

## XXI.—On the Determination of High Temperatures by means of Platinum-resistance Pyrometers.

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IN the experiments on alloys (*vide* Trans., 1890 to 1894), the results of which we have hitherto communicated to the Society, we have made use of mercury thermometers, whose fixed points were determined by the platinum-resistance method. As we are now examining alloys which melt at temperatures above the range of the mercury thermometer, it has become necessary for us to select a method of measuring high temperatures. Four methods have been commonly used for this purpose.

- (a.) Air thermometers.
- (b.) Calorimetric methods.
- (c.) The change in the electromotive force of a thermo-couple.
- (d.) The change in resistance of a platinum wire.

It was necessary, for the purpose of our experiments, to select a method which would not only rapidly indicate the temperature, but would measure small differences of temperature with accuracy. Methods (a) and (b) were consequently out of the question, and, from the results hitherto published, it appeared that (c) was wanting in delicacy. We therefore decided to adopt method (d), especially as we already had some acquaintance with it.

The method of platinum-resistance pyrometry, first suggested by Siemens, has been brought to great perfection by Callendar and Griffiths (*Phil. Trans.*, A, 1887, p. 161; A, 1891, p. 119), and the necessary apparatus is now made by the Cambridge Scientific Instrument Company in a very practical form.

The results of this paper were obtained as a necessary preliminary to a study of alloys, which is not yet completed, but which we hope to publish shortly. Our experience leads us to the conclusion that platinum-resistance thermometry is a most valuable method, although it has not yet been much used by chemists. We therefore venture to lay before the Chemical Society a somewhat full account of the work gone through by us in the determination of the temperatures of solidification of certain metals and salts.

Callendar having, so far as we know, only compared the air and platinum thermometers up to 600° C., our results beyond that temperature required confirmation. As will be seen in Section III, that confirmation is largely to be found in the excellent work of Holborn and Wien (*Ann. Phys. Chem.*, 1892, **47**, 107), and of Victor Meyer, Riddle, and Lamb (*Ber.*, 1894, **27**, 3129).

The present paper is divided into the following sections.

1. Description of the method and instruments.
2. Study of the behaviour of the pyrometers.
3. Discussion of results and comparison with those of other observers.
4. Determination of the fixed points.

## SECTION I.

### *Description of the Method and Instruments.*

In platinum-resistance thermometry, a coil of platinum wire is introduced into the space whose temperature is to be ascertained, and the electrical resistance of this coil is measured. Such a coil, properly protected and mounted, constitutes a platinum-resistance thermometer or pyrometer.

Let  $R_0$ ,  $R_{100}$ , and  $R_t$  be the resistance of the wire at the temperatures 0, 100, and  $t$  Centigrade. Then, if we assume that the change in temperature is proportional to the change in resistance, the temperature will be given by the expression

$$\frac{R_t - R_0}{R_{100} - R_0} \times 100 \dots\dots\dots (1).$$

A scale of temperatures could thus be formed, having a value similar to that of the mercury in glass scale; for this latter scale is based on the assumption that the change in temperature is proportional to the change in the apparent expansion of mercury.

But the temperature given by expression (1) would, at high temperatures, differ considerably from that of an air thermometer at the same point.

Callendar therefore assigns the name "platinum temperature" to this quantity, and denotes it by the symbol  $pt$ . We thus have

$$pt = \frac{R_t - R_0}{R_{100} - R_0} \times 100 \dots\dots\dots (2),$$

and the symbol  $t$  is reserved for the temperature that would be given by an air thermometer.

In order to convert temperatures on the platinum scale to those on the air scale, it is necessary to determine the relation between  $pt$  and  $t$ . Callendar found that, up to about  $600^\circ \text{C.}$ , the results of his comparisons between the air and platinum thermometers were well represented by the equation

$$t - pt = \delta \{ (t/100)^2 - t/100 \} \dots\dots\dots (3).$$

Here  $\delta$  is a constant, depending apparently only on the *chemical* composition of the wire used.

$R_0$  and  $R_{100}$  can be found by immersing the instrument in ice and steam in the manner usual with mercury thermometers; we can then get  $\delta$  by determining  $R_t$ , and therefore  $pt$ , for some accurately known value of  $t$  (see Section IV).

Callendar and Griffiths have, by very thorough experiments with the air thermometer, shown that the boiling point of sulphur under a pressure of 760 mm. of mercury is  $444.53^\circ \text{C}$ . (*Phil. Trans.*, 1891A, p. 119),\* and they recommend that platinum thermometers should be immersed in the vapour of boiling sulphur, and  $R_s$ , and thence  $pts$ , found. Equation (3) will then give  $\delta$ . This method has been repeatedly applied to all our thermometers. Details as to the sulphur determinations are given in Section IV. The value of  $\delta$  having been thus ascertained for a particular thermometer, it will be seen from inspection of the tables that it changes little if at all for that thermometer, even after heating to very high temperatures.

We can now tabulate, as in Table I, the values of  $t$  in terms of  $pt$ , or we can plot  $t - pt$  and  $pt$  in the manner recommended by Callendar. The curve thus made enables us to deduce the air-thermometer temperatures corresponding to the values of  $pt$  found in our experiments.

TABLE I.  $\delta = 1.50$ .

$pt$ .	$t - pt$ .	$t^\circ \text{C}$ .	$pt$ .	$t - pt$ .	$t^\circ \text{C}$ .
-100	+2.9	-97.1	600	+54.4	654.4
0	0	0	700	+79.4	779.4
50	-0.4	49.6	800	+110.7	910.7
100	0	100.0	900	+149.4	1049.4
200	+3.1	203.1	1000	+197.0	1197.0
300	+9.8	309.8	1100	+225.0	1355.0
400	+20.2	420.2	1200	+326.7	1526.7
500	+34.9	534.9	1300	+416.0	1716.0

It is evident from Equation (3) that so long as  $t$  is constant,  $t - pt$  is proportional to  $\delta$ ; hence a table or chart giving  $t - pt$  in terms of  $pt$ , which has been constructed for a particular value  $\delta$  of the constant, can be used for another value  $\delta'$ , by multiplying by the factor  $\delta'/\delta$ . In order to form some idea of the relation between  $t$  and  $pt$ , we give Table I for the case of  $\delta = 1.50$ . An error of one in the second decimal place of  $\delta$  produces an error of  $0.9^\circ$  in the computation of  $t$  at  $1000^\circ$ , and of course the error introduced at lower temperatures is proportionately less.

\* This number is lower by  $3.9^\circ$  than the commonly accepted number due to Regnault (*Mem. de l'Institut*, 26, 1862, p. 527), but they give what appears to be a satisfactory explanation of the discrepancy.

*The Pyrometer and Wheatstone's Bridge.*

—As our thermometers were designed for high temperatures, we shall in future always speak of them as *pyrometers*. They were constructed by the Cambridge Scientific Instrument Company, according to the designs of Callendar (*Phil. Mag.*, July, 1891), and have been modified by us in details only. In the type we are now using, the coil is made of the purest platinum wire obtainable, of a diameter varying in different instruments from 0.008 to 0.004 inch. The coil has a resistance of about 3.3 ohms at 0°. The wire is wound double round a frame composed of two narrow rectangular strips of thin mica. These strips are equal, and are set with their planes at right angles, so as to intersect along their longer diameters. The section of the frame is thus a cross, and the coil forms a helix of square section touching the micas at their edges only. The coil itself is (when made of 0.004-in. wire) about 20 mm., and the wire about 200 mm., long. The coil hangs very near the bottom of a porcelain tube, Fig. 1, closed at the lower end, and glazed within and without. This tube is 400 mm. long, 12 mm. in external, and 7 mm. in internal, diameter, and the mica frame slides into it easily. The leads from the ends of the coil are made of stout platinum wire (0.025 in. diameter) to near the top of the tube, where they are soldered to copper wires terminating in binding screws.

In order to avoid convection currents, and also to prevent accidental contacts between the leads inside the tube, a number of circular mica discs are threaded on the leads. These discs fit the tubes fairly tightly, and render the wires and coil more rigid.

The coil with its two leads as here

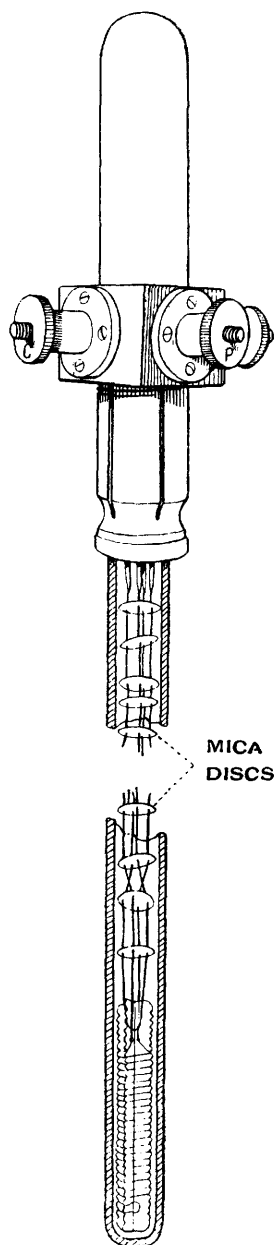


FIG. 1.—General view of the head and interior of a pyrometer.

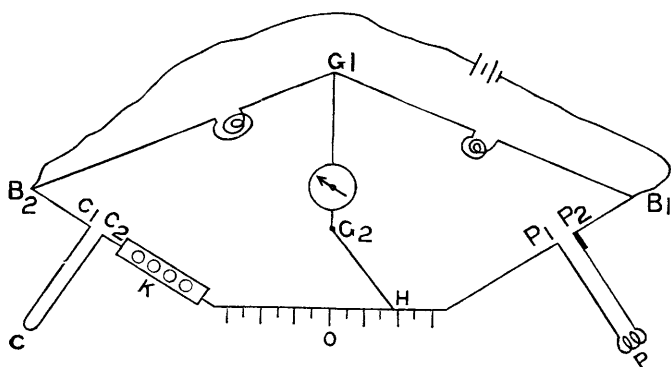
described might be made one arm of a Wheatstone's bridge, and the resistance taken in the usual way, but the disadvantage of this is that we should be measuring not only the varying resistance of the coil, but also that of the leads, parts of which will be at very different temperatures. The errors thus introduced are analogous to those due to the unimmersed part of the stem of a mercury thermometer.

To avoid this difficulty, the arms of the bridge are made equal, and the arm which contains the resistance box also contains a wire running down the tube of the pyrometer to a point just above the top of the coil, and thence back to the bridge. This wire is called the "compensator," and it should have the same resistance as the leads from the coil to the bridge; the compensator is of platinum where the leads are of platinum, and of copper where the leads are of copper. It follows that if corresponding parts of the compensator and of the pyrometer leads are near together so as to be at the *same* temperature, the resistances introduced by them into the arms of the bridge will be equal at *all* temperatures, and, consequently the balance will be independent of the temperatures of these wires.

The resistance of the leads is thus eliminated from our measurements, and we have to deal only with the resistance of the short coil, constituting what by analogy may be termed the bulb of the thermometer.

Between the top of the pyrometer tube and the binding screws of the bridge the compensator and the pyrometer leads form a fourfold insulated cable, which may be of any required length. At each end, a few inches of this cable are unravelled for attachment to the binding screws. The connections are represented diagrammatically in Fig. 2, the lettering being the same as on our apparatus.

FIG. 2.



The arms  $G_1$ ,  $B_1$  and  $G_1$ ,  $B_2$  consist of coils of equal resistance, and the arms  $B_1PH$  and  $B_2CKH$  are made equal by taking out or putting in plugs in the resistance box  $K$ , and by shifting the contact piece  $H$  on the divided bridge wire. The long leads starting from  $C_1$ ,  $C_2$  and  $P_1P_2$  form the cable to four binding screws on the head of the pyrometer tube;  $C$  and  $P$ , though apart in the diagram, are in reality close together at the lower end of the pyrometer tube. The zero of the divided bridge wire should be at  $O$ , its middle point, that is to say, if the gaps  $C_1C_2$  and  $P_1P_2$  were filled up by thick, short wires of equal resistance, the bridge should balance at  $O$ .

Then if  $R$  is the resistance of the pyrometer coil,  $r$  that introduced by the resistance box, and  $S$  that of the length  $OH$  of the bridge wire, we see that

$$R = r + 2S,$$

so that the effective value of a unit length of the bridge wire is twice its real resistance.

The coils of the box are of platinum silver with a temperature coefficient of 0.00027. The resistances are measured in a unit equal to 0.01289 true ohm. The coils form a progression in powers of 2, and are lettered as well as numbered.

Their nominal values are given in line 2 of Table II, and the corrections to be added to these nominal values are given in line 3.

TABLE II.

H.	G.	F.	E.	D.	C.	B.	A.
5 +0.105	10 +0.05	20 +0.02	40 -0.16	80 -0.1	160 +0.06	320 -0.20	640 -0.08

A unit division of the bridge wire is approximately equal to a unit of the coils. Each unit division is divided into 10 equal parts, and, by means of a vernier, tenths of each of these can be read.

A very dead beat reflecting galvanometer should be used. On account of the numerous metallic junctions in the circuit, there may sometimes be considerable thermoelectric effects. These troublesome effects were almost entirely eliminated by the use of Griffiths' thermoelectric key (*Phil. Trans.*, vol. 184 A, 398).

The current from one Leclanché cell running through 100 ohms in the battery circuit is the most suitable. This current produces no apparent heating effect in the coil of the pyrometer, but if a resistance of 20 ohms be substituted for that of 100, the heating effect of the current on the wire of the coil is perceptible, especially at low tem-

peratures (see Pyrometer 8, July 30, 1894). The heating effect shows itself by a creep on the scale of the galvanometer, lasting for some moments after the current has been put on and the first swing has ended.

The preceding statements give the most essential facts about the apparatus as it comes from the makers, but before accurate work can be done with it, the bridge wire must be calibrated and the errors of the coils determined. These are processes involving great care and a good deal of arithmetical work. An intelligible account of the methods we adopted to calibrate the bridge wire and correct the coils would be too lengthy for the present paper; a description of such methods will be found in text-books on practical physics. The result of the calibration of the bridge wire is given in Table III. Column 1 gives the bridge-wire reading, column 2 the correction, always positive, to be added to reduce it to box units.

TABLE III.

B.W. reading.	Correction.	B.W. reading.	Correction.
-10	0·26	0	0·119
-9	0·246	1	0·114
-8	0·232	2	0·121
-7	0·214	3	0·129
-6	0·193	4	0·128
-5	0·175	5	0·130
-4	0·161	6	0·129
-3	0·148	7	0·115
-2	0·138	8	0·105
-1	0·129	9	0·090

We see from Tables II and III that the corrections to be added to the bridge-wire reading may amount to more than  $0\cdot2^\circ$ , and that the coil corrections are of the same order.

When a pyrometer is first received from the makers, its FI\* is generally too great. It is adjusted by removing the tube and slightly shortening the coil by twisting the end. The twisted junction is then fused in a small oxyhydrogen flame; after this, any unfused turns are untwisted and the FI determined. With a little practice, it is easy to adjust the pyrometer so that its FI is correct to within  $0\cdot1$  per cent. If, in the process of fusing, the coil is shortened too much, it can sometimes be corrected by slightly stretching with a pin, but care must be afterwards taken to anneal the coil before determining its FI. Before making the final determination of the FI, the coil and leads should be annealed by heating the pyrometer, for about

\* The symbol FI denotes Fundamental Interval, that is,  $R_{100} - R_0$ .

two-thirds of its length, to the highest temperature of a tube-combustion furnace. The saving of time in applying corrections is so great with adjusted pyrometers, that a little labour in getting the FI within 1 per cent. of 100 box units is well repaid.

*To Record and Reduce an Observation.*—The bulb of the pyrometer being immersed in the substance whose temperature is required, a balance is obtained on the bridge, and the following points are noted.

1. The time.
2. The letters of the plugs out of the resistance box.
3. The bridge-wire reading.
4. The temperature of the coils inside the box.
5. The barometer, read to 1/10th mm. (in cases where pressure affects the result).

These are entered in the note-book, of which a sample page is given in Table IV (p. 168).

The next thing is to ascertain the corrections to be added to the observed values. Under the coil letters, we write the total corrected value of the coils in circuit taken from Table II.

Under the bridge-wire reading is placed the calibration correction from Table III. Under the box temperature comes the increased resistance of the coils in circuit due to their excess of temperature above 20°, the temperature for which Table II is correct.

If the experiment is a boiling point, we usually write, as a quantity to be subtracted, the excess of the resistance over what it would have been if the pressure had been 760 mm. We thus reduce the reading to one at normal pressure. With thermometers in which the  $R_{100} - R_0$  (or FI) is about 100 and the  $\delta$  about 1·5, we may assume that the value of  $R_{100}$  increases by 0·037, and of  $R_s$  increases by 0·072 for each millimetre of barometric pressure above 760, and conversely. For instruments in which the FI differs considerably from 100, or the  $\delta$  from 1·50, the corrections are somewhat more troublesome (see Section IV).

The numbers under (2) and (3), and the corrections under (3), (4), and (5) are now to be added, and the result is  $R$ , the resistance of the pyrometer under the given conditions.

If the fixed points are already known, we can now find

$$pt = \frac{R - R_0}{FI} \times 100$$

where FI is the symbol for  $R_{100} - R_0$ .

The  $\delta$  chart then gives us  $t - pt$ , and, therefore,  $t$ , the Centigrade temperature on the air-thermometer scale.

A resistance can generally be read with several different combina-



tions of coils and bridge wire. The results should, of course, be identical; and in practice, the groups of values of  $R_0$ ,  $R_{100}$ , and  $R_s$  got thus, do not usually differ by more than  $0.02^\circ$  from one another, and are generally much nearer. In the sample page, such groups of readings are given, but in the more condensed tables each  $R_0$ ,  $R_{100}$ , or  $R_s$  is itself the mean of such a group; the separate readings agreeing so well that it would be waste of space to give them.

TABLE IV.—*Pyrometer 14.*

	Time. 1.	Coils. 2.	Bridge wire. 3.	Box temp. 4.	Baro- meter. 5.	R.	
1894. Dec. 21 B. p. of S.	5.51	AE G 689.81	-7.022 +0.215	21.04° +0.191	759.86 +0.010	683.204	
"	5.55	AE 679.76	+3.108 +0.129	21.05 +0.193	759.84 +0.012	683.202	
"	5.59	AEH 684.865	-2.007 +0.139	21.08 +0.198	759.84 +0.012	683.207	
"	6.4	AFGH 675.095	+7.798 +0.108	21.1 +0.202	759.84 +0.012	683.215	
Ice .....	6.40	CDF 259.98	+1.778 +0.119	21.01 +0.071	.. ..	683.207 261.948	Mean $R_s$ .
	6.45	CDFH 265.085	-3.388 +0.153	21.01 +0.071	.. ..	261.921	
						261.935	Mean $R_0$ .
Steam ....	6.55	BE 359.64	+2.008 +0.120	21.06 +0.104	759.05 +0.035	361.907	
"	7.0	BEH 364.745	-3.138 +0.150	21.06 +0.104	759.00 +0.037	361.898	
"	7.5	BEG 369.69	-8.152 +0.234	21.10 +0.107	758.95 +0.039	361.918	
						361.908	Mean $R_{100}$ .
Dec. 31 Ice .....	5.40	CDF	+1.938	20.0	..	262.037	FI = 99.97
"	5.45	CDFH	-3.225	20.0	..	262.010	$\delta = 1.511$
						262.024	Mean $R_0$ .
Gold 1,200 gr. {	6.5	ABCEH	+4.80	20.25	..	1169.73	{ F. p. of Au is $1062.0^\circ$ C.
	6.10	"	+4.79	"	..	1169.73	
	6.15	ABCEG	-0.185	20.40	..	1169.73	

The third decimal place in the constants has, of course, no claim to accuracy, but, as the observed readings of  $R_0$  and  $R_{100}$  with different coils often agree to within 0.005, we think that accuracy in the second figure is gained by giving the third.

The separate readings of  $R_0$  given in Table IV do not agree quite as well as usual, and the sulphur readings agree more closely than is usual. The small discrepancy between the ice points of December 21 and December 31 is probably due to the pyrometer having been disconnected from the leads to the box in the interval. It does not affect the FI.

## SECTION II.

As one of the most important questions about platinum pyrometers is that of the constancy of their zero, fundamental interval, and  $\delta$ , after exposure to high temperatures, we have tabulated in strictly chronological order the experiments made with certain pyrometers (see Tables V to IX, pp. 170—183).

In the tables, column 1 gives the date of the experiment, 2 the hour or duration, 3 specifies the nature of the experiment, 4 symbolises the experiment, and the sub-index is the ordinal number for that species of experiment. Thus  $A_3$  means the third experiment on aluminium with the particular pyrometer.

Column 4 is useful for quickly finding an experiment.

Column 5, headed  $R_{100}^\circ$ , gives the values of the steam and ice points found on certain dates. Opposite them, in column 6, is the index number for referring to these constants; and in column 7 is the FI or  $R_{100} - R_0$ . Thus the three columns 5, 6, 7, read vertically, record the changes in the constants of the pyrometer due to the treatment it has undergone.

Column 8 gives the resistance observed during the experiments referred to in 3 and 4. Column 9 gives the corresponding *pt*, and the suffix refers to column 6, and indicates the constants used in calculating *pt*. In cases where there is no suffix, the constants immediately preceding have been used.

Column 10 gives the Centigrade temperature calculated from equation (3), or taken from a chart.

### *On the Changes in the Constants of the Pyrometers.*

By studying the columns enclosed between the thick vertical lines in the tables, we can trace the gradual change in the constants due to the treatment to which the instrument has been subjected. The change in FI is the most important.

Consider Pyrometer 7. Here, with one trifling exception, the FI rises

TABLE V.—Pyrometer 7.

Date.	Time.	Nature of Experiment.	R <sup>°</sup> <sub>100</sub> .	Index No.	Pt.	R.	$\delta = 1 \cdot 500 \cdot \frac{t}{t_0}$
1894.							
July 2	..	..	Steam	1	99.92		
" 2	..	..	Ice				
" 3	..	..	Steam	2	99.898		
" 3	..	..	Ice				
" 4	3 hours	Some hours at a red heat.					
" 5	"	F. p. of 68 grams aluminium.....	Al <sub>1</sub>	..	..	859.24	656.2
" 6	"	" 282 "	Al <sub>2</sub>	..	..	857.71	654.4
" 6	"	..	Steam	3	99.87		
" 6	"	..	Ice				
" 8	"	B. p. of sulphur (early method) .....	S <sub>1</sub>	..	..	679.39	∴ δ = 1.510*
" 15	"	..	Steam	4	99.968		
" 15	"	..	Ice	5	100.002		
" 16	"	..	Steam				
" 16	"	Extracted coil from tube and dried .....		6	100.0		
" 16	"	..	Ice				
" 16	1 hour	Heated to bright redness, then .....				1177.8	+
" 29	2 hours	F. p. of 700 grams copper in clay crucible .....	Cu <sub>1</sub>	..	..	1179.5	+
" 29	"	" 500 " plumbago do.	Cu <sub>2</sub>	..	920.9	1079.5	+
" 29	"	..	"	..	..	1179.4	+
" 29	"	..	"	..	..	1180.0	§
" 29	"	Added 100 grams copper .....	"	..	..	1180.4	
" 29	"	..	"	..	..	1180.3	1080.9§
" 29	"	..	"	..	..	1180.3	1080.9
" 29	"	..	"	..	..	1180.3	1081.0
" 29	"	Added 64 grams copper .....	"	..	..	1180.4	
" 29	"	..	Ice				
" 29	"	..	"				
" 29	"	..	Steam	7	100.05		
Aug. 1	"	..					
" 1	"	..					

Aug.

		Changed to a new tube.	Mica plate of {	Ice	253·15	8	100·08	630·06	421·58	∴ δ = 1·50*
" 6	..	coil was found to be broken.....	{	Steam	358·23	..	..	834·53	575·2 (9)	624·3
" 6	..	B. p. of sulphur after 2 hours' immersion	{	S <sub>2</sub>	..	..	..	834·33		
Dec. 17	..	F. p. of 300 grams antimony .....	{	Sb <sub>1</sub>	..	..	..			
" 18	..	..	..	Ice	258·136	9	100·192			
" 18	..	F. p. of 500 grams antimony in sala-	{	Steam	358·328	..	..	833·8	574·5 (9)	623·45¶
" 18	..	mander crucible.....	{	Sb <sub>2</sub>	..	..	..	833·7		
1895.	..	..	..	"		..	..			
Jan. 9	..	..	..	Ice	258·269	10	100·142			
9	12.40	F. p. of 500 grams pure antimony from }	{	Steam	358·411	..	..	838·50	579·41	629·38**
	1.0	tartar emetic .....	{	Sb <sub>3</sub>	..	..	..	838·50		
	1.10	..	..	"	..	..	..	838·45	579·36	629·33**
	1.20	..	..	"	..	..	..	838·52		
	6.10	..	..	"	..	..	..	838·53		
	6.25	"	"	Sb <sub>4</sub>	..	..	..	838·54	579·45	629·45**
		"	"	"	..	..	..			

\* The form of screen used to protect the pyrometer against radiation and drip of condensed sulphur was afterwards abandoned for a better one—the perforated protector. (See Sec. IV.)

† The copper had become somewhat oxidised by melting without a flux, but during the determination its surface was as usual protected by a layer of molten borax, which, when cold, was found to be deep green.

‡ In this series, there was probably no oxidation, as the borax remained colourless.

§ Surfusation was shown by a slight rise of temperature at the moment of freezing.

|| Well marked surfusion.

¶ Surfusation of many degrees.

\*\* Much surfusion.

TABLE VI.—*Pyrometer 8.*

Date.	Time.	Nature of Experiment.		R° <sub>100</sub> .	Index No.	Fl.	R.	<i>pt.</i>	$\delta = 1.504.$ $t.$
1894. July 2	..	..	Steam	359.506	1	100.174			
" 2	..	..	Ice	259.332	..	..	860.38	600	654.5
" 5	..	F. p. of 282 grams aluminium .....	Al <sub>1</sub>	..	..	..	860.86	600.48	654.8
" 5	..	..	"	..	..	..			
" 6	..	..	Ice	259.534	2	100.166			
" 6	..	..	Steam	359.700	..	..			
" 9	..	B. p. of sulphur (early method) .....	S <sub>1</sub>	..	..	..	681.52	421.29	∴ $\delta = 1.517$
" 10	..	F. p. of 805 grams copper (best com- .....	Cu <sub>1</sub>	..	..	..	1181.46	920.4 (2)	1079.2
" 10	..	mercial bar and rod) .....	"	..	..	..	1181.30	920.2 (2)	1079.0
" 10	..	..	"	..	..	..	1181.30	921.4 (3)	1080.7
" 11	..	B. p. of sulphur (early method) .....	S <sub>2</sub>	..	..	..	680.58	421.45 (3)	∴ $\delta = 1.507$
" 11	..	F. p. of same pot of copper as on July 10	Cu <sub>2</sub>	..	..	..	1181.29	921.3 (3)	1080.5
" 11	..	..	"	..	*	..	1181.18		
" 12	..	Tube contaminated with borax .....	Steam	359.36	..	..			
" 12	..	Cleansed from adhering borax .....	"	358.62	3	100.16			
" 12	..	..	Ice	258.46	..	..	658.34	399.22 (3)	419.35
" 12	..	F. p. of 700 grams zinc .....	Zn <sub>1</sub>	..	..	..	658.31		
" 12	..	" .....	"	..	..	..			
" 13	..	Heated in molten zinc for many hours.							
" 15	..	..	Ice	258.437	4	100.185			
" 15	..	..	Steam	358.622	..	..			

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\* The greatest care is needed in cleaning off any flux from the outside of the tube before determining  $R_{100}$  and  $R_0$ , otherwise  $R_{100}$  is too high and  $R_0$  too low.

† The heating effect of the current was well marked in ice, and it was necessary to pass the current through the coil for several minutes before a steady temperature was attained.

‡ This series of boiling points was carried out with the improved "perforated protector," described in Section IV. The separate readings were almost identical. We therefore use this value of  $\delta$ .

§ Perhaps insufficient immersion.

+ The heating effect of the current was well marked in ice, and it was necessary to pass the current through the coil for several minutes before a steady temperature was attained.

§ Perhaps insufficient immersion.

TABLE VI—continued.

Date.	Time.	Nature of Experiment.		R <sub>100</sub> .	Index No.	Fl.	R.	<i>p</i> l.	$\delta = \frac{1}{t} \cdot 504.$
1894. Sept 30	..	..	Ice Steam	257·436 357·401	11	99·965			
" Oct. 1	6 hours	At 700° C.	Al <sub>4</sub>	..	..	..	857·29	599·9 (12)	654·5
" 2	12 hours	F. p. of 175 grams aluminium. Flux....	Ice Steam	257·43 357·42	12	99·99	655·9 655·94	398·53	418·57
" 3	12 hours	F. p. of 400 grams zinc (in a reducing { atmosphere of coal gas) .....	Zn <sub>2</sub>	..	..	..			
" 7	..	Tube, much corroded, let water through. Dried pyrometer. New tube .....	Ice Steam	257·59 357·55	13	99·96			
" 8	..	F. p. of 189 grams aluminium. It was believed to be Schaffhausen. No flux.	Al <sub>5</sub> Al <sub>6</sub>	.. ..	.. ..	.. ..	855·2 855·4	598·0 598·2	652·2 652·4*
" 9	..	Four identical readings .....							
" 15	..	F. p. of 211 grams of same Al .....							
" 15	..	Pyrometer broken.							

\* We have reason to think that this aluminium was not so pure as the aluminium used in the other experiments.

TABLE VII.—*Pyrometer* 11.

Date.	Time.	Nature of Experiment.		R° <sub>100</sub> .	Index No.	Fl.	R.	<i>p</i> <i>t</i> .	$\delta = 1.497 \frac{t}{t_0}$ .
1891. July 14	1 hour	Annealed at a red heat.							
" 14	"	B. p. of sulphur (early method)	S <sub>1</sub>	259.793	..	..	683.402	421.41 (2)	.. $\delta = 1.51$
" 14	"	"	Ice	360.295	1	100.502			
" 15	"	"	Steam	360.331	2	100.514			
" 29	"	F. p. of 664 grams electrolytic copper..	Ice	259.817	..	..	1187.31		
			Cu <sub>1</sub>	..	..	..	1187.10	922.5 (2)	1081.5
			"	..	..	..	1187.12	921.9 (3)	1080.7
			"	..	..	..	1186.94		
" 29	"	"	"	259.895	..	..			
Aug. 1	"	"	Ice	360.447	3	100.58	1100.08		
" 1	"	"	Steam	259.868	..	..	1100.14	835.40	958.7
" 2	2 hours	F. p. of 300 grams silver .....	Ice	..	..	..	1100.13		
" 2	"	"	Ag <sub>1</sub>	..	..	..			
" 3	"	"	"	259.829	..	..	684.003	421.602 (4)	.. $\delta = 1.497^*$
" 13	"	B. p. of sulphur. Perforated protector	S <sub>2</sub>	259.87	4	100.597			
" 13	"	"	Ice	360.467	..	..			
		"	Steam	..	..	..	1102.4		
Dec. 26	5.30	F. p. of 700 grams Stas' silver .....	Ag <sub>2</sub>	..	..	..	1102.42	837.5 (4)	961.6†
" 26	5.41	"	"	..	..	..	1102.41	836.4 (5)	
" 26	5.47	"	"	..	..	..			
" 26	5.55	"	"	..	..	..	1102.43		
" 26	6.15	"	Steam	360.572	5	100.732			
" 26	"	"	Ice	259.84	..	..			

\* The only trustworthy determinations.

† We had specially purified this silver by Stas' method of precipitation with ammoniacal cuprous sulphite.



TABLE VIII.—Pyrometer 13.

Date.	Time.	Nature of Experiment.	R <sup>o</sup> <sub>100</sub> .	Index No.	F.I.	R.	pt.	δ = 1·500. t.
1894.		Annealed at a red heat.						
Aug. 3	..	F. p. of 300 grams silver (no record of { use of reducing gas during cooling) }	Ag <sub>1</sub> " Ice Steam	.. .. .. 1	.. .. .. 100·64	1100·8 1100·8 1100·8	833·2 (1)	935·9
" 4	..	Heated in sulphur.						
" 5	..	" " in molten silver.	Ice Steam	2 2	100·69	1102·3 1102·5 1102·7	834·48	957·7
" 5	..	.. .. .	Ag <sub>2</sub> "	.. ..	.. ..	686·51	421·35	∴ δ = 1·513
" 5	..	F. p. of 268 grams silver. ....	S <sub>1</sub> Ice Steam	.. 3 3	100·665			
" 7	3 hours	B. p. of sulphur (early method). ....	262·331 362·996 362·989 362·986	.. .. .. ..	.. .. .. ..	686·52 686·68 686·83	421·37 421·53 421·68	∴ δ = 1·51 ∴ δ = 1·502 ∴ δ = 1·492*
" 7	..	Stem wholly immersed in steam. ....	"	..	..	686·78		
" 9	..	Coil end only " immersion. ....	S <sub>2</sub> S <sub>3</sub> S <sub>4</sub>	.. .. ..	.. .. ..	686·82+		
" 10	..	B. p. of sulphur, 9" immersion. ....	"	..	..			
" 10	..	" " stem wholly immersed	"	..	..			
" 11	..	" " perforated protector	"	..	..			
" 11	..	" " resistance box 20° .....	S <sub>5</sub>	..	..			
" 12	..	B. p. of sulphur, perforated protector	S <sub>6</sub> Ice	.. 4	..	686·83	421·71	∴ δ = 1·49
" 12	..	resistance box 30° .....	262·283 262·271	.. ..	(100·67) † ..			
" 12	..	Connections of pyro. and box cleaned	S <sub>7</sub>	..	..			
" 12	..	" "		..	..			

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\* In this series, changes in the length of stem immersed did not affect the reading.

4. These experiments were made to test the temperature coefficient of the box.

† These values of FI are interpolations, not observed numbers.

TABLE VIII—continued.

Date.	Time.	Nature of Experiment.	R <sub>100°</sub>	Index No.	Fl.	R.	<i>p</i> t.	$\delta = 1 \cdot 500$ . t.
1894. Sept. 27	5 hours	In aluminium, then .....	363·418 Ice	12	100·846			
" 28	"	" ..	262·572 Steam	13	100·840			
" 28	"	" ..	363·400					
" 29	"	F. p. of 175 grams aluminium.....	Al <sub>2</sub> O <sub>3</sub>	..	..	867·2	599·5	653·9
Dec. 9	"	New tube and f. p. of 145 grams K <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub> (1)	..	..	1178·6	905·7 (13)	1058·6
" 10	"	New tube.....	Steam	14	100·937			
" 10	"	" ..	363·767 Ice		..			
" 10	"	F. p. of 160 grams K <sub>2</sub> SO <sub>4</sub> .....	262·830 K <sub>2</sub> SO <sub>4</sub> (2)	..		1180·6	909·2	1062·7
" 11	"	New porcelain tube.....	263·33 Ice	15	100·90	1180·6		
" 11	"	In new platinum outer tube .....	364·23 Ice	16	100·92	1180·4		
" 11	3.5 3.30 3.55	F. p. of 512 grams Na <sub>2</sub> SO <sub>4</sub> .....	263·31 Steam	17	100·88			
" 12	"	" ..	364·19 Ice	..	..	1049·43		
" 13	4 P.M.	Heated in molten Na <sub>2</sub> SO <sub>4</sub> .....	263·31	..	..	1049·69		
" 13	4.45	F. p. of about 150 grams Na <sub>2</sub> CO <sub>3</sub> .....	..	..	..	1049·63	779·4	883·2
" 13	5.20	" ..	Na <sub>2</sub> CO <sub>3</sub> (1)	..	..	1023·96	753·96	849·4*
" 13	"	" ..	"	..	..	1023·45	753·45	848·8
" 13	"	" ..	"	..	..	1022·75	752·75	847·9†
" 16	12.45	New porcelain tube .....	263·465 Ice	18	100·945			
" 16	1.10	F. p. of 71 grams Patricroft magnesium .....	364·410 Steam	..	..	851·3	582·2	632·8†
" 16	"	" ..	Mg <sub>2</sub>	..	..	851·3		

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Surfusion of at least 5°.

TABLE VIII—continued.

Date.	Time.	Nature of Experiment.		R <sub>100</sub> .	Index No.	Fl.	R.	p <i>t.</i>	$\delta = 1 \cdot 500.$ <i>t.</i>
1894.		Annealed at a red heat.	Au <sub>1</sub>	..	..	..	1183·61	908·66	1061·9
	12·5	..	"	..	..	..	1183·65	908·68	1061·9
Dec. 24	12·50	..	Steam Ice	365·986 264·781	24	101·205			
"	..	B. p. of sulphur .....	S <sub>9</sub>	..	..	..	..	..	$\therefore \delta = 1 \cdot 501$
"	..	F. p. of 700 grams silver (Stas) .....	Ag <sub>4</sub>	..	..	..	1110·52		
"	..	..	..	..	..	..	1110·62	835·76	959·5
"	..	..	..	..	..	..	1110·58		
"	..	..	..	..	..	..	1110·66		
"	..	..	Ice	265·785	..	..			
"	..	On removal from tube, the coil stuck and became unwound. We therefore think that on cooling from silver a strain may account for change in the constants.	Steam	367·358	25	101·573			

On removal from tube, the coil stuck and became unwound. We therefore think that on cooling from silver a strain may account for change in the constants.

regularly and slowly from  $99\cdot92$  to  $100\cdot19$ , while  $R_0$  decreases by a few tenths of a degree. These changes are the result of at least two heatings to over  $1100^\circ$  for two hours each, and quite half-a-dozen exposures to a bright red heat for many hours, not to speak of many minor heatings and coolings. If these changes had been altogether ignored, the maximum error introduced at  $1000^\circ$  would have been  $3^\circ$ —a quantity of very little importance in the present state of our knowledge of high temperatures.

Pyrometer 8, from July 2 to July 29, when it was broken, tells the same tale; two heatings to over  $1100^\circ$  and several minor heatings altered the FI by only  $0\cdot011^\circ$  and  $R_0$  by  $0\cdot9^\circ$ . From July 29 to October 7, its FI did not vary by more than  $0\cdot1^\circ$ , or its  $R_0$  by more than  $0\cdot3^\circ$ , although it was heated to  $1000^\circ$  on three separate occasions, and to a red heat half-a-dozen times.

Pyrometer 11 tells the same tale of a very slight and gradual increase in the FI in consequence of exposure to temperatures near  $1000^\circ$ .

Pyrometer 13 affords an excellent example of this slow secular rise in the FI; even heating in molten aluminium produces a minute but steady rise.

This appears to be the normal change in pyrometers such as ours. We are disposed to think that the change takes place, not while the coil is hot, but when it cools, and that it is due to the thickening of the mica plates on which the wire is wound. If the micas are examined after prolonged exposure to high temperature, they are found to have become opaque and brittle, and when looked at edgewise they are clearly thicker than at first. Now, the coil on being heated will expand, and the permanent thickening of the mica, which is taking place at the same time, will not cause any strain in the wire; but, as the coil cools, it will contract on to the now larger frame, become strained, and its resistance will increase.

We therefore think that the constants should be determined *before* every important temperature experiment, and providing the leads were well annealed originally, these constants should be used in calculating the *pt*, no matter what the constants may be after the experiments. Unfortunately, we did not come to this conclusion until a late date, so that in many cases constants determined just before the experiment are lacking, and a slight uncertainty is thereby introduced into the results. But the correction is a small one. In some cases we have calculated the results with constants determined both before and after the experiment to show the amount of discrepancy.

Other changes occur in the constants. If the pyrometer is unscrewed from the leads, slight changes in  $R_0$  and  $R_{100}$ , due to dirt on

TABLE IX.—*Pyrometer 16. New Sample of Wire.*

Date.	Time.	Nature of Experiment.	R° <sub>100</sub> .	Index No.	Fl.	R.	<i>pt.</i>	$\delta = 1.534.$ <i>t.</i>
1894. Dec. 19	1 hour	Two-thirds of tube containing coil and leads was heated to 800°. Later, the coil was heated to 1000°.						
"	2.40	F. p. of 577 grams K <sub>2</sub> SO <sub>4</sub> .....	..	..	..	1228.8		
"	3.10	" ..	..	..	..	1228.9		
"	5.0	" ..	..	..	..	1228.8		
"	..	In new porcelain tube .....	391.734	1	103.387	1228.7	909.6 (1)	1066.7
"	..	B. p. of sulphur. Perforated protector ..	288.347	..	..	723.640		∴ $\delta = 1.534$
"	3.25	F. p. of already fused Na <sub>2</sub> CO <sub>3</sub> .....	..	..	..	1063.1	421.02	845.3*
"	6.15	F. p. of fresh Na <sub>2</sub> CO <sub>3</sub> .....	..	..	..	1068.0	749.3	851.7†
"	6.36	" ..	..	..	..	1067.35	754.1	851.1
"	7.0	" ..	..	..	..	1067.27	753.5	851.0
"	2.35	F. p. of 782 grams gold .....	..	..	..	1227.29	753.4	1062.3
"	3.0	" ..	..	..	..	1227.20	906.74 (2)	1062.2
"	3.16	" ..	..	..	..	1227.12	906.65 (2)	1062.1
"	3.35	" ..	391.582	2	103.591		906.55 (2)	
"	..	B. p. of sulphur. Bar. 774 mm. R is not corrected for bar, but <i>pt</i> and <i>t</i> are corrected .....	287.991	..	..	725.220		∴ $\delta = 1.532$
"	4.25	F. p. of 700 grams Stas' silver .....	..	..	..	1152.93	421.061	
"	4.41	" ..	..	..	..	1152.89	884.92	960.9
"	4.50	" ..	..	..	..	1152.86		
"	8.50	" ..	391.604	3	103.591			
"	1.30	F. p. of 700 grams silver (later sample, J. and M.) .....	288.013	..	..	1152.68		

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\* This sample of  $\text{Na}_2\text{CO}_3$  had already been fused for an hour or more, and its f. p. taken with Pyrometer 17. It was falling steadily.  
 † Platinum protector used to protect the fused salts from impurities. The fused salt was quite clear at 6.15, but became opaque during the later fusing. See Pyrometer 18.  
 ‡ In the calculation of  $t$ , the value 1.532 of Dec. 25th is assumed for  $\hat{v}$ .  
 § These considerable changes are no doubt due to strain.

† In the calculation of  $t$ , the value 1.532 of Dec. 25th is assumed for  $\delta$ .

§ These considerable changes are n



the binding screws, may appear the next time the instrument is used, but the FI is not affected.

If the leads have not been sufficiently annealed in a combustion furnace, irregular changes of several degrees may occur the first few times the pyrometer is used at a high temperature.

Finally, there is a destructive change to which the pyrometers are liable at temperatures above  $1000^{\circ}$ . This is due to the melting of the glaze on the inside of the porcelain tube. The glaze at present used becomes sticky at  $1100^{\circ}$ , and melts at a somewhat higher temperature. If the frame, and especially the wire of the coil, does not touch the inside of the tube, the melting of the glaze is probably harmless. But if the wire, or even the mica, touches the fused glaze, it becomes attached to the tube, and, on cooling, a strain is produced. This may only produce an irregular alteration of the constants, and we have used successfully pyrometers in which the coil was fused to the tube. But if the glaze gets on the wire, it probably deteriorates it, and the instrument is no longer trustworthy, even its  $\delta$  altering. For temperatures above  $1100^{\circ}$ , it will be desirable to use tubes with no glaze on the inside.

#### *On Pyrometers with Different Values of $\delta$ .*

Our earlier pyrometers were made of a wire that we knew to have a  $\delta$  very near 1.50, and we were content at first with a somewhat rough verification of this fact for each pyrometer in turn. But, as we began to realise the accuracy of measurement possible with the pyrometers, it became worth while to find  $\delta$  with the greatest care, and the later determinations of  $\delta$  are those we use in calculating  $t$ . We think that in the determinations of December, 1894, the value of  $\delta$  is correct to about  $\frac{1}{1000}$ th part.

It seemed desirable also not to confine our experiments to wire with a  $\delta$  of 1.50, but to see how far consistent results could be obtained with wire having a different  $\delta$ .

Table XII of the freezing point of gold throws some light on this question. There we see values of  $\delta$  varying from 1.50 to 1.58, giving different values of  $pt$ , but the same values of  $t$ . Pyrometer 15 had an extraordinary  $\delta$  of 2.04; but still it gave, at first, the correct freezing point of gold. Similarly, Pyrometer 17, with a  $\delta$  of 2.1, gave a good freezing point for sodium carbonate. These two pyrometers, however, rapidly deteriorated, and we cannot regard them as absolutely proving that the  $\delta$  formula is applicable to such an extreme case.

## SECTION III.

*The Freezing Points of the Metals.*

The metals were usually fused in cylindrical crucibles 42 mm. wide and 105 mm. high, made either of plumbago or salamander, or of a fine, close-grained clay. When very slow cooling was required, these cylinders were placed inside another crucible, the interval between the two being filled with pieces of broken crucible. The silver, copper, and gold were fused in an ordinary Fletcher's blast furnace, whilst for the aluminium, magnesium, zinc, tin, and antimony it was sufficient to use a draught furnace. The stirring was effected by hand, except in a few experiments with aluminium, when a rotary stirrer was used. The pyrometers were heated in a muffle furnace before being put into the fused metals, and when the experiment was completed they were transferred to the muffle and allowed to cool. In this way, the life of the porcelain tubes was greatly prolonged. In order to protect the fused metals from absorption of oxygen, we passed either a current of coal gas or of hydrogen over the surface. This precaution was adopted in the cases of tin, zinc, antimony, magnesium, and silver.

*Freezing Point of Tin.*

Pyrometer 13 gave with 800 grams of tin a freezing point of  $231.91^{\circ}$ . The tin used was a particularly well crystallised sample; it was free from copper, but contained a trace of iron.

*Freezing Point of Zinc.*

Pyrometer 8 gave with 700 grams of the metal a freezing point of  $419.35^{\circ}$ , whilst the same pyrometer gave with 400 grams of zinc the number  $418.57^{\circ}$ . The zinc used was the purest distilled metal obtainable. The hydrogen produced from the solution of 50 grams, when slowly passed through a red-hot tube, did not deposit the least trace of arsenic or antimony. The zinc contained, however, a small trace of lead and a minute trace of iron, but the quantities were so small that they could only be estimated colorimetrically; no trace of cadmium could be detected.

The discrepancy between our numbers and those of Griffiths ( $417.6^{\circ}$ ) is probably accounted for by the fact that he fused his zinc in an iron crucible; this crucible was afterwards found to have been considerably attacked.

As our object was to ascertain the behaviour of the pyrometers at higher temperatures, no further experiments were made with zinc and tin.

*Freezing Point of Magnesium.*

Pyrometer.	Wt. of Mg.	<i>t.</i>
13 (1)	71 grams	632·8
13 (2)	69 „	632·5

The metal used was “commercial” distilled magnesium, obtained direct from the Patricroft Company. It is improbable that it contained more than 99 per cent. of the pure metal: hence, our value is, no doubt, too low.

The experiments on magnesium were discontinued for the present, owing to the rapid destruction of the pyrometer tubes and crucibles by the fused metal.

*Freezing Point of Antimony.*

Pyrometer.	Wt. of Sb.	<i>t.</i>
7 (1)	300 grams (commercial)	624·3
7 (2)	500 „	623·5
13 (1)	300 „	623·5

*Pure Antimony from Tartar Emetic.*

7 (3)	500 grams	629·39
16 (1)	„	629·79
7 (4)	„	629·45

The mean freezing point of antimony (pure) is 629·54°.

As we were much struck with the great discrepancy between the freezing points of our commercial antimony and the usually accepted value (440°), we made a qualitative analysis, and found that it contains considerable quantities of lead. We therefore procured some of the pure metal made from tartar emetic, and satisfied ourselves that it was free from lead, iron, and potassium. It will be seen that this pure antimony had a higher freezing point than the commercial sample, and that the discrepancy between our number and 440° was increased. It is worthy of notice that the pure antimony behaved like the pure metals, silver, gold, and copper, in having a freezing point persistent for a long time, and a melting point identical with its freezing point. The antimony was fused in a salamander cylinder placed in a small Fletcher's blast furnace, and it was protected from oxidation, when cooling, by keeping a current of coal gas passing

over the surface. After fusion for six hours, the surface remained perfectly bright, like molten silver. At the end of the experiments, the freezing point was again determined with pyrometer 7(4), and found to have undergone no change.

TABLE X.—*Freezing Point of Aluminium.*

Pyro.	Wt. of Al.	<i>t.</i>	Pyro.	Wt. of Al.	<i>t.</i>
7 (1)	68 grams	656·2	13 (3)	200 grams	654·1
(2)	282 "	654·4	(4)	180 "	655·8
8 (1)	282 "	654·6	(4)	175 "	655·0
(2)	—	655·1	(5)	175 "	655·0
(4)	175 "	654·5	(6)	175 "	654·9
13 (1)	200 "	652·5	(7)	175 "	654·1
(2)	182 "	654·0			

The mean of these values is 654·5°.

Perhaps it would be correct to reject 7 (1), on account of the small amount of metal used, and 13 (1), on account of the absence of flux, but both were good experiments, and the mean would not be altered by striking them out.

8 (3) and (5) were rejected, on account of the absence of any stir, and 8 (5) and 8 (6) on account of the kind of aluminium used in them (electrolytic from Schaffhausen), which appeared to be less pure than the metal used in the other experiments. The freezing point of aluminium is far less definite than that of the metals antimony, silver, gold, and copper. Its temperature is never quite stationary, but, during the period of solidification, falls very slowly. There is no difficulty in determining the f. p. roughly, but a sharp reading is impossible. This, no doubt, is due to the impurities present (silicon and iron) in the samples of the metal at our disposal.

The presence or absence of flux did not make a very great difference in the f. p. On some occasions we blew oxygen through the molten metal, but did not thereby alter the freezing point, although large quantities of oxide were formed. It would appear from this that the oxide is little, if at all, soluble in the metal. From the fact that the freezing point was not changed by blowing oxygen through the metal, we conclude that the impurities were not removed by the process. We found, by direct experiment, that the addition of crystalline silicon lowered the freezing point.

We generally used as a flux a fused mixture of sodium and potassium chlorides with a little cryolite. This flux underwent some chemical changes, emitting flashes of light when it was stirred, but the f. p. of the aluminium did not appear to be affected by it. The

aluminium used in the experiments given in the table above was known to contain 99·5 per cent. of pure Al.

TABLE XI.—*Freezing Point of Silver.*

Pyro.	Wt. of Ag.	<i>t.</i>	Pyro.	Wt. of Ag.	<i>t.</i>
8 (1)	300 grams	958·8	13 (4)	700 (Stas)	959·4
"	"	958·8	"	"	959·5
"	"	958·8	"	"	959·4
8 "	298 "	958·3	"	"	959·5
11 (1)	300 "	958·6	16 (1)	"	960·9
"	"	958·7	"	"	960·9
"	"	958·7	"	"	960·9
11 (2)	700 (Stas)	961·6	16 (2)	700 (J. & M.)	960·7
"	"	961·6	"	"	960·9
"	"	961·6	"	"	961·0
"	"	961·6	"	"	961·0
13 (2)	268 grams	957·5	16 (3)	298 (same as in 8 (3) )	959·6
"	"	957·7	"	"	959·6
"	"	957·9	"	"	960·4
13 (3)	"	958·3	16 (4)	284 (J. & M.)	960·4
"	"	958·5	"	"	960·6
"	"	958·5	"	"	960·4
"	"	958·5	"	"	

All these experiments were performed in salamander crucibles, and a little coal gas was allowed to burn in the furnace during cooling, so as to maintain a reducing atmosphere. With this precaution, there is no absorption of oxygen, and no spitting. If this precaution is neglected, as in 13 (1) and the first reading of 8 (1), the freezing point is always lower; Callendar has already observed this fact.

The 700 grams of silver used in 11 (2), 13 (4), and 16 (1) had been specially purified by us, using Stas' method of precipitation with ammoniacal cuprous sulphite. Its freezing point was exquisitely steady, and, as in the case of the gold, there was no difference between the melting and freezing points. The experiments 16 (2) and 16 (4) were performed with a new and specially pure sample of silver from Johnson and Matthey; its f. p. is the same as that of the Stas silver.

It seems probable also, from comparing 16 (4) and 16 (2), that 700 grams is better suited for an accurate determination than the smaller quantities. We therefore take, as the most probable value, the mean of 11 (2), 13 (4), 16 (1), and 16 (2), attaching equal weight to each group.

We thus get the number 960·7° for the temperature at which silver freezes.

TABLE XII.—*Freezing Point of Gold.*

Date.	Wt. of Au.	Pyro.	<i>d.</i>	<i>pt.</i>	<i>t° C.</i>
Dec. 23, 1894 :					
4.20	782 grams	18	1.574	903.15	1061.5
4.45	"	"	"	902.85	1061.2
Dec. 24 :					
11.40	"	13	1.500	908.60	1061.8
12.5	"	"	"	908.66	1061.9
12.25	"	"	"	908.68	1061.9
2.35	"	16*	1.532	906.74	1062.3
3.0	"	"	"	906.65	1062.2
3.16	"	"	"	906.56	1062.1
Dec. 30 :					
3.53	1200 grams	15	2.04	873.1	1061.2
4.45	"	13 A	1.553	905.8	1061.9
4.50	"	"	"	"	1061.9
4.58	"	"	"	905.7	1061.8
5.5	"	"	"	"	1061.8
6.5	"	14	1.511	907.95	1062.0
6.10	"	"	"	"	1062.0
6.15	"	"	"	"	1062.0
7.15	"	18 A	1.577	902.1	1060.1

The mean freezing point of gold is 1061.7°.

In the experiments of December 23 and 24, the 782 grams of gold was contained in a small, cylindrical, clay crucible, imbedded in a larger crucible, and heated in a Fletcher blast-furnace. The immersion of the pyrometer was from 60 to 70 mm., and the rate of cooling very slow. The period of constant temperature lasted from the commencement of freezing until the gold was a solid mass, and the melting point seemed to be identical with the freezing point.

In the experiments of December 30, with 1200 grams, the gold was contained in a single wider salamander crucible, and the depth to which the pyrometer was immersed was less than 50 mm. The rate of cooling was faster, and the period of constant temperature shorter, but the f. p. could in both cases be read to  $\frac{1}{1000}$ th of a degree. If it were not for the expense, a pot of 2000 grams of gold would afford an ideal means of obtaining the higher fixed point on platinum thermometers.

Messrs. Johnson and Matthey assayed the gold for us before the experiments; it proved to contain 99.95 per cent. of pure gold. After the experiments were finished, they again assayed the gold, and found that it had undergone no change whatever in purity.

\* A small uncertainty exists here as to the constants of 16.

TABLE XIII.—*Freezing Point of Copper.*

Pyro.	Wt. of Cu.	$t^{\circ}$ C.	Pyro.	Wt. of Cu.	$t^{\circ}$ C.
7 (2)	500 grams	1079·6	8 (1)	805 grams	1079·0
"	"	1079·5	8 (2)	"	1080·6
"	"	1080·4	"	"	1080·5
"	600 grams	1081·0	11	664 grams	1081·7
"	"	1080·9	"	"	1081·5
"	"	1080·9	"	"	1081·5
"	664 grams	1081·0	"	"	1081·3
8 (1)	805 grams	1079·2	12 (1)	"	1080·3
"	"	1079·0	12 (2)	500 grams	1081·6

The mean freezing point of copper is  $1080\cdot5^{\circ}$ .

These experiments were made in plumbago crucibles, the surface of the copper being protected from oxidation by a layer of molten borax; this layer formed a colourless glass when examined at the end of the experiment. In some cases, a little powdered charcoal was added to the borax, but this precaution does not appear to be necessary if plumbago crucibles are used. If the copper is allowed to oxidise, its f. p. is lowered, presumably by the solution of the oxide [*vide* 7 (1)].

The copper used with pyrometer 8 was the best rod and bar copper, such as is used for electrical connections. The other samples were granulated electrolytic copper from Johnson and Matthey. The pyrometer tubes were rapidly attacked by the fused borax.

#### *Experiments on the Freezing Points of Salts.*

The recent very interesting experiments of Victor Meyer, Riddle and Lamb (*Ber.*, 1894, **27**, 3129), on the melting points of salts, determined by means of an air thermometer, have led us to slightly extend our work with a view to getting another comparison with the air thermometer.

The freezing points of the salts were determined in a platinum crucible protected by an outer crucible, the space between being packed with magnesia or with broken crucible material. The porcelain tube of the pyrometer was protected from the action of the fused salts by a thin-walled platinum tube 105 mm. long, which fitted the pyrometer tube closely, like the finger of a glove.

Several sources of error were noticed.

1. The latent heat of most of the salts appears to be small, for a considerable amount of the salt crystallises before the pyrometer reaches a steady temperature.

2. Owing to the fact that the solid salt is deposited as a non-

TABLE XIV.—Freezing Points of Salts.

Time.	Pyro.	Weight of salt.	° C.	Time.	Pyro.	Weight of salt.	° C.	Time.	Pyro.	Weight of salt.	° C.
<b>K<sub>2</sub>SO<sub>4</sub>.</b>				<b>Na<sub>2</sub>SO<sub>4</sub>.</b>				<b>Na<sub>2</sub>CO<sub>3</sub>.</b>			
	13 (1)	145 grams	1061·4	3.5	13 (1)	512 grams	883	4.0	13 (1)	150 grams (about)	849·4
	"	"	1058·6	3.30	"	"	883·3	4.45	"	"	848·8
				3.55	"	"	883·2	5.20	"	"	847·9
3 P.M.	13 (2)	160 grams	1062·6	<b>Melting Point. V. Meyer's Method.</b>				2.32	17*	500	848·0
3.40	"	"	1062·7					3.25	16 (1)	"	845·3
4.0	"	"	1062·5					6.15	16 (2)	500 grams	851·7
4.0	13 (3)	577 grams	1066·2					6.36	"	"	851·1
6.0	"	"	1066·1					7.0	"	"	851·0
8.10	16 (1)	"	1066·7					7.30	18 (1)	"	849·2
	"	"	1066·8					7.50	"	"	848·4
	"	"	1066·7								
5.0	"	"	1066·6								
<b>Melting Point. V. Meyer's Method.</b>				* δ of pyrometer 17 was 2·10.							
12.10	16 (2)	1 gram	1083·9								
12.45	"	"	1085·5								
1.3	"	"	1084·3								
1.11	"	"	1083·2								



conducting layer on the surface of the pyrometer tube, which is at the same time cooling by conduction along the leads and stem, the steady temperature does not last so long as in the case of a freezing metal. For these reasons we procured a larger platinum crucible capable of holding a kilogram of the fused salts, and the only experiments we regard as trustworthy were made with large quantities in this crucible.

3. Another source of error lies in the fact that the fused salts at these high temperatures are rapidly acted on by the water vapour and reducing gases of the furnace. Our attempts to protect them were not altogether successful, owing to the necessity of keeping the crucible partly open to allow of the pyrometer being used as a stirrer, and also to the fact that platinum at high temperatures is readily permeable by gases.

The fused sulphates, when examined after the experiments, were found to be feebly alkaline, sometimes gave a black stain on a silver coin, and smelt slightly of sulphuretted hydrogen when moistened. The sodium carbonate slightly attacked the surface of the platinum, probably on account of the formation of a trace of caustic alkali.

It may be expected that changes of this kind would be roughly proportional to the duration of the experiment, and this is seen to be the case, for the f.p. of sodium carbonate becomes lower the longer it is heated. In the experiments with this salt, we can easily allow a correction for the time of heating; this gives us for the probable f.p. of freshly molten sodium carbonate a temperature very near  $852^{\circ}$ , both with pyrometers 16 and 18, and  $850^{\circ}$  for the abnormal pyrometer 17. We take  $852^{\circ}$  as the correct value, though this may turn out to be slightly too low. In the experiments with sodium carbonate, the deterioration of the salt could be watched by looking into the crucible; the first two or three times the salt was fused, it remained quite transparent, but afterwards it became opaque in consequence of some chemical change.

In the good experiments 16 (1), 13 (3), and 13 (1) with the sulphates, no progressive fall in the freezing point was detected; we therefore think that the slight chemical changes which undoubtedly occurred had no appreciable effect, and that the mean values  $1066.5^{\circ}$  for potassium sulphate and  $883.2^{\circ}$  for sodium sulphate may be accepted. The potassium sulphate used in 16 (1) was afterwards titrated with standard acid, and was found to contain 0.2 per cent. of free alkali reckoned as KOH. In a previous experiment we ascertained that 2 per cent. of sodium carbonate lowers the freezing point of potassium sulphate by  $20^{\circ}$ , and as a very rough approximation we may therefore assume that 0.2 per cent. of potassium hydroxide would cause a fall of  $2^{\circ}$ .

As the numbers we obtained for the freezing points of these salts differed from those of Meyer, Riddle, and Lamb, we determined to follow their method more closely. A sample of 1 or 2 grams of the salt was placed in a platinum test-tube 8 mm. wide and 110 mm. long, and fused at the lowest possible temperature. A platinum wire was then introduced into the fused mass, and as it solidified the wire became fixed axially in the tube. The test-tube was then secured to the pyrometer in such a position that the fused salt was on a level with and close to the coil. The pyrometer, with attached tube, was now placed in a bath, contained in our large platinum crucible, of some salt or mixture melting at a lower temperature than the salt in the tube. The free end of the platinum wire was carried over a pulley, and a weight of 50 grams attached to it. On slowly heating the furnace, the rise in temperature could be watched with the galvanometer, and at the moment when the weight pulled out the superficially-fused salt from the test-tube the temperature of the bath was taken. By repeating the experiment several times, cutting off the supply of heat while the temperature was well below that at which the pull-out took place, we could make the rise of temperature at the moment of pull-out very slow. In all cases, the wire pulled out with it the bulk or the whole of the salt.

When care is taken to make the rise in temperature of the bath very slow at the moment of pull-out, results consistent among themselves are obtained by the method, but we are disposed to think that it always gives too high a temperature. For example, with  $K_2SO_4$  we got  $1084^\circ$  for the pull-out (? melting point) and  $1066.5^\circ$  for the freezing point, the two temperatures differing by  $17.5^\circ$ . Similarly, the pull-out point for sodium sulphate exceeds the freezing point by  $19^\circ$ . As the pull-out point is determined on a rising, and the freezing point on a falling temperature, we should expect any lag of the pyrometer to produce an opposite effect to the one observed.

We think that the freezing point method is most probably correct, and that in V. Meyer's method the temperature of the bath rises considerably above the true melting point before the wire pulls out. Notwithstanding this fact, the pull-out experiments enable us to compare our thermometry with the air thermometry of Meyer, Riddle, and Lamb (Table XV, see next page).

It will be seen that in experiments with potassium sulphate, conducted in the same way, our results agree very well with those of V. Meyer, but in the corresponding experiments with sodium sulphate we are  $40^\circ$  higher. It may be inferred that a pull-out experiment with sodium carbonate would have given us a reading about  $20^\circ$  higher than Meyer's.

It is certain that these discrepancies are not wholly due to the

thermometry, but we are at present unable to localise the sources of error.

TABLE XV.

	Le Chatelier.	Victor Meyer.	Heycock and Neville.
Sodium carbonate...	810°	—	852·0°
Sodium sulphate....	867	—	883·2
Potassium sulphate..	1015	—	1066·5

*Melting Points by the Pull-out Method.*

Sodium carbonate...	—	849°	—
Sodium sulphate....	—	863	902·2°
Potassium sulphate..	—	1078	1084·0

*General Comparison of our Results with those obtained by other Observers.*

The best recent work on the melting points of silver, gold, and copper, that we are acquainted with, is contained in a paper by Holborn and Wien, "Ueber die Messung hoher Temperaturen" (*Ann. Phys. Chem.*, 1892, **47**, 107). They used a platinum rhodium couple standardised by a porcelain air thermometer.

Both their results and those of Meyer, Riddle, and Lamb, being based directly on air thermometry over the whole range studied, have a greater *à priori* claim to be regarded as standard numbers than ours, which are an extrapolation from air thermometry carried to 600° only. At the same time we would point out that a comparison of our numbers, even when obtained by pyrometers having very different constants, with those of Holborn and Wien, shows that a platinum-resistance pyrometer yields much more consistent results up to 1100° than those given by a thermo-couple.

We regard the substantial agreement of our results with those of Holborn and Wien as proving the validity of the  $\delta$  formula up to 1100°. This is, perhaps, the most important result of our work.

On account of the purity of the antimony, silver, gold, and copper used by us, we attach considerable value to the freezing points found for these metals. The other metals were probably not so pure, and there may be on that account an error of a few degrees in the values given.

The following table gives a comparative view of our results, those of Holborn and Wien, and of some other recent workers. The numbers are partly taken from Holborn and Wien's paper.

COMPARATIVE TABLE XVI.

Year . . . .	1879.	1892.	1892.	1895.
Observers .	Violle.	Holborn and Wien.	Callendar and Griffiths.	Heycock and Neville.
Tin . . . . .	—	—	231·7	231·9
Zinc . . . . .	—	—	417·6	418·96*
Antimony ..	—	—	—	629·54
Magnesium..	—	—	—	632·6
Aluminium..	625	—	—	654·5
Silver . . . . .	954	968	972·0†	960·7
Gold . . . . .	1035	1072	—	1061·7
Copper . . . .	1054	1082	—	1080·5

## SECTION IV.

*Determination of the Ice Point  $R_0$ .*—For this purpose, we use a double copper cylinder, the inner cylinder being 250 mm. high and 100 mm. in diameter, with the interval between the two cylinders packed with felt.

The ice is crushed to a fine powder by hammering it between folds of dry sail-cloth; it is then washed, drained, and transferred to the inner copper cylinder. Water from *previously melted ice* is now poured on it, and the ice and water well stirred together. The excess of water is drained off by a tube attached to the lower end of the cylinder until the water level is about an inch below the top of the ice.

Great care must be taken to remove all soluble salts from the surface of the pyrometer tube before introducing it into the ice. The measurement of the resistance can be made when the pyrometer has been in the ice about five minutes.

*Determination of the Steam Point  $R_{100}$ .*—We use a hypsometer of the ordinary form, except that it is provided at the side with a wide reflux condenser, so arranged as to deliver the condensed water into the boiler below the surface of the boiling water. Some arrangement of this sort is necessary, otherwise the steam would condense on the head of the pyrometer and injure the insulation.

Since a change of 27 mm. in the barometer produces a change of  $1^\circ$  in the boiling point of water in the neighbourhood of  $100^\circ$ , we see that  $\frac{dt}{dp} = 0.037^\circ$  per millimetre. If the thermometer is one whose fundamental interval is within  $1^\circ$  of 100, we can at once reduce

\* Meyer and Riddle by the air thermometer get  $419^\circ$  for the melting point of zinc (*Ber.*, 1893, 26, 2443).

† This number is not given by Callendar, but it can be deduced from the data he gives (*Phil. Mag.*, Feb., 1892).

$R_{100}$  to what it would have been at a pressure of 760 mm. (see Table IV).

It is absolutely necessary that the surface of the pyrometer should be free from all soluble salts when the steam point is being taken.

We used a special form of compensated sulphuric acid barometer, made by Hicks, of Hatton Garden. This barometer is the invention of Professor Callendar, and is described by him in the *Phil. Mag.*, January, 1894. It has a very open scale, one division being equal to 0.188 mm. of mercury, and is therefore much more suitable for our work than an ordinary mercury barometer. Mr. Griffiths kindly compared it daily for some weeks with his standard mercury barometer. A scale of comparison was then plotted in such a way that the readings were at once obtained on the mercury scale reduced to 0° and sea level in latitude 45.

*Determination of the Sulphur Point  $R_s$ .*—Besides finding the constants  $R_0$  and  $R_{100}$  for a platinum pyrometer, it is necessary, in order to obtain the constant  $\delta$  in the equation

$$t - pt = \delta\{(t/100)^2 - t/100\},$$

to find the resistance at some other known temperature, which should be at a considerable distance above  $R_{100}$ . We have followed Callendar and Griffiths in choosing the boiling point of sulphur, and in the details of the method pursued.

In order to obtain with accuracy a fixed point on a thermometer immersed in boiling sulphur vapour, it is necessary to pay attention to numerous small details. The following method gives the most satisfactory results.

The vessel containing the sulphur, Fig. 3, resembles the outer boiling tube of a Victor Meyer's vapour density apparatus. It is 48 cm. long by 5 cm. diameter, with a bulb at the bottom 6—7 cm. in diameter, and is made of hard glass.

The tube passes through the axis of a cone of asbestos card, the space between the cone and the tube being packed with asbestos wool. This outer cone, which is 36 cm. long and 15 cm. wide at the base, serves as a jacket, to prevent either too rapid cooling of the sulphur vapour or its superheating by the flame of the lamp. It is necessary that the liquid sulphur should reach 4 or 5 cm. up the boiling tube, in order that any superheated sulphur vapour may be washed by the liquid sulphur out of contact with the overheated walls of the bulb. If this precaution be neglected, consistent results cannot be obtained. With a single large-sized Bunsen, and using 260 grams of sulphur, it takes about  $1\frac{1}{2}$  hours before the sulphur vapour appears above the top edge of the outer asbestos cone.

The pyrometer is placed in the axis of the glass tube, as shown in

the figure, and it is absolutely necessary to protect the part containing the platinum spiral by means of a cone of thin asbestos, constructed as follows. Asbestos card, about  $\frac{1}{16}$  in. thick, is rolled into a cone 10 cm. long, with its base just wide enough to fit loosely the inside of the glass tube. This cone is stitched together with iron wire, and is perforated near its apex with three or four holes about  $\frac{1}{2}$  in. in diameter. The base of the cone is closed with a plate of asbestos, perforated at its edges, as shown in the plan B of Fig. 3.\* By means of this

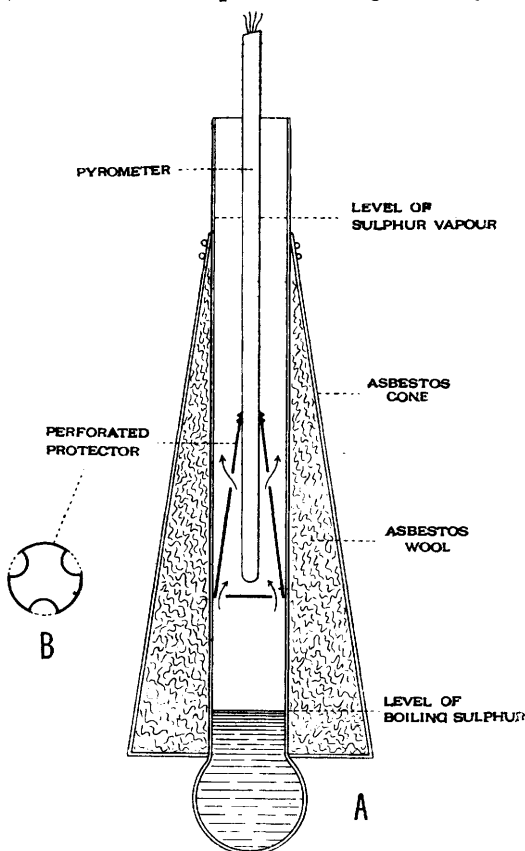


FIG. 3.—Section of sulphur-boiling apparatus showing pyrometer and inner cone. inner cone, which is bound to the pyrometer with iron wire, the sulphur vapour is made to take the path indicated by the arrows, whilst the liquid sulphur condensed above trickles either down the walls of the glass tube or over the surface of the cone, *without flowing over the bulb.*

\* This inner cone is referred to in the tables as the “perforated protector.”

A pyrometer immersed in the sulphur vapour acquires the temperature in about 10 minutes, and will not show a change of more than  $0\cdot02^\circ$  in the course of several hours, provided the barometer is steady. If the sulphur is allowed to solidify in the bulb, it can be remelted by withdrawing the glass tube from the outer cone and heating it round the surface of the sulphur, and not at the bottom of the bulb. If this simple precaution be adopted, the same tube will serve for some dozens of determinations. When the pyrometer is in the sulphur vapour, the mouth of the tube is closed with asbestos card. The sulphur used in our experiments was kindly given to us by Mr. Allhusen, of Newcastle, and was chemically pure; it was obtained by the partial combustion of sulphuretted hydrogen.

Since the *pt* temperature of boiling sulphur varies with the height of the barometer, it is necessary to introduce a correction. From Regnault's experiments we get the change of temperature due to a small change of pressure in the neighbourhood of the boiling point.

$$\frac{dt}{dp} = 0\cdot082^\circ \text{ C. per mm.}$$

This holds approximately for a change of 10 mm., either above or below the boiling point. An example will show most clearly how this pressure correction is applied.

*Example.*—Pyrometer 16 on December 21 had the following constants.

$$R_0 \dots 288\cdot347. \quad R_{100} \dots 391\cdot734. \quad R_s \dots 723\cdot788.$$

$$\text{Bar.} \dots 762\cdot04. \quad \text{Since } \frac{dt}{dp} = 0\cdot082 \text{ per mm., the sulphur was}$$

boiling at a temperature of

$$444\cdot53 + 0\cdot082 \times 2\cdot04 = 444\cdot7.$$

$$\text{Again, since } pt = \frac{Rt - R_0}{R_{100} - R_0} \times 100, \text{ we get}$$

$$\begin{aligned} Pt_s &= \frac{(723\cdot788 - 288\cdot347) \times 100}{391\cdot734 - 288\cdot347} \\ &= \frac{435\cdot441 \times 100}{103\cdot387} \\ &= 421\cdot176. \end{aligned}$$

Hence, substituting in the formula

$$\begin{aligned} t - pt &= \delta t / 100(t/100 - 1), \text{ we get} \\ 444\cdot7 - 421\cdot176 &= \delta \cdot 4\cdot447 \times 3\cdot447, \text{ therefore,} \\ \delta &= \frac{23\cdot524}{15\cdot328} = 1\cdot5347 \end{aligned}$$

We wish here to express our indebtedness to the Grant Committee of the Royal Society for their liberality in placing at our disposal a sum of money for the purchase of instruments.

To Messrs. Johnson and Matthey for lending us, free of all charge, the considerable quantity of gold necessary for our experiments, for making the assays, and for valuable information concerning the metals we have used.

To Mr. Horace Darwin, of the Cambridge Scientific Instrument Company, for the care and accuracy with which he has constructed the thermometers and other apparatus.

To Mr. E. H. Griffiths for much valuable advice concerning the thermometers, and also for practical assistance in some of the later experiments.

[*Note as to the purity of the copper used in the experiments with Pyrometers 7, 11, and 12.*—Messrs. Johnson and Matthey have made a special assay of the electrolytic copper mentioned on p. 190, and find that it contains 99·95 per cent. of copper. We have estimated the iron in 10 grams, and found 0·04 per cent.]

*Sidney Sussex College,  
Cambridge.*

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