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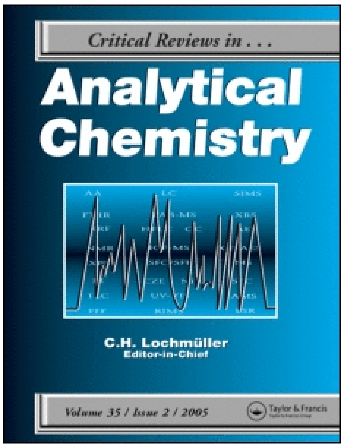

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PROBLEMS IN HIGH TEMPERATURE THERMOMETRY*

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I. INTRODUCTION

The error sources or *problems* in temperature measurement increase roughly as the difference increases between the measured temperature and room temperature. Above about 500°C, significant problems arise because metallurgical and chemical reactions affect the property used to measure temperature. For example, recrystallization, grain growth, and chemical contamination change the electrical resistivity, the thermoelectric power, or the emissivity of metals used in temperature sensors or standards. Similarly, such reactions can affect the mechanical properties of the materials used to construct these instruments. Consequently, devices and apparatus used at high temperatures tend to become inaccurate and unreliable during long-term, high-temperature service. The degree to which these reactions can be controlled or avoided directly affects the reliability of temperature measurements.

In this article, the discussion is concerned primarily with temperature measurement problems above 500°C, except in a few instances where problems at lower temperatures may affect the high temperature results. The upper limit of temperature measurement problems discussed is 3000°C, as this is the normal maximum use temperature of the techniques included in this review.

Two reviews on high temperature thermometry published by Bedford[1] and Quinn[2] deal primarily with temperature standards. Bedford's review focused on thermocouples in significant detail, whereas Quinn gave more attention to optical pyrometry. We discuss problems in applied temperature measurements, rather than in standards, and concentrate on the problems due to the high temperature limitations of the materials in the thermometer sensors.

Researchers have attempted to extend the range of temperature measurements upward and to increase their accuracy in two major ways. The most straightforward way has been attempts to extend the range of the instruments normally used at lower temperatures. Although such attempts have not been particularly successful, they have revealed inadequacies of these instruments that were not obvious at the lower temperatures. On the other hand, optical pyrometers, normally used for temperature measurement above about 800°C, are currently receiving considerable attention to improve their resolution and to increase their accuracy so that their useful range can be extended to lower temperatures.

The second way, being pursued partly because of inherent inadequacies of traditional instruments, has been to develop new methods for measuring temperature, such as ultrasonic pulse thermometry and noise thermometry. These newer instruments are not without problems, however, and are limited also by degeneration of sensor and other material properties at high temperatures.

Physical changes of materials in high temperature environments affect sensors such as resistance thermometers and thermocouples, and components such as lamps in optical pyrometers. Electrical shunting, which results from an exponential decrease of the electrical resistance of insulators as the temperature increases, can affect transmission of sensing signals through insulated cables. Chemical reactions of structural materials, or impurities in these materials and sensor materials, can affect the stability of thermometers at high temperatures. In some cases, the sensor materials may alter the system being measured by acting as a catalytic surface,[3] in which case the sensor must be protected from reactive gases or compounds in the system in which temperatures are to be measured. Protective devices around a sensor can introduce thermal conduction problems. Consequently, considerable effort must be expended to ensure that the thermometer actually measures the temperature it is meant to measure. Although thermal conduction is a problem at lower temperatures as well, other complicating effects at higher temperatures may make errors due to the thermal conduction more difficult to identify. All of these effects will be discussed in more detail below as they relate to specific instruments.

II. TEMPERATURE AND TEMPERATURE SCALES[4]

Temperature is a property of a body or system, its hotness. In the Systéme International (SI)[5] the unit of thermodynamic temperature is, "the kelvin,... defined as the fraction 1/273.16 of the thermodynamic temperature of the triple point of water." No scale is specifically mentioned, but the definition implies by the phrase, "thermodynamic temperature," that the values are expressed on the

Kelvin Thermodynamic Temperature Scale (KTTS), which requires that the ratios of absolute temperatures conform to the requirements of the second law of thermodynamics. This relationship is most often defined using reversible Carnot cycles. Using a straightforward thermodynamic argument, gas thermometer temperatures can be shown to be equivalent to thermodynamic temperatures for ideal gases when the value for the triple point of water is defined to be the same on both scales. Consequently, gas thermometry has often been used to realize thermodynamic temperatures. Because of the care and elaborate experimental apparatus required, such determinations are rarely carried out except in the national standards laboratories and even rather infrequently by them. Instead, other scales have been constructed which are more easily reproduced.

The International Practical Temperature Scale of 1968[6] (IPTS-68) was constructed to provide an accurate and precise specification for measuring values of temperature which agree closely with corresponding values of thermodynamic temperature. This scale was adopted in 1968 by the International Committee of Weights and Measures and replaced IPTS-48 (Text Revision of 1960). A revised edition of the text of IPTS-68 was adopted in 1975 by the 15th General Conference of Weights and Measures. The "Amended Edition of 1975 of IPTS-68"[7] has not changed any values of temperature measured according to IPTS-68, but changes were made to improve the clarity and precision of the language.

Measured values of temperature have no meaning without reference to a specific scale and unit. There are four sets of units and their corresponding scales acceptable for use in the SI. (1) The kelvin, symbol K, as defined above is the unit of the Kelvin Thermodynamic Temperature Scale (KTTS). The symbol "T" is used to represent values of temperature on KTTS. (2) The degree Celsius, symbol °C, which is everywhere equal to the kelvin, is the unit of the Celsius Thermodynamic Temperature Scale (CTTS) defined as

$$t = T - 273.15\ \mathrm{K} \qquad (1)$$

where "t" is the symbol for values of temperature on CTTS. (3) There is a corresponding set of symbols for temperatures measured on IPTS-68 given the subscript "$_{68}$". Thus, International Practical Kelvin Temperatures are indicated by the symbol T_{68}, with the unit K_{68}.* (4) Similarly, International Practical Celsius Temperatures are indicated by the symbol t_{68}, with the unit $°C_{68}$.* T_{68} and t_{68} are related in the same way as thermodynamic temperatures

$$t_{68} = T_{68} - 273.15\ K_{68} \qquad (2)$$

Since IPTS-68 specifies the use of non-thermodynamic thermometers, e.g., the platinum resistance thermometer and the Type S thermocouple, the units K_{68} and K are not exactly equal. This distinction is not only essential for mathematical exactness, but also should be a reminder that thermodynamic temperatures and international temperatures are fundamentally different and that international temperatures have been forced to reasonably close agreement only through considerable effort!

A. IPTS-68 Fixed Points

IPTS-68 specifies (1) values of temperature for a set of reproducible equilibrium states (phase changes) of several pure materials called "fixed points" and (2) the quality and kind of measuring instrument to interpolate between these fixed points, as well as the interpolation formulae. The values assigned as the temperatures of the fixed points were chosen to make IPTS-68 a close approximation to KTTS. This requires that determinations of KTTS temperatures of the fixed points be made by a thermometer which can be made to measure thermodynamic temperatures. In most cases, this has been a constant-volume gas thermometer, although at higher temperatures some means of radiation pyrometry must be used.

Several efforts[8-10] to measure thermodynamic temperatures have used the ratios of the total radiation from blackbody cavities as an alternative to both gas thermometry and optical pyrometry. (Optical pyrometers use only narrow spectral bands of radiation.) These studies have been limited for the most part to determinations of temperatures up to the gold point, but, as yet, the uncertainties are too large to be useful in deter-

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*Corresponds to the usage recommended in Reference 4. The Amended Edition of 1975 of IPTS-68 does not distinguish between the units of the thermodynamic temperature scales and those of the IPTS-68.

minations of the thermodynamic temperature scale. A project at the U.S. National Bureau of Standards (NBS) to determine KTTS temperatures from 100°C to the gold point (1064.43°C) is to measure the total radiant energy from a blackbody at these temperatures that reaches a calorimeter held at 2 K.[10] The triple point of water is used as the fiducial point, and temperatures can be referred directly to this primary, defining fixed point of both KTTS and IPTS-68. The sensitivity of the apparatus is about 0.002°C for a blackbody temperature of 100°C, and the estimated uncertainties in the measured thermodynamic temperatures are from 0.01°C at 100°C to 0.1°C at the gold point. The progress of this project has been impeded by internal reflections in the apparatus and diffraction losses, but these problems have been substantially solved, and the determination of thermodynamic temperatures from 100 to 1064°C will commence in 1976.[11]

A noise thermometer has been developed at the Instituto di Metrologia "G Colonetti" (IMGC)[12,13] for measurement of thermodynamic temperatures. The uncertainties in noise thermometry above 0°C at the present state of development, however, are larger than those of gas thermometry by at least an order of magnitude.

This discussion will be concerned with IPTS-68 only above 0°C where changes from IPTS-48 to IPTS-68 affect high temperature measurements. In 1968, the temperatures assigned to the fixed points were adjusted to what was believed to represent the best values of the thermodynamic temperatures of these points. The values assigned to the temperatures of the zinc, silver, and gold freezing points were based largely on gas thermometry done at the Physikalisch-Technische Bundesanstalt (PTB) in the 1950s.[14] Table 1 compares the values assigned to the respective defining fixed points by IPTS-48 and IPTS-68.

The uncertainties of these fixed points assigned at the time IPTS-68 was adopted have been shown to be unduly optimistic by gas thermometry carried out at the NBS. The table of estimated uncertainties has been deleted from the amended edition of 1975 of IPTS-68.[15] Instead, the Comité Consultatif de Thermometrie (CCT) will publish estimates from time to time of the uncertainties in fixed point temperatures arrived at by international agreement. This will preserve a reproducible and unchanging practical scale of temperature and, at the same time, will allow for periodic corrections to the relationship of IPTS-68 to KTTS thermodynamic temperatures.

Measurable differences between IPTS-68 and KTTS were shown to exist above 0°C, beginning with a new determination of the thermodynamic temperature of the steam point at NBS.[16,17] Using modern ultrahigh vacuum techniques to clean the gas thermometer system and carefully purifying the filling gas, the NBS minimized contamination of the gas thermometer system. With the new levels of cleanliness thus obtained, the difference between IPTS-68 and KTTS at the steam point was determined to be -0.027°C. Further, at 140°C the difference is -0.047°C, and there are significant differences up to 450°C. (These will be described in a forthcoming publication.) NBS plans to extend their gas thermometer measurements to the gold point (1064.43°C). If further work continues to show this trend of differences between IPTS-68 and KTTS, a new value for the thermodynamic temperature of the gold point will change KTTS temperatures above that point, because they depend on the value of the thermodynamic temperature assigned to the gold point.

TABLE 1

Defining Fixed Points of the International Practical Temperature Scale of 1948 and 1968 above 0°C in °C$_{68}$

Fixed point	1948	1968	Change
Triple point of water	0.01	0.01	0
Steam point	100	100	0
Tin point	–	231.9681	
Zinc point	419.505	419.58	0.075
Silver point	960.8	961.93	1.13
Gold point	1063	1064.43	1.43

B. IPTS-68 Interpolating Instruments

From 0 to 630.74°C, interpolation between the fixed point temperatures is defined by the resistance ratio W(t)* of a standard platinum resistance thermometer. The purity criterion for the platinum in standard thermometers was changed from the IPTS-48 value by increasing the minimum allowable "α" from 1.3920 to 1.39250. (The constant "α" is defined as W(100), the ratio of the resistance of the thermometer at 100°C to that at 0.°C.) The Callendar equation used in the earlier scales

$$t' = \frac{1}{\alpha}\,[W(t) - 1] + \delta\left(\frac{t'}{100}\right)\left(\frac{t'}{100} - 1\right) \qquad (3)$$

(δ is a constant) was supplemented by a correction equation

$$t_{68} = t' + 0.045\left(\frac{t'}{100}\right)\left(\frac{t'}{100} - 1\right)\left(\frac{t'}{419.58} - 1\right)\left(\frac{t'}{630.74} - 1\right) \qquad (4)$$

where t′ is obtained from Equation 3.

IPTS-68 allows use of the freezing point of tin (231.9681°C) in place of the steam point (100°C) because the tin point can be reproduced with a higher degree of precision and with simpler apparatus than can the steam point. Furthermore, since the tin point lies more nearly half way between the triple point of water (0.01°C) and the freezing point of zinc (419.58°C), use of the tin point improves the fit of the resistance versus temperature equation for interpolation between the fixed points.

Between 630.74°C and the gold point, IPTS-68 is defined by the equation relating the emf output of a standard platinum-10% rhodium versus platinum thermocouple to t_{68}

$$E(t_{68}) = a + bt_{68} + ct^2_{68} \qquad (5)$$

where the constants a, b, and c are calculated from the values of the emf measured at 630.74 ± 0.2°C (measured by a standard platinum resistance thermometer) and at the freezing points of silver [t_{68}(Ag)] and gold [t_{68}(Au)].

The requirements for the standard thermocouple are (1) the purity of the platinum wire must be such that the W(100) is not less than 1.3920, and (2) the emf outputs at the various calibrating points must be within the limits specified below:

$$E[t_{68}(\mathrm{Au})] = 10\,334\ \mu V \pm 30\ \mu V \qquad (6)$$

$$E[t_{68}(\mathrm{Au})] - E[t_{68}(\mathrm{Ag})] = 1186\ \mu V + 0.17\ \{E[t_{68}(\mathrm{Au})] - 10\,334\ \mu V\} \pm 3\ \mu V \qquad (7)$$

and

$$E[t_{68}(\mathrm{Au})] - E(630.74°C) = 4782\ \mu V + 0.63\ \{E[t_{68}(\mathrm{Au})] - 10\,334\ \mu V\} \pm 5\ \mu V \qquad (8)$$

While the amended edition of 1975 of IPTS-68 states that the platinum-rhodium alloy need be only nominally 10% rhodium, the values given above are for the new *exact* alloy of platinum-10 ± 0.05 wt% rhodium to agree with the new international reference characteristics for the Type S thermocouple published in 1974 in Monograph 125.[18] These new reference characteristics replaced the NBS Circular 561 tables,[19] which were based both on a *nominal* alloy (about Pt-9.91% Rh) and IPTS-48. The differences between the Monograph 125 and NBS Circular 561 tables are shown in Figure 1. Officially, the *nominal* platinum-10% rhodium versus platinum (formerly Type S) thermocouple has been dropped, but, in fact, U.S. manufacturers of platinum thermocouple materials still supply *nominal* alloy wire (as of early 1976) unless *exact* is carefully specified. (Experience at Oak Ridge National Laboratory [ORNL] has shown that even when *exact* alloy is specified, occasionally *nominal* is delivered.) Also, there exist no recognized reference characteristics or tables for a thermocouple with a *nominal* alloy positive element on IPTS-68. Calibration is required to differentiate between the two compositions, *exact* and *nominal*. The practice that has evolved at ORNL has been to reference the *nominal* Type S thermocouples to the *exact* Type S characteristics in Monograph 125 and to generate a difference curve with a second or third degree polynominal along with a set of reference tables for each thermocouple tested. The confusion which results from having two very similar

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*The resistance ratio W(t) is defined as the ratio of the resistance of the thermometer at some temperature R(t) to that at 0°C, R(0), i.e., W(t) ≡ R(t)/R(0).

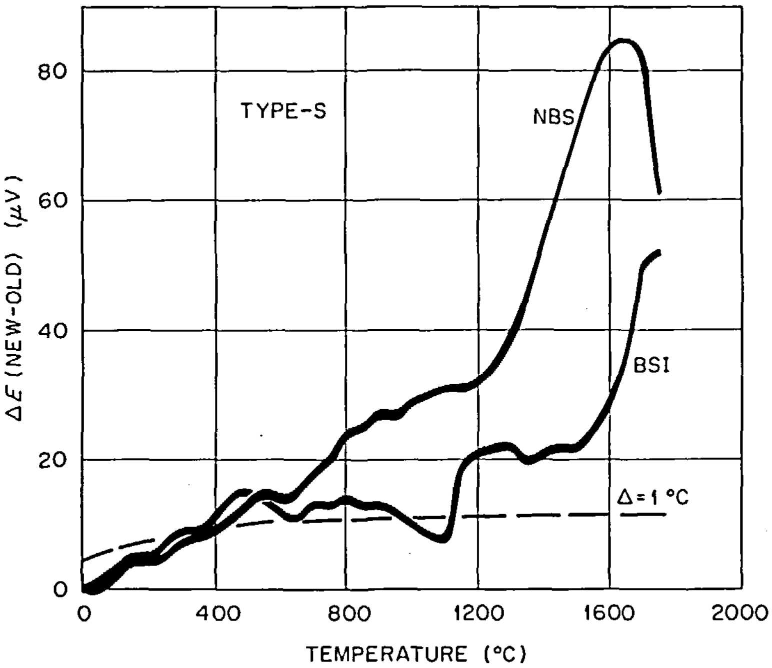


FIGURE 1. Differences between tables for "exact" and "nominal" Type S thermocouples as a function of temperature. "New" refers to National Bureau of Standards (NBS) Monograph 125 Tables; "Old" refers to: (1) NBS Circular 561 Tables, and (2) British Standards Institution (BSI) Tables B.S. 1826:1952. (From Powell, R. L. et al., *Thermocouple Reference Tables Based on IPTS-68*, NBS Monograph 125, National Bureau of Standards, Washington, D.C., 1974.)

thermocouples is likely to last for some years. In addition, many industrial instruments contain cold-junction compensation and linearization networks designed for the *nominal* Type S thermocouple and the Circular 561 tables. At 1000°C an error of about +3°C will result if an *exact* Type S thermocouple is used with such an instrument.

The Monograph 125 characteristics for the Type S thermocouple contain one peculiarity of consequence for precise work. These characteristics are based on IPTS-68, not a real thermocouple, and the second derivative of emf versus t_{68} is discontinuous at the points on IPTS-68 where there is a change in defining instruments: (1) at 630.74°C, the juncture between the standard platinum resistance thermometer and the standard Type S thermocouple; and (2) at the gold point, the juncture between the standard Type S thermocouple and the portion of the scale defined by the radiation law. Douglas[20] outlined a method for smoothing the characteristics at these points, which otherwise would introduce about a 0.1% discontinuity in properties such as heat capacity that are determined by measuring differences in temperature.

Above 1064.43°C, IPTS-68 is defined by the equation

$$\frac{L_\lambda(T_{68})}{L_\lambda[T_{68}(\mathrm{Au})]} = \frac{\exp\left(\dfrac{c_2}{\lambda T_{68}(\mathrm{Au})}\right) - 1}{\exp\left(\dfrac{c_2}{\lambda T_{68}}\right) - 1} \qquad (9)$$

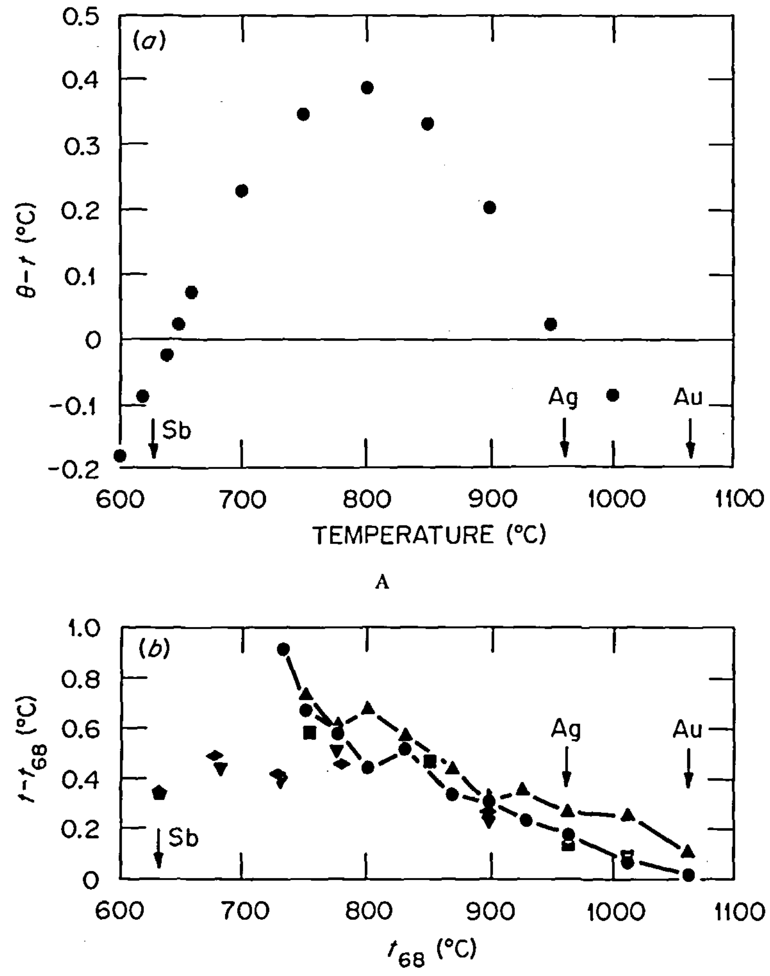
derived from the Planck radiation law, where $L_\lambda(T_{68})$ and $L_\lambda[T_{68}(\mathrm{Au})]$ are the spectral concentrations of the radiation of a blackbody at a wavelength λ (in vacuum) at T_{68} and $T_{68}(\mathrm{Au})$, respectively, and c_2, the second radiation constant is 0.014388 metre kelvin. Usually, optical pyrometers are used for interpolation of IPTS-68 temperatures above the gold point, and their measurements are based on this equation. The majority of these instruments in common use are single-wavelength instruments, but some have been designed using two[21-23] or even three wavelengths.[24]

C. Comparison of Fixed Points and Interpolating Instruments

From 630.74°C to the gold point, Evans and

Wood[25] compared interpolations between fixed points using standard Type S thermocouples and high temperature platinum resistance thermometers. Their results (Figure 2a) indicate that the difference between the scale established by the platinum resistance thermometer with a quadratic interpolation formula and the Type S thermocouple is as much as 0.4°C at 800°C. Quinn et al.[26] at the National Physical Laboratory (NPL), England, made a comparison using Type R thermocouples (Pt-13%Rh versus Pt), high temperature platinum resistance thermometers, and the NPL photoelectric optical pyrometer. Their results resembled those of Evans and Wood and are shown in Figure 2b. Bonhoure[27] has reported similar results for a comparison between an optical pyrometer and IPTS-68 at the Bureau International des Poids et Mesures, Paris.

These latter two experiments indicate that there may be about a 0.5°C difference between IPTS-68 at 750°C (defined by the Type S or R characteristics) and the radiation scale. Further-



A

B

FIGURE 2. (a) Differences between IPTS-68 Type S thermocouples and resistance thermometry scale as determined by Evans and Wood. (Adapted from Evans, J. P. and Wood, S. D., *Metrologia*, 7, 108 (1971).) (b) Differences between four Type R thermocouples calibrated against the NPL photoelectric pyrometer and IPTS-68 (connected points) and two high temperature platinum resistance thermometers using a modified quadratic interpolation formula and IPTS-68 (unconnected points). (Adapted from Quinn, T. J., Chandler, T. R. D., and Chattle, M. V., *Metrologia*, 9, 44 (1973).)

more, the results of NBS and NPL indicate that, using a platinum resistance thermometer and a quadratic interpolation formula, a scale could be made to agree more closely with the thermodynamic scale between 630.74 and 1064.43°C.

D. Secondary Reference Points to IPTS-68

Besides the defining fixed points of IPTS-68 in Table 1, some secondary fixed points are listed in Table 2. These fixed points are secondary in two senses. First, some have not been as well characterized as the defining fixed points and, second, some values depend on old determinations which were adjusted to IPTS-68 temperatures. Others, such as the boiling points of mercury and sulfur and the copper-aluminum eutectic are not as reliable, depending too much on experimental techniques and conditions. The freezing point of antimony at 630.74°C is well known, but it is difficult to realize experimentally because of the relatively large amount of supercooling (as much as 20°C) before freezing of the metal is initiated.[28] Fortunately, the aluminum point at 660.37°C appears to be as reliable, but aluminum does not supercool by more than about 1.5°C.[29]

In 1972, the freezing point of copper was determined to be 1084.83 ± 0.1°C,[30] or 0.3°C higher than the value in IPTS-68.[6] A new determination of the freezing point of platinum at the NPL has shown the value (1772°C) given in the table of secondary reference points to be about 4.1°C too high. The NPL value is reported as 1767.9 ± 0.3°C.[31] Quinn reported[15] an unpublished value of 1769.5 ± 0.5°C from the NML (National Metrology Laboratory, Japan). Combining these two values, the CCT recommended a value of 1769°C, which will be provisional until new determinations at PTB and IMGC are completed.

III. CALIBRATION TACTICS

For any temperature measuring sensor, the temperature sensitive parameter must be related to a known temperature scale. This parameter, such as the resistance of platinum wire or the emf of various combinations of thermoelements, is a property of the corresponding materials and varies slightly from sensor to sensor. It may also change

TABLE 2

Secondary Reference Points*

Equilibrium state	IPTS-68 ($^\circ C_{68}$)
Triple point of phenoxybenzene	26.87
Triple point of benzoic acid	122.37
Freezing point of indium	156.634
Freezing point of bismuth	271.442
Freezing point of cadmium	321.108
Freezing point of lead	327.502
Boiling point of mercury	356.66
Boiling point of sulfur	444.674
Freezing point of copper-aluminum eutectic	548.26†
Freezing point of antimony	630.755†
Freezing point of aluminum	660.46†
Freezing point of copper	1084.88†
Freezing point of nickel	1455
Freezing point of cobalt	1495†
Freezing point of palladium	1554
Freezing point of platinum	1769†
Freezing point of rhodium	1963
Freezing point of aluminum oxide	2054†
Freezing point of iridium	2447
Melting point of niobium	2477†
Melting point of molybdenum	2623†
Melting point of tungsten	3422

*Values taken from Amended Edition of 1975 of IPTS-68.[7]
†Indicates values changed from IPTS-68[6] or reference points added to the table.

with time, It is necessary, therefore, that some means of calibration be used to compare working sensors with laboratory standards to achieve accurate and precise temperature measurements. Means for periodic checks of the laboratory standards are also desirable.

Two methods are used to calibrate contact-type thermometers: (1) measurement of a fixed point, or (2) comparison with a standard thermometer. The former yields more accurate calibration temperatures, but only at discrete intervals. These temperature intervals may be inconveniently spaced if the characteristics of the test thermometer are not well known. The comparison method will give, overall, a less accurate calibration than the fixed point method. If the calibration range is narrow and not close to a fixed point, however, the comparison method may be more satisfactory. For example, a thermometer designed to be used, say, to only 100°C could be damaged by heating it to the tin point (231.9681°C). For thermocouples which may be cold-worked during their installation in an apparatus, a comparison in place can increase the reliability of the temperature measurements.[32]

Freezing points can be determined with a furnace and cells containing the freezing point standard. Such equipment has been described by McLaren[33] and in a more elaborate form by Riddle et al.[34] Several precautionary notes are in order. Tin can supercool as much as 5°C and requires a special freezing technique to establish a reliable freezing point temperature. Antimony also supercools excessively and requires freezing techniques that are similar to, but more elaborate than, those used for tin.[35,36] Aluminum and silver are particularly sensitive to oxygen and must be protected in an inert atmosphere.[29,37]

A test thermometer can be compared with a standard thermometer by immersing both in a stirred fluid bath or in a massive metal block which can be thermostated and made isothermal. Such a comparator block for thermocouples and platinum resistance thermometers has been described by Evans and Wood.[25] Because a constant temperature is not provided by a change of state, as in the freezing point cell, temperature in a comparison calibration will be less stable. By employing statistical designs for comparison experiments, using techniques such as those described by Youden and Conner[38] and Powell et al.,[39] not only will the accuracy of the comparison be improved, but information can be obtained about measurement uncertainties.

Table 3 lists some of the uncertainties associated with various types of calibrations. Monograph 126[34] gives a detailed analysis of the measurement errors which can occur with platinum resistance thermometers. Evans and Wood[25] also give a detailed statistical analysis of their comparison experiments.

The thermometers must be at the temperature they are assumed to be measuring. Particularly with a new type of thermometer or a new system, the immersion depth of the thermometers should be varied to determine that they are tracking the temperature of the comparison block or its equivalent, a freezing point cell. The work of McLaren and Murdock is a good example of this technique.[40] Use of heat pipes in thermometry calibrations has not been extensively reported,[41-43] but these devices probably will gradually replace massive metal blocks to establish isothermal zones.

Table 3 list types of calibrations and their accuracies. Problems specific to a type of thermometry will be discussed in the sections devoted to those thermometers.

IV. RESISTANCE THERMOMETRY

An excellent and comprehensive review of the techniques of platinum resistance thermometry for temperatures up to 630°C has been issued by the NBS as Monograph 126.[34] Most efforts to extend precision resistance thermometry to higher temperatures has been confined to thermometers made with platinum resistors. The following discussion, therefore, deals with the limitations of presently available standard platinum resistance thermometers (PRTs) and the difficulties in extending the measurements with PRTs above 630°C.

A. Limitations of Standard Thermometers

Standard PRTs currently available are not suitable for use above 630°C. They are limited primarily by the choice of sheath and insulator materials. Pyrex sheathed thermometers should not be subjected to temperatures much above 500°C to avoid softening of the glass. Metal sheathed thermometers are limited either by the oxidation resistance of stainless steel or above 650°C by contamination of the platinum sensor by migration of impurities from other high tempera-

TABLE 3

Comparison of Calibrating Standards and Instruments

Reproducibility of Fixed Points (in °C) all ±

Calibrating standard	Precision of single unit	Spread between several units
Triple point of water (0.01°C)	0.00004[34]	0.0002[6]
Freezing point of tin (231.968°C)	0.00005[36]	0.00015[36]
Freezing point of zinc (419.58°C)	0.00005[65]	0.0002[65]
Freezing point of antimony (630.74°C)	0.0003[28]	0.003[28]
Freezing point of aluminum (660.37°C)	0.0002[29]	0.0025[29]
Freezing point of silver (961.93°C)	0.002[37]	0.01[37]
Freezing point of gold (1064.43°C)	0.002[25]	0.01[30]
Freezing point of copper (1084.5°C)	0.005[30]	0.2–2
Standard strip lamp	0.01–0.09	(1064–2200°C)

Uncertainties in Interpolation (in °C)

Instrument	Uncertainty	Temp. range	Comments
Standard platinum resistance thermometer	<0.001	0–500°C	
	0.001–0.003	500–630°C	
0.25-ohm high temperature platinum resistance thermometer	0.002–0.02	630–1064°C	
Type S thermocouples:	0.2–0.3	0–1100°C	Fixed point calibration
	0.3–0.5	0–1100	Comparison
	0.2–2	1064–1500°C	NBS
	0.3–3	1064–1500°C	Other
Base metal thermocouples:	0.2–1*	0–1100°C	Freezing point
	0.5–1.0*	0–1100°C	Comparison
Optical pyrometers:			
Visual	1.6–0.3–1.5	800–1064–2400°C	NBS single observer
Photoelectric	0.06–2	1064–3525°C	NBS instrument
	2	775–1225	Commercial instrument
	4	1075–1750°C	Commercial instrument
	7	1500–2800°C	Commercial instrument
	14	2800–5800°C	Commercial instrument

*Refers only to agreement with standard tables[15] of first-time calibration. The calibration process itself causes changes in some types of base metal thermocouple materials which can result in errors of as much as 1% above 600°C. This is covered in more detail in Section V of this paper.

ture alloy sheaths. A high purity fused quartz sheath will withstand temperatures to 1100°C, but the mica insulation in standard PRTs effectively limits their use to about 630°C.

Two types of mica are used for coil supports and lead insulators in PRTs. Muscovite mica begins to dehydrate at about 540°C. This not only degrades the structural strength of the coil support, but the water vapor released reduces the insulation resistance in the thermometer. Phlogopite mica does not dehydrate below 700°C and is, therefore, used in thermometers intended for service to 630°C.[34]

Berry[44] has investigated the effects of various high temperature exposures on mica insulated PRTs. The insulation resistance of a set of six dry thermometers ranged from about 8×10^6 to 8×10^8 ohms at 600°C. For a standard PRT with an ice point resistance, R_0, of 25.5 ohms, an insulation resistance of about 10^8 ohms will cause an error due to electrical shunting of about 0.001°C at 600°C. The exponential decrease in insulation

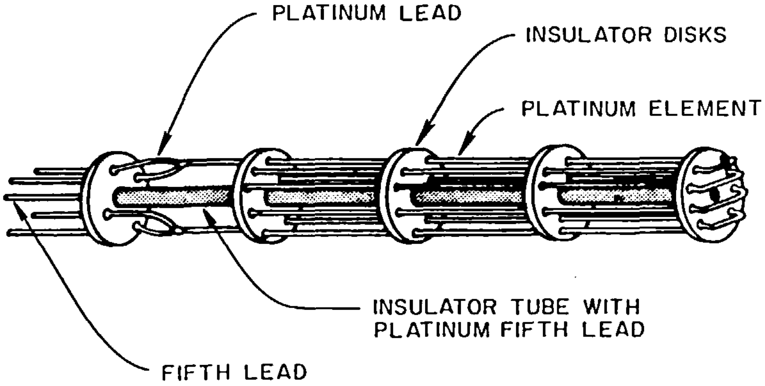


FIGURE 3. "Birdcage" high temperature platinum resistance thermometer. (Adapted from Evans, J. P. and Burns, G. W., in *Temperature, Its Measurement and Control in Science and Industry,* Vol. 3, Part 1, Herzfeld, C. M., Ed., Reinhold, New York, 1962, p. 313.)

resistance with increasing temperature will cause an error of about 0.01°C at 750°C due to the electrical shunting. With the best mica insulators, Berry estimates the useful lifetime of this type of PRT to be 1 to 4 months at 630°C and 1 or 2 days at 700°C for 1 mK accuracy. Consequently, PRTs intended for use at higher temperatures must employ other insulating materials.

B. Design of High Temperature Thermometers

Thermometers for use up to the gold point have used insulators and coil supports of high purity quartz or sapphire. Evans and Wood[25] measured a minimum value of about 4 X 10^6 ohms at the gold point for the insulation resistance in some of their high temperature PRTs. Sawada and Mochizuki[45] reported a value of 60 X 10^6 ohms at 1100°C for one of their thermometers. Curtis and Thomas[46] measured values of the order of 10 X 10^6 ohms at 1100°C. The value for the resistance of the sensor which can be used at high temperatures is thus limited by the electrical shunting due to the high temperature conductivity of the insulating materials. Berry[44] gives the error, Δt, caused by the insulation resistance S_t at 1064°C as

$$\Delta t = -7.63 \times 10^3 (R_0/S_t) \qquad (10)$$

To keep the error due to electrical shunting less than 0.001°C at the gold point, a resistor with an ice point resistance of the order of 0.1 ohm is necessary.

The majority of high temperature PRTs available commercially and those constructed for research purposes have been of the "birdcage" design described by Evans and Burns[47] (Figure 3). The resistors have been constructed of 0.5 mm platinum wire with an R_0 of 0.25 ohm and either quartz or sapphire disks. This value was chosen to both minimize the insulation shunting effects and to preserve the convenience of being able to mentally estimate changes of temperature from changes in resistance, since a change of 0.001 ohm is roughly equivalent to a change of 1°C. One defect of these thermometers is that the resistor wires serve both as the resistance element and as a part of the support structure. Differential thermal expansion between the platinum sensor and its insulating support has been a source of instability in these thermometers.

With the more sensitive AC resistance bridge developed by Cutkosky,[48] thermometers with smaller ice point resistances can be constructed with no loss in resolution in the temperature. Anderson[49] designed the "steeple" thermometer (Figure 4) which avoids problems of differential thermal expansion. A single loop of platinum wire, W, is supported by a platinum steeple, S, which is, in turn, supported by a sapphire disk, I.

Other high temperature PRTs have been constructed with helical coils similar to standard PRTs, but using a quartz coil support. Sawada and Mochizuki[45] described thermometers made with an R_0 of 25.5 ohms for use to 1100°C. The commercial version of these thermometers, however, is not recommended for use above 1000°C. NBS has constructed helical coil thermometers with an R_0 of 0.25 ohm.

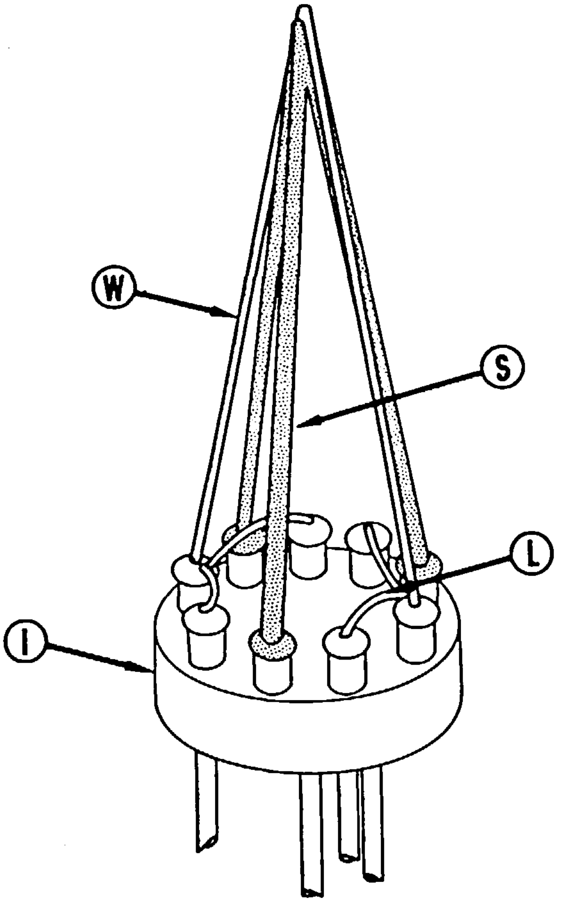


FIGURE 4. "Steeple" high temperature platinum resistance thermometer. (Adapted from Anderson, R. L., in *Temperature, Its Measurement and Control in Science and Industry,* Vol. 4, Part 2, Plumb, H. H., Ed., Instrument Society of America, Pittsburgh, 1972, p. 927.)

C. Stability of High Temperature Thermometers

Efforts to produce high temperature PRTs with a reproducibility at the gold point comparable to that of standard PRTs at lower temperatures have been frustrated by the physical and chemical changes which result from exposure to temperatures from 630 to 1100°C. The stability of these thermometers has typically been inferred from the reproducibility of their ice point resistance, R_0, and W(100). It is usually assumed that a change of resistance equivalent to 1 mK at 0°C is approximately equivalent to a change of 4 mK at the gold point. While it is clear that these are necessary conditions, other factors such as the high temperature electrical shunting may be effective only at high temperatures, so that these conditions should not be regarded as sufficient. The data of Wood[50] on the reproducibility of the silver point resistance, R(Ag), of three helical coil PRTs showed changes in R(Ag) but little or no change in R_0. Nevertheless, in practice, R_0 and α have not been constant after exposure to temperatures above 960°C. Marcarino and Crovini[51] measured changes equivalent to about 20 mK after ten silver point determinations. Changes in R_0 equivalent to 20 mK were observed after a single exposure to gold point temperatures.

Much of the data on the stability of high temperature PRTs have been reported as drift rates, i.e., changes in indicated temperature estimated from changes in R_0 per hour of exposure at high temperature.

Wood[50] has summarized work at NBS on nine PRTs, as well as a thermometer constructed from thoriated tungsten. Three of the nine were 0.25-ohm, helical coil PRTs and six were 0.25-ohm birdcage PRTs; the tungsten thermometer was of the steeple design. The drift rates reported for these thermometers at or near the gold point (1064.43°C) is 1 to 2×10^{-4} °C/hr of exposure at temperatures above 1000°C. The drift rates of helical and steeple platinum thermometers, 5 to 8×10^{-5} °C/hr at 1065°C, are less than those of the birdcage thermometers.

The most recent measurements with high temperature PRTs are those of Marcarino and Crovini.[51] They concluded on the basis of their own calibrations of a set of seven thermometers and comparison with earlier studies at NBS[25] and at NPL[52] that high temperature PRTs could be used provisionally as an alternative to the Type S thermocouple from 630.74 to 1064.43°C on IPTS-68 with about a tenfold increase in reproducibility. Furthermore, the 0.1% discontinuity at 630.74°C would be reduced to about 0.005%.

Berry[53,54] has studied the effect of oxygen content on the stability of standard PRTs. He estimated uncertainties of the order of 2 to 3 mK between 200 and 419°C from changes in R_0 which are a function of oxygen pressure and thermal cycling. (The accepted precision of 1 ppm in temperature determined with PRTs can be accounted for in part by uniformity of procedure of the experimenters.)

Anderson[49] constructed two steeple thermometers, each with a sensor wire of a single platinum crystal. He showed that elimination of grain boundaries did not eliminate the change in ice point resistance after exposure to high temperatures, and that the ice point resistance could be changed drastically by altering the oxygen content of the filling gas. Similar behavior was observed with sensor wires of either polycrystalline or sintered platinum.

The drift rate of thermometers made from sintered platinum initially was large, but gradually approached the drift rate of polycrystalline and single-crystal wires. The sintered wire was chosen because of its reported resistance to grain growth. Recently, a new material has been announced: dispersion hardened platinum.[55] The mechanical properties of this material, that is, platinum wire containing a dispersion of small, evenly distributed zirconia particles, are superior to those of pure platinum, although the electrical properties are altered. To date, no one has constructed a high temperature resistance thermometer from this material.

The resistance of metals is increased at high temperatures by lattice vacancies formed by increased thermal vibration of the atoms about their crystal lattice sites. The equilibrium concentration of vacancies increases exponentially with temperature, and at equilibrium, the effect on the resistance should be constant and reproducible at a given temperature. By cooling too rapidly, however, the vacancies can be frozen in and, as a result, the resistance of the thermometer is increased at lower temperatures. Since one requirement for thermometer stability is the reproducibility of R_0, high temperature thermometers must be cooled slowly to avoid freezing-in vacancies as the thermometers are cooled. Marcarino and Crovini[51] annealed their thermometers for 1 hr at 650°C followed by 1 hr at 480°C after cooling from higher temperatures before measuring R_0.

Berry[56] gives a relation for the change in the ice point resistance caused by the formation of vacancies at temperature T as

$$\frac{\Delta R(0^\circ C)}{R(0^\circ C)} = 1.20 \times 10^3 \exp\left(-\frac{1.51}{kT}\right) \qquad (11)$$

Even with rapid cooling, the temperature resolution of high temperature PRTs inferred from the stability of R_0 is at least a factor of 2 better than that of Type S thermocouples (Figure 5 and Table 4). If a fiducial fixed point sufficiently high in temperature is used, however, such as the aluminum point, the vacancies would rapidly assume an equilibrium concentration.

D. Thermal Radiation Piping

During their work on the freezing point of antimony, McLaren and Murdock discovered the phenomenon of "radiation piping" in PRTs.[57] Radiation piping is the transfer of heat along the walls of a quartz or pyrex sheath by internal reflections of thermal radiation. This heat transfer can be reduced to an insignificant level by roughening the surface of the sheath by gentle sandblasting or by painting the outside of the sheath with colloidal graphite to diffuse these reflections. The errors due to this effect ranged from 0.001°C at the triple point of water to almost 0.1°C at 630°C.

Some of McLaren's and Murdock's results are shown in Figure 6. The error due to radiation piping is plotted as a function of the length of the thermometer stem blackened with colloidal graphite. Similar errors could be expected in apparatus constructed from clear transparent materials such as thermometer wells, etc., and in the thermometers themselves.

E. Depth of Immersion

McLaren and Murdock[40] and Evans and Wood[25] investigated the effect of the depth of immersion on the accuracy of high temperature PRTs. Since high temperature PRTs are generally constructed with larger lead wires than standard PRTs, particularly the low resistance thermometers, the heat transfer from the sensor to the cooler portions of the thermometer is increased. This heat transfer is in addition to that transferred by radiation piping. To test for adequate immersion, a thermometer is withdrawn in increments and the temperature indicated by the thermometer is observed. When the immersion depth characteristics of PRTs are measured in metal freezing point cells, the thermometer is considered to have adequate immersion if the temperature gradient measured reproduces that induced in the freezing metal by the hydrostatic head. (The change in freezing temperature caused by the pressure exerted by the hydrostatic head of molten metal, calculated from the Clapyron equation is $+2.2 \times 10^{-5}$°C/cm depth for tin, $+2.7 \times 10^{-5}$°C/cm for zinc, and 1.6×10^{-5}°C/cm for aluminum.)

F. Resistance Measurements of 0.25-ohm Thermometers

The 0.25-ohm, high temperature PRTs require resistance measurements of high accuracy. To achieve a 1-mK resolution at the gold point, the resistance (1 ohm) must be determined to 1 ppm. The extreme care required to make such measure-

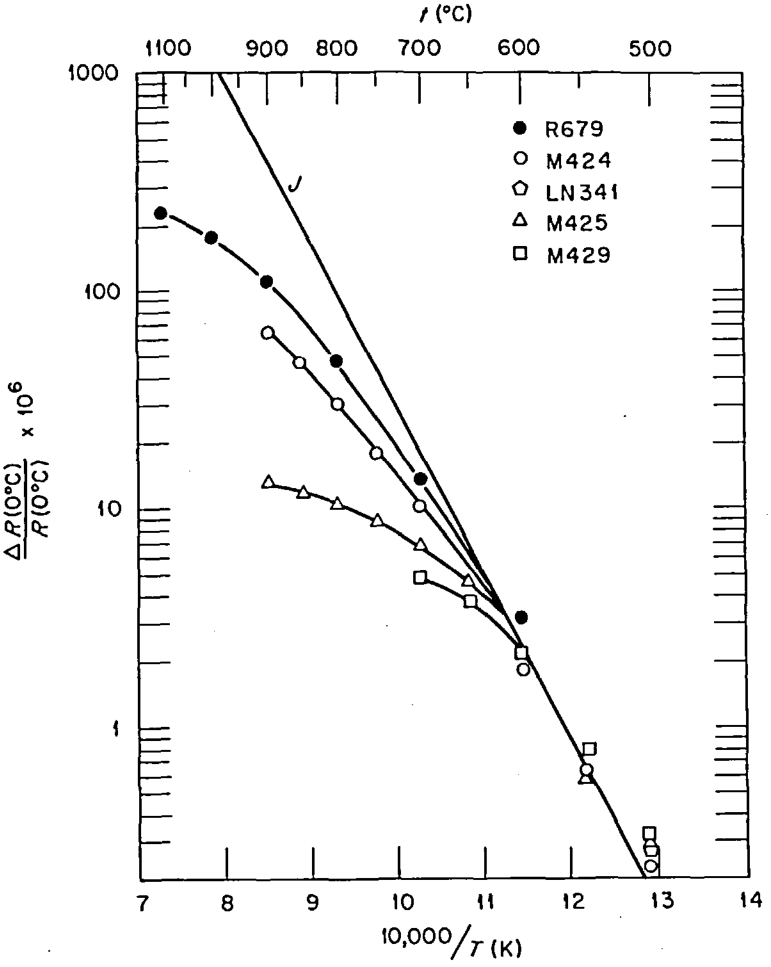


FIGURE 5. The error ΔR_0 (0°C) caused by quenched-in vacancies for several NRC platinum resistance thermometers as a function of quenching temperature. The line "J" is given by Equation 4. (Adapted from Berry, R. J., in *Temperature, Its Measurement and Control in Science and Industry*, Vol. 4, Part 2, Plumb, H. H., Ed., Instrument Society of America, Pittsburgh, 1972, p. 927.)

TABLE 4

Fractional Increase in R(0°C) of a Platinum Resistance Thermometer Produced by its Extraction from a Furnace at 1050°C at Different Rates

Extraction rate (time for 2-cm steps)	$\frac{\Delta R(0°C)}{R(0°C)} \times 10^6$	Equivalent temp. error in R(0°C) (mK)
0.1 sec	186.1	46.7
2 sec	177.2	44.5
10 sec	105.9	26.6
1 min	45.1	11.3
3 min	25.8	6.5
10 min	10.7	2.7

Adapted from Berry, R. J., in *Temperature, Its Measurement and Control in Science and Industry*, Vol. 4, Part 2, Plumb, H. H., Ed., Instrument Society of America, Pittsburgh, 1972, p. 937.

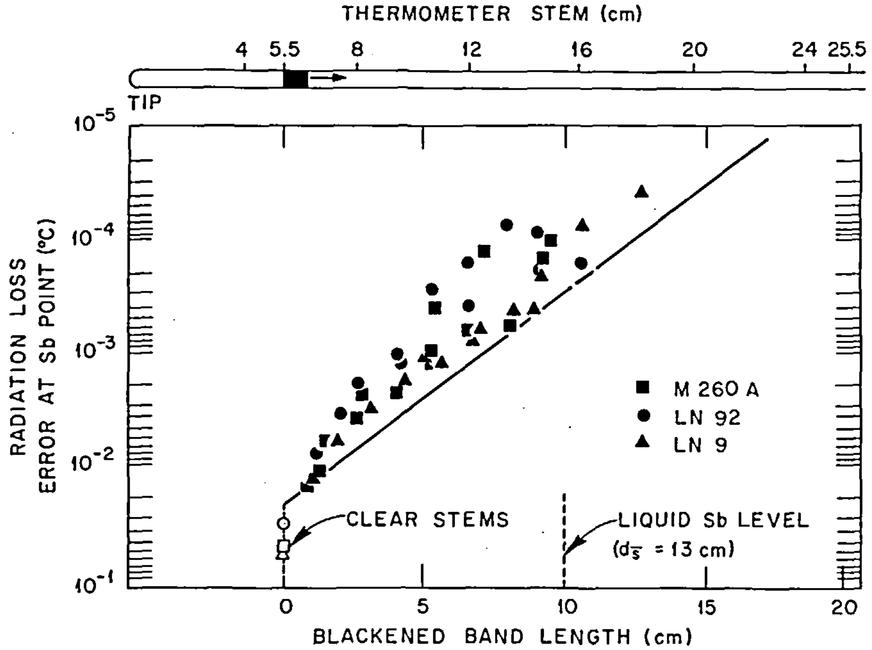


FIGURE 6. Errors caused by radiation piping in platinum resistance thermometers as a function of the length of the colloidal graphite band painted on the outside of the thermometer stem. (Adapted from McLaren, E. H. and Murdock, E. G., *Can. J. Phys.*, 44, 2631 (1966).)

ments with DC instruments has essentially confined the use of these thermometers to the national standards laboratories. Partly because of the necessity of measuring the low resistance values of high temperature PRTs, a new generation of AC resistance bridges based on ratio-transformers was developed.[48,58-61] Several features are common to all these instruments. The availability of low cost, low noise, stable operational amplifiers enabled construction of sensitive (~0.3 nV) tuned amplifiers for use as detectors. Since these amplifiers can be locked to a selected frequency, pick-up from power lines, etc., can be eliminated if the pick-up does not saturate the preamplifier stages placed in front of the filter section. Use of alternating current eliminates any effect due to changing thermal emfs in the measuring circuit. The ratios of such bridges are obtained using inductive voltage dividers rather than resistor networks. Since these ratios are established by the number of turns around high permeability magnetic cores, the fixed ratios are virtually immune from changes due to temperature or aging. Since these instruments do not require current reversals, or lead reversals as is necessary with DC instruments to eliminate the effect of thermal emfs, or contact resistances, they can be made to continuously record small temperature changes.

Furukawa[29] and Furukawa et al.[36] have reported an application of an AC bridge for recording freezing point temperatures with a precision of ~0.1 mK over extended periods (up to 12 to 16 hr). Few of these new instruments are commercially available, which also has tended to keep this powerful new technique confined to the national standards laboratories where they were developed. The uncertainty in the measurement of resistance with such instruments is from a few parts in 10^7 to a few parts in 10^8, depending on the instrument. Their freedom from thermal emfs, the inherent long- and short-term stabilities of their ratio-transformers and inductive voltage dividers, and their negligible temperature coefficient are great incentives for increased use of these instruments in the future.

There is one new type of uncertainty associated with these instruments, namely, the differences between the AC and DC resistances which can be observed with these bridges. This problem has not been completely investigated, but the few determinations reported show a dependence on the structure of the thermometer sensor. In particular, the reader is referred to a paper by Furukawa.[29] A variety of thermometers were used in these experiments, with both a DC Mueller bridge and an AC bridge of NBS design.

G. Industrial Resistance Thermometers

In many cases, it is impractical to use a laboratory standard resistance thermometer, or else its high accuracy is not needed. Widely available industrial-grade platinum resistance sensors offer improved sensitivity and stability over thermocouple thermometry to about 800°C. These thermometers are available in a variety of configurations, from long-stem and capsule types that resemble standard PRTs to small flat units for determining surface temperatures. They are also available in two-, three-, and four-lead configurations in resistance ranges from 10 to 5000 ohms.

The construction details of industrial-type thermometers vary widely. Several designs have been described by Johnson.[62] For higher temperatures (to about 800°C), some are imbedded in ceramic and others are insulated with oxide powders and encased in oxidation resistant alloys. Although such construction improves their ability to withstand mechanical shock and decreases their response time, the platinum sensor is not strain-free and sensor wire is more likely to be contaminated. Both Carr[63] and Dutt[64] have reported the performance of such sensors. One manufacturer reports that changes in their industrial-grade PRTs amounts to 0.1 to 0.25°C per year at 650°C, depending on the type of sensor. Carr's results indicate that after 6000 hr at 650°C the maximum change was ~1°C; so the manufacturer's claim may be somewhat optimistic. Since Carr's procedure of using a Type S thermocouple as a standard probably contributed an uncertainty of, at best, several tenths of a degree, his results may be unduly pessimistic. Dutt reported drift rates of about 0.1°C per year at 675°C. Carr's work, which included thermometers from a number of manufacturers, showed a 100% failure rate for thermometers from some manufacturers, but thermometers from other manufacturers survived all or most of his tests. This indicates that some care should be used in selecting a source for these thermometers.

A number of digital instruments for use with platinum resistance sensors are now available. Experience with these instruments indicates that their calibration should be checked frequently by a procedure such as connecting suitable low-temperature-coefficient, precision metal film resistors in place of the thermometer and then adjusting the instrument.

H. Calibration

Techniques for primary calibration of PRTs at fixed points on IPTS-68 are covered in NBS Monograph 126.[34] Unless a laboratory is heavily engaged in thermometry, it may be impractical to set up such elaborate equipment. It is not necessary, or even desirable, to send all thermometers to the NBS for calibration. A single thermometer, calibrated by NBS, can be designated a laboratory standard, and working thermometers calibrated against it in a comparison apparatus, such as a thermostated, massive metal block of high thermal conductivity or a stirred fluid bath, depending on the available equipment and the temperature range to be covered. Vibration in a stirred bath can work harden the sensor of a standard PRT, however, and thus change its R_0. The depth of immersion should be checked by stepwise raising the thermometer in about 1-cm increments and observing any change in the temperature indicated by the thermometer.

Since standard PRTs are delicate precision instruments, they should be checked occasionally to ensure that their calibration has not changed. A standard PRT should be routinely checked by measuring its resistance at the triple point of water (0.01°C). The resistance should not change more than the equivalent of 1 mK. (For a standard 25.5-ohm thermometer, this is about 0.0001 ohm.) With careful handling, such a thermometer can be expected to retain its calibration for years. As an example of what is meant by careful handling, a rule of thumb at the NBS is that if the thermometer strikes any solid surface hard enough to produce an audible sound, the ice point resistance has probably changed and should be checked. Long periods of use at the higher temperature end of its usable range (<500°C) can also cause a change in the ice point resistance. For laboratories not having a triple point of water cell, a well-stirred ice bath, made with distilled water and ice (also made from distilled water), can produce a fixed point of 0°C with an uncertainty of about 1 mK.

V. THERMOCOUPLE THERMOMETRY

Thermocouples are the most common thermometers used in science and industry for temperature measurements above 500°C. Contrary to common belief, thermocouples are not a panacea for high temperature thermometry, for they too have significant problems associated with their use. Accurate temperature measurements with these instruments can be achieved only when their applications are planned carefully. With the instruments now available, accurate thermocouple thermometry above about 1200°C requires extraordinary precautions, and usage above 2000°C appears quite unlikely.

This section discusses the seven sources of errors in thermocouple thermometry listed in Table 5, specifically: the temperature interval in which each source is operative; the magnitudes of the sources; differences in the sources for various types of thermocouples and environments; references that the reader may consult for more details on the sources; and, where possible, methods for minimizing, calculating, or measuring the magnitude of the errors. To aid the reader in a more fundamental understanding of error sources, a brief review of the theory of thermocouple thermometry precedes this discussion.

A. Thermoelectric Laws

From the theory of thermoelectric thermometry,[66-69] it can be shown that the thermal emf, E, of a thermocouple is given[70] by the line integral along the path ℓ from the negative to positive terminal of the thermocouple (Figure 7):

$$E = -\int^{\ell} S_i \vec{\nabla} T \cdot d\vec{x} \qquad (12)$$

where S_i is the absolute thermoelectric power (Seebeck coefficient) of the thermoelements *a* and *b*, and $\vec{\nabla} T$ is the temperature gradient at any position $\vec{x}$ along the thermoelements. Thus, E is dependent on the difference in Seebeck coefficients of the thermoelements and the temperature distribution in which the thermocouple is placed. Several important concepts related to $\vec{\nabla} T$ and S are explained in the following paragraphs.

1. Temperature Gradients

Because the temperature gradient $|\vec{\nabla} T|$ is zero in an isotherm, there is no contribution to the total E from isothermal zones of a thermocouple.

TABLE 5

Error Sources in Thermocouples Thermometry

1. Thermal shunting error
2. Electrical shunting error
3. Calibration errors
4. Decalibration errors
5. Extension wire errors
6. Reference junction errors
7. Data acquisition errors

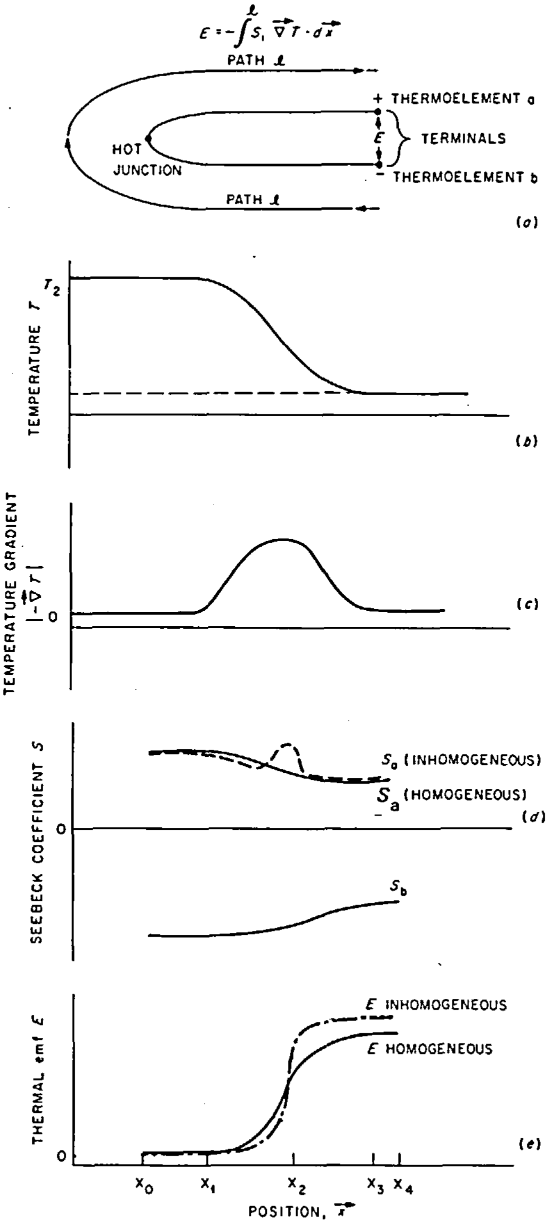


FIGURE 7. Effects of thermal gradient and inhomogeneities on the thermal emf of a thermocouple.

For example, in Figure 7, E is constant for the thermocouple for sections between positions X_0 and X_1, which includes the hot junction, and between positions X_3 and X_4 because the temperature gradient $|\vec{\nabla} T|$ is zero. The maximum contribution to E is in the vicinity of position X_2 where the temperature gradient $|\vec{\nabla} T|$ is a maximum. Therefore, a common notion that a thermocouple can be viewed as a battery at the hot junction is incorrect because normally, as in Figure 7, the hot junction per se does not contribute to E but serves only to complete the electrical circuit. This does not imply, however, that the temperature of the hot junction is unimportant. If the hot junction and a small length of thermocouple near the hot junction (X_0 to X_1 in Figure 7) are not at the temperature of the object to be measured, the measured temperature is incorrect since the integral of Equation 12 is not taken over the true temperature distribution.

Because of the importance of this concept to an understanding of this section, we restate it: the thermal emf of a thermocouple is generated only in the sections of the thermocouple that are in a temperature gradient, and the thermocouple hot junction must be at the temperature of the object whose temperature the thermocouple is measuring.

2. Seebeck Coefficient

The Seebeck coefficient, S, is an electron transport property of the materials used as thermoelements. The magnitude of S is dependent on mechanisms that scatter electrons, namely:[71] (a) displacement of ion cores from their equilibrium positions because of thermal oscillations (phonons); (b) impurity atoms; (c) imperfections in the crystal structure such as dislocations, grain boundaries, vacancies, and stacking faults; (d) electron-electron interactions; (e) ion cores with unordered magnetic moments; and (f) variations in the chemical composition or crystalline order.

During use, the section of the thermocouple in the temperature gradient is subjected to a different time-temperature-environment exposure at all points along its length. This variation in exposure may cause the thermoelements to become metallurgically and/or chemically inhomogeneous, changing the scattering mechanisms and thus S along the length of the thermocouple.

3. The Effect of Inhomogeneities

If the thermoelements are homogeneous, Equation 12 for the thermal emf of a thermocouple reduces to the more familiar form

$$E = \int_{T_1}^{T_2} (S_a - S_b)\, dT \qquad (13)$$

which means that E is a state function and depends only on temperatures T_2 and T_1 of the hot and reference junctions, respectively. If one of the thermoelements is inhomogeneous, however, the S of this thermoelement is a function of both temperature and position; that is, S has the same value at different temperatures and different positions along the thermoelement, as shown in Figure 7d for thermoelement *a* at positions near X_2.

For an inhomogeneous thermoelement, the line integral in Equation 12 is not independent of its path through the temperature gradient[72] and Equation 13 does not apply. Therefore, the E of an inhomogeneous thermocouple changes with the shape of the temperature gradient even though the hot and reference junction temperatures remain unchanged. Inhomogeneities thus produce temperature measurement errors in thermocouple thermometry which are more severe when the inhomogeneity is placed in a steep temperature gradient, as in thermoelement *a* of Figure 7.

B. Errors in Thermocouple Thermometry

The error sources in thermocouple thermometry can be divided into the seven categories listed in Table 5. The magnitude of each error depends on the application and type of thermocouple and, in general, increases with increasing temperature. Each error must be assessed and summed to yield the total temperature measurement error. Often, however, the assessment of some of these errors is difficult, and elaborate auxiliary tests or mathematical models must be employed if a realistic error value is to be obtained.

Three general categories of thermocouples, listed in Table 6, are used as examples in the detailed discussion of the seven error sources that follows. These thermocouples were chosen because they are the most commonly used in the temperature interval 500 to 3000°C, and their performance has been studied extensively. Much of what is said

TABLE 6

Thermocouples Discussed as Examples in Section V.B

Nominal composition			
Positive thermoelement	Negative thermoelement	ISA designation	Approximate melting point[a] (°C)
	Nickel-based[b]		
Nickel-10% Chromium	Nickel-5% (Silicon, Aluminum, Manganese)	K	1425
	Platinum-based		
Platinum-10% Rhodium	Platinum	S	1770
Platinum-13% Rhodium	Platinum	R	1770
Platinum-30% Rhodium	Platinum-6% Rhodium	B	1825
	Tungsten-based		
Tungsten	Tungsten-25% Rhenium	–	3120
Tungsten-3% Rhenium	Tungsten-25% Rhenium	–	3120
Tungsten-5% Rhenium	Tungsten-25% Rhenium	–	3120

[a] Melting temperature of lowest melting thermoelement.

[b] Commonly known as Chromel versus Alumel, a trade name of the Hoskins Manufacturing Co., Detroit, Michigan.

about these thermocouples can be extended to other similar types.

1. *Thermal Shunting Error*

A thermocouple, just as any other contacting temperature sensor, disturbs the temperature distribution of any object to which it is attached because the thermocouple has a finite size and conducts heat away from (or to) the object. The thermocouple itself loses heat to (gains heat from) its surroundings by conduction, convection, and radiation. This heat transfer can cause the thermocouple hot junction to be at a different temperature, higher or lower, than that of the object. This temperature difference plus any temperature change of the object due to the presence of the thermocouple are temperature measurement errors, which are called "thermal shunting" errors.

The magnitude of a thermal shunting error depends largely on the method of thermocouple installation. The ideal thermocouple installation method, which avoids thermal shunting and the resulting temperature measurement error, is one in which the portion of the thermocouple near the hot junction is isothermal and at the temperature of the object whose temperature is to be measured. Because of the wide diversity in installation techniques, it is difficult to discuss the magnitude of thermal shunting errors in a general manner; rather, thermal shunting errors must be analyzed for each specific case. For example, the errors due to thermal shunting are normally large for surface temperature measurements, especially when the thermoelements extend through a flowing fluid at a temperature below or above that of the object being measured. (From this particular case, the thermal shunting error has derived the name "fin effect" because of the high surface area presented by the thermocouple to the fluid stream.) Because of the thermal mass of the thermocouple and relatively poor heat transfer between the thermocouple and the object, thermal shunting errors are usually larger when measuring transient temperatures than those for steady-state measurements.

a. Steady-state Temperatures

Three types of thermocouple installations that minimize thermal shunting are shown in Figure 8. The one shown in Figure 8a was used in making thermal conductivity measurements by a radial heat flow technique.[73] The principal consid-

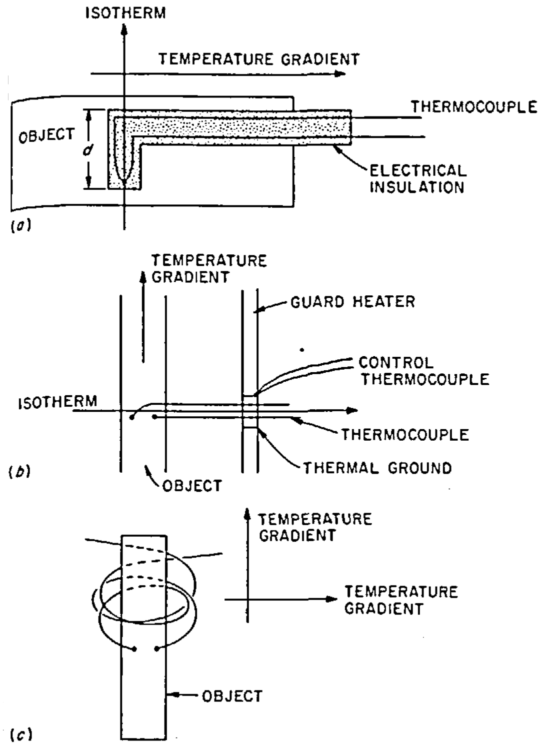


FIGURE 8. Three examples of proper thermocouple installation that minimizes thermal shunting errors: (a) use of guard heaters, (b) placement of thermocouple in existing isotherm, and (c) thermal contact of thermocouple near hot junction with object.

eration of this design is that the portion of the thermocouple near the hot junction is in an isotherm of length *d* so that the heat transferred to the hot junction is sufficient to bring it to the temperature of the object.[74] The design of Figure 8b was employed for measurements of thermal conductivity by a longitudinal heat flow technique.[32] The thermocouple passes through and is thermally grounded to, but electrically insulated from, a guard heater which surrounds the object. The guard heater is maintained at the same temperature as the object by a second control thermocouple, thereby eliminating the temperature gradients near the thermocouple hot junction. When clearly defined isotherms do not exist, as they do in Figures 8a and b, the thermocouple can be wrapped around the object in the vicinity of the hot junction. This technique (Figure 8c) was employed in making thermal expansion measurements with a quartz differential dilatometer.[75] Although the examples in Figure 8 are for bare wire thermocouples, similar techniques may be used with sheathed thermocouples. Also, the installation techniques of Figures 8a and 8c are applicable in transient temperature measurements.

If it is not possible to take the precautions shown in Figure 8 because of physical constraints, the temperature measurement error due to thermal shunting must be either determined experimentally or by mathematical modeling. The former approach may be quite difficult, whereas the results of the latter may be erroneous, depending on how well the model matches the physical conditions.

General models of thermal shunting errors with thermocouples were formulated by Jakob,[74] Otter,[76] Benedict and Otter,[77] and Leyers.[78] Most of these models concern surface temperature measurements. The models show that the principal factors that determine the magnitude of the thermal shunting error are (a) thermal conductivities of the object and the thermocouple, (b) heat transfer coefficient and area of contact between the thermocouple near the hot junction and the object, (c) heat transfer coefficients (due to radiation, convection, and conduction) between the thermocouple near the hot junction and its surroundings, (d) size of the thermocouple, and (e) size of the object.

b. Transient Temperatures

When transient temperatures are measured with thermocouples, the thermal shunting error often becomes the dominant error. The magnitude of this error depends on (a) the intrinsic ability of the thermocouple to respond to a transient and (b) the rate at which heat can be transferred to the thermocouple hot junction from the object whose temperature is being measured. When the temperature of a solid is measured, the latter normally is the predominant error source; whereas when measuring the temperature of most fluids, such as water, liquid metals, and oil, the former is.

It is common practice[77] to characterize the intrinsic ability of a thermocouple to respond to a transient by a first-order time constant τ. When the thermocouple at temperature T_1 is plunged into a bath at temperature T_2, the thermal shunting error E_s at time t is given by[77]

$$E_s = (T_2 - T_1)e^{-t/\tau} \qquad (14)$$

If the temperature of an object increases or decreases at a constant rate R, E_s is[77]

$$E_s = R\tau \qquad (15)$$

for times greater than 4τ from the start of the temperature change. The values for τ for sheathed *compacted thermocouple assemblies* (CTA) (immersed in water) vary[79] from about 5×10^{-2} to 10 sec for sheath diameters of 1 to 10 mm, respectively. Thus, for a heating rate of 10°C/sec, the thermal shunting error of a 10-mm diameter CTA would be 100°C after 40 sec of heating. (The error would be smaller at shorter times.) Bare wire thermocouples have τ values of about 10 milliseconds or less, depending on their size.[79]

When the transient temperature of a solid object is measured, the thermocouple hot junction should be welded or brazed to the object, and the section of the thermocouple near the hot junction, either sheath or insulator, should be thermally grounded to the object. Otherwise, the thermocouple response will be decreased significantly, resulting in large temperature measurement errors. When possible, an intrinsic thermocouple hot junction should be used for measuring the temperature of electrical conductors. As shown in Figure 9, the solid object (electrical conductor) itself is part of the thermoelectric circuit of an intrinsic hot junction.

The transient responses of intrinsic thermocouples were investigated by Bickle,[80] Bickle and Keltner,[81] Henning and Parker,[82] and Maglic and Marsicanin.[83] These studies show that the time constant of an intrinsic thermocouple depends on the diameters and thermal conductivities of the thermoelements and on the thermal conductivity and diffusivity of the object. Typical τ values are about 10 microseconds. This implies that with a 1000°C/sec heating rate the thermal shunting error would be about 10 millidegrees (Equation 15). However, Bickle and Keltner[81] and Maglic and Marsicanin[83] show that other errors occur with such high heating rates because a temperature gradient develops between the thermoelements due to differences in their thermophysical properties. Because of the temperature gradient across it, the object between the thermoelements contributes an error-producing emf, as given by Equation 12, to the thermal emf of the thermocouple.

2. *Electrical Shunting Error*

For most applications, the thermoelements of a thermocouple are placed in an electrical insulator to prevent their contacting each other and shorting out their thermal emf. At high temperatures, the electrical resistivities of even the best insulators are too low to prevent electrical leakage between the thermoelements. This leakage, called "electrical shunting," causes temperature measurement errors. Electrical shunting appears to be the error source that restricts the upper limit of accurate (errors $<\sim 1\%$) high temperature measurements with thermocouples to ~2000°C.

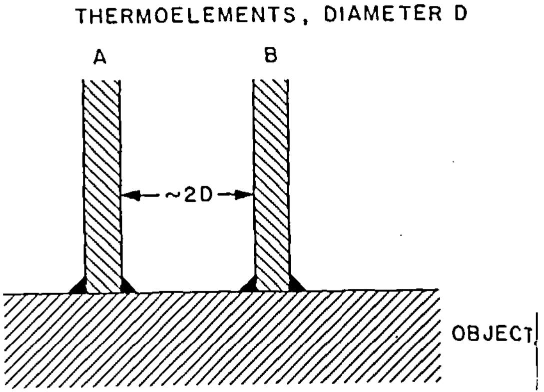


FIGURE 9. Intrinsic thermocouple consisting of two thermoelements welded to object at separation of two wire diameters (not to scale).

A seemingly obvious solution is to use bare thermoelements for that portion of the thermocouple exposed to temperatures above 2000°C. According to Williams,[84] however, thermionic emission currents between bare thermoelements and their surroundings can superimpose spurious DC voltages on the output emf of a thermocouple, which causes temperature measurement errors. His data, taken in a vacuum and low helium and argon pressures, demonstrated that the temperature measurement error due to thermionic emission is undetectable below about 1400°C but increases to about 24°C at 2200°C in his system.

The measurements of Frederikse and Hosler[85] and Loup et al.[86] suggest that thermionic emission can occur between thermoelements, even if an insulator is used. Frederikse's and Hosler's results demonstrate that the reported values of electrical resistivity of insulators between 1500 and 1800°C are similar because the current flow detected during these measurements is a result of thermionic emission between electrodes rather than from charge carriers (electrons, holes, cations, and anions) in the insulators. Applying Frederikse's and Hosler's observations to electrical shunting in thermocouples is questionable because the applied voltages in the resistivity measurements are volts.

whereas thermocouple thermal emfs are millivolts. Differences in applied voltage are important to the initiation of thermionic emission because of the work function differences of the thermoelements.

a. Factors Affecting Electrical Shunting

In most applications the magnitude of the electrical shunting error increases as the hot junction temperature increases. However, because the thermal emf of a thermocouple is produced in a temperature gradient and not at the hot junction, the shape and value of the temperatures in the gradient region of the thermocouple also determine the overall error. Because electrical shunting errors are dependent on the temperature gradient and the hot junction temperature of the thermocouple, it is not possible to correct for this error by calibration unless the calibration is performed *in situ*.

Thermocouples formed by swaging or drawing a metal sheath around crushable ceramic insulators containing the two thermoelements, the *compacted thermocouple assembly* (CTA), have the highest electrical shunting errors of any type of thermocouple assembly. The reason is that this fabrication method results in a large area of electrical contact between the insulators and thermoelements and between the insulators and sheath. Although the metal sheath contributes to electrical shunting, it is also an electrical shield that helps to eliminate thermionic emission currents from the surroundings to the thermoelements and that minimizes induced emfs. A loosely fitting metal sheath surrounding a high density, recrystallized insulator with loosely fitting thermoelements has lower leakage and good shielding characteristics. Alternatively, for some applications each thermoelement can be placed in an individual, rather than the same, insulator and sheath, but this might reduce the effectiveness of the shielding.

The larger the diameter of the insulator and thermoelements, the less the electrical shunting. However, it is impractical to compensate for the exponential decrease of resistivity with temperature (a factor of ~10 decrease in electrical resistivity of the insulators per 200°C temperature rise) by increasing the diameters of the insulator and thermoelements. Therefore, insulators and sheaths with high intrinsic eletrical resistivities and thermoelements with low electrical resistivities are required to minimize electrical shunting errors.

b. Electrical Shunting Models

The most reliable method of determining the electrical shunting error in thermocouple thermometry at high temperature is by experiment; for example, the thermocouple could be calibrated *in situ* versus a standard thermometer or an optical pyrometer. However, by equivalent circuit modeling of the insulator shunting in thermocouples, the effects of the variables controlling shunting can be investigated. The main difficulty with using a model to determine the electrical shunting error is the uncertainty in the input parameters required for the calculation. For example, uncertainties in the input values of the electrical resistivity of the insulator are due (a) to errors in the experimental measurement of this quantity and (b) to the presence of an unknown contact resistance between the insulator and thermoelements. Brown et al.[87] compensated for both these effects using an "effective" electrical resistance for the insulator. Shepard et al.[88] and Popper and Knox[89] varied the values of the insulator electrical resistivity input to their models until, by trial and error, they obtained an adequate prediction of the shunting errors determined experimentally. Once an experimentally proved model has been developed for a particular thermocouple, it can be used, in principle, to predict the electrical shunting error in any application for which the temperature gradient imposed on the thermocouple is known.

Several models of electrical shunting in thermocouples are described in the literature, and the reader is referred to a summary of them by Shepard et al.[88] and to the cross references of the summary. In general, a model is chosen to represent the thermocouple as an equivalent electrical circuit, for example, as shown in Figure 10 for a sheathed thermocouple. The resulting electrical network, which consists of a large number of modular elements, is described analytically, and the network equations are solved to derive the electrical shunting error. Normally, a numerical algorithm is coded for a digital computer to obtain the solution of the equations. As pointed out by Shepard et al.,[88] "These treatments generally assume that: (1) the insulators follow ohmic behavior; (2) the resistive and thermoelectric elements are homogeneous; (3) the temperature gradient is one-dimensional along the axis of the thermocouple, and (4) all emf's are produced thermally." Most models do not include the effect

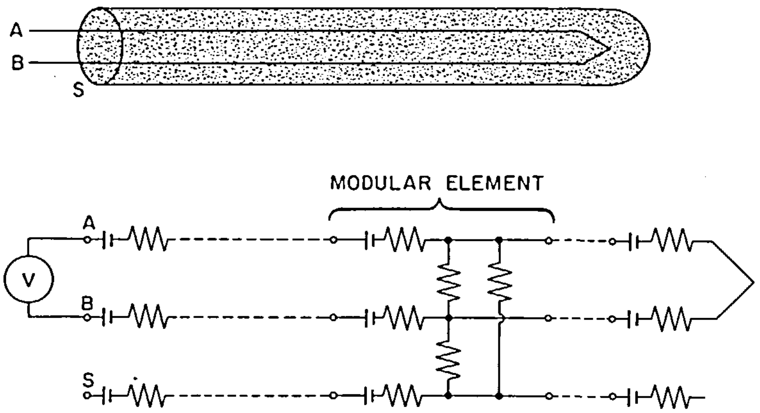


FIGURE 10. Equivalent circuit model for a sheathed thermocouple.

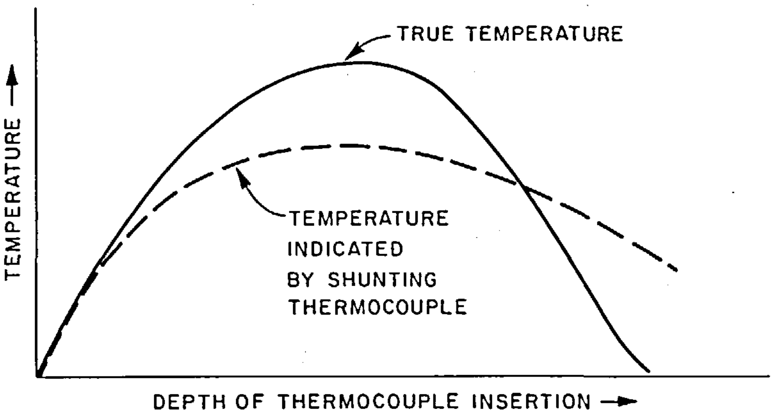


FIGURE 11. Temperature indicated by shunting thermocouple as it is inserted through a symmetric temperature distribution.

of the electrical contact resistance between the insulator and the sheath because these resistances are unknown. Also, thermally produced electron emissions are not considered. More elaborate models that consider emfs produced by chemical potentials between wires[90] and by nuclear radiation[91] have been derived.

c. Electrical Shunting Effects

Electrical shunting can cause a thermocouple to indicate too high or too low a temperature. For example, Figure 11 depicts the temperature indicated by a shunting thermocouple as it is inserted through a symmetric temperature distribution. During initial insertion, the temperatures are too low for electrical shunting to occur; thus, the indicated temperatures are correct. Further insertion results in temperatures near the hot junction high enough to cause insulator shunting, and the temperature indicated by the thermocouple would be too low. Finally, when a part of the thermocouple in the center of the temperature gradient is at a higher temperature than the hot junction, electrical leakage occurs in the hotter part of the thermocouple, resulting in indicated temperatures that are too high.

3. Calibration Errors

A thermocouple is not an absolute instrument and requires calibration to yield values of temperature on IPTS-68 (Section II). Calibration consists of a measurement of the emf* of the thermocouple at several temperatures which are determined by a standard thermometer or metal freeze

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*For accurate calibrations, the emf of the thermocouple should be measured by a potentiometer with uncertainties no greater than ±(0.01%, +0.01 μV) and a resolution of 0.01 μV. Such potentiometers are available commercially.

point (Section III). The measured emfs of the thermocouples are converted to temperature using a reference table or function.* Differences (ΔT) between those calculated temperatures and those of the standard or freeze point are usually small (several degrees) and vary smoothly with temperature. Thus, the true temperature of the calibrated thermocouple is the algebraic sum of the temperature difference (ΔT) and the table or function temperature.

At this point a word of caution about thermocouple reference tables and functions is appropriate. If the table or function is not a good representation of the emf versus temperature (E:T) relationship of the thermocouple with continuous and smooth first- and second-derivatives (dE/dT and d^2E/dT^2), temperature measurement errors will occur unless many calibration points are taken. These errors can be large, especially when the thermocouples are used to measure temperature differences, such as in thermal expansion, thermal conductivity, and specific heat measurements; the errors are amplified if the emf difference between two thermocouples is divided by the Seebeck coefficient to compute the temperature difference. Adams and Simpson[94] have studied inadequacies of this type in the NBS Circular 561 tables,[19] which for many years were the most common reference tables in use in the United States. We strongly recommend that use of these tables be discontinued and that measurements made with them be corrected by obtaining a new calibration difference curve using the functions in Reference 18. (This also will correct for temperature measurement errors due to the change from IPTS-48 to IPTS-68 scales, as discussed by Douglas.[20])

References 95–97 contain more details of thermocouple calibration methods. Table 7 shows the expected uncertainties[97] of thermocouple calibrations when fixed point or secondary reference point techniques are used or when comparison techniques employing thermocouple or optical pyrometer standards are used. The estimated uncertainties assume that reasonable care is exercised in the calibration procedure. The listed overall uncertainties are the sum of the following:

1. uncertainty of the temperature of the fixed or reference point temperature or the temperature measured by the standard interpolating instrument,
2. differences in temperature between that of the thermocouple being calibrated and the temperature of the calibration apparatus as measured by a standard or determined by the freezing point of the fixed point or secondary reference,
3. uncertainty of the measured emf of the thermocouple being calibrated,
4. uncertainty of the emf versus temperature function or table used for the thermocouple,
5. uncertainties due to inhomogeneities in the thermocouple, and
6. uncertainties due to the metallurgical state of the thermocouple due to prior heat treatment.

The first four sources of uncertainties depend on the calibration apparatus and the type of thermocouple and are discussed elsewhere.[95-97] The last two uncertainty sources are discussed next.

a. Uncertainties Due to Inhomogeneities

For a calibration to be useful, a thermocouple must be homogeneous because inhomogeneities will produce errors that are dependent on the temperature gradients impressed on the thermocouple, and seldom will the temperature gradients be the same during calibration as in use. For the most accurate temperature measurements, Laubitz and McElroy[98] recommended (a) that representative samples of each lot of thermocouples be calibrated to establish the E:T relationship and (b) that *in situ* comparisons be made with a working-standard thermometer to correct for differences between individual thermocouples. Such elaborate procedures are necessary because there are no other known methods of accurately correcting for temperature measurement errors due to inhomogeneities in thermocouples.

Although thermocouple wire produced commercially is sufficiently homogeneous for most purposes,[95] a careful experimentalist is advised to randomly check the homogeneity of each lot of thermocouple wire or CTA before use. (The

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* References 18 and 92 contain tables and/or analytical functions for the most commonly used thermocouples, and Kinzie[93] gives references to measurements of the E:T relationships of numerous less common thermocouples.

TABLE 7

Uncertainties in Thermocouple Calibration[a]

Thermoelements	Type	Temperature range (°C)	Calibration points	Calibration uncertainty: At calibration point (±°C)	Calibration uncertainty: Of interpolated values (±°C)
Fixed and secondary point calibration					
Pt-10%Rh vs Pt	S	0 to 1100	Zn, Sb, Ag, Au	0.2	0.3
Pt-13%Rh vs Pt	R	0 to 1100	Sn, Zn, Al, Ag, Au	0.2	0.5
Pt-30%RH vs Pt-6%Rh	B	600 to 1100	Al, Ag, Au	0.2	0.5
Chromel vs Alumel	K	0 to 1100	Sn, Zn, Al, Ag, Au	0.2	1.0
W-Re alloys	–	1000 to 1455	Au (1064.43°C)	0.5[b]	2.7[b]
		1455 to 1554	Ni (1455°C)	3.5[b]	4.0[b]
		1554 to 1768	Pd (1554°C)	3.0[b]	4.0[b]
			Pt (1768°C)	3.0[b]	
		1768 to 2000	Rh (1963°C)	5.0[b]	7.0[b]
Comparison to types R or S standard					
Pt-10%Rh vs Pt	S	0 to 1100	Every 100°C	0.3	0.5
Pt-13%Rh vs Pt	R	0 to 1100	Every 100°C	0.3	0.5
Pt-30%Rh vs Pt-6% Rh	B	600 to 1100	Every 100°C	0.3	0.5
Chromel vs Alumel	K	0 to 1100	Every 100°C	0.5	1.0
Comparison to optical pyrometer					
Pt/Rh	R, S, B	1100 to 1450	Every 200°C	2	3
Pt-30%Rh vs Pt-6%Rh	B	1450 to 1750	Every 200°C	3	5
W-Re alloys	–	1000 to 1300	Every 200°C	2	3
		1300 to 1600	Every 200°C	3	4
		1600 to 2000	Every 200°C	5	8

[a] This table was compiled by a committee and represents their consensus, which is not necessarily supported by experimental evidence. (See Reference 96.)

[b] These values apply only when all five calibration points are used; i.e., Au, Ni, Pd, Pt, and Rh freeze points.

Adapted from Swindells, J. F. and Burns, G. W., "Calibration of T/C's" in *Manual on the Use of Thermocouples in Temperature Measurement,* ASTM Special Publication 470A, American Society for Testing and Materials, Philadelphia, 1974, p. 106.

homogeneity of new or of seldom used thermocouple types should always be checked.) Inhomogeneities in thermocouples can be detected by the travelling gradient technique described by Fenton,[99] Carr,[100] or Moffat.[101]

One serious inhomogeneity is that encountered in the nickel-based, Type K thermocouple, known as Chromel versus Alumel* by most users.[102-103] The nickel and chromium atoms of the positive thermoelement (KP, Chromel) occupy specific (ordered) lattice sites in the crystal structure when heated to temperatures between 200 and 600°C. Above 600°C, the atoms disorder; that is, they occupy random lattice sites in the crystal structure.[102] The order-disorder transformation in the KP thermoelement is, therefore, completely reversible. Because the amount of order formed depends both on time and temperature, inhomogeneities due to ordering are produced during manufacture by differences in the time-temperature history along the KP thermoelement. Normally, the final heat treatment consists of heating to 800 to 1000°C for several minutes, followed by rapid cooling in the ambience. This treatment essentially retains the high-temperature disordered state. However, when a Type K thermocouple is fabricated in a CTA, the final distribution of the ordered state is seldom homogeneous, especially near the hot junction.[102]

b. Uncertainties Due to Prior Heat Treatments (Annealing)

Before a thermocouple is calibrated or put to use, it should be heat treated to ensure that it is free of inhomogeneities from the residual effects of cold work performed during fabrication or of other imperfections that might change the E:T relationship. Manufacturers usually supply thermocouples in the "annealed" condition. Annealing is a heat treatment in which a cold-worked metal (a metal reduced in size by low temperature plastic deformation, such as by swaging or drawing) is heated above a critical temperature T_X for a sufficient time for the metal to recrystallize, that is, to form new strain-free grains throughout the metal. Recovery, the first stage of annealing, occurs at temperatures below T_X and relieves most of the locked-in stresses due to cold work. Recrystallization, the second stage of annealing, occurs above T_X but cannot take place unless a critical minimum amount of cold-work was performed on the metal.[104] When thermocouples are annealed, the heat-treatment temperature should be above T_X, but should not exceed it appreciably; this will avoid excessive grain growth, the third stage of annealing. Large grains (resulting from grain growth) will reduce the high-temperature mechanical strength of the thermoelements. In small diameter thermoelements, grains can grow completely across the diameter of the thermoelement wire; subsequently, such thermoelements will fail mechanically at grain boundaries when they are subjected to tensile stresses as, for example, in small-diameter CTAs.[105,106]

Heat treatments to be performed prior to calibration are recommended for three general kinds of thermocouples: Type K; Types B, S, and R; and W-Re. These thermocouples are the most common employed above 500°C. Their compositions are listed in Table 6.

Type K thermocouples – Potts and McElroy,[107] from their investigation of the effects of temperature, time, and amount of cold work on the recrystallization of nickel-based thermoelements, reported that the KP thermoelement of a Type K thermocouple recrystallized in 1 hr at 735°C and the negative thermoelement (KN) at 650°C, both after 70% cold work. Lesser amounts of cold work increased T_X for both thermoelements. Both KP and KN thermoelements recovered between 100 and 450°C. Significant grain growth is known[105-107] to occur in all nickel-based alloys above 900°C.

One manufacturer[108] recommends that Type K thermocouples should be annealed between 730 and 1040°C and that the time and temperature selected should be based on the desired final hardness of the thermoelement. We recommend the following sequence of heat treatments for Type K thermocouples received from a manufacturer: (a) heat the thermocouple to 800°C for 1 hr; (b) cool the thermocouple rapidly to room temperature; and (c) preorder the KP thermoelement at temperatures between 300 and 600°C for times depending on the thermocouple application (see Reference 102).

These heat treatments should be performed in an inert atmosphere, especially if the thermocouple is not in a sheath. Unless the Type K

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*Trademark of the Hoskins Manufacturing Co., Detroit, Michigan, 48203.

thermocouples are preordered, temperature measurement errors up to +8°C occur during use because of changes in the E:T relationship caused by the order-disorder transformation in parts of the thermocouple in a temperature gradient. The reader is cautioned that when preordered Type K thermocouples are used, temperature errors will result if (a) the depth of immersion of the thermocouple is changed, (b) the temperature gradient of the thermocouple is changed, (c) the experimental thermal cycle for which the thermocouple was preordered is not rigidly maintained, or (d) the thermocouple is not calibrated after the ordering treatment.* Errors due to (a) and (b) also occur after an annealed, uniformly disordered, Type K thermocouple has been exposed to temperatures above about 350°C for several hours or 500°C for several minutes.

Types B, S, and R thermocouples – Various investigators do not agree as to the best heat treatment for Types B, S, and R thermocouples.[93] The major concern, however, is not which type of heat treatment is best to relieve strains due to cold work via recrystallation but rather which heat treatment should be used to remove oxide layers and point defects, such as impurity atoms and vacancies, from the thermoelements. This is not to say, however, that the latter is the more important consideration, for Kollie and Graves[109] have shown that cold working can cause temperature measurement errors of -7°C in Type S thermocouples, whereas McLaren's and Murdock's[40] results on point defects and oxide layers show errors of less than 3°C. It turns out, though, that heat treatments to remove oxide layers and impurity atoms from Types B, S, and R thermocouples must be performed at temperatures far in excess of the recrystallization temperature of the thermoelements. For example, the recrystallization temperature of platinum[110,111] is between 400 and 700°C, depending on prior cold work and impurities, but Bedford et al.[112] and the NBS[18] recommended that Type S thermocouples be heat treated in air "at 1450°C for 30 min and then slowly cooled (about 30 min) to room temperature." McLaren and Murdock[40] recommended that Type S thermocouples be heat treated in air "in the temperature range 1300 to 1450°C with durations up to 1 hour on the Pt element and 10 hours on the alloy element followed by a . . . 16 hours . . . vacancy defect anneal at 450°C." Both of these heat treatments are recommended for 0.5 mm diameter bare wire thermocouples.

It is not an easy matter to resolve the controversy concerning the best heat treatment for Types B, S, and R thermocouples. One desires to heat the platinum or alloyed thermoelements in air at a temperature sufficiently high and a time sufficiently long (a) to remove impurities from the thermoelements by diffusion of the impurity atoms to the surface where they are oxidized and/or volatilized; (b) to remove the Rh_2O_3 layer, formed on the alloyed thermoelements at low temperatures (600 to 850°C), by heating the alloyed thermoelements for 10 min at temperatures above the dissociation temperature of the oxide (~1100°C, see Reference 40); (c) to prevent excessive grain growth in the thermoelements, especially in the platinum, by keeping the temperature and time of heat treatment as low as possible; and (d) to prevent selective evaporation of the platinum or rhodium from the alloyed thermoelement.

A compromise must be made, therefore, between requirements (a) and (b) versus (c) and (d). The best heat treatment must be proved by additional experimentation; meanwhile our recommendations[113] for 0.25-mm diameter bare wire, Types B, S, or R thermocouples are as follows: (a) heat to 1400°C for 2 min (a more conservative treatment for a platinum thermoelement is 1300°C for 1 hr); (b) cool slowly (10 min) to 1200°C and hold at 1200°C for 15 min; (c) cool slowly (10 min) to 1000°C and hold at 1000°C for 1 hr; and (d) cool to 500°C and hold at 500°C for 2 hr. This heat treatment should be performed in air, using, for example, the technique of Roeser and Lonberger.[95] If larger (smaller) thermoelements are used, proportionally longer (shorter) times should be allowed at 1400°C. After the thermocouple has been placed in insulators, steps (c) and (d) above should be repeated. For a CTA, step (a) should be performed before fabrication, and steps (b), (c), and (d) after fabrication.

W-Re thermocouples – Davis[114] studied the recrystallization of tungsten and "doped" tung-

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*The thermocouple that is to be used should not be calibrated, per se, but rather a companion thermocouple should be heat treated with it and calibrated.

sten* wires by optical microscopy and measurements of mechanical properties of the wires. He concluded that pure and doped tungsten wires recrystallize in two stages. In the first stage, called "primary recrystallization," the fine, fibrous crystal structure produced during working transforms *in situ* to produce columnar grains in a temperature range from about 1000 to 1400°C. In the second stage, "secondary recrystallization," the columnar grains are transformed into either (a) equiaxial grains (pure tungsten), which grow into large grains, or (b) very large grains, which grow by consumption of the columnar structure (doped tungsten). Secondary recrystallization of pure tungsten wires begins at a temperature between 1500 and 1800°C, but does not occur in doped wires until the temperature is increased to between 1900 and 2300°C, depending on the dopant.

Burns and Hurst[115] concluded that W-Re alloy wires also recrystallize in two stages. They observed that secondary recrystallization occurred at a lower temperature (1525°C) and more rapidly in W-25%Re, a negative thermoelement, than occurred in either doped or undoped W, W-3%Re, or W-5%Re, positive thermoelements.

Thermocouple wire manufacturers heat treat W and W-Re alloys to produce a relatively ductile structure in which primary recrystallization is only partially complete. If used above about 1600°C, completion of primary recrystallization and the onset of secondary recrystallization cause an "emf shift," which is equivalent to a 10 to 20°C temperature measurement error, in as-received thermocouples. Only after completion of secondary recrystallization does the E:T relationship become stable for W-Re thermocouples; but in this condition, the wires are too brittle to assemble as thermocouples.[115]

Burns and Hurst[115] investigated the emf shift after heat treating W-Re thermoelements to 2725°C; they observed the emf shift to be essentially complete at 2125°C. In particular, "as-drawn," 0.25-mm diameter W-3%Re (doped) and W-25%Re were stable after 1 hr and after 10 min, respectively, at 2125°C. These thermoelements were fine grained, and still were sufficiently ductile to allow assembly. The crystal structure of the doped W-3%Re thermoelement showed advanced primary recrystallization, whereas the W-25%Re thermoelement showed partial secondary recrystallization. While lot-to-lot variation in the recrystallization and ductility of W-Re thermocouples is expected, the procedures of Burns and Hurst serve as a guide to proper heat treatment of these thermocouples.

4. Decalibration Errors

Even if a thermocouple is heat treated, assembled, calibrated, and installed with utmost care, temperature measurement errors can occur because the E:T relationship changes during use (called "decalibration" or "drift"). Temperature measurement errors due to drift have been investigated extensively and reported in the literature, for example, the review by Kinzie.[93] Unfortunately, the reported results, although showing the same trends, differ in magnitude of drift because of undetected differences in experimental variables that control the drift rates. Therefore, it is not possible to accurately predict what the drift will be for a particular type of thermocouple operating in a given environment.

Several factors cause a thermocouple to drift, for example: (a) chemical reaction of one or both thermoelements with their gaseous environment or with impurities in the environment, with the electrical insulators or impurities in the electrical insulators, or with the object whose temperature is to be measured; (b) metallurgical transformations that occur in one or both thermoelements (order-disorder reactions in Type K thermocouples and secondary recrystallization in W-Re thermocouples); (c) loss of alloying elements by selective evaporation as in Type K thermocouples used in a vacuum at high temperatures (Cr loss); and (d) transmutation by nuclear radiation of atoms of the thermoelements.

Drift rates generally increase rapidly with increasing temperature and are larger for smaller diameter thermoelements. In the following paragraphs, some conditions that contribute to the drift of sheathed and unsheathed Types K, B, S, R, and W-Re thermocouples are reviewed.

a. Type K Thermocouples

Type K thermocouples exhibit a drift due (a) to

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*Potassium, silicon, and aluminum compounds are added as "dopants" to tungsten oxide prior to its reduction to tungsten metal. The impurity oxides cause formation of gas bubble inclusions in the grain boundaries and inhibit grain growth, thereby raising the primary and secondary recrystallization temperatures.

the order-disorder transformation in the KP thermoelement and (b) to oxidation of both thermoelements during exposure to air at high temperatures. Drift in Type K thermocouples due to ordering (References 99, 101–103, 107, 116–119, and 133) and to oxidation (References 99, 101, 103, 107, 108, and 116–133) has been studied extensively; these studies reveal large drifts (>10°C) above about 800°C, especially in slightly oxidizing atmospheres. Additions to and variations of the chemical composition of the nickel-based, Type K thermoelement alloys affected some improvement in their stability.[93,107] Most of these newer alloys, however, were formulated to improve the stability while maintaining the E:T relationship of the Type K thermocouple, and, thus, the overall improvement in stability was limited.[134]

Burley[103] and Burley et al.[135] developed a new nickel-base alloy pair, Nicrosil versus Nisil; inhomogeneities due to ordering have little effect on the thermoelectric emf of this thermocouple. This thermocouple also has superior oxidation resistance at high temperatures, but its E:T relationship is about 10% different (lower emf) from a Type K thermocouple. Consequently, precalibrated Type K temperature recorders or controllers or the programs for data acquisition systems would have to be modified for use with this new thermocouple.

The order-disorder transformation is controlled by diffusion of atoms; therefore, the rate of the order-disorder transformation increases exponentially with temperature. Burley[103] has shown that 1 sec is required to complete the transformation in the KP thermoelement at 500°C, 10 min at 430°C, and 1 year at 300°C. Also, the lower the temperature the more atoms that can be ordered. Kollie et al.[102] showed a maximum change in the Seebeck coefficient of a previously disordered KP thermoelement to be 0.04% at 600°C, 0.7% at 500°C, 1.3% at 400°C, and 1.9% at 300°C. Consequently, the *magnitude* of drift due to ordering *increases* as the temperature is lowered, but the *rate* of drift *decreases* as the temperature is lowered.

Fenton[99,119] showed that the drift rate of a previously disordered Type K thermocouple is proportional to the log of time for times between 45 min and 30 days, but after 100 days the thermocouple E:T relationship is stable. The maximum drift rate caused by ordering was observed when the hot junction was at 600°C (or above); the attendant temperature measurement error was +2.5°C after a previously disordered thermocouple had been held for 30 days with a hot junction temperature of 600°C (or above). Burley,[103] without being specific, estimated that the maximum drift error due to ordering would be +8°C over a period of up to 1 year.

Fenton[99,119] showed that for certain specific applications, the errors due to ordering in the KP thermoelement could be reduced by a factor of 10 by calculating the decalibration error from drift data obtained previously for the thermocouples. Similarly, Kollie et al.[102] demonstrated for one particular application that heat treatment prior to calibration and use, to produce an optimum amount of order, reduced the drift error to 0.2°C. However, variation of the optimized heating or cooling cycles, change of the depth of thermocouple immersion during use, or modification of the temperature gradient caused errors up to 1% of the measured temperatures with preordered Type K thermocouples.

At high temperatures and exposure to air, the thermoelements of a Type K alloy oxidize, which causes the thermocouple E:T relationship to drift. If the atmosphere is strongly oxidizing, the temperature error increases positively with time at a given temperature, and most of this drift can be attributed to changes in the Seebeck coefficient of the KN thermoelement.[103,120,123] On the other hand, if the atmosphere is only slightly oxidizing, the chromium in the KP thermoelement oxidizes preferentially, causing the Seebeck coefficient of the KP thermoelement and the indicated temperature of the thermocouple to decrease with time at temperature. Because a green Cr_2O_3 surface film is formed on the KP thermoelement, the negative drift is attributed in the trade to "green rot." Thus, it is apparent that the drift of a Type K thermocouple is dependent on the partial pressure of oxygen around the thermoelements and is undoubtedly the cause for much of the disparity in reported drift data.

Table 8 lists the drift data obtained by Dahl[120] for bare, 3.3-mm diameter, Type K thermocouples in freely circulating air. Burley's results[103] agree with Dahl's, and most of the drift measured by Burley is due to the KN thermoelement. Neither investigator attempted to separate the drift due to the order-disorder transformation from that due to oxidation. Burley's data, however, show that the KP thermoelement drifts positively at 1000°C, has

TABLE 8

Drift of Bare, 3.3-mm diameter Type K Thermocouple in Freely Circulating Air

Exposure temperature (°C)	Exposure time (hr)	Drift (°C)
760	1000	+1.7
871	1000	+2.8
982	1000	+4.4
1093	1000	+10.6
1204	200	+11.7
Nicrosil-Nisil (3.3 mm diam)		
1000	700	+1.5
1100	700	−0.2
1200	700	−0.5

Adapted from Burley, N. A., in *Temperature, Its Measurement and Control in Science and Industry,* Vol. 4, Part 3, Plumb, H. H., Ed., Instrument Society of America, Pittsburgh, 1972, p. 1677.

almost no drift at 1100°C, and drifts negatively at 1200°C. Since the order-disorder transformation causes a positive drift, and a loss of chromium due to oxidation causes a negative drift at these temperatures,[136] the overall drift of a 3.3-mm diameter KP thermoelement in a strongly oxidizing atmosphere is more dependent on the order-disorder transformation below 1100°C than on oxidation (for 1000 hr of exposure).

The salient feature of the Nicrosil-Nisil thermocouple is its improved oxidation resistance in air. For comparison, Burley's results[103] for the drift of bare, 3.3-mm diameter Nicrosil-Nisil thermocouples are also shown in Table 8. At 1100°C, the stability of the Nicrosil-Nisil thermocouple is a factor of at least 50 better than that of a type K thermocouple.

The data listed in Table 8 are for large diameter (diam = 3.3 mm) thermoelements exposed to freely circulating air. In many applications, design restraints require smaller diameter thermoelements and other atmospheres than air. The data of one manufacturer[108] demonstrate that the drift of Type K thermocouples in air at constant temperatures above 1000°C is proportional to d^{-x}, where x is between one and two. At lower temperatures, the dependence of drift on diameter is smaller; for example, the drift is approximately proportional to $d^{-1/2}$ at about 870°C. The complexity of the relationship between drift and diameter is due to the presence of two drift producing mechanisms – *ordering* in the KP thermoelement, which is diameter independent and produces a positive drift, and *oxidation* in the KP and KN thermoelements, which depends on the diameters of the thermoelements and produces a positive drift in the thermocouple output for the KN thermoelement and a negative drift for the KP thermoelement.

The high-temperature performance of Type K thermocouples in other than freely circulating air atmospheres is rather poor. For example, Bennett et al.[124] measured drifts of −9 and −90°C after 50 hr at 1000°C in "stagnant" air and helium, respectively. Their measurements were performed on preoxidized, 0.5-mm diameter, Type K thermoelements and demonstrated that the majority of the drift occurred along the portion of the thermoelements in the 800 to 900°C temperature interval. Therefore, clean, oxide-free thermoelements should be used with atmospheres other than free circulating air. It is also desirable to avoid "inert" atmospheres with traces of oxygen to prevent the preferential oxidation of chromium from the KP thermoelement which produced these rapid negative drifts.

McCoy[137] investigated the drift of 0.81-mm diameter Type K thermocouples in CO and CO_2 atmospheres. After 257 hr in CO_2, he observed drifts of −80°C, −8°C, and −9°C at temperatures of 833, 722, and 620°C, respectively. Similar results were observed for Type K thermocouples by Dobovisek and Rosina.[127] In mixtures of CO and CO_2, McCoy's measured drifts were positive initially, followed by rapid negative drifts.

The stability of Type K thermocouples is improved substantially by placing the thermocouple in a protective sheath. In fact, most users of Type K thermocouples employ *compacted thermocouple assemblies* (CTA) formed by swaging or drawing a metal tube over crushable insulation to obtain a compact, rugged thermocouple assembly. When sealed, the amount of moisture and other sources of oxygen is limited to that sealed in a CTA, if the sheath is impervious to oxygen. Unfortunately, the amount of oxygen can be large because oxygen and water vapor are adsorbed and absorbed by the fine-grained, crushed insulation and trapped in the insulation voids (about 25 vol % of voids). Therefore, CTAs are not drift free.

Herskovitz et al.,[128] for example, showed that commercially available 3.2-mm diameter, stainless-steel sheathed, magnesia (MgO) insulated, Type K CTAs drifted from +5.7 to +15.6°C after 10,000 hr in air at 871°C. Presumably, the variations in drifts about the mean of +11.5°C were due to differences in the oxygen content of the assemblies, which were produced by 15 different manufacturers. After these drift tests and using an inhomogeneity test facility, Carr[131] showed that the Seebeck coefficients of the thermoelements varied significantly along the length of each assembly. In similar work, Mathieu et al.[130] showed that portions of CTAs exhibited changes in Seebeck coefficients of the thermoelements that were indicative of both slightly and highly oxidizing conditions. Mathieu et al. demonstrated that a highly oxidizing condition existed at the portion of the thermocouple where the temperature gradient was steepest due to oxygen diffusion from colder portions of the assembly. The slightly oxidizing condition near the hot junction was attributed to oxygen depletion resulting from oxidation of the thermoelements and sheath.

Bliss[132] devised an elaborate procedure for fabricating Type K CTAs in which the assemblies were baked out and purged with argon to reduce the amount of oxygen sealed in the assembly. Bliss demonstrated that assemblies manufactured in accordance with this procedure exhibited drifts of less than 10°C after 10,000 hours at 1100°C, and 2500 hr at 1200°C.

b. Types of B, S, and R Thermocouples

One of the salient features of Pt-Rh thermocouples is their excellent resistance to oxidation at high temperature. Types S and R thermocouples each have a pure platinum negative thermoelement and a Pt-10%Rh (Type S) or Pt-13%Rh (Type R) positive thermoelement, and both thermocouples can yield reliable temperature measurements up to 1600°C under well-controlled conditions. Above about 1100°C, the platinum thermoelement loses its mechanical strength and is unstable in certain environments; therefore, a Type B thermocouple (Pt-30%Rh versus Pt-6%Rh) is often a better choice[138] for temperature measurements between about 1100 and 1800°C. The type B thermocouple is also preferred[18] to the two less common combinations of Pt-20%Rh versus Pt-5%Rh and of Pt-40%Rh versus Pt-20%Rh, mainly because the emf output of the Type B thermocouple is larger at high temperatures.

Below 1000°C, the principal cause of drift in Pt-Rh thermocouples is oxidation of Rh to Rh_2O_3. The Rh_2O_3 is formed both internally and externally (a black film on surface) on the thermoelements between 400 and 850°C, but it decomposes when heated above 1100°C. The formation of this oxide causes minor drifts; for example, Darling and Selman[139] measured a -2°C drift in a Type R thermocouple after 40,000 hr at 625°C in air. They heat treated the oxidized thermocouple at 1200°C in air and observed that "the rhodium returned to the solid solution in the platinum and restored the thermocouple output."[139]

Several studies[40,138-145] were performed to determine the stability of Pt-Rh thermocouples above 1000°C. A general conclusion from these studies is that the stability of Pt-Rh thermocouples depends on the environment and that the thermocouples are more stable in air than in vacuum, and more stable in vacuum than in most inert atmospheres. Instability of the Pt-Rh thermocouples is caused (a) by reactions with impurities in the materials of construction or in the environment, or (b) by volatilization of the Pt and Rh in vacuum or at higher temperatures in air and inert atmospheres.

One of the most definitive studies of the stability of Pt-Rh thermocouples was by Walker et al.[140,141] who showed that drift of these thermocouples in air, argon, and vacuum is caused by reactions of the thermoelements with impurities in the electrical insulators. Their results prove that insulators with a low iron content yield the most drift-free assemblies. Their results for the purest insulators studied, Degussit Al23 (Al_2O_3), are summarized in Table 9. The drift of the Type B thermocouples in these insulators was less than 1°C in air for 120 hr at temperatures to 1730°C, which is slightly better than the performance of the Type S thermocouple. The drift of Types B and S thermocouples was zero after 120 hr of exposure in air, argon, or vacuum at temperatures below 1380°C. Although not shown in Table 9, the drift in air was independent of thermoelement size, but was less for larger thermoelements in argon and vacuum.

For comparison, some of the results of Glawe and Szaniszlo[144] and Hendricks and McElroy[142]

TABLE 9

Drift of Pt-Rh Thermocouples

Thermocouple (type)	Temperature (°C)	Time (hr)	Drift(°C)		
			Air	Argon	Vacuum
Walker et al.[141] (0.51 mm thermoelements; Degussit A123 Al_2O_3)					
S	1000	120	0	0	0
S	1200	120	0	0	0
S	1380	120	0	0	0
S	1600	120	–1	–11	–4
	1730	120	–1.3	–	–
B	1000	120	0	0	0
B	1200	120	0	0	0
B	1380	120	0	0	–1
B	1600	120	0	–7	–2
	1730	120	–0.3	–	–
Glawe and Szaniszlo[144] (0.51 mm thermoelements)					
R	1327	10,000	–5	–23	–23[a]
B	1327	10,000	–	–26	–13[a]
Hendricks and McElroy[142] (0.51 mm thermoelements; ΔRR Morganite Al_2O_3)					
S	1300	160	–	–	+3
		328	–	–	–3
		1035	–	–	–14
B	1300	160	–	–	+1
		328	–	–	+3
		1035	–	–	+2

[a] Open-circuit failure expected after 2000 to 4000 hr. The values shown assume the same shape of curve as for argon.

are also listed in Table 9. Glawe and Szaniszlo found that the drift rate of Types B and R thermocouples increased with time after a "few thousand hours" in argon at 1327°C and that the thermocouples failed after 2000 to 4000 hr in vacuum at 1327°C. Hendricks and McElroy concluded, "commercial thermocouples of the type $Pt_{90}Rh_{10}$ vs Pt, $Pt_{94}Rh_6$ vs $Pt_{70}Rh_{30}$ . . . were shown to be stable within ±10°C for times up to 1000 hours at pressures between 10^{-6} and 10^{-8} torr in the range 1200 to 1450°C." The results in Table 9 agree that the performance in air is better than in argon or vacuum and that the drift of Type B thermocouples is generally less than Types S or R.

Darling and Selman[139] investigated the compatibility of Pt-Rh thermocouples with four commonly used insulating materials, alumina (Al_2O_3), zirconia (ZrO_2), magnesia (MgO), and thoria (ThO_2). The ambiences were air, vacuum, and argon, and the insulating materials were fine powders (<1000 μm particles) of high purity (<100 ppm impurities). Darling and Selman state,

> Under normal oxidizing conditions platinum thermocouples are exceedingly inert with respect to the more refractory oxides. Severe reactions can occur, however, when the oxidizing potential of the surrounding atmosphere is reduced below a critical level. Alumina, zirconia, and thoria dissociate, oxygen is evolved, and platinum extracts the metal from the refractory to form dilute alloys and low melting point phases. Magnesia is very resistant to this type of decomposition and appears to be an excellent refractory for use in contact with platinum.

The amount of impurities in the powders used by Darling and Selman was less than in high-density, recrystallized oxides normally used to insulate the thermoelements of Pt-Rh thermocouples. For example, Walker et al.[140] give the impurity content of their Degussit Al23 (Al_2O_3) insulators as 5000 ppm, with 340 ppm of iron and 1000 ppm of silicon, which can be compared with only 5 ppm of iron and 5 ppm of silicon in the Al_2O_3 used by Darling and Selman, Thus, Darling's and Selman's work cannot be correlated with that of Walker et al., which shows an increase in drift with an increase in iron content of the insulators. Support for the measurements of Walker et al. is obtained from that of Cochrane[143] who showed that the thermal emf of platinum changes about 2.3 μV per ppm (by weight) of iron, indicating that small quantities of iron in solution in Pt-Rh thermocouples can cause large changes in the emf. In our opinion, Darling's and Selman's conclusion that MgO is the best insulator for Pt-Rh thermocouples can be true only if MgO can be obtained with less iron and other impurities than contained in Al_2O_3.

One conclusion from investigations of drift in bare wire, Pt-Rh thermocouples is that drift is the result of reactions that occur through the vapor phase. Therefore, when Pt-Rh thermoelements are used in a sheathed assembly where the gaseous phase is confined around the thermoelements, the drift rates are large.[142,146-151] For example, Selman[146] measured a drift of -200°C in 1400 hr at 1450°C (~-6°C/day initially) in Pt-10%Rh sheathed, MgO insulated, Type R CTAs. Selman[146] (articles by Selman and Rushforth[147] and Bard[148] are the same work, essentially) attributed the drift to rhodium migration to the pure platinum thermoelement by a vaporization-condensation mechanism involving rhodium oxide, with the rhodium coming mainly from the sheath.

Selman achieved substantial improvement in the stability of the thermocouple assemblies in several ways. One way was to heat the assembly and drive off the water vapor absorbed by the MgO insulation before the thermocouple assembly was sealed. This treatment decreased the drift a factor of 10 from -200 to -20°C after 1400 hr at 1450°C. Selman attributes this decrease to a change in the sintering properties of the MgO due to an absence of water vapor. In the thermocouple with less drift, the dry MgO "sintered to dense, impervious mass which would have almost completely prevented gaseous transfer between the metallic components. The insulation within the unstable device (thermocouple), was cracked and porous, and provided no real barrier to vapor transport." A similar observation was made by Freeman.[149] Selman obtained greater stability in another way, that is, by driving off not only the water vapor but also the oxygen (and nitrogen) from the insulation and then backfilling with about 0.3 atm of pure argon gas. (This reduced pressure avoided bursting the sheath at high temperatures.) Additional stability was obtained using a Pt-5%Rh sheath with a Type B thermocouple, which yielded an assembly whose "performance over periods up to 1000 hr at 1450°C has proved to be equal to a 13% rhodium-platinum versus platinum (Type R) thermocouple insulated and sheathed with recrystallized alumina." (This is a drift of about -2°C in 500 hr in air at 1450°C.)

Bedrich[150] analyzed Selman's and Rushforth's[147] results by calculating drift from their reported temperature gradient and change in composition of the thermoelements of a Pt-10%Rh sheathed, MgO insulated, Type R CTA sealed with air. Bedrich shows that the error due to rhodium migration is too small to account for the observed drift; therefore, he concludes that other reactions occur to cause the higher experimentally observed drift. Perhaps impurities, such as Fe_2O_3, in the insulators decompose and react with the thermoelements, as observed by Walker et al.[140,141]

If a refractory metal sheath is used instead of a Pt-Rh sheath, the drift rate of Pt-Rh thermocouples increases. For example, Hendricks and McElroy[142] measured a drift rate of ~-10°C/day at 1200°C for niobium and tantalum sheathed, MgO insulated, Type S CTAs, whereas Selman[146] found similar Pt-Rh sheathed thermocouples to be stable at 1200°C. At 1600°C, Zysk[151] measured drifts of -27°C in 90 min for an Al_2O_3 insulated, tantalum sheathed thermocouple; he measured an even poorer performance, that is, a change of -61°C in 60 min, when MgO was used instead of Al_2O_3.

There are numerous possible explanations for the poor performance of Pt-Rh thermocouples sheathed by refractory metals: (a) Toenshoff and Zysk[152] noted that the insides of refractory metal tubes used as sheaths are difficult to clean because they have corrugated surfaces (after "sink drawing") that entrap contaminants (such as residual lubricants), and these are not removed by vapor degreasing or solvent swabbing operations prior to assembly fabrication; (b) the refractory metal sheaths could have "gettered" the oxygen, producing a low oxygen partial pressure in which Pt-Rh thermocouples exhibit poor performance; (c) the tantalum sheaths, by means of a vaporization-condensation reaction, could have reduced impurities (e.g., Fe_2O_3) in the insulators, thereby causing the thermoelements to alloy with the reduced metal atoms; (d) the thermocouple fabrication techniques could have been executed poorly, causing contamination of the assembly; and (e) any combination of the above.

c. W-Re Thermocouples

Refractory metals and their alloys melt at about 3000°C. Of such materials, tungsten and tungsten-rhenium alloys are used most commonly for thermoelements.[93] These metals should not be exposed to oxidizing atmospheres or to supposedly inert atmospheres that contain a small amount of oxidizing impurities. High vacuum and pure gas, such as argon, helium, nitrogen, and hydrogen, will protect these metals at high temperature.

Lack of ductility, especially of pure tungsten and W-3%Re alloy, is another problem with some refractory metals. As discussed previously, completely recrystallized W-Re thermoelements are brittle, and it is almost impossible to fabricate these materials into thermocouples. Also, partially recrystallized thermoelements are not stable (they decalibrate) when heated, resulting in errors of 10°C or more. After use, W-Re thermocouples are brittle and must be handled carefully to avoid breakage.

Two more problems, chemical incompatibility with insulators and selective evaporation of components from the alloys, severely limit the stability of refractory metal thermocouples above about 2000°C. Indeed, these two problems and electrical shunting through the insulators and/or by thermionic emission appear to limit accurate (error <1%) thermocouple thermometry to temperatures below 2000°C.

As pointed out by Anderson and Bliss[153] and others, the methods of testing and reporting drift data of refractory metal thermocouples are not uniform. Anderson and Bliss state, "At the present time it is virtually impossible to intercompare the drift data in the literature due to the large number of variables in material and techniques." Probably the variables most difficult to control are impurities in the insulators, sheath, and atmosphere. Also, an emf shift due to recrystallization of the thermoelements could cause disparities in data because of differences in heat treatment prior to testing. For example, Burns and Hurst[115] reported a change in emf equivalent to about +45°C during annealing of as-drawn W-3%Re versus W-25%Re thermocouples at 2400°C. Consequently, shifts of up to +45°C could occur during tests or use, depending on prior heat treatments of the thermoelements.

Burns and Hurst[115] studied the drift in bare wire W-Re thermocouples in atmospheres of argon, hydrogen, helium, and nitrogen (<10 ppm vol impurities, <1 ppm vol O_2). After 1 hr at 2127°C, drifts to +18°C were noted in seven lots of as-received, doped W-3%Re versus W-25%Re thermocouples. Between 1 and 50 hr of exposure, three of the seven lots exhibited no additional drift and four exhibited an additional drift as follows: two, 1°C; one, -3°C; and one, +4°C. Continued exposure to 1000 hr in argon and nitrogen and 500 hr in helium and hydrogen showed no additional drift. Burns and Hurst[115,154] concluded that the emf shift was complete after 1 hr of exposure at 2127°C. In fact, they observed that 10 min at 2127°C was sufficient to stabilize the W-25%Re thermoelement, while retaining good ductility. Doped W-3%Re also retained good ductility after 1 hr at 2127°C.

Others[155-157] have studied the drift of bare W-Re thermocouples in argon and helium. Below 2127°C, the measured drifts were probably due to the emf shift because the drift rates are large during the first few days of exposure, then become much smaller after longer exposure. For example, Walker et al.[156] reported that, in argon, a bare tungsten thermoelement drifted +6°C in the first hour at 1525°C and only an additional +2°C during 48 hr. It can be concluded that in ultrapure inert gases, W-Re thermocouples are stable within a few degrees for several thousand hours at temperatures below 2100°C, if the thermocouples are heat treated before use as recommended by Burns and Hurst.[115]

The stability of W-Re thermocouples is not as good in a vacuum as in a pure, inert atmosphere because rhenium evaporates in a vacuum. Burns and Hurst[115] report that a W-3%Re versus W-25% Re thermocouple drifted -180°C after 500 hr at 2127°C and after only 50 hr at 2327°C in a vacuum of 10^{-8} torr. Asamoto and Novak[155] measured a drift of ±50°C after 15 hr in a vacuum at 2600°C for bare wire W-3%Re and W-5%Re versus W-25%Re thermocouples. (Ion or similar vacuum pumping systems should be used because back-streaming oil of oil diffusion pumps seriously reduces the stability of W-Re thermocouples, even at a temperature as low at 1625°C [see Reference 156].)

Impurities in insulators contribute to the drift of W-Re thermocouples. For example, Walker et al.[156] measured a significant increase in iron in W-26%Re thermoelements after 120 hr at 1625°C in argon with Al_2O_3 insulators. The impurities from the Al_2O_3 caused the W-Re thermocouples to continue to drift, even after the drift of similar bare wire thermocouples had almost ceased. Droege et al.[158] concluded that BeO must contain no more than about 100 ppm of impurities to obtain good stability with W-Re thermocouples. Several other insulators have been considered for use with W-Re thermocouples, but only thoria appears to have sufficiently high resistivity and high normal purity to be considered as an alternative high temperature insulator.

Because they lack oxidation resistance, W-Re thermocouples must be enclosed in a protective sheath for many applications. Also, BeO, the insulator used most often with these thermocouples, undergoes a phase transformation at ~2050°C. During this transformation the volume of the BeO increases and causes the insulator to disintegrate. For this reason a sheath is required to maintain the mechanical integrity of the assembly. Fabrication of W-Re in CTAs is difficult because of the limited ductility of the thermoelements. Other disadvantages of CTAs are that the emf shift is more difficult to remove, the electrical shunting effect is increased, and drift due to chemical reaction of the thermoelements with the insulation is larger.

Burns and Hurst[154] suggest that a tantalum sheathed, doped W-3%Re versus W-25%Re thermocouple containing hard-fired (instead of crushable) BeO insulators is a good alternative to a CTA. Burns and Hurst cleaned and baked the components and heat treated the thermoelements to remove the emf shift, and then they fabricated the assemblies. The drift rate for this assembly was less than 1°C per 1000 hr of exposure at 1800°C, and Burns and Hurst suggest that similar results could be achieved up to 2000°C.

Without *in situ* calibration against an optical pyrometer, accurate temperature measurements above 2000°C do not appear possible with thermocouple thermometry because of the first four error sources listed in Table 5 which have been discussed. The fifth and sixth error sources are essentially independent of the hot junction temperature, whereas the noise and pick-up errors, discussed as part of the seventh error source, are not.

5. Extension Wire Errors

For accurate thermocouple thermometry, the thermoelements are connected directly to a reference junction of known temperature, rather than being terminated at some point and connected by extension wires to the reference junction. Extension wires are substitutes, selected because of their lower cost, and should be avoided if possible. Temperature measurement errors are caused by differences in the thermoelectric properties of the thermoelements and extension wires. From Equation 13, the thermal emf E_t generated by a thermocouple with hot junction temperature T_2 and reference junction temperature T_1 is

$$E_t = \int_{T_1}^{T_2} (S_a - S_b)\, dT \tag{16}$$

where the S_i are Seebeck coefficients of thermoelements a and b. When extension wires c and d are used to replace thermoelements a and b, respectively, between T_x and T_1, the emf E_{tx} of the thermocouple plus extension wire is

$$E_{tx} = \int_{T_x}^{T_2} (S_a - S_b)\, dt + \int_{T_1}^{T_x} (S_c - S_d)\, dt \tag{17}$$

The error due to the extension wire is the difference between emfs computed by Equations 16 and 17, or

$$\text{Error} = E_{tx} - E_t =$$

$$\int_{T_1}^{T_x} [(S_c - S_a) - (S_d - S_b)]\, dt \tag{18}$$

Therefore, to reduce the extension wire error, temperature difference $T_x - T_1$ and the differences in Seebeck coefficients of the thermoelements and the extension wires, $(S_c - S_a)$ and $(S_d - S_b)$, should be minimized. Normally, thermoelement wires are used for extension wires for base metal thermocouples, whereas copper-based alloys are used as extension wires for noble metal thermocouples. The tolerances to which extension wires are manufactured are listed in Table 10. If the temperature range is narrower than shown in Table 10, the errors are (in general) reduced. For example, in a range from 1 to 20°C, Starr and Wang[159] have shown that the error for a Type S thermocouple with SX extension wire is about +3°C, which is about half of the tolerance of Table 10.

If extension wire must be used, the junction between the thermoelements and extension wire should be kept isothermal to avoid additional errors due to differences in the thermoelectric properties of the connectors used with the extension wire. Also, if the junction temperature is known, the extension wire can be calibrated and the measured thermal emf can be corrected using Equation 18.

6. Reference Junction Errors

As stated by Equation 13, the thermal emf E of a thermocouple depends on temperatures T_2 and T_1 of its hot and reference junctions, respectively. If one wishes to determine T_2 from a measurement of E, reference junction temperature T_1 must be known. At the reference junction, both thermoelements usually are joined to copper wires, which are connected to the data acquisition system. The temperature of both thermoelement reference junctions must be the same to avoid error. The copper wires should be high quality, homogeneous, and untinned so that they do not produce a differential thermal emf, which would be an additional error source.

Several types of reference junctions are in wide use. When properly installed and maintained, they produce temperature measurement errors of less than ±0.3°C. These errors are due to: (a) thermal shunting of heat to or from the reference junction; (b) electrical shunting, for example, by water condensation for reference junctions operating below room temperature; and (c) inaccurate reference junction temperature. (See References 161–165 for more details.)

a. Ice-point Reference

Most emf-temperature tables and functions, such as NBS Monograph 125 (Reference 18), are established for a 0°C reference junction temperature. Thus, an ice-point reference junction is most commonly employed when accurate temperature measurements are required. Two types of ice-point references are used: a mixture of water and melting ice held in a Dewar flask, and a mixture of ice and water maintained in equilibrium by refrigeration. To avoid electrical shunting errors, a thermocouple is usually placed in the closed end of a glass tube which is immersed in the ice-water mixture. The upper end of the glass tube is sealed gas tight to avoid electrical shunting errors that could be caused by condensation of water vapor in the tube. Either oil[69] or mercury[162] is put in the bottom of the tube at the reference junction to aid heat transfer from the mixture to the reference junction to reduce thermal shunting

TABLE 10

Tolerance for Extension Wires[a]

Thermocouple type	Extension type	Typical alloys	Temperature range (°C)	Tolerance (°C)	
				Standard	Special
E	EX	Ni-Cr/Constantan	0 to 204	±1.7	–
J	JX	Fe/Constantan	0 to 204	±2.2	±1.1
K	KX	Ni-Cr/Ni Alloy	0 to 204	±2.2	±1.1
T	TX	Cu/Constantan	–59 to 93	±0.8	±0.4
R,S	SX	Cu/Cu-Ni Alloy B	0 to 204	±6.7	–
B	BX	Cu-Mn Alloy/Cu	0 to 121	±33	–

[a]See References 159 and 160.

errors. (When mercury is used, each thermoelement must be in a separate tube.)

Using extreme care, Thomas[164] reproduced the reference point of an ice-water mixture to 10^{-4} °C, which is negligibly small for thermocouple thermometry. Sutton[163] described the technique necessary to achieve an ice-water reference accurate to 0.01°C. Caldwell[165] demonstrated that even with less stringent techniques and methods of construction of the ice-water reference junction, the errors are less than 0.05°C.

Refrigerated ice-water reference junctions are available commercially. When properly installed, the error of these reference junctions is less than 0.1°C.

b. Triple Point of Water

A triple point cell contains an equilibrium mixture of ice, water, and water vapor. The triple point temperature is +0.01°C, and the temperature of commercially available cells is accurate[161] to 10^{-4} °C. Use of a triple point cell is recommended only when the remainder of the thermometry system is of the highest accuracy.

c. Zone Box

In systems having many thermocouples, say a hundred, and not requiring reference junction errors less than ±0.2°C, all the thermocouples may be routed to a zone box where the thermoelements are joined to wires, usually copper, which extend to the data acquisition system. If the zone box is isothermal, one thermocouple, or some other thermometer such as a resistance thermometer which does not require a reference temperature, may be used to determine the zone box temperature. It is not necessary that the zone box temperature be fixed, only that its temperature change slowly in comparison with the time required to read all the thermocouple emfs connected to it. Some zone boxes operate at ambient temperatures. Others are put in ovens at about 65°C to eliminate variations in ambient temperature from the reference junction correction. Ovens are available[161] with rated temperature accuracies of 0.1 to 0.05°C, but a careful experimentalist should always measure the oven temperature. When a reference table or a function referred to 0°C is to be used, the emf E to convert to temperature using the table or function is, by Equation 13,

$$E = E_m + E_t \tag{19}$$

where E_m is the measured emf of the thermocouple, and E_t is the emf from the reference table or function for the thermocouple at the measured temperature of the zone box.

d. Electrical Compensation

Most commercially available, direct reading (in temperature) thermocouple data acquisition systems use electrical compensation instead of a reference junction. One scheme is to place a circuit with a temperature sensitive resistor in series with the thermocouple emf. The emf across the temperature sensitive resistor and its compensating circuit is chosen to give an emf (E_t of Equation 19) that is equal to that of the thermocouple at the temperature of the junction of the thermocouple with the compensating circuit. The reference junction errors of well-designed electrical compensation circuits are less than ±0.3°C.

7. Data Acquisition Errors

The errors in measuring the thermal emf of a thermocouple vary from a few millidegrees when high-quality potentiometers are used to tens of degrees when high speed data loggers are employed. Because of the large number of data acquisition systems available, these errors have not been categorized. In general, data acquisition systems designed for steady state emf measurements, such as potentiometers, are more accurate than data acquisition systems for transient measurements of emf. To paraphrase the Heisenberg uncertainty principle, the product of the *speed* of data acquisition and the *accuracy* of data acquisition is approximately constant.

Table 11 is a comparison of the temperature measurement errors of a computer-operated data acquisition system and a high quality potentiometer, both commercial units. The computer system can record 20,000 thermocouple output readings per second with an uncertainty of ±0.25% of full scale (either 10, 20, 40, 80, 160, . . . , mV). With a potentiometer, an experienced operator can read one thermocouple output in about 1 min with an uncertainty of ±(0.01%, + 0.01 μV). The computer system errors listed in Table 11 are a factor of 20 to 40 greater than those of the potentiometer for a Type K thermocouple and a factor of 30 to 300 greater for a Type S thermocouple. Thus to gain a factor of 10^6 in data acquisition speed, a factor of at least 20 must be sacrificed in temperature measurement uncer-

TABLE 11

Errors in Temperature Measurement of Type K and Type S Thermocouples Due to Data Acquisition

Temperature range (°C)	EMF range (mV)		Computer system[a] error (°C)		Pot. system[b] error (°C)	
	Type K	Type S	Type K	Type S	Type K	Type S
0–250	10	10	±0.6	±3.2	±0.02	±0.01
250–485	20	10	±1.2	±2.7	±0.03	±0.03
485–965	40	10	±2.4	±2.4	±0.07	±0.06
965–1035	40	10	±2.4	±2.2	±0.11	±0.08
1035–1372	40	20	±2.4	±4.2	±0.12	±0.10
1372–1768	–	20	–	±4.2	–	±0.14

[a] Uncertainty ±0.25% of full scale emf.
[b] Uncertainty ±(0.01%, +0.01 µV) of thermocouple emf.

tainty, which is a justifiable compromise for many applications.

In Table 11 the potentiometric errors are less for the Type S than for the Type K thermocouple, and the computer system errors for the Type S thermocouple are either equal to or less than those for the Type K thermocouple between 485 and 1035°C. These data demonstrate the fallacy of the often stated superiority of a Type K thermocouple to a Type S thermocouple because the output of the Type K is four times greater than the output of the Type S. This is no longer true with present instrumentation.

One data acquisition error that is difficult to assess is due to nonthermal emfs, often called "noise" or "pick-up," which are either induced on the thermoelements or added to the thermal emf by electrical leakage of the thermocouple insulation. Pick-up errors are common in high temperature thermocouple thermometry and may distort the thermocouple signal so as to render it useless. Errors due to the DC component of the emf pick-up are very difficult to determine; sometimes these errors can be eliminated by turning off all electrical power that might contribute to DC pick-up while the thermocouple emf is measured.

The AC component of the pick-up can be filtered out for steady state and some transient temperature measurements. However, if the thermal emf changes rapidly, filtering may cause the measured emf to lag the true thermal emf of the thermocouple, resulting in temperature measurement errors. For example, a single-pole filter with a roll-off of 3 dB at 2 Hz in series with the thermocouple would cause the thermocouple output to lag −8°C while the thermocouple hot junction experienced a 100°C/sec temperature rise. This filter would also attenuate a 3-mV, peak-to-peak, 60-Hz induced, AC emf by a factor of 30. The result would be that the AC pick-up error would be reduced from ±38°C, unfiltered, to ±9.3°C, filtered (±1.3°C for a Type K thermocouple due to AC emf passed through the filter and 8.0°C due to lag).

Numerical methods[166] have been developed for correcting the transient emf of a thermocouple that is distorted by filtering, by its time response, or by thermal shunting. This technique is known as "deconvolution" of the distorted signal to the true undistorted signal, and requires a mathematical model of the system. A more direct technique,[167] called "digital signal averaging," requires several repeated measurements. Superposition and addition of the repeated measurements allows the unwanted noise to be averaged out. Data smoothing[168] is also effective in reducing errors due to noise or pick-up.

C. Thermocouple Thermometry Conclusions

From a review of the sources of error in thermocouple thermometry, our conclusions are the following:

1. Proper installation of a thermocouple can

negate errors due to thermal shunting in steady state temperature measurements. Heat transfer modeling is usually necessary to correct for temperature lag errors due to thermal shunting during measurements of temperature transients.

2. Electrical shunting errors can be reduced by use of loosely fitting insulators and sheaths, but they are unavoidable at higher temperatures when *in situ* calibrations or electrical models must be employed to correct for the error.

3. Generally, calibration errors increase with increasing temperature, and the accuracy of the calibration depends on the method employed.

4. Decalibration of thermocouples occurs because of chemical and metallurgical changes in the thermoelements during use and limits the useful lifetime of thermocouples.

5. Extension wires should not be used in accurate thermocouple thermometry; however, errors due to their use can be minimized by calibration of the extension wire.

6. Reference junction errors can be reduced to as low as 10^{-4} °C, if desired.

7. When potentiometers are used to read the thermal emf, the data acquisition error is inconsequential. Higher-speed methods, such as analog-to-digital converters used with computers, usually introduce data acquisition errors of less than 10°C.

With the present state of the art, accurate temperature measurements using thermocouples is limited to temperatures below 2000°C because of electrical shunting and rapid decalibration of the thermocouple above this temperature. Generally speaking, the accuracy of thermocouple thermometry depends on the care exercised by the user, and the uncertainties of the measurement may vary from tenths of degrees to hundreds of degrees.

VI. PYROMETRY

Optical pyrometers are widely used to measure temperatures above 800°C. Above 1064.43°C, the freezing point of gold, they are the most convenient means of realizing IPTS-68. Although, in principle, it should be possible to realize KTTS using optical pyrometers and the Planck equation, in practice it is not possible to make such measurements with the precision required for accurate temperature measurements. Instead, the value for the thermodynamic temperature of the freezing point of gold $T_{68}(Au)$ determined by gas thermometry is defined along with a value for c_2, the second radiation constant. A radiation scale of temperature can thus be defined by the ratio of the spectral radiance at some wavelength, λ, of a blackbody at some temperature T_{68} to that at the gold point, $T_{68}(Au)$ (see Equation 9). The wavelength usually chosen is about 0.650 nm, a convenient value for visually balanced pyrometers, although modern photoelectric instruments allow a much wider freedom of choice, even down to 1.0 nm in the infrared region. Recent reviews covering optical pyrometry include, besides the more general reviews of Bedford[1] and Quinn,[2] one by Ruffino on fundamental radiation pyrometry.[169]

In its simplest form, an optical pyrometer consists of a telescope to focus the image of a glowing body onto a detector, and some reference source whose image is viewed by the detector either alternately or simultaneously. Various spectral filters and attenuators are superimposed in front of the detector. The detector may be an observer's eye when using a visual pyrometer, or it may be some type of photoelectric detector in more sophisticated instruments. In most laboratory instruments, the reference source is a miniature strip lamp whose brightness temperature is determined by calibration. In some of the more elaborate instruments developed at the various national standards laboratories, the reference source may be a blackbody cavity surrounded by freezing gold. The filters pass a narrow spectral band and define the effective wavelength of the pyrometer. Absorbing glasses may be inserted between the unknown source and the detector to extend the range of the pyrometer to higher temperatures.

The visual optical pyrometer superimposes the image of the reference lamp onto the image of the unknown source, and the current through the reference lamp is adjusted until its filament disappears against the background of the unknown source. The unknown temperature is read from a scale or meter. Most photoelectric instruments are provided with a chopper that allows the detector to alternately view the unknown source and the reference lamp. The temperature of the reference lamp is automatically adjusted to give a brightness match between the reference and unknown, and some form of readout is provided for the reference lamp current. An instrument at the PTB (Germany)[170] includes a reference lamp held at a constant brightness and a special photocell with well-determined and stable linear characteristics.

A. Problems in Optical Pyrometry

Some problems with optical pyrometry are related to the instruments themselves, and others are related to the radiative properties of materials and the particular experimental situation. Instrument uncertainties are due to drift in the reference lamps, changes in sensitivity of the detectors, noise in the detection system, and changes in the optical system (e.g., changes in transmission of the absorbing filters or collection of dust on the system optics). In addition, the accuracy of experimental measurements is affected by uncertainties in the emissivity of the object whose temperature is to be measured and absorption of radiation by gases and windows in the optical path.

Drift of the temperature-current characteristics of the reference lamps is one source of uncertainty in instruments with such lamps. Lee[171] investigated these uncertainties and observed changes of several tenths of a degree per 100 hr of use. In practical use, these drift rates are unpredictable because the degree of aging depends on the time at a temperature and the value of the temperature. These uncertainties can be minimized by periodic calibration of the pyrometer against a standard strip lamp, as discussed below.

Detector systems contribute uncertainties in both visually balanced optical pyrometers and those using photomultiplier detectors. A common laboratory and field instrument is the disappearing-filament, visual optical pyrometer. A visual reading using these instruments is somewhat subjective. Different observers were used at the NBS in determinations of the gold freezing point to evaluate such bias. The determination of different observers differed as much as 1°C, although the standard deviation of the observations of a single observer was between 0.1 and 0.25°C.[172] A number of instruments with photoelectric detectors have been designed and constructed at the national standard laboratories,[171,173-175] and several photoelectric instruments are available commercially. The standard deviation of a typical photoelectric instrument developed[171] at the NBS is 0.06 K at the gold point and 2 K at 3525°C. The largest single source of uncertainty at the gold point is due to drift in the reference lamp. At higher temperatures, uncertainties in the calibration of the absorbing glasses are the major source of error. Noise in the electronics contributes some uncertainty, but this is reduced by integrating over a period of time. Coates[175] noted that drift in a photomultiplier is strongly correlated with drift in the temperature of the photocathode. He minimized this drift by thermostating the photomultiplier tube. Kunz and Kaufmann[170] have described the photoelectric pyrometer designed at the PTB. This instrument contains a reference lamp maintained at a constant brightness temperature, a special photocell used as a linear detector, and a programmable calculator for on-line data collection. The uncertainties claimed for the PTB pyrometer range from 0.04°C at the gold point to 0.7°C at 3800°C.

Uncertainties of commercial photoelectric instruments are considerably higher, ranging from ±2°C at 1500°C to ±7°C at 2800°C, because of the unpredictable aging effects of the pyrometer lamps, uncertainties to the absorbing glasses and, in some cases, the instability of the electronics of the instrument.

Since determination of brightness ratios depends on the transmission of the optical path, the optical surfaces of the pyrometers should be kept dust free.

A problem which may be encountered in a high temperature system with a window is the change of the transmittance of the window with time owing to deposition of material on the window vaporized from the parts of the system at high temperature. Removing the window to measure its transmittance may give erroneous results. If such a window is a part of a vacuum system, as is often the case, exposure of the inner surface to air may further change its transmittance if the material deposited on the window is oxidized.[176]

For accurate work in radiation thermometry, a correction must be made for the refractive index of air or the gas between the pyrometer and the blackbody cavity, as discussed in 1972 by Blevin[177] and applied in 1974 by Quinn[178] to his measurements of the freezing point of platinum as well as of some other fixed points. The correction is small for air, amounting to 0.3 K at the platinum point.

Since radiation from the specimen whose temperature is to be determined must be viewed directly by the pyrometer, radiative heat losses through the access port can cool the target and

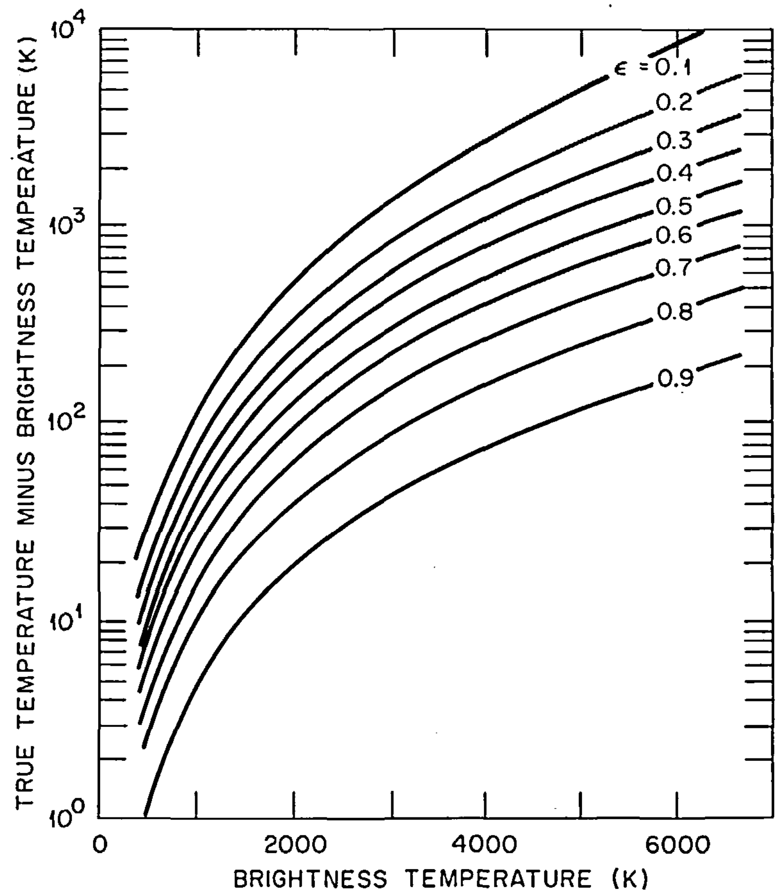

FIGURE 12. Errors that can occur in optical pyrometry, if emissivity of a surface is neglected, as a function of apparent (brightness) temperature.

cause errors amounting to as much as 5 to 6 K at 2000°C.[1]

Temperatures measured by optical pyrometers can be related to thermodynamic or IPTS-68 temperatures through Equation 9 only for ideal blackbody conditions. For nonideal conditions, the emittance is defined by

$$L(\lambda,T_s) = \epsilon(\lambda,T)\, L_b(\lambda,T) \qquad (20)$$

where $L(\lambda,T_s)$ is the radiance of a surface, $\epsilon(\lambda,T)$ is the value of the emittance of the surface at temperature T, and $L_b(\lambda,T)$ is the radiance of a blackbody. T_s is the apparent, or brightness, temperature of the surface, and T is its true temperature — all under the same wavelength conditions. Considerable effort must be expended to ensure that the emissivity of an object whose temperature being measured is known. For example, to achieve an uncertainty of about 0.1K at the gold point, the emissivity of a blackbody must be 0.999 or greater. For this reason, the design of blackbodies has received a good deal of attention, and several have been constructed[179,180] with an emissivity greater than 0.9995. Both Quinn[181] and Bedford[182] have reviewed the theories for calculating the emissivity of blackbodies of various configurations.

For most materials, the vagueness of the emissivity can give rise to very large errors when an optical pyrometer is used to measure surface temperatures. Figure 12 shows the corrections that must be made for various values of emissivity as a function of brightness temperature. As an example, consider the values of emissivity reported for Inconel (Figure 13),[183] a material widely used in high temperature systems. At 0.65 μm, the effective wavelength of most optical pyrometers, the emissivity can vary from 0.14 to 0.87 depending on the surface condition of the material. This would amount to about a 100°C

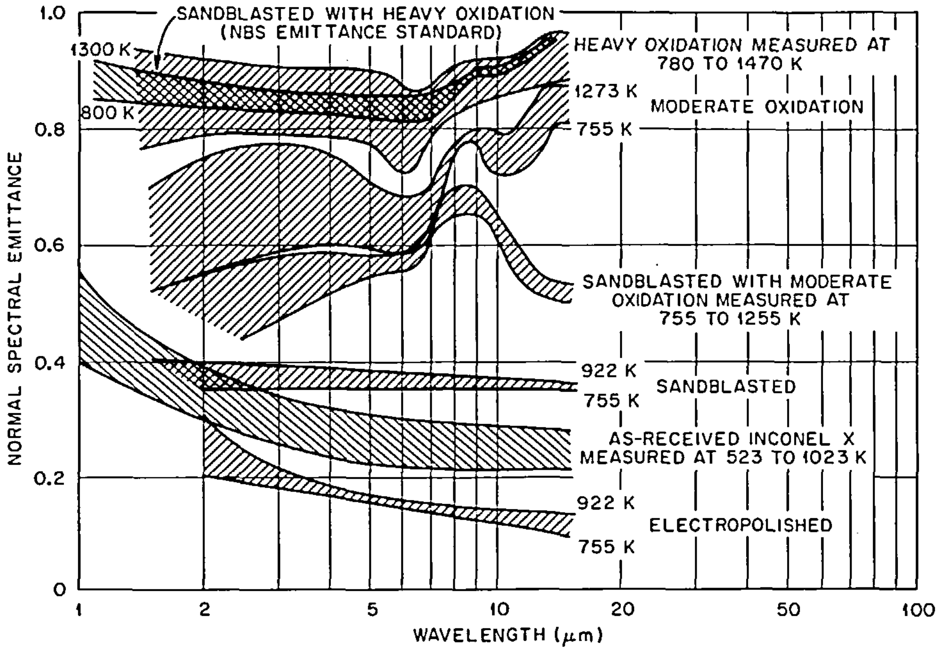

FIGURE 13. Range of emittance values for Inconel as a function of wave length. Note that in the region of 0.65 μm, the assumption of a linear change of emissivity with wavelength can be seriously in error. (Adapted from Touloukian, Y. S. and DeWitt, D. P., *Thermophysical Properties of Matter TPRC Data Series, Thermal Radiative Properties: Metals and Alloys,* Vol. 7, Plenum Press, New York, 1970, p. 1347.)

error at a brightness temperature of 1000°C. Furthermore, the surface conditions can change with time. Although there are extensive compilations of emissivity,[183] the vagueness of the emissivity of even a relatively well-characterized material such as Inconel reinforces the suggestion that precise temperature measurements should be made using only a blackbody cavity.

Two- and three-color pyrometers have been proposed[21,23,24,184] to avoid the problems of emissivity; however, these pyrometer designs are based on an assumption that the emissivity is constant or varies linearly with wavelength. Thus, to use these pyrometers, the user must know the emissive properties of the surface. As seen in Figure 14, these assumptions may be seriously in error, since the value of the emissivity strongly depends on the surface condition of the material. Furthermore, at the present time, these instruments are less sensitive than comparable single-wavelength pyrometers.

An alternative method described by Kunz[22] is to measure the ratio of adsorption of radiation energy at two wavelengths provided by lasers, and at the same time measure the change in temperature of the object with a photoelectric pyrometer at a third wavelength. The adsorption measurements give a ratio of the emittances at the two wavelengths, $r_e = \epsilon(\lambda_1)/\epsilon(\lambda_2)$, and the temperature is given by

$$\frac{1}{T} = \frac{1}{T_r} + \frac{\ln\left[\epsilon(\lambda_1)/\epsilon(\lambda_2)\right]}{c_2\,(1/\lambda_1 - 1/\lambda_2)} \tag{21}$$

where T_r is the ratio temperature measured by the pyrometer, and c_2 is the second radiation constant from the Planck equation. A more complete description of this method is given by DeWitt and Kunz.[185]

B. Calibration of Optical Pyrometers

Optical pyrometers can be readily calibrated using a calibrated strip lamp powered by a stable DC power supply, with some means of reading the lamp current (up to about 40 A). Strip lamps, when calibrated by the NBS, are supplied with a table of lamp current versus temperature. The stability of these strip lamp standards has been improved from drift rates of tenths of a degree in 100 hr to tenths of a degree in 1000 hr using improved construction techniques.[186] Lee[187] de-

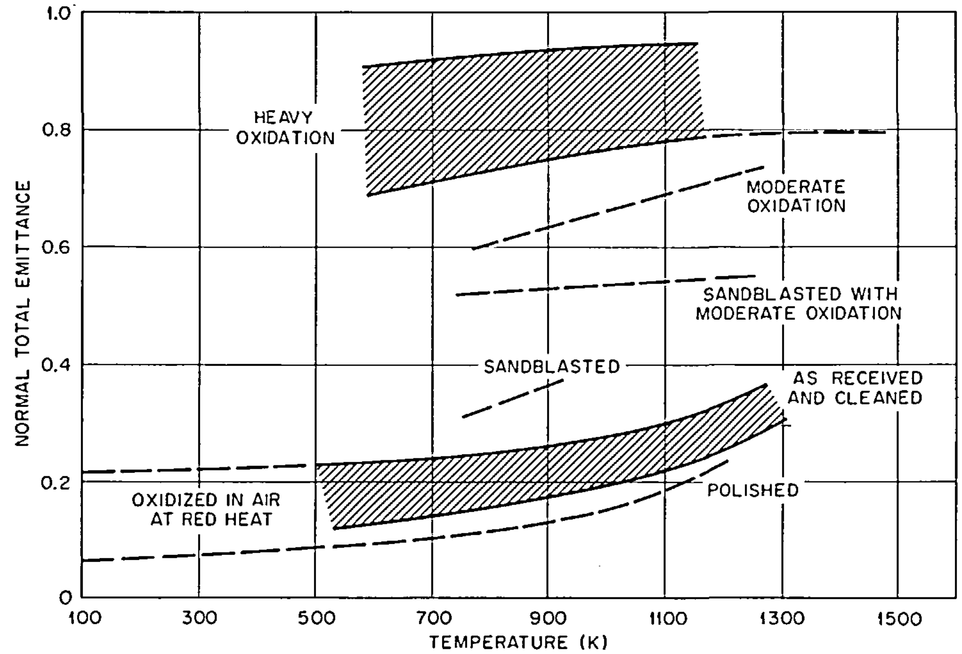

FIGURE 14. The range of values found for the total normal emittance of Inconel as a function of temperature and surface condition. (Adapted from Touloukian, Y. S. and DeWitt, D. P., *Thermophysical Properties of Matter TPRC Data Series, Thermal Radiative Properties: Metals and Alloys*, Vol. 7, Plenum Press, New York, 1970, p. 1347.)

scribed a copper-freezing-point blackbody that can be used for a single-point calibration with optical pyrometers. The pyrometer optics and the envelope should be clean and dust-free. The internal pyrometer lamp current should be checked against the manufacturer's estimated values, and if it has drifted by more than an amount equivalent to 50°C, the lamp should be replaced.

VII. OTHER TYPES OF THERMOMETERS

There has been much work done in the past few years to develop high temperature thermometers, mostly to improve existing measuring instruments. There have been, however, significant developments of new types of thermometers. Among these are a Johnson noise thermometer in which electrical noise generated in a resistor is directly proportional to its thermodynamic temperature; an ultrasonic thermometer, using either pulse or resonant techniques, with a sensor which can be as simple as a small wire with a step near the active end; edge-tone resonators[188] (somewhat reminiscent of an organ pipe) with a resonant frequency dependent on the temperature of a gas; metal film resistance thermometers[189] for high speed measurements up to about 1000°C; and microwave techniques[190] employing resonant wave-guide cavities whose resonant frequency is related to temperature through thermal expansion of the cavity. Most of these thermometers are still in a development stage; however, for certain special applications the Johnson noise thermometer shows promise.

A. Johnson Noise Thermometry

Temperature measurements based on Nyquist's theoretical explanation of the electrical noise generated in an electrical conductor have been attempted from the time Nyquist and Johnson published their papers[191,192] in the 1930s. It has been only in the past 10 years that electronic theory and circuits were developed to make the noise thermometer practicable. The chief fascination with noise thermometry is that, according to Nyquist's theory,

$$\overline{(e^2_{nv})}^{1/2} = K(4kTR\Delta f_v)^{1/2} \tag{22}$$

the rms noise voltage is related by a proportionality factor, K, to the square root of the thermodynamic temperature, T; the resistance, R, of the sensor; the bandwidth, Δf, of the detection system; and Boltzmann's constant, k.

As with gas thermometry, the concept of noise thermometry is simple, but the realization is not. In an actual noise thermometer system, the sensor leads, the electronic amplifiers, and, at times, other sources which may be difficult to identify contribute noise signals in addition to the noise signal from the sensor. Probably the most successful noise thermometers have been those developed for the liquid-helium range of temperature, using Josephson junctions as parametric amplifiers. In such a system it is possible to have a noise generating resistor that is without lead error and has an accuracy of a few percent at about 0.020 K.[193] At high temperatures, besides the problems of noise generated by the leads, the thermometer can be affected by insulation leakage.

Just as there exists a noise voltage in a resistor R at temperature T, there is likewise an associated noise current. One scheme which has been suggested is that by employing noise power, that is,

$$P = E_n i_n \tag{23}$$

the measurement of temperature could be made independent of the value of the resistance R. Such a scheme proposed by Blalock and Borkowski[194] is illustrated in Figure 15 where the output of the high-impedance voltage amplifier is given by Equation 22. Similarly, the output of the low-impedance current amplifier is given by

$$\overline{(e^2{}_{ni})}^{1/2} = K(4kT_s\Delta f_i/R)^{1/2} \tag{24}$$

The noise power is obtained by substitution into Equation 23; the result is

$$P_n = \overline{(e^2{}_{ni})}^{1/2}\ \overline{(e^2{}_{nv})}^{1/2} = CT_s \tag{25}$$

where

$$C = 4kK_iK_v(\Delta f_i \Delta f_r)^{1/2} \tag{26}$$

and does not depend on R. The values k and Δf are constants of the amplifiers. Realization of the noise power method depends on the adequacy of the noise current amplifier, which must have a very low input impedance (high transconductance). Such an amplifier was developed only recently by use of modern circuit techniques.

The noise power thermometer shows its greatest potential in special applications, such as temperature measurement in nuclear reactors where the resistance of a sensor is changed by transmutation of the sensor material and by other radiation damage effects. At least two laboratories have reported experiments with noise thermometers in nuclear reactors.[195,196] The most recent was at the ORNL where a noise power thermometer was placed in the High-Flux Isotope Reactor for about 5000 hr at temperatures from 1350 to 1500°C. The rhenium sensor was estimated to have been converted to about 75% osmium in this time; however, the temperature indicated by the noise thermometers was still within 1 to 2% of the initial value (approximately ±10°C). In contrast, thermocouple thermometers under similar conditions have decalibrated hundreds of degrees Celsius.[197]

Although the theory developed by Nyquist shows the noise thermometer to be a fundamental thermometer and not just a transducer, it has not been developed sufficiently to make a significant contribution to realization of the thermodynamic scale. Crovini and Actis[13] recently reviewed the

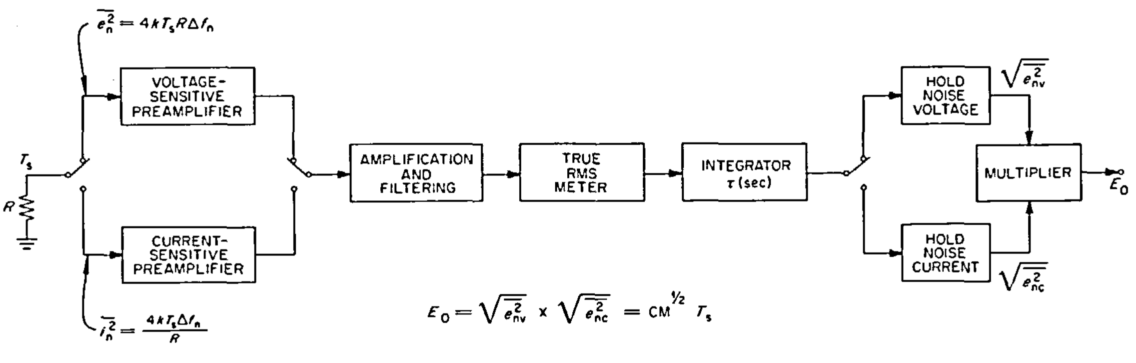

FIGURE 15. A system for measuring temperature using noise power. (Adapted from Blalock, T. V. and Borkowski, C. J., *Rev. Sci. Instrum.*, 45, 151 (1974).)

status of noise thermometry, and from electronic considerations alone, he concluded that the limit of accuracy of existing noise thermometers is about 0.03%. In contrast, the NBS gas thermometer is expected to yield the thermodynamic temperature of the gold point with an uncertainty of ~0.001%. However, the noise thermometer could conceivably be used as an interpolating instrument above the gold point as an alternative to the optical pyrometer. Furthermore, continued development of the noise amplifiers and associated circuity is expected.

B. Ultrasonic Thermometry

Two general types of ultrasonic thermometers have been developed, a resonant technique and a pulse-echo technique. Lynnworth and Carnevale[198] state that the sensor material can be a gas, liquid, or solid. One advantage claimed for the ultrasonic thermometer is its fast response time, which can be milliseconds. The feasibility of measuring temperatures in fairly exotic conditions, for example, gas flames at about 2700°C, is claimed to have been demonstrated. The complex apparatus necessary for such a measurement, however, makes it doubtful that this method will ever emerge from the laboratory. With the development of the microprocessor, such a method might be made practicable, but it would still be expensive. Very little work seems to have been done using liquids as sensors, except for feasibility studies.

There has been a substantial amount of work to develop refractory wire sensors for high temperatures. For example, Bell[199] reported good stability using a molybdenum wire resonator at 1200°C. The calibration was retained within ±2 K, both in a vacuum furnace and in a nuclear reactor. In work at ORNL[196] for proposed fuel center-line temperature measurements in a nuclear reactor, a rhenium sensor was selected, but it decalibrated several hundred degrees in a few hundred hours. The transmutation of the rhenium to osmium resulted in a change in elastic constants and a consequent change in the sound velocity in the sensor. One should remember, however, that the decalibration of high temperature thermocouple materials studied under similar circumstances was similar.[197] At present, no contact method of temperature measurement has proved adequate above 1700°C. The Johnson noise thermometer should, in principle, not be subject to the same sources of errors, but experimental work has not been extended above 1500°C.

VIII. CONCLUSIONS

With the increased emphasis today on energy research, conversion, and conservation, the necessity for accurate temperature measurements is of critical importance. Controls of all economically viable energy conversion systems known at this time, as well as those projected for the future, depend on temperature measurements. Furthermore, the design of such systems depends critically on the temperature dependence of such material properties as strength of materials, thermal expansion rates and corrosion rates, which in turn are strongly dependent on accurate temperature measurements. Even recent compilations of material properties show a great diversity of values for the same substance. A large part of these differences has been traced to errors in temperature measurement.[1] Because of these uncertainties, energy systems must be designed more conservatively, that is, less efficiently, than would be the case with more reliable thermal property data.

It is hoped that this review will result in an increased awareness of problems in high temperature thermometry and, perhaps, will even provoke some solutions.

ACKNOWLEDGMENTS

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Note: References to the proceedings of the several symposia on temperature measurement are so numerous that the following abbreviated forms have been used:

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