U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP768

Part of Journal of Research of the National Bureau of Standards, Volume 14, March 1935

METHODS OF TESTING THERMOCOUPLES AND THERMOCOUPLE MATERIALS

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ABSTRACT

This paper describes various methods used for testing thermocouples and thermocouple materials, and the precautions which must be observed in order to attain various degrees of accuracy. In particular, it describes in detail the methods developed and used at the National Bureau of Standards. It also provides some guidance to the reader in the selection of the method which is best adapted to a given set of conditions.

CONTENTS

I. 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 these temperatures 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 large portion of such measurements are 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 paper 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 we have given 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 paper were devised primarily for calibrating couples in the usual temperature ranges, but unless otherwise indicated they may be used up to the maximum temperatures at which the various types of couples 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-rhodium	0 to 1,450	0 to 2,650	1,700	3,100
Chromel-alumel	−200 to 1,200	−300 to 2,200	1,350	2,450
Iron-constantan	−200 to 750	−300 to 1,400	1,000	1,800
Copper-constantan	−200 to 300	−300 to 570	600	1,100

II. GENERAL CONSIDERATIONS

1. TEMPERATURE SCALE

The object in the calibration of any thermocouple is to determine an emf-temperature relation in which the temperature is expressed on a definite and reproducible scale. The International Temperature Scale,[1] adopted in 1927 by thirty-one nations, is now in practically universal use. The methods of realizing this scale are described in detail in the reference cited. The instruments, calibration points, and interpolation equations to be used in the various ranges of the scale are summarized in table 2.

2. GENERAL METHODS

In order to calibrate thermocouples to yield temperatures on the International Scale, it is apparent from the definition that they must be so calibrated that their indications agree with those of the platinum-resistance thermometer in the range −190 to 660° C, the platinum-10 percent rhodium thermocouple in the range 660 to 1,063° C, and the optical pyrometer above 1,063° C. The most direct procedure would therefore be to compare the couples directly with these primary instruments in the appropriate temperature ranges. However, to follow such a procedure in the calibration of every couple requires more time and apparatus than is justifiable or necessary since, 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 Scale, these standards may be used subsequently to calibrate other couples. This procedure is used far more than any other because the comparison of the indications of two couples is usually simpler than the comparison of two different types of instruments.

The temperature-emf relation of a homogeneous [2] 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 couple, temperature range, accuracy required, size of wires, apparatus available, and personal preference.

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[1] George K. Burgess. BS J. Research **1**, 635 (1928) RP22.

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

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

Temperature ranges		Instruments	Calibration points (values for pressure of one standard atmosphere)			Interpolation equations [a]
°C	°F		*Fixed point*	°C	°F	
-190 to 0	-310 to 32	Platinum resistance thermometer	Boiling point of oxygen	-182.97	-297.35	$R_t=R_o[1+At+Bt^2+C(t-100)t^3]$
			Melting point of ice	0.000	32.000	
			Boiling point of water	100.000	212.000	
			Boiling point of sulphur	444.60	832.28	
0 to 660	32 to 1,220	Platinum resistance thermometer	Melting point of ice	0.000	32.000	$R_t=R_o(1+At+Bt^2)$
			Boiling point of water	100.000	212.000	
			Boiling point of sulphur	444.60	832.28	
660 to 1,063	1,220 to 1,945	Platinum to platinum-10 percent rhodium thermocouple.	Freezing point of antimony	[b] (630.5)	[b] (1,166.9)	$e=a+bt+ct^2$
			Freezing point of silver	960.5	1,760.9	
			Freezing point of gold	1,063.0	1,945.4	
1,063 and above	1,945 and above	Optical pyrometer	Freezing point of gold	1,063.0	1,945.4	$\log_e\frac{J_2}{J_1}=\frac{C_2}{\lambda}\left(\frac{1}{1,336}-\frac{1}{t+273}\right)$

[a] R_t is the resistance at $t°$ C, R_o, the resistance at 0° C; A and B are constants determined by calibration at the boiling points of water and sulphur, 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_2 is the monochromatic visible radiation at wave length λ cm emitted by a black body at temperature $t°$ C, J_1 the radiation of the same wave length emitted by a black body at the gold point, and C_2 is 1.432 cm degrees.

[b] The value for the freezing point of the particular lot of antimony used is determined by means of the platinum-resistance thermometer.

Thermocouple calibrations are required with various degrees of accuracy ranging from 0.01 to 10 or 20° 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 couples directly with a standard platinum-resistance thermometer in a stirred liquid bath. In the range 300 to 660° C (and below if a platinum-resistance thermometer or stirred liquid bath is not available) couples are most accurately calibrated at the freezing or boiling points of pure substances. Between 660 and 1,063° C, the 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 couples are most accurately calibrated in this range by direct comparison with the standard couple calibrated as specified. Other couples may be calibrated just as accurately at the fixed points as the 10-percent rhodium couple, but interpolated values at intermediate points may depart slightly from the International Scale. Above 1,063° C, the most basic calibrations are made by observing the emf when one junction of the couple 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 couple above 1,063° C are given under melting points and under methods of interpolation.

Although the 10-percent rhodium couple serves to define the scale only in the range 660 to 1,063° C, this type of couple 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 couples 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 660 to 1,063° C any type of couple 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 Scale as the platinum-10 percent rhodium couple. In fact, at the lower temperatures certain types of base-metal couples are definitely better adapted for precise measurements.

The calibration of couples 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.

3. HOMOGENEITY

The magnitude of the emf developed by a couple depends upon the composition of the wires in the region of temperature gradients. The emf developed by an inhomogeneous couple is characteristic of the temperature of the hot 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 couple, the homogeneity of the wires must be established.

Thermocouple wire now being produced by the wire manufacturers in this country is sufficiently homogeneous in chemical composition for most purposes. Occasionally inhomogeneity in a couple 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.

While 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. 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 source of heat, such as 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 uniformily 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-rhodium couple 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 couple 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

[3] W. P. White, Phys. Rev. **23**, 449 (1906); **31**, 135 (1910). J. Am. Chem. Soc. **36**, 2292 (1914). Foote, Fairchild, and Harrison. Tech. Pap. BS **14** (1920–21) T170.

along an inhomogeneous wire depends upon the temperature distribution, it is evident that corrections for inhomogeneity are impracticable if not impossible.

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-rhodium thermocouple wire as sold by some manufacturers is already annealed, it has become regular practice in many laboratories to anneal or "stabilize" all platinum-rhodium couples, 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 1,350° C.

There is some question as to the optimum temperature or length of time at which such couples should be annealed to produce the most constant characteristics in later use. 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 couple 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. During the past ten years the practice at the National Bureau of Standards was to anneal all platinum-rhodium couples electrically for 6 hours at 1,500° C before calibration. The emf of a number of new thermocouples was determined both after annealing for 5 minutes and for 6 hours 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 hours 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-rhodium couples for 1 hour at 1,450° C.

[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 rare-metal couples, 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. Such a tube should preferably be made of metal, but one made by simply rolling up a sheet of heavy paper will do very well.

It has not been demonstrated conclusively that 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.

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] or Wenner,[7] 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 5 μv will suffice, slide-wire potentiometers of the laboratory type are sufficiently accurate. Portable potentiometers accurate within 40 to 100 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 couple.

Indicators of the galvanometric type are seldom used in making calibrations. Galvanometer indicators should be graduated for a specified external resistance of couple and leads, and the resistance of the indicator itself should be high in order to minimize the effects of changes in the resistance of the couple and leads. Detailed discussion is given and special instruments used in measuring the emf of thermocouples are described in Bureau of Standards Technologic Paper T170.

III. 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-10-percent rhodium thermocouples to realize the International Temperature Scale in the range 660 to 1,063° C. From such a calibration, together with methods of extrapolation described later, the temperature-emf relation of this type of couple may be determined with an accuracy of about 2° C at 1,500° C. Calibration at a few other selected points below 660° C will yield a working standard which 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 (1,773° 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 one standard atmosphere (760 mm of Hg) and the variations of the boiling temperatures with pressure are given in the last column.

[5] H. Diesselhorst. Z. Instrumentenk, **28**, 1 (1908).
[6] W. P. White. Z. Instrumentenk, **27**, 210 (1907).
[7] L. Behr. Rev. Sci. Instruments, **3**, 108 (1932).

TABLE 3.—*Fixed points available for calibrating thermocouples*

Thermometric fixed point	Values on the International Temperature Scale				Temperature of equilibrium (t_p) in °C as a function of the pressure (p) between 680 and 780 mm of Hg
	Assigned (Primary points)		Determined (Secondary points)		
	°C	°F	°C	°F	
Boiling point of oxygen	−182.97	−297.35			$t_p=t_{760}+0.0126(p-760)-0.0000065(p-760)^2$
Sublimation point of carbon dioxide.			−78.5	−109.3	$t_p=t_{760}+0.1443(t_p+273.2)\log\left(\frac{p}{760}\right)$
Freezing point of mercury			−38.87	−37.97	
Melting point of ice	0.000	32.000			
Boiling point of water	100.000	212.000			$t_p=t_{760}+0.0367(p-760)-0.000023(p-760)^2$
Boiling point of naphthalene			217.96	424.33	$t_p=t_{760}+0.208(t_p+273.2)\log\left(\frac{p}{760}\right)$
Freezing point of tin [1]			231.9	449.4	
Boiling point of benzophenone			305.9	582.6	$t_p=t_{760}+0.194(t_p+273.2)\log\left(\frac{p}{760}\right)$
Freezing point of cadmium			320.9	609.6	
Freezing point of lead [1]			327.3_5	621.2_3	
Freezing point of zinc [1]			419.4_8	787.0_6	
Boiling point of sulphur	444.60	832.28			$t_p=t_{760}+0.0909(p-760)-0.000048(p-760)^2$
Freezing point of antimony			630.5	1,166.9	
Freezing point of aluminum [1]			660.1_5	$1,220.2_7$	
Freezing point of Cu-Ag eutectic alloy.[2]			778.8	1,433.8	
Freezing point of silver	960.5	1,760.9			
Freezing point of gold	1,063.0	1,945.4			
Freezing point of copper [1]			1,083.0	1,981.4	
Melting point of palladium			1,555	2,831	
Melting point of platinum			1,773	3,223	

[1] 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. The values given in this table for these materials apply for the standard samples that are being issued as of the present date.
[2] 28.1 percent copper and 71.9 percent silver by weight.

In selecting the points at which to calibrate a couple, one sometimes has a choice between a boiling or a freezing point,[8] as for example, between the boiling point of sulphur (444.60° C) and the freezing point of zinc (419.48° C), between the boiling point of naphthalene (217.96° 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 (327.35° C). In determining the emf of a couple 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.

[8] In this paper "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 couple 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 couple in the freezing material, and "melting point" is used for the same point when it is realized experimentally by determining the emf of a couple 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.

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 couple is protected from contamination; (2) the couple 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. For temperatures above 600° 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-rhodium thermocouples insulated by two-hole insulating tubes 50 cm long and 4 mm in diameter with 1 mm holes. For temperatures below 600° 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-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 widemouth thermos bottle 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 lead wires should be insulated from the thermocouple wires, except where they make contact through 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 cold-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 Acheson graphite has the greatest utility and is used almost exclusively at the National Bureau of Standards for this work. It is very pure, can be machined into any desired shape, and can be used in contact with any of the freezing-point materials in table 3 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. Therefore, copper and silver must be protected from oxygen, and it is advisable also to protect aluminum and antimony from oxygen. This is 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

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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.

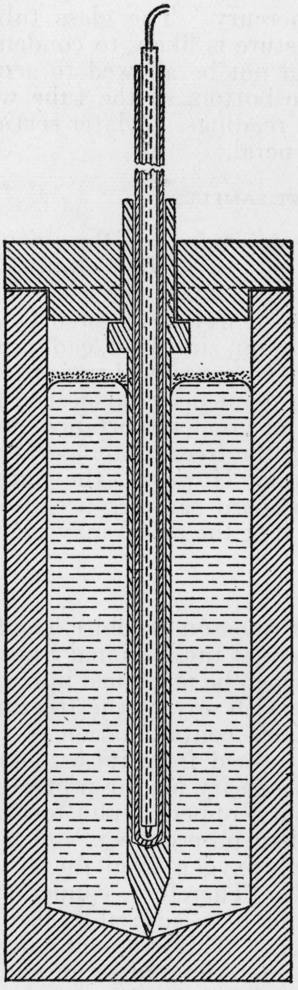

FIGURE 1.—*Arrangement for protecting a thermocouple in molten aluminum.*

(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 an alundum tube and imbedded in alundum cement. The space between the heating element and the outside wall is filled with silocel powder. Acheson-graphite diaphragms are placed above the crucible in order to minimize 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 couple, 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 stirring the metal with the thermocouple protection tube just before freezing begins. The emf of the couple 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.

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

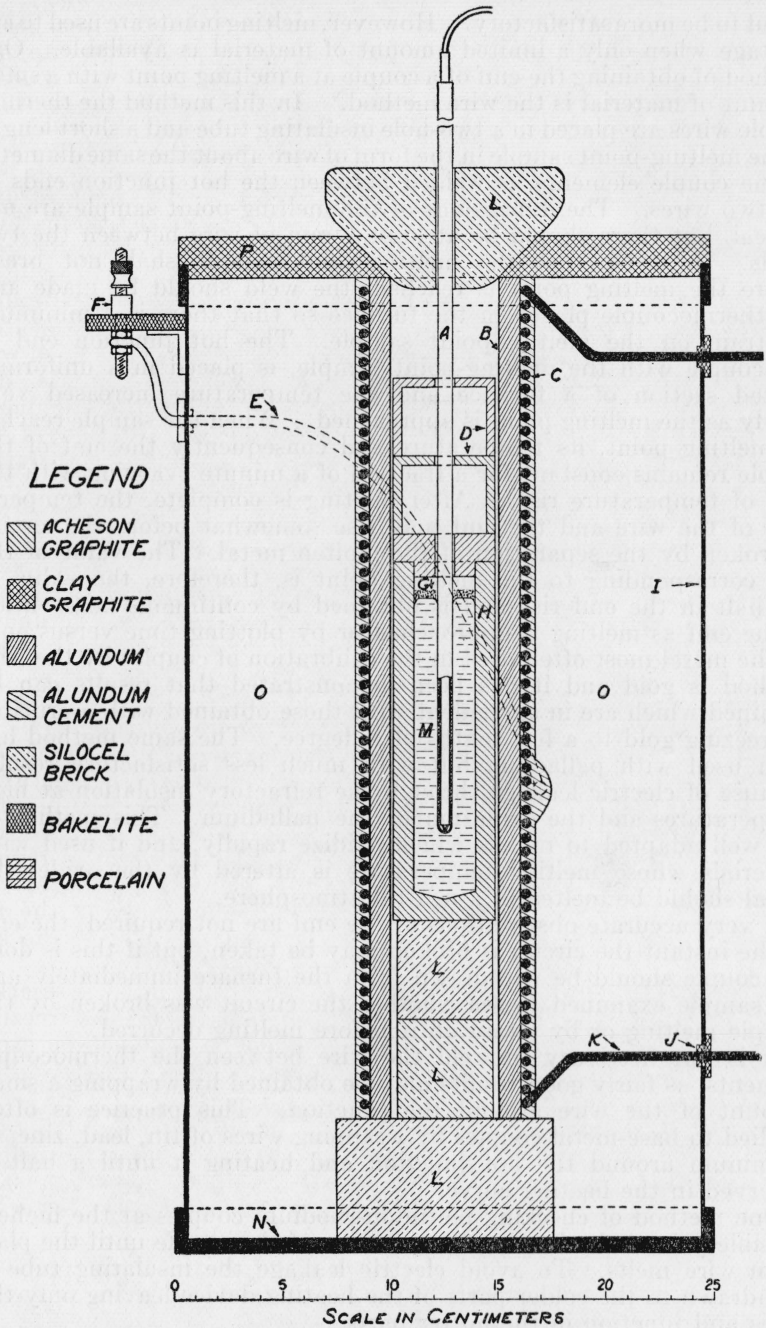

FIGURE 2.—*Furnace used in calibrating couples at freezing points of metal.*

A, porcelain protecting tube; B, alundum 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; M, freezing-point metal; N, cast-iron base; O, silocel-powder insulation.

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 couple at a melting point with a small amount of material is the wire method.[9] 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 couple elements, is welded between the hot 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 hot junction end of the couple 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 couple remains 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 couples 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 which 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 couple 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 couples by wrapping wires of tin, lead, zinc, or aluminum around the hot junction and heating it until a halt is observed in the heating curve.

One method of checking platinum-rhodium couples at the highest possible point is by heating the junction of the couple 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.

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[9] Hoffmann and Meissner Ann. Phys. **60**, 201 (1919). Fr. Hoffmann. Z. Phys. **27**, 285 (1924). Fairchild, Hoover, and Peters. BS J. Research **2**, 931. (1929) RP65.

3. BOILING POINTS

Boiling points play an important part in the definition of the International Temperature Scale, since 3 of the 4 points upon which the scale between −190 and 660° C is based, are the boiling points of oxygen, water, and sulphur. 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) 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 [10] give a detailed description of a hypsometer used in precision measurements. If the proper conditions are attained, the observed emf of the couple 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 couple. The couple for some distance from the junction must be shielded from radiation from hotter and colder surfaces. The relation between the temperature (t_p) in ° C and the pressure (p) for the range 680 to 780 mm of Hg is given by

$$t_p=100.000+0.0367\ (p-760)-0.000023\ (p-760)^2$$

The steam point as realized by utilizing the condensing vapor in a hypsometer is certainly accurate 0.01° C. An accuracy of about 1° C can be obtained by merely immersing a couple in boiling water.

(b) SULPHUR, BENZOPHENONE, AND NAPHTHALENE POINTS

These points 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 sulphur point are given in the International Temperature Scale.[11] Detailed description of the apparatus and precautions to be observed for the sulphur boiling point are given by Mueller and Burgess.[12] The procedure and apparatus for realizing the boiling points of naphthalene and benzophenone are the same as those for the boiling point of sulphur. Detailed information regarding these points is given by Waidner and Burgess [13] and by Finck and Wilhelm.[14]

(c) OXYGEN POINT

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

[10] J. Opt. Soc. Am. and Rev. Sci. Inst. **6**, 958 (1922).
[11] BS J. Research **1**, 635 (1928) RP22.
[12] BS Sci. Pap. **15**, 163 (1919–20) S339.
[13] Bul. BS **7**, 1 (1911) S143.
[14] J. Am. Chem. Soc. **47**, 1577 (1925).

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. When the thermometer tube is immersed in the bath, part of the oxygen liquefies. The temperature (t_p) in °C of the bath is related to the pressure (p) in the thermometer by $t_p = -182.97 + 0.0126\ (p-760) - 0.0000065\ (p-760)^2$ in the range 680 to 780 mm of Hg. This requires that the temperature of the bath be kept within the limits −183.9 to −182.7° 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.[15] The sublimation point of carbon dioxide may also be utilized by immersing the couple 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.

IV. 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 couple to the same temperature as the actuating element of the standard, such as the hot 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 by a liquid-in-glass thermometer. The method of bringing the junction of the couple to the same temperature as that of the actuating element of the standard depends upon the type of couple, type of standard, and the method of heating.

1. PLATINUM-RHODIUM THERMOCOUPLES

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 couples decreases rapidly at low temperatures, becoming zero at about −138° C (−216° F). These couples are usually calibrated above 300° C by comparison with standard thermocouples in electrically heated furnaces. The standard couple may be either a 10- or 13-percent rhodium couple that has been calibrated at fixed points or by comparison with other couples so calibrated.

[15] BS J. Research **10**, 381 (1933) RP538.

The method employed at the National Bureau of Standards for the comparison of two such couples permits simultaneous reading of the emf of each couple without waiting for the furnace to come to a constant temperature. In order to insure equality of temperature between the measuring junctions of the couples, 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 5μv with platinum-rhodium couples, if the periods of the galvanometers are approximately the same.

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

In order to calibrate a couple 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 the National Bureau of Standards for the routine testing of couples consists of a nickel(80)-chromium(20) tube clamped between two water-cooled terminals. The tube, which is 1$\frac{3}{16}$ inch inside diameter, 1$\frac{5}{16}$ inches outside diameter, and 24 inches 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 minimize lag no thermal insulation is used between the heating tube and the radiation shield. The middle part of this furnace for about 18 inches 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 5 minutes 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 cold junctions are maintained at 0° C.

The above method and apparatus were devised primarily for the rapid testing of couples, 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 couples 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 couples may be heated to a uniform temperature, is the flexibility of control. Electric tube furnaces 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 rheostat 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 inch in diameter and 18 inches long. Even though the furnace tube is kept fairly clean, it is advisable to protect platinum-rhodium couples 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 couple read alternately on one instrument.

When the couples 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 couples without removing them from the protection tubes, then the junctions of the couple 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 couples are completely enclosed in protection tubes. However, extension leads may be used with the couple 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 couples 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 couples 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 couples 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 couple 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.

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 couples with the exception, in some cases, of the methods of bringing the junctions of the standard and the couple being tested to the same temperature and the methods of protecting platinum-rhodium standards from contamination. One arrangement of bringing the junction of a platinum-rhodium standard to the same temperature as that of a large base-metal couple for accurate calibration is to insert the junction of the standard into a small hole (about 1.5 mm in diameter) drilled in the hot junction of the base-metal couple as shown in figure 3. The platinum-rhodium standard is protected by porcelain tubes to within a few millimeters of the hot junction, and the end of the porcelain tube is sealed to the couple by pyrex glass or by a small amount of kaolin and water-glass cement. This prevents contamination of the standard couple, with the exception of the small length of 2 or 3 mm, which is necessarily in contact with the base-metal couple. 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 couple may be welded together and the hole drilled in the composite junction. The couples 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.

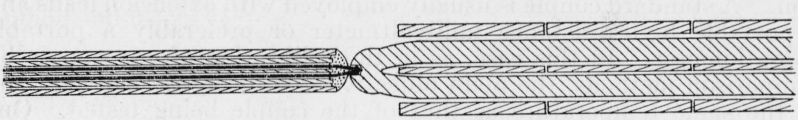

FIGURE 3.—*Arrangement to assure good thermal contact between the junction of a base-metal couple and that of a protected platinum-rhodium couple.*

In testing one or more small base-metal couples, 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 couples are to be tested at the same temperature, the method of immersing the couples 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 couples. When wires, insulators, and protection tubes of base-metal couples 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.

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 couples depends upon the temperature distribution along the wires. If possible such couples 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 couples 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 couples.

The exact method of procedure depends upon the type of installation. A standard couple is usually employed with extension leads and a portable high-resistance millivoltmeter or preferably a portable potentiometer. In this case, as in the calibration of any couple by comparison methods, the main objective is to bring the hot junction to the same temperature as that of the couple being tested. One method is to drill a hole in the furnace at the side of each couple permanently installed, large enough to permit insertion of the checking couples. The hole is kept plugged, except when tests are being made. The standard couple is immersed in the furnace through this hole to the same depth as the couple being tested, with the hot junctions ends of the protection tubes as close together as possible.

In many installations the base-metal couple and protecting tube are mounted inside another protecting tube of iron, fire clay, carborundum, or some other refractory which is permanently cemented or fastened into the furnace wall. Frequently there is room to insert a small test couple in this outer tube alongside of the fixed couple. A third method, much less satisfactory, is to wait until the furnace has reached a constant temperature and make observations with the couple being tested, then remove this couple from the furnace, and insert the standard couple 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 couple 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 couple are proportional to the temperature or to the emf. For example, it has been observed that a couple 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 couples is unsatisfactory because, in most furnaces used in industrial processes, large temperature gradients exist and there is no certainty that the standard couple is at the same temperature as the couple 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 similiarly mounted thermocouples located close together, the reading of the standard couple represents the temperature of the fixed couple 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. 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.[16] 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.[17]

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 the National Bureau of Standards, 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 transdichloroethylene, 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 [18] for temperatures down to −150° C.

A number of couples 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.

V. METHODS OF INTERPOLATING BETWEEN CALIBRATION POINTS

1. PLATINUM-RHODIUM COUPLES

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

16 Bul. BS **14**, 133 (1918–19) S301.
17 BS J. Research **6**, 401 (1931) RP284.
18 BS Sci. Pap. **20**, 619 (1924–26) S520.

calibration points, by direct interpolation between points, or by drawing a difference curve from an arbitrary reference table which closely approximates the temperature-emf relation of the couple. The method to be selected for a particular calibration depends upon such factors as the type of couple, number of calibration points, temperature range, accuracy required, and personal preference.

For the highest accuracy in the range 660 to 1,063° C with platinum to 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 couple 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 [19] of more than 0.1° C in the range 660 to 1,063° C. By calibrating the couple 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 (reference 19) 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 (reference 19) of more than 0.1° C.

For temperatures outside the range 660 to 1,063° 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 1,500° 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 $e=10\ t$, and emf as abscissas, the difference at intermediate points may be taken from the curve and added to the quantity $10\ t$ 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 the temperature-emf relation for the type of couple 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 relation of actual couples, the fewer the number of calibration points required for a given accuracy.

Reference tables [20] for platinum-rhodium thermocouples which are based on the temperature-emf relations of a considerable number of representative couples from various sources have recently been

[19] Wm. F. Roeser. BS J. Research **3**, 343 (1929) RP99.
[20] Roeser and Wensel. BS J. Research **10**, 275 (1933) RP530.

published. These tables represent accurately the shape of the relations for both the 10 and 13 percent rhodium couples in the entire range 0 to 1,700° C. The difference curve for any couple from the appropriate table is practically a straight line.

In the calibration of platinum to platinum-10 percent rhodium thermocouples to be used as working standards at the National Bureau of Standards, the emf is observed at the freezing points of gold, silver, antimony, zinc, lead, and tin and at the boiling point of water. The constants in the equation $e=a+bt+ct^2$ are computed from the observations at the gold, silver, and antimony points. Values in the range 660 to 1,063° C, computed from this equation and the four observed values below 660° C are used to construct a difference curve from the reference table mentioned previously. This difference curve is then extended graphically above 1,063° C. 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.

TABLE 4.—*Data for construction of difference curve*

Temperature, t	Observed emf thermocouple H4 e	emf values from table 2, Research Paper 530 e_t	Difference $\Delta e=e_t-e$	Temperature, t	Observed emf thermocouple H4 e	emf values from table 2, Research Paper 530 e_t	Difference $\Delta e=e_t-e$
°C	μv	μv	μv	°C	μv	μv	μv
0.0	0.0	0.0	0.0	700.0	6,269.9	6,260.0	−9.9
100.0	644.0	643.0	−1.0	800.0	7,342.4	7,330.0	−12.4
231.9	1,712.0	1,709.0	−3.0	900.0	8,447.0	8,433.3	−13.7
327.35	2,570.7	2,566.6	−4.1	960.5	9,131.0	9,117.0	−14.0
419.48	3,441.8	3,436.3	−5.5	1,000.0	9,583.9	9,569.0	−14.9
630.5	5,543.5	5,535.0	−8.5	1,063.0	10,316.7	10,301.0	−15.7

The observed values of emf at the calibration points are given in table 4 together with the values at 100° C intervals from 660 to 1,063° C computed from the equation

$$e=-335.4+8.3087\,t+0.0016106\,t^2$$

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

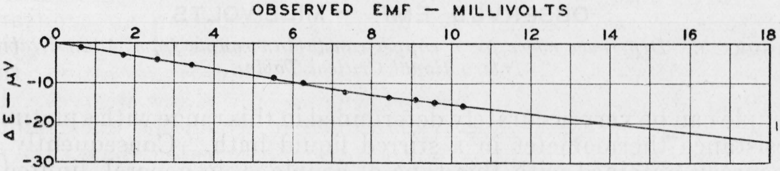

FIGURE 4.—*Difference curve for a platinum 10 percent rhodium couple from reference table in Bureau of Standards Research Paper 530.*

For accurate extrapolation above the gold point it is essential that the shape of the emf-temperature relation 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 above 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 Research Paper 530 are in most cases linear 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 for observations at fixed points. Two points (accurate to ±1° C at about 600 and 1,200° C) are usually sufficient to determine the difference curve from the tables in Research Paper 530 for either a 10- or a 13-percent rhodium couple, such that the resulting calibration is accurate to ±2° C at any point in the range 0 to 1,200° C and to ±3° C up to 1,500° C.

2. COPPER-CONSTANTAN COUPLES

The relation between the temperature and emf of copper-constantan thermocouples has been very well established in the range −200 to +300° C. The temperature of the measuring junction of such a

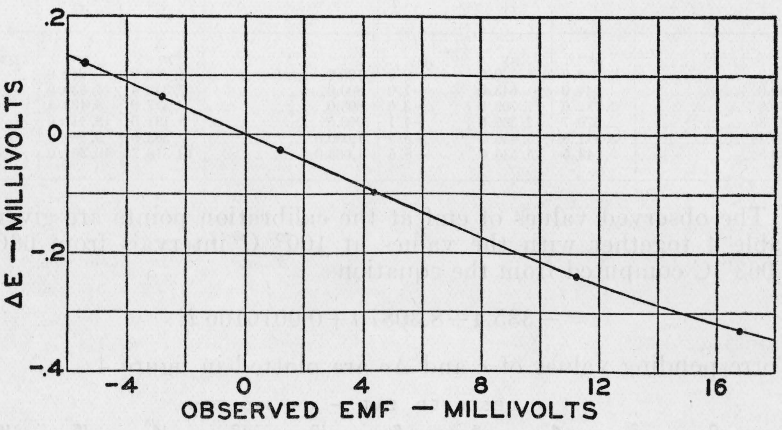

FIGURE 5.—*Difference curve for a copper-constantan couple from Adams' table in International Critical Tables.*

couple 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 couple is, in general, limited by the stability of the constantan wire above 200° C and by the accuracy of the emf measurements or the homogeneity of the wire below 100° 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 Adams' table[21] 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.

[21] L. H. Adams. Int. Critical Tables 1, 58 (1926).

Equations are used to good advantage with copper-constantan couples 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 Adams' table except when the differences are large. One convenient method of obtaining a calibration accurate to $\pm 0.2°$ C in the range 0 to 100° C is to use an equation of the form $e=at+0.04\ t^2$ where a is a constant determined by calibration at 100° C, e the emf in microvolts and t the temperature in ° 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 couple 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 2μv). 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.

3. CHROMEL-ALUMEL COUPLES

Figure 6 shows a difference curve for a typical chromel-alumel thermocouple from the standard tables published in this issue of the journal (RP767, p. 239). The difference curve from these tables

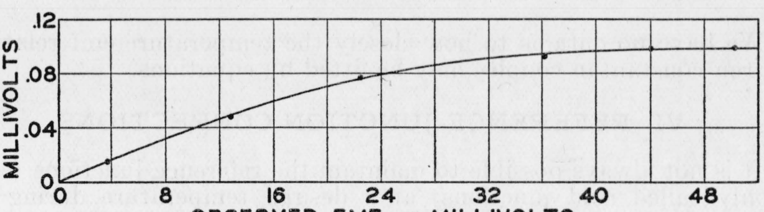

FIGURE 6.—*Difference curve for a chromel-alumel couple from table in Bureau of Standards Research Paper 767.*

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 2,000° F). These tables represent the average temperature-emf relation of chromel-alumel couples 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 $e=at+bt^2+ct^3$ will 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 2μv greater than at the calibration points.

4. IRON-CONSTANTAN COUPLES

Reference tables have not been determined as accurately for iron-constantan couples as they have for the other types. Skeleton tables are given in Bureau of Standards Technologic Paper T170, page 306, and in the International Critical Tables, volume 1, page 59. Figure 7 shows a difference curve from the table in the International Critical Tables and from a straight line, $e=57t$ (where e is in microvolts and t in °C) for a typical thermocouple. This latter method of drawing difference curves from a straight line is used at the National Bureau of Standards in the calibration of this type of couple.

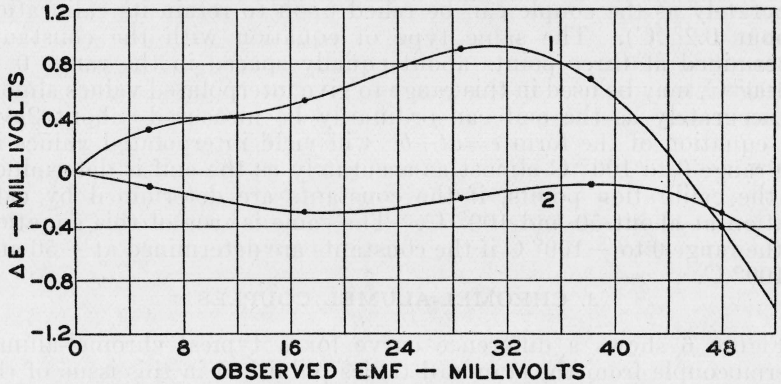

FIGURE 7.—*Difference curves for an iron-constantan couple* (1) *from a straight line; and* (2) *from the table in volume 1 of International Critical Tables.*

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

VI. 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 couple 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 couple 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-10 percent rhodium thermocouple with the measuring junction at 1,000° C and the reference junction at 25° C is 9.43 mv, and the emf of the couple with the measuring junction at 1,000° C and the reference junctions at 0° C is required. The emf of the couple when the reference junctions are at 0° C and the measuring junction at 25° C is 0.14 mv, then the sum of these emf (9.43 and 0.14) gives the desired value.

The sign of the corrections must be considered when applying these corrections, for example, suppose the observed emf of the couple with the measuring junction at 1,000° C and the reference junctions at 0° C is 9.57 mv and the emf of the couple with the measuring junction at 1,000° C and the cold junctions at 25° C is required. The emf of the couple when the reference junction is at 25° C and the measuring junction at 0° C is −0.14 mv, and when this is added to the observed emf the desired value 9.43 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 couple is lowered by bringing the junction temperatures closer together and increased by making the difference greater.

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

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

Temperature		Electromotive force			
		Platinum-rhodium [1]	Chromel-alumel	Iron-constantan	Copper-constantan
°C	°F	mv	mv	mv	mv
−20	−4	−0.101	−0.77	−1.02	−0.75
−15	5	−.077	−.58	−.77	−.57
−10	14	−.052	−.39	−.51	−.38
−5	23	−.026	−.20	−.26	−.19
0	32	.000	.00	.00	.00
5	41	.027	.20	.26	.19
10	50	.054	.40	.52	.39
15	59	.082	.60	.78	.59
20	68	.111	.80	1.05	.79
25	77	.141	1.00	1.31	.99
30	86	.171	1.20	1.58	1.19
35	95	.201	1.40	1.84	1.40
40	104	.232	1.61	2.11	1.61
45	113	.264	1.81	2.37	1.82
50	122	.297	2.02	2.64	2.03

[1] The values in this column apply for either the 10- or 13-percent rhodium couple. The difference between the average temperature-emf relations in this range does not exceed 5 μv.

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 couples are usually made of the same materials as the thermocouple wires, but in the case of platinum-rhodium couples a copper lead is connected to the platinum-rhodium wire and a copper-nickel lead to the platinum wire. Leads for any of the couples discussed here are available at all the pyrometer instrument manufacturers. Although the temperature-emf relation of the copper, copper-nickel lead wire is practically the same as that of platinum-rhodium couples, the individual lead wires are not identical thermoelectrically with the couple wires to which they are attached and, therefore, the two junctions where the leads are attached to the couple should be kept at nearly the same temperature. This is not necessary in the case of base-metal couples when each lead and couple wire to which it is attached are the same material.

VII. 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 large. 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/°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.

TABLE 6.—*Average thermal* [1] emf/°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	11.5
Platinum-13 percent rhodium	1,000	13.0
Chromel	870	31.7
Alumel	870	8.7
Iron	600	11.4
Constantan	600	47.0
Constantan	100	37.0
Copper	100	9.25

[1] Complete tables giving the average thermal emf of platinum-10 percent rhodium, and platinum-13 percent rhodium against platinum are given in Research Paper 530. The average thermal emf of chromel and of alumel against platinum are given in Research Paper 767.

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 10 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 ±2° 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.

1. PLATINUM

The thermal emf of thermocouple platinum against the standard Pt 27 is usually less than 100 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 25° C to obtain a comparison accurate to 2 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 couple and the emf measured at one or more temperatures by any of the methods described for calibrating 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 couple used to measure the temperature are one and the same. The sample or wire being tested is then welded to the junction of the couple and the emf of the couple 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.

2. PLATINUM-RHODIUM

The testing of platinum-rhodium thermocouple wire directly against platinum is exactly the same as the calibration of platinum-rhodium thermocouples. Platinum against platinum-10 percent rhodium gives 11.5 μv/°C and platinum against platinum-13 percent rhodium gives about 13 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 ± 1.5° C. Such an accuracy in temperature measurements is obtained only with a very homogeneous and accurately calibrated couple 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 0.2 μv/°C (200 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 1.5 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 ± 6° C.

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

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 junction. The junction of a standard platinum-rhodium couple 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 [22] 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 National Bureau of Standards standard Pt 27 and may be used to convert values of the thermal emf of any material against one of these

[22] Working standards of chromel and alumel prepared in this way, with certificates giving the thermal emf of the individual samples against the standard Pt 27 may be procured from the National Bureau of Standards.

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

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 relations for the various thermocouple materials against platinum are given in table 8 and may be used for making reference-junction corrections.

TABLE 8.—*Average temperature-*emf *relations of various thermocouple materials against platinum for applying reference-junction corrections*

Temperature		Electromotive force					
		Platinum-rhodium [1] *vs.* platinum	Alumel-platinum	Chromel-platinum	Constantan-platinum	Copper-platinum	Iron-platinum
°C	°F	mv	mv	mv	mv	mv	mv
−20	−4	−0.101	−0.27	−0.50	−0.64	−0.109	−0.38
−15	5	−0.077	−0.20	−0.38	−0.48	−0.084	−0.29
−10	14	−0.052	−0.14	−0.25	−0.32	−0.057	−0.19
−5	23	−0.026	−0.07	−0.13	−0.16	−0.029	−0.10
0	32	0.000	0.00	0.00	0.00	0.000	0.00
5	41	0.027	0.07	0.13	0.16	0.030	0.10
10	50	0.054	0.14	0.26	0.33	0.060	0.19
15	59	0.082	0.20	0.40	0.50	0.091	0.28
20	68	0.111	0.27	0.53	0.67	0.124	0.38
25	77	0.141	0.34	0.66	0.84	0.158	0.47
30	86	0.171	0.41	0.79	1.01	0.193	0.57
35	95	0.201	0.47	0.93	1.18	0.229	0.66
40	104	0.232	0.54	1.07	1.35	0.265	0.76
45	113	0.264	0.60	1.21	1.52	0.302	0.85
50	122	0.297	0.67	1.35	1.69	0.340	0.95

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

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.

VIII. 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.

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-10 percent rhodium	International Temperature Scale, fixed points.	660 to 1,063	Freezing point of Sb, Ag, and Au.	0.2	*Equation:* $e=a+bt+ct^2$	0.2
Platinum-rhodium [1]	Fixed points	0 to 1,500	Boiling point of water, freezing point of Sn, Pb, Zn, Sb, Ag, and Au.	0.2	Difference curve from reference table.	0.5 to 1,100 and 2 at 1,500
	NBS standard samples, fixed points.	0 to 1,500	Freezing point of Sn, Zn, Al, and Cu.	0.2	do	1 to 1,100 and 2 at 1,500
	Comparison with standard couple.[1]	0 to 1,500	About every 100° C	1	Any	2 to 1,100 and 3 at 1,500
	do	0 to 1,500	About 600 and 1,200° C (or more points).	1	Difference curve from reference table.	2 at 1,100 and 3 at 1,500
Chromel-alumel	Comparison with standard couple.[1]	0 to 1,200	About every 100° C	2	Any	3
	do	0 to 1,200	About 500, 800, and 1,100° C (or more points).	2	Difference curve from reference table.	3
	Comparison with standard resistance thermometer [2] or at fixed points.	0 to 350	About every 100° C	0.1	do	0.5
	Comparison with standard resistance thermometer.[2]	0 to −190	About every 60° C	0.1	do	0.5
Iron-constantan	Comparison with standard couple.[1]	0 to 750	About every 100° C	2	Any	3
	do	0 to 750	About 100, 300, 500, and 750° C	2	Difference curve from straight line.	4
	Comparison with standard resistance thermometer [2] or at fixed points.	0 to 350	About every 100° C	0.1	do	1
	Comparison with standard resistance thermometer.[2]	0 to −190	About every 60° C	0.1	do	1

Copper-constantan	Comparison with a standard resistance thermometer [2] or at fixed points.	0 to 300	About every 100° C	0. 1	*Equation:* $e=at+bt^2+ct^3$ or difference curve from reference table.	0.2
	Comparison with a standard resistance thermometer.[2]	0 to 100	About 50 and 100° C	0. 05	*Equation:* $e=at+bt^2$ or difference curve for reference table.	0.1
	Fixed point	0 to 100	Boiling point of water	0. 05	*Equation:* $e=at+0.04\ t^2$	0.2
	Comparison with a standard resistance thermometer.[2]	0 to −190	About every 60° C	0. 1	*Equation:* $e=at+bt^2+ct^3$ or difference curve from reference table.	0.2
	Fixed points	0 to −190	Sublimation point of CO_2 and boiling point of O_2.	0. 1	Difference curve from reference table.	0.3

[1] Either 10- or 13-percent rhodium.

[2] In a stirred liquid bath.

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 couples 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 couples at more points. The accuracy obtained with copper-constantan couples at low temperatures is usually limited by the emf measurements and in such cases the accuracy may be improved by employing a number of couples 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.

Table 10 gives the uncertainty in the thermal emf measurements of various thermocouple materials against the standard Pt 27 produced either by an uncertainty of $\pm 2°$ C in the temperature measurements

TABLE 10.—*Uncertainty in the determination of the thermal* emf *of thermocouple materials against platinum*

Material	Uncertainty in electromotive force
	mv
Platinum	----------
Platinum-10 percent rhodium	0.03
Platinum-13 percent rhodium	.03
Alumel	.02
Chromel	.07
Constantan	.10
Iron	.03

when platinum is used as a working standard, or by an uncertainty of $\pm 10°$ C in the temperature measurements when the material is compared with a working standard of the same material, the emf of which has been previously determined against the standard Pt 27 to the equivalent of $\pm 2°$ C. In the former case the uncertainty in the emf measurement is proportional to the uncertainty in the temperature measurement, whereas in the latter case it depends only slightly upon the temperature measurement provided the emf of the working standard against the standard Pt 27 is known to the same accuracy.

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 thermocouple materials are distributed with certificates giving the thermal electromotive forces of the individual samples against the standard Pt 27. The materials being distributed at present are alumel and chromel P.

(5) 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.

WASHINGTON, December 31, 1934.