

## THE PHYSICAL REVIEW.

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### THE CONSTANCY OF THERMOELEMENTS.

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ELECTRICAL thermometers are coming more and more into use, not only for the measurement of extreme temperatures and other special work, but even to secure for calorimetry an instrument superior to the mercury thermometer. Among electrical thermometers the resistance thermometer, for temperatures below  $1000^{\circ}$ , has been the one mainly used where accuracy and great sensitiveness were especially desired. The possibilities of the thermoelement in these directions have therefore remained comparatively undeveloped, while the great advantages which it frequently offers for particular kinds of work have been attainable only by the sacrifice of exactness. Palmer,<sup>1</sup> however, has already shown that the thermoelement may become an instrument of precision comparable with the best thermometers of other types; and the attainment of similar results in other cases is a matter of no great difficulty.

The errors of the thermoelement are almost entirely due to a single cause, inhomogeneity, which renders parasitic electromotive forces liable to occur at any point along the wires, and makes the reading of the element subject to change with every temperature fluctuation throughout its length. Where the trouble is due to a change in the material of the wires, it can generally be prevented by care in using the element. The inhomogeneity of the original materials can usually be diminished by making a proper selection of wires, or corrected by suitable treatment afterwards, and the

<sup>1</sup>A DeForest Palmer, *PHYS. REV.*, 21, p. 65, 1905.

detrimental effect of what remains can always be reduced by various devices.

The effect of inhomogeneities can easily be expressed by an extension of the ordinary formula, which gives the electromotive force of homogeneous thermoelements. In any metallic circuit, let  $J$  be the junction between  $E$  and  $F$ , two portions of wire, each homogeneous in itself but differing from the other in thermoelectric power by an amount,  $\Delta H$ . Suppose the middle points of  $E$  and  $F$  cooled to the same temperature,  $\theta_0$ , which may be as low as convenient. This cooling will not affect the thermoelectromotive force in the circuit, since it occurs within homogeneous portions of wire. If the temperature of  $J$  is  $\theta_J$  there will be a thermoelectromotive force between  $E$  and  $F$  equal to  $(\theta_J - \theta_0)\Delta H$ .<sup>1</sup> A similar expression obtains for every other point in the circuit at which there is a change in  $H$ . The total electromotive force therefore equals

$$\Sigma(\theta_J - \theta_0)\Delta H. \quad (1)$$

Since the temperature  $\theta_0$  may be anything we please, it can be taken equal to 0, and equation (1) becomes

$$E = \Sigma \theta_J \Delta H. \quad (2)$$

In general, the variation in thermoelectromotive power along the circuit will be continuous.  $E$  and  $F$  may then be taken to be infinitesimal; the portion cooled to the temperature  $\theta$  may be a second order infinitesimal (since the length of the cooled portion does not affect the thermoelectromotive force), and (2) becomes

$$E = \int \theta dH, \quad (3)$$

where the integration is to be carried over the whole circuit.  $dH$  of course is itself a function of  $\theta$ .

The magnitude of the error due to inhomogeneity in any given case can easily be computed in accordance with formula (3) by a graphical method. This is illustrated in the following discussion of a contaminated platinum thermoelement in an electric furnace. The upper curve ( $LMN$ ) gives the observed temperature gradient;<sup>1</sup> the next ( $PQR$ ), the approximate thermoelectric power

<sup>1</sup>  $H$ , as here used, is strictly the mean thermoelectric power, a function of the temperature interval.

along the platinum wire of the thermoelement, which was also obtained by actual measurement. The wire, as the curve itself clearly shows, was considerably altered near the hot junction.  $OK$  is the thermoelectric power of the platinum-rhodium wire which formed the other branch of this element.  $OK$  is, therefore, the thermoelectric power which would have existed at the junction had there been no contamination. In order to represent graphically the

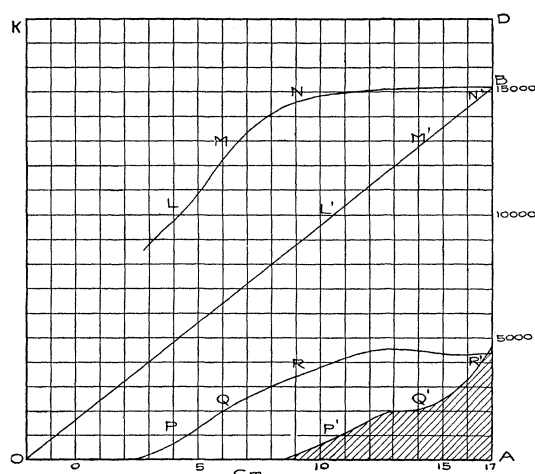


Fig. 1. Graphical method of computing the E.M.F. of an inhomogeneous element, applied to a platinum thermoelement in a resistance furnace. Upper curve, furnace temperature in microvolts (10 microvolts = approx.  $1^{\circ}$ ), with depth in the furnace for abscissa; middle curve, thermoelectric power of the wire, arbitrary ordinate, same abscissa. Lower curve, same thermoelectric power, with temperature as abscissa. Total area, normal E.M.F., shaded area, error.

product  $\theta dH$ , the coördinates should preferably be  $\theta$  and  $H$ ; that is, the thermoelectric power should be plotted as a function of temperature and not of length. The required change of coördinates is effected by the following device: The line  $OB$  is drawn with  $B$  equal to the ordinate of the maximum temperature on the diagram. The temperature curve is projected horizontally upon this line,  $L, M, N$  of the curve falling at  $L', M', N'$ . The abscissæ of  $L', M', N'$  are now proportional to their ordinates (since they lie on a straight line through the origin) and are, therefore, proportional to the tem-

<sup>1</sup> The furnace was of the type described by A. L. Day and E. T. Allen, *PHYS. REV.*, 19, p. 184, 1904; Carnegie Institution Publication, No. 31, p. 25, 1905.

peratures. The thermoelectric power curve is next shifted horizontally so that all the abscissæ are altered by the same amount as in shifting the curve  $L, M, N$ . For instance, if  $P, Q, R$ , were originally under  $L, M, N$ , they will be moved to  $P', Q', R'$ , under  $L', M', N'$ . In practice, this shifting is easily done, and consists simply in taking with a pair of dividers  $PP'$  equal to  $LL'$ ,  $QQ'$  equal to  $MM'$ , etc. The abscissæ of the curve  $P', Q', R'$ , being the same as those of  $L', M', N'$ , are likewise proportional to the temperatures. The curve  $P', Q', R'$ , therefore, has its abscissæ proportional to the temperature and its ordinates to the thermoelectric power. The area  $OADK$  represents the thermoelectromotive force which would be given by a thermoelement of homogeneous wires whose junction was at the temperature  $OK$ . The actual electromotive force is given by the area  $O, P', Q', R', D, K$ , and the lowering of electromotive force due to contamination of the wire, by the approximately triangular shaded area  $P', Q', R', A$ .

In this particular case, the effective thermoelectric power at the junction was about two thirds the normal, yet the reading of the thermoelement was lowered less than five per cent. The reason for this is, of course, that the contamination lay mainly in the region of uniform temperature, so that the maximum heat of the furnace extended out to a point where the difference in thermoelectric power between corresponding points of the two wires was much greater than at the junction. On the other hand, a small amount of contamination extending far from the junction evidently has a relatively great effect on the reading of the thermoelement—a point of importance in work with platinum thermoelements at high temperatures.

The reading of an inhomogeneous thermoelement is a function of all the temperatures throughout its length. In many cases where alterations in thermoelements have been reported, the effect observed was probably due to change in the distribution of temperature along a really unaltered element.

Since the errors of thermoelements depend upon the intermediate temperatures, their constancy can be increased by increasing that of the temperature distribution between the junctions.<sup>1</sup> This is one of the ways in which the effect of an unavoidable inhomogeneity

<sup>1</sup>Holborn and Day, *Drud. Ann.*, 2, 538; *Am. Journ. Sci.*, 10, 197, 1900.

can be diminished. Of course, the element should then be calibrated for the particular temperature distribution with which it is to be used.<sup>1</sup>

On the other hand, the behavior of an element which has been used with a constant temperature gradient affords no criterion of the excellence of that element under less favorable conditions.

The errors due to inhomogeneity in thermoelements are sometimes, but incorrectly, spoken of as due to "Thomson currents." This doubtless arises from the fact that these errors are attributable to the middle and not to the ends of the wire. The Thomson effect, however, does not depend at all upon the heterogeneity of the wire, while the errors we have been discussing are directly due to it. Indeed, for most purposes it is convenient to think of an inhomogeneous thermoelement as composed of a number of short, weak elements in series.

*Thermoelectric Testing of Wires.* — The most satisfactory way to improve thermoelements is obviously to get rid of the inhomogeneity as far as possible, and such was the object mainly in view during the following work. In this attempt, the careful testing of the thermoelectric power of wires was important, either for study of their properties and behavior, or to control the selection and arrangement of the materials from which the thermoelements were made. Several types of thermoelectric wire testers were therefore made.

The thermoelectric properties of wires have usually been tested by moving some source of heat or cold along them — a Bunsen flame, for example, or a lump of ice.<sup>2</sup> This method has the advantage of simplicity, and usually shows the presence of inhomogeneity well enough. It seemed ill adapted to the quantitative work here described, for the following reason: In a thermoelement as ordinarily used, the electromotive force is not affected by any parts of the circuit which are at uniform temperature, but depends upon the difference in thermoelectric power of two wires, each of which passes from a hot to a cold region. Similarly, when a single wire is heated at one place, the portions which contribute to the result-

<sup>1</sup> The deterioration of contaminated thermoelements is often given in degrees. Of course, any such statement is meaningless unless something is said or implied as to the conditions under which the element is to be read.

<sup>2</sup> Edwin H. Hall, L. L. Campbell and S. B. Serviss, *Proc. Amer. Acad.*, 41, 559, 1906.

ing electromotive force are those which pass from hot to cold at the edges of the heated region, and this electromotive force, therefore, measures the difference in thermoelectric power of these two portions of wire through which the temperature gradients extend. If, now, the heating is by a Bunsen flame, the two gradients are very near each other. To get the difference between two distant portions of the wire many of the short-length observations must be combined. As the error of each measurement is usually large compared to the whole variation in the wire, the result obtained by adding a number of observations may easily be in error by more than its whole value. The differences between distant points of the wire, however, are precisely those which have the greatest effect on the reading of the element.

The common method was accordingly modified by disconnecting one end of the wire and completing the circuit through an auxiliary wire which touched the other somewhere within the heated portion.

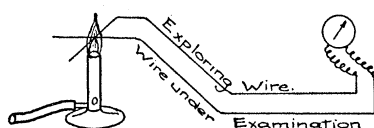


Fig. 2. Simple method of testing the thermoelectric height of a wire by means of a second exploring wire of the same material.

(Fig. 2.) The circuit then contained two temperature gradients, one on each wire, and by drawing the tested wire along, all portions of it could be compared with the same fixed portion of the other. A map of the whole wire could thus be made<sup>1</sup> and a comparison of any

two portions would contain the errors of but two observations. The auxiliary wire should be of the same material as the one tested, since otherwise large electromotive forces are introduced, whose variation, even with slight fluctuations of temperature, may quite cover up the electro-motive forces due to the differences in thermoelectric power under investigation. The temperature gradient should be at least as short as the inhomogeneities to be located. This method succeeds best where the working difference in temperature is high, since the effect of temperature irregularities away from the testing point becomes less important. With an ordinary

<sup>1</sup> As in Fig. 5 (in which, however, the comparison was with a fixed portion of the same wire). This curve corresponds to the integral of any one of the curves given by Hall Campbell and Serviss (*loc. cit.*).

Bunsen burner as source of heat, it proved excellent for studying platinum wires. A temperature of  $1000^{\circ}$  can easily be reached and kept constant within 2 per cent. A somewhat greater variation will do no harm if the wires are of the same material. Since the heating is done by a rapid current of air, the temperature gradient is sharp.

When the testing is done at ordinary temperatures, on the other hand, differences of temperature at other places on the test wire may cause disturbances. It is then better to use two exploring wires, one on each side of the temperature gradient, as in Fig. 3. The only portion of the inhomogeneous tested wire in the circuit is then the part (2 cm. or less) actually under examination. Freedom from disturbing electromotive forces will then be obtained if (1) the temperatures are constant, or (2) the exploring wires are homogeneous. As both these conditions can be nearly secured, this method gives excellent results. Most of the wire testers which were tried were constructed on this principle and differed mainly in the method of maintaining the temperature gradient. Steam was the source of heat. Ice was tried for the lower temperature, but was abandoned because it caused a condensation of moisture and thus endangered the insulation.

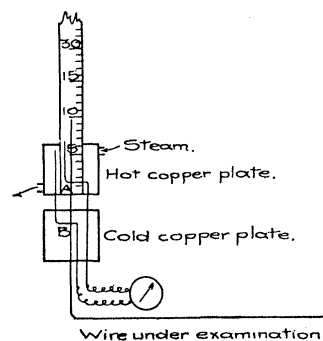


Fig. 3. Copper plate (dry) wire tester, using two exploring wires, making contact with the tested wire at A and B. The tested wire is drawn along the scale past the stationary exploring wires. Only two or three cm. of the tested wire is in circuit at one time, and all other wires exposed to temperature changes are of copper. A non-conducting pad covers the plates and wires when in use.

1. In the first form of tester, the wire ran from a hot to a cold globule of mercury. The results varied enormously with the condition of the surface of each metal. The temperature gradient was very sharp, but a sharp gradient was soon found to be seldom needed and to be obtainable by other methods; hence this form of tester was abandoned.

2. By putting a ring of lead pipe carrying steam in the top of a jar of kerosene, a sharp gradient was obtained on account of the slow conduction of heat downward from the warm layer which formed at

the top. The thermal contact of the fluid with the wire was of course excellent. This device seems to have advantages where only a few tests are needed and the construction of anything elaborate is therefore undesirable; but it cannot be made as convenient as several other forms, and the initial temperature difference steadily diminishes.

3. A small, square, wooden box was set in an oblong tin can and the whole filled with kerosene. Two bodies of kerosene were thus provided, separated by a thin vertical partition of wood. Pipes carrying steam and tap water maintained the two at different temperatures and a propeller in each caused rapid motion of the fluid at the place where the wires ran through the partition. This apparatus gave a very sharp gradient<sup>1</sup> and great freedom in arranging and connecting the wires. It was of value in several cases, but for ordinary work a more convenient arrangement is possible.

4. In the wire tester with which most of the work to be described was done, the temperature gradient was maintained by contact of the wires with hot and cold plates of copper (Fig. 3). These plates formed the tops of metal boxes, through which flowed steam and tap water respectively. They were covered with shellacked paper to insulate them from the tested wires. The wires were laid on the plates and covered with a weighted pad, which at once pressed them firmly against the plates, insured good contact with the exploring wires, and checked the escape of heat upward. The temperature distribution in the wires, secured merely by contact with a solid substance, is probably not very uniform or regular, but any variation due to this cause in the small electromotive forces measured was too minute to be noticed. In fact, the apparatus was originally constructed so as to admit of using kerosene to make better thermal contact, but experience showed that the use of this disagreeable fluid was not necessary. Of course, the temperature of the wire need not be that of the steam so long as it is constant.

If the wire to be tested is insulated, exploring wires can not be used. For such cases, various pieces of apparatus were employed whose common principle is shown in Fig. 4, where *E* is an enclosure, maintained at a constant temperature by means of steam, through

<sup>1</sup> Ninety-five per cent. of the temperature difference was within 1 cm. with platinum wires .6 mm. in diameter (No. 22).



which runs the wire in such a way that any two portions of it may simultaneously be subjected to the temperature gradient at the edge of the enclosure, and thus compared directly with each other. If one point of the wire,  $F$ , is kept always at the edge, it can be com-

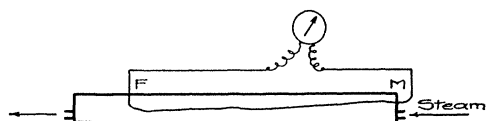


Fig. 4. Flat can wire tester. Adapted to insulated wires. The thermoelectric heights of any two portions,  $F$  and  $M$ , of the wire can be *directly* compared, and with almost no bending. A pad covers the wire when the test is made, or the wire may be inclosed between two similar cans.

pared in turn with all other points. The only essentials are that the temperature of the enclosure shall be constant and the length of wire within it capable of variation. It will not do, for example, to run the wire through a straight tube, since this requires heating a constant length of wire. The wire, however, if sufficiently flexible, can be doubled inside of a tube, when  $F$  and  $M$  will be near together at the same end. An apparatus of universal application is shown in Fig. 4. It consists simply of a long steam-heated metal case, flat on one side, against which lies the wire, covered by a thick pad of cloth. The temperature under such a pad is more uniform than that observed inside a steam-jacketed tube 14 mm. wide, and the adaptability of the method is obvious. This particular apparatus was not actually constructed, as the fine wires examined could be readily handled in tubes which we already had, but the constancy of temperature under a pad was measured carefully by means of a steam-heated varnish can. Such a can, or a flask, which can be set up almost at a moment's notice, makes a good substitute for the long metal case when the wire under examination is short.

Two types of thermoelements, one platin-rhodium, the other, constantan-copper, have been studied, with the result of improving considerably the accuracy of each.

1. *Platin-Rhodium Thermoelements.* — At the temperature of  $1000^{\circ}$  the platinum resistance thermometer begins to suffer a loss of accuracy. From that temperature up to  $1600^{\circ}$ , therefore, the thermoelement is the only satisfactory sensitive pyrometer available. Thermoelements made for high temperature work are now

tolerably familiar. Ordinarily they consist of a wire of very pure platinum, .6 mm. in diameter, joined by fusion to a wire of platinum alloyed with (10 per cent. of) rhodium or iridium. Couples containing iridium are the more sensitive at low temperatures. Their calibration curve is nearly linear. At higher temperatures, those alloyed with rhodium are nearly as sensitive and much more constant. They were the only ones studied. Connected to a voltmeter, these thermoelements form a direct-reading, convenient and accurate pyrometer of wide range. When read by means of a potentiometer, they are capable of much greater accuracy. One pair of elements has been carefully studied as far as  $1000^{\circ}$  and has never shown a disagreement greater than one half microvolt, corresponding to about  $\frac{1}{20}^{\circ}$  at the higher temperatures, and other elements have usually given results almost equally good as high as  $1500^{\circ}$ .

The principal problem presented by our thermoelements was the rather unusual one of preventing a rapid and continuous alteration of the wires when in use.

It has long been known that the reading of platinum thermoelements and resistance thermometers is easily altered at high temperatures by contamination of the metal. As far as observed until recently, the trouble always occurred in a reducing atmosphere. Holborn and Wein<sup>1</sup> found that hydrogen alone had no effect, but in the presence of silicates it liberated silicon, which attacked the platinum. Reducing gases containing carbon were also believed to be deleterious to thermoelements, but I have not been able to find satisfactory experimental confirmation of this view. Holborn and Day<sup>2</sup> subsequently found that furnaces made of fresh or imperfectly burned clay gave trouble, which was attributed to the organic matter contained in the clay. The contaminated wires were usually restored by igniting at high temperatures in the air, though it was frequently necessary to cut off portions of the element on account of impurities which could not be driven out in this way. The danger of contamination in an oxidizing atmosphere seems hitherto to have been considered negligible.

When work was begun in this laboratory, the methods used by

<sup>1</sup> Holborn and Wien, *Wied. Ann.*, 56, 373, 379, 1895.

<sup>2</sup> Holborn and Day, *loc. cit.*

Holborn and Day at the Reichsanstalt were adopted, with some improvements calculated to adapt them for use at higher temperatures.<sup>1</sup> A platinum-iridium alloy replaced the platinum or nickel of the coils, and a new insulating material consisting mainly of magnesia was substituted for clay in the body of the furnaces. Rapid deterioration of the thermoelements at the higher temperatures was soon observed, the magnitude of which was altogether unexpected and for a long time defied explanation, as special precautions had been taken to avoid the presence of reducing matter in the furnaces. The possibilities of contamination through dissociation, electrolytic action, organic or ferruginous dust (both of which abounded in the laboratory), or the volatilization of iridium from the furnace coils, were all considered; but none of these explanations seemed to account for all the facts, and the further precautions which occurred to us, such as cleaning and ventilating the porcelain tubes surrounding the thermoelements, were without effect in remedying the trouble.

For a time, therefore, furnace work was conducted by means of a provisional arrangement. The working elements were used in their contaminated condition, but were compared frequently with standards which, being in the furnace only five or ten minutes each day, kept their values very well. The simplest way to compare the two thermoelements is, of course, to read both when at the same temperature. In an electric furnace of ordinary size, temperature gradients are so steep that the only satisfactory way to bring two junctions to the same temperature is to thrust both together into one of the porcelain tubes which are made for protecting thermoelements in furnaces. This can be done if each element has but one insulating capillary, leaving the other wire bare. If care is taken to keep the bare wires on opposite sides of the porcelain tube, the elements can be pushed down without crowding, and at the same time the capillary tubes will prevent the bare wires from coming in contact. No such contact has been observed in several hundred comparisons. The thermoelements thus located are read alternately and as rapidly as the galvanometer will allow. Change in the furnace temperature can easily be allowed for. Comparisons can also be made by

<sup>1</sup> Day and Allen, *loc. cit.*

putting one element after another into the same porcelain jacket, though not so well, since five minutes are required to attain temperature equilibrium after a cold element has been inserted in the jacket. Hence the furnace must previously be adjusted to constant temperature, which requires some time, and even then results are not very certain. Simultaneous readings of two elements in separate tubes are also unreliable at high temperatures, as equality of temperature can not be assured. In a furnace at  $1400^{\circ}$ , differences of  $2^{\circ}$  have been observed between similar tubes symmetrically placed and so close to each other as to be in contact through most of their length. By comparing two elements in two such tubes and then reversing and comparing again, the difference in temperature of the tubes can be eliminated and with excellent results. The conditions, however, must be such that the temperature difference remains constant.

The comparing of thermoelements has been of the greatest value in high temperature work. It may be used as a substitute for or check upon the tedious process of calibrating by means of metallic melting points; it affords a valuable control of the extensive extrapolation which is necessary above  $1000^{\circ}$ , and insures that results obtained with different elements at these higher temperatures shall be comparable among themselves; and it serves to indicate the first signs of deterioration. Applied to elements which are much contaminated, however, it has a disadvantage obvious in the light of the previous discussion (see p. 452), since the reading of the contaminated elements, being a function of the temperatures throughout the contaminated portions, varies with the condition of the furnace. In that work which we were forced to carry on for some months with contaminated elements, this difficulty was minimized by correcting the elements immediately after the temperature reading had been taken and in the same tube, so that the temperature gradient along the element might be as nearly as possible the same for both operations. The contaminated ends of the working element were also cut off as soon as they had fallen off  $3$  or  $4^{\circ}$ . By virtue of these precautions, measurements could, in favorable cases, be made to agree within  $.3^{\circ}$  at  $1400^{\circ}$ . There was often, however, a good deal of uncertainty, which made the continual comparisons seem very irksome. We were finally driven to a consistent effort to get rid of the contamination altogether.

The systematic attack upon the problem began with an attempt to learn more of the actual condition of the contaminated elements. This study was begun by physical methods, the thermoelectromotive force of the wire furnishing a convenient and delicate means of investigation. Several of the wire testers described above were used, and contaminated elements were examined, centimeter by centimeter. The first day's work yielded results of importance and led to several surprises, in which conclusions derived from the experience of others and from our own occasional observations were found to be for the most part erroneous.

In the first place, the process of igniting the elements to free them from impurity was found to be practically useless, being almost without effect upon the contamination with which we were dealing. This practice, borrowed from the Reichsanstalt, had not seemed satisfactory, but whenever special failures were noticed, these had been attributed to a lack of thoroughness in the heating process.

Second, the thermoelectric height due to the contamination of the platinum wires proved many times greater than had been supposed. Immediately adjacent to the junctions, it was sometimes half that of the rhodium alloy of the other wire. The amount of alteration had previously been inferred from the change in the reading of the whole element when in the furnace, and thus, as is evident from the discussion of Fig. 1, above, too low an estimate had been made.

Third, a similar discovery was made regarding the rhodium alloyed wires. Nothing whatever appears to have been published upon this point; their contamination is considerably less than that of the pure platinum, and was therefore probably overlooked. The contaminating material was commonly believed to be subject to some selective absorption by which the platinum alone was affected. The tests, however, showed that the rhodium wires gained in thermoelectromotive power on the average one-fifth as much as the platinum. This information was especially important. The contamination had been supposed to be due to mere traces of foreign matter whose minuteness made the task of discovering and subsequently excluding them appear exceedingly difficult. The amount of impurity taken up by the rhodium wires, however, was evidently com-

parable to the amount of alloy (10 per cent.) initially present in them. The contaminating materials, therefore, were present in measurable quantities, and the prospect of identifying and then avoiding them appeared decidedly encouraging.

For this task, again, the wire testers were invaluable. They were capable of detecting an amount of impurity far beyond the reach of chemical analysis, and could work upon wires less than 2 cm. long. By subjecting short pieces of pure platinum wire to various possible sources of contamination, one after another, information could be obtained rapidly and at slight expense. When pure platinum wire was heated in our furnaces at  $1400^{\circ}$ , contamination occurred regularly and certainly. After an hour at this temperature, the resulting thermoelectromotive power (measured at  $100^{\circ}$ ) was about 4 per cent. of that of the ten per cent. rhodium wire. One-third of a per cent. could readily be detected. There was therefore no question as to the possibility of recognizing the presence of any source of contamination similar to that existing in our furnaces.

1. The first possibly contaminating materials investigated were reducing gases containing carbon. Wires were heated directly in a blast flame and electrically in illuminating gas and carbon monoxid, to various temperatures up to the melting point of platinum, but no contamination whatever could be found. In this particular, our results fail to confirm the observation made by Holborn and Wien that while the contaminating action of hydrogen is due to the liberation of silicon, carbon alone may contaminate thermoelements.<sup>1</sup> Carbon, like hydrogen, appears to act simply as a reducing agent, and is detrimental only in the presence of other material which yields contaminating products on reduction.

2. A pure platinum wire was then suspended in a furnace without the customary porcelain protecting tube. The usual amount of contamination occurred. The results with gas had shown that the impurities came from the materials of the furnace; this experiment showed also that they reached the wire in the form of vapor. Among the volatile materials in the furnaces, iridium (from the heating coils) was the immediate object of suspicion. Our furnaces when hot were known to be filled with iridium vapor, which con-

<sup>1</sup> Loc. cit.

densed as a black deposit on the cooler portions of the furnace in quantities sufficient for chemical identification.

3. Further light on this subject was obtained through the kindness of Mr. George B. Hollister, of the Corning Glass Works, Corning, N. Y., who loaned us a thermoelement which had been in continuous use at  $1400^{\circ}$  for four months in a glass smelter, which was heated exclusively by gas. If iridium was really the cause of the contamination, this element might have been expected to remain unaltered. It showed contamination, though comparatively little, considering the length of time it had been in use. A striking peculiarity was, however, presented by the rhodium wire, whose thermoelectromotive height was not increased at all. The contamination of this element, therefore, was clearly due to a different cause from that of our own. Furthermore, the absence of contamination in the rhodium wire suggested that that wire itself probably furnished the only contaminating material to which the platinum wire could have been exposed. The properties of the two metals are such that if iridium vapor was capable of alloying platinum in an oxidizing atmosphere, rhodium would naturally be expected to produce a similar and smaller effect. Hence, in spite of the contaminated platinum wire, the condition of this element strengthened the belief that iridium was the impurity in our own thermoelements. One and one half per cent. of rhodium has since been found in the platinum wire of the Corning element by chemical analysis, but this result was not obtained until sometime afterward.

4. A direct test of the action of iridium was of course next in order. To make it, the platinum wire must first be heated in the absence of iridium. All our furnaces contained that metal, but a means of excluding its vapor was found in the use of glazed Marquardt tubes. These glazed tubes are not recommended for use above  $1200^{\circ}$ , but their deterioration at somewhat higher temperatures is very slow, and the one used in this work gave no indication of injury from overheating after five hours at  $1500^{\circ}$ . A platinum wire heated in this tube for an hour at about  $1500^{\circ}$  showed no contamination. When the experiment was repeated with a piece of iridium-alloyed furnace coil wire beside it in the same tube, there was contamination, and about as much as usually occurred in the furnace itself with the same time and temperature.

Platinum was therefore certain to become contaminated in the presence of iridium. Since, moreover, this change agreed in amount with that acquired in the furnace, and since porcelain, a silicate, caused no injury to the wire, the inference seemed justified that the non-metallic furnace materials had no share in producing the contamination, but that it was entirely due to iridium and rhodium.

5. Further confirmation of the above results by chemical analysis now seemed feasible and desirable. Dr. Eugene T. Allen, of this laboratory, undertook the analyses, both of a wire contaminated with iridium and of the one from the Corning Works, supposed to contain rhodium. In both cases the impurity sought was found in substantially the amount expected from the observed change in thermoelectric power. Dr. Allen's report follows.

*The Detection and Estimation of Iridium and Rhodium in Thermo-elements.*—For iridium, the method in its essential features was that of Deville and Stas. The platinum-iridium alloy is dissolved in ten times its weight of pure lead, by holding the two in contact for four hours or more at about  $1000^{\circ}$ . Most of the lead is then removed by dilute nitric acid and the spongy residue extracted with ten per cent. aqua regia. The iridium remains undissolved. Several test alloys prepared by fusing pure platinum and pure iridium (from Heraeus) with ten times their weight of lead, gave invariably high results, but when the lead was increased to twenty times the weight of the platinum metals, the result was satisfactory.

	Taken.	Found.
Pure lead,	10 + gr.	
“ platinum,	0.5024 gr.	
“ iridium,	0.0117 gr. iridium	.0121 gr.

Iridium in the platinum wire of an old thermoelement.

Taken.	Found.
9 cm. platinum wire, 0.4913 gr.	Iridium, .0076 gr. = 1.54 per cent.

The metal obtained gave the following tests characteristic of iridium :

1. Mixed with sodium chloride and heated in chlorine it slowly changed to the somewhat volatile, brown sodium iridium chloride which dissolved in water with a red brown color.



2. The solution in 1 gave with ammonium chloride the rather difficultly soluble, almost black ammonium iridium chloride.

3. On boiling with alcohol and caustic soda a blue solution of iridium trichloride was formed.

4. A small portion heated with ammonium nitrate and concentrated sulphuric acid gave a blue color.

The rhodium was estimated by the method of Deville and Stas, which consists in the solution of the metal (it should be previously rolled into thin ribbon) in aqua regia, precipitation of the bulk of the platinum by saturated ammonium chloride solution, separation of the rhodium with the remaining platinum from the filtrate by long boiling with ammonium formate, and final separation of the rhodium by fusing with acid potassium sulphate, from which it is precipitated in condition to weigh, by the action of ammonium formate. The method was tested on an alloy synthesized from pure platinum and the ten per cent. rhodium alloy of Heraeus.

	Taken.	Found.
Pure platinum,	0.4440 gr.	
10% rhodium wire,	.0241 gr.	
∴ rhodium =	.0024 gr.	rhodium — .0027 gr.

The filtrate from the ammonium platinum chloride, amounting to perhaps 20 cm.<sup>3</sup>, was decidedly pink, and the color of the potassium acid sulphate fusion when hot was claret, yellow when cold. On trial it was found that one mg. of rhodium (in the form of potassium rhodium chloride<sup>1</sup>) in 10 cm.<sup>3</sup> was distinctly pink.

Rhodium in the thermoelement.

Taken — platinum wire of element,	.4484 gr.
rhodium found,	.0033 gr.
=	0.73 per cent.

The same color indications of rhodium were observed here in the filtrate from the ammonium platinum chloride and in the potassium acid sulphate fusion.

6. Although platinum wire was not injured in a gas flame, in the exhaust from a Fletcher gas furnace contamination occurred, as had, indeed, been expected. The cooler portions of the furnace

<sup>1</sup> The author is indebted to Dr. W. F. Hillebrand for a sample of this rhodium salt.

top were covered with a deposit of ferric oxide, which was so distributed as to show that iron in some form had almost certainly been brought up from the furnace by the escaping gas, oxidized, and deposited there. It therefore seemed quite probable that iron vapor, as well as silicon,<sup>1</sup> may be a contaminating material in furnaces containing a reducing atmosphere. This was confirmed by heating platinum as usual, at 1500°, in a glazed porcelain tube with a few milligrams of iron wire. Contamination resulted, although the two wires were not in contact.

7. An investigation of the behavior of iron in an oxidizing atmosphere was suggested by this last result. Ferric oxide heated as usual in a glazed porcelain tube with (but not touching) a fragment of platinum wire, failed to produce any contamination; thus strengthening the conclusion that non-metallic furnace materials are harmless in an oxidizing atmosphere.

Platinum, then, is subject to contamination at high temperatures by the vapor of iridium and rhodium, even when these are present in small quantities. The impurity is only slightly diminished by ignition in air. Besides these metals, and gold and silver, there seems to be no contaminating agency which need be feared in an oxidizing atmosphere. Commercial platinum always contains iridium, and its use within the furnace must either be avoided, if thermoelements are to be kept constant, or else some protecting arrangement, such as glazed porcelain tubes, be used. Unglazed tubes, except in metal work, are valuable only as a mechanical support. In any case, contamination of the platinum from the rhodium wire will take place, although with relative slowness. Good elements, therefore, should preferably be exposed to high temperatures for as short periods as possible. A reference to Fig. 1 shows that platinum does not become contaminated by iridium vapor below about 900°

Thermoelements alloyed with iridium are known to be less constant than those with rhodium, and the difference has usually been attributed to the loss of iridium by evaporation from the alloy. In the light of what precedes there can be little doubt that it is due

<sup>1</sup> Shown to be a contaminating material by Holborn, Wien and Mylius. Holborn & Wien, loc. cit.

rather to the absorption of some of the iridium vapor by the platinum wire. If this is so, iridium elements should be more constant if used so that the platinum and the alloyed wires were not close to each other. On inquiry, it was found that Drs. Waidner and Burgess, of the National Bureau of Standards, in this city, had actually observed that iridium elements kept their calibration better when stretched directly through the furnace than when doubled at the junctions as usual.

Beside chemical composition, the hardness of a metal affects its thermoelectromotive force, and the platinum thermoelements are liable to a temporary error from this source. New elements are usually hard from the drawing of the wire, sometimes reading as much as two per cent. high at room temperature. If they are not annealed before use, the softening of the heated portions produces inhomogeneities, which are also liable to continual change on further heating. The wire may also become hard during use from bending or other mechanical strains incident to handling, and also perhaps as a result of the brittleness (crystallization) which platinum attains when heated to moderately high temperatures—a point deserving further investigation. Fortunately, the annealing of platinum wires is very easy, on account of the absence of oxidation, so that the hardness of a platinum thermoelement need never be regarded as other than temporary. In this laboratory, only that part of the wire which is to be in or near the furnace is usually annealed. A wire of the usual size, .6 mm. in diameter, will carry 17 amperes when freely suspended, while 15 amperes is more than sufficient to soften it. There need be, therefore, no danger of melting off the wire.

The chemical purity of the original material is less under the user's control than most other causes of inhomogeneity. It is fortunate, therefore, that the chemical homogeneity of the best platinum elements now on the market is practically perfect. The platinum and rhodium wires of two thermoelements were tested throughout their length of 150 cm. at 1000° by means of a Bunsen burner, in the manner described above (p. 454). No effect due to inhomogeneity was found as great as the accidental errors of observation, which were about one-hundredth of one per cent. of the

electromotive force of the element at that temperature. In ordinary use the temperature at any one point of the element would rarely vary  $100^{\circ}$  for the same temperature at the junction, and the error due to inhomogeneity would therefore not exceed  $.01^{\circ}$ , which is considerably less than the usual error from other causes.

The last discussion suggests a point of some interest. The standard size of thermoelements (.6 mm.) was adopted after investigation by Holborn and Day, who found that finer wires did not give constant results. At that time, however, the contamination of platinum was not so well understood, nor the danger from hardening. It seems highly probable, therefore, considering the great homogeneity of thermoelement platinum, that considerably finer wires than .6 mm. would work perfectly well in very many cases. The main disadvantages would be the increased liability to contamination, and the greater danger from insufficient insulation, due to the higher resistance. Both these effects would decrease very rapidly with the temperature. The main advantages would be the lessened conductivity for heat and the reduced cost.

Any account of the present investigation would be incomplete which did not acknowledge its special indebtedness to the active interest of Dr. Arthur L. Day, of this laboratory.

II. *Copper Constantan Thermoelements.*—The second type of thermoelement investigated was of copper and constantan, and was intended for work at ordinary temperatures. The reasons for preferring a thermoelement to a resistance or mercury thermometer lay largely in the special conditions of the work for which they were to be used. The expectation of attaining greater ease and accuracy of reading than with a mercury thermometer has been abundantly confirmed.

The work of Hall, Campbell and Serviss,<sup>1</sup> and of Palmer<sup>1</sup> had apparently shown that an accuracy of  $.01^{\circ}$ , for measurements up to  $45^{\circ}$ , could readily be obtained with commercial wire. Instead of a single thermoelement, five elements connected in series were used, enclosed side by side in a common tube, constituting what may perhaps be called a thermobattery. A double advantage was expected from this mode of construction: (1) The greater electromo-

tive force made errors in the electric measurements less important, and (2) the accidental inhomogeneities in the wires would tend to neutralize each other. Insulated wire was, of course, needed, and copper was therefore substituted for the iron or steel commonly used. This change was considered an advantage, however, for another reason. Iron wire is notoriously uncertain in its thermoelectric properties, while copper is remarkably constant; hence, with wires of copper and constantan, there is only one-half the likelihood of trouble from inhomogeneity, and the electromotive force is still four-fifths as great as with constantan and iron. The constantan wire was No. 36 (.127 mm. diameter) obtained from the Driver-Harris Company, by whom it is sold under the trade name, "Advance." In order to control the accuracy of the results, two similar thermobatteries were made. Comparisons of these under various conditions showed that the readings were not constant, and that the trouble was probably due to inhomogeneity in the original material. An examination of some fresh wire from the same spool by means of a jacketed tube tester confirmed this suspicion. Three samples of wire, each 3 m. long, gave similar curves, one of which is shown in Fig. 5. The maximum variation is about .2 per cent. of the thermoelectromotive force against copper. This variation is evidently periodic.

Mr. H. C. Dickinson, of the Bureau of Standards, in conversation, has mentioned find

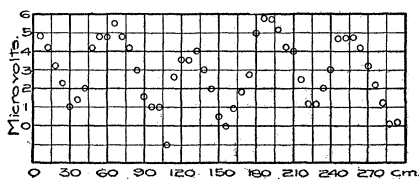


Fig. 5.

ing inhomogeneities with a period of the same length, about 60 cm., in wire of a different size obtained from the same company. I am indebted to him for the suggestion that the periodicity of the inhomogeneity points strongly toward an origin in the annealing process, when the wire may have been in coils of 60 cm. circumference. It is inconceivable that the peculiar curve of Fig. 5 should itself be the result of chemical inhomogeneity, nor are there any other irregularities greater than .013 microvolt per degree which can be due to that cause. Probably the effect of chemical inhomogeneity is even less than that, and altogether negligible.

Better wire could, therefore, doubtless have been obtained by further search, but it seemed preferable to avoid delay by using that on hand, diminishing the effect of its irregularities by the method of construction. The device employed was the one already tried, of allowing the inhomogeneities to balance each other, except that instead of trusting to the chances of partial compensation among the numerous wires, the curve in Fig. 5 was used to select two lengths of wire which could be combined so that their variations were at every point nearly equal and opposite. The resultant thermoelectromotive power, as indicated by the curve, was then constant within .013 microvolt. The probability of error from inhomogeneity with the thermobatteries thus made can be estimated as follows: Whenever a thermoelement has received an individual calibration, the errors due to inhomogeneity depend, not upon the absolute values of the intermediate temperatures, but upon their variation from the condition prevailing during calibration. The results of the calibration will, therefore, include the effect of all temperatures which regularly vary with the junction, that is, of the temperatures of the portions near the junction, which are immersed in the bath with it. The variations of temperature which may accompany a given temperature at the junction are the only ones which can cause error. As the thermobattery here described was to be used with nearly constant immersion, the greatest variation of this sort was that of the portion exposed to the air, and was not greater than  $20^{\circ}$ . The maximum error was, therefore,  $20 \times .013$ , = (about) .25 microvolt, and since the thermoelectric power was 80 microvolts for a degree, this corresponded to an error of  $.003^{\circ}$ . The result fully confirmed this estimate. Two such thermobatteries were made. Inclosed in the same tube they showed a permanent difference (which is not an error) of about .3 microvolt at  $30^{\circ}$ , which was about the limit of the sensitiveness of the galvanometer. The variation between the two was less than this, and altogether too small to measure. When both junctions of one were immersed in ice baths, the middle running through the air at about  $30^{\circ}$ , no variation from zero in the reading could be detected. With the two batteries in series, therefore, the error is not over  $.002^{\circ}$ , and probably much less, as far as the batteries themselves are concerned.

These results are not markedly better than those reported by

Palmer, except for the increased sensitiveness gained by putting the elements in series. The method by which they were obtained, however, leaves the experimenter less dependent upon good fortune in getting originally homogeneous wire. Palmer does not appear to have considered the inhomogeneities of commercial wire at all important. The very experiment which is often used to investigate the quality of a thermoelement — that of reading it with both junctions in ice — he uses to show that the temperatures of the different ice baths were identical, and he does not mention inhomogeneity at all. His results, therefore, while they show something of the accuracy attainable with the thermoelement, appear to be misleading as to the ease with which that accuracy can ordinarily be obtained with commercial wire.<sup>1</sup> Their reproduction by another will be uncertain, if not improbable, without attention both to the quality and the treatment of the wire.

On the other hand, it should not be forgotten that the extreme refinement here considered is not always needed; sufficient accuracy for many kinds of work can usually be obtained with such simple precautions as are discussed immediately below.

The permanence of the thermobatteries seemed to depend upon three things. First, freedom from mechanical strain, the hardening effect of which is well known. Whether annealing is a satisfactory remedy in the case of constantan does not seem to be settled. With insulated wires it was, of course, out of the question.

Second, protection against chemical change, which in this case means oxidation. The effect of a layer of tarnish in altering the thermoelectric power of wires is also familiar. A number 22 constantan wire (.6 mm. in diameter) which had lain exposed to the air of a well ventilated laboratory for three months had its electromotive force against copper altered over .6 per cent.<sup>2</sup> This trouble can be corrected by scouring off the tarnish, but the restoration of the original electromotive force of the wire was not considered certain. Moreover, this remedy also was inapplicable to insulated wires.

<sup>1</sup> It will not do to infer from Palmer's results even the probable homogeneity of commercial wire, since three of his elements (page 75) differ .1 per cent. among themselves, indicating that there was somewhere in the wire a variation in thermoelectric power at least half as great as that shown in Fig. 5. That amount of inhomogeneity would often produce errors considerably greater than those he actually found.

<sup>2</sup> Elements of constantan and other base metals, therefore, will not maintain their accuracy at temperatures high enough to cause oxidation.

Third, preservation of the insulation, which meant, practically, protection against moisture.

All these requirements could have been secured well enough in ways which would have left the middle portion of the wires reasonably flexible. But since, for the work in hand, rigidity was not inconvenient, it seemed better to avoid all possibility of trouble, and the elements were accordingly completely inclosed in suitably bent glass tubes.

The outside diameter of the tube inclosing the hot junction of both batteries is 3.3 mm. at the end. The time lag is 3 seconds in gently stirred water. The resistance of each is about 30 ohms.

The permanence of constantan elements can also be increased in another way. Wire is less liable to vary if initially in the condition to which use tends to bring it. Just as elements used at high temperatures, where they are certain to become annealed in part, should be annealed throughout before calibration, so those liable to be irregularly hardened in handling become immune toward that cause of inhomogeneity if thoroughly hardened in the first place. Of course, the hardening must be uniform, and the possibility of making it so seemed worth a brief investigation.

The small insulated constantan wire was easily hardened by working it back and forth over the square corner of a piece of wood. Wires thus treated, after being "aged" by heating to 100° for 15 minutes (a precaution whose necessity was immediately discovered) were tested for thermoelectric power. The total electromotive force against copper had increased .8 per cent or .33 microvolt per degree, but the greatest variation along the wire was less than the experimental error, which was about .013 microvolt per degree. This uniformity was not dependent on uniform working of the wire, as long as the hardening was thorough. The wires seemed to rapidly approach a constant condition. This would naturally be anticipated, and is essential if the method of hardening is to have much practical value. An important further consequence of it is that any variations in hardness originally present will disappear as the wire approaches the uniform condition. Hardening, therefore, supplies a method of securing initial homogeneity as well as of increasing the permanence of the element in use.



The degree of homogeneity shown to exist depended upon the experimental error in the method of testing. A more careful examination would probably show that the actual homogeneity is considerably greater than that already demonstrated. Further investigation of this question, however, while desirable, has seemed more appropriate to a laboratory not especially equipped for work at high temperatures. The original object of the present investigation was secured by the construction of the pair of enclosed thermoelements already described. For the method of hardening wires, enough seems to have been done in calling attention to its value, and showing that it is already capable of producing homogeneous thermoelements whose errors scarcely exceed those of the electrical apparatus by means of which they are likely to be read.

#### SUMMARY.

1. The main source of error in thermoelements is inhomogeneity, by the removal of which, in most cases, far greater accuracy may be attained than has hitherto been realized.
2. The electromotive force of an inhomogeneous element equals  $\int \theta dH$ , where  $\theta$  is temperature, and  $H$ , the thermoelectric power. This formula can be applied by a convenient graphical method. The errors due to inhomogeneity depend on the temperature distribution along the element also; a change in this distribution therefore produces the same result as a further alteration in the element. Such errors can be made to decrease indefinitely as the temperatures remote from the junctions of the element are made more constant.
3. Thermoelectric wire testers, of several easily constructed types, proved invaluable in these studies and in the making of thermoelements.
4. The effect of initial chemical inhomogeneity is practically negligible, as far as thermoelement work is concerned, in (Heraeus's) thermoelement platinum wires, in commercial copper, and, often if not always, in constantan.
5. The effect of physical inhomogeneity — that is the variation in hardness — in these wires can by no means be neglected. New wires are usually hard drawn. This hardness, as well as that which may result from bending, etc., can be quickly and effectually removed from platinum wires by annealing. In constantan, a

thorough hardening also produces uniformity and leaves the metal nearly free from liability to further change through handling.

6. Constantan and copper wires are apt to become chemically inhomogeneous through the formation of a film of oxide or other tarnish. Even at ordinary temperatures and in well ventilated rooms, an error from this cause amounting to as much as one half per cent. may easily develop within a few months. Cleaning off this film nearly, if not quite, restores the original calibration.

7. Platinum at high temperatures takes up impurities which diffuse into the wire. Carbon, illuminating gas, etc., produce this result only through their reducing action on other substances capable of injuring the platinum — of which iron (which reaches the platinum in the form of vapor) and silicon are perhaps the most important. In an oxidizing atmosphere, silicates and iron oxides are harmless, but contamination occurs above  $900^{\circ}$  from the presence in the hot furnace of small quantities of rhodium, and especially iridium, either pure or in alloys with platinum. All of these metals are somewhat volatile at high temperatures. The contaminating impurity can not be removed, but can be excluded by inclosure in glazed Marquardt porcelain, which, moreover, is fairly durable at  $1500^{\circ}$ .

8. Where the use of contaminated elements is necessary, fair accuracy can still be obtained by frequent comparison with standards under conditions such that the temperature gradient along the contaminated wire is always the same.

9. Frequent comparisons of platinum elements are always desirable in order to control the calibration and the unavoidable extrapolation.

10. Thermoelements of platinum-rhodium, and of constantan-copper, when used with proper precautions, have been found free from any error as great as .005 per cent. With the platinum, this amounts to less than one twentieth degree at  $1000^{\circ}$ ; with constantan, to less than  $.002^{\circ}$  for measurements up to  $40^{\circ}$ . Furthermore, this result with constantan was obtained with rather inferior wire, by uniting elements in series in such a way that the variations along the wires counteracted each other.

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