thermocouple and gradually raising the temperature until the circuit breaks, due to the melting of the interposed link, and noting the maximum reading. Only a millimeter or two of the couple wire need be lost by this operation. The best results are obtained in a clear resistance-tube furnace of small diameter; the Pt point

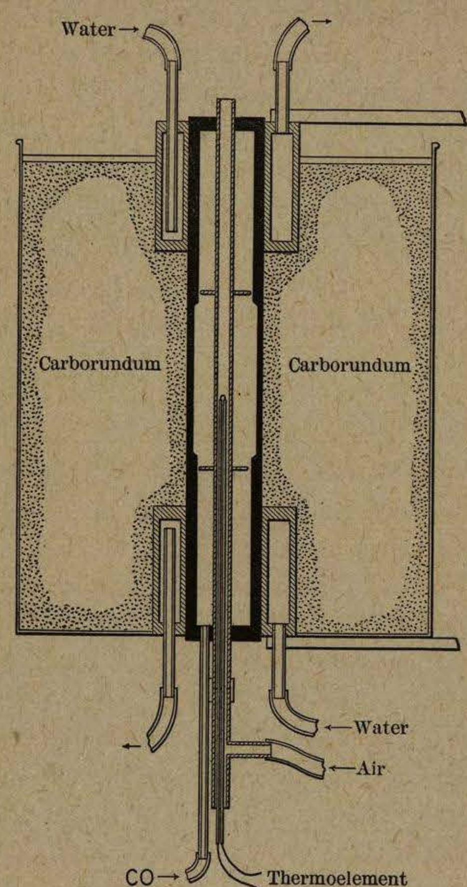

Fig. 56. Sosman's Carbon Furnace.

cannot be obtained in this way except in some special form of carbon furnace (Fig. 56), or in an iridium- or platinum-alloy furnace (see Fig. 174, Chap. XI). The wires should be protected by porcelain, quartz-glass, or magnesia tubes. In any case the link should be fused, not tied into place, and is best of nearly the same diameter as the couple wires. Very great precautions

have to be taken to guard against leaks from the furnace, it being absolutely necessary that no part of the thermocouple circuit touch any hot part of the furnace in the case of Pd and Pt melts, and the insulators of the separate leads should not touch each other within the furnace.

In general, much less reliable results will be obtained when the oxyhydrogen or other flame has to be used. The unsteadiness of the flame may be partly overcome by immersing the linked or wrapped junction in a small muffle or in a small crucible containing powdered refractory material such as alumina. For the platinum point the oxyhydrogen flame is required; the palladium point can be obtained with a strong blast, and the gold point with an ordinary Bunsen. In industrial plants advantage may be taken of flues, furnaces, etc., to give the requisite heat.

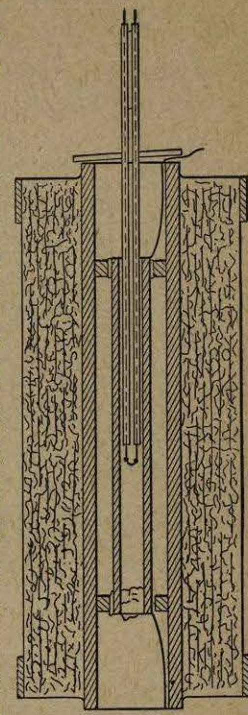

Fig. 57. Mounting for Wire Method.

The precision obtainable with the wire method is illustrated by observations of Waidner and Burgess on the melting point of palladium, carried out in an electric resistance furnace (Fig. 57), the palladium wire being inserted at the junctions of a series of Pt-Rh and Pt-Ir couples. The temperature scale of the Table, page 186, is that of the thermocouple (equation (3), page 112).

Instead of inserting the link in the thermocouple circuit, it may be put in a neighboring auxiliary circuit containing some electrical device for recognizing a break. The accuracy will be somewhat lessened, but the protected couple will remain intact by this modification.

A wire method devised by Wright suitable for use with minute quantities of salts is shown in Fig. 58. The salt is mounted at T on the slightly flattened junction within a water-jacketed electric furnace placed below a microscope, by means of which the melting or freezing is observed.

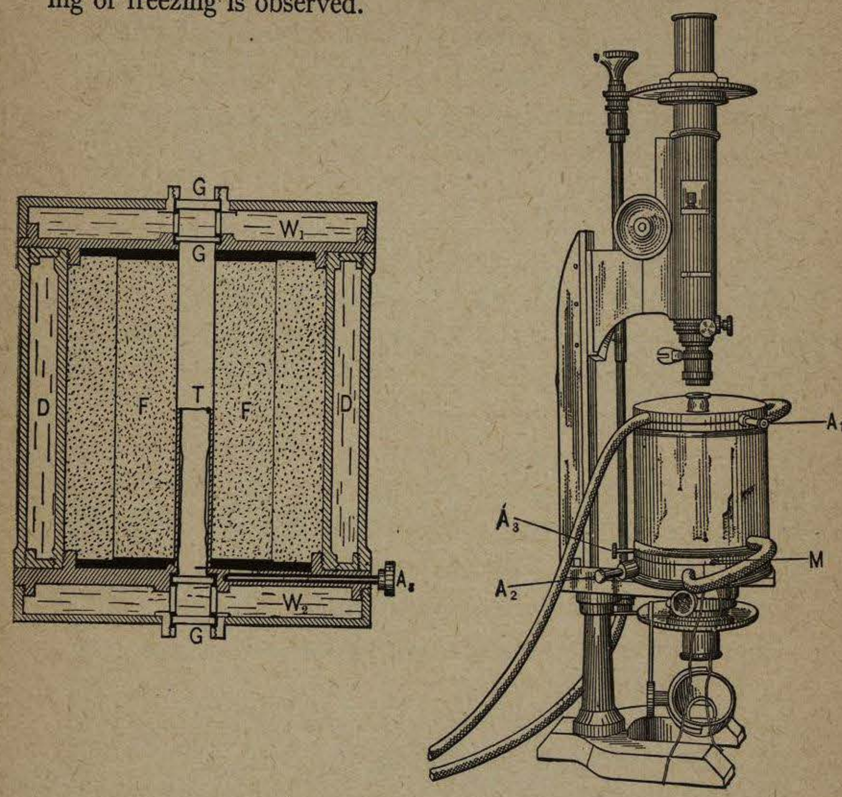

Fig. 58. Furnace and Microscope for Minute Pieces.

MELTING POINT OF PALLADIUM — WIRE METHOD.

Thermo-couple.	Number of observations.	Melting point of palladium.	Remarks.
W_1	5	1531.0°	Horizontal furnace; bare wires.
S_2	6	1530.5	Horizontal furnace; porcelain tubes.
W_3	4	1530.0	" "
P_2	5	1529.5	" "
P_1	2	1530.0	Vertical furnace; see Fig. 57.
S_2	2	1530.5	" "
P_2	2	1530.0	" "
W_1	3	1530.5	" "
W_6	6	1530.1	" "
		Mean = 1530.2°	M.P. on thermoelectric scale (equation (3), p. 112).

Boiling points, including those of the metals such as Cd and Zn, have frequently been used for the calibration of thermocouples, but the boiling metals are much more difficult to manipulate than the melting, and there is far greater danger of contamination of the thermocouples, nor is there need of resorting to them. If desired, however, the freezing points of Sn, Pb or Cd, and Zn may be replaced by the boiling points of naphthaline, benzophenone, and sulphur respectively, none of which attack the couples ordinarily used. The standard form of boiling apparatus for an accuracy of 0.05° C. or better is shown in Fig. 169, except that for naphthalene and benzophenone a side condenser tube should be added; or an air blast from a ring burner around the top of the boiling-tube may be used.

For a somewhat less accuracy the smaller portable apparatus of Barus (Fig. 59) may be used for boiling points, including also water and analine. This consists of a tube of thin glass, similar to test tubes, of 15 mm. inside diameter, 300 mm. long, with a small bulb at 50 mm. below the open end. It is surrounded with a plaster muff of 150 mm. height and 100 mm. diameter which has been cast about the glass tube inside of a thin metallic cylinder forming the outside surface. The bulb is immediately above the plaster jacket, below which the tube, closed at its lower end, extends to a distance of 70 mm. As soon as the plaster has begun to set the glass tube is taken out, giving it a slight twisting motion. The cylinder is left to dry, and the tube is again put in place. This allows, when the tube is broken, of taking it out and replacing it, which would be difficult if it adhered to the plaster. A jacketed Victor Meyer tube may also be used.

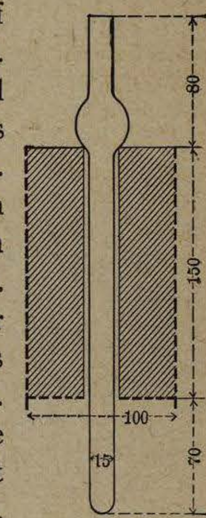

Fig. 59. Boiling Apparatus of Barus.

The lower free portion is heated by a Bunsen flame gently at first, then without any special precaution, once boiling sets in. The liquid at rest should occupy two-thirds of the height of the free end of the tube. The heating is continued until the liquid coming from the condensation of the vapor runs abundantly down the walls of the bulb. The flame is then adjusted so that the limit of condensation of the liquid, which is very sharp, remains constantly midway up the bulb. There is then a very uniform temperature in the interior of the glass tube throughout the height of the plaster cylinder. The junction of the couple is inserted and the coil of the galvanometer takes up a fixed invariable position. It is well to prevent the liquid from running down about the couple by placing a small cone of aluminium or asbestos above the junction. Electric heating may also be used.

For the boiling point of zinc, Barus made small crucibles of porcelain very ingeniously arranged, but also very complicated, besides being fragile and costly. One can make use more simply of a porcelain crucible 70 mm. deep (Fig. 60), filled with melted zinc for 50 mm. of its depth, and, above, 20 mm. of charcoal dust. A cone pierced with a central hole lets pass a small porcelain tube containing the couple. The whole is heated until there is seen a small white flame of zinc escaping from the crucible. It is indispensable that the openings for the escape of zinc vapor be large enough. They tend, indeed, to become clogged by a deposit of zinc oxide which solders at the same time the cover to the crucible, and this causes an explosion when there is no longer vent for the zinc vapors. A better form providing for the condensation of vapors was used by D. Berthelot.

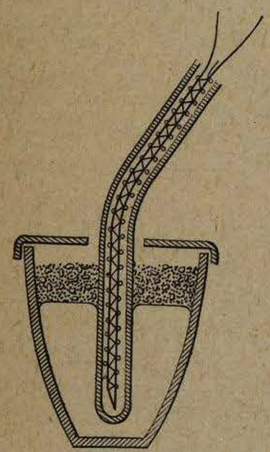

Fig. 60. Zinc-boiling Apparatus.

Technical Calibrations. — The process of calibration is greatly simplified if an uncertainty of 5° C. or more may be permitted, as is the case for most technical operations. When the crucible method is used, smaller crucibles and furnaces may be allowed

than for exact calibration, and metals and salts of less certain purity may be tolerated, although it is most certainly safer to use only very pure materials. Some metals, such as Al and Sb, have their melting points greatly influenced by small impurities, and are obtainable in sufficient purity with difficulty. Other metals, such as Sn, Pb, Zn, and Cu, can be trusted from almost any source of supply to give temperatures to within 2° C. of the melting points of the pure metals. The precautions of manipulation mentioned in the preceding paragraphs apply here, with somewhat attenuated emphasis, depending upon the accuracy desired. For example, it is often not convenient to maintain the cold junctions at 0° C., or one may desire to keep them during calibration at the average temperature to which they are subjected in use or attached directly to the pyrometer galvanometer. We have indicated elsewhere (page 155) how to make allowance for variations in cold-junction temperatures.

The galvanometer and thermocouple may be tested either together or separately, but the former method is the more convenient and eliminates the use of any auxiliary apparatus. Five or six points on the galvanometer scale are usually sufficient for a technical calibration of the couple and galvanometer together. These may be given by any of the freezing or boiling points we have mentioned. A convenient inexpensive series of the former, requiring the minimum of precautions in manipulation and suitable in crucibles of 50 or 100 c.c. in a small air-gas furnace when the couples are wires of small diameter, is the following:

Sn	232° C.	Al	657° C.
Pb	327	NaCl	800
Zn	419	Cu · CuO_2	1063

The last is copper saturated with its oxide. A piece of carbon steel (0.9 per cent C) bored with a small hole into which the couple is inserted will give on cooling a calibration temperature of about 700° C.

If it is desired to use salts only, as may be the case with certain base-metal couples of the cane type, which are plunged without protection directly into the bath, there will be some sacrifice of accuracy even when large quantities of salt are used in nickel crucibles, due in part to our uncertainty of their melting points, in part to the great effects that slight impurities exercise on these temperatures, and above all to heat conduction along the leads, as the couple is practically short-circuited by the salt near its surface. This is even more emphatically true when a couple is plunged bare into metal, which is bad practice even when the couple will stand it. The following list of salts is suggested, with considerable reserve as to the numerical values, some of which may be 10° C. or more in error:

$NaNO_3$	308° C.	$BaCl_2$	950° C.
KNO_3	336	K_2SO_4	1060
$Ca(NO_3)_2$	550	Na_2SiO_3	1088
KI	680	Li_2SiO_3	1202
KCl	780	Diopside	1391
NaCl	800	Anorthite	1550
Na_2SO_4	885		

Another sharply defined temperature which may be used is the transformation temperature of crystalline quartz at 575° C., obtained with a good quality of silica sand.

Still another method of calibration is by the comparison of the pyrometer readings with those of a standardized instrument in the same furnace. With the platinum couples and a porcelain-tube platinum-resistance furnace of 1.5 cm. diameter and 30 to 60 cm. long, results to 2 degrees or better may be obtained if special precautions are taken to insure constant temperature, such as inclosing hot junctions within a short platinum cylinder and passing them through notches in a platinum disk. When base-metal couples are compared with those of platinum, it is usually necessary to protect the latter from contamination from the former by inclosing the platinum wires and junctions in glazed porcelain or other suitable tubes. A better temperature distribution for the comparison of base-metal couples than is found usually in tube furnaces may be obtained by using large crucible furnaces in which are placed baths of mixed salts which may be stirred and contained in long iron crucibles.

Industrial and Scientific Applications. — The measurement of temperatures by thermoelectric couples has enhanced the accurate knowledge of a great number of high temperatures of which previously little or nothing was known. The earlier measurements were particularly numerous in the scientific and industrial investigations on iron. It was with the thermoelectric couple that Osmond and others, Roberts-Austen, Arnold, Howe, and Charpy made all their studies on the molecular transformations of irons and steels. The conditions of manufacture and of treatment of these metals have been improved by the introduction into industrial works of this method of high-temperature measurements.

We give below, as examples of the early use of the thermocouple, a series of determinations made by Le Chatelier in a number of industrial operations.

Steel. — Siemens-Martin open-hearth furnace:

Gas at the outlet of the gas generator	720°
Gas at the entrance of the regenerator	400
Gas at the outlet of the regenerator	1200
Air at the outlet of the regenerator	1000
Interior of the furnace during refining	1550
Smoke at the foot of the chimney	300

Glass. — Basin furnace for bottles; pot furnace for window glass:

Furnace	1400°
Glass in affinage	1310
Annealing of bottles	585
Rolling of window glass	600

Illuminating gas. — Gazogène furnace:

Top of furnace	1190°
Base of furnace	1060
Retort at end of distillation	975
Smoke at base of regenerator	680

Porcelain. — Furnaces:

Hard porcelain	1400°
China porcelain	1275

To-day, the use of the thermocouple in the most varied industries is so widespread that the above list could be indefinitely multiplied. It is not merely, however, in the determination of the temperatures entering into a great number of industrial operations that the thermoelectric pyrometer has paved the way for itself and for other types of pyrometer, but it is, above all, in the ability that is thereby given by such temperature measurements to control the quality of the products of these operations depending on temperature, and so permit the exact reproduction, within as close limits as is wanted, of any desired result, and to increase thereby enormously the efficiency of many industrial plants.

The use of the thermocouple in scientific investigations has been not less extensive or fruitful, and we have, for instance, what may be called a new science, or at least a new aspect of chemistry, namely, thermal analysis, which has grown up in recent years, based mainly on the interpretation of physicochemical phenomena at high temperatures by means of the indications of the thermocouple.

In the development of scientific metallurgy, again, the thermocouple has been almost the only temperature-measuring device which has been employed. These two generalizations are sufficient to indicate its secure position as an instrument of pyrometric research.

Conditions of Use. — Thermoelectric couples, as we have seen, may be divided for convenience into two general classes, the platinum-alloy couples and the base-metal couples, both of which are readily calibrated and easy to use. The former, by reason also of their small size and of the permanence and precision of their indications, are on the whole preferable to all other pyrometric methods for ordinary investigations, scientific or industrial, over the wide temperature range for which they are best adapted, or from 300° to 1600° C. We shall see, however, that when the highest accuracy is desired, or better than 1° C., the resistance thermometer of platinum may be given the preference to 900° C. from the very lowest temperatures, even over the thermocouple used with a potentiometer. The former also is somewhat more adapted for use with robust recording instruments. Above

1000° C., however, the platinum thermocouple is the only form of electric pyrometer which can be used with any considerable certainty; and attached either to a suitable direct-reading galvanometer or to an automatic recorder, this instrument is proving of great utility in the industries. It may also be wired readily for use in multiple on a single distant recording instrument, each couple also having its separate indicator beside it.

For temperatures below 600° C., there is gain in sensibility without serious loss in accuracy by substituting such couples as that of silver-constantan or copper-constantan, both of which can be kept small; and below 500° C. we reach the range of accurate mercury-in-glass thermometers. We have discussed elsewhere the precautions and methods of use both in work of precision and in technical work for the various types of couple.

The use of the base-metal couple is limited to the technical field, and even here great discernment has to be used to satisfy oneself that the couple in hand, with its accessories, is suitable for the use to which it is contemplated to put it. There are few base-metal couples which can be used safely above 1000° C., and some of them are of very questionable utility for any purpose.

We shall see that, even in the range for which it is best adapted, the thermocouple may in certain lines of work be replaced to advantage by still other methods, such for instance as the radiation and optical pyrometers.