ON CONSTRUCTION OF PLATINUM THERMOMETERS AND OF RESISTANCE COILS

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While zeros of platinum thermometers are generally much steadier than are those of mercury-in-glass thermometers, nevertheless the most serious difficulty in work of high precision is the zero shift. Such observed shifts may be due to many different causes. For example; (a) to shift of lead resistance with temperature or handling, (b) to shift of insulation resistance, (c) to shift of reference coils resistance, and (d) shift in resistance of the thermometer coil itself.

Causes (a) and (b) can be located with certainty and eliminated by well known methods. In this connection it might be emphasized that lamp cord is a very unsuitable material for such leads. But (c) and (d) are very difficult, indeed, to separate. In fact, what one observes always is the difference between shifts due to these two causes. Approximate separation of the shifts may be obtained by imposing temperature excursions on the thermometer, so that the time for which it is away from the reference temperature is short. This is limited to the detection of shifts in the thermometer due to temperature change. Secular shifts are also important and here the only means of separating and measuring is by reference to a non-varying resistance. The proportional variation involved in thermometer work, say for 0.001°C at room temperature, is of the order of 3 parts in a million which is probably beyond the limit of steadiness of the best standard resistances.

The causes of resistance shift of reference coil and of thermometer coil are necessarily very much alike. They may be summarized thus: (a) gradual relief from mechanical strain due to previous handling, (b) both imposition of and relief from strain during use, (c) changes in the composition of the resistance

- material from the outside as oxidization of the surface of the resistance wire, or attack by acid in the bath liquid, or contamination of the platinum wire by silicon or metallic vapors, (d) changes in the internal character of the material due, for example, to crystal growth, or to concentration changes of solid solution and so on.

Cause (a) is usually met by annealing at a temperature well above that at which the coil is to be used. This may be made fully adequate for the Pt coil by heating electrically in air. For the resistance wires, usually manganin, this is difficult to do on account of oxidization of some components in the wire which not only changes the total resistance but also its temperature coefficient. It is undoubtedly one of the principal causes of resistance shifts in newer coils and may easily remain of very objectionable magnitude over the time for which such coils are used.

Cause (b) is one of the main reasons for shift of resistance of both coil and thermometer. Thus standard resistances are wound embedded in shellac, on a metallic cylinder. The coefficients of expansion of the wire, of the shellac, and of the cylinder are all different. The result of temperature change is to impose strains on all the parts and these may or may not remain entirely elastic. If any permanent deformation occurs anywhere, it will show itself by a shift in the resistance when the reference temperature is again attained. It is easily conceivable that the readjustment of the resistance to the reference temperature state might take time and the resistance therefore drift for hours or days.

Or consider the standard method of construction of platinum thermometers.¹ The wire is wound in notches on the edges of 4 mica strips, so that it makes a square. It is wound tight at room temperature. A rise in temperature allows the wire to become loose on its support, in annealing for instance, and on cooling it grips the points of support again. If it has shifted on the support any minute amount, the bends have to accommodate it, that is, the wire is being continually re-strained. Experimentally, it was found that a wire wound in a thread cut in a nonconductor was

¹ See Summary by T. S. Sligh, Bur. of Stand. Sci. Paper, No. 407.

even worse in its erratic zero shifts, which is to be explained in the same way.

These conditions require that for the platinum thermometer, the wire be supported in such a way as not to strain it either from handling or from temperature change. As the wire must be of very small diameter to give the required resistance the supporting points must be close together. On the other hand, the support must not be a constraint. Some experimental work which the writer has had under way for years required the measurement of small differences of temperature at not exceeding 300°C . The difficulties encountered led to much experimental work. The following procedure for the construction of a thermometer for this range is a summary of this phase of the work.

A spool of metal for carrying four strips of mica is constructed as in Fig. 1, which shows, also, cross sections at the important

FIG. 1

places. The dimensions used are set by the space and resistance requirements. A cylinder of 3-4 cm long and 5 mm diameter can carry a meter of 0.05 mm platinum wire having about 50 ohms resistance at 0°C . The narrow and thin strips of mica are slipped into the radial slots of the spool bc, so that the outside edge of the mica is about flush with the cylinders. The strips need support over their length by the slots in the central rod. A light prick with a center punch beside the slot on the cylinders b and c will hold the mica in the slot during handling. The cylinders b and c have four holes, alternating with the slots, as indicated in the figure. Pieces of platinum wire about No. 20 and 2-3 cm long are covered with lead glass fused on to let it slip into the hole in "a" up

to a knob at one end. A little ring of the lead glass is slipped over the wire and fused on using a small pointed flame, with the result shown at "a." By crowding the soft glass close to the brass it is possible to leave very little play. Four such leads are each silver-soldered to a copper wire long enough to reach out of the thermometer case. These are then bound together while the coil itself is constructed. The four leads thus make a very substantial support for the spool carrying the thermometer coil with very little chance for straining the fine wire.

The spool bc with the mica strips in place is cast in wax, forming a cylinder out as far as the edges of the mica. Half beeswax—half resin is a suitable wax. This cylinder is turned down in the lathe till the surface is slightly below the ends of the spool. A double thread is cut in the wax and mica with a very pointed threading tool, the number of threads being determined by the length of wire to be carried and the diameter and length of the available spindle. It is possible to use 100 threads per inch successfully both in the cutting and subsequent use. It is, of course, not necessary that the space between the threads be cut to a sharp edge, but the groove must be sufficiently wide and deep to hold the thermometer wire securely.

The compensating lead connection of the fine platinum wire is put in first. It is led through the hole in cylinder b around a semi-circumference and back to the diametrically opposite lead. It is insulated from the metal around the holes by a thin tube of glass either fused down on the wire for its length through the hole, or only at one end to prevent it slipping along the wire. Care must be taken that the wire has slack enough not to be broken by whatever looseness the leads may have. This is only important during the handling as when the coil is in the protecting tube, the leads will be unable to move materially. It is possible to proceed here to the silver soldering of the fine wire to the heavier platinum leads but it is difficult to avoid some fusion of the wax. It is safer to seal the wire in place by bringing near the wax a warm point, and proceed to wind the main coil. The two ends of the wire are insulated and held in place, as for the short wire. The spindle is mounted in the lathe and the wire stretched in a loop from the two

fastened ends by a piece of thread tied to the loop, passed over a round bar and loaded with a weight of a few grams. The wire is annealed at a dull red heat by a suitable electric current. The two wires are then wound in the double thread with care to assure that the wires go well down into the groove and that no small shavings of wax support it irregularly. The wire near the end of the loop is caught in place by a hot point held near the wax, and the loop is then fastened at leisure by a piece of the same platinum wire passed through a fine hole bored through one of the mica strips.

All four wires are then silver soldered to their respective leads with a fine pointed flame. The operation goes more readily if the leads have been prepared with a little silver solder on the end so it is only necessary to have the fine wire in contact with the fused silver to make the joint. A little silver solder may be readily transferred from another bit of platinum wire if necessary. The making of the four joints without fusing the wax seriously required some practice and care. The wax may be protected from fusing by holding the cylinder *b* in a vise and slipping a narrow piece of mica under the wire being heated. An oxy-gas flame may be made very small and yet give the required heat and hence does the best work. The making of these joints may be delayed till the wax is removed, but the coil is then very easily injured. The wax is removed by a suitable solvent, hot turpentine serves well for the half-and-half and the turpentine can be removed by a volatile solvent like carbon tetrachloride.

The annealing just before winding assures that the coil will do no springing on removal of the wax. If it be now annealed by passing an electric current, the coil squirms all out of place. This may be entirely avoided by warming the coil gradually inside a hard glass tube by heating the tube with one or more gas flames. While hot a small current will make the wire incandescent and complete the annealing.

This results in a perfectly cylindrical coil with the wires as exactly spaced as the thread was cut. The wires are well supported at four points without any unusual bend at the point of support. Any adjustment due to temperature changes can result only in long radius bends which will not exceed the elastic limit. Ex-

perience over several years with such coils shows that they have very steady zeros, the steadiest in fact of any arrangement yet tried here. Any numerical statement of the zero shift is of little value since it is complicated by the unknown variation of the reference coils and of course though probably to a smaller extent, by the variability of the ice bath temperature.

Conduction along the leads may be minimized by threading the wire through holes in short metal cylinders which fit the case and are separated from each other by nonconductors. The leads are insulated from the metal cylinders by thin glass tubes. In between the metal cylinders these are made of much thicker glass and so serve to space the metal cylinders. The result is to improve the radial conductivity without affecting the axial, so that at each point the leads will be kept near the temperature of the material surrounding the stem. The 4 platinum-copper junctions are arranged to come in the middle of the first or second metal cylinder. These four junctions are thus held together in temperature even during changing temperature. These junctions are the main location of thermals in the circuit, and this arrangement excludes them practically completely. In the set-up used by the writer for years there are no erratic motions of the light spot with a galvanometer sensibility of 10^{-9} , and almost no zero shift. It should be added that the galvanometer circuit in the bridge is entirely copper (no brass binding posts) and is never opened: the bridge is operated by manipulating the applied potential and the slide wire contact is in the battery circuit.

The introduction of a metal spindle in the thermometer and of the metal about the leads, increases the heat capacity of the thermometer and therefore of the lag when measuring a changing temperature. Where the reduction of lag is of primary importance this type of construction may not be the best. In all cases the steadiness of the zeros is of primary importance for precise work and in many cases lag is quite secondary. It is these cases where this type of construction is particularly suitable.

It is evident that a similar type of construction should improve the steadiness of the resistance coils. The conditions are somewhat different, however. The coils can be made much larger and

longer before the size gives rise to difficulty. The manganin wire is very stiff and a very hard wax would be needed around which to bend the wire. The difficulty of preventing surface oxidization makes it desirable to use a much coarser wire. Coils were consequently built as follows.

Four grooves are milled out of a brass cylinder $\frac{1}{2}$ inch diameter and 5 inches long to give it the cross section indicated in Fig. 2a. These four grooves are filled with paraffin wax by slipping this cylinder inside a brass tube, filling with melted paraffin and after

FIG. 2

thorough cooling slipping the tube off by heating it rapidly. Four strips of mica are laid along the cylinder as indicated in Fig. 2b. The edges of the strips do not meet so that the wire when wound on does not have a complete cylindrical support but may spring in and out in each quadrant as required by the temperature conditions.

The wire is doubled for non-inductive winding and a copper wire hard soldered to the bend. This may be done with very little heating of the resistance wire by holding both wires together end on in clamps. A gas flame fed with a little oxygen enables one to heat the joint very rapidly and transfer the liquid solder from another wire with the minimum heating of the resistance wire—when done successfully less than $\frac{1}{4}$ inch of the resistance wire may show the effects of heat. The copper wire is passed through a glass sleeve inserted in a hole in a wing of the supporting cylinder as indicated in Fig. 2c. A sharp bend in the copper wire is sufficient to hold it. The ends of the resis-

tance wire are fastened in a similar manner by hard soldering each end to two copper wires, one to serve for fastening and the other as current lead.

The mica strips are bound in place with a series of ties of string or wire. The winding of the resistance wire is begun at the doubled end and the ties removed successively as they are replaced by wire. The paraffin is then melted and washed out by suitable solvents.

There is no need for covering on the wire if it be carefully spaced in winding. Also there is nothing in the construction to prevent the coil being heated to 400-500°C. With suitable vacuum protection this should be the best treatment. The procedure so far used has been to heat the coil to about 135°C for many hours in air in a space heated by boiling xylol. The surface of the wire becomes slightly discolored at this temperature which is therefore as high a temperature as one should use in the presence of air. After this treatment the wire still remains very stiff and will spring uncoiled strongly if unfastened. This is a good reason for thinking that this annealing is a long way from adequate and that a considerable portion of unrelieved strain remains in the wire. The resistance changes show also that considerable strain has been removed.

After annealing the coil is dipped in a good grade of shellac dissolved in pure alcohol, so as to make a fairly thick varnish. It is dried by holding a few hours at near 100°C. This gives a comparatively thin coating of shellac, hardly sufficient to distort the wire materially. If the shellac penetrates between the wire and the mica it can produce scarcely any strain. Nor can the change of hygroscopic condition of the shellac produce material changes in the strain.

To minimize any effect of moisture as well as to protect the wire from mechanical injury it is best to enclose each coil in a container with acid-free dry kerosene as indicated in Fig. 2. The leads are insulated from the container by mica disks under the nuts and a glass sleeve in the holes. The whole joint is set in fused shellac which is also fused on over the outside finally. The stout copper leads have small holes bored into them axially at the coil

ends and the copper leads from the resistance wire are soft soldered in these holes using resin dissolved in pure alcohol as flux. The brass cylinder is slipped on and soft soldered together with an iron using resin. The kerosene is put in through a small hole in the bottom which is finally closed with a lump of solder. The stout copper leads can be used for supporting the coils.²

Experience with such coils shows them to be materially better in steadiness than the older form. But there still remains relative variation of such a size as to be distinctly objectionable. The actual variation may easily be greater and it is these latter which come into the thermometer work.

The order of variation reached by many workers gives a fundamental interval constant to a few parts per 100 000, so that for this factor the accuracy is almost certainly better than any other associated physical measurement. But when one desires to read a small temperature difference to 0.001° or 0.0001°C the erratic or continuous variation from day to day makes such data very uncertain. This has been the writer's personal experience. Improvement in the steadiness of the system would increase one's confidence in the data very materially.

In this connection further work on manganin is very necessary. The writer has made up many coils with variations of many conditions, e. g., with and without shellac on silk insulation, with and without metallic calcium as a drying agent, oxygen and acid absorbing agent in the kerosene; on metal cylinders, or with four points of support, or without any support. Having no steady comparison resistance it has not been possible to conclude anything about the actual variation. There was always relative variation of a magnitude much greater than the limit of measurement and great enough to be very undesirable in thermometric work.

About the only experimental attack would appear to be the careful study of groups of coils made up in different ways till some means was found for reducing greatly the relative variation within a group. Differential treatment of members of the group would

² See this JOURNAL, 6, p. 175, 1922.

then enable one to judge of the effect of the different conditions. For example, how quickly does a manganin coil attain a steady resistance after a change of temperature. The writer has followed the steady drift of resistance of an iron wire coil for more than 24 hours after its resistance was changed by raising the temperature about 30°C for a short time. The change was of the order of 10^{-4} and large enough to render the coil absolutely worthless for its proposed use as a thermometer.

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