NBS CIRCULAR 590

Methods of Testing Thermocouples and Thermocouple Materials

UNITED STATES DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards

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Methods of Testing Thermocouples and Thermocouple Materials

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Contents

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Various methods used for testing thermocouples and thermocouple materials and the precautions that must be observed in order to attain various degrees of accuracy are described. In particular, the methods that have been developed and used at the National Bureau of Standards are outlined in detail, and some guidance is given to the reader in the selection of the method best adapted to a given set of conditions.

Consideration is given primarily to the calibration of platinum versus platinum-rhodium, copper-constantan, Chromel-Alumel, and iron-constantan thermocouples.

1. Introduction

Methods of testing thermocouples and thermocouple materials have been developed to supply the need of those industries to which the measurement and control of temperature are essential. The recognition by the various industries in this country that the measurement and control of temperature are essential to a uniformly high quality of product has led, in recent years, to a tremendous increase in the use of temperature-measuring equipment. Where the higher temperatures are involved, by far the greater portion of such measurements is made with thermocouples, and therefore these devices must be regarded as one of the important tools of modern industry.

The users of thermoelectric pyrometers have been demanding ever-increasing accuracy in these instruments. Thermocouple materials are being bought on closer specifications, and the pyrometer manufacturers have been setting up smaller tolerances in the inspection and calibration of their product, with the result that practically all pyrometric equipment now being sold is of very high quality. Reliable methods of testing thermocouples and thermocouple materials are required to realize the degree of accuracy now demanded. The purpose of this Circular is to describe the more important of these methods and to point out certain precautions that must be observed to secure reliable results. The essential features of many of these methods and much of the apparatus described here have been devised and described in whole or in part by various writers, but references to their papers will be made only when it is felt that a more detailed description than is given here will be helpful to the reader.

Combinations of metals and alloys extensively used in thermocouples for the measurement of temperatures in this country are listed in table 1, together with the temperature ranges in which they are generally used and the maximum temperatures at which they can be used for short periods. The period of usefulness at high temperatures depends largely upon the temperature and the diameter of the wires. The methods described in this Circular were devised primarily for calibrating thermocouples in the usual temperature ranges, but unless otherwise indicated they may be used up to the maximum temperatures at which the various types of thermocouples can be used.

TABLE 1. *Types of thermocouples and temperature ranges in which they are used*

Type of thermocouple	Usual temperature ranges		Maximum temperatures	
	° C	*° F*	*° C*	*° F*
Platinum versus platinum-rhodium	0 to 1,450	32 to 2,650	1,700	3,100
Chromel-Alumel	−190 to +1,100	−310 to +2,000	1,350	2,450
Iron-constantan	−190 to +760	−310 to +1,400	1,000	1,800
Copper-constantan	−190 to +300	−310 to +570	600	1,100

2. General Considerations

2.1. Temperature Scale

The object in the calibration of any thermocouple is to determine an emf-temperature relationship in which the temperature is expressed on a definite and reproducible scale. The International Temperature Scale, adopted in 1927 [1] [2] by 31 nations and revised in 1948 [2], is now in practically universal use. The methods of realizing this scale are described in detail in the references

[1] Now with American Machine & Foundry Co., Alexandria, Va.

[2] Figures in brackets indicate the literature references at the end of this Circular.

TABLE 2. *Instruments, calibration points, and interpolation equations of the International Temperature Scale of 1948*

Temperature ranges		Instruments	Calibration points (values for pressure of 1 standard atmosphere)			Interpolation equations [a]
° C	*° F*		*Fixed point*	*° C*	*° F*	
−182.970 to 0	−297.346 to 32	Platinum resistance thermometer.	Boiling point of oxygen.	−182.970	−297.346	$R_t=R_0[1+At+Bt^2+C(t-100)t^3]$.
			Ice point [b]	0	32	
			Boiling point of water	100	212	
			Boiling point of sulfur	444.600	832.280	
0 to 630.5	32 to 1,166.9	Platinum resistance thermometer.	Ice point [b]	0	32	$R_t=R_0(1+At+Bt^2)$.
			Boiling point of water	100	212	
			Boiling point of sulfur	444.600	832.280	
630.5 to 1,063.0	1,166.9 to 1,945.4	Platinum versus platinum-10-percent-rhodium thermocouple.	Freezing point of antimony.	[c] 630.5	[c] 1,166.9	$E=a+bt+ct^2$.
			Freezing point of silver.	960.8	1,761.4	
			Freezing point of gold	1,063.0	1,945.4	
1,063.0 and above	1,945.4 and above	Optical pyrometer	Freezing point of gold	1,063.0	1,945.4	$\frac{J_t}{J_{\mathrm{Au}}}=\frac{e^{\frac{c_2}{\lambda(t_{\mathrm{Au}}+T_0)}}-1}{e^{\frac{c_2}{\lambda(t+T_0)}}-1}$.

[a] R_t is the resistance at t°C, R_0, the resistance at 0°C; A and B are constants determined by calibration at the boiling points of water and sulfur, and C is an additional constant determined by calibration at the boiling point of oxygen. E is the emf at t°C, and a, b, and c are constants. J_t and J_{Au} are the radiant energies per unit wavelength interval at wavelength, λ, emitted per unit time by unit area of a black body at the temperature, t, and at the gold point, t_{Au}, respectively, c_2 is 1.438 cm degrees, T_0 is the temperature of the ice point in degrees K. λ, is a wavelength of the visible spectrum, and e is the base of Naperian logarithms.

[b] It is recommended that for work of the highest precision, the zero point be realized by means of the triple point of water, a point to which the temperature +0.0100° C has been assigned.

[c] The freezing temperature of the antimony used in determining these constants shall be determined with a standard resistance thermometer, and shall be not lower than 630.3° C. Alternatively, the thermocouple may be calibrated by direct comparison with a standard resistance thermometer in a bath at any uniform temperature between 630.3° and 630.7° C.

cited. The instruments, calibration points, and interpolation equations to be used in the various ranges of the scale are summarized in table 2.

Methods of improving the International Temperature Scale are subjects of continuous study in many laboratories. Although such studies may result in minor changes in the values assigned to fixed points or in the substitution of one fixed point for another, they will not alter, in general, the methods of calibrating thermocouples.

2.2. General Methods

In order to calibrate thermocouples to yield temperatures on the International Temperature Scale, it is apparent from the definition that they must be so calibrated that their indications agree with those of the standard platinum-resistance thermometer in the range −182.970° to 630.5° C, the standard platinum versus platinum-10-percent-rhodium thermocouple in the range 630.5° to 1,063.0° C, and the optical pyrometer above 1,063.0° C. The most direct procedure would therefore be to compare the thermocouples directly with these primary instruments in the appropriate temperature ranges. However, to follow such a procedure in the calibration of every thermocouple requires more time and apparatus than is justifiable or necessary because, in most cases, other methods are available which yield results sufficiently accurate. For example, a thermocouple may be compared indirectly with any of the primary instruments by determining its emf at a number of fixed points, either those which are used in defining the scale or others, the values for which have been determined with the primary instruments. If a few laboratories maintain the apparatus necessary to calibrate thermocouples as working standards to yield temperatures on the International Temperature Scale, these standards may be used subsequently to calibrate other thermocouples. This procedure is used far more than any other because the comparison of the indications of two thermocouples is usually simpler than the comparison of two different types of instruments.

The temperature-emf relationship of a homogeneous[3] thermocouple is a definite physical property and, therefore, does not depend upon the details of the apparatus or method employed in determining this relation. Consequently, there are innumerable methods of calibrating thermocouples, the choice of which depends upon the type of thermocouple, temperature range, accuracy required, size of wires, apparatus available, and personal preference.

Thermocouple calibrations are required with various degrees of accuracy, ranging from 0.1° to 5° or 10° C. For an accuracy of 0.1° C, agreement with the International Temperature Scale and methods of interpolating between the calibration points become problems of prime importance, but for an accuracy of about 10° C, comparatively simple methods of calibration will usually suffice. The most accurate calibrations in the range −190° to 300° C are made by comparing the thermocouples directly with a standard platinum resistance thermometer in a stirred liquid bath. In the range 300° to 630.5° C (and below if a platinum resistance thermometer or stirred liquid bath is not available) thermocouples are most accurately calibrated at the freezing or boiling points of pure substances. Between 630.5° and 1,063.0° C, the platinum versus

[3] A homogeneous thermocouple is one in which each element is homogeneous, in both chemical composition and physical condition, throughout its length.

platinum-10-percent-rhodium thermocouple calibrated at the freezing points of gold, silver, and antimony serves to define the International Temperature Scale, and other types of thermocouples are most accurately calibrated in this range by direct comparison with the standard thermocouple calibrated as specified. Other platinum, versus platinum-rhodium thermocouples may be calibrated just as accurately at the fixed points as the platinum versus platinum-10-percent-rhodium thermocouple, but interpolated values at intermediate points may depart slightly from the International Temperature Scale. Above 1,063.0° C, the most basic calibrations are made by observing the emf when one junction of the thermocouple is in a black-body furnace, the temperature of which is measured with an optical pyrometer. However, the difficulties encountered in bringing a black-body furnace to a uniform temperature make the direct comparison of these two types of instruments by no means a simple matter. Other methods of calibrating a thermocouple above 1,063.0° C are given under melting points and under methods of interpolation.

Although the platinum versus platinum-10-percent-rhodium thermocouple serves to define the scale only in the range 630.5° to 1,063.0° C, this type of thermocouple calibrated at fixed points is used extensively both above and below this range as a working standard in the calibration of other thermocouples. For most industrial purposes, a calibration accurate to 2° or 3° C in the range room temperature to 1,200° C is sufficient. Other thermocouples can be calibrated by comparison with such working standards almost as accurately as the calibration of the standard is known. However, it might be pointed out that outside the range 630.5° to 1,063.0° C any type of thermocouple suitable for the purpose, and calibrated to agree with the resistance thermometer or optical pyrometer in their respective ranges, has as much claim to yielding temperatures on the International Temperature Scale as the platinum versus platinum-10-percent-rhodium thermocouple. In fact, at the lower temperatures, certain types of base-metal thermocouples are definitely better adapted for precise measurements.

The calibration of thermocouples then may be divided into two general classes, depending upon the method of determining the temperature of the measuring junction, (1) calibration at fixed points and (2) calibration by comparison with standard instruments, such as thermocouples, resistance thermometers, etc.

In order to obtain the high accuracies referred to above and usually associated with calibrations at fixed points, it is necessary to follow certain prescribed methods and to take the special precautions described in detail in the following sections, but for an accuracy of about 5° C the more elaborate apparatus to be described need not be employed.

2.3. Homogeneity

The magnitude of the emf developed by a thermocouple depends upon the temperatures of the measuring and reference junctions and the composition of the wires in the region of temperature gradients. The emf developed by an inhomogeneous thermocouple is characteristic of the temperature of the measuring junction only when the region of inhomogeneity is not in a region of temperature gradients. Therefore, in order to obtain a high degree of accuracy with a thermocouple, the homogeneity of the wires must be established.

Thermocouple wire now being produced by the manufacturers in this country is sufficiently homogeneous in chemical composition for most purposes. Occasionally, inhomogeneity in a thermocouple may be traced to the manufacturer, but such cases are rare. More often it is introduced in the wires during tests or use. It usually is not necessary, therefore, to examine new thermocouples for inhomogeneity, but thermocouples that have been used for some time should be so examined before an accurate calibration is attempted.

Although rather simple methods are available for detecting thermoelectric inhomogeneity, no satisfactory method has been devised for quantitatively determining it or the resulting errors in the measurement of temperatures. Tests for inhomogeneity must be so designed that the method of testing does not of itself introduce inhomogeneities into the wire being tested. Abrupt changes in the thermoelectric power may be detected by connecting the two ends of the wire to a sensitive galvanometer and slowly moving a sharp temperature gradient, such as that produced by a piece of solid carbon dioxide, a Bunsen burner, or small electric furnace, along the wire. This method is not satisfactory for detecting gradual changes in the thermoelectric power along the length of the wire. Inhomogeneity of this nature may be detected by doubling the wire and inserting it to various depths in a uniformly heated furnace, the two ends of the wire being connected to a galvanometer as before. If, for example, the doubled end of the wire is immersed 25 cm in a furnace with a sharp temperature gradient so that two points on the wire 50 cm apart are in the temperature gradient, the emf determined with the galvanometer is a measure of the difference in the thermoelectric properties of the wire at these two points.

After reasonable homogeneity of one sample of wire has been established, it may be used in testing the homogeneity of similar wires by welding the two together and inserting the junction into a heated furnace. The resulting emf at various depths of immersion may be measured by any convenient method. Other similar methods have been described for detecting inhomogeneity [3].

Tests such as those described above will indicate the uncertainty in temperature measurements due to inhomogeneity in the wires. For example, if a difference in emf of 10 microvolts (abbreviated hereafter μv) is detected along either element of a platinum versus platinum-rhodium thermocouple by heating various parts of the wire to 600° C, measurements made with it are subject to an uncertainty of the order of 1° at 600° C or of 2° at 1,200° C. Similarly, if an emf of 10 μv is detected along an element of a base-metal thermocouple with a source of heat at 100° C, measurements made with it are subject to an uncertainty of the order of 0.2° C at this temperature. The effects of inhomogeneity in both wires may be either additive or subtractive, and, as the emf developed along an inhomogeneous wire depends upon the temperature distribution, it is evident that corrections for inhomogeneity are impracticable if not impossible.

2.4. Annealing

Practically all base-metal thermocouple wire produced in this country is annealed or given a "stabilizing heat treatment" by the manufacturer. Such treatment is generally considered sufficient, and seldom is it found advisable to further anneal the wire before testing.

Although the new platinum and platinum-rhodium thermocouple wires as sold by some manufacturers are already annealed, it has become regular practice in many laboratories to anneal or "stabilize" all platinum versus platinum-rhodium thermocouples, whether new or previously used, before attempting an accurate calibration. This is usually accomplished by heating the wire electrically in air. The entire length of wire is supported between two binding posts, which should be close together so that the tension in the wires and stretching while hot are kept at a minimum. The temperature of the wire is most conveniently determined with an optical pyrometer.[4] It is necessary, however, to add a correction to the observed apparent temperature to obtain the true temperature, which is always the higher. The correction (based on an emissivity of 0.33) amounts to 130° and 145° C, respectively, for apparent temperatures of 1,270° and 1,355° C.

There is some question as to the optimum temperature or length of time at which such thermocouples should be annealed to produce the most constant characteristics in later use [4]. As a matter of fact, there is some question as to whether annealing for more than a few minutes is harmful or beneficial. Most of the mechanical strains are relieved during the first few minutes of heating at 1,400° to 1,500° C, but it has been claimed that the changes in the thermal emf of a thermocouple in later use will be smaller if the wires are heated for several hours before calibration and use. The principal objection to annealing thermocouples for a long time at high temperatures, aside from the changes in emf taking place, is that the wires are weakened mechanically as a result of crystal growth. For a number of years prior to 1935, the practice at the National Bureau of Standards was to anneal all platinum versus platinum-rhodium thermocouples electrically in air for 6 hr at 1,500° C before calibration. The emf of a number of new thermocouples was determined both after annealing for 5 min and for 6 hr at 1,500° C, and in no case did the change in emf correspond to as much as 2° C at 1,200° C. After 6 hr of heating, the wires, particularly the platinum element, become much softer. It has been found, however, that annealing at temperatures much above 1,500° C produces rapid changes in the emf and leaves the wire very weak mechanically. The National Bureau of Standards, on January 2, 1935, adopted the procedure of annealing all platinum versus platinum-rhodium thermocouples for 1 hr at 1,450° C.

It has not been demonstrated conclusively that platinum versus platinum-rhodium thermocouples after contamination can be materially improved in homogeneity by prolonged heating in air, although it is logical to suppose that certain impurities can be driven off or, through oxidation, rendered less detrimental.

2.5. Instruments

One of the factors in the accuracy of the calibration of a thermocouple is the accuracy of the instrument used to measure the emf. Fortunately, in most instances, an instrument is available whose performance is such that the accuracy of the calibration need not be limited by the accuracy of the emf measurements. For work of the highest accuracy, it is advisable to use a potentiometer of the type designed by Diesselhorst [5], White [6], Wenner [7], or Bonn,[5] in which there are no slide wires and in which all the settings are made by means of dial switches. However, for most work, in which an accuracy of a few microvolts will suffice, slide-wire potentiometers of the laboratory type are sufficiently accurate. Portable potentiometers accurate within about 50 μv and capable of being read to about 5 μv are also available. Aside from the greater sensitivity obtained, an important advantage of using a potentiometer is the fact that the reading obtained is independent of the resistance of the thermocouple.

Indicators of the galvanometric type are seldom used in making calibrations. Galvanometer indicators should be graduated for a specified external resistance of thermocouple and extension wires, and the resistance of the indicator itself should be high in order to reduce the effects of changes in the resistance of the thermocouple and leads. A discussion of these factors is given in NBS Technologic Paper T170 (1921).

[4] The ordinary portable type of optical pyrometer is very satisfactory for this purpose. As commonly used, the magnification is too low for sighting upon an object as small as the wires of bare-metal thermocouples, but this is easily remedied by inserting an additional piece of telescoping tubing so that the objective lens of the pyrometer is about twice as far from the pyrometer lamp as it is when sighting upon distant objects, or by using an objective lens of higher magnification.

[5] Designed by N. E. Bonn, of the Rubicon Co.

3. Calibration at Fixed Points

One of the important applications of the method of calibrating thermocouples at fixed points is found in the calibration of platinum versus platinum-10-percent-rhodium thermocouples, to realize the International Temperature Scale in the range 630.5° to 1063.0° C. From such a calibration, together with methods of extrapolation described later, the temperature-emf relationship of this type of thermocuple may be determined with an accuracy of about 2° C at 1,450° C. Calibration at a few other selected points below 630.5° C will yield a working standard that is accurate to a few tenths of a degree in the range 0° to 1,100° C. Fixed points are also conveniently used with various degrees of accuracy ranging from 0.1° to 5° C in the calibration and checking of various types of thermocouples in the range −190° C to the melting point of platinum (1,769° C). The fixed points for which values have been assigned or determined accurately and at which it has been found convenient to calibrate thermocouples are given in table 3. The values in the table apply for a pressure of 1 standard atmosphere (760 mm of Hg) and the variations of the boiling temperatures with pressure are given in the last column.

TABLE 3. *Fixed points available for calibrating thermocouples*

Thermometric fixed point	Values on the International Temperature Scale of 1948				Temperature of equilibrium (t_p) in degrees C as a function of the pressure (p) between 680 and 780 mm of mercury. p_0 is standard atmospheric pressure.
	Assigned (primary points)		Determined (secondary points)		
	°C	°F	°C	°F	
Boiling point of oxygen	−182.970	−297.346	--------	--------	$t_p=-182.970+9.530\left(\frac{p}{p_0}-1\right)-3.72\left(\frac{p}{p_0}-1\right)^2+2.2\left(\frac{p}{p_0}-1\right)^3$
Sublimation point of carbon dioxide.	--------	--------	−78.5	−109.3	$t_p=-78.5+12.12\left(\frac{p}{p_0}-1\right)-6.4\left(\frac{p}{p_0}-1\right)^2$
Freezing point of mercury	--------	--------	−38.87	−37.97	
Ice point	0	32	--------	--------	
Triple point of water	--------	--------	+0.0100	32.0180	
Boiling point of water	100	212	--------	--------	$t_p=100+28.012\left(\frac{p}{p_0}-1\right)-11.64\left(\frac{p}{p_0}-1\right)^2+7.1\left(\frac{p}{p_0}-1\right)^3$
Triple point of benzoic acid	--------	--------	122.36	252.25	
Boiling point of naphthalene	--------	--------	218.0	424.4	$t_p=218.0+44.4\left(\frac{p}{p_0}-1\right)-19\left(\frac{p}{p_0}-1\right)^2$
Freezing point of tin[a]	--------	--------	231.9	449.4	
Boiling point of benzophenone	--------	--------	305.9	582.6	$t_p=305.9+48.8\left(\frac{p}{p_0}-1\right)-21\left(\frac{p}{p_0}-1\right)^2$
Freezing point of cadmium	--------	--------	320.9	609.6	
Freezing point of lead[a]	--------	--------	327.3	621.1	
Freezing point of zinc[a]	--------	--------	419.5	787.1	
Boiling point of sulfur	444.600	832.280	--------	--------	$t_p=444.600+69.010\left(\frac{p}{p_0}-1\right)-27.48\left(\frac{p}{p_0}-1\right)^2+19.14\left(\frac{p}{p_0}-1\right)^3$
Freezing point of antimony	--------	--------	630.5	1166.9	
Freezing point of aluminum[a]	--------	--------	660.1	1220.2	
Freezing point of silver	960.8	1761.4	--------	--------	
Freezing point of gold	1063.0	1945.4	--------	--------	
Freezing point of copper[a]	--------	--------	1083	1981	
Freezing point of palladium	--------	--------	1552	2826	
Freezing point of platinum	--------	--------	1769	3216	

[a] The values given in this table for these materials are the values stated in the International Temperature Scale of 1948. Standard Samples of these materials are procurable from the National Bureau of Standards with certificates giving the freezing point of the particular lot of metal.

In selecting the points at which to calibrate a thermocouple, one sometimes has a choice between a boiling or a freezing point [6] as, for example, between the boiling point of sulfur (444.600° C) and the freezing point of zinc (419.5° C); between the boiling point of naphthalene (218.0° C) and the freezing point of tin (231.9° C); or between the boiling point of benzophenone (305.9° C) and the freezing point of cadmium (320.9° C) or lead (327.3° C). In determining the emf of a thermocouple at a freezing point, the time in which observations may be taken is limited to the period of freezing, after which the material must be melted again before taking further observations. In the case of boiling points, there is no such limit in time since the material can be boiled continuously. In addition, there is sometimes a question as to the beginning and end of the interval of constant-temperature characteristic of freezing. On the other hand, it is not necessary to observe the pressure during freezing and, in general, simpler apparatus and less skill are required to obtain a given accuracy with freezing points.

[6] In this Circular, "boiling point" is used for the temperature of equilibrium between the liquid and vapor phases, although the point is usually realized experimentally by immersing the thermocouple in the condensing vapor. "Freezing point" is used for the temperature of equilibrium between the solid and liquid phases when the point is realized experimentally by immersing the thermocouple in the freezing material, and "melting point" is used for the same point when it is realized experimentally by determining the emf of a thermocouple while the material is melting. When conditions permit a choice, freezing points are preferable to melting points of metals because the molten metal can be brought to a uniform temperature just prior to freezing by stirring more easily than the solid can be brought to a uniform temperature just prior to melting, a condition that must be met to obtain accurate results.

3.1. Freezing Points

The emf developed by a homogeneous thermocouple at the freezing point of a metal is constant and reproducible if all of the following conditions are fulfilled: (1) The thermocouple is protected from contamination, (2) the thermocouple is immersed in the freezing-point sample sufficiently far to eliminate heating or cooling of the junction by heat flow along the wires and protection tube, (3) the reference junctions are maintained at a constant and reproducible temperature, (4) the freezing-point sample is pure, and (5) the metal is maintained at essentially a uniform temperature during freezing. The methods of obtaining these conditions are subject to a choice. However, the essential features of the methods employed at the National Bureau of Standards are described here.

a. Protection Tubes

Closed-end porcelain or Pyrex-glass tubes are generally used to protect thermocouples from contamination, which usually results from the thermocouple wires coming in contact with other metals or metallic vapors or from the action of reducing gases at high temperatures. In the latter case, the silica of the insulating or protecting tube is reduced to silicon, which alloys with the thermocouple wires [8]. For temperatures above 500° C, the wires should be insulated by porcelain tubing and protected from contamination by a glazed porcelain tube. It is advisable to heat these tubes before use, to about 1,200° C in an oxidizing atmosphere to burn out any carbonaceous material that may have collected in them during storage and shipping. Protection tubes 5-mm inside diameter, 7-mm outside diameter, and 50 cm long are convenient for platinum versus platinum-rhodium thermocouples insulated by two-hole insulating tubes 50 cm long and 4 mm in diameter with 1-mm holes. For temperatures below 500° C, Pyrex tubes are very satisfactory for both protecting and insulating the wires.

b. Depth of Immersion

The depth of the immersion necessary to avoid heating or cooling of the junction by heat flow along the thermocouple wires and protection tube depends upon the material and size of the wires, the dimensions of the insulating and protecting tubes, and the difference between the temperature of the freezing-point sample and that of the furnace and atmosphere immediately above it. The safest method of determining whether the depth of immersion is sufficient is by trial. It should be such that during the period of freezing the thermocouple can be lowered or raised at least 1 cm from its normal position without altering the indicated emf by as much as the allowable uncertainty in the calibration. For platinum versus platinum-rhodium thermocouples in the protection tube described above, a depth of 10 cm, which is greater than necessary, is used at the National Bureau of Standards.

c. Reference-Junction Temperature Control

The temperature of the reference junctions is most easily controlled at a known temperature by placing them in an ice bath. A wide-mouthed Dewar flask filled with shaved ice saturated with water is very satisfactory. Electrical connection between a thermocouple wire and a copper lead wire is easily made by inserting them into a small glass tube containing a few drops of mercury. The glass tubes are then inserted into the ice bath to a depth of about 10 cm. The extension wires must be insulated from the thermocouple wires, except where they make contact through the mercury. It is preferable that the insulation on the wires extends below the level of the mercury. The glass tubes should be kept clean and dry inside. Moisture is likely to condense in the tube from the atmosphere but should not be allowed to accumulate. A little moisture and dirt at the bottom of the tube will form a galvanic cell, which may vitiate the readings. A later section deals with reference-junction temperatures in general.

d. Purity of Freezing-Point Samples

The temperature at which a metal freezes depends upon the amount and kind of impurities present. The values in table 3 apply for metals, the purity of which is of the order of 99.99 percent. The freezing temperature of silver, gold, or copper may be lowered by as much as 0.1° C and that of antimony, aluminum, zinc, lead, cadmium, tin, or mercury by as much as 0.05° C by 0.01 percent of impurities. The purity of the Standard-Sample freezing-point materials issued by the National Bureau of Standards is not of great importance, as a certificate is issued with each sample giving the freezing temperature determined on that particular lot of metal. However, the purest metals available are selected for these Standard Samples because a high degree of purity is necessary in order that the metal may give a flat freezing curve.

e. Crucibles

Of the crucible materials ordinarily used, highly purified graphite has the greatest utility and is used almost exclusively at NBS for this work. It can be machined into any desired shape, and can be used in contact with any of the freezing-point materials in table 3 except palladium and platinum without detectable contamination of the metals. At high temperatures, the gases formed from its oxidation provide the reducing atmosphere usually necessary for the protection of the freezing-point metal. Copper and copper oxide form a eutectic which melts about 20° C lower than pure copper, and it is possible for molten silver to absorb enough oxygen from the air to lower its freezing point as much as 10° C [9]. Therefore, copper and silver must be protected from oxygen, and it is advisable also to protect aluminum and antimony from oxygen. This is

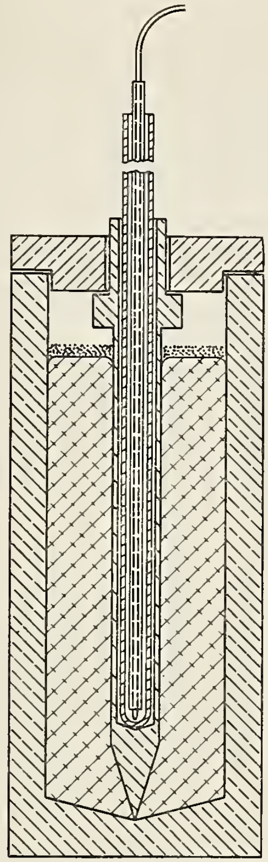

Figure 1. *Arrangement for protecting a thermocouple in molten aluminum.*

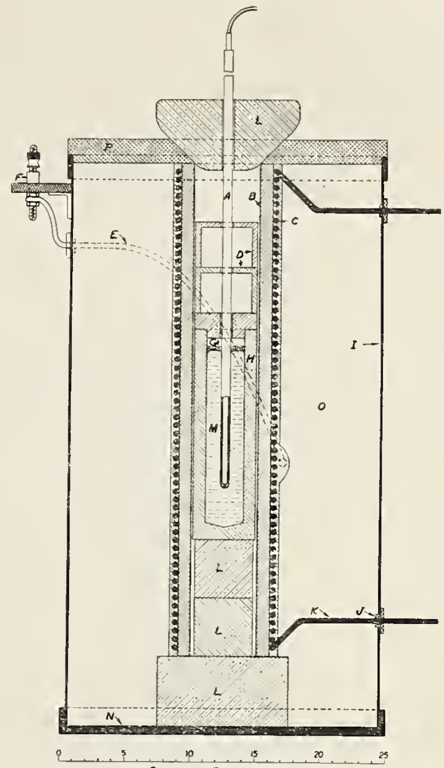

Figure 2. *Furnace used in calibrating thermocouples at freezing points of metals.*

A, Porcelain protecting tube; B, refractory furnace tube; C, heating element (80 nickel, 20 chromium); D, graphite diaphragms; E, control thermocouple (Chromel-Alumel); G, graphite powder; H, graphite crucible; I, sheet steel; L, insulating blocks; M, freezing-point metal; N, cast-iron base; O, powdered diatomaceous earth insulation.

done by using graphite crucibles with covers of the same material, and as an added precaution these freezing-point metals are covered with powdered graphite or charcoal.

Porcelain tubes or crucibles, or any material containing silica, cannot be used in contact with aluminum, as the silica is readily attacked. Aluminum is melted in a graphite crucible and the porcelain protecting tube separated from the aluminum by a very thin sheath of graphite. Figure 1 illustrates one convenient manner in which the sheath may be mounted in the crucible. The sheath is held down in the metal by the weight of the cover and is allowed to remain in the crucible after the aluminum is frozen. The thermocouple protecting tube fits snugly inside the sheath. At the National Bureau of Standards the graphite crucibles used for gold, silver, antimony, and zinc are 3-cm inside diameter and 15 cm deep. The crucibles used for copper, aluminum, lead, and tin are 5-cm inside diameter and 15 cm deep. Porcelain, silica, clay, clay graphite, and Pyrex glass are also used as crucible materials. Pyrex glass is very suitable for mercury.

f. Furnaces

Figure 2 shows the type of furnace used in the freezing-point determinations. The heating element is No. 6 or 8 gage nickel(80)-chromium(20) wire wound on a refractory tube and imbedded in refractory cement. The space between the heating element and the outside wall is filled with powdered diatomaceous earth. Graphite diaphragms are placed above the crucible in order to reduce the oxidation of the crucibles and to promote temperature uniformity in the metal.

g. Procedure

In the calibration of a thermocouple at freezing points, the thermocouple, properly protected, is slowly immersed in the molten metal. The metal is brought to essentially a uniform temperature at the beginning of freezing by holding its temperature constant at about 10° C above the freezing point for several minutes and then cooling slowly, or by agitating the metal with the thermocouple protection tube just before freezing begins. The emf of the thermocouple is observed at regular intervals of time. These values are plotted, and the emf corresponding to the flat portion of the cooling curve is the emf at the freezing point of the metal.

Antimony and tin have a marked tendency to undercool before freezing, but the undercooling will not be excessive if the liquid metal is stirred.

3.2. Melting Points

The emf of a thermocouple at the melting point of a metal may be obtained in the same manner and with the same apparatus as that just described for freezing points, but the latter are found to be more satisfactory. However, melting points are used to advantage when only a limited amount of material is available. One method of obtaining the emf of a thermocouple at a melting point with a small amount of material is the wire method [10]. In this method, the thermocouple wires are placed in a two-hole insulating tube and a short length of the melting-point sample, in the form of wire about the same diameter as the thermocouple elements, is welded between the measuring junction ends of the two wires. The dimensions of the melting-point sample are not critical, but there should be at least 1 mm of wire between the two welds. In order that the melting-point sample shall not break before the melting point is reached, the weld should be made and the thermocouple placed in the furnace so that there is a minimum of strain on the melting-point sample. The measuring junction end of the thermocouple with the melting-point sample, is placed in a uniformly heated section of a furnace and the temperature increased very slowly as the melting point is approached. When the sample reaches its melting point, its temperature and consequently the emf of the thermocouple remain constant for a fraction of a minute (varying with the rate of temperature rise). After melting is complete, the temperature of the wire and the emf may rise somewhat before the circuit is broken by the separation of the molten metal. The value of the emf corresponding to the melting point is, therefore, the value at the halt in the emf rise and is obtained by continuous observation of the emf as melting is approached or by plotting time versus emf.

The metal most often used in the calibration of thermocouples by the wire method is gold, and it has been demonstrated that results can be obtained which are in agreement with those obtained with a crucible of freezing gold to a few tenths of a degree. The same method has been used with palladium, but with much less satisfactory results because of electric leakage through the refractory insulation at high temperatures and the oxidation of the palladium. This method is not well adapted to metals that oxidize rapidly, and if used with materials whose melting temperature is altered by the oxide, the metal should be melted in a neutral atmosphere.

If very accurate observations of the emf are not required, the emf at the instant the circuit is broken may be taken, but if this is done the thermocouple should be withdrawn from the furnace immediately and the sample examined to see whether the circuit was broken by the sample melting or by strain on it before melting occurred.

It is not necessary to weld the wire between the thermocouple elements, as fairly good results may be obtained by wrapping a small amount of the wire around the junction. This practice is often applied to base-metal thermocouples by wrapping wires of tin, lead, zinc, or aluminum around the measuring junction and heating it until a halt is observed in the heating curve.

One method of checking platinum versus platinum-rhodium thermocouples at the highest possible point is by heating the junction of the thermocouple until the platinum wire melts. To avoid electric leakage, the insulating tube is withdrawn to the colder parts of the heating device leaving only the wires and junction in the hotter parts.

3.3. Boiling Points

Boiling points play an important part in the definition of the International Temperature Scale, because 3 of the 4 points upon which the scale between −182.970° and +630.5° C is based are the boiling points of oxygen, water, and sulfur. However, boiling points, with the exception of that of water, are seldom used in the calibration of thermocouples, and consequently the methods of realizing these various points will be mentioned only briefly here. References are given to complete discussions for those interested, as boiling points might profitably be employed to a greater extent, when a platinum-resistance thermometer or a stirred liquid bath is not available.

a. Water (Steam Point)

The temperature of condensing water vapor is realized experimentally by the use of a hypsometer so constructed as to avoid superheat of the vapor around the thermocouple and contamination with air and other impurities. Simple types of hypsometers are shown in various trade catalogs. Mueller and Sligh [11] give a detailed description of a hypsometer used in precision measurements. If the proper conditions are attained, the observed emf of the thermocouple will be independent of the rate of heat supply to the boiler, the length of time the hypsometer has been in operation, and the depth of immersion of the thermocouple. The thermocouple for some distance from the junction must be shielded from radiation from hotter and colder surfaces. The relationship between the temperature (t_p) (in degrees C) and the pressure (p) given in table 3 holds for the range 660 to 860 mm of Hg. The steam point as realized by utilizing the condensing vapor in a hypsometer is certainly accurate to 0.01° C. An accuracy of about 1° C can be obtained by merely immersing a thermocouple in boiling water.

b. Sulfur, Benzophenone, and Naphthalene

The boiling points of the three materials above are near the freezing points of available pure metals and are very seldom used in the calibration of thermocouples. The specifications to be followed in realizing the sulfur point are given in the International Temperature Scale [12]. Detailed description of the apparatus and precautions to be observed for the sulfur boiling point are given by Mueller and Burgess [13]. The relationship between temperature and pressure for sulfur in table 3 holds for the range 660 to 800 mm of Hg. The procedure and apparatus for realizing the boiling points of naphthalene and benzophenone are the same as those for the boiling point of sulfur. Detailed information regarding these points is given by Waidner and Burgess [14] and by Finck and Wilhelm [15].

c. Oxygen

The temperature of equilibrium between liquid and gaseous oxygen is best realized experimentally by the static method, the oxygen vapor-pressure thermometer being compared with the thermocouple to be calibrated in a suitable low-temperature bath. An oxygen vapor-pressure thermometer is nothing more than a glass tube containing very pure oxygen at a pressure of several atmospheres at room temperature, and connected to a mercury-filled manometer for measuring the pressure in the tube [16]. When the thermometer tube is immersed in the bath, part of the oxygen liquefies. The relationship between the temperature (t_p) (in degrees C) of the bath and the pressure (p) in the thermometer given in table 3 holds for the range 660 to 860 mm of Hg. This requires that the temperature of the bath be kept within the limits −184.3° to −181.8° C. This is most conveniently done by stirring liquid oxygen in a Dewar flask.

d. Carbon-Dioxide Point

Although the sublimation point of carbon dioxide is not a boiling point, the highest accuracy is obtained in utilizing this point, by employing the same method as that for the boiling point of oxygen. An instrument of this type suitable for use as a carbon-dioxide vapor-pressure thermometer is container type 3, described by Meyers and Van Dusen [17]. The sublimation point of carbon dioxide may also be utilized by immersing the thermocouple in a slush made by mixing carbon-dioxide snow with a liquid such as acetone. The slush should be stirred and the air excluded from the vapor above the surface of the slush. Whereas the accuracy obtained with a vapor-pressure thermometer is of the order of a few hundredths of a degree, an accuracy of 1° C is all that can be claimed for the temperature of the slush.

4. Calibration by Comparison Methods

The calibration of a thermocouple, by comparison with a working standard is sufficiently accurate for most purposes and can be done conveniently in most industrial and technical laboratories. The success of this method usually depends upon the ability of the observer to bring the junction of the thermocouple to the same temperature as the actuating element of the standard, such as the measuring junction of a standard thermocouple or the bulb of a resistance or liquid-in-glass thermometer. The accuracy obtained is further limited by the accuracy of the standard. Of course, the reference-junction temperature must be known, but this can usually be controlled by using an ice bath as described earlier or measured with a liquid-in-glass thermometer. The method of bringing the junction of the thermocouple to the same temperature as that of the actuating element of the standard depends upon the type of thermocouple, type of standard, and the method of heating.

4.1. Platinum Versus Platinum-Rhodium Thermocouples

Platinum versus platinum-rhodium thermocouples, either the 10- or 13-percent rhodium, are seldom used for accurate measurements below 300° C (572° F) and are practically never used below 0° C, because the thermal emf per degree of these thermocouples decreases rapidly at low temperatures, becoming zero at about −138° C (−216° F). These thermocouples are usually calibrated above 300° C by comparison with standard thermocouples in electrically heated furnaces. The standard thermocouple may be either a platinum versus platinum 10- or 13-percent-rhodium thermocouple that has been calibrated at fixed points or by comparison with other thermocouples so calibrated.

The method employed at the National Bureau of Standards for the comparison of two such thermocouples permits simultaneous reading of the emf of each thermocouple without waiting for the furnace to come to a constant temperature. In order to insure equality of temperature between the measuring junctions of the thermocouples, they are welded together. A separate potentiometer is used to measure each emf, one connected to each thermocouple, and each potentiometer is provided with a reflecting galvanometer. The two spots of light are reflected onto a single scale, the galvanometers being set in such a position that the spots coincide at the zero point on the scale when the circuits are open and, therefore, also when the potentiometers are set to balance the emf of each thermocouple. Simultaneous readings are obtained by setting one potentiometer to a desired value and adjusting the other so that both spots of light pass across the zero of the scale together as the temperature of the furnace is raised or lowered.

By making observations, first with a rising and then with a falling temperature, the rates of rise and fall being approximately equal, and taking the means of the results found, several minor errors, such as those due to differences in the periods of the galvanometers, etc., are eliminated or greatly reduced. The differences between the values observed with rising and falling temperatures are usually less than a few microvolts with platinum versus platinum-rhodium thermocouples, if the periods of the galvanometers are approximately the same.

This method is particularly adapted to the calibration of thermocouples at any number of selected points. For example, if it is desired to determine the temperature of a thermocouple corresponding to 10.0 mv, this emf is set up on the potentiometer connected to this thermocouple, the emf of the standard thermocouple observed as described above, and the temperature obtained from the emf of the standard. If it is desired to determine the emf of a thermocouple corresponding to 1,000° C, the emf of the standard corresponding to this temperature is set up on the potentiometer connected to the standard and the emf of the thermocouple being tested is observed directly.

In order to calibrate a thermocouple in the least possible time by this method, it is necessary to use a furnace that is so constructed that it will cool rapidly. The heating element of the furnace used at NBS for the routine testing of thermocouples consists of a nickel(80)-chromium(20) tube clamped between two water-cooled terminals. The tube, which is 13/16-in. inside diameter, 1⁵⁄₁₆-in. outside diameter, and 24 in. long, is heated electrically, the tube itself serving as the heating element or resistor. The large current necessary to heat the tube is obtained from a transformer. A large cylindrical shield of sheet metal is mounted around the heating tube to reduce the radiation loss. To reduce lag no thermal insulation is used between the heating tube and the radiation shield. The middle part of this furnace, for about 18 in., is at practically a uniform temperature, and the water-cooled terminals produce a very sharp temperature gradient at each end. This furnace can be heated to 1,200° C in about 10 min with 12 kw and, if all the power is shut off, will cool from this temperature to 300° C in about the same time. This type of furnace can be used up to 1,250° C (2,282° F).

The thermocouples are insulated and protected by porcelain tubes. It is essential that the two potentiometers and thermocouple circuits be separate except at the point where the junctions are welded together. The reference junctions are maintained at 0° C.

The above method and apparatus were devised primarily for the rapid testing of thermocouples, but it is not necessary to follow this method literally or to procure identical apparatus to obtain good results. If it is not convenient to weld the junctions of the thermocouples together, they may be brought into fairly good contact by wrapping with platinum wire or foil. The only advantage of the furnace described above, over any other type of furnace in which several inches of the thermcocouples may be heated to a uniform temperature, is the flexibility of control. Electric tube furnances suitable for such comparison tests can be obtained, designed to operate on either 110 or 220 v, and may be obtained equipped with an adjustable power supply for regulating the current. For temperatures up to 1,150° C (2,102° F), a furnace with a heating element of nickel (80)-chromium (20) will suffice. Furnaces with heating elements of platinum or platinum-rhodium are available for higher temperatures. A convenient size of heating tube is 1 in. in diameter and 18 in. long. Even though the furnace tube is kept fairly clean, it is advisable to protect platinum versus platinum-rhodium thermocouples by a porcelain tube. If two potentiometers are not available for taking simultaneous readings, the furnace may be brought to essentially a constant temperature and the emf of each thermocouple read alternately on one instrument.

When the thermocouples are calibrated by welding or wrapping the junctions together, the difference between the temperatures of the junctions should not be great even when the temperature of the furnace is changing. If it is necessary or advisable to calibrate the thermocouples without removing them from the protection tubes, then the junctions of the thermocouple being tested and that of the standard should be brought as close together as possible in a uniformly heated portion of the furnace. In this case, it is necessary that the furnace be brought to approximately a constant temperature before taking observations. It is usually not possible to maintain the reference junctions at 0° C when the thermocouples are completely enclosed in protection tubes. However, extension leads may be used with the thermocouple or the temperature of the reference junctions may be measured with a thermometer.

There are a number of other methods of heating and of bringing the junctions to approximately the same temperature, for example, inserting the thermocouples properly protected into a bath of molten metal or into holes drilled in a large metal block. The block of metal may be heated in a muffle furnace or, if made of a good thermal conductor such as copper, may be heated electrically. Tin, which has a low melting point, 232° C (450° F), and low volatility, makes a satisfactory bath material. The thermocouples should be immersed to the same depth with the junctions close together. Porcelain tubes are sufficient protection, but to avoid breakage by thermal shock when immersed in molten metal it is preferable to place them inside of secondary tubes of iron, nickel-chromium, graphite, or similar material. In all of these methods, particularly in those cases in which the junctions of the thermocouples are not brought into direct contact, it is important that the depth of immersion be sufficient to eliminate cooling or heating of the junctions by heat flow along the thermocouple and the insulating and protecting tubes. This can be determined by observing the change in the emf of the thermocouple as the depth of immersion is changed slightly. If proper precautions are taken, the accuracy yielded by any method of heating or bringing the junctions to the same temperature may be as great as that obtained by any other method.

4.2. Base-Metal Thermocouples in Laboratory Furnaces

The methods of testing base-metal thermocouples above room temperature are generally the same as those just described for testing rare-metal thermocouples with the exception, in some cases, of the methods of bringing the junctions of the standard and the thermocouple being tested to the same temperature and the methods of protecting platinum versus platinum-rhodium standards from contamination. One arrangement of bringing the junction of a platinum versus platinum-rhodium standard to the same temperature as that of a large base-metal thermocouple for accurate calibration is to insert the junction of the standard into a small hole (about 1.5 mm in diameter) drilled in the measuring junction of the base-metal thermocouple as shown in figure 3. The platinum versus platinum-rhodium standard is protected by porcelain tubes to within a few millimeters of the measuring junction; and the end of the porcelain tube is sealed to the thermocouple by Pyrex glass or by a small amount of kaolin and water-glass cement. This prevents contamination of the standard thermocouple, with the exception of the small length of 2 or 3 mm, which is necessarily in contact with the base-metal thermocouple. If the furnace is uniformly heated in this region (and it is of little value to make such a test unless it is) contamination at this point will not cause any error. If the wire becomes brittle at the junction, this part of the wire may be cut off and enough wire drawn through the seal to form a new junction. The seal should be examined after each test and remade if it does not appear to be good. More than one base-metal thermocouple may be welded together and the hole drilled in the composite junction. The thermocouples should be clamped in place so that the junctions remain in contact. If two potentiometers are used for taking simultaneous readings, the temperature of the furnace may be changing as much as a few degrees per minute during an observation, but if a single instrument is used for measuring the emf, the furnace temperature should be maintained practically constant during observations.

In testing one or more small base-metal thermocouples, they may be welded to the junction of the standard. If a base-metal standard is used, the best method is to weld all the junctions together. If a large number of base-metal thermocouples are to be tested at the same temperature, the method of immersing the thermocouples in a molten-metal bath or into holes drilled in a large copper block is very advantageous. If a tin bath is used, iron or nickel-chromium tubes are sufficient protection for base-metal thermocouples. When wires, insulators, and protection tubes of base-metal thermocouples are large, tests should be made to insure that the depth of immersion is sufficient to eliminate heating or cooling of the junction by heat flow along these materials.

4.3. Thermocouples in Fixed Installations

After thermocouples have been used for some time at high temperatures, it is difficult if not impossible to determine how much the calibrations are in error by removing them from an installation and testing in a laboratory furnace. The thermocouples are usually inhomogeneous after such use and in such a condition the emf developed by the thermocouples depends upon the temperature distribution along the wires [18]. If possible, such thermocouples should be tested under the same conditions and in the same installation in which they are used. Although it is not usually possible to obtain as high a precision by testing the thermocouples in place as is obtained in laboratory tests, the results are far more accurate in the sense of being representative of the behavior of the thermocouples.

The exact method of procedure depends upon the type of installation. A standard thermocouple is usually employed with extension leads and preferably a portable potentiometer, although a portable high-resistance millivoltmeter may be used. In this case, as in the calibration of any thermocouple by comparison methods, the main objective is to bring the measuring junction of the standard thermocouple to the same temper-

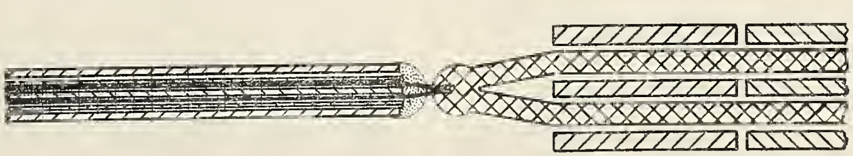

Figure 3. *Arrangement to assure good thermal contact between the junction of a base-metal thermocouple and that of a protected platinum versus platinum-rhodium thermocouple.*

ature as that of the thermocouple being tested. One method is to drill a hole in the furnace at the side of each thermocouple permanently installed, large enough to permit insertion of the checking thermocouple. The hole is kept plugged, except when tests are being made. The standard thermocouple is immersed in the furnace through this hole to the same depth as the thermocouple being tested, with the measuring junctions ends of the protection tubes as close together as possible.

In many installations, the base-metal thermocouple and protecting tube are mounted inside another protecting tube of iron, fire clay, silicon carbide, or some other refractory which is permanently cemented or fastened into the furnace wall. Frequently there is room to insert a small test thermocouple in this outer tube alongside of the fixed thermocouple. A third method, much less satisfactory, is to wait until the furnace has reached a constant temperature and make observations with the thermocouple being tested, then remove this thermocouple from the furnace, and insert the standard thermocouple to the same depth.

If desired, comparisons can be made preferably by either of the first or second methods at several temperatures, and a curve obtained for each permanently installed thermocouple showing the necessary corrections to be applied to its readings. Although testing a thermocouple at one temperature yields some information, it is not safe to assume that the changes in the emf of the thermocouple are proportional to the temperature or to the emf. For example, it has been observed that a thermocouple which had changed in use by the equivalent of 9° C at 315° C had changed only the equivalent of 6° C at 1,100° C.

It may be thought that this method of checking thermocouples is unsatisfactory because, in most furnaces used in industrial processes, large temperature gradients exist and there is no certainty that the standard thermocouple is at the same temperature as the thermocouple being tested. This objection, however, is not serious, because if temperature gradients do exist of such a magnitude as to cause much difference in temperature between two similarly mounted thermocouples located close together, the reading of the standard thermocouple represents the temperature of the fixed thermocouple as closely as the temperature of the latter represents that of the furnace.

The principal advantage of this method is that the thermocouple, leads, and indicator are tested as a unit and under the conditions of use.

4.4. Thermocouples in Stirred Liquid Baths

Thermocouples and resistance thermometers are not usually directly compared above 300° C because of the difficulty encountered in bringing the thermocouple junction and the thermometer bulb to the same temperature, but these two types of instruments may be very accurately compared below 300° C, where a stirred liquid bath can be conveniently used. A type of bath suitable for use above 0° C is shown in figure 5 of a paper by N. S. Osborne [19]. The container, which is insulated on the outside, consists of two cylindrical vertical tubes connected at the bottom and near the top by rectangular ports. A frame carrying the heating element, cooling coils if desired, and stirring propeller are inserted in one of the vertical tubes. The instruments being compared are placed in the other vertical tube and held in place by any convenient means. The chief advantage of this arrangement is that local irregularities, due to direct conduction from the vicinity of the heating or cooling elements, are eliminated. A stirred liquid bath for use below 0° C has been described by Scott and Brickwedde [20].

The liquids used in the baths should be capable of being stirred readily at any temperature at which they are used and they should not be highly flammable. At NBS oil is used between 100° and 300° C; water in the range 0° to 100° C; mixtures of carbon tetrachloride and chloroform in the range 0° to −75° C; a five-component mixture containing 14.5 percent of chloroform, 25.3 percent of methylene chloride, 33.4 percent of ethyl bromide, 10.4 percent of *trans*dichloroethylene, and 16.4 percent of trichloroethylene in the range −75° to −140° C; and commercial propane below −140° C. Propane is highly flammable, and every precaution must be taken to prevent it from mixing with liquid air or oxygen. A complete series of nonflammable liquids for cryostats is given by C. W. Kanolt [21] for temperatures down to −150° C.

A number of thermocouples can be calibrated at one time in a stirred liquid bath. Platinum-resistance or liquid-in-glass thermometers or thermocouples may be used as standards.

5. Methods of Interpolating Between Calibration Points

5.1. Platinum Versus Platinum-Rhodium Thermocouples

After a thermocouple has been calibrated at a number of points, the next requirement is a convenient means of obtaining corresponding values of emf and temperature at other points. A curve may be drawn or a table giving corresponding temperature and emf values may be prepared. The values in such a table may be obtained by computing an empirical equation or series of equations through the calibration points, by direct interpolation between points, or by drawing a difference curve from an arbitrary reference table which closely approximates the temperature-emf relationship of the thermocouple. The method to be selected for a particular calibration depends upon such factors as the type of thermocouple, number of calibration points, temperature range, accuracy required, and personal preference.

For the highest accuracy in the range 630.5° to 1063.0° C with platinum versus platinum-10-percent rhodium thermocouples, the method is that prescribed in the International Temperature Scale. An equation of the form $e=a+bt+ct^2$, where a, b, and c are constants determined by calibration at the freezing points of gold, silver, and antimony, is used. By calibrating the thermocouple also at the freezing point of zinc and using an equation of the form

$$e=a'+b't+c't^2+d't^3,$$

the temperature range can be extended down to 400° C without introducing an uncertainty [22] of more than 0.1° C in the range 630.5° to 1063.0° C. By calibrating the thermocouple at the freezing points of gold, antimony, and zinc and using an equation of the form $E=a''+b''t+c''t^2$, a calibration is obtained for the range 400° to 1,100° C, which agrees [22] with the International Temperature Scale to 0.5° C. The freezing point of copper may be used instead of the gold point, and the aluminum point used instead of the antimony point without introducing an additional uncertainty [22] of more than 0.1° C.

For temperatures outside the range 630.5° to 1063.0° C, the method of drawing a smooth curve through the temperature and emf values has just as much claim to accuracy as the method of passing empirical equations through the calibration points, because an empirical equation performs the same function as a curved ruler. For the temperature range 0° to 1,450° C, a curve for interpolation to 1° or 2° C requires calibration points not more than 200° C apart and a careful plot on a large sheet of paper, which is tedious to read. A reduction in the number of calibration points increases the uncertainty proportionately. If, however, we plot as ordinates the differences between the observed emf and that calculated from the first degree equation $e=10t$, and emf as abscissas, the difference at intermediate points may be taken from the curve and added to the quantity $10t$ to obtain values of emf corresponding to the appropriate temperature in which the uncertainty in the interpolated values is much less than in the case in which the emf is plotted directly against the temperature. If we go one step further and plot differences from an arbitrary reference table, the values of which closely represent the form of the temperature-emf relationship for the type of thermocouple in question, the maximum differences to be plotted will be only a few degrees. In this way, interpolated values are obtained in which the uncertainty in the interpolated values is not appreciably greater than that at the calibration points. The more accurately the values in the arbitrary reference table conform to the emf-temperature relationship of actual thermocouples, the fewer the number of calibration points required for a given accuracy.

Reference tables [23] for platinum versus platinum-rhodium thermocouples which are based on the temperature-emf relationships of a considerable number of representative thermocouples from various sources have recently been published. These tables represent the shape of the relations for both the 10- and 13-percent-rhodium thermocouples in the entire range 0° to 1,700° C. The difference curve for any thermocouple from the appropriate table is a smooth curve.

In the calibration of platinum versus platinum-10-percent-rhodium thermocouples to be used as working standards, the emf is observed at the freezing points of gold, silver, antimony, and zinc. The constants in the equation $E=a+bt+ct^2$ are computed from the observations at the gold, silver, and antimony points. The observed value at 419.5° C and the values calculated from the equation for the range 630.5° to 1063.0° C are used to construct a difference curve from the reference table mentioned previously. This difference curve is then extended graphically above 1063.0° C. When the highest accuracy is required at the lower temperatures, additional observations are taken at the freezing points of lead and tin and at the boiling point of water. Values taken from this difference curve when added algebraically to the values in the reference table yield the corresponding temperature-emf values at any temperature. A numerical example follows.

The observed values of emf at the calibration points are given in table 4, together with the values at 50° C intervals from 650° to 1,050° C computed from the equation,

$$E=270.73+8.15786t+0.00169396t^2.$$

Corresponding values of E and Δe are plotted in figure 4.

TABLE 4. *Data for construction of difference curve*

Temperature, t	Reference table emf NBS Circular 561, E_r	Observed emf standard thermocouple, E	Difference, $\Delta e=E_r-E$
° C	μv	μv	μv
0.0	0.0	0.0	0.0
419.5	3437.6	3443.6	−6.0
630.5	5536.8	5546.2	−9.4
650.0	5738.0	5747.6	−9.6
700.0	6259.7	6269.8	−10.1
750.0	6790.0	6800.5	−10.5
800.0	7328.9	7339.7	−10.8
850.0	7876.4	7887.3	−10.9
900.0	8432.4	8443.4	−11.0
950.0	8996.9	9008.0	−11.1
960.8	9120.0	9131.1	−11.1
1000.0	9570.1	9581.1	−11.0
1050.0	10151.8	10162.6	−10.8
1063.0	10304.4	10315.2	−10.8

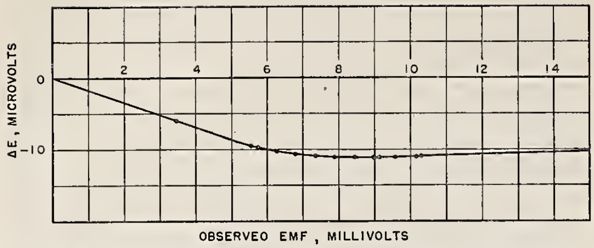

FIGURE 4. *Difference curve for a platinum versus platinum-10 percent-rhodium thermocouple, using the reference table in NBS Circular 561.*

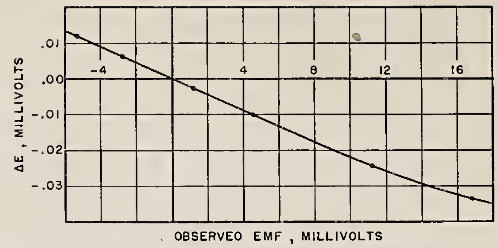

Figure 5. *Difference curve for a copper-constantan thermocouple, using the reference table in NBS Circular 561.*

For accurate extrapolation above the gold point, it is essential that the shape of the emf-temperature relationship given in the reference table conform closely to that of actual thermocouples so that the difference curves will be linear both above and below this point. If the difference curve has a large curvature or if there is an abrupt change in slope near the gold point, the extrapolation of the difference curve may involve considerable uncertainty. The difference curves of actual thermocouples both 10- and 13-percent-rhodium alloys from the reference tables given in NBS Circular 561 are in most cases smooth curves in the entire range 0° to 1,700° C and the difference curves can therefore be extrapolated with but little uncertainty. The extrapolated values for a number of thermocouples have been checked by means of actual comparison with an optical pyrometer, and in no case was the difference as great as 3° C at 1,500° C and in most cases it was not over 1° C. These differences are not much greater than the accidental errors in the comparisons.

Difference curves can be drawn from observations obtained in comparison calibrations as well as from observations at fixed points. Two points (accurate to ±0.3° C at about 600° and 1,100° C) are usually sufficient to determine the difference curve from the tables in NBS Circular 561 for either a 10- or a 13-percent-rhodium thermocouple, such that the resulting calibration is accurate to ±1° C at any point in the range 0° to 1,100° C and to ±3° C up to 1,450° C. (The reference junction temperature at which the emf difference is zero constitutes a third point.)

5.2. Copper-Constantan Thermocouples

The relationship between the temperature and emf of copper-constantan thermocouples has been very well established in the range −190° to +300° C. The temperature of the measuring junction of such a thermocouple can be very accurately determined in this range with a platinum-resistance thermometer in a stirred liquid bath. Consequently, the accuracy obtained with this type of thermocouple is, in general, limited by the stability of the wires above 200° C, and by the accuracy of the emf measurements and the homogeneity of the wire below 200° C. The stability of the larger sizes of wire is greater than that of the smaller wires under the same conditions.

Figure 5 shows a difference curve from the values in NBS Circular 561 for a typical copper-constantan thermocouple. Two points above and two below 0° C suitably spaced are usually sufficient to give an accuracy of 0.3° C.

Equations are used to good advantage with copper-constantan thermocouples for interpolating between calibration points, but it has not been demonstrated that the accuracy obtained with equations is any greater than that obtained by drawing difference curves from reference tables except when the differences are large. One convenient method of obtaining a calibration accurate to ±0.2° C in the range 0° to 100° C is to use an equation of the form $e=at+0.04t^2$ where a is a constant determined by calibration at 100° C, e the emf in microvolts, and t the temperature in degrees C. An equation of the form $e=at+bt^2+ct^3$, where a, b, and c are constants determined by calibration at three points (about 100°, 200°, and 300° C), will give interpolated values as accurately as the thermocouple can be relied upon to retain its calibration (about 0.2° C). The same type of equation with the constants determined at three points about equally spaced in the range 0° to −190° C, may be used in this range to give interpolated values almost as accurately as the emf can ordinarily be measured (about 2 μv). An equation of the form $e=at+bt^2$ will yield interpolated values in the range 0° to 100° C almost as accurately as the emf is determined at the calibration points, if the constants are determined by calibration at about 50° and 100° C. The same is true of this equation in the range 0° to −100° C if the constants are determined at −50° and −100° C.

5.3. Chromel-Alumel Thermocouples

Figure 6 shows a difference curve for a typical Chromel-Alumel thermocouple from the standard tables published in NBS Circular 561. The difference curve from these tables can be determined in the range 0° to 1,300° C (2,372° F) with an uncertainty not more than 1° C greater than at the calibration points by calibration at 500°, 800°, and 1,100° C (or at 1,000°, 1,600°, and

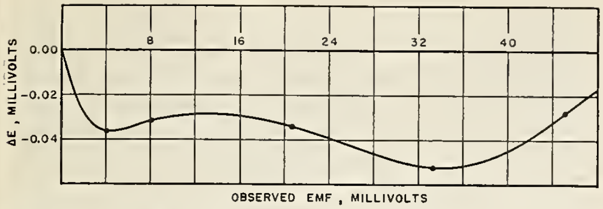

FIGURE 6. *Difference curve for a Chromel-Alumel thermocouple, using the reference table in NBS Circular 561.*

2,000° F). These tables represent the average temperature-emf relationship of Chromel-Alumel thermocouples now being manufactured.

Little success has been met in fitting equations to the calibration of Chromel-Alumel thermocouples in the range 0° to 300° C. An equation of the form $e=at+bt^2+ct^3$ may be in error by 1°C at 50° C if the constants are determined by calibration at about 100°, 200°, and 300° C. However, it will be accurate to about 0.5° C at 150° C and to about 0.2° C between 200° and 300° C. In the range 0° to −190° C, an equation through three points about equally spaced will give interpolated values in which the uncertainty is not more than 2 μv greater than at the calibration points.

5.4. Iron-Constantan Thermocouples

Until recently, several iron-constantan reference tables had been used by the suppliers of this material. One such table still being used by some Government agencies was published in a paper on "Reference Tables for Iron-Constantan and Copper-Constantan Thermocouples" [24].

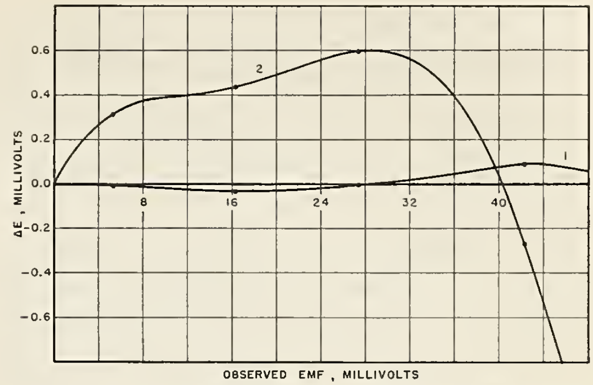

FIGURE 7. *Difference curves for an iron-constantan thermocouple, using (1) the reference table in NBS Circular 561 and (2) a straight line, e=56t.*

More recently, a reference table that closely represents the temperature-emf relationship of the iron-constantan thermocouples now being supplied by most producers of this type of thermocouple was developed. This table is not very different from that which had been in use by some producers since 1913 and consequently has been referred to as the "Modified 1913 Reference Tables for Iron-Constantan Thermocouples" [25].

Figure 7 shows a difference curve from the modified 1913 tables and from a straight line, $e=56t$ (where e is in microvolts and t is in degrees C) for a typical thermocouple. This latter method of drawing difference curves from a straight line may be used if the thermocouple does not match existing reference tables.

We have no data as to how closely the temperature-emf relationships of iron-constantan thermocouples may be fitted by equations.

6. Reference-Junction Corrections

It is not always possible to maintain the reference junctions (commonly called cold junctions) at a desired temperature during the calibration of a thermocouple, but if the temperature of the reference junctions is measured, it is possible to apply corrections to the observed emf, which will yield a calibration with the desired reference-junction temperature. If the emf of the thermocouple is measured with the reference junctions at temperature t, and a calibration is desired with these junctions at temperature t_0, the measured emf may be corrected for a reference-junction temperature of t_0 by adding to the observed value the emf which the thermocouple would give if the reference junctions were at t_0 and the measuring junction at t. For example, suppose the observed emf of a platinum versus platinum-10-percent-rhodium thermocouple with the measuring junction at 1,000° C and the reference junction at 25° C is 9.427 mv and the emf of the thermocouple with the measuring junction at 1,000° C and the reference junctions at 0° C is required. Since emf of the thermocouple when the reference junctions are at 0° C and the measuring junction at 25° C is 0.143 mv, the sum of these emf (9.427 and 0.143) gives the desired value.

The sign must be considered when applying reference-junction corrections. For example, suppose the observed emf of the thermocouple with the measuring junction at 1,000° C and the reference junctions at 0° C is 9.570 mv and the emf of the thermocouple with the measuring junction at 1,000° C and the reference junctions at 25° C is required. The emf of the thermocouple when the reference junctions are at 25° C and the measuring junction at 0° C is −0.143 mv, and when this is added to the observed emf the desired value 9.427 mv is obtained. Whether the reference-junction correction is positive or negative should not cause any confusion if it is remembered that the emf of the thermocouple is lowered by bringing the junction temperatures closer together and increased by making the difference greater.

In the calibration of thermocouples, the temperature-emf relationship is not always accurately determined in the range of reference-junction temperatures, in which case the average temperature-emf relationship of the type of thermocouple may be used. The average relations for the various types of thermocouples are given in table 5. The errors caused by using these average relations, instead of the actual relation, for a particular thermocouple are, in general, less than 1° C.

If the thermocouple is very short, so that the reference junctions are near the furnace and subject to considerable variations or uncertainty in temperature, it is usually more convenient to use extension leads to transfer the reference junctions to a region of more constant temperature than to measure the temperature of the reference junctions near the furnace. The extension leads of base-metal thermocouples are usually made of the same materials as the thermocouple wires, but in the case of platinum versus platinum-rhodium thermocouples, a copper lead is connected to the platinum-rhodium wire and a copper-nickel lead to the platinum wire. Leads for any of the thermocouples discussed here are available at all the pyrometer instrument manufacturers. Although the temperature-emf relationship of the copper versus copper-nickel lead wire is practically the same as that of platinum versus platinum-rhodium thermocouples, the individual lead wires are not identical thermoelectrically with the thermocouple wires to which they are attached and, therefore, the two junctions where the leads are attached to the thermocouple should be kept at nearly the same temperature. This is not as necessary in the case of base-metal thermocouples when each lead and the thermocouple wire to which it is attached are the same material.

TABLE 5. *Average temperature-emf relations for thermocouples for applying reference-junction corrections*

Temperature		Electromotive force			
		Platinum versus platinum-rhodium [a]	Chromel-Alumel	Iron-constantan	Copper-constantan
°C	*°F*	*mv*	*mv*	*mv*	*mv*
−20	−4	−0.103	−0.77	−1.00	−0.75
−15	+5	−.079	−.58	−0.75	−.57
−10	14	−.054	−.39	−.50	−.38
−5	23	−.027	−.19	−.25	−.19
0	32	.000	.00	.00	.00
+5	41	+.028	+.20	+.25	+.19
10	50	.056	.40	.50	.39
15	59	.084	.60	.76	.59
20	68	.113	.80	1.02	.79
25	77	.143	1.00	1.28	.99
30	86	.173	1.20	1.54	1.19
35	95	.204	1.40	1.80	1.40
40	104	.235	1.61	2.06	1.61
45	113	.266	1.81	2.32	1.82
50	122	.299	2.02	2.58	2.03

[a] The values in this column apply for either the 10- or 13-percent rhodium thermocouples. The difference between the average temperature-emf relationships in this range does not exceed 2 μv.

7. Testing of Thermocouple Materials

Thermocouples are ordinarily made up to yield a specified emf at one or more temperatures, and in order to select and match materials to do this, a convenient method of testing each element is required. One method of accomplishing this is to determine the thermal emf of the various materials against some stable and reproducible material. At low temperatures copper is sometimes used for this purpose, but platinum appears to be the most satisfactory because it can be used at any temperature up to its melting point, can be freed from all traces of impurities, and can be readily annealed in air. Two samples of platinum, both of which are spectrochemically pure, may differ slightly in thermal emf, but the same is true of any other metal. To avoid the ambiguity that might arise from this fact, the thermal emf of thermocouple materials tested at the National Bureau of Standards (since 1922) is referred to an arbitrary piece of platinum designated as standard Pt 27. This standard is spectrochemically pure, has been thoroughly annealed, and although it may not be the purest platinum that has been prepared, serves as a satisfactory standard to which the thermal emf of other materials may be referred. However, there is nothing to prevent any other laboratory from setting up a laboratory standard for their own use, but in order that the various laboratories and manufacturers may specify and express values of thermal emf on a common basis, a common and ultimate standard is necessary.

Platinum is used as a working standard for testing thermocouple materials in some laboratories, but it is generally more convenient to use a working standard of the same material as that being tested. In any case, the thermal emf of a material against the standard Pt 27 is the algebraic sum of the emf of the material against the working standard, and the emf of the working standard against the standard Pt 27 (the law of intermediate metals). When platinum is used as a working standard in testing some other material, the thermal emf measured is great. To obtain the thermal emf of the material against the standard Pt 27, the relatively small emf of the platinum working standard against the standard Pt 27 is added to the large measured emf. When the working standard is of the same kind of material as that being tested, the thermal emf measured is small. To obtain the thermal emf of the material against the standard Pt 27 in this case, the relatively large emf of the working standard against the standard Pt 27 is added to the small measured emf.

Except in the case of constantan, two samples of a similar material which will develop more than 0.5 μv/°C against one another are exceptional. In most cases, the value is less than 0.2 μv/°C. Even in the case of constantan, the thermal emf between 2 extreme samples does not exceed 3 μv/°C. Therefore, in determining the difference in thermal emf between two samples of a similar material, it is not necessary to measure the temperature accurately.

The average thermal emf per degree C of platinum against other thermocouple materials is given in table 6. It is seen that in measuring the thermal emf of these materials directly against platinum working standards, it is necessary to measure an emf which changes by a large amount for a small change in temperature. An accurate measurement of the emf corresponding to a given temperature, therefore, requires an accurate measurement of the temperature of the junctions. The necessity for this accurate measurement of temperature, however, is avoided when the measurements are made by using a working standard of material similar to that being tested, since in this case the emf developed is small and changes very little even for large changes in temperature. In the latter method, the accurate measurement of temperature is not entirely avoided but merely shifted to the laboratory that determines the thermal emf of the working standards against the standard Pt 27.

The small thermal emf of a platinum working standard against the standard Pt 27 at any temperature can be determined as accurately as the emf can be measured. These standards are subject to change during use but, if properly used and occasionally checked, can be relied upon to about 2 μv at 1,000° C. The thermal emf of working standards of other materials is determined and certified at the National Bureau of Standards to the equivalent of ±1° C at high temperatures.

In any event the testing of a thermocouple material is essentially the determination of the emf of a thermocouple in which the material being tested is one element and a working standard the other. Some of the precautions that must be observed to obtain accurate results are given in the following sections.

TABLE 6. *Average thermal [a] emf per degree C of platinum against other thermocouple materials.*

Material	Temperature	Average change in thermal emf with temperature
	°C	μv/°C
Platinum-10-percent rhodium	1,000	11.6
Platinum-13-percent rhodium	1,000	13.2
Chromel	900	31.5
Alumel	900	8.7
Iron	600	11.6
Constantan	600	46.8
Constantan	100	37.4
Copper	100	9.4

[a] Complete tables giving the average thermal emf of platinum-10-percent rhodium, and platinum-13-percent rhodium against platinum are given in NBS Circular 561. The average thermal emf of Chromel and of Alumel against platinum are given in Research Paper 767; of copper and constantan against platinum in RP1080; of iron and constantan against platinum in RP2415.

7.1. Platinum

The thermal emf of the thermocouple platinum against the standard Pt 27 is usually less than 20 μv at 1,200° C and in testing one sample of platinum against another it is not necessary to measure the temperature of the hot junction to closer than 50° C to obtain a comparison accurate to 1 μv. The reference-junction temperature need not be accurately controlled. The platinum standard (i. e., the wire previously compared with the standard Pt 27) is welded to the wire being tested to form a thermocouple and the emf measured at one or more temperatures by any of the methods described for calibrating platinum versus platinum-rhodium thermocouples. The wires should be carefully insulated and protected. Measurements at two temperatures, about 600° and 1,200° C, are sufficient to give the emf at any temperature as the emf is small and practically proportional to the temperature.

In many laboratories the platinum standard and the platinum element of the thermocouple used to measure the temperature are one and the same. The sample or wire being tested is then welded to the junction of the thermocouple and the emf of the thermocouple and that between the two platinum wires are measured simultaneously with two potentiometers or alternately with one instrument. Simultaneous readings of these electromotive forces should not be made with a millivoltmeter or with a current flowing in either circuit because one wire is common to both circuits and in this case the potential difference measured by one instrument is influenced by the current flowing in the other circuit. However, this objection is not encountered in the method described above in which the platinum standard is not the same wire as the platinum of the thermocouple.

7.2. Platinum-Rhodium Alloy

The testing of platinum-rhodium thermocouple wire directly against platinum is exactly the same as the calibration of platinum versus platinum-rhodium thermocouples. Platinum against platinum-10-percent rhodium gives 11.6 μv/°C and platinum against platinum-13-percent rhodium gives 13.2 μv/°C at 1,000° C. Therefore, in order to determine the thermal emf of a sample of platinum-rhodium against platinum to ± 20 μv, it is necessary to measure the temperature to $\pm 1.5°$ C. Such an accuracy in temperature measurements is obtained only with a very homogeneous and accurately calibrated thermocouple in a uniformly heated furnace, but if the emf of one sample of wire is known with this accuracy, it may be used to determine the emf of other samples without the necessity of accurately measuring the temperature. For example, the thermal emf per degree of any sample of platinum-10-percent rhodium against any other sample rarely exceeds 0.05 μv/°C (50 μv at 1,000° C). Therefore, if the thermal emf of one sample against platinum is known to ± 20 μv at 1,000° C, the emf of other samples against the same platinum can be determined to about the same accuracy by comparing the samples of platinum-rhodium and measuring the temperature of the hot junction to 10° or 20° C. The same applies for platinum-13-percent rhodium.

The working standard used to determine the thermal emf of the platinum-rhodium may be a sample of platinum, of platinum-rhodium, or either element of the thermocouple used in measuring the temperature. Platinum-10-percent rhodium against platinum-13-percent rhodium gives about 1.6 μv/°C at 1,000° C so that if the thermal emf of one of these materials against platinum is known to ± 20 μv at 1,000° C, the thermal emf of the other against the same platinum can be determined to ± 30 μv by comparing the two and measuring the temperature to $\pm 6°$ C.

A number of wires can be welded together and tested by any of these methods.

7.3. Base-Metal Thermocouple Materials

a. At High Temperatures

In testing base-metal thermocouple materials (Alumel, Chromel, constantan, copper, and iron) the procedure is very much the same as in calibrating base-metal thermocouples. Although such thermal-emf measurements are ultimately referred to platinum, it is not necessary to measure each sample directly against platinum. When the measurements are made against platinum (and this must frequently be done), the platinum wire should be sealed through the end of a glazed porcelain protection tube with Pyrex glass, leaving about 1 cm of the wire exposed for welding to the base-metal wire or wires. The largest uncertainty in the measurements arises from the uncertainty in the determination of the temperature of the hot junction. The junction of a standard platinum versus platinum-rhodium thermocouple may be inserted into a hole drilled in the junction formed by welding the material to platinum. This brings the junctions to the same temperature.

In the use of platinum or platinum-rhodium for testing thermocouple materials, the wires are used a large number of times before checking or scrapping. Base-metal thermocouple wires used for testing similar materials should not be used more than once if the highest accuracy is required, because there is a slight change in these materials when heated to a high temperature and if they are used repeatedly, the wires become inhomogeneous. The procedure then is to select a coil of wire and test it for homogeneity by taking several samples from different parts of the coil, welding them all together, and measuring the emf between the various samples. If the coil is sufficiently homogeneous as found from such tests, one or more samples may be taken from it and the thermal emf determined as accurately as necessary by comparison with a standard, the emf of which against the standard Pt 27 is known. The average value for the thermal emf of the few selected samples from the coil against the standard Pt 27 will apply for the remainder of the coil with sufficient accuracy for most purposes. Any sample from this coil may then be used as a working standard for testing similar materials. The accuracy with which the temperature must be measured depends upon the difference between the standard and the material being tested. In case of some materials that have been well standardized, the differences are small enough that an accuracy of 50° C is sufficient. Seldom, if ever, should it be necessary to measure the temperature closer than 10° C.

b. At Low Temperatures

Annealed electrolytic copper is very uniform in its thermoelectric properties and is often used as a standard for thermoelectric testing at temperatures below 300° C. The thermal emf of other materials against either copper or platinum may be determined very accurately by using a stirred liquid bath or fixed points. The steam point is an excellent one for this purpose.

Table 7 gives the thermal emf of annealed electrolytic copper against NBS standard Pt 27 and may be used to convert values of the thermal emf of any material against one of these standard materials to values of emf of the same material against the other standard material.

TABLE 7. *Thermal emf of annealed electrolytic copper against NBS platinum standard Pt 27*

Temperature	Electromotive force	Temperature	Electromotive force
° C	μv	° C	μv
−200	−194	100	766
−150	−354	150	1,265
−100	−367	200	1,831
−50	−242	250	2,459
0	0	300	3,145
+50	+340	350	3,885

7.4. Reference-Junction Corrections

It is not convenient for everyone to obtain the same reference-junction temperature in determining the emf of the various thermocouple materials against platinum and, therefore, corrections must be applied to arrive at values for a common reference-junction temperature. The method of applying these corrections is the same as that discussed under the testing of thermocouples. The average temperature-emf relationships for the various thermocouple materials against platinum are given in table 8 and may be used for making reference-junction corrections.

In comparing two samples of a similar thermocouple material at high temperatures, it is not necessary to measure or control accurately the temperature of the reference junctions. The emf developed by two samples of platinum-rhodium, even the 10- against the 13- percent-rhodium alloy, is practically independent of the temperature of the reference junctions between −20° and +50° C. In all other cases, with the possible exception of iron, the emf may be taken as proportional to the difference between the temperatures of the two junctions, and when the emf is small, the corrections for the temperature changes of the reference junctions are negligible. In comparing two samples of iron, the emf developed is changed more by changing the temperature of the reference junctions than by changing that of the hot junction by the same amount, for example it was observed (in one case) that the emf (320 μv) developed by two samples of iron when one junction was at 600° C and the other at 25° C changed by 0.1 μv for each degree change in the temperature of the hot junction and 1.4 μv for each degree change in the temperature of the reference junctions.

Table 8. *Average temperature-emf relationships of various thermocouple materials against platinum for applying reference-junction corrections*

Temperature		Electromotive force					
		Platinum versus platinum-rhodium [a]	Chromel versus platinum	Alumel versus platinum	Constantan versus platinum	Iron versus platinum	Copper versus platinum
° *C*	° *F*	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*
−20	−4	−0.103	−0.50	0.27	0.64	−0.36	−0.109
−15	+5	−.079	−.38	.20	.48	−.27	−.084
−10	14	−.054	−.25	.14	.32	−.18	−.057
−5	23	−.027	−.13	.07	.16	−.09	−.029
0	32	.000	.00	.00	.00	.00	.000
+5	41	+.028	+.13	−.07	−.16	+.09	+.030
10	50	.056	.26	−.14	−.33	.18	.060
15	59	.084	.40	−.20	−.49	.27	.091
20	68	.113	.52	−.28	−.66	.36	.124
25	77	.143	.66	−.34	−.83	.45	.158
30	86	.173	.79	−.41	−1.00	.54	.193
35	95	.204	.93	−.47	−1.17	.63	.229
40	104	.235	1.07	−.54	−1.34	.72	.265
45	113	.266	1.21	−.60	−1.51	.81	.302
50	122	.299	1.35	−.67	−1.69	.90	.340

[a] These values apply for either 10- or 13-percent rhodium.

8. Accuracies Obtainable

The accuracies obtained in calibrating the various types of thermocouples by different methods and the uncertainty in the interpolated values by various methods are given in table 9.

These accuracies may be obtained with homogeneous thermocouples when reasonable care is exercised in the work. More or less accurate results can be obtained by the same methods. In the case of Chromel-Alumel and iron-constantan thermocouples at low temperatures, the accuracy given in table 9 is limited by the uncertainty in interpolated values. However, this uncertainty can be greatly reduced by observing the emf of the thermocouples at more points. The accuracy obtained with copper-constantan thermocouples at low temperatures is usually limited by the emf measurements and in such cases the accuracy may be improved by employing a number of thermocouples in series (multiple-junction couples). When it is desired to test a thermocouple and leads or thermocouple, leads, and indicator as a unit by any of the methods described in the preceding sections, no additional difficulties are encountered.

The following services are provided by the National Bureau of Standards for fees covering the cost.

(1) Thermocouples are calibrated and certified as accurately as the conditions of use and the homogeneity and stability of the wires justify. The accuracies given in table 9 have been found to meet most needs.

(2) Indicators used with thermocouples are calibrated separately or in combination with a particular thermocouple.

(3) The thermal electromotive forces of thermocouple materials against the standard Pt 27 are determined and the results certified to the limits justified by the material.

(4) Standard Samples of metals are distributed, each with a certificate giving the value of the freezing point. The freezing-point metals being distributed at present are tin, lead, zinc, aluminum, and copper.

TABLE 9. *Summary of methods and accuracies obtainable in calibrating thermocouples*

Type of thermocouple	Methods of calibration	Temperature range	Calibration points	Accuracy at observed points	Method of interpolating	Uncertainty in interpolated values
		° C		° C		° C
Platinum versus platinum-10-percent-rhodium.	International Temperature Scale (fixed points).	630.5 to 1,063.0	Freezing point of Sb, Ag, and Au	0.2	Equation: $E=a+bt+ct^2$	0.3
Platinum versus platinum-rhodium.[a]	Fixed points	0 to 1,450	Freezing point of Zn, Sb, Ag, and Au.	.2	Difference curve from reference table	0.5 to 1,100 and 2 at 1,450.
	NBS Standard Samples, fixed points	0 to 1,450	Freezing point of Sn, Zn, Al, and Cu.	.2	do	.5 to 1,100 and 2 at 1,450.
	Comparison with standard thermocouple.	0 to 1,450	About every 100° C	.3	do	.5 to 1,100 and 2 at 1,450.
	do	0 to 1,450	About 600° and 1,100° C (or more points).	.3	do	1 to 1,100 and 3 at 1,450.
Chromel-Alumel	Comparison with standard thermocouple.[a]	0 to 1,100	About every 100° C	.5	Linear	1
	do	0 to 1,100	About 500°, 800°, and 1,100° C (or more points).	.5	Difference curve from reference table	2
	Comparison with standard resistance thermometer [b] or at fixed points.	0 to 350	About every 100° C	.1	do	0.5
	Comparison with standard resistance thermometer.[b]	0 to −190	About every 50° C	.1	do	.5
Iron-constantan	Comparison with standard thermocouple.[a]	0 to 760	About every 100° C	.5	Linear	1
	do	0 to 760	About 100°, 300°, 500°, and 750° C	.5	Difference curve from reference table	1
	Comparison with standard resistance thermometer [b] or at fixed points.	0 to 350	About every 100° C	.1	do	0.5
	Comparison with standard resistance thermometer.[b]	0 to −190	About every 60° C	.1	do	.5
Copper-constantan	Comparison with standard resistance thermometer [b] or at fixed points.	0 to 300	About every 100° C	.1	Equation: $e=at+bt^2+ct^3$ or difference curve from reference table.	.2
	Comparison with standard resistance thermometer.[b]	0 to 100	About 50° and 100° C	.05	Equation: $e=at+bt^2$ or difference curve from reference table.	.1
	Fixed points	0 to 100	Boiling point of water	.05	Equation: $e=at+0.04t^2$	.2
	Comparison with standard resistance thermometer.[b]	0 to −190	About every 60° C	.1	Equation: $e=at+bt^2+ct^3$ or difference curve from reference table.	.2
	Fixed points	0 to −190	Sublimation point of CO_2 and boiling point of O_2.	.1	Difference curve from reference table	.3

[a] Either 10- or 13-percent rhodium. [b] In stirred liquid bath.

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