THERMOELEMENTS OF PRECISION, ESPECIALLY FOR CALORIMETRY.

By Walter P. White.

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The advantages of the thermoelement for calorimetry and similar work of high precision have been briefly stated, and the design and arrangement of the potentiometer and other auxiliary apparatus have been described in other papers of this series.[1] The construction and use of the thermoelement itself are simple matters, yet variations, apparently slight, in design or procedure may make great differences in the labor required or the success attained. The present paper aims to treat these details more explicitly than has yet been done, as well as to present some new material.

The thermoelement is merely a bundle of suitably connected wires, and the only problems presented by its construction concern, first, the quality of the wires, and second, their insulation and protection.

I. Multiple Elements.

The simplicity of the thermoelement has this consequence: that it is about as easy to have a considerable number of wires with, of course, a corresponding gain in sensitiveness, as to use a single pair. The use of many junctions has indeed been the rule in thermoelectric apparatus generally, but in thermometric work it has been customary to employ a single couple, and the use of more has often been regarded as a matter for special mention.[2] Convenience evidently dictates exactly the opposite procedure; it is the single couple which should not be used without special reason. The number of couples which can be installed as easily as one will generally be from four to twelve, according to circumstances; with thermo-

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[1] This Journal, 36, 1859, 1876, 2011 (1914).

[2] *Nomenclature.*—The classic division of all thermoelectric apparatus into thermocouples and thermopiles is unfortunate. It classes together instruments of widely different nature and use, and lays a most inconvenient emphasis on the usually trivial distinction which comes from the number of parts. A "thermopile" is still a thermopile, whether it does the work of a dynamo, of a radiometer, or of a thermometer, but it must change and become a "thermo*couple*" whenever a single pair of metals happens to be used. What is wanted is, evidently, to have terms each of which applies to the instruments of one kind and applies to all of them. The term "Thermoelectric Thermometer," analogous to "Resistance Thermometer," is such a term. Its length, however, seems likely to prevent its general adoption; it will scarcely displace the word "thermocouple" in cases where the latter is now properly in use. But the general practice of using a single pair of metals for thermometric work has brought it about that while the word thermopile naturally suggests other than thermometric uses, the term thermoelement suggests nothing else. It therefore seems practicable to use "thermoelement," as a familiar, intelligible and convenient synonym for "Thermoelectric Thermometer." "Multiple" and single thermoelements can then be discriminated (when necessary) without concealing their essential similarity.

elements of from 25 to 100 couples, the very great precision reached is obtained at the cost of some, not serious, inconvenience.

II. Quality of the Wire.

The thermoelement, in itself, has only two sources of error: defective insulation, and inhomogeneity of the wires composing it. Of these, inhomogeneity is of course the only one peculiar to the thermoelement. Formerly a frequent cause of serious error, and still troublesome at very high temperatures, it can easily be rendered harmless in calorimetric and similar work. To this end, however, it is of course well that the maker, and to some extent the user, of the thermoelement should understand the nature of the effect which inhomogeneity produces.

1. General Law of the Inhomogeneous Thermoelement.—From the elementary facts of the thermoelectric circuit, it follows that any thermoelement may be taken as equivalent to a number of similar but shorter ones placed end to end, each measuring the temperature difference between its own terminals.[1] The most effective of these partial thermoelements, that is, the effective portions of the real thermoelement, will then be those lying in the steepest temperature gradients. Thus in Fig. 1, if A B C D E represents the temperature distribution along the thermoelement *a b c d e*, the resulting electromotive force (that is, the reading) will depend mainly on the quality of the wire *bc*, lying in the gradient B C; the portions *ab* and *ce* will have only a secondary effect. *If the gradient shifts from B C to C D the effective thermoelement will be changed; it will be no longer the portion bc but cd.*

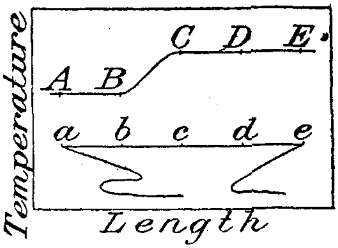

Fig. 1.

It follows that a thermoelement will be strictly constant if it is either perfectly homogeneous, so that its various portions may be indifferently substituted for each other, or else is always used with the temperature gradients in the same places; and evidently, if both these conditions are partly fulfilled neither will need, in practice, to be fulfilled completely. This is emphatically the case with calorimetric thermoelements, where the original quality of the wire is often sufficient in itself to give all needed precision, and where the gradients are also very steady.

It also follows that in any thermoelement the quality of the wire not in the temperature gradients is of less or no importance. This nearly always applies especially to the portions near the junctions,[2] a point of

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[1] The demonstration occurs in: "The Thermoelement as a Precision Thermometer," Walter P. White, *Phys. Rev.*, 31, 135–40 (1910).

[2] Since there cannot be any considerable temperature gradient near the junction, if the junction is to be at the temperature of the medium whose temperature is being measured.

great practical importance which has often been overlooked by users of thermoelements.

2. *Inhomogeneity in Particular Cases.*—The way in which inhomogeneity may affect different forms of the thermoelement is easily seen from the above.

(*a*) *Thermoelement Wholly within the Jacket.*—The simplest arrangement is where the thermoelement is wholly inside the calorimeter jacket, and runs to a second calorimeter. The total temperature gradient is then no greater than the temperature change which is to be measured. This gradient will always be at about the same place on the thermoelement; at the worst it will not shift by more than one-fourth its own length, that is, from *ac* to *bd* in Fig. 2. This is evidently equivalent to shifting one-fourth of the gradient from *ab* to *cd*, leaving three-fourths unchanged in *bc*, If we suppose that the maximum variation in thermoelectric quality is 100 per million—a high value with present methods of construction—and, moreover, that all of it exists between *a* and *c*, the uncertainty due to the shift of the gradient would be one-fourth of 0.000100, or 0.000025.

Fig. 2.

It is worth noting that the absolute value of this error would diminish with the interval. A resistance thermometer, for instance, which when at its best reads to 0.0001°, would indicate an interval of 4° as accurately as this rather inferior thermoelement, and a larger interval more accurately, but for an interval of only 0.1°, while the precision obtained with the resistance thermometer would have fallen to 1 per mille, the thermoelement would still be good for 0.025 per mille (or 0.0000025°) as far as any error due to inhomogeneity is concerned, and would be limited practically only by the delicacy of the electrical reading.

(*b*) *Thermoelement Partly Outside the Jackets.*—If the middle of the thermoelement is directly exposed to the air of the room, there will be at each end of the exposed portion a gradient whose value will change as the room temperature changes. If the wire lying in these two gradients differs in quality, any change of room temperature occurring during a determination will cause an error. If this error seems likely to be appreciable it can easily be prevented by shielding the exposed (horizontal) portion of the thermoelement with an inverted trough of sheet copper, which straddles it and dips into the jacket water on each side. With such a temperature-controlling shield made of copper 0.8 mm. thick, reaching 36 mm. above the water and 14 mm. wide at the top, the maximum variation from the temperature of the water was only 0.04 of the difference between water and air. When two such pieces of copper were used, one over the other, separated by a little blotting paper, the maximum variation on the inner one was below 0.02 of the water-air difference.

With this simple arrangement in use, then, the room temperature would have to change over 40° in order to produce an error of 0.0001°, even with the rather inferior thermoelement supposed above. With full exposure of the middle of the thermoelement to the open air, however, a change of 3° in room temperature might produce an appreciable effect in any but the most homogeneous thermoelement. Hence such an exposure should not be practiced in work of high precision, particularly since the prevention of it is so very easy.

(*c*) *Thermoelement with Ice Bath.*—If one end of the thermoelement, instead of being in a second calorimeter, is in an ice bath, there will be introduced a gradient of 20° or so, with an error in case the gradient shifts which may possibly be 0.001° but more probably as low as 0.0002°. To avoid this error, time must be allowed for equilibrium to set in after inserting the thermoelement. After that, changes due to inhomogeneity will be very slight and slow, and probably no greater than those which may result from small changes in the temperature of different portions of the bath itself. But the ice bath is not recommended for calorimetric work of the highest precision, and it is one important advantage of the methods here presented that they avoid its use.

(*d*) *Adiabatic and Non-adiabatic Methods.*—In adiabatic methods the gradient occurs at the outer edge of the jacket. If, therefore, the same arrangement is used, sometimes for adiabatic and sometimes for non-adiabatic methods, the effective thermoelement is not the same in the two cases, and the results may differ a little. The difference, however, is usually quite negligible and is, moreover, easily determined, but the possibility of its occurrence should not be wholly overlooked.

3. Selection and Testing of Wire.—Commercial copper wire is sufficiently homogeneous for precision thermoelements. Methods have been described for arranging inferior constantan wire so as to secure a very satisfactory resultant homogeneity.[1] These effective but relatively laborious methods are no longer necessary. Our study of this earlier wire convinced us sometime ago that the production of satisfactorily homogeneous constantan wire was easily possible, as soon as any manufacturer should become sufficiently interested to undertake it. The Electrical Alloy Company, of Morristown, N. J., at our request, have furnished several samples of "specially annealed" wire[2] which confirm this view. Although the 200 meters and more which have been tested contain a few (relatively) bad spots, they consist mainly of continuous stretches of wire varying less than 0.0007 in thermoelectric power against copper and therefore

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[1] "The Constancy of Thermoelements," Walter P. White, *Phys. Rev.*, **23**, 470 (1906); "The Thermoelement as a Precision Thermometer," *Loc. cit.*, 140–43.

[2] Their trade name is "Ideal," but the wire is practically the same as Constantan (40% nickel).

good enough to make, without any further selection or arrangement, thermoelements precise to better than one-ten-thousandth.[1]

It is of course possible that an occasional spool might consist mainly of inferior wire. If three samples distributed through a spool are all inferior it will probably be best to send for another spool, since the cost of the untested wire is a trifle. In general, however, judging by past experience, the chances are over 10 to 1 that any particular 30-meter length will contain much good wire, and work now in progress will probably soon render the situation still more satisfactory.[2] Meanwhile, the testing of enough wire for a very sensitive thermoelement will seldom prove long or laborious.

4. Sizes of Wire.—In general, it is desirable that the thermal conductance of a thermoelement should be small, the electrical conductance large. It is easy to show that the ratio of electrical to thermal conductance is a maximum when the ratio of the cross sections of the two kinds of wire, 1 and 2, equals $\sqrt{\frac{\sigma_1 \kappa_1}{\sigma_2 \kappa_2}}$, where σ is the electrical, κ, the thermal, conductivity. For copper and constantan this calls for a ratio of about 21.4 to 1 at 18°. A somewhat smaller ratio will do nearly as well, if it is desirable for mechanical or other reasons, but it is clear that very inefficient ratios have often been used. For the constantan, 0.25 mm. diameter (No. 30 B & S) is about the most convenient size in the great majority of cases.

5. Method of Testing.—The essential feature of all methods of testing wire thermoelectrically is to heat (or cool) successively various portions of the wire, and observe the electromotive force produced. This electromotive force at any instant measures the difference in thermoelectric power between the two ends of the heated portion. The most obvious method is to draw the wire *through* a warmed bath or tube. In that case both gradients are changing at the same time, and the interpretation of the observations is usually troublesome and unsatisfactory. The method will, however, distinguish readily enough between wire which is wholly free from irregularity and that which is not, and has been used in making some excellent thermoelements, by rejecting altogether all wire which was not clearly excellent.

It is about as easy, however, to secure more complete information,

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[1] Our last spool received shows, as far as tested, 99% of wire varying less than 0.0002, and considerable wire as good as this has been obtained from other spools.

[2] The difficulty lies in our present ignorance as to the causes of the inhomogeneities sometimes found in carefully made constantan wire. Some preliminary work on the problem failed to give definite results, and thus showed that the problem has sufficient difficulty to be probably worth while as a research. At the same time the number of factors is so small that a successful solution could be confidently expected, and its practical usefulness would be considerable. It is to be hoped that some one will take the matter up.

often resulting also in a greater economy in using the wire, by drawing the wire *out of* a heated bath, leaving one end of the heated portion unchanged during the test. All other parts of the wire, as they are successively drawn out of the heated region, are then compared with the unchanging part, and a complete map of the variations of the whole is thus obtained. It is important to be able to handle the wire readily without snarling or kinking; this can be done by running it from one drum to another, putting one of the drums in the heated bath. If the wire is insulated, as it usually will be if intended for multiple thermoelements, it is more simply and surely tested if in one single piece. The two ends then run from the drums to copper leads, which run to a sensitive galvanometer. Twisting of these portions as the drums turn is prevented by letting them wind (or unwind) about the slender axles of the drums; the small amount of wire which is thus coiled to a small radius is thrown away after the test. The wire is best brought out of the hot bath along the axle of the drum and allowed to make its small coil above in the air, where it can be easily attended to. (This is an improvement over previous published methods,[1] and was suggested by Mr. L. H. Adams of this laboratory.) Two strips of sheet copper wound around the axle, one at the surface of the liquid and the other a little higher, will keep the gradient, which will be mostly between them, constant as the drum turns.

The E. M. F. of a copper constantan couple for 80° temperature difference is over 3000 microvolts, hence in this test an irregularity of 2 microvolts is enough to cause rejection of the wire; the readings must therefore be good to a microvolt or better, and the galvanometer must accordingly be arranged for eliminating the effect of parasitic thermal forces.[2] The galvanometric precision, however, may always be less than is to be used in reading the thermoelement after it is made. The parasitic E. M. F.'s produced by ordinary irregularities of the air temperature and of the bath are of course quite negligible, when eighty degrees produce only a microvolt or two. The junctions to the two copper leads, however, must not differ by more than 0.005°. If other means fail, they can easily be kept as near as this by putting them together into a stirred bath at room temperature. The equality of temperature can be tested by seeing how nearly the galvanometer reads zero before the hot bath is heated.

The hot bath can be conveniently filled with kerosene at 100°. The wire, even when wet with kerosene, can be marked with red ink. The marks may either indicate the portions to be rejected or may be put at

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[1] In "The Thermoelement as a Precision Thermometer," *Loc. cit.*, p. 142.

[2] A regular feature of thermoelectric work of precision. Described in the first paper of this series, Walter P. White, "Thermoelement Installation, Especially for Calorimetry," THIS JOURNAL, 36, 1859 (1914).

regular intervals of a meter or two, corresponding to a note-book record of electromotive force readings. The wire should be supported so that no length greater than a foot or so hangs free in the air, for such lengths, swinging in the earth's magnetic field, cause annoying parasitic currents, which delay the observations. Normally the operation is very rapid. Wire enough for a 24-couple element can be carefully done by two persons, one to observe, and one to run the wire, in less than an hour.

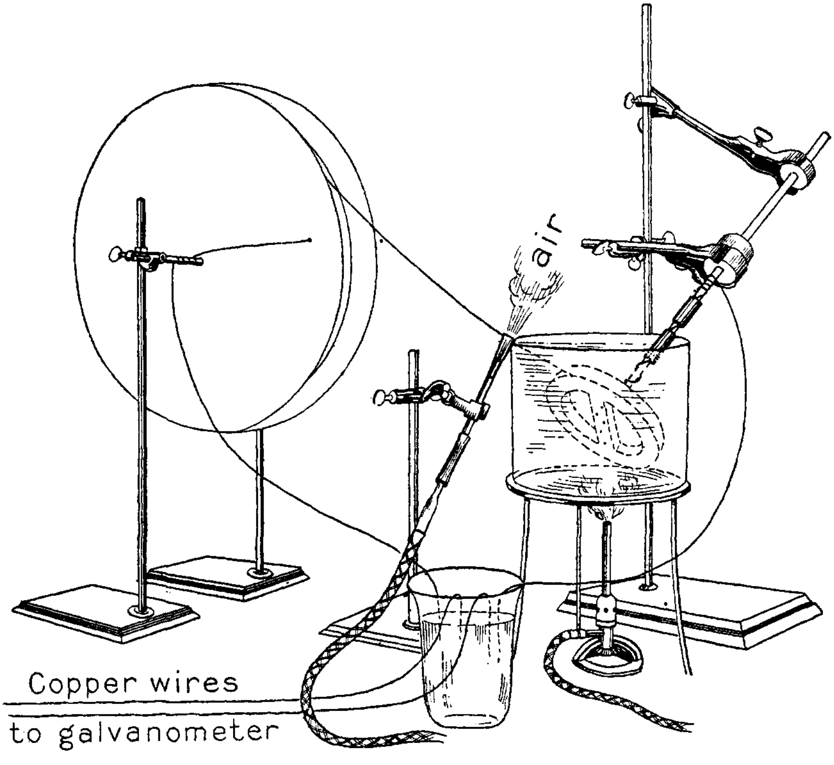

Fig. 3.—Apparatus for testing the quality of thermoelement wire.

Fig. 3 shows one of our wire testers. The drums are both of pasteboard, the axles are wooden dowel rods, the bearings of the inclined axle of the drum in the warm bath are corks, clamped to a retort stand.

6. Making Up the Thermoelement.—After the wire is tested, 2 different methods are possible for selecting the portions to go in the thermoelement. The simplest is merely to cut out the bad pieces of wire (or else put them where they will do no harm)[1] using the rest without further selection. The other method is useful whenever a continuous piece of wire

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[1] Even a very bad portion of wire will do no harm if it is 5 cm. below the level of the bath at either end of the thermoelement.

is available with very few bad spots, and long enough to make the whole, or at any rate half, of the thermoelement. It permits picking out, with certainty, the very best portions of the thermoelement to go in the gradient regions. It is accomplished by winding the wire into a ring, of circumference equal to the length of the finished thermoelement, and then shifting the ring, while partly immersed in a warmed bath, until the most homogeneous portions of the bundle are found.

To accomplish this operation effectively requires a little systematizing. Fig. 4 will give an idea of our present method. The wire is wound on a pasteboard ring, on which a scale of centimeters is marked with red pencil. A light metal rod is clamped to the ring by means of two clothespins, and turns in a bearing (which is merely twisted wire) just at the level of the fluid; thus as the ring is swung up and down, the gradient

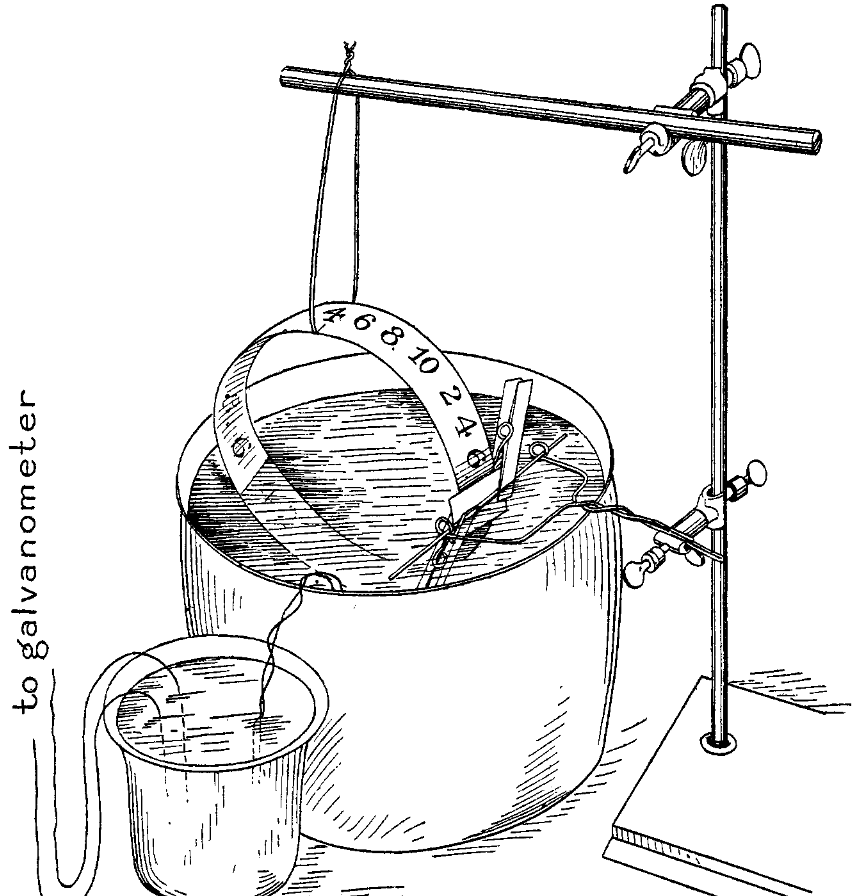

Fig. 4.—Apparatus for locating the best parts of a thermoelement before the wire is cut.

near this rod remains fixed, and the variations in the wire at the other gradient are directly measured. Two plates of sheet copper or aluminum, a few centimeters wide, clamped on with the rod, and projecting a centimeter or two above the liquid surface, will make the fixed gradient still more constant. A blast of air directed against the wires just above the movable gradient will render that gradient sharper and more quickly established after each change. At least two positions of the fixed gradient (and therefore of the rod) will be needed to cover the whole circumference. The leads should be of the same continuous wire, running to copper galvanometer leads as described above for the wire tester. The point where they leave the ring should be always either in the air or in the liquid for any one position of the fixed gradient. The observations obtained by the method just described are plotted against length, the best available portions of the ring are selected for the gradients of the finished thermoelement, and the wires are then cut accordingly. Before the cuts are made a narrow streak is drawn with white paint somewhere across the wires. It is then possible afterward, by bringing the white spots on the wires opposite each other, to be sure that the wires are in the same relative positions as during the test.

III. Construction.

1. Soldering.—In joining up an element, as in testing the wire, it is well to arrange systematically for handling, without confusion, the large amount of small wire. Our wires, therefore, after being cut, are clamped on light boards a decimeter shorter than the element, and with a width of 1 cm. for each pair of junctions. The clamps are little battens of wood, screwed on. Once in place, the wires remain clamped till they are gathered together under loosened battens for inclosure in their case. By this procedure not only is the work made easier and more orderly, but the wire is protected from mechanical strains which might impair its original homogeneity.

A compact and smooth joint is of great assistance in the subsequent operations. This is promoted if the silk insulation is cemented in place by shellac before the wire is cut. Then when the tip of the wire is scraped bare in preparation for being soldered, the adjacent silk remains closely adherent. The copper end, being smaller and more flexible, is wound around the constantan, and tweezers are used, so as to avoid contact with the fingers, which may interfere with the soldering of constantan when rosin is used. A very quick and satisfactory way to do the soldering[1] is by dipping, for the shortest possible time, in a bath of rather hot solder[2] and then snipping off the tip of the junction, thus getting rid of any projecting ends of wire or tails of solder. The exposed portion of bare wire should then be very short; not over a millimeter between the end and the place where perfect insulation begins.[3]

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[1] Compare "The Thermoelement as a Precision Thermometer," *Loc. cit.*, p. 143.

[2] Rosin is preferably used as a flux, and the rosin is apt, when melted, to loosen the end of the silk. Mr. C. W. H. Ellis, of this laboratory, has used a method which avoids this trouble. The wire, after dipping in melted rosin, is touched with a hot piece of porous fireclay, or other refractory material, which absorbs the excess of rosin, leaving just about enough to do the soldering nicely.

[3] This, of course, involves bringing the solder within half a millimeter or less

2. *Insulation.*—With the errors from inhomogeneity of the thermoelement made negligible, defective insulation is the only remaining source of error. It is also easily avoided. Some resistance thermometers are provided with special drying material, but the very sensitive inclosed thermoelement seems amply protected against water vapor by a paraffin seal at the point where the leads leave the case.[1] This has been true of thermoelements used for several years in ice baths, and in one instance, where liquid water had entered through a small hole in a defective case, the thermoelement had recovered its insulation after lying on the shelf a few months with the case still on.

We have never observed any electrical leakage in uninclosed thermoelements, though slight leakage is not altogether improbable in damp weather if the wires are not well paraffined, just as it might be in any other wires similarly situated.

The junctions, where the silk insulation has been removed for soldering, of course need special treatment. The most obvious way is to insulate by some kind of varnish,[2] and then simply bunch the junctions together in inclosing.

An easier and more effective method is to distribute the junctions along the tube, letting the inner wires come the farthest, so that the whole group forms a sort of cone with the junctions all on the outside, next the case, which is drawn to a similar cone if glass is used. This method saves the labor of reinsulating, is especially free from liability to failure and gives a thermoelement tip of minimum size and lag. The increase in required depth of immersion which it involves is usually not in the least detrimental.[3]

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of the silk without charring that. This is not difficult, with proper attention to the temperature of the solder and the time of immersion. A little preliminary practice is, of course, useful. If the solder is too cold the junction comes out rough. If the end of the silk insulation does become a little loosened, of course no great harm is done, but projecting bits of solder or wire may give considerable trouble.

[1] The thermoelement wires may, without any detriment to the readings, be paraffined throughout their length, and our thermoelements always have been so treated. This may have contributed toward the immunity from dampness which we have observed. At any rate the paraffining seems desirable, in general, for the present, as a precautionary measure. It is best done after the wires are fixed in the case.

[2] Cellulose acetate is apparently the best varnish yet tried. One sample of this gave, after staying a few years in a box, exposed to the atmospheric humidity, a strong smell of acetic acid, and became nearly insoluble in the usual solvent, thus giving strong indications of decomposition. But an 8-junction element, insulated with material from this same sample, now shows, after two years' inclosure embedded in paraffin, an insulation resistance of over 2000 megohms between the two groups of wires.

A fairly thick coating of varnish is needed, since the varnish tends to gather in the depressions of the surface, leaving the projections (for instance, the outer surface of the copper wires, if these are wound round the others) insufficiently protected.

[3] Four mm. per junction for 24 junctions is unnecessarily open, yet it requires

In cases where the junctions are too numerous to be distributed satisfactorily, or wherever any number of junctions are to be imbedded in metal, reinsulation is of course necessary. A superior method of reinsulating has recently been introduced by Mr. L. H. Adams, of this laboratory, who has kindly allowed me to quote his as yet unpublished description of it here:

" * * * The junctions are coated with an insulating layer of vulcanized rubber by the following procedure: Each junction is dipped separately into a fairly thick rubber solution consisting of pure gum rubber dissolved in a mixture of benzene and carbon disulfide. After standing an hour or so, or until dry, the coating of rubber is vulcanized by immersing, for a few seconds only, in a dilute solution of sulfur dichloride in carbon disulfide (1 to 40). If a thicker coating is desired the operation of dipping in the rubber solution and drying may be repeated several times before the vulcanization. A final drying for several hours at 40° or 50° completes the operation. The coating thus obtained is tough and elastic, and of about the hardness of ordinary sheet rubber. Where, for any reason, a much harder coat of rubber is desired, the following method may be substituted: Dip the junctions in a rubber solution in which sulfur is directly incorporated, dry as above and heat to 130–150° for an hour or so.[1] The solution is prepared by adding to the plain rubber solution an amount of precipitated sulfur equal to about 20% of the amount of rubber present.

"Either of these methods gives a tough, coherent and elastic coating of high electrical resistance. In fact, the mechanical and electrical properties even of the softer coating are so satisfactory that the junctions may be imbedded in fusible (Wood's) metal."[2]

3. Inclosure.—The ends of nearly all thermoelements must be enclosed, to allow immersion in baths, etc. A frequent weakness in the case of single or auxiliary elements is to have the inclosing tube stop just above the surface of the bath. The bending of the wire is greatest at the end of the tube, and this bending, and the consequent inhomogeneity introduced into the element, thus come in the temperature gradient, where they

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a less total depth of immersion than is demanded by many of the best calorimetric resistance thermometers. Twenty-four junctions have been successfully distributed within 2.8 cm., though this degree of concentration is nearly always unnecessary and is undesirable. The distributing can be done more freely if the copper wires are cut a few centimeters longer than the others, otherwise it is necessary to pay attention to the order in which the wires are connected.

[1] Care should be taken that this heating does not injure cotton or silk insulation.

[2] Indications of the production of copper chloride have been observed, Mr. Adams tells me, after treatment with the sulfur chloride. Thorough drying and prompt inclosure of the junctions are therefore desirable, and until more experience has been had, the hard rubber insulation appears safer.

do the maximum amount of harm.[1] The rigid inclosure should come well beyond the gradient into the region of uniform temperature. The middle of the thermoelement may then, in most cases, be left free and flexible. (A slightly flexible prolongation of the rigid tube may advantageously be added to diminish the amount of sharp bending.) With the sensitive multiple elements needed for calorimeter temperatures a complete rigid inclosure will probably be preferred in most cases.

The three main desiderata of a thermoelement end are: small heat capacity, small lag—these are luxuries rather than necessities—and negligible effect upon the reading due to heat conduction along the element from the air above the bath—this is, of course, essential. These three things are all dependent on compactness, and it is the combining of compactness with effective insulation that causes whatever difficulty there is. This difficulty occurs only at the soldered ends, where the original silk insulation has to be removed.

Three kinds of enclosure have been used, glass tubes, metal tubes, and flat metal cases.

Of these the glass inclosure is the easiest to employ, and gives the greatest security against danger of leakage, either of electricity or water. It is therefore preferable in most cases. It is readily made from ordinary soft tubing, fitting the thermoelement rather tight at the ends, and larger at the bends, around which the wires must be pushed into place.[2]

Ordinarily, both ends of a calorimetric thermoelement will turn downward, for insertion in some sort of bath, so that the whole will have much the form of Fig. 5. This figure shows more particularly a glass inclosure, which will usually consist of two L-shaped tubes. The tubes are conveniently held together by a little trough of sheet metal, into which they are either cemented with sealing wax, or clamped. The trough may be made to come at any desired part of the

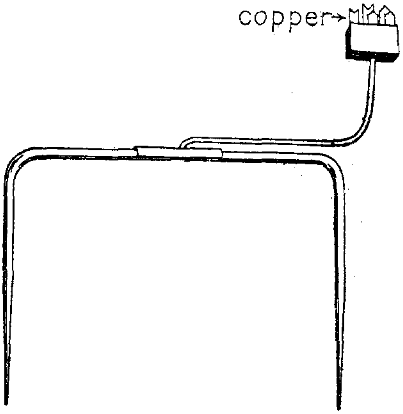

Fig. 5.—A glass inclosed thermoelement.

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[1] Compare the section on "General Law of the Inhomogeneous Thermoelement," II, 1, above.

[2] In *metal tubes* the bend is made after the wires are in, and have been tested for insulation, etc. The junctions, whether reinsulated or not, are protected from the tube by a wrapping of silk cloth. This inclosure becomes more desirable as the junctions become fewer, and the need for strength, greater.

With the *flat metal case* the idea is to diminish the lag by making the tube thin, and facilitate insulation by making it wide. The uninsulated junctions, staggered to horizontal portion, and may be used to assist in making thermal contact with a jacket.

In every inclosure the lag is diminished if the junctions are imbedded in paraffin. A fluid (xylol) was about equally effective. Naphthalin gave about half the lag of paraffin, and is therefore generally to be preferred in cases where a reduction of the lag is at all desirable. Otherwise, the paraffin is preferable, on account of its lower melting point and less volatility. Some idea of the effectiveness of different methods can be gained from Table I.

TABLE I.—THERMOELEMENT CONSTANTS.

The length in all cases was 50 cm. The *copper* wires were 0.15 mm. diameter (No. 35).

Diameter of constantan wires	0.26 mm. (No. 30)	0.47 mm. (No. 25)	0.47	0.26
Number of junctions	8	12	24	24
Total resistance	42	21	42	126
Diameter of element alone	2.6 mm.	4.2 mm.	5.2 mm.	..
Diameter of glass tube inclosure	...	5.8 mm.	7.0 mm.	5.9
Diameter of metal (brass) tube inclosure	3.3 mm.			
Lag, flat metal case, paraffin filling	0.9 sec.			
Lag, metal tube, paraffin filling	3 sec.			
Lag, glass tube, paraffin filling		9 sec.	12 sec.	
Lag, glass tube, naphthalin filling		5 sec.	7 sec.	5 sec.
Sensitiveness, microvolts per millidegree	0.3	0.5	1.0	1.0
Smallest temperature actually read	0.0003°	0.0002°	0.0001°	0.0001°
Water equivalent, 9 cm. immersion	0.8 g.		1.7 g.	

The required depth of immersion was investigated by putting both ends of the element in a stirred bath at room temperature, with one end passing through a cup containing ice, just above the water. This method is convenient, but exaggerates the effect of conduction, especially for the smaller elements. With the thicker 24-junction glass inclosed element an immersion of 5.5 cm. (average—the uppermost junction was only

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keep them apart, are cemented in one or two layers on mica strips, which are thrust into the previously made and tested end cases; the middle portions of the case, including the bends, are then soldered together around the wire. Of the three, this type of inclosure is the most troublesome and most liable to leakage of water, but has a lag and a required depth of immersion which are very low in proportion to the number of junctions.

4 cm. under) reduced the effect of heat conduction on the reading to less than 1/50,000 of the temperature difference between bath and ice.

With the 8 junctions in 3.3 mm. brass tube an immersion of 4 cm. reduced the effect of the ice to 1/4,000 the temperature difference.

4. Curvature of the Bend.—The two bends in the thermoelement of Fig. 5 will often be conveniently located just above the calorimeters, and hence in the temperature gradients. The bends must therefore not be so sharp as to materially affect the thermoelectric power of the wire by the strains produced. Just how sharp they may be without detriment has not been determined, and information on this point would be very welcome, but we have found no perceptible effect from a curve with a radius of 2.5 cm. in No. 30 wire (0.25 mm. diameter), so that this degree of curvature, at any rate, may be considered safe.

5. Terminals.—A precision thermoelement should, by all means, be divided into two equal parts, which can be connected in opposition. This gives a ready check upon temporary or permanent defects or changes in the element itself, upon defects of insulation during the construction, and upon the presence of parasitic electromotive forces in the leads outside the zero adjusting switch at the potentiometer. A convenient arrangement of terminals for this purpose, applicable also when the two halves are in separate cases, is shown in Fig. 6. When A^+ and B^+ are the terminals, with B^- and the second A^- joined, the two halves A and B are in opposition; the series arrangement has A^+ and B^- as terminals, with B^+ connected to the first A^-. The arrangement lends itself well to the use of leaves of copper as terminals, which is probably the scheme best combining simplicity with great freedom from thermal forces.

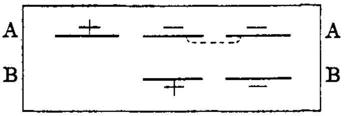

Fig. 6.—Diagram of the arrangement of thermoelement terminals.

It is well also to add another terminal so connected that 4 or 8 junctions can be read when desirable.

In our own work the thermoelement is checked up, by reversal, at the beginning and end of each day. The operation, which takes less than a minute, gives a guarantee of the integrity of the thermoelement and its insulation, and of the auxiliary switches as well. The divided thermoelement is also an ever ready auxiliary for quickly verifying the condition of the potentiometer. For this purpose one or more stationary or steadily changing temperatures are read with the whole element, and also with one-half of it. One reading, plus or minus the difference of the two halves, which is also observed, should be twice the other. Any accidental change or deterioration in the potentiometer coils used would almost certainly be indicated by a failure of this relation. It does not seem a very convenient method for a complete calibration of the potentiometer.

If the thermoelement is to be wholly within the calorimeter jacket, or if it is to be protected by the sheet copper shield of Section 2*b*, in either case the terminals are best not mounted directly upon the case. They may be situated as in Fig. 5, on the end of a slender tube, which is brazed to the sheet metal trough and carries the leads, or they may be at the end of a cable, a meter long or more, made by wrapping the leads with tape, inclosing with the leads a stout cord, a little shorter, for mechanical protection.

IV. Calibration and Testing.

A multiple thermoelement can be calibrated easily and with great precision by comparison with another thermoelement. Of course some thermoelement must have first been calibrated by another method, but this is a service appropriate to the national standardizing laboratories.[1]

All thermoelement calibration can be left to these laboratories wherever that seems desirable, but the secondary calibrations are so easy that they may often profitably be done by the individual experimenter. The checking, testing, or comparing of thermoelements also involve the same principles and precautions as the calibrating.

1. The Precision of the Calibration.—The calibration of an electrical thermometer differs from that of mercury thermometers and many other instruments in that the result can be expressed by a simple equation. It follows that in measuring temperature *intervals* the absolute effect of incorrect calibration will diminish with the interval; the proportional error will be the approximately constant magnitude. And hence, in *making* the calibration, where observations may be made at intervals of 5° to 10°, it follows (1) that the errors in electromotive force measurement will be quite negligible; (2) that errors from inhomogeneity and uneven bath temperature, which tend to increase with the temperature, though they may be noticeable, will still usually be negligible.

To illustrate: In comparing a thermoelement with a standard, dis-

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[1] In a recent paper whose authorship I shared ("The Calibration of Copper-constantan Thermoelements," *Phys. Rev.*, 31, 159 (1910)), it was assumed that thermoelements would usually need to be calibrated independently by their users, and therefore by some relatively disadvantageous method, and the supposed difficulty of independent calibration has elsewhere been accounted a very serious objection to the thermoelement. It now seems that whatever justification these views may once have had at any rate exists no longer. The resistance thermometer is unquestionably easier to calibrate independently, yet in spite of this fact the majority of the calorimetric resistance thermometers now in use in this country were calibrated at the Bureau of Standards. There therefore seems to be no reason why the thermoelement, which both stands transportation and keeps its calibration at least as well, should not be calibrated at a standardizing laboratory.

crepancies of 0.001° at 40° might sometimes be observed. It would generally be highly erroneous to conclude that the error of such a thermoelement would ever be 0.001° in calorimetric work. The error really indicated would be 25 per million, which is 0.0001° for a 4° interval, and correspondingly less for smaller intervals. If, secondly, the discrepancy of 0.001° should occur during the process of calibration, so that observations at (say) 30° and 40° failed to correspond, the calibration would be out by (in this case) one part in 10,000 through the 10 degree interval between 30° and 40°. In most calorimetric determinations, which involve intervals much less than 10°, the actual error due to the incorrect calibration would thus be much less than 0.001°.

In nearly every case, however, even if a discrepancy of 0.001° should be observed, the occurrence of any such discrepancy during calibration would be very improbable. For such discrepancies, when not due to irregularities in the bath temperature, are caused by a shift—usually a considerable shift—in the position of the temperature gradients. Observations, therefore, which are made with an unchanged depth of immersion and an unaltered ice bath are likely to be quite free from appreciable calibration error. The fact that the consistent series of observations may be 0.001°, or 25 per million, higher or lower than another possible set, is of no importance in calibrating for calorimetric work. Discrepancies, then, observed in comparing thermoelements, are of no importance unless they approach 0.001° in magnitude[1] and unless they also occur during constant conditions as to depth of immersion and arrangement of the bath. In such a case either the portion of the thermoelement used for a gradient, or else the comparing bath, is unsatisfactory.

What has just been said applies to the comparing of a thermoelement with any standard. The comparison against another nearly equal thermoelement has three special advantages:

(1) Only one reading, the difference between the two thermoelements, needs to be made with maximum precision. If the two differ by 1%, the actual temperature needs to be read with only about 0.01 the precision of the differential reading.

(2) The most precise reading is of a small magnitude, and is therefore especially easy to secure, as far as the potentiometer system is concerned.

(3) The constancy required in the bath temperature is less than in a comparison of separate thermometers.

2. *The Bath for Comparing Thermoelements.*—The ease and precision with which thermoelements can be compared are much more likely to

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[1] This is on the assumption that a final precision of 0.1 per mille is desired. For a less precision a greater tolerance is of course possible.

be realized with a suitable bath.[1] A simple but efficient bath has been made from a tall vacuum jacketed bottle of one liter capacity. The heater is four or five turns of No. 25 silk insulated constantan wire, so coiled that after being fed into the mouth of the bottle it expands and lies against the sides. The stirrer with its tube (supported by a retort stand clamp) is the only other thing required. The tube is long and well centered in the bottle, with the propeller at the bottom. The shaft is inclined slightly in the tube, so as to be near its side at the top, thus giving more space for the thermoelements; a partition surrounds the shaft so as to prevent the thermoelements from coming into contact with it, which might cause a false heating. The tube is wrapped with blotting paper, so as to increase the thermal separation between the ascending and descending columns of liquid. (The current should of course be upward in this tube.) It appears probable from our experience, and also from a consideration of the physical actions involved, that the stirring may easily be too vigorous, and that it should never furnish nearly as much heat as the heating coil, for that is equivalent to putting a considerable part of the coil directly in the tube at the bottom—a thing which no one would think of doing. By the use of a few cork pulleys, very easily and quickly made, the speed of stirring is made to vary with the temperature elevation.

3. Tests Preliminary to the Calibration.—(From here on the calibration of one thermoelement against another will be the only case considered, and 24 couples will be assumed.)

Two sources of error are to be considered in calibrating: the discrepancies in reading discussed in Section 1, and the effect of differences in the lag of the two thermoelements. It is well to determine in advance the possible magnitude of these two errors; this may save many unnecessary precautions, and will make more certain the value of the results.

The effect of a difference in lag of course depends on the rate at which the bath temperature is changing. It will probably be simplest not to determine the lag as such, but to find at once the relation of rate to error. If, for instance, a change in bath rate of 20 microvolts per minute (say, a change from +5 to —15 per minute) should produce a change of 0.2 microvolt in the differential reading for the same centigrade temperature, then for any rate under 5 per minute the effect on the differential reading would be less than 0.05 microvolt. The rate can easily and

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[1] In a previous paper a very simple and satisfactory electrically heated comparing bath was described ("The Thermoelement as a Precision Thermometer," *Loc. cit.*, p. 147) whose essential features were extreme symmetry and an upper chamber kept a very little hotter than the rest. This bath, which was packed in cotton wool, was rather slow in settling down to a constant temperature. This made its operation rather tedious with elements of large lag, for whose accurate comparison a nearly constant temperature is desirable. Accordingly, the present bath has been substituted.

quickly be made small enough by a little regulation of the bath heating current,[1] and should be measured for each determination.

The discrepancies in thermoelement readings, whether due to inhomogeneity or to uneven bath temperature, will vary as the thermoelements are moved, and especially as they are moved up and down. It is therefore possible to estimate very quickly how great are the discrepancies to be expected during the calibration. In making such estimates, it is probably safe to consider that the effective level of the calibration bath will not vary, as a result of temperature change alone, by more than 1 cm., and the addition of a copper collar around the thermoelement will make the gradient still more constant in position.

If more definite information as to the quality of the thermoelement is desired it can be satisfactorily obtained as follows: The thermoelement is clamped by the middle at such a height that two vacuum-jacketed bottles, full of ice and water, can be moved up and down while they surround the vertical ends. The gradient at either end can thus be shifted up and down without making any other change. By clamping a trough of sheet metal under the horizontal part of the thermoelement, and piling fine ice in this, the gradients can be extended around the bends and along toward the center. In one instance the effect of a shift in the ice level was practically complete in 3 minutes, in a glass-inclosed twenty-four junction thermoelement, when the gradient was moved upward.

4. Conduct of a Calibration.—In comparing thermoelements, the simplest way to treat the cold junctions is to put them in an ice bath, and this is quite accurate enough for all ordinary purposes. The bath should be adjusted 15 minutes or so before being used, and should not be stirred or disturbed during a series of observations, except that the ice melting at the top should be replaced, and the level kept as constant as possible.

With the ice bath in use it is necessary to read only (1) the total electromotive force of one of the thermoelements and (2) the difference between their readings, differentially. The total electromotive force readings, made at regular time intervals, give the bath rate. As soon as this has been made small enough, the differential reading is taken. This reading and the *corresponding* total electromotive force are the necessary data for that temperature. Since the total E. M. F. observations need be accurate only to 5 microvolts, while the bath rate must usually be less than 5 microvolts per minute, observations taken within a minute of each other will correspond sufficiently, so that the observing of two different electromotive forces presents no difficulty even with very simple potentiometer arrangements. It will save considerable work in the calculations if the data correspond to round numbers of microvolts of the total E. M. F. of the thermoelement undergoing calibration. This

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[1] A quick and convenient method, also, is to change the heating current so as to reverse a rather slow rate, and then read during the minute or two of nearly constant temperature which occurs as the rate passes through zero.

does not necessitate bringing the bath within 0.005° of the round value; it is sufficient to observe within 0.1° of it and apply a correction, or interpolate between readings on both sides. The ratio of the differential reading to the total E. M. F. may usually be taken as constant over 0.5°.[1]

5. Getting the Working Table from the Calibration Data.—The E. M. F. of most thermoelements between 0° and 100° can be expressed with high precision by a cubic equation with temperature as the independent variable, and still better by an exponential equation,[2] so that there is no difficulty in getting a complete calibration which has all the precision of the observations and the standards used. This, however, is in practice mainly a question for the standardizing laboratories, since the thermoelement user will want tables in which E. M. F. is the independent variable. No advantageous formula has yet been found for making such tables, so that the best way to get them is probably to apply small corrections to a suitable preexisting table.[3] The best preexisting table to use will generally be one derived for another thermoelement, since the differences are then most likely to follow a simple law.[4]

A good method for making the corrections is in detail as follows: It has been suggested above that the calibration points be, by an easy interpolation or otherwise, found for round values of the E. M. F. of the thermoelement calibrated. The differential readings, added to (or subtracted from) these, give the corresponding values for the standard, from which the true temperatures can of course be found. If, now, the microvolt readings E_1, E_2, ... , of the calibrated element, are taken to the preexisting table (which may be the table for the standard), tempera-

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[1] This value is calculated on the assumption that the two thermoelements differ by 1%. If the difference is greater or less than this the *safe* limits of an assumed constant ratio will change about in inverse proportion.

This nearly linear ratio may be taken advantage of to obtain a method of calibration in which the ice bath is avoided, and greater certainty thus obtained. The cold junction is put in a gently stirred bath in a vacuum-jacketed bottle, which is kept nearly constant by immersion in a thermostat, or which may be in any bath which never differs from it in temperature by more than 0.2°. A correction for the slight possible temperature variations in the bottle is readily made by using the linear ratio of electromotive force to electromotive force difference over the small intervals involved. The temperature of this bottle is accordingly measured, but with a precision which need not be better than 0.003°.

[2] L. H. Adams, "A Useful Type of Formula for the Interpolation and Representation of Experimental Results," *J. Wash. Acad. Sci.*, 3, 469 (1913).

[3] R. B. Sosman, "The Platinum-Rhodium Thermoelement from 0° to 1755°," *Am. J. Sci.*, [4] 30, 1 (1910); see also L. H. Adams, "Calibration Tables for Copper-Constantan and Platinum-Platinrhodium Thermoelements," This Journal, 36, 72 (1914). The present method, however, is in detail somewhat different from that of Sosman.

[4] Such a table, consistent to 0.00001°, has been derived, and will soon be placed at the disposal of the users of thermoelements.

ture readings θ_1, θ_2, ... will be obtained, which are not the true temperatures, since the table was not made for the *calibrated* element; but the differences between these and the true temperatures θ_1', θ_2', ..., added to the numbers in the table, will evidently give tabular values which *are* true for the calibrated element. This gives values for the temperatures taken in the calibration. To get values for other temperatures, parabolas are derived, giving the differences $\theta_1' - \theta_1$, $\theta_2' - \theta_2$, ..., in terms of the E. M. F.'s, E_1, E_2, ..., and from these parabolas other values of $\theta' - \theta$ are obtained. Since these values are derived from a smooth curve, any errors in using them will diminish with the interval measured. Experience shows that if the original intervals are 10° the maximum error introduced by assuming the absolute correctness of a parabola will not exceed 0.0002° in 5°, which is a little larger than the probable proportional error due to the calibration, but further experience may very likely reduce this limit. If the original observations are at intervals of 5°, the error in the parabolas is quite negligible. Hence a five-degree interval must, for the present, be considered the best in calibration, unless the two thermoelements differ by less than 3 per mille, when a ten-degree interval is quite sufficient.

In calculating thermoelement tables the calculations should be carried out to a precision somewhat greater than is to be used in reading the thermoelement, even if this precision is considerably better than was reached in the calibration observations, because the error due to the calibration observations will decrease with the interval measured, so that for small intervals the needless errors due to insufficient carrying out of the reckoning might be the largest present, unless these are made less than the error of reading.

6. *Working Tables.*—With a 24-couple copper-constantan thermoelement it is possible to have a calibration table which though short (and therefore easily constructed), yet gives a very easy interpolation. This possibility arises, first because the ratio of E. M. F. to temperature is nearly constant, and second, because the unit of measurement, the microvolt, corresponds very closely to a decimal submultiple of a degree, namely a thousandth.[1] This is illustrated in Tables II and III. Table II is a small portion of a table of an actual thermoelement, arranged with 100-microvolt intervals, that is, with only 10 steps per degree. Table III is the same, written so as to give the number of millidegrees which must be added to the number of microvolts in order to give the true temperature. Here the difference is only about 0.0027°, so that the interpolation is easy. (The ease of interpolation can also be readily secured in using Table II, but is more apparent in Table III.)

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[1] The possibility, therefore, may occur with the resistance thermometer, since this may be made to have the same two properties.

TABLE II.		TABLE III.		TABLE II.		TABLE III.	
Microvolts.	Degrees.	Millidegrees minus microvolts.	Diff.	Microvolts.	Degrees.	Millidegrees minus microvolts.	Diff.
8000	8.29720	297.2		8500	8.81082	310.82	
			2.78				2.65
100	8.39998	299.98		600	8.91347	313.47	
			2.73				2.62
200	8.50271	302.71		700	9.01609	316.09	
			2.73				2.61
300	8.60544	385.44		800	9.11870	318.70	
			2.70				2.59
400	8.70814	308.14		900	9.22129	321.29	
			2.68				2.57
8500	8.81082	310.82		9000	9.32386	323.86	

7. *Measurement of Intervals.*—The ease and precision of the whole system of calorimetric measurements described in the present series of papers depend, to a considerable extent, on the fact that changes of temperature, not temperatures, are the subjects of the more accurate observations. The cold junction temperature, therefore, if constant, need not be known with high precision, for it is added both to the initial and to the final reading of the calorimeter thermoelement, and its errors disappear in the resulting subtraction.[1] The ratio of microvolts to degrees, however, in copper-constantan, changes about 0.002 per degree, hence on this account the cold junction temperature must be known to 0.05° for a precision of 0.0001, and correspondingly for other degrees of precision. This requirement is easily met—by means of a moderately good mercury thermometer, for instance. If the cold junction temperature is measured in degrees, it must, of course, be reduced to microvolts before being added to the thermoelement readings. This reduction needs to be correct only to 50 microvolts or so.

Summary.

Inhomogeneity, once a serious foe to precision in thermoelements, and still often supposed to be such, can, without difficulty, be rendered practically negligible in copper-constantan thermoelements used for any precision up to 50 parts per million. Such thermoelements, accordingly, may, except for imperfect insulation, easily preventable, be free from all appreciable errors other than those (such as incomplete depth of immersion) which are possible with all thermometers. To attain this freedom from error the wire used must be tested, and the essential though easily satisfied requirements peculiar to a thermoelectric system must be observed. These this paper attempts to consider in detail, and it also describes simple but important details regarding the operations of construction, insulation, inclosure, calibration, etc., of the thermoelements.

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[1] One feature of the system is a provision for eliminating the effect of *change* in the cold junction temperature; this is treated in a subsequent paper.

Constantan wire for thermoelements has been so far improved that continuous lengths are frequently obtainable which vary (in electromotive force against copper) less than 0.0002, making sensitive thermoelements with errors usually less than 20 per million.

The testing of wire enough for a thermoelement of maximum sensitiveness takes but an hour or two, with simple apparatus.

On account of the ease with which thermoelements can be constructed, the more sensitive combination of several couples is generally preferable to a single couple, even for cruder measurements.

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EASY CALORIMETRIC METHODS OF HIGH PRECISION.

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In calorimetry by the "Method of Mixtures" a precision of 1 per mille appears to be generally counted excellent. It scarcely deserves, however, to be considered high at the present time. Calorimetric precision depends more on the adequacy of the apparatus than on any special skill exercised by the observer, and it has been found that appropriate apparatus and methods are easily attainable which will yield a precision approaching 0.1 per mille with little more labor than is needed to get 1 per mille with some customary arrangements.[1] It is true that 1 per mille appears in most cases to be quite sufficient. Errors in associated temperatures or defects in chemical purity are often such that a higher calorimetric precision would be of comparatively little value. Nevertheless, there are cases where a higher precision is desired, and these will doubtless increase with the general progress of science; often, too, the associated measurements or the chemical purity attained have probably really been governed by the limitations of the calorimeter, and would readily be improved if greater calorimetric precision should appear less difficult to get; finally, there are many determinations where, though high relative precision may not be desired, yet high absolute precision is necessary on account of an unavoidable small temperature interval (in measuring heats of dilution, for instance). A relative precision of from 1 to 0.1 per mille, and an absolute precision of from 0.001° to 0.0001° are therefore of interest, and these are in view in the present paper.

Precision in calorimetry depends first upon the temperature measurement, and second upon the determination of the heat which escapes and is determined indirectly. The control of the heat losses has been made not only sufficient for the highest precision but convenient, owing mainly

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[1] One-fiftieth per mille has been reached, under specially favorable conditions.