The Freezing Point of Platinum

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I—*Introduction*

The International Temperature Scale, which has been in force since 1927,* is based on certain values assigned to the boiling and freezing points of pure substances and on specified means of interpolation between, or extrapolation beyond, these points. The highest basic point of the scale is the freezing point of gold, defined as 1063·0° C, while for extrapolation from this temperature use is made of the Wien law of radiation, with a certain value of the constant C_2. Though any temperature above 1063° C is thus completely defined without reference to further fixed points, determinations of such points are of considerable value. In particular, they serve to indicate the degree of reproducibility of the scale by the various users of it, and, when well authenticated, to provide secondary standards for its realization. Of such fixed points the most important has been the freezing point of palladium (1555° C), but the latest developments in furnace technique and refractory materials should now enable the freezing point of platinum to be used with equal, if not greater, advantage. The qualities of platinum which render it especially valuable in this connection are as follows: its freedom from oxidation; its high standard of purity, for which a convenient electrical test is available; its high freezing point (about 1775° C) which approaches the important zone of temperature covered by the electric lighting industry. These qualities also make the platinum point especially suitable as the basis for a standard of light, as has been proposed by a number of experimenters.

It is with the two objects indicated above that the National Physical Laboratory has undertaken an investigation concerning the freezing point of platinum, the precise scope of which may be defined as follows:—

(1) To determine the value of the freezing point in terms of the International Temperature Scale.

* 'Trav. Mem. Bur. Int. Pds. et Mes.,' vol. 18, p. 94 (1927).

(2) o obtain evidence as to the suitability of the specification proposed by he Bureau of Standards, U.S.A., for a Primary Standard of Light based on the freezing point.

Both bjectives involve measurements of radiation from a black body held at the emperature of freezing platinum, but, whereas for the purposes of the secon the black body has to be realized under strictly defined conditions, no such limitation applies to the first objective. The procedure adopted has been to setup a radiator in accordance with the proposed specification and to try modifations suggested by the experience gained. The present paper is concerned with the furnace arrangements, the setting up and modification of the radiators, and the other factors involved in the determination of the freezing point. The same apparatus was used, for their observations on the proposed standard of light, by the Photometry Division of the Electricity Department, who will deal with this subject in a subsequent paper.

II—*Method of Experiment*

According to the International Temperature Scale any temperature t, above the freezing point of gold (1063° C), is determined by means of the ratio of the intensity J_2 of monochromatic visible radiation of wave-length λ cm, emitted by a black body at the temperature t, to the intensity J_1 of radiation of the same wave-length emitted by a black body at the gold point, by means of the following formula, derived from the Wien equation

$$\log_e \frac{J_2}{J_1} = \frac{C_2}{\lambda}\left[\frac{1}{1336} - \frac{1}{(t+273)}\right],$$

the constant C_2 being taken as 1·432 cm degrees. Though the definition refers to monochromatic radiation, the common practice is to use for the temperature measurement a pyrometer of the disappearing filament type fitted with a red glass transmitting a comparatively wide band of radiation. As is well known the "effective wave-length" of such a glass for any temperature interval, *i.e.*, the wave-length to which the above formula is strictly applicable, can readily be calculated from the spectral transmission of the glass and the visibility curve of the eye.

Having obtained the effective wave-length, the process of temperature measurement consists in determining the ratio J_2/J_1. For moderate temperatures this is done by employing a rotating sector disc of such aperture as will

cut down the radiation from a black body at the higher temperature to match in intensity the radiation from a black body at the gold point.

For the freezing point of platinum, however, this ratio, for a wave-length of 0·66 μ, is of the order of 300 to 1, so that if a sector disc with two symmetrically placed apertures* were used, each aperture would only be 0·6 degrees of angle. The cutting of such an aperture with the requisite precision and its measurement to an accuracy of at least 1 part in 500, or 4 seconds of arc, would be a matter of great difficulty.

Consequently it is convenient to carry out the reduction in intensity from the platinum to the gold point in two stages. This allows of the use of sectors of considerable aperture which are easily constructed and measured. It is true that the double set of observations would tend to a decrease in precision. Against this it may be mentioned that, with a pyrometer of normal construction, the field intensity most favourable to accurate observation lies considerably above the gold point. Hence, by choice of an appropriate sector, the observations, which are most limited in time, namely, those on the black body at the platinum point, can be taken at a favourable intensity, while unlimited time is available for those at less favourable intensity. On the whole, therefore, considerable advantage accrues from the system of two-stage reduction of the platinum point.

The several processes involved in a determination of the freezing point of platinum may now be summarized.

1—The determination of the spectral transmission of the red glass and calculation of its effective wave-length for the two ranges.

2—The construction and measurement of two sector discs of such apertures that the product of their transmissions gives approximately the ratio of radiation intensity of black bodies at the gold and platinum points for red light of about 0·66 μ.

3—The setting up of a black-body radiator at the freezing point of platinum and the measurement of the current through the pyrometer lamp required to match the intensity of the radiator as reduced by the rotation of one of the sector discs.

4—The adjustment of another radiator to such temperature as will, without the interposition of a sector, require approximately the same current as in 3 to give a match with the pyrometer lamp.

* It is advantageous to use two apertures since they are self-compensating for errors in centring and require a lower speed to eliminate flicker.

5.—The measurement of the current through the pyrometer lamp required to match the intensity of the radiator, referred to in 4, as reduced by the rotation of the second sector disc.

6.—The setting up of a black body radiator at the freezing point of gold and the measurement of the current through the pyrometer lamp required to match the intensity of this black body.

It is not necessary that the operation 4 should give exactly the same current as 6 since corrections for small departures can readily be determined; similarly it is not necessary that the combined effect of 4 and 5 should give exactly the same current as 6.

III—*Apparatus*

The Optical Pyrometer—The optical pyrometer used in the investigation was of the disappearing filament type of Holborn-Kurlbaum. It calls for no detailed description since its main features follow those of the instrument developed at the Nela Research Laboratory with improvements based on the work of Fairchild and Hoover. Thus use was made of their type of lamp, which has a cylindrical envelope provided with flat ends designed to allow the filament and object to be viewed at high magnification without distortion. It may be added that the filament employed had a diameter of 0·05 mm and that with diaphragms giving angles of 0·054 and 0·022 radians on the objective and eyepiece sides of the lamp respectively, a satisfactory disappearance of the filament was obtained.

The red filter used in the eyepiece of the pyrometer was of the Corning Glass known as "high transmission red 50%," and was 6 mm in thickness. Its effective wave-length was calculated in the usual way* from the spectral transmission† of the glass and the visibility curve for the eye, taking for this latter the agreed international data.‡ As is well known, the effective wave-length varies with the temperature of the glass itself, so that a correction has to be applied to any readings obtained with a sector on account of the variations in atmospheric temperature. The magnitude of this correction increases with decrease in the transmission of the sector. It so happened in the present investigation that the observations with the sector of smaller transmission had to be taken in a laboratory subject to wide changes in temperature and it

* For a specimen calculation see Fairchild, Hoover, and Peters, 'Bur. Stand. J. Res.,' vol. p. 951 (1929).

† This was determined by the Optics Division, National Physical Laboratory.

‡ 'C. R. Comm. Int. Éclairage,' p. 67 (1924).

was thought well, therefore, to control the temperature of the glass at th maximum likely to be reached, about 25° C. For this purpose the screw-o cell for attaching the red glass to the pyrometer was provided with a wate circulation which could be maintained at the required temperature.

Another point which may be mentioned in connection with the pyromete was the use of a totally reflecting prism. Normally this formed an integra part of the instrument, being attached to the end of the objective tube i such a way that the prism had one face always normal to the axis of the tub but that it could be rotated about this axis so as to allow the sighting of the pyrometer in a vertical, horizontal, or intermediate direction. Except where otherwise stated, all observations were taken with the prism attached to the pyrometer as indicated.

2—*Rotating Sectors*—As already stated, the reduction in intensity from the platinum to the gold point was effected in two stages. The intermediate temperature could, of course, range over wide limits and the considerations governing its choice in the present work were as follows. In addition to determining the platinum point (about 1773° C) in terms of the gold point it is useful to correlate its value with that for the palladium point (about 1555° C). A single sector could be used twice over to determine either of these points in a two-stage operation and the intermediate temperatures would then be 1340° C for platinum and 1270° C for palladium. It is obvious, therefore, that if either of these temperatures were chosen for the intermediate point, a total of two sectors would enable both the platinum and palladium points to be determined by the two-stage method in terms of the gold point and in relation to each other. In view of the simplification which could thus be obtained and of the fact that the temperatures in question were in a region giving a comfortable brightness of field in the pyrometer, it was decided to work at one of the temperatures and the choice was given to 1270° C. Two sectors were, therefore, constructed, one giving a reduction from 1773° C to 1270° C, and the other from 1270° C to 1063° C, the latter to be used subsequently for a determination of the palladium point. The sectors were cut from aluminium discs 0·5 mm thick and 39 cm in diameter, and were in pairs of approximately equal angles and situated opposite to each other. The peripheries of the discs were not cut through and the risk of damage to the edges was thereby diminished. The edges were trued against a radial jig and were covered with a thin layer of dull black paint.

The angular apertures of the sectors were determined by measurement of chord and radius as magnified by a simple lever system. For this purpose the

clamped to a flat steel strip, 1·5 metres in length, so as to be con-
th a pivot situated near one end of the strip and about which it could
tl in a horizontal plane. A microscope having its axis approximately
as sighted with its cross wires on one edge of the aperture to be
and the lever was rotated until the second edge came under the cross
he resulting movement of a mark on the remote end of the lever,
t a known distance from the centre of rotation, was measured by
a travelling microscope. The arrangement gave about an eight-fold
tion.

is apparatus no difficulty was experienced in measuring the apertures,
he smaller sector, to 1 part in 1000. As a check on the absence of
from the painted edges of the sector, the transmission of the sector
r aperture was compared in the pyrometer with that of a sector, of
same opening, prepared by mounting knife edges on an aluminium
rm the apertures. The calibrations of the two types were found to be
t to within the limits of observation. For prolonged series of read-
comparative absence of noise with a plain disc is a considerable
e and this type was used throughout the investigation.

Black-body Radiators at Platinum Point—As already indicated, the
stigation has been largely concerned with radiators set up in accordance
specification* recommended by the Bureau of Standards for the
on of a black body at the freezing point of platinum for the purposes
mary standard of light. The general design of the radiator will be
od by reference to fig. 1 which shows a section of it mounted in a
as used in the present investigation. The following are some of the
ints of the specification :—

(1) The crucible, etc., to be of material which does not contaminate platinum (*e.g.*, thoria) and the thermal insulation to be of the same material.

(2) The dimensions of the several parts to be as follows : internal diameter of crucible at top 22 ± 2 mm, and at bottom 17 ± 2 mm ; internal height of crucible 45 ± 5 mm ; inside diameter of sight tube 2·5 ± 0·2 mm ; wall thickness of sight tube 0·25 to 0·5 mm ; opening in cover at least 0·8 mm less than internal diameter of sight tube ; depth of powder in sight tube 10 to 15 mm.

(3) Platinum to be of such purity as to give an α coefficient of at least 0·390.

*' Rep. Com. Consult. d'Electr., Bur. Int. des Pds. Mes.,' p. 178 (1930).

(4) Electromagnetic heating to be used, freezing points only to be taken and power supply to be so controlled as to give a constant intensity for 3 minutes during the freeze.

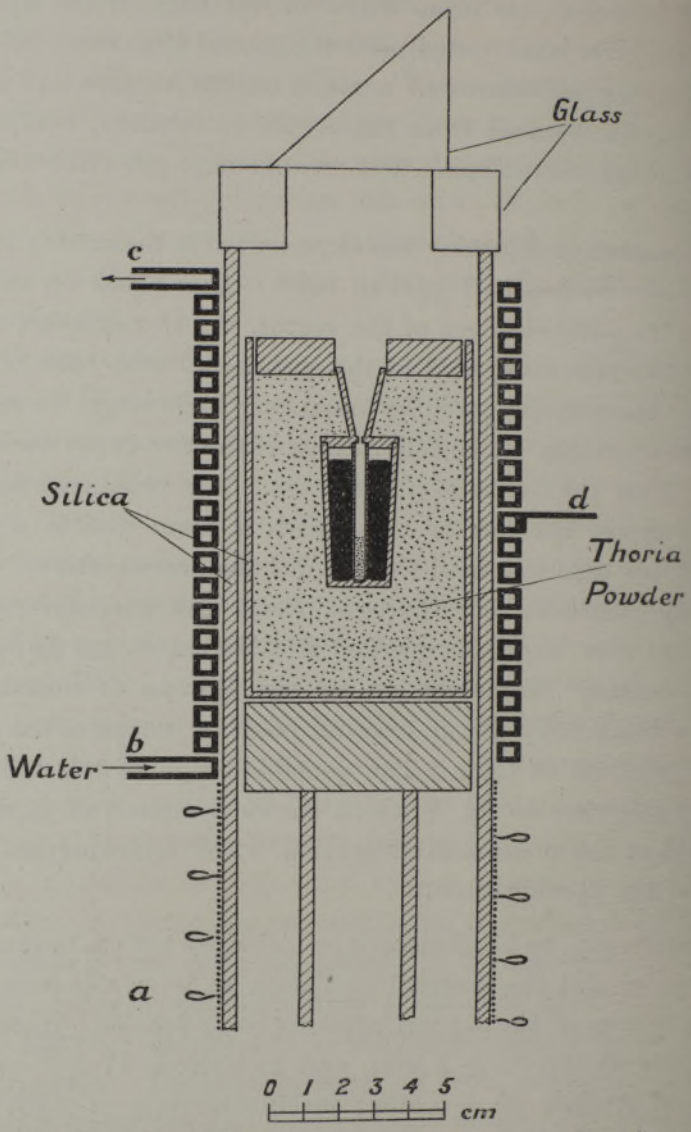

Fig. 1—Furnace assembly for platinum melting point with B.S. crucible

It is convenient at this stage to point out the slightly divergent objects of the two investigations undertaken at the Laboratory in relation to the above-mentioned specification. The investigation on the Standard of Light was concerned primarily with the reproducibility of the standard defined by the detailed specification and only secondarily with the question whether that

complies with the conditions required of a black-body radiator. ther hand, the determination of the freezing point depends funda- on the realization of a black body, no matter how obtained, and the ecification has to be considered only from this point of view.

Unfortunately no simple test is available for compliance with black-body nditions. It is therefore necessary, for this purpose, to rely on such indirect idence as the constancy of the results obtained at the freezing point under riation in the conditions of experiment, *e.g.*, in the rate of cooling and the amount of induced undercool, the constancy of the results obtained at the elting point, and the agreement between the freezing and melting points. n the present work there appeared to be a small but definite difference between he values of the melting and freezing points obtained with the specified pparatus shown in fig 1 and it was thought advisable to try some modifications f that assembly. Assuming the most likely cause of the difference to be a eparture from black-body conditions due to a longitudinal gradient of tempera- ure in the sight tube, it was considered that such an effect might be produced ither by the tapering of the ingot resulting in a differential effect in the inductive heating or by the fact that the direction of maximum heat loss was obviously upwards. Effects of this description could, of course, be additive or sub- ractive and were probably the latter in the present instance.

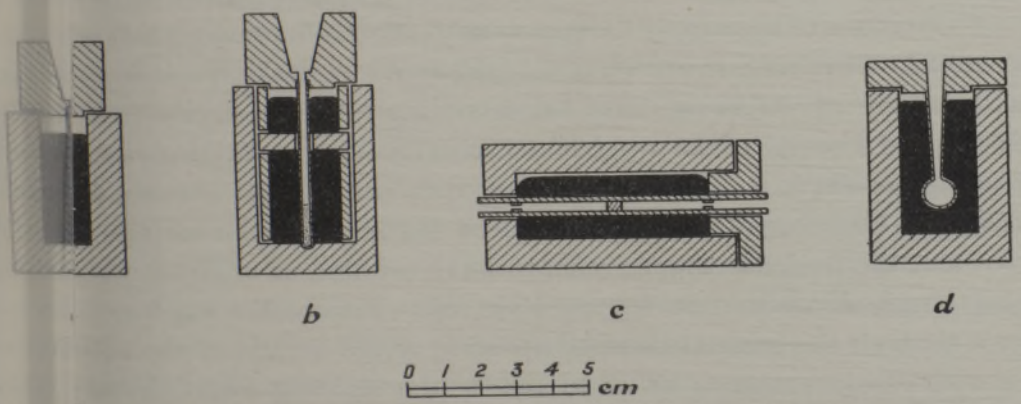

Fig. 2—Modified crucible assemblies for platinum melting point

In the modification shown in fig. 2 (*a*), the radiating tube and top are similar to those in fig. 1, but the crucible is made strictly cylindrical in form, so as to eliminate the supposed unequal heating of the ingot. In fig. 2 (*b*) the ingot is shown divided by a horizontal partition of refractory material, with the idea of solidifying, and perhaps reducing, the upward conduction of heat.

Both of these modifications gave satisfactory results, which are summariz later in this paper.

It is perhaps of interest to mention two other modifications which did n prove to be successful. In the first of these, fig. 2 (*c*), the attempt was made eliminate temperature gradient in the central region of the radiator on whi the pyrometer was sighted, by a symmetrical arrangement giving equal he loss from the two ends. It is obvious that, other things being the same, t ingot would have to be longer with this arrangement than with assymetr arrangements such as those in figs. 1 or 2 (*a*), and further that the ingot is mo conveniently placed with its axis horizontal. The use of the assembly, show in fig. 2 (*c*), had been suggested as the result of promising experiments on similar arrangement of a gold ingot, heated in a resister furnace, and also thos on a very small platinum ingot, $\frac{1}{4}$ inch in diameter and $\frac{3}{4}$ inch in length, heate inductively. This latter ingot was contained in a crucible of alumina and ha a sight tube of alumina glazed on the outside by partial fusion.* The bore o the sight tube was 1 mm and the object sighted on was a tiny fragment of alu mina at its centre. This assembly gave passable melting points, having duration of halt of from 1 to 3 minutes, and values of the same order as thos obtained with larger scale apparatus. The freezing points were less satisfactory owing to the tendency of the undercool to obscure the halt though this defect could no doubt have been minimized by taking special measures to eliminate the fluctuations in the supply voltage so as to allow a finer regulation of the rate of cooling. However, it was obviously desirable to work on a larger scale and the assembly shown in fig. 2 (*c*) was accordingly tried. In the first trial the crucible had a cavity at the top, not shown in fig. 2 (*c*), containing an extra piece of platinum which it was hoped would melt and fill the crucible to its full capacity. Unfortunately this extra piece did not entirely coalesce with the ingot and the irregular shape seems to have resulted in unsatisfactory curves being obtained for the six freezes observed. Finally the experiment broke down through the gradual bending upwards of the middle of the tube, under the hydrostatic pressure, so as to render the sighting unsatisfactory. The tube in this case was of thoria 2·5 mm in bore and 0·25 mm in wall thickness. The results were considered to be sufficiently promising to justify a second trial with a tube of the same bore but 1 mm in wall thickness. However, a breakdown again occurred through the bending of the tube and the method was accordingly abandoned.

* See description of process by Adcock and Turner in ' J. Sci. Instr.,' vol. 7, p. 327 (1930).

The other arrangement, fig. 2 (*d*), has been successfully used at lower temperatures,* but in the present work it yielded curves of unsatisfactory form on the occasion on which it was tried. The reasons for failure were not explored; probably heavy gradients were induced in the ingot by radiation from the conical surface above the bulb. The arrangement is only mentioned here because of the possible interest attaching to the refractory material used. The bulb and tube, fig. 2 (*d*), were made in one unit of pure alumina by means of a process described by Mr. Turner in the note on refractory materials appended to this paper. When heated to about 1950° C in the molten metal the material of the radiator re-crystallized into the translucent form which has great mechanical strength. It was noteworthy that, at the conclusion of the experiments, the radiator was withdrawn from the molten metal and exposed immediately to the atmosphere without fracture occurring.

The following comments may be added with regard to the refractories used for melting platinum. Except where otherwise mentioned, these were of pure thoria. The crucible assemblies of the form of fig. 1 were made at the Bureau of Standards from thoria fused by a special process as described by Swang and Caldwell,† and the other assemblies in the Metallurgy Department of the Laboratory from shrunk thoria as described in Appendix I. The behaviour of the two types did not seem to be very different and examples could be quoted of prolonged usage with each. Thus one of the shrunk thoria type, fig. 2 (*a*), was intact when it came to be broken up after some 50 melts while one of the fused thoria type, fig. 1, actually survived 300 melts. No cracks were observed in the former type of crucible, which was thick-walled, but they seemed prone to develop in the thinner-walled type of fig. 1. The most common cause of failure in both kinds of assembly arose from the particular manner of anchoring the sight tube by fitting it into recesses in the lid and the base of the crucible as recommended in the proposed specification for the Standard of Light. Any imperfection of fit, or differential shrinkage of the crucible and the tube, was liable to cause the latter to shift in position if not to come adrift. The main cause of failure with both types being as stated, it might be preferable to adopt a closed-end sight tube rigidly attached to the lid.

(2) *Black-body Radiators at the Gold Point*—With gold, as with platinum, the ingot method provides the best means for realizing a black body at the freezing

* Hoffmann and Meissner, 'Ann. Physik,' vol. 60, p. 201 (1919), also Schofield, 'Proc. Roy. Soc.,' A, vol. 125, p. 517 (1929).

† 'Bur. Stand. J. Res.,' vol. 6, p. 1131 (1931).

point. A much wider range of experimental conditions is, however, practicable at the gold point. This feature is of value in that it provides a possible means for detecting systematic error inherent in the platinum determinations, since those at the gold point can be made both with and without the restrictions applying at the higher temperature. Accordingly, a series of measurements was carried out, for the purposes of the present investigation, with a gold ingot assembled as shown in fig. 2 (*a*) and heated by means of the longer coil employed for most of the experiments on platinum (see 6, p. 803). In addition a large number of experiments have been made with ingots heated in ordinary resister types of furnace. The use of such a furnace has the advantage over inductive heating as a finer control is possible at the change point since the alteration of electrical resistance on melting of most metals, including platinum and gold, does not, as in the inductive system, tend to accelerate the process of melting or freezing. Further, the provision of special means for attaining temperature uniformity can more readily be made in the resister type of furnace.

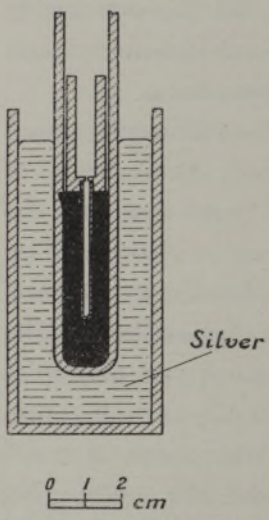

Fig. 3—Crucible assembly for gold melting point in resister type furnace

As already mentioned a gold ingot assembled as in fig. 2 (*c*) was used in a resister furnace and this gave satisfactory melting and freezing curves so long as there was an absence of longitudinal temperature gradient at the centre of the ingot. To prove the absence of gradient involves, however, the somewhat laborious process of taking simultaneous observations with two pyrometers sighted into opposite ends of the radiator and fortunately an alternative method of securing the desired uniformity came to light as a result of a parallel investigation* into the melting point of gold by means of platinum thermocouples. It was then shown that a high degree of temperature uniformity could be secured by the expedient of interposing a bath of silver between the ingot of gold and the furnace tube and this arrangement was accordingly adopted for the purposes of the present investigation in the manner indicated in fig. 3. The radiator shown consists of a fireclay tube which is cemented into a block of "mabor" material resting on the surface of the gold ingot. The ingot is contained within a "pythagoras" tube which is immersed in a bath of silver, the whole being inserted into a tubular furnace (not shown in the figure) which was wound with platinum ribbon.

* An account of this investigation will be published in due course.

(5)—*Radiator at Intermediate Temperature* (1270° C)—Any hot object having the required brightness temperature, in this case about 1270° C, could apparently be used for the purposes of the operations 4 and 5 described in Section II above, irrespective of its spectral distribution of energy. It was found convenient to employ a radiator similar to that at the gold point (see fig. 3) but without the supplementary silver bath. This assembly was inserted into a resister furnace and maintained at a steady temperature, as indicated by a thermocouple fixed beside the crucible, over the period required for the taking of the observations with and without the sector.

(6)—*High Frequency Induction Furnace*—In heating all the ingots the high frequency induction furnace designed by Bell* was employed, some modifications being made to meet the particular requirements of the investigation. Thus for the anode coil *ba*‡ it was found advantageous to use an air-cooled coil consisting of 50 turns of cotton-covered copper wire of 18 gauge spaced at 16 turns to the inch and provided with tappings at each fifth turn. The coil was covered with bakelite paint and was air-cooled by fans. For the main heating coil, *bc*, two arrangements were used each consisting of $\frac{1}{4}$ inch square section copper pipe with water cooling, one coil having 14 turns in a length of 5$\frac{1}{2}$ inches and the other 20 turns in a length of 6$\frac{3}{4}$ inches. The power condensers used were of 0·003 and 0·005 microfarads respectively.

IV—*Measurements*

In this section the observations at the gold point, the intermediate point (1270° C) and the platinum point are dealt with in order of rising temperature. A single pyrometer lamp of known constancy was used throughout the investigation, and occasional comparisons with other lamps showed no appreciable change in its calibration. All the measurements were made by two observers whose readings were in close agreement, and the values given below represent the mean of their observations.

(1) *Gold Point*—As already explained, two types of assembly were used for the determination of the freezing point of gold, namely, that shown in fig. 2 (*a*), which was heated inductively, and that shown in fig. 3, which was heated in a resister furnace. Examples of freezing and melting point curves, obtained with the two types of apparatus, are plotted in fig. 4. The ordinates are

* See ' Proc. Phys. Soc.,' vol. 40, p. 193 (1928).

† Suggested and carried out by A. Grace.

‡ The lettering in fig. 1 agrees with that of figs. 3 and 4 of Bell's paper.

pyrometer readings expressed in terms of temperature as derived from the mean reading of all the freezing points taken as 1063·0° C. Differences in reading can readily be estimated from the fact that individual observations are represented as circles of radius 0·5° C. It will be noted that in inductive heating the melting point curve shows a comparatively short halt. This was characteristic of the series and apparently arises from the considerable increase

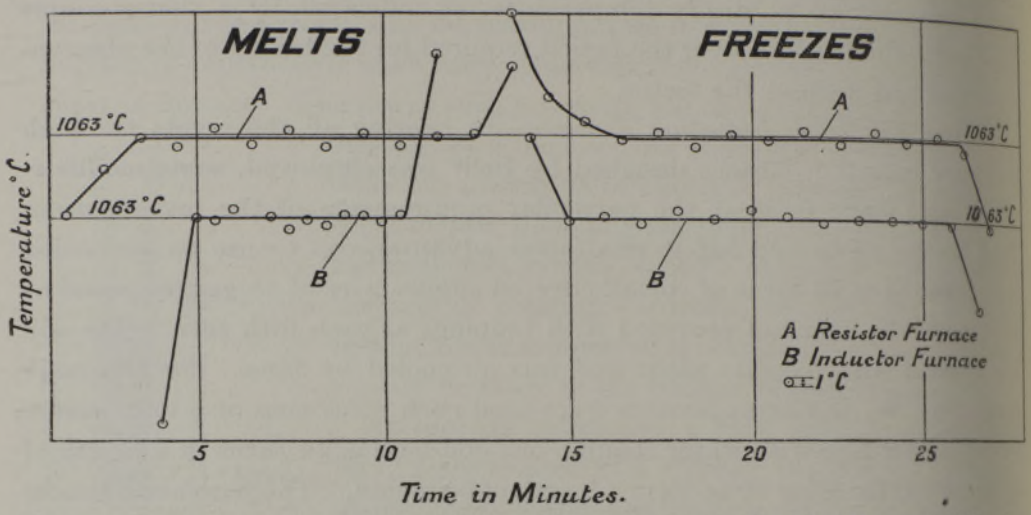

Fig. 4—Examples of curves for melting and freezing points of gold. Mean of all freezing points taken as 1063° C.

of electrical resistance of gold on melting. The results of all the experiments are summarized in Table I.

It will be seen that the mean values of freezing point given by the two methods are indistinguishable, while the mean values of the melting point in the two methods are respectively higher and lower by 0·2° C than the mean freezing points. These differences though small appear to be quite definite.

Table I—Calibration of Pyrometer at Gold Point—Pyrometer readings expressed in temperature relative to the mean of the readings for all the freezing points taken as 1063·0° C.

	Melting points				Freezing points			
Assembly	No.	Average deviation of, from mean	Mean	Probable error of mean	No.	Average deviation of, from mean	Mean	Probable error of mean
		°C	°C	°C		°C	°C	°C
Fig. 2 (*a*)	26	0·4	1062·8	±0·08	27	0·2	$1063{\cdot}0_1$	±0·04
Fig. 3	24	0·2	1063·2	±0·03	25	0·2	$1062{\cdot}9_8$	±0·04
		Mean	1063·0			Mean	1063·0	

It may be added that the mean value taken for the freezing point is based on some 400 individual observations.

Intermediate Point (1270° C)—Over 350 individual observations were taken for the purpose of linking the intermediate temperature with the gold point. They do not call for any special comment.

Platinum Point—Before dealing with the measurements on which the actual determination of the freezing point depends it may be of interest to refer to certain preliminary experiments.

At the commencement of the investigation it was thought that, since both this work on the freezing point and the standard of light involved the use of right-angled prisms to reflect the radiation from the black body in a horizontal direction, it would be convenient to adopt a common form of mounting for the prism. This mounting is shown in fig. 1. It will be seen that the prism rests on two bars of glass which span the end of the furnace tube. A slow stream of air was blown through the gap between the glass bars in order to cool the prism. This arrangement was, however, found to be unsatisfactory for two reasons. In the first place there was the possibility of error owing to the axis of the pyrometer not being normal to the face of the prism, which might result in an appreciable loss of light. An optical test was devised to check the correctness of adjustment in this respect, but was found to be somewhat troublesome to apply in conjunction with other necessary adjustments of the pyrometer. A second and more serious source of error came to light during the course of the investigation, namely, the deposit of a slight film on the face of the prism nearest the furnace. The material of this film was not identified, but it seems not improbable that it consisted of platinum.* When the film was present its absorption no doubt caused a lowering in the apparent value of the freezing point which in one extreme case amounted to 5° C. On discovering the presence of film the attempt was first made to prevent it, by greatly increasing the strength of the draught on the exposed face of the prism, but this was found to lead to error owing to the cooling of the radiator. Subsequently resort was had to cleaning the prism before commencing observations on each melt and freeze, but finally the apparatus was re-arranged so as to allow the prism to be fixed to the pyrometer tube as previously described. In this

* Incidentally it may be mentioned in support of this view that after being maintained for seven hours near the melting point, the inner surface of the cone (see figs. 1 or 2) was found to have a deposit of platinum which apparently could have reached this position only by vapourization.

position it was situated at 14 inches from the top of the furnace and no further difficulty with the formation of a film was experienced.

Another point dealt with in the preliminary work was in relation to the two induction coils described in Section III 6 above. The first experiments were made with the short coil, and gave freezing points which were higher by 1° C or 2° C than the melting points. It was considered that possibly this difference might be due to lack of uniform heating caused by variations in the strength of the inductive field covering the ingot. Observations were accordingly taken with the ingot in various positions inside the longer coil. It was found that the values of the freezing and melting points remained sensibly constant for movements of the ingot of about 1·5 cm from the central position. Though the experiments indicated that the shorter coil was probably adequate in length, the longer coil was, in fact, used for most of the experiments.

Turning now to the definitive observations, we give in fig. 5 the whole of the readings taken in a single series of experiments, in order that an idea may be formed of their general characteristics. This set has been chosen for illustration because it represents the greatest variation of conditions in a consecutive batch of experiments. Thus it will be seen that there was a variation of the order of two to one in the duration of melt or freeze and that in the latter the magnitude of the undercool ranges from zero to 70° C. Attention may also be drawn to the following points: the "spread" of the observations, from their mean values, averages less than $\pm$ 1° C; the values of melting or freezing point seem to be independent of the duration of the halt and the value of the freezing point also independent of the amount of undercool; the curves for the melts were superior to those of the freezes in sharpness of breakaway at the end of the halt.

Observations of melting and freezing points were taken on five separate ingots. The data used for calculating the absolute values are given in Appendix II and the results obtained are summarized in Table II. It will be observed that the table is divided into two parts according as the ingot is cylindrical (see fig. 2) or tapered (see fig. 1), the object of adopting this division being to throw light on the possibility of systematic difference between the two types. In the result no such difference was found and each form gave satisfactory curves.

The data in Table II may be supplemented by the following information:

Cylindrical Ingot C.1—The curves for melt and freeze were of about equal quality, the latter being somewhat better than those in fig. 5. No undercools of any magnitude were recorded.

With regard to the comparatively large drop in the value of R_{100}/R_0 which occurred with this ingot, it may be mentioned that the process of purifying the shrunk and ground thoria, used for making crucibles, was improved after the experiments with this ingot (see Appendix I).

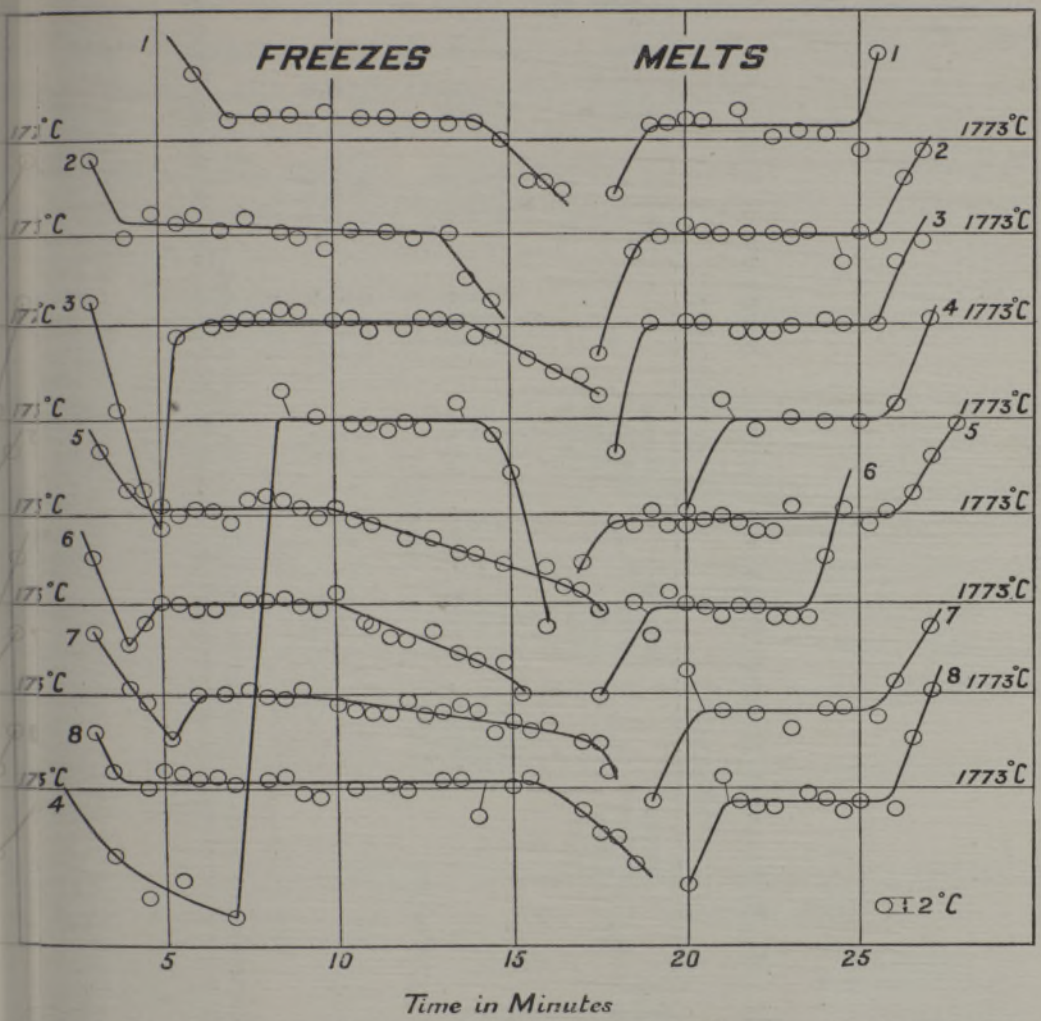

Fig. 5—Examples of curves for melting and freezing point of platinum with C.2 ingot.

Cylindrical Ingot C.2—These curves are dealt with in fig. 5 and have already been commented upon. A high value of R_{100}/R_0 is seen to have been maintained.

Cylindrical Ingot C.3—The curves for melt and freeze were the best obtained in the whole series of experiments. More than half the freezes gave curves of the same quality as those obtained with gold, fig. 4, and only slight undercools were observed.

Table II—Melting and Freezing Points of Platinum. Summary of Values

Particulars* of assembly	No. of previous melts	Melting points				Freezing points				Freezing less melting point	R_{100}/R_0	
		No.	Average deviation of, from mean	Mean	Probable error of mean	No.	Average deviation of, from mean	Mean	Probable error of mean		Before	After
			°C	°C	°C		°C	°C	°C	°C		
C.1, fig. 2 (*a*)	0	5	0·3	1772·3	±0·12	5	0·4	1773·4	±0·14	1·1	1·3916	1·3884
C.2, fig. 2 (*a*)	0	8	1·0	1772·6	0·29	8	0·6	1773·6	0·24	1·0	1·3919	1·3911
C.3, fig. 2 (*b*)	0	18	1·0	1772·1	0·22	17	0·8	1773·2	0·14	1·1	1·3895	1·3887
		Mean (C)		1772·3		Mean (C)		1773·3				
B.S.1, fig. 1	75	3	0·3	1771·7	—	5	1·1	1772·7	±0·43	1·0	1·3910	—
	200	22	1·4	1770·4	±0·24	25	1·2	1774·3	0·20	3·9	—	1·3903
B.S.2, fig. 1	10	7	1·0	1771·3	0·31	7	0·9	1772·9	0·24	1·6	—	1·3916
		Mean (B.S.)		1771·1		Mean (B.S.)		1773·3				

* C.1, C.2, C.3 refer to separate ingots of cylindrical form according to the figure indicated.
B.S.1, B.S.2 refer to separate ingots of tapered form according to the specification proposed by the Bureau of Standards.

The ingot was prepared by mixing portions of ingots which had already been much used and consequently the initial value of R_{100}/R_0 was lower than usual. The fall after use was, however, small.

*Tapered Ingot B.S.*1—The assembly was still in working condition when it came to be broken up after the ingot had been melted some 300 times for several distinct purposes, *i.e.*, experiments on the standard of light, the colour temperature scale, and the freezing point determination. In its final form the ingot was somewhat irregular in shape owing to the extrusion of metal through fissures in the crucible. A considerable number of the earlier freezing point observations, prior to the 75th melt, had to be rejected for various reasons, mainly because of the suspected presence of film on the prism as already described. Though the absolute values could not be taken into account, it should be recorded that the freezing points were higher on the average than the melting points by between 1 and 2° C.

A similar difference is seen in the short series of observations, after the 75th melt entered in the table. In the later series, after the 200th melt, the difference had increased to about 4° C, though the curves for the melts and the freezes, without undercools, were of fairly good form. However, included in the freezes were a number in which heavy undercools had been deliberately induced with the result that a series of freezing point curves were obtained of about the same average quality as those shown in fig. 5, Nos. 3 and 4. Examples of three such curves, with undercools varying from 25° to 40° C, are given in fig. 3.

In Table III the 25 freezes are divided into two groups according to the amount of undercool.

Table III—Analysis according to the amount of undercool of the 25 freezing points with B.S.1 ingot, taken after 200 previous melts

No. of determinations	Undercool		Mean freezing point, ° C
	Amount, ° C	Average, ° C	
13	0 to 5	2	1775·0
12	25 to 55	38	1773·5
25 (total)	—	—	1774·3

Taking from Table II the most probable value of the freezing point as 1773·3° C, we see that the first value in Table III, with a very small average undercool, is higher than this by 1·7° C, while the value of the melting point, given in Table II, is lower than 1773·3° C by 2·9° C. Presumably, therefore, some factor was operative in opposite directions during melt and freeze. For

example, we might surmise that material extruded from the ingot, as already mentioned, would affect the temperature distribution both as a source of heat, by electrical induction, and a sink of heat, by thermal conduction, and that one effect might predominate during melting and the other during freezing, so as actually to cause a reversal of the longitudinal gradient in the two conditions, and give rise to the differences noted.

With regard to the other group in Table III, the undercools were induced by raising the temperature of the ingot considerably above the melting point.

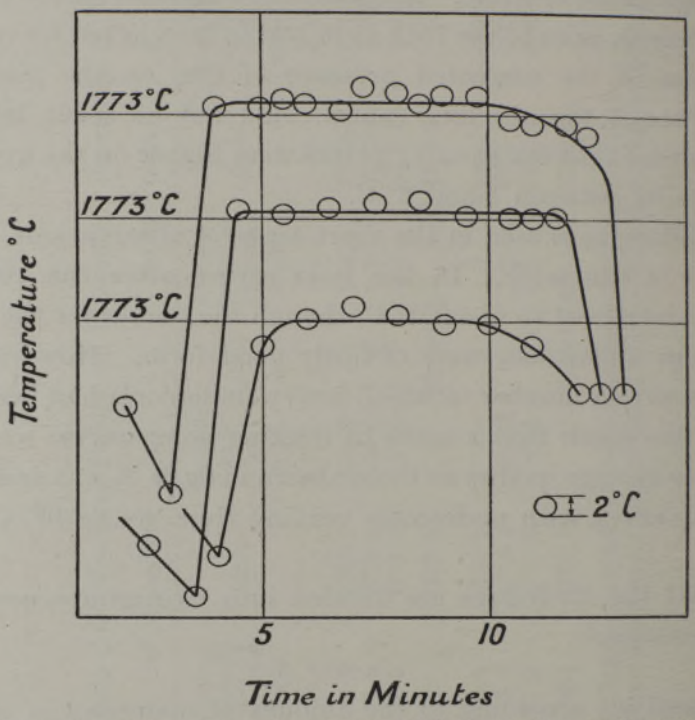

FIG. 6—Examples of freezing point curves with B.S.1. ingot after 200 melts.

The tendency of undercool was thereby increased, but it could often be terminated at will by tapping the apparatus. The sudden evolution of heat, which occurs on freezing after an undercool, might be expected to override the prevailing temperature gradients and give, for an appreciable time, a flat on the curve corresponding with the true freezing point. Although after any undercool the reading cannot apparently rise above the true freezing point, there is a certain danger that if the liquid is cooled too far the freezing point may never be reached in the subsequent rebound. When, however, curves are of the form shown in fig. 6, and with a reasonable length of halt, there seems to be very little possibility of a depression in value. In

xperiments on platinum no evidence of such depression was found ercools ranging up to 70° C, and even with an undercool of 150° C difrence in the single instance observed was only 2° C which is hardly he range of error of a single determination.

circumstances it would seem that the second value in Table III is to considerably greater weight than the first.

*Ingot B.S.*2—The melts and freezes gave curves of about average those for the freezes being without appreciable undercools.

Values in Table II—In view of the small range of the values given in the precise method of arriving at the means for each group is not of portance. For the C ingots the values have been weighted according umber of determinations, while for the B.S. ingots the arithmetic s been taken, since, for the reasons already indicated, the second value able, though representing many determinations, is not considered to ater weight than the other two. Alternatively if the second freezing lue is replaced by the more reliable second value of Table III, and the ken according to the number of determinations, practically no n would result.

V—*Discussion of Results*

bject of the investigation dealt with in this paper is to determine the ture of equilibrium of the solid and liquid phases of platinum at atmospheric pressure, which temperature has been referred to throughthe sake of brevity, as the "freezing point of platinum." Such an um temperature should be given by observation either of the freezing elting point at any atmospheric pressure, the extreme variation of this being of quite negligible effect in metals. Where, however, as not ntly happens, the values obtained from the freezing and melting points is generally recognized that the former gives the more reliable indica- hus in the specification for the International Temperature Scale it is vn that, for the purpose of realizing the Scale at the gold and silver by means of platinum thermocouples, the equilibrium temperature is en by the freezing point subject to a test for freedom from the influence rnal conditions. The test can be either a raising or lowering of the in the ingot by 1 cm without altering the reading by more than 0·1° C, rnatively an agreement between the melting and freezing points to Unfortunately an exploratory test is hardly feasible under the

conditions applying in the present investigation, while a persistent difference o at least 1° C has been noted between the freezing and melting points (se Table II). It is therefore necessary to adduce other reasons for the acceptanc of the value found for the former point. In the first place a number of argu ments can be advanced in support of the greater reliability of the freezin point in the particular circumstances of the work. For example :—

(1) Electrical induction is known to have a stirring action on the liqui which would tend to promote temperature uniformity at the onset of solidi fication.

(2) Heating by high frequency induction being a skin effect, departure from the true cylindrical form of ingot, arising, for example, from the origina shape of the crucible, or extrusion of metal through its walls, would be mor likely to produce non-uniformity of temperature in the metal when melting This seems a reasonable deduction from the fact that the energy dissipated i the skin of the ingot is relatively large during melting, being required fo raising the temperature of the surroundings in addition to that of the ingot whereas during freezing only a small amount of energy is needed to retard th natural process of cooling.

(3) Apart from the more permanent effects indicated in (2) casual irregularity of shape may arise from the contraction of the ingot on each solidification. For example, an ingot frequently solidifies with a smooth continuous skin on its top surface and a cavity may then be formed either in the body of the meta or against the side wall of the crucible. In either state non-uniformity o temperature is likely to be caused on melting.

(4) The conditions at the freezing point permit of greater variation as use may be made of the phenomenon of undercooling. Examples have been given above of the satisfactory results which can be obtained by inducing under cooling. It is not, of course, advocated that the undercool should be habitually employed, but, when used with due caution, it seems to afford a valuable means of check.

For the general reasons given above, the freezing point is to be preferred to the melting point as a means of obtaining the equilibrium temperature. In favour of acceptance of the particular value found for the freezing point of platinum in the present investigation the following special reasons may be urged : the mean values yielded by the experiments on five separate ingots, with considerable variation of assembly, have only ranged through 1·6° C, or 0·9° C if the higher value in Table III is rejected ; no appreciable change in the value of the freezing point has been found with a two-fold variation in

...lerth of freeze, or by undercooling ranging from 0° to 70° C: the prob-...lityof freedom from systematic error is increased by the fact that a similar ...pparatus used for gold gave values for the freezing point agreeing perfectly ...ith those obtained with a different assembly and with a different type of ...eating.

...So far nothing has been said concerning the effect of the uncertainties ...risingin various processes involved in obtaining the absolute value of the ...freezing point. An estimate of the limits of the most obvious of these sources ...of error is given in Table IV.

Table IV—Estimate of Errors

Source of error	Effect at platinum point °C
...hotometric matching at gold, intermediate, and platinum points.....	±0·6
...ransmission of sectors	±0·4
...fective wave-length	±0·4
Maximum error (if all of one sign)	±1·4

...For the transmission of the sectors an uncertainty of 1 part in 1000 has been ...allowed on each and treated as additive. The allowance for effective wave-...length is intended to represent the probable error in the transmission curve for ...the glass. It has been assumed that the visibility curves for two observers ...are identical with that adopted for the average eye by the international agree-...ment already referred to. It is hardly practicable to determine the visibility ...data for each individual engaged in work of this type, but the occurrence of ...any anormality in the present work is rendered unlikely by the facts that the ...ratios* of the two observers were found to be 1·00 and 1·02 respectively, ...and that no discrepancies appeared in their readings when working with or ...without sectors.

...No allowance has been made for possible depression of the freezing points ...owing to impurities in the metals. The specimens of gold used were of the ...highest purity prepared by Messrs. Johnson Matthey & Co., while the resistance ...coefficient of the platinum does not, in the worst specimen, point to impurities ...totalling more than a few parts in 100,000,† the precise effect of which is very ...difficult to assess.

* S. Crittenden and Richtmeyer, ' Bull. Bur. Stand.,' vol. 14, p. 87 (1918). The ratios given here were determined by the Photometry Division, National Physical Laboratory.

† C analyses in paper by Wensel, Roeser, Barbrew, and Caldwell, ' Bur. Stand. J. Res.,' vol. 6, p. 1108 (1931).

On the whole it would seem that the value found for the freezing point may be taken as $1773 \cdot_3^\circ$ C with an uncertainty of the order of $\pm 1^\circ$ C. It is of interest to compare this figure with former values obtained by optical pyrometer methods. For this purpose we reproduce a table of values, Table V, taken from a paper by Roeser, Caldwell, and Wensel,* and have added our own value thereto.

Table V—Determinations of the Melting Point of Platinum with Optical Pyrometer by the Ratio of Brightness Method

Observers	Date	Scale used		Value reported	Value on International Temperature Scale
		C_2	Au point		
			°C	°C	°C
Nernst and Von Wartenburg	1906	1·46	1064	1745	1763
Holborn and Valentiner	1907	1·42	1064	1789	1777
Waidner and Burgess	1907	1·45	1064	1753	1764
Hoffmann	1924	1·430	1063	1771	1769·5
Ribaud and Mohr	1931	1·432	1063	1762	1762
Roeser, Caldwell, and Wensel	1931	1·432	1063	1773·5	1773·5*
Author	1934	1·432	1063	$1773 \cdot_3$	$1773 \cdot_3$*

* Freezing point determinations.

The determination of Roeser, Caldwell, and Wensel at the Bureau of Standards in 1931 was the first made by the ingot or crucible method, which is no doubt greatly superior to those previously employed. It is satisfactory to note that, following this method with variations as described above, the present investigation has yielded a value indistinguishable from that found at the Bureau of Standards.

VI—*Acknowledgments*

Acknowledgments have been made in the course of the paper for assistance received in various ways, but special thanks are due to the Bureau of Standards who kindly presented the Laboratory with a number of crucible assemblies and to Mr. Turner, of the Metallurgy Department, National Physical Laboratory, who was responsible for the making of all the other crucible assemblies used for melting platinum. In addition the author desires to record his personal indebtedness to Mr. C. R. Barber, B.Sc., Assistant in the Physics Department, not only for sharing in the observations throughout, but for his skill in constructing apparatus and for making many valuable suggestions. Mr. A. Grace, Assistant in the Physics Department, also rendered valuable assistance by his suggestions and skill in constructional work.

* ‘ Bur. Stand. J. Res.,’ vol. 6, p. 1121 (1931).

Summary

The freezing point of platinum on the International Temperature Scale has been determined by measuring the ratio of brightness, for a certain wavelength of black-body radiators held at the freezing points of platinum and gold, the latter being the basic point of the scale for all high temperatures. The radiators consisted of hollow enclosures of refractory materials immersed in ingots of the metals which were heated by electro-magnetic induction and also for gold, in an ordinary resister type of furnace. Observations on five ingots of platinum and two of gold yielded a mean value of $1773 \cdot {}_3^\circ$ C $\pm 1^\circ$ C for the freezing point of platinum. This value is indistinguishable from the only previous one obtained by the same method.

Appendix I

Note on the Refractory Articles made for the Investigation into the Freezing Point of Platinum

By D. Turner, B.Sc. (Tech.)

Most of the articles to which reference is made are illustrated in fig. 2 of the paper. They were all made of pure thoria except for the unit, consisting of the tube and bulb, shown in fig. 2 (*d*), which was made of alumina. An account of the methods developed at the Laboratory for the preparation of special refractories, including the two mentioned, has been published by the author of this note elsewhere.* The following additional information may be given with regard to the special articles referred to in the paper.

The thoria used was of the highest quality obtainable and contained only small traces of impurity. Its treatment consisted in a preliminary calcination at a temperature of about 1650° C with the object of reducing the subsequent shrinkage during the firing and use of the article, after which the calcined powder was crushed in a steel end runner mill, for a period determined by its hardness and temperature of firing, so as to obtain a suitable grain size and particle distribution. Accurate grading of the powder was not necessary, but the whole of the material would pass a 120 I.M.M. sieve and a considerable percentage of the powder would pass a 200 mesh sieve. The powdered refrac-

* 'Trans. Faraday Soc.,' vol. 27, p. 112 (1931); 'Trans. Ceramic Soc.,' vol. 33, p. 33 (1933); (with F. Adcock) 'J. Sci. Instr.,' vol. 7, p. 327 (1930).

tory was then treated with hydrochloric acid to remove the iron introduced during the grinding process, after which filtration and thorough washing of the material was essential for maintaining its purity. In the first crucible made (referred to as C.1 in the paper) slight contamination of the platinum charge occurred which was presumably due to inadequate washing, but subsequently no trouble of this kind was experienced.

Both slip casting and moulding processes for making thoria crucibles have been developed at the Laboratory, but in the present work the latter method was employed since only thick walled crucibles were required. The prepared thoria powder was mixed with a quantity of water sufficient to provide cohesion and was then fed in small quantities into a metal mould, each filling being tamped down hard by hand, using a small wooden rod. The moulded crucible, which was sufficiently strong to be removed from the mould and to withstand careful handling, was finally fired at 1650° C. It is understood that these crucibles showed no sign of failure from cracking in spite of the further shrinkage which occurred in their use at temperatures as high as 1900° C.

A similar moulding process was used for making the lids and the large diameter tubes shown in fig. 2 (*b*).

The small bore thoria tubing was prepared by extrusion through the usual type of die, the necessary plasticity being obtained by the addition of cellulose acetate solution to the calcined and powdered material. The volatile constituents of the solution evaporated rapidly as the material left the die and the resulting tube hardened almost immediately. In this condition the tubes were strong and possessed considerable flexibility. They could be closed, cut, joined, or otherwise manipulated with ease, and could be fired immediately.

All the thoria articles, referred to above, if suitably prepared, were strong, hard, and dense after firing at 1650° C.

In articles made from alumina, which was obtained as a very pure calcined powder, no preliminary heat-treatment was required, but similar grinding and acid treatment of the material was carried out, the powdered material being prepared as an aqueous casting "slip." The tube and bulb of fig. 2 (*d*) was slip cast in one piece in a two-part coreless plaster-of-Paris mould. This portion was then fired after which the lid itself was cast around the fired tube and the whole assembly subsequently refired to 1600° C.

The small bore alumina tubing mentioned in the paper was prepared by extrusion and was glazed by surface fusion as described elsewhere.*

* Turner and Adcock, 'J. Sci. Instr.,' vol. 7, p. 327 (1930).

Appendix II

Data for Calculation of Freezing Point of Platinum on International Temperature Scale

Sectors—These had transmissions of 0·03136 and 0·11143 respectively.

Effective Wave-length of Red Glass—This was as follows for the two intervals :

For temperature 25° C, and interval 1270°–1773° C, 0·6585 μ.*

For temperature 15° C, and interval 1063°–1270° C, 0·6588 μ.

Pyrometer Observations—Mean current to match radiator at gold point was 0·19806 amp and $di/dt = 0·00025$ amp/° C.

Mean current to match radiator at platinum point as reduced by the two sectors (see operations 3–5 on p. 794) was 0·19784 amp. This latter current is seen to be equivalent to a temperature of 1062·2° C and by application of the formula in Section II above for the two sectors in succession, a temperature of 1773·3° C is obtained for the mean freezing point. The values of individual freezing points were obtained by difference from the mean value.

* This was obtained from the calculated value 0·6574 μ for 15° C by adding 0·00011 μ per° C. The value of the temperature coefficient of this type of glass was determined by Mr. Buckley ; see also Fairchild, Hoover, and Peters, ' Bur. Stand. J. Res.,' vol. 2, p. 951 (1928), and Forsythe, ' Trans. Faraday Soc.,' vol. 15, p. 21 (1920), for temperature coefficients of similar glasses.