

# The International Temperature Scale between 0 degrees and 100 degrees C

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# PHILOSOPHICAL TRANSACTIONS.

I.—The International Temperature Scale between 0° and 100° C.

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I.—Scope and Objects of the Work.

The aim of the work set out in the following paper is to secure as accurate as possible a knowledge of the difference between the scales defined by the platinum resistance thermometer and the mercury in verre dur thermometer. The readings of the former are reduced by the customary quadratic equation of Callendar, and the latter by using the corrections to the constant volume hydrogen scale, as determined by Chappuis.\*

The reasons for undertaking the intercomparison may be set out briefly as follows:— In 1887 the International Committee of Weights and Measures adopted as the standard scale of temperature that of the constant volume hydrogen thermometer set up by Chappuls at the Bureau International at Sèvres. In order to make this scale available to investigators elsewhere, primary standard mercury in verre dur thermometers were prepared by Tonnelot of Paris to the specification of the Bureau International, and Chappuis\* made a careful comparison between eight of these mercury thermometers and his hydrogen thermometer over the range - 24° C. to 100° C. The "International Hydrogen Scale" (échelle thermométrique normale) thus became defined in terms of the mean scale of certain mercury thermometers in the possession of the Bureau International, while other mercury thermometers of the same type were prepared by TONNELOT (in more recent years by BAUDIN) and circulated among the different nations, after their fundamental constants had been determined by the Bureau International. In this way the standard scale of the National Physical Laboratory, for example, over the range 0° C. to 100° C. became that defined by the particular "Tonnelot" and "Baudin" thermometers in its possession, and it remained so up to the year 1927.

During recent years, however, agreement has been reached between three national laboratories—the Bureau of Standards (U.S.A.), the Physikalisch-Technische Reichsanstalt (Germany), and the National Physical Laboratory (Great Britain) on a scale which was formally adopted as the "International Temperature Scale" at the Seventh General Conference of Weights and Measures held at Sèvres in September, 1927. The definition of the International Temperature Scale recognises the thermodynamic Centigrade scale as the "fundamental scale to which all temperature measurements

\* 'Trav. Mém. Bureau Internat. des poids et mésures,' vol. 6 (1888).

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should ultimately be referable," and proceeds to specify a scale based on fixed points, with standard means of interpolation, as the best conveniently realisable approximation to this scale. It is specified that the scale between 0° C. and 660° C. shall be defined by a platinum resistance thermometer, using the formula

$$R_t = R_0 (1 + At + Bt^2),$$

the constants R<sub>0</sub>, A and B being determined by calibration at the ice, steam and sulphur points.\* The temperature of the sulphur boiling point at 760 mm. pressure is defined as  $444 \cdot 60^{\circ}$  C., and it is specified that the ratio  $R_t/R_0$  shall be not less than  $1 \cdot 390$  when  $t = 100^{\circ} \text{ C. and } 2.645 \text{ when } t = 444.6^{\circ} \text{ C.}^{\dagger}$ 

On the "International Temperature Scale," therefore, the mercury thermometer as a standard means of interpolation is eliminated. It thus became necessary to determine what change, if any, would be made in the temperature scale used at the National Physical Laboratory by the adoption of the platinum resistance thermometer in place of the mercury in verre dur thermometer for interpolation between 0 and 100° C. An intercomparison of the Tonnelot and Baudin thermometers in use at the N.P.L. with the platinum resistance thermometer was therefore undertaken. It has been shown, however, by Waidner and Dickinson; that the scales defined by various verre dur thermometers may differ among themselves by as much as 0.02° C. in the region under consideration. It was therefore felt desirable to utilise as many mercury thermometers as could be made available with a view to securing as good a comparison as possible between the "mean verre dur scale" and the "platinum" scale. Since the differences between the scales defined by different mercury thermometers are probably mainly due to slight variations in the composition of the glass, it was particularly desirable to include thermometers made at about the same time as those used by Chappuis in his original intercomparison with the gas thermometer. Details of the thermometers used by him and of those used in the present investigation are given in Table I.

# II. The Platinum Thermometers.

The platinum thermometers used are of the potential lead type and are hermetically sealed. Fig. 1 is a diagrammatic representation of the type. The bulb is constructed of mica, in the manner devised by Callendar. The mica cross is wound with the

\* For ease in computation in the present work, the equivalent formulæ, embodying the conception of a "platinum temperature"  $(t_{pt})$ , advocated by Callendar, have been used. These formulæ are:—

$$t_{pt} = 100 \, (R_t - R_0) / (R_{100} - R_0) \text{ and } t - t_{pt} = \delta \cdot t \, (t - 100) \cdot 10^{-4}.$$

- † Equivalent to  $\delta = 1.50$  when  $R_{100}/R_0 = 1.390$ .
- ‡ 'Bull. Bur. Standards,' (Sci. paper 69), vol. 3, p. 663 (1907).
- § It is very important that the mica used should be of high quality and as free as possible from iron. When dehydrated by heating, it should take a silvery appearance: if any yellowness is apparent the specimen should be rejected. The mica used in the construction of these thermometers was "Best clear ruby mica" obtained from Messrs. Mica Products, Ltd., Langton Road, London, S.W.9.

TABLE I.

Number.	Date of manufacture.	Maker.	Scales.	Range covered in intercom- parison.	Owner.
		Thermo	meters used in the present intercon	nparison.	
4,303 4,304 4,305 4,306 4,517 4,518 4,893 4,976 11,048 11,151 15,504 15,959 16,377 16,378 18,370	May, 1884 May, 1884 May, 1884 May, 1884 Nov., 1885 Nov., 1885 Feb., 1890  —, 1891 Dec., 1892  Feb., 1893 May, 1897 July, 1903 Sept., 1905 Sept., 1905 July, 1913	Tonnelot  "" "" "" "" "" "" Baudin "" ""	3 to + 51 and + 95 to + 103 3 to + 51 and + 95 to + 103 3 to + 51 and + 95 to + 103 3 to + 51 and + 95 to + 103 3 to + 51 and + 95 to + 103 4 to + 103 5 to + 102 6 to + 103 4 to + 103 3 to + 27, + 48 to + 52 and 4 to + 102 2 to + 2 and + 47 to + 103 5 to + 52 and + 95 to + 102 4 to + 52 and + 98 to + 102 4 to + 52 and + 98 to + 102 4 to + 52 and + 98 to + 102 2 to + 2 and + 98 to + 102 2 to + 2 and + 48 to + 102 2 to + 2 and + 48 to + 102	0 to 50 0 to 50 0 to 50 0 to 50 0 to 100 0 to 100 0 to 100 0 to 26 50 to 100 0 to 50 0 to 50 0 to 50 50 to 100	Board of Trade.  "" "" "" Board of Education (Science Museum). N.P.L. University College, Cardiff. N.P.L.  "" "" "" "" "" ""
	,,	,,	Thermometers used by Chappuis.*		,,
4,428 4,429 4,430 4,431 4,479 4,480 4,481 4,482	Jan., 1885 Jan., 1885 Jan., 1885 Jan., 1885 Nov., 1885 Nov., 1885 Nov., 1885	Tonnelot   '', '', '', '', '', '', '', '', '', '	$\begin{array}{c} -5 \text{ to} + 104 \\ -32 \text{ to} + 39 \text{ and} + 95 \text{ to} + 103 \\ -32 \text{ to} + 39 \text{ and} + 95 \text{ to} + 103 \\ -32 \text{ to} + 39 \text{ and} + 95 \text{ to} + 103 \\ -32 \text{ to} + 39 \text{ and} + 95 \text{ to} + 103 \\ -32 \text{ to} + 39 \text{ and} + 95 \text{ to} + 103 \\ \end{array}$	0 to 100 0 to 100 0 to 100 0 to 100 - 24 to 0 - 24 to 0 - 24 to 0 - 24 to 0	Bureau International.  ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,,

purest obtainable platinum wire, of 0.1 mm. diameter and such length† as to make its resistance in ice lie between 30 and 31 ohms or its resistance in steam between 40 and 41 ohms. This choice of resistance has the advantage of enabling at least one fixed point on each thermometer to be read in two ways on a decade bridge. Each end of the bulb wire is fused with two leads of 0.6 mm. diameter commercial platinum wire into a bead, in such a manner that the bulb wire leaves the bead as nearly radially as possible. The lead wires are taken through mica washers in the customary manner to the head of the thermometer. The envelope of the thermometer is of "Pyrex" glass, except where the lead wires are fused in. Here there is a cap of soda glass, through which four equal short lengths of platinum are sealed in enamel, these lengths being afterwards fused to the leads attached to the bulb. The soda glass cap is drawn out to a pip for sealing off, and is fixed in the Pyrex tube through a narrow rubber

<sup>\* &#</sup>x27;Trav. Mém. Bureau Internat. des poids et mésures,' vol. 6 (1888).

<sup>†</sup> About 2.2 metres, making a bulb about 9 cm. long when wound at a pitch of 1 mm.

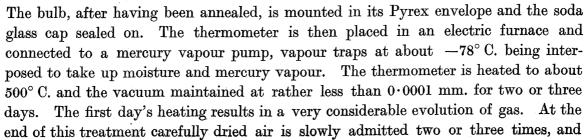
Fig. 1.

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ring, the joint being covered with De Khotinsky "medium" cement. This makes a joint which is sufficiently elastic to take up the differential expansion between the two glasses, while still remaining vacuum tight. The head is designed to prevent any

> straining of the internal leads. The external leads are made of two 12-foot lengths of 3/0.028-inch "Maconite" twin wire. heavy rubber insulation of dumb-bell section which serves as an efficient protection against the breakage of strands.

The annealing, drying and sealing of the thermometer is carried out as follows: Before being mounted in its Pyrex envelope, the thermometer is heated in a clean silica tube in a platinum furnace to a temperature of 720° C. for half an hour, the thermometer being removed and plunged in liquid oxygen two or three times towards the end of the period. The effect of this furnace heating is to dehydrate the mica completely. While this has the drawback of making the bulb much more fragile, it is felt to be desirable, in order to avoid any risk of subsequent liberation of moisture in the sealed thermometer. Dehydration starts at just about 660° C., which is the limit of the region in which the platinum thermometer is used for the purposes of the International Temperature Scale, so that if dehydration is not carried out initially, moisture would almost certainly be set free in high temperature thermometers. At the National Physical Laboratory a standard procedure for annealing has been adopted for all platinum thermometers of this type. If the furnace heating is prolonged, the platinum appears to become progressively contaminated by the mica, but the treatment outlined above has only a slight effect on the constants of the wire. After the furnace heating, the wire is given a further annealing for two hours by passing a current sufficient to maintain its temperature at 1000 to 1100° C. In the case of S1 the annealing was done at 1000° C. in a furnace over a period of 24 hours and, in consequence, the ratio  $R_{100}/R_0$  was considerably depressed. When S2 was made, electric annealing, preceded by a 4-hour furnace heating, was used, and a low  $\mathrm{R}_{100}/\mathrm{R}_{0}$  is still shown. S1 was broken and reconstructed in the course of the work, and in the case of S4, S5 and the new S1 the standard method described above was adopted.



finally the thermometer is sealed off when filled with dry air at atmospheric pressure and a temperature of about 450° C.

Thermometers S1 and S4 were made from platinum supplied by Messrs. Johnson Matthey, that for S2 was kindly given by the Bureau of Standards as a sample of their own preparation, while that for S5 was purchased from Heraeus. Thermometers S1 and S2 are about 37 and 32 cm. in length respectively, while S4 and S5 are about 70 cm. long. In order to reduce the lead resistance of the long thermometers, the leads are made of silver, except for 10 cm. of platinum adjacent to the bulb and a similar length where the leads are fused through the glass.

In the early stages of the work the thermometers had a somewhat different type of seal, but this was found to be unsatisfactory, as it broke down after a few months' use. Except when such a breakdown occurred, and moist air entered the thermometer, the zeros remained very constant, variations rarely exceeding a few thousandths of a These variations, moreover, could in most cases be attributed to the resistance bridge rather than to the thermometer, as, in general, both thermometers in use changed together,\* the original values being restored on re-calibrating the bridge.

Table II shows the fundamental constants of the thermometers used. Since the early thermometers had an R<sub>100</sub>/R<sub>0</sub> less than 1·390, a careful comparison was made to see whether the original S1 defined a scale appreciably different from that given by the other thermometers. No measurable difference was found, however, in the region explored (30° C. to 60° C.). The lag coefficient of each platinum thermometer was determined in one of the water baths used in the intercomparison, and the values found were as follows: S1, 22.5 sec., S2, 17.5 sec., S4, 15 sec., and S5, 19 sec.

# III.—The Resistance Bridge.

The bridge used is that described by Smith and is essentially a Kelvin Double Bridge, as in fig. 2. P is the thermometer bulb,  $L_1$ ,  $L_2$ ,  $L_3$  and  $L_4$  the leads, Q and aare variable resistances, and S, R, and b fixed resistances. The condition for balance of this network is:—

$$P = \frac{(Q + L_3) R}{S} + \frac{b L_2}{(a + b + L_1 + L_2)} \left( \frac{Q + L_3}{S} - \frac{a + L_1}{b} \right),$$

which, if  $L_1 = L_2 = L_3$ , a and Q are large compared with L, and a = b (R + Q)/(R - S), reduces to P = QR/S.

In the actual bridge used R is 10 ohms and S and b 1000 ohms each. The lead resistances are about 0.2 ohm in the region 0° C. to 100° C. and P is rather more than In these circumstances it can be shown that the error involved in the

<sup>\*</sup> See, for example,  $R_0$  for S4 and S5 on 19th February, 1929 (Table II).

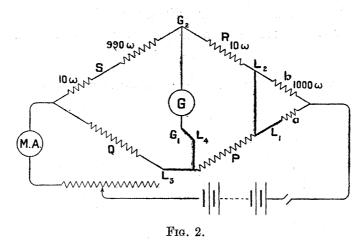
<sup>† &#</sup>x27;Phil. Mag.,' vol. 24, p. 561 (1912).

# TABLE II.

	TABLE		
Date.	$\mathbf{R}_{0}.$	$ m R_{100}/R_{0}.$	8
	S.1.		
5.7.27	29.0449		1.500
		1 99617	1.900
7.7.27	29.0453	$1.38617_{0}$	
11.7.27	29.0453	$1.38616_{0}$	
29.7.27	29.0456	1.38615,	
7.10.27	29.0455	$1.38615_{6}$	
21.1.28	29.0460	$1\cdot38615_{6}$	
	Thermometer broke	n and re-made.	
21.3.28	28.6978	$1 \cdot 39057_{9}$	1.493
27.3.28	28.6978	$1\cdot39057_{2}$	·
	Thermometer opened	l and re-sealed.	
31.5.28	28.6994	$1.39058_{7}$	
11.9.28	28.6996		1 · 493
19.9.28	28.7000	$1 \cdot 39060_3$	1 100
19.9.28	28.7000	$1.39058_{4}$	
10.0.20		1 000004	
	S.2.		•
6.7.27	29.9949	<u> </u>	1.498
7.7.27	$29 \cdot 9949$	$1.38869_{6}$ *	
11.7.27	$29 \cdot 9949$	$1.38868_{8}$	$1 \cdot 499$
29.7.27	$29 \cdot 9949$	$1.38868_{6}$	
7.10.27	$29 \cdot 9947$	$1.38869_{2}$	·
20.1.28	$29 \cdot 9950$	$1.38869_{7}$	
8.2.28	$29 \cdot 9952$	1.388692	<u> </u>
27.3.28	29.9947	$1.38868_{9}$	
	S.4.	u di ser <del>e</del> d	·
31.5.28	28.6575	1.390782	
10.9.29	$28 \cdot 6572$	*	1.493
	Thermometer opened	and re-sealed.	
31.10.28	$28 \cdot 6593$	$1 \cdot 39077_7$	programme .
1.11.28	28.6593	$1.39076_{3}$	
1.11.28	28.6593	$1.39076_{3}$	
19.2.29	28 • 6585	1.39076	
10.2.20		2 000.04	
	S.5.		
11.9.28	30.8915		1.490
19.9.28	30.8916	1.39078,	- American
19.9.28	30.8916	1.39078,	
31.10.28	30.8918	$1 \cdot 39079_{4}$	
1.11.28	30.8918	1.390783	
7 77 00	30.8918	$1.39078_{7}$	
$1.11.28 \\ 19.2.29$	30.8911	$1.39079_{\delta}$	

<sup>\*</sup> Wire when annealed according to more recent practice gives 1.3913.

approximation is about 0.0000002 ohm. An introduction of a 0.5 per cent. difference between L<sub>2</sub> and L<sub>3</sub> can cause an error of about 0.00002 ohms or 0.0002° C. This, it



should be noted, is an error in an absolute determination of the resistance and is considerably reduced where thermometry—which is essentially a differential measurement—is concerned.

The remaining source of error lies in the inexactitude of the relation

$$a = b (R + Q)/(S - R) = (Q + 10)/0.99$$

in the actual bridge.

The dials of the bridge (fig. 3) are arranged so that each "Q" coil carries with it the corresponding "a" coil equal to 1/0.99 of its value, while a coil of 10/0.99 ohms is

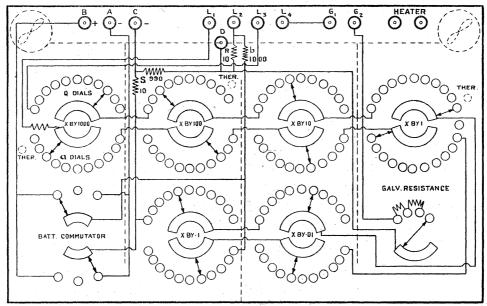


Fig. 3.—In normal use the battery is connected to A and B. To check that a = (Q + 10)/0.99, the battery connections are changed to B and C, links are inserted between L2 and D and between L<sub>1</sub>, L<sub>3</sub> and L<sub>4</sub>, and the battery commutator is set in the position shown.

permanently connected in the "a" arm of the bridge. In order to test readily whether the condition is satisfied, the "S" arm of the bridge is divided into a 10-ohm coil and a 990-ohm coil, the 10-ohm coil being adjacent to the "Q" arm. By a suitable arrangement of links it is possible to make the connections as in fig. 4, the condition for balance being:—

$$a = b (Q + S_{10})/(S - S_{10}) = b (Q + R)/(S - R)$$
, if  $S_{10} = R$ .

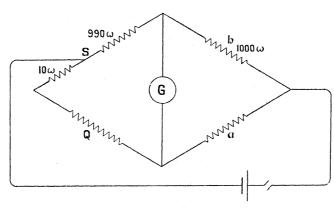


Fig. 4.

In the actual bridge in use  $S_{10}$  is equal to about 1.0003 R, but it can be shown that the error introduced into the estimate of the Q/a relationship by this cause is only about 5 parts in a million, which, it will be seen, is quite beyond the accuracy needed in the check. Further, the out-of-balance current in this network shows that the error in the relation a = b(Q + R)/(S - R) is about 1 part in 3000 and is reasonably constant at this figure. If we consider a thermometer whose resistance at 0° C. is 30 ohms and whose leads are of 0.2 ohm resistance at 0°C, and which is supposed to be about 75 per cent. immersed in the temperature measured, we find that the error introduced by this cause at the ice point (P = 30 ohms, L = 0.22 ohms) is  $-0.0004^{\circ}$  C. and in steam (P = 40 ohms, L = 0.28 ohms)  $-0.0006^{\circ}$  C., so that the error on the fundamental interval is only 0.0002° C.

In the original calibration of the bridge the resistances of all the "Q" coils were measured at 20° C. by means of a potentiometer, taking an external Wolff 100-ohm coil as standard and stepping up or down by comparing each coil with the sum of the coils in the next dial below. The resistance of the connections, brushes, etc., in this arm of the bridge was also measured and found to be about 0.005 ohm. The temperature coefficients of the 1000-ohm, 100-ohm and 10-ohm "Q" coils and of the "R" and "S" coils were determined, and the Q/a relationship was checked in the manner indicated above. Finally, the bridge was standardised by using it to measure the resistances of 10-ohm and 100-ohm Wolff coils. The Wolff coils used were kept under observation throughout the work and compared weekly with the sealed standard coils of the Electrical Measurements Department of the Laboratory.

In measuring the 100-ohm coil it was found that the bridge reading rose steadily for some time after switching on the battery current, due to the fact that when high resistances are being measured the ratio coils carry a much heavier current than the "Q" coils and the heating effect on the "S" coil is sufficient to increase the ratio perceptibly. It can be shown that if the total current given by the battery is  $i_b$ , that passing through the thermometer  $i_t$ , and the bridge be balanced at a reading Q, then

$$i_b = (Q/1000 + 1) i_t$$

The current through the "S" coil is therefore (Q/1000)  $i_t$ . The change in S with current was determined by arranging it to form one arm of a Wheatstone Bridge with a high resistance connected as a shunt on one of the arms so as to give a fine variation of resistance, and varying the current through a wide range. From the figures thus obtained a table of "ratio heating corrections" was drawn up. These were tabulated as corrections to the bridge reading for a given thermometer current and for any balanced bridge reading (Q) from 1000 ohms (below which the correction is negligible) up to 11,000 ohms. The thermometer current used throughout the present work was 4 milliamps, and the ratio heating corrections for this current on a thermometer of  $R_0 = 30$  ohms are  $-0.001^{\circ}$  C. at  $0^{\circ}$  C.,  $-0.003^{\circ}$  C. at  $100^{\circ}$  C. and  $-0.02^{\circ}$  C. at  $445^{\circ}$  C. The correction for heating of the 1000-ohm coils in the "Q" arm was found to be less than 1 part in a million for a current of 4 milliamps and has therefore been neglected.

During the progress of the intercomparisons to be described, the values of the 1000 ohm and 100 ohm coils in the "Q" arm were redetermined at intervals of about six weeks, and on each occasion the ratio R/S was redetermined by using the bridge to measure the resistance of the 100-ohm Wolff coil.

The bridge is of the oil-immersed type and is filled with pure acid-free paraffin. It was made by H. Tinsley & Co. and follows the layout of fig. 3 as regards the arrangement of the coils. The paraffin is circulated by means of two screw propellers indicated in the back corners of the bridge. Each of these propellers revolves in a vertical tube, and between the two is a compartment separated from the main body of the bridge and containing a heating coil of about 80 ohms resistance. Both screws drive downwards. The oil is drawn from the heater compartment into the top of the right-hand screw tunnel, leaving this for the main part of the bridge at the bottom. A series of baffles then arranges that it flows to the front of the bridge over the  $\times 1.0$  dial and the galvanometer key, then to the back over the  $\times 0.01$  and  $\times 10$  dials, to the front over the  $\times 100$  and  $\times 0.1$  dials, and finally back over the battery switch and the  $\times$  1000 dial into the top of the left-hand screw tunnel, whence it is returned into the heater compartment at the bottom. Three mercury thermometers divided to tenths of a degree are mounted in the oil stream in the positions marked in the diagram. It was found that if the air temperature was about 15° C. and sufficient energy was supplied by means of the heater in the bridge to maintain the temperature of the oil at about 20° C., there was a drop in temperature of about 0.5° C. during a circuit of the oil in

the bridge. As it was desired to know the coil temperatures to at least 0.1° C., steps were taken to improve the uniformity. The entire bridge was surrounded by a wooden casing, so that, starting from the outside of the bridge, the lagging was as follows:—  $1\frac{1}{2}$  inches granulated cork,  $\frac{1}{2}$  inch wood,  $1\frac{1}{2}$  inches air, and  $\frac{1}{2}$  inch wood. Heaters were placed in the air space so that its temperature could be made approximately 20° C. In hot weather the temperature of the bridge could be kept down by circulating icecold water through pipes contained in this air space, the water being fed from a tank which was kept charged with lumps of ice. In very cold weather additional heat could be supplied from a heater on the floor under the bridge, the space round it being enclosed by baize curtains. In this way it was possible to reduce the amount of energy required in the bridge heater itself to about 10 watts, and in these circumstances it is easy to keep all three thermometers within about 0·1° C. The centre thermometer is taken as giving the temperature of the ratio coils and of the 100-ohm Q coils, while the left-hand thermometer gives that of the 1000-ohm Q coils. The resistances controlling the current in the bridge heater are mounted on a board on the wall alongside the bridge. A maximum resistance of 1600 ohms, which can be cut out in steps of 25 ohms by means of a series of switches, is available, and the current is indicated by an The whole of the electrical energy for heating, cooling, stirring and illumination is taken from a board carrying a number of two-pin plugs. One of these plugs has an independent switch, but the others are all fed from the 110-volt mains through a double-pole knife switch of high-grade insulation. The current for the scale lantern is supplied from the independently controlled plug, and it is thus possible to disconnect all electric mains from the bridge and to observe if there is any effect on the balance due to electrical leakage.

With a view to eliminating as far as possible changes in resistance of the bridge coils with humidity,\* a current of dried air is continuously passed through the oil. Calcium chloride pots are also kept under the glass cover of the bridge. When not in use the glass is kept covered by a black cloth to protect the ebonite of the bridge from light, and during observations there is normally only artificial light in the room.

The current for working the bridge is supplied by a battery of 36 glass "mass type" accumulators, kept on insulated shelves in the basement immediately below the The leads are brought through the floor in an ebonite tube and pass by way of a resistance box (maximum 1111 ohms, variable by 1 ohm) and a 50-milliamp. Weston milliammeter to the battery terminals of the bridge. The four thermometer leads from the bridge are of 12 S.W.G. insulated copper wire ("Association" cable, 2500 megohm grade) and are carried on porcelain cleats throughout. They are taken to a set of four terminals on an ebonite distribution board near the bridge, and these terminals can be linked with either of two other sets. One of these connects with leads to a terminal board in the same room, conveniently placed for the water baths, hypsometer and ice bath, and the other with leads to the basement where the sulphur

<sup>\*</sup> Rosa and Babcock, 'Bull., Bur. Standards' (Sci. paper 73), vol. 4, p. 121 (1907).

bath is installed. The distribution board and terminal boards are fitted with wooden covers to protect the ebonite from light and, as an additional precaution against leakage, they are mounted on porcelain pillars.

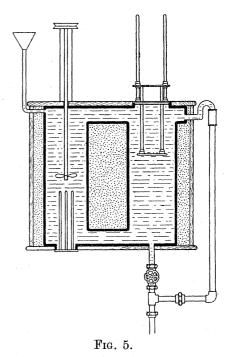
The galvanometer is a moving coil instrument made by Gambrell Bros. It has a coil resistance of 14 ohms and is used with a shunt of 100 ohms. Readings are taken with a closed galvanometer circuit by reversing the battery current, and the sensitivity is such that, with a current of 4 milliamp. in the thermometer, an error in balance corresponding to 0.001° C. would cause a deflection of about 1.5 mm. on reversal. It was not possible to use a more sensitive galvanometer owing to the amount of vibration present.

# IV. The Intercomparison Baths.

Two of the intercomparison baths designed for the Class A thermometer test work of the National Physical Laboratory were used, No. 1, shown in section in fig. 5, being

suited for immersions up to about 40 cm., and No. 2, which is similar in construction, for immersions up to about 80 cm. No. 1 bath has been used for the intercomparisons up to 50° C., and No. 2 for the higher temperatures. The baths consist essentially of two vertical metal cylinders, with communication at the top and bottom. The larger of these cylinders (about 12 cm. diameter) contains the thermometers, while the heating and stirring is effected in the other. The whole bath is lagged with granulated cork.

Each heater is made of nichrome ribbon wound round a strip of mica and subsequently made into a sandwich with two additional mica strips. heaters are pushed into thin copper pockets, which are pressed into close contact with the heaters by the In this way the heating control is head of water. made very easy, as there is very little tendency for the temperature of the bath to creep when the The maximum input of current is cut down. energy is about 1.8 kw.

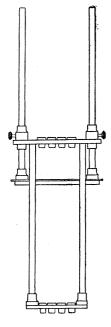


Stirring is effected by a screw arranged to lift the

The screw in No. 1 bath revolves at 590 r.p.m. and that water in the heater tube. In No. 1 bath below 50° C. no differences as great in No. 2 bath at 630 r.p.m. as 0.001° C. were found between two platinum thermometers immersed at different depths, and the same state of affairs existed up to about 70° C., over the range of immersions actually used, in No. 2 bath. At higher temperatures in No. 2 bath, the observations shown in Table III were made with a view to determining any corrections necessary on account of lack of uniformity. The immersions 60-65 cm. correspond with those of a Tonnelot thermometer of range 0-100° C., 42-50 cm., to a 50-100° C.

# TABLE III.

S.4.		S	Difference.	
Immersion.	Temperature.	Immersion.	Temperature.	Greater minu less immersion
Cms.	° C.	Cms.	° C.	° C.
58	83.686	38	83.681	+0.005
60	85.983	42	85.981	+0.002
60	87.910	42	87.907	+0.003
34	89 • 987	45	89.987	0.000
63	89.870	45	$89 \cdot 872$	-0.002
34	$92 \cdot 356$	45	$92 \cdot 356$	0.000
63	91.713	45	$91 \cdot 711$	+0.002
34	94.587	48	$94 \cdot 586$	-0.001
63	$94 \cdot 664$	48	$94 \cdot 662$	+0.002
34	95.829	48	$95 \cdot 829$	0.000
65	$95 \cdot 446$	48	$95 \cdot 457$	- 0.011
65	$95 \cdot 640$	48	$95 \cdot 631$	+ 0.009
65	$98 \cdot 291$	50	$98 \cdot 292$	- 0.001



**0**00000000

Fig. 6.

thermometer, while 34 cm. is the mean of the immersions obtainable with platinum thermometers S1 and S2, which were used in some of the earlier observations prior to the construction of S4 and S5. is evidently no systematic difference exceeding one or two thousandths of a degree over a range of immersions from 34 to 65 cms.

The thermometers are supported, four at a time, in a suitable cage" (fig. 6), which allows of ready adjustment of the immersion Loose "bosses" of different bores are used of the thermometers. to fit the various thermometers, which are supported by rubber rings cut from pressure tubing.

# V. The Ice, Steam and Sulphur Points.

The ice bath consists of a cylindrical porcelain vessel, 28 cm. deep and 15 cm. diameter. Its lower end is hemispherical and is fitted in the centre with a tube leading to a drain-cock, This vessel is mounted in an outer wooden casing large enough to allow of about 5 cm. of The porcelain vessel is furnished with granulated cork insulation. a flange so that it can be screwed tightly to the top of the wooden box, with thick rubber packing interposed, thus minimising the risk of water getting into the lagging. The ice used is specially prepared from distilled water in blocks of about 30 lb., and each block, after being given a wash to remove any surface contamination, is then planed. The

plane consists of a wooden bench through the surface of which the blade projects.

block is slid to and fro on this bench and the shavings are collected underneath in teak boxes kept exclusively for this ice. The fineness of shaving of the ice is of fundamenta importance: skilfully shaved, the product should feel like snow to the touch. ice is touched as little as possible by the hands; it is put into the ice bath a little at a time with a galvanised iron scoop, additions of distilled water being made periodically. While this is being done the ice-water mixture is continually kneaded and pressed down with a wooden stick about 1 cm. thick and 3 cm. wide. This is continued until the pot is full of a firm, close, semi-transparent mixture of ice and water. operation must be performed slowly and carefully—to fill the pot requires about ten minutes.\* When mercury thermometers are to be observed, a special holder is used. This consists of two arms vertically above one another and fitted with V-grooves in which the thermometer is held by flat springs. In using this holder the thermometer is pushed into the upper clip sideways and then gently pushed down, lifting the lower spring clip with the finger to allow the bulb to pass without pressure. putting the thermometer in the ice a hole is made by pushing a glass rod of slightly smaller diameter into the ice through the clips. Control is kept on the purity of the ice by means of conductivity measurements on the drainings from the ice bath. general, the conductivity is such as to indicate a depression of the freezing point of about 0.0003° C., the variations from this being quite small. The conductivity of the drainings from ordinary commercial ice was also investigated and gave almost equally good results, except that on rare occasions a block would be found giving an estimated freezing point of about  $-0.005^{\circ}$  C. The reproducibility of the ice point, measured with the platinum thermometer in the bath described, may be taken as being of the order of 0.001° C. The hypsometer is that used in the ordinary test work of the Laboratory and is of fairly normal design. The height of the apparatus is such as to give a clear 95 cm. of vapour above the water level, or 85 cm. above the wire gauze baffle which is fitted to prevent splashing of the thermometer bulbs. The inner tube is 10 cm. in diameter and the outer tube 17 cm. The cooling water from the condenser is fed into a constant-level device which maintains the water level in the boiler. Heating is effected electrically by heaters similar to those used in the intercomparison baths, the normal loading being 1.5 kw. A small water manometer of 13 mm. bore, graduated in millimetres on each limb, is fitted and is illuminated from behind by an opal lamp and viewed through a telescope. In normal use the excess pressure inside the hypsometer is about 2 mm. of water (0.14 mm. mercury), which is equivalent to about 0.005° C. The thermometers are supported in the same "cage" as is used in the intercomparison bath. Since the holes in the base plate of this cage are considerably larger in diameter than the stems of the thermometers, they are covered in the steam bath by a slip of asbestos paper, through which the thermometers are pushed. This does not, however, make a steam-tight joint, and the few millimetres of emergent column are kept bathed

<sup>\*</sup> For mercury thermometers the packing need not be quite so tight as for platinum thermometers which not only have a greater lag, but are continually dissipating energy from the bulb.

This condenses on the stems of the thermometers and they are kept clear by continuous brushing with a small camel-hair brush during an observation. hypsometer was mounted on the same staging as the two water baths, and, in order to get the thermometers in as nearly as possible the same condition as in water, the stirrer of one of the baths was run, thus producing a certain amount of vibration. (See also Section VIII.) The actual experimental procedure in making an observation of a steam point is similar to that adopted for the higher temperatures in the water (See Section VI.) bath.

Since the barometer in the building where the intercomparison was carried out was not capable of a higher precision than 0·1 mm. (equivalent to 0·004° C.), the barometric readings were all taken on the "principal working standard" of the Metrology Depart-This is a Fortin barometer by Casella (No. 2519) and has recently been reverified against a fundamental standard constructed in the Metrology Department Readings were taken in inches to an accuracy of 0.001 inch and converted to millimetres for use, the boiling points being taken from the Wärmetabellen of the Physikalisch-Technische Reichsanstalt (1919). The distance between the barometer and the hypsometer was about 150 yards and the difference in altitude between the water and mercury levels 1.75 metres, the hypsometer being the higher. This involves a correction to the barometer readings of -0.14 mm. The correction for gravity is based on a pendulum determination of "g" made in the Metrology Department in 1927, which gave as the local value 981·195 cm./sec.<sup>2</sup>, as compared with the standard gravity of 980·665 cm./sec.<sup>2</sup> The gravity correction to the barometer thus becomes +0.42 mm. at pressures in the region of 760 mm.

The sulphur bath is, in all essentials, that described by Mueller and Burgess.\* The boiling tube is of silica and heating is by gas. The radiation shield used is of iron and consists of a cylindrical tube, 12 cm. long and 3.5 cm. diameter, surmounted by a conical umbrella of diameter 1.5 cm. at the top, 4.5 cm. at the bottom, and of height 2.5 cm. Adequate clearance is allowed for vapour to pass between the cone and the cylinder, although it is not possible to see the thermometer winding through the gap. The bulb windings of all the thermometers used in this work are about 9 cm. in length. With this arrangement a raising and lowering of the thermometers by about 5 cm. from the mean position never alters the reading by more than  $\pm~0.01^{\circ}$  C., and often by only about  $\pm 0.005^{\circ}$  C.

It has been found that results are readily reproducible to an accuracy of better than  $0.02^{\circ}$  C., i.e.  $\delta$  is known to the nearest 0.001, which is well beyond the demands of the present work.

# VI.—Experimental Procedure.

Since it was desired to make two complete and independent series of observations on each mercury thermometer, the programme of work was divided into ten series of

<sup>\* &#</sup>x27;Bull., Bur. Standards' (Sci. paper 339), vol. 15, p. 163 (1919).

observations, each covering a range of 50°C. These series are set out in Table IV. In the discussion of results it will be found that, in general, the two independent observations at any temperature agreed to within about 0.004° C. (see Table XIII). There

TABLE IV.

	Thermometer Numbers.
Series.	0° – 50° C. 50° – 100° C.
I II III IV	4,893, 4,976, 15,959, 16,377  4,303, 4,304, 11,048, 16,378 4,305, 4,306, 15,504, 16,377  4,893, 4,976, 11,151, 18,370  4,893, 4,976, 11,151, 18,370  ———————————————————————————————————
V VI VII VIII IX	4,517, 4,518, 4,893, 4,976  4,303, 4,305, 15,959, 16,378 4,304, 4,306, 11,048, 15,504 4,517, 4,518  4,517, 4,518  4,517, 4,518, 4,893, 4,976  —  4,517, 4,518 —  —  —  —  —  —  —  —  —  —  —  —  —
X	4,517, 4,518, 11,151, 18,370

were, however, some instances of larger discrepancies, and in these cases\* a third observation was made. These check observations were begun in Series VIII and IX, when normally there would not always be four thermometers in the bath, and continued after the completion of Series X.

All thermometers which were used below normal room temperature were kept in a refrigerator at about  $-3^{\circ}$  C. for several weeks before starting work, so as to get a regular curve of zero depression. This practice was not followed in Series I, but it was found that the results obtained in that series were consistent with those for the corresponding thermometers in Series IV, V and VII, except for the inevitable difference in the zero depression curve below air temperature.

Observations were made at temperature intervals of 2° C. throughout the range, commencing at the bottom, and, as a rule, three temperatures were observed in one The ice points of the platinum thermometers in use (two were always used at a time) were determined at the beginning and end of each day's work, and those of the mercury thermometers after each temperature.

The procedure in making an observation of the zero of a mercury thermometer was as follows: The ice was packed and a hole prepared for the thermometer, which was then removed from the bath and a stop-watch started. In the case of the higher temperatures the thermometer was allowed to cool gradually (the bulb being passed through the fingers a few times) to about 50° C. and was then plunged in the ice to well above the zero line. It was given a few twists and raised so that the mercury column

<sup>\*</sup> Less than 15 per cent. of the total.

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just appeared above the surface of the ice. The stem was then wiped to remove surplus water, and observations were usually commenced a little more than two minutes after the thermometer left the bath. Readings were taken by means of an observing telescope fitted with a micrometer eyepiece. As an example, in the case of a thermometer reading between -0.1 and -0.2, the cross-wires would be set on the divisions and the mercury column in the following order: -0.1, column, -0.2; -0.2, column, -0.1; with the divisions in front of the column ("front" readings), and then repeated with the divisions behind the column ("back" readings). The taking of a mean value between these two sets serves to eliminate any error due to parallax. The time was noted at each setting on the mercury column. As is well known, when a mercury thermometer is exposed to a high temperature it suffers a temporary depression of the On plunging the thermometer into ice, the zero at once commences to recover, and the ice reading obtained after a lapse of about three minutes is not quite the same as the zero which was effective when the thermometer was in the comparison bath. It was found that, as closely as could be observed, the rate of recovery of the zero between three and ten minutes after removal from the water bath was constant, and for the purposes of an approximate correction it was assumed to be constant right back to "zero time." A second set of observations on each zero was accordingly made after a total time of about seven minutes had elapsed, and the rate of recovery deduced. In this way a correction of the observed zero to bring it to that which was effective while the thermometer was in the bath could be determined. This correction is probably not exact, but it only amounts to about 0.004° C. at its highest and is applied in a systematic manner throughout. According to the observations of Guillaume,\* the procedure adopted here would cause an under-estimate of the recovery by a constant quantity of about 0.001° C. owing to the approximately exponential form of the recovery This recovery phenomenon is for another reason an aid to accuracy in observing the ice point. It is well known that readings of high precision on a mercury thermometer should be taken on a rising meniscus in order to get the best possible regularity in capillarity effects, and the recovery ensures that the meniscus is always rising when the thermometer is in the ice bath.

The zeros used were not the actual values measured, but were taken from a mean curve plotted through the zero observations. The curve was drawn day by day, but never to within three observations of the last point plotted, so that a fair mean curve could be drawn. When, at the conclusion of the work, steam points were being observed, this method no longer applied and the individual ice readings were used.

The observations in the water bath and in the hypsometer were made by estimation through a  $\times$  12 Ross prism monocular, working at a distance of about 1 metre. The thermometers were left in the bath for at least half an hour before observing, or longer if they had not recently been used at a similar temperature. During this period they were held with a considerable length of the column exposed, so that the mercury surface

<sup>\* &</sup>quot;Traité pratique de la thermométrie de précision," p. 153. (See also Section VIII).

was never much higher in temperature than the unoccupied space above it. In this way distillation of the mercury was, to all intents and purposes, prevented.

An observation was carried out in the following way. The platinum thermometers were set so that their bulbs would be as close as possible to those of the mercury thermometers when the latter were immersed to the reading. The heating current of the bath was adjusted to give a rate of rise in temperature of about  $0.01^{\circ}$  C. per minute. The mercury thermometers were set with their columns all on the same level and with divisions in front, and were then pushed down so that only a few millimetres of the column projected above the base plate of the cage. After the lapse of about one minute readings were commenced and continued for 150 seconds. The mercury thermometers were read at a steady rate in the following order: 1, 2, 3, 4, 4, 3, 2, 1, 1, 2, 3, 4, etc., each run of four readings occupying between five and ten seconds. During the 150 seconds of the observation, one of the platinum thermometers was read at the following times: 0, 30, 60, 90, 120 and 150 seconds.

A similar set of readings was then taken with the mercury thermometers reversed ("back" reading) and finally front and back readings were taken against the other platinum thermometer. As soon as these four sets of readings were complete, the mercury thermometers were again lifted and the temperature steadied while the ice points were taken individually. The ice values were worked out as they were observed, and check values were taken (after returning the thermometer to the water bath for about a quarter of an hour) when any inconsistency with previous readings was noticed. Since distillation takes place fairly rapidly at the higher temperatures, the time of observation was cut down from 150 to 90 seconds above 75° C., below which temperature the correction for distillation becomes negligible (see Section VII).

The steam points were observed in the same way as the other temperatures above 75° C., except that readings of the barometer replaced those of the resistance thermometer. The barometer was observed at three-minute intervals commencing one or two minutes before the thermometer readings and continuing for a similar period afterwards. The barometric curve was plotted and each of the four observations (front, back, front, back) was regarded as corresponding with the barometric height at the mean time of the observation. Throughout the work the observations on the resistance thermometers were made by the author, while all mercury thermometer readings were taken by Mr. J. G. Durham, Senior Observer in the Physics Department. This procedure was followed in view of the necessity for securing as high a speed of working as possible, and of the fact that Mr. Durham's long experience in mercury thermometer observation made him peculiarly fitted for this section of the work. As a matter of interest, at one temperature observations were made with the observers interchanged, and all the values obtained agreed with those found by the normal procedure to within 0.003° C.

The order of observation of steam points depended on convenience; for example, thermometers which would not be required in the water bath for several weeks could be

used; but the majority of the observations were taken after the water bath comparisons had been completed.

Tables V and VI show specimen sets of observations in the water bath and in the The corrections applied to the platinum thermometer observations are

Water Bath No. 1. Table V.—Series VIII—Observations 964-7. April 30, 1928. Stirrer, 590 r.p.m. Barometer, 754 mm.

		T	'hermome	ters.	,		Bridge	e Tempe	rature.	Therm
Time (secs.).	S.1 Dials.	16,378.	4,304.	4,306.	15,504.	S.2 Dials.	Right.	Centre.	Left.	Posi- tion.
0		32.085	31.935	32 · 135	31.905	3-3-7-6-6-2	19.83	19.96	19.89	Front.
		32.090	31.940	$32 \cdot 140$	31.905					
,		32.090	31.940	$32 \cdot 140$	31.910					
<b>3</b> 0		32.090	31.945	$32 \cdot 140$	31.910	6-7				
		32.090	31.945	$32 \cdot 145$	31.910					
*		32.095	31.950	$32 \cdot 150$	31.915					
60		32.095	31.955	$32 \cdot 155$	31.915	7-2				
		32.098	31.960	$32 \cdot 155$	31.920					
90		32.098	31.960	$32 \cdot 160$	31.920	7-7				
		$32 \cdot 100$	31.965	$32 \cdot 160$	31.925					
		$32 \cdot 100$	31.965	$32 \cdot 165$	31.925					
120		$32 \cdot 100$	31.965	$32 \cdot 165$	31.925	8–2				
		$32 \cdot 100$	31.965	$32 \cdot 165$	31.930					
150	No. of Contract	32.100	31.965	$32 \cdot 165$	31.930	-8-7	,			
	Mean	32.0951	31 • 9539	32 · 1529	31.9175					
0		32.110	31.970	32 · 175	31.940	3-3-7- 7-0-2	19.84	20.00	19.90	Back.
	,	$32 \cdot 120$	31.980	$32 \cdot 180$	31.940					
		32.115	31.985	$32 \cdot 180$	31.940					
30		32.120	31.980	$32 \cdot 180$	31.940	0-7				
		32.120	31.985	$32 \cdot 180$	$31 \cdot 940$			1		
		32 · 120	31.985	$32 \cdot 180$	31.940			1		
60		$32 \cdot 120$	31.985	$32 \cdot 180$	$31 \cdot 945$	1-1				
		$32 \cdot 125$	31.990	$32 \cdot 185$	31.950					
		$32 \cdot 125$	31.990	$32 \cdot 185$	31.950			}		
		$32 \cdot 125$	31.990	$32 \cdot 185$	$31 \cdot 955$					
90	· Monthson	$32 \cdot 125$	$31 \cdot 990$	$32 \cdot 190$	31.960	1-6				
		$32 \cdot 125$	$31 \cdot 995$	$32 \cdot 190$	31.960					
		$32 \cdot 125$	$31 \cdot 995$	$32 \cdot 190$	31.960		-			
		$32 \cdot 130$	$31 \cdot 995$	$32 \cdot 190$	$31 \cdot 965$					
120		32.130	$31 \cdot 995$	$32 \cdot 190$	31.965	2-0			1	
		32.130	31.998	32.190	31.965					
150		$\begin{vmatrix} 32 \cdot 130 \\ 32 \cdot 130 \end{vmatrix}$	$31.998 \ 31.998$	$32 \cdot 195 \ 32 \cdot 195$	$31.970 \ 31.970$	2-5				
100										
	Mean	32 · 1236	$31 \cdot 9897$	$32 \cdot 1856$	$31 \cdot 9531$					

# Table V—(continued)

		T	hermomet	ers.			Bridge	Temper	ature.	Therm
Time (secs.).	S.1 Dials.	16,378.	4,304.	4,306.	15,504.	S.2 Dials.	Right.	Centre.	Left.	Position.
0	3-2-3-3-2-5	32.160	32.020	$32 \cdot 215$	31.995		19.84	20.03	19.91	Front
. 0	J-2-J-J-2-J	32.165	32.020	$32 \cdot 215$	31.995		13.01	20 00	10 01	I TOHO.
		32.165	32.020	32.220	31.995					
30	3-0	32.170	$32 \cdot 025$	$32 \cdot 220$	$31 \cdot 995$					
		$32 \cdot 170$	$32 \cdot 025$	$32 \cdot 225$	32.000					
60	3–5	$32 \cdot 170$	$32 \cdot 025$	$32 \cdot 225$	32.000					
		32.170	32.025	$32 \cdot 225$	32.000					
00	4.0	32.170	32.030	32 • 225	32.000					
90	4-0	$32 \cdot 175 \ 32 \cdot 175$	$32.025 \\ 32.030$	$32 \cdot 225 \\ 32 \cdot 230$	$32.000 \\ 32.000$					
`		32.175	32.030	$32 \cdot 230$	32.000					
120	4–5	32.175	32.035	32.230	32.000					
		32.180	$32 \cdot 235$	$32 \cdot 235$	32.000					
150	5-0	$32 \cdot 180$	32.040	$32 \cdot 240$	32.000					
									AND THE RESIDENCE OF THE PERSON OF THE PERSO	
	Mean	32.1714	32.0275	$32 \cdot 2257$	31.9986					
			· / ·							
				,						
0	3-2-3-3-5-7	32.185	32.040	$32 \cdot 245$	32.015		19.86	20.03	19.93	Back.
0	<i>3−2−3−3−0−1</i>	$\begin{vmatrix} 32.165 \\ 32.190 \end{vmatrix}$	32.040 $32.045$	$32 \cdot 245$	$\frac{32.015}{32.015}$		13.00	20,00	10.00	Dack.
		32.190	32.050	32.250	32.020					
30	6–2	32.195	32.050	32.250	32.020				_	
		32.195	$32 \cdot 055$	$32 \cdot 250$	32.020					
		$32 \cdot 198$	32.060	$32 \cdot 260$	32.020			5.		,
60	6–7	32.198	32.065	$32 \cdot 260$	32.020		}			-
00	<b>**</b> 0	32.200	32.065	32.265	32.025					
90	7–2	32.200	32.065	32.265	32.025					
		$\begin{vmatrix} 32 \cdot 200 \\ 32 \cdot 202 \end{vmatrix}$	$32.065 \\ 32.065$	$\begin{array}{c} 32 \cdot 265 \\ 32 \cdot 265 \end{array}$	$32.030 \ 32.030$					
120	7–7	$32.202 \ 32.205$	$32.005 \\ 32.070$	$\frac{32 \cdot 205}{32 \cdot 270}$	$\frac{32.030}{32.030}$					
-20	• • •	$32 \cdot 205$	32.070	32.270	32.035					
1		$32 \cdot 205$	32.070	$32 \cdot 270$	32.035					
150	8–2	32.205	32.075	32.270	32.035					
ŀ	**************************************								-	
	Mean	32.1982	32.0607	32.2600	32.0253					
1		( I	i		-					

Table V—(continued).—Ice Points.

		1		1
-	Position.	Front. Back.	Front. ". Back.	
	Mean Value.	C. 0.000 I.P.+0.008 E.P.+0.0007	-0.0225	c. 0.0010 0.024 0.027
15,504.	Mean Time.	125	360	125 sec.
	Read- Mean ing. Time.	-0.031 -0.031 -0.033 -0.032	-0.030 -0.030 -0.029 -0.031	Recovery per 125 sec. Corrected zero Zero from curve
	Time (secs.).	85 110 145 165	320 350 380 405	Reco Corre Zero
	Mean Value.	C. 0.0000 I.P.+0.0086 E.P.+0.0007	-0.0935	sc. 0.0010 0.094 0.095
4,306.	Mean Time.	145	385	145 seconomics of the seconomi
	Read- ing.	-0.103 -0.104 -0.102 -0.102	-0.103 -0.101 -0.100 -0.100	Recovery per 145 sec. Corrected zero Zero from curve
	Time (secs.).	105 120 160 180	345 365 400 425	Recor Corre Zero
	Mean Value.	-0.0535 C. 0.0000 I.P. +0.0076 E.P.+0.0007	-0.0452 -0.0495	3. 0.0018 0.047 0.047
4,304.	Mean Time.	120	380	120 sec
	Read- ing.	-0.054 -0.051 -0.056 -0.053	-0.046 -0.045 -0.054 -0.053	Recovery per 120 sec. Corrected zero Zero from curve
	Time (secs.).	75 105 155 170	340 360 395 415	Reco Corre Zero
	Mean Value.	C.—0.0004 I.P.+0.0090 E.P.+0.0008	+0.0562	+0.055 +0.054 +0.055
16,378.	Mean Time.	130	370	: 130 se : o : rve
	Read- Mean ing. Time.	+0.049 +0.050 +0.044 +0.044	+0.053 +0.049 +0.053 +0.051	Recovery per 130 sec. Corrected zero Zero from curve
	Time (secs.).	90 115 145 170	335 355 385 405	Reco Corre Zero

# MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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		Mercury Tl	Mercury Thermometers.		Platinum Thermometer.
Corrections.	16,378.	4,304.	4,306.	15,504.	Bridge reading:—3-3-7-6-7-4·5
		Observati	Observation No. 964.		<u> </u>
Calibration	$\begin{array}{c} 32.0951 \\ -0.0460 \\ +0.0428 \\ \end{array}$	$\begin{array}{c} 31.9539 \\ + 0.0360 \\ + 0.0352 \\ \end{array}$	$\begin{array}{c} 32.1529 \\ - 0.2150 \\ + 0.0378 \\ \end{array}$	$31.9175 \\ + 0.0840 \\ + 0.0379$	Con   300.058   Values   $70.020$   $6.745$   Zero res. $0.005$
Exernal Fressure (110 mm.)  Zero  Fundamental Interval	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} -0.0011 \\ +0.0470 \\ -0.0393 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3376.871 Temp 0.004
	32.0375	32.0317	32.0393	32.0393	hatio heating -0.021
Hydrogen Scale	0.1040	- 0.1040	0.1040	- 0.1040	$ \frac{3376 \cdot 846}{$
					: 32 Ra
Corrected Temperature	. 31.933° C.	31.928° C.	31.935° C.	31.935° C.	31.927° C. (S.2)
		Observation	Observation No. 965.		
Corrected Temperature	. 31.962° C.	31.963° C.	31.968° C.	31.971° C.	31.960° C. (S.2)
		Observation No. 966.	n No. 966.		
Corrected Temperature	. 32.009° C.	32.002° C.	32.008 °C.	32·016° C.	32·007° C. (S.1)
		Observation No. 967.	n No. 967.		
Corrected Temperature	. 32.036° C.	32.035° C.	32.042° C.	32·043° C.	32.035° C. (S.1)

# Table V—(continued).—Summary.

Mercury minus platinum.

		- <i>j</i>	F	Mean.
	°C.		° C.	°C.
16378	$-8.1 = +0.001_{5}$	16378	-8.2 = +0.004	+0.003
4304	$-8.1 = -0.002_{5}$	4304	-8.2 = +0.002	0.000
4306	-8.1 = +0.004	4306	-8.2 = +0.008	+0.006
15504	$-8.1 = +0.008_{5}$	15504	$-8.2 = +0.009_{5}$	+0.009

# Table VI.—Steam Point. Observations 1778-81. January 24, 1929.

	Time	9.	Mano	meter.	Thermo-		Thermo	meters.	
hr.	min.	sec.	Hypsometer.	Atmosphere.	meter Position.	4,893.	4,976.	4,517.	11,151.
3	41	50	1·70 cm.	1·89 cm.	Front	99·970 99·970 99·970 99·970 99·970 99·970 99·970 99·970 99·970 99·970	100 · 200 100 · 198 100 · 200 100 · 200 100 · 200 100 · 200	100 · 005 100 · 002 100 · 005 100 · 005 100 · 005 100 · 005 100 · 005	$100 \cdot 195$ $100 \cdot 195$ $100 \cdot 198$ $100 \cdot 198$ $100 \cdot 195$ $100 \cdot 195$ $100 \cdot 195$ $100 \cdot 198$
3	43	20				$99.970 \\ 99.965$	$100 \cdot 200$ $100 \cdot 200$	100.005 $100.005$	$100 \cdot 198$ $100 \cdot 198$
		-		Mean		99 • 9697	100 · 1999	100.0043	100 · 1968
3		45			Back	99·970 99·970 99·965 99·965 99·965 99·970 99·970 99·970 99·970 99·970 99·970 99·970 99·965 99·965	100·195 100·195 100·195 100·198 100·198 100·195 100·195 100·195 100·195 100·195 100·195 100·195 100·195 100·195	100·005 100·005 100·005 100·005 100·005 100·005 100·005 100·005 100·005 100·005 100·005 100·005 100·005	100·198 100·195 100·198 100·198 100·198 100·198 100·198 100·198 100·198 100·198 100·198 100·198 100·198 100·198
				Mean		99.9680	100 · 1954	100.0050	100 · 1976

# Table VI—(continued).

Time.	Mano	meter.	Thermo-		Thermo	meters.	
hr. min. sec.	Hypsometer.	${\bf Atmosphere.}$	Position.	4,893.	4,976.	4,517.	11,151.
3 45 40			Front	99.970	100 • 200	100.005	100 · 200
				$99 \cdot 975$	$100 \cdot 200$	100.005	$100 \cdot 200$
*				$99 \cdot 975$	100.200	100.005	$100 \cdot 200$
				$99 \cdot 975$	$100 \cdot 200$	100.005	$100 \cdot 200$
				$99 \cdot 975$	100.200	100.000	$100 \cdot 200$
				99.975	100.200	100.005	$100 \cdot 200$
				$99 \cdot 975$	100.200	$100 \cdot 005$	$100 \cdot 200$
			1	$99 \cdot 975$	100.200	$100 \cdot 005$	$100 \cdot 200$
			4 - 54	$99 \cdot 975$	$100 \cdot 200$	$100 \cdot 005$	$100 \cdot 200$
				$99 \cdot 975$	100.200	$100 \cdot 005$	$100 \cdot 200$
				$99 \cdot 975$	$100 \cdot 200$	100.005	$100 \cdot 200$
			1	$99 \cdot 975$	$100 \cdot 200$	$100 \cdot 005$	$100 \cdot 200$
				$99 \cdot 975$	100 • 200	$100 \cdot 005$	$100 \cdot 200$
		. "		$99 \cdot 975$	$100 \cdot 200$	$100 \cdot 005$	$100 \cdot 198$
3 47 10				$99 \cdot 975$	$100 \cdot 200$	$100 \cdot 005$	$100 \cdot 200$
		Mean		99 • 9747	100 • 2000	100.0047	100 • 1999
					100 105	100 007	100 100
$3  ext{ } 47  ext{ } 35$			Back	99.965	100.195	100.005	100.198
				99.965	100 195	100.005	100.198
				99.970	100 195	100.005	100.198
				99.970	100 195	100.005	100.198
				99.970	100 105	100.005	100.195
				99.970	$100 \cdot 195 \\ 100 \cdot 195$	$100.005 \\ 100.005$	100.195
				99.970			100.195
				$99 \cdot 970 \\ 99 \cdot 970$	$100 \cdot 195$ $100 \cdot 198$	$100.005 \\ 100.005$	$100 \cdot 195$ $100 \cdot 198$
	-			99.970	100.198 $100.198$	100.005	100.198
				99.970	100.198 $100.195$	100.005	100.198 $100.198$
				99.970	100.195 $100.195$	100.005	100.198 $100.198$
				99.970	100.195 $100.195$	100.005	100.198 $100.198$
	,			99.905	100.195 $100.195$	100.005	100.198 $100.198$
				99.970	100.195 $100.195$	100.005 $100.005$	100.198 $100.198$
3 49 5	1.69 cm.	1.90 cm.		99.970	$100 \cdot 195$	100.005	$100 \cdot 198$
		Mean		99.9690	100 · 1954	100.0050	100 · 1973

Ice Points.—Corrected Values.

	° C.
4,893	0.145
4,976	<b>-</b> 0·034
4,517	- 0.198
11,151	+0.004

# Table VI—(continued).

# Barometer Readings.

Time.		. (A	Reading. and "g" of N.P.L.)	
				mm.
3.40				$766 \cdot 88$
$3 \cdot 43$	•••	• • •	• • •	$766 \cdot 88$
$3 \cdot 46$	•••	•••	•••	$766 \cdot 93$
$3 \cdot 49$	• • •	• • •	• • •	766.90
$3\!\cdot\!52$	•••			$766 \cdot 90$

Corrections: To standard "g"

To altitude of hypsometer ...

Excess pressure in hypsometer +0.15

# Reduced Readings.

			Corr	ected Thermo	ometer Readi	ngs.
Time.	Pressure.	Boiling Point.	4,893.	4,976.	4,517.	11,151.
hr. min. sec. 3 42 35 3 44 30 3 46 25 3 48 20	$\begin{array}{c} \mathrm{mm.} \\ 767 \cdot 31 \\ 767 \cdot 34 \\ 767 \cdot 35 \\ 767 \cdot 33 \end{array}$	° C. 100·268 100·269 100·269 100·269	° C. 100·263 100·262 100·268 100·263	° C. 100·289 100·285 100·289 100·285	° C. 100·255 100·255 100·255 100·255	° C. 100·277 100·278 100·280 100·277

those set out in Sections II and III, while those for the mercury thermometers are as follows: (1) calibration, (2) internal pressure, (3) external pressure, (4) zero, (5) fundamental interval, (6) correction to constant volume hydrogen scale. (1) and (2) are taken directly from the tables supplied with the thermometers by the Bureau International. For the purposes of (3) the standard pressure was for convenience taken to be that on the bulb with the barometer at 760 mm. and with the thermometer immersed vertically up to the zero line. In ice, therefore, the correction is that given by the barometric height alone, and in the water bath allowance has to be made for a head of water proportional to the reading of the thermometer. In the hypsometer the barometric pressure must be reduced by an amount corresponding to a head of water equal to the distance between the centre of the bulb and the zero line (in general 4 mm. of mercury). (5) is taken from the tables of the Bureau International. Subsequently corrections were applied to reduce the values according to the steam points determined in the present work. The corrections (6) to the constant volume hydrogen scale are those obtained and tabulated by Chappuis.\*

<sup>\* &#</sup>x27;Trav. Mém. Bur. Internat.,' vol. 6 (1888).

The lag coefficient of a Tonnelot thermometer was measured and found to be about 3 secs. For the purpose of the lag correction in Table V, therefore, the platinum thermometer lag coefficients have been reduced by this amount so as to arrive at the differential lag. It will be noted that each temperature measurement involves, on the system of numbering exemplified in Tables V and VI, four "observations," each of which comprises about fifteen readings on each of four mercury thermometers, and six (or four) readings on a platinum thermometer. In the course of the present work 1,889 "observations" (including steam points) were made: that is, about 100,000 individual readings on mercury thermometers and about 6,000 readings on platinum thermometers.

# VII.—Special Corrections.

In making the steam point determinations the same thermometer was subjected to about the same temperature day after day, and it thus became possible to determine an approximate distillation correction. Taking a large number of observations on several thermometers, it was found that the average fall in the zero per observation was about  $0.003^{\circ}_{5}$  C. Since the zero observed is that which held at the end of each set of observations and not at the mean time, each observed zero is low by about 0.001,° C. Assuming that the rate of distillation at any temperature is proportional to the vapour pressure of mercury at that temperature, the following corrections to the observed temperatures (to the nearest 0.001°C.) were deduced: 80-96°C.,  $-0.001^{\circ}$  C.; 98 and  $100^{\circ}$  C.,  $-0.002^{\circ}$  C.

In making observations at the steam point it was unfortunately not possible to work always on a rising meniscus. Distillation causes a slow fall, so that, unless the barometer is showing a definite rise equivalent to about  $0.004^{\circ}$  C. in ten minutes, the meniscus will be falling. When this happens the meniscus tends to flatten, and, in consequence, the internal pressure on the bulb, due in part to capillarity and in part to the head of mercury in the bore, is reduced. The thermometer will therefore tend to read high.

In order to determine the magnitude of the correction to apply to falling readings, a special series of observations was made in No. 1 water bath at about 30° C. Four mercury thermometers and one platinum thermometer were used, and rising and falling readings were taken alternately, two sets of each, with the meniscus in as nearly as possible the same position for all four sets. Since differences only were required, zeros were not taken and only "front" readings were used. The values found are This experiment gives a difference of 0.002° C. between rising shown in Table VII. and falling readings.

Guillaume\* gives evidence to show that the difference between the internal pressures with rising and falling readings is of the order of 40 mm. of mercury, equivalent to about  $0.004_5$ ° C. The smaller difference found above is probably due to the fact that the agitation of the thermometers in the water bath is very considerable, since not only is there vibration from the stirrer, but the thermometers themselves are continually

Table VII.—Differences: Falling minus Rising Readings in thousandths of a degree.

		Thermome	ter Number.		
Date.	16,377.	16,378.	15,959.	4,305.	Mean.
1.2.29	+5 0 +5	$\begin{array}{c c} +1 \\ -6 \\ 0 \end{array}$	+4 +2 -5	+2 +1 -1	$\begin{array}{c c} +3 \\ -1 \\ 0 \end{array}$
7.2.29	$\begin{array}{c c} +3 \\ +6 \\ +6 \\ +1 \end{array}$	$\begin{array}{c} +7 \\ +3 \\ +5 \\ 0 \end{array}$	$\begin{array}{c c} +2\\ +6\\ +2\\ +1 \end{array}$	$\begin{array}{r} +5 \\ +4 \\ +1 \\ -3 \end{array}$	$\begin{array}{c} +4\\ +5\\ +3\\ 0 \end{array}$
				Grand Mean	+2

shaken in the bosses by the turbulent circulation of the water. Guillaume suggests the application of a correction equal to about  $+0.002^{\circ}$  C. to rising and  $-0.002^{\circ}$  C. to falling readings, but in the present work it was felt that it would be more convenient to regard rising readings as standard and to apply the full difference as a correction to falling readings.

An attempt was made to throw additional light on this question by analysing the actual steam point observations into rising and falling readings, the dividing line being taken at a rate of rise in the barometer equivalent to 0.0004° C. per minute.

TABLE VIII.

Thermometer Number.	Difference: Falling minus Rising Readings in thousandths of a degree.	Thermometer Number.	Difference: Falling minus Rising Readings in thousandths of a degree.
4,303 4,304 4,305 4,306 4,517 4,518 4,893	$\begin{array}{c} +2 \\ -2 \\ +2 \\ 0 \\ 0 \\ 0 \\ 1 \end{array}$	11,151 15,504 15,959 16,377 16,378 18,370	$ \begin{array}{c} +5 \\ -2 \\ +1 \\ +3 \\ +2 \\ +3 \end{array} $
4,976 11,048	$\begin{array}{c} +1 \\ +1 \\ +2 \end{array}$	Mean	+1

differences found are set out in Table VIII, which shows a mean value of 0.001° C. Owing to the effect of distillation, very few of the observations were taken on a rising meniscus, and a reference to Table XI and fig. 10 will show that the individual observations on the steam point are much too scattered to permit of any great weight being attached to the value given by this method.

Since Guillaume's observations apply to a thermometer not subjected to continuous vibration, it seems likely that a somewhat lower value than  $0.004^{\circ}$  C. would be suitable for observations taken in the hypsometer used in this work, as a certain amount of vibration was introduced (see Section V). On the other hand, a correction of  $0.002^{\circ}$  C., found in No. 1 water bath, would probably be too low, since the vibration in the stirred water is undoubtedly greater than that in the hypsometer. Finally, therefore, a correction of  $-0.003^{\circ}$  C. was applied to all steam point observations taken on a falling It will be noted (Section VIII, fig. 13) that, when corrected in this way, the observations at the steam point do not appear to be inconsistent with those taken in the water bath.

In the case of thermometer 15504 (range 0-50° C.) a progressively increasing difference between the mercury and platinum thermometers with rising temperature was found, although the steam observations were not consistent with this. In order to find whether any change had taken place in the calibration of the thermometer, some measurements were made on a thread of length about 50° C. If the calibration corrections of the Bureau International apply, their use should obviously give an unvarying length to the thread. Using these corrections, however, the apparent length of the thread in the region 0-50° C. was 0.017° C. greater than in the region 50-100° C. The calibration correction at 50° C. was therefore reduced by 0.009° C. and the corrections between 0 and 50° C. were changed proportionately.\* The broken thread observations, which were taken on the travelling microscope of the Metrology Department, are shown in detail in Table IX.

An estimate was made as to the magnitude of the error introduced by the fact that on the average about 0.7° C. of the mercury column was emergent during all the observations. In the hypsometer one of the Tonnelot thermometers was replaced by a small maximum thermometer, which was supported in an inverted position with just the bulb (about 1 cm. long) exposed. The reading recorded was 94° C. We may take it, therefore, that the temperature of the emergent column of a Tonnelot thermometer is not lower than 94° C. and is probably considerably higher. Taking, therefore, 94° C. and assuming 0.7° C. emergent, we get about 0.0007° C. as an upper limit to the emergent column error. Evidently, then, all errors due to stem exposure will be quite negligible.

# VIII.—Results.

Before considering the main results of the intercomparison, it will be convenient to refer to some incidental facts which were disclosed during the observations.

As has been stated earlier, the observations on the ice point were all made by measure-

\* It was not thought necessary to carry out more extended re-calibration of the bore, since below 50° C. an error of 0.014° C. in a single thermometer would be necessary to affect the final mean by as much as 0.001° C.

# Table IX.—Thermometer No. 15504.

Setting.	Micrometer Reading.	Value.	Setting.	Micrometer Reading.	Value		
**	mm.	° C.		mm.	°C.		
		Air Temperatu	re, 18·85° C.				
		Column (	)–50° C.				
$49 \cdot 6$ Column $49 \cdot 7$	$egin{array}{c} 0 \cdot 226 \\ 0 \cdot 742 \\ 0 \cdot 896 \\ \end{array}  .$	$49 \cdot 677$	$\begin{array}{c} 0 \cdot 2 \\ \text{Column} \\ 0 \cdot 3 \end{array}$	$0.046 \\ 0.411 \\ 0.718$	0.254		
$49 \cdot 6$ Column $49 \cdot 7$	$0.224 \\ 0.742 \\ 0.895$	$49 \cdot 677$	$\begin{array}{c} 0 \cdot 2 \\ \text{Column} \\ 0 \cdot 3 \end{array}$	$0.030 \\ 0.413 \\ 0.717$	0.256		
	Mean Cal. correction	$49.677 \\ +0.011$		Mean Cal. correction	$0.255 \\ 0.000$		
		49.688			0.255		
	A	Apparent Lengt	h. 49·433° C.				
		Column 50-					
98·6 Column 98·7	0.914 $1.136$ $1.591$	98 • 633	$\begin{array}{c} 49 \cdot 2 \\ \text{Column} \\ 49 \cdot 3 \end{array}$	$0.591 \\ 0.710 \\ 1.260$	49.218		
98·6 Column 98·7	0.913 $1.135$ $1.592$	98 • 633	49·2 Column 49·3	$0.593 \\ 0.713 \\ 1.263$	49 · 218		
	Mean Cal. correction	$98.633 \\ +0.012$		Mean Cal. correction	$49 \cdot 218 \\ +0 \cdot 010$		
		$98 \cdot 645$			$49 \cdot 228$		
		Apparent Lengt	th. 49·417° C.				
		Column 0					
49·6 Column 49·7	$0.848 \\ 1.203 \\ 1.526$	49.652	0.2 Column $0.3$	0·284 0·476 0·968	0.228		
49·6 Column 49·7	$0.856 \\ 1.206 \\ 1.529$	49.652	0.2 Column $0.3$	0·288 0·478 0·969	0.228		
Mean Cal. correction		$49.652 \\ +0.011$		Mean Cal. correction	$\begin{array}{c} 0 \cdot 228 \\ 0 \cdot 000 \end{array}$		
		49.663			0.228		
	A	pparent Lengt	h, 49·435° C.				
		Air Temperatur	e, 18·90° C.				

ment instead of by estimation between the tenths. This made it possible to draw conclusions as to the magnitude of any systematic errors to which the observer was liable. During the later stages of the work an estimated reading was recorded in addition to the measured value, and the difference between the two was noted in each These differences were tabulated so as to get the distribution of the errors of estimation over the space of a division, the observations being split into groups covering a range of 0.025° C. each. These results are tabulated in Table X and the graph in

TABLE X.

Estimated Reading. Hundredths of a division.	Number of Observations.	Mean Error. Hundredths of a division.
Hundredths of a division.  2 5 7 10 12 15 17 20 22 25 27 30 32 35 37 40 42 45 47 50 52 55 57 60 62 62 65 67	Observations.  14 24 42 55 29 43 49 60 40 70 58 83 54 72 83 77 35 50 40 61 31 335 24 57 48 48 48	Hundredths of a division.  - 0.8 - 0.6 - 0.7 - 0.7 - 0.6 0.0 + 0.5 - 0.2 - 0.5 - 0.9 - 1.3 - 1.4 - 1.0 - 0.7 - 0.2 - 1.4 - 0.7 - 0.2 - 1.4 - 0.7 - 0.0 + 0.2 - 1.4 - 0.7 - 0.1
70 72 75 77 80 82 85 87 90 92 95	47 15 34 19 33 15 11 11 15 10 18 6	$   \begin{array}{c}     + 0.8 \\     + 0.7 \\     + 1.0 \\     + 0.3 \\     - 0.3 \\     - 0.3 \\     - 0.8 \\     - 0.2 \\     + 0.6 \\     + 1.6 \\     + 0.9 \\     + 1.3   \end{array} $

fig. 7 is taken from this. It will be seen that, as would be expected, the curve is fairly symmetrical about the centre of the space, and it will also be seen that the maximum

error in estimation is about  $-0.002^{\circ}$  C. at four-tenths of a division or  $+0.002^{\circ}$  C. at six-tenths of a division. The same observer's estimates on divisions of much larger size drawn on paper revealed a very similar error at this point.

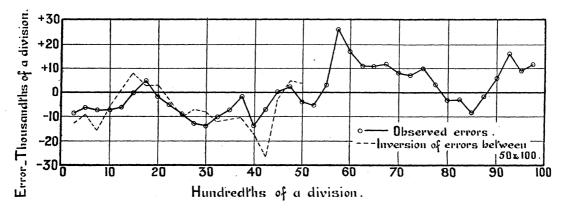


Fig. 7.

The small systematic errors shown by this test would obviously produce no appreciable effect on the mean of a series of rising readings, such as those normally obtained in the water bath, but might be taken into account in the case of the steadier steam point observations. The corrections indicated were applied to these readings in the case of several of the thermometers, but when the means came to be taken very few of them were changed by as much as 0.001° C., so that it was felt that the correction was not worth the labour of applying.

Reference has already been made (Section VI) to the method of determining the "recovery" of the zero in the ice bath. The rate of recovery per hundred seconds has been calculated for all the observations at and above 8° C. and the mean rate of recovery between three and seven minutes after each temperature is plotted in fig. 8. Each point on the curve represents the mean of about twenty observations, except in the case of the point at 100° C. which represents 544 observations.

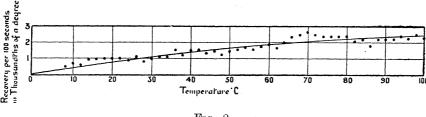
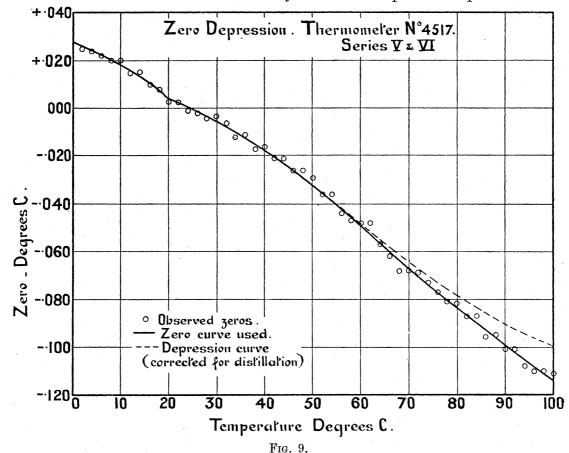


Fig. 8.

According to Waidner and Dickinson (loc. cit.), the rate of recovery after three minutes in ice is constant for all temperatures from 20° C. up to 100° C. and equal to about 0.0025° C. per hundred seconds, but the results of the present series of experiments show a definite rise in rate with temperature. Guillaume\* gives a mean recovery curve deduced from observations on the ice point after 50° C., 100° C. and 200° C. An examination of this curve shows a rate of recovery corresponding to 0.0015° C. per hundred seconds after five minutes in ice, a period which represents approximately the conditions in the present experiments. Guillaume also found no measurable variation in the rate of recovery for initial temperatures up to 200° C.



Owing to the fact that an appreciable amount of distillation takes place at the higher temperatures, it is impossible to deduce from these observations an accurate value for the depression constant of the glass. Fig. 9 is a typical curve of zeros which shows that very few of the observations are as much as  $0.003^{\circ}$  C. off the mean curve. The discontinuity at 20° C. is due to the fact that, for convenience, the curve was plotted in short sections (Section VI). A smooth curve would represent the facts better, but any errors introduced only amount to one or two thousandths of a degree in an individual thermometer. The broken line is the depression curve obtained when allowance is made for the amount of distillation estimated to have taken place as a result of observations of zeros after repeated steam points. In this way, taking a mean of all thermometers, the depression of verre dur is estimated at  $0\cdot10_5^{\circ}$  C. for

100° C., variations of about  $\pm 0.02^{\circ}$  C. from the mean being obtained with different thermometers. Previous estimates of the depression\* range from 0·100° C. to 0·115° C.

The observations at the steam point may conveniently be considered before those of the rest of the intercomparison. It is evident that these observations will be less accurate than those made in the water bath for the following reasons:

- (1) Observations are made on a nearly stationary meniscus which, as already pointed out, (a) increases errors due to capillarity, and (b) makes errors of sub-division in reading more serious, as they do not average out as in a series taken on a considerably rising temperature.
- (2) Zero readings will be less accurate because (a) the depression and recovery are both larger than at lower temperatures, and (b) the individual observation and not a point on a mean curve is taken.
- (3) Errors due to distillation are at a maximum.

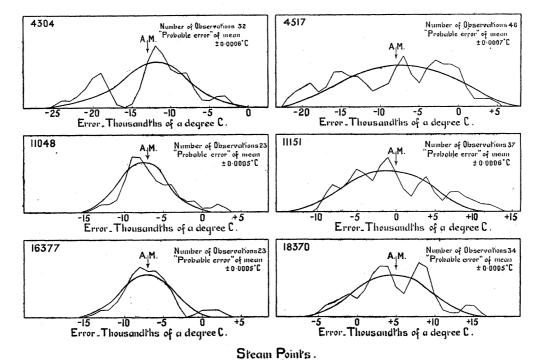
In view of these facts, observations were carried on until the distribution of the results assumed a fairly symmetrical form, similar in general appearance to a Gaussian distribution of errors. This involved from about twenty to fifty observations on each thermometer. The results are shown in Table XI, which shows "errors" of the various mercury thermometers at the steam point, when the Bureau International figures for the fundamental intervals are employed. The "probable error" is shown at the foot of the table and the distribution of the observations is shown graphically for a few of the thermometers in fig. 10. The curves have been obtained by giving a weight of two to an observation at the actual observed figure and a weight of one at ± 0.001° C. away. That is, the irregular curve represents the boundary of the area filled by recording a system of four spots for each observation—two at the actual observation and one on either side, thus:— .:.

Of the thermometers used, 11,048 gives the sharpest peak to the curve, while 4517 behaved very much more erratically than any of the others. 4304 shows a pronounced double peak, but it is possible that this would have been eliminated by a more extended series of observations: other thermometers showed a similar effect in the early stages of the observations, but the trough filled up as the work proceeded. There is a smaller effect of a similar type shown by 18,370. The other two curves, 16,377 and 11,151, may be regarded as representative of the remainder which are not shown here. "probable error" figures given in Table XI must, of course, be taken with reserve. In order to find errors such that the chances are ten to one against their being exceeded, the "probable errors" must be multiplied by six, thus giving values of about  $\pm 0.004$ ° C.

The form of the distribution curve and the fact that the arithmetic mean of the observations is in fairly accurate coincidence with the peak of the curve give some evidence that the number of observations was sufficient for the application of the

<sup>\*</sup> Guillaume, "Études thermométriques," Trav. Mém. Bur. Internat., vol. 5 (1886); Thiesen, Scheel and Sell, "Z. Instrumentenkunde," vol. 16, p. 49 (1896); Waidner and Dickinson, loc. cit.

<sup>†</sup>  $0.6754 \sqrt{\sum r^2/n(n-1)}$  when r = residual error, n = number of observations.



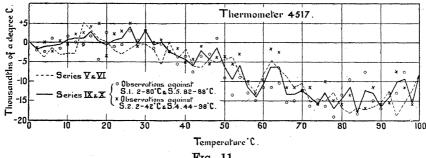
Distribution of Observations.

Fig. 10.—Steam Points: Distribution of observations.

probability laws to have reasonable validity. Further, if one takes the mean of the first half of the observations on each thermometer, it is found that the values so obtained differ from those given by the complete series by  $0.003^{\circ}$  C. in one case,  $0.002^{\circ}$  C. in one case, 0.001° C. in two cases, while with the other eleven thermometers there is exact agreement.

It is interesting to note that, if one omits the corrections for distillation and falling meniscus, the mean of all the differences between the figures of the Bureau International and those of the present intercomparison reduces to zero.

Table XII gives a summary of all the observations, using the fundamental intervals of the Bureau International, the mercury thermometers being reduced to the constant volume hydrogen scale by means of Chappuis's corrections. It will be seen that, in general, the agreement between two independent series is fairly good, but that it was felt desirable to take a third set of readings at about 14 per cent. of the points. Fig. 11



Frg. 11.

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MATHEMATICAL,
PHYSICAL
& ENGINEERING
SCIENCES

TRANSACTIONS SOCIETY A

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PHYSICAL
& ENGINEERING
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TRANSACTIONS SOCIETY A

# Table XI.—Steam Points.

" Errors" in thousandths of a degree C, when using Bureau International fundamental intervals.

Values corrected for distillation and, where necessary, for falling meniscus.

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# Table XI.—(continued).

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Table XII.

Mercury—Platinum in thousandths of a degree C. Mercury thermometer readings corrected according

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Summary of Observations.

to Bureau International fundamental intervals and reduced to constant volume hydrogen scale.

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shows, as a representative sample, a plot of the observations recorded in Table XII in the case of thermometer 4517, while, in addition, the actual readings against each of the platinum thermometers in Series IX-X are shown.

The thermometers which are in regular use at the Laboratory as standards are 16,377 and 16,378 over the range of  $0-50^{\circ}$  C. and 11,151 and 18,370 over the range of  $50-100^{\circ}$  C., and it is of interest to compare the residual differences found between these instruments in the present intercomparison with those which have appeared in the ordinary precision test work of the Laboratory. In the latter case, it must be remembered, the accuracy aimed at is not as high as in the present work,  $0.005^{\circ}$  C. being in general the highest accuracy below  $50^{\circ}$  C. and  $0.01^{\circ}$  C. above.

The results contained in the Laboratory test-books during recent years have been abstracted, and the mean difference between the two standards concerned has been calculated. Each observation has been recorded at the nearest 5° C. and about a hundred observations at each 5° C. were available. The values obtained are shown in Table XIII and it will be seen that the differences found in the present intercomparison and those deduced from general test work are in as close agreement as could reasonably be expected.

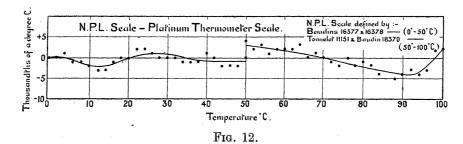


Fig. 12 shows the alterations made in the scale of the National Physical Laboratory by the change over from the mercury thermometers now in use to the platinum thermometer. The curves are plotted so as to show the values given by the mercury thermometers when reduced by using the fundamental intervals determined by the Bureau International. It will be seen that the change involved does not exceed  $0.002^{\circ}$  C. up to  $50^{\circ}$  C. or  $0.005^{\circ}$  C. between  $50^{\circ}$  C. and  $100^{\circ}$  C. These changes are evidently too small to have any effect, except in a few isolated cases, on even the most precise tests carried out by the National Physical Laboratory.

Table XIV shows the mean values of the observations recorded in Table XII after they have been corrected to the fundamental intervals found in the present intercomparison, and two groups of means are also recorded. This information is also given graphically in fig. 13. Section (a) of fig. 13 indicates in smoothed curves the amount of the differences which exist between the various individual thermometers, while section (b) shows as a full line the mean of all the curves in (a). It will be seen that the general form of this curve holds, with very few exceptions, for all the

Table XIII.—Residual differences between N.P.L. standards in thousandths of a degree C.

		16,378–16,377.	
Tempera- ture ° C.	Test Work.	Intercomparison.	Test Work minus Intercomparison.
5 10 15 20 25 30 35 40 45 50	$egin{array}{c} 0 \\ +2 \\ 0 \\ +4 \\ +6 \\ +5 \\ +2 \\ +4 \\ +4 \\ \end{array}$	$ \begin{array}{r} -1 \\ +5 \\ +2 \\ +7 \\ +8 \\ +7 \\ +5 \\ +8 \\ +2 \end{array} $	$     \begin{array}{r}       + 1 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 2 \\       - 3 \\       - 4 \\       - 2 \\     \end{array} $

		11,151–18,370.	
Temperature ° C.	Test Work.	Intercomparison.	Test Work minus Intercomparison.
50 55 60 65 70 75 80 85 90 95	$ \begin{array}{c} +9\\ +12\\ +9\\ +13\\ +10\\ +10\\ +3\\ +4 \end{array} $	$   \begin{array}{c}     + 10 \\     + 14 \\     + 13 \\     + 16 \\     + 16 \\     + 10 \\     + 8 \\     + 6 \\     + 3 \\     + 2   \end{array} $	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

thermometers. The dates of manufacture of the thermometers used (Table I) vary from 1884 to 1913, while the thermometers used by Chappuis, for which alone his corrections to the constant volume hydrogen scale can, strictly speaking, be held to be valid, were all made in 1885. It is possible that there have been variations in the composition of the verre dur used over the period 1884-1913, and, in consequence, the newer thermometers may define a somewhat different scale. Section (c) shows the result of taking the mean of those thermometers used in the present work which are nearly contemporary with those of Chappuis. Thermometers 4303, 4304, 4305, 4306, 4517 and 4518 were all made within a year of the date of Chappuis's instruments. To

TABLE "Hydrogen" minus Platinum in thousandths of a degree C. Means of values in Table XII

																			n	Con	an.			е°	C					a constant										and the second second	
Therm. No.			**********												************					ren	mpe		ur	e 	···																
therm. No.	2		4		6		8		10	1	$_2 \mid$	14	1	6	1	8	20	1	22	2	4	26	3	28		30	32	2	34	36		38	40	)	42	4	14	46	3	48	50
4,303		5		6	:	2	(	) -	- 1	+	1	(	) +	- 3	+	1	+	1 -	- 1	_	1		1		1 +	- 2	+	1	+ 4	+	2 +	- 3	+	4 -	+ {	5 +	- 1	+	1 -	<b>⊢</b> 3	+1
4,304		o		1	:	1	+ 1	L	0	+	3	(	+	- 3	+	5	+	8 +	- 7	+	4	+	6	+	5	- 2	+	5	+ 4	+	6	- 9	+	6	+10	+	- 5	+	9 -	- 6	+ 6
4,305		0		0	(	0	]	L -	- 1		0	+ 2	2 +	- 2	+	3	+	1   +	- 3	+	3	+	3	+	$2   \dashv$	- 4	+	4	+ 2	2 +	1	- 2	+	4	+ 4	+	- 4	+	4 -	- 1	+ 4
4,306		0		1	- ;	3	+ ]	L +	- 1	+	4	+ 6	3 +	- 7	+	8	+	6 +	- 9	+	8	+	6	+ .	3   +	- 6	+	9	+ 5	+	7 +	- 8	+	6	+ 6	3 +	- 4	+	5	- 6	+ 2
4,517		2		2	- :	2	<b>—</b> ]	L -	- 1		0	+ 4	4	- 4	+	$_2$	+	2 +	- 1	+	1	+	3	+ :	2   +	- 3	+	2	+ 1	. +	2	C		0	_ :	3	0		0	О	1
4,518		1		0		1	(	) +	- 1	+	1	+ 2	+	. 2	+	3	(	0	0	+	3	+	3	+ :	3 +	- 4	+	3	+ 3	4	5 +	- 4	+	1 -	+ ]	L +	- 2		2 -	- 2	0
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<b>i</b> ,976		o		0	(	0	+ 1	L -	- 5		3	_ 1	. -	. 1	_	5	(	0 +	- 3	+	$_2$	+	3	+ :	2 +	- 5	+	3	+ 6	+	6 +	- 5	+	3 -	+ 5	3 +	· .4	+	2	- 2	+ 3
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15,504	+	1 -	+	1	+ :	2 -	+ 2	2 +	- 2		0	+ 1	+	- 2	+	5	+ ;	3   +	- 5	+	3	+	2	(	)  -	- 6	+	6	+ 9	+1	0 +	- 7	+1	.0	+ 8	+	. 9	+1	1	-11	+11
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16,377		0	+	1	(	o -	1	l _	- 3		5	_ 4	_	. 1	_	3		2 +	- 2		1		0		1 -	- 2		1	— 2		2   -	- 2	+	1 -	<b>+</b> 1		. 3		3 -	- 2	+ 1
16,378		o		0	:	1 -	+ 1	L +	- 1		1	_ 2		0	+	3	+ 4	1 +	- 4	+	6	+	5	+ 4	4 +	- 4	+	3	+ 3	+	3 +	- 3	+	4 -	ի 3	+	. 1	+	2 +	-	+ 1
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ean of 4303– 976		1		1	-	1	C	)	- 1	+	1	+ 2	-	- 3	+	2	+ :	2 +	- 3	+	2	+	3	+ :	2   +	- 4	+	4	+ 4	+	5 +	- 4	+	4	<b>⊢</b> 3	+	3	+	2 +	- 3	+ 2
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A RECOGNIC OF THE SECURITY OF THE SECURITY SECUR											_															.,															

XIV.

# TEMPERATURE SCALE BETWEEN 0° AND 100° C.

corrected in accordance with the new fundamental interval determinations.

1											Ten	npera	ture	° C.											
1 1 1	52	54	56	58	60	62	64	66	68	70	72	74	76	78	80	82	84	86	88	90	92	94	96	98	Therm. No.
			_	_	_	_																			4,303
   د					_	_																_			4,304
	_			_			_							_		_									4,305
					_		_							_								_			4,306
-	- 2	- 3	_ 5	- 8	_ 4	_ 1	_ 2	- 6	_ 7	- 8	<b>–</b> 8	<b>–</b> 9	- 8	- 9	-10	-11	-10	- 8	- 8	- 8	_ 7	- 5	- 4	- 6	4,517
1	+ 1	О	- 4	_ 4	_ 2	_ 1	_ 3	- 8	- 9	- 8	_ 9	-10	_ 7	-11	- 9	<b>—</b> 9	- 9	- 9	- 8	_ 7	- 5	- 8	- 3	- 1	4,518
1	+ 3	- 4	- 4	_ 2	+1	+3	+ 5	+ 1	+ 6	+ 4	+ 4	+ 1	+ 4	+ 2	+ 1	+ 1	+ 5	+ 5	+ 1	+ 4	+ 1	+ 2	+ 3	+ 1	4,893
	0	1	0	_ 1	О	+ 1	_ 2	<b>—</b> 5	- 1	- 3	- 6	<b>—</b> 3	_ 7	- 5	<b>—</b> 6	0	0	+ 3	- 3	+ 3	- 2	— 1	_ 2	- 1	4,976
									_				_												11,048
-	+ 8	+11	+ 7	+ 9	+ 8	+ 9	+11	+ 8	+ 9	+ 8	+ 7	+ 3	+ 5	+ 3	+ 3	+ 1	_ 2	- 1	- 4	- 3	О	- 2	- 3	+ 3	11,151
NCES					—			_	-	-			_				_		-	_	_		_	_	15,504
SCIE				_		_		-	-		-					_				_	-		-	_	15,959
1						—	—	-		-	-		_								_	_			16,377
4	-	-	_		_					-	-	_						-	-	-			-		16,378
-	- 7	_ 7	- 8	- 8	- 8	- 8	- 9	-10	-10	-10	-13	-12	-10	-10	- 9	-10	-10	- 8	_ 9	-10	-10	-11	- 8	_ 4	18,370
1 1 -	<b>-</b> 1	_ 2	- 3	- 4	_ 1	+ 1	o	- 4	- 3	- 4	_ 5	_ 5	_ 4	_ 6	- 6	_ 5	_ 3	_ 2	- 4	_ 2	- 3	- 3	- 1		Mean of 4303–4976
0 -	- 1	_ 1	_ 2	_ 2	_ 1	+ 1	0	_ 3	_ 2	- 3	- 4	_ 5	- 4	_ 5	_ 5	- 5	_ 4	_ 3	- 5	_ 3	_ 4	_ 4	<b>-</b> 3		Mean of all thermometers
_																									

consider these six thermometers only, however, would be to use only two thermometer in the range 50-100° C., which, in view of the individual differences shown in Section (a) would hardly be satisfactory. For the purpose of drawing the curves in Section (c) therefore, thermometers 4893 and 4976—made about five years later—have also been included. Comparing the full line curves in (b) and (c), it will be seen that they follow one another very closely, and a reference to the means in Table XIV from which they are drawn shows only a few differences as great as  $0.002^{\circ}$  C. It is thus fairly safe to assume that there is no systematic difference with time between the thermometers made during the period in question. For further consideration, therefore, the mean of all thermometers (Section (b)) has been used.

In fig. 13 the use of inverted commas (as: "Hydrogen" scale) indicates that the particular scale so marked is arrived at by assuming (a) Chappuis's values for the differences between the constant volume hydrogen thermometer (initial pressure 1 m. of mercury) and the mercury in verre dur thermometer, and (b) that the mean of the readings of the group of thermometers represented in the curve is identical with the mean which would have been given by Chappuis's thermometers. With these reservations, therefore, the full line curve in fig. 13 (b) may be taken as representing the difference between the constant volume hydrogen thermometer and the platinum thermometer.

For the purposes of the International Temperature Scale, however, the platinum thermometer is to be used as a means of reproducing the thermodynamic scale and not the hydrogen scale. It is therefore of interest to investigate the closeness of agreement between the platinum thermometer and the thermodynamic scale. To do this, we must assume values for the differences between the hydrogen scale (v const.,  $p_0 = 1$  m. Hg) and the thermodynamic scale. According to Holborn and Otto\*  $T_{Ther.} - T_{H_2}$  is  $-0.003^{\circ}$  C. at  $50^{\circ}$  C. and  $-0.002^{\circ}$  C. at  $25^{\circ}$  C. and  $75^{\circ}$  C., while the same workers a year later† gave - 0.002° C. and - 0.001° C. Keesom and TUYNT have recalculated Holborn and Otto's results and give for the difference  $T_{Ther.} - T_{H.}$ , the values  $-0.004^{\circ}$  C. at 25° C.,  $-0.006^{\circ}$  C. at 50° C., and  $-0.005^{\circ}$  C. at 75° C., while, collecting observations by various workers at Leiden, they arrive at a value of  $-0.002^{\circ}$  C. at  $50^{\circ}$  C.

From these figures it appears that either  $-0.002^{\circ}$  C. or  $-0.003^{\circ}$  C. at  $50^{\circ}$  C. would be a sufficiently accurate figure to assume for the purposes of the present work, and in the graphs of fig. 13 the value  $-0.003^{\circ}$  C. has been used. The broken line in Section (b), then, may be taken as indicating the thermodynamic scale in terms of the platinum thermometer. This curve is reproduced as a full line in Section (d), where Chappuis's observations, on which it depends, are also plotted. These observations have, of course, been reduced to the thermodynamic scale, again assuming a difference of 0.003° C. between the thermodynamic and hydrogen scales at 50° C.

<sup>\* &#</sup>x27;Zs. für Physik.,' vol. XXIII, 1924, p. 93.

<sup>† &#</sup>x27;Zs. für Physik.,' vol. XXXIII, 1925, p. 10.

<sup>‡ &#</sup>x27;Travaux et Mémoires du Bur. Intl.,' vol. XVIII.

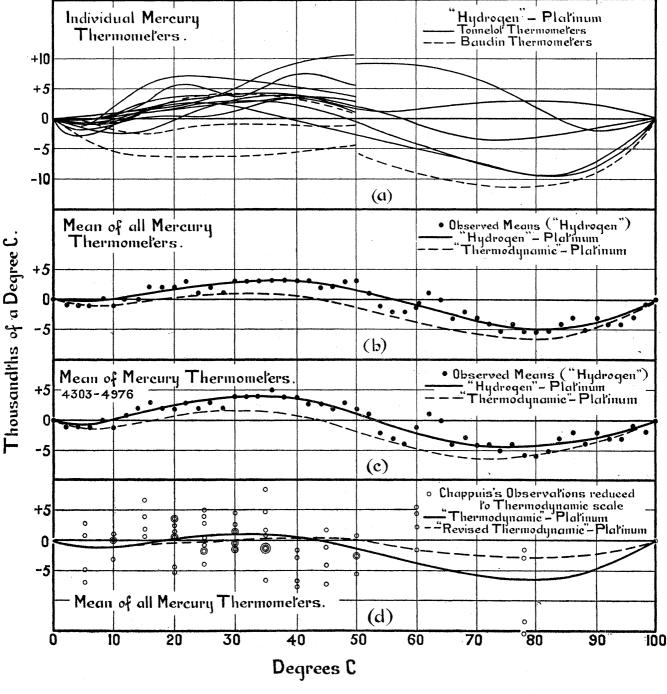


Fig. 13.

The curve depends on Chappuis's table of values for hydrogen minus mercury in verre dur, which was derived from the equation:—

$$\begin{split} T_{\rm H_2} - T_{\rm Hg} &= -0 \cdot 10921037 \; (100 - T_{\rm Hg}) \, T_{\rm Hg} + 5 \cdot 8928597 \\ &\times 10^{-4} \, (100^2 - T_{\rm Hg}^2) \, T_{\rm Hg} - 1 \cdot 1577325 \times 10^{-6} \, (100^3 - T_{\rm Hg}^3) \, T_{\rm Hg}, \end{split}$$

which he obtained by interpolation between his observations by the method of least

Chappuis's observations up to 50° C. were made in a water bath, but those at 60° C. and 78° C. were made in chloroform vapour and alcohol vapour respectively. observations above 50° C. are few in number and not so consistent among themselves as those below 50° C., so that they form a rather slender foundation for the curve between 50° C. and 100° C. The alcohol observations in particular are spread over a wide range. The two observations plotted at about  $-0.002^{\circ}$  C. were taken on June 2, 1887, and those at about  $-0.014^{\circ}$  C. on June 1, 1887.

In view of the comparatively large discrepancy (0.007° C.) between the "thermodynamic" and platinum scales, the experiment of disregarding Chappuis's observations of June 1, 1887, was tried. This led to the following revised form of his equation:

$$\begin{split} T_{\text{H}_{\text{s}}} - T_{\text{Hg}} &= -0 \cdot 108565 \, (100 - T_{\text{Hg}}) \, T_{\text{Hg}} + 5 \cdot 208236 \\ & \times 10^{-4} \, (100^2 - T_{\text{Hg}}^2) \, T_{\text{Hg}} - 0 \cdot 575027 \, \times 10^{-6} \, (100^3 - T_{\text{Hg}}^3) \, T_{\text{Hg}}, \end{split}$$

which results in the broken line curve of Section (d)—"revised thermodynamic" The numerical values for both curves in Section (d) are summarised in Table XV. From this it can be said that it has not been possible in the present work

TABLE XV.

Temperature.	Thermodynamic in thousandths	
	Chappuis's Equation.	Revised Equation.
10 20 30 40 50 60 70 80 90	$\begin{array}{c} -1 \\ 0 \\ +1 \\ +1 \\ -2 \\ -4 \\ -6 \\ -7 \\ -5 \end{array}$	$ \begin{array}{c} -1 \\ 0 \\ 0 \\ +1 \\ 0 \\ -2 \\ -2 \\ -3 \\ -2 \end{array} $

to detect any difference between the thermodynamic scale and the scale defined by the platinum resistance thermometer. It is evident that the scattered nature of Chappuis's

observations sets a limit to the accuracy which can be attained in an intercomparison when the mercury in verre dur thermometers are used as an intermediary, but it is not likely that any differences which may exist between the thermodynamic and platinum scales exceed a few thousandths of a degree between  $0^{\circ}$  C. and  $50^{\circ}$  C. or  $0 \cdot 01^{\circ}$  C. between  $50^{\circ}$  C. and  $100^{\circ}$  C.

The experiments of Henning and Heuse\* lead to a somewhat similar conclusion. These workers made a direct comparison between the platinum thermometer and the helium thermometer ( $v_{\text{const}}$ ,  $p_0 = 1$  m. Hg), and give as the observed differences, helium minus platinum: at 20° C.,  $+0.007^{\circ}$  C.; at 50° C.,  $-0.005^{\circ}$  C.; and at 80° C.  $+0.004^{\circ}$  C. Of these figures they consider that only the value of  $+0.007^{\circ}$  C. at 20° C. may be considered as slightly outside their limit of experimental error. They therefore draw the conclusion that any differences which exist between the thermodynamic scale and that defined by the platinum thermometer are less than  $0.01^{\circ}$  C. in the range  $0-100^{\circ}$  C.

## IX.—Summary.

- 1. Fifteen mercury in verre dur standard thermometers made by Tonnelot and Baudin and calibrated by the Bureau International des Poids et Mésures have been compared with four platinum thermometers made at the National Physical Laboratory.
- 2. Differences amounting to as much as  $0.02^{\circ}$  C. between individual mercury thermometers were observed.
- 3. It was found that the change from certain Tonnelot and Baudin thermometers to the platinum thermometer as a means of interpolation between 0° C. and 100° C. will not alter the temperature scale of the National Physical Laboratory in that range by more than 0.002° C. between 0° C. and 50° C. or 0.005° C. between 50° C. and 100° C.
- 4. No difference between the thermodynamic scale and the scale defined by the platinum thermometer was detected, the mercury in verre dur thermometers being used as an intermediary. It is considered that such differences probably do not exceed a few thousandths of a degree between 0° C. and 50° C. or 0·01° C. between 50° C. and 100° C.

### X.—Acknowledgments.

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