

## CHAPTER XI.

## STANDARDIZATION OF PYROMETERS.

**Thermometric Scales.**—The generally recognized standard temperature scale is that of the gas thermometer, which, as we have seen, has been realized in the form of the constant-volume nitrogen thermometer to  $1550^{\circ}\text{C}$ . This scale is fixed by the determination of certain reference temperatures, such as melting or freezing and boiling points. It would be desirable to define temperatures in terms of the normal or thermodynamic scale, which is independent of the properties of any particular substance. At the present time, however, the limit of accuracy attained in gas pyrometry does not exceed the departure of the constant-volume gas scale from the thermodynamic scale; and the scale as defined by various gases is also practically identical, so that for most practical purposes we may speak in terms of either scale interchangeably.

Above the range of the gas thermometer, we are compelled to resort to extrapolation in terms of some phenomenon varying with the temperature. For this purpose, use is usually made of the radiation laws based on the relations which have been found to exist at lower temperatures between the intensity of total and monochromatic radiation and temperature. Just as the thermodynamic scale of temperature is independent of the thermal properties of any particular substance, but would be reproduced exactly by an ideal gas, and is very nearly realized by the thermal properties of ordinary gases: similarly, the radiation scale of temperature is independent of the radiating properties of any particular substance, but would be reproduced exactly by the radiation from a black body, and is very nearly realized by the radiation from an almost completely closed, clear furnace at a uniform temperature. The radiation scale, then,

may be, and in practice is, so defined as to be the thermodynamic scale, so that we have in reality a single, continuous-temperature scale from the lowest to the highest attainable temperatures.

Unfortunately, there is not as yet a sufficiently good agreement among the few temperatures above  $1200^{\circ}\text{C}$ . determined with the gas thermometer, so that there is still considerable uncertainty in the values to assign to the constants in the radiation laws and therefore to fixed points in the higher ranges.

**Fixed Points.**—As the scale determined by the gas thermometer is the one universally recognized, it is necessary, in order to calibrate a pyrometer, to express its indications in terms of the gas scale. In general, it is not feasible to compare the readings of a pyrometer directly with those of the gas thermometer. The use of the latter becomes restricted mainly to the establishment of certain constant, reproducible temperatures or fixed points such as are given by freezing points and boiling points of the chemical elements and of certain compounds. The accuracy attainable in pyrometric researches is, therefore, limited by the exactness of our knowledge of these reference temperatures, and their determination has been and still is of the most fundamental importance in pyrometry. There have been a great many temperatures suggested for this use, but the actual number available is very small. Preference should, in general, be given to those determinations made with the gas thermometer itself, although there are others made indirectly in terms of the gas scale, as with thermocouples, optical pyrometers, and resistance thermometers, which are of considerable weight; and in fact the more common practice, when working with the gas thermometer, is to compare its readings in a furnace or bath with those of some more convenient instrument and then transfer the gas scale by means of the latter to the melting or boiling points by interpolation.

We have already called attention to many of these determinations of fixed points, among which the following may be considered in greater detail:

*Sulphur.*—(Boiling)  $444.6^{\circ}\text{C}$ . on the constant-volume scale of nitrogen, or  $444.5^{\circ}$  on the constant-pressure scale; correspond-



ing to about  $444.7^\circ$  on the thermodynamic scale, under a pressure of 760 mm.; with a variation of  $0.090^\circ$  per millimeter change of mercury in the atmospheric pressure.

The boiling point of sulphur has been the object of several series of distinct observations, among which we may cite the following, distinguishing between direct and strictly independent determinations with the gas thermometer and indirect ones by italicizing the former.

## BOILING POINT OF SULPHUR.

Observers.	Method and remarks.	S.B.P. observed.	Corr. to const. vol. $p_0=1$ at.
Regnault.....	Const. vol., about.....	$447.5^\circ$	.....
Crafts.....	Const. vol.....	445	.....
Callendar and Griffiths.....	Const. press.....	$444.53$	$444.74^\circ$
Reichsanstalt.....	Const. vol. Wiebe and Bötcher scale.....	444.5	444.5
Chappuis and Harker.....	Const. vol. corr. from $445.2^\circ$ .....	444.7	444.7
Holborn.....	Const. vol. extrapolated Pt. resistance.....	444.55	444.55
Rothe.....	Const. vol. Hg thermo. P.T.R. scale.....	444.7	444.8
	Thermocouples.....	445.0	.....
Eumorfopoulos.....	Const. press.....	$444.55$	$444.76$
Holborn and Henning.....	Const. vol.....	$444.51$	$444.51$
	Best value from above series.....		<u>444.6</u>

Regnault's figure was obtained by plunging the reservoir of the thermometer in the liquid sulphur; but this liquid will superheat, and so gives too high a value. The other eight very concordant results were obtained in the vapor.

The result first published by Chappuis and Harker, using a constant-volume thermometer, was  $445.2^\circ$ , but this difference from Callendar and Griffiths' result was shown probably to be due mainly to an incorrect value assumed for the expansion coefficient of the porcelain bulbs used by the former. Eumorfopoulos first published the value  $443.7^\circ$ , which was recognized at the time to be uncertain, as it depended upon the unknown expansion coefficient of mercury, which has since been determined by Callendar and Moss to high temperatures.

Callendar and Griffiths as well as Eumorfopoulos worked with a constant-pressure air thermometer, and it is of interest to note that the outstanding difference between several of the experimental determinations by the constant-volume and constant-pressure methods is of the order of difference to be expected between the two gas scales, — constant-volume and constant-pressure, — as seen from Callendar's table (page 31) and from Fig. 1. In fact, in work of the highest precision it will probably soon be desirable to reduce observations to the thermodynamic scale.

At the Reichsanstalt a new determination of the S.B.P. has recently been carried out by Holborn and Henning, using several gases and bulbs of glass and quartz. Their result is about  $0.2^\circ$  C. lower than would be expected from the measurements at constant pressure.

In order to reproduce the exact value of the sulphur boiling point, however, it is not sufficient to plunge the protected thermometer into the sulphur vapor, but it is necessary to guard it against superheating by radiation from the liquid and lower walls, on the one hand, and cooling by liquid sulphur condensed on the thermometer case and radiation from the thermometer, on the other hand. Unless proper precautions are taken, variations of  $1^\circ$  C. may be found. Sulphur boils very smoothly without bumping, and, in a properly constructed apparatus, condenses in a very sharp line near the top of the boiling tube. A conical or cylindrical aluminium shield with an umbrella cap fitting close about the thermometer stem serves the double purpose of shielding the instrument from radiation and condensed sulphur. A sulphur boiling apparatus with the protected thermometer in place is shown in Fig. 169, with which measurements consistent to about  $0.03^\circ$  may be obtained. Gas or electric heating may be used, and the boiling tubes may be of hard glass, porcelain, or aluminium. A study by Waidner and Burgess of the various forms of sulphur apparatus used by previous experimenters showed that they give the same temperature to a few hundredths of a degree. Commercial sulphur gives the same boiling point



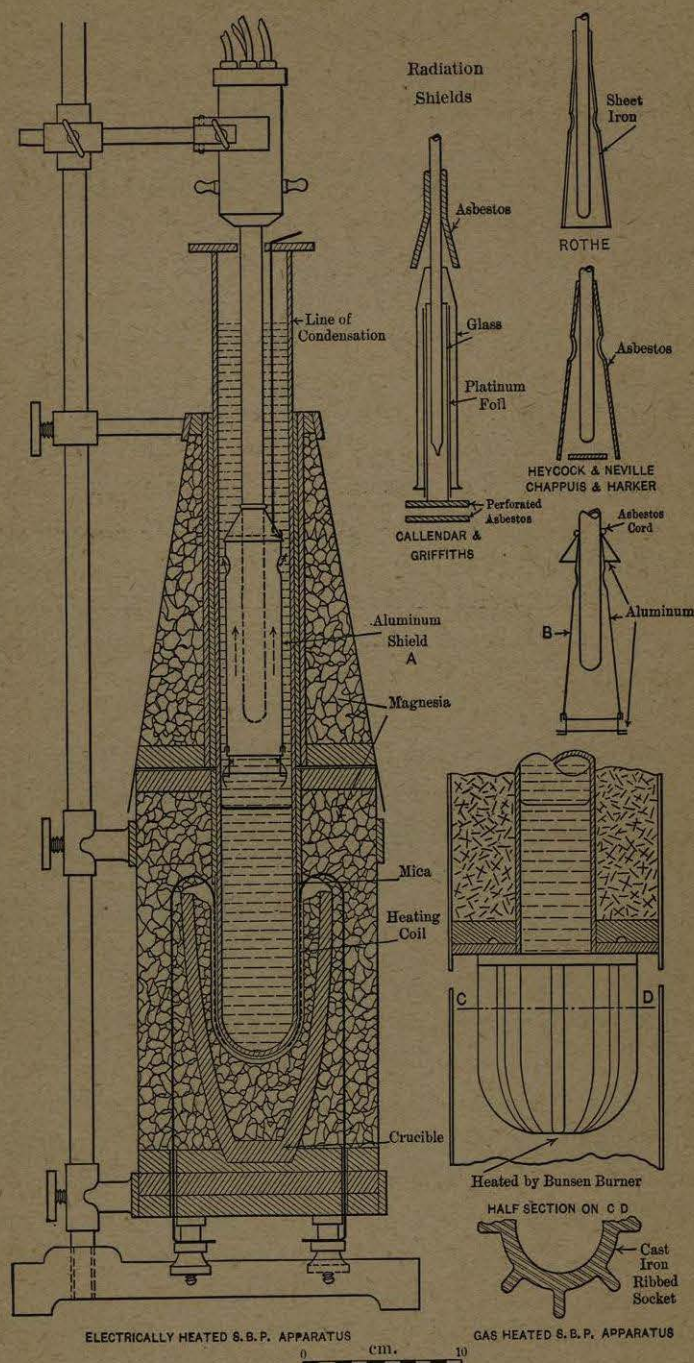


Fig. 169. Types of Sulphur Boiling Apparatus.

as the best sulphur obtainable. A criterium of satisfactory realization of the S.B.P. is the constancy of reading when a thermometer with accessories is displaced several centimeters in the vapor. Waidner and Burgess have also shown that, measured in this way, the column of vapor above boiling sulphur is constant to about  $0.03^{\circ}\text{C}$ .

In spite of the most excellent agreement of the observations in the above table, the determinations with the hydrogen thermometer by Jaquerod and Wassmer of the boiling points of naphthalene and benzophenone, and those by Day and Sosman with the nitrogen thermometer of the freezing points of zinc and cadmium, are not consistent with the value cited above for sulphur. As shown by Waidner and Burgess, using the platinum thermometer, the sulphur point as quoted would be nearly one degree too high in terms of the work of the observers mentioned above. In view of the almost universal use of the sulphur point as a calibration temperature, it is of prime importance to finally fix its value to at least better than  $0.1^{\circ}\text{C}$ .

The several determinations of the change of boiling point of sulphur with pressure are in very close agreement. For exact work, the two-term formula of Holborn and Henning, or that of Harker and Sexton, is to be preferred.

$$t = t_{760} + 0.091_2 (H - 760) - 0.044_2 (H - 760)^2.$$

**Zinc.** — (Freezing or melting)  $419.4^{\circ}\text{C}$ . Freezing points undergo unappreciable changes with variations in atmospheric pressure, and their experimental determination is somewhat easier than for boiling points if a thermocouple is used. The direct determination of a metallic freezing or melting point with a gas thermometer is beset with almost insurmountable experimental difficulties, so recourse is always had to some auxiliary pyrometer whose indications have been exactly calibrated by direct comparisons with a gas thermometer.

Zinc is easily obtained in sufficient purity. Some recent determinations of this point are:



Heycock and Neville.....	419.4 <sup>o*</sup>
Stansfield.....	418.2
Holborn and Day.....	419.0
Day and Sosman.....	418.2
Waidner and Burgess.....	419.37
Holborn and Henning.....	419.40

The first and next to the last values were obtained with the resistance pyrometer, assuming the value for the S.B.P., 444.70°; Stansfield's observation was obtained with a recording thermocouple, and the other is by direct transfer with thermocouples or resistance thermometers from the nitrogen-gas thermometer.

*Zinc.*—(Boiling) 920° C., with a variation of 0.15° for a change of 1 mm. in the atmospheric pressure.

The boiling point of zinc has been the object of a great many determinations, and yet it is one of the least known and consequently the most unreliable to try to use, and is not to be recommended. It has been the object of so much study, undoubtedly, as it was apparently the one point near the upper limit of the early experiments with the gas thermometer which could be determined directly by this instrument; but superheating effects in vapors at such high temperatures and an uneven temperature distribution are very difficult to obviate even with electrical heating.

Some of the results obtained are shown by the following table:

E. Becquerel.....	930° and 890° C.
Sainte-Claire-Deville.....	915 to 945
Barus.....	926 and 931
Violle.....	930
Holborn and Day (two observations).....	910 and 930
Callendar.....	916
D. Berthelot.....	918

The value 930° as given by Voille's and Barus' results was generally accepted until recently, but the more recent determinations indicate 930 to be over 10° high. The value adopted, 920°, is probably not in error by over 5° C.

\* The value 419.0° is obtained if an observation on an admittedly too small sample be included.

*Gold.*—(Fusion or freezing) 1063° C. This point is to-day one of the best-known fixed points, and gold possesses the advantages of being obtainable in very great purity, is not oxidizable in air, nor is it readily attacked by the silicious materials used in crucibles. Its cost is its only drawback for use in considerable quantities, but methods have been devised, as inserting a short length of wire between the leads of a thermocouple, requiring only very minute amounts of gold. These wire methods give on the average the same results as the crucible method, as shown by Holborn and Day and by D. Berthelot, although their precision is slightly less.

The early determinations of the gold point were quite discordant, but the later ones where electric heating was employed are in excellent agreement.

Pouillet.....	1180° C.
E. Becquerel.....	1092 and 1037
Violle.....	1045
Holborn and Wien.....	1070 to 1075
Heycock and Neville.....	1062
D. Berthelot.....	1064
Holborn and Day.....	1064
Jaquerod and Perrot.....	1067
Day and Sosman.....	1062

Violle's value was long quoted as the best for the gold point, but the later determinations show it to be some 20° low. Holborn and Wien's high value was obtained with a porcelain-bulb thermometer and is to be considered as replaced by Holborn and Day's value, to obtain which nitrogen in a Pt-Ir bulb was used, together with a thermocouple. The agreement of their results when working under various conditions is shown from the following observations:

Gold, sample 1.....	1064.0 ± 0.6 (crucible method)
Gold, sample 2.....	1063.5 (crucible method)
Gold, sample 2.....	1063.9 (wire method)

Not less than 300 grams was used for observations in both graphite and porcelain crucibles, while by the wire method 0.03 gram of the metal suffices.

Berthelot used his optical gas pyrometer in connection with



thermocouples and considers his result to be in error by less than 2 degrees. Heycock and Neville's result was obtained by extrapolation above the sulphur point of the platinum-resistance formula, while Jaquerod and Perrot's value was obtained in terms of a quartz-bulb constant-volume thermometer filled with various gases, the results agreeing to a few tenths of a degree. They used a modified form of the wire method, which consisted in making a small piece of gold wire a part of an alternating electric circuit, melting of the gold being noted by cessation of sound in a telephone.

Day and Sosman used their nitrogen thermometer previously described. A preliminary determination with the same apparatus by Day and Clement gave  $1059^\circ$  for the gold point on a sample found subsequently to contain iron. It was unfortunate that Holborn and Valentiner, in their gas-thermometer work to  $1600^\circ\text{C.}$ , did not repeat the gold point. An examination of their thermoelectric data shows a discrepancy of about 5 degrees at this temperature from the value here cited as most probable.

Berthelot has called attention to the fact that the later determinations are sufficiently concordant to warrant reducing them to the thermodynamic scale (see page 26).

Observers.	Gas.	Initial pressure.	Corrections.	Observed temp.	Thermodynamic temp.
D. Berthelot.....	Air	76 cm.	+ 1.36° C.	1064°	1065.6°
Holborn and Day.....	N	29 cm.	0.27	1064	1064.3
Jaquerod and Perrot.....	{ Air, N } { O, CO }	23 cm.	0.21	1067.2	1067.4
Day and Sosman.....	N	21 cm.	0.21	1062.4	1062.6

*Silver.* — (Freezing or melting)  $961.0^\circ$ . The freezing point of silver is not a constant temperature except in a reducing atmosphere, and this metal is volatile, thus making it unsafe to use under conditions in which its vapors may attack platinum wires, as of a thermocouple whose electric properties silver alters very considerably.

Many determinations of this point have been made, but it is only the recent observations that take into account the effects

of oxidizing and reducing atmospheres. Some of the determinations of the silver point follow:

	Pure Ag.	In air.
Pouillet.....	.....	$1000^\circ\text{C.}$
E. Becquerel.....	.....	960 and 916
Violle.....	.....	954
Holborn and Wien.....	970	.....
Heycock and Neville.....	960.5	955
D. Berthelot.....	962	957
Holborn and Day.....	961.5	955
Day and Sosman.....	960.0	.....
Waidner and Burgess.....	960.9	953 to 957

Melted silver exposed to the air gradually absorbs oxygen, which lowers the freezing point, and this latter is not a definite temperature, varying with the rate of cooling, mass, and surroundings. This lowering may reach 20 degrees or more. The wire method gave  $953.6 \pm 0.9$  as found by Holborn and Day. The freezing point of *pure* silver may be obtained in a graphite crucible in an atmosphere of nitrogen or of CO, or covered with powdered graphite, i.e., in conditions preventing oxidation. The melting or freezing point is equally sharp, and on account of the ease of getting very pure silver its use is strongly recommended as a fixed point.

*Copper.* — (Freezing or melting)  $1063^\circ$  in air,  $1083^\circ$  pure. Whether the gold or the copper point was the higher was long an open question in pyrometry. The great advantage in practice of copper is its cheapness, but the fact that copper apparently has two freezing points does not possess the same disadvantages as with silver, for both of the copper points are very definite, the higher one,  $1083^\circ$ , being that of the pure metal, easiest obtained with a graphite crucible, the metal being protected from the air by a layer of powdered graphite. The lower value,  $1063^\circ$ , is given by the wire method, and copper may replace gold in this way. Values intermediate between  $1063^\circ$  and  $1083^\circ$  will be obtained in crucibles for incomplete protection from air, the effect being due to the formation and solution of cuprous oxide, saturation of the copper with the oxide giving the eutectic point  $1063^\circ$  for about 3.5 per cent  $\text{Cu}_2\text{O}$ . The presence of the eutectic temperature will usually be detectable, whatever the percentage



of  $\text{Cu}_2\text{O}$  present, and this fact may be used to check the purity of copper in a crucible.

We may note the following determinations of the copper point:

Heycock and Neville.....	1080.5°
Stansfield.....	1083
Holman.....	1086
Holborn and Day.....	1084.1
Day and Sosman.....	1082.6
Waidner and Burgess.....	1083

The values obtained by Holborn and Day, and by Day and Sosman, are the only ones determined directly in terms of the gas thermometer. The difference of 20° C. between the Cu and  $\text{Cu-Cu}_2\text{O}$  points has been determined by various observers.

*Palladium.* — (Fusion) 1550°. This temperature marks the present upper limit of the gas thermometer. The following are some of the recent determinations of the palladium melting point:

Observers.	Method.	Observed melting point.	Reduced to $c_2=14,500$ .
Nernst and v. Wartenberg.....	Optical; Wien's law, $c_2=14,600$	1541°	1546°
Waidner and Burgess.....	Optical; Wien's law, $c_2=14,500$	1546	1546
Holborn and Valentiner.....	Nitrogen gas, thermocouples, and optical..... $c_2=14,200$	1575	1560
Day and Sosman.....	Nitrogen gas and thermocouples	1549	.....

Palladium may be melted in air by the wire method and therefore is a convenient control temperature for thermocouples. (See p. 186.) It will be noted that the gas-thermometer determination of Day and Sosman appears to be equivalent to a value of  $c_2 = 14,450$  in the Wien equation.

*Platinum.* — (Fusion) 1755°. Above the palladium point, resort must be had to extrapolation. There have been a great many experimental estimates made of the platinum melting point, some of them based only on extrapolation of purely empirical formulæ from temperatures below 1100° C. Such, for instance, are the thermoelectric estimates based on the formula  $E = -a + bt + ct^2$  on data which satisfy this equation only in the range 300° to 1200° C. In view of the great importance of this temperature as the best one for reference in the upper part

of the scale, all the determinations of which we are aware that have been made are included in the table. The values found prior to the year 1900 are in terms of incorrect values of the basal temperatures, and cannot therefore be correct except by accident.

#### EXPERIMENTAL DETERMINATIONS OF THE MELTING POINT OF PLATINUM.

Date.	Observers.	Method.	Published melting point.	Reduced to common scale.*
1877-1879	Violle	Calorimetric	1775-1779	.....
1892	Barus	Thermoelectric	1757-1855	.....
1895	{ Holborn and Wien	{ Thermoelectric	1780	.....
1896	{ Holman, Lawrence and Barr	{ Thermoelectric	1760	.....
1898	Petavel	Total light from Pt	1766	.....
1903	Nernst	{ Total light from black body	{ 1782	.....
1905	{ Holborn and Henning	{ Thermoelectric and optical	{ 1729	.....
1905	{ Holborn and Henning	{ Thermoelectric	1710	1755
1905	Harker	Thermoelectric	1710	1755
1906	{ Nernst and Wartenberg	{ Optical; Wien's law ( $c_2=14,600$ )	{ 1745	1751
1907	{ Waidner and Burgess	{ Optical; Wien's law ( $c_2=14,500$ )	{ 1753	1753
1907	{ Holborn and Valentiner	{ Optical; Wien's law ( $c_2=14,200$ )	{ 1782	1763
1907	{ Waidner and Burgess	{ Monochromatic radiation from Pt	{ 1750	1750
1907	{ Waidner and Burgess	{ Thermoelectric (two formulæ)	{ 1706-1730	1753
1909	Féry	{ Monochromatic radiation from Pt: Oxidizing atmos. Reducing atmos.	1690 1740	..... .....
1910	Sosman	{ Thermoelectric from Pd=1549°	1752	1755
1910	Ruff	Optical	about 1750	.....
		<b>Best Value</b> .....		<b>1755</b>

\* This scale is that for which  $c_2=14,500$  in Wien's law III, p. 251.

The published thermoelectric determinations involving extrapolation on the thermoelectric scale (equation (3), page 112) from low temperatures have little or no weight. The method used by Nernst in 1903 is not capable of great accuracy. Féry's as well as Ruff's measurements appear to have been crude, and the differences noted by the former may be due to the surface prop-



erties of the platinum in the different parts of a gas flame and not to the oxidizing and reducing atmospheres as such. All the optical measurements by the other observers were taken in an oxidizing atmosphere and are at least 50 degrees higher than Féry's oxidizing-atmosphere values. The outstanding uncertainty of the platinum point is mainly attributable to the difference assigned to  $c_2$  in the Wien formula and to the different gas scales in terms of which the extrapolations are made. The value here assigned to the platinum point, 1755, is in terms of the Day and Sosman gas scale (Pd = 1549), the optical determinations of Nernst and v. Wartenburg, and Waidner and Burgess, and the mean differences between the palladium and platinum points as found by them and by Holborn and Valentiner, thus:

Observers.	Pt-Pd.
Nernst and v. Wartenburg	204° C.
Holborn and Valentiner	207
Waidner and Burgess	207

**Rhodium.** — (Fusion) 1940°. The other members of the platinum group have had their melting points less well determined than palladium and platinum. For rhodium the following estimates, among others, have been made:

Mendenhall and Ingersoll (Pt=1755)	1932
V. Wartenberg (using a tungsten furnace)	1940

**Iridium.** — (Fusion) 2300°. Although it is questionable if temperature of 2000° C. and over can be determined in terms of the gas scale, it may, nevertheless, be found desirable to determine as exactly as may be one or more fixed temperatures in this range by other methods, as specific heat and the laws of radiation. Iridium and tungsten seem to be the most suitable for this purpose. Hardly any limit of accuracy can as yet be placed upon such determinations. For iridium the following values have been found:

Violle	1950° C.
Veder Weyde	2200
Nernst	2200 to 2240
Rasch (computed from Nernst's data)	2285
Mendenhall and Ingersoll	2300
v. Wartenberg	2360

V. Wartenberg's determination was made in a tungsten furnace in vacuo; that of Mendenhall and Ingersoll of a bead on a Nernst glower.

The recent development of furnaces suitable for use at these extreme temperatures will undoubtedly enable us to more sharply define other points in this part of the scale.

It is interesting to note that at the extreme temperature of the electric arc, 3600° C., the various radiation methods and the specific-heat method give results agreeing to about 100° C.

*Other metals melting below 1100° C., such as cadmium, lead, antimony, and aluminium, have also been used in the attempt to determine fixed points, and some of the results are given in the accompanying table for metals melting below 1100° C.*

TABLE OF FREEZING POINTS TO 1100° C.

Observers...	Stansfield.	D. Berthelot.	Heycock and Neville. Callendar.	Waidner and Burgess	Holborn and Day.	Day and Sosman.
Date.....	1898	1898-1901	1895-99	1910	1900-1901	1910
Instrument...	Recording thermocouple.	Optical interference.	Electrical resistance.	Electrical resistance.	Nitrogen ther. and thermocouple.	Nitrogen ther. and thermocouple.
Calibration data.....	0° 100 444.53	Expansion of air.	0° 100 444.53	0° 100 444.70	Pt-Ir-bulb nitrogen thermometer	Pt-Rh-bulb nitrogen thermometer
Sn.....	232.1°		231.9°	231.9°		
Bi.....	268.4		269.2			
Cd.....			320.7	321.0	321.7°	320.0°
Pb.....	325.9		327.7	327.4	326.9	
Zn.....	418.2		419.0	419.4	419.0	418.2
Sb.....			629.5	630.7	630.6	629.2
Al.....	649.2		645.5	658.0	657.0	658.0
Ag <sub>3</sub> -Cu <sub>2</sub> .....			778.5	779.2		
Ag (in air).....			955.0		955.0	
Ag (pure).....	961.5	962	960.7	960.9	961.5	960.0
Au.....	1062.7	1064	1061.7		1064.0	1062.4
Cu-Cu <sub>2</sub> O.....				1063.2	1064.9	
Cu.....	1083.0		1080.5	1083.0	1084.1	1082.6

**The Iron Group.** — A fixed point that has been frequently used is the melting point of nickel (1450°). The thermoelectric determinations based on empirical formulæ gave values varying