# A NEW DETERMINATION OF THE MELTING POINT OF PALLADIUM

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**ABSTRACT**

The melting point of palladium was determined by measuring with an optical pyrometer the ratio of brightness of the red light ($\lambda = 0.6528\mu$) emitted by black bodies at the melting points of palladium and gold, respectively. The crucible method was shown to be more reliable than the wire method. Especial attention was given to the purity of the metals. The result obtained by the crucible method, when substituted in Wien's or Planck's equation, gives the melting point of palladium as 1,556.6° C. with an uncertainty of 1°. In the computations $C_2$ was taken as 1.432 cm deg. and the melting point of gold as 1,063° C. The average of the present result, and those of six previous determinations, is 1,553° ± 0.7°. Estimating the uncertainty in $C_2$ as 0.002 and in the melting point of gold as 0.5°, it is concluded that the uncertainty in the value of the melting point of palladium on the centigrade thermodynamic scale is approximately 2°.

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## I. INTRODUCTION

When the latest determination of a physical constant is in good agreement with the best value derivable from all previous acceptable data, the situation is regarded as satisfactory. But when the modern investigator's result departs considerably from this figure, the uncertainty in the value of the physical constant is not decreased unless a reasonable explanation is offered.

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This has been the situation with the melting point of palladium since Hoffman and Meissner[2] in 1919 obtained 1,556° C. when the mean was less than 1,553° and the average departure of previous values from the mean was about 2°. Moreover, the value 1,550° obtained in 1910 by Day and Sosman,[3] using a gas thermometer, was considered by them to be good to +2°. Therefore it seemed well worth while to redetermine the value of this important fixed point of the high-temperature scale.

Since 1911 no investigator has undertaken to measure high temperatures with a gas thermometer, and there is little likelihood that such measurements above 1,500° C. will again be attempted. The experimental difficulties are too great. Radiation methods of measurement are to be preferred. Measurements of total radiation from a black body, with the application of the Stefan-Boltzmann law for the establishment of a high-temperature scale, are to be preferred on theoretical grounds to dependence on Planck's law and measurements with an optical pyrometer or spectrophotometer. However, a greater precision can be obtained in measurements with an optical pyrometer than in measurements with a total radiation pyrometer; moreover, there is an increasing belief in the validity of Planck's law for spectral distribution of radiation from a black body, and experimental data confirming the quantum theory are accumulating rapidly. The uncertainty in the value of $C_2$ of Planck's law has been reduced in recent years to the order of 0.002 in 1.432 cm deg., an uncertainty equivalent to about 1° C. at 1,550° C.

## II. METHODS

The method used was, in brief, to compare by means of an optical pyrometer the brightness of a black body at the melting point of palladium with that of a black body at the melting point of gold. There were two modifications of the method—(1) crucible method and (2) wire method.

In the crucible method the pyrometer was sighted into a black body immersed in freezing or melting metal in a crucible. In the wire method a Lummer-Kurlbaum black-body furnace was employed. Its temperature was determined by the melting of a small bit of gold or palladium wire placed within it. The wire was fused in between the hot junction ends of a thermocouple so that its emf would show a halt at the melting point while the furnace temperature slowly rose.

From the brightness measurements, or pyrometric readings, the melting point of palladium is computed according to Wien's law, which is equivalent to Planck's law for light, and such a temperature,

[2] Hoffman and Meissner, Ann. d. Phys., 60, p. 201; 1919.
[3] Day and Sosman, Am. J. Sci., 29, p. 93; 1910; 43, p. 521; 1912.

basing the calculation on the melting point of gold and the value of the constant $C_2$ of Wien's law.

## 1. OPTICAL PYROMETER

The particular instrument used in this work is shown in Figure 1. It was built at the Bureau of Standards for the purpose of studying the characteristics, sources of error, etc., of the disappearing-filament optical pyrometer. The design was developed to give high precision and reliability.

The study of the instrument extended over a period of years. Particular attention was paid to diffraction,[4] to the effects of lens imperfections, to diaphragms or stops, and to the pyrometer lamp.
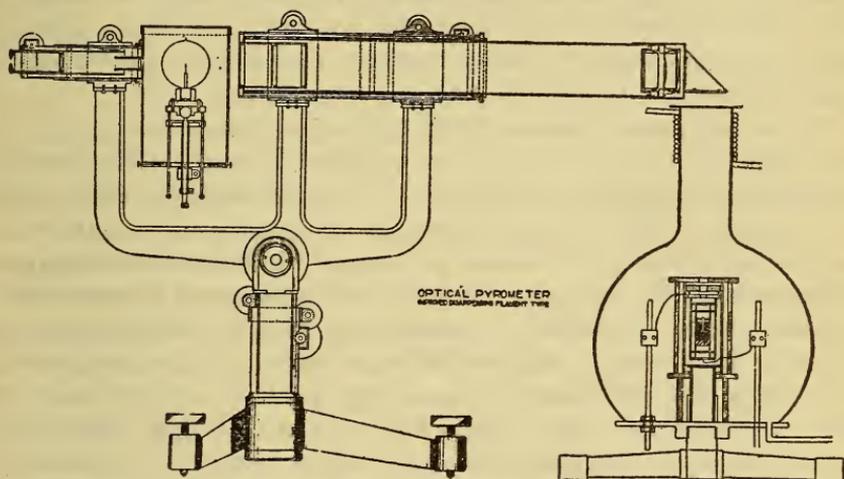


OPTICAL PYROMETER

FIGURE 1.—*Optical pyrometer furnace and crucible of metal*

The front objective is an F3 lens computed at the bureau for this instrument. The pyrometer lamp used throughout the measurements reported here is a lamp provided with flat optical-glass windows fused to the lamp bulb. The lamp, after evacuating and baking, was aged or seasoned before any measurements were made. During the measurements the current-temperature characteristic of the lamp changed only slightly, the total change being equivalent to about 1° at 1,063° C. The change was gradual and was carefully watched or checked by repeated calibrations at the melting point of gold. The advantage of the flat windows is the elimination of the uncertain effects of striated blown bulbs, and the increase in precision obtained as a result of a well-defined and undistorted photometric field.

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[4] Fairchild and Hoover, J. Opt. Soc. Am. and Rev. Sci. Inst., **7**, No. 7, pp. 543–579; 1923.

The exit aperture of the pyrometer telescope during the present work was 0.04 radian. A larger aperture could not be used to advantage,[5] although so small an aperture makes necessary added precaution in keeping dust and dirt from the optical parts. The method used to make certain of the cleanliness of the optical path was to focus the eyepiece upon each glass surface of the system in turn with a bright background for illumination. Such a procedure was found to be essential.

Throughout the work the telescope was adjusted to give a magnification of the source of about 8 diameters, and of the pyrometer-lamp filament about 15 diameters. Such a magnification was selected to give, in conjunction with the 0.04 radian exit aperture and a red glass filter, a brightness of the photometric field which was found by trial to be comfortable and favorable to precise settings. Also, at such a magnification the lamp filament is distinctly visible and is easily matched in brightness with the background.

Before any measurements at the palladium point were made, the instrument had been in use for a number of years. The precision attainable was found to be about 0.1° C. at the melting point of gold or of copper. With a lamp current at the gold point of about 0.1 ampere and a change in current per degree of about 0.00015 ampere, it is apparent that care was necessary in the electrical measurements. Currents were determined by measuring with a potentiometer the potential drop across a standard 0.1 ohm resistor in the lamp circuit. A specially designed rheostat, consisting of a box with two dials and three fixed resistors, was used. One of the dials was adjusted so that settings of the pyrometer-lamp current required a considerable rotation of the dial. Only a trained observer could successfully use this fine-control dial. Settings of the current were always made by turning the dial slowly back and forth, causing the lamp filament to appear alternately darker and brighter than the background and then estimating the midpoint at which a photometric match appeared to be obtained. The dial of the rheostat worked smoothly and turned with slight effort. The observer had no knowledge of the current values of settings during a series of readings at a fixed or constant temperature of the furnace or crucible.

## 2. CRUCIBLE METHOD

The arrangement during measurements with the crucible method is shown in Figure 1. The pyrometer is provided with a total-reflection right-angled prism mounted upon the front end of the telescope. This prism was used in all measurements, even when sighting into the horizontal furnace shown in Figure 2, thus avoiding any

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[5] See footnote 3, p. 932.

correction for its absorption. The furnace and crucible were small and mounted within an evacuated pyrex-glass globe having an optical-glass window. The furnace was made of alundum tubes and diaphragms and insulated with thoria. The insulated cover served as the upper diaphragm. Sides, bottom, and cover of the furnace were wound with platinum-rhodium alloy wire (20 per cent rhodium) to be heated electrically. "Sillimanite" porcelain crucibles, with an inner tube to serve as an immersed black body, were made by turning out the parts on a lathe, using for a cutting tool a crystal of carborundum. The porcelain was first fired to such a temperature that the lathe work was possible, and, after turning and cutting, the parts were fired again to a temperature slightly above the melting point of palladium. The crucibles barely withstood repeated melting and freezing operations, not only on account of the large difference in thermal expansion of the crucible and the palladium but probably because of slight shrinkage of the crucible during continued exposure to the high temperature. After this work had been finished Bowen and Greig [6] identified a eutectic of silica and alumina which melts at 1,545° C. This discovery fully accounts for the relatively short life of the crucibles and their tendency to crack after long heating at 1,550° to 1,560° C.

In order to prove that the immersed tube in a sillimanite crucible was a good black body, such a crucible, was filled with gold and heated in another separate furnace not illustrated. The brightness of this black body at the melting point of gold was compared directly with that of one made of graphite in a graphite crucible filled with gold. The results were quite satisfactory, and when this porcelain crucible finally failed a second crucible was not made.

Owing probably to the high thermal conductivity of gold, less trouble is experienced in obtaining freezing and melting points which agree than is the case with palladium. A necessary procedure in both cases is to heat the melting furnace uniformly. The diaphragms in the furnace shown in Figure 1 were designed to promote uniformity of temperature in the furnace, and hence in the melting or freezing metal. Under such conditions melts and freezes of both gold and palladium agreed invariably to a few tenths of 1° and frequently agreed to less than one-tenth of a degree.

The heating and cooling currents required by the furnace were determined by trial and slowly changed during the life of a furnace. Occasionally the duration of a melt or freeze was too short, and satisfactory observations were not obtained. The crucibles used in the final series at the palladium point held a charge 1.8 cm deep and 1.3 cm in diameter. The inner tube joined to the bottom of the crucible

[6] J. Am. Cer. Soc., 7, No. 4, p. 238; 1924.

had an inner diameter of 1.2 mm and an outer diameter of about 2 mm. This size of crucible and quantity of metal was sufficient to give a constant temperature at melting or freezing for over 30 minutes in the case of gold and nearly as long in the case of palladium. Usually the time during which constant readings were obtained was about 15 minutes.

### 3. WIRE METHOD

The type of furnace used in the investigation by the wire method is shown in Figure 2. It is essentially a Lummer-Kurlbaum experimental "black body" and is, in a general way, the same as the furnaces
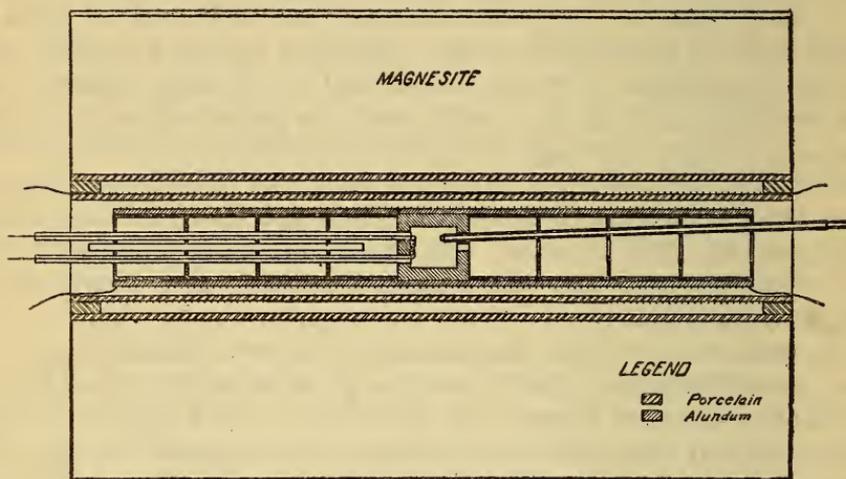


FIGURE 2.—*Black-body furnace showing control couple, test couple, and diaphragms used in wire method*

used by Hyde and Forsythe,[7] and by Hoffman and Meissner. It consists of two coaxial tubes each wound with platinum—20 per cent rhodium wire and insulated, outside of a small air space, with a refractory oxide. The larger of the two inner tubes was covered over its middle part with platinum foil in place of wire, thus compensating for the lower loss of heat from that part. This outer heating coil was shunted near one end for adjusting relative heating of front and rear of the furnace. The inner coil was wound nearly uniformly over the whole length, with a slight crowding of turns near the ends. Over this coil the space was filled with a pure grade of fused alumina called "R R Alundum" (ground to 120 mesh), a material of high thermal conductivity.

The inner tube was filled with a series of flat-bottomed, cylindrical cups of alundum placed end to end, ground to fit the tube and with bottoms drilled out with holes to serve as diaphragms and courses for

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[7] The Gold Point Palladium Point Brightness Ratio, Astrophys. J., **51**, p. 244; 1920.

tubes holding thermocouples.   The result is a central cavity with a small opening, and a conical series of openings limiting the radiation. It may be supposed that the inner middle cavity of this furnace was at a uniform temperature, maintained in such condition by preventing much radiant heat from escaping through the small hole in the cavity.

An older construction of such a furnace is shown in Figure 3.   The system of diaphragms in this furnace leads to decided departures from black-body conditions.   This was found to be the case by the authors in 1916, and by others, including Hoffman and Meissner.   These two workers tried blackening the side walls or "black wall" of their furnace and showed by such means that the side walls were, in general, hotter than the back wall when the furnace was apparently uniformly heated and the innermost opening was invisible.

The various methods employed to bring such a furnace (fig. 2 or 3) to the melting point of palladium (or gold) differ in details. Hyde and Forsythe controlled the furnace with a thermocouple led in from the rear and placed with its hot junction within the inner chamber or touching the "back wall" from behind and noted, by the
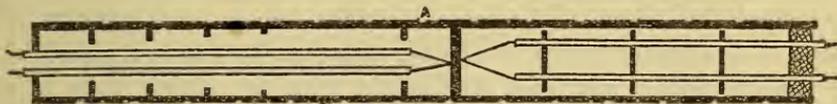
FIGURE 3.—*Older construction of black-body furnace shown in Figure 2*

ringing of an electric bell, the instant of melting through (apart) of a bit of fine palladium or gold wire welded or fused to the tips of two platinum wires led into the furnace from the front through the central diaphragms.   Hoffman and Meissner did likewise except that the moment of melting was determined by observing a halt in the rise of emf of a thermocouple, used in place of the two platinum wires. Thus the possibility of obtaining a high reading during a rise of the wire above its melting point before melting apart was removed. Hoffman and Meissner observed that melting apart occurred in many cases a degree or so above the melting point.   It does not follow, however, that such was the case with the experiments of Hyde and Forsythe, who used a finer and longer wire.   Nevertheless, the "halt" method is more certain and exact.   Apparently no attempt was made by any of these writers to adjust the furnace to a uniform temperature by means of actual measurement of the temperatures of various parts.   Uniformity was adjudged by disappearance of the outline of the innermost opening.   The measurements of brightness were made by sighting into the front of the furnace held at a constant temperature as indicated by the control couple.   This couple was calibrated in a preliminary experiment by observing its emf at the

moment of melting of the gold or palladium wire inserted from the front. There is necessarily some uncertainty as to the constancy of the relation between the melting point and the emf of the control couple, and also as to the effect of alternate insertion and removal of the porcelain insulating tubes and couple through the front diaphragms. The radiation from the front openings is greater during the brightness measurements than when the openings are partly filled by the "melt" elements. Thus the relative temperatures of front and rear of the furnace may be disturbed.

In the procedure followed by the authors temperature uniformity was controlled according to actual measurements and was not disturbed by alternate insertion and removal of the melt couple. Furthermore, no primary dependence was placed upon the constancy of the control couple.

The furnace was heated to a temperature slightly below a melting point (1,060° or 1,550°) and maintained until a steady state was reached. A control couple inserted from the rear served to indicate this condition. A second couple was inserted through holes shown in Figure 2, either in front or rear, while in the opposite end an empty tube filled the holes. The second couple, whose hot junction was placed in the center cavity or the adjacent cavity was compared with the control couple and then exchanged with the empty tube in the other end. Allowing a few minutes for a steady state to be again reached, a second comparison would give the relative temperatures of two cavities or portions of the furnace. Through such a series of measurements adjustments were made until the middle three cavities were apparently at the same temperature.

Only longitudinal temperature gradients were smoothed out by such means, and no indication was obtained of the existence or magnitude of radial gradients. The average temperature of a given cavity was estimated and adjusted. In each case the couple extended well into the cavity, almost touching or reaching the next wall. Unavoidable errors attend such measurements. First, the insertion or exchange of tubes disturbs the temperature distribution. Second, the thermocouple is, in general, inhomogeneous and gives an emf dependent on the condition of that part of it traversing the gradients at the ends of the furnace. Third, radial gradients in temperature, if present, finally render impossible a measurement of the temperature of a cavity. No single value can represent the temperature of the cavity, which is not uniformly heated, and a thermocouple inserted into the cavity will indicate a temperature above the coldest part and below the hottest part, but not, except by accident, a temperature truthfully representing the intensity of radiation issuing from the hole in the experimental black body.

By means of the series of diaphragms only a part of this radiation is allowed finally to escape, the remainder being reflected back by the diaphragms and partly replaced by radiation from the diaphragms into the hole in the inner cavity or black body. The radiation finally leaving the furnace arises mainly in the "back wall" of the inner cavity and is partly made up of light reflected by the back wall from the side walls and front of the cavity. Thus the brightness of the "black body" depends to some extent upon the emissivity of the back wall. It is impracticable to overcome this difficulty by blackening the back wall, because materials used for blackening (such as chromium oxide) are not sufficiently refractory to use at high temperatures; that is, while the melting points of some such materials may be well above 1,550° C., they are too volatile to be used adjacent to a thermocouple or the bit of palladium put into the furnace.

Temperature uniformity is increased markedly by decreasing the size of the radiating opening, but this alone can not result in a perfect black body. A corresponding decrease in the size of each of the series of openings in the diaphragms must accompany a reduction in the inner hole in order to decrease the radiation from the front wall of the inner cavity.

Having observed, before the present work was begun, that certain forms of furnaces were not sufficiently "black," the furnace was built of alundum, a comparatively good conductor of heat, and the innermost hole was made as small as practicable—about 3 mm in diameter. The cups or crucibles used to form the inner cavity and adjacent diaphragms were ground into the furnace tube, fitting it so tightly that long heating at high temperatures has resulted in permanent fusion of crucibles and tube except at the relatively colder ends of the furnace. Fortunately this did not occur until the final form of furnace had been assembled.

Preliminary measurements by the wire method were made to compare the brightness of the Lummer-Kurlbaum black body at the melting point of gold with that of a "black body" immersed in the crucible of gold. So far as we can learn such a direct comparison of the two methods has not been made before. While Hoffman and Meissner used both methods, their reported results do not include direct comparison of two black bodies at a supposed single temperature.

The first measurements at the gold point by the wire method gave a brightness exceeding by the equivalent of 2° the brightness observed by the crucible method. Inasmuch as the measurements by the crucible method included measurements on both porcelain and graphite "black bodies" which were in practically exact agreement, we sought an explanation for the discrepancy in the wire method.

34054°—29——2

It hardly seems necessary to remark that the assumption of nearly perfect blackness of the tubes immersed in metal in the crucibles does not lead to the conclusion that the Lummer-Kurlbaum black body provided a brightness greater than that of a black body. The supposition is, on the other hand, that the observed brightness in the latter instance is too great because the "average" or equivalent temperature of the inner cavity is higher than that of the bit of metal melting within it. In case the side walls of this cavity are hotter than the back wall, the brightness of the back wall may be greater than that of a perfect black body at the temperature of the back wall on account of reflection of light coming from the side walls. A bit of palladium wire held near the back wall on the axis of the furnace will remain always at a temperature below that of the side walls.

In the first arrangement of diaphragms in the furnace shown in Figure 2 there was a series of openings through the diaphragms close to one side of the furnace tube. We found that a thermocouple inserted through these holes into the inner cavity indicated a temperature 2° higher than when inserted along the axis of the furnace. This does not show that the side walls are 2° hotter than the center, but that they are more than 2° hotter than the center. In all measurements we were careful to keep all holes in the diaphragms closed except those in the centers. If a couple was withdrawn, an empty tube replaced it. The holes were made only slightly larger than the tubes.

Having found a departure from ideal black-body conditions, we replaced the parts forming the inner cavity by a single alundum piece made as follows: Two crucibles of different diameters and same height were placed one within the other with bottoms opposed, thus forming a complete inclosure. The crucibles were cemented together with alundum cement in such a way as to provide sides, front, and rear walls about 6 mm thick. One 3 mm hole was drilled through the front wall and two holes through the back wall to fit the protection tubes for a thermocouple. The inner cavity was then somewhat smaller, but we hoped this would be more than offset by the effect of more uniform temperature resulting from thick walls.

Into the inner cavity was led a thermocouple through holes just bordering the central holes left open for observations. The hot junction of this couple was about midway between the axis of the furnace and the side wall of the cavity. A bit of gold or palladium wire 0.5 mm in diameter and 2 mm long joined the elements of this "melt" couple at the "hot junction."

Observations with the optical pyrometer were taken by one observer while another observer controlled the furnace and observed the emfs of the melt couple and control couple. Having adjusted the inner

three cavities to apparently the same temperature, a degree or so below the melting point, with the furnace held constant by means of the control couple, the melt couple was inserted and the furnace current adjusted to give a rate of rise of temperature of about 1° in three minutes. Observations were made with the optical pyrometer during the time immediately preceding the melt and finally at the moment of melting, while simultaneous readings were taken of the emf of the melt couple. All but the final reading of the optical pyrometer were corrected to the melting point. The corrections could be made with an accuracy of 0.1° or better. In thus checking the melt couple immediately after optical measurements all chance of change in the melt couple was avoided, and no dependence was placed upon the control couple, which could not readily be renewed and which continually developed inhomogeneity during the work.

The thermoelectric measurements required in the wire method are described in an appendix. The precision obtained was well within that attainable in the optical measurements.

### III. SUMMARY OF RESULTS OBTAINED

#### 1. CRUCIBLE METHOD

In this section the results are expressed in terms of the current passing through the pyrometer lamp when it was matched in brightness from time to time with a black body at the melting point of palladium, viewed through a sector disk, and with a black body at the melting point of gold.

With a knowledge of the constants to be used in the application of Wien's law, a sector disk was made having a transmission approximately equal to the ratio of brightness for red light of black bodies at the melting points of gold and palladium, respectively. The disk was made of aluminum carefully hammered flat, with two sector openings edged with steel knife-edges ground or "lapped" straight. While it was intended to obtain a disk of a selected transmission, the size of the openings was such that only a rough approximation could be made without many trials. Inasmuch as a correction would have to be made in any case for the incorrect transmission of the disk, the first value found was considered close enough and was eventually found to be so. The transmission of the disk was measured on a circular dividing engine at different points along the radii and the transmission computed for the section or, rather, zone of the disk to be used. This transmission was found to be 0.7829 per cent, with a probable accuracy of better than 0.0008 per cent. When the pyrometer lamp was matched in brightness with a black body at the palladium point through this disk the current through the lamp corresponded to a temperature about 1,301° K., 35° below the melting point of gold.

This interval was determined with an accuracy of 0.1°. For this purpose the lamp was calibrated with reference to gold as a fiducial point, for the range 1,000° to 1,700° K. and an equation of current versus temperature computed. In the region of 1,300° the calibration was carefully checked by sighting through sector disks into a black body at the gold point. From this equation, $\frac{di}{dt}$, the rate of change of current with temperature, for different temperature intervals, was computed. For the interval 1,300° to 1,336°, $\frac{di}{dt}$ was found to be 0.0001414 ampere per degree.

Corrections were applied to the measurements for change in the pyrometer lamp from the initial calibration, for impurity of the palladium melted repeatedly in crucibles, and for room temperature. The transmission of the red glass filter and a glass absorption screen used in many of the measurements depended upon the temperature of the room. The absorption glass was not appreciably heated by radiation from the furnace, because of the interposition of the glass window of the furnace, a thick glass prism, and the front objective lens of the pyrometer telescope.

The temperature coefficient of spectral transmission of the red glass filter was determined by the colorimetry section of the Bureau of Standards. The authors determined the coefficient for the absorption glass pyrometrically. The two determinations were made for a 30° interval in room temperature. Temperature of the laboratory varied from 22° to 42° C. during the different series of measurements.

After an extensive study of methods of melting pure palladium sponge, a small crucible of the metal was taken for a preliminary trial of the method. The results obtained with this crucible were not satisfactory. The furnace was not heated uniformly, the crucible failed after two melts and two freezes, and during the last freeze the inner tube within the crucible broke and tipped out of alignment. The 31 readings obtained in this series were not included with later results, because the melting and freezing points were not sharply defined. Even under such circumstances, however, the crucible method appears to advantage, for the series gave for the melting point of palladium 1,554°, a value found later to be in good agreement with the final mean.

A new furnace and new crucible were made, designed to eliminate the faults found in the first instance. A little increase in diameter of both permitted an increase in the strength of the inner tube, which was about 2 mm outside diameter. The heating elements of the new furnace were changed to promote uniformity of temperature, which was also helped by a better system of diaphragming.

Before taking observations on the black body in this crucible of palladium many melts and freezes of gold in both sillimanite and graphite crucibles were made. As a mean of 156 readings at the gold point the current through the pyrometer lamp numbered F10 was 0.11542 ampere. Within experimental error no difference was found between the black bodies of graphite and of porcelain. Refer to Table 1.

TABLE 1.—*Current through pyrometer lamp, gold point, crucible method*

| Date | Current (ampere) | | Number of readings | Secular mean | Remarks |
|------|------|------|------|------|------|
| | Melt | Freeze | | | |
| September, 1922 | 0.11543 | 0.11543 | 18 | 0.11543 | New graphite crucible. |
| | | .11543 | 11 | .11543 | Do. |
| | .11543 | .11544 | 20 | | Do. |
| | | .11544 | 12 | .11544 | Do. |
| November, 1922 | .11542 | .11543 | 20 | | New porcelain crucible. |
| | .11542 | .11541 | 18 | | Do. |
| | .11545 | .11540 | 13 | | Do. |
| | .11542 | .11543 | 34 | | Do. |
| | .11541 | | 10 | .11542 | Do. |
| December, 1922 | .11542 | | 8 | | Do. |
| | .11542 | .11541 | 13 | .11542 | Do. |
| | .11546 | .11546 | 18 | | After using lamp at high temperature. |
| | .11545 | .11542 | 18 | .11545 | |
| January, 1923 | .11548 | .11542 | 17 | | Same crucible. |
| March, 1923 | .11546 | .11546 | 15 | .11545 | |
| July, 1923 | .11556 | .11556 | 22 | | Lamp again used at high temperature. |
| | .11556 | .11555 | 13 | | Another new graphite crucible. |
| | .11555 | .11554 | 18 | .11555 | Same crucible. |
| September, 1923 | .11558 | .11556 | 28 | .11557 | Do. |

Measurements with lamp F13, not given in the table, gave for the gold in a graphite crucible as a mean of 28 readings 0.28296 ampere through the lamp, and for the sillimanite crucible 0.28293 ampere. The difference is equivalent to about 0.1° and is not significant.

After these measurements the new cruicible of palladium gave. very satisfactory results. (See Table 2.) The melting and freezing points were sharply defined and agreed with each other. Readings were taken with sector disk No. 3 and with absorption glass No. 2, which had been very carefully compared. The precision of this comparison was ample to allow their alternative use. After 20 readings with the absorption glass and 66 with the sector disk the lamp F10 was checked at the gold point, giving again the value 0.11542 ampere, as shown in the table. Two weeks later 18 readings with the palladium crucible gave a mean agreeing with the previous values.

TABLE 2.—*Summarized data in terms of current through pyrometer lamp (amperes)*

| Date | Gold point — Secular mean crucible method | Gold point — Wire method | Gold point — Corrected for change lamp | Gold point — Number of readings | Palladium point — Absorption glass | Palladium point — Sector disk | Corrections — Room temperature | Corrections — Lamp change | Corrections — Melting point | Corrected value | Furnace gradient — Front | Furnace gradient — Rear | Number of readings | Method | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| August, 1922 | 0.11494 | | | 81 | | | | | | | | | | | Preliminary, data not used. |
| December, 1922 | .11542 | | | 156 | 0.11743 | 0.11005 | 0 | 0 | +0.00005 | 0.11046 | | | 31 | Crucible | Data used for comparison of absorption glass and sector. |
| | | | | | | .11041 | | | | | | | 9 | do. | |
| | .11542 | | | | .11739 | .11037 | 0 | 0 | +.00005 | .11042 | | | 11 | do. | Top of furnace visibly cool. |
| | .11542 | | | | | .11040 | 0 | 0 | +.00005 | .11045 | | | 10 | do. | New furnace cover, giving apparently uniform temperature of furnace. |
| | .11542 | | | | | .11042 | | | | .11047 | | | 17 | do. | |
| | .11542 | | | 21 | | .11042 | 0 | 0 | +.00005 | .11047 | | | 13 | do. | Succeeded by check at gold point. |
| | .11542 | | | 36 | | .11041 | 0 | 0 | +.00005 | .11046 | | | 15 | do. | Do. |
| | .11542 | | | | | .11040 | 0 | 0 | +.00005 | .11045 | | | 11 | do. | Crucible removed and Pd examined for change in purity. |
| | .11545 | | | | | .11041 | 0 | 0 | +.00005 | .11046 | | | 18 | do. | Preliminary, thin wall, black body. |
| | | | | | | .11046 | 0 | −.00003 | +.00005 | .11048 | | | 15 | do. | New thick walls. See text, furnace temperature quite uniform, opening always invisible. |
| March, 1923 | .11545 | 0.11567 | 0.11564 | 14 | | | | | | | −10 | +3 | | | |
| | .11545 | .11548 | .11545 | 7 | | | | | | | | | | | |
| | .11545 | .11549 | .11546 | 10 | .11736 | .11034 | +.0004 | −.00003 | 0 | .11035 | | | 5 | Wire | Data not used, but opening nearly invisible. |
| | .11545 | .11555 | .11552 | 10 | | | | | | | | | | | |
| July, 1923 | .11545 | | .11546 | 32 | .11745 | .11043 | +.0004 | −.00003 | 0 | .11044 | −2 | +2 | 8 | do. | Crucible removed and Pd examined. |
| | .11555 | | | 53 | .11754 | .11052 | +.0004 | −.00013 | +.00003 | .11046 | | | 16 | Crucible | |
| August, 1923 | .11555 | .11559 | | 42 | .11773 | .11071 | +.0008 | −.00013 | 0 | .11066 | +.3 | +2.3 | 28 | Wire | Two series furnace O. K. |
| | .11555 | .11559 | | | .11771 | .11064 | +.0013 | −.00013 | 0 | .11064 | +.3 | +2.3 | 10 | do. | Data used for comparison with sector. |
| | .11555 | | | | .11755 | .11069 | +.0009 | −.00013 | 0 | .11065 | +2.6 | +2.0 | 10 | do. | |
| | .11555 | | | | | .11053 | +.0009 | −.00013 | 0 | .11049 | −1.4 | +2.8 | 15 | do. | |
| | .11555 | | | | | .11082 | +.0012 | −.00013 | 0 | .11061 | −.6 | +2.2 | 15 | do. | |

The next check at the gold point followed after considerable use of the lamp for other purposes, during which use the lamp changed slightly, now requiring 0.11545 ampere, mean of 36 readings. During the same day that this check was made the last observations with the palladium crucible then in hand were made. The mean of 15 readings was slightly higher than the previous results. This ended the observations with this crucible.

Nearly a year later, after measurements by the wire method another crucible was made and filled with palladium. This was melted in the same furnace as before. Lamp F10 had changed to require 0.11555 ampere at the gold point. But one melt and one freeze of the palladium were observed for the purpose of demonstrating the reproducibility of the results obtained by the crucible method. The palladium was removed from the crucible without further melting, to be examined for impurities. The results were in satisfactory agreement with those obtained the year before.

After making all corrections to measurements, as described above, the final weighted mean current for F10 sighting into the palladium crucible through sector disk No. 3 is 0.11047 ampere. This is 0.00495 ampere below the standard current of 0.11542 ampere for the gold point. The lower reference temperature is obtained from $\frac{di}{dt} = 0.0001414$ ampere per degree and is found to be 1,301.1° K.

Employing the methods given in a later section to calculate the melting point of palladium from the measured ratio of brightness "from gold to palladium," the result is found to be 1,826.6° K., or 1,553.6° C., for $C_2 = 1.432$ cm deg.

### 2. WIRE METHOD

The initial brightness measurements by this method were made at the gold point, using a Lummer-Kurlbaum furnace as described in a section above. Referring to Table 2, the first result is found to be 0.11567 ampere as a mean of 14 readings. This is 0.00022 ampere above the value obtained with the crucibles of gold and is equivalent to a difference of nearly 2°. There seems to be no doubt that the brightness of this furnace was greater than that corresponding to a black body at 1,063° C. The furnace was very uniformly heated, according to thermocouple measurements of the temperatures of the three middle cavities. It was at this stage of the work that, as stated before, the side walls of the middle cavity were shown to be at least 2° hotter than the temperature indicated by a couple whose hot junction was near the axis of the furnace tube and close to the back wall of this cavity. After replacing the parts forming the middle cavity with the single-piece inclosure with 6 mm walls,

further measurements were in much better agreement with the crucible values but did not give satisfactory reproducibility.

The first two runs with the, thick-walled inner cavity, of 7 and 10 readings, respectively, gave mean currents of 0.11548 and 0.11549 ampere through the pyrometer lamp. While these values are only a fraction of a degree above the crucible results, the third run of 10 readings gave 0.11555 ampere. This was a real discrepancy, for a subsequent check with a crucible (sillimanite) of gold showed that the pyrometer lamp had not changed.

Immediately after the third run the furnace was heated to the melting point of palladium. Late in the evening of that day the furnace was brought to a steady and fairly uniform temperature. Two runs with palladium wire were made. In the first the front cavity was much too cold, according to actual measurements, although the middle diaphragm or innermost opening was almost invisible. A low result was obtained. In attempting to adjust the furnace to uniformity it was found that when the indicated temperatures signified uniformity the innermost opening appeared darker than the surrounding front of the diaphragm. Readings were then taken with the gradient as given in Table 2, and the result, 0.11044 ampere, was in fair agreement with those of the crucible method.

In July, 1923, two sets of measurements at the gold point, when the furnace was apparently very uniformly heated, gave as a mean of 42 readings 0.11546 ampere, a result 0.00004 ampere above the crucible values. The first set gave 0.11549 and the second 0.11543, variations from the mean quite like those obtained before. The variations could not be correlated with the slight temperature gradients in the furnace, such as were indicated by thermoelectric measurements before and after the brightness measurements.

When the furnace was heated to the palladium point, attempts were repeated to adjust it for equality of temperature in the middle three cavities; again we found that the innermost opening appeared dark under such conditions. Adjustments of the furnace were made, of course, by trial, and the measurements with the optical pyrometer proceeded when the furnace was in various states of nonuniformity, as given in the last five lines of Table 2. There is not much certainty as to the accuracy of the figures in the column headed "Furnace gradient." Possibly they are accurate to less than 1°. That they do not correctly represent the true temperature gradients there can be no doubt. However, they are consistent with the results obtained with the optical pyrometer; that is, the colder the front cavity, the lower the pyrometer reading, while the rear temperature remained according to measurements, 2° to 3° high. It is possible that further study of the wire method would disclose a

procedure and furnace design which would eliminate the effects shown here. However, it is well established that there is too much radiation escaping from the innermost cavity of the furnace as built for this work. It seems probable that with the present design the inner cavity is necessarily too cold when the furnace is adjusted to uniformity as described above. Perhaps the addition of heating elements in the diaphragms themselves would alter this condition. It would be very difficult to manipulate the furnace, in such case, at 1,550° C. Time and effort are better spent with the crucible method. At best, the wire method appears as a good but not perfect substitute. Taking the data obtained and making allowance for the departure from black-body conditions, considerable support is given to the opinion that the crucible method furnishes a nearly perfect black body but there is no way of selecting a satisfactory mean of the wire-method results. The indicated temperatures of the front and rear cavities are not those of the front and rear walls of the innermost cavity. Moreover, the side walls are in all probability hotter than the diaphragms.

A weighted mean of the results of the wire method is 0.11060 ampere for the palladium point and 0.11547 ampere for the gold point. The latter value is 0.00005 above the crucible value for gold. This difference of 0.00005 may properly be subtracted for the purpose of comparing the methods, from 0.11060 giving 0.11055 ampere for the final result from the wire method. This is 0.00008 above the crucible result, corresponding approximately to 1.1° in the melting point of palladium.

Although the difference of 1° in the results from the two methods is small, the evidence is clearly against averaging the two. The final result, therefore, will be based on the crucible method alone.

## IV. COMPUTATIONS

In order that the measurements with an optical pyrometer may be interpreted as a determination of the melting point of palladium, it is necessary to base the high-temperature scale upon Planck's (or Wien's) law for the spectral distribution of radiation from a black body and at least one previously known temperature or fixed point. The value of the constant $C_2$ in Wien's law

$$J = c_1 \lambda^{-5} e^{\frac{-c_2}{\lambda \vartheta}} \tag{1}$$

is involved, and also a computation of the effective wave length, $\lambda_e$, of the light transmitted by the red glass filter of the pyrometer. The equation for computing one temperature from a known temperature is conveniently put in the form

$$\frac{1}{\vartheta_2} - \frac{1}{\vartheta_1} = \frac{\lambda_e \log T}{c_2 \log e} \tag{2}$$

derived from Wien's law, in which $\vartheta_2$ and $\vartheta_1$ are the two temperatures involved, $T$ is the transmission of a sector disk or ratio of black-body brightnesses corresponding to the temperatures $\vartheta_2$ and $\vartheta_1$ and $e$ is the Napierian base.

The computations following are based on $C_2 = 1.432$ cm deg., on $\vartheta_1 = 1301.1°$ K. as found in the experimental results obtained by the crucible method, on $T = 0.7829$ per cent, and $\lambda_e$.

The remaining quantity with which we are concerned is $\lambda_e$. The effective wave length or mean effective wave length $\lambda_e$ is a function of the transmission of the red glass filter, visibility of radiant energy, and spectral distribution of radiant energy. The variation of $\lambda_e$ with temperature of the black-body radiation is so slight that only approximate values of black-body temperatures are required for the computation of $\lambda_e$ for any given interval of temperature.

All the photometric observations included in this report were made with the right eye of one of the writers, C. O. F., for whom visibility had been measured by two groups of workers.[8] The relative visibility for this eye as determined in the two cases is given in Table 3, together with the mean visibility for many eyes and the ratios of the two sets of measurements.

TABLE 3.—*Relative visibility versus wave length*

| $\lambda$ micron | V for C. O. F. by — | | | V many eyes by — | | |
|---|---|---|---|---|---|---|
| | Coblentz, 1917 | Gibson, 1923 | Ratio | Coblentz | Gibson | Ratio |
| 0.61 | 0.613 | 0.534 | 1.15 | 0.557 | 0.511 | 1.09 |
| .62 | .470 | .431 | 1.09 | .427 | .387 | 1.10 |
| .63 | .338 | .319 | 1.06 | .302 | .279 | 1.08 |
| .64 | .220 | .2154 | 1.02 | .194 | .184 | 1.05 |
| .65 | .135 | .1343 | 1.01 | .115 | .113 | 1.02 |
| .66 | .076 | .0784 | .97 | .0645 | .0642 | 1.00 |
| .67 | .040 | .0427 | .94 | .0338 | .0349 | .97 |
| .68 | .020 | .0223 | .90 | .0178 | .0178 | 1.00 |
| .69 | .0090 | .0112 | .80 | .0085 | .0092 | .92 |
| .70 | .0051 | .0056 | .91 | .0040 | .0045 | .89 |
| .71 | .0025 | .00273 | .92 | .00203 | .00220 | .92 |
| .72 | .0011 | .00137 | .80 | .00097 | .00108 | .90 |
| .73 | .00055 | .000686 | .80 | .00048 | .00051 | .94 |
| .74 | .00033 | .000345 | .96 | .00028 | .00026 | 1.08 |
| .75 | .00020 | .00021 | .95 | .00020 | .00014 | 1.43 |

It might be supposed that the mean of the values in the second and third columns of Table 3 should be used in our calculations. This is not the case, however. Other groups of workers have reported their results of determinations of the relative visibility for many eyes. It is apparent that the visibility for C. O. F. as given in the table could be corrected to values consistent with the mean visibility for the human

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[8] Coblentz and Emerson, B. S. Sci. Paper No. 303; 1917. Gibson and Tyndall, B. S. Sci. Paper No. 475; 1923.

eye as determined by all published measurements.  The data of Gibson are so close to such a mean that this correction is unnecessary, so we have used the values in the third column.  Moreover, while Coblentz used a flicker photometer, Gibson's photometric arrangement resembled that of optical pyrometry.

The difference in $\lambda_e$ computed from V (C. O. F.) as determined by Coblentz and by Gibson is $0.0011\mu$, equivalent to $1.2°$ in the calculated melting point of palladium.  The uncertainty in the final result arising from an uncertainty in $\lambda_e$ is discussed later.

The spectral transmission of the red glass used as a filter was measured by the colorimetry section of the Bureau of Standards. These measurements were made both photometrically and radiometrically and at two different temperatures of the red glass.  The change in $\lambda_e$ with room temperature was found to be $0.000089\mu$ per degree, equivalent to a change of $0.09°$ in the palladium point per degree change in room temperature under the conditions of the work.

The mean effective wave length of the red glass screen for a certain temperature interval $\theta_1$ to $\theta_2$ is defined as that wave length at which the ratio of black-body radiation intensity at the two temperatures is equal to the ratio of integral luminosity; that is, $\lambda_e$ is that wave length at which

$$\frac{J_2}{J_1} = \frac{L_2}{L_1} = \frac{\int_0^\infty J_2(\lambda, \vartheta_2) R(\lambda) V(\lambda) d\lambda}{\int_0^\infty J_1(\lambda, \vartheta_1) R(\lambda) V(\lambda) d\lambda} \tag{3}$$

in which the quantities $J$, $R$, $V$, and $L$ are, respectively, radiant energy, transmission of screen, visibility, and luminosity.  The mean effective wave length can be defined also from its relation to the effective wave length $\lambda_L$.  This quantity is defined as that wave length at which the rate of change of radiant energy at a given temperature is equal to the rate of change of integral luminosity. It can be shown that the reciprocal of the mean effective wave length, $\lambda_e$, for a certain temperature interval $\vartheta_1$ to $\vartheta_2$ is equal to the average value of the reciprocal of the effective wave length, $\lambda_L$, for the interval $1/\vartheta_1$ to $1/\vartheta_2$; that is

$$\frac{1}{\lambda_e} = \frac{\int_{1/\vartheta_1}^{1/\vartheta_2} \frac{1}{\lambda_L} d\left(\frac{1}{\vartheta}\right)}{\frac{1}{\vartheta_2} - \frac{1}{\vartheta_1}} \tag{4}$$

The relation between $1/\lambda_L$ and $1/\vartheta$ is found to be practically linear and approximately

$$\lambda_e = 1/2 \left(\lambda_{L1} + \lambda_{L2}\right)$$

The two methods of computing $\lambda_e$ are found to agree exactly. We present here only the calculations by the former method, which is, in this particular instance, slightly shorter. The calculation of integral luminosities is made by tabular integration of $JRV$ products, since it is not practicable to express $R(\lambda)$ in anylitical form, and an analytical expression for $V(\lambda)$ is somewhat awkward to use.

The tabular integration is performed most conveniently by Simpson's rule. The use of this rule permits the use of wider intervals of abscissas than a simple step-by-step method.

Table 4 gives the values of $JRV$ from which the integrals in equation (3) are computed. The constant $C_1$ of Wien's equation has been omitted, and only relative values of luminosity are obtained. Simpson's rule is stated as

$$A = \frac{h}{3}\left[(y_o + y_n) + 4(y_1 + y_3 + \ldots) + 2(y_2 + y_4 + \ldots)\right]$$

in which $h$ is the width of strips and $y_o$ and $y_n$ are the first and last ordinates.

From Table 4, $L_2$ is found to be $695.02 \times 10^{-7}$ and $L_1$ is $543.04 \times 10^{-9}$.

$$\frac{L_2}{L_1} = T = 127.99$$
$$\log T = 2.107176$$

From equation (2)

$$\lambda_e = \frac{C_2 \log e}{\log T}\left(\frac{1}{1,300} - \frac{1}{1,825}\right) = 0.6531_0 \text{ microns}$$

Computations using narrower strips and more digits give $\lambda_e = 0.6531_1\mu$, and the step-by-step method gives from the table $\lambda_e = 0.6530_0\mu$. The visibility data from Coblentz give $\lambda_e = 0.6519\mu$.

A great many computations have been made for this particular temperature interval, many other temperatures, and for various sets of data on visibility and red-glass transmission. Among these were computations of the errors arising from low accuracy in visibility data of the far red, and in data on red-glass transmission near the short wave-length limit. The values in Table 4 have been shortened to approximately the significant figures, and the number of wave lengths used have been limited to the minimum, the table being carefully trimmed down to the least number of figures which will give $\lambda_e$ to the nearest unit in the fourth place.

The question as to what accuracy is required in the measurements of spectral transmission of the red glass is easily answered by computations. For example, the effective wave length at 55°, room

TABLE 4.—*Relative spectral luminosity of black body, at 1,300 and 1,825° K., through 3 mm Corning H. T. red glass*

[For $C_2$=1.432 cm deg.]

| Wave length, micron | V visibility C. O. F., by Gibson | R transmission of red glass, 25° C. | VR | $J_1 \times 10^8$ for 1,300° K. | $J_2 \times 10^6$ for 1,825° K. | $J_1 VR. 10^9$ | $J_2 VR. 10^7$ |
|---|---|---|---|---|---|---|---|
| 0.615 | 0.485 | 0.000 | 0.00000 | 18.92 | 32.71 | 0 | 0 |
| .620 | .431 | .014 | .0060 | 20.99 | 34.81 | 1.27 | 2.10 |
| .625 | .375 | .085 | .0319 | 23.24 | 37.00 | 7.41 | 11.79 |
| .630 | .319 | .250 | .0798 | 25.69 | 39.28 | 20.49 | 31.33 |
| .635 | .263 | .520 | .1368 | 28.34 | 41.65 | 38.76 | 56.96 |
| .640 | .2154 | .655 | .1411 | 31.21 | 44.11 | 44.03 | 62.23 |
| .645 | .173 | .730 | .1263 | 34.30 | 46.66 | 43.31 | 58.92 |
| .650 | .1343 | .780 | .1048 | 37.63 | 49.29 | 39.42 | 51.64 |
| .655 | .101 | .798 | .0806 | 41.22 | 52.02 | 33.22 | 41.93 |
| .660 | .0784 | .809 | .0634 | 45.07 | 54.84 | 28.59 | 34.78 |
| .665 | .057 | .815 | .0465 | 49.21 | 57.74 | 22.86 | 26.82 |
| .670 | .0427 | .819 | .0350 | 53.64 | 60.74 | 18.76 | 21.24 |
| .675 | .030 | .823 | .0247 | 58.37 | 63.83 | 14.41 | 15.76 |
| .680 | .0223 | .826 | .0184 | 63.43 | 67.00 | 11.68 | 12.34 |
| .685 | .0156 | .828 | .0129 | 68.82 | 70.27 | 8.89 | 9.08 |
| .690 | .0112 | .830 | .0093 | 74.56 | 73.62 | 6.93 | 6.84 |
| .695 | .0078 | .830 | .0065 | 80.68 | 77.07 | 5.22 | 4.99 |
| .700 | .0056 | .830 | .00465 | 87.16 | 80.60 | 4.05 | 3.75 |
| .705 | .0040 | .830 | .00332 | 94.05 | 84.22 | 3.12 | 2.80 |
| .710 | .00273 | .828 | .00226 | 101.3 | 87.92 | 2.29 | 1.99 |
| .715 | .00188 | .826 | .00155 | 109.1 | 91.71 | 1.69 | 1.42 |
| .720 | .00137 | .825 | .00113 | 117.2 | 95.58 | 1.32 | 1.08 |
| .725 | .00096 | .824 | .00079 | 125.8 | 99.54 | 1.00 | .79 |
| .730 | .000686 | .823 | .00057 | 135 | 103.6 | .76 | .59 |
| .735 | .00049 | .822 | .00040 | 144 | 107.7 | .58 | .43 |
| .740 | .000345 | .821 | .00028 | 155 | 112 | .44 | .32 |
| .745 | .00028 | .820 | .00023 | 165 | 116 | .38 | .27 |
| .750 | .00021 | .819 | .00017 | 176 | 121 | .30 | .21 |
| .755 | .00015 | .818 | .00012 | 188 | 125 | .23 | .15 |
| .760 | .00011 | .816 | .00009 | 200 | 129 | .18 | .12 |
| .765 | .000u8 | .815 | .000065 | 213 | 134 | .14 | .09 |
| .770 | .00005 | .814 | .000041 | 226 | 139 | .09 | .06 |

temperature of the red glass, is found to be 0.0027 greater than at 25°, a change of less than 0.5 per cent, while the changes in spectral transmission are very marked, as shown in Table 5, particularly from $0.62\mu$ to $0.65\mu$.

TABLE 5.—*Transmission of red glass*

| λ | $T$=25° | $T$=55° |
|---|---|---|
| $\mu$ 0.615 | 0 | 0 |
| .62 | 0.104 | 0.004 |
| .63 | .250 | .130 |
| .64 | .655 | .550 |
| .65 | .780 | .750 |
| .66 | .810 | .794 |
| .67 | .820 | .810 |
| .68 | .826 | .818 |

The uncertainty in $\lambda_e$ arising from uncertainties in the data in Table 5 can be scarcely more than a few units in the fourth place, our estimate being $0.0003\mu$. The uncertainty arising from errors

in visibility is possibly somewhat larger, but we believe it is considerably less than 0.0003. The observer's eye is slightly red sensitive, but is otherwise normal, and apparently stable in spectral sensitivity or visibility.

Although the computation of $\lambda_e$ appears somewhat involved, there is good reason to believe that $\lambda_e$ is as well known as would be the case with a spectrophotometer, the slits of which must be opened to such a width as to afford the same brightness as that obtained with the optical pyrometer, in order to obtain the same photometric precision. We are supported in this statement by Forsythe and would call attention to the following statement by Hoffman and Meissner:

> As was indicated by a separate very careful investigation, the ratio of brightness at the two melting points, determined with these two slit widths (collimator slit 0.2 mm, ocular slit 0.3 mm) differed from the ratio with the slits reduced to infinitely small width, only by a negligible amount.

The absorption glass [9] employed during some of the series of measurements is a screen made up of three different-colored glasses, the combined effect of which is a transmission which approximates an exponential function of wave length. The three glasses used are Corning G171 IZ (2.57 mm thick), G554 CP (3.07 mm thick), and Jena F3815 (0.175 mm thick). The screens give a perfect color match of filament and background when sighting into a black body with the pyrometers, using a red glass in the eyepiece. Of course a very dense red glass gives by itself such a color match, but for many purposes it is desirable to use a red glass screen not too dense. The glass described above as having an effective wave length about $0.653\mu$ is sufficiently selective to give an almost perfect color match with the sector disk used at the palladium point and at the same time transmit enough light to promote ease in obtaining a photometric match. When using the absorption glass, a greater precision is possible because of more perfect disappearance of the filament than can be obtained using a sector disk of low transmission. Another advantage of the absorption glass is that in combination with the red glass it has a lower room-temperature coefficient than the sector disk and red glass combination.

The calibration of such an absorption glass or screen can be accomplished by comparison with a sector disk or by using two known temperatures. In the present case the screen was compared with a sector disk. The comparison results in a determination of the constant $A$ in

$$A = \frac{1}{\vartheta_2} - \frac{1}{\vartheta_1} = \frac{\lambda_e \log T}{C_2 \log e}$$

The constant $A$ for such a glass is not affected by small changes in the $\lambda_e$ of the red glass screen used in conjunction with it, so that

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[9] Foote, Mohler, and Fairchild, J. Wash. Acad. Sci.; November, 1917.

further measurements with the glass can be made without close attention to effective wave length. A full discussion of the theory and usefulness of this type of absorption device is not properly included here. Its use introduced no significant errors and does not enter into a discussion of the accuracy of the final results.

The sector disk used was made by mounting steel knife-edges on openings in an aluminum disk. The disk was carefully balanced and hammered flat. The steel knife-edges were ground and polished as straight as possible. Their straightness was examined on a linear dividing engine and found to be accurate to $1\mu$ or better throughout. Before measurements on the dividing engine were made, the knife-edges were aligned with the center of the disk. The angles were measured at three radii and the transmission of the disk at a particular radius taken where the apertures of the pyrometer were placed with reference to the slits in the disk. The accuracy in the determination of the transmission of the sector disk was better than 0.1 per cent of the transmission. Dividing engine measurements were made before and after rotating the sector disk at high speed (5,000 r. p. m.) to be certain that no slip of the knife-edges would take place.

The effects of diffraction by a sector disk have been made the subject of study by two of the writers,[10] from which study we were able to avoid error from loss of light by diffraction.

The calculation of the palladium melting point from the equation

$$\frac{1}{\theta_2} - \frac{1}{\theta'_1} = \frac{\lambda_e \log T}{C_2 \log e}$$

is made as follows:

$\lambda_e$ from Table 4 is $0.65310\mu$ for room temperature $= 25°$ C.

$\lambda_e = 0.65283$ for $22°$ C., the temperature on which the calculations are based.

$T = 0.007829$, $-\log T = +2.1063$.

$C_2 \log e = 6,219.1$.

$\theta'_1 = 1,301.1°$ K. as found on page 1 for a lamp current of 0.11047 ampere.

$\theta_1 = 1,063°$ C.

$\dfrac{1}{\theta_2} - \dfrac{1}{1,301.1} = -0.00022110$.

$\qquad \theta_2 = 1,826.6°$ K. $= 1,553.6°$ C.

Using these values, the ratio of brightness, $R$, of a black body at the melting point of palladium to that of a black body at the melting point of gold is obtained from the equation

$$\log R = \frac{C_2 \log e}{\lambda_e}\left(\frac{1}{\theta_2} - \frac{1}{\theta_1}\right)$$

$$R = 82.25$$

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[10] See footnote 3, p. 932.

One might suppose that a recalculation of $\lambda_e$ from Table 4 is required if another value than 1.432 is used for $C_2$, but it can readily be shown that a change in $C_2$ has a third-order effect on $\lambda_e$. Hence, the palladium point may be computed for any value of $C_2$ from the equation above.

## V. PURITY OF METALS USED

The metals used in these series of measurements were of such a high purity that chemical analyses were not attempted. The methods used to determine the quality of the metals are described below.

### 1. GOLD

The gold for filling the crucibles was obtained from the United States assay office at New York. It was very pure but was less pure than a sample obtained from the United States Mint at San Francisco, which was used as a standard for comparison. The latter sample under spectroscopic examination showed slight traces of copper, silver, and calcium. The assay-office gold contains traces of the same metals, each impurity being present in such a small quantity that estimates were placed at about 0.001 per cent or less for each.

A comparison of the melting points of the different samples of gold was made by the wire method. In applying this method a high accuracy of comparison was obtained by careful manipulation of the furnace and by the use of new well-annealed thermocouples. The thermoelectric circuits were made as free as possible from stray emfs and the measurements made on a Diesel horst potentiometer with a galvanometer of high sensitivity (15 mm per microvolt). A precision of better than 0.2 microvolt in the measurement of the emf of the thermocouple was obtained without difficulty. The gold from the assay office was found to have a melting point approximately 0.01° high. Two other samples of gold were at hand, one from a merchant and one from the Nela Research Laboratory. The former melted 0.28° low and the latter 0.17° high.

Owing to the remarkable consistency of the results obtained in observations with the optical pyrometer upon crucibles of gold, it has been unnecessary to test the contents of a crucible after use. In fact, the original graphite crucible of gold is still intact and is in use. One of the ingots from a sillimanite crucible was examined and showed no change in melting point.

We may consider it a well-established fact that the gold was sufficiently pure. It is highly probable that in the future this metal will always be readily available in so pure a state. This is fortunate because gold is not equaled by any other metal in the properties which make it useful for a pyrometric fixed point. It does not oxidize nor carbonize, nor absorb gases when melted either in air or a reducing

atmosphere. Also, it has a very high thermal conductivity, which is a valuable property for obtaining sharply defined melting and freezing points as they are indicated by a thermocouple or optical pyrometer.

## 2. PALLADIUM

Palladium sponge, lot No. 3, was prepared by W. H. Swanger from metal obtained from the United States assay office at New York. This metal had been prepared by an electrolytic process and was about 99.0 per cent pure. Four hundred and twenty grams were used in the preparation of palladium No. 3. The metal, in the form of wire about 4 mm in diameter, was dissolved in aqua regia made up from 4 volumes of hydrochloric acid (sp. gr. 1.18), 1 volume of nitric acid (sp. gr. 1.42), and 2 volumes of water. After the metal was dissolved the solution was evaporated to remove most of the excess of nitric acid. It was then diluted with water containing some hydrochloric acid and treated with an excess of ammonia without previously filtering off the small insoluble residue. The treatment with ammonia produced a precipitate of $[Pd(NH_3)_4]Cl_2.PdCl_2$ (Vauquelin's salt) which dissolved in excess of ammonia on digestion on the steam bath. The solution of tetramminepalladous chloride $[Pd(NH_3)_4]Cl_2$ was now filtered from the precipitated impurities, of which the predominant constituent was iron hydroxide.

The original insoluble matter was, of course, removed at the same time. To the filtered solution, normally yellow but in this case green because of the presence of copper, a slight excess of hydrochloric acid was added, thereby precipitating nearly all of the palladium as dichlordiamminepalladium $Pd(NH_3)_2Cl_2$. This precipitate was filtered off, washed, and redissolved by the addition of ammonium hydroxide. The ammoniacal solution was filtered and the palladium salt again precipitated by the addition of hydrochloric acid to a slight excess. This cycle was repeated twice more. In the last operation gaseous ammonia was led into the suspension of the salt in water instead of adding ammonium hydroxide. This precaution was taken to avoid contaminating the solution with impurities which might be present in the ammonium hydroxide.

The final salt was well washed, thoroughly drained on a Büchner funnel, and dried in an air oven. It was reduced to sponge by ignition in porcelain containers under an atmosphere of hydrogen. To avoid having the final sponge saturated with hydrogen the sponge was taken from the atmosphere of hydrogen while it was still warm. It oxidized slightly on cooling in the air but was reduced by moistening with a few drops of formic acid and warming sufficiently to evaporate the excess of acid. Subsequent spectrographic examination of samples prepared from this sponge indicated the absence of all of the

other platinum metals as well as the impurities found chemically in the original material.[11]

The mother liquors from the various operations were examined for impurities. The principal foreign metals found were copper, lead, silver, iron, and platinum. Small amounts of bismuth, antimony, tellurium, and silicon were also found.

Palladium sponge, lot 4, was prepared from scrap palladium obtained from various experiments with portions of palladium from lot 3 and possibly from other lots of pure palladium. It was dissolved in aqua regia and once precipitated as dichlordiamminepalladium in the manner previously described. This salt was ignited to sponge, which was then redissolved in aqua regia. The solution was filtered from traces of insoluble matter, treated with one-third its volume of concentrated nitric acid and with sufficient ammonium chloride solution to precipitate nearly all of the palladium as ammonium chloropalladate $(NH_4)_2PdCl_6$. This precipitation occurred after digesting for a short time on the steam bath. The precipitation of palladium in this way is not quantitative, but under good conditions a larger yield of palladium is obtained than in the precipitation of dichlordiamminepalladium. The use of ammonium chloropalladate in the purification of palladium is less common than the precipitation of dichlordiamminepalladium. One possible advantage is that the salt is precipitated from an acid solution. In the precipitation of palladium from an ammoniacal solution, silver chloride present in the solution would also be precipitated by the addition of hydrochloric acid.

The red salt $(NH_4)_2PdCl_6$, obtained as described, was ignited to sponge in an atmosphere of hydrogen. The sponge was redissolved in aqua regia and the palladium once more precipitated as ammonium chloropalladate in the manner described. This salt was ignited to the sponge known as lot 4.

Impurities found when examining the mother liquors were silver, iron, copper, and nickel, as well as a small amount of silica. Examination of samples from this lot, by means of the spark spectrograph, revealed no traces of the impurities or of the metals of the platinum group. Melt No. 138 was made from this sponge. This melt, made in a crucible of powdered lime, showed the principal calcium lines rather strongly. Hydrogen present in the palladium sponge probably caused some reduction of the lime in contact with the molten palladium.

In the beginning it was intended to apply three tests for comparative purity—(1) spectroscopic, (2) thermoelectric, and (3) melting

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[11] The spectrographic method used is described in B. S. Sci. Paper No. 444, Practical Spectrographic Analysis.

point.  These tests could be carried out best after preparation of the metal in the form of wire or rod.  Hence the problem of successful melting of the pure metallic sponge immediately presented itself. Furthermore, we intended to use a sillimanite porcelain crucible in the final determinations of the melting point, and for that reason we prepared samples melted in sillimanite.  Being previously informed that palladium absorbs oxygen readily when molten, and believing that melting the metallic sponge in a vacuum would result in the retention of oxidizable impurities or the absorption of reduced elements from the crucible, we prepared to melt the sponge in air and freeze the metal in pure nitrogen.  A number of attempts showed that oxygen absorbed above the melting point was eliminated exceedingly slowly while the metal was held molten in an atmosphere of pure nitrogen.  The contents of a crucible upon freezing usually gave off a small quantity of gas generating a pressure which cracked the crucible.  It is not certain that this gas was oxygen.  It may have been nitrogen.  During these trials a number of fairly solid ingots were obtained and were drawn into rods and wire.  One such ingot was found under spectroscopic examination to be purer than any other but is listed as No. 3 in the table below.  This sample and No. 138 contained only calcium, so far as known, but No. 138 was the most negative thermoelectrically and possibly the purest.

There may be some doubt as to the relative purity of the samples Nos. 1, 2, and 3 in the table, but there is a difference of only 0.1° in the melting points.  Sample No. 2 was obtained from Doctor Sosman, of the Geophysical Laboratory, and was cut from the ingot which Day and Sosman have retained since their measurements with a nitrogen thermometer.  Spectroscopic examination showed a trace of copper and more calcium than sample No. 3, but the melting point was nearly identical with that of No. 1.  The precision of the melting point comparisons is very nearly 0.1°.

The table following is presented for various reasons.  It shows that an extensive investigation was made, and that a sufficiently pure metal was obtained.  A fairly consistent relation between relative melting points and thermoelectric power is apparent.  The statement by Adams [12] that impure palladium usually melts higher than the pure metal is not confirmed.

Samples Nos. 8 and 11 were cut from ingots left after the observations on the melting point by the crucible method.  We have used the corrections of 0.4° and 0.7° in the two cases for the following reason.  It was found that palladium sponge melted in sillimanite gave a metal spectroscopically pure, when the melting was done in air (freezing in nitrogen).  Samples Nos. 8 and 11, however, were

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[12] Day and Sosman, The Dictionary of Applied Physics, "Abs. Scale of Temp.," Macmillan & Co.; 1922.

prepared by melting the sponge in sillimanite in a vacuum; in fact, in the crucible used for the temperature measurements as shown in Figure 1. (This procedure eliminated the possibility of the cracking of crucibles by evolution of gas from the freezing metal.) Whatever impurity entered the metal must have resulted from the reduction of the material of the crucible by impurities in the sponge. Subsequent examination showed the introduced impurities to be traces of aluminum, iron, silicon, and a greater amount of titanium. Furthermore, the crucible was filled by repeated melting of charges of compressed sponge, and no measurements were made until the metal had been in contact with the crucible for a considerable length of time. Of course the sponge used was tested separately, sample No. 1 (138) representing this lot of sponge (see Ann. d. Physik, 1919), and the values given are theirs and versus their purest sample. No. 15 contained platinum.

*Summary of estimated errors*

| Source of error | Equivalent in degrees |
|---|---|
| Transmission of sector disk | 0.2 |
| Effective wave length | .3 |
| Photometric matching | .2 |
| Brightness of experimental black bodies | .3 |
| Impurity of metal | .1 |
| Total | 1.1 |

A very conservative estimate of the uncertainty is 1°. We believe that the probability that the error is greater than 0.5° is very small.

Waidner, Mueller, and Foote [13] have reviewed the work of various investigators of the melting point of palladium, and their summary is given in Table 6, in which the values have been recorrected to $C_2 = 1.432$ cm deg.

TABLE 6.—*Comparison of samples of palladium*

| No. | Sample | Difference in melting point | E. M. F. at melting point | Metal melted in— |
|---|---|---|---|---|
|  |  | ° C. |  |  |
| 1 | No. 138 | 0 | 0 | Lime. |
| 2 | D. & S., 1923 | 0 | --------- | Magnesia. |
| 3 | B. of S., 1923 | −0.1 | +54 | Sillimanite. |
| 4 | D. & S. 2 | −.2 | 180 | Magnesia ?. |
| 5 | G 2 | −.3 | 160 | Lime. |
| 6 | 4 remelted | −.4 | 250 | Sillimanite. |
| 7 | W 1 | −.4 | 205 | Lime. |
| 8 | B. of S., 1923 | −.4 | --------- | Sillimanite. |
| 9 | Nela | −.6 | --------- | (?). |
| 10 | G 1 | −.6 | 490 | Lime. |
| 11 | B. of S., 1922 | −.7 | 550 | Sillimanite. |
| 12 | N. Y. A. Office | −2.3 | 2,500 | Lime ?. |
| 13 | Heraeus | +.9 | 3,800 | (?). |
| 14 | Kahlbaum | +1.0 | 5,200 | (?). |
| 15 | H & M [a] | +9.5 | 5,600 | (?). |

[a] No. 15 was an impure sample found by Hoffman and Meissner.

[13] Pyrometry Symposium, Bull. A. I. M. M. E.; 1919; also published by the institute as a book Pyrometry.

TABLE 7.—*Melting point of palladium*

[$C_2$=1.432 cm deg.  M. P. of gold=1,063° C.]

| Investigators | Method | Melting point |
|---|---|---|
| | | °*C.* |
| Nernst and Wartenberg, 1906 | Ratio of brightness Pd/Au, Wanner pyrometer. | 1, 552 |
| Waidner and Burgess, 1907 | Disappearing filament pyrometer and sector disk. | 1, 550 |
| Day & Sosman, 1910 | Gas thermometer | 1, 550 |
| Hyde, Cady, and Forsythe, 1915 | Ratio of brightness Pd/Au, disappearing-filament pyrometer. | 1, 557 |
| Mendenhall, 1917 | Ratio of brightness Pd/Au, spectral pyrometer. | 1, 553 |
| Hoffman and Meissner, 1919 | Ratio of brightness Pd/Au, spectrophotometric. | 1, 556 |
| Present authors | Ratio of brightness Pd/Au, disappearing-filament pyrometer. | 1, 553. 6 |
| Mean | | 1, 553. 1±0. 7 |

## VI. CONCLUSION

The melting point of very pure palladium has been redetermined by measuring the relative brightness of black bodies at the melting points of gold and palladium and calculating the upper temperature by means of Wien's law, which is equivalent to Planck's law, for light and such a range of temperature.  The measurements were made with an optical pyrometer sighted into a black body immersed in freezing metal.  The precision attained was about 0.1° at the gold point or 0.2° at the palladium point.  The result is 1,553.6 ± 0.5° C., based on 1,063° C. for the melting point of gold and 1.432 for $C_2$ in Planck's law.  On this basis the mean of all accepted data is 1,553.1°, with a "probable error" of 0.7°.  If we consider the uncertainty of 0.5° in the melting point of gold and 0.002 in the value for $C_2$ (accepting Planck's law), we may finally conclude that the melting point of palladium is 1,553 ± 2° on the centigrade thermodynamic scale.

It has become almost universal practice to take 1,063° C. as the melting point of gold.  The earlier work of Hollorn and Day [14] resulted in the value 1,064°, while the later work of Day and Sosman led to the value 1,062.6° ± .8°.  It is obvious that an accuracy of the order of 0.1° was not attained, and that if the value is to be given to the nearest degree, then 1,063° is logically indicated as the proper choice.

## VII. APPENDIX

### 1. THERMOELECTRIC MEASUREMENTS

Throughout this work all electrical measurements were made with potentiometers.  Part of the time a Leeds & Northrup type K slide-wire potentiometer was employed, and for more accurate work

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[14] Ann. d. Phys., **307,** p. 527; 1900.

a Diesselhorst 5-dial potentiometer was used.   It is out of place here to describe in detail well-established methods of measuring small emfs.   Attention is directed here to the special problems arising.

No special difficulty was met in measuring emfs of thermocouples at the melting point of gold.   New, homogeneous couples of platinum and platinum, 10 per cent rhodium alloy, made at the Bureau of Standards were used exclusively.

A new couple, well annealed and inserted in a clean 2-holed porcelain tube, was cut at its hot junction, and a bit of gold wire was welded to both elements.   The weld was made in such a way that a minimum of strain remained in the two legs of the couple, so that the gold would not part at the melting point.   The couple with its gold tip was inserted into the furnace just below the melting point, and after a steady state was reached the heating rate was adjusted to about 0.3° per minute.   The slow rise of emf of the couple was observed in the drift of a line of light across a galvanometer scale. When the melting point was reached, the drift ceased—the emf remained constant—for a fraction of a minute and then continued with a slight increase caused by the slight lag of the couple behind the furnace temperature.   Frequently the gold parted a degree or so above the melting point.   Occasionally the furnace was manipulated so successfully that the gold was made to freeze without having been more than a few tenths of a degree above its melting point. The freezes checked the melts fairly well but were not taken during any optical measurements.   When the gold parted, the galvanometer swung freely back to zero, indicating an open circuit.

A precision of measurement was attained which made it possible to compare thermoelectrically the melting points of different samples of gold to 0.02° corresponding to 0.2 microvolt from the couple.   It was possible to detect the melting range of samples which melted only a few tenths of a degree from the melting point of the purest samples.

Such a precision was, also attained in measurements at the palladium point, but not without practice and a study of the difficulties encountered.   These were, in particular, (1) deterioration of thermocouples, which became inhomogeneous, and (2) electrical leakage from the furnace to the thermoelectric circuit through refractory insulation.   The most refractory procelains become fairly good conductors above 1,450° C., and considerable leakage could occur when part of the furnace was 110 volts above the ground potential.   Were it not that this leakage occurred over only a short length of the couple circuit, measurements could scarcely be made at all.

First, we found that by using new annealed couples, by leaving them in the 2-holed tubes after their use had begun, and by clipping from

the end 1 cm or so after each melt that trouble with inhomogeneity was almost eliminated. It was necessary, however, to insert the couple to the same depth in the furnace each time in order to obtain satisfactory results.

Leakage caused more trouble. At first we found that at the moment of melting the emf did not always remain constant but rose and fell erratically. This was found to be caused by changes in the positions of the wires of the couple when they were relieved from a strained position by melting of the palladium. If the weld was properly made, the erratic changes at the melting point were small but were not eliminated. We tried grounding the couple and shielding it from the furnace with an intermediate grounded shield without material success.

A notable difference between gold melts and palladium melts was that when the palladium melted through, the galvanometer in the circuit was thrown violently off the scale instead of coming to a balance as on open circuit. Reversing the heating current of the furnace reversed the high potential across the galvanometer, plainly indicating the presence of leakage from the furnace winding to the couple. Believing that chemical action or electrolysis might be playing a part, we carried out a few simple tests as follows:

A couple whose hot junction had been cut open was inserted into the furnace at about 1,550° C. and emfs across the outer terminals observed under different conditions. Reversing the furnace current reversed the emf. Then we noticed that opening the heating circuit suddenly, removing high potential from the furnace, did not result in zero emf across the terminals of the couple. In one instance this emf was in excess of 1 volt but dropped so rapidly that no accurate measurement was possible.

A new couple open at the end in a new porcelain tube was inserted in the furnace at 1,550° C., and immediately afterwards the furnace current was rapidly reversed by hand, thus preventing appreciable electrolysis. After the couple had become practically as hot as the furnace, the current was suddenly cut off. The galvanometer across the outer terminals of the couple thereupon indicated no emf. After closing the furnace-heating circuit and allowing the current to pass for a minute in one direction and then again opening the circuit, the galvanometer indicated a high potential, which quickly dropped in value.

In order to obtain high precision in electrical measurements at the palladium point—that is, measurements to tenths of a microvolt—we found it best to reverse the furnace current by hand while the emf of the couple was indicating the melting of the palladium. (No steady source of alternating current was conveniently available.)

Quite satisfactory measurements were obtained which were certainly consistent to 0.5 microvolt, by exercising care in repeating melts without change in any detail. Many samples of palladium were compared as to melting point, and in a few cases of purest material special care was used.

It must not be supposed that difficulties met in thermoelectric measurements have any bearing on the results obtained with the optical pyrometer. The optical-pyrometer measurements were followed immediately by the check of the thermocouple at the melting point, without disturbing the melt couple in any way. The precision obtained in comparing different samples of palladium was necessary in identifying the purest metal but was greater than necessary in the measurements of brightness.

Washington, November 24, 1925.