have made an analysis of this which gave the following composition after desiccation at 200°:

Alumina and iron	14
Soda	3.2
Water	2.6
Silica (by difference)	80.2

It is a very finely powdered quartz to which is added 10 per cent of clay, and diluted with a solution of silicate of sodium. To use it, the matter is diluted so as to form a thick paste, and the couple is dipped in it the required length, arranging the wires parallel to each other at a distance apart of about 1 mm.

The whole may then be dried and calcined very rapidly, without fear of snapping the covering, as would happen with clay alone; but this covering is not sufficiently impermeable to protect the couple against the very volatile metals, as zinc. It is better, in this case, to use small porcelain tubes of 5 mm. inside diameter, 1 mm. thickness of wall, and 100 mm. long, straight or curved, according to the usage to which they are to be put.

The couple insulated by asbestos thread, or by a small inner porcelain tube of 1 mm. inside diameter, as has been said previously, is pushed down to the bottom of the tube. If one has not at hand such tubes of porcelain, and it is required to make a single observation at a temperature not exceeding 1000°, as, for instance, a standardization in boiling zinc, one may use a glass tube. It melts and sticks to the asbestos, which holds a thick enough layer to itself to protect the platinum. But, on cooling, the tube breaks, and it is necessary to make a new set-up for each operation. This is not practicable for continuous observations.

Fused quartz is now obtainable for insulating thermocouples and for containing sheaths. This material gradually crystallizes and crumbles above 1200°, and in the presence of a volatile reducing agent, as graphite or hydrogen, volatile silicides are formed above 1200° C., which will destroy platinum. Some types of industrial mountings used by Heræus for platinum thermocouples are shown in Fig. 42.

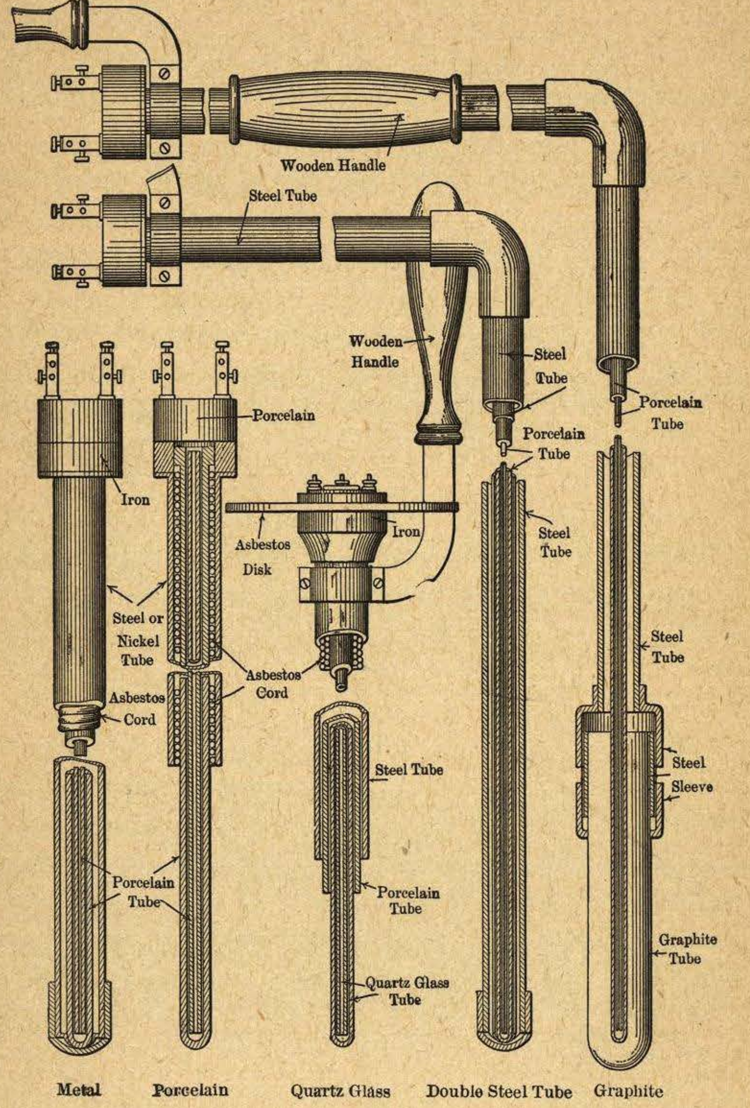

Fig. 42. Heræus' Thermocouple Mountings.

Cold Junction. — In general, in a thermoelectric element, one distinguishes the hot junction and the cold junction. The latter is supposed kept at a constant temperature. In order to realize rigorously this arrangement, three wires are necessary, two of platinum and one of an alloy connecting two junctions. This theoretical arrangement is practically without interest, and the second junction is always dispensed with. If, in fact, the temperature of the whole circuit exclusive of the hot junction is uniform, the presence or the absence of the cold junction does not affect the electromotive force; if this temperature is not uniform, the second junction is not advantageous, for there is then in the circuit an infinity of other junctions just as important to consider: the junctions of the copper leads with the platinum wires, those of the galvanometer leads and of the different parts of the galvanometer among themselves.

One must satisfy himself as well as may be as to the uniformity of temperature in the cold circuit, and rigorously of the equality of temperature between corresponding junctions, particularly those of the two platinum wires with the copper leads. These uncertainties in the temperature of the cold junctions are an important source of error in the measurement of temperatures by thermoelectric couples, but for ordinary practice they are easily eliminated. In order to realize exact measurements, precise to 1°, for instance by the galvanometer method, it will be necessary to have completely homogeneous circuits, including the galvanometer, with the single exception of the junctions of the platinum wires with the conducting leads; these should be immersed in the same bath at constant temperature. It would be necessary for this that the constructors of galvanometers limit themselves to the use of the same kind of wire for all parts of the apparatus, wires of the coil, suspending wires, leads, and parts of the coil. That is difficult to obtain.

In the standardization of thermocouples for exact work, it is customary to immerse the cold junctions, i.e., the points of contact of the copper leads and platinum-metal wires, in an oil bath in ice. With the potentiometer, irregularities due to other sources of E.M.F. in the circuit are eliminated by reversing simultaneously the battery current and the couple circuit.

The Cold-junction Correction. — In work of high accuracy with platinum couples and when the potentiometric method of measurement is used, the cold-junction correction should be experimentally eliminated by keeping the cold junctions at a constant temperature, most conveniently at 0° C.

When the galvanometer method is used, it is often not convenient to keep the junctions of the couple to the lead wires of the galvanometer at a definite temperature, although the galvanometer itself may be so removed from the furnace that its temperature changes are slight. Except in the roughest kind of work, allowance has to be made for the cold-junction temperatures, which may be measured by an auxiliary thermometer.

Calling t_0 the cold-junction temperature for which the instrument reads correctly, t the observed temperature of the cold junction, the correction to apply to the observed temperature readings of the galvanometer, otherwise supposed to read correctly for a given thermocouple, usually lies between $\frac{1}{3}(t - t_0)$ and $(t - t_0)$, depending on the type of couple and the temperatures of both hot and cold junctions. This question has been treated in detail for several types of couple by C. Otterhaus and E. H. Fischer.

That this correction depends in general upon both hot and cold junctions is due to the fact that the E.M.F.-temperature curve is not a straight line (see Fig. 24). The correction factor by which to multiply $(t - t_0)$ is numerically equal to the ratio of the tangents of this curve for the hot- and cold-junction temperatures.

As an example, we may compute the corrections to apply for a Pt, 90 Pt-10 Rh Heræus thermocouple using the E.M.F. data of Day and Sosman (page 114).

CORRECTIONS FOR COLD JUNCTION (Pt, 90 Pt-10 Rh).

Temperature of hot junction.	Correction factor for cold junctions near:		
	0°	20°	40°
100° C.	0.76	0.81	0.86
200	.65	.68	.73
300	.60	.63	.68
400	.57	.61	.65
500	.55	.59	.63
600	.54	.57	.61
700	.53	.55	.59
800	.51	.54	.57
900	.49	.52	.55
1000	.48	.50	.53
1200	.46	.49	.51
1400	.45	.48	.50
1600	.45	.48	.50

It is to be kept in mind that the E.M.F. indicated by a direct-reading galvanometer is a measure of the difference in temperature between the hot and cold junctions. If the galvanometer needle be set at zero, which is a convenient way of working, this zero reading will correspond to the temperature of the cold junction at the start; therefore the true temperature is obtained by adding to the observed temperature reading a quantity corresponding in millivolts to the cold-junction temperature, obtained as already explained. The starting point t_0 in the above is of course the temperature at which the cold junctions were kept during the original calibration, often 0° or 20° C.

Thus, if the cold junction is at 25° C. and the hot at 500°, this correction, from the above table, is $+0.60\,(25 - 0) = +15°$, if the couple was calibrated from 0° C., and the galvanometer read zero for a cold-junction temperature of 25°.

It is a simple procedure, and usually sufficiently exact when the temperature scale of the galvanometer corresponds approximately to that given by the thermocouple, to set the pointer of the galvanometer at the position on its scale corresponding to the temperature of the cold junctions. The readings of the galvanometer, otherwise corrected, will then give temperatures.

Elimination of Cold-junction Changes. — The Bristol base-metal thermocouples are provided with extension pieces of the same composition as the fire end, permitting the cold junction to be removed to a place of slight temperature change, as near the floor, and this arrangement also facilitates the convenient renewal of the short, heavy fire ends of these couples when they have to be discarded.

Bristol has also devised an automatic compensator for cold-end temperatures, shown in Fig. 43, consisting of a small glass bulb and capillary tube partially filled with mercury, into which a short loop of fine platinum wire dips. This is inserted in the thermoelectric circuit close to the cold junction. Changes in temperature cause the mercury to expand or contract, cutting in or out resistance in the circuit. This acts in opposition to the change in E.M.F. with temperature at the cold end, so that a balance may be established if the parts are properly designed.

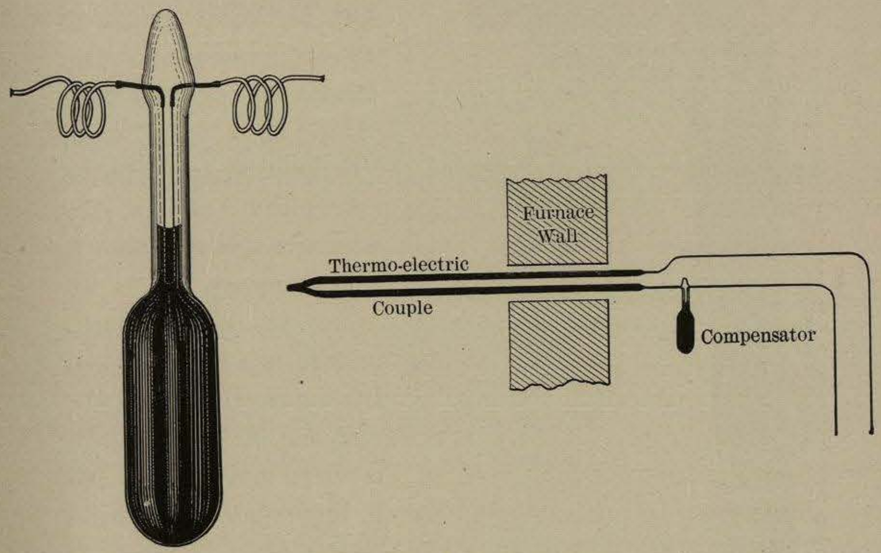

Fig. 43. Bristol's Compensator.

In the Thwing instruments, the elimination of the temperature variations of the cold ends of the couple, where they can be brought close to the galvanometer, is affected by a device consisting of a compound strip of two metals having unequal coefficients of expansion, so attached to the spring controlling the pointer that the reading of the galvanometer when no current is flowing is the temperature of the surroundings.

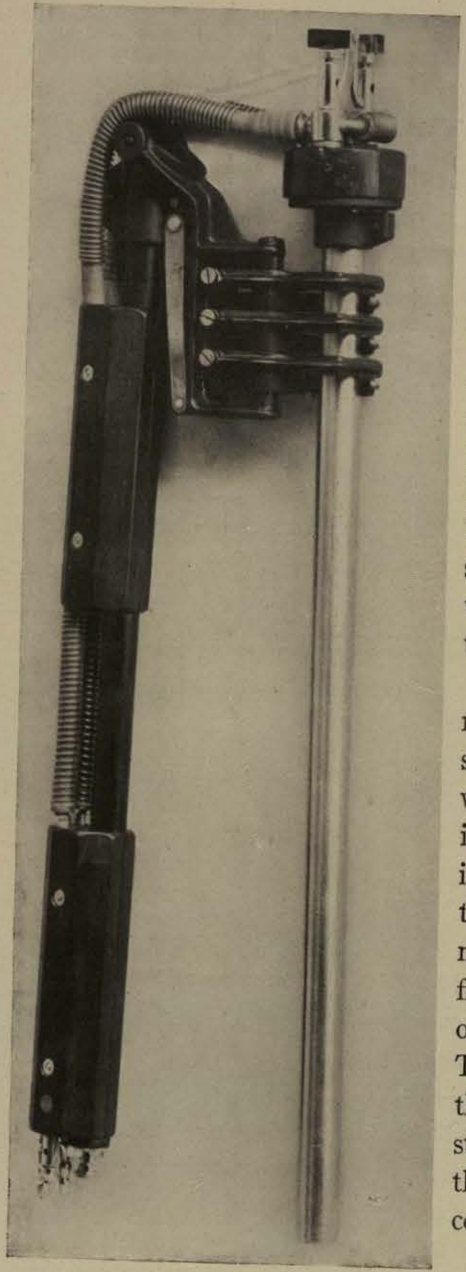

Fig. 44. Water-jacketed Cold Junction.

In many industrial establishments running water of practically constant temperature is available, and the cold end of the thermocouple can then be water-jacketed and so kept sufficiently constant in temperature, as shown in Fig. 44, which represents an arrangement for this purpose as constructed by Hartmann and Braun. The movable arm can be swung out horizontally when the thermocouple is to be immersed.

Paul provides an attachment by which an inexpensive supplementary couple, with one end water-cooled, is placed in series with and in opposition to the main thermocouple by means of nonreversible plugs which fit into sockets in the head of the pyrometer cane. The temperature difference then indicated by the instrument is that between the fire end and water-cooled end.

A Breguet spiral, to which one end of the control spring of the millivoltmeter is attached, has been devised by C. R. Darling and

sold by Paul. In this way the zero of the instrument is made to vary with its temperature.

The Crompton Company provide their instruments with a multiple scale (Fig. 45), which allows for the cold-junction temperature variations.

Finally, the cold end of the thermocouple may be buried in a box underground, for instance, and copper wires run to the galvanometer. We shall mention other such devices under the heading "Compound Thermocouples" and when discussing accessories to recorders.

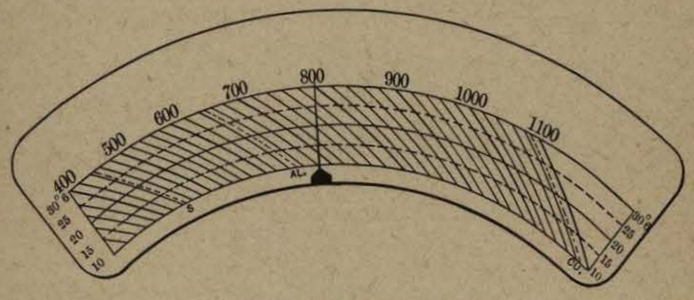

Fig. 45. The Crompton Scale.

Constancy of Thermocouples. — This matter is of the greatest importance in thermoelectric measurements both in the laboratory and in the works, as there is nothing more aggravating than the gradual deterioration of a product due to insidious, and often unnoticed until too late, changes in the controlling apparatus.

The behavior of thermocouples made of platinum and its alloys has been studied in great detail, from this point of view, by several observers, but the data are somewhat contradictory.

If a thermocouple, however well protected, is heated for a long time at a high temperature, its E.M.F. will change. It is well for accurate work to have at least two thermocouples, one of which is kept as a standard and only occasionally heated, and never above 1200° C. In this way changes in the couple ordinarily used may be readily detected. Holborn, with Henning and Austin, has made a very complete study of the effects of continued heating in various atmospheres on the loss of weight and changes produced in electric and thermoelectric properties of the platinum metals. The following table shows the results of continued heating in air on the E.M.F. of the platinum couples ordinarily used:

EFFECT OF PROLONGED HEATING ON E.M.F.
E.M.F. AGAINST PT IN MICROVOLTS.

Duration of heating, hours.	90 Pt – 10 Ir.			
	700° C.	900°	1100°	1300°
0	....	......	16,540	19,740
3	9460	12,450	15,450	18,530
6	9160	11,930	14,780	17,640
8	8840	11,560	14,300	17,050
	90 Pt – 10 Rh.			
	800° C.	900°	1000°	1100°
0	7230	8340	9480	10,670
3	7250	8380	9510	10,690
6	7270	8400	9540	......
9	7280	8410	9540	10,720
12	7290	8420	9550	......

This investigation shows that the E.M.F. of a couple, and thus the indicated temperature, changes with continued heating, very considerably for a Pt-Ir couple and about 0.5 per cent for a Pt-Rh couple for ten hours' heating. The change is greatest during the first part of the heating. The observed increase in E.M.F. of the Pt-Rh is difficult to explain unless it be due to distillation of iridium from the heating coil, as shown from Day and Sosman's work. Before use, a thermocouple should be annealed by passing a current through it at a white heat, when future changes will be slight if used in an oxidizing atmosphere. This annealing also will restore to very nearly its normal value the E.M.F. of couples which have been in contact with silicates.

Changes in temperature distribution along the wire may also affect the apparent electromotive force of the couple, causing

apparent changes in temperature as great as 20° at 1000° C. with some wires. The less homogeneous the wires the more marked is this effect. In the most exact work, therefore, the same conditions of immersion must be followed throughout, or the resulting changes in E.M.F. measured.

It follows from all this, as Holborn and Day state, that the temperature scale, once established by means of the thermocouple, can be maintained with certainty only with the help of fixed temperatures such as the melting points. Dr. W. P. White draws particular attention to the importance of that region of the wires passing through a steep temperature gradient and the great influence that inhomogeneity in this portion of the wire may have upon the temperature readings with thermocouples.

If we consider an inhomogeneous thermocouple composed of short segments each of which is supposed homogeneous, at any junction of two segments there is developed an E.M.F. proportional to the temperature t and their difference in thermoelectric power ΔH, or for the whole circuit:

$$E = (t_1 \cdot \Delta H_1 + t_2 \cdot \Delta H_2 + \ldots t_n \cdot \Delta H_n) = \Sigma t \cdot \Delta H.$$

It is evident that those portions of the circuit at constant temperature and of homogeneous material ($\Delta H = 0$) do not contribute to the value of E; but in the regions of temperature gradient of an inhomogeneous wire, the errors due to inhomogeneity depend also upon the temperature distribution along the wire. If an inhomogeneous thermocouple, therefore, is raised or lowered in a furnace at constant temperature, the reading of the couple will change. In view of these facts, it is important that those portions of the thermocouple wires passing from cold to hot regions be chemically and physically of uniform properties.

The effect of initial chemical inhomogeneity, for the platinum thermocouples, appears to be either negligible or very small, but may be considerable for base-metal couples. The region between hard-drawn and annealed wire is one of marked physical inhomogeneity. This can be, and should always be, eliminated by annealing the wires of most couples including platinum, preferably with an electric current, or by hardening in the case of constantan. The most troublesome source of inhomogeneity, however, the most difficult to remove, and the source of greatest error, particularly with platinum thermocouples, is that due to contamination from evaporation and diffusion of metal vapors into the region of temperature gradient of the platinum wire. The oxide coating which forms on some metals is also a similar source of uncertainty in the regions of variable temperature.

Regarding the effects of contamination of platinum wires, carbon, illuminating gas, and other reducing agents appear to act only through their reducing action on other substances, such as iron and silicon, capable of injuring the platinum. In an oxidizing atmosphere, iron oxides and silicates produce little or no effect; but metals such as iridium and rhodium, particularly the former, which is very volatile even from a Pt · Ir alloy wire at 900° C., and capable of alloying with platinum, will, if present, produce marked contamination of platinum wires. Amputation of the contaminated portions appears to be the only remedy in this case. Excessive local heating will also cause inhomogeneity to develop, especially in the alloy wire, probably due in part to evaporation and in part to crystallization.

Measurement of Inhomogeneity. — This is very easily and exactly effected, and should be carried out on any thermocouples to be used in work of high accuracy. Each of the wires is tested separately, its ends being kept conveniently at a constant temperature of 0°. The wire is in circuit with a sensitive galvanometer graduated in microvolts and is passed through a short electric resistance furnace kept at a constant temperature, 1000° or 1400° C. The readings of the galvanometer are taken for different positions of the furnace along the wire. The furnace may be replaced conveniently by a short length of porcelain heated by a Bunsen burner. Using a sensitive recorder, a small furnace may be pulled automatically along the wire which records its own variations. Such a device is in use at the Bureau of

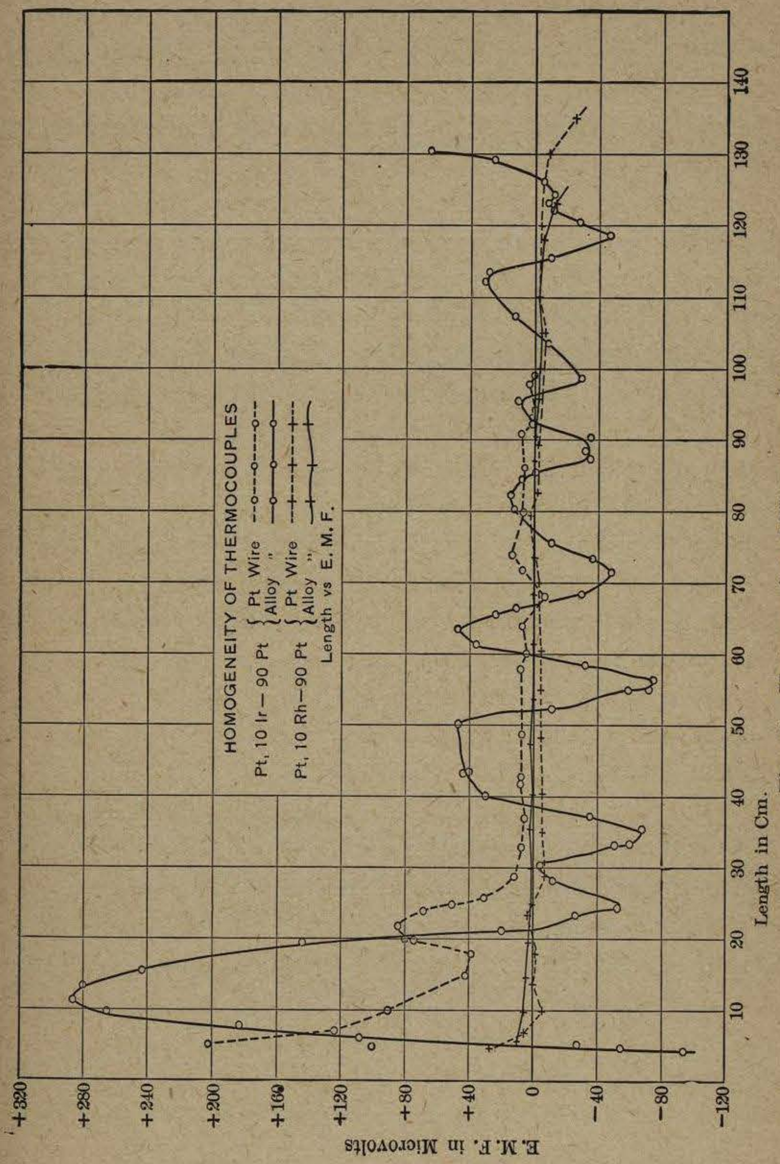

Fig. 46. Homogeneity of Thermocouples.