from 1484 to 1427. Day and Sosman find *1452* with the gas thermometer, and Ruer 1451 with the thermocouple, assuming palladium = 1541. The former find for cobalt *1490*, and, from the measurements of several observers, iron would have a melting point of about 1520 on the same scale. These metals are readily oxidized and usually contain sufficient impurities to influence their melting temperatures somewhat. They are most readily worked in an atmosphere of hydrogen. Microscopic samples melted on platinum in hydrogen, as measured by Burgess with an optical pyrometer (see p. 343), gave Ni = 1435, Co = 1464, and Fe = 1505.

Metals Melting above 2000° C. — Above the platinum point, there have been recently a considerable number of attempts to locate fixed points. With the exception of iridium and rhodium, which have already been mentioned, it appears to be necessary to work in vacuo all the elements available in this very high temperature region. A very convenient way to mount them is as filaments or strips as in incandescent lamps.

Of the elements that have been so studied, only tantalum and tungsten have been determined with a fair agreement by several observers; and tungsten is the only one which melts without excessive evaporation, and, having the highest melting point yet measured, appears to be the best adapted for an extreme fixed point.

For *tungsten* the following values have been found:

Waidner and Burgess (1906–1910) (c_2 = 14,500)....	3250–3050° C.
V. Wartenberg (1907–1910) (c_2 = 14,600)..........	2800–2900
Pirani (1910) (c_2 = 14,500)........................	3250

The value 3000° C. is probably correct to 100° C.

For *tantalum* we have:

V. Bolton (1905)................................	2250–2300°
Waidner and Burgess (1907 and 1910)...........	2910
Pirani (1910)..................................	3000
Pirani and Mayer (1911)........................	2850

Measurements of the melting points of osmium, molybdenum, titanium, and other very refractory elements have also been

made, but none of them gives promise of being as serviceable as the above for fixed points in pyrometry.

Melting Points of the Chemical Elements. — In Table II of the Appendix is given a list of the melting points for the chemical elements with some indication of our knowledge of their exactness.

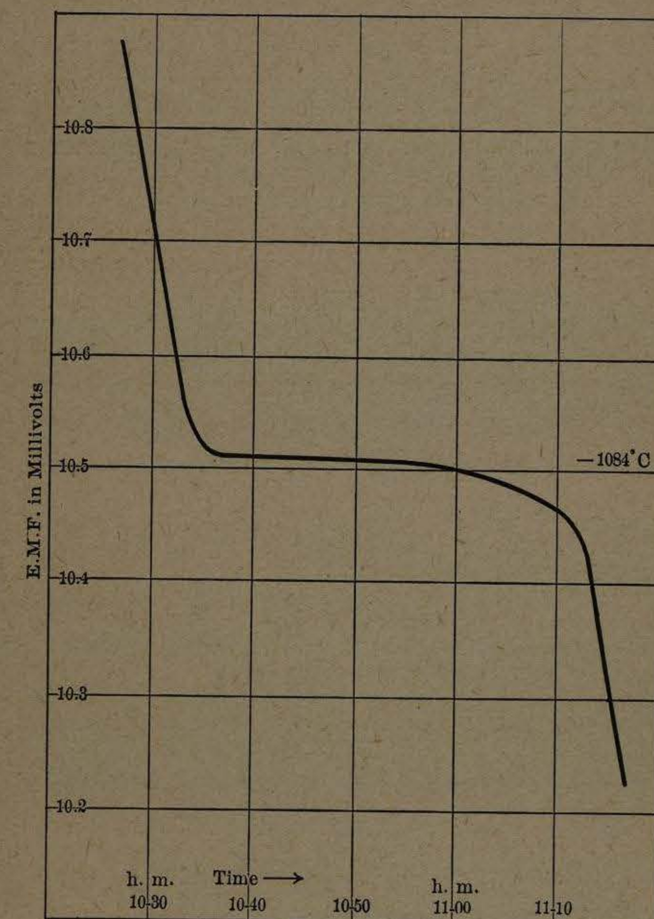

Fig. 170. Freezing of Copper.

Typical Freezing-point Curves. — The freezing-point curves of copper, antimony, silver, and aluminium are shown in Figs. 170 to 173, from data obtained at the Bureau of Standards, in which time in minutes is plotted as abscissa and E.M.F. of a 90 Pt-10 Rh

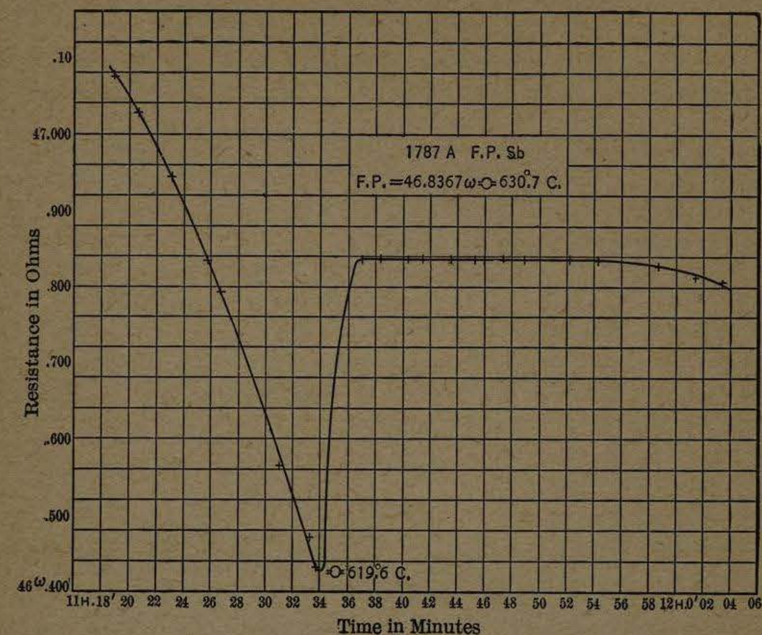

Fig. 171. Freezing of Antimony.

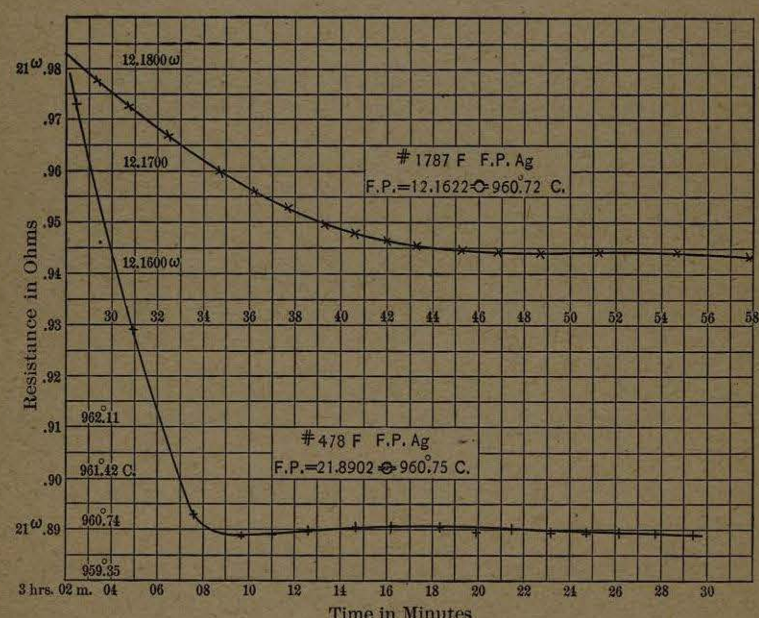

Fig. 172. Freezing of Silver.

thermocouple as ordinate for copper and aluminium, and the resistances of a platinum thermometer for antimony and silver. An inspection of the copper curve shows why this metal is desirable to use, as it gives a very flat curve. With aluminium rapid

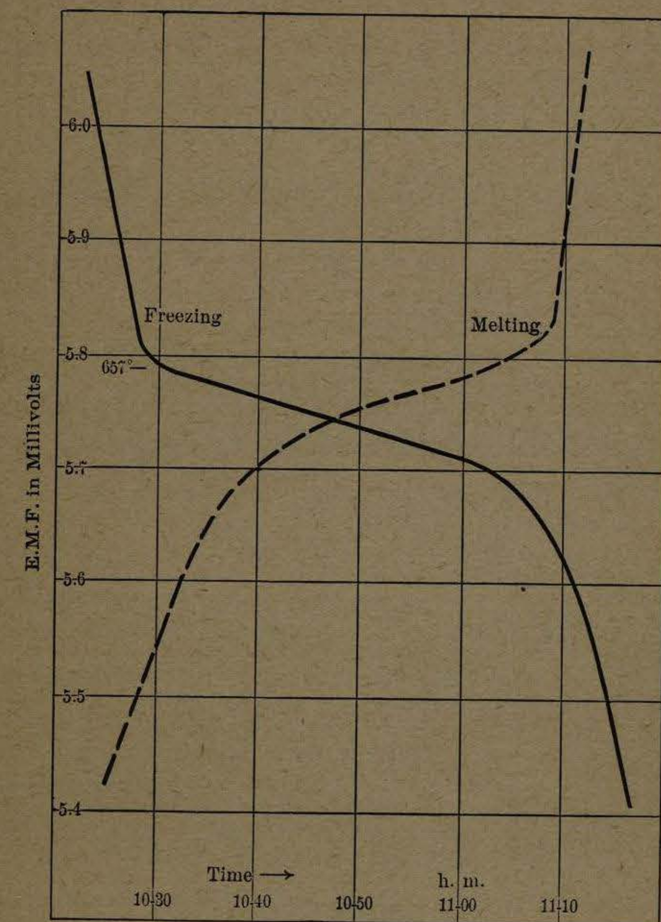

Fig. 173. Freezing and Melting of Aluminium.

cooling would be fatal to an exact determination. The slant here observed in the curve at the transition point is characteristic of the presence of impurities and of low conductivity and latent heat. For this metal the melting curve is also given, showing the melting and freezing points to differ somewhat, apparently.

Antimony undergoes great undercooling, depending on the rate of cooling, and may reach over 30° C.; but the maximum is a very definite temperature for moderate undercooling, and for a quick-acting thermometer in a charge of metal that is not too small. For silver, two rates of cooling are shown.

Boiling Points. — Sometimes it is desired to calibrate a pyrometer down to room temperature, even if in this case the use of a mercury thermometer is usually to be preferred. Use may be made of the boiling points of water, aniline or naphthaline, and benzophenone, or of the tin freezing point, 231.9°.

Water. — 100° by definition, with a variation of 0.04° for a change of 1 mm. in atmospheric pressure.

Aniline. — 184.1°, with a change of 0.05° per millimeter. This value is probably correct to 0.1°. Aniline, however, oxidizes readily.

Naphthalene. — 218.0°, with a change of 0.058° per millimeter. This point has been very carefully determined by several observers (see page 226), and naphthalene is cheap and readily obtained of sufficient purity, best tested by taking its freezing point, which should be 80.0° C.

Benzophenone.—306.0°, with a change of 0.063° per millimeter. Although expensive and difficult to get pure (melting point = 47.2°), this substance appears to be the only satisfactory one so far found possessing a sufficiently constant boiling point between 218° and 445°. The sulphur boiling-point apparatus (Fig. 169) may be used for both naphthalene and benzophenone if provided with an auxiliary condensing tube. Both these boiling points are easily kept constant to better than 0.05°.

Metallic Salts. — The different fixed points that have been mentioned are not all of a very convenient use. It would be preferable to have in the place of the metals, metallic salts for the determination of the fixed points if they can be shown to be satisfactory otherwise. These salts fortunately are for the most part without action on platinum, which is of great advantage for the standardization of thermocouples and resistance thermometers. There are few, however, whose fusing points

have been determined up to the present time in a sufficiently precise manner.

Among the salts whose freezing or melting temperatures have been carefully determined, and which may therefore be used for calibration purposes, are:

NaCl (melting) by W. P. White	801° C.
NaCl (freezing) by G. K. Burgess	800
Na_2SO_4 (melting) by W. P. White	885
Diopside ($CaMg(SiO_3)_2$) (melting) by Day and Sosman	1391
Anorthite ($CaAl_2Si_2O_8$) (melting) by Day and Sosman	1549
Lithium metasilicate (Li_2SiO_3) (melting), F. M. Jaeger	1202
Sodium metasilicate (Na_2SiO_3) (melting), F. M. Jaeger	1088

The transformation points of some salts can only be obtained satisfactorily on heating due to great undercooling when it is attempted to take their freezing points. This is true, for instance, of diopside, anorthite, and the silicates, the values for which apply only for chemically pure salts prepared artificially. Where stirring is practicable the undercooling can largely be avoided in taking freezing points of both metals and salts.

In general, salts give a less sharp melting point than metals, due mainly to low conductivity and heat of fusion of the former, and of course impurities will act in the same way. There is no difficulty, however, in keeping the melting-point curve flat to within 1° C. for some pure salts such as NaCl and N_2SO_4. There are undoubtedly other salts which might be studied to advantage, such as:

	Melting point.
1 MolNaCl+1 MolKCl	about 650°
Pb_2O_5 2 Na_2O	about 1000
$MgSO_4$	about 1150

K_2SO_4 has been used to some extent, but it appears to possess several dimorphous varieties with different melting points, like sulphur, so that the actual point observed may be uncertain. On page 367 is given a list of salts and the status of their melting points as determined by relatively less precise methods than the above.

Alloys: Eutectic Points. — In the case of certain alloys there are well-defined transition points which may be used as fixed temperatures to advantage in those temperature intervals in which there is no conveniently located and suitable metal freezing point. The most sharply defined of such transformations are the temperatures of freezing of eutectics, when, if the components are pure and the alloy is of very nearly the eutectic composition, the evolution of heat and the constancy of temperature during the transformation compare favorably, in some cases, with the freezing of a pure metal.

Such a suitable eutectic in a desirable location is that of silver and copper, which happens to have the composition Ag_3-Cu_2, whose freezing temperature has been found by Heycock and Neville to be 779.0°, and by Waidner and Burgess 779.2°. There are probably a considerable number of such transformation temperatures that could be used as fixed points to advantage. Thus the eutectics of aluminium or of antimony with the members of the iron group are probably more sharply defined temperatures than those of the commercial metals often used in standardizing thermocouples. Another well-known and fairly reproducible transformation temperature on cooling in the solid state is the recalescent point of steel (iron-carbon), of maximum effect for $C = 0.9\%$ at about 705° C. for slow cooling and somewhat lower for fast cooling.

Reproducibility of Freezing Points. — It is of great importance in pyrometry of precision and in the calibration of instruments to be able to reproduce exactly the fixed temperatures of boiling and freezing or fusion. We have seen that the materials ordinarily used for boiling points can easily be had in sufficient purity to reproduce these temperatures to within 0.05°, and that their freezing points are a delicate test of purity.

There have been several intercomparisons of the thermal reproducibility of some of the metals whose freezing temperatures are used as fixed points. Thus, Day and Allen in 1904, using thermocouples, found that the metals used in the establishment of the Reichsanstalt scale could be purchased in America, with the exception of antimony, to give the same scale to within 1° C. Waidner and Burgess, using both thermocouples and platinum-

resistance pyrometers, the latter of which is capable of the much greater sensitiveness and reliability, have made recently an exhaustive study of the reproducibility of several of the metal freezing points, as shown in the following table, in which the samples were purchased from reliable American and German firms as their best product:

Metal	Sn	Cd	Pb	Zn	Sb	Al	Cu
Number of samples...........	5	3	4	3	6	3	4
Reproducibility * in degrees C.	0.06	.26	.10	.06	2.3	1.2	1.0

There was one or more carefully analyzed sample of each metal, and this table shows that, with the exception of Sb and Al, it is very easy to get these metals pure enough from several sources. The only sufficiently pure antimony was "Kahlbaum," and the best aluminium was from the Aluminium Company of America. The uncertainty noted in the copper point is due mainly to oxidation and the uncertainties of measurement. Of the other metals often used, but not cited in the above table, silver and gold are readily obtained of the highest purity; palladium and platinum less readily so, but their purity as wires is easily tested by measuring their temperature coefficients (see Chapter V).

Temperature of the Arc and Sun. — In certain problems involving extremely high temperatures and as comparison sources for apparent stellar temperatures, the positive crater of the carbon arc and the sun's disk may be used, although the actual values to assign to their temperatures are still somewhat in doubt. In the case of measurements in terms of the radiation laws, it is to be remembered that, other things being equal and barring luminescence, the values found will be low, due to the selective radiation of carbon and of the sun's disk, or the departure of their radiation from the laws of the black body. We should expect, also, that measurements made by total-radiation methods would give lower temperatures than by spectral-radiation methods if the arc and sun have energy distributions differing from those of the black body at the same temperatures.

* The reproducibility is defined as the average deviation of the freezing points of the metals from their mean freezing point.

The following measurements have been made on the positive crater of the arc:

TEMPERATURE OF THE CARBON ARC.

Observers.	Date.	Temperature centigrade.	Method.
Le Chatelier.....	1892	4100°	Photometric; intensity of red light.
Violle...........	1895	3600	Calorimetric; specific heat of carbon.
Wilson and Gray	1895	3330	Total radiation of copper oxide, empirical relation for.
Petavel.........	1898	3830	Total light from Pt; empirical formula.
Wanner..........	1900	3430–3630	(Varying with carbons used) photometric in terms of Wien's law, page 251.
Very............	1899	3330–3730	Wien's displacement law.
Lummer and Pringsheim...	1899	3480–3930	Wien's displacement law.
Féry............	1902	3490	Total radiation; Stefan-Boltzman law.
Féry............	1904	3880	Photometric; Wien's law.
		3343	Total radiation.
Waidner and Burgess......	1904	3420	Holborn-Kurlbaum pyrometer (red and green light). Wien's law.
		3410	Wanner pyrometer. Wien's law.
		3450	Le Chatelier optical pyrometer. Wien's law.

It seems probable that the temperature of the arc is not over 3600° C., and the value 3500° C. appears to best represent the results. Considerable changes in current produce less effect on the apparent temperature than do variations in the kind of carbons used. In taking observation in the arc, it is convenient to mount the positive terminal horizontally and the negative vertically. Care should be taken to have a sufficient area at the maximum temperature, especially when using total-radiation methods. This can only be accomplished by using heavy carbons, 1.5 cm. or more in diameter, and correspondingly high currents.

Observations in terms of several of the radiation laws have been made on the apparent temperature of the sun's disk. Observation shows also that the apparent temperature falls off from the center to the limb, due to absorption in the outer layers, from which it is deduced that the photosphere has a temperature some 500° hotter than the observed value for the center of the disk.

(A) If Stefan's law is assumed to hold, and if the solar constant J as well as the coefficient σ are known, the formula $J = \sigma T^4$, with a proper choice of units, gives us T (absolute) directly; or a calibrated total-radiation pyrometer may be used if the absorption of the earth's atmosphere is corrected for.

(B) If the position of the wave length of maximum energy is known and if the spectral-energy curve for the sun resembles that of the black body, Wien's displacement law $\lambda_m T = C$ may be used if C is known.

(C) Similarly, the relation $E_m T^{-5} =$ const. may also be used.

(D) Finally, Planck's equation, $I = C_1 \lambda^{-5} \left(\epsilon^{\frac{C_2}{\lambda T}} - 1 \right)^{-1}$, gives us still another method if c_2 is known.

If these methods, including measurements with several wave lengths by (D), all gave the same temperature for the sun, using the constants characteristic of the black body in the several equations, it would follow that the apparent temperature found would be the true temperature of the sun. The spectral methods in general, however, appear to give relatively high values, indicating that the true temperature of the sun, except for luminescent effects, is higher than any of the observed values.

Some of the recent observations are given below for the apparent mean value of the temperature of the sun's disk.

SOME RECENT ESTIMATES OF THE SUN'S APPARENT TEMPERATURE.

Observers.	Mean temperature centigrade.	Method.
Millochau and Féry........	5090–5390	(A) With actinometer (solar constant = 2.8 to 2.55) and total-radiation pyrometer.
Scheiner.......	5930	(A)
Wilsing and Scheiner.....	5130–5600	(D) Using 5 wave lengths, $c_2 = 14,600$.
Nordmann.....	5050–5630	Modification of (D) with heterochrome photometer, assumes arc = 3343° C., $c_2 = 14,600$.
Abbot and Fowle	6160	(B) $\lambda_m = 0.433\,\mu$; $C = 2930$.
Abbot and Fowle	5570	(A) Solar constant = 1.95; Kurlbaum's value of σ (page 247).
Kurlbaum......	5460 or 6120	(D) Using several wave lengths and for c_2, 14,580 or 14,200.

Goldhammer has shown that (B) is probably the least reliable method, and (D) the one least subject to objection if several wave lengths are used. For measurements corrected for the earth's atmosphere, the value 6000° C. would seem to be a fair one for comparison with other celestial sources.

Table of Fixed Points. — In the actual state of our knowledge, the fixed points to which we should give preference are summarized in the table below, in which temperatures below 1600° C. are expressed in terms of the scale of the nitrogen constant-volume thermometer, which has given fairly consistent results to 1100° C., as we have seen, in the hands of several experimenters. Between 1100° and 1600° C. the results of Day and Sosman are followed, and above 1600° temperatures are expressed in terms of Wien's law (page 251), in which c_2 is taken as 14,500, as best representing the data at hand. Estimates of the accuracy with which these fixed points are known, and also of their reproducibility from a known source of supply, are given in the table. The uncertainty of some measuring device is of course included under reproducibility.

TABLE OF FIXED POINTS.

	Boiling points.	Accuracy.	Reproducibility.
Water	100.0° C.	(By definition.)	0.001°
Naphthalene	218.0	0.2	.02
Benzophenone	306.0	0.3	.03
Sulphur	444.7	0.5	.03
	Freezing points.		
Tin	231.9	0.2	0.03
Cadmium	321	0.3	0.05
Lead	327	0.3	0.05
Zinc	419	0.5	0.05
Antimony	631	1.5	0.3
Sodium chloride	800	2.0	1.0
Silver	961	2.0	0.3
Gold	1063	3.0	0.5
Copper	1083	3	1
Lithium metasilicate	1202	5	2
Diopside	1391	10	5
Nickel	1450	15	10
Palladium	1550	15	5
Platinum	1755	20	10
Tungsten	3000	100	25
Carbon arc	3500	150	50
Sun	6000	500	100

Standardization of Pyrometers. — The above discussion has shown that we possess a number of fixed points which have been established with sufficient accuracy to use them in the standardization of pyrometers. For such standardization, two courses are open besides direct comparison with a gas thermometer, a proceeding usually out of the question, and furthermore rendered superfluous by the establishment of these fixed points in terms of the gas scale. When its construction permits, a pyrometer may be calibrated by finding its indications at two or more of the fixed points, or may be compared with another which has been so calibrated. The latter method is the one used for ordinary purposes, as in the graduation of industrial instruments, but for pyrometers which are to be used as standards the former method should be used when possible.

We have discussed at some length, in their respective chapters, the methods of calibration for the various pyrometers, and it is unnecessary to dwell further on this matter, except to say that it cannot be assumed that a pyrometer once standardized is standardized for all time, especially if it is subjected to hard usage.

Standardizing Laboratories. — Recognizing the importance of establishing, preserving, and disseminating a common and authoritative temperature scale and of providing means of having pyrometers and other instruments certified as to their accuracy, some of the governments have established laboratories, such as the Physikalisch-Technische Reichsanstalt in Germany, the National Physical Laboratory in England, the National Bureau of Standards in the United States, and the Laboratoire d'Essais and the Laboratoire Central d'Electricité in France, whose functions are not only testing instruments but carrying on researches as well. The German institution, the oldest of these laboratories, has been one of the most potent factors in the development of excellency in German instruments, and has been of immense service to the industries as well as to the interests of science; and the other national laboratories are fast assuming a position of equal importance in their respective countries.

Metals and Salts of Certified Melting Points. — It would often be of great convenience, when one has to calibrate his own pyrometer, and in cases of dispute between individuals as to their respective temperature scales, to have available metals or salts the melting points of which had been certified by a standardizing laboratory. The Bureau of Standards is preparing to issue such certified metals and salts of sufficient range and number to meet the ordinary requirements of pyrometer calibration.

Electrically Heated Furnaces. — For the standardization of pyrometers as well as in many other high-temperature problems, it is necessary to preserve a constant temperature for a considerable time and to be able to reproduce a given temperature very exactly.

Electrically heated resistance furnaces best serve these ends, and great improvements have been made in their construction in recent years.

Furnaces wound with nickel wire of 1 to 2 mm. diameter on porcelain have been used considerably, but they are slow in heating up and their upper limit is about 1200° C., if the furnace is to be used frequently, although for a single heating 1400° C. may be attained with care. Platinum wire has been used to attain higher temperatures, but the use of this material in wire form is very expensive for heating.

Heræus has made electric heating to 1300° or 1450° C., depending on size of furnace, generally accessible by the substitution of platinum foil for the wire, weighing about 1.5 grams per square centimeter or having a thickness of about 0.007 mm. This reduces the cost of a platinum furnace very greatly, and has the further advantages of giving slightly greater uniformity of heating and attaining at a somewhat greater speed high temperatures than with wire-wound furnaces. Above 1500° C. chemical action sets in between the platinum and material of the tubes usually employed, so that although, as far as the platinum is concerned, 1700° C. could be maintained for a short time, yet the present safe upper limit for long periods of heating is 1400° with foil furnaces.

Their greatest weakness is the cracking of the porcelain tubes on which the foil is wound and the evaporation of the platinum when not covered with a suitable paste.

For very high temperatures, up to 2100°, the iridium-tube furnaces of Heræus may be used, as they have been with success by Nernst and others in the study of vapor pressures at these temperatures, as well as in melting point and physiochemical investigations. In Fig. 174 is shown the furnace and accessories used by Waidner and Burgess for the determination of the palladium and platinum melting points. For lower temperatures, tubes of platinum or of a platinum alloy may be used with great saving in cost.

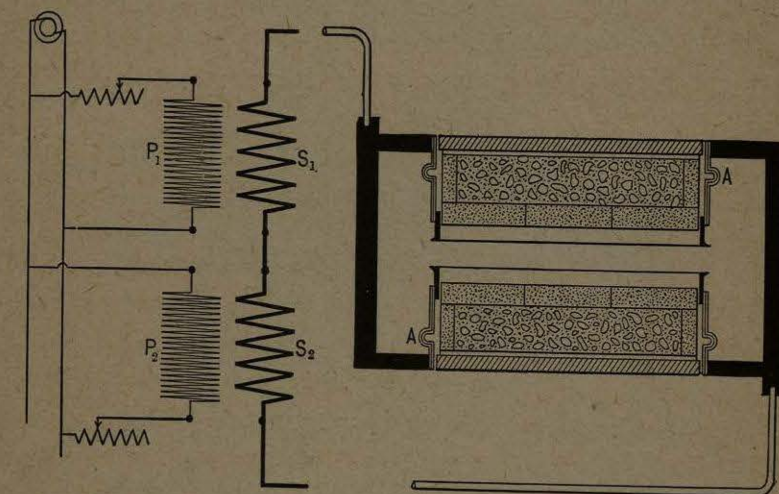

Fig. 174. Iridium-tube Furnace.

Crucible Furnaces. — A suitable form of electrically heated crucible furnace for freezing and melting point determinations to 1100° C., such as used at the Bureau of Standards, is shown in Fig. 175. The double winding with platinum ribbon gives a very delicate temperature control if connected in parallel through separate rheostats on the same battery. This furnace is designed to carry a crucible of 300 c.c. capacity, so as to give ample immersion of the thermometer at a constant temperature. If the freezing or melting of a metal is made to take twenty minutes or more, the form of the freezing or melting curve becomes a very

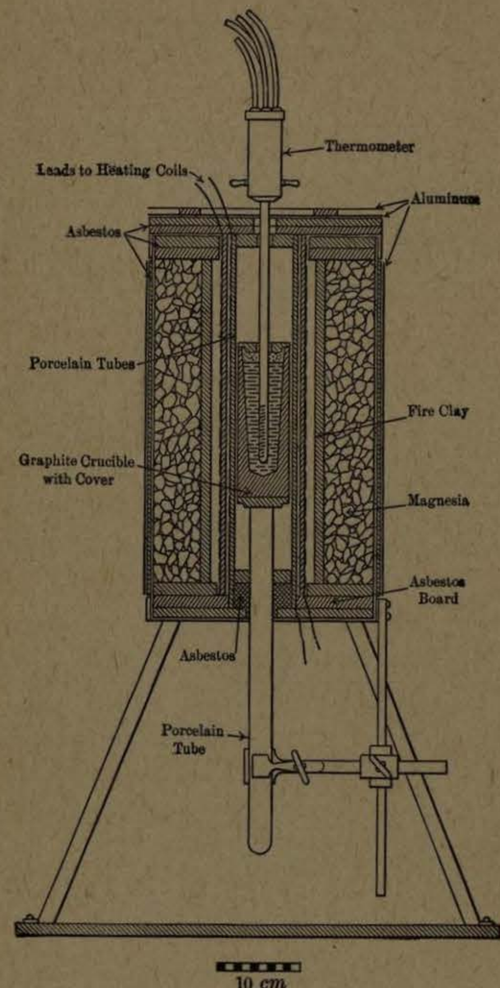

Fig. 175. Double-wound Crucible Furnace.

sensitive check on the purity of the sample. Another form of crucible furnace used successfully at the Carnegie Geophysical Laboratory to above 1600° C. is shown in Fig. 52. The characteristic of this furnace is the inwound platinum-wire heating

coil. Although of high first cost, it is a very durable furnace as constructed. Both types of furnace may be arranged for use with any desired atmosphere. Less satisfactory results will be obtained with ordinary gas furnaces to 1300° C.

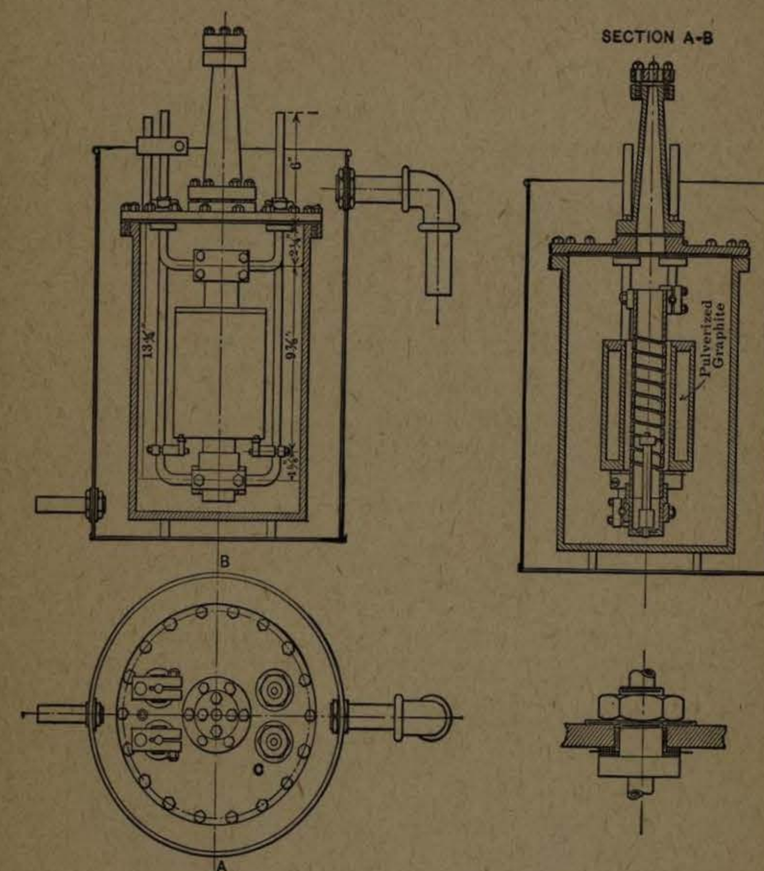

Fig. 176. Arsem Vacuum Electric Furnace.

Vacuum and Pressure Furnaces. — Mr. Arsem of the General Electric Company has developed a type of vacuum furnace which is convenient for certain melting points, such as fireclays, refractory bricks, and ashes, and chemical investigations to 2500° C. or higher. In one of its ordinary water-cooled forms, shown in Fig. 176, the heating is produced by passing an alternating current of low voltage through a graphite spiral. The highest temperatures may be reached in a few minutes. The interior is observed through a mica or glass window. Temperatures are measured with an optical pyrometer. By taking the heating curve, the transformation points for only a few tenths grams of material are easily observed. (See page 342.) Such a furnace has been in constant use at the Bureau of Standards for several years.

V. Wartenberg has successfully constructed a tube resistance furnace of tungsten mounted in vacuo (Fig. 177), and with it

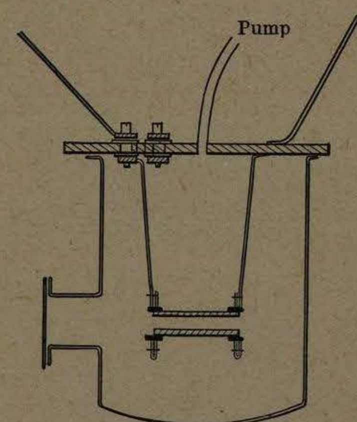

Fig. 177. Wartenberg's Tungsten Furnace.

determined the melting points of a number of refractory elements melting above 2000° C.

Messrs. Hutton and Petavel of Manchester, England, have constructed a pressure furnace for work at high temperatures, the essential parts of which are shown in Fig. 178. A vertical carbon tube was electro-coppered at the ends, soldered into brass castings, and provided with water circulation at *A* and *B*. Temperature readings were taken down the side tube of carbon, fixed into a brass tube with a window at the end, a current of hydrogen being admitted at *C*. The whole furnace was packed in crushed wood charcoal, while a thin walled graphite crucible

contained the metal to be studied. This furnace has been used by Greenwood for the determination of the boiling points of

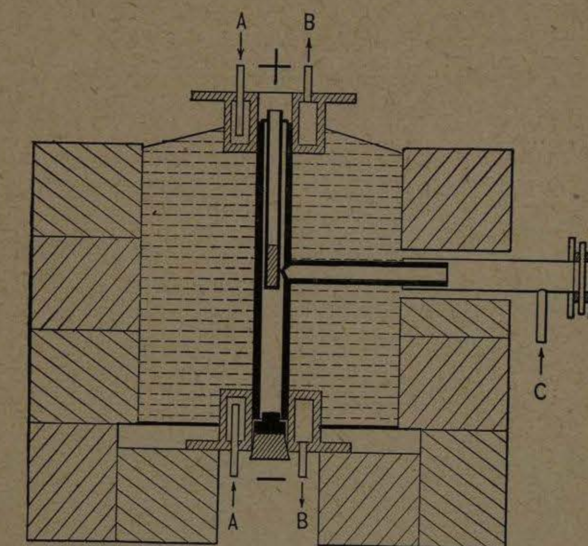

Fig. 178. Graphite Furnace of Hutton and Petavel.

some of the metals and their variation with pressure. Other types of furnace are described in Chapters II, IV, and V.