A Determination of the Specific Heat of Water in Terms of the International Electric Units

Arthur Schuster and William Gannon

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XI. *A Determination of the Specific Heat of Water in Terms of the International Electric Units.*

By Arthur Schuster, *F.R.S., Langworthy Professor of Physics at the Owens College, Manchester, and* William Gannon, *M.A., Exhibition* (1851) *Scholar, Queen's College, Galway.*

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This research was originally undertaken by Professor Schuster and Mr. H. Hadley before the authors were aware that Mr. E. H. Griffiths was engaged on a similar investigation. After a number of preliminary experiments, and just as the final arrangements for the conduct of the measurements were being definitely made, Mr. Hadley, on his appointment to the Head Mastership of the School of Science and Art, Kidderminster, had to leave Manchester. In the meantime Mr. Griffiths' important research was published; and we had to consider whether our own work, which was designed on a smaller scale, could compete with it in accuracy. We decided to complete the investigation, principally for the reason that, although we both aimed at determining what is commonly called the mechanical equivalent of heat through the heating of a certain mass of water by means of an electric current, the details of the experiments differed very materially, so that our two ways of dealing with the problem seemed to afford a useful test of the amount of agreement which may be obtained at present. Our investigation touches only a small part of that treated by Mr. Griffiths, as we did not attempt to measure the changes in the specific heat of water due to change of temperature. On the other hand, the more modest limits within which we have confined ourselves, allowed us to use a much simpler apparatus. On Mr. Hadley's departure, Mr. W. Gannon took his place. From the former gentleman we received a good deal of help in the devising and construction of some important parts of the apparatus.

The principle of the method we have used is extremely simple. The electrical work done in a conductor being measured by $\int EC\,dt$, where E is the difference of potential at the ends of the conductor, C the current and t the time, we keep the electromotive force constant, and measure $\int C\,dt$ directly by a silver voltameter. We do not therefore require to know the resistance of the wire, and we thus avoid the difficulty of having to estimate the excess of temperature of the wire over that of the water in which it is placed. We also gain the advantage of not having to measure time, and therefore are able to complete the experiment more quickly than

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we could have safely done if the length of time during which the current passed had to be measured with great accuracy.

As regards the dimensions of the apparatus, there is not very much choice. The voltameter limits the current intensity to about one ampère. The calorimeter must contain at least one litre of water, otherwise the corrections for cooling become too large; on the other hand difficulties of stirring appear when the mass of water is too great; the calorimeter in our experiments contained about 1500 grams. of water. In order to measure the rise in temperature of the water with sufficient accuracy, that rise should not be less than 2°; and it is easily calculated that if the experiment is to be completed in about ten minutes, the electromotive force—with the current and the quantity of water fixed upon—must be about thirty volts. We used Clark cells as our standard of electromotive force, and a battery of twenty cells was found sufficient for our purpose. Having fixed on the current and electromotive force, the resistance of the wire can be determined.

The accuracy which can be obtained altogether depends on the attention given to small details, and we therefore proceed to describe separately the various parts of the apparatus used.

The Clark Cells.

As standard of electromotive force we used Clark cells. It was originally intended to keep one of these cells at a constant temperature of about 25° C. in a thermostat. This cell (fig. 1), which we shall call the C.T.C. (constant temperature Clark), was constructed according to a pattern which has proved very useful when it is desirable to have a cell which can stand without damage a moderate current for a short time. A small WOULFE's bottle is taken in which the three openings have stoppers made of glass ground into the necks. The stopper fitting into the central opening has a platinum wire fused into it, and the zinc rod is attached to this wire. Of the two other openings, one carries a bent tube with a mercury trap, and the other a glass tube which passes to the bottom of the bottle. A platinum wire passes through this tube and dips into the mercury. The mercury trap is useful in the early history of the cell, as it is difficult to avoid generation of some gas at first, and the additional pressure thus produced often damages the joints of the cell. After a time the mercury may be removed, and the tube sealed off. The cells were set up with the usual precautions, and have now worked for some years satisfactorily. There is, of course, the usual difficulty of ascertaining the temperature; thermometers have been inserted into some of them, but even then, though they have proved of great utility, they are not suitable as standards when great accuracy is required, unless placed in an enclosure of constant temperature.

The comparison of our Clark cells was always made by opposing them and measuring the difference of their electromotive forces. For this purpose the current from a Leclanché cell (L, fig. 5, p. 427) was passed through a fixed resistance (R) of 10,000

Fig. 1.

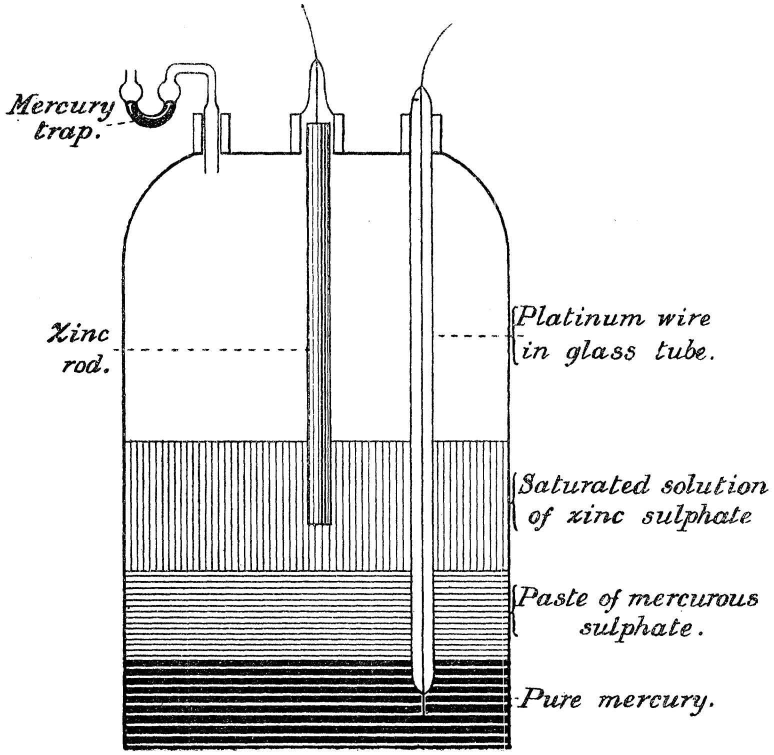
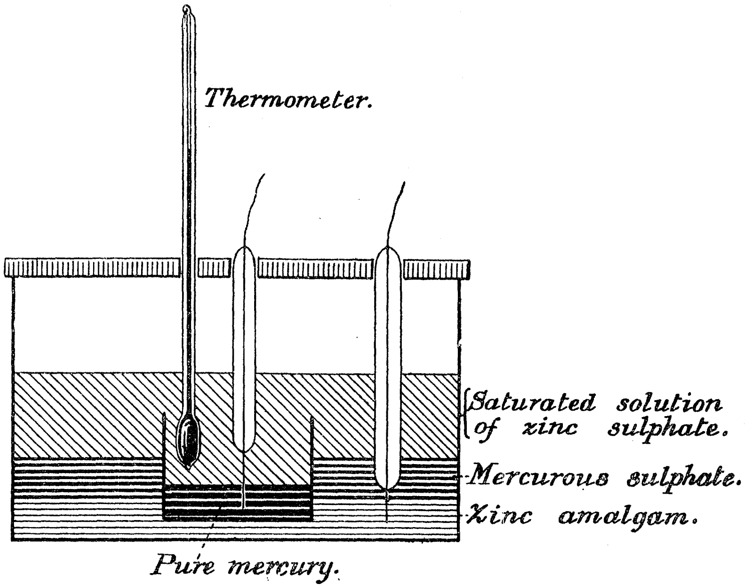

Mercury trap.
Zinc rod.
Platinum wire in glass tube.
Saturated solution of zinc sulphate
Paste of mercurous sulphate.
Pure mercury.

Fig. 2.


Thermometer.
Saturated solution of zinc sulphate.
Mercurous sulphate.
Zinc amalgam.
Pure mercury.

ohms and through a resistance box. The difference in the potential at the terminals of this box was balanced in the usual way by the residual electromotive force of the two Clark cells. If e_1, e_2, E be the electromotive forces of the Clarks and the Leclanché respectively, and r the resistance of the box when there is a balance,

$$e_1 - e_2 = \mathrm{E}\,\frac{r}{10000 + r}.$$

When two Clarks which have approximately the same temperature are compared, r would be equal to only a few ohms, and in that case we may neglect the r in the denominator, and in many cases take the electromotive force of the Leclanché equal to that of the Clark. Care was taken that the Leclanché cell had its normal electromotive force, which was measured whenever any change in its value might have produced an appreciable difference in the experiments.

Large cells can only be used as standards, if they are constructed according to the principle of Lord RAYLEIGH's H cell. In the spring of 1891 a cell was set up having the form of fig. 2. It consists of two glass vessels, one being placed inside the other. The outer vessel contains the zinc amalgam, the inner vessel the mercury. The vessel is covered by a wooden lid, through which the electrodes and a thermometer are passed. The upper part of the outer vessel is paraffined so as to prevent the creeping of the zinc sulphate over the sides. Very little evaporation takes place, and the lid is readily removed so that the cell may be refilled when necessary. It was constructed originally so that the liquid could be stirred, but it was found better not to disturb the cell. This cell has answered all requirements perfectly, and will be referred to as the "standard." The cell, which is not readily moved owing to its weight, stands in a corner of a small cupboard, and was compared at intervals with the C.T.C. between November, 1891, and June, 1892. The results are given in Table I. The thermostat, which was not adapted for temperatures as low as 25° C., had to be readjusted occasionally, hence the small variation in temperature shown in the second column. The temperature of the standard at different times varied between 11°·2 C. and 18°·3 C., and the experiments afford a good test as to the limits within which a temperature correction could be safely applied.

TABLE I.—Comparison of Standard Clark Cell with C.T.C. Cell.

1.	2.	3.	4.	5.
Date.	Temperature in thermostat.	Temperature of standard.	Observed difference reduced to 25° C.	Calculated difference.
	° C.	° C.		
1891.				
Nov. 26 .	25·26	13·9	— 68	— 67
„ 27 . .	25·2	12·7	— 78	— 77
Dec. 11 .	25·3	13·8	— 68	— 68
„ 19 . .	25·4	11·9	— 81	— 82
1892.				
Feb. 2 . . .	25·08	14·1	— 63	— 65
„ 6 . . .	25·4	12·6	— 76	— 76
„ 12 . . .	25·4	14·0	— 66	— 66
„ 12 . . .	25·45	14·4	— 65	— 63
March 1 . .	25·7	13·2	— 73	— 72
„ 3 . .	25·52	11·4	— 87	— 86
„ 5 . .	25·65	11·2	— 87	— 87
April 2 . . .	25·75	13·9	— 69	— 67
„ 5 . . .	25·7	15·9	— 53	— 52
May 9 . .	25·4	16·8	— 46	— 45
„ 20 . . .	25·8	14·9	— 53	— 59
„ 24 . . .	25·32	14·8	— 60	— 60
June 1 . . .	25·46	18·3	— 34	— 34
Mean value . .	..	13·99	— 66·3	

A small correction to the observed numbers is necessary, owing to the small variations in temperature of the C.T.C. cell. The corrected values of r are given in the fourth column. As the C.T.C. cell was not quite saturated with zinc sulphate when placed in the thermostat, the temperature coefficient ·0004 was used to reduce its value to 25°. The corrections are so small that an accurate knowledge of that coefficient is not required. The mean temperature of the standard cell in all these experiments was 13°·99, the mean value of r was 66·3. From these data we may calculate what the value of r should have been in each experiment, on the assumption that the temperature coefficient of the standard was ·00081.* The values of r, thus deduced, are given in the fifth column. With the exception of the experiment on May 20, the agreement is quite satisfactory; and we are justified in concluding that the changes in the electromotive force of our standard cell may be correctly deduced

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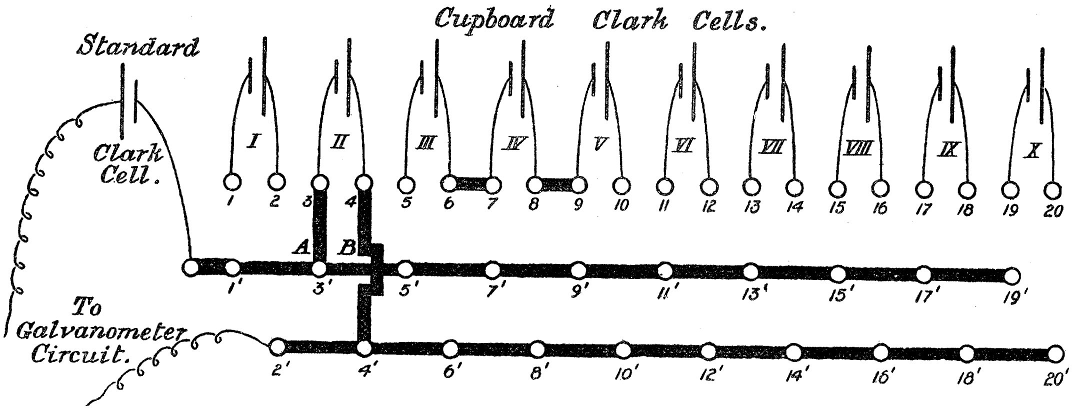
* The temperature coefficient determined by GLAZEBROOK and SKINNER ('Phil. Trans.,' vol. 183, 1892, A) is ·00076 between 0° and 15°—that is, for an average temperature of 7°·5. The temperature coefficient according to KAHLE ('Zeitschrift für Instrumentenkunde,' August, 1893) is $-{\cdot}000814-{\cdot}000007\,(t-15)$, giving an identical value for $t=7°{\cdot}5$.

from the readings of the thermometer placed in it. Recent results of KAHLE agree with our conclusions, and show that, in the H form of cell, the lag in the change of the electromotive force with change of temperature is avoided, owing to the fact that the liquid at both electrodes, being in contact with crystals of zinc sulphate, is always in a state of concentration. We have, after the conclusion of our experiments, set up a few cells according to the instructions given in the Third Memorandum of the Board of Trade. When proper precautions are taken to ensure equality of temperature, these cells agree within about one part in ten thousand with each other and our standard cell. Taking account of the determination by GLAZEBROOK and SKINNER of the electromotive force of a Clark cell—1·4342 at 15° C.—and of the slightly lower value obtained by KAHLE, we have adopted 1·4340 as the value of our standard cell in terms of the international volt. As temperature coefficient, we have adopted that given by KAHLE (see footnote on preceding page).

Fig. 3.



Arrangement for Comparison of Clark Cells.

The electromotive force at the ends of the heating coil in our experiments had to be kept balanced against twenty Clark cells. These cells form part of a battery of one hundred cells constructed in the year 1890, about eighty of which are still in good condition. A set of twenty is mounted in two rows of ten each. The cells are small, but as we had no means of keeping their temperature constant, their combined electromotive force had, whenever required, to be determined in terms of the standard cell. This could be quickly done as follows:—Ten cells of the form shown in fig. 1 were placed side by side in the same cupboard that contained the standard cell (fig. 3 and *c.c.*, fig. 5). The terminals of these cells—which we shall call the "Cupboard Clarks"—were permanently connected to mercury cups numbered 1, 2, &c. (fig. 3). A board of wood was placed in front of the Clarks and contained a series of cups 1′, 3′, 5′, &c., permanently connected by copper strips, and a second series 2′, 4′, 6′, similarly connected. The cups of the two series were placed respectively opposite the positive and negative poles of the Cupboard Clark cells and could be connected to them by means of copper bridges A and B. The standard cell being inserted and the two bridges being placed as shown in the figure, the Cell II. is opposed to the standard and the difference of their electromotive force is measured. Moving the bridges along from one set of cups to the next, the ten Cupboard Clarks may be rapidly interchanged.

The mounting of the cells also allows of their being rapidly placed in series by means of copper strips. The figure shows the Cells III., IV., V. thus connected. The galvanometer used in these comparisons (G, fig. 5) was one of Lord KELVIN's High Resistance Astatic Galvanometers. Its resistance was 5600 ohms. It was placed on paraffin blocks for better insulation. During use its sensitiveness was such that one scale division corresponded to $7{\cdot}3 \times 10^{-6}$ volt. A carbon resistance (P, fig. 5) could be thrown into series with the galvanometer when it was necessary to diminish its sensitiveness. A commutator (K, fig. 5) served to change rapidly the circuit in which the galvanometer was inserted. This commutator was made of a paraffin block containing seven mercury cups, but two sets of two were permanently connected as shown in the figure. Three copper bridges served to connect temporarily the terminals s to g, g to j or k, s' to p or q; when s was connected to g the Standard Clark was opposed to one of the ten Cupboard Clarks. When the ten Cupboard Clarks were to be opposed to one half of the battery of twenty cells, g—j and s'—p were connected; for the other half g—k and s'—q were joined. In the equivalent experiments when the battery had to be opposed to the electromotive force at the end of the heated coil, the three temporary bridges were removed.

The operation of standardising the electromotive force of our battery took about ten minutes and was carried out as follows:—

1. Reading of the thermometer placed in the Standard Clark, t_1^s.

2. Comparison of the ten Cupboard Clarks separately with the Standard. The comparison of Cell I. with the Standard gives us a relation of electromotive forces which may be written

$$\text{I.} - \text{Standard} = a_1,$$

and the addition of all such relations gives us for the ten cells

$$(\text{I.} + \text{II.} + \text{III.} + \ldots + \text{X.}) - 10 \text{ Standards} = a_1 + b_1 + \ldots = \text{S}_1.$$

3. Comparison once more of the Cell I. with the Standard gives

$$\text{I.} - \text{Standard} = a_2.$$

There may be a small difference between a_1 and a_2 owing to temperature changes.

4. Reading of the thermometers placed in the Standard, t_2^s.

5. Comparison of Sets (1) and (2) of the battery of 20 cells with the 10 Cupboard Clarks in series, giving by addition the relation

$$\text{Set (1)} + \text{Set (2)} - 2 \times (\text{I.} + \text{II.} + \text{III.} + \ldots + \text{X.}) = 2\text{T}_1.$$

6. Third comparison of the Cupboard Clark I. with the Standard, the difference being denoted by a_3.

7. Reading of the thermometer of the Standard Clark, t_3^s.

From the above measurements we obtain the electromotive forces of our battery in terms of the Standard, thus:—

$$\text{Set (1)} + \text{Set (2)} = 20 \text{ Standards} + 2(S_1 + T_1).$$

After the completion of each experiment for the equivalent, the comparisons are carried out in the reverse order, and if S_2 and T_2 denote the quantities corresponding to S_1, T_1 we may take the electromotive force of the battery during the experiment to be the arithmetical mean of that determined at the beginning and end. The relation, written as above, would be

$$\text{Set (1)} + \text{Set (2)} = 20 \text{ Standards} + (S_1 + S_2 + T_1 + T_2).$$

A small correction is necessary owing to the fact that the temperature of the Cupboard Clarks may not have been the same during their comparison with the battery as it was while they were being compared with the Standard. We may, without sensible error, assume that all Cupboard Clarks varied equally, and that, therefore, the alteration due to temperature changes, for each cell measured in electromotive force, is expressed by the difference of $\frac{1}{2}(a_2 + a_3)$ and $\frac{1}{2}(a_1 + a_2)$. Hence we correct for the change of the ten cells by adding to S_1 the quantity $5(a_3 - a_1)$. A similar correction applies to the final comparison, so that the complete relation of electromotive force is given by

$$\text{Set (1)} + \text{Set (2)} = 20 \text{ Standards} + (S_1 + S_2 + T_1 + T_2) + 5(a_3 - a_1 + a_4 - a_6).$$

The temperature of the Standard to which the equation applies is the mean between $\frac{1}{2}(t_2^s + t_3^s)$ and $\frac{1}{2}(t_4^s + t_5^s)$. The temperatures t_2, t_3 and t_3, t_4 were practically identical in every case, we may take without error $\frac{1}{2}(t_3 + t_4)$ to be the temperature of the Standard during the comparisons.

The Silver Voltameter.

The platinum bowl which served as voltameter had a diameter of 9 centims. and a greatest depth of 4 centims. A 20 per cent. solution of the nitrate of silver was used, the salt being supplied by Messrs. JOHNSON, MATTHEY, and Co., as thrice recrystallized. The silver plate serving as anode was supplied by the same firm. It was 7 centims. in diameter and 2 millims. thick. The dish rested during the experiments on tinfoil wrapped round a ring of copper, which rested on a tripod, also covered with tinfoil (V, fig. 5). The tripod stood on paraffin blocks. The silver plate, protected by filter-paper, was suspended from three platinum wires attached to a copper terminal. The insulation of the voltameter was amply sufficient, and the contacts were all sufficiently good to allow a perfectly steady current to pass. In order always to bring back the dish to the same condition, the silver deposit of the previous experiment was always dissolved away before a new deposit was made. The dish was washed successively with (1) concentrated nitric acid, (2) a solution of potash, (3) tap water, (4) distilled water. After drying in air-bath the empty dish was weighed two or three times with the usual precautions. The silver deposit was treated in the manner described by Lord RAYLEIGH. Immediately after an experiment the silver solution was removed from the dish, the deposit washed three times, and left overnight with distilled water. After washing again next morning, the deposit was dried in an air-bath, first at 100° C., subsequently the temperature of the bath was raised for 10 or 15 minutes to 160° C. The dish was then again weighed two or three times. The distilled water used in washing left no residue on evaporation from platinum foil, nor gave any visible turbidity with silver nitrate solution. The voltameter was efficiently protected from dust, which might otherwise have got entangled in the silver. The deposit always firmly adhered to the dish in characteristic radial lines, and no difficulty was ever experienced in the washing.

Correction of the Weight to Vacuo.

In correcting the weighings to vacuo we must distinguish between the bowl and the silver. As regards the bowl, it is only the difference in the density of the air when the two weighings are taken which will affect the result. We found it, therefore, most convenient to reduce the weighings to the normal state of the atmosphere instead of to vacuo. The correction k to vacuo may be written $k = w\rho\alpha$, α being a constant and $\rho = \rho_0 h_1 t_0 / h_0 t_1$, where

ρ_0 = density of air at 76 centims. and 15° C.,
h_1 = height of barometer at time of weighing,
t_1 = absolute temperature of balance case,
h_0 = 76 centims.,
t_0 = 288°.

Representing the changes in barometric pressure and temperature by dh and dt respectively, we may express the difference in the buoyancy correction from that which would hold if the temperature was 15° C. and barometric height 76 centims. by

$$dk = \frac{w\alpha\rho_0}{h_0 t_0}\{t_0\, dh - h_0\, dt\}.$$

Substituting the values which apply to our platinum bowl weighed against brass weights, viz.,

$$w = 64, \quad \rho_0 = \cdot 00122, \quad \alpha = \tfrac{1}{21\cdot 5} - \tfrac{1}{8\cdot 4} = - \cdot 0725,$$

the correction becomes

(i) for difference in temperature $+ \cdot 020\,(t - 15)$ millim.
(ii) ,, ,, pressure $+ \cdot 074\,(76 - h_1)$,,

As regards the silver deposit, the correction amounts to ·024 millim. for each gram. Neither the accuracy of our weighings nor our knowledge of the equivalent of silver render it necessary to apply so small a correction, which would alter our final result by only one part in 40,000.

The balance used was one of OERTLING'S long beam balances, and the sensibility was adjusted so that with a load equal to that of the platinum bowl 1 millim. corresponded to one scale division. The bowl was always counterbalanced by the same weights before and after the deposit, so that any error in these weights would not affect the result.

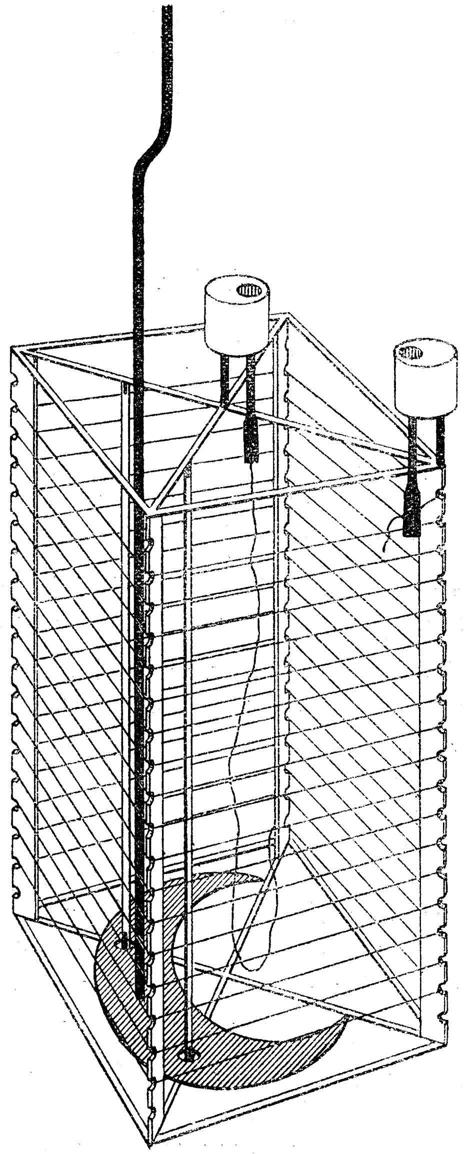
To determine the correction, if any, to the weights used in balancing the silver deposit, a brass weight of nominal value of 1 gram. was standardised by the Board of Trade, and found to weigh 1·000032 gram. The silver deposit weighing always just above ·5 gram., it was sufficient to determine the error of the $\frac{1}{2}$-gram. platinum mass which was used in all the experiments. Four experiments gave for the corrected mass: ·499966, ·500020, ·500032, ·499998, or, as a mean, ·500004 gram. It was therefore sufficient to assume the ·5-gram. weight to be correct.

The Heating Coil.

The coil in which the electric energy was converted into heat was made of a length of 760 centims. of platinoid wire, having a diameter of ·0345 centims. (29 B.W.G.) and a resistance of approximately 31 ohms. The coil used during the first few experiments was wound on a frame made of thin strips of ivory. On determining the specific heat of that substance we met, however, with a serious difficulty, as it was found to absorb a considerable quantity of water, which it gave up again on heating. Thus a fresh strip of ivory was found to lose 10 per cent. of its weight after heating in an air-bath for two hours. Even coating with shellac will not overcome the gradual absorption of water. Having had to discard ivory, we fixed on porcelain, and were supplied through the kindness of the Worcester Manufactory with strips of that material. The mounting of the frame and wire is seen in fig. 4.

Four strips of porcelain, 14 centims. long and 1 centim. broad, with 30 notches to keep the wire in position, are mounted by fixing their ends in sockets made of brass foil. These sockets were connected by stout brass wire. The ends of the platinoid wire were fixed to stout copper wire about 5 centims. long wedged into the bottom of cylindrical pieces of ebonite. The ebonite was held in position by brass supports soldered to the frame. The upper ends of the copper terminals projected into the bottom of cups drilled from above in the ebonite; these holes, which were 9 millims. wide and 15 millims. deep, were filled with mercury, and served to connect the coil with the outer circuit. The coil was insulated by a covering of shellac. To obtain a thin and uniform layer, the frame was immersed in a weak alcoholic solution of the substance, and afterwards heated for half-an-hour in an air-bath at a temperature of 130° C. This process of immersion and heating was repeated until the insulation resistance was higher than that required by the conditions of the experiment, and we

Fig. 4.



were quite satisfied with the permanence of the covering obtained. The insulation was tested from time to time and the coil re-covered when necessary. When the coil immersed in water was connected to one terminal of the battery, the second terminal being a bare wire, the resistance was generally found to be over 40,000 ohms, the electromotive force being 30 volts. That an insulation resistance equal to that amount is amply sufficient will be seen if it is remembered that leakage can only cause error in so far as the water is decomposed. If the whole of the current were to pass through the water instead of through the coil, about 1 volt would be lost, so that an error of 3 per cent. only would result. Considering the small diameter of the wire and the high resistance of distilled water, it will appear that, even if our wire had been completely uncovered, the error introduced would not have been great, and even an insulation resistance of 1000 ohms would have made it inappreciable.

The Stirring.

The stirrer is shown in figs. 4 and 5. It consisted of a piece of brass foil cut to a half-moon shape. The upper surface was soldered to fine brass tubing, 17 centims. long. Two pieces of glass tubing fixed to the frame of the coil passed through circular holes cut into the stirrer and served as guides. The stirrer was moved up and down by a wheel and crank W (fig. 5) driven by an electromotor. A piece of brass tubing, of the same kind as that attached to the stirrer, was fixed to the crank, and the motion was transmitted by a flexible joint made of several layers of thin unvulcanised india-rubber, firmly tied to each of the two parts of the brass tubing. This joint, devised by Mr. HADLEY, worked very satisfactorily, and allowed sufficient lateral play to facilitate the adjustment of the calorimeter and coil below the driving wheel of the stirring apparatus.

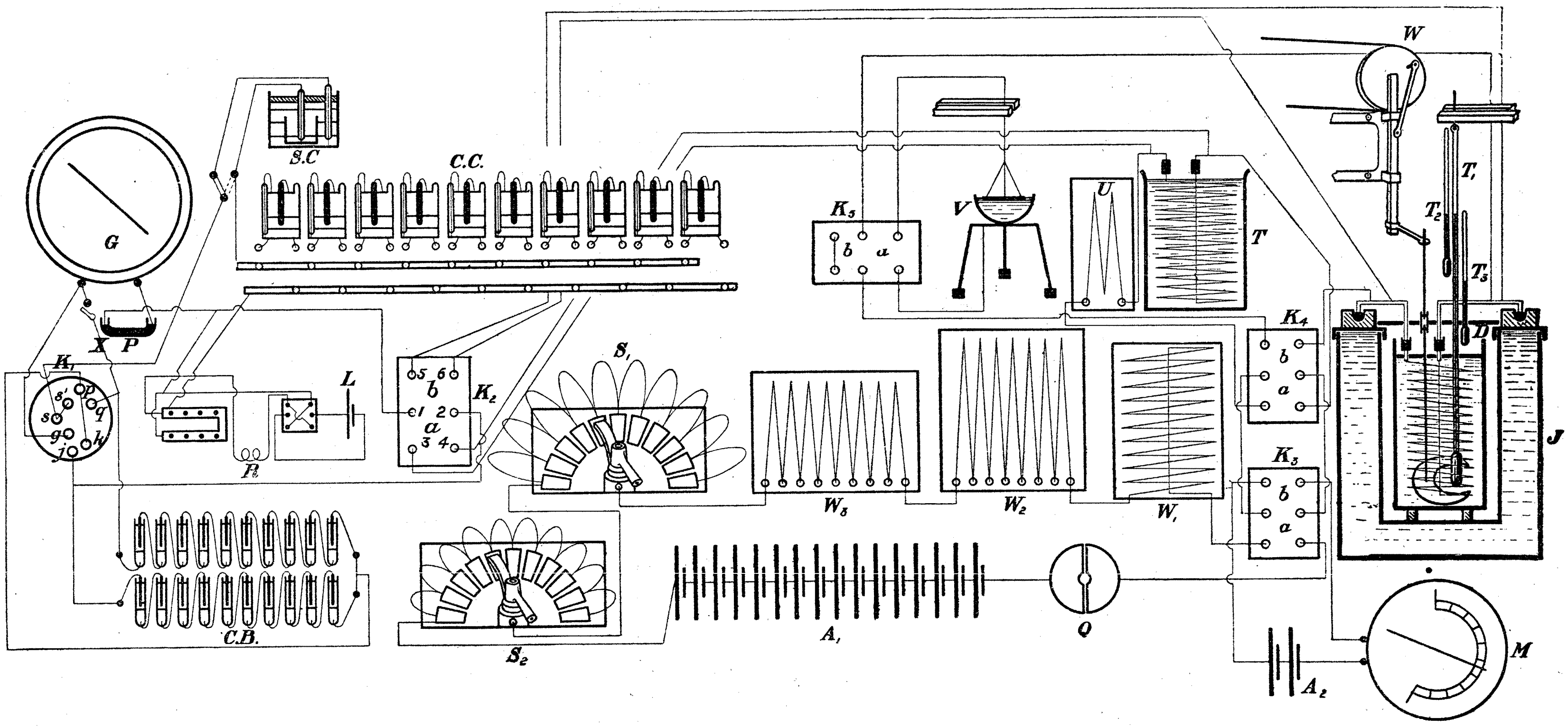
Some Questions concerning Thermometry.

The method of using mercury thermometers in accurate work has undergone considerable change in the last twenty years. In measuring a temperature, the interval between 0° and 100° used to be determined by plunging the thermometer first into a mixture of ice and water, and then into boiling water. If the two readings are T_0, T_{100}, the temperature t corresponding to an intermediate reading, T_t would be

$$t = 100\,(T_t - T_0)/(T_{100} - T_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

Owing to certain properties of the glass envelope, analogous in their effects to elastic fatigue, a thermometer when exposed to a constant temperature will not, however, take up its final indication for a time which may be considerable, and this set of the glass affects especially the zero point, the apparent zero as at first observed

Fig. 5.



$K_1K_2K_3K_4K_5$ = Mercury keys.
$W_1W_2W_3$ = Adjustable resistances.
S_1S_2 = Resistance switches.
A_1 = Main battery.
A_2 = Auxiliary battery.
M = Current-meter.
J = Water-jacket.
D = Cover over calorimter.

W = Stirrer apparatus.
T = Temporary coil.
U = Resistance in temporary circuit equal to voltameter resistance.
V = Silver voltameter.
Q = Plug key in main circuit.
G = Kelvin high-resistance astatic galvanometer.
$S.C.$ = Standard Clark.

$C.C.$ = Cupboard Clarks'.
$C.B.$ = Clark battery.
P = Carbon resistance.
r = Box of 1–40 ohm coils.
R = 10,000 ohms.
L = Leclanché cell.
T_1 = Principal thermometer (Baudin).
T_2T_3 = Auxiliary thermometer.

being dependent on the temperature to which the thermometer was previously exposed. It is found, however, that consistent results can be obtained by referring the reading of a thermometer not to a fixed zero, but to the position of the mercury thread, observed when the thermometer is plunged into ice directly after being exposed to the temperature to be measured. Calling T_0^t the zero, as thus determined, after exposure to the temperature t, that temperature measured in the mercury thermometer is now defined as

$$t = 100\,(T_t - T_0^t)/(T_{100} - T_0^{100}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

The two definitions of temperature indicated by (1) and (2) are identical if the so-called depression of the zero $T_0^0 - T_0^t$ is proportional to the temperature t, as with thermometers made of the Jena, or French standard glass. Writing in this case

$$T_0^0 - T_0^t = \alpha\,(T_t - T_0^t)$$

or

$$T_t - T_0^t = \frac{1}{1-\alpha}\,(T_t - T_0^0),$$

and similarly

$$T_{100} - T_0^{100} = \frac{1}{1-\alpha}\,(T_{100} - T_0^0),$$

we obtain by substitution in (2)

$$t = 100\,(T_t - T_0^0)/(T_{100} - T_0^0),$$

which is identical with (1), if the zero in that equation is meant to signify the position which the thermometer would take up if plunged into ice for a considerable time.

If the observations are made with English glass of recent manufacture, the identity of equations (1) and (2) does not hold, as the depressions of the zero are nearly proportional to the squares of the temperatures. It then becomes of importance to define clearly how a temperature is taken. Thus WIEBE finds that thermometers made of English glass read *lower* than the air thermometer by as much as 0°·047 at 40°, while ROWLAND states that *all* thermometers examined by him, including those of English manufacture, read *higher* than the air thermometer. The two statements are not contradictory; the discrepancy is explained by the fact that WIEBE refers all temperatures to the zero observed directly after each reading, while at the time ROWLAND's work was done, this practice, which alone converts the thermometer into an instrument fit for scientific research, and is now uniformly adopted, had not yet come into use.

It is an essential point in thermometric measurements that the work done by different observers should be comparable, and some uniform scale should be adopted.

For the present we cannot do better than use thermometers made either of standard Jena or French glass, as their behaviours have been thoroughly studied. By making use of the published investigation, we may then refer our measurements to the thermometers of Berlin or Sèvres.

In calorimetric researches it is often impossible or inadvisable to determine the zero after each measurement. The behaviour of standard glass is so regular that, after the thermometer has been in air for a few years, we may predict with considerable accuracy the position of the zero from a knowledge of the temperature to which the instrument has been exposed. The following Table will illustrate this point.

TABLE II.

1.	2.	3.	4.	5.	6.
Date.	Temperature. C.	Zero observed.	Observed zero reduced to 760 millims.	Calculated zero.	Difference.
1893.	°				
Dec. 19	12·47	·0167	·0194	·0193	+·0001
,, 5	12·55	·0194	·0183	·0193	−·0010
,, 12	13·28	·0162	·0185	·0186	−·0001
,, 13	14·14	·0150	·0187	·0178	+·0009
,, 12	22·36	·0080	·0104	·0102	+·0002
,, 13	22·46	·0086	·0123	·0101	+·0022
,, 19	22·58	·0085	·0115	·0100	+·0015

The second column gives the temperature to which our standard thermometer had been exposed previous to the zero determination; the third column gives the observed zero, measured by an eye-piece micrometer, the fourth place of decimals having no significance; the fourth column gives the observed zero corrected for change due to the varying pressure on the bulb. According to GUILLAUME, the zero of a thermometer after exposure to a temperature t, should be capable of expression in the form $z - 0{\cdot}00092\ (t^\circ - 15^\circ)$ where z is the zero corresponding to the temperature of 15°. The fifth column gives the zero reading calculated according to this formula, taking for z the value 0·0170; the sixth column shows the difference between the calculated and the observed reduced values.

The agreement is satisfactory, especially for the lower temperatures. The experiment on December 12 was made after exposure of the thermometer to the temperature of 22° during four hours, and the zero is seen to be exactly that calculated from the formula. In the two last observations the thermometer had only been kept in the water for about two and a half hours; and we conclude from the observations that the time was not quite sufficient to lower the zero through its full amount.

A little consideration is necessary to decide how far the uncertainty of the zero may introduce errors into a calorimetric measurement. With French or German standard glass the depression of the zero, corresponding to a certain interval, is less than the thousandth part of that interval. If the thermometer has been, before the experiment, sufficiently long in the calorimeter to take up its permanent position, and if the rise of temperature is then made to take place, the position of the zero in the final period must lie between its original value and that corresponding to permanent immersion in the final temperature. The error made by either assumption cannot exceed one part in a thousand, and we may form a sufficiently good estimate as to the actual zero value to reduce considerably the limits of possible mistake. But the slow set of the glass envelope which shows itself in the shifting zero, may affect our results in another way. The correction due to loss of heat by radiation and conduction is generally determined by observing the temperature of the calorimeter at the beginning and conclusion of the experiment. But even if there is no loss in the final stage, the thermometer will apparently fall slowly, owing to the imperfect behaviour of the glass envelope. Let the rate of fall be β; if the calorimetric observations are conducted in the usual way we should over-estimate that loss by the quantity β. If the time during which the calorimeter has been rising in temperature is τ, we may correct for the error made in this way by adding $\frac{1}{2}\beta\tau$ to the final temperature, or deducting $\frac{1}{2}\beta t$ from the zero. This is equivalent to saying that we may correct for the set of the glass envelope in a calorimetric measurement by taking for the zero during the final stage the zero shown by the thermometer after immersion in the final temperature during a period equal to half the length of time it has taken the thermometer to rise from its initial to its final value. In our experiments this would be between four and five minutes.

To obtain some clearer information as to time taken by our thermometers to arrive at this permanent zero a series of experiments were carried out. We had a thermometer (Baudin, 12773) which in all respects was as nearly as possible like the one used in our calorimeter experiments (12772). The former was placed in water of about 22°, and kept there for over four hours, the latter was kept during the same time at a temperature of from 10° to 12°, and then suddenly raised to the higher temperature and placed side by side with No. 12773. The two thermometers were read alternately every quarter of a minute for about a quarter of an hour, so as to obtain a good comparison. After the lapse of another hour a similar set of readings were taken at the same temperature. As the mercury threads stand between the same divisions in the two cases, a systematic difference in the reading cannot be due to any calibration errors. The following Table III. gives the results of the comparisons. The times are given in minutes reckoned from the moment that 12772 was placed beside 12773. The column headed Δ denotes the difference between the indications of the two thermometers, 12772 always reading higher.

Table III.

Date.	November 2.		November 6.		November 8.		November 13.		Mean.	
Temperature previous to comparison . . .	10°·4		13°·2		12°·0		10°·0		11°·4	
Temperature during comparison	21·2		21·2		21·3		21·2		21·2	
	Time.	Δ.	Time.	Δ.	Time.	Δ.	Time.	Δ.	Time.	Δ.
	m. 2·5 6·5 78·0	0°·0128 ·0113 ·0104	m. 2·3 5·5 69·0	0°·0108 ·0118 ·0092	m. 2·0 6·5 89·0	0°·0137 ·0132 ·0125	m. 1·5 7·0 65·0	0°·0097 ·0116 ·0098	m. 2·1 6·4 75·2	0°·0118 ·0120 ·0105

It appears from the table that the thermometer suddenly plunged into water at a temperature of about 10° higher than that to which it was previously exposed, will, during the first hour show a gradual lowering of its indications, corresponding to the lowering of its zero point, amounting to about 0°·0012. Even after the first hour the change will not be complete, as is seen from Table III.; the experiments made on Dec. 13 and 19 showing that after two hours and a half, the zero is still too high by about 0·0018. The first indications of the thermometer must have been too low therefore by about 0·004. As the total change of zero corresponding to the rise from 11°·4 to 21°·2 is 0·009, it follows that about half the depression takes place in the first few minutes.

In view of these experiments we conclude that the zero of a thermometer of French glass used in calorimetric determinations may after the lapse of a few minutes be assumed to have a position half-way between those corresponding to the lower and the higher temperatures. The extreme uncertainty of this range is less than one part in two thousand, but it is practically certain that an error of more than one part in five thousand cannot be introduced by the assumption made.

The Thermometers.

We used as primary standard a thermometer made by Tonnelot (No. 4929). A complete calibration and examination of this instrument was made for us by the "Bureau International des Poids et Mesures" at Paris. The thermometer is divided into tenths of a degree, the length of each degree being 0·58 centim. The divisions are beautifully sharp and can be read both in front and behind the mercury thread. The stem is cylindrical and has a diameter of ·45 centim. The bulb has a length of 4·8 centims. and a diameter very nearly equal to that of the stem.

A thermometer plunged into a calorimeter can only be read with convenience when the thread is a few inches above the level of the water; and if the length of a degree is short, the correction for the emergent stem becomes serious. It is important that this correction should be small, as it cannot be ascertained with great accuracy. Hence it is better for calorimetric measurements to use a thermometer with an open scale so that nearly the whole thread may be immersed. The open scale has the further advantage of being more easily read. It is generally supposed that the accuracy of thermometer measurements is increased by using a thermometer in which the length of a degree is made very large, and the manufacture of such thermometers has been pushed to ridiculous extremes. Our experience confirms the conclusion drawn by GUILLAUME ("Thermométrie," p. 180), that the uncertainties in the indications of a thermometer measured in degrees increase with an increase in the length of the degree, and that, therefore, apart from the convenience of reading, the advantage altogether is in favour of a short degree. When the whole thermometer can be plunged in water and the temperature of the water is kept sufficiently steady to allow a careful reading, a thermometer such as that of TONNELOT, divided into tenths of a degree, the divisions being half a millimetre apart, allows as accurate a determination of temperature as any mercury thermometer can give us at present.

It was the uncertainty of the correction of the emergent stem which finally decided us to use in our calorimeter a thermometer with an open scale; but it was essential that it should be made of the same glass as the standard. We chose one by BAUDIN (No. 12772), having a length of degree of 3·1 centims. approximately, and being divided into fiftieths. It contained according to the statement of the maker 33·0 grams. of mercury. It could be read at the freezing-point and between 12° and 23°. The stem was shortened by an expansion in the glass above the zero point in such a way that the distance from the division which marked 12° to the centre of the main bulb was only 8·1 centims. The radius of the bore can be calculated from the weight of mercury, and is thus found to be 0·0061 centim. From experiments made under varying pressures, the thickness of the glass bulb can be roughly estimated as ·066 centim. In order to allow us to use the thermometer for our purpose it was necessary (1) to calibrate the thermometer, (2) to compare it with the standard, (3) to determine carefully the pressure coefficient, as the comparison had to be conducted with the thermometer in a horizontal position.

The Calibration.

The calibration was conducted according to the method of THIESSEN, as described by GUILLAUME. Threads were broken off, having a length of very nearly one, two, &c., up to ten degrees, and these threads were pushed forward from degree to degree. Their lengths were measured on the thermometer in the usual way, an estimate of the overlapping of the mercury to one-hundredth part of a division being made by the eye, looking through a telescope of small magnifying power, but without a micrometer. The observations with every thread were repeated more than once, often by different observers. The final result is given in Table IV., in which the second column gives the calibration correction in thousandth parts of one division. The reductions are easily made by the method of least squares in the manner indicated by THIESSEN. The probable error of a single observation* was calculated to be ·020 division, and the probable error in the final correction at each point is ·008 division, or, as the thermometer was divided into fiftieths, the probable error in the calibration correction is 0°·00016.

TABLE IV.

Degrees.	Calibration correction of the complete series, the unit being ·001 division = 0°·00002.	Calibration correction deduced from observations made with one thread and eye estimate. 1892.	Calibration correction deduced from observations with one thread and micrometer measurements. 1894.
12	0	—	—
13	77	88	75
14	184	186	172
15	22	30	15
16	272	283	246
17	253	265	257
18	45	41	38
19	83	82	122
20	291	286	314
21	75	86	50
22	80	103	88
23	0	—	—

We conclude from this that it is extremely unlikely that our calibration is wrong by 0°·0008 at any point. In order to see how far the eye without micrometer may be trusted to carry out a calibration by means of one thread (GAY-LUSSAC'S method), we give in the third column of Table IV. the calibration corrections deduced from the observations of the thread of one degree. At the conclusion of our experiments it seemed more satisfactory to make certain that no appreciable change had taken place in the thermometer. The calibrations were, therefore, repeated, but this time only with one thread, according to GAY-LUSSAC'S method, and the readings were taken with a micrometer. The results are given in the fourth column. The greatest difference between the corrections found in 1892 and 1894 amounts to about ·04 division, or 0°·0008; the average difference amounts to less than half that value.

The observations made at the conclusion of our experiments were only intended as a check, and we feel justified in concluding that no change has taken place in the

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* By a single observation here is meant the measurement of the mercury thread in one of its positions. Several measurements in the same position are taken, and their mean value counts in the reduction as one observation.

thermometer, and that our calibration in 1892 was satisfactory. The numbers obtained from the single thread by GAY-LUSSAC's method are practically identical with those obtained by the more complete method.

The temperatures for which the corrections have been obtained being too far apart to allow us to interpolate safely for the intermediate points, a thread of 2°·5 was broken off, and by means of it the corrections for every half-degree could be deduced. The divisions of the thermometer were not equidistant, but the maker had attempted to correct for inequality of bore. This method, much in use at one time, causes a good deal of unnecessary labour, as already pointed out by GUILLAUME, whenever the instrument is to be used for accurate work; its subsequent calibration cannot be dispensed with, and the lengths of the divisions must be measured one by one, as there is no clue where a sudden change in the length may occur. We give in an appendix the method adopted to deduce the final corrections for each division of the thermometer.

Pressure Corrections.

The reservoir of a thermometer is generally subjected to an internal pressure due to the column of mercury forming the thread, and this pressure causes quite an appreciable increase in volume. If the thermometer is always used in the vertical position, no error is caused in assuming uniformity of bore; the effect of internal pressure will only be a shortening of the distance between the fundamental points. Even in this case, however, care must be taken that the range for which the thermometer is used does not include bulbs like those which are placed above the freezing point in calorimetric thermometers.

A comparison between two thermometers is more easily conducted in a horizontal than in a vertical position; and in that case, of course, the effect of pressure must be taken account of.

The effects of external pressure are easily measured by suspending the thermometer in a vessel in which the pressure can be quickly changed from the atmospheric pressure to one of a few centimetres only.

We have used a method which is a slight modification of that given in GUILLAUME's book. It is unnecessary to enter into long details, as the method will be described in another communication. Three experiments were made on March 21, 1892. The change of pressure was a sudden diminution from the atmospheric pressure to one of 2·7 centims. The observations, when reduced, give

	0°·002088
	0°·002085
	0°·002080
Mean . .	0°·002084

as the effect due to 1 centim. of mercury at 0° C. at the latitude of Manchester.

The experiments were repeated two years later, on February 22, 1894, when two different determinations gave

$$\begin{array}{rl} & 0{\cdot}002096 \\ & \underline{0{\cdot}002072} \\ \text{Mean} \;\; . \;\; . & 0{\cdot}002084 \end{array}$$

It is seen that the changes in atmospheric pressure, which may amount to several centimetres, may produce a change in the indications of a delicate thermometer which cannot be neglected.

From the effect of external pressure we may easily deduce that of internal pressure. If $P\alpha$ is the diminution of volume due to an increase of pressure P applied externally, and $P\beta$ the increase in volume of the same pressure is applied internally, then the diminution in volume due to a simultaneous increase of pressure P inside and outside is $P(\alpha - \beta)$, and this must also be equal to P/κ, where κ is the compressibility of the walls of the thermometer bulb. Hence

$$\alpha - \beta = 1/\kappa.^*$$

The reading apparently is diminished when the thermometer is raised from the horizontal to the vertical position, not only because the glass bulb expands, but also because the mercury is compressed. If κ' is the resistance to compression of mercury, a pressure P will have the same effect as an increase of volume P/κ' of the reservoir. Hence, if β now denotes the complete effect of unit increase of pressure applied internally on the reading in degrees of the thermometer, we obtain

$$\beta = \alpha + \frac{1}{\kappa'} - \frac{1}{\kappa}.$$

$\frac{1}{\kappa'} - \frac{1}{\kappa}$ is the relative compressibility of mercury and glass, which is known. AMAGAT, whose measurements doubtless are the most accurate at our disposal, finds for glass of medium hardness the relative compressibility to be $1{\cdot}707 \times 10^{-6}$, and for lead glass (*cristal*) $1{\cdot}512 \times 10^{-6}$ ('Annales de Chimie et de Physique,' vol. 22, 1891). For the French thermometer glass the coefficient will not differ much from the larger of these values.

The numbers given refer to the atmosphere as unit pressure. It is more convenient

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[*] This relation is quite general and independent of the shape of the bulb, which need not be of the same thickness throughout, provided it is of homogeneous material. The relation in GUILLAUME's book is proved in an elaborate manner for spheres and cylinders, and is then said to hold "no doubt only approximately" for thermometer bulbs.

[Since the above was written, Mr. CHREE has published a paper ('Phil. Mag.,' October, 1894), in which a proof of the relation between the internal and external pressure coefficients practically identical with the above has been given.—June, 1895.]

for our purpose to take as unit pressure that due to a column of mercury 1 centim. long, and for unit change of volume that corresponding to an increase in temperature of one degree. The relative coefficient of thermal expansion of glass and mercury between 10° and 20° C. being $1{\cdot}598 \times 10^{-4}$, the apparent compressibility of mercury reduced to the new units will be found by dividing the above number by $76 \times 1{\cdot}598 \times 10^{-4}$. The relation between β and α then becomes

$$\beta = \alpha + 0{\cdot}000141.$$

The number used by the Bureau International des Poids et Mesures, founded on some older determinations, is 0·000154, and the uncertainty of this term might be raised as an objection to the use of a thermometer in the horizontal position. But the whole term being of little importance, it does not matter much which of the different possible values we adopt. Thus the difference between GUILLAUME'S internal pressure correction and ours would produce a difference in the measured temperature range of our Baudin thermometer of one part in 25,000, and in the Tonnelot standard it would be equal to only the sixth part of that value. For the sake of uniformity we have continued to use GUILLAUME'S number, and therefore take for the Baudin 12,772,

$$\alpha = 0{\cdot}002084$$
$$\beta = 0{\cdot}002238,$$

where α and β measure in degrees the changes in the apparent temperature due to a change of pressure of 1 centim. of mercury applied to the outside or inside respectively.

A small correction was necessary to allow for the fact that the mercury in that part of the stem which is not immersed in the calorimeter is not necessarily at the same temperature as the water. To ascertain this correction two small thermometers were used, one placed in the space between the calorimeter and the disc (D, fig. 5) which covered the water jacket, while the other was placed above this disc about half-way between it and the upper end of the thread. We found that in the last period when the calorimeter had risen about 2°, that part of thread below the disc D could be assumed to be at a temperature 1° above that of the air, while that part of the thread which was above the disc had not appreciably changed its temperature. The correction was always small, as the whole rise was only 2° and only a few degrees of the stem were exposed to the air.

The thermometer was always read by means of a cathetometer telescope, the cathetometer stand being very convenient to move the telescope parallel to itself. The avoidance of parallax is of importance and can be easily secured in this way, provided the thread is always read when in the middle of the field.

Comparison of Thermometers.

Having found the calibration correction of a thermometer, it remains to determine its range. The calibration of our calorimetric thermometer was carried out between the points marked 12° and 23° respectively, and in order to find the interval between those points according to some fixed scale, it would seem most natural to compare the thermometer near the extreme points of its range with a standard. This we attempted to do at first, but found that the results of different comparisons were not as concordant as we could have wished. Two thermometers, however, carefully calibrated, will show differences when compared with each other amounting to a few thousandths of a degree, and there seems little doubt that local irregularities, either in the width of the bore, or in the nature of the surface affecting the capillary constant, render the readings of a mercury thermometer uncertain to that extent. These irregularities are more likely to occur near the ends of the scale where the tube had to be blown out into a bulb or joined to the reservoir. We decided therefore to compare the Baudin and Tonnelot along the whole scale in order to obtain as accurate a value for the Baudin as possible.

The comparisons were carried out in a horizontal bath with a slowly rising temperature. It is unnecessary here to enter into the details of the construction of the apparatus and method of comparison, as these will be furnished in another communication. Table V. shows the result. Column II. gives the reading T_B of the Baudin thermometer, corrected for calibration and division errors and reduced to the vertical position. The third column gives the correction γ which has to be applied to the Baudin thermometer in order to reduce it to the readings of the standard mercury thermometer made of French glass. The values of γ are those obtained by experiment. Calling t_B the reading of the Baudin thermometer, we require to express γ as a linear function of the temperature in the form

$$\gamma = a + bT_B.$$

Reducing the observations by the method of least squares, we found

$$a = + 0{\cdot}0194$$
$$b = - 0{\cdot}00089 \pm 0{\cdot}000047.$$

Calling γ' the value of γ calculated with the help of these data, $\gamma' - \gamma = \Delta$ will express the difference between the calculated and observed corrections to the Baudin thermometer. The fourth column of the table in which Δ is entered shows that the agreement is satisfactory. The residual differences are accounted for by errors of observation, by remaining errors of calibration of the two thermometers and by irregularities in the capillary phenomena. The probable error of a single comparison is found to be 0°·00096, that is about one thousandth of a degree, and the probable error of the interval is about one part in 20,000.

TABLE V.

I.	II.	III.	IV.
Comparison.	T_B.	γ.	Δ.
1	12°·585	+0·0072	+0·0010
2	12·643	+0·0068	+0·0014
3	12·885	+0·0073	+0·0006
4	12·923	+0·0051	+0·0028
5	13·068	+0·0068	+0·0010
6	13·315	+0·0090	−0·0014
7	13·393	+0·0088	−0·0013
8	13·687	+0·0071	+0·0001
9	14·023	+0·0075	−0·0006
10	14·103	+0·0096	−0·0027
11	14·171	+0·0074	−0·0006
12	14·184	+0·0075	−0·0007
13	14·590	+0·0067	−0·0003
14	15·132	+0·0076	−0·0017
15	15·194	+0·0065	−0·0006
16	15·538	+0·0052	+0·0004
17	15·981	+0·0057	−0·0005
18	16·018	+0·0035	+0·0017
19	16·534	+0·0037	+0·0010
20	17·226	+0·0062	−0·0021
21	17·322	+0·0037	+0·0030
22	17·964	+0·0035	−0·0001
23	17·997	−0·0005	+0·0039
24	18·032	+0·0026	+0·0008
25	18·593	+0·0032	−0·0003
26	18·999	+0·0026	−0·0001
27	19·107	+0·0023	+0·0001
28	19·464	+0·0015	+0·0006
29	19·997	+0·0041	−0·0025
30	20·011	+0·0006	+0·0010
31	20·055	+0·0021	−0·0005
32	20·545	+0·0006	+0·0005
33	21·065	+0·0028	−0·0021
34	21·103	+0·0005	+0·0001
35	21·485	+0·0006	−0·0003
36	21·501	+0·0008	−0·0005
37	22·054	+0·0004	−0·0006
38	22·145	−0·0036	+0·0033
39	22·451	−0·0010	+0·0004
40	22·831	−0·0011	+0·0002

In the comparison of the calorimetric and standard thermometers, the two were always treated exactly in the same manner, and exposed simultaneously to the same temperatures; hence we may assume that their zeros varied equally, and, as the zero of the standard was assumed that corresponding to the steady state of the thermometer after it has been exposed for a sufficiently long time to the temperature of comparison, the correction found for the Baudin applies to the ultimate reading of that thermometer at any temperature. As it has been shown that we must in our experiments take the zero to be halfway between its initial and final positions, the corrections under the condition of our experiments have to be diminished by 0·00046 ; hence, if t is any interval of temperature on the standard thermometer, and t_B that on the Baudin thermometer, we find finally

$$t = t_B (1 - \cdot 00135).$$

We have made a few observations which check the correction (·00046) we have made to eliminate the error due to the fact that, in the actual equivalent experiment, the zero of our Baudin had not reached its final state. The Baudin was placed in water at a temperature 10° above that at which it had previously been kept, and was compared after the lapse of about ten minutes with the standard. The latter instrument had been immersed in the warm water for several hours, and its zero was determined at the conclusion of the comparison. The corrections thus found on three different days for the Baudin were $-0^\circ\cdot0059$, $-0^\circ\cdot0069$, $-0^\circ\cdot0053$, or $-0^\circ\cdot0060$ in the average, at a mean temperature of 22°·6. Taking the correction at 12° to be that found above, viz., 0°·0082, we should get an interval correction of $-0^\circ\cdot00142$, holding for the conditions of the experiment closely resembling those of the equivalent experiments. The difference between this number and the one adopted ($-0\cdot00135$) is less than one part in a thousand.

The Calorimeter and Water-equivalents.

The calorimeter consisted of a copper vessel, heavily gilt outside and inside, the weight of gold deposited being about 1·6 grms. The copper vessel was of the usual cylindrical form, and had the following dimensions :—

Height	17·9 centims.
Diameter of section	11·0 ,,
Thickness of walls	0·0295 centim.
Total weight of calorimeter .	161·3 grms.

The following data will show the agreement between different determinations of the specific heat of copper :—

TABLE VI.

Observer.	Specific heat.	Range of temperature through which copper was cooled.	Mean temperature of copper.	Temperature of water.
		° °	°	°
REGNAULT (NACCARI)*	·0933	100 – 17	59	17
TOMLINSON	·0938	100 – 20	60	20
BÈDE	·0933	100 – 15	58	20
JOULE	·0921	40 – 8	24	7
TOMLINSON	·0926	60 – 20	40	20

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* REGNAULT gives a higher value, based apparently on a wrongly-assumed value of the specific heat of lead. The above value is that which NACCARI has recalculated from REGNAULT'S observations, correcting for the error.

The mean of the first set of three observations gives ·0935 for the specific heat of copper at 59°, and the mean of the last two ·0924 for the specific heat at 32°. The average temperature at which our observations were made was 19°, and, assuming the specific heat to be a linear function, we may with sufficient accuracy adopt for its value ·0918. The water-equivalent of the calorimeter, taking account of the small quantity of gold on it, is thus found to be 14·71. An error of 1 per cent. in this value would change our result by one part in ten thousand, and we may certainly trust the assumed specific heat of copper to that degree of accuracy. Our heating coil and frame were made of brass, porcelain, glass, platinoid, and shellac. After the conclusion of our experiments the whole of the heating frame, coil, and stirrer was broken up and enclosed in a cage of copper gauze, and its water-equivalent determined, with the following result:—

TABLE VII.

Experiment.	Water equivalent.	Mean temperature of copper.
		°
1	9·62	27
2	9·72	29
3	9·68	27
4	9·96	57
5	9·95	58
6	9·98	58

From these figures we calculate the water-equivalent at 19° to be 9·59.

We had originally intended to calculate the water-equivalent of our frame and coil by adding the equivalents of its parts, and we had for this purpose made some experiments on the specific heat of porcelain and platinoid. The experiments were not quite satisfactory, in the first place, because they related to a temperature higher than the one used in our experiments, and secondly because when they were made we had not quite realised what serious errors may be introduced, even with the best thermometers when the temperature during the last period is falling. Our values, for this reason, were no doubt too high. Although we trust entirely to the water-equivalent 9·59, which was directly determined with all precautions, and with a thermometer rising during the whole course of the experiments, we nevertheless give as a check the equivalents calculated from that of its parts.

TABLE VIII.

Material.	Weight.	Specific heat.	Water-equivalent.
Porcelain	23·32	·196	4·59
Platinoid	5·76	·102	·59
Glass	5·58	·190	1·06
Brass	42·55	·090	3·82
Copper terminals	2·04	·092	·19
		Total	10·25

This refers to a temperature of about 60°, and agrees sufficiently well with the equivalent 9·96 which was directly determined, if we remember that the specific heats of porcelain and platinoid are, for the reasons given, too high, and that the values for the specific heat of brass and glass were assumed to be those usually given.

We must add 0·34 to the water-equivalent belonging to a silver disc covered with gold foil, which was kept floating on the surface of the water in order to prevent evaporation as far as possible.

As regards the thermometer, we calculated the specific heat from the data inscribed on it by the maker, according to which the weights were as follows :—

Weight of mercury	33 grams.
Weight of glass bulb	1·83 grams.
Weight of glass in stem	25·79 ,,

Taking the specific heat of mercury to be 0·033, and that of glass 0·19, we calculate that the water-equivalent up to the point marked 12° was 2·05. An experiment made to determine directly the equivalent of the thermometer, showed that we could trust the figures given by the maker, the value found being identical with that calculated from his data. We may add 2·05 permanently to the water-equivalents, and in the separate experiments correct for the additional length of the stem immersed, which was slightly different on different occasions. The correction is determined by the fact that the water-equivalent corresponding to a length of 1° of the stem is 0·34. We may take, therefore, as the equivalents which were the same in all experiments :—

Calorimeter	14·71
Heating coil, frame and stirrer	9·59
Silver disc	0·34
Thermometer as far as mark 12°	2·05
Parts surrounding calorimeter	0·33
	27·02

The reason for the last item will be given in connexion with the discussion of the cooling correction.

The Total Mass of Water.

The calorimeter contained approximately 1514 grams. of distilled water in each experiment. The mass of water was determined by volume and by weight. In the estimation by volume a carefully calibrated 500 cub. centims. flask and burette were used. The weighings were taken on a balance, allowing, to estimate accurately, 0·1 gram. The buoyancy correction amounts to 1·58 gram.

As our calorimeter was not completely covered, a certain amount of evaporation took place, the mass of water during the experiment differing by about a decigram from that which was put in. A few experiments give a fairly consistent rate of ·11 gram. per hour of evaporation under the conditions of our experiment. As a check the water was nearly always weighed both before and after each experiment, and the mass during the experiment was then found by interpolation.

The Cooling Correction.

The interchange of heat between the calorimeter and its surroundings depends on conduction and radiation. If the water of the calorimeter is exposed to the air, evaporation may sensibly lower the temperature, but for the present we may disregard the effects of evaporation. The loss of heat to the outside is usually corrected for in a well-known manner. The correction depends on the assumption that the loss of heat is proportional to the difference in temperature between the calorimeter and its enclosure, and if the loss of heat is small, the assumption is generally justified. In a well-disposed experiment the temperature (u) of the calorimeter alters slowly and regularly during the preliminary period. If n observations are made at regular intervals of time T, they should be expressible with sufficient accuracy in an expression of the form $u = v + k\mathrm{T}$. It is usual to obtain the two constants of this equation v and k by graphical means; we have employed instead the method of least squares, not for the reason that we believe to have obtained a greater degree of accuracy in this way, but simply as a matter of convenience. The process of calculation takes less time than the graphical method, and the results are quite free from personal bias. The observations themselves give a series of equations,

$$\begin{aligned} u_1 &= v + k\mathrm{T} \\ u_2 &= v + 2k\mathrm{T} \\ &\vdots \\ u_n &= v + nk\mathrm{T}. \end{aligned}$$

It is required in the first place to calculate v and k. The most probable values of v and k are

$$\tfrac{1}{2}n(n-1)v = (2n+1)\mathrm{A} - 3\mathrm{B}$$
$$\tfrac{1}{6}n(n-1)(n+1)k\mathrm{T} = 2\mathrm{B} - (n+1)\mathrm{A},$$

where

$$\mathrm{A} = u_1 + u_2 + \ldots + u_n$$
$$\mathrm{B} = u_1 + 2u_2 + \ldots + nu_n.$$

The last observation being taken, the second period—in which the heat to be measured is allowed to enter the calorimeter—begins after a further interval T, and it is required to calculate, in addition to the rate of heating kT, the most probable value u_{n+1} of the temperature at the beginning of the second period. The above equations give

$$\begin{aligned} u_{n+1} &= v + (n+1)k\mathrm{T} \\ &= \frac{6\mathrm{B} - 2(n+2)\mathrm{A}}{n(n-1)}. \end{aligned}$$

In our case, where the rise in temperature was always small and regular, ten or twelve observations were considered sufficient to determine the constants, and in that case the labour of reduction is small.

After an experiment the change in temperature of the calorimeter had to be observed once more, and a value k' corresponding to k was again determined in a similar manner. From the two values k and k' the loss of heat of the calorimeter during the whole of the experiment could easily be calculated, for the rise in temperature during the actual heating was uniform. If the current passed during m intervals, each equal to T, and if $-k$ and $-k'$ denote the rates of cooling during the first and last periods, the loss of heat during the m intervals was $\tfrac{1}{2}m(k+k')$. A small correction was necessary owing to the fact that the observed values of k and k' did not correspond to the temperature of the calorimeter at the beginning and end of the second period.

We have now to examine shortly how far errors in the estimation of the cooling correction may arise. NEWTON'S law of cooling is known to be approximate only. If we had to deal simply with radiation, we should obtain greater accuracy by adopting the law of STEFAN, according to which radiation varies as the fourth power of the absolute temperature. We have calculated that the difference introduced by STEFAN'S law in the final value of the equivalent amounts to about one part in sixty thousand, and considering that the combined effect of radiation and conduction seems to follow NEWTON'S law more closely than the effect of radiation alone, we are justified in taking that law as correct. In order that the usual cooling correction should apply, it is not necessary that the different parts of the enclosure should all be at the same temperature, nor is it always necessary that the temperature of the surrounding bodies should be constant. If, as in our case, the calorimeter receives its heat at a constant rate, the temperature of the enclosure may vary as a linear function of the time during the same time without vitiating the experiment, for as long as we assume NEWTON's law, it does not matter whether the calorimeter rises uniformly or the enclosure falls uniformly or whether they both vary together. This is an important consideration, for unless we take very elaborate precautions, the enclosure must to a certain extent follow the temperature of the calorimeter. All that is requisite for a correct estimate of the cooling is that the rates should be accurately known at the beginning and ending of the second period. The change in temperature of our water jacket in the actual experiments was very small and sometimes inappreciable.

When the temperature of our calorimeter was raised 1° above that of the water jacket, the cooling amounted to about 0°·0025 per minute; the cooling surface was about 725 sq. centims.; the amount of water in the calorimeter, 1500 grams. Hence there was a loss of heat for each square centimetre of surface of 0·0052 unit per minute. In Mr. E. H. GRIFFITHS' determination, where the pressure of the surrounding space was reduced to about one-hundredth atmosphere, the corresponding number was between 0·0028 and 0·0026, taking 300 sq. centims. as the exposed surface. On the other hand, his total amount of water was always less than one-quarter of that used by us; so that the actual cooling in his experiments for one degree difference was about double ours. It is interesting also to compare our number with that corresponding to the loss from a cylindrical rod suspended horizontally in the air and quite unprotected. Mr. LEES ('Phil. Trans.,' Vol. 183, p. 490) finds for a nickel-plated rod of about 2 centims. diameter, 0·011 gramme-degree per square centimetre per minute, or about twice our number. In the latter case, the conditions of the experiment are most favourable for great loss of heat by convection; and Mr. GRIFFITHS' experiments show that by reduction of pressure to about one-third of a millimetre the loss is only reduced to about one-quarter of what it is in that case, and one-half of what it may easily be reduced to in a calorimetric experiment at atmospheric pressure. It ought to be possible by properly disposed diaphragms to reduce considerably the effects of convection currents at atmospheric pressure and so gain in a simple way the same advantage as is done by removing the air surrounding the calorimeter.

We may calculate approximately that part of the loss which is due to conduction irrespective of convection. Taking the thermal conductivity of air to be 0·000055, and the distance between the calorimeter and the enclosure as 3·8 centims., we find that thermal conductivity alone would account for a loss of roughly 0·001 gramme-degree, or about one-fifth only of the actual loss. As in Mr. GRIFFITHS' experiments the enclosure was at a greater distance from his calorimeter than ours, his observed loss by radiation and conduction is also about five times that due to conduction of air alone.

Evaporation will produce a certain amount of cooling of the calorimeter, if that is not perfectly enclosed; but unless the rate of evaporation changes with the temperature, the effect will only be a lowering of temperature by a constant quantity.

The rate of cooling can only be affected by evaporation in so far as it increases with the temperature, and since for small changes it would vary as a linear function of the temperature, any error due to evaporisation is eliminated by the cooling correction.

Some Corrections to the Water-equivalents.

1. *Correction for Surrounding Air.*—The usual method of finding the value of the correction depends on the assumption that the loss of heat is proportional to the excess of temperature, and as regards radiation this will hold whenever the variation is small. When however an appreciable quantity of heat is carried away by conduction, an error may be introduced by taking as the excess of temperature the difference observed between that inside the calorimeter and that of its jacket, for the temperature gradient in that case will not be uniform during the whole course of the experiment. Consider, for instance, a calorimeter placed on a more or less conducting material like wood or cork. If the calorimeter is suddenly heated, the temperature gradient at the surface will be large and will then slowly diminish. The cooling observed, as usual, after the lapse of a few minutes, will underrate the heat lost during the first few minutes. It is easy to see that when conduction comes into play, the amount of heat lost or gained will depend on the distribution of heat in the conducting body, and that will depend on the previous history of the calorimeter. Thus, when a calorimeter is kept heated until all the surrounding parts have reached a steady temperature, and observations are then made on the rate of cooling, we are not justified in applying the rate thus formed to the period in which heat is communicated to the calorimeter. An estimate may be made of the error introduced if the correction is applied in the usual way. We take the case of a calorimeter placed on a non-conducting slab of thickness c. At the beginning of the experiment everything is to be at temperature zero. At the time $t = 0$, the temperature (u) of the calorimeter is to be gradually and uniformly raised so that we may take $u = pt$. Finally, at a time T, the temperature is kept constant and equal to $p\mathrm{T}$. It is required to find the rate at which heat is given up by the calorimeter at any moment, and the total amount of heat which passed through its surface.

Taking the flow to be linear, the differential equation to be satisfied is

$$\partial u/\partial t = a^2\, \partial^2 u/\partial x^2.$$

Here $a^2 = \kappa/s$, where κ represents the conductivity and s the heat capacity per unit volume. We introduce the conditions

$u = 0$ if $t = 0$ for all values of x.
$u = \phi(t)$ for $x = 0$.
$u = 0$ for $x = c$ for all values of t.

Also $\phi(t) = pt$ between $t = 0$ and $t = \mathrm{T}$, and $\phi(t) = p\mathrm{T}$ if $t > \mathrm{T}$.

The solution of the differential equation can be put into the form

$$u = \phi(t)\left\{\frac{c - x}{c} - \frac{2}{\pi}\sum_{n=1}^{n=\infty}\frac{1}{n}\sin\frac{n\pi}{c}x\right\} + \frac{2\beta^2}{\pi}\sum_{n=1}^{n=\infty} n\sin\frac{n\pi}{c}x\int_0^t e^{-n^2\beta^2(t-\lambda)}\phi(\lambda)\,d\lambda,$$

where β is written for $a\pi/c$.

The first term is often omitted as it vanishes for all finite values of x. But as we shall have to consider the value of $\partial u/\partial x$ for $x = 0$, it is retained here. To perform the integration we must distinguish two cases, according as t is smaller or greater than T. Taking $\phi(\lambda) = p\lambda$, and performing the integration with respect to λ, we find

$$u = pt\,\frac{c - x}{c} - \frac{2p}{\pi\beta^2}\sum_{n=1}^{\infty}\frac{1}{n^3}\left(1 - e^{-n^2\beta^2 t}\right)\sin\frac{n\pi x}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for $t < \mathrm{T}$.

For larger values of t we have to divide the integral into two parts as the value of $\phi(\lambda)$ has a discontinuity for $t = \mathrm{T}$.

The final equation for u then becomes

$$u = p\mathrm{T}\,\frac{c - x}{c} - \frac{2p}{\pi\beta^2}\sum_{n=1}^{\infty}\frac{1}{n^3}e^{-n^2\beta^2 t}\left(e^{n^2\beta^2\mathrm{T}} - 1\right)\sin\frac{n\pi x}{c}\cdot$$

Writing $(\partial u/\partial x)_0$ for the value of $\partial u/\partial x$ at the plane $x = 0$, the quantity of heat passing out of the calorimeter up to the time T will depend on

$$-\int_0^{\mathrm{T}}\left(\frac{\partial u}{\partial x}\right)_0 dt = \frac{1}{c}\int_0^{\mathrm{T}}\left\{p\mathrm{T} + 2p\sum_{n=1}^{n=\infty}\frac{1}{n^2\beta^2}\left(1 - e^{-n^2\beta^2 t}\right)\right\}dt$$

$$= \frac{p\mathrm{T}^2}{2c} + \frac{pc\mathrm{T}}{3a^2} - \frac{pc^3}{45a^4} + \frac{2pc^3}{\pi^4 a^4}\sum_{n=1}^{n=\infty}\frac{1}{n^4}e^{-n^2\beta^2\mathrm{T}}.$$

We also obtain if $t > \mathrm{T}$

$$-\int_0^t\left(\frac{\partial u}{\partial x}\right)_0 dt = \frac{p\mathrm{T}}{2c}(2t - \mathrm{T}) + \frac{pc\mathrm{T}}{3a^2} + \frac{2pc^3}{\pi^4 a^4}\sum_{n=1}^{\infty}\frac{1}{n^4}e^{-n^2\beta^2 t}\left(1 - e^{n^2\beta^2\mathrm{T}}\right).$$

The application of these formulæ is easy when $\beta^2 t$ is so large that $e^{-\beta^2(t-\mathrm{T})}$ may be neglected. The heat H which has passed through unit surface of the calorimeter up to the time t is obtained by multiplying the right-hand side of the last equation by $k = a^2 s$.

Neglecting the last term this becomes

$$\mathrm{H} = \frac{pk\mathrm{T}}{2c}(2t - \mathrm{T}) + \frac{pcs\mathrm{T}}{3}$$

and the rate at which heat is given up at the time t is

$$dH/dt = pkT/c.$$

If the cooling correction is applied in the usual way, the rate at which heat is lost would, during the period of heating, be taken as half that corresponding to the final period, or in other words we should take loss of heat as $\frac{pkT}{2c}T$ during the period of heating, and as $\frac{pkT}{c}(t - T)$ from the time that the temperature of the calorimeter has become steady. It is seen that in this way of calculating, the term $\frac{1}{3}(pcst)$ is neglected. This term represents the amount of heat which is necessary to raise a thickness $\frac{1}{3}$ of the material through which the heat is conducted to the final temperature of the calorimeter.

We see from this investigation that a certain amount of the air surrounding the calorimeter should be added to the water-equivalent. For air a^2 is about 0·26, and in our experiments the walls of the enclosure were 3·8 centims. from the calorimeter. We may, without sensible error, neglect the error due to the curvature of the sides of the calorimeter and substitute 3·8 for c. The value of β^2 then becomes $0{\cdot}26\pi^2/(3{\cdot}8)^2 = 0{\cdot}18$.

As several minutes always intervened between the time at which the temperature of the calorimeter had become constant and the observations for the cooling correction, $\beta^2(t - T)$ was always greater than 10 and $e^{-\beta^2(t-T)}$ was therefore quite negligible. We may in this case then simply calculate the water-equivalent of a quantity of air surrounding the calorimeter, and having a thickness of $c/3$ or 1·3 centims. The total effective surface of the calorimeter being 724 sq. centims., the quantity to be added to the water-equivalent becomes 0·28.

2. *Correction for Thermometer.*—In taking the water-equivalent of the thermometer, it is usual to consider only that part which is plunged into the water, but this requires justification, as it is clear that those parts of the thermometer which are close to, but not actually in contact with the water, must be heated also. The following calculation will give an estimate of the error which may be thus introduced. We may assume, in the first instance, that the thermometer which is surrounded by air rising from the calorimeter will not give up any appreciable heat to the outside, so that we may apply the same differential equation for the flow of heat as that used in the former problem. We may treat the thermometer as a glass rod of indefinite extent, having the temperature of its surface in contact with the water raised at a uniform rate pt until $t = T$ when it is kept constant at the temperature pT.

The solution of the equation applied to this case gives us :—

$$-\left(\frac{\partial u}{\partial x}\right)_0 = \frac{2p}{a\sqrt{\pi}}\sqrt{t} \text{ for } t < \mathrm{T}$$

$$-\left(\frac{\partial u}{\partial x}\right)_0 = \frac{2p}{a\sqrt{\pi}}(\sqrt{t} - \sqrt{t - \mathrm{T}}) \text{ for } t > \mathrm{T}$$

$$-\int_0^{\mathrm{T}}\left(\frac{\partial u}{\partial x}\right)_0 dt = \tfrac{4}{3}\frac{p\mathrm{T}^{3/2}}{a\sqrt{\pi}}$$

$$-\int_0^{t}\left(\frac{\partial u}{\partial x}\right)_0 dt = \tfrac{4}{3}\frac{p}{a\sqrt{\pi}}(\sqrt{t^3} - \sqrt{(t - \mathrm{T})^3}).$$

In our experiments the average time t during which the rate of cooling was observed was with sufficient accuracy equal to 2T, reckoned from the moment the heating began. In that case, the above formulæ show that the total amount of heat which has passed into the thermometer, denoting by A the area of its cross-section, is

$$\frac{4\kappa \mathrm{A}p\mathrm{T}^{3/2}}{3a\sqrt{\pi}}[2\sqrt{2} - 1];$$

while the heat lost to the calorimeter, calculated by means of the cooling during the last period, is

$$\frac{3\kappa \mathrm{A}p\mathrm{T}^{3/2}}{a\sqrt{\pi}}[\sqrt{2} - 1].$$

The quantity to be added to the water-equivalent is obtained by dividing the difference of these values by pT, and becomes therefore

$$\frac{\kappa \mathrm{A}}{3a}\sqrt{\frac{\mathrm{T}}{\pi}}(5 - \sqrt{2}) = 1{\cdot}2\,\frac{\kappa \mathrm{A}}{a}\sqrt{\frac{\mathrm{T}}{\pi}}\,.$$

Substituting for a in terms of the conductivity κ, the capacity for heat of unit volume of glass s, this becomes $1{\cdot}2\ \mathrm{A}\sqrt{(\kappa s\mathrm{T}/\pi)}$.

Putting in the numerical values corresponding to our experiments $\kappa = 0{\cdot}0021$, $\mathrm{T} = 540$, $s = {\cdot}5$, $\mathrm{A} = {\cdot}21$, the correction is found to be 0·12.

3. *Correction for Leads.*—On the other hand, the water-equivalent of the coil was slightly over-estimated as the wires serving as leads were reckoned in, although part of them protruded out of the water. The length which was outside the water was 2·8 centims., but about 8 millims. of this was in close contact with stout copper rods, the temperature of which would not rise appreciably during the experiment. From the previous investigation, which is applicable to this case, it would appear that one-third or 0·7 centim. of the part surrounded by non-conductors should have been taken into the water-equivalent instead of the whole. The error committed in the heat capacity of 2·1 centims. of copper wire, weighing ·22 grams. per centim., that is ·08,

should be subtracted from our water-equivalents, as there were two such wires. The heat produced by the current in the leads (No. 14, I.W.G.) would, if entirely used to raise the temperature of the leads, produce a rise of 0°·2 in the time of the experiment. If the whole of this heat is imagined to enter the calorimeter it would produce a difference of 1 part in 150,000 in the total rise. No error can therefore arise through the heating of the leads.

4. *Correction for the parts of the Calorimeter not in contact with Water.*—The water in our calorimeter reached to about 1·5 centims. from the top of the vessel, but a rough estimate of the error introduced will show that we were justified in taking the whole of the calorimeter into the water-equivalent. The cooling which took place when the temperature of the calorimeter was at 1° above that of the surroundings amounted to 3·5 gramme-degree units per minute. If we assume that the heat lost was the same at every part of the calorimeter, we find that the loss due to radiation and convection of the part of the outside surface above the level of the water amounted nearly to one quarter-unit. The loss of heat towards the inside of the part not filled with water must have been small, but in order to over-estimate the loss we may assume that the part of the calorimeter which was above the water lost 0·5 heat unit per minute for a difference in temperature of 1°. This will allow us to calculate the temperature gradient along the copper close to the water surface. If κ is the conductivity of the copper, A the area of the section of the calorimeter, t the time,

$$\kappa t \mathrm{A}\, du/dx = \cdot 5,$$

and since κ is nearly unity and $\mathrm{A} = \cdot 83$, du/dx is found to be nearly ·01. The calculated temperature gradient of $\frac{1}{100}$ of a degree per centim. must have exceeded considerably the actual one, and must diminish with the distance from the water surface, but assuming it to be uniform all over the upper part of the calorimeter, the average temperature of the copper would be 0°·007 below the temperature of the water. The heat capacity of that part of the calorimeter is approximately unity, and therefore the error in the water-equivalent, considerably over-estimated, is ·007, a negligible quantity.

5. *Correction for Cork Supports.*—It only remains to discuss whether the cork supports on which the calorimeter stood added in any appreciable way to the water-equivalents. It is not possible here to estimate the effect by calculation, as the contact between the calorimeter and the cork is irregularly distributed over the cork.

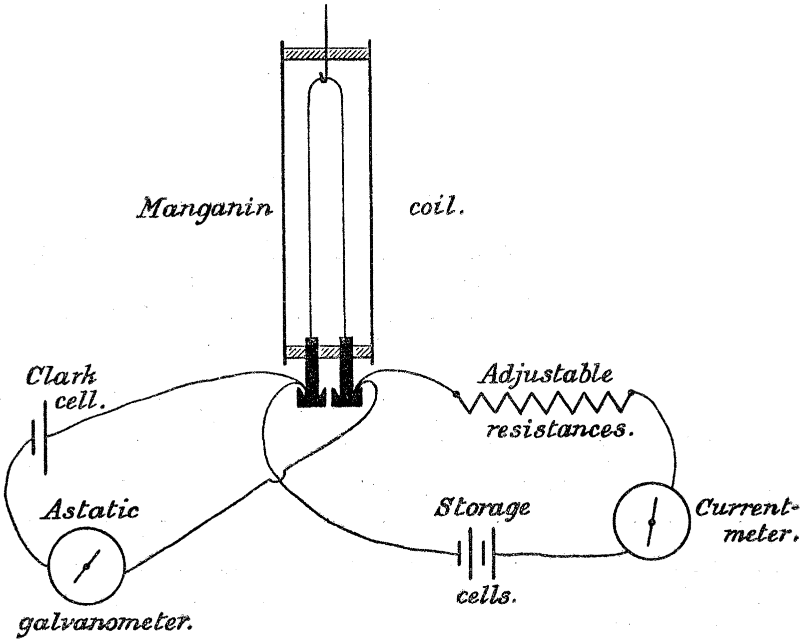
We therefore made a few experiments in which the change in temperature of the cork was directly measured by means of thermo-junctions, the calorimeter being treated exactly as during an experiment on the heat-equivalent. We found in this way that the heat which entered the three corks during the whole duration of the experiment is only ·08 unit as against 3300 units which have entered the water in the calorimeter, and as the greater part of this heat is allowed for in the cooling correction, no addition need be made to the water-equivalents on this account.

The sum of the various small corrections to the water-equivalent amounts to 0·33, or about 2 parts in 10,000 of the whole water-equivalent.

The Auxiliary Current.

In the first two series of our experiments, the thermometer was generally rising during the first, but falling during the last period. It is known that a falling thermometer will somewhat lag behind the real temperature, but we had hoped to eliminate this by applying a constant correction. Special experiments made for the purpose did not, however, give us sufficiently consistent results, and it appeared that the lag was too variable to be allowed for. Hence we decided to work only with a rising thermometer. We might have achieved this by raising sufficiently the temperature of the surrounding water-jacket, but this would have made the gain by radiation and conduction in the first period greater than we thought could be correctly measured. The plan we adopted consisted in sending through our coil, in the final period, a weak current (about 0·1 ampère) which just overbalanced the cooling. The current—which we call the auxiliary current—could be measured with sufficient accuracy to calculate the rate of heating which was due to it alone, and as the rise in temperature was observed, the loss by radiation could be deduced.

Fig. 6.



The auxiliary current was derived from two storage cells and was measured by one of Lord Kelvin's magnetostatic centiamperemeter balances placed in circuit with the coil and cells. In order to avoid any error that might arise from a possible change in the constant of the instrument due to a change in the value of the earth's magnetism, we took the precaution of calibrating the instrument immediately after each equivalent experiment. This was done as follows:—

The current from two storage cells passed in succession through the current meter, a coil of manganin wire and a set of adjustable resistances (see fig. 6). The terminals of the manganin coil were connected up through the astatic galvanometer with our Standard Clark cell, so as to oppose the E.M.F. at the terminals of the manganin coil due to the passage of the current from the storage cells to the E.M.F. of the Clark cell. If the galvanometer shows no deflection on both circuits being closed, then $e = ir$, where $e =$ E.M.F. of the Clark, $i =$ current in the current meter, $r =$ the resistance of the manganin coil.

A coil of manganin wire was chosen, since this material has a very small temperature coefficient; it was supplied by Messrs. ELLIOTT, having a composition of copper 84 per cent., manganese 12 per cent., nickel 4 per cent.; its resistance value was nearly 14 true ohms. An example will explain the calculation of the value of the current. On May 20 the current meter read 48·34 divisions (a short focus lens enabled us to read the divisions to hundredths). Temperature of the Clark cell 17°·12 C. Hence the current is equal to 1·4327/14 = 0·10234 ampère; and therefore 1 division = 0·00212 ampère. The instrument remained very constant throughout the equivalent experiments, as may be seen from the following table:—

TABLE IX.

Date.	Value in ampères of 1 division.
May 10	0·00213
" 13	0·00212
" 17	0·00212
" 20	0·00212
June 5	0·00212
" 9	0·00212
" 15	0·00212

As a check upon this method of calibrating the current meter, it was also calibrated on one occasion by measuring the current passing through it by the silver voltameter. Its constant as thus determined was 0·00212. The sensibility of the current meter was such that its readings were accurate to 1 in 400. Hence the cooling correction to be applied is accurate to 1 in 200, and from the data already given it appears that an error of that amount only affects the accuracy of the equivalent to 1 in 200,000. Knowing the value of the auxiliary current, the rise in temperature (θ) per minute of the total mass of water is calculated from the formula $\theta = (C^2R \times 60)/(J \times M)$, R being the resistance of the heating coil. The mean of several determinations of R with an Elliott P.O. box—which had been sent to Messrs. ELLIOTT for careful examination—gave a value of 31·32 B.A. units at the mean temperature of the equivalent experiments, or 30·90 true ohms, if 1 B.A. unit = ·9866 true ohm. It is clear that an approximate value of J will be sufficient in this part of the calculations. Any error in the value of J will affect the cooling correction to half its value, and as that correction amounts to 1 per cent. of the equivalent, an error of 1 per cent. in the assumed value of J would involve an error of 1 part in 20,000 of the final value. The reductions had naturally to be made before we knew what our own value of J was going to be, so we applied provisionally Mr. GRIFFITHS' value of $4·194 \times 10^7$, and although our own value is slightly lower it would have made no appreciable difference if our value had been taken instead.

The Temporary Coil.

The only part of the arrangement which has not so far been described is a coil of platinoid equal in resistance to the one in the calorimeter, in series with a resistance approximately equal to that of the silver voltameter.

This coil and resistance served for a preliminary adjustment of the circuit. It was necessary, in order to secure sufficient accuracy, that a balance of electromotive force should be obtained soon after the beginning of each experiment, and this could be done by means of this coil, which, for distinction, we shall call the temporary coil. The keys which serve to change currents were all made of paraffin blocks, and of very simple construction. The blocks had six holes filled with mercury, and copper connectors completed the circuit. The two ways in which connection could be made may be seen in the key marked k_2 (fig. 5), where the holes are numbered. In the position of the key which we shall call a, the cups 1 and 3 were connected, as well as 2 and 4; while, in the position b, 1 was connected to 5 and 2 to 6. The keys k_3 and k_4 were exactly similar, and we shall speak of the positions a and b of the keys when the corresponding connections were made. Thus, $k_3(a)$, $k_4(b)$ means that the key k_3 was in position a, and key k_4 in position b. The key k_5 served to short-circuit the silver voltameter in the final period; a copper connector could be placed for this purpose either at a or b.

Method of Maintaining a Constant Difference of Potential at the Terminals of the Heating Coil.

The difference of potential at the terminals of the heating coil was kept constant by balancing it against the battery of twenty Clark cells in the well-known way. The success of this method, when the potential difference had to be kept constant for some minutes, depends on the ability of the operator in altering the total resistance of the circuit through which the current is passing by small variable amounts. The current —which, in our experiments on the heat-equivalent, was about 0·9 ampère—tends to diminish in value, owing to (1) change in the values of the different resistances in circuit, due to change of temperature produced by the passage of the current; (2) change of the resistance of the silver voltameter; (3) running down of the electromotive force of the storage cells. In order to counteract the effects of these changes, a number of separate resistances, W_1, W_2, W_3, and two switches, s_1 and s_2 (fig. 5), were placed in series with the remainder of the circuit. W_1 consisted of coils of platinoid wire; W_2 and W_3 were platinoid wires of different resistance-values, any number of which could be connected in series by means of mercury cups and copper bridges. The resistances W_1, W_2, W_3 enabled the current to be adjusted to the proper value when running through the temporary circuit; W_2 or W_3 enabled us to make any necessary change at the moment of sending the current through the heating coil. The switches s_1 and s_2 were used to keep the spot of light in the zero position during the nine or ten minutes the current was passing through the heating coil. They consisted of a stone base, on which were arranged eleven brass studs (shown in figure) along a semicircle, having binding screws (not shown) attached to their ends. Over these studs slides a movable contact piece attached to an insulating handle. The movable arm consists of a number of thin brass plates, jointed together only at the centre, and so fitting that they form independent springs which press edgewise on the brass studs, thus ensuring good uniform contact. The resistances to be inserted are placed in the binding screws attached to the studs (soldered to ensure better contact). One switch had platinoid wires of 0·008 ohm, and the other platinoid wires of 0·006 ohm. These switches gave a much greater range than was found necessary in any experiment. When the spot of light was observed to move from the zero position, a movement of the arms of these switches brought it back. The spot of light was never as much as five small divisions from its position of rest, but even a deviation of ten divisions during the whole time of the experiment would have produced no appreciable difference in the value of the equivalent.

The current was only switched on to the principal circuit when it was found to be running with fair steadiness through the temporary circuit. After some little trouble, caused by leakage, we were able to keep the current constant without any considerable change in the value of the total resistance of the circuit.

The electromotive force that is thus measured is the difference of potential at the terminals of the heated coil, provided there is no leakage in the wires connecting these terminals to the galvanometer. The insulation of these wires was found to be 7×10^8 ohms, so that the electromotive force at the galvanometer is practically equal to the electromotive force at the terminals of the coil.

Method of carrying out an Experiment.

Two observers were required to carry out an experiment; one (A) kept the electromotive force at the ends of the coil constant and compared the Clark cells; the other (B) took all the temperature observations.

A weighed and measured quantity of water having been placed in the calorimeter, the platinum dish (after being weighed several times) was filled with 120 cub. centims. of the silver nitrate solution. The water in the jacket of the calorimeter was raised about 1° C. above the temperature of the water in the calorimeter, so as to secure a convenient rise before the heating of the coil commenced. The observations are conveniently divided into three periods. The reference to the connections will be understood with the help of fig. 5.

Preliminary Period.

A_1 being the main battery, the key Q was open at first, and the connections in the other keys were as follows: k_2 (a), k_3 (a), k_4 (a). The observer (A) compared the Clark cells with the help of the key k_1, and at the conclusion of the comparisons—which took about 8 minutes—the temporary bridges of k_1 were removed. (A) then closed the main circuit at Q, and the connections were such that the current was flowing through the temporary coil and could be adjusted till a balance was obtained against the 20 Clarks C.B. The observer (B) in the meantime observed every minute the thermometer which was plunged into the calorimeter. The rise was roughly about 0°·002 per minute, and so regular that more frequent observations would have been of no value. (B) also observed the auxiliary thermometers.

Everything being ready, a signal was given 10 seconds before the current was to be sent through the principal coil. (B) now broke connections at k_2 and joined k_5 (a).

Main Period.

(B) changed the connection k_4 (a) to k_4 (b), and the main current thus passed through the coil in the calorimeter. A signal being given that this was done, (A) makes connections k_2 (b), and thereby opposed the Clark battery to the electromotive force at the terminals of the principal coil. If the preliminary adjustment was perfect (as it was on two occasions), the spot of light remained at rest; but generally it moved slightly to one side, and then a slight readjustment of the resistances brought it back to its position of rest. (A) called out when he had obtained a satisfactory balance, and this was generally three seconds after the main current was complete. As the experiment lasted nine or ten minutes, and as the electromotive force was never as much as two in a thousand out during the first three seconds, no error in the final result can be introduced in this short period. During the heating of the coil (B) did not take any temperature observations except when half the proposed time of heating had elapsed. The object of this observation is to be able to point the telescope very near the division of the thermometer which the mercury thread would reach at the conclusion of the experiment.

Final Period.

Ten seconds before the main current was interrupted, the connection at k_2 was broken, the balance being always so steady that it could be trusted to be maintained during that interval. (B) now broke k_3 (a), and three seconds after connected k_3 (b).

(A) in the meantime had changed k_5 from a to b, k_4 being still at b. The circuit is now seen to be such that the small battery A_2 sends a current through the magnetostatic meter M and the calorimeter coil. In this final period (B) observed the thermometer and the magnetostatic meter, and also made observations on the auxiliary thermometers placed near the stem of the Baudin, in order to introduce the stem correction. (A) once more compared the Clarks.

The Results.

We divide our experiments into three series, but only attach any value to the third, as during the first two sets the thermometer was falling in the last period. We had hoped, at first, to be able to apply a small correction, to eliminate the error which is due to the fact that a falling thermometer will read too high, and we made a large number of experiments to determine the correction. We arrived, however, at the result that the indications of a falling thermometer are so irregular that no correction is possible. Consequently in our third series the thermometer was rising during the whole course of each experiment.

We think it worth while to put on record an impression that the behaviour of our Baudin thermometer has altered since we received it from the maker. As soon as it came some preliminary experiments were made, to see if we could work with the thermometer while it was falling, and the observations seemed to show that the fall was sufficiently uniform. Our first three experiments gave results which were very consistent, and a minute after the current was broken the temperature seemed to fall already in a perfectly regular manner. But as we continued our work, the behaviour of the instrument seemed to deteriorate. Thus in our experiment of March 8th the thermometer had hardly fallen three minutes after the current had stopped. It is possible that this was due to accidental circumstances, for it is well known that different places in the bore of a capillary tube behave very differently. We wish therefore to express no opinion at present as to the probability of an actual change in the behaviour of the thermometer, but only to draw the attention of other experimenters to this point which seems worth keeping in mind.

The results of the first three experiments which constitute the first series are consistent, but no value is attached to the equivalent as deduced from them, owing to the uncertainty of the water equivalent. The coil, as has been mentioned, was then wound on an ivory frame. When Mr. HADLEY, who then assisted in the work, began to experiment on the specific heat of ivory, he met with serious difficulties. The ivory contained water to begin with, as was shown by the diminution in the weight of fresh ivory when heated up; it absorbed again when placed in water; the results were consequently not to be trusted. Even when coated with shellac, the substance did not behave in a consistent manner. There were other imperfections in our calorimeter at that time which make it impossible for us to know the water equivalent with sufficient accuracy.

In the second series of experiments, the coil was wound on porcelain strips, and we were quite satisfied that the water equivalent was known with sufficient accuracy. Nevertheless the agreement of the results in this series is not satisfactory.

In experiments 4 and 6 the thermometer was falling both in the first and last period, and the cooling correction was consequently somewhat large; on the other hand the lag of the falling thermometer would affect both the first and last period, and, therefore, be partly eliminated in the result.

Experiment 5 is rendered a little uncertain by the fact that the thermometer at the beginning of the first period fell slightly, and then remained perfectly stationary; it is therefore probable that the temperature was really increasing at the beginning of the experiment. The cooling correction, calculated on the assumption of no rise, would be too large, hence the calculated equivalent too small. The result of March 8th is anomalous, and does not seem altogether accounted for by the sticking of the thermometer at the end. There was on that day an exceptionally large difference in the amount of water, as measured by weight and by volume. We took, as usual, the mass as determined by weight; had we taken the latter, the calculated equivalent would have been 4181. A final revision of our calibration correction showed a small error, which may have affected some of the results in series I. and II., by about one part in two thousand. As we do not attach any value to the numbers obtained, we have not recalculated the numbers.

The results of our third series are as consistent as could be hoped for. We thought it useless to multiply the experiments, as it did not seem to us that our results could be materially improved by repetition. Their good agreement shows that our results are correct to more than one part in a thousand, provided that we have avoided systematic errors. The difference between our results and that of Mr. GRIFFITHS must be due, on the one side or other, to errors which a multiplication of experiments could not eliminate.

We give the results of our experiments in the form of Tables.

Column I. gives the number of the experiment.

Column II. gives the date.

Columns III. and IV. state whether in the first and last period respectively the thermometer was falling or rising.

Column V. gives the value of the equivalent calculated, the temperature scale being that of a mercury thermometer made of French hard glass.

Columns VI. and VII. give the same equivalent, reduced to the nitrogen and hydrogen scale of the Bureau International des Poids et Mesures.

Column VIII. gives the temperature range of the experiment.

TABLE X.

Series I.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	1892. April 2	Rising	Falling	4·164 × 10^7	4·175 × 10^7	4·177 × 10^7	15°·2—17°·2
2	,, 5	,,	,,	4·168	4·178	4·180	16·8—18·8
3	June 9	,,	,,	4·169	4·177	4·178	19·9—21·9
			Mean . . .	4·167	4·177	4·179	17·3—19·3

TABLE XI.

Series II.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
4	1892. July 5	Falling	Falling	4·188 × 10^7	4·197 × 10^7	4·198 × 10^7	18·2—20·1
5	,, 12	?	,,	4·177	4·187	4·189	16·4—18·4
6	1893. Feb. 11	Falling	,,	4·192	4·203	4·205	15·4—17·6
7	,, 22	Rising	,,	4·185	4·196	4·198	14·9—17·1
8	Mar. 1	,,	,,	4·186	4·198	4·200	14·3—16·5
9	,, 8	,,	,,	4·169	4·179	4·181	16·4—18·6
			Mean . . .	4·183	4·193	4·195	15·9—18·1

TABLE XII.

Series III.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
10	1893. May 13	Rising	Rising	4·1824 × 10^7	4·1927 × 10^7	4·1940 × 10^7	17°·4—19°·6
11	,, 17	,,	,,	4·1807	4·1910	4·1923	17·2—19·4
12	,, 20	,,	,,	4·1807	4·1910	4·1923	17·3—19·7
13	June 5	,,	,,	4·1804	4·1902	4·1916	17·9—20·1
14	,, 9	,,	,,	4·1776	4·1872	4·1884	18·2—20·4
15	,, 15	,,	,,	4·1822	4·1908	4·1919	20·2—22·4
		Mean of first four		4·1810	4·1912	4·1934	17·4—19·7
		,, last two		4·1799	4·1890	4·1901	19·2—21·4
		,, Series III. . . .		4·1804	4·1905	4·1917	18·0—20·3

Our final value is

$$J = 10^7 \times \begin{cases} 4{\cdot}1804 \text{ on the mercury scale of hard French glass,} \\ 4{\cdot}1905 \text{ on the nitrogen scale,} \\ 4{\cdot}1917 \text{ on the hydrogen scale,} \end{cases}$$

at a temperature of 19°·1.

This result depends on the assumption that the electrochemical equivalent of silver is 0·001118, and that our standard Clark cell had an electromotive force of

$$1{\cdot}4340\ (1 - \alpha\,\overline{t - 15}) \text{ volts,}$$

where $\alpha = {\cdot}000814 + {\cdot}000007\ (t - 15)$ as given by KAHLE ('Zeitschrift für Instrumentenkunde,' vol. 13, p. 310, 1893). GLAZEBROOK and SKINNER's coefficient refers to a mean temperature of 7°·5, and is identical with the above at that temperature.

Discussion of Results.

The comparison of the results of different observers will be facilitated by Table XIII., in which we compare ergs with the foot-pound at Greenwich and the kilogram-metre at Paris.

TABLE XIII.

Ergs × 10^{-7}.	Foot-pounds at Greenwich.	Kilogram-metres at Paris.
4·160	772·83	424·07
4·165	773·76	424·58
4·170	774·68	425·09
4·175	775·61	425·60
4·180	776·54	426·11
4·185	777·47	426·62
4·190	778·40	427·13
4·195	779·33	427·64
4·200	780·25	428·15
4·205	781·19	428·66
4·210	782·12	429·17

This table has been calculated on the assumption that g at Paris is equal to 980·96, and at Greenwich equal to 981·24.

We have prepared another table (XIV.) which will give at any temperature the correction of an interval measured on our mercury thermometer to an interval measured on the nitrogen and hydrogen thermometers. This table has been calculated with the help of the equation given by CHAPPUIS for the correction to the thermometer made of French hard glass.

TABLE XIV.

	10°.	12°.	14°.	16°.	18°.	20°.	22°.	24°.
Correction to nitrogen thermometer. . . .	–0°·00369	·00337	·00305	·00275	·00247	·00220	·00194	·00170
Correction to hydrogen thermometer. . . .	–0°·00418	·00381	·00346	·00313	·00280	·00249	·00219	·00190

In comparing our results with those of other observers, we have in the first place to consider the value which Mr. GRIFFITHS has obtained in his very excellent series of measurements. His final result ('Proc. Roy. Soc.,' vol. 55, p. 26; Phil. Trans., vol. 184, 1893, A., p. 361), is

$$J = 4{\cdot}1982\,(1 - {\cdot}000266\,\overline{\theta - 15}) \times 10^7.$$

This refers to the nitrogen thermometer. At a temperature of 19°·1 the value would be reduced to 4·1936, which corresponds to our 4·1905 at the same temperature. GRIFFITHS' value is to be increased slightly owing to the fact that he really measures the difference between the specific heat of water and of air. This would increase the value of J by ·0011 about, so that the value of J at 19°·1 would be raised to 4·1947 × 10^7, which is exactly one part in a thousand larger than ours. The difference is small, but must be due to some systematic error, as both GRIFFITHS' value and our own agree so well with each other, that ordinary observational errors and accidental disturbance could not have produced so large a difference in our result. The least satisfactory part of a calorimetric measurement must always be the cooling correction, and we have considered it of great importance to reduce that correction as much as possible. The uncertainty of the cooling correction does not necessarily depend on its value; thus, we can much diminish it by starting, as we have done in our last series, with the initial temperature of the calorimeter about as much below that of the water-jacket as the final temperature is above it. Yet the *uncertainty* of the correction does not seem to us to be diminished by that process. We may reasonably estimate the uncertainty due to the cooling correction by calculating what the error in the observed rate of cooling, either at the beginning or end of the experiment, must have been in order to produce a difference of one part in a thousand in the final result. We find in our own experiments that the error must have amounted to more than 15 per cent. We consider it unlikely that so large an error occurred always in the same direction. Apart from the cooling correction, however, it is difficult to see how a difference of one-tenth per cent. is produced unless by accumulation of a number of small errors.

The weak point of Mr. GRIFFITHS' determination is the small quantity of water he uses, his result depending on the introduction of about 120 grams. into his calorimeter. The highest water equivalent with which he worked was about 350 grams., of which 85 are due to the calorimeter itself. The chief objection to the use of such small quantities lies in the great cooling correction. In the experiment quoted by him on p. 482, the loss of heat due to radiation and conduction at the end of his experiment amounts to about 9 per cent. of his heat supply. If such loss has been wrongly estimated to 1 per cent., an error of $\frac{1}{10}$ per cent. would result in the final value. The consistency of Mr. GRIFFITHS' results shows that if an error occurred due to that cause, it must have been systematic, and we may point out how, with such large cooling correction, serious errors may arise. In applying the cooling correction it is always assumed that the loss of heat depends *only* on the difference of temperature between the calorimeter and enclosure; but, as has been already pointed out, this is not the case as regards conduction. Mr. GRIFFITHS' calorimeter was suspended by three stout glass tubes, through one of which the stirrer was passing. The exhaustion in the space surrounding the calorimeter was never sufficient to do away with the conduction of air, so that we may take the larger part of the cooling to be due to conduction and convection. The loss of heat in that case must to some extent depend not only on the temperature, but on the *rate of change* of temperature. Whether the part which depends on the rate of change is sufficient to produce a sensible difference in the result, it is not easy to say, but the error produced would with different currents and quantities of water be the same in all cases, and could not, therefore, be detected by the inconsistencies thereby introduced into the results.

The difference between our value of the equivalent and that of Mr. GRIFFITHS is, however, of smaller importance than the difference which exists between them and the equivalent, as determined directly by JOULE, ROWLAND, and MICULESCU. JOULE'S latest value, which is the only one which needs consideration, is 772·65 foot-pounds at 61°·7 Fahrenheit. The number refers to the degree as measured by JOULE'S mercury thermometer. ROWLAND adds to this a correction to the air thermometer of about 3, and another small correction for a change in the heat capacity of the apparatus, which brings the value up to about 776. The correction to the air thermometer has been obtained by means of a comparison made by JOULE himself with one of ROWLAND'S thermometers. JOULE'S original thermometers have been temporarily placed by Mr. B. A. JOULE in the hands of Professor SCHUSTER, in order that an accurate comparison may be instituted between them and modern thermometers. A full description of the comparisons made will be given on another occasion. The result arrived at shows that the correction is less than that assumed by ROWLAND, and would bring his value up to only 775 at the temperature indicated.

GRIFFITHS compares his result with that deduced by ROWLAND from JOULE'S observations. ROWLAND combined the different values obtained by JOULE in his various investigations, attaching weights according to his judgment as to their relative merits. Griffiths finds in this way that the difference between himself and Joule amounts to one part in 350, but, if equal weights are attached to all Joule's results, the difference is reduced to one part in 4281. Little value can be attached, however, to a combination of Joule's results which gives equal weights to that obtained in 1847 and that deduced from his latest and most careful work. There is, moreover, in Rowland's table a misprint or error in the reduction of Joule's 1847 result from foot-pounds to kilogram-metres, which lowers the value as given by Griffiths from 779·2 to about 778. It does not seem to us advisable to go beyond Joule's 1878 results, and the value assigned by him in this latest research should be taken as giving his final judgment on the matter. Reducing to the nitrogen thermometer of the Bureau International, Joule's result is 775 foot-pounds at Greenwich, at a temperature of 16°·5 C. At the same temperature Griffiths' number is 779·8.

Great weight must be attached to Rowland's determination, which, at the temperature to which Joule's number applies, is 777·6, and at 19°·1, 776·1, corresponding to our 778·5. Rowland's value is, therefore, just halfway between our own and Joule's result. But it must be taken into consideration that if the comparison between Rowland's and Joule's thermometers, as made by the latter, is to be trusted, Rowland's value referred to the "Paris" nitrogen thermometer would be slightly reduced. At any rate, it seems probable that if his value is in error, it is rather in the direction of being too high. We have, therefore, a difference of at least three parts in a thousand to account for between our result and that of Rowland, and of nearly four parts in a thousand between Griffiths' and Rowland's at a temperature of 19°·1. These results are summarised into the following table :—

Table XV.—Equivalent in foot-pounds at Greenwich, at 19°·1, referred to "Paris" nitrogen thermometer.

Joule.	Rowland.	Griffiths.	Schuster and Gannon.
774	776·1	779·1	778·5

We now turn to an investigation by Miculescu ('Annales de Chimie et de Physique,' vol. 27, 1892) in which the mechanical equivalent of heat is measured directly by what seems an excellently devised series of experiments. His result is $4·1857 \times 10^7$. He does not state the exact temperature to which this applies, but all his experiments seem to have been made between 10° and 13°, so that we may assume 11°·5 to be the mean temperature of his experiments. Rowland's value at that temperature is $4·199 \times 10^7$. We must draw attention to one point in Miculescu's work, which requires clearing up before we can give to it any decisive value. Everything in the experiments depended on the measurement of a couple, the arm of the couple being the distance between two knife-edges, one of which had to support a weight of more than 43 kilos. The distance between the knife-edges is said to have been 28 centims. in all experiments. Very insufficient information is however given how that distance was measured, and it would almost seem as if the author had trusted to the maker in adjusting the central knife-edge to the zero point of its scale. If the apparatus is still in existence it might be well to make sure that no error has been introduced through a wrong estimate of the length of the lever arm.

In order to compare MICULESCU'S value with that of others we must apply a temperature correction which is somewhat doubtful, but taking the mean of ROWLAND'S and GRIFFITHS' values as the most probable at present, we obtain at 15° the following values :—

TABLE XVI.—Equivalents in foot-pounds at Greenwich, at 15°, referred to the "Paris" nitrogen thermometer.

JOULE.	ROWLAND.	MICULESCU.	GRIFFITHS.	SCHUSTER and GANNON.
775	778·3	776·6	780·2	779·7

If we remember that ROWLAND'S number referred to the "Paris" nitrogen thermometer would probably be smaller by one unit, we are struck with the fair agreement there is on one hand between the results of JOULE, ROWLAND, and MICULESCU, and, on the other hand, between GRIFFITHS and ourselves. As far as we can draw any conclusions from the comparison, it seems to point to a difference in the value obtained by the electrical and direct methods. Whether this method is due to some remaining error in the electrical units or to some undiscovered flaw in the method adopted by Mr. GRIFFITHS and ourselves remains to be decided by further investigations.

Appendix.

We give the observations and the calculation of the result of the experiment on 20th May, which is typical of the other experiments. The symbols used are the same as those on pp. 421 and 422.

(1.) *The Electromotive Force.—Comparison of the Clark cells.*

Before the experiment	After the experiment
Time: $11^h\ 43^m$	Time: $12^h\ 16^m$
$t_1^s = 17°\cdot06$	$t_6^s = 17°\cdot23$
I.—Standard = $-3\cdot2$ (a_1)	I.—Standard = $-4\cdot0$ (a_6)
II.— ,, = $-4\cdot6$	II.— ,, = $-5\cdot8$
III.— ,, = $+1\cdot0$	III.— ,, = $+0\cdot5$
IV.— ,, = $+1\cdot4$	IV.— ,, = $+0\cdot5$
V.— ,, = $-0\cdot5$	V.— ,, = $-1\cdot0$
VI.— ,, = $-0\cdot7$	VI.— ,, = $-1\cdot8$
VII.— ,, = $+1\cdot4$	VII.— ,, = $+0\cdot3$
VIII.— ,, = $-0\cdot1$	VIII.— ,, = $-1\cdot4$
IX.— ,, = $+2\cdot4$	IX.— ,, = $+1\cdot4$
X.— ,, = $+2\cdot0$	X.— ,, = $+1\cdot2$
$s_1 = -0\cdot9$	$s_2 = -10\cdot1$
I.—Standard = $-4\cdot0$ (a_2)	I.—Standard = $-4\cdot0$ (a_5)
$t_2^s = 17°\cdot12$	$t_5^s = ?$
Set 1.—(I. + II. + . . . + X.) = $+4\cdot0$	Set 1.—(I. − II. + . . . + X.) = $+15\cdot0$
Set 2.—(I. + II. + . . . + X.) = $+2\cdot0$	Set 2.—(I. − II. + . . . + X.) = $+13\cdot2$
I.—Standard = $-3\cdot2$ (a_3)	I.—Standard = $-4\cdot1$ (a_4)
$t_3^s = 17°\cdot12$	$t_4^s = 17°\cdot17$
Time: $11^h\ 53^m$	Time: $11^h\ 06^m$

The observations in the column headed "After the experiment" were made from below upwards, the interval between $11^h\ 53^m$ and $12^h\ 06^m$ being taken up by the experiment on the equivalent. The correction due to temperature change here is

$$5 \times (a_3 - a_1 + a_4 - a_6) = 0\cdot5.$$

Hence

$$\text{Set (1)} + \text{Set (2)} = 20 \text{ standards} + 6\cdot6 \text{ (see p. 422).}$$

As the total resistance of the circuit differed very little from 10,000 ohms, and the electromotive force of the Leclanché used was 1·45 volts, the correction to the battery of Clark's becomes $6\cdot6 \times 1\cdot45 \times 10^{-4} = 0\cdot0010$ volt.

The average temperature of the Clark cells during the above experiment was 17°·5. Hence the electromotive force calculates out as follows :—

20 Clark cells at 15° C.	28·6800 volts.	
Correction to 17°·15, taking the change for each cell to be 0·00115 volt per degree	− 0·0493	,,
Correction of battery to standard	+ 0·0010	,,
Electromotive force of battery . . .	28·6317	,, (E).

(2.) *Total Water Equivalent.*

	Weights.
Calorimeter + coil	270·14 grams.
Calorimeter + coil + water	1781·54 ,,

(At 12h 45m.)

Hence

Water	=	1511·40
Evaporation correction . .	=	·05
Buoyancy ,, . .	=	1·58
Equivalents 27·02 ·34 . . .	=	27·36
Total water . . .		1540·39 (W).

The equivalents include 27·02, the constant value throughout all the experiments (see p. 441), and 0·34 for the part of the thermometer stem above 12°, which was immersed in the water.

(3.) *Weight of Silver Deposit.*

Date of Weighing.	Observed weight of dish.	Temperature.	Barometer.	Temperature correction in milligrams.	Barometer correction in milligrams.	Corrected weight.	Mean.	Difference.
May 19	64·263487	17°·0	749·7	+·040	+·076	64·263603	·263612	·62034
,, 20	·263510	16·9	749·9	+·038	+·074	·263622		
,, 23	·883859	16·9	758·2	+·038	+·013	·883910	·883953	
,, 23	·883943	17·0	758·2	+·040	+·013	·883996		

The silver deposit was thus 0·62034 gram. (W).

The weighings are supposed to be correct to ·1 millim., and in the mean of any two observations the second decimal may be retained as having some significance. The temperature and pressure corrections were calculated for safety to ·001 millim., and it was found more convenient to carry out the calculations to that place, cutting off the unnecessary figure at the end.

(4.) *Temperature Observations.*

The temperature was measured by subdividing a thermometer division of 0°·02 to the 100th part by the eye; each reading is probably right to 0°·0004.

Time.	Temperature.	Time.	Temperature.
h. m.	°	h. m. s.	
11 48	17·2200	12 11	Main circuit broken
9	30	5	Auxiliary circuit made
50	80	12	19°·7512
1	·2312	3	24
2	60	4	56
3	96	5	80
4	·2432	6	?
5	80	7	·7616
6	·2516	8	40
7	60	9	76
8	·2604	20	96
9	36	1	·7712
12 00	86	2	36
1	Circuit made	3	56
		4	80

By the method of least squares, we obtain from the preceding observations:—

Mean rate of rise per minute in the first period = 0°·00406
Temperature at $12^h\ 1^m$ . . . . = 17°·2722
Mean rate of rise per minute in the third period = 0°·00227
Temperature at $12^h\ 12^m$ . . . . = 19°·7508

The readings of the centiampere balance at equal intervals of time were

62·06
61·86
61·46
60·56
60·36,

or a mean reading of 61·26.

The calibration of the balance immediately after the experiment showed that 1 division = 0·00212 ampere, so that the mean value of the current flowing through the measuring coil in the final period was equal to 0·12987 ampere. From this and the data: resistance of coil = 31·32 B.A. units, 1 B.A. unit = ·9866 × 10^9 C.G.S. unit, J. (assumed) = 4·194 × 10^7, total water = 1540·50 grams.; we easily obtain that the rise per minute due to auxiliary current = 0°·00484. As the observed rise per minute was 0°·00227, the cooling per minute in the final period was equal to 0°·00257.

We require to know the temperature at 12 h. 11 m. Since the cooling per minute at a mean temperature of the calorimeter of 17°·25 was − 0°·00406, and at a mean temperature of 19°·76 was + 0°·00257, a slight calculation will show that the cooling per minute at 17°·27 was equal to − 0°·00401, and at 19°·75 was + 0°·00254.

We are now able to calculate the temperature rise.

Temperature at 12 h. 12 m. = 19°·7508
Rise in temperature during 55 seconds, due to auxiliary current = ·0044
Cooling for 1 minute = ·0025
Therefore temperature at 12 h. 11 m. = 19°·7489
Calibration correction at this point = − 0°·0054
Therefore corrected temperature at 12 h. 11 m. = 19°·7435
Temperature at 12 h. 1 m. = 17°·2722
Calibration correction at this point = − 0°·0050
Therefore corrected temperature at 12 h. 1 m. = 17°·2672
Difference of these temperatures. = 2°·4763

To this difference we must add the following corrections:—

(*a*) For the cooling during the time the main circuit was closed, $10 \times \frac{1}{2}$ (·00254 − ·00401) = − 0°·00735
(*b*) To correct for the wrong interval of the Baudin thermometer − 0·00135 × 2·47 = − 0°·00333
(*c*) For the emergent stem. = + 0°·00126
(*a*) + (*b*) + (*c*). = − 0°·0094
Therefore corrected rise in temperature = 2°·4669 (*t*)

$$J = w\mathrm{E}/(\cdot 001118\,\mathrm{W}t) = 4\cdot 1807.$$

THE following Table includes the Values of the Quantities necessary for the Final Calculation of the Heat Equivalent in the Experiments of the Third Series.

Date of experiment.	Weight of deposit in grams.	Electro-motive force.	Total water in grams.	Temperature change.	Value of J. on mercury thermometer.	Mean temperature of water.
13th May .	0·55938	28·6349	1543·07	2·2200	4·1824 × 10^7	18·3°
17th ,, .	·55881	28·6330	1540·32	2·2224	4·1807	11·2
20th ,, .	·62034	28·6317	1540·39	2·4669	4·1807	18·5
5th June .	·55684	28·6050	1540·41	2·2125	4·1804	19·0
9th ,, .	·55780	28·5878	1534·34	2·2251	4·1776	19·3
15th ,, .	·55952	28·5418	1539·91	2·2180	4·1822	21·3