

III. *On the Capacity for Heat of Water between the Freezing and Boiling-Points, together with a Determination of the Mechanical Equivalent of Heat in Terms of the International Electrical Units.—Experiments by the Continuous-Flow Method of Calorimetry, performed in the Macdonald Physical Laboratory of McGill University, Montreal.*

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*Communicated by Professor H. L. CALLENDAR, F.R.S.*

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Sec. 1.—*Introduction.*

THE unsatisfactory state of our knowledge of the Mechanical Equivalent of Heat and, inseparably connected therewith, of the capacity for heat of water, is the more surprising when we consider the large number of physicists who have devoted their attention to this subject during the century just closed. Since the remarkable pioneer experiments of Count RUMFORD, undertaken just 100 years ago, to determine the nature of heat, the subject has been advanced step by step by different investigators. Conspicuous among these we may mention REGNAULT, who gave us the first idea of the mode of the variation of the specific heat of water with temperature, without, however, giving us any knowledge of the mechanical equivalent of heat; JOULE, who gave us the first measurements of the mechanical equivalent without attempting to study the thermal unit at different temperatures; ROWLAND, who by the remarkable accuracy of his experiments gave us not only a direct determination

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of the mechanical equivalent, but also the variation of the thermal unit over a limited range. More recently we have the exceedingly careful experiments of MICULESCU, of GRIFFITHS, of SCHUSTER and GANNON, and of REYNOLDS and MOORBY.

It is evident from only a cursory glance at the work of these and the host of other investigators, that the science of calorimetry must be regarded as incomplete and approximate so long as its fundamental unit remains in doubt. To obtain, as is urgently needed, a complete series of determinations of the capacity for heat of water over the entire range of temperature is manifestly impossible by the older methods of calorimetry. A new method has long been required, more completely free from the influence of extraneous surrounding conditions.

During a conversation which I had with Professor CALLENDAR, in the autumn of 1896, we discussed the unsatisfactory state of our knowledge of the specific heats of water and mercury. Professor CALLENDAR pointed out that what was required was a new method of calorimetry, which would reduce to a minimum many of the larger corrections inherent in, and making uncertain, the older methods. Such he considered possible in a continuous, or steady, flow method, in which a stream of liquid could be made to continuously carry off a definite and measurable supply of heat. This method he considered capable of great accuracy and free from nearly all the errors in the older methods. I very gladly consented to assist Professor CALLENDAR in developing this method, which we commenced as a joint work early in 1897.\*

The early experiments with mercury will be discussed in full in another paper, and cannot be more than mentioned in this place. They were satisfactory in many respects, but must be considered more as preliminary attempts, the experience of which served so much to aid in later measurements with water. A calorimeter, designed for the determination of the specific heat of water, was set up and tested just previous to the meeting of the British Association at Toronto, to which body a preliminary note was sent describing the method in general terms. On the re-opening of the College session, in September of that year (1897), Professor CALLENDAR was unfortunately obliged, through stress of work, to relinquish his connection as a joint observer in the experiments. My own duties, however, were such as to allow of a certain amount of time to be devoted to research, so that the work was carried on at intervals throughout the winter. During this session Mr. RUSSELL W. STOVEL, B.Sc., joined our graduate classes and devoted a large part of his time to assisting in the work. It is largely to his skill as an observer that it was possible to continue the work during this time.

In the spring of 1898 Professor CALLENDAR was called to London to fill the Quain Chair of Physics in University College, and was obliged to sever his connection entirely with the experiments. It was with extreme regret that we realized this, as

\* For theory of experiment and work done prior to 1897, see the paper by Professor CALLENDAR above, pp. 55-148.

so much was due to his kind supervision in perfecting different portions of the apparatus. Mr. STOVEL also was obliged to leave at this time, so that the work was somewhat delayed.

During the summer of 1898, Mr. CHARLES SHEFFIELD, B.Sc., was kind enough to devote his entire time to the work, and made himself exceedingly useful through his untiring efforts until late in the autumn. University duties being closed, it was possible for us to devote all our time to the work. The measurement of the mechanical equivalent we obtained will be described further on, but it must be regarded as a preliminary attempt owing to a source of error in the method, which was not discovered until some time after. We made a careful study of the general theory of the method, which, as will be explained in its place, was affected somewhat by the error above mentioned. On comparing these determinations with later ones, and more particularly in applying the theory of the method to different calorimeters, we met with such large discrepancies, much larger than any possible error in the instrumental readings, that we were forced to abandon the greater part of our earlier results, and re-organize the experiment.

Unfortunately Mr. SHEFFIELD was called away at this time and was unable to continue his work on the method. It is with extreme regret that I have to record the death of Mr. SHEFFIELD, since leaving this laboratory, which occurred recently at Niagara Falls, where he occupied a position in the capacity of electrical engineer. His death at so early an age and under such trying circumstances is all the more sad, as he had proved his worth and ability in so many ways as an accurate observer and faithful worker.

During the winter of 1898-99 I was obliged to undertake the sole responsibility of the work, with the exception of some temporary assistance in taking observations from my colleague, Mr. H. M. TORY, M.A., to whom I am also indebted for many helpful suggestions. As at that time there was no prospect, until the close of the session, of finding an experienced observer who could devote sufficient time to help in taking observations, it was necessary for me to arrange the conditions of the experiment so as to be able to take all the observations, both thermal and electrical, myself. With a little practice I was soon satisfied that this could be done, although not quite so quickly as with two observers, yet with sufficient accuracy to satisfy the conditions of the experiment. It became chiefly necessary to produce perfectly steady and uniform conditions, over a more extended period of time, conditions which demanded greater refinements in the apparatus. The experiments from this time on, as they became little by little improved and extended, were so steady and consistent, and fulfilled the conditions demanded by the theory so perfectly, that it was deemed unnecessary to break the continuity of the work by introducing a second observer. From January, 1899, to the close of the work, the complete set of observations for nearly every experiment was taken by one observer.

The results of the work from  $4^{\circ}$  C. to  $60^{\circ}$  C., obtained between January and June

of that year, were communicated by Professor CALLENDAR and myself to the meeting of the British Association, at Dover, in September. A reprint of this communication, slightly modified, to contain some later determinations above  $60^{\circ}$ , was published in the 'Physical Review' of April, 1900.

In the present communication I desire to record the complete set of experiments obtained for the mode of variation of the specific heat of water over the entire range  $0^{\circ}$  C. to  $100^{\circ}$  C., feeling confident that they represent, to an order of accuracy approaching 1 in 10,000, the true values, and to point out the wonderful verification they give of the work of REGNAULT over the range where his experiments are the most trustworthy, a verification so complete that the present work may be said to extend over the entire range where it is possible to maintain water in the liquid phase.

I desire, at this time, to record my thanks to Professor JOHN COX, Director of the Macdonald Physical Laboratory, for placing every facility at my disposal that could aid me in the work; to Mr. J. W. FRASER, B.Sc., Demonstrator in Physics in this laboratory, for his observations on the comparisons of our 1-ohm resistance standards; and to Mr. G. W. SCOTT for his kindness in helping me prepare figures for this paper.

I am also indebted to Messrs. EIMER and AMEND, of New York, for the very efficient way in which they made three glass calorimeters, and the great trouble they took to exhaust very perfectly the vacuum-jacket connected with each one.

### Sec. 2.—*General Theory of the Method of Continuous Calorimetry.*

If we have a flow of liquid,  $Q$  per second, continuously heated by an electric current in a fine tube enclosed in a vacuum-jacket, the walls of which are maintained at the temperature of the liquid flowing into the fine tube, then, when equilibrium has been established,

$$Js Qt (\theta_1 - \theta_0) + (\theta_1 - \theta_0) ht = ECt,$$

where

$J$  is the mechanical equivalent of heat,

$s$ , the specific heat of the liquid,

$\theta_0$ , the temperature of the inflowing liquid,

$\theta_1$ , the temperature of the outflowing liquid,

$h$ , the heat-loss per degree difference in temperature between the surface of the fine tube and the walls of the vacuum-jacket,

$EC$ , the electrical energy generated per second, and

$t$ , the time of flow.

If the liquid be a conductor of electricity, such as mercury, then  $E$  represents the difference of potential maintained across the column of liquid in the fine tube, and  $C$  represents the current flowing through the tube. If the liquid be a non-conductor,

such as water, then  $E$  represents the difference of potential across a conducting wire passed through the tube in which the current  $C$  flows.

We will deal entirely in this place with the method as applied to this latter case, such as a steady flow of water, and replace  $J_s$  in the general equation by  $J$ , or the number of joules in one calorie.

Let  $J = 4.2 (1 \pm \delta)$ , where  $\delta$  is a small quantity varying with the thermal capacity of the water, then we may write the general equation,

$$4.2 (1 \pm \delta) Qt (\theta_1 - \theta_0) + (\theta_1 - \theta_0) ht = ECt.$$

Dividing through by  $t$ , and re-arranging the terms, we have

$$4.2 Q (\theta_1 - \theta_0) \delta + (\theta_1 - \theta_0) h = EC - 4.2 Q (\theta_1 - \theta_0).$$

This we will call the general difference equation.

The total heat-loss from the water will be made up of radiation from the surface of the tube through which the water is flowing, conduction from the ends of the tubes containing the thermometers for measuring the temperature of the inflowing and outflowing water, and convection currents due to insufficient stirring around the thermometer bulbs. There will be a small gain in heat due to work done by the water in flowing through the fine tube. To study the effect of these upon the general difference equation it will be necessary to refer to the diagram of the continuous-flow electric calorimeter in its simplest form, given in fig. 1.

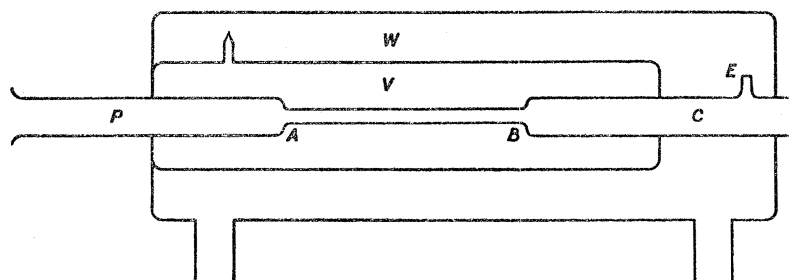


Fig. 1. Diagram of Calorimeter.

In this  $AB$  represents the fine tube in which the water is heated while flowing through,  $V$ , the vacuum-jacket, and  $C$  and  $P$  the inflow and outflow tubes connected to  $AB$ , in which the thermometers are placed. The water-jacket is shown at  $W$ , and includes the vacuum-jacket and inflow-tube  $C$ . The water enters the calorimeter at  $E$  from a reservoir separate from that supplying the water for the jacket, but maintained at the same temperature. The electric heating current passes through the fine tube  $AB$  through a platinum wire extending the whole length, but is arranged so as not to generate heat in the vicinity of the thermometer bulbs. The thermometer in  $C$  measures the temperature  $\theta_0$  of the inflowing water, and that in  $P$

the temperature  $\theta_1$  of the outflowing water, warmed by the passage of the electric current. The temperature of the water increases rapidly from B to A, and gradually decreases from A towards P.

*Radiation.*—The loss of heat through the vacuum-jacket will consist of the cooling of the surface of the glass in the flow-tube by radiation, by convection currents of residual vapour in the jacket, and by radiation from the molecules of the water itself. Provided the vacuum is good, these are all included in the  $h$  term of the general difference equation. This radiation term obviously should not vary, but should remain independent of the quantity of water flowing, provided it can be assumed that the temperature gradient from B to A remains the same for all flows. This assumption can be justified only if the temperature gradient is linear. If it is not linear then we may have either one of two conditions:—

1. When the distribution of heat in the water column AB is such that the water is hotter in the centre than the sides, in which case the temperature of the glass surface of the fine tube will be that represented in (1) fig. 2, and will depend on the thermal conductivity of the different layers of

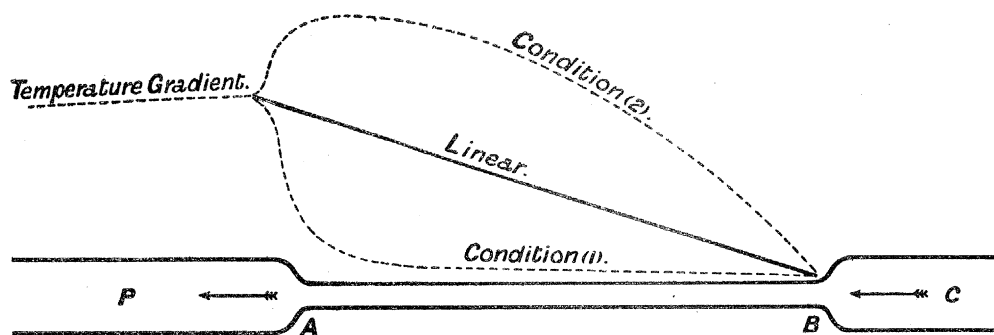


Fig. 2.

water between the centre and the sides, which will be conditioned by the rapidity of flow. This condition is fulfilled perfectly when the water column is receiving heat from a central wire conductor and flowing at velocities less than the critical velocity for the tube in question. In this case the water flows in parallel stream-lines, and does not mix. The higher the velocity of flow up to the critical velocity, the more gradual will be the slope of the temperature gradient of the glass surface from B to A. At A, the water is mixed around the thermometer bulb and the temperature of the glass suddenly increases. For any given temperature  $\theta_1$  of the water, as indicated by the outflow-thermometer, the total heat-loss from the water will decrease with increasing velocity of flow in proportion to the slope of the temperature gradient along BA.

2. The case where the sides of the water column are hotter than the interior, or where the water is receiving heat from the surface of the fine tube. The

temperature gradient will then be represented by (2) fig. 2. The water flowing through the interior of the tube will receive less and less heat from the layers along the sides as the velocity of flow increases. To attain the given temperature  $\theta_1$  on the outflow-thermometer, the temperature gradient from B to A will rise rapidly, and suddenly decrease as the water is mixed around the bulb. The total heat-loss from the water will then increase with increasing flow in proportion to the slope of the temperature-gradient from B to A. This condition would be perfectly fulfilled by replacing the fine glass tube by one of metal through which the electric heating current could be made to flow. Less perfectly it is fulfilled when the heating wire lies along the sides of the tubes, and supplies heat to the layers of water nearest the walls of the tube.

In both these cases the heat-loss would not be independent of, but would depend on, some function of the flow. To ensure a perfectly uniform temperature, equal to that of the flow-tube, throughout any section of the water column, it is necessary to produce thorough mixing at all points, and avoid the formation of stream-lines. If this is fulfilled, we can be safe in assuming the temperature gradient at least approximately linear from B to A in both the above cases. Also that the total quantity of heat lost per second by radiation from the water in its passage through the length of tube included in the vacuum-jacket is the same, quite independent of the velocity of flow.

An experimental study of the two cases above given, where the water flowing in parallel stream-lines receives heat from a platinum wire, which may be moved from the centre to the sides of a 3-millim. bore flow-tube, will be given in Section 7.

*Conduction.*—The heat-loss by conduction from the ends of the calorimeter will evidently be very small where a bad thermal conductor, such as water, is used. Where metal wires are introduced to convey the electric current to the central heating wire, the conduction of heat from the water by the wires assumes a much more serious character, more especially when the calorimeter and jacket are maintained at a temperature very different to that of the surrounding air. At the inflow end the effect, when the calorimeter is at a higher temperature than that of the air, is to lower the temperature  $\theta_0$  of the inflow water by a small amount. The effect at the outflow end is similar, but smaller, on account of the direction of flow. It is evident that this can always be measured and eliminated for any given flow by recording the temperatures of the inflow and outflow thermometers before the electric heating current is turned on. The only conduction effect that these “cold” readings will not take account of is the conduction from the outflow-tube due to the rise of temperature ( $\theta_1 - \theta_0$ ). This must be separately measured in other ways. It can be estimated and its maximum effect obtained, for any given difference in temperature, by surrounding the outflow-tube beyond the water-jacket by a water circulation, the temperature of which can be changed at will. If it is made as small as possible by

replacing the water circulation by heavy lagging; its effect can be measured by varying the flow of water, as will be shown further on. This conduction effect will be independent of the difference in temperature between the jacket water and the outside air, and depend on the rise of temperature  $(\theta_1 - \theta_0)$  directly, and on the velocity of flow inversely.

*Convection.*—We have already discussed the effect of the stream-line flow on the radiation correction, when the water is not stirred in its passage through the flow-tube. It is proposed further on to treat this more in detail, as it has an important bearing on the general validity of this method applied to a non-conducting liquid. The effect of convection currents around the thermometer bulbs is avoided by suitably stirring the water. Strictly speaking, the thermal stream-lines in the flow-tube should not be classed as convection currents, but I have included them here for the sake of convenience.

*Gain of Heat.*—The work done by the water in flowing through the fine tube may be measured by determining the difference in water-pressure between the inflow and outflow-tubes, for any given flow. The work done by any other flow can then be determined by measuring the change in temperature on the outflow-thermometer due to the change in flow.

If  $W_1$  be the work done by the flow  $Q_1$  per second,  
 $W_2$            "           "           "           "           "           "  
 $Q_2$            "           "           "           "           "           "

then

$$W_1 = JQ_1(\theta_1 - \theta_0) + (\theta_1 - \theta_0)h \quad \text{and} \quad W_2 = JQ_2(\theta_2 - \theta_0) + (\theta_2 - \theta_0)h,$$

where  $\theta_0$  is the temperature of the inflowing water as before,

$\theta_1$  and  $\theta_2$  the temperatures of the outflowing water for the flows  $Q_1$  and  $Q_2$  respectively, and

$h$  the heat-loss per degree rise, as before.

Then  $W_1 - W_2 = J(Q_1 - Q_2)(\theta_1 - \theta_2) + h(\theta_1 - \theta_2)$ .

But  $h$  is small, and  $(\theta_1 - \theta_2)$  is small, so that we may neglect it in comparison to  $(Q_1 - Q_2)$ . If we find that  $(\theta_1 - \theta_2)$  is negligible for a large value of  $(Q_1 - Q_2)$ , then we have  $W_1 - W_2 = 0$ .

For the limits of flow and the size of flow-tubes I adopted in the present experiments, no measurable effect could be obtained on the outflow-thermometer. Even if the work done was appreciable, the method adopted of obtaining the "cold" readings for each flow would eliminate it, except if it varied with the change in the viscosity of the water, heated through the temperature  $(\theta_1 - \theta_0)$ .

*Method of Measuring the Specific Heat.*—Referring to the original difference-equation, we see that

$$4.2 Q (\theta_1 - \theta_0) \delta + (\theta_1 - \theta_0) h = EC - 4.2 Q (\theta_1 - \theta_0),$$

in which there are the two terms  $\delta$  and  $h$  to be determined. If we take two flows of



water,  $Q_1$  and  $Q_2$ , for the same inflow temperature  $\theta_0$ , then we have the two equations

$$\begin{aligned} 4.2 Q_1 (\theta_1 - \theta_0) \delta_1 + (\theta_1 - \theta_0) h &= E_1 C_1 - 4.2 Q_1 (\theta_1 - \theta_0), \\ 4.2 Q_2 (\theta_2 - \theta_0) \delta_2 + (\theta_2 - \theta_0) h &= E_2 C_2 - 4.2 Q_2 (\theta_2 - \theta_0). \end{aligned}$$

If the electric current is adjusted for the two flows so that  $\theta_1 = \theta_2$ , then

$$(\theta_1 - \theta_0) h = (\theta_2 - \theta_0) h,$$

and  $\delta_1 = \delta_2 = \delta$ , and hence by direct subtraction and writing  $d\theta = (\theta_1 - \theta_0) = (\theta_2 - \theta_0)$ ,

$$4.2 (Q_1 - Q_2) d\theta \delta = (E_1 C_1 - 4.2 Q_1 d\theta) - (E_2 C_2 - 4.2 Q_2 d\theta),$$

and

$$\delta = \frac{(E_1 C_1 - 4.2 Q_1 d\theta) - (E_2 C_2 - 4.2 Q_2 d\theta)}{4.2 (Q_1 - Q_2) d\theta},$$

from which  $J$ , or the number of joules per calorie  $= 4.2 (1 \pm \delta)$ . By substituting  $\delta$  in either difference-equation,  $h$  can be obtained.

The value of  $J$  thus obtained will be the mean over the range  $d\theta$  through which the water is heated, and apply to the mean temperature

$$\theta_0 + \frac{1}{2} (\theta_1 - \theta_0) = T \text{ (mean).}$$

If the variation of the value of  $J$  is not linear over this mean temperature, then for different values of  $\theta_0$  and  $\theta_1$  for the same value of  $T$  (mean), the value of  $J$  will be slightly different.

*Application of the General Difference Equation to Test the Theory of the Method.*—  
In order to test the accuracy of the assumptions made in regard to

- (a) The dependence of the heat-loss on the rise of temperature,
- (b) The dependence of the heat-loss on the flow, including the conduction correction,

we will consider the general difference equation. We have as before

$$4.2 Q (d\theta) \delta + (d\theta) h = EC - 4.2 Q (d\theta).$$

Dividing through by  $d\theta$ , the equation is expressed per degree rise, or

$$4.2 Q \delta + h = \frac{EC - 4.2 Q d\theta}{d\theta} = \Delta.$$

If  $h$  depends only on  $d\theta$ , then for different values of  $d\theta$ , for the same mean temperature and flow, we have

$$4.2 Q \delta + h = \Delta = \text{constant.}$$

This relation should hold provided the temperature coefficient of both  $\delta$  and  $h$  is linear. A small variation from lineality can, however, be safely neglected.

If we vary the flow and keep the rise of temperature constant, then we have in the equation already given

$$4.2 Q \delta + h = \Delta.$$

The value of  $\Delta$  for different values of  $Q$  will vary in proportion to  $4.2 Q \delta$ , but the variation will be a linear one, provided we are not neglecting any term on the left-hand side varying inversely as the flow. If  $\delta = 0$ , then

$$h = \frac{EC - JQ d\theta}{d\theta}$$

for any value of  $Q$ .

In Section 5 the experimental proof of these considerations is given, and it is shown that within wide limits of flow it holds with great accuracy. For very small values of  $Q$  the conduction becomes measurable, but the limits chosen in the present series of experiments are seen to hold for the higher temperatures as perfectly as for the lower.

### Sec. 3.—*Measurement of Fundamental Constants.*

Owing to the importance attached to the measurement of the different constants in the general equation of the method, it is proposed to treat each one separately in this section, dividing them up under the two heads electrical and thermal. In the first we have the Clark cell, standard resistance and potential measurements, and in the second the measurement of temperature, weight and time.

The general plan of the electrical connections is given in fig. 3. A large 4-cell accumulator, of 200 ampere-hours each, supplied the steady heating current to the calorimeter through the resistance and rheostat. Potential terminals were taken from the calorimeter and resistance, and from two Clark cells in series, to the paraffin block, where they were placed in mercury cups cut in the solid paraffin. Wires leading from two holes, placed equi-distant from the other cups in the block, were carried to the potentiometer shown to the left, and included a galvanometer in the circuit. By interchanging two connections, the Clark cell, calorimeter or resistance could be connected through the galvanometer to the potentiometer. By altering the rheostat or connecting a smaller number of cells, the heating current could be

adjusted for a change of water flow in the calorimeter, so as to produce the same rise of temperature.

If  $X_0$  is the reading of the potentiometer for the balance point of the Clark cell,

$X_1$  potentiometer reading for difference of potential on calorimeter,

$X_2$  the same for resistance  $R$ ,

$e$  the E.M.F. of Clark cell,

$R$  the value of the resistance,

then  $E$ , the potential across the calorimeter, is  $X_1/X_0 \times 2e$ , where the two Clark cells are used in series.

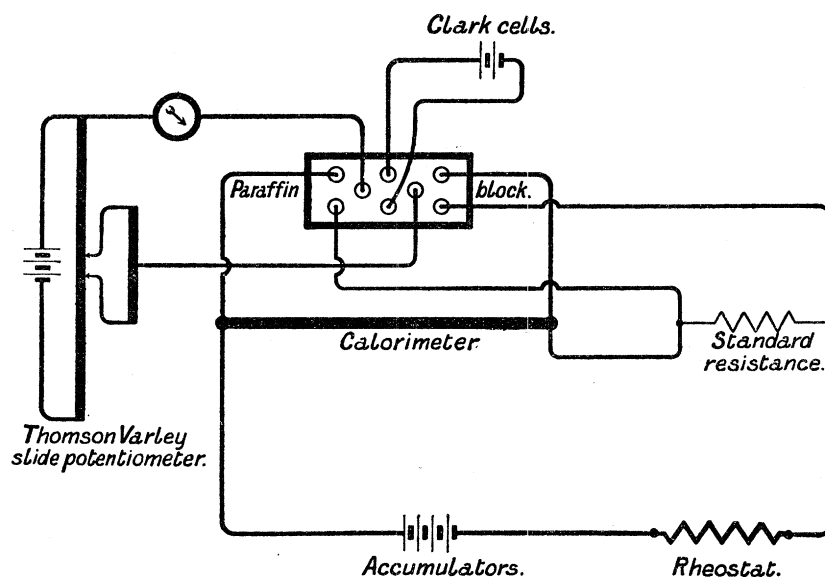


Fig. 3.

Also the current  $C$  in the circuit is  $X_2/X_0 \times 2e/R$ , from which we get the total watt energy per second supplied to the calorimeter, when the conditions have become steady, and used in heating the water,

$$EC = \frac{X_1 X_2 e^2}{X_0^2 R}.$$

The experimental error involved in the measurement of  $EC$  will depend on the accuracy of the measure of  $X_1$ ,  $X_2$ , and  $X_0$  and on the constancy of  $e$  and  $R$ .

### Sec. 3a.—Clark Cell.

Some time previous to my undertaking the present series of experiments, I made a careful study of the Clark cell with Professor CALLENDAR in order to become more conversant with its behaviour, as well as to devise, if possible, a more reliable form of cell than the one in vogue at that time. The result of this work has already been

published in full ('Proc. Roy. Soc.,' vol. 67, p. 117 (1897)), and in consequence may be passed over here with but a brief mention. A thorough study of the old form of cell recommended by the Board of Trade formed one of our chief objects, including measurements of the diffusion lag on a sudden and definite change of temperature. It was shown that for a change of 15° C. the time required for a B.O.T. cell to assume its true value was of the order of 14 days when left undisturbed, but only 2 days when shaken three times at different intervals. In cells where the saturated solution of zinc sulphate was replaced by moist zinc sulphate crystals, no such effect could be noticed, but the cells assumed their normal value on a sudden change in temperature in 10 or 15 minutes, or, in other words, in only such time as was required for the cell to assume the temperature of the surroundings.

These modified B.O.T. cells were studied in every detail, but more particularly as regards the formula governing the variation of the E.M.F. with temperature and their reproducibility. The remarkable constancy of these cells, their agreement amongst themselves, and the closeness with which they followed the temperature expression deduced, was a matter of much satisfaction. It was found that the temperature change of the E.M.F. depended on two conditions, a change of temperature and a change of strength of solution. These two changes were about equal and formed one-half of the total change. By keeping the strength of the solution constant and varying the temperature, the change was practically the same for all strengths, and equal to that found by Professor CARHART for the Carhart-Clark cell. If the temperature was kept constant and the strength of solution varied, then the E.M.F. followed the concentration in the linear relation in millivolts and grammes per cub. centim.,

$$dE = 42.0 - 88.0w.$$

The variation with temperature was followed for higher temperatures, and the transition point for the inversion of the heptahydrate (normal) crystals at 38.78° C. fixed. Various types of cells were devised which have been designated as the B.O.T. "crystal" cell, which is the modified Board of Trade form; the "sealed" cell, which is a form hermetically closed by glass fusion; and the "inverted" cell, which is a B.O.T. crystal cell reversed so as to place the negative electrode (zinc amalgam) at the bottom. These all have an identical temperature formula, which may be expressed in millivolts,

$$E_t = E_{15} - 1.200(t - 15^\circ) - .0062(t - 15^\circ)^2$$

between 0° and 30° for a mean temperature of 15°, or

$$E_t = E_{39} - 1.635(t - 39^\circ) - .0140(t - 39^\circ)^2$$

for a mean temperature of 39°.

For a cell about the mean temperature of  $39^\circ$ , with the hexahydrate crystals as solid phase, the formula

$$E_t = E_{39} - 1.000(t - 39^\circ) - .0070(t - 39^\circ)^2$$

was obtained. For temperatures above  $30^\circ$ , as the second formula shows, the values given by the first formula diverge from the observed values, due probably to a secondary change produced by the decomposition of the mercurous sulphate. If the first formula is corrected by the additional term

$$- .00006(t - 15^\circ)^3,$$

the calculated values from  $30^\circ$  to  $40^\circ$  C. are brought into very close agreement with the observed values.

The Clark cells I have used in the present work are some of the original crystal cells described in the paper by Professor CALLENDAR and myself, "On the Variation of the Electromotive Force of the Clark Standard Cell," already referred to. These cells have been in the laboratory since 1895, and frequent comparisons made of their E.M.F. with newer cells constructed at different times, both by myself and the advanced electrical engineering students. As these cells are the originals from which the temperature formulæ already given were obtained, the constancy of the E.M.F. maintained to the present time is a matter of some surprise, considering the severe treatment they were subjected to during our earlier experiments. They were made in the generally accepted way in a test-tube, and sealed by means of a cork, on the top of which marine glue was melted. The life of such a cell is necessarily dependent on the speed with which the crystals commence to dry, and this fact has been raised against the use of moist crystals in place of a saturated solution. I have found however, that in point of usefulness our crystal cells have outlived several cells with saturated solution which were made at the same time. It appears that the crystals retain the moisture more tenaciously than the saturated solution does, so that whereas a solution may be reduced to one-third of its original bulk, with deposition of crystals, a mass of crystals retains its moisture without diminishing in bulk or uncovering the zinc rod. Owing to the dryness of the Montreal climate, the question of the slow evaporation of liquid from the cells is a serious one. Our cells have been re-sealed on one occasion by simply re-melting the marine glue, but apparently without harm except to one ( $X_3$ ), which when left undisturbed for several months returned to its original normal condition, and is at present as good as the others.

Several sealed cells, inverted cells, and a number of new crystal cells have since been made in the laboratory, and have served to check the constancy of the original crystal cells. Independently several cadmium cells were made in 1897, in the inverted form, which proved to be quite satisfactory, and a comparison of the mean of these cells was made with the mean of the crystal cells. These cadmium cells

I have described in another place, and have shown that they cannot be relied on, as an accurate laboratory standard, to quite the same order of accuracy as a Clark cell, although as a commercial instrument they have distinct and unquestionable advantages over the Clark cell.

The method of keeping the Clark cells at a constant temperature has been already described in my earlier papers. Briefly it consists of a water thermostat with gas regulator, which is capable of maintaining the temperature constant to  $\cdot 02^{\circ}$  C. over extended periods. Whenever one of the experiments on the specific heat of water was performed, the bath was set to regulate as near  $15^{\circ}$  as possible, and throughout hardly ever varied more than  $\cdot 01^{\circ}$  or  $\cdot 02^{\circ}$ , unless some sudden change in the gas-pressure or water supply introduced a disturbance of too sudden a nature to be at once rectified by the regulator. The bath was supplied by a stream of water from a constant-level head through a spiral of copper tubing about 2 millims. diameter, and was heated by the gas flame, controlled by the regulator, as it passed through. During the winter, the water-supply in the laboratory was always between  $8^{\circ}$  and  $10^{\circ}$  C. at the place where the bath was located, so that there was no difficulty in maintaining the bath at  $15^{\circ}$ . During the summer, however, the water sometimes reached  $18^{\circ}$  or  $20^{\circ}$ , and it became impossible to keep the bath at  $15^{\circ}$  without running the inflowing water through an ice tank before it entered the bath. As this entailed considerable trouble, the bath was allowed simply to take the temperature of the inflowing tap water, and rose and fell in temperature slowly with it. There was no special object after all in keeping the cells at  $15^{\circ}$ , on account of the accuracy of the temperature coefficient, and the complete agreement of all the cells with one another at all the temperatures of comparison. The temperature of the bath was taken with a Geissler thermometer reading to  $\cdot 01^{\circ}$ . This thermometer was reduced to the nitrogen scale by comparisons, with a platinum thermometer, made both by Professor CALLENDAR and myself in 1896. It has seldom varied more than a few degrees either way from  $15^{\circ}$  since then, and as it was a somewhat old thermometer at the time of comparison with the platinum, it is unlikely that its readings have changed much since. Moreover, our later tests on the temperature coefficient made with this thermometer and thermometers calibrated by it, have agreed so well with the earlier measurements that there is no reason to doubt the correctness of its readings.

The comparison of the E.M.F. of the different cells was made on a specially constructed potentiometer, but as it has already been described it will be unnecessary to more than mention it here. Special attention was given to having the readings sufficiently sensitive to the order of accuracy we attempted, and defective insulation was amply guarded against. For differences in E.M.F. the potentiometer read directly in millivolts, at the rate of  $\cdot 01$  mv. for each millimetre of scale. A 6000-ohm galvanometer in the circuit was sensitive to a scale distance a little less than 1 millim.

In Table I. I have arranged the complete series of comparisons made on six of our

TABLE I.—Differences Expressed in Hundredths of a Millivolt from Mean.

	1898.										
	March.								April.		
	9.	10.	11.	14.	16.	23.	25.	31.	2.	12.	20.
X <sub>1</sub> . . . . .	- 5	- 6	- 4	- 4	- 5	- 4	- 4	- 4	- 5	- 4	- 4
X <sub>2</sub> . . . . .	+ 7	+ 8	+ 8	+ 7	+ 9	+ 7	+ 8	+ 8	+ 8	+ 8	+ 9
X <sub>3</sub> . . . . .	—	—	—	—	—	—	—	—	—	—	—
X <sub>5</sub> . . . . .	-17	-15	-13	-16	-16	-16	-14	-16	-17	-16	-16
X <sub>10</sub> . . . . .	+14	+12	+10	+15	+15	+15	+13	+14	+14	+14	+13
X <sub>11</sub> . . . . .	+ 1	+ 1	- 1	0	+ 1	0	+ 1	- 1	- 1	0	- 1
Temperature of comparison	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°
	1898.										
	May.				June.		July.	Sept.	Oct.	December.	
	4.	5.	9.	28.	13.	17.	23.	10.	14.	14.	16.
X <sub>1</sub> . . . . .	- 4	- 3	- 4	- 3	- 5	- 4	- 6	- 2	- 4	- 8	- 8
X <sub>2</sub> . . . . .	+ 6	+ 6	+ 6	+ 7	+ 5	+ 5	+ 4	+14	+10	+15	+16
X <sub>3</sub> . . . . .	—	—	—	—	—	—	—	—	—	—	+ 1
X <sub>5</sub> . . . . .	-17	-17	-18	-18	-20	-20	-21	-15	-21	-20	-19
X <sub>10</sub> . . . . .	+15	+15	+16	+15	+17	+18	+18	+21	+16	+15	+15
X <sub>11</sub> . . . . .	- 1	- 1	- 1	- 2	0	0	+ 1	+ 4	- 2	- 5	- 3
Temperature of comparison	15°	15°	15°	15°	18°	18°	20°	19°	14°	15°	15°
	1898.		1899.					1900.			
	December.		Jan.	March.	May.	June.	Oct.	February.		March.	
	19.	27.	17.	24.	6.	16.	25.	5.	12.	14.	
X <sub>1</sub> . . . . .	- 8	- 8	- 9	-12	- 9	-10	-10	-17	-14	-15	
X <sub>2</sub> . . . . .	+17	+15	+14	+11	+15	+15	+17	+17	+20	+14	
X <sub>3</sub> . . . . .	+ 3	+ 1	+ 2	+16	—	—	—	+18	—	+17	
X <sub>5</sub> . . . . .	-20	-19	-20	-23	-17	-18	-21	-23	-18	-24	
X <sub>10</sub> . . . . .	+15	+15	+14	+12	+16	+18	+15	+11	+16	+12	
X <sub>11</sub> . . . . .	- 5	- 3	- 3	- 6	- 2	- 2	- 2	- 8	- 3	- 7	
Temperature of comparison.	15°	15°	15°	15°	15°	16°	16°	15°	16°	15°	

original cells from the date of the last comparison given in Table VII., Section 25, p. 151 (*loc. cit.*), to the close of the present series of experiments. Various other tables are given here in order for the other types of cells, and I have designated the different cells by capital letters indicating the type, and by a suffix to indicate the number of the particular cell. The crystal cells are given as X, the sealed cells by S, the inverted cells by XR, and the cadmium cells by Cd. In the original table of comparison already referred to, cells X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>5</sub>, X<sub>6</sub>, X<sub>10</sub>, and X<sub>11</sub> were given. Of these cells, all are at present in existence, with the exception of X<sub>6</sub>, which was taken away from the laboratory and since broken. Table I. may be taken as a continuation of the older table. The relative differences in these cells, although somewhat larger than is usually obtained in constructing a number of cells from the same lot of materials, have been maintained so consistently that over extended periods a constancy of 1 in 100,000 can be easily assumed. Later results show that cells X<sub>1</sub> and X<sub>5</sub> have lowered somewhat, but even in these two cases the drop is less than .1 mv., and takes place so gradually as to be easily corrected for. It is highly probable that all these cells will eventually become lower in value as they become older, on account of the drying up of the crystals.

During the winters of 1897-98 and 1898-99 a number of tests were made by some of the advanced students on cells prepared by themselves under my supervision. These cells were all subjected to a temperature cycle of 15° to 0°, to 15° to 30°, to 15°. The first batch of cells made during 1897-98 were in the inverted form, and were made in the usual way in a long test-tube for immersion in the water-bath. A 10 per cent. zinc amalgam was placed in the bottom of the test-tube and covered to the depth of about 2 centims with moist zinc sulphate crystals. The paste of mercurous sulphate and zinc sulphate crystals placed on top of the crystals was made in the usual way by mixing moist crystals with pure washed Hg<sub>2</sub>SO<sub>4</sub>. The positive electrode consisted of a platinum wire flattened at one end, amalgamated, and inserted in the paste. The wire was protected by a small glass tube and reached to the top of the test-tube, where the glass was melted around the wire to form a mercury cup. The negative electrode was a platinum wire protected in a similar way and thrust into the amalgam while still warm before the cell was filled with the other ingredients. The cell was sealed by shoving a cork down the test-tube, with the two electrodes passing through holes made for them, to within a few millims. of the ingredients. The cork was about 1 centim. thick, and was sealed by inserting particles of marine glue and melting them in place by carefully warming the glass over the cork. The crystals of zinc sulphate were prepared by re-crystallizing the ordinary pure heptahydrate salt after neutralization with zinc oxide, and treating with a small quantity of the washed Hg<sub>2</sub>SO<sub>4</sub> when in solution in the usual way.

The cells made in 1898-99 were of the older type, with an amalgamated zinc rod with positive electrode at the bottom of the test-tube. They differed from the original crystal cells in having an amalgamated flattened platinum wire in place of



the metallic mercury. In preparing the crystals for these cells it was deemed unnecessary to follow the old prescription, inasmuch as they were made from the purest anhydrous salt purchased from Merck. However, a few of the cells were made from crystals that had been treated when in solution with a small quantity of  $\text{Hg}_2\text{SO}_4$ , but filtered out before re-crystallizing.

In the table of comparison now given the inverted cells are expressed as difference from the mean of the five crystal cells  $X_1$ ,  $X_2$ ,  $X_5$ ,  $X_{10}$ , and  $X_{11}$ . The temperature changes between  $15^\circ$  and  $0^\circ$ , and  $15^\circ$  and  $30^\circ$  are also given, as determined by the different students who made the cells.

TABLE II.—Comparison of Inverted Cells to Mean "Crystal" (1897-98).

Cell.	Difference from mean crystal in mvolts.	E.M.F. changes between	
		$15^\circ-0^\circ$ .	$15^\circ-30^\circ$ .
XR <sub>11</sub> . . . . .	+0.16	+16.67	-19.45
XR <sub>12</sub> . . . . .	+0.17	16.67	19.46
XR <sub>13</sub> . . . . .	+0.20	16.69	19.58
XR <sub>16</sub> . . . . .	+0.19	16.66	19.60
XR <sub>17</sub> . . . . .	+0.10	16.67	19.61
XR <sub>18</sub> . . . . .	+0.20	16.69	19.55
XR <sub>19</sub> . . . . .	+0.24	16.60	19.51
Means . . . . .	0.166	16.67	19.54

These tests are sufficient to show that the inverted cell gives a value somewhat in excess of the older crystal cells. The temperature change between  $15^\circ$  and  $0^\circ$  is also somewhat larger than the value given by the crystal cells, which was +16.62 mvolts. The reason for this may possibly be, as I have already pointed out in another place, that the sensitive electrode (negative) is at the bottom of the cell and deeply immersed in the bath, whereas in the crystal cells the negative electrode is a zinc rod at the top of the cell, and although immersed below the level of the liquid in the temperature bath, may yet conduct an appreciable amount of heat and be at a slightly different temperature to that of the cell.

I have used the term sensitive for the negative electrode because a small difference of temperature between it and the other parts of the cell influences the E.M.F. very considerably. This can be very forcibly shown in the case of an inverted cell by removing it from the  $15^\circ$  bath and standing it on a cold surface. This produces a larger change (increase) in the E.M.F. than if the complete cell were immersed at the cooler temperature; and in a similar way for a higher temperature, the negative electrode being warmer than the other parts of the cell, the E.M.F. decreases more than it would were all the cell at the same temperature. Hence, in the crystal cell,

when immersed at a temperature above or below  $15^{\circ}$ , the possibility of the zinc rod being at a slightly different temperature to that of the cell is thinkable, and would act in such a way as to make the positive change between  $15^{\circ}$  and  $0^{\circ}$ , as well as the negative change between  $15^{\circ}$  and  $30^{\circ}$ , appear smaller than the true values.

Later on in the year, on September 10, a comparison was made of the old crystal cells with two of the original sealed cells, made in 1896, and at that time still in the possession of the laboratory, as well as three new sealed cells. This comparison is given in Table III. and gives the differences in millivolts between each sealed cell and the mean of the old crystal cells, the comparisons of which were given in Table I.

TABLE III.—Comparison of Sealed Cells with Old “Crystal” Cells.

Cell.	Difference from mean of old cells.
S <sub>1</sub> . . . . .	+0·18 mv.
S <sub>5</sub> . . . . .	+0·34 ”
S <sub>11</sub> . . . . .	+0·20 ”
nS <sub>11</sub> . . . . .	+0·23 ”
S <sub>12</sub> . . . . .	+0·21 ”
	} Mean +0·23 mv.

The agreement of the new sealed cells with the old sealed cells is good, but both show that the mean of the old crystal cells is too low. This makes the mean of the sealed cells, on comparing Tables II. and III., agree with the mean of the inverted cells to ·06 mv.

A comparison of the six crystal cells X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>5</sub>, X<sub>10</sub>, and X<sub>11</sub>, with six of the newer crystal cells made by the students in 1899, was made on March 14, 1900, when the last comparison of the old crystal cells given in Table I. was obtained. In Table IV. this comparison of the six new cells is given, and the differences expressed in millivolts from the mean. Cell X<sub>2</sub> is included, and differenced from, but not included, in the mean.

TABLE IV.—Comparison of New “Crystal” Cells, on March 14, 1900.

Cell.	Difference from mean.
X <sub>21</sub> . . . . .	-0·24 mv.
X <sub>23</sub> . . . . .	+0·05 ”
X <sub>27</sub> . . . . .	-0·05 ”
X <sub>29</sub> . . . . .	+0·05 ”
X <sub>31</sub> . . . . .	+0·11 ”
X <sub>33</sub> . . . . .	+0·08 ”
X <sub>2</sub> . . . . .	-0·17 ”

During the winter previous, when all these new cells were made, the tests on the temperature changes between  $15^{\circ}$  and  $0^{\circ}$ , and  $15^{\circ}$  and  $30^{\circ}$  gave the mean

values  $+ 16.60$  and  $- 19.45$  respectively, which agree very closely with the values given by the old cells, but are smaller than the values given by the inverted cells.  $X_2$  in the above table is seen to be lower than the mean of the new crystal cells by  $- .17$ . Under date March 14, in Table I., it is seen to be  $+ .14$  mv. above the mean of the old crystal. This would make the mean old crystal lower than mean new crystal by  $.31$  mv. This excessively low value is influenced by cells  $X_5$  and  $X_1$  on the mean, which have apparently gone down since the earlier tests. If we reject these two cells from the mean, as being too low, the mean value of the four remaining cells is increased by  $.10$  mv. and the difference between mean old crystal and new crystal reduced to  $.21$  mv. In Table II. it was seen that the inverted cells in January, 1898, were  $.17$  mv. higher than the mean old crystal. If we reject cell  $X_5$  from the mean of the old crystal cells, as being too low, then the difference between the two sets of cells is reduced to  $.12$  mv. Also in Table III. the mean of the old cells is seen to be  $.23$  mv. lower than the mean of the new and old sealed cells. If we reject  $X_5$  as before from the mean, the difference is reduced to  $.17$  mv.

If now we can assume that the mean inverted and mean sealed was the same as the mean new crystal (which unfortunately could not be verified by a direct comparison), then we see that the old cells have lowered in value since January, 1898, by  $.06$  mv., or 4 parts in 100,000. Another indication that the cells have all lowered somewhat in value is afforded by a comparison as early as 1896 with six sealed cells, including  $S_1$  and  $S_5$  of Table III. The mean value of the sealed cells was  $.08$  mv. higher than the mean old crystal including cell  $X_5$ , which was more nearly in agreement with the mean at that time. (See Table VII., page 151, *loc. cit.*) It is evident that for some reason the old crystal cells, even from the first, are lower than what may be taken as the true Clark-cell value, if we may assume that the mean old sealed, mean new sealed, mean inverted, and mean new crystal are all within a few hundredths of a millivolt of each other, and of the true Clark-cell value.

In 1896 the old crystal cells were lower than the sealed cells by  $.08$  mv. ; in 1898 lower than the inverted cells by  $.12$  mv., than the new sealed cells by  $.17$  ; and in 1900 lower than the new crystal cells by  $.21$  mv. This indicates that the mean value of the old crystal cells is  $.14$  mv. lower than the most probable value that we can assume, combining all our Clark cells, and this within the limits of error of perhaps  $.02$  mv.

We can now, from the table of comparisons, assign individual values for the two Clark cells which were used throughout in the present investigation. These cells were  $X_2$  and  $X_{10}$  of the old crystal cells. From January to December, 1898,  $X_2$  was  $.08$  mv. higher than the mean of the crystal cells, and  $X_{10}$  was at the same time  $.15$  mv. higher. If we neglect cell  $X_5$  from the mean, as being too low, then this gives for cells  $X_2$  and  $X_{10}$  in series the values  $+ .03$ ,  $+ .10$ , or  $+ .13$  mv. above the mean. But as mean crystal, neglecting  $X_5$ , is  $.14$  mv. lower than what we have

reason to believe is the true Clark-cell value, two mean crystal cells in series would be .28 mv. lower. Therefore, cells  $X_2$  and  $X_{10}$  in series are lower than the true value by .15 mv. During 1899, cell  $X_2$  was on an average .15 mv. above the mean crystal cells. Neglecting  $X_5$  but not  $X_1$  this difference is reduced to .10.  $X_{10}$  was also +.15 or, neglecting  $X_5$ , .10. This gives for  $X_2 + X_{10}$  the value +.20 mv., or different from the true Clark-cell value by  $-.08$  mv. During the early part of 1900, cell  $X_1$  commenced to go down more rapidly, partially through the introduction of cell  $X_3$  again into the mean. If we take the comparisons on February 5th and March 24th, we find for  $X_2$  the value +.16 mv., and for  $X_{10}$  +.12 mv. Neglecting  $X_1$  as well as  $X_5$  from the mean, the value of  $X_2 + X_{10}$  becomes +.06 + .02, or equal to +.08 mv., the difference from the true Clark-cell value being now  $-.20$  mv. Summarizing we have, if  $e$  represents the true E.M.F. of the Clark cell in volts

In 1898	$X_2 + X_{10}$	$2 \times e$	$-.00015$	}	Mean value $-.00014$ .
In 1899	,,	,,	$-.00008$		
In 1900	,,	,,	$-.00020$		

This gives the mean error, if we assume from 1898 to 1900 the mean value  $2 \times e - .00014$  as representing the true E.M.F. of the two Clark cells used in these measurements, as in

$$1898, +4 \times 10^{-6}; 1899, -2 \times 10^{-5}; 1900, +2 \times 10^{-5};$$

all of which are less than 1 part in 10,000, and outside the possible limits of error of the other measurements.

Whenever the temperature of the Clark cell was other than  $15^\circ$  C., the E.M.F. was calculated, assuming a value at  $15^\circ$ , by the temperature formula obtained between  $0^\circ$  and  $30^\circ$  for a mean temperature of  $15^\circ$  which has already been given. As a matter of verification of this formula, which was deduced from the old crystal cells, I have summarized in Table V. the observations that have been made since, both by myself and the students under my supervision.

TABLE V.

Type of cell.		Change in millivolts between—	
		$15^\circ$ and $0^\circ$ .	$15^\circ$ and $30^\circ$ .
Old B.O.T. crystal . . . . .	1896	+16.62	-19.48
Sealed . . . . .	1896	+16.62	-19.58
Portable B.O.T. crystal . . . . .	1897	+16.60	-19.40
Inverted . . . . .	1898	+16.67	-19.54
Portable B.O.T. crystal . . . . .	1899	+16.60	-19.45
Temperature formula . . . . .	—	+16.60	-19.40
Values obtained by Dr. KAHLE . . . . .	—	+16.40	-19.40

The values obtained by Dr. KAHLE at the Reichsanstalt are somewhat lower. They were obtained for the H-form of cell with negative electrode, zinc amalgam.

The portable crystal cell in Table V. refers to the case where the metallic mercury for positive electrode is replaced by a flattened platinum wire amalgamated. The portable cells in Table VII., original paper, p. 152, made by the students in 1897, and from which the tests (in 1897) in Table V. are taken, were compared with the old crystal cells rather too soon after setting up, to use in determining the true value of the E.M.F. of the old cells, as we have done for the latter cells and the sealed cells in 1896. The mean value of all these cells is very close to the crystal cells, but later tests showed that some of them gave too low a value at first.

*Ratio of Clark to Cadmium Cells.*—In 1897, to check the value of the Clark cells made by us in the laboratory, several Weston cadmium cells were constructed. These were made in the inverted form, and one was made in the H-form after type III. described by JAEGER and WACHSMUTH ('Wied. Ann.,' vol. 59, p. 580, 1896) in their paper on the cadmium cell. All the cells had a cadmium amalgam of 1 to 6 proportion, as recommended by JAEGER and WACHSMUTH, except two, which were made after the B.O.T. "crystal" cell type with cadmium stick. These two cells, however, as was expected, gave much too high an E.M.F. and were only made as a matter of interest. I have described these cells in another place ('Journ. Phys. Chem.,' vol. 4, 1900), with comparisons which were obtained in 1897.

The temperature coefficient obtained for these cells was a little in excess of that found by JAEGER and WACHSMUTH for their cells, but is more in agreement with the value found by DEARLOVE ('Electrician,' vol. 31, p. 645, 1893) and the original value given by WESTON. The expression is a linear one, and reads

$$E_t = E_{15} - \cdot 086 (t - 15^\circ),$$

and holds with great accuracy over the range 15° to 40° C. At 15° a change of state occurs in the cadmium sulphate, so that no formula can be made to hold below that point.

I made a determination of the ratio of these cadmium cells to the old crystal cells, by means of the cylinder potentiometer and 6000-ohm galvanometer which were used in the earlier comparisons of the Clark cell, given by Professor CALLENDAR and myself in our original paper (p. 121). The potentiometer was repeatedly calibrated by comparison with the Thomson-Varley slide potentiometer, described in another place.\* The corrections for uniformity were somewhat large, but were exceedingly consistent, and were determined by myself, as well as by a large number of the students in the ordinary course of their work. The cells, both cadmium and Clark, were immersed at a constant temperature near 15° throughout the test. Table VI. contains the result of this test.

\* CALLENDAR, 'Phil. Trans.,' A, 1902, p. 63.

TABLE VI.—Comparison of Clark and Cadmium. March 6, 1897.

Cell.	Potentiometer reading corrected to 15°.	Corrected for uniformity.
X <sub>1</sub> . . . .	68225	68290
Cd <sub>3</sub> . . . .	48453	48575
Cd <sub>4</sub> . . . .	48460	48582
Cd <sub>5</sub> . . . .	48458	48580
Cd <sub>II</sub> . . . .	48460	48582

Correcting reading of X<sub>1</sub> to mean of old crystal cells and reducing mean cadmium reading to 20° by the formula,

$$E_t = E_{15} - .086 (t - 15^\circ),$$

the ratio of Clark to cadmium becomes

$$\frac{\text{Clark } 15^\circ}{\text{cadmium } 20^\circ} = \frac{68294}{48558} = 1.40644.$$

The ratio obtained by KAHLE for the cells in the possession of the Reichsanstalt was ('Wied. Ann.,' vol. 67, p. 35, 1899),

$$\frac{\text{Clark } 15^\circ}{\text{cadmium } 20^\circ} = 1.40663.$$

The value of our ratio is somewhat lower than the value given by KAHLE, which may be explained by either assuming the cadmium cells too high or the Clark cells too low. We have seen, however, that the mean of the old crystal cells is lower than the most probably true Clark-cell value obtained by comparison with later tests by .14 mvt., or 1 part in 10,000.

Correcting the ratio by this amount, it becomes 1.40658, a value nearly identical with the value obtained by KAHLE.

*The Absolute Value of e.*—The assignment of the true value of *e* to the cells used in the present work is, at present, somewhat difficult. GLAZE BROOK and SKINNER found on standardizing the B.O.T. form of test-tube cell by means of the silver voltameter, and assuming the value .001118 gram.-sec. for the electro-chemical equivalent of silver as determined by Lord RAYLEIGH and Mrs. SEDGWICK, that the value was 1.4342 international volt at 15° C. More recently we have the measurements made by Dr. KAHLE at the Reichsanstalt with the Helmholtz Electrodynamometer ('Wied. Ann.,' vol. 59, p. 532, 1896, and 'Zeit. für Instk.,' June, 1898), which give a result independent of the value assigned to the silver voltameter. We have also the value obtained recently by Professors CARHART and GUTHE, at Ann

Arbor, Michigan University ('Physical Review,' vol. 9, p. 288, 1899), with a type of dynamometer designed by themselves. The results of these measurements show a wide divergence. The values found are

GLAZEBROOK and SKINNER . . .	1.4342	volt at 15°.
KAHLE . . . . .	1.43285	„ „ „
CARHART and GUTHE . . . . .	1.4333	„ „ „

The large discrepancy in the value of the mechanical equivalent of heat obtained by the electrical methods used by Professor GRIFFITHS and Professors SCHUSTER and GANNON, as compared to the value given by the direct mechanical method, has so far hinged on the value to be assigned to the Clark cell. The older, and for so long a time accepted, value, 1.4342, there is every reason now to think is too high. The value given by Dr. KAHLE, *i.e.*, 1.43285 volt, is at the same time probably a little too low. The value found by CARHART and GUTHE depends on the mean of three determinations differing in the extreme by .5 mvt. These three determinations were made for two Clark cells in series, one of which was afterwards compared to the Reichsanstalt cells and found to be in good agreement.

At present there is a grave uncertainty in the absolute value of this fundamental constant, which requires immediate attention. It has been pointed out that the value of the mechanical equivalent of heat found by GRIFFITHS would be brought into harmony with the values found by ROWLAND by the direct mechanical method, by assuming the Clark cell 2 mv. lower than the value found by GLAZEBROOK and SKINNER. The value found by SCHUSTER and GANNON requires a somewhat smaller correction in the same direction.

In the face of these uncertainties in the value to be assigned to  $e$ , I have adopted the older value, 1.4342 international volt, as the basis of my calculations of the absolute value of the mechanical equivalent, in order to bring my results into comparison with those of GRIFFITHS and of SCHUSTER and GANNON. On this basis I have had the temerity to combine the mean value of the mechanical equivalent obtained by integrating the curve of absolute values between 0° and 100° with the determination of the mean value obtained by REYNOLDS and MOORBY, and have obtained by that way an absolute measure of the Clark cell in terms of the mechanical units, which is probably as accurate a value as has yet been obtained, provided the values assumed for my resistance standards are correct.

The discrepancy in the two values of the mean mechanical equivalent, the one obtained by integrating the variation curve, and the other obtained as a direct determination, is .132 per cent. As I have used the value  $e$  of the Clark cell in my measurements squared, this reduces to .066 per cent. on 1.43420, and shows that the value assumed for my cells is too high by this amount. The true value of the Clark cell I have assumed for calculation is 1.4342, which would give for the two

cells  $X_2 + X_{10}$  in series, the value 2·8684, provided they were equal to the true value. We have seen, however, that these two cells differ from the most probable true value of the Clark cells made in this laboratory by ·00014 volt, which would give for the true value of  $X_2 + X_{10}$  2·86826, or 1·43413 each. Reducing this value by ·066 per cent., we have, as the value of each of my Clark cells,

1·43318 int. volt,

and the most probable true Clark-cell value

**1·43325 int. volt at 15° C.**

which is in remarkable agreement with the absolute measurements of CARHART and GUTHE for their Clark cells.

From the ratio of the Clark to cadmium, the value of the cadmium cell is found to be

**1·01895 int. volt at 20° C.**

### Sec. 3b.—*Measurement of Resistance.*

Next in importance to the value of  $e$  for the Clark cells, which we assume for the calculation of the absolute value of the mechanical equivalent of heat, is the value to be assigned to  $R$  for the resistance used in these experiments.

At the outset we were exceedingly fortunate in having the laboratory equipped with a large number of 1-ohm resistance standards certified by the Electrical Standards Committee of the British Association, which were obtained in 1893. The work, therefore, of standardizing the resistances which were made for the present series of experiments was reduced to a minimum by the facility with which they could be compared to these standards on a Nalder type of Carey-Foster commutator-bridge. This bridge was supplied with a set of ratio-coils and bridge-wires which could be interchanged at will, and selected to be comparable in size with the resistances compared. During the first experiments which we made on the specific heat of mercury and the early trial experiments with the water calorimeter, the electric heating current was passed through a 1-ohm manganin coil for standard, which was immersed in paraffin oil. The difference of potential across the terminals of this specially-constructed resistance was of the same order as that across the column of liquid in the fine flow-tube in the mercury-calorimeter, and also equal to that across the platinum heating-wire in the first water-calorimeter. This was arranged for convenience in balancing on the potentiometer.

The coil was made from two manganin wires, 1 millim. in diameter, connected in parallel and wound on an ebonite frame. Connections were made to the coil at the bottom of the frame, which was held vertical, by two heavy copper-wires,  $\frac{1}{4}$  inch in diameter, so arranged as to have 3 or 4 inches immersed in the oil-bath with the coil.



The wires were bent into an inverted U and made to fit into mercury-cups, either on the commutator-bridge or in the main calorimeter circuit from which the potential terminals were taken to the potentiometer. For the later experiments with the water calorimeter it was found advisable to alter the resistance of the heating-wire to .5 ohm, so that another manganin-resistance was made similar to the first one and connected in parallel with it in the calorimeter circuit. Our numerous comparisons of these ohms with the certified standards were far from satisfactory, but the cause was at first sight not apparent.

The resistance of both the coils was found to increase, after carrying currents of from 4 to 8 amperes in a series of experiments, of the order of 2 or 3 parts in 10,000 in two weeks. This was somewhat annoying, and necessitated repeated comparisons with the standards and numerous corrections. It was also a matter of doubt whether the resistance of the coils remained the same when the heavy currents were passing, seeing that they produced such a large permanent change in the resistance. We finally commenced to suspect the real cause of the trouble to be at the point where the manganin-wire was soldered on to the heavy copper-wire. In the face of this uncertainty it was decided to abandon these resistances altogether for others made of platinum-silver wire according to a different design. Both these new 1-ohm resistances have proved to be so reliable and constant since they were made, in May, 1898, that it is proposed to give a short description of them here. They were both made on an exactly similar design.

The frame-work consisted of two heavy plates of mica,  $4'' \times 2\frac{1}{2}''$ , placed side by side, and separated about  $\frac{3}{4}$  of an inch by ebonite strips at each narrow end. Both ebonite strips were split from end to end, parallel to the mica plates and half-way between them. The strips were fastened to the mica plates by ebonite washers and small screws, shown in fig. 4, which gives a general view of a resistance. The plates were arranged so that they could be separated or put together quickly by removing two screws at either end, clamping the ebonite strips together. Two  $\frac{1}{4}$ -inch copper-wires were passed through holes bored for them through the splits in the ebonite strips at each end, in such a way that they were clamped in place by the ebonite. These heavy wires, when in place, connected the space between the mica plates with the outside of the frame-work. At each end the two wires were bent at right angles so as nearly to meet, and were inserted and soldered into holes made for them on the opposite faces of a small copper block. Heavy copper-wires ( $\frac{1}{4}$ -inch) were soldered into holes in these copper blocks and bent into an inverted U for connecting to the commutator-bridge.

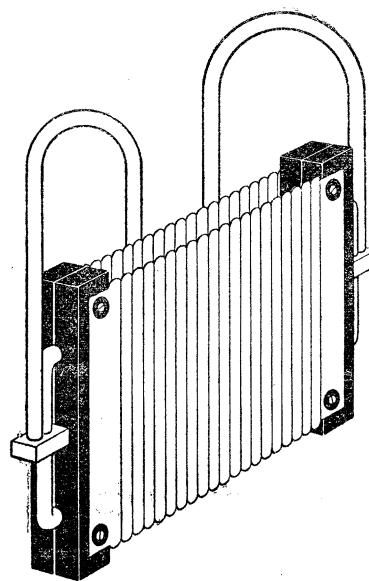


Fig. 4.

Each of the two mica plates was serrated on the two long edges and two bare platinum-silver wires, .4 millim. in diameter, wound on side by side. After winding, the ends of the platinum-silver wire were fused to copper-wires of the same size in a blow-pipe flame. The wires on the frames were then annealed at a low red heat by passing a heavy electric current through them. After the two mica plates were clamped together so as to include the heavy copper-wires at both ends, the copper-wires that were fused to the platinum-silver wires were soldered to the end faces of the copper-wires protruding into the space between the mica plates. There being in all eight ends to be soldered and four heavy copper-wires to solder into, each large copper-wire was connected to two of the small copper-wires fused to the platinum-silver wire. Each 1-ohm consisted thus of four bare platinum-silver wires, 16 millims.

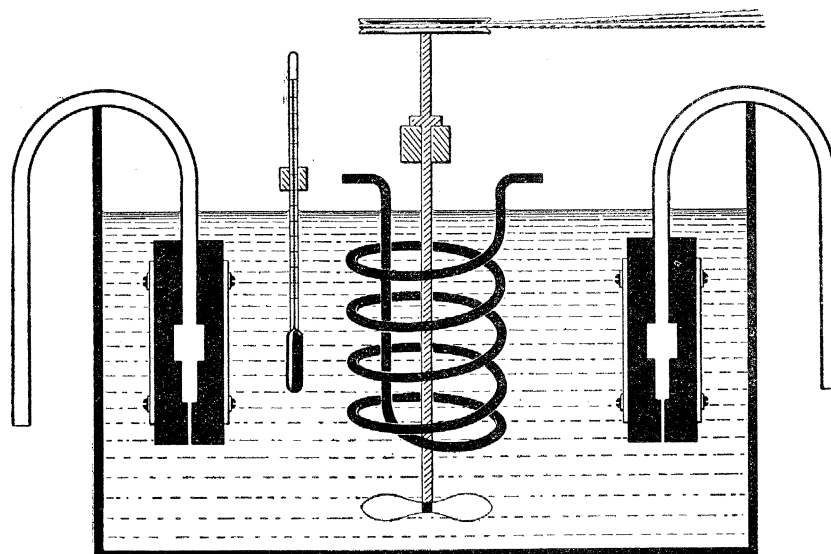


Fig. 5.

in diameter, in parallel; direct solder joins of platinum-silver with copper were avoided, and the mica plates were arranged so as to give the best possible circulation when immersed in an oil-bath.

The paraffin oil-bath was made from a square ebonite box, and included, besides the two 1-ohm coils, a stirrer and coil of metal tube for a water circulation, fig. 5. The coils always remained fastened in the bath, and when it was necessary the bath, including the ohms, could be removed from the position assigned for it in the experiment where the ends of the two inverted U-shaped connections from the coils were immersed in mercury-cups in two heavy copper forgings in the calorimeter circuit. When a comparison was made on the commutator-bridge, the bath was conveyed to the place where the bridge was always kept. During a comparison, the stirrer was run by a small electric motor and the temperature of the oil taken by a thermometer immersed in the bath. For the determination of the temperature coefficient of the

coils, water at different temperatures was run through the circulating tube so as to change the temperature of the oil.

Up to the time of writing, I have been unable to compare these ohms directly with official standards. It will, therefore, be necessary for me to describe a series of comparisons of these ohms with eleven certified ohms in the possession of this laboratory, together with a standard 1-ohm coil from the German Reichsanstalt, sent us for comparison by the Physical Department of the Massachusetts Institute of Technology. By means of these comparisons, we may possibly arrive at a result for the value of  $R$  somewhere near the truth.

Throughout the present work I have used only one of the certified standards (No. 4086) to check the constancy of the two platinum-silver ohms, as it was of a better and more convenient form to use on the bridge than the others and had a much smaller temperature coefficient.

Before describing the tests I will briefly review the method of comparing the ohms and the method of finding the value of the bridge-wire used on the Carey-Foster bridge throughout these tests. The 1-ohm pair of coils supplied by the makers of the bridge were used for the ratio coils, and a bridge-wire having a resistance of about .002 ohm per centim. was used. The bridge-wire was just 10 centims. long, with a scale graduated into half centimetres and millimetres. A lens was also supplied for reading the position of the balance point. The galvanometer for obtaining the balance point was a very sensitive 9-ohm Thomson reflecting galvanometer, which was used for the thermometer work. It had a telescope and scale, and was sensitive to 50 scale-divisions for 1 millim. of bridge scale, which, of course, was far more sensitive than was required, or even quite convenient to work with. The current supplied to the coils was from one accumulator through 20 ohms external circuit. By simply lifting the commutator from the mercury cups on the bridge and revolving it through half a revolution, the connections could be made so as to reverse the position of the two resistances relative to the ratio coils. If  $P$  and  $Q$  are the ratio coils,  $R$  and  $S$  the resistances to be compared, then, when the current is reversed in  $R$  and  $S$ , but not in  $P$  and  $Q$ , we have,  $R/S - S/R = \rho(d_1 - d_2)$ , independent of  $P$  and  $Q$ .

Here  $d_1$  and  $d_2$  are the readings of the balance points on the bridge-wire, and  $\rho$  a constant to reduce to ohms.

Let  $R/S = (1 + r)$ , where  $r$  is a small quantity; then  $S/R = (1 - r)$  and

$$R/S - S/R = 2r = \rho(d_1 - d_2).$$

To find  $\rho$ ,  $S$  may be changed to  $S_1$  by shunting with a known large resistance, say 100 ohms.

We have then, if  $R/S_1 = 1 + r + dr$ ,  $S_1/R = 1 - r - dr$ , and reversing the current as before,

$$R/S_1 - S_1/R = 2(r + dr) = \rho(d_3 - d_4),$$

from which

$$\rho = \frac{2dr}{(d_3 - d_4) - (d_1 - d_2)},$$

therefore

$$r = \frac{dr(d_1 - d_2)}{(d_3 - d_4) - (d_1 - d_2)},$$

the value of  $dr$  being  $\left(S - \frac{S}{S + 100}\right)$ .

This gives for  $R$  the value  $S(1 + r)$ , where  $S$  is the known standard. The value of  $\rho$  was obtained a number of times, both by myself and a number of the students. The values obtained since 1897 are in ohms—·001022, ·001015, ·001019, ·001011, ·001028, ·001028.

This gives a mean value of ·001020 ohm per division for bridge-wire C.

The following is a list of the standard 1-ohm coils used in the comparisons. Each coil had a certificate signed by the secretary of the Electrical Standards Committee, and dated either in 1892 or 1893.

#### LIST of Certified Standards.

##### PLATINUM-SILVER Wire Coils (embedded in Paraffin Wax).

No. 3565	certificate,	·99957	true ohm at	16·4.
„ 3566	„	·99960	„	16·5.
„ 3567	„	·99949	„	16·4.
„ 3568	„	·99961	„	16·5.
„ 3569	„	·99964	„	16·5.
„ 3402	„	·99971	„	16·7.
„ 3403	„	·99967	„	16·5.
„ 3404	„	·99970	„	16·7.
„ 3405	„	·99960	„	16·3.
„ 3406	„	·99960	„	16·3.

##### MANGANIN Wire Coil (in Oil-bath).

No. 4086 certificate, ·99978 true ohm at 15·9.

##### REICHSANSTALT Standard.

No. 1214 marked 1 true ohm at 20° C.

From 3565 to 3406 each ohm was of the older form, with the wire embedded in paraffin wax and made to insert in a water-bath, with long heavy wire connectors for the terminals of the Carey-Foster bridge. No. 4086 was the best form to use with the bridge, as the method of having the other coils always in paraffin wax is bad, and it is never possible to know exactly the true temperature of the coils. The German standard was evidently made of manganin wire on account of its very small temperature coefficient. Unfortunately coil 4086, to which all of my results were referred ('B.A. Report,' 1899), seems to be different to the others by as much as 6 parts in 10,000. It is difficult to see how it could have been injured in any way since it came into the possession of this laboratory, and, as will be seen presently, the comparisons of this ohm with both of the specially constructed platinum-silver ohms does not indicate any possible change since May, 1898. The cause that has been at work to alter its resistance has left it entirely unaffected during the last two years.

Two tables of comparisons are now given of all the 1-ohm coils. The first set in Table VII. was taken by myself and expresses all the ohms, except 3566 and 1214, in terms of 4086. For the second set in Table VIII. I am indebted to Mr. FRASER. For reducing the values of the ohms to one temperature, temperature coefficients were used which were obtained either by myself or Mr. FRASER in duplicate by special experiment, and verified repeatedly by the students. All the platinum-silver standard ohms were found to have the coefficient  $+ \cdot 000254 t^{\circ}$ .

The manganin ohms 4086 and 1214 were found to have the coefficients  $+ \cdot 000018$  and  $+ \cdot 000022$  respectively.

The different columns of Table VII. are arranged so that the first gives the number of the ohm, the second the certified resistance at temperature given in the third column, and the fourth column gives the length of bridge-wire multiplied by  $\cdot 001020$  to reduce to ohms, which represents the difference in resistance between each ohm and No. 4086. In the fifth column is given the temperature of the different ohms during the comparison, and in the sixth the temperature of 4086. The seventh column contains the value of 4086 at the temperature of comparison found from the certified value by the temperature coefficient. As all the platinum-silver standard ohms were larger than 4086, the eighth column is obtained by adding columns 4 and 7. This gives the resistance of each ohm in terms of 4086. In the last column, for comparison, I give the value of each ohm in terms of its own certificate, and corrected to the temperature of comparison in column 5 by the temperature coefficient. The values in the eighth column in terms of 4086 are all systematically smaller than the values in the ninth column, whereas they should be equal. The observations differ amongst themselves somewhat, but they are as good as can be expected from the difficulty of knowing the true temperature of the coils embedded in the wax.

In all these tests the standard ohms were left for several hours near the place of test, so that they could assume, as nearly as possible, the temperature of the air.

TABLE VII.—Comparison of 1-ohm Standards in Terms of 4086.

Number of standard.	Resistance by certificate.	Temperature when certificate is correct.	Difference in ohm from 4086.	Temperature of standards during test.	Temperature of 4086 during test.	Resistance of 4086 by certificate.	Resistance of standards in terms of 4086.	Certified resistance corrected by temperature coefficient.	Difference involving error.
3565	.99957	16.4	+ .000370	21.4	21.6	.99988	1.00025	1.00089	.00064
3567	.99949	16.4	+ .000565	22.0	21.8	.99989	1.00046	1.00091	.00045
3568	.99961	16.5	+ .000483	21.4	21.7	.99989	1.00037	1.00085	.00048
3569	.99964	16.5	+ .000657	21.8	21.8	.99989	1.00055	1.00099	.00044
3402	.99971	16.5	+ .000545	21.7	21.8	.99989	1.00044	1.00103	.00059
3403	.99967	16.5	+ .000616	21.6	21.8	.99989	1.00051	1.00096	.00045
3404	.99970	16.7	+ .000555	21.7	21.8	.99989	1.00045	1.00098	.00053
3405	.99960	16.3	+ .000482	21.6	21.7	.99989	1.00037	1.00095	.00058
3406	.99960	16.3	+ .000565	21.7	21.8	.99989	1.00046	1.00097	.00051

TABLE VIII.—Comparison of 1-ohm Standards in Terms of 3569.

Number of standard.	Resistance by certificate.	Temperature when certificate is correct.	Difference in ohm from 3569.	Temperature of standards during test.	Temperature of 3569 during test.	Resistance of 3569 by certificate.	Resistance of standards in terms of 3569.	Certified resistance corrected to temperature of test.	Difference involving error.
3565	.99957	16.4	- .00015	13.3	13.3	.99883	.99868	.99878	- .00010
3566	.99960	16.5	- .00010	13.1	13.1	.99878	.99868	.99874	- .00006
3567	.99949	16.4	- .00026	13.1	13.1	.99878	.99852	.99865	- .00013
3568	.99961	16.5	- .00009	13.3	13.3	.99883	.99874	.99880	- .00006
3402	.99971	16.7	- .00009	13.0	13.0	.99875	.99866	.99877	- .00011
3403	.99967	16.5	+ .00008	13.3	13.3	.99883	.99891	.99886	+ .00005
3404	.99970	16.7	- .00010	13.3	13.3	.99883	.99873	.99884	- .00011
3405	.99960	16.3	- .00010	13.3	13.3	.99883	.99873	.99884	- .00011
3406	.99960	16.3	- .00005	13.2	13.2	.99880	.99875	.99881	- .00006
4086	.99978	15.9	+ .00145	14.8	13.6	.99890	1.00035	.99976	+ .00059
1214	1.0000	20	+ .00098	14.1	13.7	.99893	.99991	.99988	+ .00003

A thermometer placed in the hole extending through the middle of the embedded coil was taken as the temperature of the coil. As No. 4086 was arranged with a stirrer, a thermometer could be placed in the oil in contact with the coil, and the true temperature obtained. The current used on the bridge was not sufficient to cause perceptible heating.

Table VIII. contains the comparisons of the ohms, at an entirely different temperature. These tests were made in the basement of the building, where the temperature was considerably lower than where the tests in Table VII. were made. In this case also the coils remained at least a day or two at the temperature of test, and did not vary to any extent from that. The table is arranged as in Table VII., only the comparisons were made in terms of No. 3569. This shows a very good agreement of all the platinum-silver standard ohms, including the Reichsanstalt ohm, 1214, but shows that by assuming the corrections of 3569, the value of 4086 is very much above that given in its certificate. This difference indicates an error of  $\cdot 00059$  ohm assuming 3569 as correct, or  $\cdot 00065$  referred to the mean of all the ohms. In Table VII. we saw that the platinum-silver ohms were all lower than their certified values when calculated assuming 4086 to be correct, the mean difference being  $\cdot 00052$ . These differences are both in the same direction as regards the relationship of 4086 to the other ohms. The difference of 1 in 10,000, obtained by Mr. FRASER and myself between the two values, *i.e.*,  $\cdot 00065$  and  $\cdot 00052$ , must be ascribed to the wide difference in temperature of our respective tests, as well as to the uncertainty of knowing accurately the true temperature of the paraffin-embedded coils.

We are forced now either to accept the certificate of 4086, and reject all the other 11 ohms as being in error, including the Reichsanstalt Standard, or to reject the certificate of 4086, and accept the certificates of all the others. The alternative of giving 4086 equal weight in the mean seems to be hardly justifiable considering the mass of evidence against it.

I have decided to reject the certificate of 4086, and I have accordingly corrected it in the following way: in terms of the platinum-silver standard ohms, 4086 is equal to its certified value  $+\cdot 00052$  by the comparison made at  $22^{\circ}$  C. By the comparison made at  $13^{\circ}$  C. it becomes equal to its certificate  $+\cdot 00065$ . By comparing directly with 1214, the value of 4086 becomes equal to its certificate  $+\cdot 00056$  in one test, and  $+\cdot 00061$  in another test, or equal to  $+\cdot 000585$  in the mean. This agrees very closely with the mean value of the two separate determinations with the other ohms, which comes out  $+\cdot 000585$ . We may, I think, then safely assume that the value of 4086 is equal to its certified value  $+\cdot 00058$ , which comes out  $\cdot 99978 + \cdot 00058$  at  $15^{\circ}\cdot 9$ , or  $1\cdot 00036 + \cdot 000018$  ( $20^{\circ} - 15^{\circ}\cdot 9$ ), or equal to  $1\cdot 00043$  true ohms at  $20^{\circ}$  C.

A summary of the various comparisons made of the two new platinum-silver ohms is given in Table IX. in terms of 4086, assuming for convenience that it is exactly 1 ohm at  $20^{\circ}$  C. The resistance of each ohm is reduced to  $20^{\circ}$  C. in column 4 of each

set by means of the temperature coefficient found from the tests given in Table X. Most of the comparisons up to September 10, 1898, were made by Mr. SHEFFIELD, and from that date on, by myself. The maximum variation from the mean is  $5 \times 10^{-5}$  ohm, and is within the limits of error for a series of comparisons such as these. As a rule the agreement is very much closer than this. Taking the value of 4086 as equal to 1.00045 true ohms at 20° C. in place of the value assumed for calculation in the table, we find Coil 1,  $1.00132 + .00043 = 1.00175$  true ohms at 20° C., and Coil 2, 1.00043 ohms. At any other temperature the coefficients  $+ .000250$  for Coil 1, and  $.000246$  for Coil 2, are used, which were obtained from the experiments detailed in Table X.

The value of the two 1-ohms in parallel is very easily determined on a small slide-rule, by assuming the ohms equal to  $(1 + d_1)$  and  $(1 + d_2)$  respectively, where  $d_1$  and  $d_2$  are equal to the small differences from unity, then

$$\frac{(1 + d_1)(1 + d_2)}{(1 + d_1) + (1 + d_2)} = .5 + \frac{\frac{1}{2}(d_1 + d_2)}{2 + d_1 + d_2},$$

neglecting products and powers of  $d_1$  and  $d_2$ .

At 20° C. the value of the fraction is

$$R = .5 + \frac{.00109}{2.0021} = .500544 \text{ ohm.}$$

At 10° C., when No. 1 is equal to  $(1 - .00077)$ , and No. 2  $(1 - .00205)$ ,

$$R = .5 - \frac{.00141}{1.99718} = .499294 \text{ ohm.}$$

We may accept then for calculation the most probable value of the two platinum-silver ohms in parallel to be

$$.500544 \text{ true ohm at } 20^\circ \text{ C., } .499294 \text{ true ohm at } 10^\circ \text{ C.,}$$

where one true ohm = 1.01358 B.A. unit, as given in all the certificates of the standard ohms.

*Current Heating.*—It is a matter of importance to determine the true resistance of the two coils when the maximum current used in these experiments was passed through. For the largest flows of water, when the largest heating current was required, this amounted to 8 amperes. This current was divided between eight .4-millim. platinum-silver wires immersed bare for their entire length, about 1 metre, in oil, which was vigorously stirred. Each wire was required to carry then only 1 ampere, or develop only 4 watt-seconds heat energy. It was impossible to imagine that the temperature of the wire could have been sufficiently different to that of the oil to appreciably affect the resistance. A difference of .1° between the wire and oil



TABLE IX.—Comparison of Platinum-Silver ohms, with 4086 taken as 1 ohm at 20° C.

Date of comparison.	Coil 1.			Coil 2.		
	Temperature of comparison.	Resistance at temperature of comparison.	Resistance corrected to 20° C.	Temperature of comparison.	Resistance at temperature of comparison.	Resistance corrected to 20° C.
1898.						
May 26th . . .	19·2	1·00113	1·00133	19·4	·99983	·99999
„ 28th . . .	20·9	1·00158	1·00136	20·9	1·00017	·99995
„ 31st . . .	20·8	1·00146	1·00127	20·9	1·00021	·99999
June 11th . . .	16·9	1·00053	1·00131	18·1	·99956	1·00002
„ 25th . . .	20·8	1·00147	1·00128	20·9	1·00023	1·00001
September 10th .	19·1	1·00112	1·00133	19·2	·99981	1·00000
1899.						
February 22nd .	15·6	1·00022	1·00132	15·9	·99900	1·00000
May 8th . . .	17·5	1·00071	1·00133	17·6	·99939	·99998
August 9th . . .	19·4	1·00118	1·00133	19·5	·99988	1·00000
September 21st .	17·0	1·00059	1·00134	17·0	·99930	1·00003
October 4th . . .	15·2	1·00016	1·00135	15·3	·99889	1·00004
1900.						
May 26th . . .	16·9	1·00056	1·00133	16·8	·99926	1·00005
Means . . . . .	18·27	—	1·00132	18·46	—	1·00001

Observer, SHEFFIELD.  
Observer, BARNES.

TABLE X.—Temperature Coefficient of Platinum-Silver ohms.

Coil 1.			Coil 2.		
Temperature of Pt-Ag coil.	Difference from 4086 at 20° in ohms.	Calculated from curve.	Temperature of Pt-Ag coil.	Difference from 4086 at 20° in ohms.	Calculated from curve.
21·1	+·001590	+·001590	21·0	+·000258	+·000250
14·0	-·000242	-·000200	13·0	-·001741	-·001750
6·5	-·002027	-·002055	6·9	-·003170	-·003220
20·0	+·001337	+·001310	20·3	+·000070	+·000070
19·9	+·001245	+·001290	19·3	-·000190	-·000190
12·8	-·000458	-·000495	14·5	-·001345	-·001375
8·7	-·001346	-·001520	11·4	-·002130	-·002130
5·3	-·002417	-·002370	5·9	-·003497	-·003490

Observer, BARNES.  
Observer, SHEFFIELD.

would have produced an error less than '00002 ohm, or less than 2 parts in 50,000, whereas it is probable the actual difference in temperature did not make an error one-tenth of this amount.

Sec. 3c.—*Measurement of Temperature.*

By far the most important factor that determines the character of the curve for the variation of the specific heat of water with temperature is the particular thermometric scale to which the results are referred. This was most forcibly brought out by ROWLAND in his memoir, and it was pointed out by him that without the greatest care in reducing his mercurial thermometers to the air scale, the value of the specific heat of water would have apparently remained constant in terms of the mercurial scale over the range of his experiments. The discovery of the rapid decrease in specific heat with increase of temperature from 0° to 30° C. was only made through this careful reduction.

In the present series of experiments there were no thermometric difficulties such as are to be met with in the use of a mercurial standard owing to the use of platinum thermometers. In working to the 10,000th part of a degree Centigrade, such corrections as a change of zero, pressure on the bulb, capillary and stem corrections, are so large in the case of the mercurial standard, that for large intervals of temperature the readings are far from reliable. With the platinum thermometer we still have to deal with the question of a change of zero and a stem correction, but these are so small that with sufficient care they may be eliminated altogether.

In speaking of these possible sources of error in connection with the measurement of temperature with the platinum thermometer, I am referring to a limit of accuracy seldom required in most determinations. The first source of error is already well known, and has often been subject of controversy over the reliability of the platinum thermometer, though chiefly, I am convinced, by those who are either prejudiced or who require more experience in this class of work. I have met with no difficulties of this nature that could not be attributed to my own carelessness, or could not be easily avoided with sufficient patience and care. In regard to the second source of error, I have never seen it referred to before in connection with this subject, and will therefore speak about it somewhat further on. We should, strictly speaking, include with the electrical measurements the subject of platinum thermometry. We shall, however, include it with the thermal constants and treat it entirely from that point of view.

The measurement of temperature by the change in resistance of a platinum wire has been carefully studied by Professor CALLENDAR, and his work is already too well known to make it necessary for me to dwell on the fundamental part of it. His introduction of the idea of a platinum temperature which depends on the term,

$$pt = \frac{R_t - R_0}{R_{100} - R_0} \times 100,$$

where  $R_0$ ,  $R_{100}$  and  $R_t$  are the measures of the resistance of any one particular sample of platinum wire at  $0^\circ$ ,  $100^\circ$ , or at a temperature  $t$ , has been now almost universally accepted.

The reduction of the platinum temperature to the air-scale was obtained from a series of comparisons with the nitrogen air thermometer at three fixed points  $0^\circ$ ,  $100^\circ$  and  $444^\circ$ , which led to the well-known parabolic formula,

$$t - pt = \delta \left( \frac{t^2}{100^2} - \frac{t}{100} \right),$$

where  $t$  is the air temperature, and  $\delta$  a constant depending on the purity of the platinum wire, the same for any particular purity of wire.

In selecting the wire for use in the present measurements, I was exceedingly fortunate in possessing a sample of the original wire standardized by Professor CALLENDAR and Mr. GRIFFITHS, who found its  $\delta$  equal to 1.50.

The chief difficulty in selecting a form of thermometer for use in the calorimeter lay in choosing a size of bulb which would give a sufficiently large change in resistance for the rise of temperature produced in the water. On a rise of temperature of  $10^\circ$ , it was necessary to be sure of the measurement to  $\cdot 001^\circ$ , and to obtain the readings to  $\cdot 0001^\circ$  to have them comparable with the accuracy of the other measurements. At the same time it was impossible to have the bulbs too long, as it introduced increased possibilities of error in the outflow-tube of the calorimeter. For the size of wire used ( $\cdot 15$  millim.), and the size of the units in the resistance-box for compensating the change in resistance, it was necessary to use about 4 metres of wire for each thermometer.

The first thermometers made were from some of the original sample of wire, which had been silk covered. Four metres of this wire were coiled up into a bulb, about 6 centims. long, and half a centim. in diameter, which served the purpose very well. Two sets of thermometers were made this way at different times, and will be described further on. The chief difficulty with this form was that, after bending into the coil, the wire could not be annealed well enough. Annealing for a length of time at  $150^\circ$  C. served to give fairly steady results. The difficulty, caused by the exciting current, of heating in the interior of the coiled wire, was also a serious question, which had to be carefully considered.

A pair of thermometers was made for the first tests with the water calorimeter, which were in the usual form of bare-wire wound on a mica frame. To keep the length of bulb within reasonable bounds, it was necessary to have these thermometers only one-half as sensitive as the others. However, this form was far preferable to the other, so that to produce the same sensitiveness as was required, with the most

convenient length of bulb, a smaller wire was adopted than is usually employed for thermometric work. A thermometer was finally obtained which gave the required sensitiveness, and had a length and diameter of bulb quite suitable for the calorimeter. In point of steadiness and accuracy, the two thermometers forming the differential pair made in this way could hardly be surpassed.

I propose to describe the tests made on the various thermometers used during the course of this series of experiments. Before doing so, I must briefly describe the resistance boxes and method used for compensating the change in resistance in the wire due to a change of temperature.

The general plan of WHEATSTONE'S bridge connections for the thermometer-circuit is already familiar. The wires leading to the bulb of the thermometer are compensated for a change in resistance due to a change in temperature by similar wires placed side by side with them, but connected to the opposite arms of the bridge circuit. The change in resistance in the thermometer is compensated by resistance coils on an opposite arm of the bridge, and a final adjustment made on a short bridge-wire, of which the coils are suitable multiples. A change in resistance is referred to a change in units of the box, rather than measured in ohms. It is evident that a change in the temperature of the resistance coils, while compensating a change in resistance in the thermometer, will produce an apparent change in the thermometer reading. This can be corrected for either by taking the temperature of the coils in air, or by immersing them in oil at a constant temperature. For very accurate work, however, it is better to introduce a different arrangement. If each resistance coil on the bridge is wound with another coil, which has the same temperature coefficient, but a different specific resistance, then if these second coils are connected with an opposite arm of the bridge system, any change in temperature of the bridge coils cannot affect the balance point on the bridge wire. This method, which was devised by Professor CALLENDAR, works exceedingly well.

Through the kindness of Professor CALLENDAR I have had the use of such a compensated resistance box throughout the greater part of my measurements. This box was exhibited to the Royal Society in June, 1893, by Professor CALLENDAR. Besides the compensated resistance coils, the special features of this box are the bridge-wire scale, which has a compensating device for a change in length due to a change in temperature, so that the galvanometer contact point always reads at the same point on the scale, and mercury cup contacts for each set of coils. The resistance coils were multiples of the bridge-wire, commencing from the smallest coil, which was equivalent to 10 centims. of bridge-wire, and doubling always as the coils became larger, *i.e.*, 10, 20, 40, 80, 160, &c., up to 2580. The resistance of the bridge-wire was  $\cdot 0088$  ohm per centim., so that the ten coil was rather less than  $\cdot 1$  ohm. The bridge-wire scale was of brass, very carefully divided to half-millims., and supplied with a vernier with lens reading to  $\cdot 01$  millim. The total length of bridge-

wire was 40 centims., but it could be read only between 6 and 34 centims., leaving a margin of 6 centims. at each end.

Professor CALLENDAR was kind enough to allow me to make a resistance box after this design. This box I have used in my later determinations of the specific heat. It differs from Professor CALLENDAR'S box in having a slightly greater unit, *i.e.*, 1 centim. of bridge-wire equal to .0095 ohm, and the coils were made from bare wire wound on mica frames and annealed. Solder joins were avoided between the wire forming the resistance coils and the copper connecting wire, by fusing directly to the copper.

Each of the larger coils, before putting in place in the box, was tested for compensation in a specially constructed oil-bath, the temperature of which could be changed quickly at will in a way similar to the paraffin-bath used in the standard resistance determinations. Each coil was also made of either two or three wires in parallel, .15 millim. in diameter, so as to avoid current heating. They were specially designed for immersion in oil when in place in the box, but this was not found necessary. It was not deemed necessary to test the small coils, from 10 to 40, for compensation, as the test of the larger coils showed that the calculation of the lengths of wire necessary was so nearly correct as to leave little room for error in the smaller coils over a wide range of temperature. The ratio coils in the box were made from .15-millim. platinum-silver wire wound in parallel on a mica frame, and were adjusted to equality on the Thomson-Varley slide box. The resistance coils were connected to mercury cups and short-circuited when not in use by thick copper connectors.

The calibration of these boxes consists in determining the errors in the different box coils and the calibration of the bridge-wire and scale.

In determining the total change in resistance of the thermometers between 0° and 100°, which is termed the fundamental interval, or briefly F.I., the largest that it was necessary to use was coil 640. It is evident that, provided this coil is accurately compensated, it is the best one to which to refer the F.I. It is entirely unnecessary to know its absolute value in ohms provided we assume it equal to 640 even units, and refer the other coils, including the bridge-wire, to it.

From 640 down every coil differs from the sum of all the rest by very nearly 10 centims. of bridge-wire, or the size of the smallest coil. If we compare the lengths of bridge-wire obtained by differencing the coils in this way, we obtain the usual series of equations of the form

$$640 - \text{sum}_1 = \alpha_1; 320 - \text{sum}_2 = \alpha_2; 160 - \text{sum}_3 = \alpha_3, \text{ \&c.,}$$

where  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  are very nearly 10 centims. and involve the coil errors.

If we eliminate the sum from any two equations, remembering that the next lowest sum differs from the one before by the lesser coil, then we have a series of the form

$$640 - 2 \times 320 = a_1 - a_2; \quad 320 - 2 \times 160 = a_2 - a_3, \text{ \&c.},$$

which should equal 0 if  $a_1 = a_2 = a_3$ .

If we let the error in 640 be equal to 0, then the error in  $320 = \frac{1}{2}(a_1 - a_2)$  in terms of 640 even units,

$$160 = \frac{1}{2} \left\{ \frac{1}{2}(a_1 - a_2) - a_2 - a_3 \right\},$$

and so on for all the coils.

The error in the bridge-wire, which we will call the bw. correction, is determined from the error in coil 10 obtained in terms of 640 even units. The calibration of the bridge-wire was done by inserting a small resistance, equal to about 3 centims. of bridge-wire, into the bridge circuit, so that by short-circuiting it by a heavy copper connector placed in mercury cups, the bridge-wire reading could be shifted the same amount at any part of the wire. The reading was found to vary .0005 centim. per centimetre on either side of the middle point, 19, in such a way as to increase towards 30 and decrease towards 0. This showed that the wire was slightly smaller towards the zero end, and hence its resistance greater. As the equivalent length of 10 centims., obtained in the calibration of the box coils, never occurred at exactly the same spot on the bridge-wire, there is a small correction to be applied to the values of  $a_1$ ,  $a_2$ , and  $a_3$ , due to their position. The correction is worked out so as to reduce the values to a length of bridge-wire extending over the middle point, between 14 and 24. The correction is very small, however, and would produce no appreciable error to the results if neglected altogether. In my own box the agreement of the equivalent length for the 10 coil above and below the middle point of the bridge-wire caused me to neglect this correction altogether.

In Table XII. I give a complete series of readings taken to determine the coil corrections in the first box. In Table XIII. a summary of tests is given extending over a period of a year.

Table XIV. contains the same obtained for my own box. The corrections in this latter case are somewhat larger. The reason being that it was more difficult to adjust the coils exactly when fused joints were used instead of solder, and at the same time preserve complete compensation. My aim was to be sure of having this latter condition fulfilled at the expense of the former, as the coil correction is always a definite and measurable quantity, and easy to apply.

The signs are affixed to the corrections in the way they should be applied to the reading. The bridge-wire correction is given per centimeter of length. In taking the readings the galvanometer was used which has already been referred to in connection with the comparison of the standard resistances. The sensitiveness was obtained so as to give from 40 to 50 scale divisions per millimetre of bridge-wire on reversing the current. For the small coils an external resistance of 350 ohms was

TABLE XII.—Set of Readings for determining Box Coil Corrections.

Coils.	640-sum.	320-sum.	160-sum.	80-sum.	40-sum.	20-sum.	10-sum.
Reading of bridge-wire . . . . .	24·979	21·970	20·645	19·711	25·113	27·640	28·787
Equivalent length . . . . .	14·950	12·096	10·631	9·815	15·135	17·624	18·911
Correction to mean bridge-wire	10·029	9·874	10·014	9·896	9·978	10·016	9·876
Corrected length . . . . .	0	+·002	+·003	+·004	-·001	-·002	-·004
Differences, 640-2 × 320, &c. .	10·029	9·876	10·017	9·900	9·977	10·014	9·872
Correction in terms of 640 coil	—	+·153	-·141	+·117	-·077	-·037	+·142
	0	-·077	+·032	-·043	+·017	+·027	-·057

TABLE XIII.—Box Coil Corrections in Terms of 640 even Units. Box 1.

Date.	320.	160.	80.	40.	20.	10.	Bridge-wire.
1898.							
May 6th . . . . .	-·087	+·027	-·038	+·021	+·034	-·050	+·008
„ 21st . . . . .	-·072	+·028	-·038	+·018	+·026	-·055	+·007
„ 25th . . . . .	-·077	+·027	-·036	+·017	+·028	-·051	+·007
1899.							
January 7th . . . . .	-·055	+·033	-·044	+·019	+·030	-·051	+·007
„ 9th . . . . .	-·063	+·040	-·042	+·020	+·030	-·050	+·007
„ 12th . . . . .	-·069	+·029	-·045	+·019	+·024	-·055	+·008
April 27th . . . . .	-·077	+·032	-·043	+·017	+·027	-·057	+·007
Means . . . . .	-·071	+·030	-·040	+·019	+·029	-·053	+·007

TABLE XIV.—Box Coil Corrections in Terms of 640 even Units. Box 2.

Date.	320.	160.	80.	40.	20.	10.	Bridge-wire.
1900.							
February 10th	-·029	-·054	+·210	+·144	-·033	-·074	+·0066
„ 13th	-·025	-·048	+·210	+·149	-·030	-·071	+·0061
„ 26th	-·030	-·053	+·208	+·149	-·031	-·072	+·0062
Means . . . . .	-·028	-·052	+·210	+·148	-·032	-·072	+·0064

required, which was reduced gradually to 150 ohms for the 640 coil in order to preserve the same sensitiveness throughout the test, with one accumulator. The galvanometer contact was arranged so that it could be held in contact with the bridge-wire. Therefore instead of obtaining an exact balance and reading the vernier, the contact was placed to the nearest millimetre or half-millimetre mark on the scale, with the help of the vernier, and the deflection of the galvanometer recorded. Accurate account was always kept, by repeated verification, of the sensitiveness of the galvanometer, which never altered as much as one scale division due to external disturbances.

For the sake of convenience, the diagram of the complete thermometer circuit is given in fig. 6. This shows the relative position of the resistance and compensating coils in the bridge system, the position of the ratio coils and bridge-wire. When

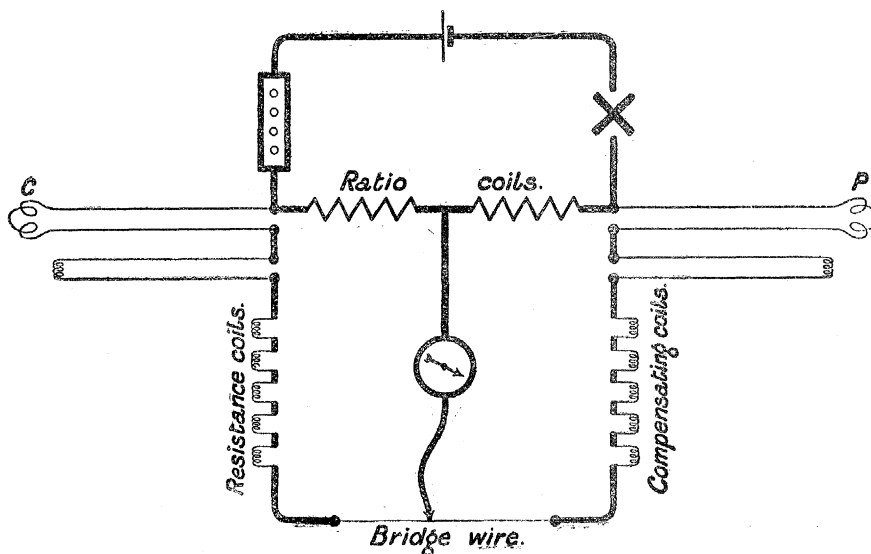


Fig. 6.

differential thermometers are used we have them connected on opposite arms of the bridge, at P and C, and arranged so that the compensating leads for thermometer P are in series with thermometer C, and the compensating leads for C connected with P. Where P and C are at the same temperature, and of the same resistance, it is evident that the bridge system is in equilibrium with the galvanometer contact at the middle of the bridge-wire. For a change in the temperature of either P or C the bridge reading shifted either to the right or left, and when too great to be read on the wire, was compensated by the resistance coils. A change of temperature in C higher than P, however, could not be recorded beyond the bridge-wire. It was therefore necessary to arrange that P should always be used for measuring a change in temperature higher than C. The resistance coils were brought into the circuit by removing the heavy copper contacts from the mercury cups. When these contacts



were removed, the contacts of each corresponding compensating coil were removed at the same time. To obtain the fundamental constant ( $R_{100} - R_0$ ) or interval, F.I., both C and P are balanced when immersed in melting ice, and then with C in ice and P in steam. To obtain the difference between the intervals of the two thermometers both are read when in steam. This gives the data required for converting into degrees a change of resistance in P relative to C.

During the progress of the present experiments, five pairs of differential thermometers were made and tested. In describing these, I shall letter them A, B, C, D, and E, respectively. The thermometers of pair A were made of the original silk-covered .15-millim. platinum-wire, about 25 ohms resistance each. The bulb of each thermometer was about 6 centims. long and was fastened by solder joints to flexible copper leads placed side by side with compensating leads. The protecting tube was of glass, about 25 centims. long and a few millims. in diameter. The ends of the compensating leads near the bulb were connected by a small piece of platinum-wire about 4 centims. long. This was to correct any conduction error on the wire in the thermometers by heat conduction from the leads. This device was also used for all the other thermometers.

Thermometer B was made of  $12\frac{1}{2}$ -ohms resistance, or one-half the sensitiveness of the other pair. Each thermometer of the pair was wound in the usual way on a mica frame, from the 6-millim. bare platinum-wire, and annealed at a low red heat. As these thermometers proved eventually to be too bulky for convenience in the calorimeter, they were soon discarded. It will, therefore, not be necessary to give them further mention.

Thermometer C was made from a pair of silk thermometers similar to A. The platinum-wire was fused to copper-wires, which in turn were soldered to copper leads. These thermometers proved satisfactory in many ways, although they finally gave trouble from defective insulation and had to be abandoned. These thermometers were used in our first preliminary measurements of J during the summer of 1898.

Thermometer D was the first pair made from .10-millim. platinum-wire. This wire was some sent out to Mr. R. O. KING by the Cambridge Scientific Instrument Company. Its  $\delta$  was given as 1.50, which was subsequently verified by Mr. TORY in the course of his work. Each thermometer was about 20 ohms. in resistance, and was made by winding on a mica frame. The bulb was about 5 centims. long and between 6 and 7 millims. in diameter. Owing to the inconveniently small F.I. of this pair of thermometers (about 700 units of the box instead of 1000 for 100° C.), it was supplanted by pair E.

Thermometer E is by far the most important pair, as with it all the later measurements of the specific heat were obtained. The wire used in making each thermometer of the pair was drawn down to .10 millim. from the original 6-millim. platinum-wire. The resistance of the thermometers was about 25 ohms each, and gave a F.I. about 970 units of the box. The bulbs were about 7 millims. in diameter and about

6½ centims. long, and were made, as in thermometer D, of the bare wire wound on a mica frame. The first arrangement was with the platinum-wire fused to about No. 18 copper-wire, which in turn was soldered to the copper leads about 6 centims. above the bulb. This was changed to having the wire fused to much longer copper-wires, which were soldered to the leads at a point considerably beyond the glass-tubes containing the bulbs. This avoided the changing of the temperature of the solder-joints in the glass-tube. The final arrangement was to have the wire gold-soldered to heavy platinum-wires, which in turn were fused to copper-wires about 6 centims. above the bulbs. These wires were then soldered to the main leads at a point sufficiently beyond the glass-tube so as to remain unaffected by a change in temperature in the interior of the glass-tube. All these changes were made to improve the thermometers, although the last one was not really necessary. A very considerable uncertainty was introduced with the first arrangement, which was removed on removing the solder-joints from the interior of the thermometer-tubes.

The .10-millim. wire is exceedingly delicate to use for thermometric work, and great care had to be exercised in constructing the thermometers and in handling them. They gave, however, exceedingly consistent results. As a check, a sample of the wire was given to Mr. TORY, who very kindly determined its  $\delta$  by comparing it with a piece of the original .15-millim. wire. This came out 1.502, and showed that no change had been produced in the  $\delta$ , due to its having been drawn from the larger size.

The fixed points 0° and 100° upon which the accuracy of the F.I. depends, were obtained as usual with a mixture of finely-cracked ice and water, and the usual form of hypsometer. In regard to the constancy of these points, the former depends on the percentage of ice or water present in the mixture, and its rate of melting, while the latter depends on the accuracy of reading of the barometer, accepting in both cases the purity of the ice or water. Great care was always taken with the freezing-point mixture, to have it compact and firmly placed in a copper vessel, heavily lagged, and in which water could be made to circulate through the ice around the thermometer bulbs. The thermometers were as far as possible placed side by side, separated only by a thin partition of ice.

After obtaining the balance-point with both thermometers in ice, one, P, was removed to the steam-jacket, leaving the other, C, still in ice. The change in resistance in P was compensated by the resistance-coils until the reading was brought on to the bridge-wire. When a sufficient time was allowed (about 15 minutes was generally sufficient) for the attainment of a steady temperature, as shown by the steadiness of the balance-point, the reading of the bridge-wire was recorded. Thermometer P was then returned to the ice-bath, and the first reading repeated, which gave a measure of any change of zero in P. The sensitiveness of the galvanometer changed slightly between the two points owing to the increase in resistance in the two arms of the bridge system, but this was determined always at both points.

In the tests to be described, an external resistance of at least 40 ohms was inserted in the battery circuit, which was supplied from one accumulator. The current was never as much as .02 ampere in each thermometer, and current-heating could be safely neglected. In view, however, of a possible effect of current-heating on the differential readings, the F.I. of thermometer D was determined for different external resistances, but no effect could be measured. The current was left continuously running during a test, and was always the same as that used in the calorimetric experiments.

Three Fortin barometers, supplied by ELLIOTT BROS., of London, were used to obtain the steam-point. They were Nos. 571, 572, and 573. They had all been filled originally by ELLIOTT. During the preliminary part of the experiments, barometer 572 was used, but owing to an accident was replaced later by 571. Barometer 571 was, however, re-filled later as a check, by boiling out with mercury, and was compared with 573, to which most of the later steam readings were referred. As a check also the scale of barometer 572 was verified, and found correct to within .1 millim. This was of sufficient accuracy for the determination of the F.I., as the mercury height could be measured accurately only to .1 millim. with the vernier supplied with the scale. It was possible to estimate to .02 millim. with a little care.

A comparison of 572 re-filled with 573, made on February 26, 1900, is given below.

No. 573, 75.415 centims.,  $t = 17.5$ ; No. 572, 75.410 centims.,  $t = 17.3$ .

Second setting,

No. 573, 75.415 centims.; No. 572, 75.400 centims.

The temperature of the mercury column was taken from a thermometer embedded in the barometer case. I decided to adopt the readings of the highest barometer as likely to be most accurate. It is probable that barometer 573 was correct to .01 centim. in its readings over different dates. An error of .01 centim. in setting and reading the height of mercury would produce an error of about .004° on the steam point, which is about the order of agreement given in the measurement of the F.I. from time to time. In repeating readings of the F.I., where it was not necessary to alter the setting of the barometer, much closer agreement than this was attained. The barometer readings were reduced to 0° C. and latitude 45°, and corrected for temperature by the formula

$$H_0 = H(1 - .0001614t)(1 - .000033) + .0002t \text{ centim.}$$

The essential scheme followed for the determination of the F.I. has already been laid down. The following tables contain the results of the tests made on the different instruments used in these experiments. Owing to the importance attached to thermometer E, it is given first place. For this thermometer it will be necessary to divide the tests into four groups.

Group I. contains the results when the .10-millim. platinum-wire is fused to short copper-wires, which in turn are soldered to the leads *inside* the glass-tubes of the thermometers, so that the solder-joints are subject to the temperature change  $0^{\circ}$  to  $100^{\circ}$ .

Group II. gives the tests when the solder-joints inside the glass-tubes were done away with.

Group III. contains the results in the case when the .10-millim. wire was gold-soldered to heavy platinum-wire, which was fused to the copper leads.

Group IV. contains the determination of F.I. in terms of the second box. It comes smaller owing to the resistance of the unit being greater than in the first box.

In Group I. the variation from the mean value is somewhat larger than the errors of reading the barometer, amounting in the extreme case to  $.007^{\circ}$ . This was attributed to an uncertainty in the solder joins.

Group I.—Coils  $640 + 320 + 10 = 969.876$  units. Thermometer E.  
10 units =  $1^{\circ}$  C. nearly. Box 1.

Date.	Bridge-wire corrected.	Total units.	Barometer corrected.	F.I. corrected to 76.00 centims.
February 24, 1899 . . . . .	+2.964	972.840	76.196	97.2141
"   24   "   . . . . .	+4.597	974.473	76.630	97.2217
"   27   "   . . . . .	-1.396	968.480	74.938	97.2260
"   28   "   . . . . .	-2.022	967.854	74.789	97.2162
"   28   "   . . . . .	-2.399	967.477	74.683	97.2160
Mean . . . . . 97.2188				

Group II.—Coils  $640 + 320 + 10 = 969.876$  units. Thermometer E.  
10 units =  $1^{\circ}$  C. nearly. Box 1.

Date.	Bridge-wire corrected.	Total units.	Barometer corrected.	F.I. corrected to 76.00 centims.
May 15, 1899. . . . .	+3.006	972.882	75.985	97.2935
"   15   "   . . . . .	+2.495	972.371	75.844	97.2926
"   18   "   . . . . .	+1.669	971.545	75.616	97.2916
August 10, 1899. . . . .	+1.302	971.178	75.492	97.2991
"   10   "   . . . . .	+1.279	971.155	75.485	97.2993
September 11, 1899. . . . .	+2.320	972.196	75.792	97.2939
"   11   "   . . . . .	+2.211	972.087	75.760	97.2944
"   21   "   . . . . .	+0.670	970.546	75.314	97.2993
Mean . . . . . 97.2955				

In Group II. the agreement is much better, and it can hardly be said that the variations can be attributed to other causes than the setting of the barometer. For tests made on the same date, where the interval was repeated with but a small change in barometric reading, which could be followed by the vernier without other adjustments, the readings are as a rule exceedingly consistent.

The two tests in Group III. are given in full.

Group III. Date, September 26, 1899.

First determination.

Both in ice, reading of bridge-wire . . . 23·173. No coils.  
 C in ice ; P in steam . . . . . 23·757 + coils, 640 + 320 + 10.

Second determination.

Both in ice, reading of bridge-wire . . . 23·175, 23·172. No coils.  
 C in ice ; P in steam . . . . . 23·646 + coils, 640 + 320 + 10.  
 Both in steam . . . . . 25·143. No coils.

Barometer in first determinations. Uncorrected, 75·073 centims. at temp. 18°·9 ; corrected, 74·851.

Barometer in second determinations. Uncorrected, 75·092 centims. at temp. 18°·8 ; corrected, 74·870.

	In first determination.	In second determination.
Bridge-wire . . . . .	— 0·584	— 0·473
Bw. correction . . . . .	4	3
	— 0·588	— 0·476
Coils . . . . .	969·876	969·876
	969·288 in box units.	969·400 in box units.
Barometer correction . . . . .	+ ·4093°	+ ·4025°
F.I. . . . .	97·3381 in degrees.	97·3425 in degrees.
Mean value . . . . .	97·3403.	

Group IV.—Coils 640 + 160 + 80 + 20 = 900·128 units.

9 units = 1° C nearly. Box 2.

Date.	Bridge-wire corrected.	Total units.	Barometer corrected.	F.I. corrected to 76·00 centims.
February 14, 1900 . . . . .	+4·143	904·271	75·778	90·5009
„ 14 „ . . . . .	+2·195	902·323	75·191	90·5006
„ 16 „ . . . . .	+4·307	904·435	75·816	90·5037
„ 16 „ . . . . .	+4·328	904·456	75·838	90·4994
„ 16 „ . . . . .	+4·361	904·489	75·846	90·5002

Summarizing we have the F.I.'s of thermometer E, as measured by the two boxes, as follows:—

Group I.—97·2188	measured with 1st box.
„ II.—97·2955	„ „ „ „
„ III.—97·3403	„ „ „ „
„ IV.—90·5009	„ „ 2nd „

This gives the corrections to be applied to the readings to make 100 10-units equal to 100° on the platinum scale:

Group I.—2·8610 per cent.	Group III.— 2·7324 per cent.
„ II.—2·7795 „	„ IV.—10·4962 „

The difference in the corrections, with the exception of Group IV., is due to the change in the lengths of the thermometer wire in changing the leads. No change was made to the thermometers themselves between Groups III. and IV.

The various tests on the other thermometers are given now as under. With thermometer D no difference could be noted in the F.I. measured with 80 ohms in the external circuit, or with 50 ohms. The tests with thermometer A are important as illustrating the results to be obtained from silk-covered wire thermometers, and also as they were the thermometers used in the mercury experiments.

#### THERMOMETER A. Box 1.

Date.	F.I. corrected.
May 22, 1897 . . . . .	99·9327
„ 24 „ . . . . .	99·9245

With thermometer C, also silk-covered thermometers, the tests are not so satisfactory.

#### THERMOMETER C.

Date.	F.I. corrected.	Date.	F.I. corrected.
April 30, 1898 . . . . .	101·4031	July 11, 1898 . . . . .	101·3908
May 2 „ . . . . .	101·3931	August 8 „ . . . . .	101·4006

## THERMOMETER D. Box 1.

Coils 640 + 160 = 800.030 units.

8 units = 1° C., nearly.

With 80 ohms external circuit.

Date.	Bridge-wire corrected.	Total units.	Corrected barometer.	F.I. corrected to 76.00 centims.
July 21, 1898 . . . . .	- 4.679	795.351	75.806	79.5924
” ” . . . . .	- 4.655	795.375	75.816	79.5913
” ” . . . . .	- 4.614	795.416	75.826	79.5925
With 50 ohms external circuit.				
” ” . . . . .	- 4.651	795.379	75.816	79.5917

All these fundamental intervals, of course, only apply to thermometer P of each pair, or the one which is used to determine the rise of temperature in the water.

No separate determinations are required when both the thermometers are at the same temperature over the scale between 0° and 100°. The correction is simply to thermometer P in its reading relative to thermometer C, when the water is heated through so many degrees in the outflow end of the calorimeter. The “cold” reading of the thermometers, when in place in the calorimeter, at any temperature of the water-jacket, will be the differential reading of the thermometers at the temperature indicated by the thermometer of the water-jacket. The effect of conduction from the ends of the calorimeter will appear as a slight change in this differential reading, but this is never more than .01° or .02°, and only comes in at the extremes of the range.

In regard to the errors referred to in the first of this section, to be met with in the practical employment of platinum thermometers for very accurate work, the first one, due to a change in zero, can always be avoided by sufficient annealing and offers no difficulty. The second one is by far the most important, and is caused by the conduction of heat away from the air around the bulbs through the metal leads. This is rendered worse rather than better by the presence of the compensating leads, because of the greater amount of good conducting material introduced into the thermometer tubes. The employment of a small length of wire to connect the compensating leads cannot rectify it, nor will the prevention of convection currents of air in the glass tubes render it harmless. It can be reduced to a negligible quantity only by immersing a sufficient length of the thermometer tube, and can always be measured by withdrawing the thermometer tube more or less from the vessel or steam-jacket in which it is immersed, and determining the drop in temperature

indicated by the bulb. I took special care to reduce this correction, which could easily amount to  $\cdot 01$  or even more in the steam-jacket, to a negligible quantity, so that it could not have affected the F.I. as determined in my experiments to as much as  $\cdot 001^\circ$ , and probably much less. Convection currents in the stem of the thermometer enclosed in the glass-tube were avoided in all my thermometers by lagging the leads down to within a few centims. of the bulb with cotton-wool.

The insulation between the leads of the thermometers could be detected very quickly by a very simple adjustment in one of the box contacts, so that the battery in series with the galvanometer could be made to detect at once the smallest leak between the connecting and compensating leads.

In correcting the differential readings to the air scale two of the ordinary parabolic formulæ are combined.

If  $pt_1$  and  $t_1$  be the platinum and air temperatures for one thermometer of the differential pair and  $pt_2$  and  $t_2$  be the same for the other, then for one we have

$$t_1 - pt_1 = \delta \left( \frac{t_1^2}{100^2} - \frac{t_1}{100} \right),$$

and for the other

$$t_2 - pt_2 = \delta \left( \frac{t_2^2}{100^2} - \frac{t_2}{100} \right),$$

from which we have, for the differential reading,

$$(t_1 - pt_1) - (t_2 - pt_2) = \frac{\delta}{10,000} (t_1 - t_2) (t_1 + t_2 - 100).$$

The correction is always small, and amounts to  $\cdot 1^\circ$  in the extreme at the ends of the scale for a difference of  $8^\circ$ . It vanishes altogether at  $50^\circ$ , changing sign at that point.

In determining the correction  $pt_1$  and  $pt_2$  may be substituted in the right-hand side for a first approximation. A second approximation generally gives the correction with sufficient accuracy.

### Sec. 3d.—*Measurement of Time.*

The method of measuring the average rate of flow over the time of any experiment was to divide the total weight of water by the time of flow. This total time of flow was generally of the order of 15 minutes, or 900 seconds. The interval was recorded on a chronograph, which marked seconds 1 centim. long, from a standardized clock. The drum of the chronograph revolved at the rate of one revolution per minute, and the record of each second was made by a lateral kick in a continuous line from a pen



marking an attached sheet of paper. The pen was connected to a relay, which was excited by an electric current whenever the pendulum of the clock swung through a globule of mercury at the middle of each stroke. The stream of water from the calorimeter could be made to flow out of either one of two nozzles before it entered the tared flask for obtaining its weight. The switch-over device was made from a 3-way glass tap, and so arranged that when the tap was turned so as to change the flow from one tube to another, the time of closing one and opening into the other was recorded by the pen on the chronograph sheet. Between the opening and closing, the flow was shut off altogether, but as this only amounted to from two to three-tenths of a second, the expansion of the rubber tube connections in the water circuit prevented the flow of water through the calorimeter from being interrupted, and any sudden shock to the conditions was avoided.

Fig. 7 gives a general plan of the switch-over device. The handle of the glass tap was connected to a long arm, which could be moved between two stops, representing the position when either nozzle was open. At the time of switching over, two marks were recorded on the chronograph, the mean of which was taken in estimating the interval of any flow. These two marks could each be estimated to  $\cdot 01$  sec. very easily with a millimetre scale, and were probably in all cases accurate to  $\cdot 02$  sec. on 900 seconds.

The standardization (indirectly to standard time) of the clock marking the seconds was done at frequent intervals during the course of the present series of experiments by comparison with a Frodsham and Keen ship's chronometer.

The rate of this chronometer was determined not only by direct comparison with the standard clock at the University Observatory, but by repeated telephonic communication between an observer at the Observatory and myself in the Physics Building. This rate, which was a slight gain, was extraordinarily constant. The rate of the clock, a loss, varied considerably between winter and summer, although the variation was very consistent and regular. The rates during the corresponding months of a year agreed almost to 1 second a day.

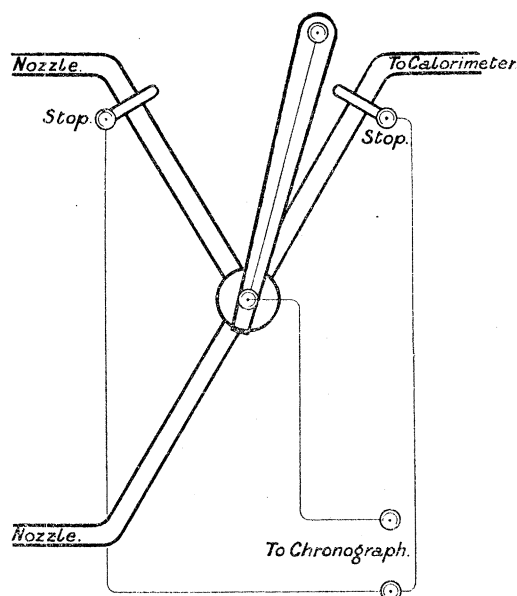


Fig. 7.

TABLE XVI.—Clock Comparisons.

	1898.							1899.		
	May.	June.	July.	Aug.	Sept.	Oct.	Dec.	Jan.	Feb.	March.
	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.
1	—	28	35	35	—	38	—	—	—	—
2	—	27	32	36	—	—	—	24	—	—
3	—	27	—	36	—	—	—	24	—	—
4	—	27	33	33	—	—	—	—	—	18
5	—	28	33	—	—	—	—	25	—	—
6	—	28	35	35	—	—	—	25	—	—
7	—	—	33	—	—	—	—	25	20	—
8	—	—	33	35	—	—	—	—	—	18
9	—	—	36	37	—	—	—	24	—	—
10	—	—	—	35	—	—	—	24	—	—
11	—	—	33	35	—	—	—	23	—	—
12	—	—	35	36	—	—	—	24	—	—
13	—	—	—	35	—	—	—	23	22	—
14	—	—	33	—	36	—	29	—	—	—
15	—	—	34	—	—	—	28	—	—	—
16	—	—	34	—	37	—	29	23	—	—
17	—	—	—	—	—	—	28	—	—	—
18	—	—	33	—	—	—	—	—	—	—
19	—	—	34	—	—	—	28	23	—	—
20	—	—	32	—	—	—	27	23	—	—
21	—	—	34	—	39	—	26	23	—	—
22	—	22	32	—	—	—	25	—	18	—
23	—	24	35	—	37	—	26	22	—	—
24	—	30	—	—	—	—	25	—	—	19
25	—	32	34	—	—	—	23	—	—	—
26	—	—	34	—	—	—	24	—	—	—
27	—	32	34	—	—	—	25	—	—	—
28	25	32	35	—	—	—	25	—	—	—
29	26	33	35	—	—	—	25	—	—	—
30	26	33	34	—	—	—	26	21	—	—
31	27	—	—	—	—	—	25	—	—	—



The following Table contains the results of the comparisons for the chronometer obtained by telephonic communication :—

TABLE XV.

Date.	Gain.	Date.	Gain.
Jan. 3 to Jan. 4, 1899 . . .	6·5 secs.	Jan. 11 to Jan. 14, 1899 . . .	19·5 secs.
„ 4 „ „ 5, „ . . .	6·5 „	„ 14 „ „ 16, „ . . .	12·0 „
„ 5 „ „ 6, „ . . .	7·0 „	„ 16 „ „ 23, „ . . .	48·5 „
„ 6 „ „ 7, „ . . .	6·5 „	„ 23 „ „ 30, „ . . .	49·0 „
„ 7 „ „ 9, „ . . .	12·5 „	„ 30 „ Feb. 6, „ . . .	46·0 „
„ 9 „ „ 10, „ . . .	7·0 „	Feb. 6 „ „ 13, „ . . .	48·5 „
„ 10 „ „ 11, „ . . .	7·0 „	„ 13 „ „ 20, „ . . .	48·5 „
Mean gain . . . . . 7·0 secs. in 24 hours.			

From March 20 to March 21 of the same year (1899) the gain was 7·0 secs. ; from February 9 to February 10, 1900, the gain was 7·0 secs. ; from February 10 to February 12 it was 15·0 secs.

In August, 1898, the chronometer was taken to the Observatory for two weeks, and daily comparisons were made with the standard clock. Its rate was found to vary between 6 and 9 seconds gain per day, which is a somewhat greater irregularity than I obtained, although the mean value agrees very well with the later comparisons. In rating the clock, I considered it safe to assume the rate of the chronometer constant to within a second from day to day, and equal to a gain of 7 secs.

In Table XVI., I give the comparison of the clock with the chronometer from May, 1898, to the close of the present work. The seconds represent the loss of the clock per day, and are not corrected for the rate of the chronometer.

In Table XVII., a summary of the previous Table is given, showing the greatest and least loss per month, with the mean loss corrected for the chronometer, which is obtained by subtracting 7 seconds. As far as possible, the rate of the clock was obtained over any day in which an experiment was obtained.

TABLE XVII.—Summary of Clock Comparisons.

Month.	Greatest loss in seconds.	Least loss in seconds.	Mean loss in seconds.	Mean loss corrected for rate of chronometer.
May, 1898 . . .	26	25	26	19
June, " . . .	33	27	30	23
July, " . . .	36	32	34	27
August, " . . .	37	33	35	28
September, " . . .	39	36	38	31
December, " . . .	29	23	26	19
January, 1899 . . .	25	21	23	16
February, " . . .	22	18	20	13
March, " . . .	19	18	19	12
April, " . . .	20	18	19	12
May, " . . .	23	21	22	15
June, " . . .	35	29	32	25
September, " . . .	38	37	38	31
October, " . . .	40	38	39	32
November, " . . .	39	31	35	28
February, 1900 . . .	23	22	23	16
March, " . . .	23	19	21	14

The rate of loss diminishes in winter and just doubles during summer. This is probably due to the effect of the dry furnace heat in the building during winter on the wooden pendulum of the clock, in contrast to the more humid climate of the summer months. The furnace fires are started about the month of November and discontinued some time in April.

### Sec. 3e.—*Measurement of Weight.*

In all the older methods of calorimetry, the question of evaporation of the water becomes a serious one for consideration. In the present experiments there were no such difficulties. The stream of water flowing from either one of the two nozzles on the outflow end of the calorimeter was caught in a weighed flask, which was fitted with a rubber stopper through which the nozzle passed. Through a second hole in the stopper a tube was fastened containing calcium chloride, so that the air in the flask, displaced by the inflowing water, passed through the calcium chloride. At no point between the calorimeter and the interior of the flask did the water come in contact with air.

In fig. 8 a drawing of the flask is given, showing the position of the calcium-chloride tube. The hole through which the nozzle of the calorimeter is thrust is closed, when the flask is removed, by a glass stopper. A similar stopper closes the end of the calcium-chloride tube and prevents the absorption of water vapour from the air.

The capacity of each of the two flasks, which were used in the experiments, was about 750 cub. centims., but the amount of water weighed in them was never more

than 650 cub. centims., and usually varied from 350 to 600 grammes. The weight of the flasks was taken empty, just previous to a determination of the flow and after they had stood for some time unstoppered inside the balance case. The interior of the

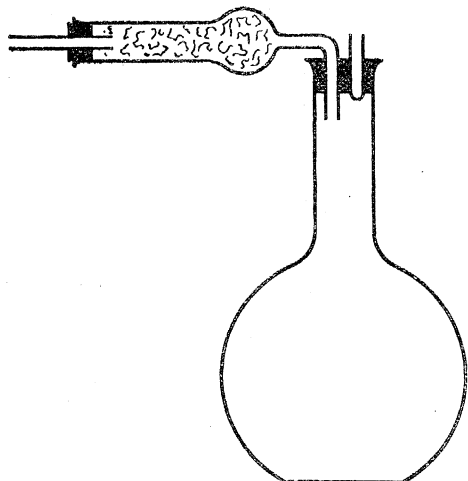


Fig. 8.

flasks was always wet on account of the water which had been weighed in them on a previous occasion.

The weight was taken on a large Oertling balance, which proved to be most suitable for the purpose. It was sensitive to less than 1 milligramme with 500 grammes, which gave a measure of the weight to a sufficient accuracy. The weights used were brass, and were one of several sets supplied us by OERTLING. They were kept entirely for the present purpose. It is exceedingly unlikely that their errors would amount to as much as 1 milligramme, especially as the several sets sent us by OERTLING agreed much closer than that, and the different weights

in the same set agreed very closely amongst themselves. Even if it could be imagined that the sum of the errors of the weights used in any given weighing could have amounted to 10 milligrammes, that would have produced an error in the estimation of the flow of only 1 part in 50,000, whereas it is most probable that the error was not so much as a tenth of this.

The correction to be applied to the weight for the ratio of the arms of the balance was found to be less than 1 in 100,000 for the weights used.

In the reduction of the weight of the water in the flask to weight in vacuum, it is necessary to correct for the presence of water-vapour in the displaced air. This water-vapour is retained in the calcium-chloride tube when the air is driven out and therefore appears not only in the weight of the flask empty, but when it contains the weight of water. It is consequently eliminated from the final weight. The actual weight of air displaced, however, is less than it otherwise would be, by the presence of the water-vapour. In applying this correction it may be assumed that the air inside the flask is completely saturated with water-vapour at the temperature of weighing.

Where brass weights are used the ratio of the weight in vacuum to the weight in air is given by the expression

$$\frac{W_{vac.}}{W_{air}} = \left(1 + \frac{\lambda_t}{S} - \frac{\lambda_t}{8.4}\right),$$

where for the calculation of  $\lambda_t$  we can use the formula

$$\lambda_t = \frac{\lambda_0}{(1 + .00366t)} \frac{p - \rho}{P}.$$

In this case  $\lambda_0 = .001293$ ;  $P = 760$ ;  $p =$  the observed barometric pressure at the time of weighing;  $\rho =$  the vapour-tension of water at the temperature of weighing.

This latter correction for the water-vapour is small and amounts to about 2 parts in 100,000 on the flow at the usual room temperature. In applying this correction, it was necessary to have the water enter the flasks at the temperature of the room, which was very nearly the temperature of the balance case. This was important, especially when the calorimeter was at a temperature very different to the room temperature. A cooler, consisting of a bath through which a constant stream of water could be made to flow, was arranged adjacent to the calorimeter, so that the outflowing water from the calorimeter was passed through a spiral of copper tube immersed in the water before passing through the switch-over device into the flasks. The temperature of the cooler was maintained near the temperature of the room by controlling the temperature of the stream of water by a gas flame. A stirrer was also fitted up for the bath.

A small change in temperature of the cooler, during the time of an experiment, required a small correction to the flow. This depended only on the readings of a thermometer in the cooler-water just previous to the switching over of the flow into the weighed flask, and just after it was turned off from the flask at the end of the interval. If  $dt$  represents the change in temperature obtained from the two readings,  $v$  the weight of water filling the copper-spiral in the cooler, and  $\alpha$  the coefficient of expansion of water, then the correction to be applied to the flow is  $\alpha v dt$ . When  $dt$  is of the order of a degree, this correction is just negligible for the volume of the total length of copper-tube used, which contained about 22 grammes of water.

#### Sec. 4.—*Description of the Apparatus and Method of Making the Experiments.*

*The Calorimeter.*—A general plan of the calorimeter is shown in fig. 1 (p. 153). The first three calorimeters were made at Bonn, and sent out to the laboratory unexhausted. We exhausted the vacuum-chamber of two of these, but the third one was not used owing to the adoption in later experiments of a slightly different design. They all had the same dimensions, with a fine-bore flow-tube 2 millims. inside diameter and 50 centims. long, which was fused at both ends to larger tubes 25 centims. long and 1.8 centim. inside diameter. These larger tubes were sealed into the vacuum-jacket made from a glass-tube 4 centims. in diameter. The seal at each end was made at about the middle of the larger flow-tubes, at a point about 11 centims. from the end where the fine-bore tube was sealed on. Two side tubes were sealed into the larger tubes at each end, but were eventually done away with in the later design, with the exception of one on the inflow end. The vacuum-jacket was exhausted on a large five-fall Sprengel pump with a McLeod gauge for determining the vacuum, and connected to the pump by a side tube fused into the glass of the chamber. When exhausted sufficiently, to a vacuum of about .002 millim. as shown by the gauge, the

connecting tube was fused together on the pump so that the vacuum chamber was permanently and hermetically sealed. The jacket was carefully heated during exhaustion so as to drive off water-vapour and occluded gas from the glass.

Three other calorimeters have been made by ELMER and AMEND of New York, since September, 1898. The vacuum jackets of these were all exhausted by them while heating the calorimeter in an asbestos oven. These calorimeters were of a similar design to the earlier ones, except in having only one side tube at the inflow end, and in having fine-bore flow tubes of different sizes, ranging from 2 millims. to a little over 3 millims. One of the calorimeters was prepared with phosphorus pentoxide in the vacuum chamber, but this proved to be rather a drawback than otherwise, because of the greater capacity for heat of the calorimeter introduced by the  $P_2O_5$ . It was essential to have the jacket very perfectly exhausted to avoid the heat-loss due to convection currents of air, which acted in such a way as to make the radiation loss appear large and uncertain. Small losses, however, from conduction and convection in the residual vapours in the jacket produced no errors on account of the steady temperature conditions during an experiment. The radiation loss would depend on the state of the glass surface, but would apparently be increased at the lower temperatures, after the calorimeter had been maintained for several hours during an experiment at one of the higher points. It was impossible always to count on the constancy of the heat-loss from one experiment to another, even with one calorimeter at the same temperature, as it depended so much on the past history. The change in heat-loss occasioned by the driving-off of occluded gases and vapours from the glass when the calorimeter was at a high temperature took place so slowly that, during an experiment extending over several hours, no measurable alteration in it could be noticed. This same effect of a slight change in heat-loss from time to time was also noted in the calorimeter used for the mercury experiments.

In fig. 9 is given a cross-section of the calorimeter and interior fittings in place, in the water-jacket. The thermometer bulbs are shown included in their glass cases. These cases were about 9 millims. in diameter, and extended the full length and a little beyond the ends of the outflow and inflow tubes. The ends of the thermometer cases over the bulbs were enclosed in thin copper cylinders, gold-plated, about 10 centims. long. These copper cylinders served the double purpose of preventing generation of heat in the vicinity of the thermometer bulbs by the electric heating current, and of helping to equalize the temperature of the water around the bulbs. The heating current was conveyed to the copper cylinders by eight No. 12 copper wires at each end, which were soldered into slits cut for them in the ends. The cylinders were made with closed ends, in one of which a hole was made for soldering in the platinum heating wire, and in the other a special screw clutch for catching the wire after the cylinders were put in place in the calorimeter. Sections of the cylinders are given in fig. 10.

The central heating wire for the fine-bore tube was made in three ways; either



a central solid platinum wire about .4 millims. in diameter, or six strands made up of 6-millim. platinum wire in parallel, or a flat wire twisted into a spiral down the fine tube. Of these the first proved to be the most satisfactory and gave the steadiest results when held central in a tube by a silk-covered rubber cord wound around it in spirals of about 1 centim. The stranded heating-wire, although excellent, was more difficult to handle, especially in putting the fittings of the calorimeter together. The flat wire did not require to have the rubber band wound around it, and it was of the full width of the tube. It was very difficult indeed to arrange the interior of the

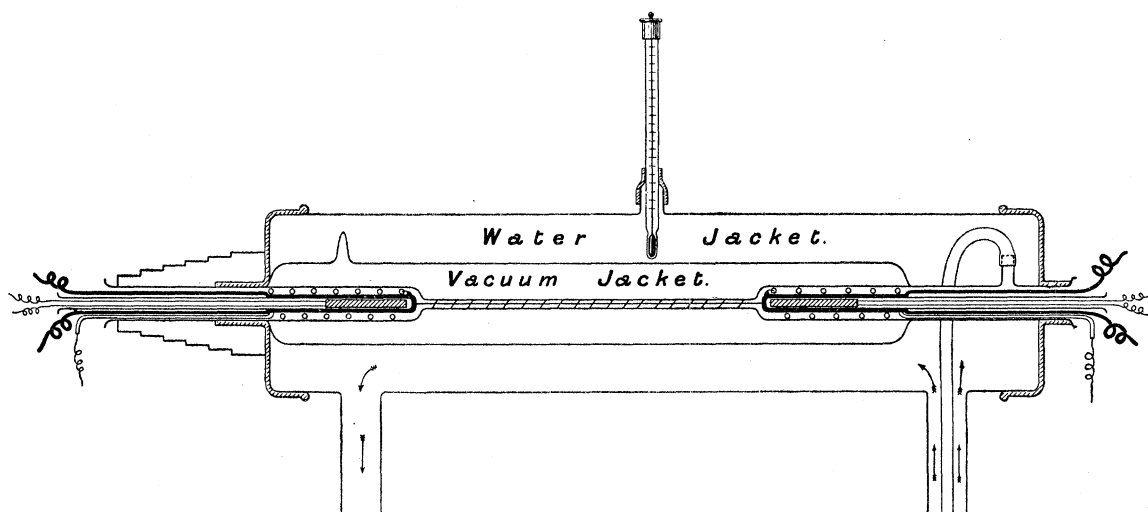


Fig. 9. Diagram of Continuous Flow Calorimeter.

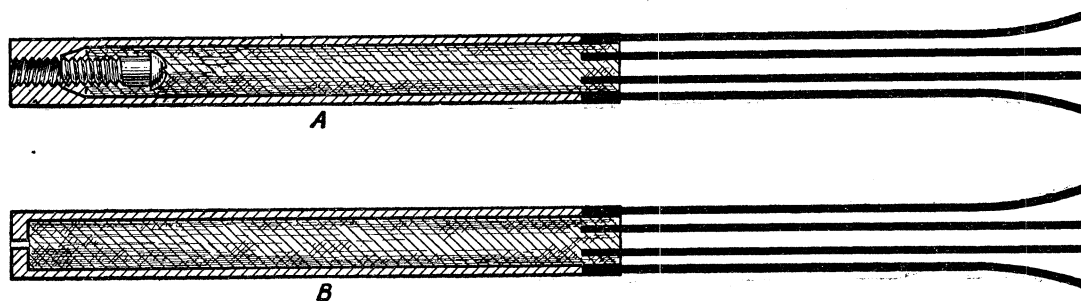


Fig. 10.

calorimeter when using this form of twisted heating-wire, as a small strain on the wire was almost sure to tear it apart. Moreover, in all experiments such as these, where water is heated by an electric current conveyed in a wire, the temperature of the wire is always above that of the water, so that as this form of wire touched the sides of the glass-tube the heat-loss was increased by the heating of the glass-tube at the points where it was in contact with the wire. Still, this arrangement gave excellent results for two calorimeters in which it was tried, and served as a satisfactory check on the results obtained by the other heating-wires. The solid heating-wire was finally adopted as offering the least mechanical difficulties.

In fitting the copper cylinders into place, they were each wound with a small rubber tube, shown in section, in fig. 9. Through these rubber tubes on the two cylinders small copper wires were placed, and soldered to the ends near the heating-wire. These copper wires served both as potential terminals as well as a method of holding the rubber tubes in place on the copper cylinders. The rubber tube served three purposes; the holding of the cylinders central and firm, the stirring of the water as it flowed around the thermometer bulbs, and the insulation of the potential leads.

The platinum heating-wire was fused at one end to a copper wire of the same size, which was in turn soldered with pure tin into the hole in the end of cylinder B, fig. 10. The other end of the heating-wire was soldered with tin directly to three copper wires, which served to draw the platinum wire into place in the fine-bore tube.

When cylinder B, which was placed in the outflow end of the calorimeter, was shoved down into place as far as it would go, the heating-wire was about 3 centims. shorter than the fine tube at the further or inflow end. The three copper wires, which were attached to the heating-wire and protruded from the calorimeter tube, were pushed through slits cut for them between the copper screw and nut (shown in fig. 10) on cylinder A. These three wires could be drawn through readily with the screw only partly in place, and in this way by pulling the wires through, cylinder A was shoved down the calorimeter tube into its place in the inflow tube. When in place a screw-driver was inserted, and a jack to hold the cylinder from turning, and the copper screw turned into place. When it reached the part of the thread where the slits ended, the three wires were firmly gripped between the thread and screw. The copper screw was smoothed on the end so as not to cut through the wires, but simply to jamb them against the screw thread. When sufficiently firm a specially constructed cutter was introduced, and the wires cut off just at the head of the copper screw, this left the cylinder firmly attached to the heating-wire by the three copper wires. The glass-tubes for the differential thermometers were placed in the two ends of the calorimeter, and slid into the two cylinders prepared for them. The tubes were put in empty, as it was found better to introduce the thermometers themselves after the calorimeter was fitted up and in place in the water-jacket. The ends of the calorimeter were closed watertight by means of a rubber stopper placed on each glass thermometer tube near the end of the calorimeter tube. The eight copper wires at the ends were placed in slits prepared for them in the rubber stoppers together with the two rubber tubes containing the potential terminals. Rubber cement was then placed over the surface and allowed to dry. A strip of rubber sheet, also covered with rubber cement, was placed so as to surround each rubber stopper and a portion of the end of the calorimeter, and on being cemented together formed a sleeve. This rubber sleeve was then firmly wired in place around the rubber stopper and wires, and also around the calorimeter tube. The ingress for the water

was by the glass side tube in the inflow end. The egress was by a glass-tube placed through a hole in the rubber stopper closing the outflow end.

The calorimeter was held in place in the water-jacket by heavy rubber caps specially made to withstand hot water. On the inflow end of the calorimeter the cap was placed at the end so as to include the whole length of tube in the water-jacket. On the outflow end the cap was drawn up to the vacuum-jacket. Side tubes, cemented into the rubber caps, served to hold them on the calorimeter. The calorimeter was shoved lengthwise through the water-jacket and the caps sprung into place over the ends.

The length of outflow tube protruding from the jacket was heavily lagged with flannel strips wound round it. As the outflowing water was made to flow the complete length of the outflow tube over the wires leading in the electric current, and as the tube itself was well protected from outside influences, the loss of heat from the water in the outflow tube was made as small as possible. This was shown very effectively by withdrawing the outflow thermometer, when the water was heated through about 8°, and determining the temperature at different points down the tube.

The glass-tube placed through the stopper closing the outflow end of the calorimeter was connected with a short rubber tube to the coil of tubing in the water cooler, which in turn was connected in a similar way to the switch-over device.

*Water-jacket and Circulating System with Electro-thermal Regulator.*—The water-jacket was an oval tube of  $\frac{1}{32}$ -inch copper, 2 ft. 9 in. long, with two lateral tubes 1 inch from each end on the under side. The jacket was 6 centims. wide and 8 centims. high. On the other narrow end of the oval two other lateral openings were made, one in the middle for a thermometer to obtain the temperature of the jacket water, and the other, which could be closed or opened at will, for an exit for accumulated air from the circulating water. The water in the jacket was circulated by means of a centrifugal pump run by a water-motor attached to the high-pressure mains in the laboratory. The water was drawn from the bottom of a large 10-gallon copper tank through the jacket to the pump, when it was thrown back again into the top of the tank. The whole system of circulating tubes formed a chain round which the water was constantly circulating. No water either left or entered the system, except that lost by evaporation, and that was exceedingly small except for the higher points. The circulating tubes were about 4 centims. in diameter, and the pumping was sufficient to supply a solid column of water from the tubes into the tank. The tank as well as the water-jacket and circulating tubes were all heavily lagged. For the higher temperatures a device was fixed to the tank to make up for the evaporation from the hot water, and to keep it always at the same level. This was most important, to prevent the exposure of part of the bulb of the thermo-regulator by the lowering of the water level in the tank.

In order to maintain the jacket at a constant temperature, a thermo-regulator was

fitted up in the large tank, similar to the one described by GOUY ('Journ. de Physique,' vol. 6, p. 479, 1897). Fig. 11 contains a drawing of this regulator with its attachments. A bulb of glass A, containing about 300 cub. centims. of toluene resting on a mercury surface B, is connected to a fine heavy-walled tube about 1 millim. inside diameter, through which the mercury at B is made to pass by the expansion or contraction of the toluene. A three-way glass tap allows the mercury to pass either into the reservoir C, or up into the tube E. A platinum wire point is attached to a copper wire and drawn up and down about 4 millims. by a pivot on the wheel F, worked by a worm-wheel from the pulley C<sub>1</sub>.

In this method, which is the distinctive feature of the Gouy regulator, the platinum point never sticks to the mercury surface, and consequently gives a sharper

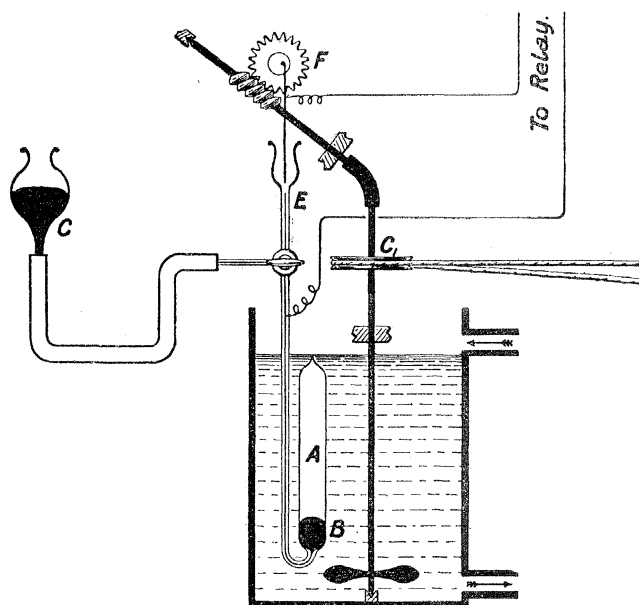


Fig. 11.

and more definite electrical connection between the thread of mercury in E and the wire. Connections were taken from this to a telegraphic relay, which was so arranged as to throw in and out a heating lamp placed in the tank. The arrangement is shown in fig. 12.

When the relay is inactive, the terminals of the lamp are short-circuited by the arm extending between the mercury cups *a* and *b*, and the full current is permitted to pass through the lamp B. When the relay is excited, the arm *ab* is raised and the circuit broken at *a*, so as to bring the lamps A and B in series. Lamp A was a 16-candle-power lamp of 200 ohms resistance, while B was either a 32-candle-power lamp of 100 ohms resistance, or a 50-candle-power lamp of about 60 ohms resistance. Either of the two heating lamps in series with lamp A was reduced in heating power over one-fourth of its full amount. The relay was made active by the closing of the

connection between the wire and mercury column, and was supplied by either one or two accumulators. This form of regulator works exceedingly well, and is much to be recommended.

The electric heating lamp has practically no lag, so that the effect known as "hunting" was not apparent. The bulb of the regulator was long and narrow, and extended the whole height of the water in the tank. For high temperatures, lamp B could not supply enough heat to make up for the loss from the circulating system to the surrounding air, so that an auxiliary gas flame was necessary, which was placed under the centrifugal pump, and was supplied by a large constant-pressure gas regulator situated in the basement of the building. The final amount of heat necessary to keep the apparatus at the temperatures of the experiment required, was supplied by the lamp B, which thus acted as a fine adjustment over and above the heat supplied by the gas flame. For very high points it was necessary to maintain a second gas flame under the large copper tank, which was arranged on three brick supports for this purpose.

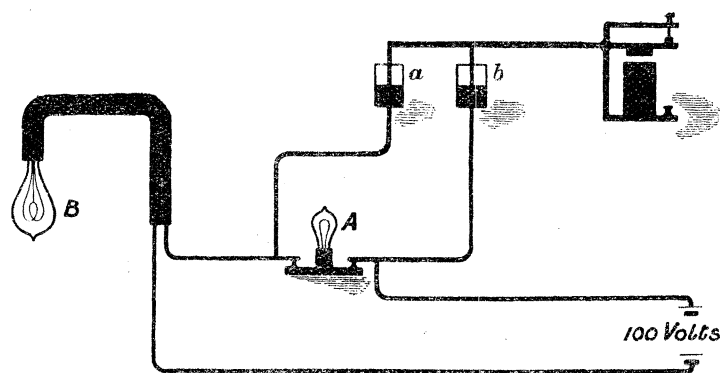


Fig. 12.

The water-motor which operated the pump in the circulating system ran at a very constant speed, on account of the very steady pressure of the water in the high-pressure mains. This aided very much in ensuring perfect regulation. Several stirrers in the apparatus were also operated by the water-motor from a pulley directly connected to it. One of the stirrers was placed in the tank and shown connected with the pulley C, in fig. 11. This helped to keep the water throughout the tank thoroughly mixed. It was connected to the pulley of the water-motor by a leather strap. Another cord was taken to the stirrer in the standardized resistance oil-bath, and a third to the stirrer in the cooler in the outflow end of the calorimeter shown in fig. 13. A general idea may be obtained of the arrangement of the apparatus by reference to fig. 13.

The accompanying photographs are added to give some idea of the appearance and arrangement of the apparatus. Fig. 14 is a side view, and fig. 15, a bird's-eye

view, taken from the ceiling. Corresponding parts of the apparatus are indicated by the same letters in the two plates.

Fig. 14, is taken looking towards the slate slab along one side of the laboratory on which the greater part of the apparatus was arranged. The water-motor A, which supplied the driving power for the circulation and all the stirrers, is seen on the extreme right. B is the heater, containing a centrifugal pump driven direct from the motor, which delivers the water into the regulator tank C (fig. 14) through a large rubber hose. Behind the tank is the hypsometer T, which was employed for pre-heating the distilled water at the higher temperatures, and the water-bath P, containing the tube resistances for regulating the flow of the distilled water. The distilled water reservoirs were on the floor above. D is the ebonite box containing the standard resistances for current measurement immersed in oil with a stirrer driven by the central pulley (fig. 5). E is the copper water-jacket (fig. 11) containing the calorimeter, swathed in flannel, and connected by rubber hose on one side to the regulator tank C, and on the other to the circulating pump B. F is the switch-over

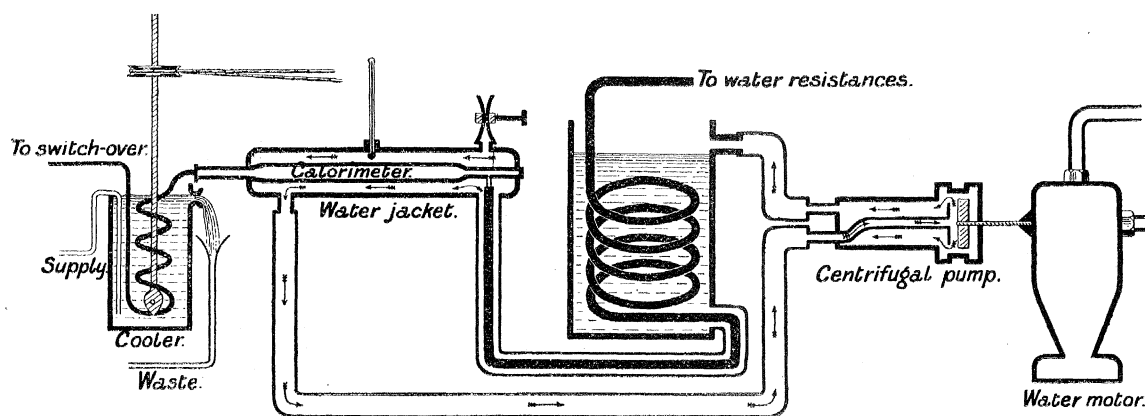


Fig. 13.

tap (fig. 7) for delivering the flow into either of the two flasks G (fig. 8), and automatically recording the time of the switching over on the electric chronograph, the cylinder of which is marked Q in fig. 15. In the background of fig. 14, on the slate slab to the left are seen, H the Thomson-Varley slide-box, and K the 100,000-ohm galvanometer. Nearer the middle at M is the 20-ohm galvanometer for the platinum thermometers. These are all beyond the range of fig. 15. L is the zigzag platinoid rheostat for regulating the main current so as to obtain the desired rise of temperature in each case.

On the small table at the side in fig. 15 is seen the compensated resistance box R for the differential platinum thermometers, with small auxiliary boxes for current regulation. S is the rubber tube containing the leads to the heating lamp in the tank C. The relay, (fig. 14) worked by the regulator in the tank, and the shunt lamp are seen at Q in fig. 14, but are hidden by the jacket E in fig. 15. The Clark

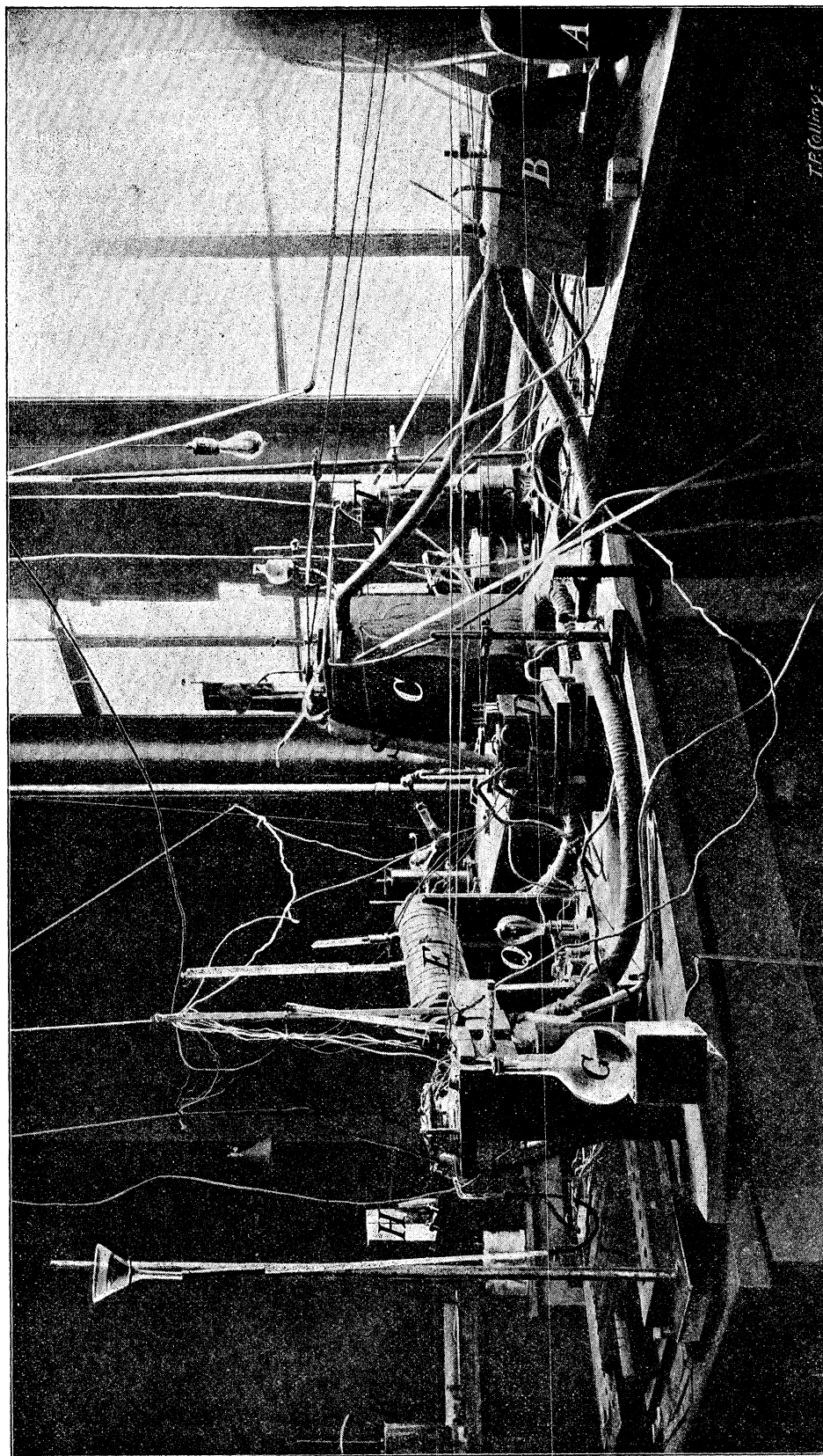


Fig. 14.

cell tanks and regulator are not shown in either view. They were at the other end of the laboratory.

*Water Supply for Calorimeter.*—The water supplied to the calorimeter passed through 40 feet of pure block-tin tube,  $\frac{1}{4}$  inch in diameter, coiled up in the constant temperature tank. After passing through this and taking the temperature of the jacket water, it was passed from the tank to the water-jacket and into the calorimeter through a rubber tube placed inside the water circulating tube. By this means the water, after entering the tank, was entirely in the circulating system until it flowed out of the calorimeter. The head of water to maintain a steady flow was supplied from a reservoir placed on the floor above, and was connected to the apparatus by a glass-tube passed through a hole in the floor. In order to vary the supply, the water was passed through a series of fine tubes acting as resistances, which could be short-circuited by larger tubes connected across them. These larger tubes, offering no resistance, were thick-walled rubber tubes and connected to the ends of the fine tubes by T-pieces. When the water was to be passed through the fine tubes, the rubber tube was simply closed with a pinch-cock. The resistance tubes were two principal ones, 1 metre long and 1 millim. in section, and three lesser ones for fine adjustments. These were all immersed in a water-bath to keep them from changing in temperature suddenly, and thereby producing a change in the flow by changing the viscosity of the water.

No device was used to maintain a constant head, as a slight falling-off in the flow was rather an advantage than otherwise, as it tended to compensate for the slight falling-off in the electric current supplied to the calorimeter by the large accumulators. Two large bottles, holding about 4 gallons each, formed the head and were connected in parallel. A layer of heavy paraffin oil was put over the water to prevent absorption of air by the distilled water, which was always used for the experiments. This was supplied to the bottles in sufficient quantity for about two experiments, and was run in under the oil through a T-connection in the tube connecting the two bottles together and with the supply tube for the apparatus. The water was first boiled in a large copper tank, and while still boiling was siphoned over into the bottles. It was allowed to cool before being used for an experiment. This method of boiling the water was used for all the earlier experiments below 60° C.; but it was found impossible to obtain steady conditions of flow above this limit, owing to the liberation of air inside the calorimeter even from the boiled water. This was somewhat surprising and delayed the attainment of the final measurements at the high temperatures. It appears that to remove the last trace of air from boiled water, it is necessary to submit it to extreme agitation. Sufficient agitation was supplied to the water, as it ran through the fine-bore tube of the calorimeter, to set free some of the air retained by the boiling water when it was run into the bottles under the oil.

It was found necessary to devise some method of preparing absolutely air-free water before readings at the higher points could be obtained. To do this I found,



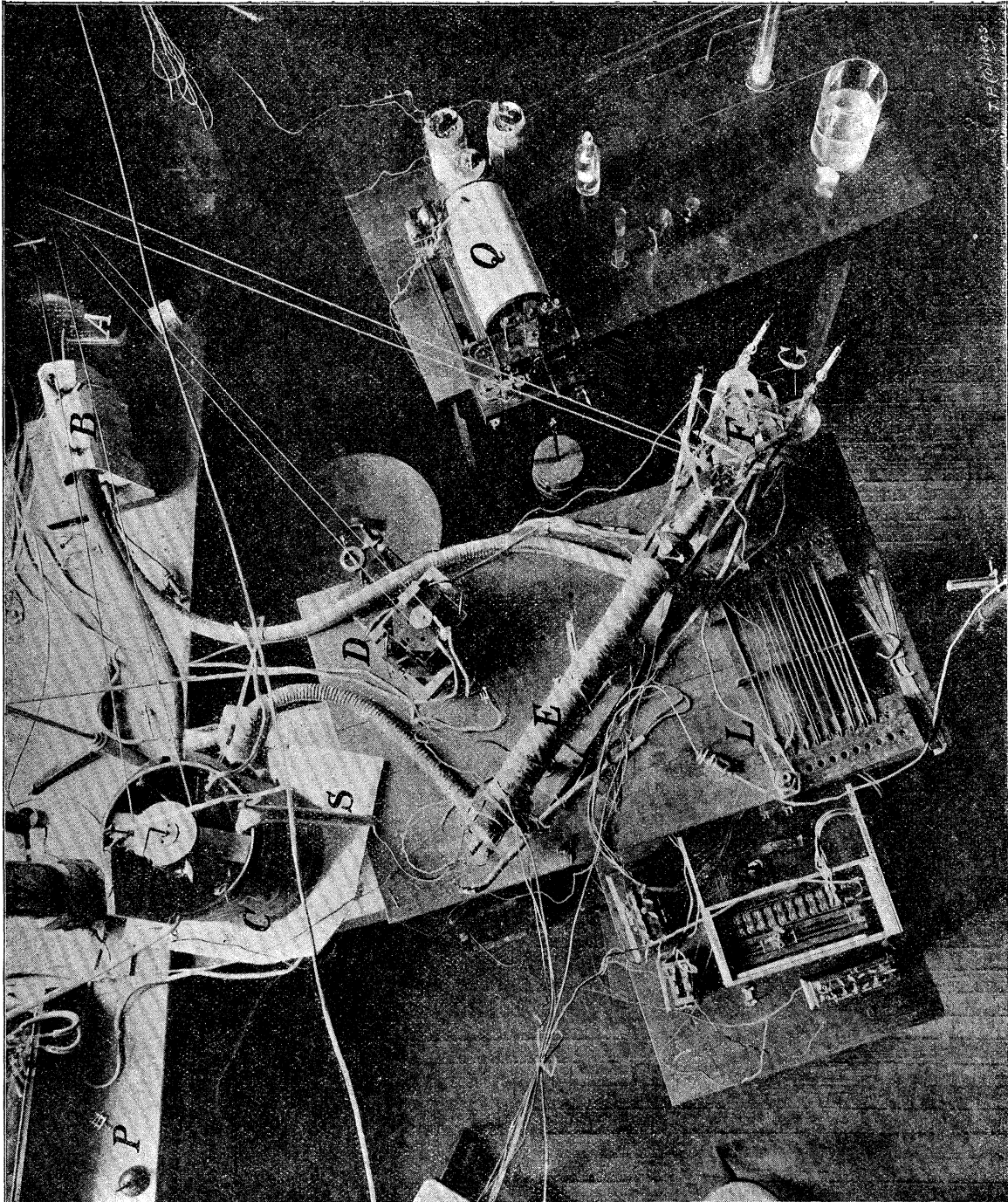


Fig. 15.

after repeated trials with other arrangements, that it was necessary, in order to separate the air from the water, to drive the latter into steam and condense it again in an air-free medium, and at the same time draw off the air before it had a chance to dissolve again. The method adopted finally was to exhaust the air over the oil in the two bottles by connecting with a water-pump while the boiling water from the copper tank was running in. In this way, by introducing a slight constriction in the siphon tube, such as a connection made from a small-bore rubber tube, the water in the tube separated into steam just past the constriction, and was condensed in the cold water already in the bottles from a previous filling. The air was at the same time sucked up through the oil and carried off by the pump. It was a matter of considerable surprise to see the amount of air thus drawn off.

After adopting this method of filling the bottles, there was no further trouble from air appearing inside the calorimeter, even as high as  $90^{\circ}$  C. When working at high temperatures, the distilled water, before it passed into the constant temperature tank, was passed through a spiral of tin tube in a steam-jacket. Instead of increasing the heat-loss of the circulating system by introducing cold water into the tank, a small quantity of heat was supplied by this means to the tank by the water flowing in from the steam-jacket. Moreover, the steam-jacket was a check on the state of the water, air bubbles being generated if the water was not perfectly air-free. The water which was run through the calorimeter was never used a second time, although it might just as well have been. Fresh distilled water was so easily prepared by means of a small water still in the laboratory that it was deemed unnecessary to use it twice.

A constant-level head was arranged near the apparatus to supply water for the cooler for the outflowing water; at the same time it also supplied the water circulation for the standardized resistance oil-bath, for the constant-level device of the tank, and for the condenser on the steam-jacket used at the higher temperatures.

*Method of Making an Experiment.*—Obviously various expedients were necessary in order to have the jacket maintained at a constant temperature at any point on the scale between  $0^{\circ}$  and  $100^{\circ}$  C. For the experiments near  $0^{\circ}$  C. the regulator was removed entirely from the tank, which was then filled with cracked ice and water. A wire sieve was placed over the stirrer in the bottom of the tank, so as not to have its action interfered with by the ice, as well as to prevent any ice from being drawn into the circulating tubes. Wonderfully steady conditions were produced in this way, and maintained without the variation of a hundredth of a degree for over an hour at a time. Between the measurements with each flow of water used, which lasted about an hour, the tank was replenished with ice. Not a great deal of ice was required for this replenishing; since only about one-quarter of the tank-full of ice was melted in the hour. From 50 to 60 lbs. of ice were melted during a complete experiment, although considerably more was used to cool the apparatus down to the ice-point before the experiment was started. From 100 to 150 lbs. of ice was

generally required for a complete ice determination. It may be said, however, that these experiments were among the easiest to obtain.

At temperatures intermediate between the ice-point and room temperature, the regulator was used, and a stream of cold water run through a coil of metal tube placed in the tank. Water direct from the water mains usually sufficed for the cooler, but for lower temperatures the tap water was run first through a coil of tube immersed in a tank of ice. The desired temperature was attained through the equilibrium between the heat supplied by the lamp in the tank and the heat absorbed by the water flowing through the circulating tube. The tap water in the high-pressure mains varied, from about  $5^{\circ}$  in winter to about  $18^{\circ}$  in summer, in the laboratory where the apparatus was located. A temperature at least  $2^{\circ}$  lower than the desired temperature of regulation was required in the cooling water. The temperature of the laboratory varied from about  $18^{\circ}$  to  $25^{\circ}$  during the different seasons; but, in general, was steady to  $1^{\circ}$ , and often less during an experiment lasting 3 or 4 hours. When not using cooling water in the tank, the temperature of the apparatus had to be maintained a few degrees above the laboratory, so that the regulator could make up for the loss of heat to the surrounding air. Hence a temperature of about  $26^{\circ}$  or  $27^{\circ}$  in the tank was the most convenient point at which to work, which for an  $8^{\circ}$  rise in the calorimeter gave a mean temperature of about  $30^{\circ}$  C.

As the temperature of the jacket was increased more and more above the room temperature, more and more gas was required to aid the electric-heating lamp in maintaining a constant temperature. At a temperature of the jacket of about  $90^{\circ}$  C. two gas flames were required, and, in addition, the 50 c.-p. lamp. Even for the highest points the regulation proved to be most satisfactory, so long as the gas pressure did not vary. It was found that the high temperature experiments had to be taken at times when there was no other gas being used in the building, as even in using the large constant-pressure gas governor fluctuations in the gas pressure in the building caused perceptible alterations to the regulator. Where the fluctuations were small and regular, the jacket water seldom varied as much as  $.01^{\circ}$  during the time for obtaining the observations for each flow, even at the highest point attained. The wonderful efficiency of the regulator and circulating system, together with the preparation of air-free water, made it possible to obtain the observations at the higher temperatures with almost *the same degree of accuracy* as at the lower points.

At whatever temperature the jacket was maintained, and before the electric-heating current was turned on, the calorimeter water was allowed to flow through the apparatus for some time after the steady conditions were attained by the regulator. The balance-point so obtained for the differential thermometers we have already termed the "cold" readings, in contra-distinction to the readings obtained when the electric-heating current is turned on. The second balance-point, together with the

requisite number of bridge resistance-coils required to compensate the rise in temperature in the water, we will term the "hot" reading. The conduction errors at the ends of the apparatus remained the same for both readings, except (as has already been pointed out) the conduction error due to the rise in temperature,  $d\theta$ , in the out-flow end. It was therefore possible for any temperature over the scale between  $0^\circ$  and  $100^\circ$  to eliminate the conduction errors at the ends of the apparatus by the "cold" readings in a very simple manner, and reduce the only conduction error to be considered, *i.e.*, that due to the rise  $d\theta$ , to the *same amount all over the scale*. Unless this procedure had been followed, large errors would have been incurred, especially at the inflow end where the conduction effect was the largest.

The adjustment of the electric current to any given flow was made by varying the number of accumulators, or by inserting a number of platinoid strips, .02 ohm, in series in the rheostat. While the conditions became steady in the calorimeter after turning on the electric current, requiring 10 to 15 minutes, the weights of the empty flasks were obtained as already described. One of these was then affixed to one of the nozzles on the calorimeter. The temperature of the cooler was then adjusted, and the preliminary readings of the potential difference across the standard resistance and calorimeter obtained. The chronograph being started, the accurate balance of the two Clark cells in series was obtained, together with the temperature of the Clark-cell bath. The other conditions remaining steady (including the thermo-regulator in the tank, the jacket circulation and the different water circulations to the resistance oil-bath, cooler, constant-level device and steam-jacket when used, as well as the thermo-regulation in the Clark-cell bath) the flow was switched over into the weighed flask at a given moment, which was recorded automatically on the chronograph. The complete set of observations then followed in order for 15 minutes. These, besides the temperature of the cooler at the beginning and end of the interval, were made every minute—first minute the deflection of the galvanometer at the nearest millimetre on the bridge-wire for the balance-point of the differential thermometers, then, in succession at every even minute, the potential balance of the standard resistance, the reading of the differential thermometers, potential across the calorimeter, reading of the thermometers, potential across standard resistance, and so on, including at the half-minutes the reading of temperature of standard-resistance oil-bath, jacket water, air temperature and temperature of thermometer resistance box, although this last was not really necessary.

At the end of the 15 minutes, to the nearest second by the watch used in starting the interval, the flow was switched over to the other nozzle, and the time automatically recorded. The balance-point of the Clark cells was then obtained, together with their temperature. On changing the full flask for a second empty one, a second set of readings for 15 minutes was obtained, without otherwise altering the conditions. The extreme steadiness of the potential balance for the Clark cells made it quite unnecessary to have it recorded oftener than just before and just after the 15-minute interval.

For each 15 minutes 8 readings in all were obtained of the differential thermometers, which were separated by 2 minutes each, the last one being taken just before switching over the flow, 3 readings of the potential across the calorimeter separated by 4 minutes, and 4 of the potential across the standard resistance also separated by 4 minutes. These readings were always corrected to the middle of the interval to correspond to the time of average flow. The thermometer readings sometimes increased and sometimes decreased during the interval, depending on the flow, but the change was never more than  $\cdot 02^\circ$  or  $\cdot 03^\circ$  over the 15 minutes, and generally much less. The question of the lag of the thermometers and of the thermal capacity of the calorimeter, which amount to such large corrections in all older calorimetric methods, was reduced therefore to a negligible quantity. The potential readings on the Thomson-Varley slide-box of the calorimeter and standard resistance generally fell off in a regular way throughout the interval, although quite often they remained steady altogether. The fall was seldom as much as 1 part in 1000 during the entire interval; hence a greater number of readings was unnecessary, since all the readings were taken at stated times, which were even minutes recorded from the seconds' hand of the watch used to start the flow over the interval.

In the earlier experiments, where two observers took the observations, simultaneous readings could be made of the temperature and potential difference every minute. This arrangement was of course preferable to the other, but where the conditions remained steady a large number of readings was really not necessary. When any sudden change in the conditions occurred, such as in the regulation, electric current or flow, so as to make the readings unsteady, these readings were either repeated during another interval where it was possible to restore the conditions in a short time, or they were abandoned altogether until such other time as the complete experiment could be repeated. My aim was, as far as possible, to produce a series of measurements, over the entire range of temperature between  $0^\circ$  and  $100^\circ$ , under as steady and uniform conditions as possible.

The number of flows usually taken in a complete experiment was two, but sometimes three. Other flows were tried to test the theory of the method beyond the limits of flow chosen for the actual experiments. In all the flows two intervals of 15 minutes were taken, which, when worked out, gave a complete check on the steadiness of the conditions and the accuracy of the observations.

None of these measurements depend very much on the absolute readings of mercury thermometers except the Clark cell. The temperature of the standard-resistance was always taken with the thermometer used in its calibration with the standard ohm, which in turn had such a small temperature coefficient that it made it of very little importance whether the thermometer used to obtain its temperature was in error by as much as  $\cdot 5^\circ$ . As a matter of fact, by direct comparison, all the thermometers used agreed with our standard thermometer to within  $\cdot 1^\circ$ . The thermometer used to obtain the temperature of the jacket-water between  $0^\circ$  and  $50^\circ$  C., was a new Müller

graduated to  $\cdot 1^\circ$  and reading to  $\frac{1}{100}$ ths. Its error was determined by comparison with the standard thermometer, and its readings were found to be  $\cdot 03^\circ$  too large. The standard thermometer was a Geissler reading to  $\frac{1}{100}$ th between  $-2^\circ$  and  $50^\circ$  C., which has been in the possession of the laboratory for several years, as before stated. In 1896 both Professor CALLENDAR and I separately determined its error, and reduced its readings to the nitrogen scale over the entire range by comparison with a platinum thermometer. The error was very consistent, and showed its readings too high by  $\cdot 11^\circ$  to  $\cdot 12^\circ$  from  $0^\circ$  to  $50^\circ$ . This thermometer was used in the Clark-cell bath and has already been referred to in that section. For jacket-temperatures between  $50^\circ$  and  $90^\circ$  C., a second Müller thermometer, reading between  $50^\circ$  and  $150^\circ$ , was used, which was graduated to  $\frac{1}{5}$ th of a degree.

#### *Specimen Tables of Observations.*

[*Added April 20th, 1901.*—H.T.B. Owing to the necessity of condensing the tables since the communication of this paper, I have considered that it would be of advantage to give specimen tables of observations as recorded during a complete experiment. I have therefore included here two sets, made as typical as possible, which illustrate more clearly the remarkable steadiness of the conditions. The experiments selected are those given under date October 27, 1899, and March 10, 1900. They include two calorimeters and different-sized flow-tubes (Calorimeters C and E), as well as flat and round heating wires. One of the sets includes the observations taken for the measurement at the highest point of the range. In the first set box 1 was used, on the second set box 2. The order in which the readings were obtained has been described in Section 4. In all cases the time of taking the readings was as closely as possible on the even minute. The time for the start and finish of an interval, during which the flow was measured, is of course given, as recorded on the chronograph, to  $\cdot 01$  second. The reading of the contact point on the bridge-wire (b.-w.) is given in centims. (10 centims. =  $1^\circ$  C.), and the deflections of the galvanometer noted, it being accurately set to the nearest millimetre by means of the vernier reading to hundredths of a millimetre. The sensitiveness of the galvanometer remained very constant, but was repeatedly checked during a set of observations. The balance-point on the bridge-wire was calculated by interpolation from the observations of the deflection. In the electrical readings of the potential, S stands for the balance-point for the difference of potential across the standardized resistance, and P for the same across the calorimeter heating-wire. These readings are of course uncorrected for the errors in the Thomson-Varley slide coils. The temperature of S is that of the oil in which the standardized resistance was immersed, and the temperature of the Clark cells is here uncorrected for the thermometer error. The inflow temperature is the same as the temperature of the jacket. In some cases

the air temperature was recorded just at the calorimeter, as well as the temperature of the balance case, but in general these never differed much from the temperature of the air as recorded on the barometer case, which was always taken with the reading of the barometer. The weights are given here in grammes, just as recorded during the experiment. The Abridged Tables sent in with the paper give the summary of these observations, together with the necessary corrections.]

[*Added May 28th*, 1902.—H.T.B. The comparative failure of my attempts to obtain consistent results in the experiments carried out previous to my discovery of the effect of stream-line motion on the distribution of heat in the fine bore flow-tube, appears to me to have been largely due to the fact that the stranded conductor was in nearly all cases annealed before being inserted in the calorimeter. This caused the different strands to lie together more in the nature of a solid conductor. It is probable that better results would have been obtained in these early experiments had the wires been stiffer, the flow-tube smaller, and had it been possible to distribute the strands more thoroughly in the water column, and at the same time to prevent them from changing their relative position in the tube between the experiments.]

SPECIMEN Table of Observations XXXVI. October 27, 1899. Calorimeter E (3 millims.).  
Flat Heating Wire. Mean Temperature, 29°·92.

Large flow.					Small flow.						
Cold readings.			Weights.		Cold readings.			Weights.			
Time.	B.-W.	Deflec.		First interval.	Second interval.	Time.	B.-W.	Deflec.	First interval.	Second interval.	
2:33	23·600	11 c.p.	Flask (1) . .	99·379	—	3:55	23·600	8 c.p.	Flask (1) . .	99·162	—
34	"	11 c.p.	" (2) . .	—	120·793	56	"	8 c.p.	" (2) . .	—	120·255
35	23·700	25 s.a.	" (1) full	659·755	—	57	"	8 c.p.	" (1) full	444·392	—
36	"	24 s.a.	" (2) "	—	680·500	58	23·700	29 s.a.	" (2) "	—	464·695
37	"	24 s.a.				59	23·600	8 c.p.			
38	23·600	12 c.p.				4:00	"	8 c.p.			
39	"	10 c.p.	Barometer . .	76·57		01	"	8 c.p.	Barometer . .	76·57	
40	23·700	25 s.a.	Temperature . .	18·2					Temperature . .	18·2	
41	"	25 s.a.									
42	"	26 s.a.									
43	23·600	11 c.p.	Temperature balance case not taken.						Temperature balance case not taken.		
4:4 Electric heating current on.					4:02 Electric heating current on.						
3:04:00:42 Start. Pot. bal. C.C. 63004. Box coil 80.					4:19:00:62 Start. Pot. bal. C.C. 62998. Box coil 80.						
05	22:100	11 s.a.				20	22:000	2 s.a.			
06	"	15 s.a.	Pot. bal. S. 70251	Temp. C.C. . 16·14		21	"	3 c.p.	Pot. bal. S. 55596	Temp. C.C. . 16·14	
07	"	"	" P. 76282	" inflow 25·74		22	"	"	" P. 60235	" inflow 25·75	
08	"	19 s.a.	" S. 70246	" air . 18·8		23	"	4 c.p.	" S. 55591	" air . 18·8	
09	"	"	" P. 76277	" S. . 14·0		24	"	6 c.p.	" P. 60231	" S. . 13·5	
10	"	19 s.a.	" S. 70241			25	"	5 c.p.	" S. 55589		
11	"	"	" P. 76274			26	"	4 c.p.	" P. 60227		
12	"	21 s.a.	" S. 70238	" S. . 14·0		27	"	4 c.p.	" S. 55586	" S. . 13·5	
13	"	"	"			28	"	3 c.p.	"		
14	"	21 s.a.				29	"	"			
15	"	"				30	"	"			
16	"	23 s.a.				31	"	"			
17	"	"				32	"	"			
18	"	30 s.a.				33	"	"			
18:30	"	"				33:30	"	"			
3:19:00:12 Flow switched over.					4:34:00:12 Flow switched over.						
3:22:00:29 Start. Pot. bal. C.C. 63004. Second interval.					4:59:01:05 Start. Pot. bal. C.C. 62997. Second interval.						
23	22:000	Bal.				5:00	21:900	4 c.p.			
24	"	1 s.a.	Pot. bal. S. 70230	Temp. C.C. . 16·13		01	"	Bal.	Pot. bal. S. 55571	Temp. C.C. . 16·14	
25	"	"	" P. 76263	" inflow 25·75		02	"	"	" P. 60211	" inflow 25·75	
26	"	5 s.a.	" S. 70227	" air . 19·0		03	"	1 c.p.	" S. 55570	" air . 19·3	
27	"	"	" P. 76262	" S. . 14·0		04	"	2 s.a.	" P. 60208	" S. . 13·5	
28	"	8 s.a.	" S. 70224			05	"	2 s.a.	" S. 55567		
29	"	"	" P. 76257			06	"	5 s.a.	" P. 60206		
30	"	9 s.a.	" S. 70219	" S. . 14·0		07	"	9 s.a.	" S. 55567		
31	"	"				08	"	"			
32	"	14 s.a.				09	"	"			
33	"	"				10	"	"			
34	"	22 s.a.				11	"	"			
35	"	"				12	"	"			
36	"	29 s.a.				13	"	"			
36:30	"	"				13:30	"	"			
3:37:00:16 Flow switched over.					5:14:00:59 Flow switched over.						
Pot. bal. C.C. 63003 Temp. C.C. . 16·13					Pot. bal. C.C. 62996 Temp. C.C. . 16·13						



SPECIMEN Table of Observations LIII. March 10, 1900. Calorimeter C.  
Solid Heating Wire. Mean Temperature 91°·55.

Large flow.					Small flow.						
Cold readings.			Weights.		Cold readings.			Weights.			
Time.	B.-W.	Deflec.		First interval.	Second interval.	Time.	B.-W.	Deflec.	First interval.	Second interval.	
3:08	22:600	2 c.p.	Flask (1) . .	97·683	—	5:23	22:400	10 c.p.	Flask (1) . .	97·538	—
09	"	7 c.p.	" (2) . .	—	121·207	24	"	12 s.a.	" (2) . .	—	121·034
10	"	7 c.p.	" (1) full	678·004	—	25	"	44 s.a.	" (1) full	459·847	—
11	22:700	29 s.a.	" (2) "	—	699·584	26	"	40 s.a.	" (2) "	—	481·545
12	"	28 s.a.				27	"	38 s.a.			
13	22:600	7 c.p.				28	22:300	5 c.p.			
			Barometer . .	75·77		29	"	3 s.a.	Barometer . .	75·77	
			Temperature . .	22·0		30	"	9 s.a.	Temperature . .	22·0	
			Temperature of balance case taken as that of air.			31	"	6 s.a.			
						32	"	5 c.p.			
						33	"	2 c.p.			
						34	"	Bal.			
						35	"	1 s.a.			
						36	"	4 s.a.			
						37	"	5 c.p.			
3:14 Electric heating current on.					5:38 Electric heating current on.						
3:38 00:30 Start. Pot. bal. C.C. 63562. Box coil 80.					6:09 00:45 Start. Pot. bal. C.C. 63557. Box coil 80.						
39	29:200	Bal.	Pot. bal. S.	74004	Temp. C.C. .	10	28:600	16 c.p.	Pot. bal. S.	59290	Temp. C.C. .
40	"				15:27	11	"	10 s.a.	"	59290	15:24
41	"	20 s.a.	"	P.	76674	"	"	10 s.a.	"	61350	inflow 87·43
42	"		"			13	"	12 s.a.	"		
43	"	8 s.a.	"	S.	73990	"	"	12 s.a.	"	S. . .	6·6
44	"		"			15	"	29 s.a.	"	S.	59287
45	"	9 s.a.	"	P.	76658	16	"	29 s.a.	"	P.	61347
46	"		"			17	"	11 s.a.	"	S.	59283
47	"	20 s.a.	"	S.	73976	18	28:500	11 s.a.	"	P.	61347
48	"		"			19	"	13 s.a.	"	S.	59283
49	"	Bal.	"	P.	76647	20	"	15 s.a.	"	P.	61343
50	"		"			21	"	15 s.a.	"	S.	59281
51	"	24 s.a.	"	S.	73965	22	28:400	15 s.a.	"	P.	61343
52	"		"			23	"	46 s.a.	"	S.	59281
52:30	"	25 s.a.	"			23:30	"		"		
3:53:00:69			Flow switched over.			6:24:00:40			Flow switched over.		
3:56:00:82 Start. Pot. bal. C.C. 63562. Second interval.					6:27:00:42 Start. Pot. bal. C.C. 63557. Second interval.						
57	29:100	3 s.a.	Pot. bal. S.	73949	Temp. C.C. .	28	28:200	7 c.p.	Pot. bal. S.	59277	Temp. C.C. .
58	"				—	29	"	14 c.p.	"	59277	15:22
59	"	10 s.a.	"	P.	76621	"	28:100	14 c.p.	"	61338	inflow 87·43
4:00	"		"			31	"	14 c.p.	"		
01	"	21 s.a.	"	S.	73939	32	"	14 c.p.	"	S. . .	6·6
02	"		"			33	"	21 c.p.	"	S.	59274
03	29:000	10 c.p.	"	P.	76613	34	"	11 c.p.	"	P.	61336
04	"		"			35	"	6 c.p.	"	S.	59272
05	"	1 s.a.	"	S.	73930	36	"	6 c.p.	"	P.	61334
06	"		"			37	"	10 s.a.	"	S.	59270
07	"	8 c.p.	"	S.	73921	38	"	22 s.a.	"	P.	61334
08	"		"			39	"		"	S.	59270
09	"	Bal.	"	S.	73921	40	"		"		
10	"		"			41	"		"		
10:30	"	5 s.a.	"			41:30	"		"		
4:11:01:30			Flow switched over.			6:42:01:12			Flow switched over.		
			Pot. bal. C.C. 63561	Temp. C.C. .	15:24				Pot. bal. C.C. 63557	Temp. C.C. .	15:20

*Abridged Tables Showing Method of Correction.*

To illustrate the method of correction and calculation of results, we here append the corresponding Abridged Tables giving the correction and reduction of the means of the observations taken during each interval for the two specimen tables of observations already given. As it would have been impracticable to place on record the complete observations for the whole work, the abridged tables only were sent in with the paper. The greater part of these tables consisting of small corrections of no intrinsic interest, it was felt to be unnecessary to reproduce them in full. They have been preserved in the Archives so as to be available for reference and verification if required. The samples here given will sufficiently illustrate the nature of the information they contain.





Sec. 5.—*Experimental Proof of the Theory of the Method.*

In Section 2 it was shown that the conditions to be studied in the general difference equation of the method were the relations of the heat-loss to the rise of temperature and to the flow. In the present section I wish to summarize the different experiments which have a more particular bearing on the theory of the method. In the first place in regard to the question, which arises in all experiments where a quantity of water is heated by an electric current conveyed in a wire, of the excess temperature of the wire over the water, it may be said that in the present method the measurement of the electrical energy is completely independent of any value to be assumed for the resistance of the heating-wire, and not only that, but owing to the steady temperature conditions inside the apparatus, no uncertainty of a change in resistance in the wire with a change in temperature is introduced. When the temperature inside the calorimeter has arrived at a steady state, only such energy is used in warming the water as is supplied to the calorimeter by the electric-heating current. The fact that the results were completely independent of the resistance of the heating-wire was shown by using heat-wires of very different resistances.

In regard to the insulation of the platinum heating-wire and of polarization and similar effects, it was considered that these played no part in the results. The resistance of the water column through which the heating-wire passed was enormously high and equal to a column of water 50 centims. long and 2 millims. in diameter, hence in comparison with the resistance of the central heating-wire, which varied from .4 to .8 ohm, was quite negligible. This is true even if it is admitted that the conveyance of the electric current by the water itself could have produced any error on the final result.

Polarization by the naked wire in the water, I am satisfied, did not take place. Not the slightest trace of gas was ever generated in the calorimeter which could not be referred to the liberation of air in the water, and this was verified by watching the column of water in the fine tube when the calorimeter was removed from the water-jacket and a large electric current passed through. The effect of reversing the electric current in the apparatus, and making it flow either with or against the water flow, was tried in some of the earlier experiments, but it was found to produce no effect on the heat-loss as measured by the difference between the electrical and thermal measurements. The effect, if any, on the electrical readings was entirely negligible.

The first experiments which were tried to test the method, were on the relation of the heat-loss to the flow, and were made by varying the flow over a wide range and at the same time keeping the inflow temperature and rise of temperature constant.

The following list of calorimeters, used in the present work, will aid in describing these and subsequent experiments:—

Calorimeter A.—The first one of the set of three obtained from Germany, with the fine-bore tube 2 millims. in diameter. This was the first one tried in the trial experiments in 1897.

Calorimeter B.—Second of the same set, with same dimensions, and used in the preliminary measurements of the mechanical equivalent.

Calorimeter C.—This was the first one made by EIMER and AMEND, after the later design. It had a 2 millims.-bore tube, and has been used for the greater number of the later experiments.

Calorimeter D.—The second E and A calorimeter, with the fine-bore tube 2·8 millims inside diameter and  $P_2O_5$  in the vacuum chamber.

Calorimeter E.—The third from E and A, with the fine-bore tube 3 millims. inside diameter.

The results of the experiments made to determine the relation of the heat-loss to the flow, are now given. They have been taken from the experiments detailed in Tables I., II., III., and IV. in Section 8. The results are taken from the observations on two calorimeters with fine-bore flow-tubes of different sizes, the heating wire in the two cases being made up of either the six strands of ·15-millim. platinum wire or the solid wire, and held central by the silk-covered rubber elastic wound round it. The water was therefore completely stirred in its passage through both the tubes, and stream-line motion avoided.

For convenience in showing the relationship I have expressed the difference between the electrical and heat watts by using the value of  $J$  obtained from the experiment for two flows in place of 4·2 joules. In this case the value of the heat-loss per degree rise should come constant for all of the flows as long as the conduction effect is negligible.

The first set comprises observations made with Calorimeter D at a mean temperature of 28° C. The flow was varied from ·67 gramme per second to ·25, and the rise of temperature was kept approximately the same by adjusting the electric heating current.

CALORIMETER D.—Mean Temperature, 28°·01 C. February 15, 1899.

$$\delta = -\cdot00485. \quad J = 4\cdot1797.$$

$d\theta.$	Q.	$(EC - JQ d\theta)/d\theta.$	Difference from mean, ·07128.
7·5234	·674106	·07122	-·00006
7·8882	·496655	·07147	+·00019
7·7745	·399290	·07130	+·00002
7·9463	·390196	·07113	-·00015
8 0033	·248234	·07197	+·00069

It will be seen that over the range of flow from .67 gramme to .39, the value of the heat-loss remains constant to within the limits of error of the different measurements, and gives a mean value of .07128 in watt-seconds per degree rise. The largest variation from the mean is for a flow of .49 gramme per second, and amounts to .00019 watt on a total supply of 2.1 watts per degree, which is less than 1 in 10,000. For the small flow, the difference from the mean of the other flows amounts to .00069 watt on 1.1 watts. This shows an increase in the heat-loss of nearly 7 parts in 10,000, and is *much too large* to be included within the limits of error. It is evident, then, that for flows below .3 gramme per second, the conduction effect commences to be measurable, and cannot be eliminated by the method of "cold" readings.

For Calorimeter C, the measurements for the different flows are given under date February 20, 1899. These are for double intervals of 15 minutes each, and include the same limits of flow as for Calorimeter D. I have taken  $\delta = .00490$ , instead of  $-.00469$  as given from these measurements, so as to give results comparable with the other sets of observations made at about this time.

CALORIMETER C.—Mean Temperature, 29°·09 C. February 20, 1899.  
 $\delta = .00490.$        $J = 4.1794.$

$d\theta.$	Q.	$(EC - JQ d\theta)/d\theta.$	Difference from mean, .04997.
8.2608	.398498	.04972	-.00025
8.2560	.398540	.04988	-.00009
8.2199	.501957	.05016	+.00019
8.2301	.501026	.04998	+.00001
7.9646	.666042	.05009	+.00012
7.9775	.664388	.04999	+.00002
8.2281	.258114	.05057	+.00060
8.2284	.257947	.05070	+.00073

The largest variation from the mean value of the heat-loss is  $-.00025$  watt, and amounts to a little more than 1 in 10,000. For the small flow, the divergence from the mean of the other flows amount to .00067 watt, and shows that the heat-loss has been increased, which agrees very closely with the result obtained for Calorimeter D. The agreement of the results for the two calorimeters, the one with a 3-millim. bore tube and the other with a 2-millim., seems to prove fairly conclusively that the increase in the heat-loss taking place below a certain limit of flow, cannot be attributed to a change in the radiation loss from the fine-bore tube, but can only be

referred to conduction from the outflow tube, which was the same size in both calorimeters.

The observations under February 22 and March 2 were taken with Calorimeter C, using the limits of flow which I have since adopted for the present measurements.

CALORIMETER C.—Mean Temperature,  $29^{\circ}\cdot11$  C. February 22, 1899.

$$\delta = \cdot00490. \quad J = 4\cdot1794.$$

$d\theta.$	Q.	$(EC - JQ d\theta)/d\theta.$	Difference from mean, $\cdot04938.$
8·2680	·392606	·04939	+ ·00001
8·2635	·392663	·04937	- ·00001
8·1938	·496708	·04928	- ·00010
8·1844	·496591	·04946	+ ·00008
7·9031	·660865	·04945	+ ·00007
7·9083	·658741	·04932	- ·00006

CALORIMETER C.—Mean Temperature,  $29^{\circ}\cdot21$  C. March 2, 1899.

$$\delta = - \cdot00499. \quad J = 4\cdot1790.$$

$d\theta.$	Q.	$(EC - JQ d\theta)/d\theta.$	Difference from mean, $\cdot04968.$
8·4310	·375154	·04963	- ·00005
8·4304	·375076	·04967	- ·00001
8·3979	·472489	·04967	- ·00001
8·4060	·471670	·04986	+ ·00018
8·3390	·590477	·04960	- ·00008
8·3439	·589356	·04969	+ ·00001

The agreement of the heat-loss is very satisfactory, and the variations from the mean value are easily within the limits of error of all the measurements, and are all less than 1 part in 10,000.

The three sets of readings for Calorimeter C show a small difference between the values of the mean heat-loss. This shows, as has been pointed out, that the absolute value of the radiation loss for one calorimeter cannot be relied on from time to time, but will vary, for many reasons. However, this never produced any error in the measurements of the specific heat of the water, on account of the method adopted of always eliminating the heat-loss from at least two different flows taken within a



short time of each other, between which the temperature of the calorimeter never varied.

In selecting the limits of flow to be used in all the measurements, the accuracy of the limits was tested for two other temperatures by recording observations for three different flows at 13° and at 60° C. In these cases the theory of the method was given a severe test.

I have tabulated here the two sets, one for a mean temperature of 13° C. and the other for a temperature of 60° C. I have taken the values of  $\delta$  for each set from the variation curve.

CALORIMETER C.—Mean Temperature, 13°·79 C. March 9, 1899.

$$\delta = -\cdot00208. \quad J = 4\cdot1913.$$

Temperature of surrounding air, 19° C.

$d\theta.$	Q.	$(EC - 4\cdot2 Q d\theta)/d\theta.$	Difference from mean, $\cdot03940.$
8·5768	·372746	·03946	+ ·00006
8·5803	·372262	·03947	- ·00007
8·5586	·459149	·03923	- ·00017
8·5683	·458194	·03930	- ·00010
8·5499	·573318	·03953	+ ·00013
8·5616	·571920	·03940	·00000

CALORIMETER C.—Mean Temperature, 59°·80 C. June 17, 1899.

$$\delta = -\cdot00360. \quad J = 4\cdot1849.$$

Temperature of surrounding air, 22° C.

$d\theta.$	Q.	$(EC - JQ d\theta)/d\theta.$	Difference from mean, $\cdot07254.$
8·3805	·612400	·07277	+ ·00023
8·3835	·611227	·07263	+ ·00009
8·3158	·462971	·07236	- ·00018
8·3395	·461364	·07240	- ·00014
8·3534	·388491	·07261	+ ·00007
8·3674	·387534	·07242	- ·00012

The variation from the mean value in both sets is less than 1 part in 10,000. It is a matter of interest to compare the balance points on the bridge-wire for the

“cold” readings of the differential thermometers, when in place in the calorimeter, for the different flows at different parts of the scale.

The three “cold” readings at  $60^\circ$  are, for the largest flow 23·681, for the next 23·582, and for the lowest 23·544. A decrease in the bridge-wire reading means that the inflow thermometer is at a lower temperature than the outflow. The heat conduction at the inflow end, through the copper wires leading in the electric current, which depends only on the difference existing between the temperature of the calorimeter water and the temperature of the laboratory, can affect the temperature of the inflowing water less for the largest flow than for the smallest flow, and therefore explains the difference in the “cold” readings for the different flows. For the flows used in the present work, the effect of the conduction at the outflow end on the temperature, as indicated by the outflow thermometer, must have been very small indeed, even at the highest points of the range. All of the “cold” readings at the high points are slightly less than the interpolated reading from the differential ice and steam-points. For the “cold” readings at the ice-point, the effect was, as might be expected, reversed, and conduction of heat into the calorimeter from the laboratory took place.

The readings given in Table XLIV., on November 18, 1899, are—

For a flow of ·59 gramme . . . .	23·330
„ „ ·39 „ . . . .	23·392

on November 22, 1899, Table XLV.—

For a flow of ·62 gramme . . . .	23·329
„ „ ·37 „ . . . .	23·398

The peculiar exception to this seems to be in the experiment made at the ice-point on March 24, 1899 (Table XV.), when the “cold” reading for the small flow was lower than for the high. I have not an exact record of the conditions under which this experiment was taken, but it is possible that the outflow end may not have been properly lagged, which would produce the effect indicated by the readings. As the observations, when reduced, give such a consistent measurement of the specific heat, even in the face of this apparent exception, additional evidence is given of the necessity of the “cold” readings to render the results independent of extraneous conditions. The “cold” readings for experiments with the jacket water at the temperature of the laboratory were, as a rule, all at the same point on the bridge-wire, and identical with the interpolated reading from the differential ice and steam-points.

The radiation loss increases only very slightly as the temperatures of the calorimeter and jacket are raised, and this is of course on account of the temperature of the calorimeter flow-tube being always the same amount above the jacket water at all

points of the scale (when the water is heated by the electric current). The increase is from the temperature coefficient of the radiation, and appears to be almost exactly linear over the range  $0^{\circ}$  to  $100^{\circ}$ .

To show the relation between the heat-loss and the rise of temperature, I have summarized the observations in Tables XXXIII., XXXIV., XXXV., for rises of  $8^{\circ}$ ,  $5^{\circ}$ , and  $2^{\circ}$  respectively. These were made with Calorimeter C, but the flat heating-wire was used in place of the central heating conductor with rubber elastic.

## RELATION of heat-loss to rise of temperature.

Calorimeter C.—Mean Temperature,  $28^{\circ}\cdot6$  C. October 14, 18, and 19, 1899.

$d\theta$ .	Q.	$(EC - 4\cdot2Q d\theta)/d\theta$ .	Difference from mean value, $\cdot04535$ .
Large flow.			
8·3069	·626436	·04521	- ·00014
8·3212	·625128	·04533	- ·00002
5·1009	·636545	·04518	- ·00017
5·1086	·635186	·04573	+ ·00038
2·2054	·620890	·04544	+ ·00009
2·2096	·619353	·04525	- ·00010
Small flow.			Mean value, $\cdot05047$
8·2446	·381577	·05044	- ·00003
8·2446	·381454	·05021	- ·00026
5·0887	·388460	·05058	+ ·00011
5·0894	·388232	·05066	+ ·00019
2·2417	·376414	·04951	- ·00096
2·2433	·375879	·04992	- ·00055

The observations were taken for different inflow temperatures so as to give approximately the same mean temperature for the different values of  $d\theta$ , in consequence of which I have used the value 4·2 joules in obtaining the heat watts, the value of  $\delta$  being the same for the different values of  $d\theta$ . For the large flows, the agreement of the values of the heat-loss is good, and much better than might be expected, having obtained the values from experiments made on different dates, although they were within a day or two of each other, and the calorimeter did not vary more than a few degrees between each experiment.

The values for the small flow do not agree so well for the  $2^{\circ}$  rise, but the values for

the 5° and 8° show that the lower value given by the former must be exceptional. Here is an error of nearly 1 part in 1000, to be accounted for by assuming either that for the small flows the heat-loss is not proportional to the rise in temperature, in which case the value of the heat-loss per degree rise increases with rise of temperature, and the value for the 8° rise or the value for the 5° rise must be regarded as exceptional, or that the error in question was due to some uncertainty at that time in the experimental conditions. The latter must be regarded as the most probable on account of the greater difficulty of measuring so small a rise of temperature to the same order of accuracy. Moreover, the second 15-minute interval shows a decided increase, and would possibly have attained the correct value given by the mean of the other readings if the experiment had been further continued. An error of only .001° on the 2° rise would account for the error in the second interval.

Besides the observations I have just given, which were selected from a series of trial experiments on the flat heating-wire, a large number of the other experiments were taken with rises of temperature ranging from 1° to 12°. These are detailed in the tables to be given later, and include results with the central heating-wire as well. It was a matter of convenience only that governed my choice of a rise of temperature for any experiment, and it sometimes happened that it was more convenient to change the mean temperature of an experiment by changing the rise of temperature in the water rather than by altering the inflow temperature—for example, in obtaining a measure of the specific heat in the neighbourhood of the zero point, where it was impossible to maintain the inflowing water at a temperature lower than 0° C.

#### *Heat Capacity of the Calorimeter.*

Although nearly always negligible in the calculation of results, the thermal capacity of the calorimeter is of value in showing the size of error introduced by a change in temperature in the calorimeter water. To determine this, the electrical supply was suddenly cut off from the calorimeter at a given moment and the rate of fall in temperature recorded. This was done for both the limits of flow used in the present work. The lag, on breaking the circuit of the thermometer before it commenced to fall, was in both cases not more than 2 or 3 seconds. If  $\theta$  be the temperature indicated by the outflow thermometer above that of the inflow thermometer, then at any time after shutting off the heat supply, the value of  $\theta$  will be approximately  $\theta = ke^{-at}$ , from which

$$d\theta/dt = kae^{-at} = a\theta.$$

But  $C d\theta/dt = dH/dt$ , where  $C$  is the thermal capacity of the calorimeter, and  $H$  is the total quantity of heat carried off by the water.

Writing  $JQ\theta$  for  $dH/dt$ ,  $Ca\theta = JQ\theta$ , and  $C = JQ/a$ .

The following set of observations was obtained for Calorimeter C :—

Flow, .598 gramme per second.

Time in seconds, after breaking electric current.	Temperature of outflow thermometer.
0	8.375
35	3.968
54	1.721
73	0.574
101	0.237
159	0.008
187.5	0.002
202.5	0.000
$a = .0386$	$C = 50.5$ joules.

Flow, .392 gramme per second.

Time in seconds, after breaking electric current.	Temperature of outflow thermometer.
0	8.068
48	3.646
77	1.400
114	0.264
152	0.142
179	0.032
228	0.010
266	0.005
299	0.003
320	0.000
$a = .0311$	$C = 54$ joules.

The logarithmic relation can of course hardly be said to hold with accuracy, or to be even approximately true for the relation between the fall in temperature and time, as given by the above series of readings, on account of the sudden descent of the temperature during the first two minutes. For changes in temperature in the outflowing water, occasioned by a change in the electrical supply or flow, greater than .02° during the 15-minute intervals, the thermal capacity as calculated by the above relation is of sufficient accuracy for the application of a small correction. It was seldom that the variation in temperature of the outflowing water amounted to more than .02° during a set of readings, and was nearly always less than .01° for the small flows.

Sec. 6.—*Effect of Stream-line Motion on the Distribution of Heat in the Fine-flow Tube.*

In Section 2 we discussed two conditions possibly existing in the fine-flow tube of the calorimeter, and explained generally the effect of these conditions on the temperature gradient of the glass surface and its influence on the heat-loss. In the present section I shall give briefly the experimental sequel to the theoretical considerations. In the light of the recent experiments of Professor HELE-SHAW,\* so beautifully illustrating stream-line motion for water flowing at velocities under the critical velocity, and of Mr. T. E. STANTON† on ‘The Passage of Heat between Metal Surfaces and Liquids in Contact with them,’ the results might have been anticipated which I am about to describe. I do not think, however, that the effect of stream-line motion in fine tubes has been at all sufficiently appreciated.

As the critical velocity at which the stream-line motion breaks down is so great (of the order of 10 feet per second) for tubes of from 2 to 3 millims. in diameter, the effect is inseparably connected with all experiments having to do with tubes of this size. More especially does the flow tend to become linear, and to divide up into distinct and parallel lines, when a change of viscosity is introduced with a change of temperature.

I must, in treating this part of the subject, apologise for the present incompleteness of my experiments, but I feel that I must give such as I have at present, not only to justify myself for the time and trouble I have taken to completely eliminate the effect of stream-line motion from my calorimetric measurements, but also as a beginning to some experiments on the distribution of heat from a metal conductor in water flowing at different velocities through fine tubes, which I hope to continue in the near future, and which I hope may at the same time throw some light on the difference in the rate of flow from the centre to the sides of the tube.

My earlier experiments in 1898 were made with Calorimeter B, with a 2-millim. bore tube and central heating conductor, but with no special device for preventing stream-line motion.‡ The measurement which we obtained of the mechanical equivalent at that time, as I have already pointed out, is affected to a certain extent by this, which was at once apparent when I came to use Calorimeter D, with a 3-millim. bore tube. I undertook two sets of observations with Calorimeter D under two conditions, one with the heating wire, which was made of six strands of 6-millim. platinum wire, resting all along the edge of the tube, the other by drawing the wire, as best I could, straight through the centre of the tube.

The results are as follows :—

\* ‘Proc. Inst. Naval Arch.’ (1897), (1898); ‘Proc. Royal Inst.’ (1899); ‘Proc. Liverpool Eng. Soc.’, 20, 37, (1898).

† ‘Phil. Trans.’ A, vol. 190, 67 (1897).

‡ See note p. 219, *supra*.

FIRST SET.—Heating wire resting on sides of fine-bore tube.  
Mean Temperature, 26°·1 C. November 4, 1898.

$d\theta$ .	Q.	$4 \cdot 2 Q d\theta$ .	EC.	Difference.	Diff./ $d\theta$ .
Large flow.					
8·2666	·600605	20·8528	21·6696	·8158	·09870
8·2759	·599645	20·8429	21·6624	·8195	·09902
Small flow.					
8·3056	·276991	9·6624	10·3699	·7075	·08518
8·3043	·276888	9·6573	10·3668	·7095	·08544

SECOND SET.—Heating wire drawn straight through fine-bore tube.  
Mean Temperature, 27° C. November 21, 1898.

$d\theta$ .	Q.	$4 \cdot 2 Q d\theta$ .	EC.	Difference.	Diff./ $d\theta$ .
Large flow.					
8·4676	·600527	21·3571	21·6677	·3106	·03668
8·4861	·599570	21·3696	21·6695	·2999	·03534
Small flow.					
8·8111	·271465	10·0460	10·6749	·6289	·07138
8·8144	·271088	10·0358	10·6724	·6366	·07223

The mean temperature in the two sets is so nearly the same that in comparing the two we can for the moment neglect the temperature coefficient of the radiation loss from the glass surface. Without otherwise disturbing the experimental conditions, the heat-loss for a flow of ·60 gramme per second has been reduced exactly one-third by simply drawing the heating-wire central. The temperature of the outflowing water being the same in the two cases, the difference in the heat-loss between the two sets gives a measure of the space represented by the diagram in fig. 2 (p. 154), between the lines drawn for condition 1 and condition 2.

The value of the heat-loss for the same calorimeter and same flow, but introducing the device for eliminating stream-line motion, is very nearly ·06 watt per degree rise, which lies midway between ·09 and ·03 watt as given here respectively. For the small flow, as might be expected, the heat-loss is more nearly the same in the two

cases, on account of the greater opportunity for conduction throughout the water column ; but the effect is still shown. It is of interest also to calculate the actual temperature of the same heating wire in the two cases.

Flow per second.	Resistance of heating wire.	Corrected to a mean temperature of 26°·1.
	First set.	
·60	·52427 ohm.	·5243
·28	·51740 „	·5174
	Second set.	
·60	·53460 ohm.	·5331
·27	·52383 „	·5225

Correcting to the same mean temperature by the temperature coefficient of the platinum, the results show that, as might be expected, the wire held central is hotter than when in contact with the glass. This means that the central wire is surrounded by a cloak of hot water moving parallel with it, and the more completely prevented from diffusing the greater the velocity of the flow. This is shown conclusively by comparing the temperature of the wire, as indicated by its resistance, with the temperature of the same wire measured “cold” and reduced to the same mean temperature. A measurement of this for a current through the wire, not sufficient to cause a rise in temperature of more than ·1° in the outflowing water, gave the value ·5100 ohm.

For the case where the wire is held central in the largest flow and the conditions are most perfect for the formation of a moving cloak, the mean temperature of the wire, as given by its increment of resistance, over and above the mean temperature of the water column in the flow-tube, is of the order of 12° C. This shows that, at the very most, only one-quarter of the total quantity of water flowing through the 3-millim. flow-tube per second was receiving heat from the wire.

In the case where the wire touches the sides of the tube for its full length, a greater area of water is heated by conduction and diffusion throughout the layers along the sides of the tube, which do not move at such a high rate of velocity as in the centre. The increment of resistance for the large flow given in the first set of readings for this case shows that the wire was of the order of 7° hotter than the mean temperature of the water, and indicates that about one-half of the total flow was employed in carrying off the heat from the wire. When the water is thoroughly stirred around the heating wire, and in particular where the flat heating wire, twisted into spirals down the flow-tube, is employed, the mean temperature of the



wire is much more nearly the same for the two flows and more nearly equal to that of the water column, the differences being of the order of  $1^{\circ}$  C. only.

Sec. 7.—*Preliminary Measurements of the Mechanical Equivalent.*

Our first measurements of the mechanical equivalent in the summer of 1898 were made with Thermometer C and Calorimeter B. This had a flow-tube slightly less than 2 millims., and, with the exception of the device for eliminating stream-line motion, was fitted up in a similar way to the later calorimeters. It is a matter of interest to determine the way in which the heat-loss varies with rise of temperature for this case. I have summarized the observations which we made at that time to determine this, and expressed them here in terms of the same values for the units as the later measurements. The results are corrected to the same value of  $Q$ , and were all obtained approximately at a mean temperature of  $30^{\circ}$  C.

RELATION of Heat-loss to Rise of Temperature.

Large flow. $Q = \cdot 54000$ gramme per second.		Small flow. $Q = \cdot 27300$ gramme per second.	
$d\theta.$	$(EC - 4 \cdot 2 Q d\theta)/d\theta.$	$d\theta.$	$(EC - 4 \cdot 2 Q d\theta)/d\theta.$
3·0462	·04445	2·9717	·04941
5·9427	·04403	5·8891	·04904
8·9131	·04298	9·0285	·04982
12·2129	·04070	11·9785	·04809

The readings for the large flow are very consistent, as shown by the plot in fig. 14. For the small flow the variations in the observations are far from satisfactory, but they show a similar decrease in the value of the heat-loss with rise of temperature as for the large flow. The decided bend in the curves shows that, as the temperature of the out-flowing water is decreased, the temperature gradient down the fine-bore tube approaches more nearly a straight line (*cf.* fig. 2, p. 154.) The decrease in the heat-loss with increase of temperature points to the more perfect confinement of the heated water around the wire in its passage through the tube, which is occasioned by its greater difference in density.

The small flow allows of the more perfect distribution of heat throughout the water column in the flow-tube, and the curve approaches a limiting value, as the temperature is lowered, much sooner than in the case of the large flow. If we may assume the two limiting values of the heat-loss per degree rise in the calorimeter for the two flows by extrapolating for a value of  $d\theta = 0$  in the two cases, and accept

these values as being true for any rise where the temperature distribution is uniform throughout the water column and stream-line motion avoided, then the value of  $d$  may be calculated. The two values of the heat-loss per degree rise so obtained were for a flow of

·54000 gramme per sec., ·04445 watt.      ·27300 gramme per sec., ·04965 watt.

The latter value has not to be corrected for the small conduction effect for the small

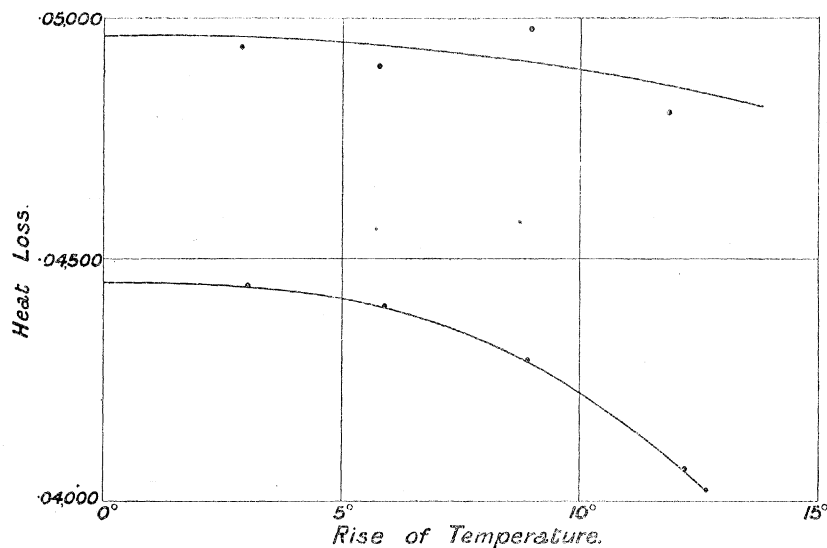


Fig. 16.

flow on account of the method of treatment. Hence the value of  $d$  comes out — ·00464, from which

$$J = 4.2(1 - 0.00464) = 4.1805 \text{ joules, at } 30^\circ \text{ C.}$$

The value of  $J$  at the same temperature, obtained with the other calorimeters for any rise of temperature when using the various devices for obviating stream-line motion, is 4.1780 joules, which agrees to 1 part in 2000 with this value. This is quite as good an agreement as can be expected from the manner of treating the observations, and the want of agreement in the observations themselves for the small flow, which is no doubt occasioned by the uncertainty introduced by the stream-lines.

#### Sec. 8.—*Experiments between 0° and 100° C.*

As soon as it became clear that the main cause of error had been removed in eliminating the effect of stream-line motion in the calorimeter, I commenced a series of experiments to extend over the entire range of temperature. These experiments are summarized in the following table from I. to LV., and include upwards of 46

complete experiments. They extended over a period of just a year, and divide themselves naturally into 8 separate series.\*

Series 1. Nos. I. to XV.

This series includes experiments with Calorimeter C, between 4° and 35° C., and Calorimeter D, at 28°. Both calorimeters were fitted with a stranded platinum heating-wire with the silk-covered rubber cord wound round. The distilled water supplied to the calorimeter was boiled before running under the oil, in bottles forming the head, but no special care was taken to keep it hot while running in. A large quantity of the air was driven off in the process of boiling, but subsequent results have shown that the water in the head must still have contained a considerable quantity of dissolved air. Several of the experiments include other flows, besides the flows used throughout the entire series of experiments. These have been already summarized in Section 5. The correction for Thermometer E is that given under Group I., Section 3, *c*.

Series 2. Nos. XVI. to XXVII.

Between Series 1 and 2 several alterations were made to the apparatus, one of the chief being the introduction of 40 feet of tin tubing into the constant temperature tank to replace a similar amount of copper tubing used previously. This was found necessary owing to the gradual formation of copper rust in the tube. This rust was carried into the small rubber tube conveying water from the tank to the calorimeter, and gradually reduced the flow. The experiments were extended from 22° up as far as 60° C., where they had to be discontinued in order to further refine the regulating attachments. The calorimeter was fitted with a solid platinum heating-wire, with silk-covered rubber cord. The agreement of the results at the lower points between 22° and 35° with those in Series 1 is very satisfactory. Above 45° the results are not so consistent, probably on account of the fluctuations in gas-pressure supplying the main heat to the circulating system. The experiment at 60° was taken, however, when no other gas was being used in the building, and the conditions were unusually steady. Rises of temperature of 11° and 5° were tried as a check on the measurements. The correction for Thermometer E is that obtained in the test in Group II., Section 3, *c*.

Series 3. Nos. XXVIII. to XXXII.

This series includes another attempt to obtain the high temperatures, but nearly all the experiments were spoiled by the liberation of air inside the calorimeter. The experiment at 67° is given as an illustration of the effect produced by the appearance of air. In this series the air bubbles were found in the calorimeter water after the experiment, in spite of the fact that the distilled water was kept continuously boiling as it was supplied to the head bottles, and was cooled from 100° C. only by the cold

\* In the following *d* is used instead of the  $\delta$  of Sec. 2.

water already in the bottles. The correction to the fundamental interval of Thermometer E is the same as for the last series.

Series 4. Nos. XXXIII. to XXXV.

This series includes experiments with Calorimeter C, using the flattened platinum strip for heating wire, instead of the central wire conductor and elastic strip. These observations are summarized in Section 5. The use of the flat wire was found to produce more irregularity in the heat-loss between the different flows, especially apparent on the small flows, and no doubt occasioned by the fact that the wire touched the sides of the tube. The correction for the fundamental interval of Thermometer E is that given under Group III., in Section 3, *c*.

The agreement of the value of J with the other measurements is very satisfactory, and the more so because the heating conductor was changed not only in form but in resistance.

Series 5. Nos. XXXVI. and XXXVII.

Experiments with Calorimeter E with flat heating strip. The fine-bore tube was slightly over 3 millims. in diameter, and was the largest tried in these experiments. The first experiments with this calorimeter were made with the central wire conductor and large rubber cord, but were neither satisfactory nor consistent. The effect of the stream-line motion apparently began to come in, with the helical motion in the water, probably from the size of the flow-tube compared to the size of the heating-wire. The thermometer was the same in every respect to that used in Series 4.

Series 6. Nos. XXXVIII. to XLVIII.

In this series, Calorimeter C was refitted with central solid platinum heating-wire with silk-covered rubber cord. Thermometer E, Group III., was still used. Measurements from  $20^{\circ}$  to  $0^{\circ}$  were made, and the values obtained under Series 1 and 2 completely verified. The observations were extended below  $4^{\circ}$ , and the lowest point obtained was for a rise of temperature of  $1^{\circ}$  above  $0^{\circ}$ . In this experiment only one flow was obtained, but the value of  $d$  may be calculated with some degree of approximation by assuming the value of the heat-loss for the two other determinations with inflow-water at  $0^{\circ}$ , and correcting for the temperature coefficient of the radiation. This experiment was done principally to test the rapid increase of the specific heat at the freezing-point. An attempt was also made to obtain the high points, but with no more success than in the previous attempts.

Series 7. Nos. XLIX and L.

Between Series 6 and the present series, various devices were tried to obviate the effect of dissolved air in the boiled water. The plan was finally adopted of preparing

absolutely air-free water, as described in Section 5, and from this time on the work at the higher points progressed more favourably. In this series observations were obtained at  $30^{\circ}$  and  $86^{\circ}$ , but the latter unfortunately with only one flow. The second flow could not be taken on account of the rapid evaporation of water from the tank, the constant-level device not being used at that time. Here again, extrapolation for the heat-loss from the value at  $30^{\circ}$  can be made, but the procedure can hardly be justified with a greater accuracy than 1 in 1000. The agreement with the later results is, however, extraordinarily good.

Series 8. Nos. LI. to LV.

This series was made with box 2 and Thermometer E, involving the F.I. correction in Group IV. It extends from  $32^{\circ}$  C. to  $92^{\circ}$  C., and in many respects is the most important series of the whole. The Calorimeter C was refitted throughout so as to give an entirely new set of observations. The complete agreement of the measurement of the specific heat at  $32^{\circ}$  C. with the other measurements with box 1, eliminates any possible error due to the box and its connections. The four sets of observations at the higher points are exceedingly consistent, and distinctly show that the previous trouble to obtain the measurements in this region was due to the effect of the air in the water. Not the slightest trouble was experienced with air making its appearance in the calorimeter in these experiments. The order in which these observations were taken was as follows:  $32^{\circ}$ ,  $74^{\circ}$ ,  $92^{\circ}$ ,  $80^{\circ}$  and  $68^{\circ}$ , between which the calorimeter cooled down to the temperature of the laboratory, and had to be heated up to the desired point each time. The measurement at  $86^{\circ}$  in Series 7 is in very good agreement with these. The beautiful consistency of this last series of measurements might make it desirable to repeat the observations between  $50^{\circ}$  and  $60^{\circ}$  C. with air-free water. I did not consider this was necessary, however, as the continuity of the observations at the two ends of the range is so good, and the divergence in the results obtained between  $50^{\circ}$  and  $60^{\circ}$  C. is so clearly explained by unforeseen and extraneous causes.

The calculation of the results in the tables just given for the determination of the value of the electrical and heat energy has been very much facilitated by the use of the Brunsviga calculating machine, which is very much to be recommended for this class of work. For the application of the small correction factors, and for the final estimation of the values of  $d$  and  $h$ , the Fuller cylindrical slide-rule has been constantly used. The values of the electrical and heat watts given in the summary at the foot of each table may therefore be in error by 2 or perhaps 3 in the fourth decimal place, but no more, but I feel confident that in the estimation of the mean value, upon which the value of  $d$  depends, this error tends to disappear, and that the value of  $d$  given by the measurements in any of the tables, represents the observations to an accuracy of 1 part in 100,000.

*Summary of Results of Observations.*

The following table contains a summary of the observations arranged and abstracted by Professor CALLENDAR. The original tables (abridged), giving details of corrections and calculations, are preserved for reference in the Archives of the Royal Society.

The first column gives the number and date of the corresponding Abridged Table preserved in the Archives. The second column gives the temperature of the jacket water or inflow, taken by means of a mercury thermometer, and corrected to the nearest hundredth of a degree. The third column gives the mean difference of temperature,  $d\theta$ , between the inflow and outflow, observed to the ten-thousandth of a degree by means of a pair of differential platinum thermometers, and reduced by the parabolic difference formula, assuming the boiling-point of sulphur to be  $444.53^\circ$  C. The fourth column gives the flow of water,  $Q$ , through the calorimeter, in grammes per second, reduced to vacuum. The fifth column gives the value of the product,  $4.2 Q d\theta$ , for comparison with the power,  $EC$  in watts, given in the next column. The seventh column gives the difference,  $EC - 4.2 Q d\theta$ , of the numbers in the two previous columns divided by  $d\theta$ . This quotient is denoted by  $D$ , and is used in calculating the results given in the last column, by means of the difference equation

$$EC/d\theta - 4.2 Q = D = 4.2 Q d + h,$$

in which  $d$  expresses the fractional variation of the specific heat of water in terms of an arbitrary unit 4.200 joules, as defined by the relation  $J = 4.200 (1 + d)$ , and the symbol  $h$  denotes the rate of heat-loss in watts per degree rise of temperature. The value of  $d$  is found by combining the observations for the two different flows  $Q'$  and  $Q''$ , which give the relation

$$d = (D' - D'')/4.2 (Q' - Q'').$$

The values of  $h$  and  $J$  follow immediately from that of  $d$ . The values of  $EC$  and  $J$  are calculated assuming the E.M.F. of the Clark cell at  $15^\circ$  C. to be 1.4342 volts, but this does not affect the relative values.

In cases where more than two different flows were taken at the same temperature, the values of  $d$  and  $h$  are calculated from the largest and smallest flow. These values of  $d$  and  $h$  are then assumed to calculate a value of  $D$  for the intermediate flow for comparison with the value of  $D$  deduced from the observations.

TABLE XVIII.—Summary of Results of Observations.

Number and date.	Jacket. Temp. °C.	Temp. rise. $d\theta$ , °C.	Flow Q. gm./sec.	Product. $4.2 Q d\theta$ .	Watts. EC.	Diff./ $d\theta$ . D.	Results. $d, h, J$ .
Series I. Calorimeter D. Stranded Conductor. Thermometer E, I.							
I. Feb. 15, 1899.	24°03	7°5234	·674106	21·3006	21·7331	·05749	$d = -\cdot00485$ , $h = +\cdot07122$ , $J = 4\cdot1796$ , at 28°·01 C.
	(Not repeated)						
	24·04	7·7745	·399290	13·0379	13·5290	·06317	
	24·02	7·9463	·390196	13·0225	13·5245	·06318	
II. Feb. 15, 1899.	24·00	7·8882	·496655	16·4544	16·9383	·06135	$d = -\cdot00533$ , $h = +\cdot07247$ , $J = 4\cdot1776$ , at 28°·01 C.
	(Not repeated)						
	24·01	8·0033	·248234	8·3447	8·8802	·06691	
		(Not repeated)					
Calorimeter C. Stranded Conductor. Thermometer E, I.							
III. Feb. 20, 1899.	25°03	7°9646	·666042	22·2800	22·5697	·03637	$d = -\cdot00469$ , $h = +\cdot04944$ , $J = 4\cdot1803$ , at 29°·10 C.
	25·03	7·9775	·664388	22·2607	22·5504	·03632	
	25·06	8·2608	·398498	13·8260	14·1689	·04151	
	25·06	8·2560	·398540	13·8194	14·1634	·04167	
IV. Feb. 20, 1899.	25·03	8·2281	·258114	8·9199	9·2922	·04525	$d = -\cdot00546$ , $h = +\cdot05123$ , $J = 4\cdot1771$ , at 29°·09 C.
	25·03	8·2284	·257947	8·9144	9·2879	·04539	
	25·06	8·2199	·501957	17·3294	17·6567	·03982	
	25·06	8·2301	·501026	17·3186	17·6450	·03966	
V. Feb. 22, 1899.	25·07	7·9031	·660813	21·9361	22·2194	·03585	$d = -\cdot00489$ , $h = +\cdot04937$ , $J = 4\cdot1795$ , at 29°·11 C.
	25·07	7·9083	·658690	21·8800	22·1628	·03576	
	25·07	8·2680	·392575	13·6334	13·9749	·04131	
	25·07	8·2635	·392362	13·6280	13·9692	·04129	
VI. Feb. 22.	25·07	8·1938	·496670	17·0937	17·4137	·03906	D calc. = ·03917.
	25·07	8·1844	·496553	17·0700	17·3911	·03924	
VII. Mar. 2, 1899.	25·01	8·3390	·590477	20·6807	20·9912	·03723	$d = -\cdot00499$ , $h = +\cdot04965$ , $J = 4\cdot1790$ , at 29°·21 C.
	25·01	8·3439	·589356	20·6536	20·9653	·03734	
	25·01	8·4310	·375154	13·2841	13·6363	·04177	
	25·01	8·4304	·375076	13·2807	13·6362	·04181	
VIII. Mar. 2.	25·01	8·3979	·472489	16·6652	16·9992	·03977	D calc. = ·03975.
	25·01	8·4060	·471670	16·6524	16·9885	·03998	
IX. Mar. 9, 1899.	9·51	8·5768	·372746	13·4272	13·7377	·03620	$d = -\cdot00208$ , $h = +\cdot03946$ , $J = 4\cdot1913$ , at 13°·79 C.
	9·51	8·5803	·372262	13·4153	13·7261	·03622	
	9·51	8·5499	·573318	20·5876	20·8827	·03452	
	9·51	8·5616	·571920	20·5654	20·8595	·03439	
X. Mar. 9.	9·51	8·5586	·459149	16·5046	16·8060	·03522	D. calc. = ·03546.
	9·51	8·5683	·458194	16·4889	16·7912	·03529	
XII. Mar. 11, 1899.	13·30	8·7411	·357638	13·1298	13·4508	·03673	$d = -\cdot00309$ , $h = +\cdot04139$ , $J = 4\cdot1870$ , at 17°·69 C.
	13·30	8·7241	·358131	13·1222	13·4428	·03675	
	13·31	8·9195	·566221	21·2117	21·5153	·03404	
	(Second interval, regulator failed)						

TABLE XVIII.—Summary of Results of Observations—*continued*.

Number and date.	Jacket. Temp. °C.	Temp. rise. $d\theta$ , °C.	Flow Q. gm./sec.	Product. $4.2 Q d\theta$ .	Watts. EC.	Diff./ $d\theta$ . D.	Results. $d, h, J$ .
Series I. Calorimeter C. Stranded Conductor. Thermometer E, I.— <i>continued</i> .							
XIII. Mar. 16, 1899.	19° 95 19° 95 19° 95 19° 95	8° 4978 8° 5149 8° 4695 8° 4963	·373778 ·372934 ·587077 ·584879	13·3404 13·3371 20·8834 20·8686	13·6769 13·6734 21·1846 21·1708	·03960 ·03950 ·03556 ·03557	$d = -\cdot 00446$ , $h = +\cdot 04655$ , $J = 4\cdot 1813$ , at 24° 20 C.
XIV. Mar. 17, 1899.	30° 15 30° 16 30° 16 30° 17	8° 6230 8° 6154 8° 6037 8° 6283	·358452 ·358388 ·567099 ·565123	12·9819 12·9682 20·4924 20·4794	13·3758 13·3639 20·8450 20·8314	·04568 ·04593 ·04099 ·04080	$d = -\cdot 00561$ , $h = +\cdot 05424$ , $J = 4\cdot 1765$ , at 34° 47 C.
XV. Mar. 24, 1899.	0° 13 0° 13 0° 13 0° 13	8° 3170 8° 3407 8° 2833 8° 2883	·559701 ·557801 ·361401 ·360873	19·5511 19·5402 12·5730 12·5622	19·9014 19·8913 12·8992 12·8898	·04212 ·04210 ·03938 ·03953	$d = +\cdot 00330$ , $h = +\cdot 03437$ , $J = 4\cdot 2138$ , at 4° 28 C.
Series II. Calorimeter C. Solid Conductor. Thermometer E, II.							
XVI. June 6, 1899.	18° 17 18° 16 18° 17	7° 9225 7° 9999 7° 9672	·404339 ·633704 ·401420	13·4542 21·2922 13·4324	13·7653 21·5737 13·7441	·03927 ·03519 ·03913	$d = -\cdot 00413$ , $h = +\cdot 04619$ , $J = 4\cdot 1827$ , at 22° 16 C.
XVII. June 8, 1899.	27° 29 27° 30 27° 30 27° 30	8° 2190 8° 2310 8° 1357 8° 1545	·618698 ·617503 ·394624 ·393530	21·3573 21·3472 13·4843 13·4780	21·6793 21·6712 13·8447 13·8404	·03918 ·03936 ·04430 ·04444	$d = -\cdot 00542$ , $h = +\cdot 05334$ , $J = 4\cdot 1773$ , at 31° 40 C.
XVIII. June 9, 1899.	27° 97 27° 97 27° 97 27° 97	8° 4281 8° 4467 8° 3590 8° 3803	·602990 ·601265 ·383786 ·382529	21·3447 21·3305 13·64739 13·4640	21·6740 21·6632 13·8410 13·8360	·03908 ·03939 ·04392 ·04439	$d = -\cdot 00536$ , $h = +\cdot 05282$ , $J = 4\cdot 1775$ , at 32° 17 C.
XIX. June 12, 1899.	36° 82 36° 82 36° 83 36° 84	8° 3641 8° 3726 8° 3746 8° 3717	·636775 ·635489 ·381973 ·381800	22·3694 22·3469 13·4352 13·4245	22·7438 22·7246 13·8606 13·8493	·04476 ·04511 ·05068 ·05074	$d = -\cdot 00540$ , $h = +\cdot 05939$ , $J = 4\cdot 1773$ , at 41° 02 C.
XX. June 12, 1899.	41° 30 41° 30 41° 30 41° 30	8° 3720 8° 3892 8° 4063 8° 4068	·632463 ·630617 ·397132 ·396628	22·2389 22·2195 14·0213 14·0043	22·6538 22·6331 14·4785 14·4633	·04956 ·04931 ·05439 ·05460	$d = -\cdot 00514$ , $h = +\cdot 06306$ , $J = 4\cdot 1784$ , at 45° 49 C.
XXI. June 14, 1899.	45° 70 45° 70 45° 69 45° 70	7° 9687 7° 9689 7° 9639 7° 9648	·666393 ·665414 ·419567 ·418914	22·3033 22·2705 14·0339 14·0136	22·7174 22·6825 14·4908 14·4700	·05197 ·05171 ·05737 ·05730	$d = -\cdot 00531$ , $h = +\cdot 06669$ , $J = 4\cdot 1777$ , at 49° 68 C.
XXII. June 14, 1899.	50° 52 50° 52 50° 50 50° 53	8° 2051 8° 2065 8° 1496 8° 1528	·631248 ·630085 ·401674 ·400859	21·7537 21·7173 13·7486 13·7261	22·2358 22·2001 14·2543 14·2374	·05876 ·05884 ·06206 ·06272	$d = -\cdot 00372$ , $h = +\cdot 06867$ , $J = 4\cdot 1844$ , at 54° 61 C.



TABLE XVIII.—Summary of Results of Observations—*continued*.

Number and date.	Jacket. Temp. ° C.	Temp. rise. $d\theta$ , ° C.	Flow Q. gm./sec.	Product. $4.2 Q d\theta$ .	Watts. EC.	Diff./ $d\theta$ . D.	Results. $d, h, J$ .
Series II. Calorimeter C. Solid Conductor. Thermometer E, II.— <i>continued</i> .							
XXIII. June 17, 1899.	55° 64 55° 64 55° 61 55° 61	8° 3805 8° 3835 8° 3534 8° 3674	·612400 ·611227 ·388491 ·387534	21·5553 21·5217 13·6299 13·6191	22·0876 22·0532 14·1874 14·1760	·06351 ·06339 ·06674 ·06656	$d = -\cdot 00341$ , $h = +\cdot 07220$ , $J = 4\cdot 1849$ , at $59^{\circ}\cdot 80$ C.
XXIV. June 17.	55° 61 55° 61	8° 3158 8° 3395	·462971 ·461364	16·1699 16·1595	16·7134 16·7052	·06536 ·06542	D calc. = ·06559.
XXV. June 20, 1899.	27° 15 27° 15 27° 17 27° 17	11° 3447 11° 3383 11° 3324 11° 3428	·642348 ·641338 ·402771 ·402108	30·6064 30·5410 19·1703 19·1562	31·0604 30·9955 19·6835 19·6715	·04002 ·04008 ·04529 ·04542	$d = -\cdot 00528$ , $h = +\cdot 05429$ , $J = 4\cdot 1778$ , at $32^{\circ}\cdot 81$ C.
XXVI. June 20.	27° 16 27° 17	11° 2504 11° 2418	·489797 ·488845	23·1437 23·0811	23·6345 23·5726	·04363 ·04372	D. calc. = ·04345.
XXVII. June 22.	27° 98 27° 98 27° 99 27° 99	5° 1297 5° 1365 5° 1579 5° 1613	·610593 ·608831 ·383538 ·382650	13·1551 13·1344 8·3086 8·2948	13·3565 13·3379 8·5392 8·5256	·03926 ·03962 ·04471 ·04472	$d = -\cdot 00555$ , $h = +\cdot 05364$ , $J = 4\cdot 1767$ , at $30^{\circ}\cdot 54$ C.
Series III. Calorimeter C. Thermometer E, II. Solid Conductor.							
XXVIII. Sept. 4, 1899.	25° 44 25° 44 25° 45 25° 45	8° 0202 8° 0343 8° 0981 8° 1079	·634819 ·632988 ·384855 ·384098	21·3838 21·3596 13·0896 13·0797	21·7067 21·6841 13·4580 13·4487	·04026 ·04039 ·04549 ·04552	$d = -\cdot 00496$ , $h = +\cdot 05352$ , $J = 4\cdot 1792$ , at $29^{\circ}\cdot 47$ C.
XXIX. Sept. 6, 1899.	27° 14 27° 14 27° 14 27° 14	8° 0488 8° 0548 8° 1703 8° 1808	·630942 ·630005 ·380614 ·379886	21·3290 21·3131 13·0608 13·0526	21·6566 21·6420 13·4412 13·4340	·04070 ·04083 ·04656 ·04662	$d = -\cdot 00544$ , $h = +\cdot 05518$ , $J = 4\cdot 1771$ , at $31^{\circ}\cdot 22$ C.
XXX. Sept. 12, 1899.	34° 60 34° 60 34° 60 34° 60	8° 3187 8° 3139 8° 3018 8° 3159	·394336 ·394088 ·626817 ·625193	13·7775 13·7609 21·8555 21·8360	14·2055 14·1916 22·2412 22·2225	·05145 ·05180 ·04647 ·04648	$d = -\cdot 00530$ , $h = +\cdot 06041$ , $J = 4\cdot 1777$ , at $38^{\circ}\cdot 76$ C.
XXXI. Sept. 14, 1899.	63° 33 63° 33 63° 33 63° 33	8° 3443 8° 3517 8° 3782 8° 4042	·390990 ·390431 ·627514 ·625068	13·7027 13·6952 22·0812 22·0633	14·3302 14·3256 22·6775 22·6657	·07520 ·07547 ·07117 ·07168	$d = -\cdot 00395$ , $h = +\cdot 08182$ , $J = 4\cdot 1834$ , at $67^{\circ}\cdot 52$ C.
XXXII. Sept. 18, 1899.	50° 41 50° 42 50° 43 50° 43	8° 2923 8° 2990 8° 2824 8° 2965	·393061 ·392595 ·626272 ·624643	13·6893 13·6841 21·7855 21·7658	14·2326 14·2267 22·2875 22·2722	·06552 ·06538 ·06061 ·06104	$d = -\cdot 00473$ , $h = +\cdot 07325$ , $J = 4\cdot 1801$ , at $54^{\circ}\cdot 57$ C.

TABLE XVIII.—Summary of Results of Observations—*continued.*

Number and date.	Jacket. Temp. °C.	Temp. rise. $d\theta$ , °C.	Flow Q. gm./sec.	Product. $4.2 Q d\theta$ .	Watts. EC.	Diff./ $d\theta$ . D.	Results. $d, h, J$ .
Series IV. Calorimeter C. Spiral strip, no rubber cord. Thermometer E, III.							
XXXIII. Oct. 14, 1899.	24° 64	8° 3069	·626436	21·8557	22·2313	·04521	$d = -\cdot 00493$ ,
	24·64	8·3212	·625128	21·8476	22·2248	·04533	$h = +\cdot 05826$ ,
	24·65	8·2446	·381577	13·2130	13·6288	·05044	$J = 4\cdot 1793$ ,
	24·65	8·2446	·381454	13·2087	13·6226	·05021	at 28°·77 C.
XXXIV. Oct. 18, 1899.	25·97	5·1009	·636545	13·6372	13·8676	·04518	$d = -\cdot 00497$ ,
	25·97	5·1086	·635186	13·6286	13·8622	·04573	$h = +\cdot 05870$ ,
	25·98	5·0887	·388460	8·3024	8·5598	·05058	$J = 4\cdot 1791$ ,
	25·98	5·0894	·388232	8·2987	8·5565	·05065	at 28°·52 C.
XXXV. Oct. 19, 1899.	27·38	2·2053	·620890	5·7508	5·8510	·04544	$d = -\cdot 00427$ ,
	27·38	2·2095	·619353	5·7475	5·8475	·04525	$h = +\cdot 05645$ ,
	27·38	2·2416	·376414	3·5437	3·6547	·04951	$J = 4\cdot 1821$ ,
	27·38	2·2432	·375879	3·5412	3·6532	·04992	at 28°·49 C.
Series V. Calorimeter E (3 millims.), spiral strip. Thermometer E, III.							
XXXVI. Oct. 27, 1899.	25° 74	8° 3281	·623288	21·8013	22·1831	·04584	$d = -\cdot 00542$ ,
	25·75	8·3360	·622427	21·7919	22·1727	·04566	$h = +\cdot 05994$ ,
	25·74	8·3310	·384073	13·4387	13·8652	·05119	$J = 4\cdot 1772$ ,
	25·75	8·3436	·383177	13·4377	13·8551	·05122	at 29°·92 C.
XXXVII. Nov. 1.	17·02	7·7440	·689271	22·4184	22·7443	·04208	$d = -\cdot 00404$ ,
	17·02	7·7488	·687919	22·3883	22·7199	·04280	$h = +\cdot 05414$ ,
	17·08	7·7804	·485563	15·8671	16·2241	·04589	$J = 4\cdot 1830$ ,
	(Flow not repeated)						at 20°·92 C.
Series VI. Solid Conductor. Thermometer E, III. Calorimeter C.							
XXXVIII. Nov. 3, 1899.	16° 01	8° 2408	·603561	20·8901	21·1857	·03587	$d = -\cdot 00384$ ,
	16·01	8·2549	·602250	20·8804	21·1744	·03598	$h = +\cdot 04567$ ,
	16·01	8·2575	·375191	13·0122	13·3381	·03947	$J = 4\cdot 1838$ ,
	16·01	8·2554	·375065	13·0043	13·3325	·03976	at 20°·18 C.
XXXIX. Nov. 4, 1899.	16·00	2·1866	·576497	5·2944	5·3737	·03627	$d = -\cdot 00310$ ,
	16·00	2·1878	·575717	5·2901	5·3699	·03647	$h = +\cdot 04387$ ,
	16·00	2·1855	·357957	3·2857	3·3713	·03917	$J = 4\cdot 1870$ ,
	16·00	2·1866	·357600	3·2841	3·3699	·03924	at 17°·09 C.
XL. Nov. 6, 1899.	17·57	5·0878	·606172	12·9531	13·1370	·03615	$d = -\cdot 00397$ ,
	17·57	5·0992	·604361	12·9433	13·1274	·03611	$h = +\cdot 04622$ ,
	17·59	5·1071	·377173	8·0903	8·2943	·03995	$J = 4\cdot 1833$ ,
	17·60	5·1142	·376515	8·0874	8·2916	·03993	at 20°·13 C.
XLI. Nov. 14, 1899.	16·34	8·1889	·608476	20·9275	21·2381	·03793	$d = -\cdot 00420$ ,
	16·34	8·2003	·607098	20·9093	21·2208	·03799	$h = +\cdot 04867$ ,
	16·36	8·2198	·383107	13·2261	13·5703	·04188	$J = 4\cdot 1824$ ,
	16·38	8·2261	·382518	13·2159	13·5613	·04199	at 20°·45 C.

TABLE XVIII.—Summary of Results of Observations—*continued*.

Number and date.	Jacket. Temp. ° C.	Temp. rise. $d\theta$ , ° C.	Flow Q. gm./sec.	Product. $4.2 Q d\theta$ .	Watts. EC.	Diff./ $d\theta$ . D.	Results. $d, h, J$ .
Series VI. Solid Conductor. Thermometer E, III. Calorimeter C.— <i>continued</i> .							
XLII. Nov. 16, 1899.	14.65	2.1581	.581584	5.2715	5.3533	.03790	$d = -.00254$ ,
	14.65	2.1614	.579646	5.2620	5.3464	.03905	$h = +.04467$ ,
	14.63	2.1391	.363655	3.2672	3.3543	.04072	$J = 4.1893$ ,
	14.63	2.1420	.362870	3.2646	3.3521	.04085	at $15^{\circ}.71$ C.
XLIII. Nov. 17, 1899.	7.50	2.1065	.587245	5.1955	5.2791	.03969	$d = +.00022$ ,
	7.57	2.1050	.586733	5.1873	5.2720	.04024	$h = +.03943$ ,
	7.67	2.0664	.372448	3.2325	3.3141	.03949	$J = 4.2009$ ,
	7.70	2.0577	.372092	3.2158	3.2982	.04044	at $8^{\circ}.66$ C.
XLIV. Nov. 18, 1899.	0.15	2.1993	.592582	5.4737	5.5842	.05024	$d = +.00512$ ,
	0.15	2.1982	.591463	5.4606	5.5714	.05041	$h = +.03759$ ,
	0.15	2.1909	.389629	3.5853	3.6861	.04601	$J = 4.2215$ ,
	0.15	2.1916	.389077	3.5813	3.6820	.04594	at $1^{\circ}.35$ C.
XLV. Nov. 22, 1899.	0.15	5.0561	.616583	13.0935	13.3381	.04838	$d = +.00370$ ,
	0.15	5.0694	.614942	13.0929	13.3344	.04764	$h = +.03842$ ,
	0.15	5.0738	.369790	7.8802	8.1040	.04410	$J = 4.2155$ ,
	0.15	5.0772	.369335	7.8758	8.1007	.04429	at $2^{\circ}.68$ C.
XLVI. Nov. 22.	0.15	1.0483	.598234	2.6339	2.6880	.05160	$d = +.00597$ ,
	0.15	1.0493	.597057	2.6313	2.6863	.05241	$h = +.0370$ .
XLVII. Nov. 27, 1899.	25.22	8.4686	.601120	21.3807	21.7224	.04035	$d = -.00497$ ,
	25.22	8.4910	.599162	21.3675	21.7149	.04093	$h = +.05316$ ,
	25.21	8.4064	.377559	13.3304	13.7105	.04522	$J = 4.1791$ ,
	25.21	8.4159	.376851	13.3205	13.7023	.04537	at $29^{\circ}.43$ C.
XLVIII. Nov. 29, 1899.	46.77	8.5495	.592608	21.2822	21.7592	.05579	$d = -.00513$ ,
	46.78	8.5767	.590139	21.2580	21.7367	.05582	$h = +.06855$ ,
	46.79	8.4380	.370080	13.1155	13.6267	.06058	$J = 4.1785$ ,
	(Not repeated)						at $51^{\circ}.02$ C.
Series VII. Calorimeter C. Solid Conductor. Thermometer E, III. Air-free Water.							
XLIX. Jan. 1, 1900.	24.94	8.3727	.579770	20.3878	20.7297	.04083	$d = -.00488$ ,
	24.94	8.3774	.579087	20.3751	20.7219	.04140	$h = +.05299$ ,
	24.95	8.3435	.355436	12.4554	12.8365	.04567	$J = 4.1795$ ,
	24.95	8.3449	.355120	12.4465	12.8282	.04574	at $29^{\circ}.13$ C.
L. Jan. 6.	81.56	8.0278	.646259	21.7898	22.5230	.09133	$d = -.00052$ ,
	81.60	8.0325	.644355	21.7383	22.4762	.09186	$h = +.0930$ .
Series VIII. Calorimeter C. Solid Conductor. Thermometer E, IV. Box II.							
LI. Feb. 24, 1900.	28.15	8.2035	.645683	22.2468	22.6039	.04358	$d = -.00521$ ,
	28.15	8.2223	.643769	22.2317	22.5931	.04396	$h = +.05791$ ,
	28.16	8.2468	.404207	14.0003	14.4041	.04897	$J = 4.1781$ ,
	28.16	8.2613	.403213	13.9904	14.3966	.04917	at $32^{\circ}.26$ C.

TABLE XVIII.—Summary of Results of Observations—*continued*.

Number and date.	Jacket. Temp. ° C.	Temp. rise. $d\theta$ , ° C.	Flow Q. gm./sec.	Product. $4.2 Q d\theta$ .	Watts. EC.	Diff./ $d\theta$ . D.	Results. $d, h, J$ .
Series VIII. Calorimeter C. Solid Conductor. Thermometer E, IV. Box II.— <i>continued</i> .							
LII. Feb. 28, 1900.	69°85 69°85 69°86 69°86	8°3152 8°3226 8°4472 8°4893	·622088 ·620830 ·385739 ·383723	21·7257 21·7011 13·6853 13·6816	22·3864 22·3672 14·3733 14·3761	·07947 ·08044 ·08146 ·08181	$d = -\cdot00189$ , $h = +\cdot08469$ , $J = 4\cdot1920$ , at $74^{\circ}\cdot05$ C.
LIII. Mar. 10, 1900.	87°42 87°41 87°43 87°43	8°2361 8°2513 8°2768 8°3168	·645077 ·642851 ·402934 ·400935	22·3142 22·2783 14·0069 14·0049	23·1450 23·1161 14·8450 14·8398	·10088 ·10155 ·10130 ·10030	$d = +\cdot00042$ , $h = +\cdot10011$ , $J = 4\cdot2017$ , at $91^{\circ}\cdot55$ C.
LIV. Mar. 17, 1900.	76°12 76°12 76°12 76°12	8°5262 8°5570 8°5224 8°5433	·617742 ·615198 ·388311 ·387095	22·1213 22·1099 13·8992 13·8897	22·8806 22·8747 14·6692 14·6603	·08894 ·08938 ·09036 ·09021	$d = -\cdot00117$ , $h = +\cdot09218$ , $J = 4\cdot1951$ , at $80^{\circ}\cdot38$ C.
LV. Mar 21, 1900.	63°84 63°84 63°82 63°82	8°6883 8°6760 8°8222 8°8494	·387767 ·387527 ·604663 ·601956	14·1499 14·1212 22·4047 22·3732	14·8324 14·8029 23·0757 23·0488	·07856 ·07858 ·07606 ·07634	$d = -\cdot00262$ , $h = +\cdot08283$ , $J = 4\cdot1890$ , at $68^{\circ}\cdot21$ C.

Each single line in the above table represents the mean results of the observations of temperature and potential difference taken, as explained and illustrated by the specimen tables of observations, during a period of 15 minutes, for which the corresponding value of the flow was measured. In nearly all cases the observations were repeated during a second period of 15 minutes under conditions as nearly as possible the same, except for a slight diminution of the flow, due to the fall in the water level. The order of accuracy of the readings can be estimated by comparing the corresponding values of D for the two similar flows. The two values of D should agree, except that the falling-off of the flow tends to make the second value in each case slightly the larger when  $d$  is negative. In comparing the values it must be remembered that 3 in the fifth place of D corresponds to only 1 part in 100,000, with a heat supply of 24 watts and a rise of  $8^{\circ}$ . The differences seldom exceed 1 in 10,000, whereas with the method of mixtures it is very difficult to obtain an order of agreement of 1 in 1,000 in repeating an experiment under identical conditions.

The values of  $d$  as directly measured and expressed in the different series just given, I have plotted in fig. 17. From the smooth curve drawn so as to include the observations, I have taken the following values of  $d$  and calculated the corresponding values of J. These are summarized here (p. 250). The values of J are, of course, in absolute measure, and the values of  $d$  in terms of a thermal unit equal to  $4\cdot2000$  joules, which occurs at  $9^{\circ}$  C. and  $88^{\circ}\cdot5$  C. The mean value of

J, 4·18876 joules, is exactly coincident with the values at 15°·7 and at 68° C. In selecting a thermal unit to which the values of the specific heat may be referred, it seems desirable to adopt one at a temperature which, if at the same time at a convenient part of the scale, may also represent the mean value over the whole range. Such a convenient point appears to be indicated at either 15° or 16° C. I propose, at the present time, to adopt the value at 16° C., and shall in consequence express the specific heat of water in terms of this unit, which is equal to 4·1883 joules, and which differs from the mean value by only 1 part in 10,000.

The following table (p. 252) includes the values of the specific heat of water in terms of a unit at 16°. No one simple formula can be fitted to the complete curve between 0° and 100° with any degree of accuracy, on account of the change which occurs at 37°·5, which is the point of minimum specific heat. Two formulæ can be

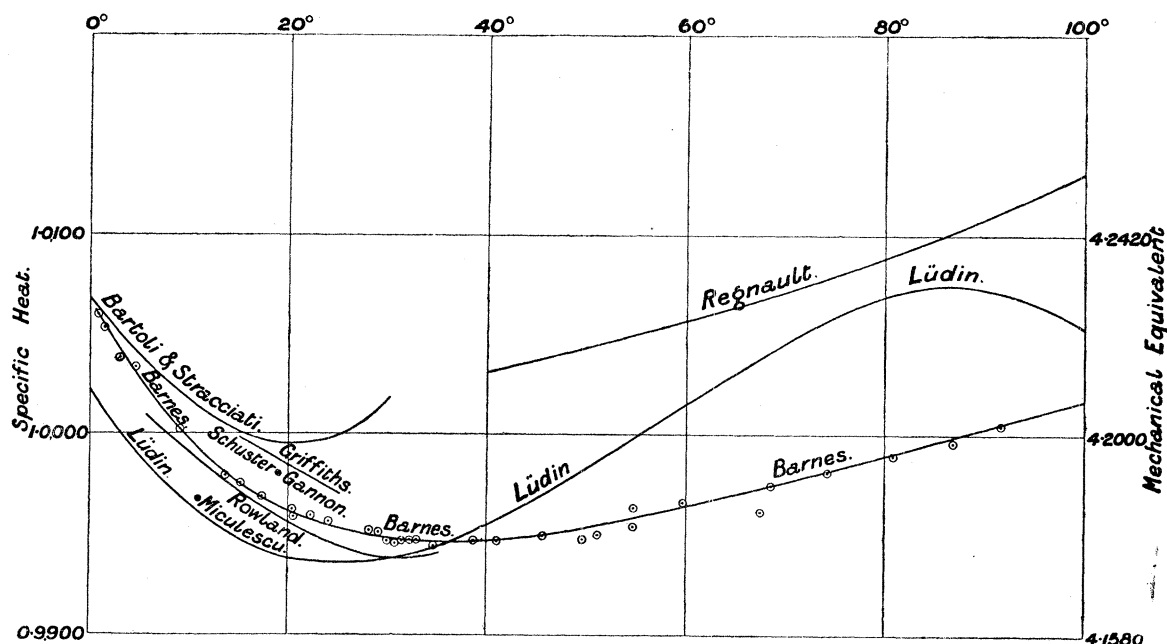


Fig. 17.

fitted together, however, over the range with great accuracy. Between 5° and 37°·5 the expression representing the specific heat in terms of a unit at 16° C. is

$$S_t = \cdot99733 + \cdot0000035 (37\cdot5 - t)^2 + \cdot00000010 (37\cdot5 - t)^3.$$

The same expression reads above the minimum point, as far as 55°, in this form :

$$S_t = \cdot99733 + \cdot0000035 (t - 37\cdot5)^2 + \cdot00000010 (t - 37\cdot5)^3.$$

At 55° and upwards the values diverge more and more from this formula, and follow

a different curve. The slope of the curve above  $60^\circ$  is very nearly the same as the well-known formula of REGNAULT, but the rate of increase is very much smaller. The following expression, which is very nearly a linear relation, holds between  $50^\circ$  and  $100^\circ$ :

$$S_t = \cdot99850 + \cdot000120 (t - 55^\circ) + \cdot00000025 (t - 55)^\circ.$$

These two formulæ I have represented in the last table in column 3. They represent the variation of the specific heat of water very clearly with the exception of the rapid increase at  $0^\circ$ , and are entirely independent of the values assigned to my electrical units. They can be changed to fit a unit at any other temperature by simply changing the constant term.

Since it would be a matter of great labour to determine the specific heat of superheated water, and since the variation curve of the specific heat shows no discontinuity as the boiling-point is reached at atmospheric pressure, this last formula may be said to hold with some claim to accuracy above  $100^\circ$  throughout the entire range covered by REGNAULT'S experiments.

COMPARISON of Observed and Calculated Values.

Temperature.	Observed <i>d.</i>	Calculated <i>d.</i>	J observed.	J. calculated.
Series I. February to March, 1899.				
28·01	−·00485	−·00509	4·1796	4·1786
29·09	−·00469	−·00517	4·1803	4·1783
29·11	−·00489	−·00517	4·1795	4·1783
29·21	−·00499	−·00519	4·1790	4·1782
13·79	−·00208	−·00210	4·1913	4·1912
17·69	−·00309	−·00328	4·1870	4·1862
24·20	−·00446	−·00460	4·1813	4·1807
34·46	−·00561	−·00545	4·1765	4·1771
4·28	+·00330	+·00310	4·2138	4·2130
Series II. January 6–22, 1899.				
22·16	−·00413	−·00425	4·1827	4·1822
31·40	−·00542	−·00532	4·1773	4·1777
32·17	−·00536	−·00536	4·1775	4·1775
41·02	−·00540	−·00539	4·1773	4·1774
45·49	−·00514	−·00515	4·1784	4·1784
49·68	−·00531	−·00480	4·1777	4·1799
54·61	−·00372	−·00430	4·1844	4·1819
59·80	−·00341	−·00370	4·1849	4·1845
32·81	−·00528	−·00540	4·1778	4·1773
30·54	−·00555	−·00528	4·1767	4·1779

COMPARISON of Observed and Calculated Values—*continued*.

Temperature.	Observed <i>d.</i>	Calculated <i>d.</i>	J. observed.	J. calculated.
Series III. September 4–18, 1899.				
29·47	–·00496	–·00520	4·1792	4·1782
31·22	–·00544	–·00530	4·1771	4·1778
38·76	–·00530	–·00545	4·1777	4·1771
67·52	–·00395	–·00275	4·1834	4·1885
54·57	–·00473	–·00430	4·1801	4·1820
Series IV. October 14–19, 1899.				
28·77	–·00493	–·00515	4·1793	4·1784
28·52	–·00497	–·00510	4·1792	4·1786
Series V. October 27 to November 1, 1899.				
29·92	–·00542	–·00523	4·1772	4·1781
20·92	–·00404	–·00404	4·1830	4·1830
Series VI. November 3–29, 1899.				
20·18	–·00383	–·00384	4·1838	4·1839
17·09	–·00310	–·00310	4·1870	4·1870
20·13	–·00397	–·00383	4·1833	4·1839
20·45	–·00420	–·00400	4·1824	4·1832
15·71	–·00254	–·00270	4·1893	4·1887
8·66	+·00022	+·00020	4·2009	4·2008
1·35	+·00512	+·00560	4·2215	4·2235
2·68	+·00370	+·00430	4·2155	4·2181
29·43	–·00497	–·00520	4·1791	4·1782
51·02	–·00513	–·00470	4·1785	4·1803
Series VII. January 1–6, 1900.				
29·13	–·00488	–·00517	4·1795	4·1783
85·60	–·00052	–·00036	4·1978	4·1985
Series VIII. February 24 to March 21, 1900.				
32·26	–·00521	–·00535	4·1781	4·1776
74·05	–·00189	–·00189	4·1920	4·1920
91·55	+·00042	+·00042	4·2017	4·2017
80·38	–·00117	–·00110	4·1951	4·1954
68·21	–·00262	–·00270	4·1890	4·1887
Time of flow, 900 seconds automatically recorded.				

## SUMMARY of the Specific Heat of Water from Smoothed Curve.

Temperature ° C.	<i>d.</i>	J.
5	+ ·00250	4·2105
10	- ·00050	4·1979
15	- ·00250	4·1895
20	- ·00385	4·1838
25	- ·00474	4·1801
30	- ·00523	4·1780
35	- ·00545	4·1773
40	- ·00545	4·1773
45	- ·00520	4·1782
50	- ·00480	4·1798
55	- ·00430	4·1819
60	- ·00370	4·1845
65	- ·00310	4·1870
70	- ·00245	4·1898
75	- ·00180	4·1925
80	- ·00114	4·1954
85	- ·00043	4·1982
90	+ ·00025	4·2010
95	+ ·00090	4·2038
	Mean value . . . .	4·18876

VARIATION of the Specific Heat of Water in Terms of a Thermal Unit at  
16° C. = 4·1883 joules.

Temperature ° C.	Observed values from curve.	Calculated values from formulæ.
5	1·00530	1·00446
10	1·00230	1·00206
15	1·00030	1·00024
20	1·99895	0·99894
25	0·99806	0·99807
30	0·99759	0·99757
35	0·99735	0·99735
40	0·99735	0·99735
45	0·99760	0·99757
50	0·99800	0·99807
55	0·99850	0·99894
60	0·99910	0·99910
65	0·99970	0·99972
70	1·00035	1·00036
75	1·00100	1·00100
80	1·00166	1·00166
85	1·00237	1·00233
90	1·00305	1·00301
95	1·00370	1·00370
Mean value . .	1·00012	



*Temperature Coefficient of the Radiation Loss.*

It is not possible to obtain a very accurate measure of the temperature coefficient of the radiation correction from the present experiments. At the same time we may, from the different series covering different ranges of temperature, form some idea. During a series of experiments the radiation loss remained exceedingly steady, except that repeatedly after the calorimeter had returned from a high point the heat-loss was found to have been increased, but tended to return to its old value with lapse of time. On account of the slowness of the change, this occurred without producing any serious effect on the measure of the specific heat of the water. These changes were attributed to the effect of the small trace of occluded gases and vapour left in the glass vacuum-jacket. It is interesting in the case of Calorimeter C to trace the gradual alteration in the heat-loss, from series to series, during the time of the experiments.

All of the experiments made at a mean temperature of about 30° are given in the following table :—

Date.	Temperature.	$h$ observed.	$h$ corrected to 30° C.	Remarks.
February 20. . .	29°·09	·04944	·05008	
"    22. . .	29°·11	·04937	·05000	
March 2 . . .	29°·21	·04965	·05021	
June 8 . . .	31°·40	·05334	·05235	After trial experiment at 40°.
"    9 . . .	32°·17	·05282	·05138	
"    20 . . .	32°·81	·05429	·05230	"    an experiment at 60°.
"    22 . . .	30°·54	·05364	·05326	
September 4. . .	29°·47	·05352	·05389	"    experiments at 60° and 70°.
"    6. . .	31°·22	·05518	·05432	
November 27 . . .	29°·43	·05316	·05356	"    experiments at 0°.
January 1 . . .	29°·13	·05299	·05361	
February 24. . .	32°·26	·05791	·05631	"    an experiment at 86°.

The values of the heat-loss per degree rise from the experiments on October 14 and October 18, with rises of temperature of 8° and 5° respectively, when the flat heating-wire was used, are :—

October 14. . . . .	28·77	·05826	·05913
"    18. . . . .	28·52	·05870	·05975

These values show a decided increase in the heat-loss, but was due, no doubt, to the wire being in direct contact with the glass flow-tube of the calorimeter.

In regard to the temperature coefficient of the radiation loss, this may be calculated from the observations in any of the different series. Series II. is the most suitable, extending at different temperatures between 22° and 60°, over the middle of the

range. The best average of the values of  $h$  given in this series is a line represented in the form

$$H_t = H_t + \cdot 000708 (t_1 - t),$$

where  $t$  is the temperature corresponding to the measurement of  $H_t$ , and  $t_1$  is the temperature corresponding to the value of  $H_{t_1}$ . From further consideration of the changes in the value of  $h$  from the other series, this appears to represent the temperature change of the radiation not only for Calorimeter C, but for Calorimeter E, for the two determinations between  $30^\circ$  and  $20^\circ$ .

Taking the different values of Series II., we have, on tabulating the values of the heat-loss, both observed and calculated, and accepting the value at  $22^\circ$  for  $H_t$  in the expression given above, the following values :—

Temperature.	H observed.	H calculated.
22·16	·04619	·04619
31·40	·05334	·05273
32·17	·05282	·05328
41·02	·05939	·05954
45·49	·06306	·06271
49·68	·06669	·06562
54·61	·06867	·06916
59·80	·07220	·07285
32·81	·05429	·05373
30·54	·05364	·05212

The values at  $50^\circ$  and  $55^\circ$  are not very consistent, but it will be remembered that the measurements at these points are not so trustworthy owing to the variation in the experimental conditions.

On returning to  $30^\circ$ , as seen by the last two readings, the value of  $h$  has increased in both cases. These two values were obtained with a rise of temperature of  $11^\circ$  and  $5^\circ$  respectively.

In regarding these large variations in the heat-loss from time to time, it must be again emphasised that the value of the specific heat of water, owing to the method of treatment, in no way depends on the absolute value, but only on the constancy throughout the period of an experiment.

To prove that this was so, the order of one of the experiments in Series VIII. at the higher points was reversed, and instead of taking the observations for the large flow first, as was followed for all the other experiments in this series, the observations for the small flow were obtained before those for the large flow. By this, any gradual change in the heat-loss during the time of the experiment would have produced an effect on the value of  $d$  in an opposite direction to the values given by the other experiments, and would have produced twice the error.

For Calorimeter E we have the two values at  $29^{\circ}\cdot92$  C. and  $20^{\circ}\cdot92$ , which are

$$\cdot05994 \quad \text{and} \quad \cdot05414.$$

These give for the coefficient of  $t$  in the radiation expression, the value  $\cdot000645$ ; or, applying the first formula, the value of the radiation loss at  $29^{\circ}\cdot92$  from the value at  $20^{\circ}\cdot92 = \cdot06051$ . This is within 6 parts in 10,000, and is comparable in size with the variations from the calculated values for calorimeter C. Doubtless there would be slight differences in the temperature coefficient of the radiation loss for different calorimeters with different degrees of vacuum.

In Series VI., for Calorimeter C, the decrease in the radiation loss takes place with decrease in temperature well in agreement with the other series until the experiments at  $0^{\circ}$ , when the value of the heat-loss is increased by nearly 3 parts in 1000. The two experiments at  $1^{\circ}\cdot35$  and  $2^{\circ}\cdot68$ , both with the inflowing water at  $0^{\circ}\cdot15$  C., agree however very closely with the formula as regards the temperature change in  $h$ . The explanation of the apparent increase at these points is not altogether clear, but may be looked for in the very high value of the specific heat of water in the neighbourhood of  $0^{\circ}$ , which would influence the validity of the method adopted of eliminating the heat-loss from the large and small flows. A similar increase, although much smaller, was noticed in the heat-loss for the same calorimeter at  $4^{\circ}$ , in Series I. Owing to the small conduction effect at the inflow end of the calorimeter, the water in the large and small flows enters the flow-tube, where it is heated by the electric current, necessarily at a slightly different temperature, as was pointed out before.

Whereas this would produce no error at a part of the range where the value of  $d$  was not changing rapidly with the temperature, at the freezing-point, where a very small difference in temperature produces a large change in the value of  $d$ , it cannot be regarded as equal in the difference equations for the two flows for the same value of  $d\theta$ . Taking this into consideration, I have calculated the value of  $d$ , for the two experiments under consideration, by extrapolating for the value of the heat-loss from the curve for the other observations in the same series between  $20^{\circ}$  and  $8^{\circ}$ . By this means, the value of  $d$  for each flow in the same experiment differs nearly 1 part in 1000 in the extreme case. The following are the values so obtained:—

Date.	Mean temperature.	$d$ large flow.	$d$ small flow.
November 18 . . .	$1^{\circ}\cdot35$	+ $\cdot0066$	+ $\cdot0073$
„ 22 . . .	$2^{\circ}\cdot68$	+ $\cdot0051$	+ $\cdot0060$
„ . . .	$0^{\circ}\cdot67$	+ $\cdot0072$	

The mean value for each experiment is larger than the value calculated in the usual way, but for the same value of the flow the values of  $d$  are very consistent for the

different experiments, and all give identically the same temperature coefficient of variation. For the ice experiment on March 24, of Series I., the value of  $h$  is very nearly in agreement with the extrapolated value from Series I. and II. Hence the above method of treatment for this experiment would give an almost identical value of  $d$  to the one obtained by eliminating the heat-loss from the two flows.

It is important to notice that the value of  $d$  in this experiment, obtained from the two flows, is more in agreement with the mean value of  $d$  for the other ice experiments, obtained by extrapolating from the values of  $h$  in Series VI. than for the values obtained by eliminating the heat-loss in the usual way. This points to the fact that the values given above are more nearly correct than the values given in the tables for the same experiments. If this be so, the indication is, that the value of the specific heat of water rapidly approaches an exceedingly high value at  $0^\circ$ , and in a remarkable way substantiates the suggestions made by ROWLAND in his memoir in regard to this. Further investigation is needed, however, in the neighbourhood of the freezing-point of water, before we can say that the specific heat of water approaches an infinite value as that point is reached. Such questions, as the continuity of the curve for under-cooled water, render the idea quite unthinkable at present. In view of this uncertainty, I have adhered to the lowest of the values of the specific heat given by these measurements, and have consequently included them both in the tables and plot. Even in this case, the change of specific heat with temperature is very rapid, and no effect is shown by the observations taken below  $4^\circ$  which would indicate a change at the point of maximum density. This, however, is not surprising when it is considered that the point of minimum specific heat in no way corresponds to the density curve for water.

Unfortunately, only one complete set of observations could be obtained with Calorimeter D, with the device for getting rid of stream-line motion, owing to a crack which, shortly after, started in the fine flow-tube inside the vacuum-jacket, and admitted water into the jacket. This calorimeter is of special interest, as the vacuum-jacket was supplied with a quantity of phosphorus pentoxide. The value of the heat-loss is larger than for any of the other calorimeters, including calorimeter A, which we exhausted ourselves to a vacuum of at least  $\cdot 002$  millim. of mercury. This indicated that the  $P_2O_5$ , instead of improving the vacuum as we at first thought, was really a disadvantage. The values of the heat-loss for the four calorimeters included in these measurements are, at  $30^\circ$  C. :—

Calorimeter A	. . . .	1.8 millim. flow-tube	. . . .	$\cdot 0509$ watt.
„ C	. . . .	2 „ „	. . . .	$\cdot 0500$ „
„ D	. . . .	2.8 „ „	. . . .	$\cdot 0726$ „
„ E	. . . .	3.1 „ „	. . . .	$\cdot 0600$ „

Sec. 9.—*Relation of the Present Measurements to the Work of other Observers.*

It will hardly be necessary for me to enter into a lengthy discussion of the work of other observers, more especially as it has been already carefully done in the original memoirs of ROWLAND,\* GRIFFITHS,† and SCHUSTER and GANNON.‡ Since the publication of these papers, however, a very elaborate and exhaustive series of experiments has been made by REYNOLDS and MOORBY§ to determine, by a direct mechanical method, using a Reynolds brake and a steam-engine, the energy required to raise water from a temperature slightly above freezing to the boiling-point. The value of the mean mechanical equivalent which they obtained is entitled to a great deal of weight, from the minute accuracy of their measurements and the careful discussion of possible sources of error.

It is fortunately possible, by means of the present series of experiments, on account of their great range, to connect the experiments of REYNOLDS and MOORBY with the experiments of ROWLAND, also by the direct mechanical method, which extends between 6° and 36° C. The absolute value of the mean mechanical equivalent obtained by REYNOLDS and MOORBY is 4·18320 joules, which is obviously less than the same mean value obtained in the present experiments (*i.e.*, 4·18876 joules) by as much as 0·132 per cent.

This discrepancy in the two results may be caused by an error in the present measurements at the extremities of the range, due to the neglecting of some correction factor which would cause the variation curve to increase less rapidly than it does; but it is far more probably due to an error in the value of one of the constants for the determination of the electrical or heat energy. Of this latter possibility the value of the Clark cell is still in doubt, although the value of the ohm is fairly well fixed in absolute measure, as defined in the 'British Association Report' of 1892. All of the thermal measurements are expressed in our two results to the same scale, so that the error resolves itself into an error in the E.M.F. of the Clark cell, which, as it enters into the equation for the determination of the electrical energy to the second power, has twice the effect. This has been already pointed out under the Section devoted to the Clark cell, where it was shown that if all the error between the value of the mean mechanical equivalent obtained by the direct mechanical method and the value obtained by the electrical method (assuming the Clark cell equal to 1·43420 volt and the international ohm equal to 1·01358 B.A. units) could be attributed to the Clark cell, the value 1·43420 would have to be

\* 'Proc. Amer. Acad.,' vol. 15, p. 75 (1879).

† 'Phil. Trans.,' A, vol. 184, p. 361 (1893).

‡ 'Phil. Trans.,' A, vol. 186, p. 415 (1895).

§ 'Phil. Trans.,' A, vol. 190, p. 300 (1898).

reduced to 1.43325 volt at 15° C. Such a reduction is necessary to bring my measurements into absolute agreement with REYNOLDS and MOORBY'S result. This reduced value of the Clark cell is so nearly identical with the later absolute dynamometer measurements as to give a most remarkable, if not coincident, agreement between the electrical and mechanical units.

If we compare the value of the mean mechanical equivalent obtained by integrating the values obtained by ROWLAND between 6° and 36°, which have been recently corrected to the Paris Scale by a comparison of ROWLAND'S thermometers with the Paris Scale, with the integrated value over the same range from the present experiments, we find the difference between ROWLAND'S value, 4.1834 joules, and my value, 4.1872, in terms of the Clark cell value, 1.43420 volt, equal to .091 per cent. This is a difference of only 1 part in 2000, as deduced from the comparison of the complete curve with REYNOLDS and MOORBY'S result, a discrepancy which, if not within the limits of error of our several determinations, is relatively small considering the great range covered by these experiments. The reduced value of the Clark cell according to ROWLAND would be 1.43355 volt, which differs from the value according to REYNOLDS and MOORBY by only .3 millivolt. Owing to the slight difference in the temperature coefficient of the specific heat between ROWLAND'S values and my own, the agreement of our absolute values at any one temperature will be different at different temperatures. At 25° our measurements, when expressing mine in terms of REYNOLDS and MOORBY'S, are almost exactly coincident; at 13° my value is lower than ROWLAND'S by 1 part in 1000, but at 6° we are in agreement again.

Of the other direct mechanical determinations which have been made recently, we have the work of MICULESCU\* in 1892, which is deserving of some mention. Although his work is by no means above criticism, as was clearly pointed out by SCHUSTER and GANNON in their paper, it is of interest as showing the kind of error which may occur between measurements by the direct method, which may be at the same time very carefully and accurately carried out. His value, which appears to be a mean value between 10° and 13°, is 4.1857 joules. ROWLAND'S value at the same temperature, about 11° C., is 4.194, while my own in terms of REYNOLDS and MOORBY'S value is 4.1903 joules, which, although less than ROWLAND'S value, is larger than MICULESCU'S.

Perhaps the most difficult part of the comparison of the present experiments with the work of other observers is in relation to the results obtained by the electrical method used by GRIFFITHS and SCHUSTER and GANNON. It is at once apparent from fig. 17 (p. 249) that my values are widely different to the values obtained by both these investigators, although expressed in the same values of the units used. The explanation might at once be looked for in an error in either my Clark cells or resistance standard; but if it is attributed to the Clark cells used in the present work, then the several sets of cells made at different times and from different

\* 'Ann. de Chimie,' vol. 27 (1892).

materials must all have involved the same error, always in the same direction. At the same time my cadmium cells must also have been in error to exactly the same amount and in the same direction, in order to give a ratio to my Clark cells identical with that obtained for the cells at the Reichsanstalt, which have been compared directly with the Cavendish standards used by GRIFFITHS. If the error is attributed to the value of my resistance, then we must reject the signed certificates of 11 standard ohms from the Electrical Standards Committee of the British Association, as well as a true ohm from the German Reichsanstalt, as being in error. It is far more likely that the values of my constants agreed to 1 in 10,000 with those used by GRIFFITHS and by SCHUSTER and GANNON respectively, and that the difference in our results is to be attributed to some constant source of error as yet undiscovered in our methods of calorimetry. However, the values obtained by these observers using the same method differ by nearly 1 part in 1000 from each other, which is not so good an agreement as exists between the measurements of REYNOLDS and MOORBY, ROWLAND, and myself, using widely different methods. At the same time the method used by ROWLAND is essentially the same as that used by GRIFFITHS, and is subject to similar calorimetric errors. Owing to the great care and trouble taken by GRIFFITHS to carry out his experiments, it is difficult to see where the difference between our two results can be. Moreover, the temperature coefficient obtained by GRIFFITHS, although a linear one over the range of his experiments, is almost exactly a mean to the curve in my experiments over the same range.

The individual observations by the present method agree very well amongst themselves, but although it may be correctly said that the mere repetition of observations does not necessarily eliminate errors of experiment, yet it is possible to vary the conditions so thoroughly by the continuous flow method of calorimetry as to leave little room for any systematic error. In addition to varying rise of temperature, water flow and electric current, the present measurements have been made to the same order of accuracy by varying the shape and resistance of the electric heating conductor, by using flow-tubes of different sizes, and by employing calorimeters with different values of heat-loss, this last being identical to the cooling correction in the older methods of calorimetry.

It may be questioned whether the separate determination of the cooling effect by special experiment and its subsequent application as a correction to calorimetric experiments, can be relied on to an accuracy greater than 1 part in 1000. The variations in the radiation loss measured from time to time in the present experiments are so large that unless it had been separately determined and eliminated from the final result for each experiment, large errors would have been introduced. Indeed, it appears that the cooling correction is a far more uncertain factor in methods of calorimetry than has been hitherto sufficiently realized. All questions, however, relating to the absolute values of the standards used in the present results in no way

affect the accuracy of the relative results, as regards the variation of the specific heat of water.

It is interesting to compare the absolute value of the Clark cell obtained by assuming GRIFFITHS' absolute value of the mechanical equivalent at  $15^{\circ}$ , and to express my mean value in terms of his experiments. By so doing the absolute value becomes 4.1975 joules, which differs from REYNOLDS and MOORBY'S value by .34 per cent, or, assuming the error to be due to the Clark cell, equal to .17 per cent. on 1.4342, which would reduce this value to 1.4318 volt at  $15^{\circ}$ . This, however, even referred to the lowest of the latest absolute determinations, seems to be too low a value, by as much as 1 millivolt, to be reconciled with the most probable true value of the Clark cell.

It might be thought advisable, in view of the uncertainty in the electrical units, to accept ROWLAND'S corrected values and express the present series of experiments in terms of his results, which would give a mean value quite sufficiently in accord with REYNOLDS and MOORBY'S mean determination. This could be done either from the integrated value over the range of his experiments, which would tend to eliminate errors in his method at the two extremes of the range, or by accepting his absolute value at a temperature where he could obtain the most accurate measurement. The present experiments over the range between  $4^{\circ}$  and  $60^{\circ}$  have already been published ('B.A. Report,' 1899), and were referred to ROWLAND'S absolute measurement at  $20^{\circ}$  C., but I think that the uncertainty in the thermometric standards used by ROWLAND at that time do not warrant an accuracy greater than 1 part in about 2000, and that the mean result over the complete range of temperature referred to REYNOLDS and MOORBY'S determination is more near the truth.

The value of the mean specific heat between  $0^{\circ}$  and  $100^{\circ}$  C., 4.232 joules, obtained by DIETERICI ('Wied. Ann.,' vol. 33, p. 417, 1888) in terms of the electrical units, is obviously too large to be accounted for by an error in the electrical units, or to be reconciled with the direct determination of REYNOLDS and MOORBY. The curve obtained by BARTOLI and STRACCIATI ('Beiblätter,' vol. 15, p. 761, 1891) for the variation of the specific heat of water between  $0^{\circ}$  and  $30^{\circ}$  by the method of mixtures in terms of a thermal unit at  $15^{\circ}$  C. passes through a minimum point at  $20^{\circ}$  C., above which it shows a far too rapid increase in the specific heat to be reconciled with measurements extending as far as  $100^{\circ}$  C., unless the values pass through a maximum point.

In 1895, LÜDIN (Dissert. Zürich and 'Beiblätter,' 1897) determined the variation of the specific heat between  $0^{\circ}$  and  $100^{\circ}$  by the method of mixtures and showed a minimum point at  $25^{\circ}$ , but also a maximum point at about  $80^{\circ}$ . His results are in good agreement with the present series of experiments over a range  $0^{\circ}$  to  $25^{\circ}$ , as shown in fig. 17 (p. 249), where I have plotted them in terms of a mean unit between  $0^{\circ}$  and  $100^{\circ}$  C. The excessively low minimum point shown by BARTOLI and STRACCIATI and by LÜDIN respectively, both using similar methods, suggests a



source of error common to the two. The limitation of the method of mixtures is, however, too well known to give the complete variation curve to any degree of accuracy.

I have arranged in the following table the absolute values of the specific heat of water every 5 degrees between 0° and 100° from my measurements for a value of the Clark cell equal to 1.43325 int. volts, and assuming the true ohm as correct, which gives the values in terms of the mechanical units in REYNOLDS and MOORBY'S experiments. For comparison, I also include the measurements of ROWLAND and MICULESCU, and those of GRIFFITHS and of SCHUSTER and GANNON, to the same value of the Clark cell.

The minimum point of the specific heat, which ROWLAND found at 30°, really occurs at about 37°·5, but this was considered as likely by ROWLAND, for he says in his memoir (p. 199), "The point of minimum cannot be said to be known, though I have placed it provisionally between 30° and 35° C., but it may vary much from that." And in another place (p. 200) he says, "There may be an error of a small amount at that point (30°) in the direction of making the mechanical equivalent too great, and the specific heat may keep on decreasing to even 40°."

ABSOLUTE Value of the Thermal Capacity of Water in Joules per Calorie for Different Temperatures between the Freezing and Boiling-points, expressed in terms of a Clark Cell Value 1.43325 international volts at 15° C., and the Value of the true ohm 1.01358 B.A. Units.

Temperature.	BARNES.	ROWLAND.	MICULESCU.	GRIFFITHS.	SCHUSTER and GANNON.
° C.					
5	4.2050	4.206	—	—	—
10	4.1924	4.196	4.1857	—	—
15	4.1840	4.188	—	4.1927	—
20	4.1783	4.181	—	4.1871	4.1874
25	4.1746	4.176	—	4.1816	—
30	4.1725	4.174	—	—	—
35	4.1718	4.175	—	—	—
40	4.1718	—	—	—	—
45	4.1727	—	—	—	—
50	4.1743	—	—	—	—
55	4.1764	—	—	—	—
60	4.1790	—	—	—	—
65	4.1815	—	—	—	—
70	4.1843	—	—	—	—
75	4.1870	—	—	—	—
80	4.1899	—	—	—	—
85	4.1927	—	—	—	—
90	4.1955	—	—	—	—
95	4.1983	—	—	—	—
Mean . . .	4.18326				
REYNOLDS and MOORBY'S value . . . 4.18320.					

ROWLAND'S values are those given by W. S. DAY ('Physical Review,' vol. 7, p. 193, 1898), corrected to the Paris scale. GRIFFITHS' values are those quoted by SCHUSTER and GANNON in their paper. At 20° and 25° GRIFFITHS' own temperature coefficient is used. SCHUSTER and GANNON'S value is given in their paper at a temperature of 19°·1 C. I have reduced it to 20° by the temperature coefficient obtained in my experiments, which is very similar to GRIFFITHS' over a short range. It will be seen that the values of GRIFFITHS and SCHUSTER and GANNON are brought into closer agreement when corrected to the same value of the Clark cell.

Extrapolating for the values of J above 100° C. we obtain from the formula

$$J_t = J_{55} (1 + \cdot 000120 (t - 55^\circ) + \cdot 00000025 (t - 55^\circ)^2)$$

the following values :—

Temperature Centigrade.	J. ( $J_{55} = 4\cdot 1819$ ).	J. ( $J_{55} = 4\cdot 1764$ ).
°		
110	4·2127	4·2072
120	4·2190	4·2135
130	4·2255	4·2199
140	4·2321	4·2265
150	4·2390	4·2334
160	4·2461	4·2405
170	4·2534	4·2479
180	4·2610	4·2554
190	4·2687	4·2631
200	4·2767	4·2711
220	4·2931	4·2875

A glance at the complete curve for the variation of the specific heat of water with temperature reveals at once a most interesting relation. Why should the values drop so rapidly from the freezing point and at 37°·5 the complete character of the curve change? There is no discontinuous or sudden change occurring at this point that is indicated either in the outward physical state or in the density of the water, nor do we see any connection between the curious anomaly in the density curve at 4° C. and the specific heat at that point. It is evident we have to do here with a new, and as yet unexplained, phenomenon.

The ideas advanced by ROWLAND in this connection are not, it seems to me, altogether correct when he says :—“ However remarkable the fact may be, being the first instance of the decrease of the specific heat with rise of temperature, it is no more remarkable than the contraction of water to 4°. Indeed, in both cases the water hardly seems to have recovered from freezing. The specific heat of melting ice is infinite. Why is it necessary that the specific heat should instantly fall, and then recover as the temperature rises? Is it not more natural to suppose that it continues to fall even after the ice is melted, and then to rise again as the specific

heat approaches infinity at the boiling-point? And of all the bodies which we should select as probably exhibiting this property, water is certainly the first."

The identification of latent heat and specific heat which ROWLAND makes when he says "the specific heat approaches infinity at the boiling-point" and that "the specific heat of melting ice is infinite" is hardly tenable. Moreover, the character of the curve as the boiling-point is reached shows no indication of approaching an infinite value, and is entirely independent of the pressure which determines the boiling-point. The idea of an infinite value of the specific heat at  $0^{\circ}$  can hardly be reconciled with the idea of the continuity of the curve for under-cooled water. It is highly probable that the specific heat approaches an exceedingly high, but measurable value, as the freezing point is reached, and that the character of the curve below the minimum point indicates an entirely different physical state of the water to that above. The law governing the variation of the specific heat with temperature above  $37^{\circ}\cdot 5$  is directly in accord with what knowledge we already possess of other substances, and of what our preconceived ideas might lead us to expect.

We can draw no analogies from other liquids, since our knowledge, with the exception, perhaps, of mercury, is now only exceedingly meagre. As the temperature is reduced below  $37^{\circ}\cdot 5$ , may it not be that the water commences to anticipate the formation of the solid phase, even before  $0^{\circ}$  is reached, and that the rapid increase in specific heat indicates the effort being made to resist parting with the internal energy necessary for formation of ice, and to form a more and more close aggregation? If this be true, it suggests at once the same effect for other liquids. Can we expect to find a minimum point in the specific heat curve for other liquids in the light of the above considerations? I can do no more than suggest such a possibility at present.

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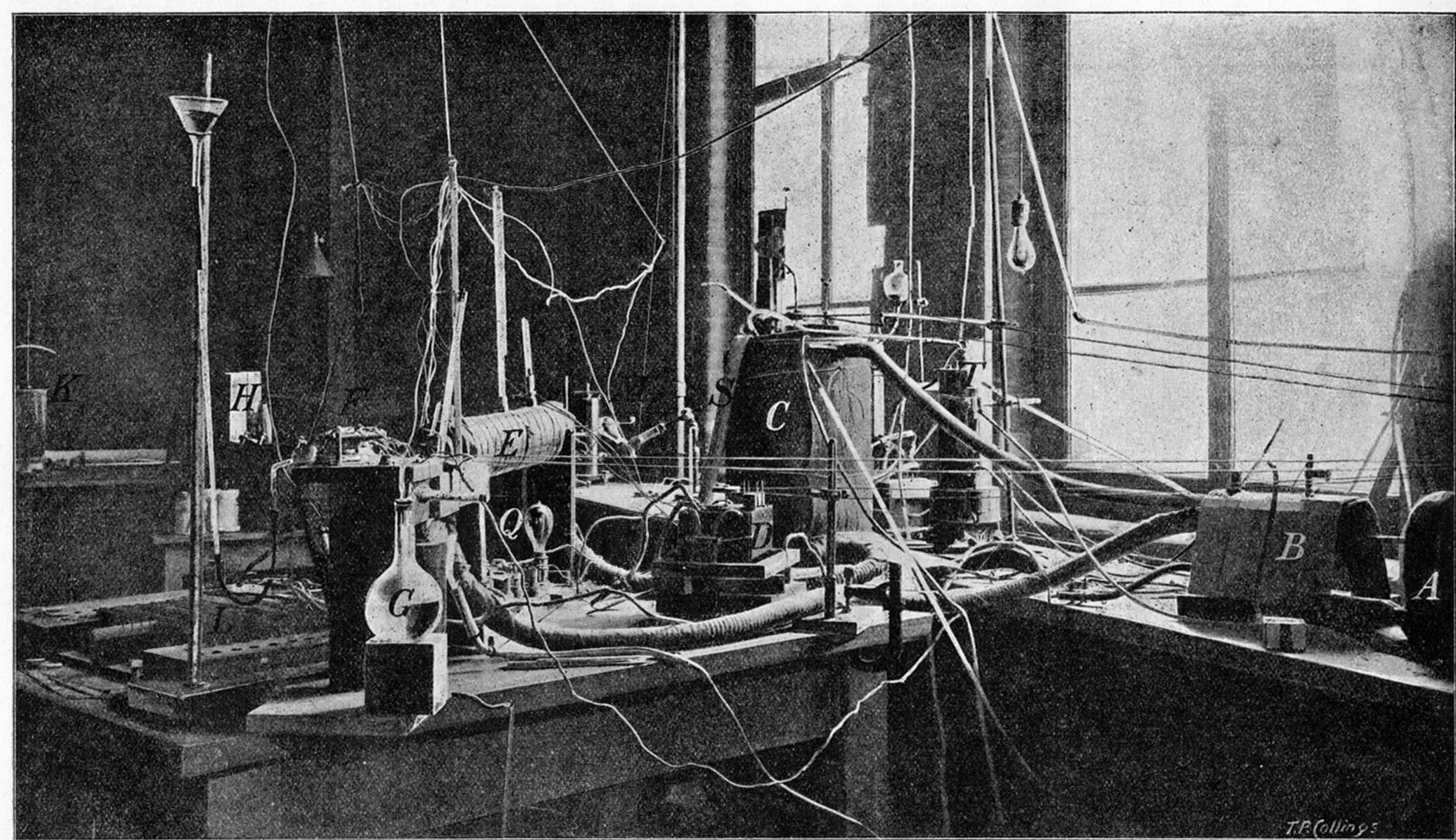


Fig. 14.

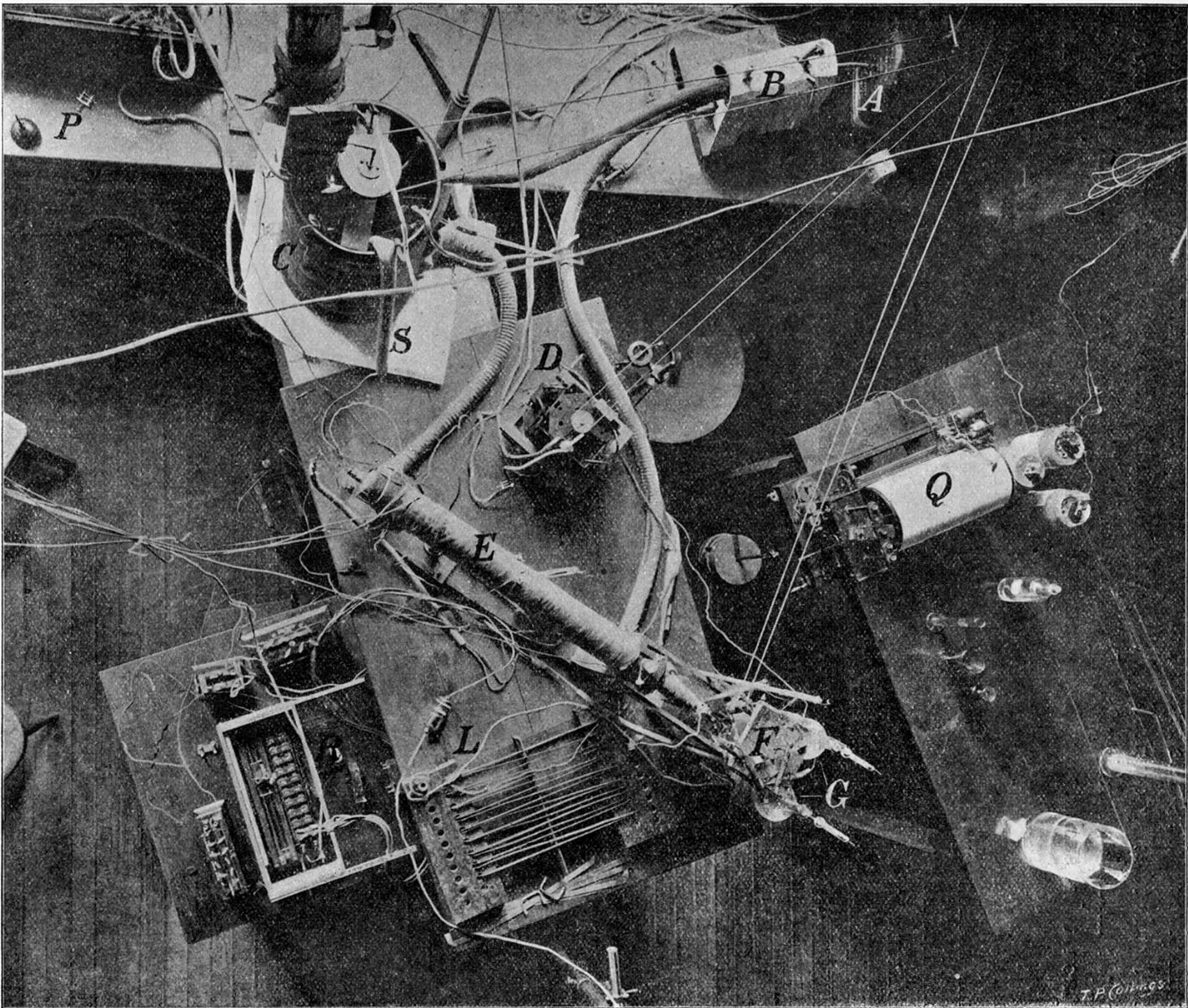


Fig. 15.