

T H E

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ART. VIII.—*The Nitrogen Thermometer from Zinc to Palladium*; by ARTHUR L. DAY and ROBERT B. SOSMAN; with an Investigation of the Metals, by EUGENE T. ALLEN.

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1. *Introduction and Plan.*

THE measurements of absolute temperature here offered were undertaken in direct continuation of those published from the Geophysical Laboratory two years ago,* with the purpose of extending the gas scale to 1600° , or as near it as might prove practicable. Except in explanations of new or particularly important features, descriptive details have accordingly been omitted here and must be sought in the first paper. Substantially the same methods and apparatus have been employed throughout.

One conclusion in particular which was brought out at that time is entitled to even greater emphasis, namely, that the existing uncertainties in the absolute temperature scale at 1000° and above are the result of experimental limitations and not of any failure of the principles involved. The experimental conditions were scrutinized with great care throughout the first investigation, and not only were the known correction factors all redetermined, but their total magnitude was reduced nearly 75 per cent. This success, after so long and painstaking

* Arthur L. Day and J. K. Clement, this Journal (4), xxvi, 405-463, 1908.

ing a study of the correction factors, led the authors to believe that the upper end of the existing gas scale (melting point of pure copper), which has been vacillating in a somewhat irregular way in various hands for three-quarters of a century, had been finally confined to the limits $\pm 0.5^\circ$, or within 1° . Although this ideal had been affectionately cherished for a good many years, its triumph has been shortlived. The present investigation has discovered a source of error which appears to have passed unnoticed before, which operates to raise the temperature scale at the copper point about 1.4° . This kind of history has repeated itself with remarkable persistence all through the record of high temperature research, and may, of course, do so again, but the limits of uncertainty are continually becoming narrower, and it appears to the authors unlikely that further investigation will again reveal errors aggregating 1° .

On the other hand, the detailed study of temperature distribution about the bulb (page 102) in which the present error was discovered, cannot but convince an experienced observer that the limit of refinement in an electrically heated air bath has been practically attained, and that higher accuracy in gas thermometry must be sought in a liquid bath which can be stirred.

Since the publication of the Reichsanstalt scale* in 1900, it has remained the standard for all temperature measurements between 400° and 1100° . Its limit of accuracy as an absolute scale was estimated to be about 3° at 1000° .

The work of Day and Clement was mainly directed to the following essential features of the problem of absolute measurement with a constant volume gas thermometer: (1) An absolutely gas-tight bulb of definite volume; (2) uniform distribution of temperature over the bulb surface during the measurements; (3) the reduction of the error due to the unheated capillary tube connecting the bulb with the manometer; (4) a more accurate determination of the expansion coefficient of the bulb itself.

The results accomplished by them in these directions may be outlined seriatim as follows: (1) The bulb chosen (90 parts platinum, 10 parts iridium) is quite rugged enough for measurements as high as 1500° , and no difficulty was experienced in maintaining a nitrogen atmosphere in it without loss by diffusion or leakage. At high temperatures the material becomes considerably softer, but with the help of a gas-tight furnace in which nitrogen could be maintained at the same pressure outside the bulb as within, neither diffusion through the bulb walls nor mechanical strain was encountered. Variations in the zero point of the thermometer, which have been

* L. Holborn and A. L. Day, *Ann. d. Phys.* (4), ii, 505, 1900; this *Journal*, (4), x, 171, 1900.

very persistent and inaccessible errors throughout the history of gas thermometry, have therefore now become practically negligible. This gas-tight furnace possessed the further advantage that the initial pressure of the gas, and consequently the sensitiveness of the instrument, could be varied within considerable limits. A sensitiveness as great as 1^{mm} of the manometer scale per degree was regularly employed. The iridium alloy has the disadvantage that platinum thermoelements, which are necessary for recording variations in the temperature over the surface of the bulb, and for transferring the gas thermometer temperatures to standard melting points, become contaminated in the presence of iridium at all temperatures above $900^{\circ}\text{C}.$; the higher the temperature and the longer the time of exposure, the greater the degree of contamination.

(2) It was sought to obtain a uniform temperature over the surface of the bulb by winding the (pure platinum) furnace coil on the inside of a refractory magnesia tube which contained sufficient iron oxide and other impurities to be a fairly good conductor of heat. The winding was somewhat closer at the ends than in the middle. This was further supplemented by secondary coils of smaller wire extending a few centimeters into the tube from each end. The current in the three coils could be independently regulated with the help of thermoelements attached to the bulb and giving its temperature at the middle and upon each shoulder (positions 2, 4, and 6, fig. 1). When these temperatures had been adjusted so that the differences between them were smaller than 0.5° , it was assumed that the temperature over the whole surface of the bulb was constant within those limits. (For the oversight in this assumption, see pages 99 and 102.)

(3) The platinum capillary and connections between the bulb and the manometer were much diminished in volume. Compared with the total volume of the bulb (195.7^{cc}) this connecting volume amounted to $.0015$ in their instrument, and reduced the total correction for the "unheated space" to less than 5° at 1100° , a correction factor not more than one-fourth as large as the best previous attainment in this direction. The uncertainty of the temperature distribution in the "unheated space" was perhaps 10 per cent, making the probable error from this source about 0.50° .

(4) A special bar 25^{cm} in length, made up from the same alloy as the bulb, was provided with a scale and its length measured in a special form of comparator at temperature intervals of 50° up to 1000° . The expansion was found to be $10^{\circ}\beta = 8.84 + 0.00131t$, with an error of about 0.5 per cent. An irregularity was detected both in the expansion and subsequent contraction in the region below 300° , which appeared variable with the rate of cooling or heating, and in character resembled the hysteresis which appears in a bar which has been subjected

to stress. If the bar was cooled down very slowly, it returned nearly to its initial length; if cooled rapidly, it required several days to return to its original dimensions. This irregularity makes up most of the 0.5 per cent uncertainty mentioned above.

Plan.—Above 1100° considerable uncertainty has existed in the temperatures of various fixed points. The melting point of nickel, considered as 1484°,* has been frequently employed. The curve of the platinum-rhodium thermoelement, extrapolated beyond the copper-point, has been still more generally used, but like any extrapolation, may lead to quite erroneous results. The only gas thermometer comparison that has been made in this region is that of Holborn and Valentiner,† but by their own estimate the accuracy of the upper portion of their scale is not greater than $\pm 10^\circ$. The chief purpose of our work was, therefore, to establish the temperature of several fixed points between 1100° and 1600° and to find what curve is followed by the platinum-rhodium thermoelement in this region, with an accuracy comparable to that obtained in the lower portion.

The plan of the work is simple. It consists, first, in selecting certain fixed thermometric points, usually melting points of metals, and in determining their reproducibility; second, in making a measurement of the true temperature on the nitrogen scale at or close by one of these fixed points; third, in transferring this known temperature by means of a thermoelement over to the fixed point in question. This transference by the thermoelement is necessary because the thermometer bulb cannot be put directly into melting or solidifying substances at high temperatures. The relation of electromotive force to temperature for any particular kind of thermoelement does not enter into the problem when the temperatures measured are close to the fixed points; a linear correction is then abundantly accurate. The interpolation curve, for any element, between the fixed points established by the gas thermometer, is therefore a separate matter.

The questions which remain to be answered are, then: (1) How exact and uniform can the temperature of the gas in the bulb be made (independently of any effort to measure this temperature)? (2) How accurately can its pressure be measured in order to establish that temperature on the nitrogen scale? (3) How accurately can this temperature be transferred from the thermometer and compared with the fixed melting point? (4) How accurately can the fixed points be reproduced for purposes of calibration of secondary measuring devices?

As has been stated, our experience has convinced us that the most of the variations in the gas scale temperatures of the

* Holborn and Wien, *Wied. Ann.*, xlvii, 107, 1892; and lvi, 360, 1895.

† *Ann. d. Phys.* (4), xxii, 1, 1907.

fixed points commonly in use, as given by various observers, are due, not to differences in the properties of different gases used, nor to differences in pressure, nor to differences between the constant-volume and constant-pressure scales, all of which have been frequently discussed from the theoretical standpoint; but to systematic errors residing in the apparatus and the methods employed. A large portion of the present work has therefore been devoted to finding out experimentally the effect of variations in all those conditions which might affect the results systematically.

2. *Apparatus.*

In all essential particulars the gas thermometer apparatus is that developed by Day and Clement and already described by them in detail (*loc. cit.*). It consists of four principal parts: (1) bulb, (2) furnace, (3) furnace jacket, and (4) manometer.

(1) *The Bulb.*—A great deal depends upon the material of which the bulb is made. Primarily and obviously, the bulb must be able to hold the expanding gas without absorbing or losing any portion of it throughout the temperature range of the measurements.

A secondary requirement, the importance of which increases rapidly when high accuracy is sought, is that it shall be possible to use several thermoelements in the furnace with the bulb without their readings being endangered by contamination from the bulb material. As long as this intermediary role of the thermoelement remains a necessary one and alloys of platinum continue to provide the only successful bulb material, the contamination* of the platinum wire of the element by the alloyed iridium or other platinum metal in the bulb will remain a serious consideration in all temperature measurement above 900°.

Although the platin-iridium bulb served well as a gas container, the contaminating effect of the iridium upon the thermoelements made the life of the latter, for measurements of such extreme accuracy, very short. Accordingly, at the close of the first series of experiments, a change was made from the platin-iridium bulb to one of platin-rhodium (80 parts platinum, 20 parts rhodium) 160^{mm} long and 47^{mm} in diameter. Inasmuch as one of the wires of the thermoelement itself contains 10 per cent of rhodium to which the platinum wire is always exposed (and which gradually contaminates it, too, although very slowly), it was thought that the substitution of a rhodium alloy in the bulb might serve to retain the necessary qualities of stiffness and regularity of expansion with a minimum of disadvantage in the matter of contamination. These expecta-

*For a detailed account of the behavior and treatment of contaminated thermoelements, see Walter P. White, *Phys. Rev.*, xxiii, 449, 1906.

tions have been completely realized. Although the rhodium alloy is less rigid at temperatures of 1000° and beyond than the iridium alloy, and requires more careful adjustment for equal pressure within and without, no sagging of the bulb walls or deformation from the gas pressure has appeared up to 1550° . Meanwhile, the contamination of the thermoelements in the presence of the rhodium alloy is now reduced in magnitude about 80 per cent for a given temperature and time of exposure.

(2) *The Furnace*.—The common practice of recent observers (Callendar, Harker, Holborn and Day, Jacquerod and Perrot, Day and Clement) has been to use a cylindrical bulb in which the length was three or four times the diameter, enclosed in a concentric furnace tube (air bath) heated by the electrical resistance of a coil of wire wound upon or within it. To this bulb the heat is applied radially over its cylindrical surface, but no heat is supplied at the ends. The furnace tube itself and the winding of the coils have been changed at different times and in a variety of ways in order to vary the distribution of the heat supply. The arrangement used in most of our experiments consisted of one main coil of platinum wire 1.2^{mm} in diameter, wound on the inside of a refractory magnesia tube 36^{cm} long and 2^{cm} thick. As has been our habit for some years, the windings near the ends of the coil are somewhat closer together than those at the middle, but this device is not of itself sufficient* to compensate for differences of temperature along the bulb at all temperatures. In a particular case a favorable arrangement will provide an almost perfect temperature distribution at 500° , but will overcompensate the ends at 1000° sufficiently to spoil the measurements. The conductivity of the bulb metal is wholly inadequate to help out this overcompensation by conveying surplus heat from the ends to the middle of the bulb. On the other hand, a change in the winding which will correct the overcompensation at 1000° provides insufficient compensation at 500° . The arrangement which has become usual with us is therefore to wind the coil somewhat more closely at the ends than in the middle, with the idea of providing partial compensation for the inevitable heat losses at the ends of the furnace in this way, and in addition, to insert supplementary coils of smaller wire in the ends of the furnace tube in order to provide a small, independently regulated heat supply which can be superposed upon that of the main coil and give the desired uniformity at any temperature likely to be employed. A furnace tube arranged in this way, except for accidental variations, caused, for example, by the flaking off of the fur-

* Day and Clement, loc. cit., p. 411.

nace lining, affords uniform temperature distribution over a length of 20^{cm} in the center of the tube for a range of temperature from 300° to 1550°, and no one temperature is more difficult to regulate than another. This arrangement contains a limitation, however, of considerably greater magnitude than was at first suspected. The ends of the bulb face the comparatively cold ends of the furnace tube and radiate a sufficient quantity of heat toward these cold ends to reduce the temperature of the end surfaces of the bulb some 6 or 8° below the mean temperature of the cylindrical surface.

In so far as this may appear to be a rather obvious condition to be overlooked, it may be remarked parenthetically that it is a common practice of physicists to assume that the temperature is constant over a radial cross-section near the center of a cylindrical furnace which is reasonably long in comparison with its diameter. With this in mind, the probability is even greater that a metallic conductor only 4^{cm} in diameter (the end surface of the bulb) perpendicular to the axis in such a furnace will have a uniform temperature between its center and periphery. The fact is that neither of these assumptions is justified, even in furnaces as long as twenty times the diameter. This was shown in a number of actual measurements made under varied conditions, differences of several tenths of a degree being found as low as 300°, and of several degrees at 1000° and higher.

This situation demonstrates the futility of depending upon metallic conductivity (of platinum) to equalize a steep temperature gradient, and again emphasizes the fact, if further emphasis is necessary, that the air bath, or, more explicitly, the temperature distribution within the heating chamber, is the most uncertain factor remaining in gas thermometry.

On account of difficulties in manipulation and accidental leakage into the thermoelement system, we preferred not to introduce additional heating coils into the furnace tube, and accordingly undertook to stop the loss of heat by inserting thin, platinum-covered diaframs opposite the ends of the bulb. The situation was still further safeguarded, in exchanging the platin-iridium for the platin-rhodium bulb by adding a reentrant tube at the lower end of the bulb, to enable us to measure the actual temperature prevailing at its center as well as over the surface. In this way, we thought to obtain a more representative integral of the surface temperature and a competent comparison of this integral with the temperature actually prevailing at the center of the bulb.

(3) *The Furnace Jacket.*—The furnace jacket was water-cooled and could be closed air-tight around the furnace and bulb together, so that the pressure could be maintained the same within and without the bulb to avoid deformation.

(4) *The Manometer*.—The bulb communicated, by a capillary tube leading out through the furnace jacket, with the manometer, which consisted of two glass tubes communicating through a steel reservoir. At the top of the shorter arm, where the capillary joined it, was a fixed reference point to which the mercury was brought for each measurement of the pressure. A detailed description of the manometer will be found in the previous paper.*

3. Details, Errors and Corrections.

The gas thermometer for high temperatures has now reached a stage of development where it becomes necessary to examine many small sources of error. These will be discussed in the succeeding paragraphs without attempting to classify separately the variable errors of observation, and the systematic errors which may arise from conditions of the measurements or from constant corrections.

To bring out the plan of investigation of these errors, it will be well to recall the derivation of the gas thermometer formula. The gas scale, as is well known, is defined by the relation

$$\frac{pv}{1 + \alpha t} = K \quad (1)$$

in which K and α are constants and t is a function of p and v , the pressure and volume of a fixed mass of the gas. K and α are determined by two further conventions:

When $p = p_0$ and $v = v_0$ (at melting point of ice), $t = 0$ (2)

When $p = p_{100}$ and $v = v_{100}$ (at boiling point of water), $t = 100$ (3)

It is then evident that

$$\alpha = \frac{p_{100} \frac{v_{100}}{v_0} - p_0}{100 p_0}$$

which defines α as the mean pressure coefficient of the gas between 0° and 100° (when v_{100} and v_0 are nearly equal); and

$$K = p_0 v_0.$$

The temperature, t , is therefore defined by the formula:

$$t = \frac{p \frac{v}{v_0} - p_0}{\alpha p_0} \quad (4)$$

the scale depending upon the gas chosen, the value of p_0 , and the ratio $\frac{v}{v_0}$. In the theoretical constant-volume thermometer,

* Loc. cit., p. 415, and this article, p. 107.

this ratio $\frac{v}{v_0}$ is unity, but in the experimental constant-volume thermometer it always varies considerably from 1. We have preferred therefore to treat equation (4) as the fundamental equation, introducing in place of $\frac{v}{v_0}$, however, the proper function of the expansion coefficient of the bulb material.

Since apparatus designed for high-temperature work is not suited for the most accurate determination of α , α has been treated in this discussion as a separately determined constant.

In the experimental gas thermometer, there is always a small space in the tube connecting with the manometer which is at various temperatures other than t . The pressure (p' or p_0') actually measured is not therefore the p or p_0 of the formula. Imagine that this supplementary space is heated up to the uniform temperature t , without any change in its volume, and let the resulting corrected pressure be p (or p_0 as the case may be). Furthermore, let

V = volume of bulb at t° .
 V_0 = " " " " 0° .
 v_1 = " " " unheated space" which is at temperatures other than t (or than 0°).
 t_1 = temperature of this space.
 β = linear expansion coefficient of the bulb material.

Under these conditions, formula (4) becomes :

$$\begin{aligned} t &= \frac{1}{p_0 \alpha} \left[p \frac{V + v_1}{V_0 + v_1} - p_0 \right] \\ &= \frac{1}{p_0 \alpha} \left[p \left(1 + \frac{3\beta t}{1 + \frac{v_1}{V_0}} \right) - p_0 \right] \quad * \end{aligned} \quad (5)$$

In this formula $\frac{v_1}{V_0}$ is a very small correction term ; while the important quantities to be measured are p_0 , p , α and β . The ratio $\frac{v_1}{V_0}$ becomes of importance, however, in determining the corrected pressure p from the measured pressure p' . The derivation of this correction is as follows :

The mass of the gas in the unheated volume under the actual conditions of measurement is proportional to $\frac{p'v_1}{1 + \alpha t_1}$;

$$* \quad \frac{V + v_1}{V_0 + v_1} = \frac{\frac{V}{V_0} + \frac{v_1}{V_0}}{1 + \frac{v_1}{V_0}} = \frac{1 + 3\beta t + \frac{v_1}{V_0}}{1 + \frac{v_1}{V_0}} = 1 + \frac{3\beta t}{1 + \frac{v_1}{V_0}}$$

the mass of the gas within the bulb is proportional to $\frac{p'V}{1+at}$.

If we now suppose the unheated space raised to the uniform temperature t without change of volume, the pressure being thereby raised to p , the total mass is proportional to $\frac{p(V+v_1)}{1+at}$.

Therefore,

$$\frac{p'v_1}{1+at_1} + \frac{p'V}{1+at} = \frac{p(V+v_1)}{1+at}$$

whence

$$p-p' = p' \left(\frac{v_1}{V+v_1} \cdot \frac{at-at_1}{1+at_1} \right)$$

This correction is easily calculated and tabulated; or, better, the factor in parenthesis (in the second member of the equation) is plotted against temperature. In practice, the volume v is divided into three portions at temperatures t'_1 , t''_1 , and t'''_1 as explained on p. 109, and the corrections obtained from the curve for each of these portions are simply added together to obtain the total correction $p-p'$. With these corrected pressures, p_0 and p , the temperature t is calculated by formula (5) on page 101.

The discussion of errors and corrections will now be taken up under the general outline sketched on page 96.

A. Temperature of the Gas in the Bulb. (a) *Uniformity.*—Above the temperatures where a liquid or vapor bath can be used to secure uniformity, the differences of temperature between different parts of a furnace has always been a serious limitation to the accuracy of the gas thermometer. This variation, even in a furnace containing well-conducting materials, is much larger than has usually been assumed, and the three equalizing factors of conductivity, radiation, and convection by air-currents, are all credited with much greater influence in bringing about uniformity than they really possess. It sometimes happens that our faith in these factors is inversely proportional to our quantitative information.

To remove this source of uncertainty, Day and Clement introduced two auxiliary heating coils in the furnace, one at each end, and by varying the three independent currents, brought the temperature at the middle and at both ends, on the outside of the bulb, to equality.

In our first measurements with the new bulb, the end elements were placed on the axis of the bulb, in positions 1 and 9 (fig. 1), instead of on the outside surface. It became evident at once that the supporting tube in the bottom of the furnace, used in the work of Day and Clement, had a consid-

erable cooling influence on the central portion of the bottom, an effect which would tend to make their results low. This effect was largely obviated by using, in place of the heavy magnesite tube, a thin Marquardt porcelain tube in the top of which was placed a Marquardt crucible, cut out into a three-pronged support. The bottom of the crucible acted as a screen to prevent radiation from the bottom of the bulb, and the smaller thickness and thermal conductivity of the tube practically prevented the loss of heat from the bottom by conduction. Later, a second diafram was added, about 1^{cm} lower down, primarily

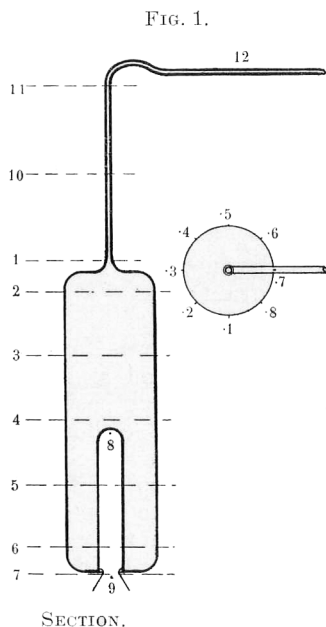


FIG. 1a.

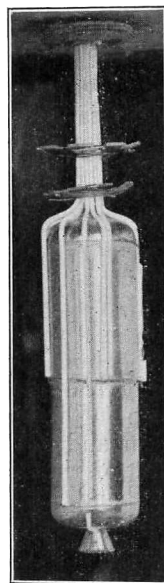


FIG. 1. Numbers indicate the positions of the thermoelements grouped about the bulb.

FIG. 1a. A photograph of the bulb made after the palladium-point determination showing all the elements and the diaframs in position.

for the purpose of centering the tube and bulb in the furnace, but without noticeable effect on the temperature distribution.

In addition to the three thermoelements mentioned, a fourth was located inside the reentrant, in position 8.* Several trials under varied conditions confirmed the fact that this element, when the other three were set equal, was 2° to 3° hotter than the one on the outside. A thorough exploration of the dis-

* See fig. 1, and note, p. 104.

tribution of temperature over the surface of the bulb was therefore undertaken.

Since the number of wires which could be led out through the packed joints was limited, the plan was adopted of using the bulb itself as a differential thermoelement, single platinum wires being tied to the bulb at points whose temperature was to be determined. Each of these wires formed, with the platinum of the standard element tied to the bulb at the middle, a differential element which would read zero if the wires were alike and if no difference of temperature existed between the two points on the bulb.

The relation of the wires was established by sealing each in turn to the platinum of the standard, and measuring their E.M.F. at various temperatures. The readings varied, according to the quality of the wire, from 0 to 40 microvolts. The method of evaluating differences of temperature, when such existed, is discussed on page 118.

The distribution of temperature lengthwise of the bulb was first investigated, and auxiliary wires were placed at the levels 1 (base of stem), 2 (top shoulder), 6 (bottom shoulder), 7 (bottom, outside of funnel), in addition to thermoelements at 4 (middle outside), 8 (inside reentrant), and 9 (bottom, just inside of funnel).*

With this system of thermoelements, it was found that at 1082°, when 9 was brought to equality with 4 and 1, the bottom of the bulb was superheated 6 to 8° at position 6, and about 4° at 7, due entirely to the fact that the thermoelement at 9, not being in contact with the bulb, lost sufficient heat by conduction and radiation downward to keep its temperature below that of the metal surrounding it. The element at 8, on the other hand, received heat by conduction up the reentrant tube and by radiation from below, which made it read higher than the element at the same level outside. The element at position 9 was therefore discarded and each setting of temperature made with reference only to the elements which were attached directly to the bulb.

The temperature between the middle and the top shoulder was also examined in several experiments. The temperature at this position was found to be within 0.5° of the other two, with a tendency to be lower than these.

Further experiments showed that in addition to the possibility of vertical variation of temperature, there was a varia-

* The system of numbering the positions of elements on the bulb is shown in fig. 1. The figure before the decimal point indicates the horizontal level, the figure after the decimal indicates the orientation around the bulb. For instance, an element in position 3.5 would be about half way between the top and middle and on the side of the bulb away from the front of the apparatus.

tion around the circumference of the bulb. This amounted in the worst case (at 1450°) to a variation of 1.3° from the mean, four elements being used around the circumference to make the test. This variation seemed to be due either to unequal conductivity of the furnace material at different points or to the falling off of small portions of the furnace lining, leaving exposed places on the wire. Variations of this character are probably an unavoidable result of using a furnace where the heat supply is so near to the point where it

FIG. 2.

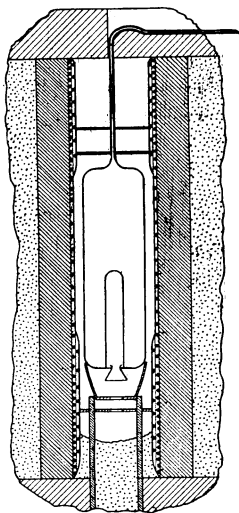


FIG. 3.

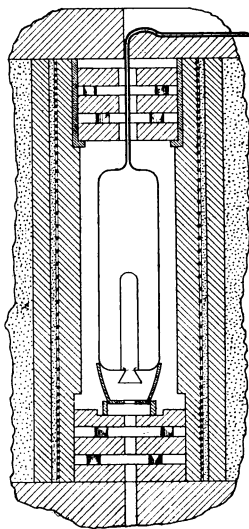


FIG. 2. Section of furnace and bulb showing the arrangement of coils and diaframs about the bulb which gave the most uniform temperature distribution in the measurement of both high and low temperatures. The supplementary end coils were independently heated and regulated.

FIG. 3. A special arrangement of the heating coil and diaframs designed to give a very uniform temperature distribution about the bulb. The coil was heavily ballasted inward with a good heat conductor and outward with a poor conductor. The heating coil was also divided into three sections which could be independently regulated. This furnace was used at the copper point only.

is measured, as is the case with the furnace which is wound on the inside. This form of winding is necessary, however, in order to reach the highest temperatures, so that absolute uniformity of temperature around the bulb had to be sacrificed to increased range of the instrument.

After this variation was discovered, measurements were always made with four elements at equal distances around the

circumference of the bulb and the mean of their readings was taken.

In order to be perfectly certain that no systematic error was being introduced by using this one form of furnace (fig. 2.) throughout, it was replaced temporarily by a furnace of platinum wire wound on the *outside* of a similar tube. In this way a heavy mass of good heat-conducting material was introduced between the source of heat and the bulb, with the expectation that a more uniform temperature might thereby be obtained in the inside space. The two types of furnace are shown in figs. 2 and 3.

A measurement at the copper point with the outside-wound furnace gave as the melting point of copper 1082.6° , which differs only 0.4° from 1082.2° , the mean of the results obtained at the same pressure with the other furnace, and is identical with the final mean of all the results, thus proving that no systematic error was to be feared from the inside-wound type of furnace. The horizontal uniformity obtained in the outside-wound furnace was better than that in the inside-wound, but the furnace was more difficult to regulate and to hold at a given temperature.

(b) *Constancy of Conditions.*—Several causes interfered with the establishment of a constant temperature for observation. The three heating currents required constant observation and readjustment with the gradual extension of the heated zone toward the outside of the furnace. This comes to equilibrium for a particular temperature after about half an hour, after which the bulb was held steady 15–30 minutes longer before readings of the pressure were taken. The temperature thus established could be relied upon to remain constant to within 1 to 3 microvolts (0.1° to 0.3°) during the course of the pressure measurements.

Above 1100° a noticeable leakage of current from the heating coil into the bulb and thermoelements frequently appeared. This may have been due in part to conductivity across the narrow air space between bulb and coil, but was probably chiefly due to accidental contact between the protecting tube of one of the thermoelements and the furnace wall. To obviate any uncertainty from this cause, it was found necessary to use alternating current for all temperatures above 1100° . This was less easy to regulate than the direct current from storage batteries, but by careful regulation of the voltage of the motor generator supplying the alternating current, equally satisfactory results were obtained.

The constancy and exactness of the temperature at 0° were beyond question. On several occasions pressure measurements at 0° were made at intervals of one-half to one hour and no

measurable difference found. Similarly, repacking the bulb in a fresh supply of ice gave exactly the same value.

B. Definition of Temperature by Measurements of Pressure.—The procedure in measuring the pressure, p' , was as follows: First the three mercury thermometers on the manometer were read to determine the temperature of the mercury column and scale; then three to four settings of the barometer were made, alternating with measurements of the manometer. The mercury thermometers were read again at the close. During this interval the other observer made as many readings as possible of all the thermoelements.

Before the manometer was connected to the bulb, the point on the scale corresponding to the reference point of the manometer* was determined once for all before the manometer was connected to the bulb, by connecting the two arms and raising the mercury to the point, as in a regular pressure measurement. Subsequent manometer readings were subtracted from this fixed level, and the resulting difference corrected for the temperature and calibration corrections of the scale and then reduced to 0° . The barometer reading was similarly corrected. The algebraic sum of the two gave the pressure p' , in terms of a centimeter of mercury at 0° and at the latitude and elevation of the laboratory. Since the absolute value of the pressure does not enter into the gas thermometer formula, corrections for altitude and latitude are superfluous.

Errors and Corrections in p' .—The level of the fixed reference point of the manometer varies with the temperature of the room because of the difference in expansion of the brass scale on the one hand and of the glass tube of the manometer which carries the fixed point on the other. This correction can be calculated from the expansion coefficients of the materials and amounts to 0.04^{mm} per 5° . Its direction and amount were checked experimentally by determining the fixed point at two temperatures differing by about 10° , the room being open on a cold day for the one case, and then closed and heated for the other. The difference found was 0.09^{mm} , and that calculated 0.08^{mm} .

The lengths of the divisions of the brass scale were corrected for change of temperature by a formula determined for this scale at the Normal-Aichungs-Kommission, the absolute length of the scale having been determined at 16° . In addition, calibration corrections, determined for each millimeter of the scale, were applied. The total scale correction was always less than 0.15^{mm} , hence the temperature measurement by the adjacent mercury thermometers was abundantly accurate for this purpose.

* p. 100.

The length of the mercury column was reduced to 0° by the expansion coefficient given in the Landolt-Börnstein-Meyerhoffer Tabellen. This correction varied from 0 to about 3.00^{mm} . As the mercury thermometers were calibrated and read to 0.1° , the uncertainty in this correction due to uncertainty in the room temperature may amount to 0.05^{mm} . For the calibration the mercury thermometers were compared with a Richter standard thermometer calibrated at the Reichsanstalt.

The barometer reading was corrected to 0° by the Landolt-Börnstein-Meyerhoffer table for barometer with brass scale. Two Fuess barometers were used. Both had been tested by the Bureau of Standards; one had an absolute correction of 0.06^{mm} , the other was exact. This was checked by direct comparison of the two. The variable error in the barometer is probably about the same as in the manometer reading (0.05^{mm}). On a very windy day or during the approach of a storm, the barometer was too unsteady to permit satisfactory measurements to be made.

A further small correction to the barometer was necessary to allow for the weight of the air column between the cup of the barometer and the top of the mercury in the open manometer column. This correction was appreciable, amounting to 0.16^{mm} in the extreme case.

To give some idea of the effect of these small corrections upon the final temperature measurement, it may be added that 1.00^{mm} corresponds approximately to 1° .

To determine the corrected pressure, p , from the measured pressure, p' (see page 101), the volume of the unheated space, v_1 , connecting the bulb with the manometer, must be known.*

TABLE I. — *Unheated Space.*

Space	Volume, c.c.		Uncertainty		Max. effect at Cu. pt. of errors
	Before Apr. '09	After Apr. '09	of vol.	of temp.	
Pt-Rh capillary, bulb to top furnace (v_1')	0.055	0.055	0.002	100°	0.04°
Pt-Rh capillary, top to outside furnace (v_1'')	0.086	0.086	0.003	50°	0.20°
Pt-Rh capillary to gold capillary	0.102	0.054	0.015	0.5°	0.20°
Gold capillary	0.094	0.066			
Pt capillary and Ni valve	0.025	0.025			
Space above meniscus	0.023	0.023			
Total	0.385	0.309			0.45°

* See discussion of this correction, Day and Clement, loc. cit., p. 410.

This was calculated from the dimensions of the capillary. The figures are given in Table I. This volume was reduced in April, 1909, by bringing the manometer closer to the furnace, since the water jacket of the furnace cut off the heat so completely that there was no risk in bringing the manometer as close as possible (35^{cm}). The volume v_1 was thereby reduced from 0.39^{cc} to 0.31^{cc}, and the ratio $\frac{v_1}{V_0}$ from 0.00187 to 0.00150.

The volume, V , which enters into the correction term (see page 102) was determined by weighing the bulb empty, and filled with distilled water at a known temperature. A very accurate determination of this volume was not necessary, the important requirement being that the volume should not change during a run. A check on change of volume was obtained in the measurement of the value of p_0 . The volume of the bulb at 0°, up to the base of the capillary stem, was found to be :

On 13 June, 1908 (new) - - - - -	205.74 ^{cc}
On 18 " " (after 1450°) - - - - -	205.75 ^{cc}
On 20 Apr., 1909 - - - - -	205.82 ^{cc}

The volume of the unheated space, v_1 , was arbitrarily divided into three portions for the convenient determination of its average temperature, t_1 . The first portion, v_1' , extended from the base of the stem to the top of the upper brick of the furnace (see fig. 2); the second portion, v_1'' , included the capillary stem as far as the outside of the furnace; the third portion, v_1''' , extended to the surface of the mercury in the manometer and included all of that portion of the unheated space which remained at room temperature.

The temperatures of the portions v_1' and v_1'' were determined by placing a thermoelement at different points along the stem during several of the runs. As this temperature does not need to be known accurately, a few measurements gave a sufficient indication of the distribution of temperature in the portion of the "unheated space" within the furnace.

A liberal estimate of the degree of uncertainty in the values of v_1 and t_1 has been made and is included in Table I, together with the effect which such errors would have on the calculated temperature, t , at the copper point.

Errors and Corrections in p_0' .—The same instrumental corrections apply to p_0' as to p' , but their proportional magnitude is, of course, larger. The values of the uncertainty in t due to these small errors will be found in Table IV.

Changes in the value of p_0 (the ice point) after heating to high temperatures have always been disturbing factors in gas thermometer measurements and have introduced uncertainties of a very intangible kind. This was especially true of the

porcelain bulbs formerly used, where both changes of volume and emission or absorption of gases by the walls occurred. The restoration of the platinum metals to favor as materials for the gas thermometer bulb has practically eliminated this uncertainty. During the present work small changes in the value of p_0 have frequently occurred after heating to a high temperature, which seem not to be due to any change in volume, for the determinations of the volume, V_0 , given above (p. 109), show a total change after a year's work corresponding to less than 0.1^{mm} in p_0 . In the early part of the work, the passage through the bulb wall of hydrogen or some other gas produced by the reducing action of wood fiber in an asbestos board insulator within the furnace, was suspected as being the cause of irregularity, particularly in view of the fact that Holborn and Valentiner had difficulties from this cause. Further, it was several times observed that heating the furnace and bulb to a higher temperature than they had reached before, caused a slight increase in the value of p_0 ,—whether due to some gas passing in from the outside, or coming out of the wall of the bulb, is not known. Air dried over calcium chloride was used outside of the bulb in the furnace enclosure throughout the work, and no indication was ever obtained of the passage of either oxygen or nitrogen through the wall of the bulb, since measurements at a given temperature (after the first heating to that temperature) gave the same value of p_0 within the error of measurement.

On one occasion an almost inappreciable leak in the manometer connection caused some uncertainty. All measurements affected by this error, when it was discovered, were rejected.

α .—Since the gas thermometer apparatus as arranged for high temperature measurements is not suited to a determination of the value of α (the pressure coefficient of the gas from 0 to 100°) with an accuracy comparable to that attained by Chappuis,* the value of α was treated as a constant. The figures used were:

$$\text{For } p_0 = 345 - 347^{\text{mm}}, \alpha = 3665.8 \times 10^{-6}$$

$$\text{For } p_0 = 217 - 221^{\text{mm}}, \alpha = 3664.0 \times 10^{-6}$$

A number of independent determinations of α for different pressures were made by Day and Clement† with the platinum-iridium bulb, but they show no appreciable difference from those by Chappuis within the experimental error of the apparatus. The probable error in Chappuis' results is not great enough to affect the high temperature values.

* Trav. Mem. Bur. Int., vi and xii, 1888 and 1902.

† Day and Clement, loc. cit., p. 442.

Pure nitrogen was used throughout as the thermometric gas.* The storage tank was refilled several times so that not all the gas was from the same original supply; the filling of the bulb was also changed several times. The bulb was first completely evacuated and heated to a high temperature, after which the connections and bulb were rinsed out several times with the purified gas before the final filling.

Expansion Coefficient of the Bulb. (β).—The substitution of a new alloy in place of the platin-iridium made necessary a new determination of the expansion coefficient of the bulb material. The method of its determination and the comparator used for the purpose were fully described in the earlier article† and do not require to be repeated here.

Three additional precautions were taken in carrying out the measurements: The bar was increased in length to 0.5 meter, and in diameter to 6^{mm}, in order to increase the sensitiveness of the determination and the uniformity of temperature along the bar respectively. In this case the bar was also made at the same time and from the same alloy as the bulb itself, and was therefore identical with it in composition.‡

In ruling the bar, the lines were spaced 0.2^{mm} apart instead of 0.5^{mm}, as in the previous investigation. This enabled a greater number of observations to be made within a narrow region than heretofore, and has thus made it possible for us to avoid the error from parallax described in the previous paper.§

The third precaution involved a slight change in the comparator itself, and was made at the suggestion of Chappuis. Our custom had been to verify the distance between the fixed hairs of the microscopes before and after each heating by measuring this distance in terms of a standard brass bar calibrated at the Bureau of Standards. The brass bar was then replaced by the platin-iridium bar before the heating began, and the length of the latter was measured in terms of the initial distance between the fixed hairs, at intervals of 50° or

* It was prepared by dropping a solution of 200 grams of sodium nitrite dissolved in 250 grams of water, into a warm solution containing 350 grams of ammonium sulphate and 200 of potassium chromate in 600 of water. It was passed through a mixture of potassium bichromate and sulphuric acid and stored over water. For use in the gas thermometer it was purified by passing through calcium chloride, hot copper gauze, potassium bichromate in sulphuric acid, 2 bottles potassium pyrogallate solution, sulphuric acid, calcium chloride and phosphorous pentoxide.

† Day and Clement, loc. cit., p. 425.

‡ The new bulb, as well as the bar, were made with the utmost care by Dr. Heraeus, of Hanau, Germany, for this investigation. We have had repeated occasion in the past to make public expression of our indebtedness to Dr. Heraeus for his interest and assistance in this work, and it is a pleasure to repeat this acknowledgment here.

§ Day and Clement, loc. cit., p. 435.

100° up to 1000°. This mode of procedure involved the assumption that the agreement of the measurements made before and after heating afforded adequate proof that no change had taken place *during* heating. The justification for this assumption lay in the fact that, (1) the furnace was completely water-jacketed to prevent any heat reaching the microscopes from the furnace; (2) suitable insulating material introduced between the observer and the microscopes cut off any disturbing influence from the near approach of the observer's body; (3) the microscopes themselves, and the carriages upon which they were mounted, were connected by carefully selected invar bars

FIG. 4.

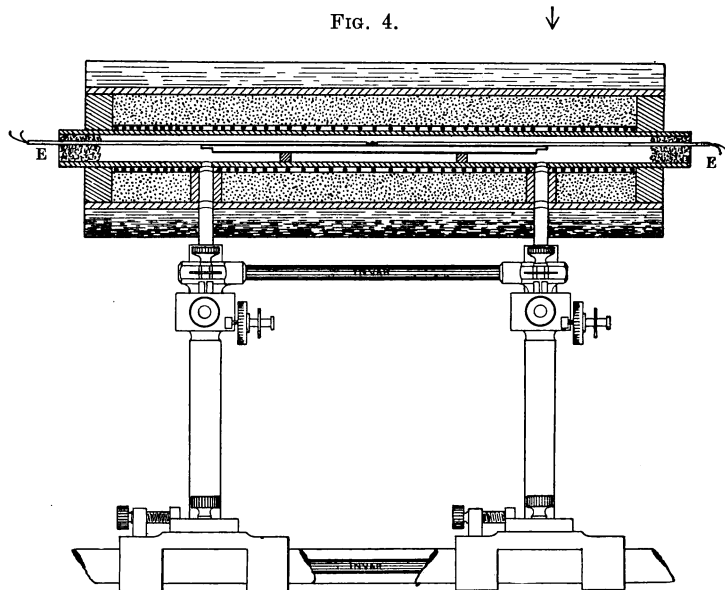


FIG. 4. Section through furnace showing bar, thermoelements (E, E) and microscopes in position. A section through the arrow is shown in fig. 5.

of negligible expansion coefficient, and, finally, (4) the faithful agreement of all the measurements before and after the many heatings left no reason for suspecting a variation.

Notwithstanding these conditions, it appeared to Chappuis that some positive proof should be offered that the distance between the cross-hairs remained unchanged while the heating was going on, inasmuch as all the measurements were made in terms of this distance. Accordingly, at his suggestion, it was arranged to retain a standard unheated bar in the field of the microscopes throughout the readings, so that the distance between the cross-hairs would be subject to check at any time

during the observations. The arrangement made for the purpose is very simple and effective, as can be seen from the neighboring diagrams (figs. 4 and 5). The last two series of measurements were made with this appliance, and the fixed distance was found to remain constant throughout the series to within 0.003^{mm} , although on first setting up the apparatus a gradual adjustment of strain, amounting to 0.012^{mm} , took place during the first two days.

The determination of β is subject to two errors; the first is uncertainty of temperature, the second occurs in the measure-

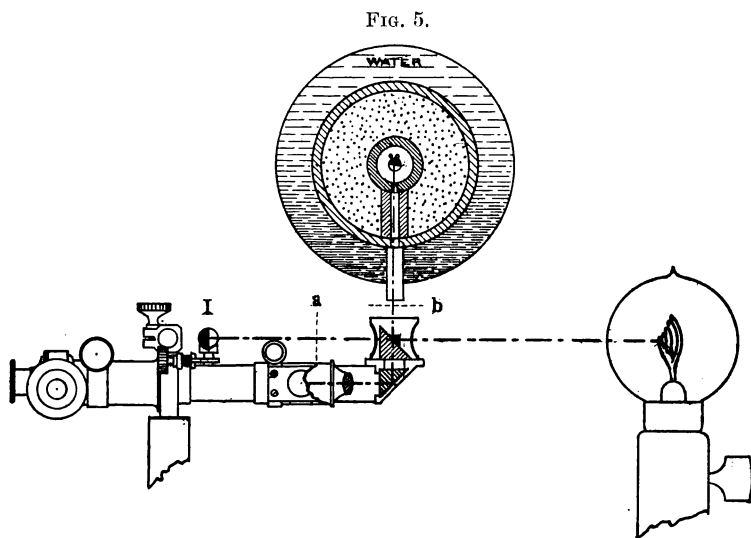


FIG. 5. A section through the furnace at one of the openings, showing the method of illumination of the heated bar and the standard cold bar (I) together with an arrangement for checking the distance apart of the cross hairs at each temperature. With a screen inserted at *a* only the hot bar is visible; with the screen at *b* only the cold bar.

ment of the change in length. It was impossible to wind the furnace (70^{cm} long and 2^{cm} inside diameter, with two side openings) so as to give a perfectly uniform temperature along the bar; but as the furnace winding and consequent distribution of temperature were varied considerably for each run, the uncertainty from this cause was eliminated in the average of all the observations. The error in the temperature measurement itself was probably not over 2° , which would give an error of less than 0.2 per cent at the highest temperature. Two thermoelements with a common junction were used, one entering from each end of the furnace. This not only gave a second temperature reading in confirmation of the first, but

a positive check upon the appearance of contamination in the thermoelements.*

With a half meter bar and a temperature interval extending from zero to 1400° , the total expansion amounts to about 7.8^{mm} . The micrometers reading the expansion were read with an accuracy of 0.002^{mm} .

There was some indication of a very small hysteresis in the expansion and contraction. Although the amount was not much greater than the experimental error, the measurements indicate that the bar was slightly shorter after heating than before, and that it gradually regained its original length.

The measurements at room temperature are given in Table II. The five measurements in this table which were made

TABLE II.—*Length of Platinum-Rhodium Bar.*

Date	Max. preceding temperature	Length at 0°	Date	Max. preceding temperature.	Length at 0°
1 July 1908	(New)	500.068	26 Sept. 1908	1150°	500.094
6 " "	900°	500.110*	1 Oct. "	25°	500.119
9 " "	28°	500.105	6 " "	1300°	500.034†
13 " "	900°	500.098*	27 " "	900°	500.108*
17 Sept. "	900°	500.108*	30 " "	1400°	500.096
19 " "	1200°	500.090	6 " 1909	28°	500.103
20 " "	23°	500.105	12 " "	22°	500.108*
22 " "	1200°	500.087	13 " "	1000°	500.109
24 " "	24°	500.096	15 " "	1400°	500.074†

* After interval of 4-7 days.

† Bent, after heating beyond last temperature at which measurements were made.

within a few hours after the bar had cooled from a high temperature, excluding the two where the bar was bent, average 500.095; while the ten measurements (excluding the first) which were made two days or more after heating, average 500.106. The difference is only 0.002 per cent of the total length, or 0.12 per cent of the total expansion to 1500° , or about 0.7 per cent of the expansion to 300° . This effect is, therefore, probably responsible for the observed irregularities between 0° and 300° , at which temperature most of the measurements were begun.†

C. *Transference of Temperature by the Thermoelement.*—The electromotive forces of the elements attached to the bulb were measured by a Wolff potentiometer. The standard of

* Day and Clement, loc. cit., p. 419.

† Kammerlingh-Onnes (Konink. Ak. Wet. Amsterdam, Proc., x, 342, 1907) has found the same effect after cooling platinum to very low temperatures.

electromotive force used was the true volt, in terms of which the E.M.F. of the Clark cell is 1.4328 at 15°, and of the saturated cadmium cell used, 1.01918 volts at 25°.

Several small corrections are necessary in order to obtain the true E.M.F. of the thermoelement. The calibration corrections of the potentiometer (Reichsanstalt calibration) were all negligible except that for the fixed resistance to which the standard cell was attached. This correction amounted to 1.3 microvolts in 10,000. The correction for the change of resistance with temperature of the potentiometer was also negligible. The E.M.F. of the standard cell varies with the temperature; hence the temperature of the cell was read at each measurement and a small correction applied. The readings were correct at 21.5°. For a variation of 5° from this temperature the correction was 2.2 microvolts in 10,000 microvolts. The resistance of the contacts of the potentiometer, and the small E.M.F.'s existing at contact points in the circuit of the thermoelement, introduced another small error which was determined by placing the thermoelement in ice and reading the E.M.F. This correction varied for the different elements from -1 to +4 microvolts.

As a check upon the absolute value, a Weston standard cadmium cell (calibration by the Bureau of Standards) whose E.M.F. was read directly on the potentiometer, was compared with the saturated cell each day. The agreement of the corrected values was usually within 0.5 microvolt. As in the case of the pressure measurement, the absolute value of the E.M.F. is not of importance, since it is used only for transference from the fixed points to the gas thermometer; the above corrections were applied, however, to reduce the readings to a common standard.

The effect of contamination of the thermoelement wires in furnace readings was much greater than the above mentioned errors.* Up to 1100° the contamination was not serious, but above that temperature the wires take up iridium together with some rhodium. It was hoped that the replacement of iridium in the bulb by rhodium, which is very much less volatile, would do away with this error, but there appeared still to be a very small percentage of iridium in the furnace wire, enough to affect the thermoelement wires appreciably, even though this furnace wire had been especially purified for this purpose.

Although the task became much longer and more laborious, it was thought wise to make an effort to avoid the error from contamination, even of this diminished magnitude, rather than to attempt to compromise with it by any scheme of approxi-

* For a more thorough discussion of this effect, see Day and Clement, *loc. cit.*, p. 419; and W. P. White, *Phys. Rev.*, xxiii, 449, 1906.

mate evaluation. Accordingly, after every exposure of sufficient length to endanger the thermoelectric readings, all the thermoelements were removed from the furnace and their wires tested for homogeneity. Where contamination was found, the contaminated portion of the wire was at once cut off. This is the only absolutely safe method of avoiding errors from this cause, for it amounts to the use of new thermoelements exclusively in all the determinations of temperature distribution within the furnace as well as for establishing the absolute temperature of the metal melting points.

A very simple method of testing the wires for contamination has been developed which consists in connecting the junction end of the wire to be tested, together with an uncontaminated wire, to the potentiometer and moving the free end of the standard wire along the wire to be tested, while heating the contact point of the two with a blast lamp.* The variation of the E.M.F. produced at this junction indicates the degree of contamination of the wire; in the uncontaminated portion this E.M.F. is small and constant within 3 mv. The temperature obtained by the blast lamp flame is sufficiently constant for the purpose and lies between 1460° and 1500°.

The wires could be relied upon to give a constant E.M.F. within 2 mv. at 1000° over a length of at least 50^{cm}, so that redeterminations of the fixed points were not necessary after cutting off each small portion of contaminated wire. Each test for contamination was continued over the 50^{cm} of wire adjacent to the hot junction and so served as a test for the homogeneity of the new wire which replaced the portion cut off. In two cases a sudden change of E.M.F. along the unused wire amounting to about 10 mv. showed the probable presence of a junction point in the original sample from which the wire was drawn. Such a junction point was of course not introduced into the heated portion of the furnace.

In this connection, it should be pointed out that the relative weight to be given to the element inside the bulb, as compared with the outside elements, is greater at temperatures above 1100° than at temperatures below, for two reasons: (1) The temperature at the middle of the bulb is not so much influenced above 1100° by the temperature of the lower part of the furnace, as it is below 1100°; (2) the outside elements are much more subject to contamination than the inside element by reason of the protection afforded by the intervening bulb walls against contaminating material from the heating coils. This is well shown by the data in Table VIII on the melting points of diopside, nickel and cobalt. In the first measurements of these temperatures, the elements were left on the bulb through

* W. P. White, loc. cit.

several runs, in consequence of which the temperatures derived by the outside elements steadily increase through the series (i. e., the readings of the outside elements on the bulb steadily decreased), whereas the temperatures derived from the inside element are fairly constant. Its contamination was found to be less in amount and distributed over a region of more constant temperature.

For insulating the thermoelement wires from the bulb and furnace, capillary tubes, both of Marquardt porcelain and of silica glass, were employed. The Marquardt tubes are open to the objection that they are very porous and offer little protection against contamination. The silica glass capillaries protected the wires very much better, but at 1100° and above they devitrified rapidly and at the end of a measurement at 1400° or over fell from the wires in small fragments, so that the wires had to be taken off and reinsulated after a single run.

For the convenience of others who may confront similar problems, it may be added that such extreme precautions as cutting off the elements at the first sign of contamination are excessive for most purposes. The region of highest temperature, and therefore of most rapid contamination in a good furnace, is also a region of constant temperature. Contamination would therefore produce little effect upon the reading of the thermoelement until it had crept out into the colder parts of the furnace, which it will do slowly during long exposures. The distribution of the contamination in an aggravated case is shown in the accompanying table, which is arranged in such a way that not only the magnitude of the contamination but also its distribution with respect to the bulb is roughly shown. The electromotive forces are determined, as has been explained, by bringing successive points of the contaminated

		Before Heating. Microvolts	After Heating. Microvolts
	40 ^{cm}	—4	—4
	35	—6	—8
Outside of furnace	30	—8	—7
	25	—9	—6
Bend of stem	20	—6	—10
	15	—5	—3
	12	—5	+2
	10	—5	+9
Shoulder of bulb	8	—5	+83
	6	—5	+83
	4	—6	+41
	2	—6	+55
Middle of bulb	0	—8	----

wire into contact with an uncontaminated one in a blast flame (temperature, 1460–1500°), the cold junction being maintained constant at 0°. The absolute magnitude of the numbers in the column “before heating” represents the electromotive force between two uncontaminated platinum wires of (nominally) equal purity. Its constant value is a measure of the homogeneity of the new wire. Its departure from this constant value “after heating” is a measure of the contamination it has received. Slight irregularities are the result of variations in the blast flame temperature. Such observations merely serve to furnish information about the distribution and approximate amount of contamination received by the element, but do not of themselves provide the data to correct its reading in a particular furnace.

Integration of Temperatures over the Bulb.—By the method which has been already described (p. 104) the differences of temperature between the ends of the bulb and the middle were determined differentially by means of platinum wires attached to the bulb itself. Temperatures about the circumference were measured by separate thermoelements, as it was not practicable to measure these differences differentially because of the necessity of passing a platinum binding wire around the bulb to hold the four elements in position. A check on the accuracy of this differential method was obtained by using in one case a thermoelement at the top shoulder of the bulb and thus measuring the temperature at this point both directly and differentially by means of the platinum wire of this element. The two temperatures agreed within 0.8° when the deviation from the middle was 6°; when the temperatures at the middle and top were nearly equal, the two methods agreed to 0.1°.

Table III contains values of $\frac{\Delta E}{\Delta t}$, the rate of change of E.M.F. with temperature at various temperatures from 400° to 1500°, both for the 10 per cent rhodium alloy and for the 20 per cent

TABLE III.—Values of $\frac{\Delta E}{\Delta t}$ for the alloys 90 Pt. 10 Rh. and 80 Pt. 20 Rh.

Temp.	90 Pt. 10 Rh.	80 Pt. 20 Rh.
400°	9.4	11.5
600°	10.1	12.8
800°	10.8	14.2
1000°	11.4	15.6
1200°	11.8	16.9
1400°	12.2	17.5
1500°	12.4	17.8

alloy of which the bulb was made. The data for the 20 per cent alloy (which need be only approximate) were obtained by two methods: (1) An element was made up by combining a platinum wire with the 20 per cent rhodium bar used for the expansion coefficient determination, and its readings compared directly with those of a 10 per cent rhodium element in the melting point furnace. (2) A platinum wire was connected from the stem of the gas thermometer bulb outside of the gas thermometer furnace to the ice box, and the E.M.F. determined against the standard platinum wire attached to the middle of the bulb. In both cases, the E.M.F. of the junction of platinum with the rhodium alloy at room temperature was applied as a correction.

In order to obtain the true E.M.F. corresponding to the temperature as measured by the pressure of the gas in the bulb, it is necessary to integrate the various readings over the surface of the bulb. The following arbitrary weights were given to the different positions of elements on the surface:

Top axis	(position 1)	5
Top shoulder	(" 2)	20
Middle	(" 4)	55
Bottom shoulder	(" 6)	15
Bottom axis	(" 7)	5

The elements on the axis at both top and bottom, although sometimes deviating rather widely from the others, have comparatively small weight, as they affect only a small portion of the total volume. The element at the lower shoulder of the bulb is given less weight than that at the top because of the smaller volume of the lower half, due to the presence of the reëtrant tube.

It was easy to show experimentally that it matters very little what these relative weights assigned to the different readings may be, since the total correction was usually small. In a number of cases, two different settings of the temperature distribution were made at each temperature, one in which the elements at the top and bottom shoulders of the bulb were made equal to the middle, and one in which the elements at top and bottom on the axis of the cylinder were made equal to the middle. The pressures corresponding to these two settings, reduced to the same reading of the standard element, are shown for several typical cases in the table below.

Date	Temp.	Pressure when 1, 4, and 7 were equal	Pressure when 2, 4, and 6 were equal
22 Jan. 1909	1082°	1038.82 ^{mm}	1038.64 ^{mm}
2 July 1909	1395°	1285.43	1285.17
17 Sept. 1909	1489°	1331.40	1330.63

It is evident that even without any correction for the different distribution in the two cases, the readings agreed within $0.2\text{--}0.8^{\text{mm}}$, or about $0.2\text{--}0.9^{\circ}$, so that the variation between any two arbitrary sets of weights which might be given to the different readings must lie well within this limit.

The Transfer to the Fixed Points.—After the thermoelements are removed from the bulb, their E.M.F. at the fixed points must be determined by immersing them in melting or freezing metals or salts. The instrumental corrections to the readings so obtained were the same as in the case of the gas thermometer readings. The error due to contamination was also present above 1100° , just as in the gas thermometer furnace, and was a very disturbing factor in determining the melting points of nickel, cobalt and palladium. Its source, however, was not usually iridium vapor from the furnace or rhodium from the wire of the element, but was either vapor of the melting metal itself, or (when a hydrogen atmosphere was used) the products of reduction of silica. In the presence of hydrogen, silica rapidly deteriorates platinum wire by reduction and alloying, as has been shown in this laboratory by Shepherd,* and elsewhere by several observers. The contamination can be partly prevented by the use of a glazed porcelain tube surrounding the thermoelement, instead of an unglazed magnesia tube; but an additional uncertainty is thereby introduced through the contamination of the melting metal by the melted glaze on the porcelain. For this reason nickel and cobalt did not prove to be as satisfactory fixed points as had been hoped, since it was necessary to melt them in an atmosphere of hydrogen. Palladium, however, can be melted in the open air and serious contamination by silicon thus be avoided, although the palladium itself gradually contaminates the wire.

Above 1100° it is better to make direct comparisons of all the elements with one or two whose fixed points have been determined, rather than to contaminate them all by a direct determination. For making these comparisons, the plan first used was to bring a crucible of molten silver to a constant temperature and insert the elements (protected by a glazed Marquardt porcelain tube) successively into the silver bath. There is an uncertainty, however, in these measurements of 2 to 3 mv., caused by small differences of temperature within the tube and to the slight cooling produced by introducing cold wires into the furnace. A better method is to join together the two platinum wires and the two alloy wires of the elements to be compared, and determine the small E.M.F.'s of each pair at several temperatures, from which the difference between the

* This Journal (4), xxviii, 300, 1909.

elements at those temperatures can be obtained by algebraic addition. This method offers a great advantage in that the temperature need be only approximately constant and approximately known, since the differences in most cases amount to only a few microvolts. By this method the comparison can be very quickly made at 1500° in the blast-lamp flame, which, with a little care, can be made to give a temperature constant to 20°.

D. Fixed Points.—Considerable attention was given in the previous paper to the standard melting points which serve to establish the gas thermometer scale for general use. In particular, a study was made of the purity of the zinc, silver, gold, and copper used, and of the magnitude of the errors likely to arise with the ordinary metals obtainable in the market.* During the present work, attention has been more particularly directed to the technic of melting point determination itself.†

All the metal melting points here described, except that of palladium, were made in an upright cylindrical furnace through which passed a glazed porcelain tube which could be tightly closed above and below and therefore permitted the atmosphere about the melting metal to be perfectly controlled. An effort was first made to accomplish this by placing the entire furnace inside a gas-tight bomb in which the atmosphere could be similarly varied, but the persistent retention of gases by the various clay insulating materials used about the furnace made this method slow, cumbersome, and very uncertain in its results. The only success which these bomb furnaces attained was to permit melting points to be measured in an approximate vacuum (about 1^{mm} pressure). But it has since been found so much simpler to operate with a neutral or reducing atmosphere in the closed tube passing through the heated zone, that the vacuum furnace has not been used for this work.

The chief disadvantage in the use of a tube of this kind is its effect upon the temperature gradient along the furnace axis. More heat is diverted toward the ends of the furnace and the central constant temperature zone becomes shorter. It offers no difficulty except that greater care must be taken in locating the crucible within the constant temperature region.

The qualities desired in fixed thermometric points for establishing and reproducing a scale are:

(1) Exact reproducibility of the temperature in repeated determinations with the same charge of material and with a different charge independently obtained. This means that the metal or salt must be either perfectly pure or obtainable with a constant amount and kind of impurity.

* E. T. Allen, in paper of Day and Clement, loc. cit., p. 454.

† See also W. P. White, Melting Point Determination and Melting Point Methods, this Journal (4), xxviii, 453 and 474, 1909.

(2) Independence of particular experimental arrangements. The melting point of a metal, for instance, must be sharp and definite enough so that with different kinds of furnaces and different rates of heating, the same temperature will be obtained.

(3) Convenience and safety of manipulation. A melting point which can only be obtained by the use of elaborate experimental arrangements is undesirable, even though it be reproducible and sharp. Furthermore, the substance must not injure the instrument to be calibrated.

(1) *Reproducibility*.—No extensive experiments have been made in the present work to test a large number of samples of different origin. It appeared sufficient to assure ourselves that all of the metals here used are obtainable in such degree of purity, or with such a constant amount of impurity, that the variations in their melting points are well within the limits of error in the scale itself. Waidner and Burgess* have recently made comparisons of various samples of pure zinc, antimony, and copper, and have found no differences exceeding 0.3° .† Our experience has been the same. All of the metals in the present investigation are readily obtainable from the ordinary sources of supply. They have been carefully analyzed in this laboratory by Dr. E. T. Allen, and the results are given in section 6.

(2) *Independence of Experimental Conditions*.—A number of experiments were made to test the effect of different experimental arrangements on the points. Two different furnaces were tried, one 65^{mm} inside diameter and 150^{mm} long, the other 55^{mm} inside diameter and 230^{mm} long. The region of constant temperature in the second furnace was longer than in the first and accordingly there was a larger range in which the crucible could be moved about without affecting the temperature. This furnace was used for all work after March 6, 1909. The ultimate test was always the agreement between the melting and freezing points. Any serious disagreement of these two shows that some influence is entering from without.

The results of the study were briefly as follows: (1) The best dimensions for a charge of metal are about 25^{mm} diameter by 45^{mm} deep. (2) The thermoelement tube should be about 5^{mm} above the bottom of the crucible. (3) There is a region within the furnace in which the melting and freezing points agree and are independent of the rate of heating or (within limits) of the depth of immersion of the thermoelement; it is necessary to find this position of the crucible by trial. With this position once determined, the temperature of the zinc, antimony, silver, gold, and copper points can be relied upon

* Phys. Rev., xxviii, 467, 1909. Bull. Bur. Stds., vi, 149-230, 1909.

† In the case of antimony, this statement applies only to Kahlbaum's metal.

within 0.2° . With large charges and facilities for stirring the metal, Waidner and Burgess have found the zinc point to be reproducible in a given furnace, with a given sample, within less than 0.1° .

White* showed that the temperatures of the two silicate points used for the present scale are reproducible within 1.0° independently of the dimensions of the furnace or the rate of heating. For a mineral melting point, the charge should be small (about 3 grams), the heat should approach the thermal junction from the side and not from the ends, and a position in the furnace should be found in which the melting point, determined by a bare thermoelement, does not vary with the rate of heating.

The possibility has been several times suggested that the temperature of the thermoelement inside of the tube might possibly be lower by a small constant amount than the temperature of the metal outside of the tube, and that this error might not be brought to light by such experiments as have been described. Several melting and freezing points of copper were, therefore, determined by enclosing the entire thermoelement wire in a thin capillary of silica glass which was slipped over the wire, bent double, and melted down upon the wire at the junction by heating in the oxyhydrogen flame. This was dipped directly into the molten copper to within 5^{mm} of the bottom, so that there was practically no possibility that the temperature of the junction could be lowered by radiation or conduction upward. The melting point on element D obtained in this way was 10,473 microvolts as compared with 10,473 microvolts in the closed glazed tube. There appears to be no error from this cause.

Convenience and Safety of Manipulation.—Zinc and gold are the most convenient of manipulation, as they require no special atmosphere and the temperatures are easily reached. Antimony, silver, and copper require an atmosphere of carbon monoxide and are somewhat less convenient. More care needs to be taken with copper than with silver and antimony because of the considerable effect of a very small amount of oxide. Antimony, silver, gold, and copper were all melted in carbon monoxide, made by dropping formic acid into warm sulphuric acid, and purified by passage through sodium hydroxide, lead nitrate, and sulphuric acid. The lead nitrate was introduced to make certain that no trace of hydrogen sulphide, which might be formed if the acid became too dilute or too warm, could pass into the metal.

The two silicates (diopside and anorthite) and palladium were melted in air. The silicate points are very convenient to

* Diopside and its Relations to Calcium and Magnesium Metasilicates, this Journal (4), xxvii, p. 5, 1909.

arrange and manipulate, provided the furnace is well insulated so that the temperature can be reached without difficulty. Palladium strains the platinum resistance furnace near to its limit of endurance on account of the high temperature, but has the great convenience of not requiring a reducing atmosphere. Special pains need to be taken, however, in this case, to protect the thermoelement from contamination.

Nickel and cobalt were melted in an atmosphere of hydrogen which was made by electrolysis in a large glass and earthenware generator, and purified by passage through potassium pyrogallate and sulphuric acid. Just before the thermoelement was introduced, the hydrogen was displaced by pure nitrogen drawn from a steel tank in which it was stored under pressure. The supply contained a trace of hydrogen and was, therefore, purified by passing over hot copper oxide and through calcium chloride and sulphuric acid. The extreme lightness of this gas compared with the outside air (especially when it is heated to 1450°) makes necessary special precautions in order to keep out any trace of air. Furthermore, hydrogen always caused contamination in the thermoelement, which was not prevented even when the hydrogen was replaced for a short time during the melting by pure nitrogen. Nickel and cobalt are, therefore, not recommended for frequent use in the calibration of thermoelements, if the two points, diopside and palladium (or diopside and anorthite), give a sufficient calibration for the purpose in hand.

The apparatus used for the melting points of nickel and cobalt is shown in section in fig. 6. The top of the large porcelain tube (Marquardt, glazed outside only) was closed by a sliding cup of brass in which the thermoelement tube and two others for introducing hydrogen were fastened by heating the cup and pouring in molten solder. The porcelain tube extended far enough out of the furnace to keep the brass cup cool. A groove near the base of the cup carried a piece of asbestos cord which made a gas-tight joint with the porcelain tube and permitted the whole to be raised and lowered without moving the crucible or opening the top of the tube. Two diaphragms of Marquardt porcelain above the crucible also prevented any considerable radiation upward to the brass cup.

In zinc, antimony, silver, gold, and copper, the thermoelement was protected by a glazed Marquardt tube of 5^{mm} inside and 8^{mm} outside diameter. In the case of antimony, the tube was further protected by a thin tube of graphite which fitted into the cover of the crucible. With diopside and anorthite, some contamination from iridium in the furnace may take place, but can be largely prevented by surrounding the tube with pure platinum. A glazed Marquardt tube cannot be used in

this case, for the glaze flows readily at these temperatures and may make its way into the charge. With nickel and cobalt, glazed Marquardt tubes and also pure magnesia tubes of the same size were used, but neither protects the element from contamination. In palladium only the pure magnesia tubes were used.

Zinc, antimony, silver, gold, and copper were melted in graphite crucibles 27^{mm} in diameter and 80^{mm} deep inside, and 37^{mm} in diameter and 100^{mm} high outside. The charge of metal was from 45^{mm} to 55^{mm} deep. Diopside and anorthite were melted in small platinum crucibles 10^{mm} in diameter and 18^{mm} deep, as described and illustrated in the paper already referred to.* Nickel was melted in an unglazed Marquardt porcelain crucible, lined with a paste consisting of about 90 per cent Al_2O_3 and 10 per cent MgO ; and also in a Berlin "pure magnesia" crucible. The charge was about 25^{mm} in diameter and 30^{mm} deep. Cobalt could not be melted in the alumina lined crucible, as the metal penetrated through the lining and attacked the porcelain. It was, therefore, melted in a "pure magnesia" crucible made by the Königliche Porzellan Manufaktur. The material of these crucibles probably contains a small percentage of silica. Palladium was melted in a crucible made in this laboratory from a specially pure magnesia made by Baker and Adamson. The magnesia was first shrunk by heating to a temperature higher than that at which the crucible was to be used, and was then made into a paste with water and a little magnesium chloride, spun into form, and baked.

Particular details regarding each of the substances used will now be taken up in the order of their temperatures.†

* W. P. White, this Journal (4), xxviii, 477, 1909.

† See, also, E. T. Allen, in paper of Day and Clement, loc. cit., p. 454.

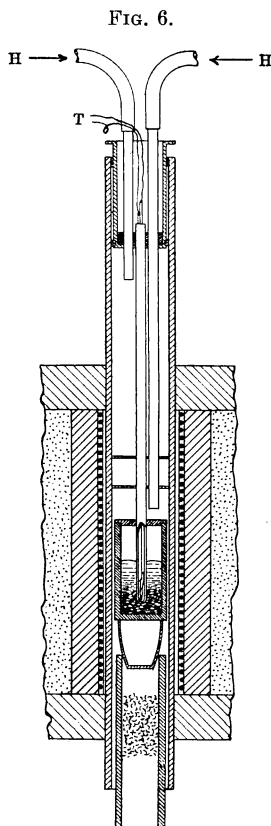


FIG. 6. The furnace in which the standard metal melting points were made, showing the position of the metal with respect to the coil, the thermoelement (T) and the arrangement (H) for maintaining a hydrogen or nitrogen atmosphere.

Zinc.—Two samples of “C. P. sticks” were used, both from Eimer and Amend. No appreciable difference could be observed between their melting points. Both melting and freezing points were sharp and measurable to a fraction of a microvolt. Successive readings did not differ by more than one microvolt. The charge was about 200 grams. The analysis has been published.*

Antimony.—Two samples of metal were used, both from Kahlbaum, and no appreciable difference was found between their melting points. An analysis of the first sample is given in section 6. The charge weighed about 150 grams. The melting point is sharp and does not differ from the freezing point by more than one microvolt, provided the undercooling which always precedes solidification does not exceed 15° . If the metal is undercooled too far to give an accurate freezing point, the fact is easily recognized by observing that the thermoelement does not return to a sustained constant temperature, but merely rises to a maximum, then falls again. The amount of undercooling is greater the higher the metal has been heated above its melting point after the melting is complete.

Silver.—The charge weighed about 260 grams. Only one supply was used, a specially purified sample obtained from the Philadelphia Mint, of which an analysis is given in the previous paper.* The melting and freezing points were sharp and agreed within one microvolt.

Gold.—A new charge of gold was used, weighing 350 grams. This was obtained from Dr. Eckfeldt of the Philadelphia Mint. No analysis was deemed necessary.*

Copper.—The copper was obtained in the form known as “copper drops cooled in hydrogen” (Eimer and Amend). Only one supply was used. The melting and freezing points were not quite as sharp as was the case with silver, but always agreed within 1 microvolt. The temperature is very susceptible to a trace of oxide, which not only lowers the temperature appreciably but makes it more uncertain, so that if a little oxidation has taken place it is recognizable at once. Waidner and Burgess† found that the best commercial electrolytic copper showed an average difference of 0.2° in the melting point from the purified copper drops. Charge, about 210 grams.

Diopside.—Two samples of diopside were used, one from the preparation of Allen and White‡ and the other made up in 1909 by G. A. Rankin. No appreciable difference was found

* E. T. Allen, in paper of Day and Clement, p. 454.

† Loc. cit., p. 469 (Phys. Rev.); p. 174 (Bull.).

‡ This Journal (4), xxvii, 1, 1909.

between the melting points. No freezing point can be obtained as the mineral undercools considerably. The charge used was 3 grams.

Nickel.—A sample of specially purified electrolytic nickel was obtained from Kahlbaum. The analysis showed less than 0.2 per cent total impurities. Care must be taken in the case of nickel that no oxide forms, as a fairly sharp break can be observed about 10° below the melting point, which may represent the eutectic of nickel and nickel oxide. This break disappeared when the nitrogen was replaced for a few minutes by hydrogen. This lower point may easily be mistaken for the melting point of the metal, and this mistake seems to have occurred in several of the published determinations of the melting point of nickel. Nickel absorbs hydrogen and possibly also nitrogen, and after cooling frequently showed excrescences and signs of "spitting" such as occur with silver in air.

Cobalt.—Kahlbaum's purest cobalt was used, containing less than 0.05 per cent total impurity. It was in the form of fine black powder, which was compressed into blocks for convenience in handling. The results obtained were not quite as satisfactory as with nickel on account of the higher temperature and more rapid contamination of the thermoelement. The absorption of gases seemed to be less than was the case with nickel.

Samples of Eimer and Amend's "98 to 99 per cent pure" nickel and cobalt were also tried. The difference between the two samples of nickel was not greater than the uncertainty in the melting point caused by contamination of the thermoelement. The "98-99 per cent pure" cobalt melted about 3.5° lower than the pure sample. Since the impurities in nickel are usually chiefly iron and cobalt, and those of cobalt are chiefly iron and nickel, and since the melting points of all three are close together, the melting points of the slightly impure metals can not be expected to lie far from those of the pure metals.

Anorthite.—Only one preparation of anorthite was used, made by G. A. Rankin 1909. The charge was about 3 grams. The melting point is not quite as sharp as that of diopside. Only the melting point can be obtained, as the mineral undercools considerably; it may even cool to glass without crystallization, in which case of course no melting point will be obtained on the following heating.

Palladium.—About 350 grams of pure palladium, in the form of sheet, was loaned to us by Dr. Heraeus. It melts and freezes quite sharply, making an excellent substance for a fixed thermometric point. The greatest uncertainty is caused by the vaporization of the metal and consequent contamination of the thermoelement wire. The charge used weighed 128-210 grams

In addition to the fixed points which have just been described, two other metal melting points, cadmium and aluminum, were incidentally determined. Only one measurement of the cadmium point was made on the gas thermometer, and this chiefly for the purpose of checking the extrapolation below the zinc point. The conditions of melting were the same as for zinc. The sample was obtained from Eimer and Amend, and its analysis has been given in a paper by Day and Allen.* The charge weighed 215 grams.

A sample of pure aluminum obtained from the Aluminum Company of America was melted in a graphite crucible of the usual size in an atmosphere of carbon monoxide. On account of the sensitiveness of aluminum to silicon contamination, the tube carrying the thermoelement was also provided with a thin protecting cover of graphite so that the metal came in contact only with pure graphite. The freezing point was sharp and constant. The melting point was less sharp but lay within 0.5° of the freezing point.

The effect on the final temperature of all the errors and corrections which have been discussed in this section, is shown in summarized form in Table IV.

The figures of Table IV serve to emphasize the statements already made, that the greatest present uncertainty in the high temperature gas scale arises from the lack of uniformity in an air bath, which not only leads to uncertainty as to what is the true temperature of the gas in the bulb, but also to errors in the transference by the thermoelement. The next largest uncertainty, due to the limitations of the materials used for fixed points, is not directly chargeable to the gas thermometer. In this connection, considerably more work needs to be done on the high thermometric points, comparable in thoroughness to the work in low temperature thermometry of Richards, Dickinson, and others, on the sodium sulphate transition point.

4. *Experimental Data and Calculated Results.*

A. Expansion Coefficient.—In Table V are given the experimental data on the expansion coefficients of the alloy 80 per cent platinum, 20 per cent rhodium. In the first column is given the date of the series, in the second and third columns the readings of the thermoelements at the middle of the bar, corrected for zero error and the temperature of the cadmium cell. The 12 other readings taken with each element at each temperature at different points along the bar cannot be given here, but the fourth and fifth columns contain the readings of the thermoelement corrected to represent the integrated tem-

* Arthur L. Day and E. T. Allen, *Phys. Rev.*, xix, 180, 1904.

TABLE IV.—*Estimated Errors and their Effect on the Value of t.*

Quantity affected	Source of error	Amount of error		Effect on <i>t</i>	
		at 400°	at 1500°	at 400°	at 1500°
(A) Temperature of gas	Temperature differences over bulb surface	2 mv.	5 mv.	± 0.2°	± 0.4°
	Variability	0	1 mv.	0	± 0.1°
(B)	<i>p</i> ₀				
	Reference point	0.02 mm.	0.02 mm.	± 0.04°	± 0.15°
	Manometer setting	0.02 mm.	0.02 mm.	± 0.04°	± 0.15°
	Scale corrections	0.01 mm.	0.01 mm.	± 0.02°	± 0.07°
	Temperature of mercury	0.05 mm.	0.05 mm.	± 0.10°	± 0.38°
	Barometer setting	0.03 mm.	0.03 mm.	± 0.06°	± 0.23°
	Temperature of barometer	0.05 mm.	0.05 mm.	± 0.10°	± 0.38°
	Variations in <i>p</i> ₀	0	0–0.05 mm.	0	0 to ± 0.3
	<i>p</i>				
	Reference point	0.02 mm.	0.02 mm.	± 0.02°	0
	Manometer setting	0.02 mm.	0.02 mm.	± 0.02°	0
	Scale corrections	0.02 mm.	0.02 mm.	± 0.02°	0
	Temperature of mercury	0.07 mm.	0.20 mm.	± 0.07°	± 0.05°
	Barometer setting	0.03 mm.	0.03 mm.	± 0.03°	± 0.01°
	Barometer temperature	0.05 mm.	0.05 mm.	± 0.05°	± 0.01°
	Unheated space { <i>v</i> ₁ <i>t</i> ₁	0.020 cc. 0.5–50°	0.020 cc. 0.5°–100°	± 0.07° ± 0.01°	± 0.5° ± 0.1°
	<i>β</i>	1.0°	2.0°	± 0.02°	± 0.11°
	Expansion	0.005 mm.	0.008 mm.	± 0.02°	± 0.09
	Hysteresis in expansion	0.01 mm.	0.01 mm.	± 0.04°	± 0.10°
(C)	E.M.F.				
	Instrumental correction	1 mv.	2 mv.	± 0.1°	± 0.2°
	Contamination	0	0–12 mv.	0	0 to +1.0°
	Integration over bulb	3 mv.	12 mv.	± 0.3°	± 1.0°
(D)	Fixed points				
	Instrumental corrections	1 mv.	2 mv.	± 0.1°	± 0.2°
	Contamination	0	0–10 mv.	0	0 to –1.0°
	Variation in given charge	Specific 1–10 mv.		Specific 0.1–1.0°	
	Variation between different charges	Specific 1–20 mv.		Specific 0.1–2.0°	

perature along the bar. For convenience, the integration was made in terms of microvolts instead of degrees. The sixth and seventh columns contain the temperatures corresponding

TABLE V.—*Observations of Expansion Coefficient, β .*

Date	Thermoelements				Temperature			Expansion from 0°	
	W	Z	W cor.	Z cor.	by W	by Z	Mean	mm on 500 mm	10 ⁶ β
1908									
Sept. 21	2261	2251	2312	2298	301.4°	301.4°	301.4°	1.404	9.32
	3197	3187	3273	3258	404.6	405.4	405.0	1.912	9.44
	4169	4153	4257	4237	506.0	507.1	506.6	2.434	9.61
	5157	5140	5237	5212	603.9	605.1	604.5	2.950	9.76
	6197	6178	6286	6262	705.4	707.2	706.3	3.500	9.91
	7264	7238	7362	7333	806.2	807.8	807.0	4.064	10.07
	8361	8335	8457	8420	905.9	906.7	906.3	4.640	10.24
	9509	9470	9599	9552	1006.9	1006.8	1006.8	5.241	10.41
	10662	10611	10733	10675	1104.5	1103.4	1104.0	5.828	10.56
	11963	11896	12018	11921	1215.3	1210.2	1212.8	6.469	10.67
Sept. 25	1817	1801	1848	1831	248.7	248.4	248.6	1.154	9.28
	2756	2735	2791	2768	353.4	352.9	353.2	1.666	9.43
	3699	3674	3726	3702	451.8	452.0	451.9	2.158	9.55
	4686	4655	4691	4662	549.7	550.3	550.0	2.668	9.70
	5711	5679	5691	5660	648.2	649.2	648.7	3.191	9.84
	6820	6788	6772	6742	751.2	752.6	751.9	3.757	9.99
	7847	7813	7754	7720	842.2	843.2	842.7	4.262	10.11
	8980	8945	8845	8809	940.8	941.4	941.1	4.827	10.26
	10140	10102	9939	9901	1036.4	1037.0	1036.8	5.403	10.42
	11368	11327	11109	11063	1136.9	1136.4	1136.7	6.012	10.58
Oct. 3	2291	2272	2302	2283	300.3	299.8	300.1	1.384	9.22
	3228	3205	3250	3228	402.2	402.2	402.2	1.899	9.44
	4208	4181	4243	4215	504.6	504.9	504.8	2.432	9.63
	5205	5175	5247	5216	604.8	605.5	605.2	2.964	9.79
	6238	6206	6281	6249	704.9	705.9	705.4	3.511	9.95
	7297	7263	7342	7309	804.4	805.5	805.0	4.069	10.11
	8401	8365	8446	8408	904.9	905.6	905.3	4.644	10.26
	9536	9497	9576	9534	1004.9	1005.2	1005.1	5.231	10.41
	10675	10647	10710	10670	1102.6	1103.0	1102.8	5.830	10.57
	11884	11857	11926	11875	1207.5	1206.2	1206.8	6.466	10.71
Oct. 29	8419	8377	8366	8324	897.4	898.0	897.7	4.618	10.29
	9551	9507	9436	9392	992.6	992.8	992.7	5.169	10.41
	10706	10663	10539	10496	1088.0	1088.2	1088.1	5.752	10.57
	11884	11849	11786	11751	1195.6	1195.7	1195.7	6.401	10.70
	13137	13104	13134	13101	1309.9	1309.8	1309.9	7.154	10.92
	W	D	W cor.	D cor.	by W	by D			
1909	2304	2301	2235	2232	293.0	293.0	293.0	1.352	9.23
	6222	6217	6180	6175	695.2	695.9	695.6	3.452	9.92
Oct. 14	9501	9494	9493	9486	997.6	998.1	997.9	5.190	10.40
	9540	9536	9542	9544	1001.9	1003.1	1002.5	5.200	10.37
	10666	10663	10690	10691	1101.9	1102.5	1102.2	5.811	10.54
	11839	11836	11783	11783	1195.4	1195.7	1195.6	6.410	10.72
	12998	12993	13121	13120	1308.9	1308.6	1308.8	7.156	10.93
	14183	14170	14390	14372	1413.4	1411.6	1412.5	7.832	11.09

to the readings in columns 4 and 5, and the eighth column, the mean of these two temperatures. The micrometer readings are not given, but in column 9 will be found the expansions reduced to millimeters for that portion of the bar lying between the 0 and 50^{cm} marks on the ends. Each of these represents the mean of eight settings at each end of the bar. In the last column are given the values of the mean expansion coefficient from 0°, calculated by dividing the expansion by the length at 0 and by the temperature.

For convenience of comparison, the values of β at the nearest round temperatures were interpolated linearly between the observations in each series, and the results are given in Table VI. Values interpolated between these values are given in parentheses.

TABLE VI.—*Values of $10^6 \beta$ at Round Temperatures for the alloy 80 Pt, 20 Rh.*

Temp.	21 Sept. 1908	25 Sept. 1908	3 Oct. 1908	29 Oct. 1908	13 Oct. 1909	14 Oct. 1909	Mean
250		9.28					
300	9.31	(9.36)	9.22		9.24		9.28
350	(9.37)	9.43	(9.33)		(9.33)		9.36
400	9.43	(9.49)	9.44		(9.41)		9.44
450	(9.52)	9.55	(9.53)		(9.50)		9.52
500	9.60	(9.62)	9.62		(9.58)		9.61
550	(9.67)	9.70	(9.71)		(9.67)		9.69
600	9.75	(9.77)	9.79		(9.76)		9.77
650	(9.83)	9.84	(9.86)		(9.84)		9.84
700	9.90	(9.92)	9.94		9.93		9.92
750	(9.98)	9.99	(10.02)		(10.01)		10.00
800	10.06	10.06	10.10		(10.09)		10.08
850	(10.14)	10.12	(10.17)		(10.16)		10.15
900	10.23	(10.20)	10.25	10.29	(10.24)		10.24
950	(10.31)	10.27	(10.32)	(10.36)	(10.32)		10.32
1000	10.40	(10.36)	10.40	10.42	10.40	10.37	10.39
1050	(10.47)	10.44	(10.48)	(10.50)		(10.45)	10.47
1100	10.55	(10.52)	10.57	10.59		10.54	10.55
1150	(10.60)	10.60	(10.64)	(10.65)		(10.63)	10.62
1200	10.65	(10.67)	10.71	10.71		10.73	10.69
1250				(10.81)		(10.82)	10.81
1300				10.90		10.92	10.91
1350				(10.99)		(10.99)	10.99
1400						11.07	11.07
1450							(11.15)
1500							(11.23)

The table shows that the percentage error at 300° is greater than that at 1200° and above, probably on account of the larger effect of the hysteresis in the expansion and contraction, already discussed on page 114. The agreement of the results is very satisfactory, particularly in view of the fact that each

series represents an entirely different curve of temperature variation along the bar. In some cases the temperatures at the ends were lower than at the middle, in others higher than at the middle, and in one series one end was higher and the other lower. The mean of all, therefore, probably eliminates any error which might arise from variation of temperature along the bar.

The results are represented within the limits of error by the straight line equation :

$$10^6\beta = 8.79 + 0.00161t.$$

This may be compared here with the expansion coefficients between 300° and 1000° determined by the authors for the 10 per cent iridium alloy,* and of Holborn and Day† for the 20 per cent iridium alloy and for pure platinum :

$$80 \text{ Pt. } 20 \text{ Ir. } 10^6\beta = 8.20 + 0.00142t$$

$$90 \text{ Pt. } 10 \text{ Ir. } 10^6\beta = 8.84 + 0.00131t$$

$$\text{Pt. } 10^6\beta = 8.87 + 0.00132t.$$

B. Gas Thermometer Data and Fixed Points.—In Table VII are given the observed gas thermometer data.‡ In the first column is the date of the measurement. The measurements are numbered chronologically in the second column for convenience of reference. In the third column is the measured pressure, p' (or p'_0) in millimeters of mercury at 0°, corrected as described on pages 107 and 108. The application of the correction for unheated space (see p. 108) gives the pressure p (or p_0) which is found in the fourth column. In the fifth column is the value of the temperature, t , calculated by formula (5) on page 101. In column 6 are given the readings of the standard thermoelements in microvolts, and in column 7 the positions of these elements on the bulb; for the significance of these figures see fig. 1 and note on page 104. In the last column are given the other elements which were used on the bulb, together with their positions designated in the same way. The italicized letters represent single platinum wires instead of thermoelements.

A few measurements in which the value of p_0 changed by more than 0.1 per cent have been omitted; their position is shown by the absence of their corresponding serial numbers.

* Published in paper of Day and Clement, loc. cit., pp. 425–441.

† This Journal (4), xi, 374, 1901.

‡ For the measurements in the table, seven furnaces were employed, using three supplies of platinum wire of about 400 grams each. One of these furnaces was wound on the outside, the other six on the inside of the tube. It was possible to rewind the wire at least once after the furnace had burned out. Failure always occurred several cms. away from the bulb in the end portions of the furnace, which, in order to secure uniformity of temperature over the bulb, had to be considerably superheated. Only one measurement was made at the palladium point, as this one rendered the furnace unfit for further use; the conditions of this measurement, were, however, perfect.

TABLE VII—Observed Gas-Thermometer Data.

Date	No.	p' (or p_0')	p (or p_0)	t	Standard Elements	Position	Other elements and positions
1908		GAS FILLING No. 1					
30 Nov.	1	217·65	217·63	0°	-----		
"	2	1037·77	1042·72	1079·87	W10443 } X 10491 }	4 8	Z (1), S (9)
1 Dec.	3	217·45	217·43	0	-----		
2 Dec.	5	217·10	217·08	0	-----		
3 Dec.	6	948·81	952·84	960·59	W 9061 } X 9100 }	4 8	Z (1), S (9)
4 Dec.	7	217·12	217·10	0	-----		
16 Dec.	8	217·08	217·06	0	-----		
17 Dec.	9	1038·50	1043·48	1083·61	W10483 } X 10555 }	4 8	Z (1), S (9)
18 Dec.	10	217·18	217·16	0	-----		
19 Dec.	11	1038·57	1043·56	1083·77	W10473 } X 10512 }	4 8	Z (1), S (9)
21 Dec.	12	217·06	217·04	0	-----		
23 Dec.	15	217·49	217·47	0	-----		
24 Dec.	16	1242·38	1249·71	1365·71	A 13866 } X ----- }	4 8	Y (1), S (9)
28 Dec. 1909	17	217·57	217·55	0	-----		
22 Jan.	18	1039·78	1044·74	1082·84	A 10502 } Y 10612 }	4 8	Z (9), B (1·3) W (2·3), S (6·7) X (7·3)
"	19	1038·82	1043·79	1081·87	A 10506 } Y 10584 }	4 8	Do.
"	20	1037·85	1042·83	1080·89	A 10498 } Y 10555 }	4 8	Do.
23 Jan.	21	217·36	217·34	0	-----		
25 Jan.	22	543·01	544·07	418·40	A 3414 } Y 3436 }	4·5 8	Do.
"	23	542·27	543·32	417·43	A 3408 } Y 3435 }	4·5 8	Do.
26 Jan.	24	703·78	705·81	629·80	A 5510 } Y 5550 }	4·5 8	Do.
"	25	702·64	704·67	628·34	A 5501 } Y 5529 }	4·5 8	Do.
"	26	949·56	953·63	960·22	A 9090 } Y 9159 }	4·5 8	Do.
"	27	948·15	952·23	958·41	A 9075 } Y 9119 }	4·5 8	Do.
"	28	1039·03	1044·05	1083·01	A 10515 } Y 10593 }	4·5 8	Do.
"	29	1037·92	1042·93	1081·56	A 10505 } Y 10556 }	4·5 8	Do.
27 Jan.	30	217·33	217·31	0°	-----		
28 Jan.	31	542·87	543·92	418·30	A 3410 } Y 3436 }	4·5 8	Do.
"	32	542·07	543·11	417·25	A 3404 } Y 3425 }	4·5 8	Do.
"	33	704·06	706·07	630·21	A 5514 } Y 5553 }	4·5 8	Do.

TABLE VII—(Continued)

Date	No.	p' (or p_0)	p (or p_0)	t	Standard Elements	Position	Other elements and positions
28 Jan.	34	703·35	705·37	629·31	A 5510 } Y 5537 }	4·5 8	Z (9), B (1·3), W (2·3), S (6·7) X (7·3)
"	35	948·96	953·05	959·46	A 9087 } Y 9142 }	4·5 8	Do.
"	36	949·86	953·97	960·69	A 9098 } Y 9163 }	4·5 8	Do.
"	37	1038·50	1043·57	1082·23	A 10511 } Y 10576 }	4·5 8	Do.
"	38	1038·99	1044·06	1082·90	A 10512 } Y 10585 }	4·5 8	Do.
"	39	1039·61	1044·68	1083·68	A 10509 } Y 10617 }	4·5 8	Do.
29 Jan.	40	217·37	217·35	0°	----		
"	41	949·32	953·38	959·78	A 9086 } Y 9156 }	4·5 8	Do.
"	42	948·58	952·66	958·81	A 9085 } Y 9131 }	4·5 8	Do.
"	43	1039·29	1044·34	1083·15	A 10515 } Y 10595 }	4·5 8	Do.
"	44	1038·49	1043·56	1082·09	A 10511 } Y 10568 }	4·5 8	Do.
"	45	1039·63	1044·71	1083·58	A 10508 } Y 10617 }	4·5 8	Do.
30 Jan.	46	217·39	217·37	0	----		
GAS FILLING No. 2							
18 Feb.	47	346·74	346·70	0	----		
22 Feb.	48	346·78	346·74	0	----		
23 Feb.	49	745·09	746·19	319·55	A 2487 } D 2483 } Z 2462 }	4·5 4·5 8	W (1·3), B (2·2), X (6·2), S (7·3), Y (12)
"	50	866·47	868·15	418·40	A 3414 } D 3406 } Z 3385 }	4·5 4·5 8	Do.
"	51	995·97	998·38	524·71	A 4451 } D 4439 } Z 4413 }	4·5 4·5 8	Do.
"	52	1122·39	1125·61	629·37	A 5510 } D 5495 } Z 5463 }	4·5 4·5 8	Do.
24 Feb.	53	346·67	346·63	0	----		
26 Feb.	59	346·24	346·20	0	----		
"	60	1657·03	1665·07	1083·17	A 10508 } D 10473 } Z 10422 }	4·5 4·5 8	W (3·3), B (2·2), X (6·2), S (7·2), Y (12)
27 Feb.	61	346·45	346·41	0	----		
1 Mar.	62	1388·84	1394·13	853·76	A 7895 } D 7869 } Z 7829 }	4·5 4·5 8	B (3·2), W (2·3), X (6·2), S (7·2), Y (12)
"	63	1513·67	1520·20	960·29	A 9086 } D 9055 } Z 9010 }	4·5 4·5 8	Do.
"	64	1632·03	1639·78	1062·15	A 10265 } D 10229 } Z 10178 }	4·5 4·5 8	Do.

TABLE VII—(Continued)

Date	No.	p' (or p_0')	p (or p_0)	t	Standard Elements	Position	Other elements and positions
1 Mar.	65	1655·77	1663·81	1082·84	A 10511 } D 10474 } Z 10420 }	4·5 4·5 8	B (3·2), W (2·3), X (6·2), S (7·2), Y (12)
2 Mar.	66	346·20	346·17	0			
3 Mar.	67	1386·28	1391·55	852·44	A 7885 } D 7861 } Z 7820 }	4·5 4·5 8	W (3·3), B (2·2) X (6·2), S (7·2) Z (8), Y (12)
"	68	1511·95	1518·48	959·81	A 9088 } D 9059 } Z 9013 }	4·5 4·5 8	Do.
"	69	1628·71	1636·46	1060·24	A 10257 } D 10221 } Z 10169 }	4·5 4·5 8	Do.
"	70	1654·46	1662·50	1082·73	A 10511 } D 10478 } Z 10444 }	4·5 4·5 8	Do.
5 Mar.	71	345·98	345·94	0	----		
GAS FILLING No. 3							
4 June	72	345·31	345·27	0	A ---- } E 3403 }	4·1 4·3	Y (1), a (2·4), b (6·4)
"	73	861·67	862·94	417·07	F 3414 } G 3416 } Z 3370 }	4·5 4·7 8	
"	74	1118·50	1120·83	629·11	A 5516 } E 5535 } F 5528 }	4·1 4·3 4·5	Do.
"	75	345·31	345·27	0	G 5529 } Z 5461 }	4·7 8	
5 June	76	1510·50	1515·27	959·77	A 9090 } E 9114 } F 9099 }	4·1 4·3 4·5	Do.
"	77	1628·08	1633·64	1060·53	G 9108 } Z 9002 }	4·7 8	
"	78	1652·36	1658·10	1081·28	A 10258 } E 10285 } F 10266 }	4·1 4·3 4·5	Do.
"	79	345·50	345·46	0	G 10279 } Z 10161 }	4·7 8	
10 June	80	345·52	345·48	0	A 10503 } E 10529 }	4·1 4·3	
18 June	81	1512·96	1517·69	961·21	F 10510 } G 10523 }	4·5 4·7	
"	82	1630·94	1636·53	1062·53	Z 10404 } F 9129 } E 9128 }	8 4·1 4·3	a (1), b (2·4), c (6·4), e (7·3)
"					A 9080 } G 9122 }	4·5 4·7	
"					Z 9015 } F 10299 }	8 4·1	Do.
"					E 10300 } A 10252 }	4·3 4·5	
"					G 10292 } Z 10181 }	4·7 8	

TABLE VII—(Continued)

Date	No.	p' (or p_0')	p (or p_0)	t	Standard Elements	Position	Other elements and positions
18 June	83	1653·61	1659·37	1082·14	F 10534 } E 10534 } A 10487 } G 10526 } Z 10403 } F 10536 } E 10534 } A 10485 } G 10525 } Z 10426 }	4·1 4·3 4·5 4·7 8 4·1 4·3 4·5 4·7 8	a (1), b (2·4) c (6·4), e (7·3)
"	84	1654·51	1660·27	1082·91	F 10536 } E 10534 } A 10485 } G 10525 } Z 10426 }	4·1 4·3 4·5 4·7 8	Do.
19 June	85	345·51	345·47	0	----		
GAS FILLING No. 3a							
19 June	86	219·73	219·71	0	----		
"	87	710·34	711·83	627·61	F 5520 } E 5520 } A 5484 } G 5516 } Z 5437 } F 9139 } E 9136 } A 9089 } G 9131 } Z 9036 }	4·1 4·3 4·5 4·7 8 4·1 4·3 4·5 4·7 8	a (1), e (2·3) c (6·3), f (7·3)
"	88	962·21	965·23	961·71	F 10540 } E 10538 } A 10490 } G 10531 } Z 10428 }	4·1 4·3 4·5 4·7 8	Do.
"	89	1051·74	1055·41	1082·75	H 14251 } E 14227 } F 14222 } G 14245 } Z 14121 } H 14282 } E 14247 } F 14241 } G 14274 } Z 14156 }	4·1 4·3 4·5 4·7 8 4·1 4·3 4·5 4·7 8	Do.
21 June	90	219·74	219·72	0	----		
22 June	92	220·65	220·63	0	----		
24 June	93	220·62	220·59	0	----		
25 June	95	220·56	220·53	0	----		
2 July	96	1283·36	1288·82	1391·97	H 14251 } E 14227 } F 14222 } G 14245 } Z 14121 } H 14282 } E 14247 } F 14241 } G 14274 } Z 14156 }	4·1 4·3 4·5 4·7 8 4·1 4·3 4·5 4·7 8	Do.
"	97	1285·43	1290·89	1394·89	H 14213 } E 14214 } F 14196 } G 14216 } Z 14099 } H 14264 } E 14242 } F 14235 } G 14259 } Z 14156 }	4·1 4·3 4·5 4·7 8 4·1 4·3 4·5 4·7 8	Do.
3 July	98	221·02	220·99	0	----		
"	99	1281·97	1287·45	1393·34	H 14213 } E 14214 } F 14196 } G 14216 } Z 14099 } H 14264 } E 14242 } F 14235 } G 14259 } Z 14156 }	4·1 4·3 4·5 4·7 8 4·1 4·3 4·5 4·7 8	Do.
"	100	1284·05	1289·54	1396·17	----		
6 July	101	220·62	220·60	0	----		

TABLE VII—(Continued)

Date	No.	p' (or p_0')	p (or p_0)	t	Standard Elements	Position	Other elements and positions
GAS FILLING NO. 4							
8 July	102	216·81	216·79	0	H 14235 } E 14216 } F 14209 } G 14232 } Z 14124 } H 14249 } E 14229 } F 14199 } G 14236 } Z 14155 }	4·1 4·3 4·5 4·7 8 4·1 4·3 4·5 4·7 8	a (1), e (2·3) c (6·3), f (7·3)
“	103	1261·35	1266·80	1391·15			
“	104	1263·13	1268·59	1393·55			Do.
9 July	105	217·36	217·33	0	H 14251 } E 14236 } F 14233 } G 14241 } Z 14123 } H 14240 } E 14236 } F 14235 } G 14233 } Z 14152 }	4·1 4·3 4·5 4·7 8 4·1 4·3 4·5 4·7 0	Do.
“	106	1261·71	1267·15	1391·64			Do.
“	107	1263·01	1268·46	1393·44			Do.
10 July	108	217·35	217·33	0	H 15019 } E 15020 } F ---- } G ---- } Z 14903 }	4·1 4·3 4·5 4·7 8	Do.
“	109	1306·60	1312·52	1455·37			
12 July	110	217·36	217·34	0	H 14978 } E 14980 } F ---- } G ---- } Z 14867 } H 14980 } E 14960 } F 14947 } G ---- } Z 14872 }	4·1 4·3 4·5 4·7 8 4·1 4·3 4·5 4·7 8	Do.
“	111	1305·53	1311·35	1453·52			Do.
“	112	1305·46	1311·28	1453·31			Do.
13 July	113	217·40	217·38	0			
10 Sept.	114	217·38	217·36	0			
11 Sept.	115	1328·68	1334·79	1484·70	H ---- } E 15389 } F 15374 } G ---- } A 15357 } H ---- } E 15411 } F 15417 } G 15418 } A 15421 }	4·1 4·3 4·5 4·7 8 4·1 4·3 4·5 4·7 8	a (1), c (2·3) e (6·7), f (7·3)
“	116	1332·18	1338·32	1489·60			Do.
13 Sept.	117	217·62	217·60	0			

TABLE VII—(Continued)

Date	No.	p (or p_0)	p (or p_0)	t	Standard Elements	Position	Other elements and positions
15 Sept.	118	1329.92	1336.03	1487.36	H ----- E 15391 F 15389 G 15399 A 15382	4.1 4.3 4.5 4.7 8	α (1), c (2.3) e (6.7) f (7.3)
16 Sept.	119	217.51	217.49	0	H ----- E 15386 F 15376 G 15368 A 15379	4.1 4.3 4.5 4.7 8	Do.
17 Sept.	120	1329.68	1335.78	1486.95	H ----- E 15397 F 15396 G 15389 A 15412	4.1 4.3 4.5 4.7 8	Do.
"	121	1331.40	1337.51	1489.34	H ----- E 14991 F 14996 G 14957 A 14982	4.1 4.3 4.5 4.7 8	Do.
18 Sept.	122	217.52	217.50	0	H ----- E 14979 F 14984 G 14952 A 14996	4.1 4.3 4.5 4.7 8	Do.
21 Sept.	123	1306.75	1312.72	1454.83	H ----- E 10618 F 10626 G 10622 G 10616 C 10567	4.1 4.3 4.5 4.7 8	α (1.5), J (2.4) c (6.2), e (7.2)
"	124	1307.28	1313.25	1455.60	H ----- E 12002 F 12003 G 12010 C 11914	4.1 4.3 4.5 4.7 8	Do.
22 Sept.	125	217.45	217.43	0	H ----- E 12006 F 12003 G 12010 C 11914	4.1 4.3 4.5 4.7 8	Do.
27 Nov.*	126	1045.80	1049.49	1090.59	H ----- E 13106 F 13112 G 13115 C 13007	4.1 4.3 4.5 4.7 8	Do.
29 Nov.	127	217.28	217.26	0	H ----- E 14246 F 14250 G 14248 C 14146	4.1 4.3 4.5 4.7 8	Do.
9 Dec.	128	1129.52	1133.91	1206.63	H ----- E 11940 F 11946 G 11951 C 11887	4.1 4.3 4.5 4.7 8	α (1), J (2.3), c (6.2), e (7.1)
"	129	1194.81	1199.74	1298.01	H ----- E 11946 F 11951 G 11949 C 11887	4.1 4.3 4.5 4.7 8	Do.
"	130	1261.16	1266.68	1391.45	H ----- E 11946 F 11951 G 11949 C 11887	4.1 4.3 4.5 4.7 8	Do.
10 Dec.	131	217.30	217.28	0	H ----- E 11946 F 11951 G 11949 C 11887	4.1 4.3 4.5 4.7 8	Do.
20 Dec.	132	1125.92	1130.29	1201.50	H ----- E 11946 F 11951 G 11949 C 11887	4.1 4.3 4.5 4.7 8	Do.

* Outside-wound furnace. See page 106.

TABLE VII—(Concluded)

Date	No.	p' (or p_0')	p (or p_0)	t	Standard Elements	Position	Other elements and positions
20 Dec.	133	1302.40	1308.33	1450.03	H 14950	4.1	a (1), J (2.3) c (6.2), e (7.1)
					E 14958	4.3	
					F 14962	4.5	
					G 14955	4.7	
					C 14882	8	
					H 16156	4.1	
“	134	1372.16	1378.78	1550.15	E 16160	4.3	Do.
					F 16170	4.5	
					G 16148	4.7	
					C 16075	8	
21 Dec.	135	217.29	217.27	0	----		

(Continued from p. 132.)

The melting and freezing points of the metals and salts, measured with the various thermoelements used during the investigation, as well as the frequent comparisons of thermoelements with each other, are too numerous to be published here, especially as they are practically all summarized in Table VIII.

Table VIII contains the final temperature of each thermometric point studied. In the first column is the number of the experiment corresponding to that in Table VII. In the second column is the correction in degrees to be applied to each of the thermoelement readings on the *outside* of the bulb, integrated from the readings of the auxiliary elements as described on page 119; in the third column is given the corresponding correction in microvolts. In the fourth column are the readings of the standard elements on the *outside* of the bulb, corrected as above mentioned. In the fifth column are the readings of the same thermoelements at the fixed point in question, as obtained in the melting or freezing of metal or salt; these figures usually represent the mean of a considerable number of determinations.

In the sixth and seventh columns are the corresponding figures for the element *inside* of the bulb. In this case, however, no correction has been applied to the reading of the element, since, being located practically at the center of the bulb, it might be expected to represent the mean temperature of the entire volume of the bulb.

In the eighth and ninth columns are the temperatures of the fixed points derived from the preceding four columns. In the last column is given the weight assigned to each measurement. In assigning these weights the number of standard thermoelements used, the amount of variation in p_0 , and other incidental variables were taken into consideration.

As has been pointed out on page 116, the relative weights to be assigned to the inside and outside elements are different at

different temperatures; (1) on account of the difference in contamination, and (2) on account of the fact that the inside element is subject to the influence of conduction and radiation from below. The weights assigned were as follows:

Temperatures	Outside Element	Inside Element
400–1100°	3	1
1100–1300°	2	1
1300–1550°	1	1

The final weighted mean of the inside and outside elements is given at the head of each section of the table.

In the last section of the table are given various points which were determined to aid in interpolating between the fixed points by means of the thermoelement.

The only comment which need be made here on the data in Table VIII concerns the figures given under the heading "copper point." In this section of the table, the values derived at the two different initial pressures (217–221^{mm} and 346–347^{mm}) are quoted separately in order to bring out the fact that the difference between the temperatures obtained from these two pressures is less than the experimental error. In the other sections of the table the data obtained at the two pressures are not separately arranged. Above the copper point only the low pressure was used, as the high pressure would have exceeded the range of the manometer.

The significance of the comparison between the inside-and outside-wound furnaces, which appears in the first half of the section on the copper point, has been commented on elsewhere (see p. 106).

5. Interpolation Between the Fixed Points.

The preparation of formulae to represent the relation between the temperature defined by the gas thermometer and the electromotive force of a thermoelement has always been a cause of considerable dissatisfaction, both to the maker and the user. The chief reason for this is perhaps the fact that the formulae used have been applicable only to limited portions of the curve and have therefore given no suggestion of physical significance. In the Reichsanstalt publication* the data extended from 300° to 1100° and included several good fixed points (melting points of pure metals) between which no interpolation, however rough, could go far astray. Accordingly, in so far as interpolation was concerned, but little attention required to be given to the formulation of this relation. It was sufficient that a simple formula of the form

$$E = -a + bt + ct^2$$

could be made to represent the observations between 300° and 1100° within the limits of the errors of observation.

* Holborn and Day, 1900, loc. cit.

TABLE VIII—*Temperatures of the Fixed Points.*

Exp. No.	Integrated correction to outside elements		Standard Elements				Temperature		Weight
			Outside Corrected	Fixed Pt.	Inside Uncorrected	Fixed Pt.	By Outside Element	By Inside Element	
	Degr's	M. V.							
Zinc Point. 418.2°									
22	0.0°	0	A 3414	3411	Y 3436	3436	418.1°	418.4°	2
23	−0.3	−3	A 3405	3410.5	Y 3445	3435	418.0	418.4	2
31	0.0	0	A 3410	3410.5	Y 3436	3435	418.3	418.2	2
32	−0.2	−2	A 3402	3410	Y 3425	3434	418.0	418.1	2
50	−0.1	−0.5	A 3413	3411	Z 3384.5	3382	418.2	418.2	3
			D 3405.5	3406			418.4		
73	−0.2	−2	A 3401	3413.5	Z 3370	3382	418.4	418.3	4
			E 3417	3429			418.3		
			F 3412	3429			418.8		
			G 3414	3429			418.6		
			418.5	418.3					
Weighted Mean,							418.2°	418.3°	
Antimony Point. 629.2°									
24	−0.1	−1	A 5509	5503	Y 5550	5546	629.2°	629.4°	2
25	−0.5	−5	A 5496	5503	Y 5529	5545	629.0	629.9	2
33	−0.1	−1	A 5513	5503	Y 5553	5544	629.2	629.3	2
34	−0.5	−5	A 5505	5503	Y 5537	5543	629.1	629.9	2
52	−0.5	−5	A 5505	5503	Z 5463	5460	629.6	629.1	2
			D 5490	5492			629.2		
74	−0.2	−2	A 5514	5504	Z 5461	5461	628.2	629.1	4
			E 5533	5530			628.8		
			F 5526	5530			629.5		
			G 5527	5530			629.4		
			629.0	629.1					
87	−0.3	−3	F 5517	5530	Z 5437	5461	628.9	629.9	4
			E 5517	5530			628.9		
			A 5481	5504			629.9		
			G 5513	5530			629.3		
			629.2	629.9					
Weighted Mean,							629.1°	629.5°	
Silver Point. 960.0°									
6	+0.8	+9	W9070	9057	X 9100	9071	959.4°	958.0°	1
26	−0.3	−3	A 9087	9083	Y 9159	9141	959.9	958.6	2
27	−0.8	−9	A 9066	9083	Y 9119	9141	959.9	960.4	2
35	−0.7	−8	A 9079	9082	Y 9142	9141	959.7	959.4	1
36	−0.1	−1	A 9097	9082	Y 9163	9141	959.4	958.7	1
41	−0.3	−3	A 9083	9081	Y 9156	9141	959.6	958.5	2
42	−0.8	−9	A 9076	9081	Y 9131	9141	959.3	959.7	2
63	−0.6	−7	A 9079	9084	Z 9010	9019	960.7	961.1	2
			D 9048	9058			961.2		
			960.9	961.1					

TABLE VIII—(Continued)

Exp. No.	Integrated correction to outside elements		Standard Elements				Temperature		Weight
			Outside Corrected	Fixed Pt.	Inside Uncor- rected	Fixed Pt.	By Outside Element	By Inside Element	
	Degr's	M. V.							
Silver Point—(Cont.)									
68	−0.7	−8	A 9080 D 9051	9085 9058	Z 9013	9019	960.3° 960.4 960.4	960.3°	2
76	−0.2	−2	A 9088 E 9112 F 9097 G 9106	9082 9113 9113 9111	Z 9002	9018	959.2 959.7 961.2 960.2 960.1	961.2	4
81	+0.3	+3	F 9132 E 9131 A 9083 G 9125	9113 9113 9082 9111	Z 9015	9018	959.5 959.6 961.1 960.0 960.0	961.5	4
88	+0.3	+3	F 9143 E 9139 A 9093 G 9135	9113 9113 9082 9112	Z 9026	9018	959.0 959.4 960.7 959.6 959.7	960.1	4
Weighted Mean,							959.9°	960.2°	
Gold Point, 1062.4°									
64	−0.3	−3	A 10262 D 10226	10265 10233	Z 10178	10193	1062.4° 1062.8 1062.6	1063.4°	2
69	−0.4	−4	A 10253 D 10217	10266 10234	Z 10169	10193	1061.4 1061.7 1061.6	1062.3	2
77	−0.3	−3	A 10255 E 10282 F 10263 G 10276	10263 10295 10296 10294	Z 10161	10193	1061.2 1061.6 1063.4 1062.1 1062.1	1063.3	4
82	+0.4	+4	F 10303 E 10304 A 10256 G 10296	10296 10295 10263 10294	Z 10181	10193	1061.9 1061.8 1063.1 1062.4 1062.3	1063.6	4
Weighted Mean,							1062.2°	1063.2°	
Copper Point, 1082.6° (Lower Pressure, p ₀ =217–221 ^{mm})									
2	+1.2	+14	W10457	10478	X 10491	----	1081.7	----	1
9	+1.0	+12	W10495	10478	X 10555	----	1082.2	----	1
11	+1.2	+14	W10487	10478	X 10512	----	1083.1	----	1
18	+0.7	+8	A 10510	10502	Y 10612	10573	1082.2	----	2
19	−0.4	−5	A 10501	10502	Y 10584	10573	1082.0	1081.0	3

TABLE VIII—(Continued)

Exp. No.	Integrated correction to outside elements		Standard Elements				Temperature		Weight
			Outside Corrected	Fixed Pt.	Inside Uncor- rected	Fixed Pt.	By Outside Element	By Inside Element	
	Degr's	M. V.							
Copper Point (Lower Pressure)—Cont.									
20	−0·8	− 9	A 10488	10502	Y 10555	10573	1082·1°	1082·5°	3
28	−0·3	− 4	A 10512	10501	Y 10593	10573	1082·1	1081·4	3
29	−0·9	−10	A 10494	10501	Y 10556	10573	1082·2	1083·0	3
37	−0·6	− 7	A 10504	10501	Y 10576	10573	1082·0	1082·0	2
38	−0·3	− 4	A 10509	10500	Y 10585	10573	1082·2	1081·9	2
39	+0·7	+ 8	A 10517	10500	Y 10617	---	1082·3	---	2
43	−0·3	− 4	A 10512	10500	Y 10595	10573	1082·2	1081·3	3
44	−0·9	−10	A 10501	10499	Y 10568	10573	1082·0	1082·6	3
45	+0·6	+ 7	A 10515	10499	Y 10617	----	1082·3	----	2
89	+0·5	+ 6	F 10546	10534	Z 10423	10432	1081·8	1083·1	4
			E 10544	10534			1081·9		
			A 10496	10503			1083·4		
			G 10538	10533			1082·4		
							1082·4		
							1082·2		
							1082·6		
							1083·0		
							1083·0		
							1082·7		
126*	+0·4	+ 5	E 10631	10534	C 10567	10470	1082·5	1082·5°	4
			F 10627	10534			1082·2		
			G 10621	10533			1082·6		
			H 10623	10535			1083·0		
							1083·0		
							1082·7		
							1082·5		
							1082·5		
							1082·5		
							1082·5		
Weighted Mean							1082·2°	1082·2°	
Copper Point—Cont. (Higher Pressure. $p_0=346\text{--}347^{\text{mm}}$)									
60	−0·7	− 8	A 10500	10502	Z 10422	10432	1083·4°	1084·1°	1
			D 10465	10470			1083·6		
65	−0·8	− 9			Z 10420	10432	1083·5	1083·9	2
			A 10502	10503			1083·0		
			D 10465	10471			1083·4		
70	−0·3	− 4			Z 10444	10432	1083·2	1081·8	2
			A 10508	10504			1082·4		
			D 10475	10472			1082·6		
78	−0·1	− 1			Z 10404	10432	1082·5	1083·7	4
			A 10502	10503			1081·4		
			E 10528	10534			1081·8		
			F 10509	10534			1083·4		
			G 10522	10533			1082·3		
83	+0·1	+ 1			Z 10403	10432	1082·2	1084·6	4
			F 10535	10534			1082·1		
			E 10535	10534			1082·1		
			A 10488	10503			1083·5		
			G 10527	10533			1082·7		
							1082·6		

* Made with outside-wound furnace. See page 106.

TABLE VIII—(Continued)

Exp. No.	Integrated correction to outside elements		Standard Elements				Temperature		Weight
			Outside Corrected	Fixed Pt.	Inside Uncor- rected	Fixed Pt.	By Outside Element	By Inside Element	
	Deg'rs	M. V.							
Copper Point—Cont. (Higher Pressure)									
84	+0.7	+ 8	F 10544 E 10542 A 10493 G 10533	10534 10534 10503 10533	Z 10426	10432	1082.0° 1082.3 1083.8 1083.0 1082.8	1083.5	4
Weighted Mean,							1082.7°	1083.7°	
Mean of 2 pressures,							1082.5°	1082.9°	
Diopside Point. 1391.2°									
96	0.0	0	E 14227 F 14222 G 14245 H 14251	14228 14229 14229 14231	Z 14121	14103	1392.1° 1392.5 1390.7 1390.4 1391.4	1390.5°	1
97	+1.0	+13	E 14260 F 14254 G 14287 H 14295	14228 14229 14229 14231	Z 14156	14103	1392.4 1393.0 1390.4 1389.9 1391.4	1390.5	1
99	−0.1	− 1	E 14213 F 14195 G 14215 H 14212	14228 14229 14229 14231	Z 14099	14103	1394.5 1396.0 1394.4 1394.8 1394.9	1393.7	1
100	+0.7	+ 9	E 14251 F 14244 G 14268 H 14273	14228 14229 14229 14231	Z 14156	14103	1394.4 1395.0 1393.1 1392.9 1393.8	1391.8	1
103	−0.4	− 5	E 14211 F 14204 G 14217 H 14230	14228 14229 14229 14231	Z 14124	14103	1392.5 1393.1 1392.1 1391.2 1392.2	1389.4	3
104	+1.0	+13	E 14242 F 14212 G 14249 H 14262	14228 14229 14229 14231	Z 14155	14103	1392.5 1394.9 1392.0 1391.1 1392.6	1389.3	3

TABLE VIII—(*Continued*)

Exp. No.	Integrated correction to outside elements		Standard Elements				Temperature		Weight
			Outside Corrected	Fixed Pt.	Inside Uncor- rected	Fixed Pt.	By Outside Element	By Inside Element	
	Degr's	M. V.							
Diopside Point—(Cont.)									
106	−0·6	− 8	E 14228 F 14225 G 14233 H 14243	14228 14229 14229 14231	Z 14123	14103	1391·7° 1392·0 1391·3 1390·7 1391·4	1390·0°	2
107	+0·9	+12	E 14248 F 14237 G 14245 H 14252	14228 14229 14229 14231	Z 14152	14103	1391·9 1392·8 1392·2 1391·8 1392·2	1389·4	2
130	−0·6	− 7	E 14243 F 14241 G 14249 H 14239	14228 14230 14230 14228	C 14146	14153	1390·2 1390·6 1389·9 1390·6 1390·3	1392·0	3
Weighted Mean,							1392·0°	1390·4°	
Nickel Point. 1452·3°									
109	+0·7	+ 8	E 15028 H 15027	14977 14980	Z 14903	14850	1451·2° 1451·6 1451·4	1451·1°	1
111	0	0	E 14980 H 14978	14977 14980	Z 14867	14850	1453·2 1453·7 1453·5	1452·1	2
112	+0·9	+11	E 14971 F 14958 H 14991	14977 14978 14980	Z 14872	14850	1453·8 1454·9 1452·4 1453·7	1451·5	2
123	−0·6	− 7	E 14984 F 14989	14977 14978	A 14982	14945	1454·3 1453·9 1454·1	1451·8	2
124	+0·8	+10	E 14989 F 14994	14977 14978	A 14996	14945	1454·6 1454·3 1454·5	1451·5	1
133	−0·3	− 4	E 14954 F 14958 G 14955 H 14946	14977 14976 14981 14977	C 14882	14898	1451·9 1451·5 1452·2 1452·5 1452·0°	1451·3°	4
Weighted Mean,							1453·0°	1451·6°	

TABLE VIII—(Continued)

Exp. No.	Integrated correction to outside elements		Standard Elements				Temperature		Weight
	Degr's	M. V.	Outside Corrected	Fixed Pt.	Inside Uncor-rected	Fixed Pt.	By Inside Element	By Outside Element	
Cobalt Point. 1489·8°									
115	+0·1	+ 1	E 15390	15439	A 15357	15409	1488·7°	1488·9°	3
			F 15375	15435			1489·6		
116	+1·4	+ 17	E 15428	15439	A 15421	15409	1490·5	1488·6	3
			F 15434	15435			1489·7		
			G 15435	15441			1490·1		
							1490·1		
118	-0·5	- 6	E 15385	15439	A 15382	15409	1491·7	1489·6	2
			F 15383	15435			1491·6		
			G 15393	15441			1491·3		
							1491·5		
120	-0·4	- 5	E 15381	15439	A 15379	15409	1491·7	1489·4	1
			F 15371	15435			1492·1		
			G 15363	15441			1493·3		
							1492·7		
121	+0·7	+ 9	E 15406	15439	A 15412	15409	1492·0	1489·1	1
			F 15405	15435			1491·8		
			G 15398	15441			1492·8		
							1492·2		
							1490·6°		
Palladium Point. 1549·2°									
134	-0·7	- 9	E 16151	16143	C 16075	16058	1549·5°	1548·8°	
			F 16161	16138			1548·3		
			G 16139	16145			1550·6		
			H 16147	16145			1550·1		
							1549·6°		
Anorthite Point. 1549·5°									
134	-0·7	- 9	E 16151	16148	C 16075	16060	1549·9°	1549·0°	
			F 16161	16141			1548·6		
			G 16139	16148			1550·9		
			H 16147	16145			1550·0		
							1549·9°		
Interpolation Points.									
49	-0·1	- 1	A 2486	2492	Z 2462	2465	320·2°	319·9°	
			D 2482	2486			320·0		
Mean for cadmium,							320·1	525·1	
51	0·0	0	A 4451	4450	Z 4413	4417	320·0°		
			D 4439	4442			524·6		
			Mean for A = 4450,						
							524·8	525·1	
							524·9°		

TABLE VIII—(Concluded)

Exp. No.	Integrated correction to outside elements		Standard Elements				Temperature		Weight
			Outside Corrected	Fixed Pt.	Inside Uncor- rected	Fixed Pt.	By Inside	By Outside	
	Degr's	M. V.					Element	Element	
<i>Interpolation Points—(Cont.).</i>									
62	0.0	0	A 7895 D 7869	7900 7881	Z 7829	7848	854.2° 854.9 854.6	855.5°	
67	−0.2	−2	A 7883 D 7859	7900 7881	Z 7820	7848	854.0 854.5 854.3 854.7°	855.0	
Mean for A = 7900,									
128	−0.2	−2	E 12004 F 12001 G 12008 H 12000	12000 12001 12001 12003	C 11914	11928	1206.3 1206.7 1206.1 1206.9 1206.5 1206.0 1205.3 1205.8 1206.8 1206.0 1206.4°	1207.8	
132	+0.1	+1	E 11947 F 11952 G 11950 H 11941	12000 11097 12001 12003	C 11887	11928	1206.0 1205.0 1205.0	1205.0	
Mean for E = 12000,									
129	−0.6	−5	E 13107 F 13102 G 13110 H 13101	13100 13101 13101 13103	C 13007	13028	1297.4 1297.9 1297.2 1298.1 1297.7 1298.5°	1299.3	
Mean for E = 13100,									

(Continued from p. 140.)

If the investigator's responsibility could be made to end with the representation of his own observations, no serious difficulty would arise, but such a formula when published is placed in the hands of many who do not realize that no physical significance was attached to the formula by its author and that its extrapolation in either direction would be fraught with grave danger. A mere inspection of the equation is sufficient to show that the electromotive force does not become zero for zero temperature, thereby immediately proving that extrapolation downward does not correspond to the observed readings of the thermoelement. In the Reichsanstalt equation this constant term was in fact sufficiently large to lead to absurdities if the extrapolation was continued far below 300°.

Notwithstanding the warning contained in this situation, extrapolation upward of the thermoelectric curve has been

employed almost universally for the determination of temperatures above 1100° , not only for direct determinations of temperature with the thermoelement itself, but also for the calibration of optical pyrometric apparatus. The absence of absolute determinations in this region has left this practice in undisturbed security until recently, when some doubt has been thrown upon the validity of irresponsible upward extrapolation by various observations. (1) The increase in the accuracy now attainable with the optical pyrometer has given an independent thermal scale comparable with that of the thermoelement and overlapping the same region. The two curves have not been found to correspond. (2) Experimental determinations of the melting point of platinum by continuing observations of the thermoelement up to a point where a portion of its platinum wire melts, have been undertaken in the national laboratories of Germany, England and the United States, and have yielded a value measured upon the extrapolated thermoelectric curve of about 1710° . The agreement in the different determinations was good and the result found general acceptance for a time. More recently, Holborn and Valentiner have made successful measurements with the gas thermometer at the temperature of melting palladium, and although high accuracy was not attempted, it became clear that the palladium point obtained by extrapolating with the thermoelement was much too low and by inference the platinum point also, for the various optical methods give opportunity for a very good determination of the temperature difference between the melting points of the two metals. The most recent estimates of the platinum melting point obtained in this way place it between 1750° and 1775° , indicating that the upward extrapolation with the thermoelement has given rise to an error of about 50° at the platinum point.

The data obtained in the present investigation throw much light upon this situation. If we take the observations of our series over the range covered by the Reichsanstalt scale (300° to 1100°) and write an equation for these of the same type as that used at the Reichsanstalt, it will read,

$$E = -302 + 8.2356t + .0016393t^2$$

and this equation will reproduce the temperatures of the standard melting points which fall in this region with a maximum error of 3 microvolts, an accuracy far within the errors of observation. But if we extrapolate this curve in accordance with the general practice above described, and compare the resulting electromotive forces with our observations between 1100° and

1550°, a somewhat startling surprise awaits us. Although the curve below the copper point is a practically perfect reproduction of the observations, it diverges from the gas thermometer scale at the melting point of palladium by 245 microvolts, which represents a temperature error of nearly 20°. This comparison is made in the table below :

	Temperature	Observed Microvolts	Calculated Microvolts	Observed— Calculated Microvolts
Zinc	418.2°	3429	3429	0
Antimony ...	629.2	5530	5530	0
Silver	960.0	9113	9115	—2
Gold	1062.4	10295	10298	—3
Copper	1082.6	10534	10534	0
<i>Extrapolation.</i>				
	1207.1	12000	12027	—27
	1298.8	13100	13161	—61
Diopside	1391.2	14228	14338	—110
Nickel	1452.3	14945	15112	—167
Cobalt	1489.8	15439	15608	—169
Palladium ...	1549.2	16143	16388	—245

If, on the other hand, we follow Day and Clement, and represent t as a function of E , using the same data as before, the equation will take the form

$$t = 47.2 + .11297E - 1.3946(10)^{-6}E^2$$

This curve passes through the fixed points below 1100° nearly as accurately as the previous one, and is also quite competent to interpolate temperatures throughout the range of the old standard scale. Extrapolating this in turn up to the palladium point and comparing it with our gas thermometer measurements in the higher region leads to temperatures about 40° too low.

	Observed	Calculated	Observed— Calculated
Zinc	418.2°	418.2°	0°
Antimony ...	629.2	629.3	—0.1
Silver	960.0	960.9	—0.9
Gold	1062.4	1062.4	0
Copper	1082.6	1082.5	+0.1
<i>Extrapolation</i>			
	1207.1	1202.0	+5.1
	1298.8	1287.8	+11.0
Diopside	1391.2	1372.0	+19.2
Nickel	1452.3	1424.0	+28.3
Cobalt	1489.8	1459.0	+30.8
Palladium ...	1549.2	1507.0	+42.2

The untrustworthiness of the present practice of extending thermoelement values obtained below 1100° into the region above that temperature is therefore abundantly demonstrated.*

We were unable to find a simple parabola with which to represent the whole series of observations between 300° and 1550° within the errors of observation. The simplest procedure is therefore to divide the long curve into two parts. This plan is carried out below in the form in which it will probably be found most useful. A parabola passing through zinc, antimony and copper reproduces the results over that temperature range within the errors of observation. A similar parabola through copper, diopside and palladium gives the upper temperatures as accurately as they were measured. These two equations offer a means of safe and convenient interpolation throughout the entire range of the gas thermometer measurements. In this series are included certain gas thermometer measurements given at the end of Table VIII which were made at temperatures between the fixed melting points, for the purpose of checking the interpolation formula, together with a single gas thermometer determination of the cadmium melting point. The temperature 854.1 appears here corrected by -0.6° , since the series, of which this measurement formed a part, showed a systematic difference of about this amount from the final average of antimony and silver, which lie on either side of this point.

Cadmium to Copper

$$E = -302 + 8.2356t + .0016393t^2$$

	Temperature	Observed Microvolts	Calculated Microvolts	Observed— Calculated Microvolts
Cadmium	320.0°	2504	2501	+3
Zinc	418.2	3429	3429	0
	524.9	4470	4472	-2
Antimony	629.2	5530	5530	0
	854.1	7927	7928	-1
Silver	960.0	9113	9115	-2
Gold	1062.4	10295	10298	-3
Copper	1082.6	10534	10534	0

Copper to Palladium

$$E = -1941 + 11.1746t + .00032161t^2$$

Copper	1082.6	10534	10534	0
	1207.1	12000	12010	-10
	1298.8	13100	13112	-12
Diopside	1391.2	14228	14228	0
Nickel	1452.3	14977	14967	+10
Cobalt	1489.8	15439	15421	+18
Palladium	1549.2	16143	16143	0

* For an account of some of the dangers of careless interpolation, see Day and Clement, loc. cit., p. 453.

It is possible to write a cubic equation which will reproduce the entire series from zinc to palladium without error greater than the normal accuracy of the observations themselves. The equation offered makes no pretensions to a least square solution with balanced residuals, but is arranged so that the greatest uncertainties are found in that portion of the curve where the greatest experimental error lies. The coefficients were rounded off for convenience of computation.

Cadmium to Palladium

$$E = -169 \cdot 7 + 7 \cdot 57t + 0 \cdot 002648t^2 - 0 \cdot 0000004724t^3$$

	Temperature	Observed Microvolts	Calculated Microvolts	Observed— Calculated Microvolts
Cadmium	320·0°	2504	2509	— 5
Zinc	418·2	3429	3425	+ 4
	524·9	4470	4466	+ 4
Antimony	629·2	5530	5525	+ 5
	854·1	7929	7934	— 5
Silver	960·0	9113	9121	— 8
Gold	1062·4	10295	10296	— 1
Copper	1082·6	10534	10530	+ 4
	1206·4	12000	11988	+ 12
	1298·5	13100	13091	+ 9
Diopside	1391·2	14228	14215	+ 13
Nickel	1452·3	14977	14963	+ 14
Cobalt	1489·8	15439	15424	+ 15
Palladium	1549·2	16143	16157	— 14

6. *Analysis of Metals.* (By E. T. Allen.)

The object of these analyses was primarily, of course, to decide whether the metals should be used or rejected for the temperature scale, and those selected were examined very carefully so that in the future, when more is known about the specific lowering which the various impurities produce on the melting point, corrections may be made if desirable.

The accuracy of the determinations is problematical. There is of course the possibility of increased solubility of difficultly soluble compounds in the comparatively concentrated solutions of the metals from which the impurities have to be precipitated, viz., 5 to 6 g. in 250^{cc} volume. Also, when it is necessary to separate the bulk of the metal by precipitation from the impurities, as it sometimes is, one cannot be sure that the impurity sought is not occluded by the precipitates. In most cases, the latter source of error is probably the more serious. Only methods worked out synthetically with materials laboriously prepared could decide these questions. Large quantities of metal, 25 to 100 g., were generally taken for analysis, and

since the impurities were weighed to the tenth of a milligram, the results are generally stated to the ten-thousandth of a percent. This does not mean that the results are considered accurate to this figure. The variation in successive determinations comes in the thousandths, so that the fourth decimal place may have about as much value as the second in an ordinary analysis. Great pains have been taken to purify precipitates, often by many precipitations, so that in all cases the figures given may be regarded as minima. In all cases, too, I have endeavored to avoid missing anything, by repeating every process, rejecting no precipitate or solution until it was decided that nothing more was to be gotten from it. In any reasonable case of suspicion, blank determinations were made with the reagents.*

Heraeus' Palladium.

The palladium was naturally suspected to contain other metals of the platinum group. It is well known that the separation of these metals is a problem of unusual difficulty. The plan here was therefore to precipitate most of the palladium from solution as one of its characteristic compounds and, while the filtrate was reserved for impurities, to redissolve and again precipitate the metal as another characteristic compound. In this way it was hoped that those impurities which were retained by the first precipitate would not be occluded by the second. The sheet metal was first cut into shavings on a milling machine which was especially cleaned for the purpose. Then the shavings were boiled a short time with dilute hydrochloric acid to remove any iron from the surface, washed and dried. After an unsuccessful endeavor to dissolve the palladium in nitric acid (insoluble brown hydroxide (?) always formed), it was dissolved in aqua regia and rid of nitric acid by successive evaporations with excess of hydrochloric acid. It was then dissolved in dilute hydrochloric acid and diluted further to about 1 l. Ammonia was added in excess.† A precipitate came down and redissolved on warming—all but a little ferric hydroxide which was filtered off. The filtrate was then evaporated again to about 250 cc, diluted and precipitated with stirring, by dilute hydrochloric acid. The voluminous precipitate of $\text{PdCl}_2 \cdot 2\text{NH}_3$ was now filtered and washed on a Büchner porcelain funnel, using suction. The filtrate we will call "solution A." The precipitate was then dried and

* After considerable experience in the examination of these "pure" metals, the writer has reached the conclusion that a 10 g. portion, in the great majority of cases, will give as satisfactory results as a larger portion and with far less labor.

† E. F. Smith and H. F. Keller, Amer. Chem. Jour., xiv, 423, 1892.

ignited in a large porcelain crucible. The resulting metal was dissolved in aqua regia and freed of nitric acid. This solution was diluted and precipitated by potassium iodide, and the filtrate—"solution B"—removed as above.

From solutions A and B, separately, the platinum metals were first removed by long boiling with ammonium formate. The metal—1 to 2 g. in weight, mostly palladium—was filtered and the filtrate and washings were examined further for other heavy metals by the usual methods.

Separation of the Palladium from the Platinum Metals.—Considering now the ammonium formate precipitate, Erdmann and Makowka* have obtained satisfactory separations of palladium from platinum and iridium by treating the solution of the mixed chlorides with acetylene. Palladium comes down as acetylide and the other metals are unprecipitated. I found also that *rhodium* solutions even on heating were not precipitated by acetylene. As for osmium, the ease with which it oxidizes and the high volatility of its oxide makes its elimination, in the process of preparing the palladium, fairly certain. Ruthenium, the rarest element among the platinum metals, need hardly be looked for; still it was sought for in the iridium found. The acetylene method was used, for lack of a safer one, though very tedious. In solutions at all concentrated, I find the palladium ceases to precipitate long before it is entirely removed from solution. Perhaps this is due to the accumulation of acid liberated in the process. At least, when the solution is separated from the acetylide, evaporated and diluted again, acetylene brings down another portion. After five or six operations, a residual solution was obtained on which acetylene had no further action. The acetylide was now carefully ignited with a little ammonium nitrate, the metal redissolved, and the whole process repeated. The residual solution was then added to the first and from it NH_4Cl brought down platinum. In the chlor-platinate no iridium was found. It was ignited and the metal was entirely soluble in a few drops of aqua regia. It was again precipitated with NH_4Cl and finally weighed as platinum— $\text{Pt} = 1.6 \text{ mg.} = 0.007 \text{ per cent.}$ No rhodium was found in the filtrate. In the attempt to dissolve in aqua regia the several portions of metal formed by igniting the acetylide, tiny insoluble residues accumulated. These were fused with KHSO_4 , which, as is well known, dissolves palladium and rhodium but not iridium or platinum if the temperature is kept low. The soluble portion was dissolved in water and precipitated with ammonium formate. It turned out to be palladium, since it was precipitated by potassium iodide and no trace of rhodium was found.

* Zeitschr. anal. Chemie, xlv, 146, 147, 1907.

The portion insoluble in KHSO_4 was freed from silica (which came from the dish) by $\text{HCl} + \text{HF}$, ignited, and weighed. $\text{Ir} + [\text{Ru}] = 1.9 \text{ mg.} = 0.008 \text{ per cent.}$ When fused with $\text{K}_2\text{CO}_3 + \text{KNO}_3$, some blue insoluble IrO_3 was formed, but the fusion showed no yellow color, and in view of the minute quantity of material, it was not thought worth while to search more carefully for ruthenium.

The final precipitate of palladium acetylide was changed to chloride, diluted, and saturated with SO_2 for gold, but none appeared.

Nothing else was found in the metal except a trace of copper. The iron found earlier had to be reprecipitated several times from chloride solution by ammonia to get rid of palladium. The precipitate was finally transformed into sulphate and determined volumetrically.— $\text{Fe} = 2.6 \text{ mg.} = 0.10 \text{ per cent.}$

Analysis of Palladium.

Au.....	none
Ru.....	none
Rh.....	none
Pt.....	0.007%
Ir.....	0.008%
Cu.....	trace
Zn.....	doubtful trace
Fe.....	0.10%
	<hr/>
	0.025%

Kahlbaum's Electrolytic Nickel.

Two 50 gram portions were dissolved separately in measured quantities of nitric acid and then carried to white fumes with excess of sulphuric acid. Both portions were then dissolved in water and filtered. There was a small dark residue which was washed thoroughly and extracted with aqua regia, leaving a little silica from the dish. The yellow chloride obtained was freed from nitric acid, saturated with SO_2 and left to stand. *No gold.* Changed to chloride again and tested with caustic soda and H_2O_2 . *Still no gold.* Acidified and reprecipitated with NH_4Cl , a characteristic yellow precipitate was obtained. Confirmed by dissolving the chlor-platinate in hot water and precipitating by hydrogen. $\text{Pt} = 2.3 \text{ mg.} = 0.0023 \text{ per cent.}$ The main solution was then precipitated by H_2S ($v = 2 \text{ l.}$). The small black precipitate obtained was worked over for gold and platinum with the above.

Other heavy metals were tested for in the ordinary way. $0.2 \text{ mg. PbSO}_4 = \text{about } 0.1 \text{ mg. Pb.}$ $\text{Cu} = 52.3 \text{ mg.} = 0.0523 \text{ per cent.}$

Ammonium Sulphide Group.—The voluminous solution was now freed from hydrogen sulphide by evaporation, some

ammonium persulphate was added and a stream of air passed through the solution for some time. *No manganese.* $\text{Fe}_2\text{O}_3 = 6.1$ mg., after repeated precipitation. $\text{Fe} = 4.2$ mg. Repeated efforts were made to separate zinc with H_2S on the principle of the lower solubility of ZnS in dilute acids, but without satisfaction. First I tried to precipitate a small fraction of the nickel, hoping to get all the zinc with it. The volume of the solution was about 5 l. But unless so much acid was added that strong doubts were entertained of recovering any zinc that might be present, the fraction of the nickel precipitate was far too great. Again, all the nickel was precipitated and the precipitate was digested with cold 10 per cent solution of hydrochloric acid. Here one had to fear either the failure to remove the zinc or the removal of too much nickel to handle without so many precipitations that a small quantity of zinc would probably be lost. It is doubtful whether we have any method which will give very small amounts of zinc in metallic nickel.

The whole solution was now tested for cobalt as follows: It was freed from H_2S by evaporation, acidulated with HCl and precipitated by α -nitroso- β -naphthol in 50 per cent acetic acid. This was added in several portions. After long standing the precipitate was collected and washed. The voluminous precipitate was very cautiously burned in a capacious porcelain crucible. Much tar was formed. The residual oxide was dissolved in nitric acid and the cobalt separated from nickel by KNO_2 in the usual way. The potassium cobalto-nitrite was finally decomposed by sulphuric acid and precipitated electrolytically from ammoniacal solution. $\text{Co} = 101.4$ mg. + 4.9 mg. recovered from filtrate and weighed as sulphate. Total = 0.1063 per cent. Fe and Co were also determined in a separate 10 g. portion of metal. $\text{Fe}_2\text{O}_3 = 0.7$ mg. $\text{Fe} = 0.49$ mg. = 0.0049 per cent. $\text{Co} = 10.3$ mg. = 0.1030 per cent. A separate 10 g. portion was taken for sulphur. It was dissolved in nitric and evaporated on the water bath. This solution was diluted and precipitated with a slight excess of sodium carbonate. The filtrate was just acidulated, evaporated, and treated with barium chloride. No precipitate.

Analysis of Nickel.

Au	none	Bi	none
Pt	0.0023%	Cd	"
As	none	Zn	none found
Sb	"	Co	0.1063%
Sn	"	Mn	none
Pb	0.0001%	Fe	0.0042%
Cu	0.0523%	S	none
		<hr/>	
		0.165%	

Kahlbaum's Cobalt.

Two 25 g. portions of the metal in the form of powder were dissolved in 150^{cc} water + 35^{cc} concentrated H_2SO_4 . The analysis was quite similar to that of the nickel. In the H_2S group were found: $\text{Cu} = 8.9 \text{ mg.} = 0.0178 \text{ per cent.}$ $\text{PbSO}_4 = 12.9 \text{ mg.}$ $\text{Pb} = 0.0176 \text{ per cent.}$ In the $(\text{NH}_4)_2\text{S}$ group manganese was tested for as in the nickel. None was found. $\text{Fe}_2\text{O}_3 = 0.9 \text{ mg.}$ $\text{Fe} = 0.0006 \text{ per cent.}$ As the tests for Ni and Zn were unsatisfactory, another portion of 25 g. was dissolved in dilute sulphuric acid and precipitated by H_2S . The filtrate from the sulphides was filtered and freed from excess of H_2S by evaporation. Then it was diluted to 1 liter and divided into two portions. Both were neutralized by sodium carbonate. In the one, manganese was sought for by ammonium persulphate. In the other nickel was looked for. A little ammonia was added and then an alcoholic solution of dimethylglyoxime. A precipitate containing much cobalt was obtained. This was worked over for nickel but none was found. For sulphur the method used in the analysis of nickel was followed. $\text{BaSO}_4 = 14.4 \text{ mg.,}$ blank = 5.1 mg., difference = 9.3 mg., $\text{S} = 0.013 \text{ per cent.}$

Analysis of Cobalt.

Ag.....	none	Cu.....	0.0178%
Au.....	"	Bi.....	none
Pt.....	"	Cd.....	"
As.....	"	Zn.....	"
Sb.....	"	Ni.....	"
Sn.....	"	Fe.....	0.0006%
Pb.....	0.0176%	Mn.....	none
		S.....	0.013%
			<hr/>
			0.049%

Aluminum.

Owing to the difficulty of handling this metal, small portions (10 g.) only were taken for analysis. *Heavy metals*, except arsenic and antimony, were sought for in the hydrochloric acid solution by ordinary methods. Only a trace of copper was found.

Phosphorus, Arsenic, and Sulphur.—For these elements, a separate portion was dissolved in caustic alkali in a special apparatus entirely of glass. The vessel was first filled with purified hydrogen and then the alkali was introduced and the gases evolved were passed through silver nitrate solution. At the end, the gases remaining in the vessel were displaced by hydrogen. The precipitated silver was worked over for the different elements. *No As nor Sb.* A separate portion was used for sulphur. $\text{BaSO}_4 = 1.4 \text{ mg.}$ $\text{S} = 0.002 \text{ per cent.}$

Silicon.—10 g. metal were dissolved in a mixture of nitric and sulphuric acids, using a platinum dish. With hydrochloric acid alone nearly all the silicon is lost as hydride. The brown amorphous residue was filtered, washed and fused with sodium carbonate. From the fusion silica was obtained in the usual way. $\text{SiO}_2 = 41.4$ mg. $\text{Si} = 0.194$ per cent. Repetitions gave 0.189 per cent and 0.190 per cent.

Carbon.—10 g. metal were dissolved in NaOH and filtered through glowing asbestos, washed first with water, then with dilute acid and finally with water and dried at 105° . The asbestos and residue were then transferred to a combustion tube and burned in air free from CO_2 . The gases were passed through standard $\text{Ba}(\text{OH})_2$. A considerable precipitate was obtained, while a blank gave no trace. The excess of $\text{Ba}(\text{OH})_2$ was the titrated with standard acid using phenolphthalein as indicator. 5.05 mg. CO_2 found. $\text{C} = 0.014$ per cent. A duplicate in which the metal was dissolved in KOH gave 0.012 per cent.

Iron.—10 g. metal were dissolved in hydrochloric acid, and to the solution was added tartaric acid free from iron. From this solution the iron was precipitated by colorless ammonium sulphide. The precipitate was finally changed to sulphate and determined volumetrically. $\text{Fe} = 4.6$ mg. Blank determination gave 0.3 mg. $\text{Fe} = 0.043$ per cent.

Calcium, Sodium, and Potassium were sought for in the hydrochloric acid solution, by precipitating with ammonia, washing the large precipitate and testing the evaporated filtrate. *No Ca.* Some alkaline chloride was found, but a blank showed that it came from the ammonia, as there was only a difference of 1.6 mg. between the chloride of the blank and that in the determination. *No Na or K.*

Analysis of Aluminum.

As	none	C	0.013%
Sb	"	S	0.002%
P	"	Ca	none
Cu	0.003%	Na	"
Fe	0.043%	K	"
Si	0.190%		
			0.251%

Antimony.

25 g. metal were powdered in an agate mortar and treated with 35 per cent HNO_3 on the steam bath. As soon as the reaction was practically complete, the antimonious acid was extracted

with hot dilute nitric acid, transferred to a filter and washed with water. The filtrate and washings were then evaporated to dryness with hydrochloric acid, while the antimonie acid was digested repeatedly with yellow sodium sulphide till the soluble portion was dissolved. The residue, after a little washing, was dissolved in nitric acid, evaporated to dryness, freed from nitric by hydrochloric acid, and the chlorides united with the first extract. The whole was precipitated by hydrogen sulphide. The washed sulphides were then extracted with colorless ammonium sulphide. From this solution the sulphides were thrown down by acid, filtered and washed. Then they were dissolved in hot dilute caustic potash. The solution was boiled with perhydrol for complete oxidation, and arsenic sought for by Fischer's method, viz., reducing by ferrous ammonium sulphate and distilling in a current of hydrochloric acid gas. *No As.*

A separate portion of 5 g. was taken for tin. McCay's method was tried.* $\text{SnO}_2 = 1.3 \text{ mg.}$ $\text{Sn} = 1.0 \text{ mg.} = .02 \text{ per cent.}$

A separate portion of 25 g. was used for sulphur. The metal was oxidized by nitric acid as before, and the soluble portion separated and evaporated. The residue was then heated with a small excess of sodium carbonate and filtered. The residue was also boiled out several times with sodium carbonate solution. The two solutions were then acidified with hydrochloric acid and treated with barium chloride. The portion soluble in nitric acid gave a slight precipitate, which was further purified, after the usual washing and drying, by fusion with sodium carbonate. The water extract containing the soluble sulphate was acidified and precipitated a second time. $\text{BaSO}_4 = \text{trace.}$

Analysis of Antimony.

As.....	none	Cd	none
Sn.....	0.02 (?)	Ni	"
Ag.....	none	Co	"
Pb.....	trace (?)	Mn.....	"
Cu	0.004	Zn	"
Bi.....	none	Fe.....	0.007%
		S	trace (?)
			<hr/>
			.031%

In the following table, the results of these and previous† analyses of metals for the temperature scale are summarized:

* Private communication.

† Day and Clement, loc. cit., p. 454.

Summarized Analyses of Metals.*

Impurities stated in fractions of 1%	Metals							
	Palla- dium	Cobalt	Nickel	Copper	Silver	Alum- inum	Antimony	Zinc
Pt	0·007	none	·0023	·0011†	·0001			
Ir	·008							
Rh	none							
Ru	"							
Au	"	none	none	none	·0005			
Se				"				
Te				"				
As		none	none	"	none	none	none	none
Sb		"	"	"	"			·002
Sn		"	"	"	"		·02 (?)	
Hg					"		none	
Ag		none	none	·0006			"	none
Pb	none	·0176	·0001	none	·0008			·051
Bi	"	none	none	"	none		none	none
Cu	trace	·0178	·0523		trace	·003	·004	none
Cd	none	none	none	none	none		none	·004
Ni	"	"		"	"	none	"	none
Co	"		·1063	"	"	"	"	"
Fe	·010	·0006	·0042	·0038	·0011	·043	·007	·006
Zn	trace ?	none ?	none ?	·0007	none		none	
Mn		none	none				"	
Si				none		·190		none
C					·0003	·013		
S		·013	none	·0020	·0004	·002		none
P						none		
Ca						"		
Na						"		
K						"		
Total	·025	·049	·165	·008	·003	·251	·031	·063

* A blank opposite any impurity means that it was not looked for.

† Means platinum metals.

7. Conclusion.

It is now something over five years since the Geophysical Laboratory took up the task of redetermining the absolute temperature scale from 300° to 1100° with the nitrogen thermometer, and of extending it, if it should prove practicable to do so, to 1600° C., for it is in this upper region that most of the mineral relations which it is the chief purpose of the laboratory to study are found. Two preliminary publications have been made during the investigation. One, a brief summary of preliminary work up to 1100°, was given before the National Academy of Sciences and the American Physical Society in April, 1907,* the second covered the same ground at con-

* Abstract, Phys. Rev. xxiv, 531, 1907.

siderable length in 1908.* The present paper extends the observations to 1550° , and completes the work contemplated under the original plan.

No attempt will be made to offer an inclusive summary of the whole investigation. It is a record of experimental measurements covering an unusually wide range of details which do not admit of brief classification. The errors which have heretofore been present in measurements with the nitrogen thermometer have been reduced by the present investigation to about one-fourth their former magnitude and the certainty of their evaluation is at least proportionately increased.

The chief source of present uncertainty is the temperature distribution over the surface of the bulb in an air bath. No indication of a limit to the temperature attainable with the nitrogen thermometer or to its ultimate accuracy was discovered during the present investigation.

The magnitudes of the errors, and their effects on the temperature, are summarized in Table IV, page 129. The determinations of the expansion coefficient of the bulb material (80 Pt. 20 Rh) are summarized on pp. 131–132.

The melting temperatures of the metals and salts which have been used as fixed points to establish the new scale are brought together in the table below, together with the conditions under which the determinations were made. The generally accepted Reichsanstalt scale is printed beside it for convenient comparison. The analyses of the metals are summarized on p. 159.

To this table has been added a new estimate of the melting temperature of platinum, of which we could make no direct determination. Its general acceptance and availability as a fixed point of reference, and the wide disagreement between the direct determinations heretofore made of it, form a sufficient reason for its inclusion. The estimate is arrived at in this way: There is a remarkably close agreement between independent determinations of the *temperature interval* between the melting points of palladium and platinum:

Nernst and von Wartenberg†	204°
Holborn and Valentiner (at the Reichsanstalt)‡	207°
Waidner and Burgess (at the Bureau of Standards)§	207°

If we therefore simply add 206° to our determination of the palladium point, we obtain 1755° as the melting point of pure platinum, with an absolute error of perhaps no more than $\pm 5^{\circ}$. The table follows:

* This Journal (4), xxvi, 405, 1908.

† W. Nernst and H. von Wartenberg, Ber. d. Deutsch. phys. Ges., iv, pp. 48, 146, 1906.

‡ L. Holborn and S. Valentiner, Ann. d. Phys. (4), xxii, 1, 1907.

§ C. W. Waidner and G. K. Burgess, Bull. Bur. Standards, iii, p. 163, 1907.

Substance	Point	Atmosphere	Crucible	Temperature	The Reich- sanstalt Scale
Zinc	Melting and freezing	Air	Graphite	418.2° ± 0.3	419.0°
Antimony	Do.	Carbon monoxide	Do.	629.2 ± 0.5	630.6
Silver	Do.	Do.	Do.	960.0 ± 0.7	961.5
Gold	Do.	Do.	Do.	1062.4 ± 0.8	1064.0
Copper	Do.	Do.	Do.	1082.6 ± 0.8	1084.1
Diopside (pure)	Melting	Air	Platinum	1391.2 ± 1.5	
Nickel	Melting and freezing	Hydrogen and Nitro- gen	Magnesia and Magne- sium Alum- inate	1452.3 ± 2.0	
Cobalt	Do.	Do.	Magnesia	1489.8 ± 2.0	
Palladium	Do.	Air	Pure Mag- nesia	1549.2 ± 2.0	1575.*
Anorthite (pure)	Melting	Do.	Platinum	1549.5 ± 2.0	

In addition, the following temperatures were incidentally obtained :

Cadmium	Melting and freezing	Air	Graphite	320.0 ± 0.3	321.7
Aluminum	Freezing	Carbon monoxide	Do.	658.0 ± 0.6	657.
Platinum	Melting	Air		1755.	

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D. C., December 24, 1909.

* Holborn and Valentiner, loc. cit.