

**THE
ENCYCLOPAEDIA
OF
THERMOMETRY**

Volume 1 Number 1, 1st Quarter 1990

THE ENCYCLOPAEDIA OF THERMOMETRY

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TABLE OF CONTENTS

PAGE	WELCOME TO THE ENCYCLOPAEDIA OF THERMOMETRY The Editors
1	FUNDAMENTALS OF THERMOMETRY, PART 1 Henry E. Sostmann
19	PRACTICAL CALIBRATION OF THERMOMETERS ON THE INTERNATIONAL TEMPERATURE SCALE OF 1990 Henry E. Sostmann
31	PLATINUM RESISTANCE THERMOMETERS AS INTERPOLATION STANDARDS FOR ITS-90 John P. Tavener

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W E L C O M E T O T H E E N C Y C L O P A E D I A
O F T H E R M O M E T R Y

V O L U M E 1 N O . 1

It is with a genuine sense of trepidation that we undertake to found and publish a new Journal. How shall we justify this rash act to our-selves and to our colleagues in temperature metrology? How can we explain what motivates us to add yet one more periodical to the number which annually crosses our desks?

First, we recognize that there is no publication which is aimed specifically at good thermometry, in its principles and in its practice. Metrologia deals with the cutting edge of measurement science, and sometimes with thermometry. Industry association journals print occasional articles on practice. We read these publications. No journal is dedicated to temperature measurement alone, from theory to practice, from laboratory to plant floor.

Second, we recognize that the respected agencies to which we used to look for refreshment and enlightenment (and indeed excitement) in our discipline are in a waning phase. There are serious reductions, in staff and effort, in thermometry at NIST, NRC, NPL, BIPM, etc. It seems as if, with the completion of work on the International Temperature Scale of 1990, it has been decided by the budget officers that temperature measurement is a matured field; a ledger to be closed as complete and perfected. We know that isn't so, and we further know that what is to come next is most likely the responsibility of the private sector.

Last, we feel that we have experience to share, and a wide circle of friends on whom we can prevail to share theirs.

We hope to bring you, in the next issues, informative articles on a variety of subjects; for example:

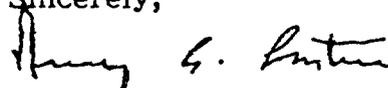
Fundamentals of thermometry; how Scales are developed, how the basic references are determined, what equipment and manipulations are required to calibrate an interpolation instrument. This issue includes the first part of a series of articles which will deal with these questions in depth.

What is the new International Temperature Scale of 1990, which became effective on January 1 just past? What is needed to calibrate a thermometer on the new Scale? What algorithms are prescribed for the calculation of ITS(90) temperatures?

We expect to publish papers on good practice in practical measurement, invited papers from respected experts in the field, reviews of current literature, news, books, and products. We practice a discipline rich in history, and we intend, when it is appropriate, to reprint landmark papers in that discipline. Because we are a commercial house, producing the world's broadest product line of equipment for both fundamental and workaday thermometry, we will not hesitate to publish information about things we make and how to use them best.

And so, welcome. You are invited to be a partner in this enterprise of publication. Subscribe; then let us know what you want to see in these pages, and if you have something to contribute, we urge you to think of yourself as a potential author.

Sincerely,



Henry E. Sostmann, Editor



John P. Tavener, Editor and
Publisher

FUNDAMENTALS OF THERMOMETRY

PART I

by Henry E. Sostmann

1: THE ABSOLUTE OR THERMODYNAMIC KELVIN, TEMPERATURE SCALE

Temperature is a measure of the hotness of something. For a measure to be rational (and useful between people), there must be agreement on a scale of numerical values (the most familiar of which is the Celsius or Centigrade Scale), and on devices for interpolating between the defining values.

The only temperature scale with a real basis in nature is the Thermodynamic Kelvin Temperature Scale (TKTS), which can be deduced from the First and Second laws of Thermodynamics. The low limit of the TKTS is absolute zero, or zero Kelvin, or 0K (without the mark), and since it is linear by definition, only one nonzero reference point is needed to establish its slope. That reference point was chosen, in the original TKTS, as 273.15K, or 0°C.

0°C is a temperature with which we all have a common experience. It is the temperature at which water freezes, or, coming from the other side, ice melts; at which water exists under ideal conditions as both a liquid and a solid under atmospheric pressure. In 1954 the reference point was changed to a much more precisely reproducible point, 0.01°C. This is known as the triple point of water, and is the temperature at which water exists simultaneously as a liquid and a solid under its own vapor pressure. The triple point of water will be the subject of extended discussion in a later article in this series of articles. It is the most important reference point in thermometry.

The unit of temperature of the TKTS is the Kelvin, abbreviated "K". The temperature interval °C is identically equal to the temperature interval K, and °C or K (the latter without the ° symbol) may be used also to indicate a temperature interval. The difference between 1°C and 2°C is 1K or 1°C, but the temperature 1°C = the temperature 274.15K.

Measurements of temperature employing the TKTS directly are hardly suitable for practicable thermometry. Most easily used thermometers are not based on functions of the First and Second Laws. The practicable thermometers that will be discussed later in this series of articles depend upon some function that is a repeatable and single-valued analog of, or consequence of, temperature, and they are used as interpolation devices of utilitarian temperature scales (such as the International Temperature Scale) which are themselves artifacts. The main purpose for the realization of the TKTS is to establish relationships between the Thermodynamic Scale of nature and the practical scales and thermometers of the laboratory or of industry, so that measurements made by non-thermodynamic means can be translated into terms of the TKTS, and rational temperature scales can be constructed on a basis related to realizable physical phenomena.

There exists in nature a number of what are called thermometric fixed points. These are physical states in which some pure material exists in two or three of the three possible phases simultaneously, and temperature is constant.

A two-phase equilibrium is represented by the earlier example of the freezing point of water, or, more properly, the coexistence of liquid and solid water. For this equilibrium to represent a constant temperature, 0°C, pressure must be specified, and the specification is a pressure of 1 standard atmosphere, 101325 Pascal. (A two-phase fixed point at 1 standard atmosphere is called the "normal" point). The variation due to pressure from the defined temperature of a liquid-solid equilibrium is not large (which is not to say that it may not be significant). The freezing point of water is reduced approximately 0.01K for an increase of pressure of 1 atmosphere. The variation due to pressure for a liquid-vapor equilibrium is relatively very large.

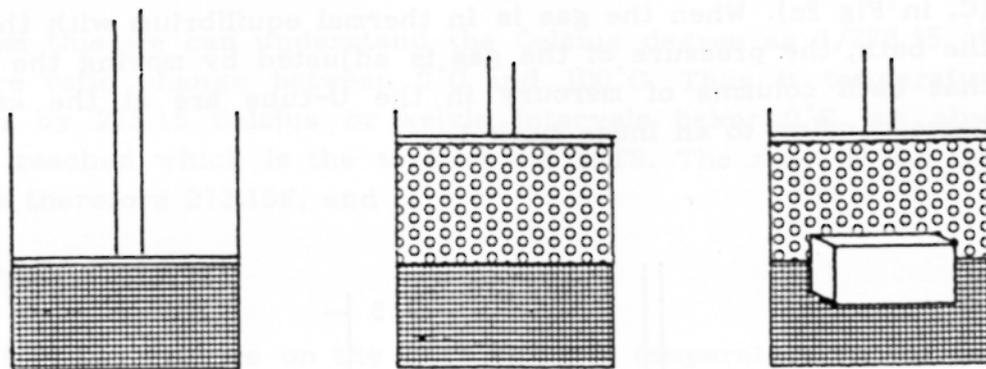
A three-phase equilibrium is represented by the triple point of water, the coexistence of liquid and solid water under its own vapor pressure, at 0.01°C. Because all three possible phases are determined by the physical state, it is generally possible to realize a triple point more accurately than a two-phase point.

This may be seen from the Phase Rule of Gibbs:

$$P - C - 2 = F$$

Eq.1

where P is an integer equal to the number of phases present, C is the number of kinds of molecule present (for an ideally pure material, C = 1) and F is an integer giving the number of degrees of freedom. Obviously, for the two-phase equilibrium there is one degree of freedom, pressure, and for the three-phase equilibrium F = 0; that is, the temperature is independent of any other factor. Fig.1 illustrates one, two and three-phase equilibria.



1a	2a	3a
P = 1	P = 2	P = 3
C = 1	C = 1	C = 1
F = 3	F = 2	F = 0

Fig. 1: The Phase Rule of Gibbs. P = the number of phases present; C = the number of components (1 for a pure material); F = the degrees of freedom. 1a is uncontrolled. 1b is a melt or freeze point. 1c is a triple point.

A typical device for realizing the TKTS is the helium gas thermometer, since the vapor pressure of an ideal gas is a thermodynamic function (or rather a statistical mechanical function, which for the purpose is the same thing). The transfer function of a gas thermometer may be chosen to be the change in pressure of a gas kept at constant volume, or the change in volume of a gas kept at constant pressure. Since it is easier to measure accurately change in pressure than it is to measure change in volume, constant-volume gas thermometers are more common in use than constant-pressure gas thermometers.

A rudimentary gas thermometer is shown in Fig 2. Its operation will be illustrated by using it to show that the zero of the TKTS is 273.15K below the temperature of the normal freezing point of water, 0' on the Celsius Scale.

Fig. 2 shows a cylindrical bulb of constant volume, connected by tubing defined as constant-volume, to a U-tube manometer. A second connection to the manometer leads to a reservoir of mercury, which contains a plunger, P, by means of which the column height of the manometer may be varied. The constant-volume bulb and tubing contain an ideal gas. The bulb is first surrounded by an equilibrium mixture of ice and water (C, in Fig 2a). When the gas is in thermal equilibrium with the slurry in the bath, the pressure of the gas is adjusted by moving the plunger so that both columns of mercury in the U-tube are at the same height, corresponding to an index mark 1.

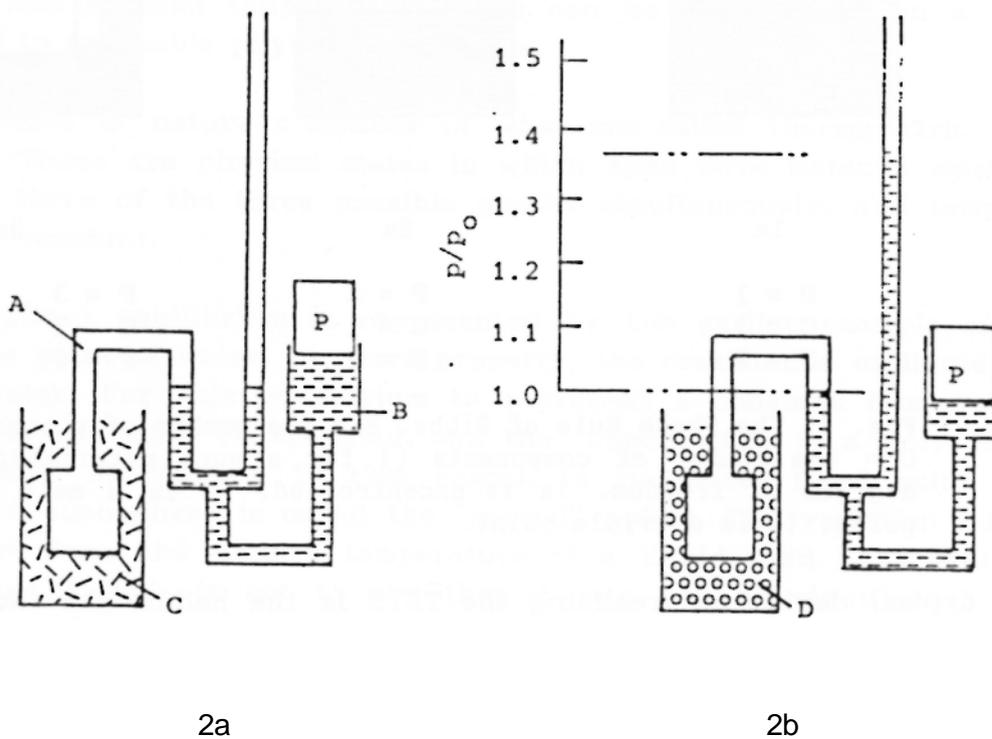


Fig.2: A rudimentary gas thermometer. A = helium gas. B = mercury, C = water + ice (0 C), D = water + steam (100°C), P = a plunger for adjusting mercury level.

Next, the ice bath is removed and replaced with a bath containing boiling water, or more correctly, an equilibrium mixture of liquid and vapor water at a pressure of 1 standard atmosphere, (D, in Fig 2b). As the manometric gas is heated by the boiling water it expands, and the mercury in the manometer is displaced. The plunger is actuated to re-position the surface of the mercury in the left leg at the index mark 1, restoring the criterion of constant volume in the closed gas system, a condition shown in Fig 2b. However the mercury in the right, open leg is not now at the index mark 1, but measurably higher. In fact, the difference in heights indicates that the pressure of the enclosed gas at the boiling point is 1.366099 times the pressure at the freezing point. We can then calculate:

$$(100^{\circ}\text{C} - 0^{\circ}\text{C}) / (1.366099 - 1) = 273.15 \quad \text{Eq. 2}$$

and from this we can understand the Celsius degree as $1/273.15$ of the pressure ratio change between 0°C and 100°C . Thus if temperature is reduced by 273.15 Celsius or Kelvin intervals below 0°C , an absolute zero is reached which is the zero of the TKTS. The zero of the Celsius Scale is therefore 273.15K, and

$$T = t + 273.15 \quad \text{Eq.3}$$

where T is temperature on the TKTS and t is temperature on the Celsius Scale. Note that the temperature interval and the zero of the TKTS have been defined without reference to the properties of any specific sub-stance.

All constant volume gas thermometer measurements can be expressed in terms of the equation

$$P_1 / P_2 = (T_1 - T_0) / (T_2 - T_0) \quad \text{Eq.4}$$

where the Ts are temperatures on the TKTS, the natural temperature Scale, and the T_0 s are the zero of that Scale.

This relationship assumes an ideal gas. The reader will have observed that the gas thermometer reflects Charles' or Boyle's law, if the pressure or the volume of the gas, respectively, be held constant. An ideal gas, is a gas whose behavior can be predicted exactly from Boyle's or Charles' Law, which obeys it through all ranges of temperature or pressure, and where the relationship between concentration (n/V), absolute temperature and absolute pressure is

$$(n/V)(T/P) = 1/R = \text{a constant} \quad \text{Eq.5}$$

more commonly written as

$$PV = nRT \quad \text{Eq.6}$$

where R is the gas constant, identical for all ideal gases. $R = 0.082053$, and is known to about 30ppm.

A second condition is that there be no intermolecular forces acting, thus the internal energy, V , does not depend on the molecular distances, and

$$(dE / dV)_T = 0$$

Eq.7

Unfortunately there is no real ideal gas, and the uncertainty of 30ppm is a large number. Helium comes closest, carbon dioxide varies most widely from ideality. However real gases approach ideality as their pressures are reduced, reflecting a reduction in density. Since it is not possible to measure the change in pressure of a gas at zero pressure (or the change in volume of a gas at zero volume) the requirement for an ideal gas is approached by making a number of measurements at a number of pressures and extrapolating to zero pressure. Such a system of measurements is shown in Fig. 3. Regardless of the nature of the gas, all gas thermometers at the same temperature approach the same reading as the pressure of the gas approaches zero.

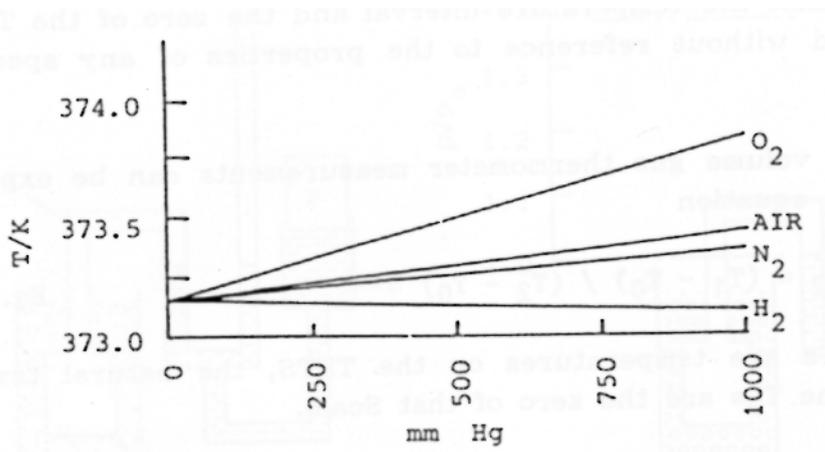


Fig 3: Pressure ratios of various gases at various pressures at the condensation point of steam.

Several authors have proposed modifications of the ideal gas law to account for the non-ideality of real gases. One which is much used, that of Clausius, is the virial equation, which is a series expansion in terms of the density of the gas, and is written:

$$PV = nRT \left(1 + \frac{nB_v}{v} + \frac{n^2 C_v}{v^2} + \frac{n^3 D_v}{v^3} + \dots \right) \quad \text{Eq.8}$$

where the coefficients B, C, D, etc., are called the second, third, fourth, etc., volume virial coefficients, and are constants for a given gas at a given temperature. Over the usual range of gas densities in gas thermometry, it is seldom necessary to go beyond the second virial coefficient.

The departure of real gases from ideality is only one of the problems of accurate gas thermometry. A second is the purely mechanical matter of dead space. There must be a real connection to convey the pressure from the bulb to the manometer. It is inconvenient to locate the bulb and the manometer in the same thermostatted enclosure, and a common practice is to use two separate enclosures, each carefully thermostatted. Fig. 4 is a modification of Fig. 2 to illustrate this configuration.

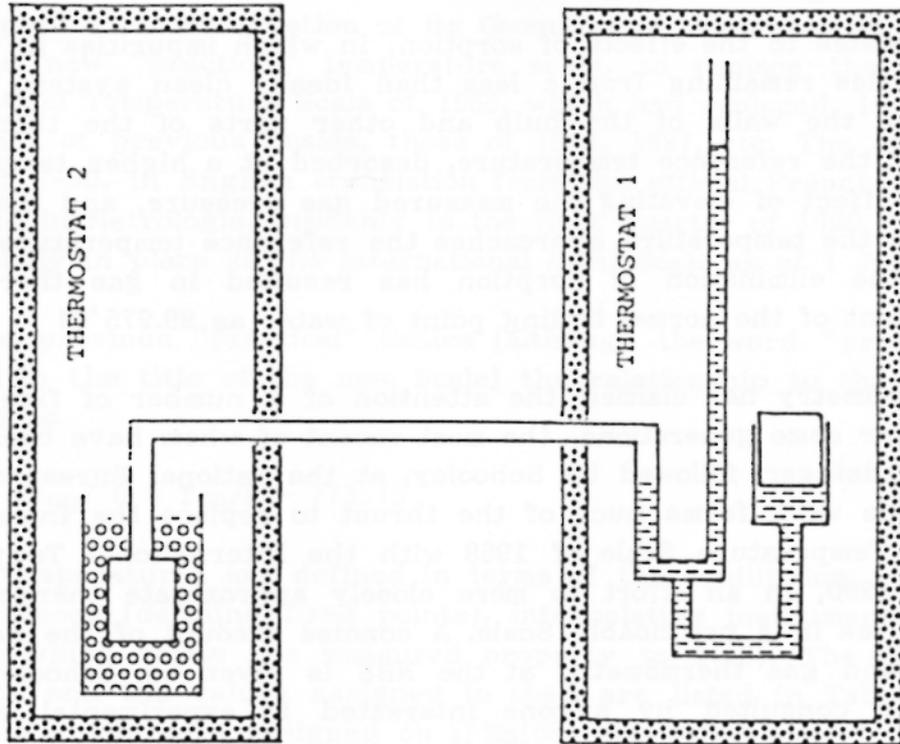


Fig.4: Thermostatted gas thermometer. The U-tube manometer and the gas bulb are separately kept at constant temperature; the (long, perhaps many meters) capillary is not.

The price paid is that there is a capillary tube, generally of some length, which goes through the wall of each of the two thermostats and whose temperature is essentially uncontrolled. The solutions are care and compromise. The bulb volume can be made as large as possible relative to the capillary volume. The temperature distribution along the capillary length can be measured at suitable intervals. The capillary volume can be kept small by providing a capillary of small diameter, but not so small as to introduce thermo molecular pressures where the tube passes through a temperature gradient, or, conversely, a correction for thermo molecular pressure can be made.

A third obvious problem is that of the thermal expansion of the materials of construction. An ideal constant-volume gas thermometer assumes that only the contained gas is subject to thermal expansion, while in reality the whole system is subject to temperature changes, which must be known or estimated, and for which correction must be made.

A fourth correction required is for the hydrostatic head pressure of the gas in the system, including that of the gas column itself.

A fifth relates to the effects of sorption, in which impurities in the gas, or impurities remaining from a less than ideally clean system, are absorbed on the walls of the bulb and other parts of the thermometer system at the reference temperature, desorbed at a higher temperature, with the effect of elevating the measured gas pressure, and then reabsorbed as the temperature approaches the reference temperature. Attention to the elimination of sorption has resulted in gas thermometry measurement of the normal boiling point of water as 99.975°C!

Gas thermometry has claimed the attention of a number of fine experimenters for some generations, the most recent of whom have been Guildner and Edsinger, followed by Schooley, at the National Bureau of Standards. This work forms much of the thrust to replace the International Practical Temperature Scale of 1968 with the International Temperature Scale of 1990, in an effort to more closely approximate thermodynamic temperatures in a practicable Scale. A concise account of the gas thermometer and gas thermometry at the NBS is given by Schooley, and should be consulted by anyone interested in experimental elegance. Schooley provides an example of the accuracy and precision of this work:

Fixed point	Gas therm	IPTS-68	Uncertainty
°C	°C	°C	
Steam pt	99.975	100.000	±0.005
Tin pt	231.924	231.9681	±0.015
Zinc pt	419.514	419.58	±0.03

With the conclusion of work in preparation for ITS-90, gas thermometry is considered to be a finished matter at the NBS. The gas thermometer itself, which should have been preserved as a national shrine or monument, is now in the process of dismemberment.

As a generality, gas thermometry has led the development of thermodynamic values of the thermometric fixed points, and a variety of other methods have been used largely to check its accuracy and consistency. These include acoustic thermometry, dielectric-constant gas thermometry, noise thermometry and radiation thermometry, each appropriate to a portion of the range of the temperature Scale.

2: THE INTERNATIONAL SCALE OF 1990 (ITS-90)

On October 5, 1989, the International Committee on Weights and Measures accepted a recommendation of its Consultative Committee on Thermometry for a new "practical" temperature scale, to replace the International Practical Temperature Scale of 1968, which had replaced, in turn, a succession of previous Scales, those of 1948, 1927, etc. The official text of the ITS-90, in English translation from the official French, will be published in Metrologia, probably in the first quarter of 1990. The ITS-90 is officially in place as the international legal Scale as of 1 January, 1990.

As in previous "practical" Scales (although the word "practical" is not used in the title of the new Scale) the relationship to the TKTS is de-fined as

$$t_{90}/^{\circ}\text{C} = T_{90}/\text{K} - 273.15 \quad \text{Eq.9}$$

and temperatures are defined in terms of the equilibrium states of pure substances (defining fixed points), interpolating instruments, and equations which relate the measured property to $T(90)$. The defining fixed points and the values assigned to them are listed in Table 1, and the values which were assigned on IPTS(68) are listed also, for comparison. It is to be remembered that, while the Scale values assigned to a fixed point may have been changed, the fixed point has the identical hotness it always had.

Several deep cryogenic ranges are provided. These are:

- From 0.65K to 5.0K using a helium vapor pressure interpolation device
- From 3.0K to the triple point of neon (24.5561K) using a constant-volume gas thermometer
- From 4.2K to the triple point of neon with ^4He as the thermometric gas
- From 3.0K to the triple point of neon with ^3He or ^4He as the thermometric gas

These ranges are probably of interest to only a limited number of specialists, and will not be dealt with in detail in this paper. The resistance thermometer portion of the Scale is divided into two major ranges, one from 13.8033K to 0°C and the other from 0°C to 961.68°C , with a number of sub ranges. There is third short range which embraces temperatures slightly below to slightly above 0°C , specifically -38.8344°C to $+29.7646^{\circ}\text{C}$. The Scale ranges are summarized in Table 2.

The interpolations are expressed as the ratios of the resistance of platinum resistance thermometers (PRTs) at temperatures of $T(90)$ and the resistance at the triple point of water; that is:

$$WT(90) = RT(90)/R(273.16\text{K}) \quad \text{Eq.10}$$

a change from the definition of IPTS(68) which used the resistance at 0°C , 273.15K, as denominator.

The PRT must be made of pure platinum and be strain free; it is considered a measure of these requirements if one of these two constrains are met:

$$W(302.9146K) >- 1.11807 \quad (\text{gallium melt point}) \quad \text{Eq.11}$$

$$W(234.3156K) >- 0.844235 \quad (\text{mercury triple point}) \quad \text{Eq.12}$$

and a PRT acceptable for use to the freezing point of silver must also meet this requirement:

$$W(1234.93K) >- 4.2844 \quad (\text{silver freeze point}) \quad \text{Eq.13}$$

The temperature T(90) is calculated from the resistance ratio relation-ship:

$$WT(90) - W_rT(90) = dWT(90) \quad \text{Eq.14}$$

where WT(90) is the observed value, W_rT(90) is the value calculated from the reference function, and dWT(90) is the deviation value of the specific PRT from the reference function at T(90). (The reference functions represent the characteristics of a fictitious "standard" thermometer; the deviation function represents the difference between that thermometer and an individual real thermometer). The deviation function is obtained by calibration at the specified fixed points, and its mathematical form depends upon the temperature range of calibration.

THE RANGE FROM 13.8033K TO 273.16K

The reference function for this range is

$$\ln[W_rT(90)] = A_0 + \sum_{i=1}^{12} A_i \{ [\ln(T(90)/273.16K) + 1.5] / 1.5 \}^i \quad \text{Eq.15}$$

where the values of A₀ and A_i are given in the text of the Scale.

If the PRT is to be calibrated over the entire range, down to 13.8033K, it must be calibrated at specified fixed points and also at two temperatures determined by vapor pressure or gas thermometry. Such thermometers will most likely be calibrated only by National Laboratories, and this paper will not include details, but assume that the sub ranges of general interest to the primary calibration laboratory begin at 83.8058K (-189.3442°C), the triple point of argon.

The sub range from -189.3442°C to 273.16°C requires calibration at the triple point of argon (-189.3442°C), the triple point of mercury (-38.8344°C) and the triple point of water to obtain the coefficients a and b. The deviation function is:

$$dW = a[W(T(90)) - 1] + b[W(T(90)) - 1] \ln W(T(90)) \quad \text{Eq.16}$$

THE RANGE FROM 0°C TO 961.78°C

For the range from 0°C to 961.78°C, the freezing point of water to the freezing point of silver, the reference function is:

$$W_r T(90) = C_0 + \sum_{i=1}^9 C_i [(T(90)/K - 754.15)/481]^i \quad \text{Eq.17}$$

and the coefficients C_0 and C_i are specified in the text of the Scale.

The PRT to be used over this entire range must be calibrated at the triple point of water and the freezing points of tin, zinc, aluminum and silver. The coefficients a, b and c are derived from the tin, zinc and aluminum calibrations respectively, and the coefficient d is derived from the deviation of $WT(90)$ from the reference value at the freezing point of silver. For temperature measurements below the freezing point of silver, $d = 0$. The deviation function is

$$dWT(90) = a[WT(90) - 1] + b[WT(90) - 1]^2 + c[WT(90) - 1]^3 + d[Wt(90) - W(933.473K9)]^2 \quad \text{Eq.18}$$

PRTs may be calibrated over the whole range or for shorter ranges terminating at the freezing points of aluminum or zinc. For the shorter ranges of Eq. 18, the equation is truncated as follows:

<u>Upper limit</u>	<u>Coefficient</u>
Aluminum	$d = 0$
Zinc	$c = d = 0$

For the still shorter range from the triple point of water to the freezing point of tin, calibrations are required at the water triple point and the freezing points of indium and tin. The deviation function is:

$$dT(90) = a[WT(90) - 1] + b[WT(90) - 1]^2 \quad \text{Eq.19}$$

For the range from the triple point of water to the freezing point of indium, calibrations are required at the triple point of water and the freezing point of indium. The reference function is:

$$dWT(90) = a[WT(90) - 1] \quad \text{Eq.20}$$

For the range from the triple point of water to the melting point of gallium, calibrations are required at these points, and the deviation equation is the same as Eq.20 except for the coefficients.

For the range from the triple point of mercury to the melting point of gallium - a most useful range for near-environmental thermometry - calibrations are required at the mercury and water triple points and the gallium melting point, and the deviation equation is

$$dT(90) = a[WT(90) - 1] + b[WT(90) - 1]^2 \quad \text{Eq.21}$$

However the reference function must be calculated from Eq.15 for the portion of the Scale below 0°C, and from Eq.17 for the portion above 0°C.

For a relatively simple polynomial approximation over the resistance thermometer range from -200°C to +600°C, accurate to 1mK above 0°C and 1.5mK below, see the article "Realizing the ITS(90)" in this issue of the Isotech Journal.

The temperature range above the freezing point of silver employs a radiation thermometer as interpolating instrument, and the relationship is:

$$L_{\lambda}(T_{90})/L_{\lambda}(T_{90}(X)) = (\exp[c_2/\lambda T_{90}(X)] - 1) \quad \text{Eq.22}$$

$$/(\exp[c_2/\lambda T_{90}] - 1)$$

where $L_{\lambda}(T_{90})$ and $L_{\lambda}(T_{90}(X))$ are the spectral concentrations of radiance of a blackbody at wavelength λ in vacuum at T_{90} and at $T_{90}(X)$. $T_{90}(X)$ may be the silver point, the gold point or the copper point. $C_2 = 0.014388$ mK.

3: THE 1990 VALUE OF THE OHM

The National representations of the standard ohm also change in 1990. The change was made because the quantum Hall effect, the new international standard of resistance, permits correction of the slight but not insignificant differences in the value assigned to the ohm by the various national laboratories, due to drift over years of the standard resistors which were kept as National standards of resistance. The following adjustments were made by England, the United States and West Germany:

NPL (England) increased the value of their ohm by +1.61 ppm. Thus a perfectly stable 1 ohm resistor calibrated at NPL prior to January 1, 1990, has a new value of 0.99999839 ohm. A 10 ohm resistor has a new value of 9.9999839 ohm.

$$1\text{O (NPL 90)} = 1.000001612 \text{ (NPL 89)}$$

$$1\text{O (NPL 89)} = 0.999998392 \text{ (NPL 90)}$$

NIST (United States) increased the value of their ohm by +1.69 ppm. A drift-free 1 ohm resistor calibrated at NIST prior to January 1, 1990, has a new value of 0.99999831 ohm. A 10 ohm resistor has a new value of 9.9999831 ohm.

$$1\text{O (NIST 90)} = 1.000001692 \text{ (NBS 89)}$$

$$1\text{O (NBS 89)} = 0.999998312 \text{ (NIST 90)}$$

PTB (West Germany) increased the value of their ohm by +0.56 ppm. A drift-free 1 ohm resistor calibrated at PTB prior to January 1, 1990, has a new value of 0.99999944 ohm. A 10 ohm resistor has a new value of 9.9999944 ohm.

$$1\text{O (PTB 90)} = 1.00000056 \text{ O (PTB 89)}$$

$$1\text{O (PTB 89)} = 0.999999944 \text{ O (PTB 90)}$$

Other laboratories adjusted the ohm as follows: VNIIM (USSR) -0.15ppm (a decrease); France, +0.71ppm; BIPM, +1.92ppm.

The effects on the calibration of a standard platinum resistance thermometer calibrated by in 1989, with a typical resistance value at 0°C (for example 25.524904) and at 650°C (for example 85.288424) are as follows:

t(89)	NBS 89 O	NIST 90 O	d(O)	d(t)
0°C	25.52490	25.52486	-0.00004	+0.000393
650°C	85.28842	85.28828	-0.00014	+0.001705

where d(O) is the decrease in resistance measured for the same hotness and d(t) is the increase in hotness represented by the same resistance.

In addition, practicable resistance standards as maintained in most thermometry

laboratories have a small but real resistance dependence upon temperature, written as

$$R_1 = R_0 [1 + a(t_1 - t_0) + \beta(t_1 - t_0)^2] \quad \text{Eq.23}$$

(values of a and β are given in the calibration report for the individual resistor).

The value of resistance is conventionally reported at 25°C, and will continue to be. However

$$25^\circ\text{C} (t_{68}) = 24.994^\circ\text{C} (t_{90}) \quad \text{Eq.24}$$

The change in the value of the ohm may be significant in precision thermometry. It is unlikely that the difference in the value of the reference temperature for the resistor will require consideration. Certainly the β term can be ignored.

In our next issue, we will discuss in detail the physical embodiment of the fixed points and of the equipment and operations involved in realizing them.

TABLE 1
FIXED POINTS OF THE IPTS-68
AND OF THE ITS(90) AS ADOPTED BY CIPM, OCTOBER 5 1989

SUBSTANCE	STATE	CELSIUS TEMP. IPTS-68	CELSIUS TEMP. ITS-90
e-H₂	Trip	-259.34	-259.3467
O₂	Trip	-218.789	-218.7916
Ar	Trip	-189.352	-189.3442
N₂	Boil	-195.802	-195.794
Hg	Trip	-38.842	-38.8344
H₂O	Trip	0.01	0
Ga	Melt	29.772	29.7646
In	Freeze	156.634	156.5985
Sn	Freeze	231.9681	231.928
Zn	Freeze	419.58	419.527
Al	Freeze	660.46	660.323
As	Freeze	961.93	961.78
	Freeze	1064.43	1064.18
Cu	Freeze	1084.88	1084.62

Notes:

e-H₂ represents hydrogen in equilibrium between the ortho and para molecular forms.

Boiling, melt and freeze points are at 1 standard atmosphere = 101 325 Pa.

TABLE 2

RANGES OF THE ITS-90
 THE PURCHASER OF A CALIBRATION MUST STATE THE RANGE REQUIRED*

<u>LOW LIMIT</u>	<u>HIGH LIMIT</u>	<u>FIXED POINTS REQUIRED</u>
-259.3467	0.01	e-H (TP), e-H ₂ (VP), Ne (TP), O ₂ (TP), Ar (TP), Hg (TP), H ₂ O (TP)
-218.7916	0.01	O ₂ (TP), Ar (TP), Hg (TP), H ₂ O (TP)
-189.3442	0.01	Ar (TP), Hg (TP), H ₂ O (TP)
0.01	29.7646	H ₂ O (TP), Ga (MP)
0.01	156.5985	H ₂ O (TP), Ga (MP), In (FP)
0.01	231.928	H ₂ O (TP), Ga (MP), Sn (FP)
0.01	419.527	H ₂ O (TP), Sn (FP), Zn (FP)
0.01	660.323	H ₂ O (TP), Sn (FP), Zn (FP), Al (FP)
0.01	961.78	H ₂ O (TP), Sn (FP), Zn (FP), Al (FP), Ag (FP)
-38.8344	29.7646	Hg (TP), H ₂ O (TP), Ga (MP)

(TP) = triple point,

(VP) = a vapor pressure determination,

(FP) = freezing point at 1 standard atmosphere,

(MP) = melting point at 1 standard atmosphere

*The purchaser may choose to specify a combination of several ranges, for example, -189.3442° to +419.527°, or some extrapolation, for example, -200° to +500°.

TABLE 3
THE COEFFICIENTS OF THE REFERENCE FUNCTIONS

The values of the coefficients A_i and C_i of the reference functions of Eq. 15 and 17

Eq.15		Eq.17	
CONSTANT OR		CONSTANT OR	
COEFFICIENT VALUE		COEFFICIENT VALUE,	
A_0	-2.135 347 29	C_0	2.781 572
A_1	3.183 247 20	C_1	1.646 509
A_2	-1.801425 97	C_2	-0.137 143
A_3	0.717 272 04	C_3	-0.006 497
A_4	0.503 440 27	C_4	-0.002 344
A_5	-0.618 993 95	C_5	0.005 118
A_6	-0.053 323 22	C_6	0.001 879
A_7	0.280 213 62	C_7	-0.002 044
A_8	0.107 152 24	C_8	-0.000 461
A_9	-0.293 028 65	C_9	0.000 457
A_{10}	0.044 598 72		
A_{11}	0.118 686 32		
A_{12}	-0.052 481 34		

TABLE 4
VALUES OF $W_r(t_{90})$ AT THE RESISTANCE THERMOMETER FIXED POINTS

FIXED POINT $W_r(T_{90})$		FIXED POINT $W_r(T_{901})$	
e-H ₂ (TP)	0.001 190 07	Ga (MP)	1.118 138 89
Ne (TP)	0.008 449 74	In (MP)	1.609 801 85
O ₂ (TP)	0.091 718 04	Sn (FP)	1.892 797 68
Ar (TP)	0.215 859 75	Zn (FP)	2.568 917 30
Hg (TP)	0.844 142 11	Al (FP)	3.376 008 60
H ₂ O (TP)	1.000 000 00	As (FP)	4.286 420 53

FUNDAMENTALS OF THERMOMETRY, PART 1, REFERENCES GAS

THERMOMETRY AND THE THERMODYNAMIC SCALE

James F. Schooley, *Thermometry*, CRC Press, Boca Raton, Florida (1986) especially on gas thermometry at the NBS

T. J. Quinn, *Temperature*, Academic Press, London and New York (1873)

F. Henning, H. Moser, *Temperaturmeßung*, Springer-Verlag, Berlin and New York, 3rd edition (1977). German text; fine section on vapor-pressure thermometry by W. Thomas

THE INTERNATIONAL TEMPERATURE SCALE

H. Preston-Thomas, *The International Practical Temperature Scale of 1968 (revision of 1975)* Metrologia 12, 1 (1976)

Supplementary Information for the IPTS-68 and the EPT-76, Bureau International des Poids et Mesures, Sevres, France. This publication continues to be valuable, but will be revised at some future date to include ITS-90

R. E. Bedford, G. Bonnier, H. Maas, F. Pavese, *Techniques for approximating the International Temperature Scale of 1990*, BIMP, when published; no projected date is known. Our reading of unofficial copies of a late draft indicate that this will be of great value.

The International Temperature Scale of 1990 is the title of the official text of the new Scale, and it will be published in Metrologia. Metrologia advises that it will be published in Vol. 27 No. 1 (February 1990).

THE 1990 OHM

Changes in the Value of the UK Reference Standards of Electromotive Force and Resistance, National Physical Laboratory, Teddington, England (1989)

N. Belecki et al, NIST Technical Note 1263, *Guidelines for Implementing the New Representations of the Volt and the Ohm*, U.S. Department of Commerce (1989)

V. Kose, H. Bachmair, *Neue Internationale Festlegung für die Weitergabe elektrischer Einheiten*, Physikalisch-Technische Bundesanstalt PTB-E-35, Braunschweig FRG (1989)

PRACTICAL CALIBRATION OF THERMOMETERS ON THE INTERNATIONAL TEMPERATURE SCALE OF 1990

by Henry E. Sostmann

ABSTRACT

I discuss the stipulations of ITS(90) over the platinum resistance thermometer range (13.8K to 961.78°C), and means for the calibration of thermometers in primary and secondary laboratories.

INTRODUCTION

There exists only one temperature scale with an absolute basis in nature. This is the Thermodynamic Kelvin Temperature Scale (TKTS). The TKTS is represented by a straight line with its origin at absolute zero (OK or -273.15°C), passing through a single defining fixed point (273.16K or $+0.01^{\circ}\text{C}$) and extending upward indefinitely toward higher temperatures. Along this straight line, it is possible to assign values to other natural conditions, fixed points other than and in addition to OK and 0.01°C , which may be adopted as defining characteristics of other temperature scales. The thermodynamic temperatures of these fixed points are established by any of a number of means (commonly constant-volume gas thermometry) and if possible, confirmed by other direct means. A discussion of the realization of the TKTS (and a full description of ITS(9)) is given in an article in this issue of the *Isotech Journal of Thermometry*, entitled "Fundamentals of Thermometry, Part 1", referred to hereafter as "Fundamentals 1".

Instruments for the direct measurement of thermodynamic temperatures do not easily permit the measurement of temperatures in the working world. It has been necessary to develop other schemes, other temperature scales, of a more practicable nature.

A thermometer can be made of any physical principle which is a function of temperature, and which, while it is not thermodynamic, is yet repeat-able and monotonic. Examples of such properties (and all of them have been employed in practicable thermometers) are the expansion or contraction of solids and liquids, change in the electrical properties of conductors, the color and brilliance of light emitted from a very hot source, the frequency of a temperature dependant oscillator. Such thermometers can be related to the TKTS, over their useful range, by calibration at the fixed points established along the TKTS, and by agreement on a consensus temperature scale, which takes into consideration the properties of the thermometer and describes mathematical relationships which govern interpolation of temperature values which lie between the calibration fixed points.

I have not space here to go into the fascinating history of the development of practical temperature scales, but the interested reader will do well to consult at least the references given. The Scale which will concern us is the International Temperature Scale of 1990 (ITS(90)), which on January 1, 1990, replaced the International Practical Temperature Scale of 1968, itself a successor to the Scales of 1948 and 1927. The ITS(90) is a construct of the International Committee for Weights and Measures, under the Treaty of the Metre, and is the legal Scale for all signatories to that Treaty.

The ITS(90), like its predecessors, stipulates a number of fixed points which define the Scale, and specifies interpolation devices acceptable for its realization. In the Scale of 1968, these interpolation instruments were a specifically-characterized platinum resistance thermometer (SPRT) over the range from 13.81K to 630.74°C, a platinum/platinum-rhodium thermocouple over the range from 630.74°C to 1064°C, and any radiation thermometer obeying Planck's Law above 1064°C.

In the ITS(90), the lower limit of the Scale is extended downward to 0.6K, using constant-volume gas thermometers or vapor-pressure thermometers for interpolation to 13.8K. The noble-metal thermocouple, with its inherent problems of stability and repeatability, is eliminated entirely, and the range of the SPRT is now 13.8K to 961.78°C. The radiation range is extended downward to 961.78°C and upward indefinitely.

In addition, most of the values given for the fixed points are changed, and some new fixed points (some of which were secondary points of IPTS(68)) added. Table 1 of Fundamentals 1 lists the fixed points of the ITS(90) and, for comparison, those of IPTS(68).

Although the ITS(90) is now legally in place, there are several National approaches to its effective date in commerce and industry. It is my understanding that NPL considers it to be effective immediately (although the official text has not yet been published); that West Germany has decreed a period of 18 months after which it is to be effective; that NIST has asked that it be effective as soon as possible. What is crucially important is that any temperature-related data developed in science and industry identifies the Scale on which data is reported.

CALIBRATION LABORATORY REALIZATION OF THE ITS(90)

The objective of the thermometer calibration laboratory is to establish a relationship between a specific unit working thermometer and the ITS(90), within required limits of uncertainty. I intend to describe two approaches to this objective, one as primary and as precise as possible, and the other secondary, more economical of time and equipment (and more flexible) with reduced precision and accuracy.

The ITS(90) provides for a larger number of calibration ranges than did the IPTS(68); there are, in fact, 11. It is no longer necessary to calibrate a thermometer over the full range if only a portion of it is of concern. It becomes the obligation of the purchaser of a calibration service to specify in his order to the laboratory the range of ranges over which he wants his thermometer calibrated. The ranges of the ITS(90), and the fixed points required to calibrate them, are shown in Table 2 of Fundamentals 1. Certainly there will be economic advantage to limiting the calibration range to that actually needed.

There are many thermometers in service which have relatively recent calibrations on IPTS(68). One may ask whether they now require full re-calibration to ITS(90). Most suppliers of calibration services (some of the National Laboratories, and Isothermal Technology) are prepared to furnish ITS(90) tables for thermometers recently calibrated and presumably still within calibration, although these suppliers cannot accept

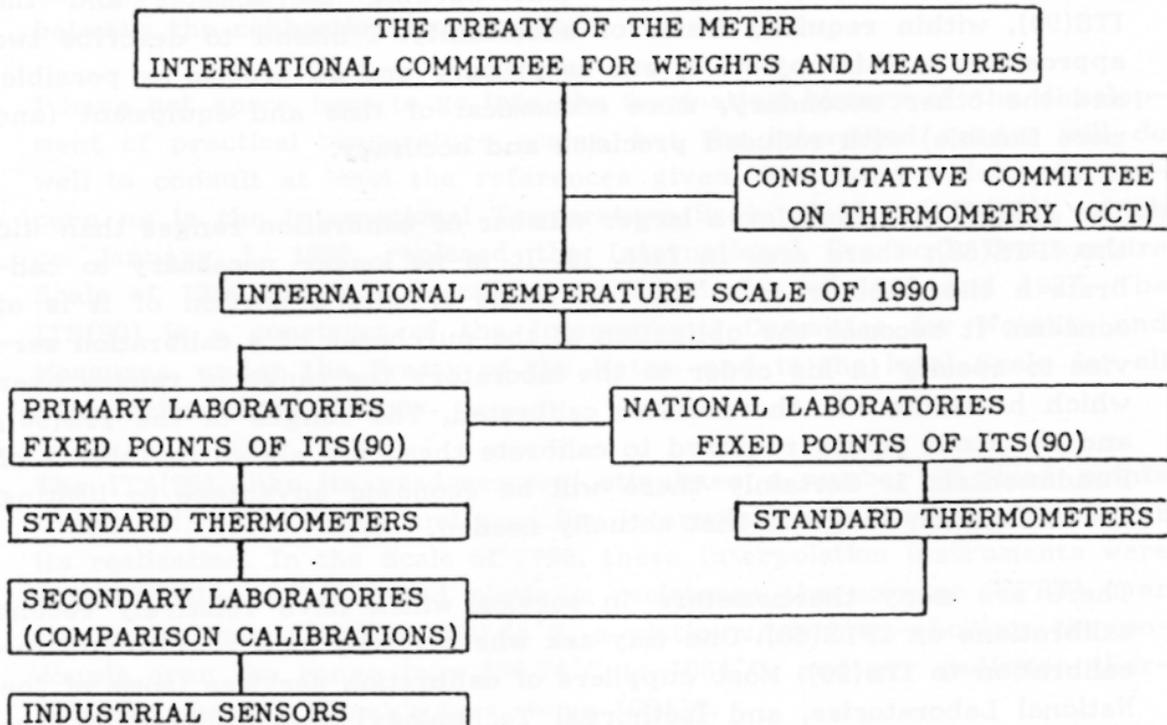
responsibility for the validity of the data used (for example, if a thermometer has drifted since the original calibration). Isothermal Technology has available for sale a complete ITS(90) interpolation program for MS-DOS microcomputers, using which a laboratory can do its own updates.

The chart on the next page illustrates the relationship between the CIMP, the ITS-(90), national, primary and secondary laboratories, and users of thermometers:

THE PRIMARY LABORATORY

The function of the primary laboratory is the calibration of thermometers at fixed points of the ITS(90). This discussion will be limited to the calibration of thermometers over the range of the platinum resistance thermometer from -189°C to $+961.78^{\circ}\text{C}$. Below this lower limit, I believe that calibration requirements are best referred to the National Laboratories; that calibrations requiring constant-volume gas thermometry or vapor-pressure thermometry at cryogenic temperatures are of limited interest to and beyond the probable scope of most non-Government laboratories.

HIERARCHY OF THERMOMETRY



With this limitation, the equipment requirements are as follows:

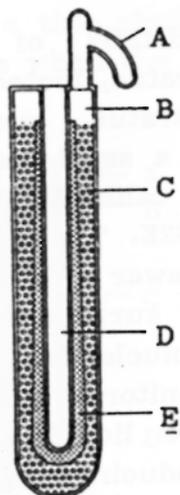
- Apparatus for realizing the fixed points of the Scale

- Platinum resistance thermometers, having valid National Laboratory calibration tables, and suitable for the ranges. The resistance thermometer ranges of the ITS(90) cannot be accommodated by a single design of platinum resistance thermometer. The traditional long-stem 25.52 SPRT with its mica cross is not suitable for use below approximately -200°C nor above $+650^{\circ}\text{C}$, and use even at 650°C should be limited. Mica is a natural crystalline material bound by water, which is given up more rapidly as temperature increases, with the results of vapor in the sheath and eventual deterioration of the mica structure. A mica-based thermometer should not be used to the aluminum point. For the range which extends down to 13.8K the 25.52 capsule thermometers remains the sensor of choice. For the range to $+961^{\circ}\text{C}$, new high-temperature platinum resistance thermometers (HTSPRTs) are now available, usually with resistance at 0°C of 0.252, and with a lower practicable limit of -50°C .

- Resistance-measuring bridges, current comparators, etc., capable of resolution of 1ppm or 0.1ppm, and reference resistors of suitable range (12 and 1052, for example) having valid calibrations to the 1990 ohm. (The 1990 redefinition of the ohm, and its effect on previously calibrated standard resistors, is discussed in Fundamentals 1.

Table 2 shows a list of commercially available equipment and approximate price. I have not hesitated to include such a list, because there are limited, and in many cases only one, sources for this equipment. The fixed points and thermometers required will be determined by the ranges over which thermometers are to be calibrated.

You will have noticed that the triple point of water is required for every range. Any laboratory engaged in thermometry, whether primary or secondary, should be equipped to realize this most fundamental of the fixed points. The measured resistance at this temperature is the denominator of the W ratio of SPRT calibration tables on ITS(90), and for the most accurate thermometry, must be measured immediately after the measurement of any other temperature. (This measurement also provides assurance that the thermometer has not suffered a trauma in use). Those experiences most likely to cause shift in an SPRT (cold work, strain, and oxidation) are closely proportional to $R(t)$, and have little effect on $W(t)$. Also, $W(t)$ is independent of the base unit used to measure $R(t)$, and so all measurements made using the same reference resistor and instrument are independent of the absolute ohmic value of that resistor.



Furthermore, it is a good quality-assurance technique to record all water-triple point measurements on a control chart for the individual thermometer. If the thermometer has not shifted at the water triple point, it is almost certainly in calibration over its range. It is also a good idea to measure the resistance at the water triple point whenever the thermometer has been returned from a National Laboratory calibration, and compare it to the certificate value, to determine that it has not suffered in transportation. The water triple point is inexpensive and easy to realize to an accuracy better than 200pK. In a commercially-available bath, Isotech Model ITL-M-18233, it is possible to maintain the triple-point state for many

weeks or months, so that this most fundamental fixed point is constantly available.

A water triple point cell is shown in Fig.1. Letter A is a convenient handle; B is the water vapor space; C is pure liquid water; D is the thermometer well, and E is ice frozen at the well.

A word here on the question of calibration intervals for SPRTs. Not only are full calibrations expensive, but they usually involve shipping the thermometer, which is to be avoided unless absolutely necessary. I do not believe in the fixed calibration interval. A thermometer used seldom and carefully might require recalibration in 5 years; one used often and carelessly might require it in 5 minutes. The time to recalibrate is when the resistance shift at the water triple point is no longer acceptable; say 500 pK for the primary laboratory. (For laboratories concerned with environmental temperatures, records at the gallium melt point may be preferred).

Beginning at the low end of the long-stem SPRT range, the low fixed point is the triple point of argon, -189.34°C . The point is expensive to realize, and I do not know personally of a commercial apparatus for it. Most primary laboratories will choose to perform calibrations in the vicinity of this temperature by comparison with SPRTs having National Laboratory calibrations. Indeed, some National Laboratories will calibrate thermometers submitted to them by comparison, using reference thermometers which are their own standards and calibrated only infrequently at the argon triple point itself. In its publication "Adoption of ITS(90)", NPL makes the following statement:

"Most thermometers (submitted for calibration) will involve...a comparison with NPL standards in a bath of liquid nitrogen (about -196°C)"

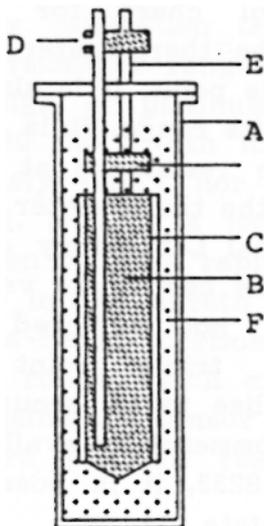


Fig.2 shows the major details of a low temperature comparison apparatus, Isotech Model ITL-M-18205. In this apparatus, comparison calibrations may be done for a small fraction of the cost of triple-point calibrations, with uncertainties less than $\pm 0.002\text{K}$. The apparatus comprises a stainless steel Dewar (A), an inner copper equalizing block (B) surrounded by a porous blanket for uniform nucleation (C), top connections for filling and monitoring the height of liquid coolant (inexpensive liquid nitrogen) and a manifold (D) for introducing helium gas between the thermometers and the wells (optional) for superior thermal conductance. (E) are three wells for thermometers; (F) is the liquid nitrogen coolant. With regard to electrical measurements of thermometers by comparison, using a resistance bridge which employs a single reference resistor, a good technique is to connect the thermometer under test as the unknown resistance and a reference thermometer

as the *standard* resistor, and, at temperature, read the ratio of one to the other. The unknown resistance can then quickly be calculated from the calibration table for the reference thermometer. The temperature need not be exact nor even precisely known.

The triple point of mercury, -38.8344°C , is required for four ranges of ITS(90). Cells are available in which mercury as pure as 15ppb is sealed within a welded stainless steel housing (which avoids any potential problem of environmental hazard) under its own vapor pressure.

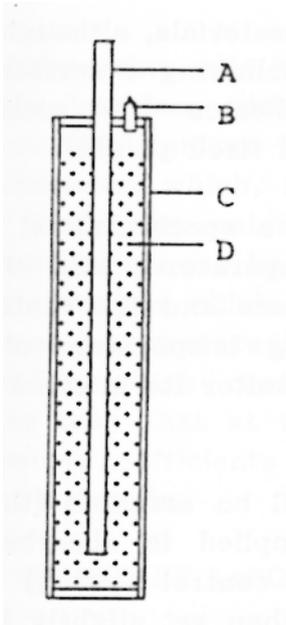
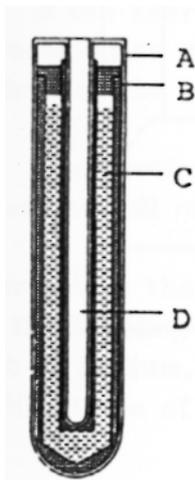


Fig.3 shows the construction of the Isotech mercury cell, Model ITL-M-17724. It is most easily used in the Isotech ITL-M-17725 Mercury Triple Point Apparatus, a self-contained housing which includes mechanical refrigeration and a control system, and makes the realization of the point almost automatic. (A) is the thermometer well; (B) is the welded-off evacuation tube; (C) is the fusion-welded steel housing; (D) is pure mercury.

The melting point of gallium, 29.7646°C , is required for four ranges. The ITL-M-17401 Gallium Cell can be operated in any closely-controlled fluid or water bath, but, as an alternative, the ITL-M-17402A Gallium Melt Apparatus automates the melt cycle to the extent that it can be switched on by a time clock before the beginning of the working day, and ready for use when the day begins.

Freezing points of high-purity metals are specified for the five ranges whose low end is 0°C . A typical freezing-point-of-metal cell is shown in Fig.4.



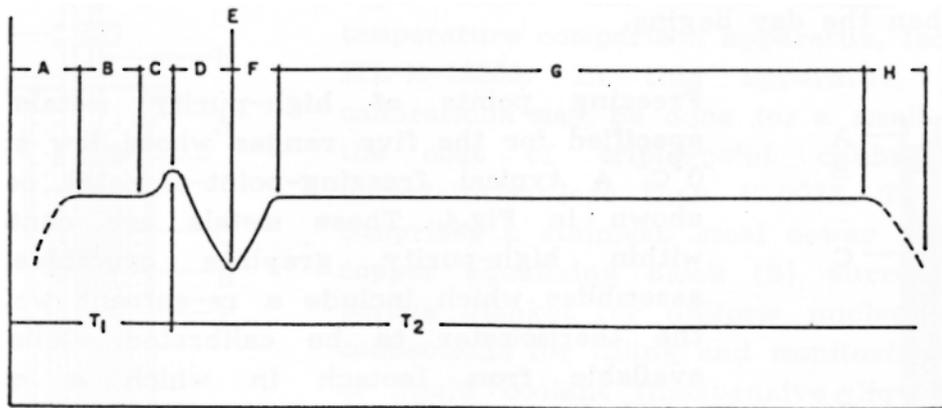
These metals are contained within high-purity graphite crucibles, in assemblies which include a re-entrant well for the thermometer to be calibrated. Cells are available from Isotech in which a quartz envelope completely surrounds the crucible, so that the cell can be filled, in manufacture, with an inert atmosphere which will be 1 standard atmosphere at the freezing temperature, and completely sealed. Sealed cells avoid any risk of contamination from outside sources, and remove the need to make pressure corrections. They are easily used in furnaces such as ITL-M-17701 (150° to 500°C) and ITL-17702 (500° to 1000°C).

The realization of a fixed point is similar for all materials, although details will differ, depending upon the metal. The following describes the cycle of a metal freeze point. Table 3 indicates the estimated reproducibility of the ITS(90) using the prescribed fixed points.

A cell containing a pure metal is assured to be in a specific state; for a metal freeze point kept at laboratory ambient temperature, this will be the solid state. The cell is inserted into the furnace and the controller set a few degrees above the anticipated melting temperature of the material. A thermometer is placed in the well to monitor its

internal temperature rise.

At the onset of melting, the temperature rise will be arrested (this is called the "melt arrest"), because the heat supplied is absorbed in phase change, and will rise again (to the furnace control setting) when all the metal has been liquefied. The controller is then set slightly below the melt temperature. As the temperature drops, a "freeze arrest" will be observed, for most metals preceded by an undercool. The freeze arrest is maintained by the latent heat of the metal, and its temperature is a physical constant for the specific metal. During the freeze plateau, which may be maintained for as much as 12 hours, temperature is fixed, and thermometers may be calibrated. Fig.5 shows a typical melt-freeze cycle.



Triple points, such as the water and mercury triple points, are independent of the pressure of the ambient atmosphere. Freeze points and melt points demonstrate some pressure dependence. For measurements of the highest precision, a pressure correction should be made.

All fixed-point cells including triple point cells define their temperatures at the interface with either the atmosphere or with their vapor pressures. This surface is not the location of the sensitive element of the thermometer, which, instead, is located some distance down a well into the fixed-point material. For measurements of the highest precision a correction should be made for the pressure of the hydrostatic head. (For materials which expand upon freezing, like water and gallium, the surface temperature is warmer than that seen by the thermometer. For materials which contract upon freezing, the surface temperature is cooler than that at the thermometer). Table 4 is a list of the ambient pressure coefficients and the hydrostatic head coefficients for fixed-point materials.

THE SECONDARY LABORATORY

Secondary laboratory calibrations are almost always comparison calibrations, made by comparing the resistance of a test thermometer to the calibration of an SPRT in an isothermal situation. Secondary calibrations are made where reduced accuracy and precision is appropriate, and/or:

- the throughput must be high; there are many thermometers to be calibrated in the laboratory cycle and the calibration cost must be kept low

- the thermometers are parts of systems, requiring total system calibration
- the thermometers are of such size, shape, thermal mass, or other characteristics that they will not fit into or operate within the constraints of the primary calibration apparatus.
- calibrations must be done over a closely-spaced range of temperatures, not all of which exist as fixed points.

Nevertheless the secondary laboratory should be equipped with at least one fixed point, most probably the triple point of water or the melting point of gallium, to maintain quality assurance and to avoid unnecessary recalibrations of its own standard thermometers. In general, the equipment requirements of the secondary laboratory are dictated by the thermometers to be calibrated.

Comparison calibration baths which are to operate below 0°C require cooling. Baths for temperatures between -196°C and -80°C commonly use liquefied gases to cool, and may be dedicated to a specific temperature (at which the liquid coolant boils) or may be varied over a limited range of temperature by varying ambient pressure, by isolating the equalizing block from the coolant, or by controlling the coolant level. Baths for temperatures between -80°C and slightly above ambient are usually cooled by mechanical refrigeration or Peltier cooling. Many such baths employ stirred silicone or other oils as thermal transfer media and are continuously variable. Such a bath may include heating as well as cooling, and be variable over the range of -80°C to +300°C with several changes of medium as the variation of oil viscosity with temperature may demand.

At temperatures above 300°C, a limit is the flash point of the oil medium. One may choose from a wide range of block furnaces, with ranges as high as 600°C, in which the thermometer is inserted into a well-fitting hole in a heated metal block, or a bath of air-levitated finely-divided aluminum oxide, which can be used to 700°C. Last, furnaces are available for the calibration of thermocouples to 1100°C and higher.

The most productive approach may be to define the requirement and to enlist the aid of equipment manufacturers in selecting the appropriate equipment for the specific work to be done. Isotech manufactures a full range of such baths and furnaces.

AN ALGORITHM APPROXIMATING ITS(90)

A full discussion of the mathematical structure of the ITS(90) is given in Fundamentals 1. However for those whom it may serve, we offer a simplification, an algorithm due to NPL, accurate to 0.001K over the range from 0° to 630°C and to 0.0015K over the range from -200° to 0°C.

$$t_{90} - t_{68} = S \sum_{i=1}^8 a_i (t/630)^i$$

where

i=	1	2	3	4
a_i=	-0.148759	-0.267408	1.080760	1.269056
i=	5	6	7	8

a_i= -4.089591 -1.871251 7.438081 -3.536296

TABLE 2
EQUIPMENT FOR THE PRIMARY CALIBRATION LABORATORY
FOR THE REALIZATION OF THE FIXED POINTS

	Source	Price*
Low temp furnace (150° to 500°C)	ISO	\$13000
High temp furnace (500° to 1000°)	ISO	15500
Indium fixed-point cell	ISO	10500
Tin fixed-point cell	ISO	6800
Zinc fixed-point cell	ISO	6000
Aluminum fixed-point cell	ISO	6000
Silver fixed-point cell	ISO	10500
Mercury triple-point cell	ISO	4000
Mercury triple-point apparatus	ISO	8500
Gallium melt-point cell	ISO	3000
Gallium melt apparatus	ISO	3500
Liquid nitrogen or argon comparator	ISO	5500
Water triple-point maintenance bath	ISO	13000
Water triple-point cells	ISO	1500
	NPL	1500
	JAR	1000

STANDARD PLATINUM RESISTANCE THERMOMETERS

25.5 ohm, -200° to +650°C	ISO	3500
	YSI	3500
0.25 ohm, -50° to +1000°C	ISO	3500

BRIDGES FOR RESISTANCE MEASUREMENT

Precision Current Comparator, 9975	GUI	35000
Automatic AC bridge, F-18	ASL	35000

MS-DOS COMPUTER PROGRAM FOR INTERPOLATION

ITS(90) interpolation program	ISO	250
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Note: This Information is for convenience, prices are an indication of price range only.

ISO = Isothermal Technology Ltd., Southport, England
 YSI = YSI Inc., Yellow Springs, Ohio USA
 GUI = Guildline Instruments, Smith Falls, Ontario, Canada
 ASL = Automatic Systems Ltd, Leighton Buzzard, England

NPL = National Physical Laboratory, Teddington, England
 JAR = Jarrett Instrument CO., Wheaton, Maryland, USA

TABLE 3
REALIZABLE ACCURACIES OF THE FIXED POINTS
WITH RESPECT TO ITS(90)

FIXED POINT	REALIZABLE ACCURACY, KELVINS
Argon, nitrogen, by comparison method	0.002
Mercury, triple point	0.0005
Water, triple point	0.00015
Gallium, melt point	0.0004
Indium, freeze point	0.0005
Tin, freeze point	0.001
Zinc, freeze point	0.001
Aluminum, freeze point	<0.002
Silver, freeze point	<0.004

TABLE 4
ATMOSPHERIC AND HYDROSTATIC PRESSURE CORRECTIONS

Substance	Equilib. Temp T₉₀	Pressure Effects	
		Atmospheric	Hydrostat
		mK per std. atmos	mK per M liquid head
e-H (tp)	13.8033	*	0.25
Neon (tp)	24.5561	*	1.9
Oxygen (tp)	54.3584	*	1.5
Argon (tp)	83.8058	*	3.3
Mercury (tp)	234.3156	*	7.1
Water (tp)	273.16	*	-0.73
Gallium (mp)	302.9146	-2.0	-1.2
Indium (fp)	429.7485	4.9	3.3
Tin (fp)	505.078	3.3	2.2
Zinc (fp)	692.677	4.3	2.7
Aluminium. (fp)	933.473	7.0	1.6
Silver (fp)	1234.93	6.0	5.4

Note: * indicates that a triple point is independent of atmospheric pressure, since it is defined as an

equilibrium point under its own vapor pressure.

P L A T I N U M R E S I S T A N C E T H E R M O M E T E R S A S I N T E R P O L A T I O N S T A N D A R D S F O R I T S — 9 0

by John P. Tavener

ABSTRACT

The requirements of the International Temperature Scale of 1990 (IT-90) extend the high-temperature end of the range of the Standard Platinum Resistance Thermometer (SPRT) from 630°C to 962°C, extend the low end of the radiation thermometer to 961°C, and eliminate the platinum/platinum-rhodium thermocouple.

Three years ago, Isotech began development of a new high-temperature Standard Platinum Resistance Thermometer (HTSPRT) in anticipation of these requirements. Results of extensive testing show excellent stability, the average change in R_0 being less than 1mK per 100 hours at 1000°C. The annealing time required in manufacture to achieve this stability is 100 to 150 hours at 1000°C. The changes in R_0 are typically less than 1mK after rapid cooling from 1000°C and annealing at 480°C for 1/2 hour.

Problems of gas and metal-ion transport across the quartz thermometer sheath at high temperatures are addressed.

INTRODUCTION

The International Scale of 1990 stipulates platinum resistance thermometers as the interpolation instrument from 13.8K (-259.2°C) to +962°C; an included temperature range of 1221°C! No single thermometer can span this range. At least three types are required, with overlapping range capability.

- 1: The capsule thermometer
Normal range 13.8K to about 250°C
Nominal R_0 25.5 Ω

This thermometer's sheath length is usually about 50mm, and it is intended to be installed in equipment with thin lead wires so as not to convey heat into a cryogenic apparatus.

- 2: The traditional long-stem thermometer (SPRT)
Range -200° to 630° or 670°C
Nominal R_0 25.5 Ω

This thermometer will probably continue to be the most common in the laboratory, since its temperature range includes most measurement requirements. In its traditional construction, using mica as a coil former, it can be used with caution and infrequency to 630°C, but is suitable for calibration at no fixed point higher than zinc (419°C), and the uncertainty of the extrapolation to 630°C is on the order of 8mK for a primary calibration. A construction employing a quartz former, permitting calibration also at the aluminium point (660°C) would reduce the uncertainty due to extrapolation to essentially zero. Isotech

produces such a standard thermometer, Model 909.

The ITS-90 defines 11 calibration ranges, each of which has a fixed point at both ends. Thus, on the ITS-90, a thermometer which cannot be calibrated at the aluminum point is restricted to a calibration range whose upper end is the zinc point. The longest calibration range for the mica-based 25.52 thermometer is from -189.3442° to $+419.527^{\circ}\text{C}$, and for Isotech's Model 909 is -189.3442° to $+670^{\circ}\text{C}$.

- 3: New high-temperature long-stem thermometers (HTSPRT).
Range -50° to 1000°C
 R_0 0.25 to 2.00

The low R_0 of the HTSPRTs permits the use of heavier platinum wire and relieves the problem of insulation leakage, but may require a reassessment of a laboratory's ability to measure electrical resistances of low level and, at the higher temperatures, often in the presence of noise.

Such long-stem HTSPRTs have now been developed specifically to meet the requirements of the new ITS-90. This paper describes the evolution of the Isotech ITL-M-962 High Temperature Standard Platinum Resistance Thermometer.

DEFINING THE PROBLEMS - DESIGN CONSIDERATIONS

- 1: Resistance value. The traditional long-stem SPRT has a nominal resistance value of 25.5 Ω at 0°C , chosen many years ago because it allowed an easy first estimate of temperature; 0.12 is approximately 1.0°C over the range from 0° to 100°C . While this is hardly a consideration at 960°C , HTSPRTs generally have been made in submultiples of 25 Ω ; 0.25 Ω and 2.5 Ω . Clearly, the lower the element resistance the smaller the effect of the unwanted shunting resistances from the structure, which at high temperatures are unavoidable. Also, the lower the resistance the greater cross-section of wire can be used, and the more likelihood of a mechanically stable element at temperatures where platinum has very low structural strength. I chose heavy wire and 0.25 Ω for my first thermometers. Higher resistances, which would reduce the electrical measurement problem, will be assayed later.
2. Diameter of sheath. The constraint is that the thermometer must fit into the thermometer well of fixed point calibration devices, dictating a sheath diameter between 7.5 and less than 8mm.
3. Length: The length must be such that the thermometer can be calibrated in conventional fixed-point devices, and so that the junction between its internal platinum lead wires and the external copper cable is outside the hot area. I chose 65 cm.
4. Sheath material: For a long time, the only material used has been quartz. Metal sheaths emit vapors and metal ions which are poisonous to platinum, and also give an illusory sense of ruggedness in what is necessarily a fragile device.

THE INTERNAL CONSTRUCTION

1. The sensing element configuration: Many configurations have been used. The main options seem to have been a cross shape or a spade shape, with suitable edge notching to retain the separation of the wires wound on it. I chose the spade shape,

recognizing that the best quartz is an only imperfect insulator at 1000°C, because it reduced the number of contacts between platinum and quartz to one-half. The notches were laser-cut, which had the effect of providing a polished surface on which the wire could ride as it moved under the influence of thermal expansion and contraction. Figure 1 shows the element construction.

2. The lead wires: Again, there seemed to be two options. These were (a) the four lead wires fed through short (50mm or so) quartz capillaries, and at the ends of the quartet of capillaries the wires located by passing through a four-hole disc, or (b) single lengths of quartz capillary over the entire length of each lead wire. I chose (b). This choice is crucial, since all of the failures I know of in HTSPRTs have been caused failures of lead wires from thermal working.
3. The handle, or head: In the handle, or head, the internal platinum lead wires connect to the external copper cable. The head needs to be light-weight, so as not to add a bulky mass to the end of a fragile stem, and also to provide a degree of isothermality across the plane of the junctions.
4. Cleanliness in construction: It is absolutely necessary to assure that the total assembly and all of its constituent parts start clean and remain clean, so that, over the thermometer's useful range of temperature, they do not contribute any substances which would change the characteristics of the platinum wire or of the insulation. This requires scrupulous care in manufacturing, and the proper application in the proper sequence of cleaning materials, acids, alkalis, oxidizers, rinses, and other techniques which have been described adequately elsewhere.

MECHANICAL CONSIDERATIONS

1. Temperature coefficients of materials of construction: Quartz has the property that its thermal coefficient of expansion is very low; 0.5×10^{-6} M/M/°C over the range 0° to 1200°C. The coefficient of platinum is approximately 9×10^{-6} . For the given length of internal lead wire, this can result in an expansion of the leads relative to the sheath of as much as 5mm, and this may not be permitted to stress, strain or work-harden the platinum.
2. The unwanted and unexpected: During his researches, John Evans discovered contaminants in his platinum which were eventually traced to external influences, and concluded that these were the results of metal-ion transport through the quartz sheath at high temperature. Isotech has eliminated this effect with its (patented) Model ITL-M-960 Vapor Ionizer.
3. The guard ring: An electrical guard ring, provided somewhere along the length of the leads, or at several such locations, has been an almost mythical provision of high-temperature thermometers. The most cogent authority I have consulted believes that, because of the large thermal gradients along the sheath, it is of dubious function and value. My own, frankly commercial, approach has been to offer a guarded and a non-guarded version; or one may simply elect to not use the guard of a guarded thermometer.

WHAT PERFORMANCE CAN BE EXPECTED OF SUCH A THERMOMETER?

The HTSPRT, used to 962°C or 1000°C, can hardly be expected to exhibit the accustomed stability of the traditional SPRT. I quote the following from a recent Information Bulletin issued by the National Physical Laboratory of England (NPL):

"Possibly the most significant change (of the ITS-90) is the removal of the platinum/platinum-rhodium thermocouple, by extension upward of the platinum resistance thermometer range to 962°C ...

This will overcome both the errors of interpolation which arise in IPTS-68 above 630°C, and the discontinuity in the first derivative at that temperature ... By present standards, the thermocouple is not adequately reproducible for use as a defining instrument, being capable of 0.2°C at best, whereas platinum resistance thermometers can be a factor of 10 more precise (0.02°C).

"... since exposure to high temperatures inevitably causes metallurgical and chemical changes to the platinum wire, a calibration extended to 962°C cannot carry the same uncertainties as those restricted to 660°, 420°C, or lower temperatures ..." (1)

The statement of Paragraph 2 is given a quantitative sense by NPL in their provisional statement of the calibration uncertainties (at the 2 σ confidence level) offered for their calibrations. The NPL Table is reproduced here: (2)

TEMP, °C	RANGE 1	RANGE 2	RANGE 3	RANGE 4	RANGE 5
-189.3442		0.002	0.002	0.002	
-38.8344	0.0005	0.0005	0.001	0.002	
0.01	0.0005	0.0005	0.001	0.002	0.005
29.7646	0.0005				
156.5985		0.001			
231.928		0.001	0.001	0.002	0.005
419.527			0.001	0.002	0.005
660.323				0.004	0.010
961.78					0.020

As far as I know, this is the first attempt by anyone to describe the short-term stability expected from a HTSPRT on ITS-90, and gives at least some guidance to manufacturers and users.

THE PERFORMANCE OF THE ISOTECH HTSPRT, MODEL 962

Throughout testing, we used 25Hz a-c ratio bridges (either an ASL F-17 with accuracy of 1mK, or an ASL F-18 with accuracy of 0.1mK) to measure thermometer resistance. The reference resistor was a Wilkins 1Q dc/a-c resistor in current calibration. The current supplied to the thermometers was uniformly 10mA, giving rise to self-heat of less than 1mK.

Initially, each thermometer was annealed in a quartz-lined tube furnace for 100 hours at approximately 1000°C, and checked for stability. In general, an anneal for 150 hours was sufficient, but a few thermometers required a longer anneal period. Subsequently, thermometers were annealed and/or temperature cycled for various lengths of time to evaluate shifts in R_0 with time and temperature.

(1) Adoption of the International Temperature Scale of 1990, ITS-90, National Physical Laboratory, Teddington, Middlesex TW11 OLW, England

(2) Calibration Uncertainties for Platinum Resistance Thermometers on the ITS-90, *ibid.*

More than 20 thermometers have been manufactured, in 3 batches, at the time this paper was written. The batches comprised:

Batch A, prototypes, made with clear quartz sheaths so that the construction could be observed and any physical changes noted,

Batch B, whose sheaths had the bottom 2" - 3" sandblasted to reduce heat piping,

Batch C, with sheaths sandblasted for the entire length (some Batch B thermometers were resheathed to C).

The distribution of R_0 shifts for 14 thermometers cycled to 1000°C a varying number of times is shown in Fig. 2. Table 1 shows the characteristics of 9 thermometers.

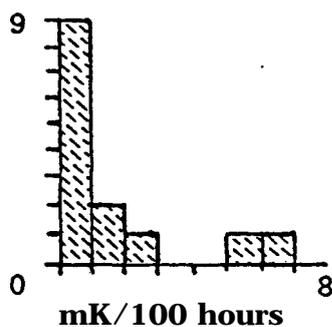


FIG. 2

It has not been possible to evaluate all the thermometers, because a number were requested by national laboratories which wanted to begin with the "raw" product. The characteristics of 9 evaluated thermometers are shown in Table 2. The 9 represent thermometers from each batch produced to date. After each anneal, the temperature was dropped rapidly to 650°C with the thermometer in the furnace, followed by a slow cool to 480°C over a period of 1/2 hour. The thermometers were then withdrawn into ambient temperature.

Table 2 shows results from 4 thermometers cycled to 1000°C. In general, the change in R_0 due to rapid cooling is less than 1mK.

To date, we have made many hundreds of measurements after cycling and during plateau. Three thermometers, one from each batch, have had in particular extensive series of measurements. These are reported in detail in Tables 3, 4 and 5. It should be noted that, since this work was done in 1989, temperatures are on the Scale IPTS-68; and since most of us still think in terms of a , this criterion has been retained. From the Tables, we note the very high values of a , which indicates that the platinum is clean and remains clean and uncontaminated.

Table 3 in particular shows a very high a for Serial 002. Two calibration cycles are reported, in which each value is the mean of at least two measurements. The shift in R_0 can be seen to be +1.9mK for the first cycle and +2mK for the second; subsequent annealing reduced the R_0 by 0.2mK. The reproducibility of the silver point is between 2mK and 5mK. The W value at silver was 4.2861458, which compares favorably with the minimum required 4.2844 of the ITS-90. The quartz sheath of this thermometer was

unroughened during these tests, and it is expected that the value will increase when heat piping is eliminated by sandblasting the sheath.

CONCLUSION

We believe that Model 962 is well-suited as a High Temperature Platinum Resistance Thermometer interpolation standard for the ITS-90, and that extensive further testing and field experience will support this belief.

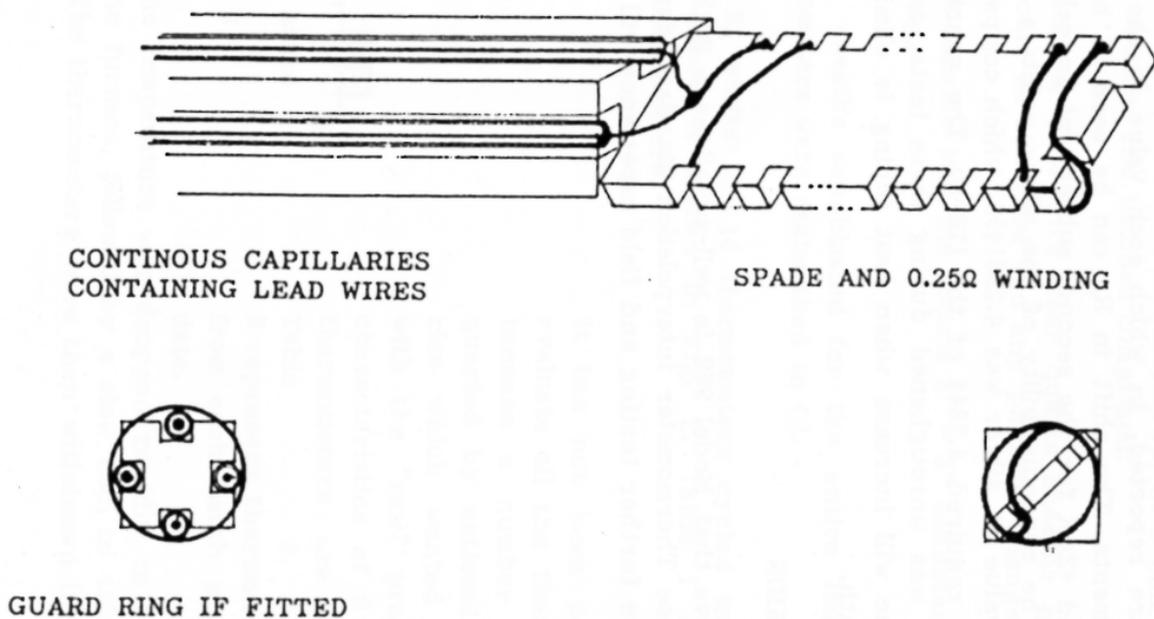


FIGURE 1 - CONSTRUCTION

TABLE 1
CHARACTERISTICS OF 9 ISOTECHT SPRTs

SERIAL	002	005	003	009
R ₀ OHMS	.1982634.	.2197977	.238681	.2352255
SELF-HEAT mK/10mA	.9	9	.9	.9
ALPHA X 10 ⁻⁴	.392781	.392751	.92788	.39276
TIME AT 1000° C(HR)	500	200	200	200
R ₀ SHIFT (mK)	1	1	1	2
BATCH	A	A	B	B

SERIAL	011	020	021	022	027
R ₀	.2430826	.2366538	.2368497	.2640155	.2397467
SELF-HEAT	.9	.9	.9	.9	.9
ALPHA	.392707	.392779	.392787	.392733	
TIME	200	250	250	250	250
R ₀ SHIFT	1	1	2	3	1
BATCH	B. C	C	C	C	C

TABLE 2
TEMPERATURE CYCLING/ANNEALING
RESISTANCE AT THE TRIPLE POINT OF WATER

SERIAL	020	021	022	027
TIME AT 1000° C PER CYCLE (HRS).				
100	.2366547	.2368497		.2397477
16	.2366544	.2368492		
16	.2366547	.2368503		
16	.2366545	.2368505	.2460155	.2397469
16	.2366545	.2368505		
64	.2366545	.2368485		
16	.2366544	.2368480		
18	.2366545	.2368480	.2460205	

280
4

.2460207

.2397459
.2397470

TABLE 3

CALIBRATION RESULTS OF SERIAL NO. 002

This unit has been used for 750 hours before these tests

R ₀ Ohms	Wt(68)	Status
0.1982638		Initial value
0.1982634		After anneal
	2.569156	Mean zinc
	1.8929761	Mean tin
	3.927811 x 10 ⁻³	Alpha
	1.492762	Delta
	3.3761571	Mean aluminium
	4.2861218	Mean silver
0.1982653		After anneal
	2.5691578	Zinc
	1.8929741	Tin
	3.927793 x 10 ⁻³	Alpha
	1.49745	Delta
	3.3761438	Mean Aluminium
	4.2861458	Mean silver
0.1982673		R ₀
	3.3761726	Mean aluminium
	2.5691544	Mean zinc
	1.8929707	Mean tin
	3.927774 x 10 ⁻³	Alpha
	1.49737	Delta
0.1982683	After 3 hours at 500°C	
0.1982681	After 2 hours at 500°C	
0.1982681	After 1 hour at 500°C	

The Table shows two complete calibration cycles from 0° to 962°C. Each measurement value reported was the mean of at least 2 measurements. The shift in R₀ was +1.9mK for the first cycle and +2mK for the second; subsequent annealing reduced the R₀ by 0.2mK. The reproducibility of the silver point. was between 2 and 5 mK; the W value was 4.2861458, well above the required value.

TABLE 4
CALIBRATION RESULTS OF SERIAL 005

R_o ohms	Wt(68)	Status
0.2386771		Initial value
0.2386766		After anneal
	2.5692919	Mean zinc
	1.8930330	Mean tin
	3.928001 x 10 ⁻³	Alpha
	1.49648	Delta
	3.3764866	Mean aluminium
	4.2869410	Mean silver
0.2386777		After anneal
	2.5692789	Mean zinc
	1.8930320	Mean tin
	3.928015 x 10 ⁻³	Alpha
	1.49684	Delta
	3.3764639	Mean aluminium
	4.2869381	Mean silver
0.2386794		After anneal

This table shows the performance of Serial 005 over two complete calibration cycles. The high alpha value indicates that the assembly has been made cleanly and without contamination. The shifts in R_o after the first and second cycle were 1.0mK and 1.7mK respectively. The reproducibility of the silver point was between 2 and 5 mK. The W value for silver was 4.28642, higher than required by ITS-90.

TABLE 4
CALIBRATION RESULTS OF SERIAL 027

R_o or R_g ohms	R(t-68)	Treatment
0.2680726 (R _g)		Initial value
0.2680727 (R _g)	.4538229	Tin
0.2680727 (R _g)	.6159397	Zinc
0.2680726 (R _g)	.4538235	Tin
0.2680731 (R _g) 0.2397477 (R _{tp})	.6159337	Zinc
0.2680736 (R _g) 0.2397469 (R _{tp})		40 hrs at 980°C + anneal
0.2680729 (R _g) 0.2397459 (R _{tp})	W(Ga) 1.1181542)	285 hrs at 980°C + anneal
0.2397473 (R _{tp})		4 hrs 960°C, slow cool to 400°C
0.2397475 (R _{tp})	W(A1) 3.3763	Mean W Al (ITS -90)
0.2397476 (R _{tp})	W(AL) 3.376335	Mean W Al (ITS -90)
0.2397473 (R _{tp})	W(Al) 3.3763312	Mean W Al (ITS -90)

Serial 027 is from one of our later batches of 962 HTSPRTs. The unit had been annealed for only 150 hours (and our triple point of water system was required for another demand during part of the testing; initial tests were performed using the melting point of gallium as reference.)

The stability of R(gallium) was better than 1mK after over 300 hours in 3 cycles at 980°C. the reproducibility of the aluminium point was better than 1 to 2 mK over the three cycles. Tests at the silver point had not yet been made at this writing.

PLATINUM RESISTANCE THERMOMETERS AS INTERPOLATION STANDARDS FOR THE ITS-90, REFERENCES

The development of high-precision platinum resistance thermometers has been evolutionary, and a great number of eminent works have contributed to the continually-advancing state of the art. It is therefore difficult to cite all of the appropriate references; the following list must therefore be a sampling.

The International Temperature Scale of 1990, Metrologia 27, 1 (to be published in February, 1990)

H.L.Callendar, *On the Practical Measurement of Temperature*, Philosophical Transactions of the Royal Society of London, Vol. 178 (1887). Also: *On the construction of platinum thermometers*, Phil. Mag., 5th Series, 32, 104 (1891)

J.L.Riddle, G.T.Furukawa, H.H.Plumb, *Platinum Resistance Thermometer*, NBS Monograph 126 (1973)

C.H.Meyers, *Coiled-filament resistance thermometers*, J. Res. NBS, 9, 807 (1932). We will reproduce this landmark paper in a future issue.

J.P.Evans, *High temperature platinum resistance thermometry*, Temperature, Its Measurement and Control in Science and Industry, Vol 4, Instrument Society of America, Pittsburgh, (1972). Also: with S.D.Wood, *An intercomparison of high temperature platinum resistance thermometer and standard thermocouples*, Metrologia, 7, 108, (1971). Also, with G.W.Burns, *A study of the stability of high temperature platinum resistance thermometers*, Temperature, Its Measurement and Control, Vol 3 Part 1 Reinhold (1962). Also, *Evaluation of some high-temperature platinum resistance thermometers*, J. Res. NBS (1984).

Li Xumo, Zhang Jinde, Su Jinrong, Chen Deming, *A new high-temperature platinum resistance thermometer*, Metrologia R, 203 (1984)

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