.3.1 REALIZATION AND APPLICATION OF THE TRIPLE POINT OF WATER

In preparation for producing an ice mantle that is required for realizing the triple-point temperature of water, the thermometer well of the cell is wiped thoroughly dry, sealed with a rubber stopper, and the cell placed in an ice bath to cool to a few degrees above the ice point. When the cell has been cooled in this manner, an ice mantle of fairly uniform thickness can be obtained. Withdraw the cell from the ice bath, set it upright on a stand, and place one drop of ethyl alcohol at the bottom of the well. Introduce small amounts of crushed Dry Ice into the bottom of the well and continue to do so until a thick mantle is formed at the bottom. Then, fill the well with crushed Dry Ice to the water level of the cell. Continue to add crushed Dry Ice to the well so as to maintain the level of Dry Ice at the water level. If the Dry Ice level becomes low before more is added, the ice mantle may crack. If the cell were precooled as indicated above, a solid ice bridge may form at the water level. If such a bridge forms, melt it immediately with heat from the hands while gently shaking the cell. The solid ice bridge can completely seal the cell at the top and any subsequent formation of ice could produce enough pressure to rupture the glass cell. When a mantle of approximately the desired thickness (4 to 8 mm) is formed, stop adding Dry Ice, replace the cell in the ice bath with the well opening slightly above the water surface of the ice bath, and leave the cell there until all of the Dry Ice evaporates. Then, fill the well with ice water and store the cell in an ice bath or ice pack for a day before using it. When the ice mantle is frozen by using Dry Ice, a process that usually requires less than one hour, the strains in the ice cause the "triple-point temperature" to be about 0.2 mK low. These are removed by letting the mantle anneal for one day.

Other methods can be used also to prepare the ice mantle. With ethyl alcohol in the thermometer well, any "cold finger" technique can be used. This technique includes successively inserting liquid nitrogen cooled rods, using a closed-end tube containing crushed Dry Ice, or using a heat-pipe cooler. These methods require more time to freeze the mantle, but the strain produced in the ice will be less than those produced by the Dry Ice technique.

After the strains in the ice mantle have been relieved by storing the cell in an ice bath for at least one day, insert momentarily a glass rod into the well in order to melt a thin layer of ice next to the well. This forms an ice-water interface immediately adjacent to the thermometer well. The test for this "inner melt" is made by giving the cell a rotatory impulse to determine whether

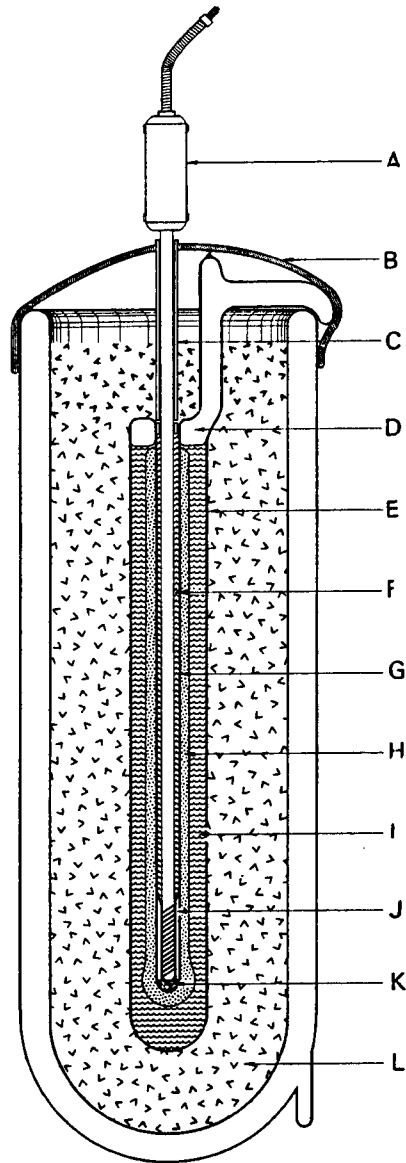


Figure 7. An SPRT in a Type A triple point of water cell immersed in an ice bath.

A -- platinum resistance thermometer, B -- heavy black felt to shield against ambient radiation, C -- polyethylene tube for guiding the SPRT into the thermometer well (the tube has a small hole near the top of the thermometer well to allow water, but not ice, to enter the tube.), D -- water vapor, E -- borosilicate glass cell, F -- water from the ice bath, G -- thermometer well (precision bore glass), H -- ice mantle, I -- air-free water, J -- aluminum bushing with internal taper at the upper end to guide the SPRT into its close-fitting inner bore, K -- polyurethane sponge for cushioning the SPRT, L -- finely divided ice and water.

the ice mantle rotates freely about the axis of the thermometer well. The outer ice-water interface guards and thermally stabilizes the inner ice-water interface temperature that is measured with the SPRT.

Figure 7 shows a triple point of water cell immersed in an ice bath with an SPRT inserted into the thermometer well. An SPRT should be precooled in a glass tube of water in an ice bath before it is inserted into the triple-point well so that the thickness of the water layer next to the thermometer well will not become excessive. Also, the time required for the SPRT to come into thermal equilibrium will be shortened. Heavy felt cloth should be used to cover the ice bath in order to prevent ambient radiation from entering the bath and reaching the thermometer element, which otherwise would cause the thermometer to give a slightly high (erroneous) reading. A plastic foam cushion should be placed at the bottom of the thermometer well to protect the well and the SPRT. Since water is a poor thermal conductor, a close fitting aluminum sleeve should be used to enhance the thermal conduction.

The thermometer current should be imposed immediately after insertion of the SPRT into the cell so that readings can be made under conditions of steady-state self heating. Five to ten minutes or longer may be required before steady-state conditions are reached. To avoid errors due to variations in the self heating that arise from variations in the thermal contact of the thermometer with its surroundings, it is best to read the SPRT at two currents and extrapolate the readings to zero power in the SPRT.

3.2.4 FREEZING, MELTING, OR TRIPLE POINTS OF METALS: Hg, Ga, In, Sn, Zn, Al, Ag, Au, or Cu

The realization of metal fixed points requires the continuous presence of liquid-solid or liquid-solid-vapor phases in thermal equilibrium. With SPRTs, the liquid-solid interface, i.e., the equilibrium whose temperature is measured, must surround and must be as close to the temperature sensing element as possible. Since the first cryoscopic constants of metals are relatively low, the fixed-point metal samples should be at least 99.9999% pure. Figure 8 shows idealized liquid/solid equilibrium conditions inside fixed point cells used in freezing and melting experiments. Figure 9 shows a representative arrangement of an SPRT inserted inside a metal fixed point cell. Ideally, and similar to the water triple-point cell, an outer liquid-solid interface, which completely surrounds the inner interface, exists close to the container wall. This outer interface, which has a temperature very close to that of the inner interface, thermally protects and thermally stabilizes the inner interface. In freezing experiments, a layer of solid is first formed at the crucible wall, then a thin layer of solid is induced on the thermometer well by inserting cooling rods. As freezing advances, the outer interface approaches the inner interface until all of the material is solid. In melting experiments, a layer of liquid is first formed next to the crucible, then a thin layer of liquid is formed next to the thermometer well by inserting a warming rod or a long heater. As melting advances, the outer liquid/solid interface approaches the inner interface.

Since different furnace or bath designs are required for fixed-point cells operated at different temperatures, they will be discussed along with each of the fixed points, or references will be made to appropriate sources of

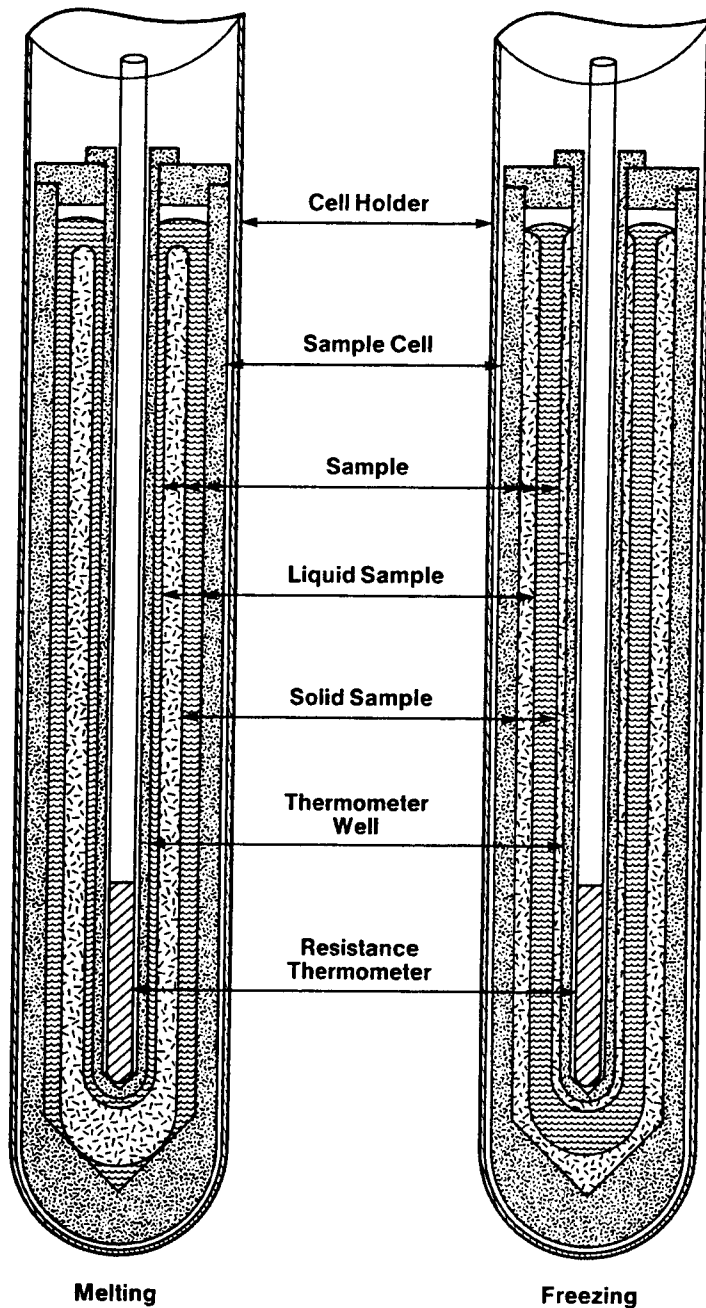


Figure 8. Idealized liquid/solid equilibrium conditions inside fixed point cells used in freezing and melting experiments. In freezing experiments, a layer of solid is first formed at the crucible wall, then a thin layer of solid is induced on the thermometer well by inserting cooling rods. In melting experiments, a layer of liquid is first formed next to the crucible, then a thin layer of liquid is formed next to the thermometer well by inserting a warming rod or a long heater. As melting advances, the outer liquid/solid interface approaches the inner interface.

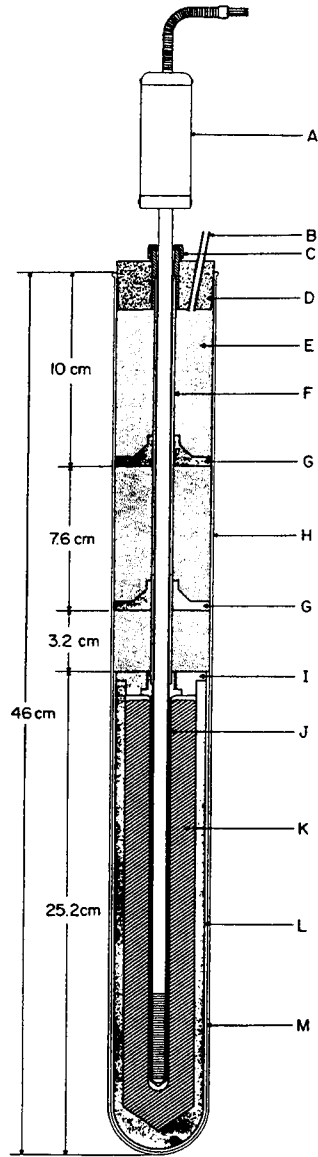


Figure 9. An SPRT in a metal freezing-point cell.

A -- platinum resistance thermometer, B -- to helium gas supply and pressure gauge, C -- thermometer gas seal with silicone rubber, D -- silicone rubber stopper, E -- thermal insulation (washed Fiberfrax), F -- thermometer guide tube [precision bore tube, ground (matt finish) to uniform outside diameter], G -- heat shunt (graphite) in close contact with F and with H, H -- borosilicate glass cell [precision bore tube ground (matt finish) to uniform outside diameter], I -- graphite cap (lid) for the graphite crucible, J -- graphite thermometer well, K -- metal sample, L -- graphite crucible, M -- thermal insulation (Fiberfrax paper) between the graphite crucible and the borosilicate glass cell.

descriptions.

In radiation thermometry, the liquid-solid phase of the metal fixed point must completely surround the blackbody radiator cavity.

3.2.4.1 CONTAINER MATERIAL

Containers for the fixed-point metals must not contaminate the metal sample, and the container material must be rugged enough to retain its integrity under thermal cycling between the temperature of use and ambient temperature. The container material preferably should be inert to air at temperatures of use; if not, e.g., graphite above about 200 °C, the container plus the fixed-point material must be protectively enclosed in an inert gas, such as nitrogen, argon, or helium, using either a borosilicate or fused silica glass envelope. It should be assumed that the fixed-point material itself will react chemically with air and, thus, the material must be protected.

3.2.4.2 METAL FIXED POINT DEVICES FOR CALIBRATING SPRTs

Figure 9 shows a representative fixed-point cell that can be used for calibrating long-stem type SPRTs. In the following sections, individual types will be described.

3.2.4.2.1 MERCURY TRIPLE POINT

3.2.4.2.1.1 MERCURY SAMPLE

On the ITS-90, the triple point of mercury (equilibrium phase state of mercury solid, liquid, and vapor phases) is assigned the value 234.3156 K (-38.8344 °C). Depending upon the choice of container material and operating procedure, it may be more practical to realize the mercury freezing point at one standard atmosphere, the value being 234.3210 K (-38.8290 °C). Mercury samples with impurity content of 1 part in 10^8 or less can be prepared by potassium hydroxide and nitric acid washings, followed by triple distillation [48]. The alkali and acid washings can be carried out by vigorously bubbling clean filtered air through the mixture of mercury and the alkali or the acid. To remove any remaining oxidizable impurities, the first two distillations should be carried out under reduced pressures with a fine stream of clean filtered air bubbling into the mercury in the distillation container. The third distillation should be done under high vacuum to remove the noble metals. With the high-purity mercury (99.999999%), both freezing and melting techniques give triple-point temperatures that agree to within ± 0.1 mK over most of the liquid-solid range. [The first cryoscopic constant of mercury is 0.00503/K. Consequently, the liquidus point of an ideal mercury solution of 99.999999% purity would be approximately 0.002 mK lower than that of 100% pure mercury.]

3.2.4.2.1.2 CONTAINERS FOR MERCURY

Any container material can be used with mercury that is sufficiently rigid and does not dissolve in, or chemically react with, mercury in the temperature range of storage and application. The choice will depend upon whether the mercury fixed-point cell is to be used at its triple point, at its freezing point, or

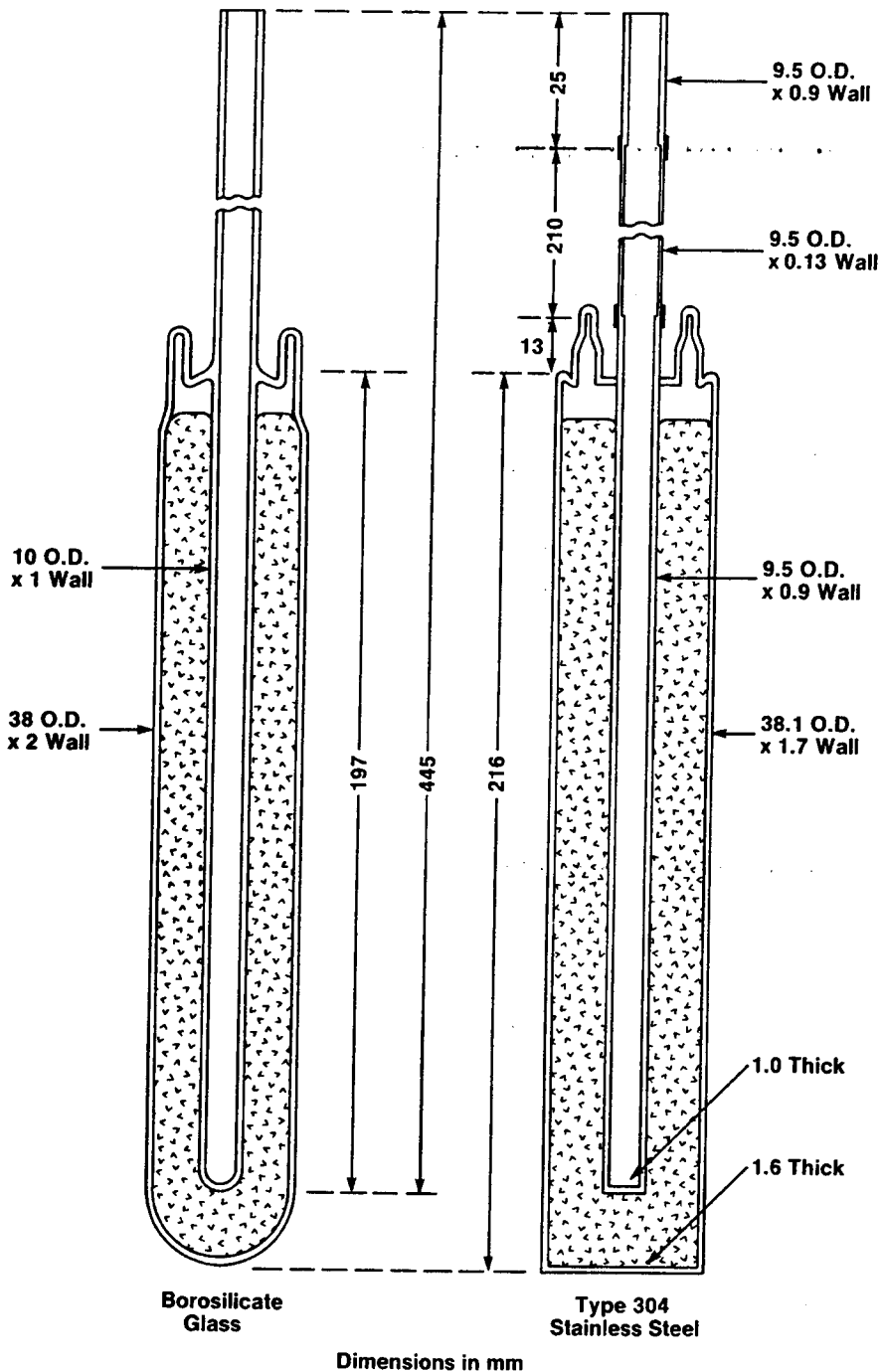


Figure 10. Two mercury triple-point cells, one constructed of borosilicate glass and one of Type 304 stainless steel. The two small-diameter tubes at the top facilitate the cleaning of the cells before filling and sealing. The glass cell is sealed by melting the small-diameter tubes, but the stainless steel cell is sealed by pinching flat the small-diameter tubes and electric-arc welding them, thereby severing them at the middle of the flat.

at either one.

3.2.4.2.1.3 METAL CONTAINERS

Mercury is capable of dissolving most metals, at least at the low levels of impurity content (<1 ppm) that are the permitted maxima for metal fixed points. Iron, nickel, chromium, and tantalum have been reported to be soluble at only 1 ppm or less; hence, stainless steel is an adequate container for mercury in most temperature standard applications [53,103]. (Note: the solubility of nickel in mercury may be close to the limit of 1 ppm.) Mercury triple-point cells can be prepared by pinching and welding the small diameter tubes used for cleaning, evacuating, and filling (see fig. 10).

3.2.4.2.1.4 CONTAINERS OF GLASS

It is expected that some metal impurities in glasses [single metal oxide (e.g., fused silica glass) or mixed metal oxides (e.g., borosilicate glass)] or "ceramics" can be leached out by mercury when the mercury is stored in them for many years. Traditionally, "soft glass" has been considered suitable for storing mercury [48]; however, soft glass, without special treatment, may be susceptible to breakage when thermally shocked. Borosilicate glass and fused silica glass are more practical choices for mercury containers. Figure 11 shows a borosilicate glass mercury triple-point cell inside a stainless steel holder.

3.2.4.2.1.5 CONTAINERS OF PLASTIC

Organic plastics, such as polyethylene, polytetrafluoroethylene (Teflon), or polytrifluorochloroethylene (Kel-F), all of which are free of metals, can be used to contain mercury and be used at the mercury freezing point. A stainless steel holder similar to that used for the glass mercury cell and for the stainless steel mercury cell (see fig. 11) or similar to the holder used for the indium cell (see fig. 12) could be used as the external holder for a plastic mercury cell. Although plastic cells have not been used yet in preparing mercury fixed-point cells, it would be practical and desirable to use plastic cells for realizing the mercury fixed point. Since the vapor pressure of mercury at room temperature is sufficiently high that mercury vapors can be transported under vacuum conditions, the vapors should be confined by an atmosphere of helium or other inert gases.

3.2.4.2.1.6 ASSEMBLY OF MERCURY CELLS

A purified mercury sample can be vacuum distilled into glass containers, with the glass filling tube then sealed under vacuum with a flame [43]. The mercury sample may be vacuum distilled into stainless steel containers and the filling tube pinched, and then cut and sealed using electric-arc welding techniques [43].

3.2.4.2.1.7 REALIZATION AND APPLICATION

When the total impurity content of a mercury sample is about one part in 10^8 , both freezing and melting techniques yield triple-point temperatures agreeing to within ± 0.1 mK over most of the liquid-solid range. A dual-stage

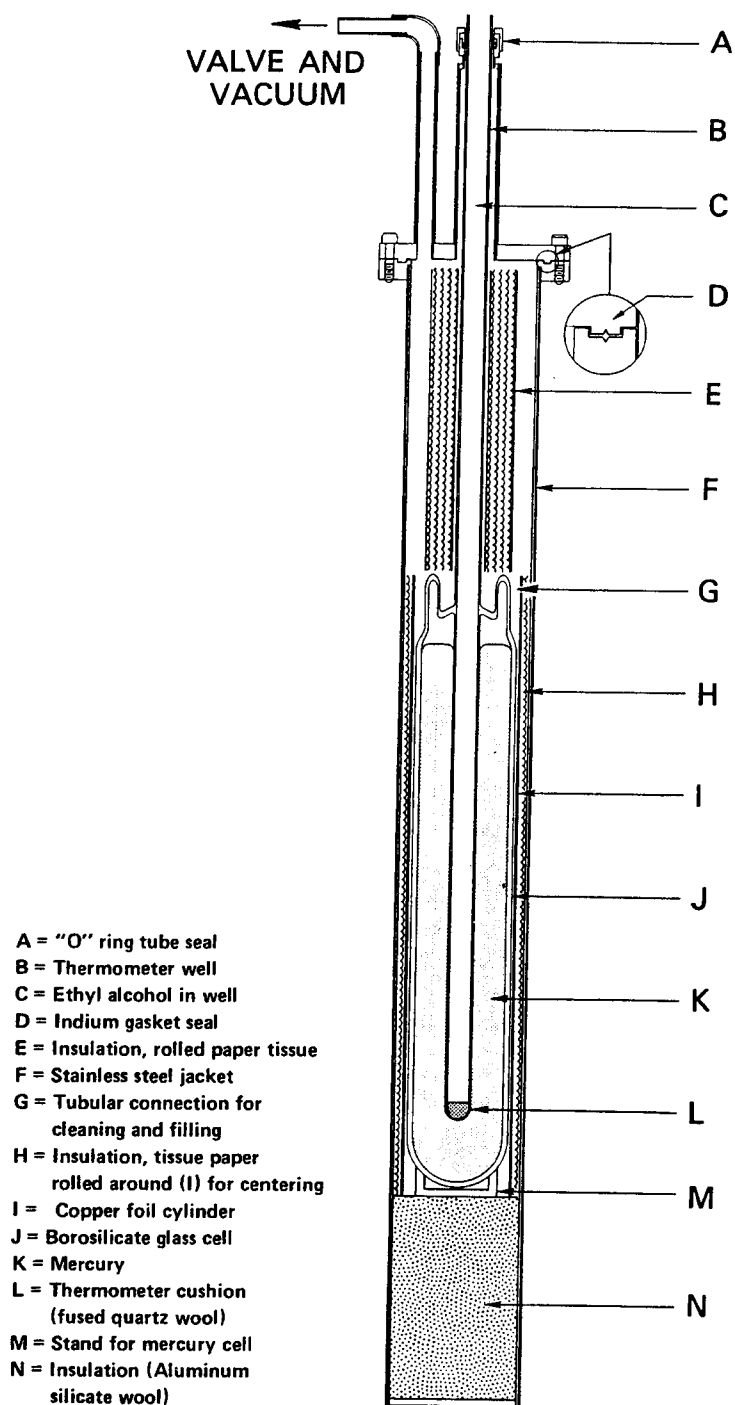


Figure 11. A borosilicate glass, mercury triple-point cell in a stainless steel container. A stainless-steel, mercury triple-point cell may also be mounted inside the stainless steel container. With the high-purity mercury sample, both freezing and melting techniques yield triple-point values agreeing to within ± 0.1 mK over most of the liquid-solid range.

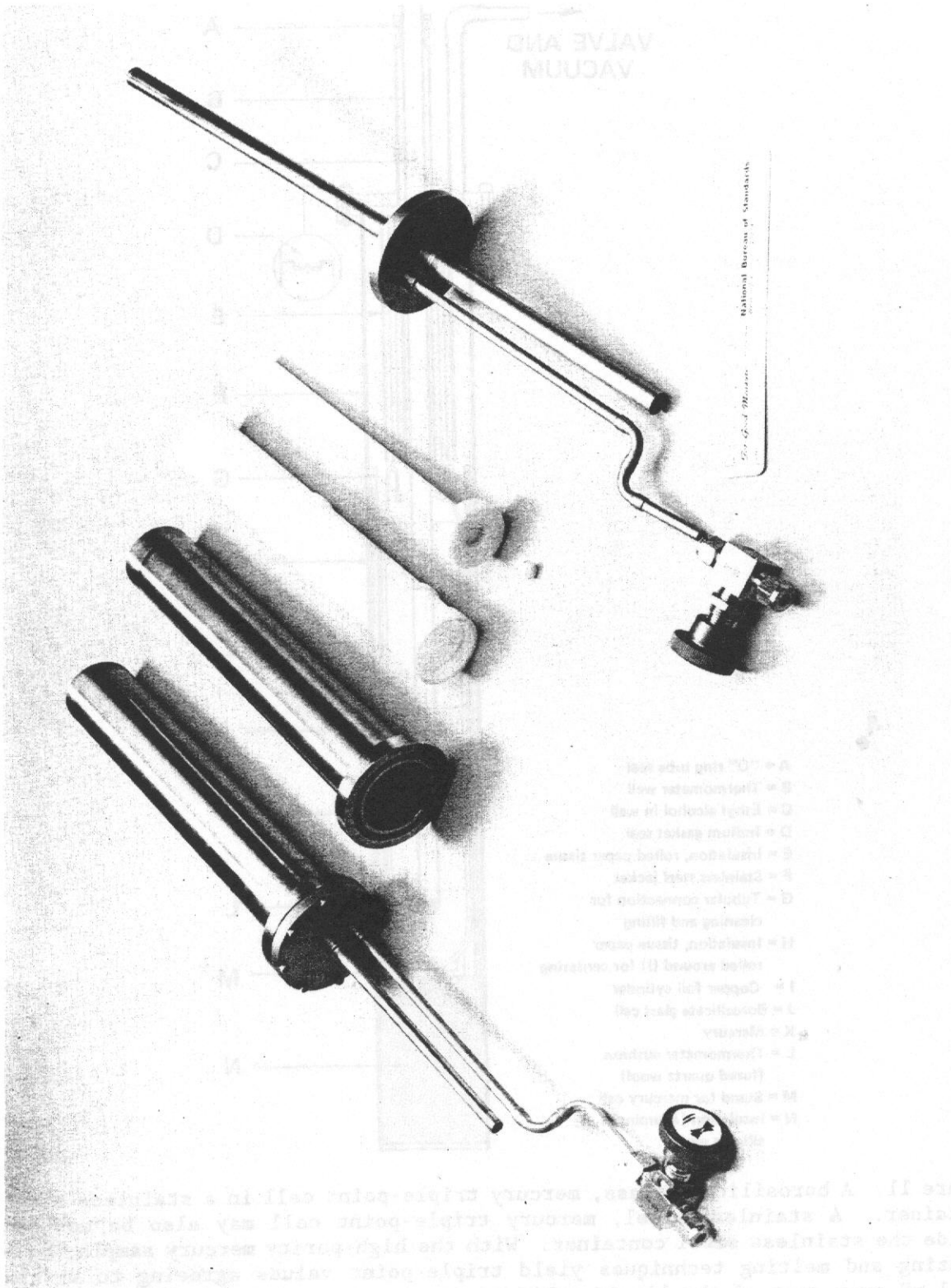


Figure 12. Photograph of an all-plastic indium cell and its stainless steel container.

refrigerator can yield a temperature near $-40\text{ }^{\circ}\text{C}$ and, hence, could be used for freezing mercury, but a much simpler stainless steel vacuum enclosure placed in a Dry Ice/ethyl alcohol mixture ($-78\text{ }^{\circ}\text{C}$) can reduce the freezing rate of mercury to give a freeze duration of about 10 hours or more with 2.2 kg of mercury, and that is perfectly adequate. Figure 11 shows such a stainless steel enclosure that has been used with a borosilicate-glass mercury cell at the NIST.

To start a freeze, fill the stainless steel enclosure that contains the mercury triple-point cell with dry air and immerse it in a Dry Ice/ethyl alcohol bath. Fill the thermometer well with ethyl alcohol and insert therein an SPRT for monitoring the temperature of the cell. Usually, mercury supercools about $6\text{ }^{\circ}\text{C}$ in a borosilicate glass cell but only about $3\text{ }^{\circ}\text{C}$ in a stainless steel cell. When recalescence is observed, evacuate the stainless steel holder. Remove the monitoring SPRT from the well and replace it with a thin-wall stainless steel tube that contains ethyl alcohol and that has been cooled in a tube of ethyl alcohol immersed in a Dry Ice/ethyl alcohol bath. Insert successively into the stainless steel tube two or three liquid-nitrogen cooled glass rods, for about 5 minutes each, in order to freeze a thin layer of mercury around the thermometer well. The purpose of the stainless steel tube is to collect the frost that forms on the rods when they are removed from the liquid nitrogen. Remove the stainless steel tube and replace it with the monitoring SPRT, which has been cooling in the tube of cold ethyl alcohol. Switch on the thermometer measuring current. (Note: it may be necessary to refill the thermometer well with a small amount of cold ethyl alcohol from the Dry-ice cooled tube before the monitoring SPRT is inserted into the well. The well should be completely filled with ethyl alcohol when the SPRT is in the well.) With the induced inner freeze around the thermometer well, temperature equilibrium is reached in about 5 minutes. After the resistance of the monitoring SPRT is read, other cooled SPRTs are successively inserted into the mercury cell and calibrated. The final reading in a cell is made with the monitoring SPRT in order to check the extent of the freeze. This final reading of the monitoring SPRT must agree with the initial reading to within $\pm 0.1\text{ mK}$. See reference [43] for more details on the calibration procedure at the mercury triple point.

3.2.4.2.2 MELTING POINT OF GALLIUM

The melting point of gallium is assigned a temperature of 302.9146 K ($29.7646\text{ }^{\circ}\text{C}$) on the ITS-90. Gallium of 99.99999% purity can be obtained commercially. At such high purity, both freezing and melting techniques should yield liquid-solid equilibrium temperatures that agree to within $\pm 0.1\text{ mK}$. Since the metal expands about 3% on freezing, plastic containers, such as polyethylene, polypropylene, or polytetrafluoroethylene, are the most suitable. These are sufficiently flexible at around $30\text{ }^{\circ}\text{C}$ to accommodate the volume change in the gallium. In assembling the gallium fixed-point cell, the supercooled metal can be poured directly into the container. A second more rugged container of Nylon, glass, or stainless steel should enclose the flexible container so that the pressure of the inert gas over the metal can be controlled at one atmosphere or be evacuated to observe the triple point. A gallium fixed-point cell, consisting of an all plastic container, that is used at the NIST is shown in figure 13. Since gallium supercools as much as $25\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$, depending upon the plastic material that is in contact with it, the most convenient method of observing its liquid-solid equilibrium temperature is the melting technique. [The first

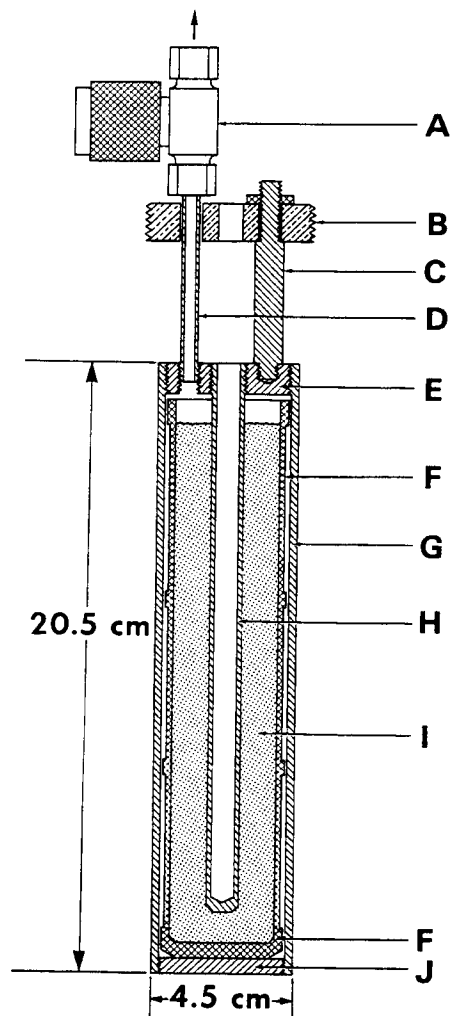


Figure 13. An all-plastic gallium melting/triple-point cell. The triple point is realized by using the melting technique. The cell is periodically evacuated through the valve.

A -- valve (Zytel), B -- bath lid (Plexiglas), C -- support rod (Nylon), D -- pumping tube (polyethylene), E -- cap (Nylon), F -- sample container (Teflon), G -- case (Nylon), H -- thermometer well (Nylon), I -- gallium metal, J -- base of the case (Nylon).

cryoscopic constant of gallium is 0.00732/K. Consequently, the liquidus point of an ideal gallium solution of 99.99999% purity would be approximately 0.01 mK lower than that of 100% pure gallium.]

3.2.4.2.2.1 REALIZATION AND APPLICATION

In order to solidify the gallium metal in a fixed-point cell, initially in the supercooled state (e.g., at room temperature), first insert successively two or three liquid-nitrogen-cooled copper rods into the thermometer well of the cell to induce nucleation, and then place the cell in an ice bath for about one hour or longer. The cell with the solidified gallium may then be placed in an oil bath at a temperature of about 40 °C to partially melt the sample to form an outer liquid-solid interface. To form a liquid-solid interface next to the thermometer well (an inner melt), the bath oil may be circulated through the thermometer well by pumping the oil through a tube placed in the well. After about 20 minutes in the hot oil bath, about 25% of the gallium will be melted. The inner liquid-solid interface can also be prepared by using an electric heater in the well. The amount of electric energy required, e.g., to form about a 1 mm shell of liquid around the thermometer well, can be calculated from the outer dimensions of the thermometer well and the heat of fusion of gallium (see table 7). The gallium cell is then securely mounted, completely immersed so that the thermometer well will be filled with the bath oil, in a stirred oil bath, controlled at a temperature about 10 mK above the liquid-solid equilibrium temperature (melting point or the triple point). Also, the cell can be immersed in a fairly close-fitting, oil-filled aluminum or copper block, controlled at a temperature about 10 mK above the equilibrium temperature. The monitoring SPRT is heated and then inserted into the thermometer well of the gallium cell. Readings are taken after about 20 minutes of equilibration in the cell. The monitoring SPRT is replaced in the cell with a preheated test SPRT and measurements on it are made after about 20 minutes. A number of SPRTs can be successively calibrated in the same "melt". When all of the test SPRTs have been calibrated, a final measurement in the cell is made on the monitoring SPRT. This reading of the monitoring SPRT should agree with the initial reading to within ± 0.1 mK. Also, measurements with different melts should agree to within ± 0.1 mK. See references [16,26,65,68,94].

3.2.4.2.3 FREEZING POINT OF INDIUM

The freezing point of indium is assigned the value 429.7485 K (156.5985 °C) on the ITS-90. Metal samples of 99.9999% purity and higher are commercially available. The freezing point of indium is at a sufficiently low temperature to permit the use of containers of high temperature plastics [polytetrafluoroethylene (Teflon), polyimide/amide, and others], borosilicate glass, and stainless steel [4,69,74,92]. See figure 14 for an example of a Teflon container used for indium at the NIST. As used with metals that freeze at higher temperatures, graphite can also be used with indium. The metal is available in the form of small pellets, wire, and rods. Suitable amounts for a sample can be easily weighed into the container. [The first cryoscopic constant of indium is 0.00212/K. Consequently, the liquidus point of an ideal indium solution of 99.9999% purity would be approximately 0.5 mK lower than that of 100% pure indium.]

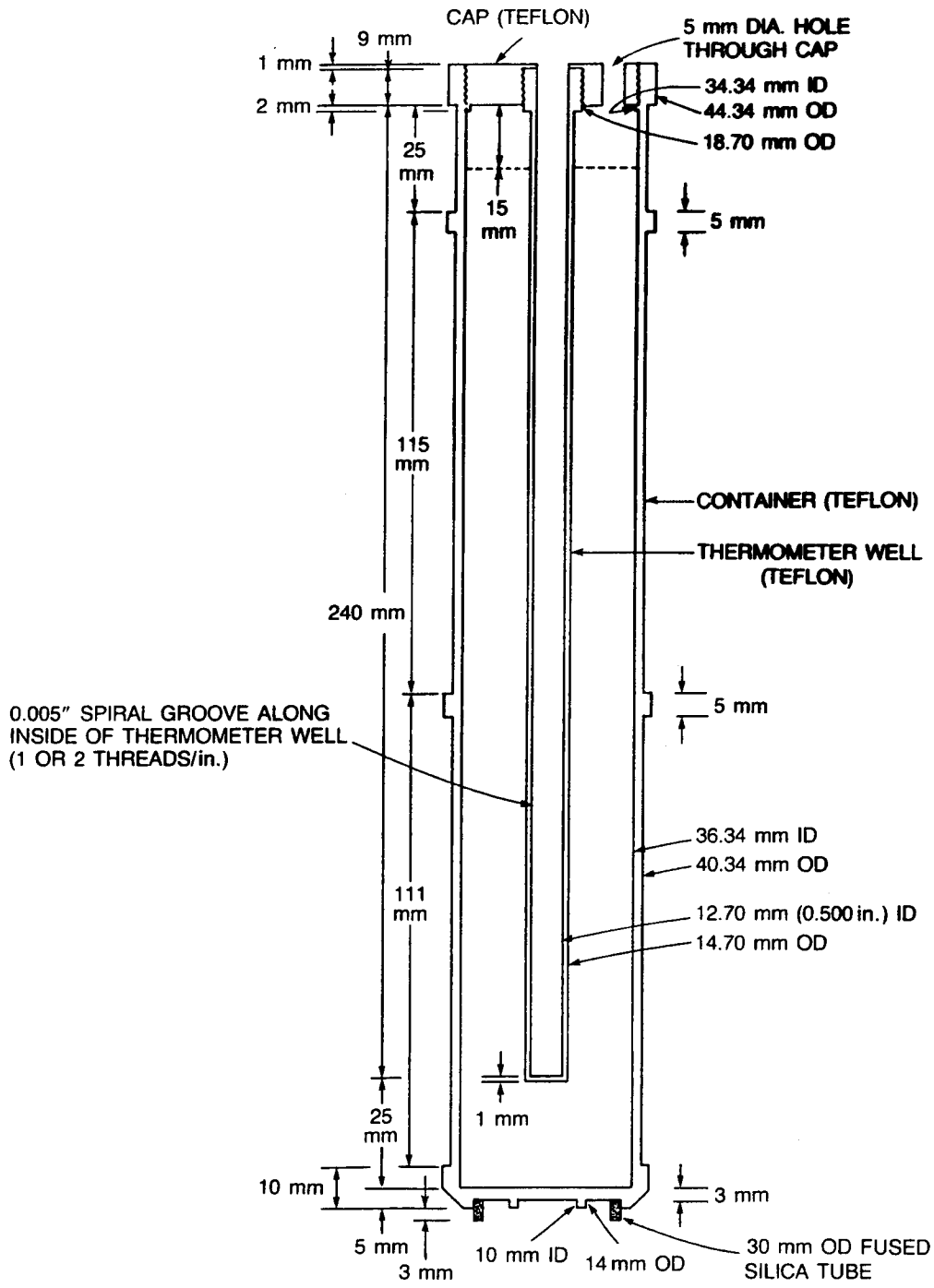


Figure 14. An all-plastic indium freezing-point cell to be used in a stainless steel container, such as that shown in figure 12. The argon gas pressure inside the stainless steel container is adjusted to one atmosphere at the freezing point. A similar all-plastic cell and stainless steel container may be used to realize the mercury freezing point or melting point at one atmosphere.

3.2.4.2.3.1 REALIZATION AND APPLICATION

A tube furnace containing the indium-point cell is controlled about 5 °C above the freezing point of indium until the metal is completely melted. (It is convenient to control the furnace temperature automatically and melt the metal sample overnight so that the freezing of the metal may be started in the morning.) Insert the check SPRT into the cell well and when the SPRT indicates that the sample is about 5 °C above the freezing temperature, change the furnace temperature control settings to control at 5 °C below the freezing point. When the check SPRT indicates recalescence, change the furnace temperature control settings to control at 1 °C to 0.5 °C below the freezing point. Withdraw the check SPRT from the cell well and insert successively in the well two fused silica glass rods, each initially at room temperature, for about 5 minutes each and then insert the cool check SPRT in order to freeze a thin mantle around the thermometer well. (To avoid the consequence of inserting borosilicate glass rods into the aluminum or silver point cell to form the mantle around the thermometer well, all glass rods used for this purpose in the laboratory should be fused silica glass.) Within 20 to 30 minutes, the readings on the check SPRT should indicate that the cell is at temperature equilibrium. After the readings on the check SPRT are completed, test SPRTs, that have been heated in an auxiliary furnace, are successively inserted into the cell well and calibrated. After all of the test SPRTs have been calibrated, the preheated check SPRT is inserted again into the cell well and read. This second reading should agree with the first to within ± 0.1 mK. See references [4,69,74,92].

3.2.4.2.4 FREEZING POINT OF TIN

The freezing point of tin is assigned the value 505.078 K (231.928 °C). Metal samples of 99.9999% purity are commercially available. Graphite containers are commonly and successfully used for tin. Although the use of materials such as boron nitride (BN) has not been reported, it could be a suitable container for tin. High purity tin has been found to supercool 25 °C or more [73,76]; hence, the freeze is nucleated by rapid cooling outside the furnace. The metal is available in the form of small pellets and in rods suitable for filling the graphite container. A method for filling graphite containers and installing the graphite thermometer wells is described in reference [46]. [The first cryoscopic constant of tin is 0.00329/K. Consequently, the liquidus point of an ideal tin solution of 99.9999% purity would be approximately 0.3 mK lower than that of 100% pure tin.]

3.2.4.2.4.1 REALIZATION AND APPLICATION

A tube furnace [46] containing the tin freezing-point cell is controlled about 5 °C above the freezing-point temperature until the metal is completely melted. (It is convenient to control the furnace temperature automatically and melt the metal overnight so that freezing of the metal can be started early in the morning.) Insert the check SPRT into the cell well and, when the SPRT indicates that the sample temperature is about 5 °C above the freezing point, change the furnace temperature control settings to control at 1 °C to 0.5 °C below the freezing point. When the check SPRT indicates that the cell temperature is close to the freezing-point value, withdraw the cell and the SPRT from the furnace. The cell will then cool rapidly and when the SPRT detects recalescence,

replace the cell in the furnace. Withdraw the check SPRT from the cell well. Insert successively in the well two fused silica glass rods, each initially at room temperature, for about 5 minutes each, and then the cool check SPRT in order to freeze a thin mantle around the thermometer well. Within about 20 to 30 minutes, the readings on the check SPRT should indicate that the cell is at temperature equilibrium. After the readings on the check SPRT are completed, test SPRTs, that have been heated in an auxiliary furnace, are successively inserted into the cell well and calibrated. After all of the test SPRTs have been calibrated, the check SPRT is heated and inserted again into the cell well and read. This reading should agree with the initial reading to within ± 0.1 mK. See references [43,46,73,76].

3.2.4.2.5 FREEZING POINT OF ZINC

The freezing point of zinc is assigned the value 692.677 K (419.527 °C). Metal samples of 99.9999% purity are commercially available. High purity liquid zinc has been found to supercool about 0.02 °C to 0.06 °C; hence, unlike the freezing procedure used with the tin-point cell, its freeze can be initiated in the furnace without withdrawing the cell from the furnace. Graphite containers are commonly and successfully used for zinc. Although the use of materials such as boron nitride (BN) has not been reported, it could be a suitable container for zinc. The metal is available in the form of small pellets and in rods suitable for filling graphite containers. [The first cryoscopic constant of zinc is 0.00185/K. Consequently, the liquidus point of an ideal zinc solution of 99.9999% purity would be approximately 0.5 mK lower than that of 100% pure zinc.]

3.2.4.2.5.1 REALIZATION AND APPLICATION

A tube furnace containing the zinc-point cell is controlled about 5 °C above the freezing point until the metal is completely melted. If the furnace temperature is maintained at a higher temperature, the zinc will melt faster, but the zinc should never be heated by more than about 5 °C above its melting point. (It is convenient to control the furnace temperature automatically and melt the zinc sample overnight so that the freezing of the metal can be started early in the morning and the calibration of six or more test SPRTs can be completed during the same day.) Insert the zinc-point check SPRT into the cell well. When the SPRT indicates that the melt is about 5 °C above the freezing point, change the furnace temperature control settings to control at 5 °C below the freezing point in order to initiate rapid cooling for nucleation. When the check SPRT indicates recalescence, change the furnace temperature control settings to control at 1 °C to 0.5 °C below the freezing point. Withdraw the check SPRT from the cell well and insert successively into the well two fused silica glass rods, each initially at room temperature, for about 5 minutes each, and then insert again the cool check SPRT. This freezes a thin mantle around the thermometer well. Within about 20 to 30 minutes, the readings on the check SPRT should indicate that the cell is at temperature equilibrium. After the readings on the check SPRT are completed, test SPRTs, that have been heated in an auxiliary furnace, are successively inserted into the cell well and calibrated. After all of the test SPRTs are calibrated, the preheated check SPRT is inserted again into the cell well and measurements made on it. This second reading should agree with the first to within ± 0.1 mK. See references [43,73,75].

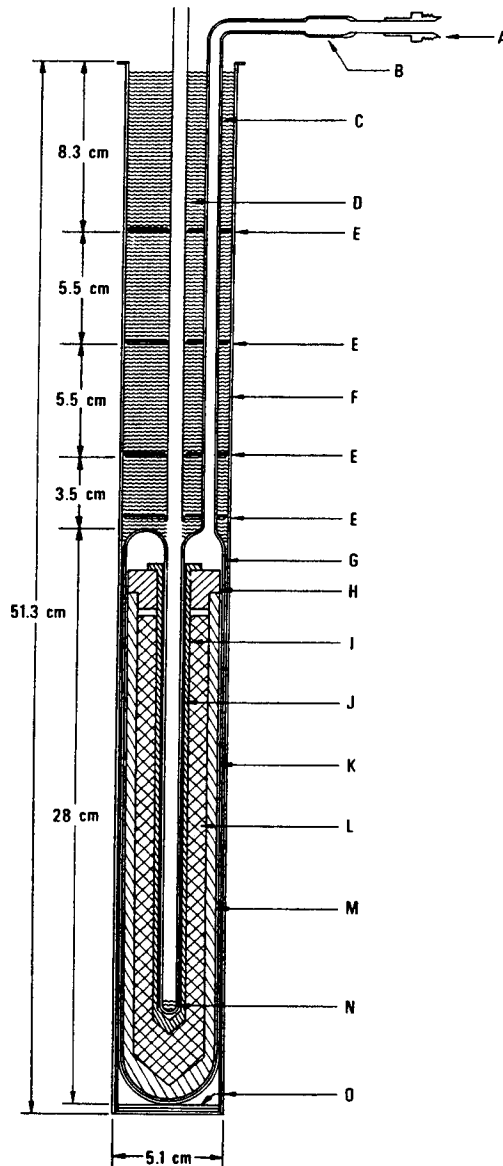


Figure 15. A graphite freezing point cell enclosed inside a fused silica tube with tube connection to high vacuum, purified argon gas source, and pressure gauge.

A -- connection to high vacuum, purified argon source, and pressure gauge, B - - fused-silica-to-Kovar graded seal, C -- fused-silica connecting tube, outer surface matte finished to minimize radiation piping, D -- thermometer guide tube, E -- heat shunts (Inconel disks), F -- thermal insulation (Fiberfrax), G - - fused-silica outer envelope, H -- graphite lid, I -- graphite thermometer well, J -- fused-silica thermometer well, K -- fused-silica fiber-woven tape for cushioning the graphite freezing-point cell inside the fused-silica enclosure, L -- metal sample, M -- graphite crucible, N -- fused-silica fiber pad for cushioning the thermometer, O -- Fiberfrax paper liner.

3.2.4.2.6 FREEZING POINT OF ALUMINUM

The freezing point of aluminum is assigned the value 933.473 K (660.323 °C). Metal samples of 99.9999% purity are commercially available. High purity graphite containers have been used successfully with aluminum. High purity liquid aluminum has been found to supercool about 1 °C to 2 °C; hence, its freeze can be initiated in the furnace without withdrawing the cell from the furnace. Aluminum is highly reactive, particularly at elevated temperatures; liquid aluminum is capable of dissolving many metals. Liquid aluminum reacts with moisture, forming the oxide and dissolving the hydrogen. The compounds Al_4C_3 and aluminum oxycarbide have been found in aluminum samples cast in graphite at 1000 °C. Because of the high chemical reactivity of aluminum, the graphite cell containing the metal must be completely protected by enclosing the cell in a fused silica envelope (see fig. 15). The argon or helium gas that is used to pressurize the freezing metal at one atmosphere must be thoroughly devoid of moisture, hydrogen, oxygen, hydrocarbons, and other substances that would react with liquid aluminum. The cell must not be heated more than 5 °C above the aluminum freezing point. [The first cryoscopic constant of aluminum is 0.00149/K. Consequently, the liquidus point of an ideal aluminum solution of 99.9999% purity would be approximately 0.7 mK lower than that of 100% pure aluminum.]

3.2.4.2.6.1 ASSEMBLY OF AN ALUMINUM-POINT CELL

High purity aluminum can be obtained in the form of shots or rods. Determine the internal volume of the graphite container, taking into account the thermometer well. Determine the mass of liquid aluminum required to fill the cell to within 0.5 cm of the graphite lid. Weight out aluminum shots or cut and clean aluminum rods that correspond to this mass. The rods should be cut with a carbide tipped tool and cleaned by etching in a hot (about 200 °C) solution consisting (by volume) of reagent grade phosphoric acid (15 parts), sulfuric acid (5 parts), and nitric acid (1 part), and then carefully rinsing many times in distilled water. Load the graphite crucible with the aluminum sample and then slide it into an extra-long fused-silica test tube such as that shown in figure 16. Insert the test tube into the tube furnace and evacuate it. While continuing to evacuate the tube, set the furnace temperature to control at about 5 °C above the melting point of aluminum. When the sample has completely melted, cool it to room temperature, while continuing to pump the tube. If aluminum shot, or rods of odd sizes, are used, the graphite cell will require several loadings and meltings before the desired amount of total sample has been loaded into the cell. When the graphite crucible is appropriately loaded with the sample, replace the silicone rubber stopper at the mouth of the extra-long test tube of figure 16 with the device for inserting the graphite thermometer well and lid (see reference [45] or fig. 17). Insert the test tube into the tube furnace, evacuate it, and then fill it with high purity argon to a pressure slightly above ambient. Melt the aluminum sample and push the graphite well and lid into the cell. Cool the sample to room temperature, while maintaining the argon pressure in the test tube slightly above the ambient pressure. Finally, assemble the graphite cell containing the aluminum sample into the desired freezing-point cell configuration (see references [43,45,70] or fig. 15).

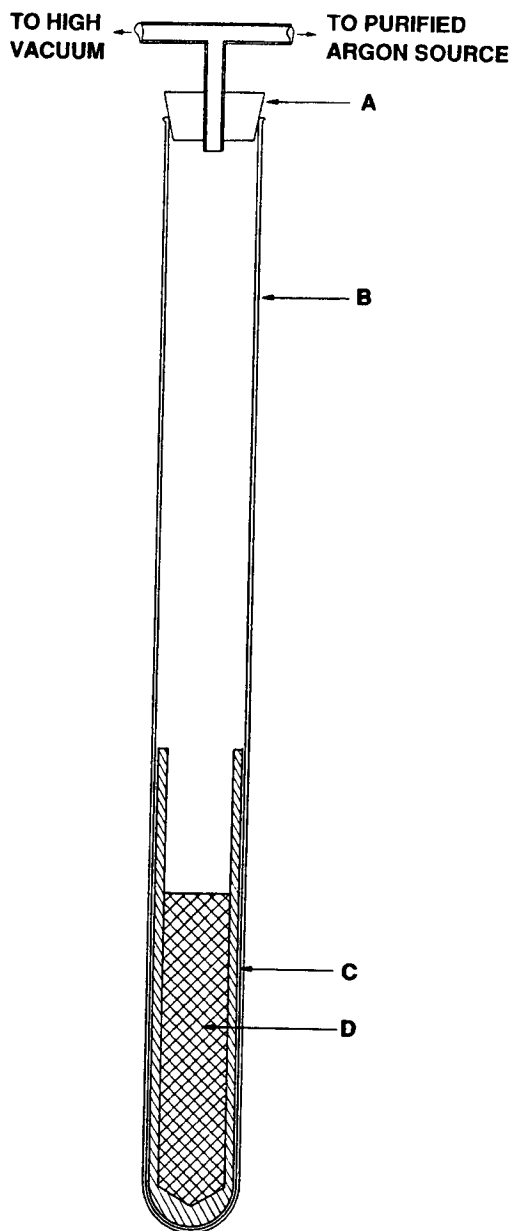


Figure 16. A method for filling a graphite freezing-point cell by melting the metal sample in the graphite crucible. The required amount of sample is placed in the graphite crucible and the crucible is inserted into the fused silica tube. To protect the sample, the fused silica tube is evacuated or filled with an inert gas (e.g., purified argon) before melting the metal in a tube furnace. Depending upon the geometry of the sample, the melting of two or more batches of sample may be required.

A -- Silicone rubber stopper, B -- fused silica tube, C -- graphite crucible, D -- metal sample.

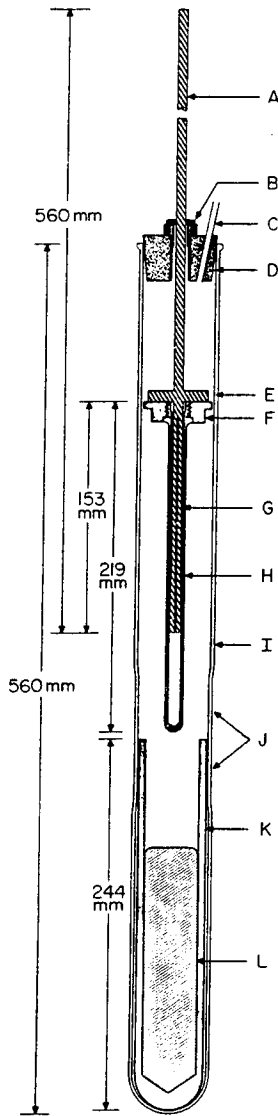


Figure 17. An apparatus for installing a graphite thermometer well and lid in a graphite crucible containing a molten metal sample.

A -- stainless steel pusher rod, B -- silicone rubber gas seal (permits linear motion of the pusher rod A), C -- inlet for purified argon gas that is used in purging and maintaining positive pressure of the gas during the assembly process, D -- silicone rubber stopper, E -- stainless steel flange attached to the pusher rod for pressing against the graphite lid and thermometer well during assembly, F -- graphite lid for the crucible, G -- slit on the pusher rod (the two halves spring outward to hold the graphite thermometer well and lid while melting the metal sample), H -- graphite thermometer well, I -- fused-silica tube, J -- a part of the fused-silica tube where its I.D. matches closely with the O.D. of the crucible and its lid so that the lid can be easily guided onto the opening of the crucible, K -- graphite crucible, L -- molten metal sample.

3.2.4.2.6.2 REALIZATION AND APPLICATION

SPRTs that are to be calibrated at the aluminum point and higher must have fused silica, sapphire, or ceramic insulation for the resistance element and its extension leads. Such high temperature SPRTs should be handled by procedures that avoid thermally shocking them.

A tube furnace containing the aluminum-point cell is controlled about 5 °C above the freezing point of aluminum until the metal is completely melted. It is convenient to control the furnace temperature automatically and melt the metal overnight so that the freezing of the metal can be started early in the morning and the calibration of two or three test SPRTs completed during the same day. Insert the aluminum-point check SPRT stepwise into the cell well. Since the SPRT will cool considerably between the time it is withdrawn from any auxiliary preheat furnace and inserted into the aluminum point cell, the SPRT is heated in the section of the thermometer guide tube that is maintained close to the furnace temperature. The SPRT is inserted initially to a location where its tip is about 3 cm above the graphite cell lid. After about 5 minutes, the SPRT is inserted an additional 5 cm and after another 5 minutes, another 5 cm, and so on until the tip of the SPRT is at the bottom of the thermometer well. When the SPRT indicates that the sample is about 5 °C above the freezing point, change the furnace temperature control settings to control at 5 °C below the freezing point in order to initiate rapid cooling for nucleation. When the check SPRT indicates recalescence, change the furnace temperature control settings to control at 1 °C to 0.5 °C below the freezing point. Withdraw the check SPRT stepwise from the cell, first to a location about 3 cm above the graphite cell lid. After about 5 minutes, withdraw the SPRT another 5 cm, and after another 5 minutes, another 5 cm, and so on until the SPRT is completely out of the thermometer guide tube. Next, insert successively into the cell well two fused silica glass rods, each initially at room temperature, for about 5 minutes each to freeze a thin mantle of solid aluminum around the thermometer well. Again insert the check SPRT stepwise, as described above, into the cell. Within 20 to 30 minutes, the readings on the check SPRT should indicate that the cell is at temperature equilibrium. After the readings on the check SPRT are completed, the SPRT is removed from the cell stepwise, as described above. The test SPRTs are then successively inserted stepwise, calibrated, and removed stepwise as described for the check SPRT. After all of the test SPRTs have been calibrated, the check SPRT is inserted again into the cell well and measurements made. This second reading at temperature equilibrium should agree with the first to within ± 0.1 mK.

When SPRTs are cooled rapidly from the aluminum point to ambient temperature, lattice vacancies are quenched in and these must be removed before the SPRTs are calibrated at the triple point of water. To relieve any quenched in lattice vacancies, the SPRTs that have been calibrated at the aluminum point should be heated in an auxiliary furnace at about 660 °C for about 30 minutes and then gradually cooled to about 500 °C over 3 hours or more before withdrawing from the furnace to cool at ambient temperature. See references [43,45,70].

3.2.4.2.7 FREEZING POINT OF SILVER

The freezing point of silver is assigned the value 1234.93 K (961.78 °C). Metal

samples of 99.9999% purity are commercially available in the form of pellets.

High purity graphite containers have been used successfully with silver. Liquid silver has been found to supercool not more than 0.5 °C; hence, its freeze can be initiated in the furnace without withdrawing the cell from the furnace. See references [3,15,72,98].

Oxygen is known to "dissolve" in liquid silver and lower the freezing point. Although the dissociation pressure of Ag_2O is expected to be quite high at the freezing point of silver, the lowering of the freezing point may be a combination of the solution of Ag_2O and of oxygen in liquid silver. (The dissociation pressure of Ag_2O is given as 414 atmospheres at 507 °C.) In a graphite environment at the freezing point of silver, a small amount of the oxygen will eventually react with the graphite; however, a newly prepared cell should be pumped at high vacuum at about 1000 °C for a week before back filling to one atmosphere with purified argon, nitrogen, or helium. [The first cryoscopic constant of silver is very small (0.000891/K). Consequently, the liquidus point of an ideal silver solution of 99.9999% purity would be approximately 1.1 mK lower than that of 100% pure silver.]

3.2.4.2.7.1 REALIZATION AND APPLICATION

The freezing-point cell of silver may be assembled by a procedure similar to that used with aluminum. See section 3.2.4.2.6.1.

SPRTs that are to be calibrated at the silver freezing point must have fused silica, sapphire, or ceramic insulation for the resistance coil and its extension leads. Such high temperature SPRTs should be handled by procedures that avoid thermally shocking them.

A tube furnace containing the silver freezing-point cell is controlled at about 5 °C above the freezing point until the metal is completely melted. (It is convenient to control the furnace temperature automatically and melt the metal overnight so that the freezing of the metal can be started early in the morning and the calibration of two or three test SPRTs completed during the same day.) Insert the silver-point check SPRT stepwise into the cell well. Since the SPRT will cool considerably between the time it is withdrawn from any auxiliary preheat furnace and inserted into the silver-point cell, the SPRT is heated in the section of the thermometer guide tube that is maintained close to the furnace temperature. The SPRT is inserted initially to a location where its tip is about 3 cm above the graphite cell lid. After about 5 minutes, the SPRT is inserted an additional 5 cm, and after another 5 minutes, another 5 cm, and so on until the tip of the SPRT is at the bottom of the thermometer well. When the SPRT indicates that the temperature of the sample is about 5 °C above the freezing point, change the furnace temperature control settings to control at 5 °C below the freezing point in order to initiate rapid cooling for nucleation. When the check SPRT indicates recalescence, change the furnace temperature control settings to control at 1 °C to 0.5 °C below the freezing point. Withdraw the check SPRT stepwise from the cell well, first to a location about 3 cm above the graphite cell lid. After about 5 minutes, withdraw the SPRT an additional 5 cm, and after another 5 minutes, another 5 cm, and so on until the SPRT is completely out of the thermometer guide tube. Next, insert successively into the cell well

two fused-silica glass rods, each initially at room temperature, for about 5 minutes each in order to freeze a thin mantle of solid silver around the thermometer well. Then, insert again the check SPRT stepwise, as described above, into the cell. Within about 20 to 30 minutes, the readings on the check SPRT should indicate that the cell is at temperature equilibrium. After the readings on the check SPRT are completed, it is removed from the cell stepwise, as described above. The test SPRTs are then successively inserted stepwise, calibrated, and removed stepwise as described for the check SPRT. After all of the test SPRTs have been calibrated, the check SPRT is inserted again into the cell well and read. This second reading should agree with the first to within ± 0.2 mK.

When SPRTs are cooled rapidly from the silver point to ambient temperature, lattice vacancies are quenched in and these must be removed before the SPRTs are measured at the triple point of water. To relieve any quenched in lattice vacancies, the SPRTs that have been calibrated at the silver point are heated in an auxiliary furnace at about 960 °C for 30 minutes or so and then gradually cooled to about 500 °C over 3.5 hours or more before withdrawing from the furnace to cool at ambient temperature. In order to protect the platinum of the SPRT from contamination by diffusion of metals at high temperatures (above 660 °C), the SPRTs should be enclosed in a platinum tube or other protective device.

3.2.5 CONTROL CHARTS OF CHECK THERMOMETERS

Control charts should be kept for all of the check thermometers associated with the various fixed points. Each of these charts will usually consist of a chronological graph of the check thermometer resistance value, $R(X)$, obtained from measurements in the fixed-point cell X , and of the ratio, $W(X) = R(X)/R(TPW)$, of the resistance value $R(X)$ to the resistance value, $R(TPW)$, obtained from measurements in a triple point of water cell. Presumably, such charts have been kept by those involved in precision thermometry. Entries on such control charts are made each time the particular fixed-point cell is used. Since those involved in precision thermometry would have used triple point of water cells for their work based on the IPTS-68 and they would have used $W(X)$, the same control chart can be continued with the ITS-90. The reason, of course, is that the behavior of the fixed-point cells is independent of the scale. Not all of the fixed points of the ITS-90, however, are the same as those of the IPTS-68. The ITS-90 uses some of the IPTS-68 fixed points but it also uses other fixed points. See reference [64].

Some metrologists may not have used $W(X)$ as defined above, but may have used the $W(t)$ of the IPTS-68. In that case, there will be a discontinuity in their control charts involving W when they implement the ITS-90 and begin using $W(X)$. The magnitude of the discontinuity will simply be the ratio $R(273.16 \text{ K})/R(273.15 \text{ K})$.

Control charts involving only $R(X)$ as a function of time will not have any discontinuity due to the change in the scale. Depending on the temperature of interest, of course, there may be need to start additional control charts.

3.3 RADIATION THERMOMETRY

Above the freezing point of silver (1234.93 K), the ITS-90 is defined in terms of Planck's radiation law. The values of temperatures T_{90} on the ITS-90 are obtained from the observed ratios of the spectral concentrations of the radiance L_λ of a blackbody at the wavelength (in vacuum) λ at T_{90} and at the reference temperature $T_{90}(X)$ according to eq. (31).

Inside a closed cavity, the radiation densities at different wavelengths λ depend only upon the temperature of the cavity walls. When a practical radiator is designed with a small hole in the wall to observe the radiation density at λ , there arises the question of how much the observed radiation departs from the blackbody radiation for a radiator design of a given geometry and material of construction. There are numerous papers on the theoretical analysis of the emissivities associated with cavity geometry and construction materials and descriptions of radiator designs that have been used in radiation thermometry [8,9,34,35,54,77,87,89,95]. The emissivities of cavities constructed of specular reflectors and diffuse reflectors have been analyzed [87]. It is expected that at high temperatures many materials become oxidized and, consequently, become diffuse reflectors. Although it is difficult to determine the actual temperature gradients in a cavity, the effect of temperature gradients has also been treated [10,11]. The effective emissivity of a graphite blackbody cavity has been computed to be 0.99997 ± 0.00003 [77].

For radiation thermometer calibrations at the silver, gold, or copper fixed point, the blackbody cavity should be constructed of graphite and surrounded by the freezing or melting metal contained in graphite to retain the high purity of the metal that is used. [The first cryoscopic constants of all three of these metals are extremely low (silver: 0.000891/K; gold: 0.000831/K; Cu: 0.000857/K). Consequently, the ideal-solution liquidus points of these metals of 99.9999% purity would be approximately 1.1 mK to 1.2 mK lower than that of 100% pure metals.]

References [27,55,56,57,62,77] give some details of construction of suitable graphite fixed-point blackbody cavities. The metal should be protected from air using an inert gas, such as argon, nitrogen, or helium, at a pressure slightly above ambient. The graphite container or auxiliary graphite scavengers can remove small amounts of oxygen impurities. For the blackbody cavity at the platinum point, pure alumina has been used in an oxidizing atmosphere to avoid the reaction between platinum metal and alumina in which oxygen gas is formed and metallic aluminum is dissolved in the platinum [33,86].

Usually, optical pyrometers or photoelectric pyrometers are used to determine the ratio of the radiances of a source of unknown temperature with that of the reference source. The optical system of the instrument is designed to focus a nearly monochromatic image of the radiation source onto a photodetector, which until about the mid-1950's was only the human eye; now the eye has been replaced in high precision measurements by photoelectric detectors because of their greater accuracy and their suitability for automation of the measurements. Two methods are commonly used to determine the ratios of spectral radiances. Either the photoelectric pyrometer is designed for comparing the two radiation sources by null-detection operation, similar in principle to the disappearing filament

optical pyrometers using suitable neutral filters or sectored discs for attenuating the radiation of one source, or for measuring directly the radiation density in terms of the detector output, e.g., photocell current. The latter requires high stability and linearity of signal processing [34,77]. The optics of the system may comprise refracting components (lenses) or reflecting components (mirrors) [28,34,54,57,87].

Equation (31) requires the ratio of monochromatic radiances. Usually, interference filters are used for this purpose. The bandwidth should be narrow with high transmittance while completely blocking out wavelengths outside the desired band. The temperature error is smaller the narrower the bandwidth. The temperature of the filters should be controlled, since they are sensitive to temperature changes. The photoelectric detector should be protected from undesired radiations from outside the solid angle defined by the aperture of the blackbody cavity. Where the output of the photocell is used to determine the ratio of the radiances, the linearity of the detector should be carefully checked or calibrated.

For details of optical pyrometer operation and attendant sources of errors, see references [28,34,54,57,77,87].

4. CALIBRATION OF THERMOMETERS ON THE ITS-90 AT VARIOUS LEVELS OF UNCERTAINTY AND SOME APPROXIMATIONS OF THE SCALE

In a standards laboratory, the design of apparatus and equipment for calibration of thermometers on the ITS-90 should be based on the desired accuracy, the number of thermometers and thermometric instruments that must be calibrated per year, the cost of realizing the ITS-90 (the fixed points and the measurement equipment), the cost of applying and maintaining the ITS-90, and the cost of research to maintain and make necessary improvements on the realization of the ITS-90. In a national standards laboratory, the efforts are directed toward the accurate realization of the ITS-90.

On 1 January 1990, no laboratory was able to calibrate thermometers over the complete range of the ITS-90 in accordance with the strict definition of the scale. Also, it is thought that on that date there was no immediate, wide-spread requirement for "experimental calibration conversion" from the IPTS-68(75) to ITS-90 over the complete range. Since the differences between IPTS-68(75) and ITS-90 were known, "arithmetical conversions" should have met most of the immediate requirements. Also, where stable thermometers have been used to maintain the EPT-76 or parts of the IPTS-68(75), the scales on those reference thermometers could be converted to ITS-90, using the published approximate differences between the scales, and then those thermometers can be used to calibrate other thermometers on the ITS-90. To realize the ITS-90 as defined and for international traceability, however, it is essential for the national calibration laboratory to have all of the fixed-point apparatus and measurement equipment. Furthermore, without continued research and comparison with other standards laboratories, the question regarding the accuracy of the realization of the scale will remain. The ITS-90 temperature calibrations are based on the thermal equilibrium states (vapor-liquid or liquid-solid equilibrium at known pressures, or vapor-liquid-solid triple points) of pure substances. Substances, however, have some impurity content; the amount must be small enough to have

negligible effect on the measurement of temperature. Obviously, the fixed-point device and the experimental procedure must be designed so that during calibration, the thermometer will be in thermal equilibrium with the equilibrium state of the defining fixed point. A method for checking whether or not the thermometer is in thermal equilibrium with a metal fixed-point standard device is to reduce the immersion in the device a known amount or vary the experimental conditions. The observed temperature change of the thermometer must correspond with the hydrostatic head effect of the liquid metal in the device, or there must be no observed temperature change with experimental conditions (such as changing furnace temperatures of metal fixed-point cells).

In order to determine the precision of the calibration process, it is essential to use check thermometers with every calibration. The results of the check thermometers will show whether the calibration process is "under statistical control" or not. The accumulated results show the precision of the "gross" calibration process.

Since some parts of this section deal with approximations of the ITS-90, and will make reference to the scale differences given in table 1, the methods by which the table was constructed will be described. The differences ($T_{90} - T_{76}$) between 5 K and 27 K were obtained using the same relation [99] as that used for ($T_{NPL-75} - T_{76}$), namely,

$$(T_{90} - T_{76})/\text{mK} = -0.0056(T_{90}/\text{K})^2. \quad (40)$$

The differences ($T_{90} - T_{68}$) between 14 K and 100 K were obtained by Working Group 4 of the CCT by graphical interpolation of data from the published literature. The differences ($T_{90} - T_{68}$), or ($t_{90} - t_{68}$), between -200 °C and 630 °C were obtained by Working Group 4 of the CCT from published data on two SPRTs, one SPRT covering the range below 0 °C, and the other covering the range from 0 °C to 630 °C. A polynomial of the form:

$$(t_{90} - t_{68})/^{\circ}\text{C} = \sum_{i=1}^8 a_i (t_{90}/630)^i. \quad (41)$$

was fitted to the data from -200 °C to 630 °C and the coefficients are:

$$\begin{array}{ll} a_1 = -0.148759 & a_5 = -4.089591 \\ a_2 = -0.267408 & a_6 = -1.871251 \\ a_3 = 1.080760 & a_7 = 7.438081 \\ a_4 = 1.269056 & a_8 = -3.536296 \end{array}$$

The polynomial with these coefficients reproduce the tabulated differences [83] to within 1 mK above 0 °C and to within 1.5 mK below 0 °C. The differences ($t_{90} - t_{68}$) between 630 °C and 1064 °C were obtained by Working Group 4 by graphical interpolation from published data [14]. The differences ($t_{90} - t_{68}$) above 1064 °C were obtained from the equation:

$$(t_{90} - t_{68})/^{\circ}\text{C} = -0.25 [(t_{90}/^{\circ}\text{C} + 273.15)/(1337.33)]^2. \quad (42)$$

In section 3, we discussed the direct realization of the ITS-90, using the

standard instruments of the scale, i.e., the realization of the scale at the lowest level of uncertainty. Of course, even the standard interpolating instruments used at the same thermodynamic temperature will indicate temperatures that differ slightly due to the devices having nonideal behavior and the scale being expressed in as simple a form as possible. The differences in indicated temperatures, however, are negligible for all practical purposes, being of the order of $\leq \pm 0.5$ mK for temperatures above about 5 K (i.e., assuming no errors in calibration). The realization of the ITS-90 in the liquid helium range of temperatures (0.65 K to 5.0 K) through helium vapor pressure-temperature relations can be accurate to about ± 0.1 mK or ± 0.2 mK.

For nonstandard types of thermometers used to approximate the ITS-90, the level of uncertainty is higher than the numbers just given because of the inherent instability of these thermometers. In all cases, these types of thermometers are calibrated by comparison with one or more standard instruments of the scale, e.g., vapor-pressure thermometry; vapor-pressure thermometry and gas thermometry; vapor-pressure thermometry, gas thermometry, and platinum resistance thermometry; gas thermometry and platinum resistance thermometry; platinum resistance thermometry; or pyrometers or spectral radiometers.

The NIST offers calibration services for various thermometers and pyrometers covering the range from 0.65 K to 4200 °C (see NIST SP 250). Of this range, the Chemical Process Metrology Division offers calibrations for contact thermometers covering the range from 0.65 K to 2400 K, and the Radiometric Physics Division offers calibrations for non-contact thermometers (radiation pyrometers) covering the range from 1234.93 K (961.78 °C) to 4200 °C. Calibrations of only contact-type thermometers will be discussed here. The types of contact thermometers calibrated include rhodium-iron resistance thermometers (RIRTs), germanium resistance thermometers (GRTs), standard platinum resistance thermometers (SPRTs), thermocouples (t/c), liquid-in-glass thermometers, thermistor thermometers, industrial platinum resistance thermometers (IPRTs), digital thermometers, and other special thermometers that are compatible with the NIST calibration equipment.

4.1 RHODIUM-IRON RESISTANCE THERMOMETERS

At temperatures below 13.8033 K, RIRTs and GRTs are, at the present time, the only thermometers that are suitable for precision temperature measurements. Also, RIRTs (and to a lesser extent GRTs) are suitable for use at temperatures up to the triple point of neon (24.5561 K). In the range from 0.65 K to about 25 K, RIRTs have reproducibilities of about ± 0.2 mK. Consequently, RIRTs don't degrade the realization of the ITS-90 significantly.

When the ITS-90 is realized, as defined, at NIST, some NIST RIRTs will be calibrated at many temperatures through the use of vapor-pressure thermometry and gas thermometry to produce reference-standard RIRTs, which will be periodically recalibrated. The resistance-temperature data of these RIRTs will be represented by a polynomial.

Customer RIRTs are calibrated by comparison with reference-standard RIRTs. A polynomial is fitted by the method of least squares to the RIRT resistance-temperature data so obtained and the results are reported in terms of the

polynomial that is selected.

Until the NIST completes the development of the CVGT and vapor-pressure thermometry apparatus with which the reference-standard RIRTs will be calibrated, calibrations of customer RIRTs are performed by comparison against reference-standard RIRTs that have been calibrated on the NPL-75 Scale [13] or on the EPT-76 and converted to the ITS-90.

To convert a calibration of an RIRT on the EPT-76 to an approximate calibration on the ITS-90, use the EPT-76 calibration resistance-temperature data, change the T_{76} values to T_{90} values using the $(T_{90} - T_{76})$ differences given in table 1, or calculated with eq (40), to produce a new set of resistance-temperature values, and then fit a polynomial of the required degree to these data. Using the coefficients of the polynomial so determined, produce the desired calibration table. A typical calibration report on the EPT-76 and one on the ITS-90 are given in appendix 3, sections 6.3.6 and 6.3.7, respectively.

4.2 GERMANIUM RESISTANCE THERMOMETERS

GRTs are comparable with, but not quite as stable as, RIRTs. They are calibrated in a manner similar to that of the RIRTs and their results similarly reported. At NIST, customer GRTs are calibrated by comparison with reference-standard RIRTs.

Anyone with a calibration on the EPT-76 may convert it to an approximate ITS-90 calibration by the same procedure as just outlined for RIRTs.

4.3 STANDARD PLATINUM RESISTANCE THERMOMETERS

Both capsule and long-stem type SPRTs are calibrated at the NIST. They will be discussed separately.

4.3.1 CAPSULE SPRTs (13.8033 K TO 429.7485 K OR 505.078 K)

For temperatures in the range from 13.8033 K to 273.16 K, capsule SPRTs are the most suitable thermometers. NIST has reference capsule SPRTs that have been, or will have been, calibrated at the defining fixed points in this range. Those SPRTs are used in calibrating customer thermometers by the comparison technique over the range from about 13 K to 84 K. The temperatures at which comparisons are made are at, or within a few mK of, the defining fixed-point temperatures of the ITS-90 and at temperatures approximately mid-way between the fixed-point values. Data at the temperatures intermediate to the fixed-point values are incorporated as a check on the calibration process. At and above the argon triple point (83.8058 K), customer capsule SPRTs are calibrated by the fixed-point method. See section 6.3 for an example of how to calculate the coefficients of the deviation functions.

4.3.2 LONG-STEM TYPE SPRTs (83.8058 K TO 1234.93 K)

Long-stem type SPRTs are used in the range from 83.8058 K to 1234.93 K. Two different long-stem type SPRTs are required to cover this whole range, one type being the customary SPRT having a nominal 25.5 Ω resistance at 0 °C and used in

the range from 83.8058 K to 692.677 K or to 933.473 K, and the second type having a somewhat longer stem and having a nominal 0.25 Ω or 2.5 Ω resistance and used in the range from 273.15 K to 1234.93 K. Such thermometers are very stable if handled carefully. In this range of temperature, SPRTs are calibrated by the fixed-point method, different sets of fixed points being required for different temperature subranges. The required fixed points for the different subranges were specified in section 2 of this document. In the fixed-point method, corrections for hydrostatic heads and gas pressures over the metals of the freezing-point and melting-point cells are made (see table 6). Similarly, corrections for hydrostatic heads present in metal and in gas triple-point cells are made. As a check on the accuracy of the calibration, measurements are made at one or more "redundant" defining fixed points lying within the temperature range of calibration or at a well characterized secondary fixed point, such as the cadmium freezing point, that lies within the temperature range of calibration. The value of the temperature of a check point calculated from the calibration constants should agree closely with the accepted value of that point. If not, then either an error was made in the calibration, one or more fixed-point cells are defective, or the thermometer is defective.

The procedures indicated in section 3.2 for realizing the various fixed-point temperatures and for handling SPRTs are followed carefully during calibration of platinum thermometers, especially so for calibration at the aluminum and silver freezing points (see sec. 3.2.4.2.7.1 for a discussion of lattice defects). See section 6.3 for an example of how the coefficients of the deviation functions are calculated from the data for the two sets of fixed points.

4.3.3 CONVERSION OF THE IPTS-68 CONSTANTS AND $W(T_{68})$ TABLES TO APPROXIMATE ITS-90 CONSTANTS AND $W(T_{90})$ TABLES

For SPRTs that have been calibrated recently on the IPTS-68(75), their calibrations may be converted to approximate calibrations on the ITS-90 at temperatures between the triple point of equilibrium hydrogen (13.8033 K) and the freezing point of zinc (692.677 K).

To make the conversion, first obtain values of $W(T_{68})$, i.e., $R(T_{68})/R(0\text{ }^{\circ}\text{C})$, from the IPTS-68(75) calibrations at values of T_{68} corresponding to the temperatures of the relevant fixed points of the ITS-90 in the appropriate range in which the conversion is desired. [Note: for a fixed point, the temperature values T_{68} and T_{90} are different, but the "hotness" is the same and so the resistance of a given SPRT remains unchanged. The temperature values on the two scales are defined to be the same only at the triple point of water and at the absolute zero of the temperature scales. Due to the nature of the scales, however, there are other temperature values of these scales that are also the same, which are fortuitous. See fig. 1, which shows the difference of t_{90} and t_{68} as a function of t_{90} .] Using these values of $W(T_{68})$ at the appropriate ITS-90 fixed-point temperatures, calculate values of $W(T_{90})$, i.e., $R(T_{90})/R(273.16\text{ K})$, by dividing the values of $W(T_{68})$ at the appropriate fixed-point temperatures by the value of $W(273.16\text{ K})$, i.e., the value of $W(T_{68})$ at the triple point of water. Table 8 shows samples of such conversions for a capsule-type SPRT and for a long-stem type SPRT calibrated on the IPTS-68(75). The calibration constants of the IPTS-68(75) equations for the two SPRTs are given also in table 8. The values of $W(T_{90})$ so

Table 8. Example of conversion of calibrations of SPRTs on the IPTS-68 to approximate calibrations on the ITS-90

Capsule SPRT, S/N 1812284 : e-H₂ TP to Sn FP

IPTS-68 CALIBRATION CONSTANTS

$R(0\text{ }^{\circ}\text{C}) = 25.4964808$	$\alpha = 3.9262754 \times 10^{-3}$	$\delta = 1.4964667$
$A_1 = -1.6314209 \times 10^{-4}$	$B_1 = -8.7377446 \times 10^{-7}$	$C_1 = -4.0321350 \times 10^{-7}$
$D_1 = 1.4525327 \times 10^{-8}$		
$A_2 = -2.1616630 \times 10^{-4}$	$B_2 = -1.7113512 \times 10^{-6}$	$C_2 = 6.6163769 \times 10^{-8}$
$D_2 = -2.2572375 \times 10^{-10}$		
$A_3 = -4.5449999 \times 10^{-4}$	$B_3 = 7.7242433 \times 10^{-6}$	$C_3 = -3.9028516 \times 10^{-8}$
$A_4 = 3.0860000 \times 10^{-7}$		$C_4 = -1.0880791 \times 10^{-4}$

ITS-90 CALIBRATION CONSTANTS CONVERTED FROM THE IPTS-68 CONSTANTS

$R(273.16) = 25.4974973$		
$a_1 = -2.5239001 \times 10^{-4}$	$b_1 = -1.2277862 \times 10^{-4}$	$C_1 = -2.3783015 \times 10^{-6}$
$a_9 = -2.5287142 \times 10^{-4}$	$b_9 = -1.1130131 \times 10^{-5}$	$C_2 = -4.3892024 \times 10^{-6}$
		$C_3 = -1.5608728 \times 10^{-6}$
		$C_4 = -2.1374663 \times 10^{-7}$
		$C_5 = -1.0344171 \times 10^{-8}$

Long-Stem SPRT, S/N RS8YA-5 : Ar TP to Zn FP

IPTS-68 CALIBRATION CONSTANTS

$R(0\text{ }^{\circ}\text{C}) = 25.5086208$	$A = 3.9856609 \times 10^{-3}$	$B = -5.8762238 \times 10^{-7}$
	$\alpha = 3.9268986 \times 10^{-3}$	$\delta = 1.49640322$
$A_4 = 2.6581418 \times 10^{-14}$		$C_4 = 9.3183900 \times 10^{-7}$

ITS-90 CALIBRATION CONSTANTS CONVERTED FROM THE IPTS-68 CONSTANTS

$R(273.16\text{ K}) = 25.5096386$	
$a_4 = -9.3225823 \times 10^{-5}$	$b_4 = -9.9914440 \times 10^{-6}$
$a_8 = -9.1058813 \times 10^{-5}$	$b_8 = -7.6061559 \times 10^{-6}$

obtained may then be used with the appropriate relations described in section 2 to obtain the constants of the ITS-90 deviation equations for the SPRTs. In table 8, we list the values of the deviation constants that were calculated from the sample data presented there. For comparison, values of the conversion from $W(T_{68})$ to $W(T_{90})$, as well as measured values of $W(T_{90})$, for the various relevant fixed-point temperatures T_{68} and T_{90} , respectively, are given in table 9. The deviations in the values of the last two columns of table 9 for the capsule SPRT reflect the inconsistency between the NBS-IPTS-68(75) wire scale and the difference between the IPTS-68(75) and the ITS-90 as given in table 1. Note that for the long-stem SPRT, the zero deviations for tin and zinc are a consequence of those fixed points having been used in both cases and the

Table 9. Values of $W(T_{68})$ and $W(T_{90})$ for various fixed-point temperatures T_{68} and T_{90} , respectively

<u>Capsule SPRT (S/N 1812284)</u>					
Fixed Point	T_{68}/K	$W(T_{68})$ meas.	T_{90}/K	$W(T_{90})$ calc.*	$W(T_{90})$ meas.
e-H ₂ TP	13.81	0.00119822**	13.8033	0.00119817	0.00119721
e-H ₂ BP	17.04200	0.00231120**	17.0357	0.00231111	0.00231049
e-H ₂ BP	20.280	0.00425962**	20.2711	0.00425945	0.00425815
Ne TP	24.5616	0.00848337**	24.5561	0.00848303	0.00848391
O ₂ TP	54.361	0.09182547**	54.3584	0.09182180	0.09182102
Ar TP	83.79723	0.21598575**	83.8058	0.21597714	0.21597795
Hg TP	234.3086	0.84421212**	234.3156	0.84417846	0.84417781
H ₂ O TP	273.16	1.00003987	273.16	1.00000000	1.00000000
Ga MP	302.9218	1.11815352**	302.9146	1.11810895	1.11810896
In FP	429.7848	1.60970773**	429.7485	1.60964355	1.60964566
Sn FP	505.1181	1.89263856	505.078	1.89256311	1.89256311

Long-Stem SPRT (S/N RS8YA-5):

Ar TP	83.79723	0.21592943**	83.8058	0.21592084	0.21592281
Hg TP	234.3086	0.84418993**	234.3156	0.84415637	0.84415625
H ₂ O TP	273.16	1.00003976	273.16	1.00000000	1.00000000
Ga MP	302.9218	1.11817175***	302.9146	1.11812729	1.11812699
In FP	429.7848	1.60980450***	429.7485	1.60974050	1.60974062
Sn FP	505.1181	1.89278557	505.078	1.89271033	1.89271033
Zn FP	692.73	2.56885786	692.677	2.56875573	2.56875573

* Values of $W(T_{90})$ calc. were obtained by conversion of corresponding values of $W(T_{68})$ meas.

** These values were calculated from NBS-IPTS-68 calibration constants, based on the NBS wire scale and calibration at the triple point of water and the freezing point of tin (and the freezing point of zinc for the long-stem SPRT).

*** These values were calculated from IPTS-68 calibration constants determined from fixed points.

conversion process having been consistent. The deviations for the other fixed points (Ar, Hg, Ga, and In) reflect the non-uniqueness of this SPRT and possible errors incurred in measurements at those fixed points.

The results of tables 8 and 9 for the long-stem SPRT, with regard to the differences between temperatures determined from an actual ITS-90 calibration and those determined from an IPTS-68(75) calibration but then calculated for approximate ITS-90 values, are shown in figure 18. Note that at temperatures above 273.16 K, the zero deviation of figure 18 is a consequence of the fact that the same fixed points (tin and zinc) have been used in both cases and the conversion process having been consistent.

Difference Between ITS-90 Calibration and IPTS-68 Calibration
 Converted to ITS-90, Chino RS8YA-5, 25.5 ohm

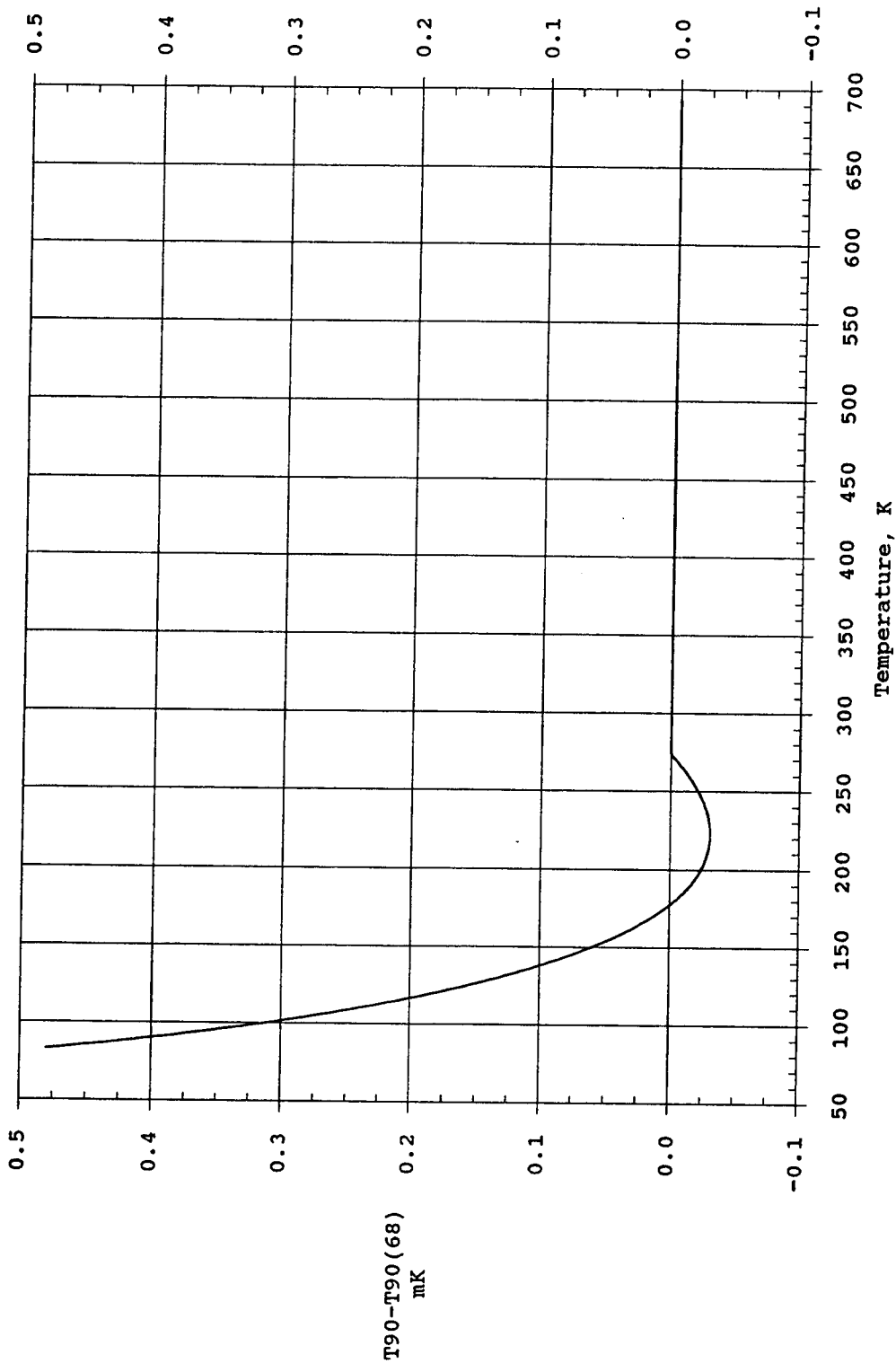


Figure 18. Differences between T_{90} and (T_{90}) as calculated from IPTS-68 calibration for the long-stem SPRT, S/N RS8YA-5, of table 8.

4.3.4 UNCERTAINTIES OF CALIBRATIONS AND THEIR PROPAGATION

Both systematic and random errors of measurements introduced in a calibration are propagated throughout the temperature range of the calibration. It is the total uncertainty arising from both of these types of errors, however, that is of interest to the customer and user of a calibrated thermometer. International comparisons of fixed-point cells below 90 K [79] and other data suggest that the uncertainties (at the 1σ level) in the realizations of the defining fixed points of the ITS-90 are about ± 0.2 mK for the triple points of hydrogen and neon, ± 0.1 mK for the triple point of oxygen through the melting point of gallium, ± 0.7 mK at the freezing point of indium, ± 1 mK from the freezing point of tin through the freezing point of aluminum, and ± 2 mK for the freezing point of silver.

The uncertainty of temperature measurements in the liquid helium range (0.65 K to 5.0 K) results from the uncertainty of the helium vapor-pressure measurements. The uncertainty (at the 1σ level) throughout this range of temperature is estimated to be approximately ± 0.1 mK to ± 0.2 mK.

For the CVGT, the uncertainty in the measured temperature over its temperature range (3.0 K to 24.5561 K) arises from uncertainties of realizations of the triple points of neon and of equilibrium hydrogen, of the measurement of the CVGT gas pressure, and of the measurement of the vapor pressure of helium. The uncertainty (at the 1σ level) throughout this range of temperature is estimated to be approximately ± 0.1 mK to ± 0.2 mK. Uncertainties introduced by a particular CVGT design may add to these uncertainties.

In the calibration of SPRTs over any given subrange, the possible error in the realization of each of the fixed points and any error of measurement must be considered and they will be propagated independently of that incurred at the other fixed points involved. The total uncertainty of measurements at a given temperature is then the root-mean-square of the appropriate contributing uncertainties. Curves showing the propagation of a \pm (unit error) incurred at each of the defining fixed points of the two major ranges are shown in figures 19 and 20. Figure 19 shows the propagation of errors associated with the fixed points below 273.16 K; and figure 20 shows curves for the fixed points used in the calibration of SPRTs in the range from 273.15 K to 1234.93 K. The labels on the various curves indicate the fixed-point in which there is the unit error in its temperature, and the other fixed points without error. As an example, consider the curve labelled Sn(Ag, Al, Zn) of figure 20. The symbol Sn indicates that the unit error occurs in the Sn freezing-point temperature; that is clearly indicated by a unit offset of the curve at that point. The symbols in parenthesis, i.e., (Ag, Al, Zn), indicate that the Ag, Al, and Zn freezing points were the other fixed points involved in the calibration and that measurements were made at those fixed-point temperatures without error. Also, it is assumed that the measurements at the triple point of water were without error. The other labelled curves are similarly interpreted. The straight lines labelled TPW show the errors propagated for an error of ± 0.1 mK made by the user in the triple point of water.

4.3.5 ESTIMATES OF POSSIBLE ERRORS INTRODUCED BY EXTRAPOLATIONS BEYOND THE RANGE OF CALIBRATION

It is unwise and is poor practice to use any thermometer beyond the temperature range over which it was calibrated. Nevertheless, some users persist in doing just that. In some cases, especially if the extrapolation is for only a few kelvins, the error introduced may be rather small. The errors of some typical extrapolations, calculated and depicted for NIST SPRTs, are shown in figures 21, 22, 23, 24, and 25.

The curve in figure 21 shows the error introduced for a NIST SPRT by extrapolating the deviation function, determined from calibration over the range from the triple point of argon to the triple point of water, downward from the argon triple point to 54 K. Extrapolating downward to about the boiling point of nitrogen (77 K) results in a fairly insignificant error in this case and, thus, can be done with the usual caution that some thermometers may not be as good as that of figure 21.

Figure 22 depicts the results for another NIST SPRT. The curve shows the error introduced by extrapolating the deviation function, determined from calibration over the range from the triple point of mercury to the melting point of gallium, downward from the mercury triple point to 84 K.

Figure 23 displays the results for the same NIST SPRT as used for figure 22, but the curve in this case shows the error introduced by extrapolating the deviation function, determined from calibration over the range from the triple point of mercury to the melting point of gallium, downward from the mercury triple point to only 200 K. A sizable error is shown for observations that would be made at Dry Ice temperatures (-78 °C).

Figure 24 depicts the results for several NIST SPRTs, but the curves in this case show the errors introduced by extrapolating their deviation functions, determined from calibration over the range from the triple point of water to the freezing point of zinc, downward from the triple point of water to -50 °C.

Figure 25 displays the results for several NIST SPRTs, but in this case the curves show the errors introduced by extrapolating their deviation functions, determined from calibration over the range from the triple point of water to the freezing point of zinc, upward from the freezing point of zinc to 934 K (660 °C).

As a general rule and good practice, one should never extrapolate any of the ITS-90 deviation functions beyond their range of application. If, however, the estimated uncertainty introduced by extrapolating a deviation function beyond the range of calibration is acceptable, then the user may do so, but with the knowledge that his particular thermometer may yield results with a larger uncertainty than that estimated. The user that makes such extrapolations should realize that not all SPRTs will behave as indicated in figures 21 through 25. The results depicted in these figures are examples only and are valid for only those SPRTs indicated. Other SPRTs may be better or worse.

ITS-90 Propagation of Calibration Errors
in Platinum Resistance Thermometry

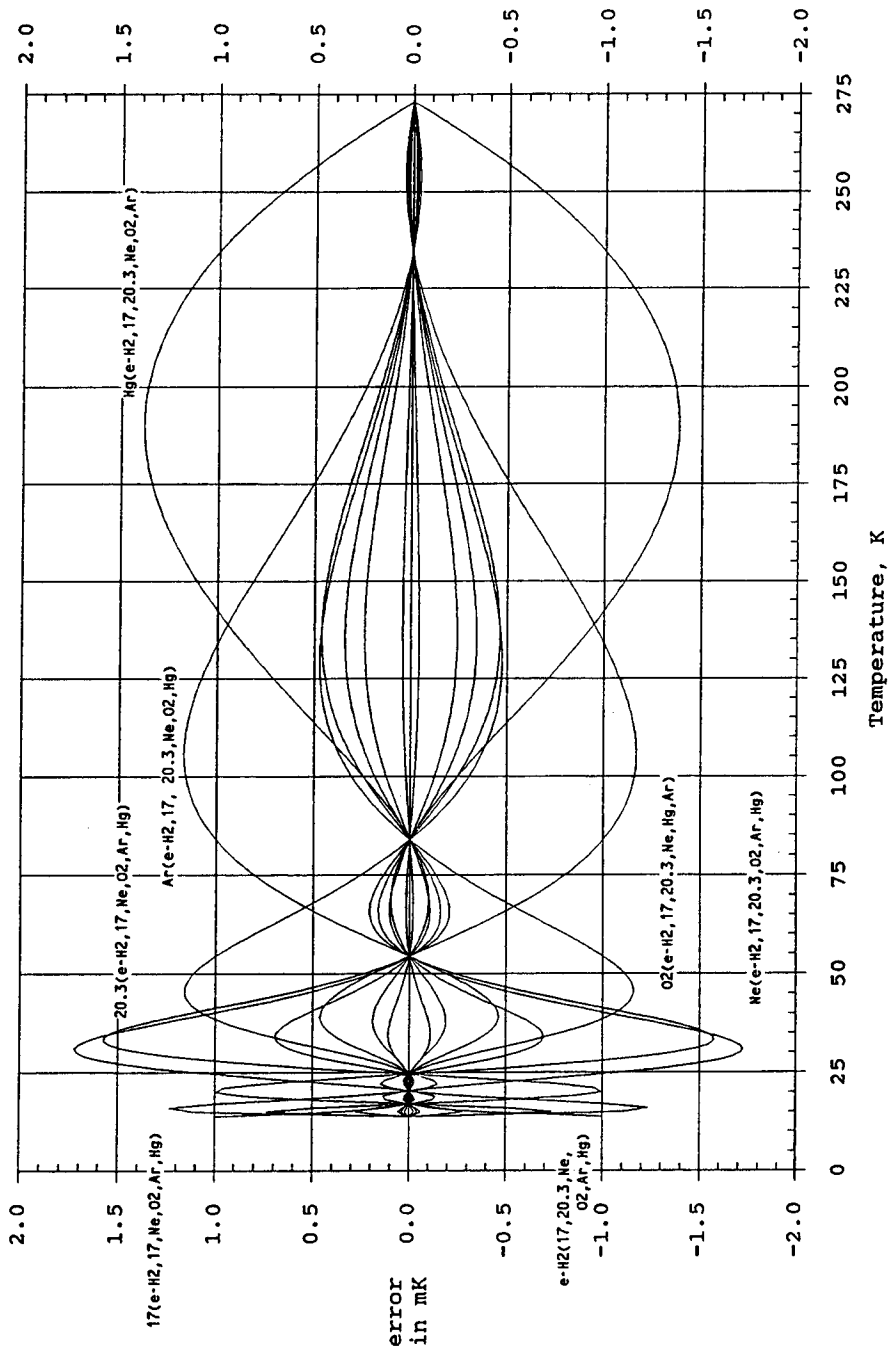


Figure 19. Propagation of errors from errors of calibration of SPRTs between 13.8033 K and 273.16 K. The curves show the error in the temperature values caused by a unit positive or unit negative error of calibration at each of the fixed points in the range, namely, the triple points of equilibrium hydrogen, neon, oxygen, argon, and mercury. The calibration at the triple point of water is assumed to have been made without error. The curves are identified by the fixed point with error outside the parenthesis and the fixed points without error inside the parenthesis.

ITS-90 Propagation of Calibration Errors
in Platinum Resistance Thermometry

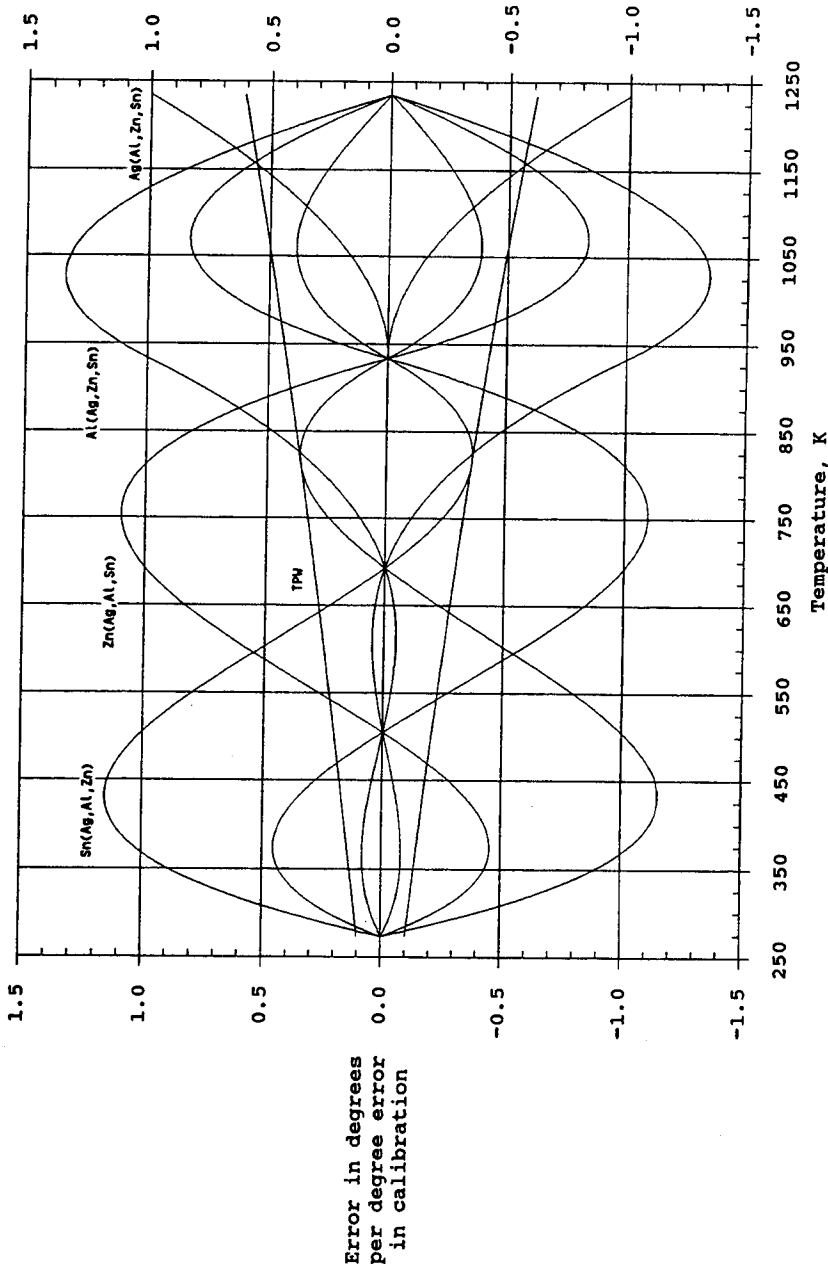


Figure 20. Propagation of errors from errors of calibration of SPRTs between 273.15 K and 1234.93 K. The curves show the error in the temperature values caused by a unit positive or unit negative error of calibration at each of the fixed points in the range, namely, gallium, indium, tin, zinc, aluminum, and silver points. The calibration at the triple point of water is assumed to have been made without error. The curves are identified by the fixed point with error outside the parenthesis and the three fixed points without error inside the parenthesis. Also included in this figure are error curves for errors made by the user at the triple point of water; these curves show propagation of ± 0.1 mK errors incurred at the triple point of water.

ITS-90, 25.5 ohm Capsule PRT 1812284
Oxygen Subrange - Extrapolated Argon Subrange

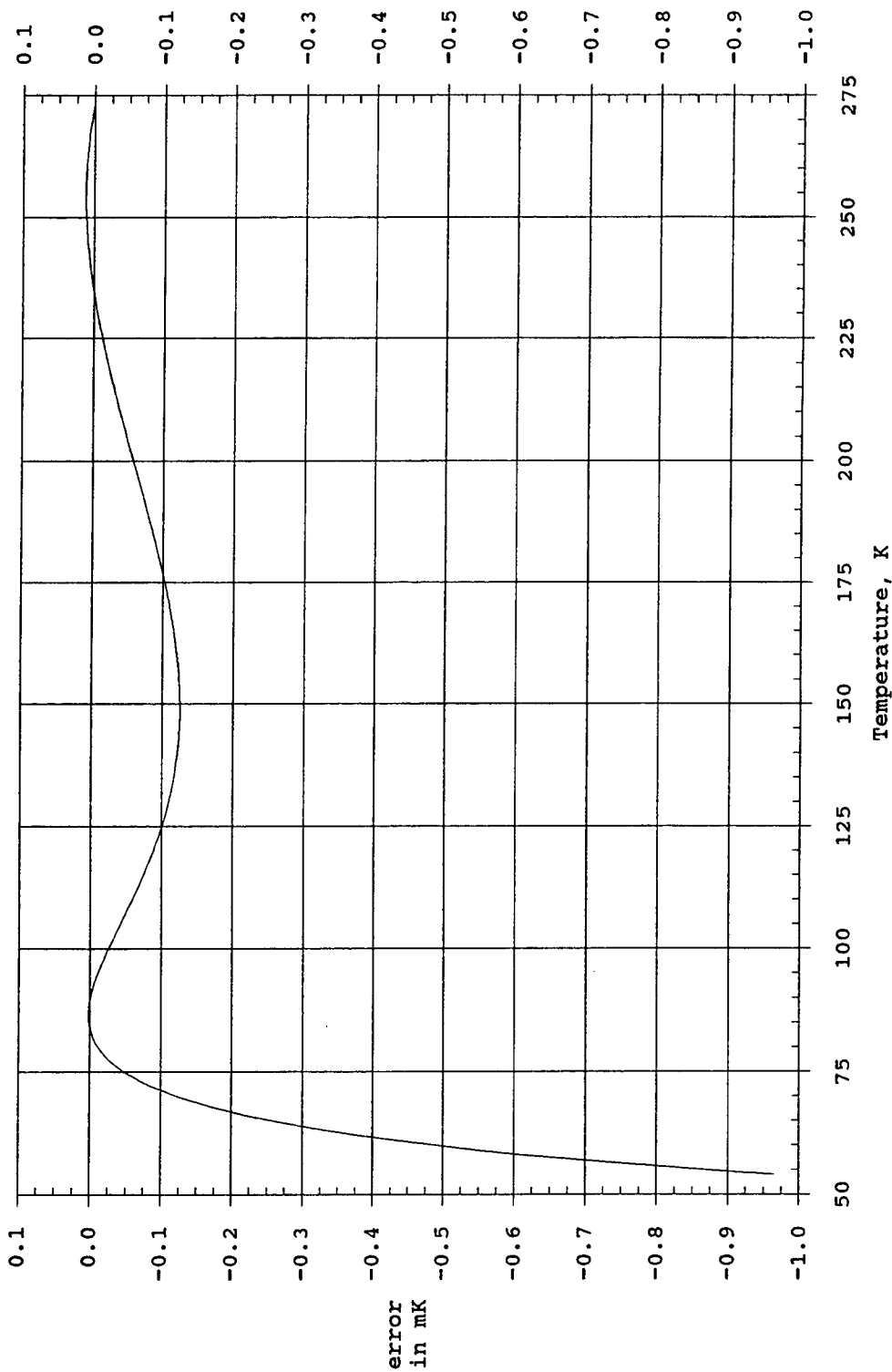


Figure 21. Error curve for a NIST SPRT; the curve shows the error introduced by extrapolating its deviation function, determined from calibration over the range from the triple point of argon to the triple point of water, downward from the triple point of argon to 54 K.

ITS-90, Chino Model R800-2, RS8YA-5, 25.5 ohm
Ar to T3 Subrange - Extrapolated Hg to Ga Subrange

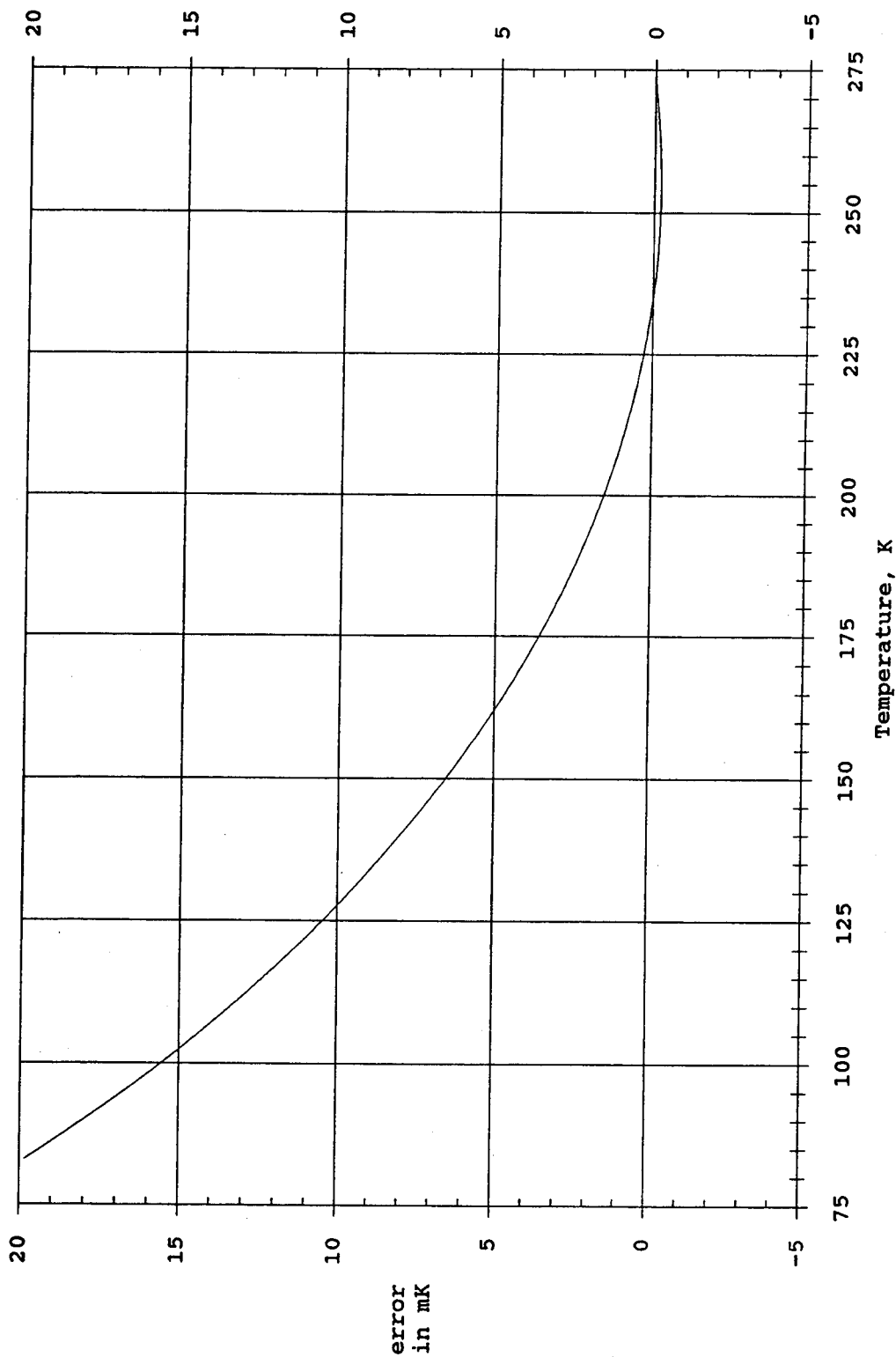


Figure 22. Curve for a NIST SPRT that shows the error introduced by extrapolating its deviation function, determined from calibration over the range from the triple point of mercury to the melting point of gallium, downward from the triple point of mercury to 84 K.

ITS-90, Chino Model R800-2, RS8YA-5, 25.5 ohm
Ar to T3 Subrange - Extrapolated Hg to Ga Subrange

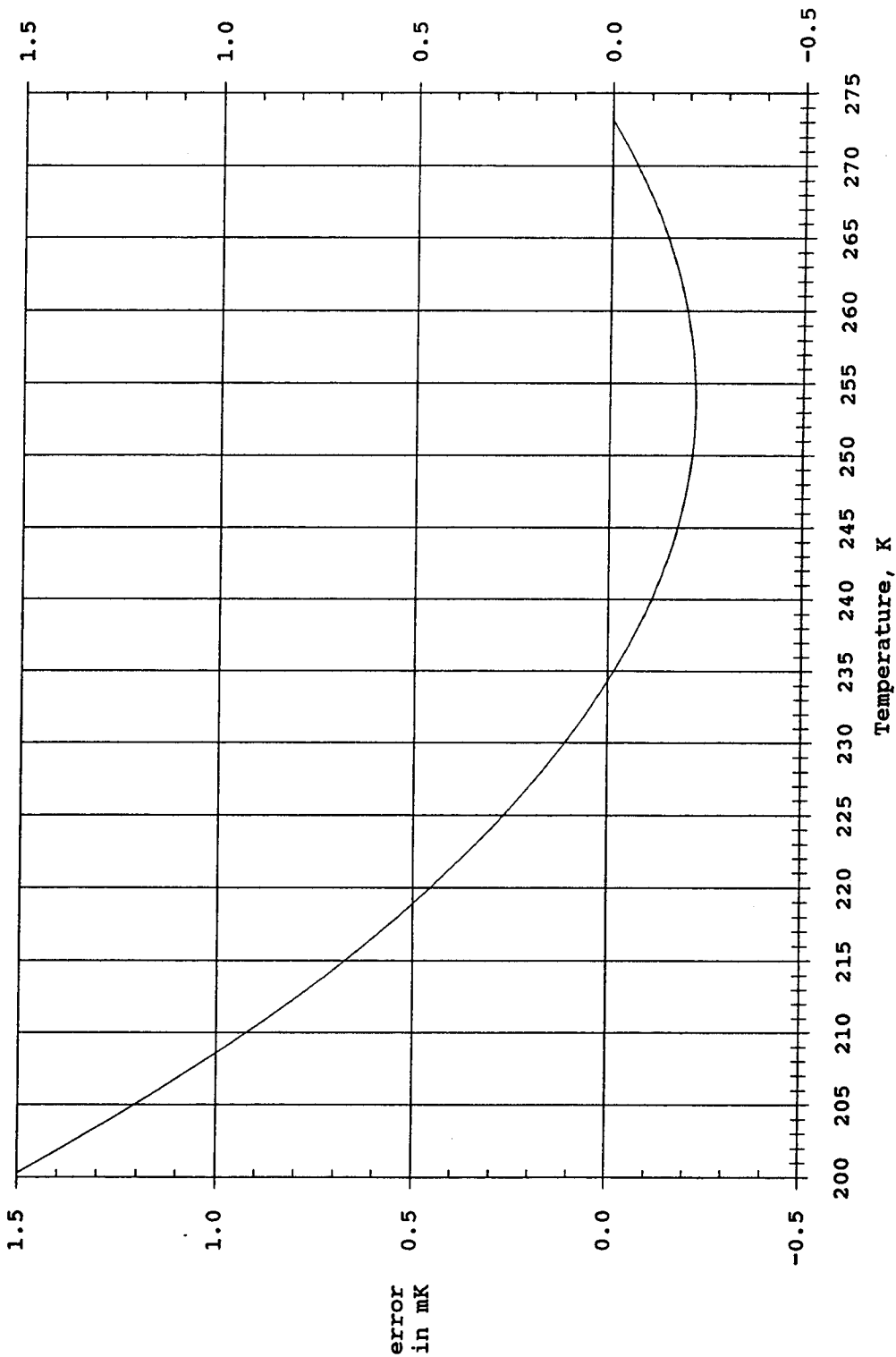


Figure 23. Curve for the NIST SPRT of figure 22 that shows the error introduced by extrapolating its deviation function, determined from calibration over the range from the triple point of mercury to the melting point of gallium, downward from the triple point of mercury to only 200 K.

ITS-90, 25.5 ohm PRTs
Ar Subrange - Extrapolated Zn Subrange

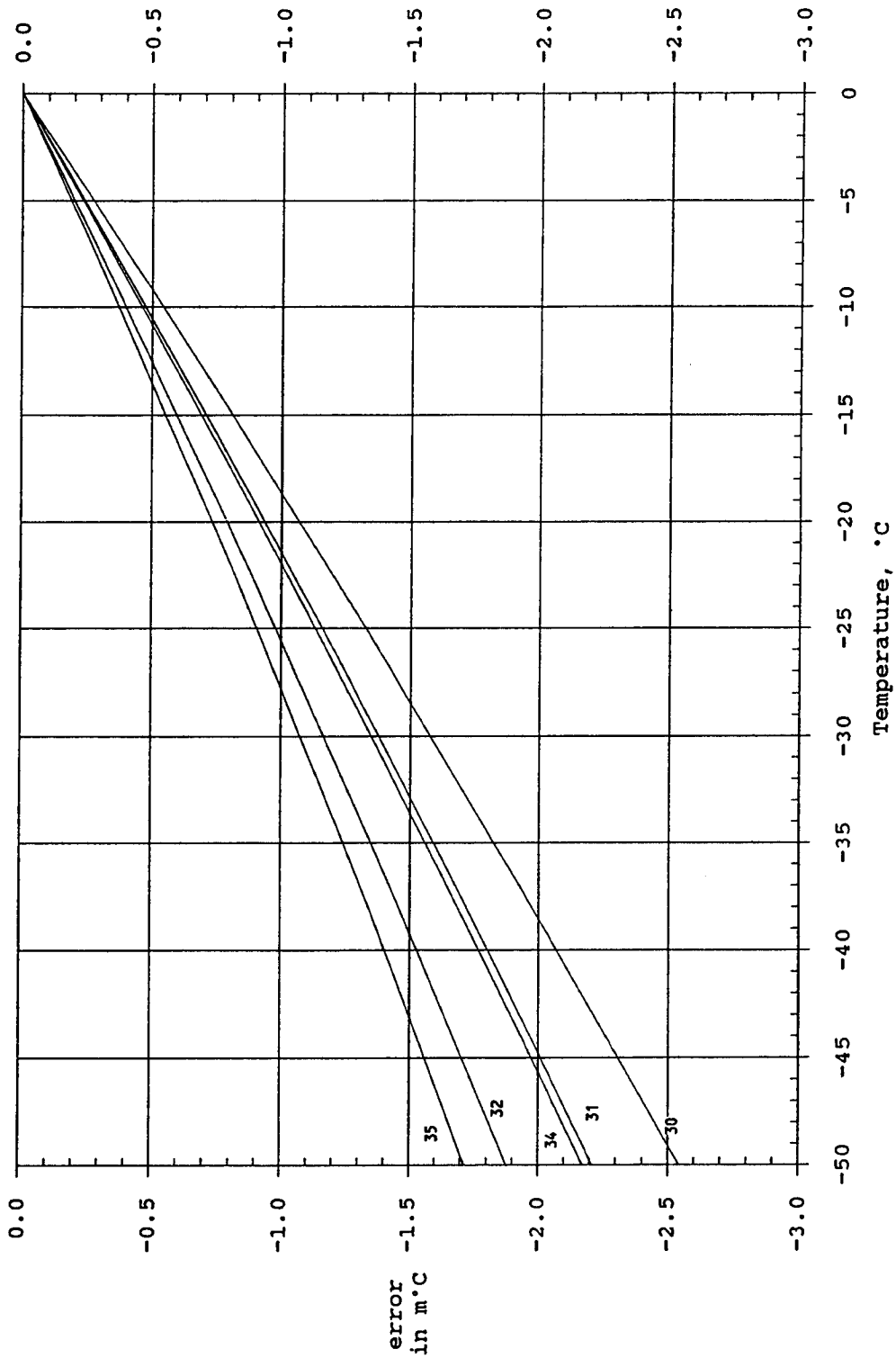


Figure 24. Curves for several NIST SPRTs that show the errors introduced by extrapolating their deviation functions, determined from calibration over the range from the triple point of water to the freezing point of zinc, downward from the triple point of water to -50 °C.

ITS-90, 25.5 ohm PRTs
Al Subrange - Extrapolated Zn Subrange

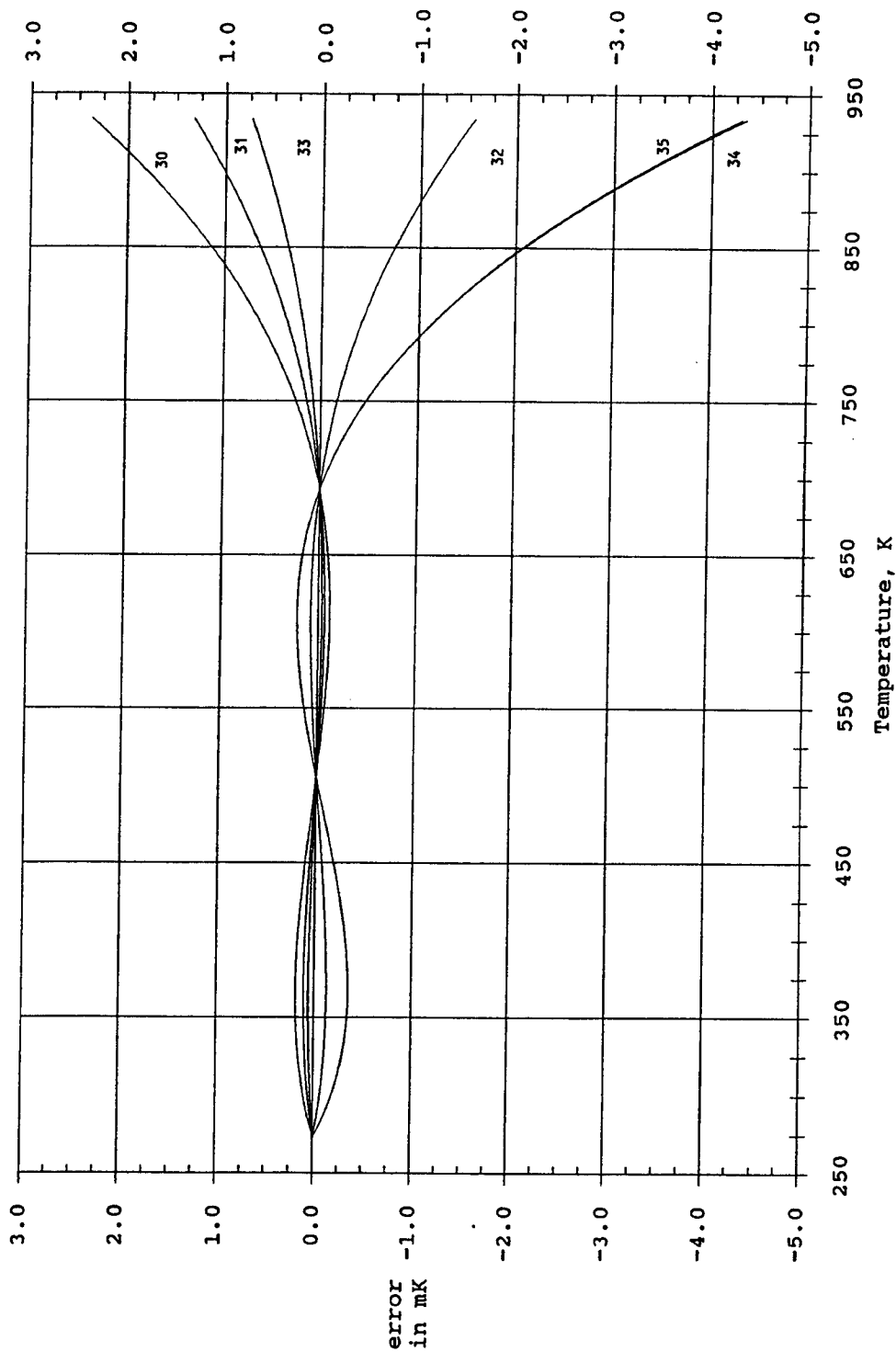


Figure 25. Curves for several NIST SPRTs that show the errors introduced by extrapolating their deviation functions, determined from calibration over the range from the triple point of water to the freezing point of zinc, upward from the freezing point of zinc to 934 K (660 °C). Also shown are subrange inconsistencies for the subrange triple point of water to zinc, relative to the subrange triple point of water to aluminum.

4.4 THERMOCOUPLES (77 K TO 2400 K)

There are numerous letter-designated types of thermocouples. The Type S thermocouple was the standard instrument of the IPTS-68(75) in the range from 630.74 °C to 1064.43 °C, but it is not a standard instrument of the ITS-90. Customer thermocouples are calibrated at NIST by using a set of temperature fixed points, by comparison with SPRTs, or by comparison with reference-standard thermocouples that have been calibrated either by comparison with an SPRT or a radiation pyrometer, or through the use of fixed points. For details of the calibration procedures and of the uncertainties involved, see NIST SP 250-35 [22] and NIST Monograph 175 [23] (or Monograph 125 [82]).

Usually, the calibration data for most types of thermocouples are analyzed relative to reference tables, such as those given in NBS Monograph 125 [82]. Monograph 125, of course, has reference tables for thermocouples based on the IPTS-68(75). This monograph has been revised and updated to give reference tables for all letter-designated thermocouples based on the ITS-90. The revised version of Monograph 125 is Monograph 175 [23] and it supersedes Monograph 125.

The electromotive-force-temperature data for a thermocouple calibrated on the IPTS-68(75) can be converted to an approximate ITS-90 calibration through the use of the differences ($t_{90} - t_{68}$) given in table 1 of this document and the S values in mV/°C for the relevant thermocouple given in Monograph 175 or Monograph 125. An example of this conversion is given in table 10. A typical calibration report is presented in appendix 3 (see sec. 6.3.8).

4.5 LIQUID-IN-GLASS THERMOMETERS

Liquid-in-glass thermometers have uncertainties of realization as small as ± 30 mK in the temperature range from 0 °C to about 100 °C, but deteriorates at lower and higher temperatures. Liquid-in-glass (primarily, mercury-in-glass) thermometers are calibrated at NIST by comparison with SPRTs in liquid baths of various kinds that cover different temperature ranges. For details of the calibration procedures and of the uncertainties involved, see NIST SP 250-23 [105]. An example of a calibration report, based on the IPTS-68(75), of a liquid-in-glass thermometer is given in appendix 3 (see sec. 6.3.9). A calibration report for the same thermometer, with the IPTS-68(75) calibration converted to an approximate ITS-90 calibration through the use of ($t_{90} - t_{68}$) differences given in table 1 is given also in appendix 3 (see sec. 6.3.10).

4.6 INDUSTRIAL PLATINUM RESISTANCE THERMOMETERS

Industrial platinum resistance thermometers (IPRTs) are designed primarily for use in the temperature range from about 77 K (approximate liquid nitrogen boiling point) to 500 °C. Typically, the manufacturer of IPRTs quotes minimum instabilities of the IPRTs at the ± 0.1 K level over this range of temperatures. Some IPRTs may be somewhat better than this but others may be considerably worse. As seen from table 1, the maximum difference of ($T_{90} - T_{68}$) below 500 °C is about 0.08 K, and therefore the difference in temperature due to the change in temperature scales is within the instability of many IPRTs. Continued use of the IPTS-68(75) and of equations and standards [American Society for Testing and Materials (ASTM) Standard, E 1137, and International Electrotechnical Commission

Table 10. Example of a conversion of calibration values of a type K thermocouple on the IPTS-68 to an approximate calibration on the ITS-90

Calibration Values on IPTS-68					Calibration Values on ITS-90	
t_{68} (°C)	emf_{68} (mV)	S (mV/°C) Monograph 125	$t_{90}-t_{68}$ (°C) Table 1	Δ [$-S \cdot (t_{90}-t_{68})$] (mV)	t_{90} (°C)	emf_{90} ^a (mV)
0.0	0.000	0.0395	0.000	0.000	0.0	0.000
100.0	4.092	0.0414	-0.026	-0.001	100.0	4.093
200.0	8.130	0.0400	-0.040	-0.002	200.0	8.132
300.0	12.195	0.0415	-0.039	-0.002	300.0	12.197
400.0	16.383	0.0422	-0.048	-0.002	400.0	16.385
500.0	20.633	0.0426	-0.079	-0.003	500.0	20.636
600.0	24.904	0.0425	-0.115	-0.005	600.0	24.909
700.0	29.136	0.0419	0.20	0.008	700.0	29.128
800.0	33.288	0.0410	0.34	0.014	800.0	33.274
900.0	37.338	0.0400	-0.01	0.000	900.0	37.338
1000.0	41.281	0.0389	-0.19	-0.007	1000.0	41.288
1100.0	45.118	0.0378	-0.26	-0.010	1100.0	45.128

^a $emf_{90} = emf_{68} - \Delta$

(IEC Standard, Publication 751] referenced to the IPTS-68(75), therefore, would result in an increase in uncertainty of temperature of only about 0.1 K if the temperature were expressed as being on the ITS-90. (Note: the ASTM and the IEC are converting their respective IPRT tables from the IPTS-68(75) to the ITS-90. ASTM Committee E-20 on Temperature Measurements is responsible for this conversion for the ASTM).

When IPRTs are calibrated on the ITS-90, of course, they may be calibrated in the same manner as is used for SPRTs. A better method of calibrating IPRTs, however, is to obtain resistance-temperature data by comparison with a calibrated SPRT at numerous temperatures over the range of interest and then fit a polynomial in t_{90} to $R(t_{90})$, to $R(t_{90})/R(0\text{ }^{\circ}\text{C})$, or to $R(t_{90})/R(0.01\text{ }^{\circ}\text{C})$ data by a least squares technique.

4.7 THERMISTOR THERMOMETERS, DIGITAL THERMOMETERS, AND OTHER TYPES OF THERMOMETERS

Thermistor thermometers, digital thermometers (with resistance, thermocouple, or diode sensors), and other types of thermometers are calibrated at NIST by comparison with SPRTs in liquid baths. The calibration procedures followed are similar to those used with liquid-in-glass thermometers. The uncertainties of calibration range from as small as ± 2 mK for thermistor thermometers to tenths

of kelvins for the others. The temperatures of calibration for these types of thermometers usually lie somewhere within the range from about 77 K to 850 K. Bead-in-glass probe type thermistors used in the moderate temperature range are quite stable and they may be used to approximate the ITS-90 at a level of about ± 1.5 mK to ± 2.0 mK [67]. In their case, a polynomial, the degree of which depends on the temperature range of the calibration, is fitted to resistance-temperature data and the results reported in terms of that polynomial. A calibration on the IPTS-68(75) may be converted to an approximate ITS-90 calibration by the same procedure as outlined for RIRTs.

4.8 THE LOGO OF THE NATIONAL CONFERENCE OF STANDARDS LABORATORIES FOR THE ITS-90

The National Conference of Standards Laboratories (NCSL) formed an Ad Hoc Committee on the Change of the Temperature Scale at the beginning of 1988 in order to publicize the new temperature scale (ITS-90) and to facilitate its implementation. At the NCSL meeting in July 1989, the Ad Hoc Committee adopted a logo, available from the NCSL [1800 30th Street, Suite 305B, Boulder, CO 80301, Tel. (303) 440-3339], that may be affixed to thermometers that have been calibrated on the ITS-90. The purpose of the logo, illustrated in figure 26, is to indicate at a glance, without having to refer to documentation, those thermometers in a laboratory that have been calibrated on the new scale. This is particularly useful for those laboratories that have their various thermometers calibrated on a prescribed schedule, with different thermometers being calibrated at different times.



Figure 26. The NCSL ITS-90 logo.

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