

THE FREEZING POINT OF PLATINUM

By Wm. F. Roeser, F. R. Caldwell, and H. T. Wensel

ABSTRACT

In determining the freezing point of platinum on the International Temperature Scale, measurements were made of the ratio of brightness of black bodies maintained at the freezing points of gold and platinum. The black bodies used were hollow inclosures of fused thorium oxide immersed in the molten metals. Observations were made during the freezing of the metals. Two optical pyrometers were used and observations were obtained on two separate lots of pure platinum by three observers. The metals were heated in air using a high frequency induction furnace to secure automatic stirring of the freezing metals and to avoid contamination from furnace windings.

The freezing point was found to be $1,773.5^{\circ}\text{C}$.

CONTENTS

	Page
I. Introduction.....	1119
II. Previous work.....	1120
III. Present work.....	1122
1. Temperature scale used and computation methods.....	1122
2. Experimental procedure.....	1124
3. Results.....	1126
4. Sources of error.....	1127
IV. Summary.....	1129
V. Acknowledgments.....	1129

I. INTRODUCTION

Since the International Temperature Scale¹ adopted in 1927 by the General Conference on Weights and Measures defines temperatures above the freezing point of gold by means of Wien's law of radiation, any determination of the melting or freezing point of platinum on this scale must be based upon measurements of the radiation emitted at some known wave length from a black body maintained at the temperature in question.

There are a number of methods by which a black body may be brought to or maintained at the melting or freezing point of a metal. Worthing² has used hollow cylinders of the metal carrying an electric current controlled so as to bring the metal slowly up to the melting point. Observations may then be made on the radiation emitted from a small opening in the side of the cylinder at the instant of melting. Mendenhall³ has used a strip of the metal folded into a hollow wedge, the angle of the wedge being so small that the radiation from the inside of the wedge approximated that from a black body. Such methods are, in some cases, the only ones available, but where feasible the methods described below are to be preferred.

Another method which has been much used is to heat a furnace to such a temperature that a small bit of the metal located in the

¹ G. K. Burgess, B. S. Jour. Research, **1**, p. 635, October, 1928.

² A. G. Worthing, Phy. Rev. N. S., **10**, p. 377; 1917.

³ C. E. Mendenhall, Astrophy. J., **33**, p. 91; 1911.

furnace will just melt or freeze. The bit of metal, the melting or freezing of which serves to indicate the proper time to make observations, is usually welded between thermocouple elements at the hot junction, melting or freezing being indicated by a constant value of the emf of the thermocouple for a short period of time while the temperature of the furnace is changing slowly. This method, commonly referred to as the wire method, has been studied by Fairchild, Hoover, and Peters,⁴ who have discussed its limitations in great detail. The one obvious disadvantage of the wire method is that the melting or freezing metal indicates the temperature of only a very small region of the furnace, whereas the radiation measured depends on the temperature of other parts of the furnace as well. At the temperature of freezing platinum one would be very fortunate if the equivalent temperature of the radiation emitted from the furnace did not differ by several degrees from the temperature of the furnace at the point where the melting sample was located.

A better method, which is termed the crucible method, is to immerse a hollow inclosure in a bath of the metal and to make observations during the time the metal is melting or freezing. Since no considerable temperature differences can exist in such a bath of metal, this method insures that the radiation measured is very nearly that from a black body at the melting or freezing point in question. Freezing points are preferable to melting points, since temperature gradients are likely to be smaller in liquid than in solid metal. If, finally, the freezing is done in a high frequency induction furnace with reduced power on the furnace, the action of the electromagnetic field on the currents induced in the metal produces a violent stirring, and the possibility of appreciable temperature gradients is further reduced.

In spite of the fact that the crucible method appears to be the ideal one for accurate melting or freezing point determinations, it has not been very widely used. For example, no determination of the freezing or melting point of platinum by this method is to be found in the literature. One reason for this is probably the fact that the crucible method demands refractories from which crucibles may be made which in prolonged contact with the molten metal will produce no appreciable contamination. The freezing points of palladium⁵ and nickel⁶ have recently been accurately determined in crucibles which produced no perceptible contamination, and the recent development of fused thorium oxide⁷ provides a refractory in which pure platinum may be repeatedly melted without detrimental contamination. In view of the importance of the platinum point and the uncertainty felt regarding its temperature, determinations have been made by the crucible method, using crucibles of fused thorium oxide and melting the metal in an induction furnace.

II. PREVIOUS WORK

Since 1912 two determinations of the melting point of platinum have been reported. In 1924 Hoffmann,⁸ using the wire method in an iridium wound furnace, obtained the value 1,771° C. on the scale

⁴ Fairchild, Hoover, and Peters, *B. S. Jour. Research*, **2**, p. 931; May, 1929.

⁵ Fairchild, Hoover, and Peters, *B. S. Jour. Research*, **2**, p. 931; May, 1929.

⁶ Wensel and Roeser, *B. S. Jour. Research*, **5**, p. 1309; December, 1930.

⁷ Swanger and Caldwell, *B. S. Jour. Research*, —, p. —, 1931.

⁸ Fr. Hoffmann, *Zeits. f. Phys.*, **27**, p. 285; 1924.

then in use at the Physikalisch-Technische Reichsanstalt, based on $1,063^{\circ}$ C. for the melting point of gold and a value of 1.430 cm degrees for C_2 . This value reduces to $1,769.5^{\circ}$ C. on the present International Temperature Scale based on $C_2=1.432$ cm degrees. Since the completion of the work described in this paper Ribaud and Mohr⁹ reported measurements on tubes of platinum, such as were used by Worthing in the case of tungsten, and obtained a value of $1,762^{\circ}$ C. Int.

Reviewing the literature, we find 14 independent determinations of the melting point of platinum. Nine of these, listed in Table 1, were made by employing uncertain extrapolation methods and although they were of value at the time they were made, they are now considered to be of historical interest only. The remaining five, including the two recent determinations noted above, are listed in Table 2. These five determinations were made by measuring with an optical pyrometer the ratio of brightness of black bodies at the melting points of gold and platinum, respectively, and calculating the platinum point by means of Wien's law of radiation.

TABLE 1.—*Determinations of the melting point of platinum by extrapolation methods*

Observers	Date	Property extrapolated	Reported value	Corrected value on present scale
	Year		$^{\circ}$ C.	$^{\circ}$ C.
Vielle ¹	1877	Specific heat.....	1,779	-----
Barus ²	1892	Electromotive force.....	1,855	-----
Holborn and Wien ³	1892	do.....	1,780	-----
Harker ⁴	1905	do.....	1,710	-----
Holborn and Henning ⁵	1905	do.....	1,710	-----
Do. ⁵	1905	Spectral emissivity.....	1,729	1,739
Waidner and Burgess ⁶	1907	Electromotive force.....	1,731	-----
Do. ⁶	1907	Spectral emissivity.....	1,750	1,761
Day and Sosman ⁷	1912	Electromotive force.....	1,752	-----
Mean.....			1,755	-----

¹ Vielle, Comp. Rend., 85, p. 543; 1877.

² Barus, Bull., 54, U. S. Geological Survey; 1889. Die Physikalische Behandlung und die messung hoher Temperaturen, Leipzig; 1892.

³ Holborn and Wien, Wied, Ann., 47, p. 107; 1892.

⁴ Harker, Royal Society, A., 76, 1905.

⁵ Holborn and Henning, Sitz. Ber. d. Koen Preuss. Akad. Wis., p. 311; 1905.

⁶ Waidner and Burgess, B. S. Bull., 3, p. 163; 1907.

⁷ Day and Sosman, Am. J. Sci., 33, p. 517; 1912.

TABLE 2.—*Determinations of the melting point of platinum with optical pyrometer by the ratio of brightness method*

Observers	Date	Scale used		Value reported	Value on the International Temperature Scale
		C_2	Au point		
	Year	cm deg.	$^{\circ}$ C.	$^{\circ}$ C.	$^{\circ}$ C.
Nernst and Von Wartenburg ¹	1906	1.46	1,064	1,745	1,763
Holborn and Valentiner ²	1907	1.42	1,064	1,789	1,777
Waidner and Burgess ³	1907	1.45	1,064	1,753	1,764
Hoffmann ⁴	1924	1.430	1,063	1,771	1,769.5
Ribaud and Mohr ⁵	1931	1.432	1,063	1,762	1,762
Authors.....	1931	1.432	1,063	1,773.5	1,773.5

¹ Nernst and Von Wartenburg, Verh. d. Deut. Phys. Ges. p. 48; 1906.

² Holborn and Valentiner, Ann. d. Phys., (4) 22, p. 1; 1907.

³ Waidner and Burgess, B. S. Bull., 3, p. 163; 1907.

⁴ Fr. Hoffmann, Zeits. f. Phys., 27, p. 285; 1924.

⁵ G. Ribaud and P. Mohr., Comp. Rend., 192, p. 37; 1931.

⁹ G. Ribaud and P. Mohr, Comp. Rend., 192, p. 37; 1931.

III. PRESENT WORK

1. TEMPERATURE SCALE USED AND COMPUTATION METHODS

On the International Temperature Scale adopted in 1927, the temperature t , in $^{\circ}\text{C}$., of a black body above the freezing point of gold ($1,063^{\circ}\text{C}$. or $1,336^{\circ}\text{K}$.) is defined by the formula:

$$\log_e R = \log_e \frac{J}{J_1} = \frac{1.432}{\lambda} \left(\frac{1}{1,336} - \frac{1}{t+273} \right) \quad (1)$$

(where)

$$J_1 = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda 1,336}} \quad (2)$$

$$J = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda(t+273)}} \quad (\text{Wien's law}) \quad (3)$$

and $C_2 = 1.432$ cm deg.

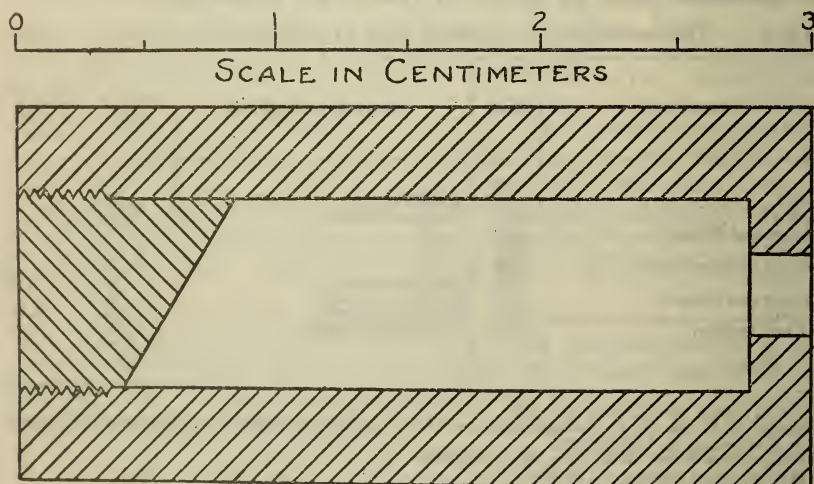


FIGURE 1—Platinum black body used in calibrating optical pyrometers

The brightness ratio $\frac{J}{J_1}$ for the platinum point, using red light, is approximately 300, and consequently a sector disk of about 1° angular opening would be required to measure this ratio in one step. The uncertainty in the measurement of such an opening would be about 20 seconds of arc corresponding to an uncertainty of nearly 1° in the computed temperature. The use of sector disks of larger openings to measure the ratio in two steps very materially reduces the uncertainty due to the errors of measurement of the angular opening. For example, two of the sectors, No. 3 and No. 2, used in this work transmit, respectively 0.7611 and 2.6258 per cent of light, an uncertainty of 20 seconds in the measurement of the angular opening corresponding to only 0.4° and 0.1°C ., respectively.

In measuring the ratio of brightness in two steps, the hollow platinum cylinder shown in Figure 1 was used to obtain measurements at intermediate temperatures. The cylinder was inclosed to prevent

air currents produced by the rotating sector disk from causing fluctuations in the temperature of the cylinder. The inclosed space was evacuated to prevent overheating of the glass window. The thick walls and the form of the platinum cylinder insure a fairly high degree of temperature uniformity inside the cylinder and by the use of storage batteries for supplying power to the furnace, the temperature could be maintained very nearly constant.

The procedure followed in taking observations and the methods of computing the freezing point of the platinum will appear from the following examples. The value given in (b) of each example was obtained by observer W. F. R. as the mean of all observations with this pyrometer, sector, and ingot. All other values given in these examples are the means for the three observers. The mean for the three observers at the gold point and at the intermediate temperatures were used throughout, since the variations among the values by the various observers were equivalent to not more than 0.3°C .

The first example is for pyrometer lamp F10 when using sector No. 2 (transmission 2.6258 per cent).

- (a) The telescope was sighted into the black body immersed in freezing gold and the lamp current required to obtain a brightness match was found to be 0.11680 ampere. (No sector used.)
- (b) The telescope was sighted through sector No. 2 into the black body immersed in freezing platinum and the lamp current required to obtain a brightness match was now found to be 0.14944 ampere.
- (c) The telescope was sighted through a sector disk of 13.013 per cent transmission into the black body shown in Figure 1, the temperature of which was adjusted so that a match was obtained when the current through the lamp was 0.11680 ampere.
- (d) With the temperature of the black body maintained constant at the same temperature as in (c), the sector was removed and the lamp current now required to obtain a match was found to be 0.14911 ampere.
- (e) Substituting in the equation (1) defining the temperature scale:

$$\frac{1}{0.13013} \text{ for } \frac{J}{J_1}$$

and 0.6537×10^{-4} cm for λ , the effective wave length for the temperature interval in question, the temperature of the black body was found to be $1,252.8^{\circ}\text{C}$.

- (f) From the temperature $1,252.8^{\circ}\text{C}$ for 0.14911 ampere and the corresponding value of $\frac{di}{dt}$ for lamp F10, we find that 0.14944 ampere corresponds to $1,254.6^{\circ}\text{C}$.
- (g) The equation:

$$\log_e \frac{J}{J_m} = \frac{1.432}{\lambda'} \left(\frac{1}{1,254.6 + 273} - \frac{1}{t + 273} \right) \quad (4)$$

similar to equation (1), may be derived from Wien's law and upon substituting for $\frac{J}{J_m}$, $\frac{1}{0.026258}$, and for λ' , 0.65226×10^{-4} cm, the effective wave length of the red screen for the temperature interval used here, we obtain $1,772.6^{\circ}\text{C}$ for the freezing point of platinum from this particular set of observations.

The next example is for pyrometer lamp F10 when using sector disk No. 3. (Transmission 0.7611 per cent.)

- (a) The current required to obtain a brightness match at the freezing point of gold was 0.11680 ampere as before.
- (b) The telescope was sighted through sector disk No. 3 into the black body immersed in freezing platinum, and the current required to obtain a brightness match was found to be 0.12781 ampere.

- (c) By using sector disks with various openings, the current-temperature relation of the lamp was determined by the method employed in (c), (d), and (e) of the first example.
- (d) From this relation, we find that the current of 0.12781 ampere corresponds to a temperature of 1,133.5° C.
- (e) Using the equation:

$$\log_e \frac{J}{J_m} = \frac{1.432}{\lambda''} \left(\frac{1}{1,133.5 + 273} - \frac{1}{t + 273} \right) \quad (5)$$

also similar to equation (1), and substituting $\frac{1}{0.007611}$ for $\frac{J}{J_m}$ and for λ'' , 0.65262×10^{-4} cm, the effective wave length of the red screen for the temperature interval used here, we obtain 1,773.4° C. for the freezing point of platinum from this set of observations.

The mean effective wave length, λ , of the red glass screen for a given temperature interval θ_1 to θ_2 is that wave length at which the ratio of black body radiation intensities at the two temperatures is equal to the ratio of the brightness of a black body at θ_1 to that of a black body at θ_2 , both viewed through the red screen. The values of λ were computed from the spectral transmission of the red glass filter and the average observer's visibility curve as described by Fairchild, Hoover, and Peters.¹⁰ Characteristics of the red glass screen are given in that paper.

All the sector disks used had two openings and were made by mounting steel strips on aluminum disks. The edges of the steel strips were ground or "lapped" straight and aligned to be radial with the aid of a circular dividing engine.

2. EXPERIMENTAL PROCEDURE

The observations on the freezing point of platinum were made upon the same crucibles of platinum as were used in the work on "The Waidner-Burgess Standard of Light"¹¹ reported elsewhere in this journal. The platinum (approximately 185 g) containing the immersed black body is shown in Figure 2. The sight tube or immersed black body, and the crucible were of a very pure grade of fused thorium oxide as described elsewhere¹² in this journal. The crucibles and sight tubes used with both the platinum and the gold were identical in all respects. The metals were both melted in air, by means of a high-frequency induction furnace. There are several advantages to be gained by the use of this type of furnace, the important ones being the stirring of the molten metal mentioned earlier and the freedom from contamination such as might occur from the metallic vapors from the winding in a resistance type of electric furnace. Cracking of the crucible caused no trouble, since the molten metal will not flow through narrow cracks in the crucible unless heated greatly above the melting point.

Two separate lots of platinum designated as ingot No. 1 and ingot No. 2 prepared at this bureau especially for this purpose, and two lots of gold, the purest obtainable from the Bureau of the Mint, were used. The tests made of the purity of the platinum are described elsewhere¹³ and indicate that the degree of contamination was

¹⁰ See footnote 4, p. 1120.

¹¹ Wensel, Roeser, Barbrow, and Caldwell, *B. S. Jour. Research*, **6**, p. 1103; 1931.

¹² Swanger and Caldwell, *B. S. Jour. Research*, **6**, p. 1131; 1931.

¹³ Wensel, Roeser, Barbrow, and Caldwell, *B. S. Jour. Research*, **6**, p. 1103; 1931.

scarcely great enough to affect the freezing point by more than 0.2°C . It is estimated that the total impurities were always less than 0.003 per cent during the course of this work.

Two optical pyrometers were used, each provided with a lamp having optically flat windows. The first of these pyrometers, shown in Figure 3, has been described by Fairchild and Hoover.¹⁴ The

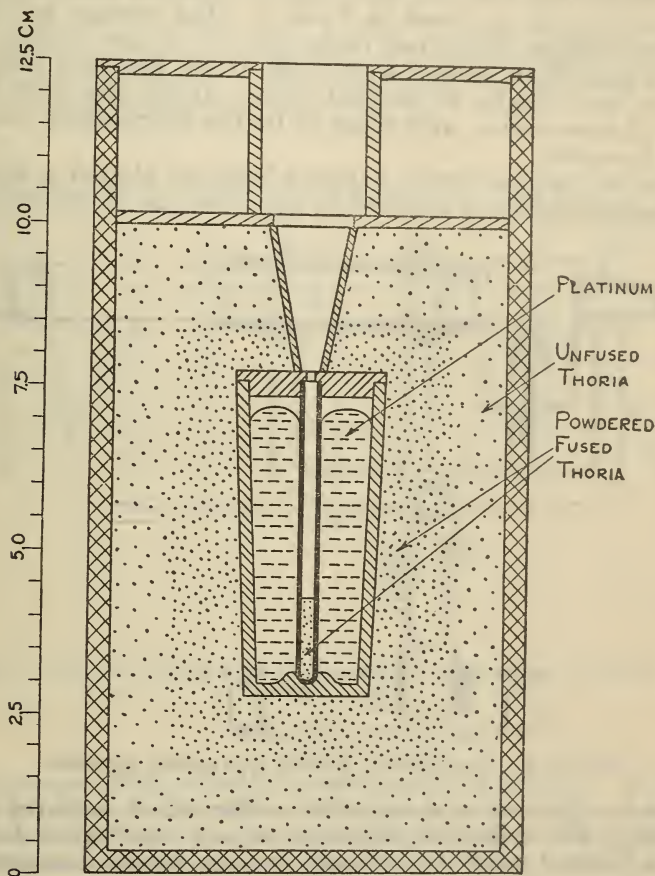


FIGURE 2.—Cross-section showing platinum, sight tube, crucible, and insulation

other pyrometer similar to the first, but giving a much higher magnification, was designed for use as a micropyrometer. The precision attainable with this pyrometer containing lamp F15, was slightly less than that attainable with the first, containing lamp F10, but the mean of the series of values obtained with it was nevertheless given the same weight as each of the two series obtained with the other pyrometer.

The telescopes were equipped with 45° total reflecting prisms so that the telescopes were horizontal while the crucibles were vertical.

¹⁴ Fairchild and Hoover, *J. Opt. Soc. Am. and Rev. Sci. Instrs.*, **7**, No. 7, p. 543; 1923.

3. RESULTS

All three of the authors served as observers. A value for the freezing point was calculated from the results of each observer using each sector disk with each lamp on each lot of platinum, excepting that lamp F15 was not used on the first lot of platinum, ingot No. 1. The 18 values thus obtained, representing 43 freezes of platinum and 47 freezes of gold are listed in Table 3. The average number of pyrometer settings during one freeze was 12, so that slightly more than 500 pyrometer settings were made at the platinum point and about the same number at the gold point. Approximately the same number of observations were made to fix the intermediate temperatures as described.

The values obtained during a typical freeze are plotted in Figure 4. The pyrometer field was matched at time intervals of approximately

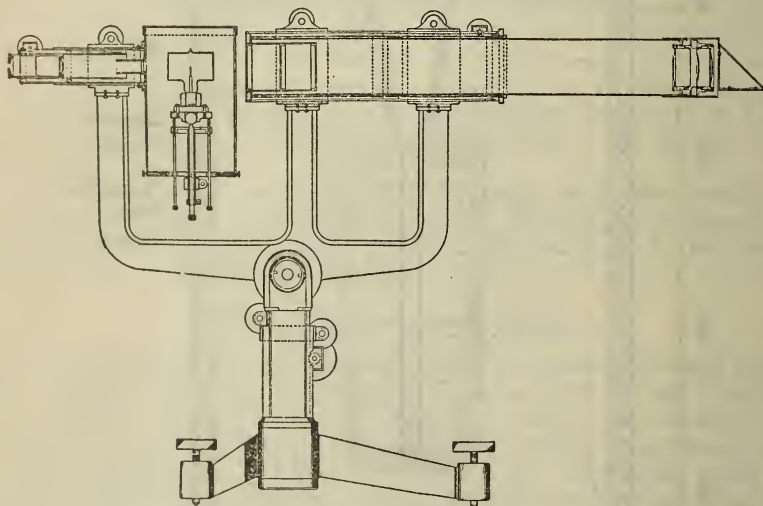


FIGURE 3.—Disappearing filament type optical pyrometer

30 seconds. The curve shows undercooling which occurred almost invariably. The maximum deviation of any observation from the mean in Figure 4 is 0.8°C. , although in some freezes it amounted to 1.0°C.

TABLE 3.—Summary of determinations of the freezing point of platinum

Observer	Ingot No. 1 lamp F10		Ingot No. 2 lamp F10		Ingot No. 2 lamp F15		Mean for observer
	Sector No. 2	Sector No. 3	Sector No. 2	Sector No. 3	Sector No. 2	Sector No. 3	
	°C.	°C.	°C.	°C.	°C.	°C.	°C.
H. T. W. -----	1, 773. 7	1, 774. 0	1, 773. 0	1, 773. 7	1, 774. 0	1, 775. 8	1, 774. 0
W. F. R. -----	1, 774. 1	1, 773. 7	1, 772. 6	1, 773. 4	1, 773. 6	1, 775. 3	1, 773. 8
F. R. C. -----	1, 772. 1	1, 771. 9	1, 771. 9	1, 773. 3	1, 773. 2	1, 774. 0	1, 772. 7
Mean-----	1, 773. 3	1, 773. 2	1, 772. 5	1, 773. 5	1, 773. 6	1, 775. 0	1, 773. 5
Mean-----	1, 773. 2		1, 773. 0		1, 774. 3		-----
Mean-----							-----
	F. P.=1, 773. 5° C. Int.						

The observations on the crucible of gold taken throughout the work indicated that any change which took place in the pyrometer lamps corresponded to not over 0.1°C ., the limit that can be detected with the pyrometers used. After the observations on the platinum were completed, a new crucible of gold was made up and observations with each lamp on the second crucible differed by less than 0.1°C ., from those on the first crucible.

The values of $1,773.5^{\circ}$ and $1,063.0^{\circ}\text{C}$., for the freezing points of platinum and gold correspond to a brightness ratio of 299.0 for $\lambda=0.6528\mu$, the effective wave length of the color filter for the temperature interval $1,063^{\circ}$ to $1,773.5^{\circ}\text{C}$.

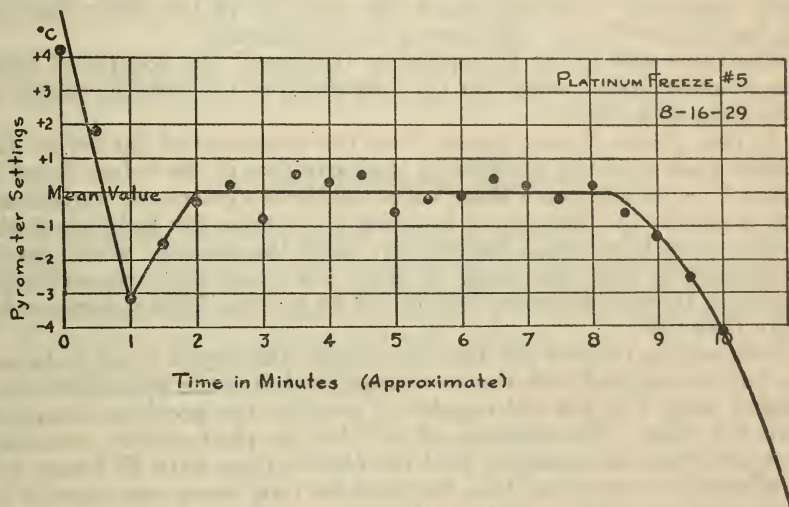


FIGURE 4.—Sample freezing curve, showing variations of pyrometer settings about the mean

4. SOURCES OF ERROR

A summary of the estimated errors is given in Table 4. All of these estimates are maximum values. The errors in the transmission of the sector disks, in the effective wave length, and in the photometric matching are not difficult to estimate, since these factors have been studied for a period of years. The estimate of 0.3°C . for the maxi-

TABLE 4.—Summary of estimated errors

Source of error	Equivalent in degrees	
	Sector No. 2	Sector No. 3
Transmission of sector.....	0.1	0.4
Effective wave length.....	.4	.4
Photometric matching.....	.5	.5
Temperature gradients and lack of black body conditions.....	.3	.3
Impurity of metal.....	.2	.2
Maximum error if all are of same sign.....	1.5	1.8

imum error due to the lack of black body conditions and temperature gradients in the walls of the sight tube is based upon measurements made at the freezing point of gold using thorium oxide and graphite black bodies. A hollow inclosure of graphite immersed in a freezing metal may be taken as a 100 per cent black body for this purpose and the temperature drop through the wall may be neglected, since the thermal conductivity of graphite is known to be high. The measurements indicated that the brightness of the thorium oxide black body was higher than that of the graphite black body by an amount equivalent to 0.1°C . This difference is opposite in sign to the difference that one deduces from a consideration of the physical properties of these materials. However, since the accuracy of the determination was only 0.15°C ., the difference is not significant.

The error due to the impurities in the metal was computed from simple assumptions regarding the depression of the freezing point by impurities in solution.

At first glance it may appear that the estimates of the errors are smaller than would be justified by the variations in the values listed in Table 3, especially since these values indicate systematic variations. For example, the differences between the values for individual observers point to errors in the effective wave lengths used which result in differences from the mean of 0.5° , 0.3° , and 0.8° , respectively. The final average, however, should not be in error from this cause by more than 0.4° .

It should be pointed out that the largest differences occur between the values obtained with the two lamps, and that the pyrometer containing lamp F15 was not capable of yielding the precision obtained with the other. The estimate of 0.5° for the photometric matching does not mean, for example, that the observations with F15 may not be affected by more than this, but that the final mean can scarcely be in error by more than 0.5° from this cause. Moreover the variations in Table 3 are not all due to one cause. A different red screen was used with the two pyrometer lamps, requiring an independent determination of the spectral transmission from which to compute the effective wave length to be used.

While the less precise observations with lamp F15 have apparently been given equal weight with those taken with lamp F10, this is really not the case. Of the 43 freezes taken, 30 were obtained with ingot No. 2. Of these 30 freezes, 12 were obtained with F10 and 18 with F15, but these 18 have been given equal weight with the 12 with F10. Moreover, since two-thirds of the values in Table 3 were obtained with lamp F10, the final average is determined largely by the results obtained with the pyrometer of greater precision. On the whole, the agreement between the values obtained with the two pyrometers is all that could be expected under the circumstances, and the final mean does not depend greatly on the method used in averaging the results.

The probable error of the mean, based on the agreement among themselves of the 18 values of Table 3, is 0.15°C . The value obtained for the freezing point, $1,773.5^{\circ}\text{C}$. Int., is considered to be accurate to 1° .

IV. SUMMARY

The freezing point of platinum has been determined on two distinct lots of metal of exceptionally high purity. Measurements were made by three observers using two precision optical pyrometers.

Hollow inclosures of fused thorium oxide were immersed in molten platinum and in molten gold. The metals were melted in air in fused thorium oxide crucibles by means of a high frequency induction furnace. Observations of the relative brightness, at wave length 0.6528μ , during the freezing of the metals yielded $1,773.5^{\circ}\text{C}$. for the freezing point of platinum on the International Temperature Scale on which the freezing point of gold is $1,063^{\circ}\text{C}$. and the value of C_2 , the second constant in Wien's law, is 1.432 cm degrees . The ratio of brightness for the above wave length was found to be 299.0.

The value obtained for the freezing point is considered to be correct within $\pm 1^{\circ}\text{C}$.

V. ACKNOWLEDGMENTS

The authors wish to express their appreciation to L. R. Kleinschmidt and H. A. Buchheit for preparation of the platinum sponge, to W. H. Swanger and J. S. Acken for melting the sponge into ingots, to E. Wickers for the chemical analyses, and to W. F. Meggers and B. F. Scribner for the spectrochemical analyses.

WASHINGTON, March 4, 1931.