Standards. Another method is that shown in Fig. 47, which permits a point-to-point study of the phenomenon. In Fig. 46 are shown the homogeneity curves, taken by the first method, of the wires of two thermocouples, the one (Pt-Rh) new and of fresh, pure materials, the other (Pt-Ir) old and impure. These methods are easily sensitive enough to differentiate the various grades of platinum wire used in thermocouple manufacture.

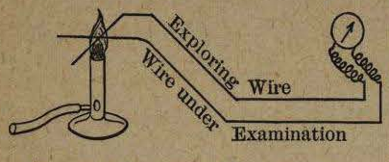

Fig. 47. Testing of Homogeneity.

We have already called attention to the inhomogeneity of base-metal thermocouples. We shall return to this question in a later paragraph.

Reproducibility of Thermoelectric Apparatus. — It is often of considerable convenience in all kinds of measurements, especially on a large scale with numerous working units of the same kind, to be able to duplicate or replace corresponding parts without having resort to new calibrations. This is equally desirable in temperature measurements, and in recent years there has been a large measure of success in the attempt to produce thermocouples and manufacture pyrometer galvanometers which are interchangeable.

As an example of the former, we may cite the case of the well-known 10 per cent platinum-rhodium normal thermocouples of Heræus. They are reported to have maintained the following constancy for the past six years:

AVERAGE E.M.F. AT 1000° C.

Year.	Millivolts.
1904	9.52
1905	9.53
1906	9.53
1907	9.57
1908	9.59
1909	9.55

Regarding the interchangeability of pyrometer galvanometers, the art of electrical instrument manufacture has so advanced in recent years that equivalent instruments, in error absolutely and with respect to each other by less than 10° C. throughout their scales, are produced currently by several makers.

Base-metal Thermocouples. — There appears to be an insistent demand, on the part of many in charge of technical processes requiring temperature control, for inexpensive and robust measuring apparatus. For this reason, if for no other, the use of the base-metal thermocouple has become firmly established. Its success has been due to several causes, principal among them being the production of fairly satisfactory alloys of high E.M.F. with temperature change, which can be made into practically unbreakable pyrometric canes of very low resistance; and the simultaneous development of pivot millivoltmeters suitable for use as galvanometers with this type of couple.

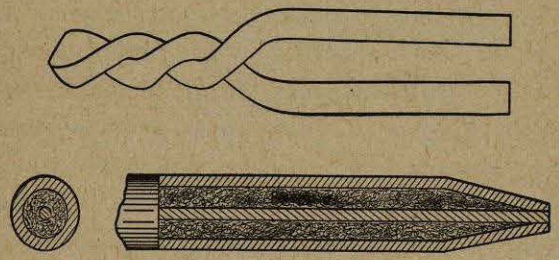

Fig. 48. Heavy Base-metal Welds.

Such canes can be had, for example, with a resistance as low as 0.05 ohms cold, increasing by only 0.01 ohm when heated to 1000° C. Even with a commercial millivoltmeter of only 1 ohm resistance, the calibration will remain constant, under these conditions, to 10° C. for any depth of immersion of the couple (see page 120). It is indispensable in such cases that *all* junctions be of negligible resistance, and they are preferably soldered. In Fig. 48 are illustrated two types of weld for base-metal couples.

A very considerable error, however, in the estimate of the temperature of regions into which are thrust thermocouples of considerable cross section and insufficient length, may arise from heat conduction along the pyrometer, the effect being to chill the hot junction below the temperature of its surroundings. It is important that such pyrometers be calibrated to allow for this effect.

The thermoelectric power of many of these base-metal couples is over 20 microvolts per 1° C., and some of them are 40 or more as compared with 10 microvolts per 1° C. for the ordinary platinum-rhodium couple. The low-resistance pivot galvanometers of 20 or 40 millivolts range, suitable for use with the base-metal couples, may be made more cheaply and robust than instruments suitable for use with platinum couples for the same sensibility.

As the base-metal couples receive hard usage, are cheap, and often require frequent replacing, it is of great advantage to make use of material of uniform thermoelectric properties, so that burned-out " fire ends " may be readily replaced as required without retesting. It is of course safer, and necessary in many instances, to calibrate each new fire end, either by comparison with a standard, or, as may be done conveniently even in technical plants, by taking the reading in salt baths of known freezing points (see page 190). In the case of the use of alloys or metals possessing critical regions, accompanied by the absorption or liberation of heat, it should be emphasized that discordant results may be obtained on reheating, the actual E.M.F.-temperature relation depending upon the internal structure of the material of the couple, and this in turn upon the rate of heating or cooling through these critical regions. These effects are particularly marked in couples of considerable size, and are enhanced by varying the depth of immersion of the couple in the test bath or furnace. We shall mention later some specific instances of these effects.

Although a very considerable number of base-metal thermocouples have been put upon the market in recent years, there appears to be very little certain knowledge available as to the exact composition, thermoelectric properties, and behavior of most of them, some of which are quite complex alloys, as for example of Ni, Cr, Al, and Cu. It should perhaps be noted that our use with base-metal couples of the adjectives " constant," " reproducible," etc., is not to be taken in the same rigorous sense as for the platinum couples.

Nickel-copper. — Various combinations of these metals have been used and recommended for temperatures as high as 900° C. According to the investigations of M. Pécheux, the most satisfactory one seems to be that with the alloy constantan (known also as "advance"), 60 Cu − 40 Ni, as one wire and pure Cu as the other. The E.M.F.-temperature curve for this thermocouple approximates a fairly flat parabola, but appears to require an equation of the third or fourth degree in t to express the results with some exactness to 900° C.; or this interval may be divided into three, each of which is represented, to a fraction of a degree, by a parabola of the form $E_{t_1}^{t_2} = a + bt + ct^2$. Between 0 and 250° C. the numerical equation is roughly $E_0^t = 40\,t + 0.03\,t^2$ in microvolts for the copper-constantan thermocouple. Those with a smaller percentage of nickel have less flat curves, lower thermoelectric powers, and guard their original calibration less well than does the copper-constantan couple.

The limiting case in this series, that of pure nickel against pure copper, is of some interest, as it gives a good illustration of the effects of molecular transformation on thermoelectric behavior. Nickel undergoes such transformation between about 230° and 390° C., which causes both its electrical resistance and thermoelectric power to depart from their normal trend in this region. These effects are shown in Fig. 49, the data on resistance being from some measurements made by Somerville, on nickel wire, and on thermoelectric power of the Ni-Cu couple from the observations of M. Pécheux.

When, for such a couple, or any thermocouple in which nickel or any substance possessing regions of molecular transformation, its rate of heating or cooling is varied, the E.M.F. readings of the couple will not in general be the same for a given temperature within this region; and for rapid cooling, in some cases, especially for wires or rods of considerable diameter, the E.M.F.-temperature relations may be changed at all temperatures below this region as well, due to the retardation or partial prevention of the complete transformation by chilling. Reannealing and slow cooling will oftentimes restore the original annealed condition. The importance of annealing all such couples before their first calibration becomes apparent from the above considerations.

The presence of impurities appears to be a further source of considerable uncertainty in the constancy of these couples with continued use, it being noted, by Pécheux for example, that couples with very pure nickel remained more constant in use than those with the less pure metal.

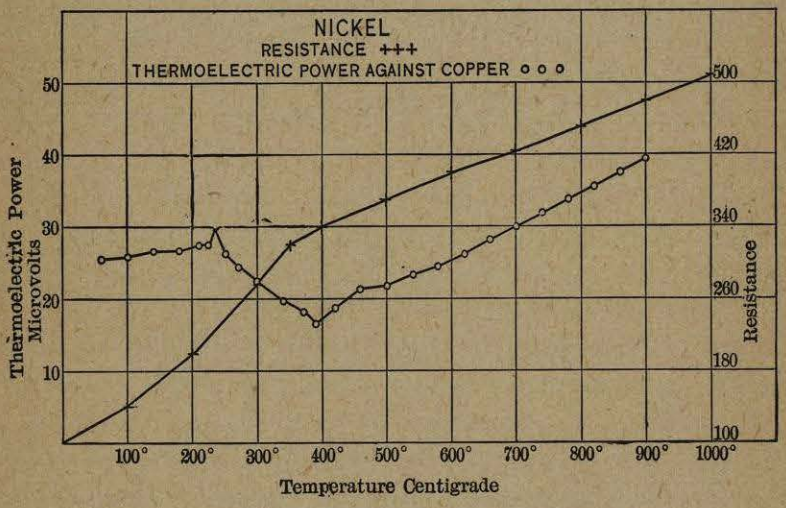

Fig. 49. Resistance and Thermoelectricity of Nickel.

The addition of zinc in any proportions to the copper-nickel alloy, giving the German silvers, appears to be detrimental in all respects.

The upper limit of 900°, assigned by Pécheux for the copper-constantan couples, is better replaced by 600°, or even less, for continued use with any considerable precision; and even at 600° both wires will oxidize and soon become fragile.

Nickel-iron. — We have already called attention to the behavior of iron wires and the enormous parasite E.M.F.'s that they may develop. Nevertheless, a favorite industrial thermoelectric combination has been, and still is in some quarters, a tube of soft iron inclosing a nickel wire. Nickel, associated with any other metal or alloy, will furnish a couple possessing anomalies in $\frac{dE}{dt}$ below 400° C., due to its molecular transformation region. Similarly, iron and also the various carbon- and alloy-steel wires have been found to introduce erratic thermoelectric behavior when used as one element in thermocouples.

Harrison, Barrett, Belloc, and others, who have studied in detail the behavior of such thermocouples, find, for example, that there are considerable changes in E.M.F.'s due to oxidation, carburization, reheating, rate of cooling, the nature of the furnace atmosphere, maximum temperature reached, and time of heating at any temperature; and in general, within any region of molecular transformation, the E.M.F. on cooling will differ from that on heating, producing E.M.F.-temperature cycles or hysteresis. The couples containing iron are most unreliable above 800° C., and all such couples, as well as those with wires of steel, nickel, copper, and many of their alloys, become brittle above 700° C.

The effect of reheating in producing hysteresis is shown in an experiment of Barrett on the change in temperature of the neutral point of a copper-steel couple:

NEUTRAL POINT OF COPPER-STEEL.

	Heating.		
	First.	Second.	Third.
When heating...........	328	283	268
When cooling...........	258	241	241

The E.M.F. is not always higher during heating, however, the following alloy for example giving lower E.M.F.'s against Cu, Pt, or Fe on heating. This alloy (Fe = 68.8, Ni = 25.0, Mn = 5.0, C = 1.2), due to Sir Robert Hadfield, also possesses the remarkable property of giving against a nearly pure iron an E.M.F. constant to within 4 per cent from 300° to 1050° C.

The variation in electromotive force with composition of steels against platinum has been studied by Belloc, whose results are shown in a somewhat idealized form in Fig. 23, page 110, from which it is evident that any changes in composition due to heating or atmosphere will produce great changes in the E.M.F. of such couples below 350° C. and above 700° C. By heating a platinum, 1.2 per cent carbon-steel couple fifteen times to 1000°, its E.M.F. per degree at 800° changed from 11 to 19 microvolts.

On the other hand, for relatively low temperatures, very exact measurements have been made with thermocouples made of iron or nickel and a base-metal alloy. Thus Palmer, working in the range 0° to 200° C. with an iron-constantan couple, gets a precision of 0.04 per cent when the residual E.M.F.'s, including those due to mechanical strains, are eliminated.

Complex Alloy Couples. — Several manufacturers have sought to produce base-metal couples which are free from some of the defects usually present in this type. The work done so far gives promise that this field of investigation is worthy of further development. Most of the effort has been on the modification of the iron and nickel elements by the addition of other metallic components such as tungsten, copper, chromium, cobalt, silicon, and aluminium. We may mention the Bristol, Thwing, and Hoskins couples as examples. One of the last, a robust nickel-chromium combination (Ni, 90 Ni − 10 Cr), has an E.M.F. about four times that of the ordinary Pt-Rh couples, the E.M.F.-temperature relation is nearly linear to 1400° C. without any recalescence disturbances of sufficient magnitude to seriously affect the temperature readings in technical work, and after annealing this couple retains its readings sufficiently for many commercial uses, even when heated to over 1300° C. for short periods.

For high temperatures, the Hoskins Company now use principally the couple nickel aluminium (2% Al) − nickel chromium (10% Cr); and for low temperatures, nickel copper (65% Cu) − nickel chromium (10% Cr). The characteristics of the materials used in the Hoskins couples are given by M. A. L. Marsh, as shown in the accompanying table:

HOSKINS' THERMOCOUPLE CALIBRATIONS.
COLD JUNCTION AT 25° C.

Couple.		Millivolts.					
Positive element.	Negative element.	100° C.	232° C.	419° C.	657° C.	800° C.	1065° C.
Nickel..........	Nickel chromium, 10% Cr.	3.21	9.34	16.88	26.0	31.50	41.80
Nickel aluminium, 2% Al..........	Nickel chromium, 10% Cr.	....	9.35	17.60	28.10	34.53	46.20
Nickel aluminium, 3⅓% Al..........	Nickel chromium, 10% Cr.	....	8.75	17.20	28.25	35.00	47.20
Nickel aluminium, 5% Al..........	Nickel chromium, 10% Cr.	....	8.25	16.67	.....	.....	47.00
Cobalt..........	Nickel chromium, 10% Cr.	3.09	9.93	20.96	33.18	.....	45.58
Nickel copper, 65% Cu..........	Nickel chromium, 10% Cr.	4.39	13.15	27.27	44.66	.....	75.40
Copper..........	Nickel chromium, 10% Cr.	1.48	4.15	7.73	11.27	.....	13.57

ELECTRICAL RESISTANCE OF THERMOCOUPLE ELEMENTS.

Element.	Resistance per foot, 0.40 m/m. wire, at 25° C.	Specific resistance at 25° C.	Temperature coefficient per degree C.
Nickel....................	0.26 ohm	10.34	0.00415
Nickel aluminium, 3⅓% Al..	.63	25.0	.00274
Cobalt....................	.356	14.15	......
Nickel copper, 65% Cu.....	.99	39.3	......
Copper....................	.043	1.75	.00388
Nickel chromium, 10% Cr...	1.76	70.0	.00051

A difficulty met with in the manufacture of complex alloy couples is the reproducibility of the same E.M.F.-temperature relation from one casting to another. The identity of behavior is, however, highly desirable in cheap commercial couples which are frequently replaced, as it obviates the necessity of recalibration or adjustment of the galvanometer scale for each couple.

The Noble Metals: Geibel's Data. — We have already discussed the thermoelectric behavior of the platinum-rhodium alloys, page 116. Some of the platinum group metals and alloys have been studied by Holborn and Day, Rudolphi, Doerinckel, and others. The most thorough and reliable investigation, however, of the electrical and mechanical properties of the noble metals and their alloys, in view of their availability for temperature measurement, has been made by W. Geibel in the laboratory of the Heræus platinum works, using materials much purer than could be obtained by Barus or Le Chatelier twenty-five years ago. The data of Geibel show wide differences from the earlier results of these observers.

PROPERTIES OF THE NOBLE METALS AND THEIR ALLOYS. (GEIBEL.)

Metal or alloy.	Electromotive force (millivolts) against platinum.												Electrical conductivity $\times 10^{-4}$ at 0° C.	Temperature coefficient between 0° and 160°.	Tensile strength in kg. for 1 mm. wire.	Melting begins. From various observers.
	100°	200°	300°	400°	500°	600°	700°	800°	900°	1000°	1100°	1200°				
Pd I	......	......	− 1.1	− 1.6	− 2.4	− 3.3	− 4.5	− 5.8	− 7.3	− 8.9	......	......	9.47	0.00328	30	1550
Pd II	......	− 1.1	− 1.8	− 2.6	− 3.4	− 4.6	− 6.0	− 7.5	− 9.2	−11.0	−13.0	−15.0	......	......	......	......
Pd−Au 10	......	− 1.9	− 2.9	− 4.1	− 5.4	− 6.9	− 8.4	−10.2	−12.1	−14.0	......	......	7.01	.00224	36	1545
Pd−Au 40	......	− 4.1	− 6.4	− 9.4	−12.5	−16.0	−19.7	−23.4	−27.3	−30.9	......	......	3.96	.00079	43	1500
Pd−Au 60	−3.8	− 7.0	−10.5	−15.0	−19.7	−24.2	−28.8	−33.5	−38.2	−42.7	......	......	4.05	.00034	49	1450
Pd−Au 80	−0.5	− 1.0	− 1.7	− 2.5	− 3.4	− 4.4	− 5.5	− 6.8	− 8.2	− 9.8	......	......	7.94	.00064	45	1350
Au	+0.8	+ 1.8	+ 3.1	+ 4.5	+ 6.2	+ 8.0	+ 9.9	+12.0	+14.2	+16.5	......	......	47.52	.00326	21.5	1063
Pd−Ag 10	−0.9	− 2.0	− 3.3	− 5.0	− 6.8	− 9.0	−11.4	−14.2	−17.0	......	......	......	4.85	.00117	42	1500
Pd−Ag 20	−1.8	− 3.5	− 5.7	− 8.5	−11.7	−15.2	−19.2	−23.2	−27.4	......	......	......	3.26	.00066	49.5	1450
Pd−Ag 40	−3.7	− 6.8	−10.7	−15.3	−20.2	−25.4	−31.0	−36.5	−42.1	......	......	......	2.38	.00005	51	1350
Pd−Ag 80	−0.1	− 0.2	......	− 0.3	......	− 0.4	......	− 0.5	− 0.6	......	......	......	9.58	.00047	40	1110
Ag	+0.7	+ 1.7	+ 2.9	+ 4.4	+ 6.1	+ 8.2	+10.6	+13.1	+15.9	......	......	......	63.72	.0041	31	960
Pd−Pt 10	+0.3	+ 0.6	+ 0.8	+ 1.0	+ 1.0	+ 0.8	+ 0.6	+ 0.1	− 0.6	− 1.5	− 2.5	− 3.7	6.93	.00214	33	1570?
Pd−Pt 30	+0.8	+ 1.6	+ 2.5	+ 3.5	+ 4.4	+ 5.3	+ 6.2	+ 6.8	+ 7.4	+ 7.9	+ 8.1	+ 8.2	4.57	.00128	(39)	......
Pd−Pt 60	+0.7	+ 1.5	+ 2.3	+ 3.3	+ 4.4	+ 5.4	+ 6.5	+ 7.6	+ 8.5	+ 9.5	+10.6	+11.5	3.78	.00096	(43)	......
Pd−Pt 90	+0.3	+ 0.7	+ 1.2	+ 1.7	+ 2.3	+ 2.7	+ 3.2	+ 3.7	+ 4.2	+ 4.7	+ 5.2	+ 5.7	5.38	.00136	42	1730?
Pt	......	......	......	......	......	......	......	......	......	......	......	......	9.94	.00348	24	1755
Pt−Ir 5	+1.1	+ 2.1	+ 3.2	+ 4.3	+ 5.4	+ 6.5	+ 7.6	+ 8.7	+ 9.7	+10.7	+11.8	......	5.61	.00188	40	1780?
Pt−Ir 10	+1.3	+ 2.6	+ 4.1	+ 5.8	+ 7.4	+ 9.1	+10.7	+12.3	+14.0	+15.7	+17.3	+19.0	4.34	.00126	48	......
Pt−Ir 25	+1.2	+ 2.6	+ 4.3	+ 6.2	+ 8.2	+10.4	+12.6	+14.8	+17.1	+19.4	+21.8	+24.3	3.17	.00066	98	......
Pt−Ir 35	+1.1	+ 2.5	+ 4.1	+ 5.9	+ 7.9	+ 9.9	+12.1	+14.4	+16.8	+19.1	+21.6	+24.3	2.71	.00058	126	......
Ir*	+0.65	+ 1.5	+ 2.5	+ 3.6	+ 4.8	+ 6.1	+ 7.6	+ 9.1	+10.3	+12.6	+14.5	......	......	......	......	2300
Rh*	+0.65	+ 1.5	+ 2.6	+ 3.7	+ 5.1	+ 6.5	+ 8.1	+ 9.9	+11.7	+13.7	+15.8	......	......	......	......	1920
Au−Pt 10	Not constant, variations as great as 2 millivolts at high temperatures.												9.76	.00098	32	1630
Au−Pt 20													5.57	.00054	52	1510
Au−Pt 40													3.06	.00037	69	1340
Ag−Pt 10	+0.2	+ 0.4	+ 0.7	1.3	1.8	2.4	3.1	3.8	4.7	Before heating			......	......	......	1450?
				1.0	1.5	2.1	2.8	3.6	4.5	After heating			......	......	......	......
Ag−Pt 30	−0.4	− 0.8	− 1.4	2.0	2.6	3.5	4.5	5.5	6.6	Before heating			......	......	......	1200?
				2.1	2.8	3.7	4.7	5.7	6.8	After heating			......	......	......	......

* Holborn and Day.

Some of his results, taken from a very complete series, on E.M.F. against platinum, electrical conductivity, temperature coefficient, and tensile strength, are given in the accompanying table. Wires of 1.3 mm. were first glowed and then cold-drawn to 1 mm. Compositions are per cent by weight. The tensile strength may be taken as giving an approximate measure of hardness.

One of the most satisfactory combinations for use as thermocouple to say 1000° C. appears to be 40 Pd · 60 Au − Pt, which at 1000° C. gives four times the E.M.F. of the ordinary Le Chatelier couple. This Pd · Au alloy also has a very low temperature coefficient and resembles the 10 per cent iridium alloy of platinum in hardness.

The alloys of platinum with gold or silver are evidently unsuitable for use in thermocouples, due to great changes in E.M.F. with prolonged heating. Geibel gives also data showing the effect of annealing at various temperatures upon tensile strength for some of these alloys. The effect is most marked for those alloys which show corresponding changes in E.M.F. For the Pt-Ir alloys there is little effect of annealing until 600° is reached, but after annealing above 800° the tensile strength (cold) falls off rapidly with increase in temperature. For pure