platinum this decreases regularly from 32 kg. for the hard-drawn to 17 kg. after annealing at 1300° C.

The alloy 60 Pd · 40 Ag has nearly a zero temperature coefficient. If of sufficient permanence in its properties, when joined to 90 Pt · 10 Ir, for example, we should have a couple of nearly constant resistance seven times as sensitive as 90 Pt · 10 Rh – Pt at 900° C.

All the alloys noted in the table appear to be solid solutions with no transformation or critical points.

Special Couples. — We may mention certain couples that can be classed neither as base-metal nor as platinum thermocouples, some suitable for relatively low temperatures and others for the very highest.

Silver-constantan is a combination that is used considerably and appears to give satisfaction to temperatures as high as 700° C.

Silver-nickel has also been used by Hevesy and Wolff from −80° to 920° C. The thermoelectric power is about three times that of the Pt-Rh couple, but is quite variable, and there is no simple formula expressing the E.M.F.-temperature relation even above 400° C.

Iridium-ruthenium. — The upper limit for the continued use without frequent recalibration of the platinum-rhodium couple is about 1600° C., although the melting point of platinum may be reached with it. Heræus has met the need for a couple that can be used to very much higher temperatures by constructing one having for one lead pure iridium and for the other an alloy of 90 parts iridium to 10 parts ruthenium, with which temperatures to about 2100° C. may be measured. The E.M.F.-temperature relation for these couples is not quite linear.

Calibrations may be made in a suitable furnace by comparison with a Pt-Rh couple or by taking readings at the melting points of Au, Pd, and Pt, above which temperature extrapolation must be resorted to unless pure Rh is available as a calibration point, or comparison be made with an optical pyrometer.

The indications of this couple remain fairly constant with repeated heatings considering the extremely high temperatures to which it may be exposed. Inhomogeneity will of course develop. A serious source of error, noninherent in this couple alone, is that due to heat conduction along the thick leads, which may amount to 50 degrees at the higher temperatures unless allowed for by observing some known temperature, as the Pt point, with the same immersion as used in the experiments.

This thermocouple, on account of its very great fragility when cold, is not suited for any ordinary industrial uses, and must be handled with the greatest care; it is also, of course, very expensive.

Compound Thermocouples. — These are of two kinds, the object of the first being to give greater sensibility to the couple by increasing its E.M.F. This is usually accomplished by putting two or more thermocouples in series, when the available E.M.F. is increased in the proportion to the number of couples. It should be remembered, however, that, by this operation, the electrical resistance of the circuit is also proportionally increased, and this may introduce considerable errors when indicating galvanometers of relatively low resistance are used; and in this case also, the sensibility may not be increased enough to warrant the additional couples, which are, of course, expensive if the platinum metals are used. The effects of varying depths of immersion of the couple wires in the heated space and changes of zero are also accentuated by this method, which, with the recent development of galvanometers which are both sensitive and robust, becomes superfluous in ordinary cases. For measuring small temperature differences, however, as in detecting transformation points, this method has its advantages.

The other kind of compound thermoelectric couple, which in the following form appears to be due to Bristol, was designed for the elimination of a portion of the expensive platinum and platinum-rhodium wires. It consists in the substitution of inexpensive alloys for the part of the couple which is not exposed to a temperature above a red heat, as shown in Fig. 50, these alloys being so chosen as to give the same E.M.F.-temperature relation as the platinum-rhodium couple; so that the resultant E.M.F. generated by the compound couple is the same as if the entire couple were of platinum and platinum-rhodium.

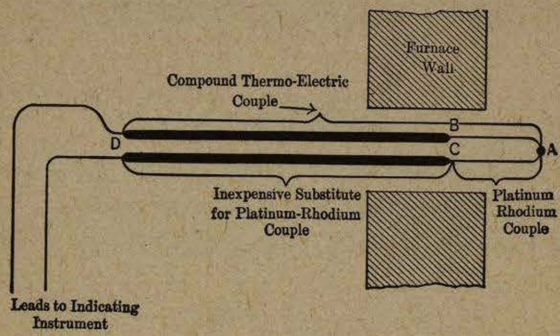

Fig. 50. Bristol's Compound Couple.

In England, Peake proposes to use, with platinum-iridium or rhodium couples, such compensating leads, made with one wire of copper and the other of cupronickel (Ni from 0.1 to 5 per cent). That good compensation may be obtained by this method is shown by the following table from products used by the Cambridge Scientific Instrument Company:

PEAKE'S COMPENSATING LEADS.

Temperature.	Pt – Pt · Ir couple.	Compensating leads.
° C.	Millivolts.	Millivolts.
0	0	0
50	0.59	0.60
100	1.25	1.25
150	1.95	1.90
200	2.68	2.60
250	3.42	3.40
300	4.20	4.25

The compensating couple of Chauvin and Arnoux is the result of an attempt to eliminate the considerable length of wire and relatively high resistance of the platinum thermocouple, and at

the same time keep the advantages of such a couple for industrial measurements to 1600° C. with a pivot instrument of robust type in those cases where it is not necessary to have a considerable length of wire exposed to the hottest temperatures. The arrangement shown in Fig. 51 consists in measuring the temperature in two steps. The platinum-iridium couple is in series with one of iron-constantan, whose hot junction is placed beside the cold junction of the platinum couple. On account of the greater E.M.F. of the iron-constantan couple, it is necessary to shunt this last with a resistance to give the same temperature difference. This shunt reduces the total resistance and so facilitates the use of long canes.

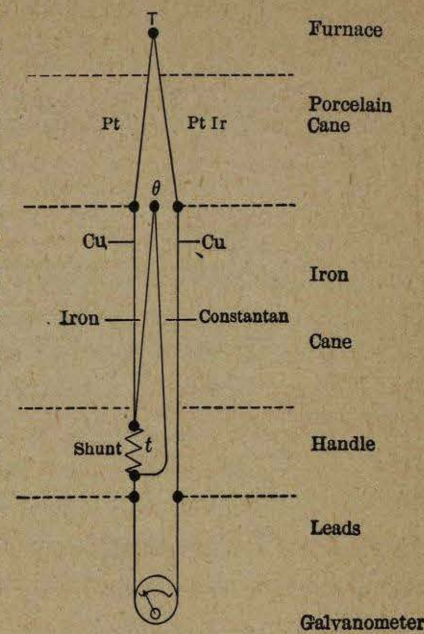

Fig. 51. Compound Couple of Chauvin and Arnoux.

Referring to the figure, we have for the platinum-iridium couple:

$$e = f(T - \theta),$$

and for the iron-constantan couple:

$$e_1 = f'(\theta - t).$$

Now, if the alloys are properly chosen in composition, it appears to be possible to so adjust the shunt as to obtain E.M.F.-temperature curves superposable for the two couples between θ and t, which is equivalent to having a single platinum-iridium couple, whence:

$$E = e + e_1 = f(T - t).$$

The value of the shunt resistance can be shown to depend only on the resistance of the compensating couple and on the ratio of the two thermoelectric powers.

The temperature θ should not exceed 800° C., and a very pure iron tube should be used to prevent anomalies around 700° C.

Calibration of Thermocouples. — With the several national standardizing laboratories organized and equipped for such work as the calibration of pyrometers, it is no longer necessary for an individual to concern himself with this matter. Nevertheless, it is often desirable to be able to carry out such calibrations simultaneously with other investigations or with the apparatus in hand. We shall not concern ourselves with descriptions of the calibration of the electrical measuring apparatus used, such as millivoltmeters and potentiometers; they will be found in any book on the testing of electrical apparatus. It is rare that an individual is so situated as to have the equipment necessary for these electrical calibrations, when recourse must be had to the standardizing laboratories. In the case of thermocouples, however, used with pyrometer galvanometers possessing a millivolt scale which is approximately correct or a scale of equal parts, the calibration of the thermocouple and galvanometer may be effected simultaneously to a relatively high degree of accuracy by taking a sufficient number of fixed points with the couple joined to its galvanometer.

We shall assume, therefore, either that the measuring apparatus is correct or that it may be sufficiently well calibrated by the operations carried out on the thermocouple.

We shall consider first the requirements for the highest accuracy attainable with platinum-metal thermocouples suitable for high temperatures, and then methods applicable to industrial practice and for base-metal couples.

Precision Calibration. — We have seen that for an accuracy of better than 5 degrees, or in many cases of 10 degrees, it is necessary to use the potentiometric method of measurement. The cold junctions of the couple should be kept at 0° C., and the wires of the couple should be annealed and shown to be sufficiently homogeneous. Only couples of the platinum metals should be used, at least for temperatures above 600° C.

The calibration may be carried out by the use of melting and boiling points of known values, or by comparison in a suitable furnace with one or more standardized pyrometers. Great care has to be taken with the insulation of the thermocouple circuit, especially at high temperatures and when electric heating is used. Reversal of the heating circuit will show this effect. It is also necessary to insure sufficient depth of immersion in the bath or furnace to avoid errors due to heat conduction along the wires of the couple. This can be tested by changing the depth of immersion in the region of constant temperature, when the readings should not change, provided of course the wires are homogeneous.

Crucible Method. — In the case of the metals or salts which are used to give the temperature of their freezing or melting points, it is usually better in exact work to use crucibles containing a considerable quantity of the material, 300 c.c. or more, although a skilled observer using a suitable furnace can get good results with very small quantities of material. Either gas or electric furnaces may be used. The latter permit a more delicate control both of the rate of cooling and of the atmosphere in which the melting or freezing is carried out, but the former can usually be heated much more rapidly. For work to 1° it is better to keep to the electric furnace.

As to the choice between melting and freezing points, the consensus of opinion is in favor of the latter when possible as being usually sharper, although sometimes complicated by undercooling, as in the case of the metals antimony and tin. With some salts this phenomenon is prohibitive of using the freezing point.

The crucibles should of course be of material that does not react with the charge or the atmosphere of the furnace, dissolve in the former, or let the furnace atmosphere penetrate into the charge when they react with each other. For salts, the best material for the crucible is platinum, but nickel crucibles will also answer in many cases, and they are inexpensive. Fire-clay crucibles, and even those of porcelain, may be used with certain salts. For the nonoxidizable metals there are several substances available, such as porcelain, magnesia, lime, alumina, graphite, and quartz. The oxidizable metals which do not dissolve graphite are best melted in graphite crucibles, those of the Acheson Company being almost pure graphite. A crucible only partly of graphite, such as the Dixon crucibles, is often sufficient, and lasts longer than those of pure graphite, and is to be preferred when a gas furnace is used. These crucibles should have covers, and in addition the surface of the metal should be covered with powdered graphite. In some cases a gas, such as CO or H, which acts as a reducing agent, or prevents oxidation such as N, must be led into the furnace. With the gas furnace, it is well to prevent the direct play of the flames on the crucible by surrounding the latter with a cylinder of metal such as wrought iron, which helps equalize temperature within the crucible.

There are a considerable number of makers of crucible furnaces, both gas and electric, suitable for ordinary freezing-point determinations. For the attainment of the higher temperatures with the former an air blast is necessary, and for the latter a rheostat and ammeter or voltmeter are necessary auxiliaries.

The electric method of heating was first used in pyrometric work for the determination of fixed points by means of the thermocouple by D. Berthelot in France and Holborn and Day in Germany. The earlier furnaces were constructed by winding pure nickel or platinum wire on porcelain tubes inclosed in an outer tube of porcelain and wrapped in asbestos. The nickel-wound furnaces may be used up to 1300° C. for a short time with care and they are readily rewound when burnt out. Their life is prolonged by packing the wire so as to prevent access of air. The platinum-wire furnaces are very expensive, but may be used up to 1500° C. These last have since been pretty generally displaced by furnaces of the Heræus type, which are made by winding platinum *foil* of about 0.007 mm. thickness on porcelain tubes covered with an aluminium earth paste which does not attack platinum at high temperatures. These furnaces are inexpensive

and very durable to 1300° when carefully used. Heræus also manufactures iridium resistance furnaces with which temperatures over 2000° C. may be reached, and a very constant temperature maintained. With this type, special precautions have to be taken to prevent the evaporation of iridium on to thermocouple wires. A further advantage, in some cases, of the electric furnace is the absence of reducing gases.

The use of electric heating has rendered the standardization of the thermocouple and all other pyrometers a relatively easy matter and increased greatly the

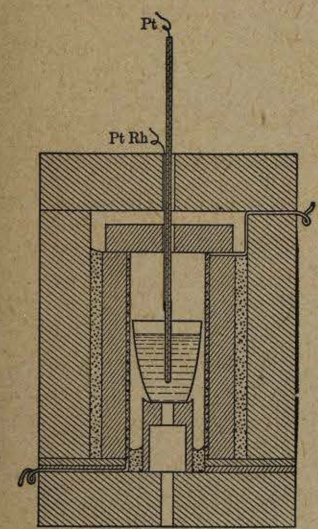

Fig. 52. Electrical Crucible Furnace.

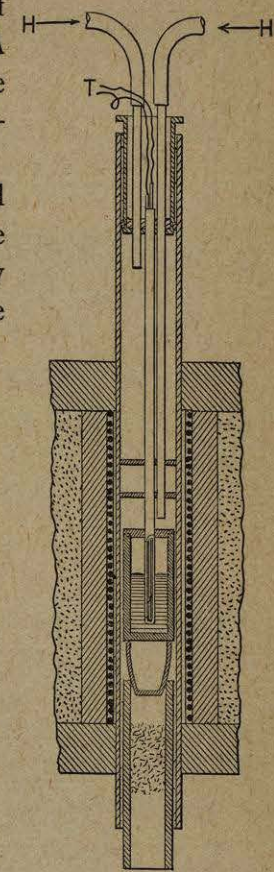

Fig. 53. Electrical Crucible Furnace.

accuracy and range attainable in establishing the fixed points in pyrometry.

Types of electric crucible furnaces are shown in Figs. 52, 53, and 175. In those of the Geophysical Laboratory (52 and 53), the platinum heating coil is embedded in Marquardt mixture.

Among the gas crucible furnaces we may mention those of the

Buffalo and the White Dental companies, the American Gas Furnace Company, and the Méker furnaces. A form of furnace that Le Chatelier found very serviceable is shown in Fig. 54. It is a furnace of English design, which has the advantage to resist almost indefinitely the action of heat and to be very easily repaired. The principle of the construction of these furnaces is to make them of two concentric layers. The outer covering of fire clay, bound together by iron, gives solidity to the furnace; it receives but indirectly the action of the heat, and is not exposed to cracking by shrinkage under the action of too high temperatures. The inner envelope, which alone receives the action of the heat, is made of large-grained quartz sand, grains of 1 mm., mixed with a small amount of a flux. At a high temperature the quartz does not shrink as does clay; it expands, on the contrary, passing over to the form of amorphous silica with a change of density from 2.6 to 2.2. But this transformation is effected only with extreme slowness, otherwise it would burst the furnace. If by chance this inner lining falls down, it is easily replaced by putting into the furnace a glass jar of suitable diameter, surrounded with a sheet of oiled paper, and packing about this coarse quartz sand slightly moistened with a sirupy solution of alkaline silicate. The furnace is heated by means of a lateral opening with a Fletcher lamp, which has the advantage of being sturdy, or with an ordinary blast lamp.

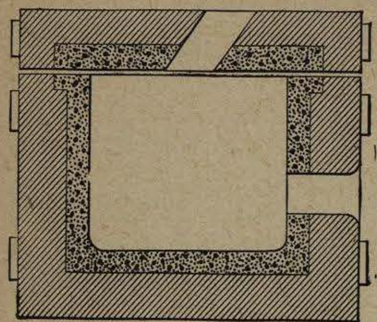

Fig. 54. Gas Crucible Furnace.

Among the metals which can be used, or which are not too expensive for the calibration of thermocouples by the crucible method, are Sn, Cd, Pb, Zn, Al, Sb, Ag, Cu, Ni, Fe, and Co. The last four are readily oxidizable, as is also Sb, but its oxide does not appear to dissolve in the metal; while Ag absorbs oxygen from the air unless protected. Al attacks crucibles containing silica, and is difficult of manipulation. The behavior of these

metals is discussed at length in Chapter XI. If only three points are required, Zn, Sb, and Cu will suffice if the last two are manipulated in a strictly reducing atmosphere. It is, of course, absolutely essential that the purity of the metals used can be vouched for. The eutectic Cu-Cu_2O is well fixed, as is also the alloy Cu_2-Ag_3, to serve for thermo-couple calibrations.

The exact values of the freezing point of very few salts are well known, as is shown on page 190. NaCl is perhaps the most certainly determined and is conveniently located between Sb and Cu to serve as a fourth calibration point; other well-known salts are Na_2SO_4 and chemically prepared diopside ($CaSiO_3 \cdot MgSiO_3$). A thin platinum detachable crucible used at the Geophysical Laboratory with small quantities of salt, into which the couple may be dipped, is shown in Fig. 55.

Some of the salts will attack the porcelain sheath about the thermocouple. A metal one, platinum or nickel, may be substituted, taking care to keep the wires of the thermocouple insulated. The metals act variously on the porcelain tubes. If left in zinc they will invariably break on cooling. If withdrawn from liquid aluminium, unless greatly overheated, they will likewise break if any metal adheres to the porcelain. The Al also dissolves silica. They may be left in copper, however, and reheated without cracking. The best practice is to always withdraw from the liquid the porcelain or other protecting tube without any substance sticking to it after finishing the observations with any metal or salt. The use of quartz-glass protecting tubes will in general prove disappointing.

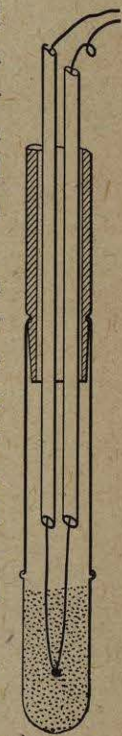

Fig. 55. Detachable Platinum Crucible.

Wire Method. — Measurements of the melting points of a precision of one or two degrees may be obtained with the nonoxidizable metals, which can be drawn, such as Au (1063°), Pd (1550°), and, to a slightly less precision, Pt (1755°), by inserting a short length of wire between the two wires of the hot junction of the