VI. *The Value of the Mechanical Equivalent of Heat, deduced from some Experiments performed with the view of establishing the relation between the Electrical and Mechanical Units; together with an Investigation into the Capacity for Heat of Water at different Temperatures.*

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Received January 19,—Read February 16, 1893.

[Plates 2–4.]

Contents.

Introduction.

The necessity for a re-determination of the value of the mechanical equivalent may not be obvious at first sight. The classic determinations by Joule have undergone but little alteration at the hands of succeeding observers, and the researches of Rowland (1879) into this matter were of such an exhaustive nature that there would appear to be little room left for further investigation. It should, however, be remembered that even JOULE's later determinations differ by as much as 1 part in 100[*]; and that marvellous as is the agreement, amongst themselves, of the results obtained by ROWLAND, they, since his method of investigation was unaltered throughout, stand in need of confirmation by different methods of observation. Again, ROWLAND, as far as I have been able to ascertain, stands practically alone in his conclusion that the specific heat of water diminishes as the temperature rises from 0° to 30° C. It is difficult to conceive of a more important investigation (for the purposes of accurate physical measurements) than the determination of the capacity for heat of water at different temperatures, and it is to me a matter of extreme surprise that greater efforts have not been made to trace the variation (if any) in its value. The science of calorimetry must be regarded as in its infancy so long as its fundamental unit is a matter of doubt.

Other observers who have attempted to obtain the value of the mechanical equivalent, by means of the work done by an electric current, have been hampered by constant perplexities as to the absolute values of the electrical units adopted. The science of electrical measurements has now arrived at such a stage that its units may be regarded as sufficiently established,[†] and, therefore, the time seems particularly appropriate for an enquiry into the relation between those units and the mechanical ones.

The difficulties of such an investigation are, of course, great, as is shown by the divergence of the results obtained by those observers who, in recent years, have adopted the electrical method. One cause of inaccuracy has been present in all determinations I have examined, viz., the increase in temperature of the conductor above the temperature of the medium in which it was placed, and the consequent alteration in its resistance. ROWLAND[‡] writes as follows :—"There can be no doubt that experiments depending on the heating of a wire give too small a value of the equivalent, seeing that the temperature of the wire during heating must always be higher than that of the water surrounding it, and hence more heat will be generated than there should be."

An account is given in the following pages of the manner in which this difficulty has been overcome, and I think it will be seen that this objection to the electrical method of investigation is now removed.

The difficulties with regard to measurement of temperature are not peculiar to the electrical method of investigation, and, therefore, I need not dwell upon them. I would, however, venture to add my expressions of astonishment to those of ROWLAND that so many enquirers have attached so little importance to this point; many investigators, whose methods have otherwise been of a high order of accuracy, having contented themselves with the mercurial thermometer as a standard. The importance

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[*] See Table XLV., *infra.*

[†] 'Report Brit. Assoc.,' 1892.

[‡] 'Proceedings American Academy,' June, 1879, p. 153.

of close attention to the thermometry is shown by the fact that the difference between the air and mercury readings, even at low temperatures, will more than account for a change of decrease into increase in the specific heat of water as the temperature rises. An indirect result of my present investigation is to add further proof (if that is necessary) to the accuracy of the measurements of temperature by platinum thermometers, and it is remarkable that so exact and easy a method is not more generally applied to that most difficult subject, thermometry.

Another difficulty which meets any enquirer into calorimetric measurements, is the uncertain nature of the thermal unit ordinarily adopted. I take it that the thermal unit is usually defined as the "amount of heat required to raise unit mass of water from 0° to 1° C." The obvious objections to this unit are that no one has more than a vague idea as to its magnitude, and that in choosing such a range of temperature we have selected, without doubt, the most difficult of all temperatures at which to ascertain it. Again, it is not improbable that over such a range water may exhibit greater changes in its properties than it does at other temperatures. The consequence is that investigators, such as ROWLAND, are compelled to express their results in terms of a variable unit, the theoretical one being an unascertained and indefinite quantity. To escape this difficulty I have taken as my standard the quantity of heat required to raise unit mass of water through 1° C. of the air-thermometer at 15° C. (*i.e.*, from 14°·5 to 15°·5 C.); in other words, I assume the specific heat of water at 15° C. to be 1, and I venture to suggest that (for want of a better) the above definition be accepted as that of the thermal unit.*

I have not included in this paper any prolonged analysis of the work of previous observers. ROWLAND has given a most complete summary, with references, of all results anterior to 1880, and the agreement between later observers is not sufficient to warrant any modification of his conclusions.†

The main portion of this communication is devoted to an account of the experiments performed in my laboratory during 1892, and, in order to avoid the introduction of redundant matter into that account, I here give a brief summary of my previous investigations.

I commenced this work in 1887, and the general principle on which I proposed to proceed was that of eliminating the effects of conduction, radiation, &c., rather than of ascertaining the actual loss or gain due to such causes. If a calorimeter is suspended in a chamber whose walls are kept at a constant temperature, it is obvious that if the initial temperature of the calorimeter is below that of the external envelope, and if the calorimeter has its temperature steadily raised by means of a

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* Personally I should have preferred to select a higher temperature, since a temperature above that of our ordinary surroundings is, at all times, more easily obtainable than a lower one; but as 15° C. has become so commonly accepted as a standard of temperature in electrical measurements, I have adopted it as my standard.

† MICULESCU gives all results published before January, 1892. See 'Annales de Chimie et de Physique,' vol. 27, p. 206.

current, a time will come when the loss by radiation, &c., must equal the gain experienced by the calorimeter during the time it was below the temperature of the surrounding space. The temperature at which the effects of radiation, &c., are eliminated, I term the "null point," and an investigation into its position indicates that if t_1 be the time that the calorimeter was beneath the external temperature, and t_2 the time required to raise it from its initial temperature to the same number of degrees above, that it was previously beneath, the temperature of the surrounding envelope, then the calorimeter would arrive at its null point at a time somewhere between $2t_1$ and t_2. In the Appendix will be found an investigation into the exact position of this point.

1887–1889.—During these years my whole attention was directed to an effort to ascertain the heat developed by the current while the calorimeter was passing from its initial temperature to this null point. Attractive as the method appeared, I ultimately relinquished it, for I wished to direct my attention as much to the investigation of the changes in the specific heat of water as to the determination of the mechanical equivalent, and, although the method is an admirable one for the latter, it is not so suitable for the purposes of the former enquiry.

My general method of conducting the experiments was the same as that observed in 1892 and described in the succeeding pages. From the outset, I had determined to vary all the conditions as much as possible, believing that it was only by such means that constant sources of error could be detected. The agreement amongst individual experiments taken under the same conditions was, if anything, at times more marked than in the experiments of 1892; nevertheless, when the final reduction of the results took place, fatal discrepancies invariably showed themselves. For example, the water equivalent, as deduced from the experiments, increased when the mass of the water was increased, and experiments conducted with a high electromotive force invariably gave too great a value for the time as compared with that obtained when a lower electromotive force was used. These discrepancies, as it now appears, may be attributed to two causes:—

(1.) To insufficient stirring;
(2.) To the rise in temperature of the wire, previously referred to.

Throughout these experiments I was conscious of the error introduced by ignorance of the actual temperature of the wire, but it was not until the summer of 1892 that a satisfactory method of estimating this difference of temperature was adopted.

Unfortunately, many of my experiments in past years were conducted with wires coated with a thick insulating covering, and it is, therefore, impossible to apply the correction obtained this year to the reduction of the earlier results. The observations were excellent in themselves, and some hundreds of experiments were performed. They all give too high a value of J (almost invariably above $4 \cdot 2 \times 10^7$), and are of no value except for the experience gained by their means and the improvements they suggested in the apparatus.

Again, the thermometry was not of a sufficiently satisfactory nature. The thermometers were standardized by direct comparison with B.A. thermometers calibrated at Kew.[*] As these B.A. thermometers were only divided into $\frac{1}{10}$ of a degree, the $\frac{1}{100}$ of a degree had to be estimated,[†] and the order of accuracy was not sufficient.

1890.—Throughout this year I devoted my attention entirely to the measurement of temperatures by platinum thermometers, and I, at that time, proposed to use such thermometers in place of mercurial ones during my J experiments. Excellent, however, as platinum thermometers are, for the accurate determination of temperature, they are not suitable when the observations have to be taken at exact intervals of time. A thermometer, whose readings are at all times visible, must be used in such a case.

1891.—By the kind permission of the Master and Fellows of Sidney College, the Chemical Laboratory was placed at my disposal during this summer. This building was unsuitable for physical work, for the traffic in the adjoining street was so great that galvanometers became at times unmanageable, and many of the observations had to be taken during the night, under conditions somewhat conducive to personal errors.

The steel regulating chamber, described in Section III., was first used in this year (1891), and the results are therefore of more value than the preceding ones; but the same persistent error in the measurement of R still remained, and the form of stirrer adopted was unsatisfactory. The summer's work was, however, of some value, as it gave sufficient data for calibrating the mercury thermometer *when rising.*

A platinum wire coil, having a single coating of amber varnish, was used, and it is reasonable to suppose that its increase of temperature above the surrounding water was of a similar order to that ascertained to be the case in the coil of 1892. Assuming the increase of its resistance to bear the same ratio to its total resistance as in the case of the 1892 coil, and, applying a similar correction to our results, we obtain

$$J = 4{\cdot}188 \times 10^7$$

expressed in terms of water at $18^\circ{\cdot}88$ C, and assuming the coefficient of the change in specific heat of water obtained in 1892, we get

$$4{\cdot}192 \times 10^7 [‡]$$

as the value expressed in terms of the thermal unit as previously defined.

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[*] The accuracy of the Kew corrections for the inequality of the bore has been previously discussed, see 'B.A. Report,' 1890.

[†] I find that many observers, by means of such thermometers, determine temperatures (without using a micrometer scale) to $\frac{1}{1000}$ of a degree. I envy, but cannot lay claim to, such powers of observation.

[‡] The wires connecting the lid of the calorimeter with the steel chamber (see fig. 2, *infra*) had (in 1891) a slightly higher resistance than those used in 1892. I am unable to make the necessary correction, as I have not sufficient data. The effect of the correction (which would certainly be less than in 5000) would be to slightly increase the value of J here given.

This agrees within 1 in 2000 with our later determinations.*

1892.—The difficulties experienced in obtaining an altogether suitable room for the work compelled me to have a special building erected in which to carry on the investigation.

The apparatus is so involved and complicated that it requires weeks to put it together and to get it into working order, and such spare time as I had in the early part of this year was devoted to these preparations. On previous occasions the constant day and night changes in temperature of the rooms in which experiments were conducted had been a cause of uncertainty; for the numbers, obtained by using resistance boxes or Clark cells whose temperature is constantly changing, are always of doubtful accuracy. I therefore designed a regulator which, except in cases of severe frost or extreme heat, automatically maintained the room at a constant temperature. I found this arrangement so effective that I have, in the hope that it may be useful to others, given a short description of it in Appendix II.

If I endeavoured to adequately describe how much I owe to the assistance of others during this investigation I should unduly increase the length of this introduction. I must, however, express my thanks to the Council of the Royal Society, to Lord KELVIN, Lord RAYLEIGH, Professor G. DARWIN, Professor HICKS, Professor J. J. THOMSON, Dr. FEUSZNER, Dr. GUILLAUME, Mr. CALLENDAR, Mr. VERNON HARCOURT, Mr. HEYCOCK, Mr. LARMOR, and Mr. NEVILLE for the encouragement and assistance they have afforded me. More especially am I indebted to Mr. GLAZEBROOK, not only for his advice and help, but for the careful and laborious comparison of my resistance box with the standards of the B.A.; and also to Mr. SKINNER for his repeated comparison of my Clark cells with the Cavendish standards. My thanks are also due to Mr. A. IVATT, B.A., Christ's College, Cambridge, for his assistance in the experimental work during 1887 and part of 1888.

Nearly the whole of the apparatus (some of it of a novel and intricate character) was constructed by, or under the direction of, Mr. F. THOMAS, Jesus Lane, Cambridge. Had it not been for his unremitting attention and skill, the results of my investigation would have been far from satisfactory.

From 1888 onwards I was assisted by Mr. G. M. CLARK, B.A., Sidney College, Cambridge, who has from the commencement of our joint work been indefatigable in his exertions. Our respective contributions are so intimately associated that I find it impossible to make the remainder of this communication in the first person, and although, by his own wish, his name does not appear on the title-page, it should, in justice, be regarded as a joint contribution.

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* The Clark cells used as our standards of E.M.F. are those given in Table IX. of Messrs. GLAZEBROOK and SKINNER'S paper, 'Phil. Trans.,' A, 1892, p. 605.

SECTION I.—GENERAL DESCRIPTION.

Let R be the resistance of a conductor at a certain standard temperature θ, then if the ends of the conductor be kept at a constant difference of potential E

$$\frac{dQ_\epsilon}{dt} = \frac{E^2}{J\,.\,R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

where Q_ϵ is the quantity of heat generated by the current, t is time, and J the mechanical equivalent of heat.

If the wire is immersed in water, and if the capacity for heat of the water and the calorimeter at the standard temperature θ is M, then

$$\frac{dQ}{dt} = M\,.\,\frac{d\theta}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

It is necessary to distribute the heat generated in the wire throughout the whole calorimeter as quickly as possible, otherwise we cannot accurately observe $d\theta/dt$, hence, since work must be done when stirring, we have to deal with a mechanical as well as with an electrical supply. Let the rise in temperature per second due to the mechanical supply be σ, and let $Q_{\epsilon,\,\sigma}$ denote the quantity of heat generated by both electrical and mechanical sources. Then

$$\frac{dQ_{\epsilon,\,\sigma}}{dt} = \frac{E^2}{J\,.\,R} + \sigma M = M\,.\,\frac{d\theta}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

It is certain that some heat will be gained or lost by radiation, conduction, and convection. Let ρ be the rise or fall per second in temperature due to radiation, &c., when the difference between the external and internal temperatures is 1° C. Denote the temperature of the surrounding envelope by θ_0, and the temperature of the calorimeter at any time by θ_1; also suppose that M becomes M′ and R becomes R′ when θ becomes θ_1.

We now have

$$\frac{dQ_{\epsilon,\,\sigma,\,\rho}}{dt} = \frac{E^2}{J\,.\,R'} + \sigma M' - \rho M'(\theta_1 - \theta_0)^* = M'\frac{d\theta_1}{dt} \quad . \quad . \quad . \quad . \quad (4),$$

where $Q_{\epsilon,\,\sigma,\,\rho}$ denotes the gain of heat due to all causes, hence

$$\frac{E^2}{J\,.\,R'\,.\,M'} + \{\sigma - \rho(\theta_1 - \theta_0)\} = \frac{d\theta_1}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

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* It is shown in Section XII. that we are justified in assuming that NEWTON's law of cooling holds true over our range of temperature.

If $E = 0$, this becomes

$$\sigma - \rho(\theta_1 - \theta_0) = \left(\frac{d\theta_1}{dt}\right)^*_{\sigma,\rho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

Provided that the mechanical supply is regular, and θ_0 is kept constant, we can, by a sufficient number of observations over small ranges, determine the values of $(d\theta_1/dt)_{\sigma,\rho}$ for different values of θ_1, and by substituting in equation 5, we obtain the value of $E^2/J.R'.M' = A$, where A is known.

Assuming that over small ranges the values of R′ and M′ are linear functions of θ_1,† we have

$$R' = R\{1 + k(\theta_1 - \theta)\}‡, \text{ and } M' = M\{1 + l(\theta_1 - \theta)\},$$

hence

$$\frac{E^2}{J.R.\{1 + k(\theta_1 - \theta)\}\,M.\{1 + l(\theta_1 - \theta)\}} = A \quad . \quad . \quad . \quad . \quad . \quad . \quad (7).$$

Now the values of E and R at the standard temperature can be ascertained by comparisons with the standards, and the value of k can be ascertained by direct measurements of R′ at different temperatures, hence

$$J.M.\{1 + l(\theta_1 - \theta)\} = \frac{E^2}{A.R.\{1 + k(\theta_1 - \theta)\}} = B, \text{ where B is known} . \quad (8),$$

we have thus one equation connecting the three quantities, J, M, and l.

Let w and w_x be the capacities for heat of the water and the calorimeter respectively at the standard temperature θ, and let the temperature coefficients of their specific heats be f and g respectively, then

$$M\{1 + l(\theta_1 - \theta)\} = w\{1 + f(\theta_1 - \theta)\} + w_x\{1 + g(\theta_1 - \theta)\},$$

hence equation (8) becomes

$$J[w\{1 + f(\theta_1 - \theta)\} + w_x\{1 + g(\theta_1 - \theta)\}] = B \quad . \quad . \quad . \quad . \quad (9).$$

If observations are taken with different weights (w_1 and w_2) of water, we obtain B_1, B_2 the corresponding values of B, thus

$$J[w_1\{1 + f(\theta_1 - \theta)\} + w_x\{1 + g(\theta_1 - \theta)\}] = B_1$$

and

$$J[w_2\{1 + f(\theta_1 - \theta)\} + w_x\{1 + g(\theta_1 - \theta)\}] = B_2;$$

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* In this, and similar cases, we use the suffix to denote the sources of heat.

† The value of $d\theta$, during our experiments, was about 1° C.

‡ The true value of $R' = R\{1 + k(\theta_1 + \beta - \theta)\}$ where β is the excess of the temperature of the wire above θ_1 the temperature of the calorimeter. See Section XIV., p. 478.

by subtraction we obtain

$$J\,(w_1 - w_2)\,(1 + f\,\overline{\theta_1 - \theta}) = B_1 - B_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10).$$

Hence, when $\theta_1 = \theta$, the value of J can be found without ascertaining the value of the water equivalent or the temperature coefficient of the specific heat of water. As J is a constant quantity we can, by repeating the observations at different temperatures, obtain from equation (10) the value of f.

Or we can obtain f without finding J, for repeating the observations at temperatures θ_1 and θ_2

$$J\,(w_1 - w_2)\,(1 + f\,\overline{\theta_1 - \theta}) = B_{1,1} - B_{2,1}$$

and

$$J\,(w_1 - w_2)\,(1 + f\,\overline{\theta_2 - \theta}) = B_{1,2} - B_{2,2}$$

the second suffix of B denoting the temperatures.

Hence, by division, we obtain

$$\frac{1 + f\,\overline{\theta_1 - \theta}}{1 + f\,\overline{\theta_2 - \theta}} = \frac{B_{1,1} - B_{2,1}}{B_{1,2} - B_{2,2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11).$$

An alternative method of finding J is to first find f by equation (11), and then to find the value of w_x and g.* The value of J can then be deduced from a single experiment by means of equations (8) or (9), and as this method enables us more easily to compare the results of individual experiments we have, as a rule, adopted it in our reductions.

In the remainder of this section we briefly indicate the manner in which we have determined the various quantities grouped together and denoted in the above equations by B.

The calorimeter was suspended by means of glass tubes in an air-tight chamber whose walls were kept at a constant temperature. The pressure of the dry air in this chamber was reduced to under ·5 millim. The water in the calorimeter was stirred at a very rapid rate throughout the experiments, and the value of $(d\theta/dt)$ ascertained at all parts of the range 14° to 26° C.; firstly, when the work was done by the stirrer only, secondly, when the rise was due to both the electrical and the mechanical supply of heat.

The masses of water used during the experiments varied in the ratio of about 1 to 3, and the difference of potential at the ends of the coil was so altered that the heat developed by the current was changed in the proportion of 1 to 9.

As shown by equation (10) *supra*, there was no necessity to ascertain the water equivalent of the calorimeter, although it was found convenient, as a check upon the

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* These values can be obtained from the preceding equations without first determining J. The process is fully explained in Section XIV.

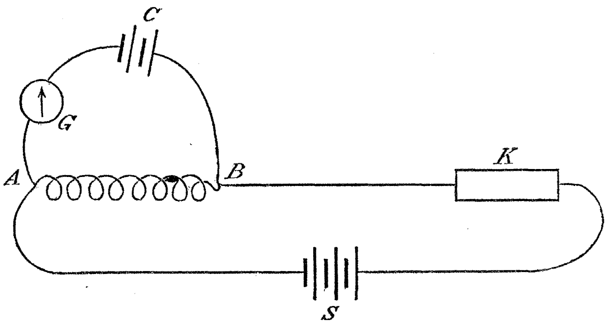
calculations, to deduce it from the differences in time caused by differences in the mass of the contained water.

The walls of the chamber containing the calorimeter were maintained at a constant temperature throughout each experiment, this being, in general, the mean temperature of the above-mentioned range. Direct observations of the changes in $(d\theta_1/dt)_{\sigma,\rho}$, caused by changes in θ_1, enabled us to ascertain the values of both σ and ρ.

(1.) *Potential* (E).—A detailed account is given in Section VI. of the method by which the ends of the calorimeter coil were maintained at a constant potential difference. Briefly, the principle on which our method depended was as follows.

The extremities of the wires *CA*, *CB*, will (when the galvanometer *G* shows no deflection) be maintained at a difference of potential equal to that due to the cells at *C*.

Fig. 1.



Let *K* be an adjustable resistance placed in the circuit which communicates with *S* (the storage cells), and let R be the resistance of the wire *AB*. Whatever variations may take place in R and in the E.M.F. at *S* it is always possible (provided the adjustment of *K* is sufficiently under control) to maintain, by close attention to the indications of the galvanometer, the points *A* and *B* at a constant difference of potential.

A special rheostat was designed by means of which it was found possible, in spite of variations in the resistance of *AB*, to maintain the potential-difference unchanged throughout an experiment, and we believe that in no case did the variations exceed $\frac{1}{10,000}$ of the mean difference of potential during each experiment.

The Clark cells (which were placed at *C*) were constructed by us according to the directions of Messrs. GLAZEBROOK and SKINNER, and have, on several occasions, been directly compared with the Cavendish and indirectly with the Berlin standard.

Their differences from the standard are small, and their mean E.M.F. at 15° C. = 1·4344 volts (see Section VI.).

(2.) *Resistance* (R).—Had it been possible to maintain a constant value for R it would have greatly simplified both the experimental work and the calculations. In the year 1890 we devoted much time to the examination of the various copper-manganese-nickel alloys, and we performed a series of determinations with a coil whose tempera ture-coefficient was practically zero. The reasons which led us to reject these alloys and adopt a platinum wire will, we think, be found sufficient (see section VII.).

The value of R was first determined by a dial-box (legal ohms) constructed by Messrs. ELLIOTT.[*] Mr. GLAZEBROOK has been so kind as to perform a complete standardization of this box by means of the B.A. standards. The resulting corrections have been applied, and the values of R expressed in true ohms, as defined by the B.A. Report, 1892.

The method by which we ascertained the true temperature, and therefore, the resistance of the wire when traversed by a current, is fully described in Section VII. We found that the difference in temperature between the wire and that indicated by the thermometer could be accurately determined, and, other conditions being equal, varied as C^2.

The arrangement of our connections enabled us to dispense with exterior resistance, as the ends of the coil itself were maintained at a constant potential-difference.

(3.) *Current* (C).—The current was maintained by storage cells of the (L) type, supplied to us by Messrs. BAILEY and GRUNDY. The E.M.F. of these cells was wonderfully constant. This constancy, although not a necessity, was a convenience. As previously pointed out, C was not directly measured.

(4.) *Time* (T).—An electrical clock with a seconds pendulum was used as our standard for time. It was carefully compared at intervals with a chronometer by DENT. A chronograph was controlled by this clock. The rate of the clock was a losing one until August 21st, but after that date its error was less than 1/25,000, and no correction was necessary.

(5.) *Mass* (M).—A balance sensitive to a change of 1/100,000 of the least mass measured by us, and a set of OERTLING'S weights,[†] were used in our determination of mass.

(6.) *Temperature* (θ).—At the time of writing (December, 1892) our thermometry is based on measurements made by platinum-thermometers. We propose to make, at an early date, a direct comparison of our standard thermometer with the air thermometer by means of the apparatus described by Mr. CALLENDAR,[‡] who has been so kind as to promise his assistance.

In a previous paper[§] the details of a careful comparison of the platinum and the air-thermometer have been given. It was then shown that the platinum-air difference curve $\delta\,[\overline{\theta/100}|^2 - \theta/100]$ gave values of θ at all temperatures from 0° to 100° C., accurate within ·01° of the real value of θ, and that discrepancies appeared to have an experimental origin. The experience of two years' work with platinum-thermometers has but increased our confidence in them.[||] Should a direct comparison with the

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[*] Particulars of this box have been given in a previous paper. 'Phil. Trans.,' A., 1891, p. 44.

[†] These weights were re-standardized by Messrs. OERTLING in August, 1892.

[‡] 'Roy. Soc. Proc.,' Jan., 1891.

[§] See 'Phil. Trans.,' 1891, A, p. 155.

[||] 'Philosophical Magazine,' December, 1892.

air-thermometer modify our determinations of differences of temperature (and it is only differences which are important to us), our results will be modified accordingly. This will not, however, necessitate any repetition of the experimental work, as the corrections involved will be of a numerical order only.

Measurement of the Heat generated by Stirring.

The difficulties that we have met with in this portion of our work have been very great. As will be shown in Section XI., we have, against our will, been compelled to increase the work done by the stirrer until the heat thus generated became about 1/10 of the whole supply. We found continuous and very rapid stirring to be a necessity. Variations in R and in the thermometer readings and in the water equivalent of the calorimeter invariably followed if the mixing was insufficient. Commencing in 1888 with a stirrer revolving at the rate of about 100 revolutions per minute, the rate was gradually increased until, in our last series, we aimed (with, it is true, a different form of stirrer) at a rate of nearly 2000 revolutions per minute.

The accurate measurement of the heat thus generated is only second in importance to the determination of the heat due to the current, and, accordingly, a great portion of our time and attention was directed to it. Fortunately, we were able to completely establish the law that, with our form of stirrer, the work done varied directly as r^3, r being the rate of rotation. From this time our difficulties rapidly diminished.

Radiation, Conduction, Convection, &c.

We endeavoured, as far as possible, to diminish loss or gain due to the above causes.

BOTTOMLEY* has shown that there is a rapid fall in the rate of loss or gain by radiation and convection when the pressure of the surrounding gas falls below 1 millim. Most of our observations were taken with the surrounding pressure under ·5 millim.

The calorimeter itself had a bright polished surface, and the walls of the enclosing chamber were clothed with bright speculum metal. In Section XI., we show that throughout our range of temperature, NEWTON'S law of radiation holds—*i.e.*, the loss or gain varies directly as the differences of temperature. It must, however, be remembered that we have not endeavoured to separate the partial effects of the radiation, conduction, and convection, and hence we can only say that the combined effect obeys this law. The total loss or gain, due to the above causes, was determined separately for each change in the contained mass.

Any error in this part of our work would have but a small effect on the mean value of J, since, in each experiment (if taken as a whole), the total loss or gain by conduction, convection, and radiation, must have been small.

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* 'Phil. Trans.,' 1887, A, p. 445.

SECTION II.—THE CALORIMETER AND COIL. (See Plate 2, fig. 2.)

The calorimeter, which was of a cylindrical form, was made of "gilding metal"—73 per cent. copper and 27 per cent. zinc.

The weight of the lower part was 501·84 grms.; of the lid 245·67 grms.

The internal diameter and the depth were each 8 centims.

Its capacity was therefore about 400 cub. centims.

The weight of the calorimeter may appear excessive for this capacity. However, as any "panting" of the lid or base would have thrown the stirrer out of adjustment and as the pressure on the flat base of the calorimeter would amount to about 120 lbs., when the space surrounding it was vacuous, it was evident that considerable thickness was necessary to secure rigidity. The two parts of the calorimeter were held together by eight screw bolts; a lead ring previously placed between the parts was crushed by the tightening of the screws and thus the join was rendered air-tight. It was therefore necessary to make both the lid and the projecting lip of the calorimeter sufficiently strong to bear the strain without bending.

As we expected to determine the water equivalent with as much accuracy as other quantities, the large mass of the calorimeter did not appear to be a serious objection.

The whole of the calorimeter was heavily gilded both inside and out, and the surfaces polished. The lead ring* was covered with gold leaf because considerable quantities of $PbCO_3$ were formed if the water had access to it; thus, no metal except gold was exposed to the action of the water. An advantage of the gold exterior was that its surface did not tarnish, and thus its coefficient of radiation remained constant.

Fixed on the interior of the lid were eight metal tubes, 1 centim. in length. Three of these were 18 millims. in diameter and served to hold the glass tubes by which the calorimeter was suspended. The others were 5 millims. in diameter and supported the glass rods on which the coil was wound. These rods reached to within a couple of millimeters of the base when the lid was placed in position. Two copper rods, 7·5 centims. in length (14 B.W.G.) passed from the insulated junctions at M and N (fig. 2, p. 382) to nearly the bottom of the calorimeter. These were also heavily gilded, and the ends of the platinum wires were fastened to their lower extremities. The last coil used by us was about 13 inches in length, and was wound round the lower end of the glass rods in such a manner, that the difference of potential of any two adjacent points could never be great. Thus the first 6 inches were wound on one side, the remainder on the further side of the calorimeter. A depth of 1·5 centim. of water completely covered the whole coil.

The glass tubes passing through the lid were held in position by perforated india-rubber corks. Great pressure had to be exerted to force the tubes "home," and

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* A pure gold ring was tried, but it was found impossible to crush it sufficiently to render the join air-tight.

several were broken in the process. The external diameter of the glass tubes was 14 millims., the interior diameter of the gold tubes 18 millims.; thus the annulus of india-rubber was very thin. The lower ends of the glass tubes were turned outwards so as to nearly cover the lower end of the india-rubber, of which the small exposed surface was originally coated with gutta-percha; but (as explained elsewhere) this was removed after J 19, and replaced by amber varnish.* The india-rubber corks, where they appeared above the lid, were, from the commencement, coated with amber varnish. No diffusion appeared to take place through these corks, and, as other observers seem to have been troubled by such diffusion when using india-rubber, it is probable that the coating of amber varnish (which adheres very firmly to the rubber) is an effective remedy. In any case it prevented any contact between the rubber and the contained water. We may thus assert that the water came into contact with the following substances only—gold, amber, glass, agate, gutta-percha (before experiment J 20) and (after experiment J 20) some hard shellac,† very small quantities of which were used to prevent slipping of the coil on the glass rods, the substance previously used for this purpose being gutta-percha. The platinum coil itself was coated with amber varnish, but it is possible, that owing to cracks in its coating caused by movements of the wire, the water had access to it in places. The small slabs of ebonite used at the junctions *M* and *N* (fig. 4, p. 396) were also covered with several layers of the same invaluable varnish.

SECTION III.—THE METHOD OF MAINTAINING THE WALLS SURROUNDING THE CALORIMETER AT A CONSTANT TEMPERATURE.

The necessity of maintaining at a constant temperature the walls of the chamber containing the calorimeter is so obvious that it seems unnecessary to dwell upon it. In our earlier experiments, the calorimeter was suspended in a copper vessel which was immersed in a large tank, and the uniformity of the temperature depended on the skill of the observer in adjusting the temperature of the tank water by altering the supply of hot and cold water admitted. The method adopted by us in 1891 and 1892 worked automatically, and enabled us to maintain a chamber at any temperature within the range of our experiments, whether that temperature was above or below that of the room. Briefly, the arrangement may be described as an enormous thermometer-bulb within which was the calorimeter.

A section and plan, on a scale of $\frac{1}{3}$, are shown on Plate 3. The steel chamber, *A, B, C* (a very fine piece of work) was constructed by Messrs. WHITWORTH and Co. A detailed description of its various parts is unnecessary, as all particulars are given in the plate referred to. The annular space (coloured black) was filled with mercury.

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* *See Note*, p. 392, *infra.*

† The shellac was melted on, and not deposited from its solution. A hard surface is rarely obtained by the latter method.

As it was advisable to free that space from air bubbles, the screw plug *P* was removed before the insertion of the mercury, and replaced by a tube leading to a GEISSLER'S mercury pump. A tube from *D* dipped into a basin of hot mercury, and in this tube was a tap which was at first closed. The air in the annular space was withdrawn until the pressure was a small fraction of a millimeter, and the hot mercury was then slowly admitted—the exhaust pump being worked at intervals. When the mercury became visible within the tube at *P*, the tube was cautiously removed, and the air-tight screw plug replaced. The mercury necessary to fill the space weighed 70 lbs.

So true were the surfaces of the two parts of the metal chamber, which were screwed together by the bolts at *A* and *C*, that, although no packing except the finest possible coating of grease had been placed upon them, they proved absolutely air-tight. These two portions of the chamber were each formed from a single block of steel and, when placed together, somewhat resembled a double hat-box. The inner and outer surfaces were turned smooth and true, and then were nickel-plated. Two holes on opposite sides were bored down between the mercury chamber and the inner surface, as shown at *E* and *F*. These holes were filled with mercury and, their inner walls being very thin, the thermometer placed in them would accurately indicate the temperature of the inner surface of the chamber. This inner surface, as also the base of the chamber, was, in our more recent experiments, covered with highly-polished speculum metal. A ring of lead wire was placed round the top edge of the chamber, on which was laid that portion of the lid shown in section at *G* and *H*, and in plan at *G′* and *H′*, and the twelve bolts securing it were screwed home. Many as have been our difficulties with regard to air-tight joints, those made in this manner, viz., by the crushing of a lead ring between two surfaces, have never given us any anxiety. The second lid, from which the calorimeter was suspended, and whose section is shown at *K L*, and plan at *K′ L′*, was secured in a similar manner.

The necessity for this double lid is not, at first sight, obvious, but it must be remembered that it was impossible to separate the calorimeter from the portion of the lid to which it was attached, and, therefore, a heavy steel plate would have been inconvenient, and have rendered any direct weighings impossible. On the other hand, the total pressure on this lid, when the chamber was exhausted, was very great, and, had the whole of it consisted of one thin piece, it is probable that it would not have withstood the strain without "panting," and, as it was necessary on account of the stirring rod, &c., that the whole apparatus should be absolutely rigid, it was essential to avoid any phenomenon of this kind. The first lid, therefore, is of considerable thickness, and the orifice in it only just sufficient to allow for the introduction of the calorimeter. Again, if the lid had been of one piece, it would have been impossible to remove it without disturbing the tubes *M* and *N*.

The tube *M* communicated with a five-way Sprengel pump and a McLeod gauge; the tube *N* with a Geissler pump and a water pump. The arrangements for drying and exhausting by means of these tubes is described in Section V.

The steel chamber, together with the mercury, weighed nearly 2 cwts. It stood on a small tripod in a galvanized iron tank, whose capacity was about 20 gallons. The tank itself was placed on a bed of Portland cement before the cement had hardened, and thus the whole erection was firm and stable. When the outer tank was filled, the surface of the water was about 3 inches above the lid of the steel chamber and was maintained at that level by a constant inflow of water, which entered almost above the screw *Q* and left by an overflow pipe shown at *W*. The screw at *Q* rotated in such a direction that the water was forced downwards, passed under the steel chamber, and returned across the lid. The screw revolved about 800 times a minute, and the stirring was very thorough, so that it was impossible to detect any difference of temperature in different portions of the tank, even when hot water was being admitted, unless the thermometer was held immediately against the entrance pipe. A glass tube with narrow bore (Sprengel tubing) was fixed into the steel tube at *D* and communicated with the regulating apparatus shown in Plate 4, fig. 1. *R* is the regulator—the gas entering at *A* and leaving at *B*. The tube *R* was about 1 inch in diameter and was drawn to a fine opening at its lower end. The thin glass partition *C* passed down the centre of this tube and projected at its lowest extremity into the narrow opening. To render the partition air-tight, its edges were coated with hard shellac, and after it had been thrust into position, the tube was warmed until the shellac melted. The top of the tube was closed with shellac, thus the gas, entering at *A*, could only arrive at *B* by passing round the lower end of this partition, and a very small movement of the mercury in the narrow neck sufficed to cut off the supply. We adopted this form of regulator after considerable experience of the ordinary form, in which the supply passes down an inner tube and up the annular space around it, which labours under the defect that the adhesion between the mercury and the inner tube causes the gas to remain cut off for some time after the mercury has commenced to contract. The form here shown is free from this defect, as it is found that the mercury does not adhere to the thin glass partition. Beneath the narrow tube a small reservoir (capacity about 3 cub. centims.) at *E* allowed considerable contraction to take place, and yet permitted the mercury to be kept in view. A side tube passed from *E* to the three-way taps *F* and *H*, and thus, by means of the tap at *F*, mercury could be withdrawn when necessary. The tubes *HK* and *HL* were about 4 feet in length—*K* terminating in a thistle-funnel, in which a supply of mercury was placed.

The tube *L* was connected with the three-way tap *M*, by which communication could be made with the exhaust water-pump, or with the open air. Behind the tube *L* was fixed a vertical scale of millimeters, and the whole of the tubing was rather wide-bore Sprengel. Through the tap at *H* mercury from the arm *KH* could be passed into the arm *KL* to any convenient height. By means of the taps *H* and *F* any portion of this mercury could be passed into the regulator, and, if necessary, the *same amount* could at any time be withdrawn by connecting *L* with the exhaust (by means of tap *M*) and opening *F* and *H*—independently of the level of the mercury in the regulator. This contrivance, therefore, rendered it possible to "set" the instrument so as to produce any required change of temperature in the tank; for it was found that the transference of about 312 millims. of the column *HL* into the regulator caused a difference of 1° C. in the temperature of the tank. It was thus possible to adjust the temperature to a very small fraction of a degree.

The connecting tube from *E* to *D* was bent into a spring of sufficient length to allow of some play to the lower end, and thus it was possible to withdraw the end from *D* without moving the whole edifice. The glass work was supported on a vertical board, about 5 feet in height, and the various taps were placed within easy reach of the observer. All gas admitted at *A* was dried by passing through tubes containing quicklime, as it was found that the regulator worked in a much more satisfactory manner when the surface of the mercury was clean. After leaving *B*, the gas entered a tube about 2 feet long, containing a very large number of small pin-holes. The tube was connected by two cross pieces containing similar small holes, with two pilot lights fed by an independent supply. A change of $\frac{1}{500}$ of a degree in the tank visibly affected the brilliancy of the tiny gas jets, and a change of less than $\frac{1}{100}$ made all the difference between total eclipse and a complete series of bright blue jets. The supply of gas through the regulator was, however, sufficient when the mercury had receded far enough to maintain the jets at a length of nearly $\frac{3}{4}$-inch.

Placed above this row of jets, but so far from the pilot lights as to be unaffected by them, was a flat silver tube, the section of whose bore was a rectangle of about 1 inch wide and $\frac{1}{16}$ inch deep, and, through this tube, the water passed on its way to the tank. The supply was regulated by a small "constant level" tank of the usual pattern, suspended from the ceiling by a string. Alterations in the level of this tank afforded a fine adjustment—the temperature depending on the rate of flow. The water was supplied direct from the main, and hence, even in the hottest summer weather, it was possible to maintain the tank at a temperature as low as 14°; in winter, as low as 3° or 4° C. Any temperature above this minimum was, of course, obtainable, but we considered it unadvisable to raise it above 40° C. on account of the ebonite, &c. This regulator proved itself to be a most satisfactory instrument. Although, when set to give a new temperature, it was slow in its action (the capacity for heat of the tank and its contents being great) it was none the less sure, and, after about half-an-hour from the readjustment, the temperature would be found to have become steady. If set to give a higher temperature, the thermometer at *E* (Plate 3) would pass that temperature by about $\frac{1}{15}$ of a degree, and, after this preliminary oscillation, would become steady, although it is probable that this first was followed by other oscillations, which were too small to be apparent. It is possible that the temperature of the inner surface of the steel chamber was, to some extent, affected by the temperature of the calorimeter. The change must, however, have been very small, since it was insufficient to affect the thermometer at *E*. It must be remembered that any such change would at once produce an effect on the mercury, and, by its action on the regulator, reproduce the original condition.

SECTION IV.—THE MOTOR AND ITS CONNECTIONS.

A belt passed from the motor to a vertical shaft fixed near the back of the tank. This shaft carried "speed-wheels," from which ran two cords, one to the stirrer in the outer tank, the other to the stirrer in the calorimeter. In order to prevent any "slipping," with which we were at one time much troubled, all these cords ran through loose pulleys hung by strings, which, passing over small fixed pulleys, were connected with pans containing shot. The tension of the cords could thus be regulated by altering the weight of shot, and any change in their length, due to stretching, &c., was of no consequence. The shaft of the calorimeter stirrer was connected with the revolving piece above it by a double HOOKE's joint. Until experiment J 19 a short piece of brass tubing with a cross wire at each end served as the HOOKE's joint, with the exception of J's 17 and 18, when only a single HOOKE's joint was used. A difference in the "stirring supply" was shown in these two experiments (see p. 450), probably due to some difference in pressure between the agate cylinder at the bottom of the stirring-rod and the ring surrounding it. After experiment J 19 the connection was made by a small circle of thin wire, which passed through a hole in the revolving shaft and dropped into a slit in the top of the stirring-rod. Thus all rigidity in the connection was avoided, and the stirring effect was more regular after the change. Above the stirring-shaft was a HARDING's counter, whose axis carried at its upper extremity a V-pulley, and at its lower extremity the HOOKE's joint (see Plate 2, fig. 2). These counters move in steps, and not with a continuous sliding motion, and, as it was essential that we should be able to read with considerable accuracy the time of each 1000 revolutions, this form of counter was the best adapted to the purpose. The wear that these instruments will stand is surprising, for, on many occasions, nearly a quarter of a million revolutions per day were recorded, and the same counter was used by us throughout our experiments of 1891 and 1892, with the exception of experiments J 20 to 34, when the original counter, having shown some slight signs of wear, was replaced by another.

The motor (one of the fan type) was by BAILEY and Co., and of the usual pattern. When working at the Sidney Laboratory in 1891, the changes in pressure, and therefore in the speed of the motor, were so frequent that we were compelled to relinquish our attempts to perform our J experiments during the day, and the observations had, therefore, to be taken between 10 p.m. and 2 a.m. Even during these hours, the regularity was far from satisfactory.

As has been explained in the introduction a special room was built for the experiments of 1892. Here the supply pipe to the motor led directly from the main, but the irregularities of pressure were still so great as to render some improvement imperative. The form of regulator devised, although it did not insure that absolute uniformity which we could have wished, was yet so effective that we venture to describe it at length, in the hope that it may prove useful to others who have met with the same difficulty.

AB (see Plate 4, fig. 2) was a flexible diaphragm made of india-rubber of one ply. This was bolted between two brass saucer-shaped discs with tinned surfaces. The lower of these discs was connected with a tube leading to the motor; the upper, by means of *E*, *F*, *G*, with an iron reservoir (a mercury bottle) placed on the floor. A thin metal rod was attached to a plate in the centre of the diaphragm, and at its lower extremity were fixed two cylinders placed so as to form a balance valve. The ends of these cylinders were grooved in such a manner that any upward movement diminished, and any downward movement increased the size of the channels through which the water had to pass. The water from the main entered at *C*, and after passing through the grooved channels followed the path indicated by the arrows, until it arrived at the injector of the motor. An iron tube about 6 feet high was supported by a vertical plank, which reached from the floor to the roof of the laboratory. The lower end of this tube entered the iron reservoir *G* at the bottom, and to the upper extremity was fastened about 4 feet of high pressure tubing of which the free end was lashed to a mercury jar *H*, similar to the hand one used in a GEISSLER'S pump. This jar rested on a movable shelf which, by means of a rope and pulley, could be raised from about 4 feet to 10 feet above the vessel *G*. Sufficient mercury was placed in this jar to fill the flexible tube and the lower 3 or 4 inches of the iron vessel *G*. The taps at *K*, *F*, and *L*, were then opened and water passed into the tube *E*, *K*, and the vessel *G*. As the pressure increased, the mercury was forced up the tube *M*, *N* until its surface became visible in *H*. The tap at *F* was then closed and the screw plug at *E* opened to allow any air in the pipes, or above the diaphragm, to escape. *E* was then closed and first the tap *L* was opened, then the tap *F*, until the mercury again appeared in *H*. *F* was then finally closed and would not again be used unless it was necessary to refill the apparatus. The pressure above *AB* could now be adjusted at will by altering the elevation of *H*, and the effective pressure could thus be changed from 20 lbs. to 60 lbs. per sq. inch. When the tap *L* was opened, if the pressure due to the tap-water on the lower side of *AB* exceeded the pressure on the top, the valve was lifted and the flow to the motor diminished until the pressure of the water which had passed the valves became the same as that above the diaphragm. Conversely, if the water pressure diminished, the flow to the motor increased. The tap at *K* was only used to remove the pressure of the mercury column from the top of the diaphragm when the instrument was not in use. Within certain limits, this regulator acted excellently; but if the water pressure fell so low that the diaphragm assumed its lowest position, it ceased to be effective. By altering the elevation of the movable shelf at *H*, the rate of the motor could be adjusted at will, and a scale being fixed to the vertical plank, the extent of the adjustment necessary to produce a given alteration was approximately known after a few observations.

[Note by E. H. G. Added April, 1893. Lord RAYLEIGH has discussed the principles which should be observed when using a motor of the fan type ('Proc. Soc. Roy.,' 1881, p. 109), and has shown that when the motor is run at high speed the curves of work and of resistance cut each other at a greater angle than is possible when the rate of revolution is small, and thus a more uniform motion is obtained in the former, than in the latter, case. Our speed wheels were so arranged that the motor under ordinary circumstances ran at about 16 revolutions per second, which appeared to be as high a speed as was necessary.]

SECTION V.—THE PRESSURE IN THE SURROUNDING SPACE.

As already mentioned, the tubes *M* and *N* (see Plate 3) led to the pumps and McLeod gauge. The circuit embraced several yards of glass tubing, a large number of junctions and four taps, of which three had to be absolutely air-tight. In addition there were the four insulated junctions in the steel and the two in the calorimeter lid, and also the six openings (three in the steel and three in the calorimeter), through which the glass tubes which supported the calorimeter passed. All who have worked with low pressures will appreciate the difficulty of making such a series of joints sufficiently air-tight.

The manner in which the difficulty was overcome in the openings through the steel and calorimeter is described in Section VII. In what we may term the external circuit the greatest difficulty was experienced in the joints between the glass and the steel tubes *M* and *N*. Throughout 1891 we used telescopic joints. The glass tubes, which closely fitted into the steel ones, were coated with hard shellac, and, when both glass and steel had been warmed, were pressed into position. There is no doubt that such joints can be made absolutely air-tight; but they cannot be trusted to last for any length of time. It is possible that shellac is sufficiently viscous to yield to long continued pressure, or, on the other hand, it may crack when exposed to sudden changes of temperature. Whatever the cause may be, we have found such joints most treacherous. Their very perfection when first made renders them the more dangerous, for they inspire the observer with a false confidence.

Our experiences during 1891 led us to reject the use of shellac in any form.* In 1892 the connection between the glass and steel was made by platinum tubes of small bore, soldered into the steel at one end and fused into the glass at the other. However, the latter form of junction could not be relied on unless the diameter of the platinum was small, and this constriction of both the passages leading to the pumps greatly increased the labour of exhausting, for the process of diffusion through

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* From the commencement we avoided the use of india-rubber tubing.

such narrow tubes is very slow when the difference of pressure at the ends falls below 1 millim. As we could find no way out of this difficulty we had to content ourselves with a higher pressure than we had proposed to work with.

The taps used were of a kind that has a diagonal hole through the stopper and a mercury cup at each end; they appear to be very perfect, and any leakage from either end can be detected by its effect on the mercury. One of these taps was in each glass tube leading from *M* and *N*, and, by their means, all the rest of the circuit could be cut off from the calorimeter.

The tube connected with *M* led to a five-way Sprengel and a McLeod gauge (both by Hicks). The tube from *N*, after passing the first tap, branched into two arms, one of which led to a Geissler pump, while in the other was a three-way tap establishing connection with the water pump, or with a series of drying bottles, containing H_2SO_4. A tube containing $Ba(HO)_2$ was fixed between the drying bottles and the calorimeter, as we thought it just possible that, otherwise, sufficient H_2SO_4 vapour might pass into the chamber to produce some action on the steel surfaces.

When the apparatus was fixed together the temperature of the tank was raised to about 40° C.; the air was then exhausted down to about 16 millims. by the water pump, dry air was passed in slowly, and this process was repeated several times. Finally the pressure was reduced as far as possible by the water pump (to about 12 to 14 millims.), and the Sprengel and Geissler brought into play.

It took about 100 double strokes with these pumps to bring the pressure down to 1 millim., so the labour involved was great, and want of time alone prevented our reducing the pressure further than we did. By increasing the number of the platinum tubes we hope to be able in future to work with much better vacua.

The absence of leakage is indicated by the fact that the lapse of a week made no perceptible difference in the reading of the McLeod gauge, although a change of ·01 millim. could have been easily detected.

It was long before this degree of perfection was attained, for the difficulty of ascertaining the position of a slight leakage, in such a circuit, was very great, and many weary hours were expended in leak hunting and in consequent taking to pieces and putting together again the various portions of the apparatus.

Section VI.—The Method of Maintaining a Constant E.M.F.

General plan of the electrical connections* (fig. 2, p. 382):—

Leads passing through points numbered 1 and 3 belong to the Clark cell circuit.

Leads passing through points numbered 2 and 4 belong to the storage cell circuit.

The leads 1 and 2, as also 3 and 4, unite at the lid of the calorimeter itself, as shown in the small sketch.

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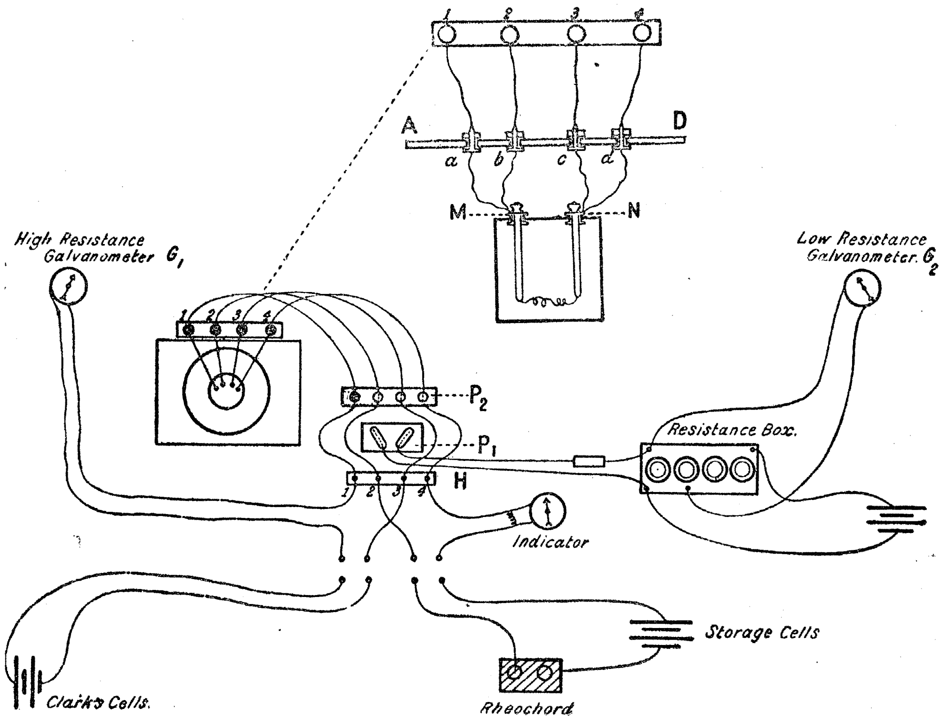
* The actual position of the galvanometers, &c., was different from the sketch, which is only intended to indicate the nature of the arrangement.

All connecting wires of any length were carried overhead, and hung by silk threads from a net suspended about 7 feet above the table. Thus all were visible, and could be traced without difficulty. All keys and instruments through which communication with earth could be made were placed on slabs of paraffin or ebonite, and the accumulators were also insulated. Each lead was placed as close as possible to its return to avoid any electro-magnetic action. The resistance of the galvanometer G_1 was about 9000 ohms. Instruments of such high resistance speedily indicate any leakage in the circuit, and it was not until we had given considerable time and attention to the insulation that we were free from trouble on this account.

Fig. 2.



The galvanometer (an astatic one manufactured by the Scientific Instrument Company, and the field so adjusted that the time of a single oscillation was about 4 seconds) showed no deflection unless connected with the Clark cells, although, at times, the difference of potential between the screws 2 and 4 amounted to 10 volts. If the fingers were placed on the ends of the wires communicating with it, the spot of light could be thrown nearly off the scale. The galvanometer was placed at the farther end of a tunnel (4 feet in length) of which the nearer end was closed by a sheet of ground glass. The beam of light was thrown in through the side of the tunnel, reflected on to the galvanometer mirror and thence on to the ground glass, which was protected by a hood from other illumination. Thus the "spot" was easily visible, even in bright day-light, by either of the observers when in the situations they occupied during the experiments. The extreme sensitiveness of this galvanometer will be illustrated when dealing with the comparison of our Clark cells.

The method of maintaining the ends of the coil at a constant potential difference has been indicated in Section 1. The experimental accuracy of the method depends entirely upon the action of the rheostat at *K* (fig. 1, p. 370). This instrument should be capable of a fine, as well as a rough, adjustment, and, above all, there should be no possibility of uncertain contact.

The majority of rheostats establish connection by the pressure of a sliding piece upon a wire, which is, at the best, an unreliable form of contact. The instrument devised by us has, however, proved to be so free from this defect that we describe it at some length.

It is well known that the electrical contact between a moving platinum wire and mercury is, under ordinary circumstances, an unsatisfactory one; its uncertain nature being probably due to the air-film attached to the wire.* We found that in vacuo the contact was in every way satisfactory.

A and *B* (see Plate 2, fig. 3) are two glass tubes about 7 feet long, with a platinum wire running through the interior of each—the ends of the wires projecting at *A* and *B*. The resistance of the wire in *A* is about 6 ohms per foot, and of that in *B* 1·7 ohm per foot. *C* and *D* are two wide tubes about 3½ feet long, closed at the lower ends.

A and *B* were carefully filled through a capillary tube with hot mercury, and inverted so as to stand in *C* and *D*. Practically, *A* and *B* are two barometers having tubes of about twice the usual length. *C* and *D* are firmly fixed in a stand, and *A* and *B* are raised or lowered by handles at the side, connected with gearing wheels which move two racks, fixed upon the rods carrying *A* and *B*. In their lowest position the barometer column reaches almost to the top of the tubes; in their highest, about 4 feet of the wire is left above the mercury. Spiral wires are attached to the projecting ends of the platinum wire at the top, and the ends of a copper fork, carrying a screw connector (*E*) at the bend, communicate with the mercury in *C* and *D*.

The current enters at *F*, passes down the wires in *A* and *B* (which are thus in parallel arc), and leaves the instrument at *E*. The wire from *F* to *B* is so arranged that additional resistance can be placed in it if required.

The mean resistance of the calorimeter coil used by us this year was about $8{\cdot}5\omega$; the minimum external resistance about $1{\cdot}3\omega$. The E.M.F. of each storage cell was about 1·4 times the E.M.F. of one Clark cell. Denoting our external resistance by r, and the coil resistance by R, it is evident that (when the number of storage and Clark cells were equal) an approximate balance would be obtained if $(\mathrm{R} + r)/\mathrm{R} = 1{\cdot}4$, which gives $r = 3{\cdot}4$, *i.e.*, when the rheostat resistance was about $2{\cdot}1\omega$.

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* If the wire is amalgamated the mercury is apt to cling to it when the wire is withdrawn.

It was found that by raising *A* about 6 inches, *B* about 24 inches, and introducing a resistance of 4ω into *FB*, an approximate balance was obtained. The resistance of *A* was then about ·3ω, and *B* 7·30ω. *B* thus acted as a shunt, and a considerable alteration in it caused only a small change in *r*. By altering their relative positions the ratio A/B could be changed, and the sensitiveness of the instrument could thus be altered when required. When arranged as above, a movement of 1 inch in *B* would throw the galvanometer spot off the scale, while the effect of a change of 1/25 inch was distinctly visible.

Thus a rise of 1 inch in B would change *r* from $(\cdot 3 + 7\cdot 3) / (\cdot 3 \times 7\cdot 3)$ to $(\cdot 3 + 7\cdot 44) / (\cdot 3 \times 7\cdot 44)$, *i.e.*, a change of ·0003ω.

And thus the ratio *r*/R would change from 1·3 / 8·5 to 1·3003 / 8·5, a change of less than 1 / 50,000.

The scale on the galvanometer screen had divisions of about 1 inch in length, and a deviation of 1 scale division, during a whole experiment, was exceptional. It thus appears that the variations in E were certainly within 1 / 100,000 of the mean value during the experiments, and, therefore, changes in E, consequent on changes in R or S, might be disregarded.* It was necessary that throughout each experiment one observer should give his entire attention to the adjustment of the rheostat. As the temperature of the coil rose steadily the value of *r* had to be increased, its total increase (over our range) being about ·005ω, *i.e.*, a rise of about 36 inches in B.† No doubt this adjustment took place in steps. The spot was observed to cross the zero line and was then thrown back to the further side—a rise of 1 millim. in B being, as a rule, sufficient for this purpose. As the handle had a large radius, this small change was effected without difficulty. The effect of such small oscillations about the zero position would probably "mean out," and if not, would be negligible.

Other possible causes of alterations in the value of E are—

(1) Polarization, as a consequence of the current required to affect the galvanometer. The high resistance of the galvanometer rendered any perceptible polarization extremely improbable. In our earlier experiments an additional resistance of 10,000ω was placed in the circuit; contact was intermittent and established by a key which was worked by a water motor.

Throughout our 1891 experiments we made it a rule to compare before and immediately after each experiment the E.M.F. of the cells used‡ with others which were kept as standards, and, as we were unable to detect any change, these excessive precautions were abandoned. On twenty-six occasions when no extra resistance was introduced these cells were compared before, and at the close of, an experiment.

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* When the external circuit became heated by the current at the commencement of an experiment considerable adjustment was required, but it was made without difficulty.

† This increase is in *addition* to the increase in *r* due to the heating of the external circuit.

‡ The Clark cells used in 1891 belonged to the Cavendish Laboratory, and are the ones referred to in Table IX., 'Phil. Trans.,' A, 1892, p. 605.

POGGENDORFF'S method was used ; a change of one plug indicated a change of E/6000, each cell was balanced against the standard ones in the manner adopted by Messrs. GLAZEBROOK and SKINNER, and in no case could any alteration whatever be detected. This point having been satisfactorily established, we considered it unnecessary to repeat the observations in a similar manner this year, but contented ourselves with occasional comparison of the cells used with others which we kept as standards.

(2) The second difficulty was not surmounted so satisfactorily. As before mentioned (Introduction) the laboratory was maintained in cold weather at a constant temperature of about 16° C., by an automatic regulator. However, during the months of August and September, 1892, while the nights were cool, the temperature during the day was extremely high, and occasionally rose in the laboratory to over 20° C. The Clark cells were contained in a tank of water, but their temperature at times changed by 3° or 4° C. ; and under such circumstances the difficulty was to know what temperature to take.

Messrs. GLAZEBROOK and SKINNER have shown that the E.M.F. does not change with the thermometer, but lags considerably. A difference between the "virtual" and "real" temperature of 1° C. would cause a difference of 1 in 1000 in our corrected times, and we believe that many of the irregularities in our results, especially in experiments before August 15, are attributable to this cause. On that date we got into working order a regulator which much diminished this source of error. A large bulb of mercury was immersed in the tank, and was connected by a narrow tube with a trap of the ordinary gas regulator pattern, through which cold tap-water, instead of gas, was kept flowing. When the mercury expanded, the water ceased to flow through the regulator, and diverged by a bye-way into the tank ; when the mercury contracted, the cold water passed into a waste pipe, instead of into the tank. The pressure of the water was kept constant by a small supply cistern, with an overflow pipe, which was suspended by a string, and the head of water could thus be regulated. This apparatus worked most satisfactorily—a change of $\frac{1}{4}^\circ$ C. turning the inflowing water from the tank to the waste. Unfortunately the weather became so warm that even the tap-water at that end of the laboratory rose to about 16° C. The changes, after the introduction of the regulator, were, however, much diminished, and rarely amounted to $0^\circ{\cdot}5$ C. As regards the errors thus introduced, although they seriously affect individual experiments, they must tend to eliminate when a large number of observations are taken.

The Clark cells used for the 1892 experiments were constructed during January and February of that year. Particulars of their construction are given in an Appendix to Messrs. GLAZEBROOK and SKINNER'S paper ; therefore it is unnecessary to give here more than a brief summary.

Although the method of preparing the solutions for different batches of six was varied, the E.M.F. of all the cells is practically the same. In all cases, the platinum wires were amalgamated by being dipped in mercury when red hot. The mercury, which was freshly distilled, was about 1 centim. in depth, and was nearly touched by the ends of the zinc rods. About 1 centim. of the "paste" was placed on the mercury, then, about 1·5 centim. of $ZnSO_4$ solution and some crystals of $ZnSO_4$. Above this solution was fixed a thin cork, on which was a thin layer of paraffin wax. On this was placed about 6 centims. of glass-wool and then about 2 centims. of marine glue. The diameter of the cell was about 2·5 centims. The platinum wire was sealed into a thin glass tube, the end of which projected above the marine glue. In most cases the upper end of the zincs was completely buried.

Nos.[*] 31 to 42.—Hg_2SO_4[†] unwashed but shaken up with Hg and the $ZnSO_4$ solution filtered at 30° C., zincs not amalgamated.

Nos. 43 to 48.—Prepared by following out the Board of Trade directions exactly.

Nos. 49 to 54.—Boiled the $ZnSO_4$ solution with ZnO, allowed to cool to 30° C. Filtered at 30° C. Added to this a small quantity of Hg_2SO_4 paste. Filtered off resulting black precipitate, warmed filtrate, and again filtered at 30° C. The cells made with this solution appeared to settle down to their final E.M.F. immediately after their manufacture, unlike the others, which were some time before they became steady.

About thirty comparisons of these cells were made between January and September, 1892. Nos. 31 to 42 remained at the Cavendish Laboratory for some time, and were repeatedly compared with the Rayleigh Standard by Mr. SKINNER, to whom we owe our best thanks for the trouble he took in this matter.

We select as examples comparisons made on three different dates. The results of the comparisons on other dates are as close, but it is unnecessary to give them at length.

No discrepancy showed itself except after rapid changes of temperature, and in the most extreme case the difference from the mean did not amount to 1 in 2000. The comparison of cells 31 to 36 with the Cavendish Standard, on February 13th and 20th, gave precisely similar results. These comparisons were only the last of a series. On both dates the temperature of the standard was slightly higher than that of the cells, and therefore the equality was very close. Mr. SKINNER, writing on February 20th, said, "You may take it that Nos. 31 to 36 are now equal to our standard, and no further comparison is necessary." In our comparisons the cells were, in each case, placed in opposition to No. 31.

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[*] These cells are numbered 131 to 160 in Messrs. GLAZEBROOK and SKINNER's paper, 'Phil. Trans.,' A, 1892, pp. 622 to 624. Numbers 154 to 160 were not used by us during this investigation.

[†] Chemicals supplied by Messrs. HARRINGTON.

TABLE I.

	Feb. 13 and 20, 1892. Comparison with Cavendish Standard. (Diff. in 6000 parts.)	May 1, 1892. Comparison with No. 31. (Diff. in 6000 parts.)	July 3, 1892. Comparison with No. 31. (Diff. in 6000 parts.)	Sept. 6, 1892. Comparison with No. 31.* (By potentiometer.)
31	+ 1 +	0	0	1·00000
32	+ 1	+ 2 +	+ 2 −	+ ·00002
33	+ 1	+ 1	0 +	− ·00003
34	+ 1	− 1	− 1 −	− ·00013
35	+ 2 +	− 1	0	− ·00011
36	+ 2 +	0	+ 1	·0
37		0	+ 1	+ ·00001
38		0	+ 1	+ ·00002
39		0 −	+ 1	+ ·00001
40		0	+ 1	− ·00006
41		0 −	0 +	− ·00006
42		0 −	0 +	− ·00007
43		+ 2	+ 3	+ ·00022
44		+ 1	+ 2	+ ·00013
45		0 +	+ 2 +	+ ·00014
46		+ 2 +	+ 3	+ ·00020
47		+ 4	+ 3	+ ·00014
48		+ 3 +	+ 5	+ ·00016
49		0 +	0 +	− ·00001
50		+ 1	+ 1 −	·0
51		− 1	0 +	− ·00002
52		− 1	0 +	− ·00009
53		0 −	+ 1 −	− ·00007
54		− 1	0 +	·0
	Temperature . . .	12°·2	17°·2	16°·04

On May 1 and July 3 the total resistance of the two boxes used was 12,000ω, so the numbers given represent the differences in 6000 parts. In the comparison on September 6 a CLARK's potentiometer (constructed by Messrs. ELLIOTT) was used. Readings can be taken with an instrument of this kind, with much greater ease and certainty than when using two resistance boxes.

It may be worth mentioning that on September 6, the instrument was adjusted by one observer and the readings taken by the other, who then moved the handle, thereby compelling a fresh adjustment by the first observer. The galvanometer used was the high resistance one, G_1, previously referred to, and gave a distinct deflection for a change of $1/10^{-6}$ in R.

Several comparisons were also made at different dates with some cells belonging

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* We have not reduced the potentiometer readings to the same form as that adopted in the previous columns, as a difference of ·00017 corresponds to 1 in 6000, and the differences shown on September 6 would only amount to + 1 + in the most extreme case.

to the Cavendish Laboratory.* These cells† were (early in August) in close agreement with No. 31, and also with the Cavendish. They have since been compared with the Berlin Standard, and appear to exceed that standard by about ·0002 volt.

It will be noticed that the results of the comparison on September 6th are in much closer agreement than those of previous dates. This is partially due to the potentiometer, since the adjustment in this case has not to proceed by steps. It must be remembered also that the cells had been kept (by the regulator above described) at a steady temperature for a considerable time; and the great importance of a constant temperature is rendered evident by the figures given in Table I., and illustrates the truth of Mr. GLAZEBROOK'S remark that many discrepancies are due to the different "lag" of the cells when their temperature is changing.

A consideration of the above facts will, we believe, bear out the conclusion that the mean value of our Clark cells may be regarded as exceeding that of the Cavendish standard by not more than ·0002 volt (*i.e.*, by about 1 in 7000). During our J experiments we always used a considerable number of these cells, placing several in parallel arc, and in no case did we use less than nine of them at any one time. Thus no correction for individual cells is necessary.

A reference to GLAZEBROOK and SKINNER'S paper will show that but a short time elapsed between their determination of the absolute value of the Cavendish standard, and the comparison of our cells with that standard. The absolute value of the standard is given by them as 1·4342 volt;‡ we are therefore justified in assuming the mean value of cells No. 31 to 54, as

$$1{\cdot}4344\ \{1 + {\cdot}00077\ (15 - t)\}.$$

[Note by E. H. G., added April, 1893. All the cells mentioned above practically maintain their relative positions at this date. I have recently taken a series of observations in the hope of throwing some light on the gradual approximation of the cells, as shown by Table I. I find that if the temperature is suddenly raised, and then kept quite constant, the initial differences steadily decrease with lapse of time, and that the cells continue to converge after the lapse of many days, and even weeks. The cells prepared by my method of adding some Hg_2SO_4 to the solution before filtering, appear to settle into their final state more rapidly than the others.]

SECTION VII.—THE MEASUREMENT OF RESISTANCE.

The coil used by us in 1888 was of platinum-iridium wire, and had a mean R of about 19 ω.

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* We take this opportunity of thanking Professor THOMSON for his kindness in permitting us to borrow many pieces of apparatus belonging to the Cavendish Laboratory.

† These are the cells Nos. 65, 69, 70, 77, 78, and 79, mentioned in Messrs. GLAZEBROOK and SKINNER'S paper. No. 65 may be regarded as equal to our No. 31. See 'Phil. Trans.,' A, 1892, pp. 605, 623, and 625.

‡ 'Phil. Trans.,' A, 1892, p. 582.

In 1889 we used two coils of 2 and 4 ω, one of German silver and one of platinum, both covered with a layer of gutta-percha.

In 1891 we used a coil of about 10 ω covered with amber varnish and made of copper-manganese-nickel alloy, and also a platinum wire of about the same value.

This year we have contented ourselves with a platinum wire of about 8·5 ω.

Since $H \propto E^2/R$ and E is, throughout each experiment, a constant, therefore $H \propto 1/R$· Hence if a coil of large resistance is used, the quantity of heat developed will be small, unless E is great.

It appeared to us desirable to keep the value of E as low as possible, for the greater the difference of potential at the ends of the coil, the greater is the loss arising from imperfect insulation, &c. On the other hand, if the coil is too short the development of heat is too localized, and its even distribution throughout the calorimeter rendered more difficult. Our experience in the earlier experiments, as also a consideration of the masses of water, &c., led us to the conclusion that a difference of potential equal to that of from 3 to 5 Clark cells* and a resistance of 8 to 10 ω would balance the opposing influences in the manner best adapted for our purpose.

Platinum would at first sight appear to be an unsuitable metal of which to form the coil, for its temperature coefficient is very great, and the element of change thus introduced involves much arithmetic in the final calculations. For the same reason the error due to its rise in temperature above the surrounding water is likely to be more serious than if the coil was formed of an alloy. These considerations carried so much weight that we undertook (in the summer of 1890) a series of investigations into the resistance of the various copper-manganese-nickel alloys, which had been recently introduced by Dr. FEUSZNER of Berlin. Some of these alloys were made for us by Messrs. JOHNSON and MATTHEY, and several specimens were given to us by Dr. FEUSZNER, to whom we owe our best thanks for his kindness; others were obtained from Messrs. WOLFF, Berlin.

The behaviour of these alloys was investigated over a range of from − 20° C. to 100° C. The different wires passed down a tube about 4 feet long, together with a platinum wire, cut from the same coil as that from which one of our platinum thermometers was made. The resistance of this wire (*in situ*) was determined in ice and steam, and the value of δ being known, by its determination when in our platinum thermometer, the mean temperature of the wires surrounding it could be deduced with great accuracy.

We hoped to proceed with an analysis of the composition of all the wires used but time has not been sufficient.

The results are summarized in the following table.

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* Had we felt certain that the insulation of the wire was perfect, we should have had no hesitation in increasing the potential difference, in which case we could have worked with larger masses of water. The uncertainty as to the temperature of the wire when thickly coated would, however, more than counterbalance any advantage gained by the use of larger masses.

DATE—July 24 to September 18, 1890.

A = Platinum wire, diameter ·005, same as thermometer H (previously annealed).
B = Copper wire (commercial).
C = Copper-manganese alloy made by Messrs. JOHNSON and MATTHEY—approximate composition—·4 per cent. manganese (previously annealed in carbon).[*]
D = Copper and manganese (J and M), 16 per cent. manganese (previously annealed in carbon).
E = Copper and manganese alloy presented to us by Dr. FEUSZNER (Mn 10 per cent. and Cu 90 per cent.).
F = Copper-manganese-nickel alloy from Dr. FEUSZNER (diameter ·17 millim.), rather more Mn than G and H.
G = Copper-manganese-nickel alloy from Dr. FEUSZNER (diameter ·14 millim.), Mn 12 per cent., Ni 3 per cent., Cu 85 per cent.
H = Copper-manganese-nickel alloy from Dr. FEUSZNER (diameter ·10 millim.), Mn 12 per cent., Ni 3 per cent., Cu 85 per cent.
J = Copper-manganese-nickel alloy supplied by WOLFF (diameter ·24 millim.), Mn, Ni, and Cu, but composition uncertain.
K = Copper-manganese-nickel alloy supplied by WOLFF (diameter ·17 millim.) Mn, Ni, and Cu, but composition uncertain.
L = Copper-manganese-nickel alloy supplied by WOLFF (diameter ·10 millim.), Mn, Ni, and Cu, but composition uncertain.
M = German silver.

TABLE II.—(Temperatures by Air Thermometer.)

	– 20°	0	10	15	20	25	50	75	100	
A (Pt)	·9288	1	1·0352	1·0525	1·0700	1·0874	1·1745	1·2608	1·3468	
B (Cu)	·9382	1	1·0306	1·0468	1·0627	1·0790	..	..	1·3054	
C	·9805	1	1·0097	1·0147	1·0195	1·0244	1·0485	1·0733	1·0977	
D	·9968	1	1·0014	1·0021	1·0027	1·0033	1·0058	1·0078	1·0096	
E	·9976	1	1·0009	1·0013	1·0017	1·0020	1·0032	1·0036	1·0031	Max. at 75° C.
F	·9983	1	1·0008	1·0012	1·0015	1·0019	1·0032	1·0042	1·0052	
G	·9966	1	1·0014	1·0022	1·0030	1·0037	1·0084	1·0104	1·0134	
H	·9999	1	1·0000	·9999	·9999	·9998	·9991	·9979	·9967	Max. at – 5° C.
J	.9987	1	1·0005	1·0007	1·0009	1·0011	1·0015	1·0014	1·0004	„ 55° C.
K	·9989	1	1·0006	1·0009	1·0011	1·0014	1·0023	1·0026	1·0027	„ 90° C.
L	·9986	1	1·0005	1·0007	1·0008	1·0010	1·0014	1·0014	1·0011	„ 65° C.
M (calculated)	·9920	1	1·0040	1·0060	1·0080	1·0100	1·0200	1·0300	1·0400	

The above resistances were taken with an E.M.F. of four Leclanché cells, and the arms of the bridge were 1000/10. A double set of electrodes was used, and the

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[*] We have to thank Mr. C. T. HEYCOCK for his kindness in making an analysis of this alloy.

external resistance determined for each observation. Also the resistance of the platinum wire was observed before and after each determination of the other wires. The current was reversed on each occasion to eliminate thermal effects. The total swing of the galvanometer averaged about 150 scale divisions for a difference of $\cdot 01\ \omega$, and thus the next figure could be determined with accuracy. The actual resistance of the wires used varied from 1 to 50 ω; but in the above table the resistance of each at 0° C. is assumed as 1 ω. It must be remembered that the temperatures are expressed in the *air* (not mercury) scale.

According to the analysis given by Dr. FEUSZNER, G and H have the same composition, and differ only in their diameters, yet the difference in their behaviour is very marked. It is possible that this difference is due to the effect of the "drawing."

The *calculated* value of German silver alloy is given for the sake of comparison. We regret that we did not include a wire of that substance. It is, of course, improbable that its increase is proportional to its temperature—from 0° to 100° C.

Our observations on these wires* extended from July 24 to September 18, 1890, and we were unable to detect any change in their resistances during that time.

The behaviour of the alloy C is curious. Our figures, which were carried to a place beyond that given in the above table, prove that, over the above range the increase in resistance varied strictly as θ. In order to test the straightness of its line beyond the above range, we constructed a thermometer which had this wire for its coil, but which was, in all other respects, constructed in the same manner as a platinum thermometer with double electrodes.

This thermometer gave $R_0 = 12 \cdot 972$, $R_1 = 14 \cdot 255$, and R_s (*i.e.*, resistance in sulphur vapour at 760 millims.) $= 18 \cdot 677$. Assuming the straight line we have

$$\theta_s = (R_s - R_0)/(R_1 - R_0) \times 100 = 444 \cdot 6.$$

According to an investigation subsequently conducted as to the boiling point of sulphur† the true air temperature ought to be $444^\circ \cdot 53$ C. It is difficult to imagine a closer approximation. A thermometer thus constructed is, therefore, a very simple and accurate instrument. It would, however, be exceedingly difficult to make another specimen of the alloy of a precisely similar composition, and the above table shows that the effect of small changes may be considerable.

A consideration of the results led to the conclusion that the wire marked H was the one most suitable for our purpose. Its change in resistance from 10° to 25° C. was only 1 in 5000, and since the resistance diminished as θ increased, it was easy to compensate by the addition of a little of the C wire. All difficulties connected with change of resistance consequent on the rise of temperature of the water, or of the

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* All these wires had been previously heated to a temperature of about 150° C.

† It must be borne in mind that the date of this determination preceded the work of CALLENDAR and GRIFFITHS on this subject, and at this time (July 27, 1890) the boiling point of sulphur was accepted as $448^\circ \cdot 4$ C. (REGNAULT).

difference in temperature of the wire and the water, appeared, therefore, to have been overcome. This conclusion, however, led to the loss of many weeks' work, and was the cause of much disappointment and delay. In the summer of 1891 we commenced a series of direct determinations of J, the arrangement of the apparatus being very nearly the same as that of 1892. Our coil consisted of about 30 inches of the above wire, H, which was first annealed at a temperature of about 200° C. in an atmosphere of CO_2. The fine white silk covering was allowed to remain, and it was painted with Mr. LAURIE's amber varnish.*

The resistance of this coil, and of the leads from it to the calorimeter lid when *in situ* and immersed in rapidly stirred water, is shown in the following table.

TABLE III.

Temperatures . . .	14°	16°	18°	20°	22°	24°
August 21, 1891 . .	R=10·5214	10·5220	10·5223	10·5225	10·5226	10·5225

RESISTANCE of the coil at temperature 14° C., on different dates.

Aug. 22		10·5228		
,, 23, 11 A.M. . .		10·5275		
,, 23, 11 P.M. . .		10·5299		
,, 24		10·5342		
,, 25		10·5398		
,, 27,	before exp. J_3	10·5559;	after exp. J_3	10·5600
,, 28,	,, ,, J_4	10·5570;	,, ,, J_4	10·5632
,, 29,	,, ,, J_5	10·5618;	,, ,, J_5	10·5696
,, 30,	,, ,, J_{6a}	10·5760;	,, ,, J_{6a}	10·5860
,, 31,	,, ,, J†	10·5867;	,, ,, J†	10·5962
,, 31,	,, ,, J_{6b}	10·5953;	,, ,, J_{6b}	10·5977
Sept 1,	10 A.M. . .	10·5968;	(some current passed) 11 P.M.	10·5982

The resistance of the wire at different temperatures was also ascertained in the observations taken August 21 to 25.

It is unnecessary to give the resistance at temperatures other than 14° C., since the resulting curves are all parallel to the one on August 21. The alteration caused by a rise of 10° C. being only 1 in 10,000, the steady diurnal rise in the resistance (at the same temperature) amounts to nearly 1 in 500 in the above interval of time. We trusted that this might be a result of the annealing, and that the wire would assume a stable condition in course of time.

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* Mr. LAURIE was so kind as to allow us to have a bottle of this varnish prepared by himself; for particulars concerning this varnish, see 'Proceedings Cambridge Phil. Soc.,' vol. 7, part 2, p. 52.

It should be noticed that on the above dates we were constantly passing currents through the coil in order to adjust the temperature of the calorimeter during our stirring experiments. As, however, there was but little current when ascertaining the resistance of the wire at different temperatures, the curves were not appreciably altered, and we did not recognize the fact that the rise was a consequence of the current.

On August 27, we performed one of our "J" experiments. We then had a current of about half ampère passing through the coil for about $1\frac{1}{2}$ hours. We had determined the resistance at the commencement of the experiment, and, on repeating our observations at its close, we found that the value of R had risen from 10·556 to 10·560. It would thus appear that the rise was a function of the current rather than of the time. We continued the series of experiments until September 1, when we decided to abandon the use of this alloy.* The labour thus expended was not altogether lost, for, as will be explained, in the section on the measurement of temperature, the results were of considerable value to us.

Had the rise been a function of the time it would not have been so disastrous, since we could have deduced the resistance during each experiment. As, however, the change was caused by the current, it was impossible to determine (with sufficient accuracy) the actual value of R at each stage of the experiment. It appeared probable that electrolysis of some kind took place. If, after a current had been passing for some time, the ends of the wires from the coil were connected with the galvanometer, a considerable deflection was produced, and it was impossible to determine the resistance of the coil for about half an hour after the completion of an experiment, owing to the disturbance of the galvanometer thus caused. The effect was apparently due to polarization rather than to thermal, or "Thomson" effects, and decreased regularly until it might be neglected, although the differences of temperature in the circuit were maintained unaltered. Much time and energy having already been expended in experimenting with these various alloys, we decided to retrace our steps and revert to a platinum wire coil. Another consideration which influenced us, was that we had, during the past few years, given considerable time and attention to the behaviour of platinum wires when used in platinum thermometers, and we considered that the experience thus gained of the changes in the resistance of such wires under varied conditions, might enable us to proceed with more confidence.

The smaller the diameter of the wire the less its capacity for heat and, in comparison, the greater its cooling surface. The wire selected for this year's experiments was supplied by Messrs. Johnson and Matthey. It had a diameter of ·004 in., and

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* Mr. Skinner has recently conducted some experiments with the same coil immersed in paraffin instead of in water; and although he has passed far greater currents than any used by us, he was unable to trace any signs of consequent increase in R. The increase shown during our experiments was, therefore, probably due to some action between the wire (when carrying a current) and the water, this is not unlikely when we remember that one of the metals present was Mn.

was of as pure platinum as could be obtained. The length used was about 13 in., and the wire was so disposed that parts near to each other should have only a small difference of potential. This wire was covered with a coating of the amber varnish before referred to. Several coatings form an excellent insulating covering for such a wire, but we contented ourselves with a thin skin. The better the insulation between the wire and the water the slower the flow of heat across the insulator, and the greater the difference in temperature between the surfaces which it separates.

If the insulation was not perfect we have little doubt but that it was sufficient. In order to throw more light on this point we decided to make a careful determination of the value of R, with the coil immersed in a pure paraffin (pentane), but otherwise under the same conditions as those of the experiment. We selected pentane (1) because it would be difficult to find a more perfect non-conductor; (2) if pure, it would be easy to free the calorimeter from all traces by passing through it a current of warm, dry air. The latter was an important consideration, for any substance such as ordinary impure paraffin might so alter the interior surfaces of the calorimeter as to change the stirring coefficient.

On December 8, 1892, about 250 cub. centims. of pentane* were introduced into the calorimeter, which had previously been dried with extreme care, and the resistance of the coil was taken at twelve different temperatures. A summary of the results is given at the end of this section (see p. 413), and a very slight increase in the resistance is observable, amounting to one part in 22,000. It is satisfactory to find that, whatever may be the effect of conduction through the water, it is, in this case, so small as to be unimportant.

The measurements of R were made when the coil was immersed and the water stirred in the same manner as during the experiments, hence it follows that if the water acted merely as a conductor it would in no way affect our results.

Even if its conductivity changed with the temperature our values of R include the effects of such change, and the manner in which R is built up at each temperature is of no consequence.

Again, if electrolysis takes place (of which, however, we have had no sign), polarization must ensue. The best proof of the absence of polarization is the fact that when the storage and Clark cell circuits were reversed (and this was invariably done more than once during each J experiment) no readjustment of the rheochord was required when using the platinum coil, although when using the manganine coil a considerable readjustment was necessary.

Had electrolysis occurred, it is almost certain that HNO_3 would have been formed. In our earlier experiments (both in the platinum and silver calorimeters),

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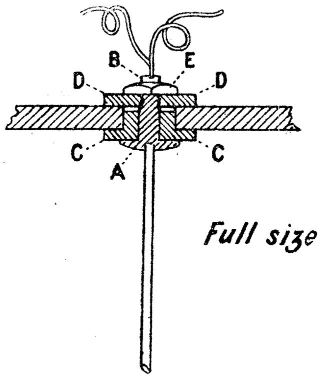
* Great difficulty was experienced in obtaining this specimen of pentane, and it was only through the kindness of Mr. VERNON HARCOURT that we were able to procure it. It was prepared under his own direction and was free from all impurities, except some traces of tetrane and hexane.

although the same water was never used for two experiments, we found that it became acid—in some cases strongly so.

This year the water remained unchanged for twenty consecutive experiments and we were unable to detect any acidity, although all water withdrawn from the calorimeter was invariably subjected to a careful examination.

The insulation of the leads passing through the steel cover and the lid of the calorimeter was a troublesome matter, as there was great difficulty in making the insulating junctions absolutely air-tight.

Fig. 3.



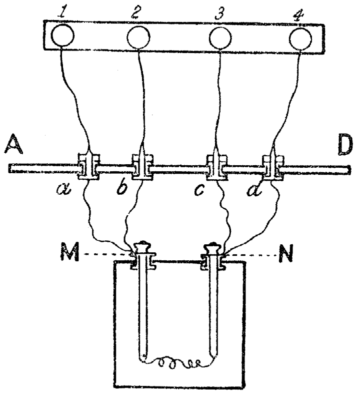
A, *B* was a brass pin, which had a screw thread on the end *B* and terminated in a nut at *A*. *C* was a ring of ebonite fitting tightly into the hole in the metal plate and having a projecting flange at the lower end.

The surface of the ebonite was moistened with gutta-percha solution (made by dissolving gutta-percha in chloroform); the ring, *C*, was then forced into the hole and the brass pin passed through it. A ring of ebonite, *D*, was then threaded on to the pin and a brass nut, *E*, firmly screwed down—the ends of the wire being soldered on at *A* and *B*.

This form of joint proved to be an excellent one, and when once adopted (after the failure of many other contrivances) gave no further trouble. The steel lid was pierced by such junctions in four places, and the calorimeter lid in two. As tap-water was continually flowing over the top of the steel lid it was necessary to insulate the exposed parts at *B*. A piece of wide india-rubber tubing enveloped the wire, the lower end fitted over the ebonite ring *D*, and was wired firmly on to it. The upper end of this tubing projected above the surface of the water in the tank. The tubes themselves were filled with distilled water to prevent any rise in temperature of the leads. The general arrangement is shown in Plate 2, fig. 2.

Leads 1 and 3 (fig. 4, p. 396) were connected with the Clark cells, and thus no current passed along them. 2 and 4 carried the current. Any heat developed in the parts above *AD* passed into the water of the outside tank, and might be disregarded. A portion of the heat developed in the wires *bM* and *dN* would pass to the water in the calorimeter. By sufficiently diminishing the resistance of *bM* and *dN* the heat thus developed could be diminished indefinitely; on the other hand, the conduction of heat between the calorimeter and the steel chamber would be increased. The wire selected was of pure copper (No. 21, B.W.G.), and each arm was about 10 centims. in length. The resistance of $bM + dN$ was carefully determined, and found to be ·0068ω. It is probable that half the heat generated in these wires would find its way to the inner, and half to the outer, vessel. We may, therefore, in order to determine the heat thus added to the calorimeter, assume this external resistance (r) as ·0034ω.

Fig. 4.



Let R be the coil resistance. Then in any time T, the quantity of heat developed in the calorimeter, will be $\mathrm{J.H} = \mathrm{C}^2(\mathrm{R} + r)\mathrm{T}$. Now $\mathrm{C} = \mathrm{E}/\mathrm{R}$, and since M and N are maintained at a constant difference of potential, therefore

$$\mathrm{J.H} = \frac{\mathrm{E}^2}{\mathrm{R}}\left(1 + \frac{r}{\mathrm{R}}\right)\mathrm{T},$$

therefore the effective value of the resistance $= \mathrm{R} - r$ (neglecting terms involving r^2/R and higher powers of r). Since the mean value of R is about 8·7, the correction is, in any case, a small one.

In order to test the insulation an arm of the bridge was constructed, which included wire No. 4, the insulators, and the steel casings—good connection with the steel being insured by passing a wire into the mercury contained in the thermometer-hole. High battery power was used, and the resistance was found to be greater than we could measure—that is, greater than 10 megohms. Since No. 4 was in connection with all the junctions in the plate *AD*, the insulation of all the junctions through the steel was thus established.

The arm was then made to include No. 4, the insulators in the lid of the calorimeter, and a copper wire, which was passed down the glass tubes until in contact with the floor of the calorimeter. The resistance of the two calorimeter junctions was, in the same way, found to be greater than 10 megohms.

Method of finding R.

P_1 and P_2 (see fig. 2, p. 382) were blocks of paraffin. The wires leading from the calorimeter to the junctions on the ebonite rod H passed through the block P_2, down which holes were then bored until the wires were exposed. These exposed portions were carefully amalgamated and the holes filled with mercury. Two thick pieces of copper were so bent that communication could be established between any of the holes in P_1 and the two troughs in P_2. When placed in position, the ends of these connecting strips rested on the conductors at the bottom of the holes. Two thick wires led from the troughs in P_1 to the resistance box, and, in order to bring their resistance up to a convenient quantity, a coil was introduced into one of these leads.

Denoting the total resistance of the conductors from the box to the lid of the calorimeter by r_1, r_2, r_3, r_4, it is obvious that all the following resistances could be taken by a movement of the connectors between P_1 and P_2, viz., $r_1 + r_2$, $r_1 + \mathrm{R} + r_3$, $r_2 + \mathrm{R} + r_4$, $r_3 + r_4$. The determinations were always made in the order thus given.

If N_1, N_2, N_3, and N_4 are the resulting numbers, we have

$$\mathrm{R} = \{(\mathrm{N}_2 + \mathrm{N}_3) - (\mathrm{N}_1 + \mathrm{N}_4)\}/2.$$

The galvanometer used had a resistance of about 8ω, and was fitted with a microscope containing a micrometer eyepiece by ZEISS. The image of a black line placed on a slip of paper in front of the mirror was thrown on to the micrometer scale.

A galvanometer fitted in this way is a very convenient instrument, for the swings can, with practice, be read with greater ease and accuracy than when the ordinary lamp and screen arrangement are used.

When a resistance was taken (whether of the coil or of a platinum thermometer) the order of the observations was as follows :—

Having determined between which plugs the resistance lay, the swing corresponding to the lower one was taken, the battery inverted and the swing in the opposite direction read. This process was repeated when the higher plug was in place. In this way all thermal or other effects are practically eliminated, and the method is independent of small changes in the zero position of the spot.

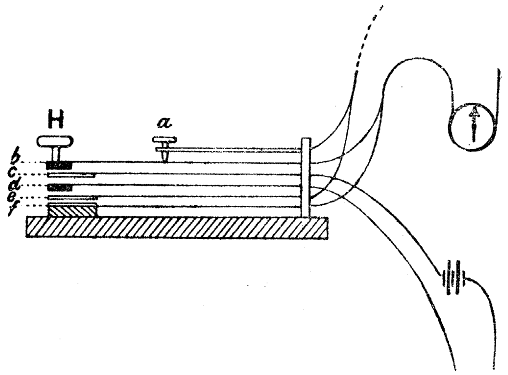
In some cases, as when working with platinum thermometers at high temperatures, the thermal effects are considerable, and the position of the zero point becomes so changed that the spot is thrown off the scale when connection with the galvanometer is made, although the battery circuit is not connected. To meet this difficulty a special key was constructed.

The ends of a and b (fig. 5) and also of e and f are connected with the galvanometer circuit, the ends of c and d with the battery. The screw at a is so arranged that, when the key is untouched, the galvanometer circuit from the box is completed.

The position of the spot at any time, therefore, is that due to the influence of any

E.M.F. in the circuit exterior to the battery circuit. Thus the spot can be placed in a convenient position by the control magnet, although a perceptible current is passing through the galvanometer. When *H* is sharply pressed down the connection at *a* is first broken; then the battery circuit is established by *c* and *d* and the galvanometer circuit by *e* and *f* (the projecting blocks on *b* and *d* being insulators). By proper adjustment of the key, the whole operation, performed by one movement, is accomplished in a small fraction of time. Thus the observed swing is due to the difference of potential caused by the battery and bridge, and is independent of any electro-thermal effects.

Fig. 5.



We have described this form of key at some length because, simple as it is, we have not seen any similar arrangement, and we have found it a great convenience, especially when working with platinum thermometers.

As an example of our method of observation, we give one of our determinations of the value of R.* It should be remembered that, although the exterior leads were made as equal as possible, the measurement of R does not depend on their equality and N_1 and N_4; N_2 and N_3 are not necessarily equal. Arms of bridge 1000/10. E.M.F. that of 2 Leclanché cells. When measuring N_1 and N_4 a resistance of 1400ω was thrown into battery circuit, in order to make the total swing a convenient size.

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* A summary of our determinations of R is given at the end of this section (see Table XVI., p. 413); the value of R in the last column but one of Table IV. has yet to be corrected for box errors, &c.

TABLE IV.

	Galv. swings.		Obs. R.	Temp. E_m.*	Temp. box.	R.	R corrected for temp. of box.	Temp. C.
	272	53						
N_1	227	398	$59\frac{45}{390}$					
	45	345						
	333	110						
N_2	183	411	$932\frac{150}{452}$					
	150	301		311·2	16·65	8·73205	8·73058	19·560
	348	124						
N_3	200	426	$932\frac{148}{450}$					
	148	302						
	330	138						
N_4	276	477	$59\frac{54}{393}$					
	54	339						

$$R = \{(N_2 + N_3) - (N_1 + N_4)\}/2.$$

A large number of similar observations were taken at temperatures ranging from 13° to 26° C. Observations at certain temperatures were repeated at regular intervals, and no change of any kind could be detected. The resulting resistance curve was the characteristic platinum one, and in no way differed from those given by our platinum thermometers. This in itself seems to us to be an adequate proof that the insulation of the coil was sufficient.

On September 4, the calorimeter was taken to pieces, and the method of fastening the wire to the glass rods within the calorimeter was altered. The wire was a little strained during the operation; but the only effect was to slightly increase its resistance at all temperatures. A new resistance curve, however, had to be drawn, and new values of R used after that date.

It may be mentioned that this coil was often used by us as a platinum thermometer to determine the temperature of the calorimeter when below, or above, the range of E_m.

The reversing keys in the storage and Clark cell circuit (see fig. 2, p. 332) were of the ordinary "rocker" form, but so constructed that as the wires on one side passed out of the mercury cups, the wires on the other almost immediately made

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* See Section X. The mercury thermometer E_m was used throughout all observations on the temperature of the calorimeter.

contact; the interval of time between the break and make being less than we could measure.

If a current be passed through a naked wire, immersed in water, it is certain that the temperature of the wire will be greater than that of the water, even when the latter is rapidly stirred.

Had we been able to use the alloy wire previously referred to this would have been a matter of small importance. Since, however, the value of R, when a platinum wire is used, varies greatly with the temperature of the wire, we felt it necessary to commence a series of investigations into the extent of the change. Hence we proceeded to determine the resistance of the coil when there was a considerable difference of potential at its ends. Our first trial was a modification of POGGENDORFF'S method of comparing E.M.F.'s. The storage cells were put in circuit through the coil, and a potentiometer arranged in series. One end of the Clark cell circuit was connected to the storage end of the coil, the other forming a sliding contact on the potentiometer; thus when the galvanometer in this circuit showed no deflection,

$$\frac{\text{E.M.F. of Clark cells}}{\text{E.M.F. of storages}} = \frac{R_1}{R_1 + \rho},$$

when R_1 is the resistance of the coil and part of the potentiometer, and ρ the resistance of the rest of the storage circuit. We had supposed that the internal resistance of the storages might be neglected so that ρ could be determined directly after adjustment by throwing the storages out and completing the circuit by a short length of wire. The ratio of the E.M.F.'s could also be obtained by the usual method through the potentiometer, and thus, by noting the temperature of the coil when adjustment was perfect, we had sufficient data from which to calculate the resistance of the coil. The results obtained by this method were very unsatisfactory, owing probably to the following causes :—

(1.) The heating up of the circuit ρ in the same manner as the coil itself.

(2.) The internal resistance of the storages, although almost zero when no current is passing, increases when the circuit is established, and hence

(3.) The ratio of the E.M.F.'s is not the true one.

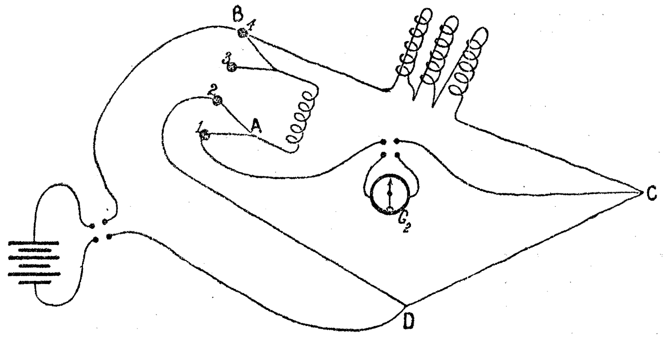
Of these, the first was probably the greatest source of error, although this circuit was entirely composed of naked wires, which had a large cooling surface.

We therefore relinquished the attempt to find the whole resistance of the coil, and devised a method whereby we could find the increment of the resistance due to increasing electromotive force; the resistance when $E = \cdot 004$ volt having been found at all points of our range as described above (Table IV.). For this purpose a temporary WHEATSTONE'S bridge was arranged, constructed as follows :—

The arm *AB* (fig. 6) was formed by the coil alone. *BC* contained three large coils of uncovered wire, the first of which (Cavendish Laboratory coil) was of German silver and had a resistance of 5ω; the second, also of German silver (belonging to the

British Association), had a resistance of $2{\cdot}5\omega$; and the third, of copper, had a resistance of $\cdot 5\omega$.*

Fig. 6.



The arms *AD*, *DC* (about 6 feet each) were made of uncovered copper wire. A preliminary rough adjustment could be made at *D* and the final adjustment of the whole bridge was made by altering the temperature of the coil in the arm *AB*. This alteration in temperature was produced by the heat developed in the wire itself, and thus the whole calorimeter was under the same conditions as those prevailing during our determination of J.

The temperature on thermometer E_m was read at the moment when the galvanometer (G_2) showed no deflection. The behaviour of the galvanometer indicated that the flow of heat from the coil was not quite steady, but took place in gushes, owing probably to the coating of insulating varnish on the wire; for when the key was depressed, the mirror did not swing steadily back to its zero, but oscillated about it, and the moment had to be estimated when the mean of these oscillations coincided with the zero. That this could be done with considerable accuracy is shown by the fact that the individual observations agreed well amongst themselves.

The general conduct of a series of these experiments was as follows.

We first found the temperature of the coil when the bridge was in adjustment, the E.M.F. at the ends of the coil being that used when taking a resistance in the ordinary way. When the calorimeter was cooled down, the E.M.F. was raised and the coil allowed to warm up until a new balance was obtained and the temperature at that moment noted.

As the temperature and consequently the resistance of the arm *BC* remains constant, and since the arms *AD*, *DC* are practically equal, their ratio remains unchanged. The resistance of the arm *AB* (the coil) must also be the same as before, hence the difference in the two observed temperatures gives us the number of degrees that the coil is hotter than the surrounding water; or we can express the result in terms of increase in resistance, as the resistance (when $E = \cdot 004$) at all temperatures is known.

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* The total mass of metal in this arm of the bridge amounted to several pounds.

TABLE V.

The following Table gives a series of observations taken on August 22, 1892 :—

Time.	Battery in circuit.	Temp. E_m.	Temp. C.	R when E = ·004.	δR.
		At which bridge balances.			
5.35	1 Leclanché	344·7			
6.22	,, ...	343·9	20·397	8·7519	
6.47	1 Storage	337·8	20·240	8·7471	·0048
6.55	2 Storages	316·5	19·698	8·7311	·0208
6.58	,, ...	316·7			
7.15	1 Leclanché	343·7	20·395	8·7518	
7.40	3 Storages	277·0	18·684	8·7010	·0507
7.45*	,, ...	279·0 (?)			
7.55	,, ...	276·8			
8.17	1 Leclanché	344·4	20·409	8·7021	
9.9	,, ...	342·5	20·361	8·7508	
9.40	4 Storages	221	17·286	8·6600	·0899
9.50	,, ...	221·2			
10.13	5 Storages	137	15·231	8·5995	·1485
10.22	,, ...	139			
10.44	1 Leclanché	337·9	20·243	8·7472	

When the readings obtained by using 1 Leclanché differ (the change being probably due to changes in the temperature of the bridge), intermediate values are deduced from the times.

It seemed absolutely immaterial whether the current was on for only a few seconds or indefinitely. In the above set, when three storage cells were being used, the current was not broken at all, the calorimeter being cooled down by the ether apparatus† in defiance of the heat developed in the coil. Although a quarter of an hour elapsed between the observations, they were in very good agreement.‡

To determine the E.M.F. at the ends of the coil, the various batteries used were compared with the Clark cells. This method was therefore open to the sources of error mentioned on p. 400, Nos. (2) and (3). The resistance of the other parts of the bridge were then determined and were as follows :—

Resistance of whole bridge 4·30ω.
,, large coils 7·69ω.
,, coil and its ratio arm 9·17ω. Hence coil = 8·75, arm ·42.
,, large coils and ratio arm 8·06ω. Hence coil = 8·75, arm ·369.
,, wires forming battery circuit ·030ω.

The E.M.F.'s were determined by the ordinary POGGENDORFF'S method in terms

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[*] This observation was uncertain; the observer at the galvanometer remarking so, before he knew that the reading of the temperature was different.

[†] See p. 419, *infra*.

[‡] This would show that the increase in resistance of the other arms of the bridge was not appreciable.

of the Clark cell at temperature 16°·8 C., hence E.M.F. = 1·434 volts; another set of storage cells being used to give the current through the potentiometer.

TABLE VI.

Battery.	Potentiometer readings.		E.M.F.
	For battery.	For Clark cells.	
		No.	
1 Leclanché	32·232 32·225	1 . 33·832	1·366
1 Storage	23·915 23·936	1 . 17·188	1·994
2 „	47·735 47·734	2 . 34·195	4·004
3 „	72·088 72·083	3 . 51·347	6·039
4 „	64·105	4 . 45·602	8·064
5 „	79·844 79·857	5 . 57·029	10·040

To determine the internal resistance of the batteries, the current from them was sent through the coil and balanced in our usual manner with the mercury rheostat (see Section VI.). The temperature being noted, when the galvanometer was steady, the resistance of the whole battery circuit external to the coil, was immediately taken; then if x is the internal resistance of the battery, R the resistance of the coil approximately corrected for the rise due to the current, then,

$$\frac{\text{E.M.F. of Clark cell}}{\text{E.M.F. of battery}} = \frac{R}{R + \rho + x},$$

but this ratio was given by the potentiometer comparison, hence we found x, the internal resistance of the storages, = ·018ω, and of the Leclanchés 2·24ω.

Hence we have the following results:—

TABLE VII.

Battery.	E[*]. At end of coil.	δR. 1 Leclanché being called 0.	δR. E = ·004.
1 Leclanché . .	1·035	0	·0016
1 Storage . . .	1·90	·0048	·0064
2 „	3·81	·0208	·0224
3 „	5·74	·0507	·0523
4 „	7·67	·0899	·0915
5 „	9·55	·1485	·1501

---

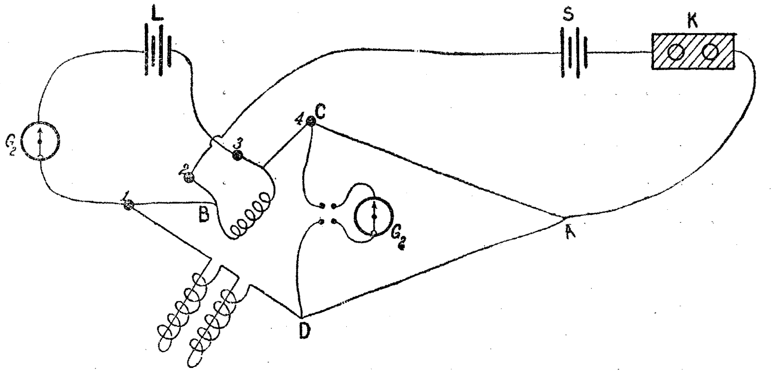
[*] It is probable that the values of E are too high, for (as before pointed out) these are the values of

These observations will be seen to agree fairly well with the parabola

$$\delta R = \cdot 00160\ E^2.$$

This method, although the results were concordant, was unsatisfactory in the manner in which the difference of potential at the ends of the coil had to be calculated. We therefore adopted the following arrangement (fig. 7), which possessed the great advantage of at once giving us the difference of potential at the ends of the coil in terms of our standards. The Clark cell circuit was connected to the ends 1 and 3 of the coil, and the mercury rheostat introduced into the storage circuit; thus, by adjustment of the rheostat the E.M.F. at the ends of the coil could be made equal to that of 1, 2, 3, &c., Clark cells. No difficulty was experienced in working the two galvanometers together, the observer at the low resistance one being entirely unaware whether the high resistance circuit was made or broken. As it was felt that the whole success of the method depended on the non-heating of the large coils, the two smaller were replaced by one large one of German silver, wound double, so as to expose a very great surface to the air. The resistance of this coil was selected so that when placed in series with the Cavendish large coil,* their united resistance was very nearly equal to that of the calorimeter coil; thus the remaining arms of the bridge were more nearly equal than before, and were made of stout German silver wire, so that each arm was about 5 feet in length and had a resistance of $\cdot 3\omega$. We believe that these results were quite satisfactory, since (1) there was no difficulty in the measurement of E; (2) the mass of metal in the large coils was very great, their cooling surface large (a thermometer placed on the coils never showed any tendency to rise) and their temperature coefficient small; (3) the other arms of the

Fig. 7.



E when the exterior resistance is infinitely great, hence the value of α (in the equation $\delta R = \alpha E^2$) is too low.

[*] The Cavendish coil was a triple strand one, containing nearly 1400 feet of single German silver wire, the other coil had a double strand and contained more than 400 feet of a stouter wire.

bridge were so nearly equal, and were so arranged, that they would be affected to the same degree by any temperature changes.

The figure shows the connections—

BC is the arm containing the coil.
BD contains the two large German silver coils.
AC, *AD* the two German silver wires forming the remaining arms of the bridge.
G_1, G_2 the high and low resistance galvanometers.
L, *S* the Clark cells and storages.
K the mercury rheostat.

TABLE VIII.—The following Table gives the observations taken September 20, 1892.

Time.	No. of Clark cells.	Temperature at which bridge is balanced.		R at C° (in Legal ohms).	δR.
		E_m.	C°.		
3.40	1	376·3	21·226	8·7790	x
3.46		376·3			
3.54	2	360·7	20·818	8·7671	$x+{\cdot}0119$
3.56		360·2			
4. 3		360·4			
4.17	3	332·5	20·100	8·7458	$x+{\cdot}0332$
4.21		332			
4.25		332·1			
4.33	4	292·5	19·080	8·7157	$x+{\cdot}0633$
4.36		292·8			
4.38		292·3			
4.50	5	240	17·760	8·6771	$x+{\cdot}1019$
4.59		240·5			
5.50	6	177·5	16·202	8·6316	$x+{\cdot}1474$
6. 0		176·8			
7.12	1	379·4	21·306	8·7814	x
7.18	2	363·4	20·895	8·7692	$x+{\cdot}0122$
7.26	3	333·4	20·130	8·7468	$x+{\cdot}0346$
7.30		333·6			
7.45	4	292	19·067	8·7156	$x+{\cdot}0658$
8. 0	5	240·4	17·765	8·6772	$x+{\cdot}1042$

Of the second series of experiments, the first was taken immediately after entering the laboratory, when the arms *AC*, *AD* (being very near one observer, and the gas having been lighted) had not probably reached a state of thermal equilibrium, but they evidently did so during the series.

TABLE IX.*

The following numbers were plotted:—		δR (Legal ohms.)	δR deduced from $\delta R = \cdot 00422 n^2$.
No. of cells.	Increase.		
0	$-x$	0	0
1	0	·0042	·0042
2	·0120	·0163	·0168
3	·0333	·0376	·0378
4	·0638	·0681	·0675
5	·1023	·1066	·1055
6	·1478	·1516	·1519

Hence $x = \cdot 0042$,

and the above agree within the limits of experimental error with the parabola

$$\delta R = \cdot 00422 \times n^2; \text{ where } n \text{ is number of CLARK's cells.}$$

In this case there can be no doubt about the actual D.P. at the ends of the coil. The results of the previous investigation (p. 404) are of great importance, in so far as they confirm the conclusion that $\delta R = \alpha E^2$, but are of little use for determining the value of α.

In order to complete these experiments variations in the rate of stirring were tried. It was found, as would be expected, that the more perfect the stirring, the less the wire became heated; but, within the limits of our rate of stirring, the change was so slight that no correction was thought necessary.

The observer at the high-resistance galvanometer could, however, always detect minute changes in the rate of stirring by the irregular behaviour of the spot. These changes, although thus rendered very evident, had an exceedingly small effect and thus they served as a proof that the oscillations observed during our J experiments also indicated variations too minute to affect our measurements.

[NOTE.—As illustrating the importance, as also the accuracy, of the correction rendered necessary by the difference between the temperature of the wire and of the water, we here give a summary of the results of J 9 and J 34. These two experiments were performed in order to subject the corrections (both for radiation, &c., and for the difference in the temperature of the wire) to a severe test, the heat developed per second in the wire during J 34 being nine times as great as that developed per second throughout J 9.

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* In comparing the last two columns, it must be remembered that a difference of ·0010 corresponds to a difference of but 1 in 8600 in R.

	J 9.	J 34.
E.M.F. (expressed in terms of a Clark cell at 15°)	2	6
Weight of water + water equivalent = (M) =	273·77 grms.	345·20 grms.
Mean rise per 1″ (after correction for stirring, radiation, &c.) = γ =	$8225^\circ \times 10^{-7}$	$5778^\circ \times 10^{-6}$
Mean temperature	19°·540 C.	19°·540 C.
Hence, thermal grms. generated per 1″, when E is that due to 1 Clark cell = $\left(\gamma \times \frac{M}{E^2}\right)$ =	56295×10^{-6}	55404×10^{-6}
Now, resistance of wire at 19·540, as determined by box in the ordinary manner = (R_0) =	8·7084	8·7122*
Hence, thermal grms. per 1″ if R = 1ω; $\left\{\left(\gamma \times \frac{M}{E^2}\right) R_0\right\}$ =	49026×10^{-5}	48270×10^{-5}
These quantities (which ought to be equal, and from which we deduce the value of J) here differ by nearly 1 part in 60.		
If, however, we deduce the values of R_{2E} and R_{6E} from Table IX., we get 8·7084 + ·0168 and 8·7122 + ·1519	8·7252	8·8641
Hence $\left(\gamma \times \frac{M}{E^2}\right) R_1$ =	49111×10^{-5}	49110×10^{-5}

We did not see how to apply a more severe test, and we, therefore, considered it unnecessary to carry the investigation further, although we had supposed that a repetition would be necessary.]

Comparison of our Resistance Coils with the Standards.

The resistance box was taken to the Cavendish Laboratory on October 31, 1892, to be compared with the standard coils in possession of the British Association.

In order to be able to standardize each coil separately, two plugs were made, half ivory and half brass, so that good contact was secured with the outer circle of the dials through the brass, but no contact was possible with the inner circle through the ivory. The insulation of these plugs was, however, defective, the shunt so formed being sufficient to bring the 10 legal ohms down to 10 B.A. ohms.

Two brass bridges were then made which rested over the outer circles of the dials, one end of each bridge fitted into the plug-holes, but was cut away so as not to

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* The resistance of the coil had been altered between these two experiments (see p. 411).

touch the central circle. By tightening up a screw in the other end of the bridge a good and regular contact was secured. To the centre of each bridge a binding screw was fixed, and connection was made by thick wire leads from these to the Carey-Foster bridge.

In the comparison of the units and tens, the Carey-Foster bridge belonging to the B.A. was used, and the difference between the standard and the box-unit was found in terms of a length of bridge-wire. In the comparison of the 100's and 1000's, the bridge described by GLAZEBROOK ('B.A. Report,' 1883) was always used.*

The standard coils used, and their values, are given in the following Table :—

TABLE X.

Coil.	Value.
ELLIOTT 269	$1 + {\cdot}000282\,(t - 15{\cdot}1)$
" 270	$1 + {\cdot}000286\,(t - 15{\cdot}3)$
" 288	$10 + {\cdot}00265\,(t - 16{\cdot}2)$
" 289	$10 + {\cdot}00260\,(t - 15{\cdot}4)$
NALDER 3634	$100 + {\cdot}0308\,(t - 17{\cdot}2)$
" 3637	$100 + {\cdot}0308\,(t - 17{\cdot}05)$
1000 *b.w.d.*	${\cdot}05000 + {\cdot}0000715\,(t - 18{\cdot}2)$

The same thermometer (HICKS, No. 352,601) that had been employed in all our determinations was again used in the standardization, and, since its bore was very nearly uniform, no correction was necessary. The B.A. thermometer (K.O., 75,149) was used for the temperatures of the standards; its correction was − ·10 at the temperatures of our observations.

The resistance of the connections between the box and bridge was taken in terms of the bridge-wire of the Carey-Foster bridge.

The results of observations on different days agree well, the average departure from the mean being less than $\frac{2}{1000000}$.

The differences could, in most cases, be easily accounted for by small temperature changes in the interior of the coils, which could not be indicated by the thermometer.

The accompanying Table gives the results.

(Although the coils in the 1000 dials were not used during the determinations of the resistance of the calorimeter coil, we have included them in this Table, since many of them were required when ascertaining the platinum temperatures, and also because a complete standardization of this kind is interesting, as it shows the order of accuracy of boxes of this pattern.)

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* In comparing the 100 and 1000 ohms coils, two Leclanché cells were used. The currents in the battery circuit were ·090 and ·023 ampère respectively.

TABLE XI.

Coil.	Unit dial.			Ten dial.			Hundred dial.					Thousand dial.				
	Nov. 16.	Nov. 17.	Mean.	Nov. 7.	Nov. 9.	Mean.	Nov. 10.	Nov. 10.	Nov. 11.	Nov. 14.	Mean.	Nov. 12.	Nov. 13.	Nov. 13.	Nov. 14.	Mean.
1	..	·99523	·99523	9·9764	9·9759	9·9762	99·796	99·793	99·801	..	99·797	998·31	..	998·40	..	998·35
2	·99888	·99894	·99891	9·9826	9·9826	9·9826	99·779	99·779	99·784	..	99·780	997·71	..	997·80	..	997·75
3	·99687	·99693	99690	9·9708	9·9709	9·9708	99·798	99·797	99·802	..	99·799	997·96	..	998 07	..	998·01
4	·99595	·99600	·99597	9·9792	9·9789	9·9791	99·784	99·783	99·790	99·789	99·787	997·69	..	997·78	..	997·75
5	·99793	·99808	·99800	9 9748	9·9747	9·9747	99·803	99·805	99·811	99·811	99·809	997·97	..	998·10	..	998·04
6	·99654	·99661	·99658	9·9774	9·9772	9·9773	99·725	99·721	99·736	..	99·727	997·94	..	998·01	..	997·98
7	·99820	·99822	·99821	8·9738	9·9735	9·9736	99·862	99·859	99·870	..	99·864	..	998·12	998·10	..	998·11
8	·99952	·99959	·99956	9·9717	9·9711	9·9714	99·823	99·823	99·830	..	99·825	..	998·38	998·38	..	998·38
9	·99714	·99723	·99719	9·9713	9·9711	9·9712	99·780	90·780	99·792	99·786	99·784	..	997·91	997·90	..	997·90
Bridge R	..	..	..	9·9811	9·9808	9·9810	..	..	99·841	..	99·841	997·79	997·95	997·92	997·82	997·87
„ L	..	..	..	9·9733	9·9735	9·9734	..	..	92·815	..	99·815	997·81	997·91	997·89	997·78	997·85

NOTE.—The box is marked by Messrs. ELLIOTT as "Legal ohms at 17° C.," hence the value of each coil, in terms of a True ohm, should be ·99757. The mean value of all the coils is ·99801, at a true temperature of 16°·92 C., or 17° by its own thermometer.

As the terminals were used for testing at the time the box was constructed, the resistance of the connections through the dials was then taken. This is sufficient to account for the apparently low value of the first unit, as the resistance of the box with all the plugs at 0 is ·00334. In testing the arms of the bridge, the centre and end terminals were used in the same manner as when the box itself formed the bridge. so that no plug resistance correction had to be applied.

A table was constructed, giving the total difference between the reading and the real value (in terms of legal ohms) for every position of the plugs in each dial. This difference we termed the "plug correction."* Having made this correction, we then had to correct for any inaccuracy in the ratio of the arms of the bridge, and as all determinations of the calorimeter coil resistance were made with the 1000 (right) and 10 (left) as the arms, it is here only necessary to give the correction for these coils.

Now $10L/1000R = 10{\cdot}0077/1000{\cdot}30 = {\cdot}0100047$. This we termed the "bridge correction."

The resulting values are expressed in legal ohms, and true ohms = reading in legal ohms $(1 - {\cdot}0024275)$.

By applying the corrections in the above form it was possible to perform all the operations by means of the slide rule,† as it was only necessary to determine the quantity to be added or subtracted in one case to three, and in the other to four figures.

(When working with platinum thermometers the last two corrections are omitted, as it is only necessary that the resistances should be expressed in terms of the same unit, the absolute value of that unit being unimportant).

Table XII. gives the values of R, when the calorimeter coil was in water, stirred in the same way as during a "J" determination. Each number in the column R was obtained in the manner given in full on p. 399, and includes the correction for temperature. The "plug correction" cannot be deduced from column R, because the difference between the correction on $R + r$ and r has to be used in each case. The plug correction however is, in every case, about the same as that required by the values of $R + r$ and r as given in Table IV.

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* The correction for the temperature of the box was made before applying the "plug correction." The values of the temperature coefficient for each dial had been previously determined by Messrs. ELLIOTT, and the accuracy of the coefficients has been exposed to severe tests.

As the temperature of the box was controlled by a special regulator, it never differed greatly from 17° C. (See 'Phil. Trans.,' vol. 182, A, p. 45.)

† FULLER's spiral slide rule gives results correct to 1 in 20,000 or 30,000.

TABLE XII.

Date.	C°.	R (at 17°).	R corrected for "plugs."	R corrected for bridge.	True ohms.
Aug. 6 . . .	18·701	8·70152	8·70514	8·70923	8·68809
,, 6 . . .	13·133	8·53685	8·54041	8·54442	8·52368
,, 10 . . .	25·217	8·89343	8·89701	8·90119	8·87958
,, 17 . . .	19·231	8·71690	8·72046	8·72456	8·70338
,, 24 . . .	20·337	8·74906	8·75260	8·75671	8·73545
,, 31 . . .	17·066	8·65267	8·65627	8·66034	8·63932
Sept. 4 . . .	15·325	8·60104	8·60459	8·60863	8·58773

Between September 4 and 11 the coil was readjusted, and was probably somewhat strained in the process. The value of R was slightly increased.

TABLE XIII.

Date.	C°.	R (at 17°).	R corrected for " plugs."	R corrected for bridge.	True ohms.
Sept. 11 . . .	19·560	8·73058	8·73416	8·73827	8·71706
,, 11 . . .	25·522	8·90563	8·90923	8·91342	8·89178
,, 11 . . .	13·280	8·54471	8·54826	8·55228	8·53152
,, 11 . . .	15·086	8·59816	8·60171	8·60575	8·58486
,, 11 . . .	22·154	8·80618	8·80975	8·81389	8·79250
,, 11 . . .	23·274	8·83966	8·84326	8·84742	8·82594
,, 14 . . .	16·952	8·65268	8·65628	8·66035	8·63933
,, 19 . . .	18·697	8·70415	8·70777	8·71186	8·69072

The sixth figure is, of course, unnecessary. The numbers in the first and last columns were plotted on a very large scale, so that the fifth figure could be read distinctly. The resulting curves differ in no respect from those given by platinum thermometers. The difference between the curve reading (at *any* of the above temperatures) and the corresponding value in the table in no case exceeds ·0005 (*i.e.*, 1 in 17,000).

The values of R after September 4 exceed the values before that date (when the temperature is the same) by ·0038.

The values of R (true ohms) at other temperatures than those in the above tables were obtained from the curves.*

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* In order to trace the changes in the specific heat of water throughout our range, we had decided to find the time of rising 1° at each of the following temperatures, viz., 14°, 15°, 16°, 18°, 20°, 22°, 24°, and 25° C. It would have been difficult, if not impossible, to arrange our actual observations throughout our experiments so that they were exactly grouped about these points. The value of each millim. of our thermometer stem varied as the temperature changed, and the above temperatures in no case corresponded with any integral number. The values of our variables at these temperatures had to be obtained by

As mentioned (p. 394) the resistance of the coil when immersed in pentane was ascertained. The observations were taken in the same manner and with the same rate of stirring as those whose results are given in the above tables.

TABLE XIV.

C°.	Determination of R in pentane.	
	R at (17°).	True ohms (after "plug" and bridge corrections).
13·632	8·55513	8·54195
14·010	8·56516	8·55197
14·982	8·59544	8·58223
16·202	8·62941	8·61612
17·161	8·65892	8·64557
18·214	8·69058	8·67699
19·164	8·71857	8·70506
20·502	8·75805	8·74443
21·702	8·79354	8·77989
23·001	8·83186	8·81812
24·699	8·88218	8·86836
24·699	8·88204	8·86822
24·713	8·88275	8·86891

The results must be compared with those in Table XIII., since the observations were made after the change in the coil.

In order to find what difference, if any, was caused by the change from water to pentane, the values of R in water at the above temperatures were taken from the curve plotted from Table XIII.

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large scale curves. No purpose would be served by reproducing any of these curves in this paper, because if drawn on a small scale they would be useless and misleading; for they would give an exaggerated idea of the accuracy of our results—the discrepancies being imperceptible. In every case we give data by which the curves could be reproduced, and where any marked departure is shown by an individual observation we mention it.

TABLE XV.

C°.	R (pentane).	R (water).	Difference.*
13·632	8·5420	8·5419	+·0001
14·010	8·5520 ?	8·5528	−·0008 ?
14·982	8·5822	8·5818	+·0002
16·202	8·6161	8·6148	+·0013
17·161	8·6456	8·6456	+·0000
18·214	8·6770	8·6766	+·0004
19·164	8·7051	8·7046	+·0005
20·502	8·7444	8·7444	+·0000
21·702	8·7799	8·7794	+·0005
23·001	8 8181	8·8176	+·0005
24·699	8·8683	8·8676	+·0007
24·713	8·8689	8·8680	+·0009

Mean difference = ·0004,

showing a rise of about $\frac{1}{22000}$ when in pentane.

The specific heat of pentane is so small that it is possible that the wire would be at a slightly higher temperature than when in water, as it would not be robbed so rapidly of the heat supplied by the current, and thus some portion of the small rise observable might be due to this cause.

The following tables give the resistances used by us for the reduction of our "J" experiments :—

R_0 denotes the resistance when the current is so small as to produce no visible change in R.

(R_0 = R, as deduced from Table XIII., diminished by ·0034, see p. 396.)

R_E, R_{2E}, &c., the resistance when the difference of potential at the ends of the coil is that due to 1, 2, &c., Clark cells.

($R_{NE} = R_0 + \delta R_0$, where $\delta R_0 = \cdot 00421 \times n^2$ true ohms, see p. 406.)

TABLE XVI.—Series II. Values of R. For Series I. subtract ·0038.

C°.	R_0.	R_{2E}.	R_{3E}.	R_{4E}.	R_{5E}.	R_{6E}.
14·477	8·5626	8·5794	8·6012	8·6307	8·6686	8·7149
15·581	8·5959	8·6127	8·6337	8·6632	8·7011	8·7474
16·682	8·6282	8·6450	8·6660	8·6955	8·7334	8·7797
17·683	8·6578	8·6746	8·6956	8·7251	8·7630	8·8093
18·688	8·6876	8·7044	8·7254	8·7549	8·7928	8·8391
19·835	8·7214	8·7382	8·7592	8·7887	8·8266	8·8729
21·115	8·7592	8·7760	8·7970	8·8265	8·8644	8·9107
22·409	8·7972	8·8140	8·8350	8·8645	8·9024	8·9487
23·862	8·8399	8·8567	8·8777	8·9072	8·9451	8·9914
25·006	8·8735	8·8903	8·9113	8·9408	8·9788	9·0250

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* The differences in the last column show a slight tendency to increase as the temperature rises, indicating a decrease in the resistance of water.

SECTION VIII.—THE MEASUREMENT OF TIME.

As previously mentioned, an electrical clock (made by Mr. THOMAS) was used as our standard. The energy required was supplied by two Leclanché cells. The pendulum (a seconds one) was very heavy, weighing about $\frac{1}{4}$ cwt. Its rod was of wood, and we were unable to detect that any appreciable change in rate was caused by the small changes of temperature to which it was exposed. The working parts of an electrical clock of this kind are so simple that, when once standardized, it is a very reliable instrument. The pendulum was fitted with a rough and a fine adjustment, and comparisons were made at regular intervals with a ("rated") DENT'S chronometer. Until August 21, 1892, the rate of gain was $-$ 1 in 2424; after that date the rate of gain was certainly less than 1 in 25,000, and such variations as were observed may have been due to temperature changes, as they were irregular and, in any case, so small as to render corrections unnecessary. All observations of time made before the above date (August 21) were corrected for clock error, before they were used in the calculations. The actual uncorrected observation is, however, the one given in all columns headed "time."

The chronograph, which was worked by a separate battery, was of a somewhat peculiar construction. It was contrived so that on "making" the circuit connecting it with the clock, the tape was at once started, and, on breaking that circuit, the tape came to rest. Thus the observer could, without moving his position, start or stop the chronograph by pressing a key.*

We rarely, however, used this contrivance, because, as our observations lasted over considerable intervals of time, the instrument had to be continuously at work. The regulator was so adjusted that the tape passed through about $\frac{3}{4}$ of an inch per second —the fractions of a second being rapidly read off by means of glass scales. The labour of numbering the seconds was great, for the instrument was not so contrived that it could make a distinguishing mark every tenth second.†

Immediately before the observer were placed two keys connected with the chronograph, one of which made permanent connection with the clock pendulum, the other was a spring key for recording the times of passing certain temperatures, or the time of each 1000 revolutions of the stirrer.

Some preliminary observations indicated that the personal error (*i.e.*, the difference between the actual time and those read off from the tape) amounted to about $\frac{3}{10}$ of a second. As, however, all times were recorded by the same observer, this constant "lag" was of no consequence.

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* It was found necessary to place the chronograph at a considerable distance from the galvanometer.

† The Table XIX., given in Section XII., shows that one experiment alone lasted more than 10,000 seconds.

SECTION IX.—THE MEASUREMENT OF MASS.

ROWLAND, in the paper to which reference has already been made, takes objection to WEBER's determination of "J," on the ground that he used only 250 grms. of water. Also M. ARNOUX in the discussion which followed D'ARSONVAL's paper said, "Its determination has always been carried out in diminutive apparatus . . . in which the losses by radiation attained a high figure. With large apparatus the loss by radiation becomes negligible since the volume increases as the cube and its radiating surface as the square only of the linear dimensions. With appliances capable of transforming into heat a few hundred kilogrammetres per second, we ought to succeed in determining the mechanical equivalent to three or four (*sic*) places."* Now as the quantity of water used by us was small, it will be well to point out the considerations by which we were influenced.

Besides the mass of water, which is used in the calorimeter, account must be taken of what is usually termed the "water equivalent" of the calorimeter. [We take this opportunity of remarking that when we, in subsequent statements, use the word "equivalent" we refer to the water equivalent of our calorimeter, and do not use the word in the sense in which it occurs in ROWLAND's paper as meaning "the mechanical equivalent;" this we have designated by the letter "J."] Now it is the very difficulty of satisfactorily determining this equivalent, rather than the estimation of loss by radiation, which has led experimenters to prefer a large mass of water, when practicable, in order to make any error in the equivalent one of the second order.

Up to the time of writing, only two methods seem to have been generally adopted for determining the equivalent, (1) the method of mixtures, (2) the method by calculations from the specific heats and masses of the component parts of the calorimeter. Of the first of these we need say but little, for JOULE himself obtained values which varied amongst themselves by 12 per cent.† We did not, however, dismiss this method without trial, for having applied it, with every conceivable precaution, to one of our calorimeters, we obtained numbers whose differences were so great as to render them useless for the purposes of this investigation.

The second method is attractive on account of its simplicity, but since the specific heats have probably been determined by the application of the first method,‡ the accuracy is not of a superior order. Of greater weight is the consideration that a calorimeter has no definite limits, it being impossible to foretell to what extent and in what manner the necessary supports, connections, and surrounding envelopes have to be introduced. The method which we have adopted of making the experiments

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* ROWLAND's calorimeter, when full, weighed over 12 kilos., JOULE's about 6 kilos.

† See Table, p. 639, 'JOULE's Scientific Papers,' vol. 1.

‡ We may quote from Prof. EVERETT's 'Units and Physical Constants,' "Specific Heat of Liquids." "We have omitted decimal figures after the fourth, as even the second figure is different with different observers." To this we may add that the specific heat of solids will bear no closer scrutiny.

themselves give us the value of the equivalent appears, to us, to be the only way in which this difficulty can be successfully overcome, and, as our results will show, the equivalent was determined with the same accuracy as the other quantities.*

There does not appear to be any argument in favour of using a small mass of water when the value of "J" is to be determined according to JOULE'S original method by the friction of water; but the complexion of the case is completely changed if the mode of investigation is altered, for in each different method the accuracy of the result will be some function of the variables at our disposal, and, since we cannot apply the calculus, these ought to be so selected from general considerations, as to make that accuracy a maximum. In the method which we have adopted the variables are the mass of water, the resistance of the coil, the difference of potential at its ends, and, dependent upon these, is the rate of rise in temperature.

Now the most satisfactory method of ascertaining the rate of rise in temperature, consists in timing the transit of the mercury column across the spider-wire of a reading telescope. This wire, being set along the graduations of the thermometer, several successive transits are recorded at different parts of the range and the mean time is taken at each place. Although the rate of rise ought to be fairly great, in order to diminish the importance of radiation losses, if the rate is too rapid the observer has not sufficient time to set his cross-wire to the successive graduations, and only one observation can be recorded at each part of the range. The confusion which would be introduced by attempting to observe every other scale division need scarcely be mentioned. It was only by constant practice that one of the observers was able to take observations with accuracy at the rate we adopted.

If, on the other hand, the advance of the column is too slow, the time of apparent contact with the telescope wire is uncertain and, at the same time, the phenomenon of "sticking" is rendered more probable. As during these experiments the strain on the observer was very great, mere personal fatigue would be sufficient to prevent accurate observations being taken if the duration of the experiment was extended beyond an hour. In the case of the experiments on the heat developed by the stirrer, it will be seen by reference to the tables that these sometimes lasted three or four hours; but the nature of these experiments not being so complicated, the strain was less and the observer had short intervals of rest.

The rate of rise in temperature thus practically determines the values which we must assign to the other quantities at our disposal, for to make the rate great we must either diminish the mass or resistance, or else increase the difference of potential. The considerations which led us to give to E and R the limiting values assigned to

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* The value of J can be obtained without ascertaining the value of the water equivalent (see p. 481), and the determination of the changes in the capacity for heat of water is entirely independent of it. Our conclusions are based on observations of differences in time caused by differences in the mass of water, and we see no reason why such differences could be ascertained with greater accuracy if the water equivalent was diminished. The total times would be decreased, but the differences would remain unaltered.

them during these experiments have already been mentioned on p. 389. We were thus restricted to masses of water varying from 130 to 300 grms.

As the determination of the equivalent and the change in capacity of the whole mass due to increase of specific heat are fully discussed in another section, it is only necessary here to deal with the mass of water added to the calorimeter. The balance used by us was by BECKER, carrying 500 grms. and turning with a milligramme. As this type of balance is not provided with a rider-arm, it was found convenient to add weights to the nearest 5 milligrms. above and below, and to interpolate by the method of oscillations. Nearly the whole of the measurements were conducted by the ordinary method of direct weighing, as the balance, when once in good adjustment, remained so. The adjustment was however, occasionally checked by the method of double weighing.

Holes were bored through the bottom of the balance case and the top of the cupboard on which it stood, and wires suspended from the pans for use when weighing flasks, &c. As it was necessary to open this cupboard whenever a flask had to be weighed, it would have been difficult to keep the air within the cupboard in a state of dessication, and thus if proper precautions had not been taken a considerable error might have been introduced in the weighing of glass vessels of large area, owing to the hygroscopic nature of their surfaces. The usual simple expedient of taring one glass vessel against another of approximately equal surface appeared eminently satisfactory, as the weighings could be repeated at varying intervals of time (generally a few hours, but in one test case four days) and the results were always found to agree to a milligramme.

In our earlier series of experiments (1887–1890) the calorimeter could be rapidly taken to pieces, dried, any required mass of water added by means of a fine dropping-pipette, weighed, and put together again. As, however, those experiments had shown us the necessity of keeping the outer space perfectly dry, we now decided to reduce, if possible, the pressure to less than 1 millim., since, in this case, radiation, &c., would be considerably diminished, and any moisture present would immediately be detected.

It thus became impossible to take the calorimeter to pieces, and means had to be devised for introducing and withdrawing water through the supporting glass tubes.

The impossibility of removing the calorimeter without destroying our vacuum led to another difficulty, for, at the end of the experiment, the water had been heated to the highest point of our range, and before we could conduct a second experiment we had either to cool the whole apparatus down, which would have been an extremely slow process, owing to the smallness of the radiation, and would also have rendered it necessary to throw the regulator of the outer bath entirely out of adjustment; or else withdraw part of, or all, the water in the calorimeter, adding sufficient cold water to bring the temperature down below the point at which our observations commenced. During the earlier part of our 1891 series we withdrew a portion only of the water by means of a modified form of weighed pipette, and then, by the same means, added a weighed quantity of cold water. This method was in some respects satisfactory, except that every withdrawal involved four weighings, so that, after a short time, the mass of water in the calorimeter was dependent upon a very great number of weighings, and small errors in each, if cumulative, might have become serious. We, therefore, soon abandoned this as a general method, and only resorted to it occasionally. Since then we have always used the following method of adding a known mass of water to the calorimeter :—

Pairs of glass flasks (with india-rubber stoppers), of 100, 200, and 300 cub. centims. capacity, were selected and carefully cleaned. One of each pair was kept as a tare for its fellow. In introducing the water into the calorimeter it was necessary to avoid loss either by accident or by evaporation, and to guard against losses of this kind the following device was employed :—A thin glass tube, 30 centims. in length, had a wider piece, about 7 centims. long and 2 centims. in diameter, fused to its upper end, thus forming a funnel. Up the centre of this wide portion a piece of glass rod was fixed, its upper extremity projecting above the top of the wider tube, so that the lip of the flask, from which water was poured, could rest against it, and thus prevent any drops running down the outside of the flask or tube. By forming a slight support, it also somewhat relieved the difficulty of the operation, which, even with its aid, was a trying one. A cork was fixed to the stem of the funnel, in such a manner as to permit its lower end to dip into the calorimeter. This funnel was provided with a case, consisting of a length of glass tube closed permanently at the lower, and temporarily at the upper, end by an india-rubber stopper. A piece of similar tubing, closed at both ends, was used as a tare. The full flask and funnel having been weighed, the funnel was withdrawn from its case, placed in one of the tubes leading to the calorimeter, and the water poured down it from the flask. This is the only part of the process during which evaporation could possibly take place, and any such loss, during the few seconds the operation lasted, would be a matter of no consequence. The empty flask was immediately re-stoppered, the funnel withdrawn and returned to its case, and the weight ascertained at any convenient time. This method also enabled us to add water below the dew-point of the room without any error due to moisture condensed on the flask and funnel, for it was only necessary to first weigh the flask, then cool it, and pour its contents into the calorimeter. The exterior of the funnel was dried before returning it to its case, and the stoppered flask placed in a dessicator for some time before the final weighing. This method appeared to be satisfactory, and, although it was impossible to add exactly the same amount on different occasions, still, as the difference was only the fraction of a gramme, it was easy to apply any necessary correction to the resulting numbers. A glass tube, reaching to the bottom of the calorimeter, was connected with an exhaust pump, which enabled us to withdraw nearly all the water, and the remaining moisture was removed by passing a current of hot dry air through the calorimeter for several hours.

Owing to some difficulty with regard to the air-tight joints, we were obliged to take the calorimeter to pieces at the beginning of July, 1892, and to our astonishment we found, although we had, as we thought, dried completely, there still remained several cub. centims. of water. We subsequently ascertained that the calorimeter could be properly dried in the above manner, provided that sufficient time was allowed; but the hot air had to pass for several days before a drying tube, suspended within the calorimeter for 12 hours, showed no increase in weight. Now, as the first method involved too many weighings, and the second was unsafe, unless two or three days elapsed between each experiment, we were compelled to seek a different mode of procedure. Thus, as we could neither withdraw any portion of the water, nor cool the whole calorimeter down without great labour, means had to be devised for cooling it from within. A tube, through which a freezing mixture could be forced, was evidently objectionable, as there would always be uncertainty as to whether all the freezing mixture had been removed. We found the following arrangement worked admirably, for the temperature of the calorimeter fell as rapidly when cooling, as it rose when the current was passing. We were thus able to use the same water again and so save a numerical reduction.

A very thin glass tube, closed at its lower end, passed down the support tube *F* (Plate 2, fig. 1) of the calorimeter, just clearing the base, and the upper end, which was open, projected about $\frac{1}{2}$ inch above the top of the tube *F*. Care was taken to so fix this tube that no water could find its way up the annular space between the two tubes. When not in use, the upper end was closed by a cork, so as to prevent air-currents circulating down to the calorimeter. When used for cooling, this tube was partially filled with ether, through which a rapid current of *dried* air was sucked by means of the arrangement shown in Plate 2, fig. 1. The fine capillary point reached just to the bottom of the closed tube, so that, when the cooling had proceeded far enough, the remaining ether could be withdrawn by reversing the connections to the exhaust pump and the H_2SO_4 drying bottles. Any ether or impurity left at the bottom of this tube would have caused great irregularities in the experiments, so, as a precaution, only freshly distilled ether was used,* and when the temperature had been sufficiently lowered, *dry* air was passed for a considerable time and, finally, the cooling tube thoroughly cleaned by means of an absorbent mop. The joint at *G* was made by slipping a small ring of india-rubber tubing round the projecting end of the cooling tube, and, by slightly splaying out the mouth of the aspirating portion, a sufficiently good union was effected, the extreme thinness of the walls rendering a ground glass joint impracticable. The entrance tube *K* was used for adding fresh ether as occasion required.

As soon as we perceived that this method of cooling was a success, it was at once evident that it could be applied to finding the latent heat of evaporation of liquids, for by regulating the rate of evaporation we could make the cooling effect such as to counterbalance the heat developed by a known current. We have already made a few rough determinations, but prefer to postpone their publication until we have applied the method with greater precautions.

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* The ether was always redistilled by us immediately before use—at a temperature under 40° C.

SECTION X.—THE MEASUREMENT OF TEMPERATURE.

When commencing this account of our experiments, we proposed to give full details of the calibration and standardization of the mercury thermometer E_m, upon which all our measurements depend. Nearly half of our time and attention has been devoted to this part of the subject, and there are but two courses open to us, viz., to give a full account of our method of standardization, with the tables upon which our conclusions are based; or to reserve a detailed description for a further communication, and give a short summary of the results in the present paper. We have decided to adopt the latter course, for the following reasons:—

(1.) We are (with the help of Mr. CALLENDAR) now entering on a careful direct comparison of thermometer E_m with a new form of air thermometer, which, there is every reason to believe, will give very accurate results; but we are unable to assign any definite limit to the time that this investigation may take.

(2.) Dr. GUILLAUME is now* engaged in the comparison with the Paris standard of a thermometer specially constructed for us by M. TONNELOT, and some time must elapse before this comparison can be completed.

(3.) The dimensions of this communication are already very great, and if, in addition, we gave a full account of our thermometric comparisons, its length would become immoderate.

(4.) We consider that the success of the method of exact determination of temperature by platinum thermometers may now be regarded as established, and that the accuracy of the results obtained by platinum thermometers in our possession is proved by communications already published.†

(5.) The results of our J experiments may themselves be taken as a proof of the accuracy of the method of time-calibration adopted by us, and described on pp. 423 and 424, *infra*.

Assuming the accuracy of the calibration it is possible we are in error—

(1.) In the actual elevation;

(2.) In the value of our total range.

No. (1) may be disregarded, for it is only the changes in the specific heat of water which render the actual elevation of any consequence whatever. Now it is impossible that we are in error by 0°·2 C., for the comparisons we have made with the B.A. thermometers, which have been carefully standardized at Kew, would alone have been sufficient to detect any error of that kind, and an error of 0°·2 C. in elevation would mean an alteration of only 1 in 20,000 in the value of J.

No. (2) is, of course, of vital importance.

In 'Phil. Trans.,' vol. 182, A, p. 155, will be found the results of a comparison of one

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* December, 1892.

† 'B.A. Report,' 1890; 'Phil. Trans.,' vol. 182, A, pp. 43–72 and 119–157; 'Phil. Mag.,' December, 1891; 'Chem. Soc. Journ.,' 1890, p. 656.

of our platinum thermometers (H) and the air thermometer over a range of 0° to 100°, and the numbers there given show that the probable limit of error at *any* point in the above range is 0°·01 C. This limit may be further diminished by the "plug corrections" (see p. 410), then neglected by us. It must be remembered that this limit of error refers to the actual elevation, and is probably decreased when we come to consider differences over a range of 11° C. Further, the table there given is a record of only a single series of observations, and must include experimental errors, which would tend to mean out if sufficient observations were taken.

Again as regards *differences*, the quantity which chiefly affects us (apart from experimental errors, etc.) is the value of δ in the equation

$$d = \theta - pt = \delta \{ \overline{\theta/100}|^{2} - \theta/100 \} ;$$

and it is therefore important to point out to what extent the variations we have observed in the value of δ may influence our results.

We have standardized our mercury thermometer E_m by means of the platinum thermometer N.* (For particulars see 'Phil. Trans.,' 1891, A, p. 151.) This thermometer contained two wires, and by placing these in series a third resistance could be determined; it thus practically contained three coils, which we denote by A + B, A, and B.

The fixed points (R_s, R_1, and R_0) of this thermometer have been re-determined at regular intervals during the past two years, and no change of any consequence has been observed.

The values of its constants are as follows†:—

	A + B.	A.	B.
R_0	9·8636	5·9881	3·8762
R_1	13·2987	8·0743	5·2252
R_s	24·2703	14·7631	9·5343 hence
δ	1·641	1·645	1·640

Now, the value of d at 14° C. and 25° C. obtained by assuming the above values of δ are $-$ ·198 and $-$ ·308, and it is on the *difference* between these numbers (·110) that possible error in the value of our range depends. Assume it as possible that the true value of δ is as high as 1·70 or as low as 1·60 (our greatest differences in any determinations of this constant have been ·009) we should then get $-$ ·205, $-$ ·319,

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* The coil of thermometer H was so long that it was barely contained in the calorimeter, and, as it required complete immersion, it was not suitable for use in this case.

† The constants differ slightly from those previously published ('Phil. Mag.,' December, 1892), as the "plug correction" (see p. 410), has, for the first time, been applied to them. By assuming that $R = 0$ we get for the absolute zero $-$ 270·66, $-$ 270·55, and $-$ 270·86 instead of the numbers there given.

and — ·193 and — ·300 as the differences, thus causing changes of ·004 and ·003, respectively, in our range, although causing differences of ·010 and ·008 in the elevation.

Apart from errors of observation, we may, therefore, regard the limit of our range error as ± ·003 in 11° C., *i.e.*, 1 in 4000; and we believe it to be much less.

As to experimental errors, it must be remembered that we have made the comparison of the platinum and mercury thermometers under the most favourable circumstances. Both were immersed in the calorimeter, the cooling tube (Plate 2, fig. 2), having been removed to allow of the insertion of the platinum thermometer. The observer, with his eye at the telescope and his hand on the key could, by means of the current, set the temperature with extreme exactitude to any required reading E_m, stirring being maintained at the same rate as during an experiment. Observations could thus be repeated at the same reading as often as necessary.

Again, the observations taken by the observer at the galvanometer were entirely independent of the readings of the observer at the telescope, yet a difference of 0°·004 C., on the repetition of an observation, was very unusual.

Many hundreds of comparisons were made, the particulars of which we reserve for our second communication.

We may mention that the comparisons made in 1892 differ from those of 1891 by ·003 in range, but show a rise of about ·010 in the actual elevation of E_m.

E_m was one of three thermometers specially constructed for this work by HICKS. We set him a somewhat difficult task, as the dimensions of the bulb were strictly limited both in length and diameter, and the weight of mercury was also specified.

The stem was divided into millimetres, about 40 millims. to 1° C., and the lower 18 centims. were out of sight within the calorimeter tube, the graduation marked 0 being within this tube and the 26th millimetre just appearing above it.

The reading 87·5 = 13°·990 C.; the reading 537·5 = 25°·471 C.

The graduations continued to 580 millims.

Our method of observation obviated the necessity of attempting to divide the millimetres by eye. The thermometer was fixed in such a position that the view of the bore was unimpeded by any of the shorter graduations. When timing changes of temperature the spider-wire of the telescope was placed on these graduations and the time of contact with the spider-wire observed. No attempt was made to take any reading terminating in 0 or 5, as these graduations extended across the bore and obscured the edge of the mercury column for about 1/20th millim. Thus to obtain the time of passing a given point we were limited to the observation of four consecutive transits, and for this reason, our "fixed points" were determined at 87·5, 127·5, &c., and the time of passing these points deduced from the times at 86, 87, 88, and 89, &c.

A consideration of the behaviour of this thermometer (as well as of other narrow bore ones) rendered it evident that the ordinary method of calibration was insufficient if the thermometer was to be used for the determination of changing temperatures. We believe that no calibration can be considered satisfactory unless made under the *same circumstances* as those in which the thermometeris to be used. As an illustration of our meaning we may mention that the range 87·5 to 127·5 $E_m = 0°·975$ C. when the thermometer was stationary, but $= 0°·973$ C. when rising at the normal rate of our experiments, *i.e.*, in addition to calibration for inequalities in the bore, a thermometer used under circumstances similar to ours must be calibrated for "sticking" and for certain periodic alterations in the rate of advance which are probably due to the behaviour of the glass bulb. Whatever may be the case with other thermometers, a close and prolonged study of the thermometer E_m has rendered it certain that the rate of advance of the column (when the rise in temperature is uniform) is influenced by other conditions than mere irregularities in the bore, but that these changes in rate will, under the same conditions, almost always recur at the same places.

During 1891 the times of rising every 10 millims.* throughout the whole range were observed and the observations repeated on more than thirty occasions with varying rates of rise. Nearly half of these observations were taken with the alloy wire, whose resistance did not increase as the temperature rose, the remainder with a platinum wire. During this series of observations the weights of water were different, the supply of heat was trebled, the exterior temperature was shifted from the bottom to the top of our range, the pressure changed from 1 to 760 millims., and, in fact, all the conditions were altered. The times of rising 10 millims. under all these different circumstances were thus determined at 42 points in our range, and the results plotted; the mean path in each case was, of course, different, but the deviations from it were regular in their occurrence and similar in their nature. Such deviations as invariably occurred throughout all the altered conditions must have had their *origin in the thermometer itself.*

We hope to publish some of these curves in our further communication for, although the changes in the curves themselves are great, the steady repetition of lag and acceleration is both curious and interesting. This year these differences recurred with another coil and a different method of stirring.

The mean values of these deviations, which were repeated throughout the whole of the experiments, were expressed in terms of the curve-reading at each point and plotted as ordinates on a straight line,† and the remainder of the calibration completed in the usual manner. The effect of the application of the resulting corrections to the numbers obtained from our J experiments is a sufficient proof of the accuracy of the method. An error of 0°·001 C. in the comparative value of any of our ranges would produce a difference of from ·4 to ·7 second between the "mean times" given

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* 10 millims. on thermometer $E_m = 0°·25$ C. approximately.

† *E.g.*, if t'' was observed time over a small range $\theta_2 - \theta_1$, and if t' was the value over that range as given by the smooth curve, then t''/t' was plotted as ordinate and $\frac{1}{2}(\theta_2 - \theta_1)$ as abcissa, and the areas thus obtained were integrated, &c.

in columns 5, 9, 14, 18, and 22, Table XL., and the curve numbers in the succeeding columns. Further, this difference would *recur in each experiment.* No persistent discrepancy of any consequence is observable. In our own work we have expressed the value of these ranges to another figure, but we refrain from printing it until we produce more evidence. One possible cause of error in our total range yet remains, viz., the difference caused by unequal lag at the beginning and end of that range, and this difficulty cannot be surmounted by means of the same method as that used for determining the comparative values of the smaller ranges.

Our experiments on this point were of the following nature :—

A platinum thermometer E (Pt) of exceedingly small capacity for heat (the external diameter was only 3/16 inch) was placed in the calorimeter. The coil of this thermometer was pressed tightly against its glass envelope, which was of egg-shell thinness, and thus the thermometer was rendered extremely sensitive. Its stem passed down a condenser-tube, through which the tank water was continually drawn by means of the water pump. The stem-resistance, therefore, remained constant, and thus only *one* observation was required, whereas with N three observations had to be taken to accurately determine a temperature. The value of R when the temperature of the calorimeter was steady was determined at the initial and final points of our range. The temperature was then lowered to our usual starting-point (10° C.), and raised in the same manner as during an experiment. The value of R was ascertained when the reading of E_m (mercury thermometer) again indicated the initial and final points. No doubt the platinum thermometer also lagged, but we proved by independent experiments that it did so to an extremely small extent, and, if uniform, the lag was of no consequence, as it would only affect the elevation and not the range. Now in the platinum thermometer we have no "sticking," &c., and there is every probability that the lag *is* regular. The observer at the galvanometer called at the moment when the "spot" was seen to pass the zero point, the other observer taking the mercury readings at the same instant. This was done over four or five consecutive plugs, and the resistance deduced at the moment of passing the required points. The results indicated that the lag of the mercury thermometer was greater at the commencement than at the end of our range by (at our normal rate of rise) about 0°·008 C.* The "stationary range" would, therefore, require diminishing by about ·008 in 11° C., or by 1 in 1400.

In order to investigate this point more fully another platinum thermometer (Q), having a naked wire, was placed in the calorimeter. The coil of this thermometer had fifty turns to the inch, and thus the different parts of the wire were very close together. The results were not satisfactory, the conduction across the water, under

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* The average lag of the mercury thermometer proved to be less than we anticipated. It, of course, depends, in a great measure, on the thoroughness of the stirring; but when the mass of mercury that has to be heated is considered, the extreme lag, observed at our rate of rise, viz., ·025, is surprisingly small.

such circumstances, being sufficient to render the galvanometer uncertain and to produce irregularities in our results. We propose to repeat these "lag" determinations, using the naked wire, but placing pentane instead of water within the calorimeter. In the meantime we have left our total range uncorrected for the difference in the initial and final lag, as our own data are not at present sufficiently accurate for us to apply the correction, which is certainly less than 1 in 1400. Its effect would be to increase the value of J,[*] but it would not affect the changes in the specific heat of water or the calorimeter.

The correction will only have to be applied to the final result.

The exterior temperature was determined by a mercury thermometer A (by HICKS), which was similar in most respects to E_m, but its range was not so open—about 27 millims. = 1° C. It was placed in the calorimeter with E_m and the readings compared at every 5 millims. of E_m. When conducting our experiments we only required to know accurately the difference between the internal and external temperature, and, for such a purpose, this comparison was sufficient. As A was to be used for the reading of stationary temperatures, a careful calibration of the usual kind was made by means of the Cavendish dividing microscopes.[†]

Our method of experimenting eliminated several of the errors which are associated with the use of mercury thermometers.

(1.) Changes of temperature of stem.

The exposed portion of the stems of A and E_m was always immediately above the surface of the water in our twenty-gallon tank. The water was always maintained at a constant temperature (see p. 454) and (as we ascertained by direct measurements) the temperature of the air above it varied but slightly. The lower portion of the stem passed through a tube immersed in this tank water, and thus the stem temperature remained steady when the temperature of the bulb was rising. The change in the temperature of even the upper portion of the stem never exceeded three or four degrees throughout the year, and the change in the average stem temperature must have been much smaller. At the time of determination of the values of the ranges, the stem was, therefore, under exactly the same conditions as those prevalent during an experiment.

(2.) The effect of changes of pressure on the bulb.

The only changes to which it was exposed were atmospheric ones, which, even if they affected the elevation, would not affect the range. Again, A and E_m were so

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[*] ROWLAND appears to have paid no attention to the effect of this difference in initial and final lag. It is probable, therefore, that the correction, if it was possible to obtain it, would cause a greater increase in his value than it is likely to effect in ours, since his average rate of rise was three times as great.

[†] This calibration is in practical agreement with another calibration of A conducted by platinum thermometers; the inequalities as determined by the latter method are, however, always greater than those shown by the former. This is to be expected when the *length* of the mercury thread used in the ordinary method of calibration is considered.

similar in construction and dimensions that the result of such changes would be nearly the same in both. Thus the differences of temperature deduced from the readings would not be altered to any appreciable extent, and it was only with such differences that we had to deal.

(3.) The changes in zero caused by the sudden changes in temperature.

The history of thermometer E_m* was much the same from day to day. During the night it remained about the temperature of the tank. Before an experiment, its temperature was lowered to 10° C. and, during an experiment, it was steadily raised from 10° C. to 25° C., no readings being taken until it reached 13°·9 C. When determining the fixed points, the same routine was, as nearly as possible, observed; thus the conditions were, in all cases, so alike that the effects were probably similar. In any case, we have been unable to detect any irregularities arising from this cause.

TABLE XVII.—Values of "Fixed Points" on Thermometer E_m when the Temperature is Steady.

E_m.	C.
87·5	13·990
127·5	14·965
177·5	16·198
217·5	17·187
257·5	18·180
297·5	19·196
347·5	20·474
397·5	21·755
447·5	23·061
507·5	24·662
537·5	25·471

The following Table shows the difference between the comparative values of the ranges when the thermometer is steady and when rising.

Range E_m.	Range C. Thermometer steady.	Range C. Thermometer rising.
87·5–127·5	·975	·973
127·5–177·5	1·233	1·235
177·5–217·5	·989	·987
217·5–257·5	·993	·995
257·5–297·5	1·016	1·016
297·5–347·5	1·278	1·278
347·5–397·5	1·281	1·282
397·5–447·5	1·306	1·307
447·5–507·5	1·601	1·598
507·5–537·5	·809	·811

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* E_m remained in the calorimeter from the commencement to the close of our work except on the few occasions when water was added or withdrawn.

The calibration of those portions of the thermometer between our "fixed points" was conducted in the same manner as the calibration over the whole range.

[Note by E. H. GRIFFITHS, added March 31st, 1893.

On February 14 I received the thermometer by M. TONNELOT (No. 11048), which had been standardized both by Dr. GUILLAUME, and under his direction, at the Bureau International des Poids et Mesures.

This thermometer is of hard glass, with transparent stem, and is divided into tenths of a degree Centigrade. The scale is continuous from — 3° to 27° C. when there occurs a bulb, then a narrow portion giving readings 48° to 52° C., then a second bulb, and, finally, readings from 98°·5 to 101°·5 C. The length of each degree is about 10 millims.

The study of this thermometer has been a most exhaustive one; two separate calibrations were performed for the most useful part (10° to 26°·5 C.)—the *greatest* difference between any two values given by the separate determinations being 0°·0028 C. The fundamental interval and the coefficients of external and internal pressure were repeatedly determined. Several hours must have been occupied in the mere copying of the observations forwarded to me—although the record consists, almost entirely, of numerals. I mention this as indicating the labour which has been devoted to this standardization, and I owe my warmest thanks to the Bureau International for the care and attention bestowed upon it.

The papers include printed tables for the reduction of the corrected mercury readings both to the hydrogen and the nitrogen scale as resulting from the comparisons of Dr. CHAPPUIS.

The comparison between this thermometer (denoted hereafter by P) and the thermometer E_m was conducted in the outer tank, for had the comparison been made in the calorimeter, the lower readings of P would have been invisible. E_m was, therefore, under the same conditions as during our J experiments, except in the following particulars:—

(1.) The external pressure was increased by about 110 millims. of water. A series of observations proved that the resulting correction was — ·3 millim. (rather less than 0°·001 C.) and this correction was always made before entering the reading of E_m.

(2.) When in the calorimeter, the lower portion of the stem passed through tubes washed by the tank water. About 60 millims. were thus maintained at a constant temperature, whatever the extent of alteration in the bulb temperature. About 50 millims. intervened between the top of the calorimeter and the lower end of this constant temperature portion. We may consider that this 50 millims. assumed the mean temperature between the tank and the calorimeter. Thus a length of (60 + 25) millims. of the stem, which during our previous experiments was at the tank temperature 19°·26, assumed, during this comparison, the temperature of the bulb θ_1.

The correction in millimeters is given with sufficient accuracy by the formula

$$85\,(\theta_1 - 19{\cdot}3) \times {\cdot}00016,$$

and as the mean value of 1 millim. is $0^\circ{\cdot}025$ C., the resulting correction is

$$85\,(\theta_1 - 19{\cdot}3) \times {\cdot}00016 \times 0^\circ{\cdot}025 \text{ C.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\alpha).$$

This amounts in the greatest case to $0^\circ{\cdot}002$ C.

The readings of P were taken by a microscope (re-levelled before each observation) which was fitted with a micrometer scale. The one hundredth of a degree Centigrade was thus read directly and no difficulty was experienced in estimating the one thousandth, the scale being an unusually clear one, made by the Cambridge Scientific Instrument Company.

The thermometer was placed in a tube, open at the lower extremity, and an opening at the upper end was connected with a rubber tube leading to the waste pipe. This arrangement was used as a siphon and the thermometer stem was thus maintained at the bulb temperature, and, therefore, as the mercury column rose, any alteration in the stem immersion was rendered unnecessary.

In order that the readings might be obtained under the exact conditions observed by Dr. GUILLAUME, I implicitly followed the instructions given in a printed note added to the certificate. After the tank had arrived at the required temperature, at least half-an-hour was allowed to elapse before taking a reading, and immediately after the observation the thermometer P was transferred to ice, and a series of readings taken to obtain the greatest zero depression. The admirable methods adopted by the Bureau International are less known, or, if known, are less practised in this country than they deserve to be. I therefore give one example in full showing the various corrections.

COMPARISON of the Reading 87·5 on E_m with P (March 15, 1893).

	Temperature reading by P. millims.	Zero point. millims.
Barometer (corrected)	754·1	754·1
H_2O pressure (expressed in terms of Hg)	12·1	4·4
Total external pressure	766·2	758·5
Observed reading	14·025	— ·036
Calibration correction	— ·026	0
External pressure correction	— ·001	0
Internal ,, ,,	+ ·026	+ ·008
Zero	+ ·028	— ·028
Fundamental error correction	— ·006	
Sum corrections	+ ·021	
Correction for stem E_m [see (α), *supra*]	— ·002.	

Hence reading on the mercury scale = 14·044.
Correction to H scale — ·067; to N scale — ·059.

Hence

Reading E_m.	Hydrogen scale.	Nitrogen scale.
87·5	13·977	13·985

I confess that I did not know until I adopted in detail the precautions advised by Dr. GUILLAUME in his "Traité de Thermométrie," that it was possible to regard the mercury thermometer as an instrument of precision, and I had considered such corrections as too refined for so rough an instrument. I am, however, now convinced that, given the *right conditions*, it is possible to ascertain temperatures by a mercury thermometer with a limit of error of 0°·002 or 0°·003. It is rarely, however, that such conditions prevail. The labour involved in the previous standardization of the thermometer is enormous, and there are but few men capable of constructing thermometers on which such labour may be profitably expended. The actual operation of observing and reducing the results is also considerably greater than is the case when platinum thermometers are used.

The following table gives the results of all observations made with the micrometer eye-piece. I had previously made several comparisons whose mean result is in fair agreement with those here given; but, as the last two figures of the readings had to be estimated, the discrepancies are greater, and the results of less value.

COMPARISON of E_m with the French Standards.

Reading E_m.	87·5	127·5	177·5	217·5	257·5	297·5	347·5	397·5	447·5	507·5	537·5
	θ_1 on the corrected mercury scale.										
March 14	—	—	—	—	—	--	20·541	21·828	—	—	—
„ 15	14·044	15·022	16·260	17·249	—	—	—	—	—	—	—
„ 16	14·044	15·020	—	—	—	—	—	—	—	—	—
„ 17	14·045	15·023	16·259	17·248	18·245	19·261	20·544	—	—	—	—
„ 18	—	—	—	—	—	—	20·545	21·832	23·140	24·740	25·552
„ 19	—	—	—	—	—	—	—	—	23·138	24·738	25·550
Mean . .	14·044	15·022	16·260	17·249	18·245	19·261	20·543	21·830	23·139	24·739	25·551
	Hence θ_1 on the hydrogen scale.										
H	13·977	14·952	16·186	17·172	18·165	19·178	20·457	21·741	23·048	24·645	25·455
	And θ_1 on the nitrogen scale.										
N	13·985	14·960	16·193	17·181	18·174	19·188	20·467	21·751	23·058	24·655	25·466
	θ_1 as determined from platinum thermometers (see Table XVII.).										
Table XVII.	13·990	14·965	16·198	17·187	18·180	19·196	20·474	21·755	23·061	24·662	25·471
Difference between N and Table XVII.	·005	·005	·005	·006	·006	·008	·007	·004	·003	·007	·005

Mean difference N—XVII = — ·0055.
Mean discrepancy from the mean ± ·0011.
Difference in range between 14° and 25° : ·001.

It thus appears that our temperatures, as deduced by platinum thermometers, exceed those of the Paris Hydrogen and Nitrogen Standards in actual elevation by 0°·014 C. and 0°·005 C. respectively, but that the value of our total temperature range is practically the same by both methods of standardization.*

It is true that slight discrepancies appear in the value of the smaller ranges, but here I am inclined to place greater reliance on our previous determinations than on those obtained by the comparison with P, for mistakes of observation are far less likely to occur when using platinum, than when reading mercury, thermometers, and also the former values are deduced from the observation of several different resistances at each temperature, all of which after the correction given by the standardization of the resistance-box (see p. 408, *supra*) are in practical agreement, although the actual values of R differ greatly.

The difference in actual elevation is of no consequence, although it is interesting to notice that the agreement with the Paris Nitrogen Scale is nearer than that with the Hydrogen Scale. This was to be expected, since the boiling-point of sulphur was ascertained by Mr. CALLENDAR and myself by means of an *air* thermometer, and our values of d depend on that determination.

We have not, as yet, been able to commence, by means of Mr. CALLENDAR'S new form of air thermometer, our direct comparison with the nitrogen scale, for the calibrating and cleaning of the instrument have occupied much time. Pending the completion of that work the results of the above comparison are of great value, and, in the meantime, we are justified in assuming that the temperature range values, as determined by us, are in such close agreement with the Paris nitrogen thermometer as to render any alteration in our results unnecessary. The reduction of our temperature from the air, to the absolute, scale would diminish the value of our total temperature range by nearly ·002, but I do not consider the accuracy of our results of such an order as to render the resulting correction (about 1 in 5000) more than a matter of form.

I have forwarded this note to Dr. GUILLAUME with the request that he would be so good as to add his opinion as to the probable limit of error of the observations with thermometer P, together with any other comments which he may think advisable. His remarks are as follows :—

"Le résultat fort remarquable des comparaisons faites par M. GRIFFITHS est sans doute le meilleur critérium de la limite d'erreur, tant des observations du thermomètre que de son étude ; et l'estimation que j'en aurais faite *à priori* aurait été sensiblement plus élevée. En effet, dans le résultat final viennent s'ajouter toutes les causes d'erreurs suivantes :—

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* The range value on the corrected *mercury* scale is (in the case of this thermometer) 11·508, and this would *diminish* our value of J by 1 part in 367.

1°. *Étude du thermomètre* P.

a. Calibrage (y compris l'interpolation dans la supposition que la division est équi distante);

b. Détermination du coefficient de pression;

c. Détermination de l'intervalle fondamental.

Les corrections résultant de ces deux dernières études n'agissent que sur le *range;* et sont de peu d'importance (moins de ·001 degré) sur un intervalle de 10 degrés. Le calibrage, au contraire, peut introduire de point en point des erreurs irrégulières. J'ai montré autrefois* que, dans un calibrage fait avec tous les soins possibles par un observateur très-exercé, l'extrême limite d'erreur, pour un thermomètre divisé en dixièmes de degré est de ·001; le calibrage du thermomètre P a été fait avec soin, mais par une méthode abrégée et l'on peut s'attendre à des erreurs de ·002 environ sur les points déterminés directement; le tube étant assez irrégulier les erreurs des points interpolés peuvent atteindre ·003.

2°. *Réduction au thermomètre à azote.*

Cette réduction se fait au moyen des tables générales déterminées par la comparaison, faite une fois pour toutes, d'un groupe de thermomètres en verre dur avec le thermomètre à gaz. Dans l'application de cette table au thermomètre P, on suppose que les corrections sont les mêmes, c'est-à-dire que le verre et le mercure de ce thermomètre sont identiques à ceux des thermomètres-étalons. Cette identité thermique a été vérifiée approximativement par des comparaisons précises faites sur un grand nombre de thermomètres; mais si l'on songe: (*a*) que le verre est un corps chimiquement compliqué, et dont la dilatation est soumise à des lois singulières; (*b*) qu'il suffit d'une différence relative de $\frac{1}{400}$ ($2 \cdot 10^{-11}$ en valeur absolue) dans le coefficient de θ^2 dans la formule de la dilatation linéaire du verre pour provoquer une différence de ·001 degré dans les indications du thermomètre à 50°, on ne peut être que fort étonné d'une telle concordance, qui résout la question vitale du thermomètre à mercure, et détruit tous les préjugés que l'on avait contre cet instrument, aussi bien que sur la dilatation du verre.

3°. *Comparaisons.*

Celles-ci comprennent:—

(*a.*) les observations à diverses températures;

(*b.*) les déterminations du zéro.

On peut vraisemblablement s'attendre à ce que les erreurs de température, les défauts de l'éclairage, les irrégularités du ménisque provenant en partie des irrégu-

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* "Etudes thermométriques," 'Travaux et Mémoires du Bureau International des Poids et Mesures,' tome 5, p. 23 (1886).

larités du tube, enfin les erreurs de l'estimation produisent au total des discordances de ·001 degré au minimum dans (*a*) et dans (*b*).

Toutes les causes mentionnées ci-dessus et ne concernant que le thermomètre P auraient pu, sans aucune doute, conduire dans la réduction au thermomètre à azote à des erreurs irrégulières atteignant ·005.

La *différence systématique* de θ_1 ·005 en moyenne s'explique suffisamment par deux causes :—

(*a.*) Pression capillaire moindre dans la colonne toujours descendante à zéro que dans la colonne à ménisque le plus souvent ascendant ou en équilibre moyen aux autres températures.

Dans les tubes de thermomètres l'angle de raccordement varie entre 46° et 75° environ, ce qui, dans les tubes de ·1 millim. de diamètre, correspond à une variation de pression de 50 millims. de mercure au maximum.

(*b.*) Le zéro se relève dès l'instant où le thermomètre est plongé dans la glace ; ce relèvement au moment initial est à peu près indépendant de la dépression, et dépasse ·001 degré par minute.

Ces deux causes réunies suffiraient à expliquer des différences constantes plus fortes même que celle qu'a trouvée M. GRIFFITHS ; pour la plupart des recherches, comme dans le cas actuel, elles sont sans nulle conséquence. Il me sera permis en terminant d'insister sur la sécurité que donne aux mesures de températures le contrôle si indirect et en même temps si parfait qui résulte des comparaisons de M. GRIFFITHS, et d'exprimer le vœu que la vérification soit bientôt étendue à un intervalle de température aussi large que possible. Jusqu'à ce jour, l'étude du thermomètre à mercure au Bureau International a été faite entre − 25° et + 100° ; l'échelle sera prochainement étendue jusqu'à 200°. Le thermomètre à toluène a été parfaitement étudié et comparé au thermomètre à hydrogène jusqu'à − 75° ; à cette température la discordance entre divers instruments étudiés individuellement n'atteint pas ·05 degré."]

SECTION XI.—THE HEAT DEVELOPED BY THE STIRRING.

During our earlier experiments (1887) we stirred by means of a screw which revolved about 200 times per minute. Throughout 1888 and 1889 we continued to use the same form of stirrer, but endeavoured to make the mixing more efficient by increasing the rate of revolution. As our experience increased we became strongly impressed with the necessity of *thorough* mixing. Any slackness in this respect makes itself evident (*a*) in changes in resistance of the wire, owing to changes in its rate of cooling ; (*b*) irregularities in the radiation and conduction, probably owing to varying temperatures of the lid ; (*c*) irregularities in the thermometer readings ; (*d*) in the water equivalent, which then is found to alter to some extent with the mass of the contained water.

One assumption underlies all the calculations, viz., that whatever the mass of the contained water, the water equivalent of the calorimeter remains constant.* We find this assumption is not correct, unless the water is thrown against every part of the calorimeter throughout each experiment. At first sight it would appear that, whatever might be the "lag" of any unwetted portion of the calorimeter when the flow of heat had become steady, the quantity of heat absorbed by it for each rise of 1° C. would be the same, and that it would only be at the commencement of each experiment that differences would be observable. It must, however, be remembered that the radiation coefficient of the whole calorimeter would be altered by the existence of this colder portion; and, as this cause of error would continue to exist throughout the whole experiment, the effect would be appreciable.

In 1891 we adopted a new form of stirrer. An ebonite shaft, passed down the central tube, and terminated at its lower extremity in an agate point, which rested on a metal bearing on the base of the calorimeter. Two gold tubes joined together in the form of a V were fastened to this shaft, the apex of the V being downwards and immediately above the agate point. This stirrer acted as a centrifugal pump, and, when revolving at a rate of about 1200 per minute, threw the water upwards and outwards with great rapidity—the whole contents of the calorimeter being removed in a few seconds when the lid was off. There could be no doubt that, provided there was sufficient water to at all times cover the lower openings of the tubes, the stirring was sufficient, and that no portion of the calorimeter could remain for any appreciable time at a different temperature to the water. This form of stirrer appeared to us so satisfactory that we did not attempt to improve upon it during our experiments in 1891; and it was this misplaced confidence which was the chief cause of our failure, in that year, to obtain satisfactory results.

Its defects may shortly be summed up as follows:—

(1.) As the depth of water in the calorimeter increased, the work expended in forcing the tubes through the water also increased; and the rate of rise in temperature (which ought to have diminished) was much greater when the mass of the water was large.

(2.) This change in the quantity of heat developed would not have been fatal, since it could have been determined separately for each mass of water used, and we persevered in our attempts to thus determine it. Unfortunately, however, it varied capriciously, even when the mass of water and rate of revolution were constant; and we have never arrived at any satisfactory explanation of these variations. It appears probable, however, that their origin was due to differences in pressure between the

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* If the water equivalent varies, the fact is rendered very evident when the values of J deduced from different masses of water are compared. Until, in 1891, we adopted forms of stirrers which threw the water against the roof of the calorimeter, our experiments were rendered useless by this constant source of error. The agreement between the values obtained in 1892 is a satisfactory proof that this difficulty had been overcome.

agate point and its bearing, the slightest variation in the position of the shaft of the stirrer causing very different quantities of heat to be generated. The quantity of heat generated by the stirrer varied from about one-sixth to one-fifteenth of the heat generated by the current, according to the electromotive force used; and as the capricious changes above referred to amounted, in some cases, to 5 or 6 per cent. of the heat due to the stirring, they might affect our ultimate result by as much as a half and, in some cases, nearly 1 per cent. The quantity of heat appeared to vary with the rate of revolution in such a manner that $tr^{5/2}$ was a constant, where t was the time of rising 1° C. and r the rate of revolution.

Our experience of this stirrer led to the following conclusions:—

(1.) The ideal stirrer must be able to throw the water from the bottom to the top of the calorimeter whatever the mass of the water.

(2.) The "work done" by the stirrer should be the same, whatever the depth of the water.

(3.) The "work done" by the stirrer should be, as far as possible, employed in throwing the water upwards to the lid, rather than in simply causing a rotation of the water near the bottom of the calorimeter.

(4.) The whole of the energy should, if possible, be employed in lifting the water and not in overcoming the friction between solid surfaces, *i.e.*, the bearings should be outside the calorimeter.

Although we found it impracticable to devise a form which would entirely fulfil the above requirements, the one adopted by us during our 1892 experiments was satisfactory.

During the spring of 1892, we made a large number of trial experiments with different forms of stirrers, and it should be borne in mind the form it ultimately assumed was an example of the "survival of the fittest." A section will be found in Plate 2, fig. 2.

A cylindrical tube *AB*, 1 inch in diameter, closed at the lower end, rested on four little feet about 1/16 of an inch in length, which were fixed to the base of the calorimeter. The plate at the lower end was perforated in the centre, so as to allow the end of the revolving shaft to pass through without touching it. Round this centre hole were four slits through which the water in the calorimeter passed into the cylinder. The end of the revolving shaft was fitted with a small cylinder of agate, which hung loosely within a ring fixed to the base of the calorimeter at *C*. The end of the agate was not in contact with the base of the calorimeter. The bearing by which the stirrer was supported was fixed at the top of the central glass tube, and thus any increased downward thrust of the stirrer did not alter the friction within the calorimeter. The stirrer consisted of an inverted cone with nearly vertical paddles at its extremities (a section is shown at *D*). When the stirrer revolved, the water was drawn in through the base of the cylinder, thrown outwards by the paddles, and, being unable to escape at the lower end, mounted rapidly to *A*, whence it was ejected with considerable violence against the roof of the calorimeter. If the rate exceeded about twenty-six revolutions per second, it was found that when the lid was removed, the water was thrown many inches above the top of the cylinder, while the stirring-shaft remained dry. A small window at *E* caused a stream of water to be continually thrown on to the top of the thermometer bulb.

The bearings at the top of this shaft ultimately assumed the form shown at *H.* A small block of steel was fastened by a screw to the shaft, and the lower end of this steel terminated in a projecting ring, which revolved in a brass bearing of the form shown at *H.* This brass bearing was, as already mentioned, fixed to the top of the central glass tube. A drop of oil placed in the channel, on the top of the brass, rendered this bearing practically air-tight, at all events, sufficiently so to prevent any possibility of evaporation.* The shaft from *H* to the top of the calorimeter was about 8 inches long, and made of ebonite; the conduction of heat along this shaft was, therefore, very small. The heat generated in the bearing at *H* passed almost entirely into the water of the outer tank, for the brass tube which terminated there was continued downwards to the steel lid, and thus the lower three inches were immersed in the water.

The portion at *D* was at first shaped like a horizontal paddle-wheel. It was, however, found that although it would work excellently for a time, a gradual accumulation of air at the centre of the paddle-wheel greatly diminished its efficiency. Many attempts were made to surmount this difficulty, and it was only by the conversion of the upper portion into the form of an inverted cone that it was finally overcome.

To adjust the stirrer, the screw in *S* was loosened and the shaft lowered until the end of the agate touched the base of the calorimeter. The stirrer was then raised about 1 millim., and fixed in that position by means of the screw at *S.* When investigating the action of these stirrers, the lid of the calorimeter was replaced by a sheet of glass which prevented the contents from being ejected. As far as it was possible to see the interior through the shower of water that poured against the glass, the water without the cylinder assumed a slow circular movement only. At the same time, there can be but little doubt that the entire contents passed from the bottom to the top within the space of a second or two. As long as the volume of the contained water exceeded 130 cub. centims., the throw appeared to be the same, whatever the quantity, and, as the figures will show, the work done altered only slightly.

Our first series of experiments was performed with the object of ascertaining (1) If, under the same conditions, the work done by the stirrer was constant; (2) In what respect the work done varied, if at all, with the mass of water; (3) If there was any constant relation between the heat developed and the rate of revolution.

The results of our preliminary series are given in the following table, the rise in temperature being expressed in millimeters of thermometer E_m, since our object at this time was not to determine the actual quantity of heat developed, but to investigate the points mentioned in the above headings.

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* It was found that this "join" would support a pressure of 7 or 8 inches of water without leakage.

TABLE XVIII.—Experiments indicating that tr^3 = constant.
(t = time of rising 1 millim. r = rate of revolution in seconds.)

Date, 1892.	Weight.	Exp.	Range in millims. E_m.	Time in seconds.	r.	t.	tr^3 $\times 10^{-3}$.	Remarks.
July 12 . .	104·015	1	276–296	900·5	29·19	Preliminary.		Outer temp. 286·5 E_m.
„ 12 . .	. .	2	276–296	912·9	28·76	Stirrer not in adjustment.		
„ 12 . .	. .	3	279–294	832·3	27·34	55·49	1134	
„ 13 . .	. .	4	279–294	533·9	31·71	35·60	1135	
„ 13 . .	. .	5	279–294	845·6	27·27	56·37	1143	
„ 13 . .	. .	6	279–294	907·0	26·62	60·47	1141	
„ 13 . .	. .	7	279–294	466·9	32·95	31·13	1114	Motor very irregular.
„ 14 . .	. .	8	279–294	803·0	27·70	53·53	1138	
„ 14 . .	. .	9	279–294	628·2	30·05	41·88	1137	
							1134	
July 14 . .	194·200	10	281–292	642·1	30·13	58·37	1596	Outer temp. 286·5 E_m.
„ 14 . .	. .	11	283–290	507·4	28·01	72·49	1593	
„ 14 . .	. .	12	281–292	514·8	32·38	46·80	1590	
„ 14 . .	. .	13	283–290	618·3	26·33	88·33	1511	
„ 15 . .	. .	14	281–292	711·9	29·15	64·72	1603	
„ 15 . .	. .	15	280–293	643·7	31·87	49·37	1603	
„ 15 . .	. .	16	282–291	648·5	28·11	72·06	1600	
							1600	
July 18 . .	194·190	31	283–290	483·1	28·62	69·01	1619	Outer temp. 285·5 E_m.
July 15 . .	239·73	17	283–290	439·6	30·78	62·74	1830	Outer temp. 286·5 E_m.
„ 15 . .	. .	18	283–290	628·2	27·44	89·74	1850	
„ 16 . .	. .	19	283–290	544·6	28·73	77·80	1846	
							1842	
July 18 . .	239·27	30	283–290	606·0	27·69	86·57	1839	1843 for wt. 239·73.
July 16 . .	285·37	20	282–291	767·0	29·10	85·22	2100	Outer temp. 286·5 E_m.
„ 16 . .	. .	21	280–293	909·2	30·98	69·95	2080	
„ 16 . .	. .	22	283–290	793·7	26·60	113·4	2134	
„ 16 . .	. .	23	283–290	711·2	27·57	101·6	2129	
„ 17 . .	. .	24	282–291	841·1	28·39	93·45	2138	
„ 17 . .	. .	25	282–291	703·8	30·02	78·20	2116	
„ 17 . .	. .	26	282–291	735·3	29·68	81·70	2135	
							2119	
July 17 . .	275·40	27	283–290	608·9	28·82	87·00	2081	Outer temp. 286·5 E_m.
„ 17 . .	. .	28	282–291	635·5	30·61	70·61	2025	
„ 18 . .	. .	29	282–291	821·5	28·39	91·27	2089	
							2065	

From the above results we drew the following conclusions :—

(1.) That under the same conditions the quantity of heat developed was the same.

(2.) That the work done increased slightly with the mass of water.

(3.) That tr^3 was a constant quantity.*

If Nos. 1 and 3 were established, No. 2 was of little consequence, as we proposed to determine the heat developed for each mass of water.

When it is remembered that our "rate" varied in the above experiments from 26 to 34 revolutions per second, the close approximation of tr^3 to a constant is remarkable, and, as we proposed to maintain a rate of, as nearly as possible, 30 revolutions per second throughout our experiments, it was evident that any assumption based on this conclusion, could lead to no appreciable error. Again, a considerable variation in the value of tr^3 would have but little effect on the value of t, *i.e*, the time of rising 1° C.

These experiments were regarded as only preliminary, and no special care was taken with regard to external temperature or pressure, and, it is probable, that many of the apparent discrepancies arose from such causes. Again, when the movement of the mercury column was so slow that from 50 to 100 seconds were taken in rising 1 millim., it was difficult to estimate with great precision the time of apparent contact of the mercury column and the spider wire of the telescope. Personal errors of this description must, however, in the long run, tend to "mean out" and give a true average.

Had we been able to bring our mechanical arrangements to such perfection that the rate of revolution was absolutely constant, it would have rendered the above investigation unnecessary, for the stirring correction would have been constant whenever the mass of water was the same.

Although by the pressure regulator, described p. 378, the regularity of the motor was increased to an extent which those accustomed to the behaviour of these instruments hardly anticipated, we were unable to ignore the residual variations. It was, therefore, necessary to record the revolutions (the time per 1000 being taken in each case) throughout all our experiments. The labour, both of observing and calculating, was thereby greatly increased; but as we had no better means at our disposal, we had to submit to the inevitable.

The establishment of the law that (with this stirrer) tr^3 might be regarded as constant, enabled us to apply with certainty the necessary corrections.

As previously stated, our object was to deduce the rise in temperature per 1 second, at rate 30. If t is time of rise of 1° in any scale, then $1/t = \mathrm{K}r^3$, therefore, $\delta \,.\, 1/t = 3\mathrm{K}r^2 \,.\, \delta r$. Knowing $1/t_2$ (the rise per 1 second at any observed rate), and $1/t_1$ (the rise at rate 30), we know $1/t_1 - 1/t_2$, that is the term required to reduce the observation to the rate 30.

The accuracy of the correction can be estimated by means of the above table. For

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* t = time rising 1° (in any scale), in seconds.
r = rate of revolution, *i.e.*, number of revolutions per second.

example, the mean value of tr^3 for the weight 194·20 is 1600, the greatest departure from the mean is 1611 in Experiment 13. By assuming $tr^3 = 1600$, we find the rise per 1 second at rate 30 = ·001687 (expressed in millims. of E_m), whereas if we assume that $tr^3 = 1611$ and correct Experiment 13 (rate 26·33) to rate 30, we get ·001676.* Again, the mean value of tr^3 for weight 285·37 is 2119, which gives the rise at rate 30 as ·001274. Experiment 22 (rate 26·60) is an extreme case; this would give ·001265 at rate 30.

Experiment 7 (weight 104·02) shows a greater divergence from the mean value, since it would give a rise of ·00242 per 1 second as against ·00238, the value as given by the mean tr^3. As, however, we discarded all J experiments where the weight of water was less than 130 grms., this extreme case did not affect our results.

During our J experiments our rate was always between 29 and 31 (generally between 29·8 and 30·2), hence the divergences in the cases, above selected, are far greater than any which occurred during our experiments.

The value of tr^3 appeared to increase very regularly as the quantity of water increased, and thus changes in its value caused by small changes in the mass could be deduced. Thus experiment 30 (239·27 grms.) gave a value of 1839. Hence we deduced that, if the weight of water was 239·73 (as in Nos. 17 to 19), the value of $tr^3 = 1843$ as against 1842, the mean of the actual experiments with the latter weight.

Had the work done by the stirrer been independent of the quantity of water, we could have deduced the water equivalent of the calorimeter from the values of tr^3, for, if K_1, K_2, etc., are the values of tr^3 when W_1, W_2 are the weights, we have $\frac{W_2K_1 - W_1K_2}{K_2 - K_1}$ as the value of the water equivalent. Using the values of K deduced from Table XVIII., we get

W.	K.	Water equivalent.	M/K.
104·02	1134	115·5	·1418
194·20	1600	105·7	·1740
239·73	1843	73·5	·1769
285·37	2119		·1753

We ultimately ascertained that the water equivalent was as nearly as possible 86·0. Assuming this value and denoting by M the mass of contained water + water equivalent, then, if the work done by the stirrer was constant, M/K would be constant The numbers in the last column show that the quantity of heat developed increases rapidly at first and arrives at a maximum.

This maximum, as well as we can estimate, occurs when the quantity of water is

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* We required but *three* significant figures when we applied a similar correction to our J experiments.

sufficient to fill the calorimeter to about the top of the tube up which the water is thrown, and it is possible that the conditions would, at this depth, change slightly.

In any case, the work done by the stirrer alters but very little as the height of water changes, provided that 130 cub. centims. is regarded as the minimum quantity.*

The examples given above show that the limit of error introduced by applying this method of reduction to variations far exceeding any occurring during our experiments is less than 1 per cent., and as the heat generated by the stirrer during the majority of our 1892 experiments varied from about $\frac{1}{9}$ to $\frac{1}{16}$ of the heat due to the current, it is evident that any error must be less than $\frac{1}{1000}$ of the whole supply. Bearing in mind the small variations which actually occurred, we may safely regard the limits of error as a small fraction of this $\frac{1}{1000}$.

As will be seen later on, we performed an experiment in which the current was so diminished that the stirring supply was half that due to the current (see J 9), and another in which the current was so increased that the proportions were as 1 : 20 (see J 34). Any inaccuracy in the determination of the stirring supply would have caused considerable divergence in the corrected results; but the numbers obtained are themselves a proof of the accuracy of the method adopted. (See note, p. 406.)

It appeared possible that changes in the viscosity of water at different temperatures would have an influence on the results.

This may be the case, although our experiments do not lead to that conclusion (see p. 448). If so, however, it would not affect us, for the total heat lost or gained by the calorimeter at different temperatures (independently of the current supply) was directly determined for each weight of water, and therefore although our values of the radiation coefficient, &c., might be modified, the expression for the total loss or gain would remain unchanged.

Want of time alone prevented our investigating this matter more fully, but the consideration that neither the value of J, nor the changes in the specific heat of water would be affected thereby, justified its postponement to another season.

No use was made of the numbers obtained in Table XVIII.; our only object being to establish the law $tr^3 = K$. This was fortunate, for on afterwards examining the water used for this series we had reason to believe that it had become slightly soiled. We found that the lead ring used in the calorimeter lid had been insufficiently gilded, and also we had not allowed the gutta-percha varnish, which we used as a "size" for the gold leaf, to harden sufficiently before introducing the water.

The results of nearly ninety additional experiments of a similar kind indicate that the irregularities of the numbers in the above table are unusual, and that the actual values of tr^3, obtained from them, are unreliable, but that the conclusion drawn (viz., that under the same circumstances tr^3 is a constant) is correct.

Very small changes in the adjustment caused considerable changes in K, but its

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* This minimum quantity, 130 cub. centims., is deduced from the results of later experiments.

value remained constant so long as the adjustment was unaltered. Any alteration in the fixing of the stirring shaft necessitated a re-determination of K.

After experiment J 19, the whole apparatus was taken to pieces. It was then found that small fragments of gutta-percha had, by the continued impact of the water, been detached from the ring of gutta-percha which had been placed between the cooling tube and the tube down which it passed. Many of these fragments had collected beneath the base of the cylinder at B* and must have considerably impeded the flow of water. In consequence, therefore, before putting the apparatus together again, we removed all remaining gutta-percha surfaces which were exposed to the action of the water. The values obtained for K were, from this time, very different from preceding ones, and, once obtained, remained constant as long as the same mass of water was used.

The experiments J 20 to 34, are in better agreement amongst themselves than the earlier ones, and the cause no doubt is that just indicated.

The mean result of the earlier experiments is satisfactory as likewise the mean time of each experiment, but the times over small ranges (especially in experiments Nos. J 5 to 12) leave much to be desired. The fact that the quantity of heat developed by the stirrer was increased by the removal of the gutta-percha fragments is a proof that the flow of water was appreciably diminished by the obstruction.

SECTION XII.—THE GAIN OR LOSS BY RADIATION, &C.

It has already been pointed out that the method of observation adopted enabled us to determine, with sufficient accuracy, the total loss or gain of heat per second at any temperature, apart from the supply due to current. We propose to use the phrase "non-electrical supply" to denote heat due to all other sources than the current.

By the method described in Section XI., we were enabled to deduce the rise per second when the rate of revolution of the stirrer was 30, although the actual rate differed slightly from our standard one. The rate of rise, when radiation, &c., was eliminated, was first ascertained by noting the time of a small rise across the outside temperature. The temperature of the calorimeter was then gradually raised through the whole range by means of stirring only, and the times ascertained of small changes at the different temperatures. Assuming the "stirring heat" to be the same at all temperatures (when the rate is the same), we can deduce the radiation coefficient. (By radiation coefficient we denote the loss or gain in temperature per second, due to the combined effects of radiation, conduction, and convection, for a difference in temperature of 1° C).

One advantage of this method is, that all observations of temperature are taken on

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* Plate 2, fig. 2.

a rising thermometer, for "sticking" is far less likely to occur when the mercury is advancing than when receding.

We have found that all observations of slowly falling temperatures (when taken with a mercury thermometer) are unsatisfactory for the above reason. Again, the conditions resemble more nearly, in every respect, those prevalent during a "J" experiment. On this account, we did not desire to reduce the "stirring heat," even if we had been able to do so, since the loss, due to radiation, &c., would, at the higher portions of the range, have mastered the stirring supply, and the observations would have had to be taken on a falling thermometer, a mode of observation which, guided by the results obtained in previous years, we had decided to reject.

It appeared unlikely that NEWTON'S Law of Radiation would hold over our range, and we anticipated a decided curvature in the line showing our "non-electrical supply."

We first proceeded to determine isolated points on this curve (ordinate = rise in temperature per second, abscissa = difference in temperature between the calorimeter and the outside temperature), but these appeared to fall so nearly on a straight line, that we decided to follow its course over our range of temperature, using a small mass of water so that the changes in the value of the rise should be as marked as possible. A very large number of experiments were made in order to decide this point—for, if the exponential formula given by DULONG and PETIT holds, the curvature ought to have been marked. Although changes in the specific heat of water and of the calorimeter would influence the inclination of the line, it appeared unlikely that they would affect it in such a manner as to straighten it; and further, the effect of such changes would alter as the mass of water changed.*

The numbers alone resulting from these observations half fill a large note-book, and to give them in full would occupy too much space. As an example, we venture to give experiments 51 to 54, exactly as they appeared in our notes. As the method employed never varied, we will, in other cases, simply give results, and we select this series because it was the first done by us with the object of tracing the "non-electrical supply" curve throughout the greater part of our range.

The numbers in the columns marked "time," are those given by the chronograph tape. New tapes were used after the readings at 343, 407, and 458, and the times of rising between these temperatures were not noted; therefore, the experiments at those ranges are numbered as separate experiments although taken consecutively.

No temperatures were taken whose readings ended in 0 or 5 because, as these were

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* We may state at once that (although some slight signs of curvature are visible when the mass of water is great) by assuming the non-electrical supply to be a linear function of the temperature (when the rate of stirring is constant), we introduce no error sufficient to affect our results, and this conclusion is based on the data supplied by more than 100 "stirring and radiation" experiments. If the results were expressed in terms of the mercury thermometer scale, the curvature would, of course, be marked.

denoted by longer lines on the thermometer scale, the time of contact with the "spider wire" was not sufficiently definite, and the thickness of the graduation would have made a considerable difference in the value of *t*.

We did not attempt to record the time for every individual 1000 revolutions, but sufficient observations were taken to enable us to detect any change in rate.

The pressure in the annular space round the calorimeter was high (·98 millim.) during experiments 51 to 54, as we had only recently commenced re-exhausting.

TABLE XIX.—Experiment LI. Aug. 11, 1892.

McLeod gauge = 62 millims. Outside temp. = 241·3 A, = 300E$_m$.
Pressure = ·98 millim. Mass of water (*in vacuo*) = 103·01 grm.
Clock error = + ·0004125.

Experiment.	Temperature E$_m$.	Time.	Revolutions.	Time.
		seconds.	thousands.	seconds.
LI.	86	111·0	6	0·8
	87	137·9	8	67·6
	88	164·8	10	134·0
	89	193·0	1	167·4
	91	248·4	2	200·7
	92	275·9	3	234·3
	93	302·5	4	267·7
	94	330·2	5	300·9
	96	386·0	6	334·0
	97	412·5	7	367·3
	98	..	9	433·5
	99	469·3	21	501·0
	101	524·4	2	533·9
	102	552·8	3	567·2
	103	579·8	4	601·0
	104	609·8		
	..	..	38	1065·2
	121	1095·6	9	1098·4
	122	1124·2	40	1131·6
	123	1154·4	1	1164·8
	124	1183·3	2	1197·9
	126	1244·3	4	1264·6
	127	1274·0		
	128	1304·0	7	1364·7
	129	1334·2	8	1397·8
	131	1394·6	50	1463·9
	132	1425·4	1	1497·3
	133	1455·3	2	1530·5
	134	1485·0	53	1563·5
	136	1546·0		
	..	..	76	2332·4
	161	2345·9	7	2365·8
	162	2379·4	8	2399·3
	163	2412·0	9	2432·6
	164	2444·9	80	2466·0
	166	2511·2	1	2499·3
	167	2544·0	3	2565·8
	168	2578·0	4	2599·4
	169	2611·7	5	2632·5
	..	..	109	3435·0

Table XIX.—continued.

Experiment.	Temperature E_m.	Time.	Revolutions.	Time.
		seconds.	thousands.	seconds.
LI.	193	3440·9	110	3468·3
	194	3477·5	1	3501·6
	196	3548·0	3	3568·2
	197	3583·8	4	3601·8
	198	3619·6	5	3635·0
	199	3656·6	6	3668·5
	201	3727·2	7	3701·7
	..	..	8	3735·0
	226	4665·0	145	4633·2
	227	4704·5	7	4699·9
	228	4743·0	8	4733·2
	229	4782·0	9	4766·6
	231	4859·9	150	4800·0
	232	4900·0	1	4833·3
	233	4939·2	2	4866·6
	234	4978·8	4	4932·9
	..	..	155	4966·2
	252	5719·8	178	5732·0
	253	5762·9	180	5798·9
	254	5806·7	2	5865·9
	256	5892·1	4	5932·4
	257	5935·8	6	5999·3
	259	6023·0	8	6066·0
	261	6110·6	190	6132·8
	262	6154·6	2	6199·3
	276	6787·7	210	6797·6
	277	6834·6	2	6864·3
	278	6881·9	5	6964·4
	279	6929·4	6	6997·5
	281	7021·3	8	7064·0
	282	7071·5	9	7097·3
	296	7763·0	240	7797·7
	297	7813·7	1	7831·0
	298	7864·7	3	7897·8
	299	7917·1	245	7964·5
	301	8020·9	6	7998·0
	302	8073·4	8	8064·9
	303	8127·0	250	8131·9
	304	8179·4	2	8198·6
	306	8285·9	4	8265·6
	322	9163·7	280	9133·5
	323	9220·8	3	9234·2
	324	9277·9	5	9301·4
	326	9393·5	7	9368·0
	327	9452·2	9	9435·4
	328	9510·6	291	9502·2
	337	10044·7	307	10038·0
	338	10104·8	310	10138·9
	339	10167·3	2	10206·0
	341	10290·8	4	10272·5
	342	10350·2	6	10339·2
	343	10411·5	8	10406·0

TABLE XX.—Experiment LII.–LIV. Aug. 11, 1892. The constants are the same as for LI.

Experiment.	Temperature E_m.	Time.	Revolutions.	Time.
		seconds.	thousands.	seconds.
LII.	403	1·0	0	15·0
	404	93·7	3	116·4
	406	281·6	6	217·1
	407	378·5	10	352·3
	408	472·0	3	453·4
	409	465·5	6	554·2
	411	757·4	9	655·0
			21	722·0
LIII.	456	1·0	3	36·8
	457	149·6	6	137·4
	458	297·4	10	271·6
	459	438·5	4	405·5
	461	732·0	22	673·6
	462	883·7	8	875·6
LIV.	507	1·1	3	13·8
	508	290·5	10	247·8
	509	560·2	2	314·4
	511	1179·9	20	580·3
			39	1215·2

Method of reducing the results in the above Table.

The time over any range is the mean time obtained by taking the observations in pairs—thus the time over the range 87·5–97·5 E_m is the mean of the times taken in rising from 86–96, 87–97, 88–98, and 89–99. Thus each number in column 4 of the following Table is the mean of, at least, four intervals of time.

TABLE XXI.

Range E_m.	Range C.	Mean Temperature C.	Time.	Rate of stirring.	$\frac{\text{Range}}{\text{Time}} \times 10^6$	(Correction to rate 30) $\times 10^6$.	(Rise, in degrees, per second at rate 30) $\times 10^6$.	Calculated rise $[\sigma \pm \rho(\theta_1 - \theta)] \times 10^6$.	Difference between last two columns.
87·5– 97·5	·242	14·110	274·4	30·01	883	0	883	880	+ 3
92·5–102·5	·242	14·232	277·6	30·00	873	0	873	871	+ 2
102·5–122·5	·487	14·597	572·9	30·14	851	− 7	844	844	0
122·5–132·5	·246	14·963	300·8	30·07	816	− 3	813	817	− 4
127·5–162·5	·864	15·395	1106·9	29·96	780	+ 2	782	784	− 2
167·5–197·5	·740	16·321	1041·2	29·93	711	+ 4	715	716	− 1
197·5–227·5	·742	17·063	1122·1	30·03	661	− 1	660	661	− 1
227·5–232·5	·124	17·495	195·9	30·02	632	− 1	631	629	+ 2
232·5–252·5	·498	17·805	822·1	30·02	606	− 1	605	605	0
257·5–277·5	·504	18·432	901·2	30·02	560	− 1	559	559	0
277·5–297·5	·510	18·940	981·6	29·98	520	+ 1	521	521	0
297·5–302·5	·128	19·260	259·7	29·92	493	+ 4	497	497	0
302·5–322·5	·512	19·580	1092·7	29·92	469	+ 4	473	473	0
322·5–337 5	·382	20·028	883·2	29·83	433	+ 8	441	440	+ 1
327·5–342·5	·383	20·156	900·2	29·86	425	+ 7	432	431	+ 1
404·5–409·5	·130	22·002	473·3	29·69	275	+ 16	291	293	− 2
456·5–461·5	·133	23·367	732·9	29·74	181	+ 10	191	192	− 1
507·5–510·5	·081	24·701	879·5	29·96	92	+ 2	94	93	+ 1

Mean rise due to stirring alone = ·0004971.

Hence $tr^3 = 5420 \times 10^4$. (The "Correction to rate 30" is deduced from this value of tr^3.)

The outside temperature throughout the above experiments was 19°·260 C. The actual observation across that temperature was over a range of 0°·128 C. only, and an error of 0°·001 C. in the range would make a difference of 4 in the number in the last column. As the rise at this point was one of the most important of all, a straight line was drawn through the numbers obtained from the pairs of observations on each side of it, the resulting value being ·000497. Assuming this to be the rise due to stirring only (at rate 30), we get radiation coefficient $(\rho) = (\gamma - {\cdot}000497)/(19{\cdot}260 - t)$, where γ is rise (gain) per second due to all non-electrical sources.

The mean temperature of the first four observations is 14°·475 C., and the mean value of $\gamma = {\cdot}853 \times 10^{-6}$, hence

$$\rho = {\cdot}000744.$$

The straightness of this "non-electrical supply line" is a matter of extreme importance, as if there were any marked curvature it would seriously affect our conclusions as to the specific heat of water. In the last columns of the above Table we give the numbers obtained by direct calculation, assuming $\rho = {\cdot}000744$ and $\sigma = {\cdot}000497$, also the difference between the calculated and experimental results. The irregularities are obviously experimental ones, and are to be expected when it is remembered that an error of 0°·001 C. in the "range" would account for nearly all of them. Again, we are here dealing with our smallest mass of water, and the individual experiments are in better agreement when the depth of water is greater. The even distribution of the numbers about a straight line is rendered more evident to the eye when plotted on a large scale than when presented in rows of figures. The Table also illustrates the accuracy of the correction for differences in rate of stirring.*

Assuming the value of the water equivalent of the calorimeter as 85·70, the value of M (mass of water + water equivalent) = 103·01 + 85·70 = 188·71, we get ·0140 as the number of thermal grammes lost or gained by radiation, &c., per second for a difference in temperature of 1° C.

In order to test to what extent any change in the viscosity of the water caused a change in the stirring heat, we performed a few experiments with different external temperatures.

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* This "non-electrical supply curve" being a straight line, we are enabled to deduce the values of both ρ and σ by two experiments only, conducted at any two different temperatures.

TABLE XXII.

Date.	Exp.	Range E_m.	Range C.	Mean temperature and temperature of outer bath.	Time.	Rate.	$\frac{\text{Range}}{\text{Time}} \times 10^6$.	(Rate correction) $\times 10^6$.	(Rise per second at rate 30) $\times 10^6$.
Aug. 12, 1892	LV.	87·5–108·5	·509	14·251	1009·2	29·99	504	+ 1	505
"	LVI.	394·5–409·5	·389	21·873	802·7	29 80	485	+10	495
"	LVII.	494·5–503·5	·241	24·433	470·9	30·21	512	−11	501

As we regarded these experiments only as preliminary, they were somewhat hurriedly performed, and we proposed investigating this point more fully later on. It has been previously pointed out (p. 440) that, in any case, the conclusions arrived at would not affect our results, and we only give them to show that no marked change is indicated. Some similar experiments performed in 1891 had led to the same conclusion.

During this year's (1892) experiments we were not troubled by any air, or water, leakages into the annular space between the calorimeter and the steel chamber. A great portion of our time and attention in previous years having been devoted to leak-hunting, we had considerable (unwished for) opportunities of investigating the effects of changes of pressure, or alterations in the dryness of the surrounding medium.

The smallest trace of moisture has a most astonishing effect on the radiation coefficient. The change in the rate of rise is most marked, and if the moisture present is sufficient to saturate the space when the calorimeter is cooled down, all attempts to obtain a radiation coefficient are hopeless. Any trace of aqueous vapour could immediately be detected by its effect on the rate of rise, and on one or two occasions was sufficient to prevent any rise whatever.

Considerable effect was also caused by changes in pressure, and when comparing the results obtained from different masses it must be remembered that the pressure was frequently changed. Although we were then not conscious of the full importance of this point, we endeavoured to maintain the pressure unaltered from the time that any set of stirring determinations were made until the corresponding J experiments were completed.

Results of the Stirring and Radiation Experiments.

Throughout the remainder of this section the following notation is adopted :—

W = weight of water (*in vacuo*).
$M = W +$ water equivalent of calorimeter.
p = pressure in annular space.
t = time of rising 1° C.
r = rate of revolution of stirrer (revolutions per 1 second).
K = value of tr^3.
σ = rise per 1 second (in degrees C.) due to stirring only.
ρ = gain or loss (in degrees C.) per 1 second due to radiation, conduction, and convection, when the difference of temperature = 1° C.
Q = thermal grms. lost or gained per 1 second by radiation, conduction, and convection = $M\rho$.

Experiments 1 to 31 (see Table XVIII.).—These were all observations taken acros the outside temperature only, and were used to establish the relation $tr^3 = K$.

Experiments 32 to 40.—Are only of use for the same purpose, but they bear out the conclusion that $tr^3 = K$.

As the calorimeter was taken to pieces after Experiment 40 (before any of our J experiments were commenced) the results are of no special value.

Experiments 41 to 50 :—

$$W = 103{\cdot}01$$
$$\sigma = {\cdot}000498$$
$$\rho = {\cdot}0000743$$
$$Q = {\cdot}0104. \quad p = 1{\cdot}15 \text{ millims.}$$

Experiments 51 to 57.—(Tables XIX., XX., and XXII.) (Nos. 41 to 54 were used in the reduction of J 1 to 4.)

Experiments 58 to 65.—During this series the value of σ began to show signs of alteration. The cause has already been mentioned; flakes of gutta-percha having collected at the base of the inner cylinder, the "throw" of the stirrer became less regular. Also (as we were not at this time aware of the importance of maintaining the pressure unaltered), we both diminished and increased the pressure during this series. Fortunately, however, we performed sufficient radiation experiments to enable us to deduce the probable values of the variables appropriate to the respective J determinations. $W = 188{\cdot}065$ throughout this series.

Experiments 58 and 59 :—

$$\left.\begin{array}{l} \sigma = {\cdot}000354 \\ \rho = {\cdot}000490 \\ Q = {\cdot}0134. \quad p = {\cdot}40 \text{ millim.} \end{array}\right\} \text{J 5 to 7.}$$

Experiments 60 and 61 :—

$$\left.\begin{array}{l}\sigma = \cdot000358\\ \rho = \cdot000478\\ Q = \cdot0131. \quad p = \cdot37 \text{ millim.}\end{array}\right\} \text{J 8 and 9.}$$

Experiments 62 to 65 :—

$$\left.\begin{array}{l}\sigma = \cdot000360\\ \rho = \cdot000483\\ Q = \cdot0132. \quad p = \cdot37 \text{ millim.}\end{array}\right\} \text{J 10 to 12.}$$

Experiments 66 to 80.—The cause of irregularity had not yet been ascertained, and therefore not removed. During this series we made several changes in the connections between the stirring rod and the revolving shaft above it, and also in the pressure around the calorimeter.

W = 277·971 throughout this series.

Experiments 66 to 71 :—

$$\left.\begin{array}{l}\sigma = \cdot000276\\ \rho = \cdot000361\\ Q = \cdot0131, \quad p = \cdot37 \text{ millim.}\end{array}\right\} \text{J 13 and 14.}$$

Experiments 72 and 73.—The position of the revolving shaft and counter was slightly altered, and the whole of this portion of the apparatus re adjusted.

$$\left.\begin{array}{l}\sigma = \cdot000272\\ \rho = \cdot000374\\ Q = \cdot0136. \quad p = \cdot38 \text{ millim. ?}^{*}\end{array}\right\} \text{J 15 and 16.}$$

Experiments 74 to 78.—The double HOOKE's joint was now removed and replaced by a single one in the hope of diminishing the vibration of the stirring rod, the pressure was at the same time somewhat reduced.

The value of σ showed considerable alteration.

$$\left.\begin{array}{l}\sigma = \cdot000267\\ \rho = \cdot000363\\ Q = \cdot0132. \quad p = \cdot37 \text{ millim.}\end{array}\right\} \text{J 17 and 18.}$$

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[*] There is probably some error here. We have only a single note of the pressure during this day (August 28), and we have no means of checking it since Experiment 74 was not performed until August 30. Now (as we find recorded in our notes), we gave twenty-three strokes to the mercury pumps on August 29, the resulting pressure on August 30 being ·37 millim.; it appears almost certain, therefore, that the pressure on August 28 must have exceeded ·38 millim.

Experiments 79 and 80.—The simple HOOKE's joint was now replaced by a light ring of wire, which passed through holes in the stirring rod and the revolving shaft.

$$\left.\begin{array}{l}\sigma = \cdot000272 \\ \rho = \cdot000374 \\ \mathrm{Q} = \cdot0136. \quad p = \cdot44 \text{ millim.}\end{array}\right\} \text{J } 19.$$

It thus appeared that both σ and ρ had resumed their former values.

Experiments 81 and 82.—These two experiments were intended to be the first pair of a series. On commencing J 20, the same evening (September 4), it was discovered that the coil in the calorimeter had become loose. The calorimeter had, in consequence, to be taken to pieces, and a week elapsed before we were able to resume our J determination. These two experiments are consequently of no use, but they are interesting as showing the kind of accuracy obtainable.

$$\begin{array}{l}\mathrm{W} = 140\cdot270. \\ \sigma = \cdot000439. \\ \rho = \cdot000578. \\ \mathrm{Q} = \cdot0130. \qquad p = \cdot36 \text{ millim.}\end{array}$$

Experiments 83 to 93.—After Experiment 82 a marked difference is observable in the value of σ. Between September 4 and 10 the calorimeter had been thoroughly cleaned, and all gutta-percha surfaces removed from its interior. The "throw" of the stirrer was evidently improved, and as a consequence the value of σ was raised.

The series of J Experiments (Series II., J 20 to 34), performed after this change, are so much superior to their predecessors that we base our conclusions almost entirely upon them. We feel it right, therefore, to give more particulars concerning their "non-electrical supply" determinations than we have considered necessary in the case of Series I. (J 1 to 19). The following table is a summary of the "stirring experiments" used in the reduction of J 20 to 25.

TABLE XXIII.—W = 139·776.

Date.	Range E_m.	Range C.	Time.	Rate.	$\frac{\text{Range}}{\text{Time}}$.	Rate correction × 10^6.	Rise at rate 30.	Mean temperature C.
Sept. 10 .	292·5–307·5	·384	752·05	29·93	·000510	+ 3	·000513	19·260
„ 10 .	87·5–127·5	·973	1173·43	30·35	·000829	− 18	·000811	14·476
„ 10 .	292·5–307·5	·384	746·75	30·07	·000514	− 4	·000510	19·260
„ 11 .	292·5–307·5	·384	733·6	30·18	·000523	− 9	·000514	19·260
„ 11 .	292·5–307·5	·384	753·22	29·96	·000510	+ 2	·000512	19·260
„ 11 .	442·5–452·5	·263	899·23	30·31	·000293	− 13	·000280	23·064
„ 13 .	292·5–307·5	·384	723·05	30·20	·000522	− 10	·000512	19·260
„ 13 .	87·5–127·5	·973	1168·85	30·39	·000832	− 20	·000812	14·476
„ 13 .	442·5–452·5	·263	890·65	30·30	·000296	− 15	·000281	23·064

Hence

$$\left.\begin{aligned} {}^{*}\sigma &= \cdot000512, \text{ therefore } tr^3 = 5273 \times 10^4 \\ \rho &= \cdot000620 \\ Q &= \cdot0140. \qquad p = 1\cdot15 \text{ millims.} \end{aligned}\right\} \text{ J 20 to 25.}$$

Experiments 94 to 102.

TABLE XXIV.—W = 199·674.

Date.	Range E_m.	Range C.	Time.	Rate.	$\frac{\text{Range}}{\text{Time}}$.	Rate correction × 10^6.	Rise at rate 30.	Mean temperature C.
Sept. 14 .	292·5–307·5	·384	898·68	30·10	·000428	− 4	·000424	19·260
„ 14 .	442·5–452·5	·263	1161·05	29·81	·000227	+ 8	·000235	23·064
„ 14 .	442·5–452·5	·263	1110·62	30·04	·000237	− 2	·000235	23·064
„ 14 .	87·5–127·5	·973	1481·7	30·16	·000657	− 7	·000650	14·476
„ 15 .	292·5–307·5	·384	856·65	30·52	·000448	− 22	·000426	19·260
„ 15 .	87·5–127·5	·973	1519·8	29·77	·000640	+ 10	·000650	14·476
„ 16 .	292·5–307·5	·384	880·98	30·25	·000437	− 11	·000426	19·260

Hence

$$\left.\begin{aligned} \sigma &= \cdot000426, \text{ therefore } tr^3 = 6353 \times 10^4 \\ \rho &= \cdot000485 \\ Q &= \cdot0138. \qquad p = \cdot48 \text{ millim.} \end{aligned}\right\} \text{ J 26 to 29.}$$

Experiments 103 to 110.

TABLE XXV.—W = 259·500.

Date.	Range E_m.	Range C.	Time.	Rate.	$\frac{\text{Range}}{\text{Time}}$.	Rate correction × 10^6.	Rise at rate 30.	Mean temperature C.
Sept. 16 .	292·5–307·5	·384	1081·6	30·03	·000355	− 1	·000354	19·260
„ 17 .	292·5–307·5	·384	1025·7	30·50	·000374	− 18	·000356	19·260
„ 17 .	87·5–127·5	·973	1816·5	29·78	·000536	+ 8	·000544	14·476
„ 18 .	87·5–127·5	·973	1784·2	30·05	·000545	− 2	·000543	14·476
„ 18 .	292·5–307·5	·384	1081·8	30·03	·000355	− 1	·000354	19·260
„ 18 .	292·5–307·5	·384	1078·7	30·03	·000356	− 1	·000355	19·260
„ 18 .	442·5–452·5	·263	1335·7	29·88	·000197	+ 4	·000201	23·064
„ 18 .	442·5–452·5	·263	1284·1	30·10	·000205	− 4	·000201	23·064
„ 18 .	452·5–462·5	·265	1278·6	29·78	·000207	− 14	·000193	23·327

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* The values of σ and ρ given at the end of the Tables are derived from large scale curves, and thus give the mean of all the observations.

Hence

$$\sigma = \cdot000355 \qquad tr^3 = 7606 \times 10^4$$
$$\rho = \cdot000399$$
$$Q = \cdot0138 \qquad p = \cdot48 \text{ millims.}$$

The reduction of our observations involved so much arithmetic that the whole series of experiments was concluded before we were able to get the results in the form now given.

Although we were prepared to find a rapid reduction in the value of Q as the pressure diminished, we had not realized the importance of small changes in the pressure. This was unfortunate, for, as the figures show, our average pressure was just that at which small alterations produced the greatest effect. We usually considered it sufficient to record the pressure each day, whereas it appears that a careful observation of the pressure during each stirring experiment ought to have been made. It is evident that we should have done better to select pressures of not less than 1 millim., and thus small variations would have had but little effect.

At the time of the observations we did not know the real value of the water equivalent. It was thus impossible for us to obtain Q with any accuracy, and it is only by the changes in the value of Q that the effects of changes in pressure are rendered evident.

The results compare very favourably with the conclusions arrived at by BOTTOMLEY.*

Collecting the numbers given in this section (with the exception of Experiments 72 and 73, see note, p. 450), we get

TABLE XXVI.

Date.	Experiment.	Mass of water.	Pressure in millims.	Thermal grms. per second.
Sept. 10–13 . . .	83– 93	139·78	1·15	·0140
Aug. 8–10 . . .	41– 50	103·01	1·15	·0140
„ 11	51– 54	103·01	·98	·0140
Sept. 14–16 . . .	94–102	199·67	·48	·0138
„ 16–18 . . .	103–110	259·50	·48	·0138
Aug. 26	79– 80	277·93	·44	·0136
„ 14–26 . . .	58– 59	188·07	·40	·0134
„ 24, 25 . . .	62– 65	188·07	·37	·0132
„ 30, 31 . . .	74– 78	277·93	·37	·0132
„ 26, 27 . . .	66– 71	277·93	·37	·0131
„ 17, 18 . . .	60– 61	188·07	·37	·0131
Sept. 4	81– 82	140·27	·36	·0130

These numbers are plotted in fig. 8 the abscissæ denoting pressures and the ordinates the number of the thermal grms. gained per second. When it is remembered that adjacent points are obtained from very different masses of water, the close agreement is a proof of the accuracy of the observations. The sudden change in the value of Q

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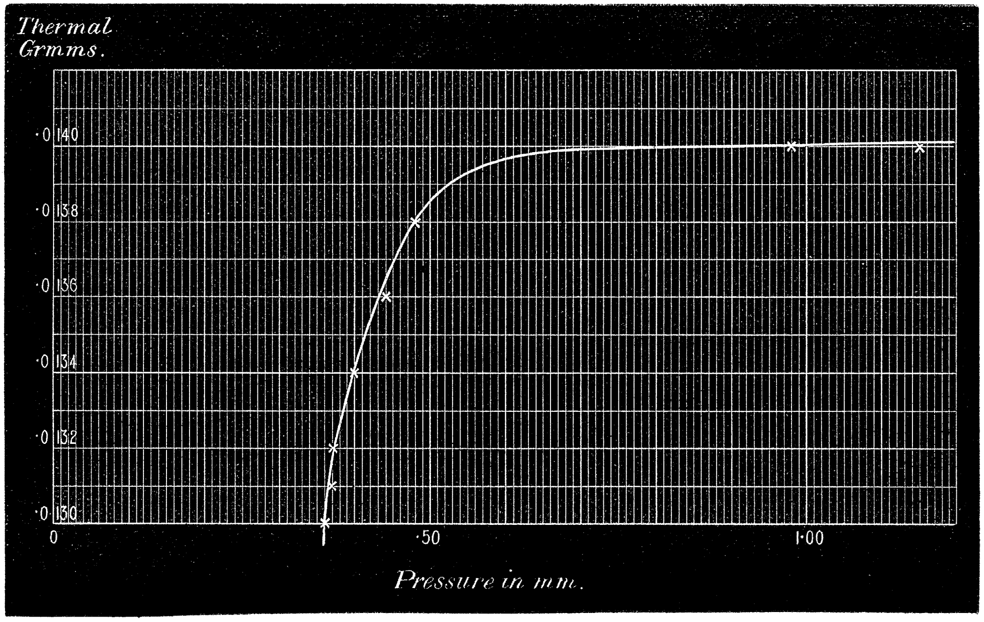
* 'Phil. Trans.,' 1887, A.

when the pressure falls below ·50 millim. is remarkable; but a reference to BOTTOMLEY's paper will show that the curve given by him is of a similar type, although the critical point is at a higher pressure and the bend in the curve is less sharp.

Fig. 8.



Although all the observations on the "non-electrical supply" have been brought together in this section for the purposes of comparison, they were not taken continuously but in groups. Each group of observations was used for the reduction of J experiments performed at the same time and on the same weight. The stirring experiments were usually performed during the daytime, the corresponding J experiments in the evening, and it was rarely that two sets of J observations were taken on the same day. Throughout the whole of the experiments J 1 to 34, as also their corresponding stirring experiments, the surrounding temperature was maintained at 300 E = 19·260 C.*

If θ_1 = temperature of calorimeter, then $(\theta_1 - 19{\cdot}260)\,\rho$ gives the rise or fall in temperature per second due to radiation, &c., hence $\sigma + (\theta_1 - 19{\cdot}260)\,\rho$, gives the rise in temperature per second due to the whole "non-electrical" supply. As previously pointed out (see note, p. 411) we proposed to reduce the numbers obtained from our J experiments at certain fixed temperatures and the following Table gives the changes in temperature per 1 second, due to the "non-electrical" supply at these points. The numbers were obtained from large-scale curves, but can be calculated from the values of σ and ρ given in this section.

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* In previous years we had performed several pairs of experiments in which the outside temperature was, in one case at the bottom, and in the other at the top, of our range. By "meaning" the reciprocals of the times of rising 1°, the effect of radiation, &c., could be eliminated. We hoped to repeat these experiments this year, but want of time prevented our doing so.

TABLE XXVII.—Rise per second due to non-electrical supply, at temperatures required for the reduction of the J experiments.

J (expts.) =	1–4.	5–7.	8–9.	10–12.	13–14.	15–16 and 19.	17–18.	20–25.	26–29.	30–34.
W =	103·010	188·065	188·065	188·065	277·931	277·931	277·931	139·776	199·674	259·500
$\sigma \times 10^6$ =	498	354	358	360	276	272	267	512	426	355
$\rho \times 10^6$ =	743	490	478	483	361	374	363	621	483	399
VALUE of $\{\sigma + \rho\,(19{\cdot}260 - \theta_1)\} \times 10^6$.										
Temp. C.										
14·477	853	587	587	591	449	451	441	809	658	546
15·581	771	534	534	538	409	410	401	741	604	502
16·682	690	480	481	485	369	368	361	672	551	458
17·683	615	431	433	436	333	331	324	610	502	418
18·688	541	382	385	388	297	293	288	548	454	378
19·835	455	326	331	332	255	250	246	476	397	332
21·115	360	263	269	270	209	203	200	397	336	281
22·409	264	200	207	208	162	154	153	316	273	229
23·862	156	128	138	138	110	100	100	226	203	171
25·006	71	78	83	82	69	57	58	155	148	125

The above Table is deduced from "stirring" experiments Nos. 41 to 110. Th values of ρ and σ, obtained by repeating an experiment under the same conditions, rarely show any difference as great as ·000004, and thus a difference from the mean value of ·000002 may be regarded as our limit of experimental error. Now a change of two in the last digit would, when 5 Clark cells were used, cause a difference of less than 1 in 4000 in the resulting value of J; but as the numbers in each column are obtained from independent experiments, and as all the columns are used in the final determination of J, it is probable that the mean resulting error is of very small dimensions.

[Note by E. H. G. Added April, 1893. The statement that the loss or gain by radiation, convection, and conduction is, in our apparatus, a linear function of the difference in temperature may at first sight appear to differ from the conclusions arrived at by DULONG and PETIT, MACFARLANE, and other observers, but I think that the contradiction is more apparent than real. The curve which shows the absolute loss or gain (fig. 8, p. 454) indicates that, if we had reduced the pressure to something under one-thousandth of a millimetre, the loss or gain by radiation, convection, and conduction might almost have been disregarded over our range, and hence it is evident that convection plays by far the greatest part at such pressures as those with which we were working; and the wonderful experiments of Professor DEWAR (the account of which had not been published when the preceding section was written) appear to place this conclusion on a firm foundation. Now DULONG and PETIT make the loss or gain by convection vary directly as the difference in temperature when the density of the gas remains constant. In our apparatus the density of the air surrounding the calorimeter must have remained nearly constant throughout each experiment, and therefore our observations appear to corroborate, rather than to contradict, the conclusions arrived at by DULONG and PETIT.]

SECTION XIII.—THE METHOD OF PERFORMING A J EXPERIMENT.

The general method of procedure was as follows.

Freshly distilled ether having been placed in the cooling tube, the temperature of the calorimeter was lowered until the resistance of the coil indicated a temperature of 10° C., any remaining ether was then withdrawn and dried air passed through the cooling apparatus for about ten minutes. The aspirating portion of the apparatus was removed and the cooling tube cleaned by a small mop of absorbent cotton wool. The open end was closed by a long cork, and a metal tube placed over the whole of the projecting portion, the lower end of this tube being washed by the tank water.

The storage circuit was then completed and the rheostat adjusted until the balance with the Clark cells was obtained. About twenty minutes elapsed before the temperature rose to 86 E_m—the point at which we commenced our observations. During this interval the chronograph circuit was tested, and any final adjustment of the motor and external circuit completed.

The task of one observer was invariably that of maintaining the potential balance by means of the rheostat, and also inverting the currents at regular intervals. The attention of the second observer was directed to recording the group of transits about each fixed point, the chronograph key being placed at the base of the telescope stand. In the intervals he recorded the times of the revolutions of the stirrer, which were distinguished on the tapes from the temperature records by double marks. He also occasionally recorded the readings of thermometer A (the external temperature), but these were as a rule so regular as to render this observation a matter of form.

Thus, during the progress of an experiment, no notes had to be taken unless some exceptional incident occurred. We believe this to be an important matter during observations of this description, for the mechanical operation of note-taking greatly distracts the attention.

The chronograph required rewinding about every twenty minutes, and in the press of the other observations this was sometimes forgotten. Some of the omissions in the tables are due to this cause. The duration of a whole experiment varied from 40 to 80 minutes, according to the weight of water present and the E.M.F. used.

At the end of an experiment, the chronograph tape was counted and the results tabulated in the form shown in Tables XXVIII. to XXXIII. These six experiments are typical of the rest, and have not been in anyway selected, except that they are the first performed on each weight, in Series II., with different E.M.F. s.

TABLE XXVIII.—Series II. J 20. September 11, 1892.

Weight of water (*in vacuo*) = 139·776 grms.

Clark Cells.* $n = 4$. Nos. **(37, 38, 39)**, **(40, 41, 42)**, **(43, 44, 45)**, **(46, 47, 48)**.

Temperature = 15°·05 C.

External temperature throughout experiment = 241·2 A = 300 E = 19°·260 C.

Pressure = ·97 millim.

Calorimeter cooled to 10°·00 C. before commencing experiment. Connections reversed at †.

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolutions.	Rate.
	seconds.		thousands.	seconds.	
86	7	. .	4	4	
87	11·8				
88	16·8				
89	21·8	. .	5	36·8	
Mean					
126	206	199	10	200·2	
127	211	199·2			
128	216	199·2			
129	221·2	199·4	11	233·2	
Mean	. .	199·2	. .	. .	30·54
176	464·2	258·2	17	431	
177	469·2	258·4			
178	474·7	258·7			
179	479·8	258·5	19	496·6	
†Mean	. .	258·45	. .	. .	30·37
216	673·8	209·6			
217	679·1	209·7			
218	684·5	209·8			
219	689·9	210·1	25	693·5	
Mean	. .	209·8	. .	. .	30·47
256	888·3	214·5	30	857·5	
257	893·8	214·7			
258	899·2	214·7			
259	904·8	214·9	32	922·8	
Mean	. .	214·7	. .	. .	30·53

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* The cells in brackets were placed in parallel arc.

TABLE XXVIII.—(continued).

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolutions.	Rate.
	seconds.		thousands.	seconds.	
296	1111·3	223	37	1087	
297	1116·9	223·1			
298	1122·7	223·5			
299	1128·3	223·5			
Mean	..	223·38	..	..	30·45
346	1398	286·7	46	1383·5	
347	1403·9	287			
348	1409·6	286·9			
349	1415·4	287·1			
Mean	..	286·93	..	..	30·35
396	1691·5	293·5			
397	1697·4	293·5			
398	1703·4	293·8			
399	1709·5	294·1	56	1712·4	
†Mean	..	293·75	..	..	30·41
446	1997·4	305·9			
447	2003·7	306·3			
448	2010·0	306·6			
449	2016·2	306·7	66	2039·6	
Mean	..	306·38	..	..	30·56
506	2380·8	383·4	76	2366·7	
507	2387·5	383·8			
508	2394·2	384·2			
509	2400·8	384·6	78	2431·5	
Mean	..	384	..	..	30·54
536	2579·8	199	82	2563·8	
537	2586·8	199·3			
538	2593·5	199·3			
539	2600·3	199·5	84	2629·7	
Mean	..	199·38	..	..	30·42

TABLE XXIX.—Series II. J 23. September 12, 1892.

Weight of water (*in vacuo*) = 139·776 grms.

Clark cells. $n = 3$. Nos. **(37, 38, 39), (40, 41, 42), (43, 44, 45)**. Temperature 15°·21 C.

External temperature. 241·2 A = 300 E = 19°·260 C. Pressure = ·78 millim.

Calorimeter cooled to 10°·10 C. before commencing experiment. Connections reversed at †.

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolution.	Rate.
	seconds.		thousands.	seconds.	
86	− 9·5 ?				
87	− 1·7				
88	6				
89	14	..	7	21	
Mean					
126	305·2	314·7 ?			
127	313·2	314·9			
128	321	315			
129	329·5	315·5	17	354·2	
Mean	..	315·03	..	..	30·01
176	714·2	409			
177	723·6	409·4			
178	731	410			
179	739·2	409·7	29	753·4	
†Mean	..	409·52	..	..	30·06
216	1050·3	336·1			
217	1058·7	336·1			
218	1067·3	336·3			
219	1076	336·8	40	1120	
Mean	..	336·33	..	..	30·01
256	1397·2	346·9			
257	1406	347·3			
258	1415	347·7			
259	1423·9	347·9	50	1453	
Mean	..	347·45	..	..	30·02

TABLE XXIX.—(continued).

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolution.	Rate.
	seconds.		thousands.	seconds.	
296	1760·9	363·7	59	1753·6	
297	1770·2	364·2			
298	1779·7	364·7			
299	1789	365·1	61	1820·3	
Mean	..	364·43	..	..	29·95
346	2231·5	470·6	73	2219·9	
347	2240·9	470·7			
348	2250·5	470·8			
349	2260	471	75	2286·7	
Mean	..	470·78	..	..	30·02
396	2719	487·5	87	2686·6	
397	2729	488·1			
398	2739	488·5			
399	2749·3	489·3	89	2753	
†Mean	..	488·35	..	..	30·02
446	3233·9	514·9	103	3219·3	
447	3244·8	515·8			
448	3254·9	515·9			
449	3265·8	516·5	105	3286	
Mean	..	515·78	..	..	30·02

Owing to the breakage of a wire in the clock and chronograph circuit, the records of the times from 449 to 539 are so uncertain that we have decided to omit them.

TABLE XXX.—Series II. J 26. September 14, 1892.

Weight of water (*in vacuo*) = 199·674 grms.
Clark cells. $n = 4$. **(37, 38, 39), (40, 41, 42), (43, 44, 45), (46, 47, 48).**
Temperature 15°·12 C.
External Tempereture 241·2 A = 300 E = 19·260° C. Pressure = ·48 millim.
Calorimeter cooled to 10°·00 C. Connections reversed at †.

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolutions.	Rate.
	seconds.		thousands.	seconds.	
86	45·2	..	0	19·6	
87	51·7				
88	57·9				
89	64·1	..	2	86·1	
126	297·7	252·5	8	285·3	
127	304	252·3			
128	310	252·1			
129	316·8	252·7			
Mean	..	252·4	..	..	30·10
176	623·8	326·1	18	617·6	
177	630	326			
178	636·7	326·7			
179	643	326·2	19	650·8	
† Mean	..	326·25	..	..	30·12
216	888·6	264·8	26	883·2	
217	895·2	265·2			
218	902	265·3			
219	908·9	265·9	27	916·4	
Mean	..	265·3	..	..	30·12
256	1160·7	272·1	34	1148·8	
257	1167·1	271·9			
258	1174	272			
259	1181	272·1			
Mean	..	272·03	..	..	30·10

TABLE XXX.—(continued).

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolutions.	Rate.
	seconds.		thousands.	seconds.	
296	1442·1	281·4	42	1414·6	
297	1449·4	282·3			
298	1456·5	282·5			
299	1463·8	282·8	44	1481	
Mean	..	282·25	..	..	30·12
346	1804·3	362·2	53	1780·3	
347	1811·7	362·3			
348	1818·9	362·4			
349	1826·5	362·7	55	1847·3	
Mean	..	362·4	..	..	30·02
396	2175	370·7	64	2147	
397	2182·9	371·2			
398	2190·5	371·6			
399	2198	371·5	66	2213·7	
† Mean	..	371·25	..	..	30·02
446	2562	387	76	2546·4	
447	2569·9	387			
448	2577·7	387·2			
449	2585·6	387·6	78	2613	
Mean	..	387·20	..	..	30·05
506	3046	484	90	3012	
507	3054·3	484·4			
508	3062·8	485·1			
509	3071·2	485·6	92	3078·5	
Mean	..	484·78	..	..	30·08
536	3297·4	251·4	97	3244·7	
537	3305·9	251·6			
538	3314	251·2			
539	3322·6	251·4	98	3278	
Mean	..	251·4	..	..	30·07

TABLE XXXI.—Series II. J 27. September 15, 1892.

Weight of water (*in vacuo*) = 199·674 grms.

Clark cells. $n = 5$. Nos. **(37, 38, 39)**, **(40, 41, 42)**, **(43, 44, 45)**, **(46, 47, 48)**, **(52, 53, 54)**.

Temperature 15° C.

External Temperature 241·1 A = 299·8 E = 19°·258 C. Pressure = ·48 millim.

Calorimeter cooled to 10°·01 C. Connections reversed at †.

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolutions.	Rate.
	seconds.		thousands.	seconds.	
86	76·7	..	7	22·9	
87	80·9				
88	85·2				
89	89·4				
Mean					
126	249·7	173	13	223·7	
127	254	173·1			
128	258·4	173·2			
129	262·6	173·2	15	290·7	
Mean	..	173·13	..	..	29·88
176	471·8	222·1	20	457·5	
177	476	222			
178	480·6	222·2			
179	485	222·4	21	490·5	
Mean	..	222·18	..	..	30·13
†216	651·6	179·8	25	623·2	
217	656	180			
218	660·5	179·9			
219	665	180	27	689·5	
Mean	..	179·95	..	..	30·15
256	834·7	183·1	31	822·4	
257	839·5	183·5			
258	844	183·5			
259	848·8	183·8	32	855·6	
Mean	..	183·48	..	..	30·22

TABLE XXXI.—(continued).

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolutions.	Rate.
	seconds.		thousands.	seconds.	
296	1024·4	189·7	37	1021·6	
297	1029	189·5			
298	1034	190			
299	1038·6	189·8	38	1054·8	
Mean	..	189·75	..	..	30·12
346	1267·2	242·8	44	1254·4	
347	1271·8	242·8			
348	1276·7	242·7			
349	1281·6	243	45	1287·5	
Mean	..	242·83	..	..	30·08
396	1513·6	246·4			
397	1518·6	246·8			
398	1523·6	246·9			
†399	1528·8	247·2	53	1553·2	
Mean	..	246·83	..	..	30·11
446	1769·3	255·7	59	1752·6	
447	1774·7	256·1			
448	1779·9	256·3			
449	1785	256·2			
Mean	..	256·08	..	..	30·10
506	2087·5	318·2	68	2051·1	
507	2092·8	318·1			
508	2098·4	318·5			
509	2103·7	318·7	70	2117·3	
Mean	..	318·38	..	..	30·16
536	2251	163·5	73	2216·6	
537	2256·8	164			
538	2262·2	163·8			
539	2267·9	164·2			
Mean	..	163·88	..	..	30·22

Table XXXII.—Series II. J 33. September 18, 1892.

Weight of water (*in vacuo*) = 259·500 grms.

Clark cells. $n = 5$. **(37, 38, 39), (40, 41, 42), (43, 44, 45), (46, 47, 48), (52, 53, 54).**

Temperature 15°·06 C.

External temperature 241·2 A = 300 E = 19°·260 C. Pressure = ·44 millim.

Calorimeter cooled to 10°·10 C. Connections reversed at †.

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolutions.	Rate.
	seconds.		thousands.	seconds.	
86	42·9	..	8	18	
87	48				
88	53·1				
89	58·5	..	10	84·6	
Mean	..	..	..	..	
126	251·7	208·8			
127	257	209			
128	262·2	209·1			
129	267·7	209·2	16	283·8	
Mean	..	209·03	..	..	30·10
176	520·4	268·7			
177	525·7	268·7			
178	531·2	269			
179	536·5	268·8	24	549·2	
Mean	..	268·75	..	..	30·15
†216	737·7	217·3			
217	743	217·3			
218	748·5	217·3			
219	754·1	217·6	31	781·6	
Mean	..	217·38	..	..	30·12
256	959·3	221·6	36	947·4	
257	965	222			
258	970·6	222·1			
259	996·5	222·4	37	980·7	
Mean	..	222·03	..	..	30·14

TABLE XXXII—(continued).

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolutions.	Rate.
	seconds.		thousands.	seconds.	
296	1188·9	229·6	43	1180·3	
297	1194·7	229·7			
298	1200·4	229·8			
299	1206·2	229·7	44	1213·6	
Mean	..	229·7	..	..	30·06
346	1482	293·1	52	1479·7	
347	1487·8	293·1			
348	1493·6	293·2			
349	1499·2	293	53	1512·9	
Mean	..	293·1	..	..	30·07
396	1780	298			
397	1786·2	298·4			
398	1792·3	298·7			
399	1798·4	299·2	62	1812	
Mean	..	298·58	..	..	30·10
†446	2088·8	308·8	70	2077·7	
447	2095	308·8			
448	2101·2	308·9			
449	2107·7	309·3	71	2110·9	
Mean	..	308·95	..	..	30·11
506	2472	383·2	81	2441·7	
507	2478·6	383·6			
508	2485·2	384			
509	2491·7	384	83	2507·6	
Mean	..	383·7	..	..	30·25
536	2669·7	197·7	87	2639·8	
537	2676·4	197·8			
538	2682·9	197·7			
539	2689·9	198·2			
Mean	..	197·85	..	..	30·26

TABLE XXXIII.—Series II. J 34. September 18, 1892.

Weight of water (*in vacuo*) = 259·500 grms.

Clark cells. $n = 6$. Nos. **(37, 38, 39)**, **(40, 41, 42)**, **(43, 44, 45)**, **(46, 47, 48)**, **(49, 50, 51)**, **(52, 53, 54)**. Temperature 15° C.

External temperature 241·2 A = 300 E = 19°·260 C. Pressure = ·48 millim.

Calorimeter cooled to 10°·01 C. Connections reversed at †.

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolutions.	Rate.
	seconds.		thousands.	seconds.	
86	65·9	..	0	18·5	
87	69·6				
88	73·7				
89	77·3	..	2	85·5	
126	217·4	151·5	5	184	
127	221·4	151·8			
128	225·2	151·5			
129	228·9	151·6	7	250	
Mean	..	151·6	..	..	30·23
176	411·5	194·1	11	382·5	
177	415·4	194			
178	419·3	194·1			
179	423·2	194·3	13	448·5	
†Mean	..	194·13	..	..	30·25
216	568	156·5	16	547·5	
217	572	156·6			
218	576	156·7			
219	580	156·8	18	613·5	
Mean	..	156·65	..	..	30·30
256	727·5	159·5	21	712·4	
257	731·5	159·5			
258	735·5	159·5			
259	739·6	159·6	22	745·4	
Mean	..	159·53	..	..	30·23

TABLE XXXIII.—(continued).

Reading E_m.	Time.	Time over interval.	Revolutions.	Time of revolutions.	Rate.
	seconds.		thousands.	seconds.	
296	891·7	164·2	26	877	
297	895·8	164·3			
298	900	164·5			
299	904·2	164·6	27	910	
Mean	..	164·4	..	..	30·28
346	1100·8	209·1			
347	1104·8	209			
348	1109	209			
349	1113	208·8	34	1140·3	
Mean	..	208·98	..	..	30·40
396	1312·5	211·7	39	1304·7	
397	1317	212·2			
398	1321	212			
399	1325·4	212·4	40	1337·7	
Mean	..	212·08	..	..	30·40
†446	1531·2	218·7			
447	1535·7	218·7			
448	1540	219			
449	1544·6	219·2	47	1567·7	
Mean	..	218·9	..	..	30·43
506	1802·7	271·5	54	1797·8	
507	1807·2	271·5			
508	1811·9	271·9			
509	1816·5	271·9	55	1830·6	
Mean	..	271·7	..	..	30·43
536	1942·3	139·6	58	1929·8	
537	1947	139·8			
538	1951·7	139·8			
539	1956·3	139·8			
Mean	..	139·75	..	..	30·33

For convenience of reference in the succeeding Tables, we repeat here the Table showing the values we have assigned to each range on the rising thermometer.

TABLE XXXIV.

No. of range.	E_m.	C.	Mean.	$d\theta$.
1	87·5–127·5	13·990–14·963	14·477	·973
2	127·5–177·5	14·963–16·198	15·581	1·235
3	177·5–217·5	16·198–17·185	16·682	·987
4	217·5–257·5	17·185–18·180	17·683	·995
5	257·5–297·5	18·180–19·196	18·688	1·016
6	297·5–347·5	19·196–20·474	19·835	1·278
7	347·5–397·5	20·474–21·756	21·115	1·282
8	397·5–447·5	21·756–23·063	22·409	1·307
9	447·5–507·5	23·063–24·661	23·862	1·598
10	507·5–537·5	24·661–25·471	25·006	·811

We consider it unnecessary to give more of our original observations in full, but have collected in Tables XXXV. and XXXVI. the unreduced experimental results of all the J experiments, with the exception of J 1 to 4. (See p. 475.)

TABLE XXXV.—Series I. Experiments 5–19.

Group B. W = 188·065 gr.

Date and number.	Temperature and number of Clark cells.		Ranges (see Table XXXIV.).									
			1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Aug. 14 5	16·20 5	Time Rate	168·87 30·21	216 73 30·21	175·85 30·10	179·47 30·06	185·60 30·08	236·90 30·07	— —	250·00 30·05	311·46 30·04	160·12 30·13
Aug. 14 6	16·50 5	Time Rate	— —	— —	175·65 30·13	179·47 30·22	185·41 30·19	236·43 30·35	241·01 30·23	250·20 30·18	311·31 30·17	160·45 30·11
Aug. 16 7	16·70 5	Time Rate	168·97 30·02	217·34 30·00	175·92 30·02	179·70 29·99	186·23 29·92	237·28 30·05	241·18 29·97	250·40 29·97	311·78 30·01	160·40 30·16
Aug. 17 8	15 95 4	Time Rate	249·22 29·87	321·71 29·93	261·36 29·97	267·71 29·97	277·59 30·10	356·73 29·97	364·13 29·94	381·01 30·04	475·88 30·00	246·55 30·00
Aug. 18 9	16·30 2	Time Rate	— —	— —	755·64 29·81	792·83 29·86	844·13 29·90	1116·16 29·90	— —	— —	— —	— —
Aug. 23 10	16 55 4	Time Rate	246·20 31·20	317·62 31·16	258·03 31·14	264·75 31·11	275·23 31·18	351·64 31·22	359·96 31·22	— —	— —	— —
Aug. 24 11	16·60 4	Time Rate	249·84 29·48	322·12 29·66	262·47 29·26	269·52 29·19	279·60 29·15	357·90 29·20	368·69 29·43	378·83 30·36	471·63 30·71	245·38 30·81
Aug. 25 12	16·60 4	Time Rate	248·28 30·20	320·77 30·19	260·30 30·21	267·63 30·24	277·55 30·16	355·27 30·18	364·93 30·04	380 52 30·11	476·35 30·07	246·63 30·06

Table XXXV.—(continued).

Group E. W = 277·931 grms.

Date and number.	Temperature and number of Clark cells.		Ranges (see Table XXXIV.).									
			1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Aug. 26 13	16·15 4	Time Rate	330·52 29·77	426·35 29·80	346·63 29·82	355·30 29·87	368·82 29·79	472·58 29·84	484·37 29·78	504·48 29·78	633·02 29·74	327·63 29·71
Aug. 27 14	16·15 4	Time Rate	330·70 29·72	426·22 29·82	347·08 29·84	355·22 29·83	368·75 29·82	473·43 29·61	485·32 29·68	504·85 29·77	632·50 29·78	327·73 29·76
Aug. 28 15	16·05 5	Time Rate	223·60 30·34	287·18 30·38	232·62 30·44	237·23 30·54	245·22 30·52	313·25 30·58	319·28 30·54	330·47 30·61	411·63 30·63	211·52 30·47
Aug. 28 16	16·05 5	Time Rate	224·45 29·87	288·35 29·88	233·45 29·89	238·40 29·90	246·47 29·91	314·65 29·89	320·45 29·85	332·18 29·81	412·50 29·79	213·10 29·77
Aug. 30 17	16·50 4	Time Rate	331·12 30·17	426·88 30·13	346·82 30·02	355·98 30·04	370·02 29·95	473·83 29·92	485·20 30·10	505·12 30·14	633·10 30·11	327·83 30·11
Aug. 31 18	16·10 4	Time Rate	329·57 30·16	427·18 29·68	346·70 30·22	353·90 30·36	367·97 30·39	471·68 30·33	483·25 30·35	504·15 30·31	629·47 30·37	327·50 30·37
Sept. 1 19	16·00 5	Time Rate	224·52 29·73	288·33 29·84	233·50 29·59	238·80 29·79	246·80 29·54	314·42 29·82	320·60 30·03	331·33 29·77	412·60 29·75	211·07 31·52

TABLE XXXVI.—Series II. Experiments 20–34.

Group A. W = 139·776 grms.

Date and number.	Temperature and number of Clark cells.		Ranges (see Table XXXIV.).									
			1	2	3	4	5	6	7	8	9	10
Sept. 11 20	15·05 4	Time Rate	199·20 30·54	258·45 30·37	209·80 30·47	214·70 30·53	223·38 30·45	286·93 30·35	293·75 30·41	306·38 30·56	384·00 30·54	199·38 30·42
Sept. 11 21	15·00 5	Time Rate	136·60 30·36	175·98 30·37	142·45 30·31	145·63 30·13	150·60 30·12	191·98 30·26	195·38 30·37	202·70 30·34	252·33 30·37	130·20 30·40
Sept. 12 22	15·00 4	Time Rate	202·40 29·48	260·60 29·53	211·60 29·67	217·00 29·64	225·30 29·66	289·05 29·58	296·72 29·69	308·97 29·68	387·40 29·68	201·25 29·63
Sept. 12 23	15·10 3	Time Rate	315·03 30·01	409·53 30·06	336·33 30·01	347·45 30·02	364·43 29·95	470·78 30·02	488·35 30·02	515·78 30·02	— —	— —
Sept. 13 24	15·00 5	Time Rate	136·13 30·82	175·28 30·89	142·05 30·87	144·73 30·80	149·65 30·96	190·60 31·04	194·38 30·97	201·35 31·06	250·75 31·26	— —
Sept. 13 25	15·25 4	Time Rate	199·80 30·25	258·68 30·18	210·45 30·18	215·68 30·21	223·88 30·24	287·40 30·21	294·58 30·23	307·38 30·25	384·90 30·26	199·68 30·27

TABLE XXXVI.—(continued).

Group C. W = 199·674 grms.

Date and number.	Temperature and number of Clark cells.		Ranges (see Table XXXIV.).									
			1	2	3	4	5	6	7	8	9	10
Sept. 14 26	15·10 4	Time Rate	252·40 30·10	326·25 30·12	265·30 30·12	272·03 30·10	282·25 30·12	362·40 30·02	371·25 30·02	387·20 30·05	484·78 30·08	251·40 30·07
Sept. 15 27	15·00 5	Time Rate	173·13 29·88	222·18 30·13	179·95 30·15	183·48 30·22	189·75 30·12	242·83 30·08	246·83 30·11	256·08 30·10	318·38 30·16	163·88 30·22
Sept. 15 28	15·10 4	Time Rate	252·40 30·10	326·00 30·14	265·18 30·15	272·08 30·05	282·10 30·13	361·28 30·33	369·15 30·40	384·95 30·44	482·15 30·47	249·00 30·70
Sept. 16 29	15·00 5	Time Rate	172·70 30·25	221·88 30·36	179·65 30·39	183·25 30·33	189·60 30·27	241·98 30·34	246·00 30·43	255·30 30·39	317·70 30·42	163·73 30·39

Group D. W = 259·500 grms.

Sept. 16 30	15·05 5	Time Rate	209·33 29·93	269·10 29·93	217·80 29·93	222·30 29·85	230·48 29·50	294·45 29·50	300·05 29·47	310·50 29·58	386·40 29·61	199·03 29·70
Sept. 17 31	15·20 5	Time Rate	209·46 30·00	269·23 30·07	217·95 30·05	222·40 29·98	230·00 30·00	293·23 30·07	298·63 30·08	309·63 30·19	384·60 30·18	198·28 30·20
Sept. 18 32	14·80 5	Time Rate	209·13 30·00	268·97 30·11	217·78 30·08	222·38 30·04	229·68 29·92	293·80 29·83	298·95 29·95	309·38 30·15	384·58 30·14	198·25 30·19
Sept. 18 33	14·80 5	Time Rate	209·03 30·10	268·75 30·15	217·38 30·12	222·03 30·14	229·70 30·06	293·10 30·07	298·58 30·10	308·95 30·11	383·70 30·25	197·85 30·26
Sept. 18 34	15·00 6	Time Rate	151·10 30·23	194·13 30·25	156·65 30·30	159·53 30·23	164·40 30·28	208·98 30·40	212·08 30·40	218·90 30·43	271·70 30·43	139·75 30·33

Observations on Tables XXXV. and XXXVI.

Experiments 1 *to* 4.

These have been rejected and the observations are not included in the Tables. The discrepancies over the shorter ranges are absurdly great, and the mean times far too large. During these experiments we had great difficulty in maintaining the potential-balance; this ought to have been sufficient to indicate the source of error, but, at the time, we attributed it to want of practice in the observers.

It must be borne in mind that it was not until many weeks after the close of our observations that the reductions were completed, so that, at the time of experimenting, we were wholly in the dark as to the actual value of our results. Our only means of obtaining any glimpse of the value of a particular experiment was its resemblance to some other one taken under similar conditions, but, as all the conditions were never precisely the same, we could thus obtain little information.

We have now no hesitation in assigning the following cause to the failure of these four experiments. With this weight of water, the depth in the calorimeter, when the stirrer was at rest, was only 2 centims., and as, when rapid stirring took place, a great portion of the contents must have been within the cylinder and in the upper portion of the calorimeter, it is evident that the higher parts of the coil must have been at times uncovered, since it required 1·5 centims. for complete immersion. This would account (1) for the irregular behaviour of the potential-balance, and (2) for the great lengthening of the times shown in these experiments. We at no time anticipated success with so small a mass of water, but the excellent results obtained from our stirring experiments on this weight (see Table XXI.) justified the attempt.

Experiments 5 *to* 12. (*Group B.*)

These experiments are only slightly more satisfactory than those we have rejected. The cause is partly that so frequently alluded to in Section XII., viz., obstructions in the openings at the base of the internal cylinder, the resulting irregularities in the throw of the stirrer affecting not only the non-electrical supply, but also changing the coefficient of increase in the resistance of the wire. That this is the case is indicated by the results of Experiment 9, where the E.M.F. was so reduced that the current was only ·1 ampère, and the changes in the temperature of the wire were less marked. This experiment was performed in order to test the accuracy of our various corrections, rather than as a serious effort to determine the value of J. The observations in this experiment only extended over $\frac{2}{5}$ of our total range, for, had we endeavoured to carry it out through the upper ranges, its duration would have extended over some hours.

In every case (excepting as above stated, Experiments 1 to 4) we have given all the numbers recorded, because, however bad individual observations may appear, we have no sufficient grounds for their rejection. The omissions in the table represent experimental mistakes; in No. 5, Range 7, the storage circuit was broken for a second or two by an accident with the reversing key; in No. 6, the chronograph refused to work throughout the first two ranges; in No. 10, some contact must have taken place between the wires of the coil, as the potential-balance was entirely destroyed after the 7th range. No. 11 was an exceptionally bad experiment, especially in the latter half; the changes in water pressure were so rapid and violent as to pass beyond the control of the motor-regulator, the rate changing from 29·43 to 30·36 in two consecutive observations. Had it not been for our desire to present our results in full, we would certainly have rejected this experiment.

Experiments 13 to 19. (*Group E.*)

In this group, our heaviest weight, the observations although still somewhat irregular are in better agreement. As might be anticipated the throw of the stirrer was less affected by the obstructions at the base when the depth of water was greater. The alterations made in the connections of the stirring rod have been already alluded to.

Our conclusions as to the value of J and the changes in the specific heat of water are based almost entirely on the results of Series II. Although the results deduced from Nos. 13 to 19 are in almost perfect harmony with those from Series II., the agreement, for the reasons given above, must be in part fortuitous. The mean value of J deduced from Nos. 5 to 12 agrees with the most probable value, but the change in the specific heat of water alters from positive to negative according as the group is compared with the results obtained from a lighter or a heavier weight.

Series II.

This series contains but fifteen experiments, which may appear a small number on which to base our conclusions. We would, however, point out that these are only the concluding series of many hundred J experiments conducted by the same observers, who are therefore in the best position to judge of their value. Furthermore, these fifteen experiments are conducted on very different weights of water and with very different currents, and our conclusions would be but little altered if they were based on any two individual experiments rather than on the mean results of all. Want of time alone prevented our increasing their number, but we believe that such increase would have given them small additional weight. The results of Series I. are quite sufficient to corroborate the value of J, although the least trustworthy group of that series gives contradictory values for the change in specific heat of water.

Such irregularities as are observable in the members of these series, are we believe inseparable from the use of mercury thermometers. Although many irregularities which would otherwise be apparent have been eliminated by the method of calibration adopted (Section X.), there yet remain residual ones, not strictly recurrent, whose effect can only be eliminated by taking the mean path of a series of observations over consecutive ranges. The magnitude of such irregularities can be estimated by a comparison of the columns headed "mean" and "from curve" in Table XL.

None of these experiments call for special comment, with the exception of No. 34. This was performed with the object of testing the accuracy of the correction given by the formula $\delta R = \alpha C^2$ (Section VII., Table IX.), and we did not anticipate from it results of much value. The irregularities in ranges 8, 9, 10, of Group D, Column 21, Table XL., are clearly an example of the eccentric behaviour of the thermometer when rising at this rapid rate; their mean however is excellent.

SECTION XIV.—THE CALCULATION OF THE RESULTS.*

The method which we have adopted in our calculations can be put into a general form, thus:—

Suppose a to be the rate of production of heat in the calorimeter at some standard temperature θ, whilst a' denotes the value of a at any other temperature θ_1;

ρ the change in temperature per one second due to radiation, &c., when the difference between the external and internal temperature is 1° C;

M the capacity for heat of the calorimeter and its contents at the standard temperature θ, M′ its value at θ_1;

Then if θ_1 is the temperature of the calorimeter at any time t, the rate (α') of production of heat is

$$M' \frac{d\theta_1}{dt} + M'\rho\,(\theta_1 - \theta_0),$$

where θ_0 is the temperature of the surrounding envelope.

Thus the equation of condition is

$$M' \frac{d\theta_1}{dt} = \alpha' - M'\rho\,(\theta_1 - \theta_0) \quad \text{. . . . .} \quad (1).$$

Now, by JOULE'S law,

$$JM \frac{d\theta_1}{dt} = C^2R \quad \text{. . . . .} \quad (2),$$

therefore

$$\alpha_\epsilon = M \frac{d\theta_1}{dt} = \frac{C^2R}{J} = \frac{n^2E^2}{JR} \quad \text{. . . . .} \quad (3),$$

where α_ϵ is the rate of production of heat due to the electrical supply, and E is the E.M.F. of a Clark cell, and n is the number of cells used.

But since the rate of production of heat is dependent on the resistance of a platinum wire, and E is kept constant, this rate will diminish as the temperature rises, or,

$$\alpha'_\epsilon = \alpha_\epsilon \{1 - k\,\overline{\theta_1 - \theta + \beta}\} \quad \text{. . . . .} \quad (4),$$

---

* We have changed the notation adopted in Section I. to one more suited for arithmetical operations.

where k is the resistance temperature-coefficient of the wire, and β is the number of degrees that the wire is hotter than the water in contact with it.

Similarly

$$M' = M\{1 + l\,\overline{\theta_1 - \theta}\}$$

where l is the mean coefficient of increase of specific heat of the water and calorimeter.

For the non-electrical supply, we have shown that $tr^3 = K$ (p. 438), where t is the time of rising 1° C. and r is the rate of revolution of the stirrer, and therefore the rise per second is given by

$$\sigma = r^3/K \quad \ldots\ldots\ldots\ldots \quad (5),$$

and

$$\delta\sigma = \frac{3r^2}{K}\,\delta r \quad \ldots\ldots\ldots\ldots \quad (6).$$

By (6) we can reduce all observations to the standard rate r.

Equation (1) after introducing terms due to stirring becomes

$$M'\frac{d\theta_1}{dt} = \alpha'_{\epsilon.\rho.\sigma.} + (\sigma - \rho\,\overline{\theta_1 - \theta_0})\,M',$$

that is,

$$M[1 + l(\theta_1 - \theta)]\frac{d\theta_1}{dt} = \frac{n^2E^2}{JR}\{1 - k\,\overline{\theta_1 + \beta - \theta}\} + (\sigma - \rho\,\overline{\theta_1 - \theta_0})\,M(1 + l\,\overline{\theta_1 - \theta}) \quad (7);$$

or

$$\frac{d\theta_1}{dt} = \frac{n^2E^2}{JRM}\cdot\frac{1 - k(\theta_1 + \beta - \theta)}{1 + l(\theta_1 - \theta)} + \sigma - \rho(\theta_1 - \theta_0) \quad \ldots\ldots \quad (8^*).$$

If we write

$$\left(\frac{d\theta_1}{dt}\right)_\epsilon \text{ and } \left(\frac{d\theta_1}{dt}\right)_0$$

for the electrical and non-electrical terms in this expression,

$$\frac{d\theta_1}{dt} = \left(\frac{d\theta_1}{dt}\right)_\epsilon + \left(\frac{d\theta_1}{dt}\right)_0 \quad \ldots\ldots\ldots\ldots \quad (9).$$

---

[*] Equation (8) may be expressed in the following form—

$$d\theta_1/dt = A + \lambda\theta_1,$$

where A is the sum of quantities independent of θ_1, and λ is the sum of a number of small quantities.

The range $d\theta_1$ is reckoned from slightly below θ_1, say from θ', to slightly above θ_1, say θ''; hence if t' and t'' are the times at θ' and θ'', we may assign to $d\theta_1/dt$ the value $(\theta'' - \theta')/(t'' - t')$.

Strictly speaking, the equations ought to be integrated from $t = t'$, when $\theta_1 = \theta'$, to $t = t''$, when $\theta_1 = \theta''$, but the error introduced by the above method may, provided the ranges are sufficiently small, be neglected.

We have adopted throughout our experiments ranges of from 1° to 1°·5 C. It does not appear probable that increased accuracy would have resulted from the adoption of smaller ranges, for the effect of errors in the thermometry is increased as the size of the ranges is diminished.

The experiments on the heat developed by the stirrer give us the values of

$$\left(\frac{d\theta_1}{dt}\right)_0 = \sigma - \rho\,(\theta_1 - \theta_0).$$

(See Table XXVII.)

1. The first step in the calculation of our observations has been to correct, where necessary, all times for the clock error, which was + ·0004125, up to J 9 inclusive. This correction has been applied in Table XXXVIII.

2. We found the value of $d\theta_1/dt$, *i.e.*, the rise per second produced by the combined effect of all sources of gain or loss (Table XXXVII., col. 4).

3. Since the rate of revolution throughout an experiment was always nearly 30 per second, we eliminated irregularities in the rate by reducing to rate 30 by means of the formula given in (6). Thus we obtained the value $d\theta_1/dt$ would have had, had the rate been uniformly 30 per second. This reduction is shown in Table XXXVII., cols. 5 and 6.

4. In order to be able to more readily compare experiments performed under almost identical circumstances, the next correction applied was that for the temperature of the Clark cells. Lord Rayleigh gives the formula

$$E_{15} = E_t\,\{1 + {\cdot}00077\,(t - 15)\}$$

hence

$$E^2_{15} = E^2_t\,\{1 + {\cdot}00154\,(t - 15)\}\; \ldots\ldots\ldots \quad (11),$$

where t is the temperature of the Clark cells.

This correction cannot be applied to $d\theta_1/dt$ as a whole (equation 9) but only to the portion $(d\theta_1/dt)_\epsilon$ the electrical supply. As the correction was always very small, it was sufficient to find the approximate value of $(d\theta_1/dt)_\epsilon$ by subtracting, at any temperature, the value of $(d\theta_1/dt)_0$ as given in Table XXVII., and then find the correction on the value of $(d\theta/dt)_\epsilon$ so obtained by formula (11). The result of this correction gives col. 7, Table XXXVII.

The correction was applied in this order as we could thus compare all the experiments performed with the same E.M.F.'s so long as the values of σ and ρ were the same. The results at this stage of their reduction are given in Tables XXXVIII. and XXXIX.

5. Table XXXVII., col. 8, gives the value of $(d\theta/dt)_0$ taken from Table XXVII. This subtracted from col. 7 gives the value of $(d\theta/dt)_\epsilon$, *i.e.*, the rise per second due to the current only, the difference of potential at the ends of the coil being n Clark cells (col. 9).

Hence equation (8) is reduced to

$$\left(\frac{d\theta_1}{dt}\right)_\epsilon = \frac{n^2E^2\{1 - k\,\overline{\theta_1 - \theta + \beta}\}}{\mathrm{JRM}(1 + l\,\overline{\theta_1 - \theta})}.$$

6. In the section on resistance in Table XVI. we have collected the values of $\frac{R}{1 - k(\theta_1 - \theta + \beta)}$ at the mean temperature of each range. The value of n, the number of Clark cells used, is given with each experiment. Substituting their values we obtain the time of rising 1° C. with unit resistance and one Clark cell, or

$$\frac{J}{E^2}\mathrm{M}(1 + l\,\overline{\theta_1 - \theta}) = \mathrm{T} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (12).$$

This gives column 10 of Table XXXVII.

7. The results of all the experiments were then meaned and plotted, the columns headed "Mean" and "From curve" in Tables XL. and XLI. giving the results. From these smoothed curves the values of the required constants were calculated thus:—

8. If W_x is the water-equivalent of the calorimeter, and f and g are the temperature coefficients of the specific heat of water and of the calorimeter respectively, and suffixes written to W, l, T, denote the values of these quantities for different weights of water, then from (12) we obtain

and

$$\left.\begin{aligned} \frac{J}{E^2}(W_1 + W_x)(1 + l_1\overline{\theta_1 - \theta}) &= T_1 \\ \frac{J}{E^2}(W_2 + W_x)(1 + l_2\overline{\theta_1 - \theta}) &= T_2 \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \quad (13),$$

where

$$l_1 = \frac{fW_1 + gW_x}{W_1 + W_x} \quad \text{and} \quad l_2 = \frac{fW_2 + gW_x}{W_2 + W_x} \quad . \; . \; . \; . \; . \; . \; . \quad (14).$$

Hence, subtracting equations (13), we get

$$\frac{J}{E^2}(W_2 - W_1)(1 + f\,\overline{\theta_1 - \theta}) = T_2 - T_1$$

or

and

$$\left.\begin{aligned} \frac{J}{E^2}(W_2 - W_1)(1 + f\,\overline{\theta_0 - \theta}) &= T_{2,0} - T_{1,0} \\ \frac{J}{E^2}(W_2 - W_1)(1 + f\,\overline{\theta_2 - \theta}) &= T_{2,2} - T_{1,2} \end{aligned}\right\} \quad . \; . \; . \; . \; . \quad (15),$$

where the observations are taken at two temperatures θ_0 and θ_2, the second suffix of the T's referring to these temperatures.

Hence, by division, we obtain the value of f, the temperature-coefficient of the specific heat of water.

And, if θ_0 is our standard temperature, the value of J is found without any knowledge of the water-equivalent of the calorimeter.

Now $W_1 (T_{2,0} - T_{1,0})/(W_2 - W_1)$ is the time that W_1 grms. of water at temperature θ_0 would take to rise 1° C. Subtracting this from $T_{1,0}$ and dividing by $(T_{2,0} - T_{1,0})/(W_2 - W_1)$ we obtain the number of grms. of water at θ_0, to which the calorimeter also at θ_0 is equivalent . . . . (16).

Similarly the expression

$$\frac{T_{1,2} - W_1 (T_{2,2} - T_{1,2})/(W_2 - W_1)}{(T_{2,0} - T_{1,0})/(W_2 - W_1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (17)$$

gives the number of grammes of water at θ_0 to which the calorimeter at θ_2 is equivalent. Thus we obtain both the water-equivalent of the calorimeter and also its temperature-coefficient g.

Finally J is calculated from

$$J = \frac{E^2 . T}{M(1 + l\,\overline{\theta_1 - \theta})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18).$$

The following Table gives the complete working out of J 20. This experiment was selected, because it was the first of which we have given the experimental details (See Table XXVIII.).

TABLE XXXVII.—Experiment J 20.

Date, September 11, 1892. W = 139·776 grms. Clark cells, $n = 4$ at 15°·05 C.

$\sigma = \cdot 000512$. $\rho = \cdot 000621$. $tr^3 = 5232 \times 10^4$.

$d\theta_1$.	dt.	Rate.	$\frac{d\theta_1}{dt} \times 10^6$.	Rate correction × 10^6.	$\frac{d\theta_1}{dt} \times 10^6$ at rate 30.	$\frac{d\theta_1}{dt} \times 10^6$ corrected for temperature of Clark cells (+ 0·3).	$\left(\frac{d\theta_1}{dt}\right)_0 \times 10^6$.	$\left(\frac{d\theta_1}{dt}\right)_\epsilon \times 10^6$.	T.*	Mean temperature.
·973	199·20	30·54	4884	− 28	4856	4856	809	4047	458·1	14·477
1·235	258·45	30·37	4779	− 19	4760	4761	741	4020	459·4	15·581
·987	209·80	30·47	4704	− 24	4680	4681	672	4009	459·0	16·682
·995	214·70	30·53	4636	− 28	4608	4608	610	3998	458·7	17·683
1·016	223·38	30·45	4548	− 24	4524	4524	548	3976	459·7	18·688
1·278	286·93	30·35	4454	− 18	4436	4437	476	3961	459·6	19·835
1·282	293·75	30·41	4364	− 21	4343	4343	397	3946	459·4	21·115
1·307	306·38	30·56	4266	− 29	4237	4237	316	3921	460·3	22·409
1·598	384·00	30·54	4161	− 28	4133	4134	226	3908	459·7	23·862
·811	199·38	30·42	4067	− 22	4045	4045	155	3890	460·3	25·006
1	2	3	4	5	6	7	8	9	10	11
REFERENCES.										
Table XXXIV.	Table XXVIII.	Table XXVIII.	p. 479, 2	p. 478, eq. 6, p. 479, 3.	p. 479, 3	p. 479, 4, eq. 11	Table XXVII.	p. 479, 5	p. 480, 6 Table XVI.	Table XXXIV.

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* These values can be compared with Table XL., cols. 11–15. Taking the differences between the individual results of Experiment 20, and the mean numbers of all the experiments on this weight, we get by the method of least squares, mean probable error ± ·075 second. This does not include the inevitable errors arising from the thermometry, the values of the ranges being only given to the nearest $\frac{1}{1000}$ of a degree, such errors can only be removed by the smoothed curve.

The two following Tables, XXXVIII. and XXXIX., give the values of $(d\theta_1/dt) \times 10^6$, corrected to rate 30 and for the temperature of the Clark cells. They correspond to Col. 7 of Table XXXVII. :—

TABLE XXXVIII.—Series I. Values of $(d\theta_1/dt) \times 10^6$.

Group B. W = 188·065.

No. of experiment.	No. of Clark cells.	Mean temperature of each range.									
		14·477	15·581	16·682	17·683	18·688	19·835	21·115	22·409	23·862	25·006
9	2	—	—	1314·6	1261·7	1208·9	1150·3	—	—	—	—
8	4	3914	3847	3782	3722	3661	3588	3526	3434	3362	3293
10	4	3916	3853	3801	3725	3655	3597	3523	—	—	—
11	4	3922	3854	3801	3727	3671	3599	3509	3444	3369	3282
12	4	3919	3851	3791	3716	3663	3598	3519	3438	3359	3294
	Mean	3919	3853	3798	3723	3663	3598	3517	3441	3364	3288
5	5	5769	5701	5622	5554	5482	5404	—	5238	5142	5071
6	5	—	—	5629	5551	5488	5406	5326	5232	5143	5064
7	5	5776	5698	5626	5554	5475	5400	5333	5236	5142	5065
	Mean	5773	5699	5626	5553	5482	5403	5329	5235	5142	5067

Table XXXVIII.—(continued).

Group E. W = 277·931.

No. of experiment.	No. of Clark cells.	Mean temperature of each range.									
		14·477	15·581	16·682	17·683	18·688	19·835	21·115	22·409	23·862	25·006
13	4	2955	2906	2857	2809	2766	2712	2658	2603	2535	2487
14	4	2955	2907	2852	2811	2764	2714	2655	2600	2535	2484
17	4	2940	2895	2851	2801	2748	2704	2646	2591	2526	2477
18	4	2953	2905	2845	2806	2754	2705	2649	2590	2532	2470
The above four experiments cannot be meaned here, as the values of σ and ρ are different. (See p. 450).											
15	5	4349	4299	4238	4185	4135	4070	4006	3945	3889	3826
16	5	4346	4290	4238	4183	4131	4070	4010	3947	3884	3817
19	5	4347	4291	4245	4178	4135	4075	4004	3956	3884	3804
	Mean	4347	4293	4240	4182	4134	4072	4007	3949	3886	3816

TABLE XXXIX.—Series II. Values of $(d\theta_1/dt) \times 10^6$:

Group A. W = 139·776.

Number of experiment.	Number of Clark cells.	Mean temperature of each range.									
		14·477	15·581	16·682	17·683	18·688	19·835	21·115	22·409	23·862	25·006
23	3	3090	3014	2935	2864	2791	2713	2624	2534	(2431)*	(2351)*
20	4	4856	4761	4681	4608	4524	4437	4343	4237	4134	4045
22	4	4834	4763	4681	4604	4526	4442	4336	4246	4141	4049
25	4	4859	4768	4683	4604	4528	4437	4342	4240	4139	4048
	Mean	4850	4764	4682	4605	4526	4439	4340	4241	4138	4047
21	5	7102	6995	6904	6825	6740	6641	6541	6428	6303	6208
24	5	7103	6996	6904	6831	6743	6650	6543	6425	6301	—
	Mean	7103	6995	6904	6828	6741	6646	6542	6426	6302	6208

* Obtained by producing the curve through the preceding numbers. (See Table XXIX.)

TABLE XXXIX.—(continued).

Group C. W = 199·674.

Number of experiments.	Number of Clark cells.	Mean temperature of each range.									
		14·477	15·581	16·682	17·683	18·688	19·835	21·115	22·409	23·862	25·006
26	4	3852	3781	3717	3652	3596	3526	3454	3375	3295	3224
28	4	3852	3783	3717	3654	3596	3523	3457	3377	3296	3226
	Mean	3852	3782	3717	3653	3596	3525	3455	3376	3295	3225
27	5	5625	5554	5479	5414	5349	5264	5188	5101	5013	4939
29	5	5623	5550	5478	5415	5347	5266	5192	5102	5012	4936
	Mean	5624	5552	5478	5415	5348	5265	5190	5102	5013	4937
Group D. W = 259·500.											
30	5	4650	4592	4536	4482	4426	4359	4291	4225	4149	4086
31	5	4646	4585	4529	4476	4419	4357	4290	4222	4151	4082
32	5	4651	4586	4528	4473	4425	4355	4289	4219	4148	4083
33	5	4649	4589	4535	4475	4419	4357	4289	4225	4154	4088
	Mean	4649	4588	4532	4476	4422	4357	4290	4223	4150	4085
34	6	6431	6352	6290	6229	6171	6101	6032	5956	5867	5791

Table XL. gives the values of T (equation 12), *i.e.*, the times of rising 1° C. with unit R, and E = 1 Clark cell at 15° C.

TABLE XL.—Times of rising 1° C. = T.

Series 1.

	Group B. W = 188·065.					Group E. W = 277·931.			
No. of cells.	2	4	5			4	5		
No. of experiments performed.	1	4	3			4	3		
Temperature.				Mean.	From curve.			Mean.	From curve.
14·477	—	557·3	556·6	557·0	557·1	740·1	740·6	740·4	740·4
15·581	—	557·6	556·5	557·1	557·2	739·7	740·3	740·0	740·5
16·682	558·5	557·0	556·6	557·0	557·3	740·4	739·7	740·1	740·5
17·683	557·0	558·0	557·3	557·6	557·5	740·4	741·2	740·8	740·6
18·688	558·3	558·2	557·8	558·1	557·6	742·2	740·7	741·4	740·6
19·835	558·7	558·0	558·1	558·1	557·7	741·0	741·5	741·3	740·6
21·115	—	558·0	557·0	557·5	557·8	741·2	741·8	741·5	740·7
22·409	—	558·7	558·0	558·4	557·9	740·4	740·4	740·4	740·7
23·862	—	557·3	557·6	557·4	558·0	739·9	738·6	739·3	740·7
25·006	—	558·3	558·2	558·3	558·2	741·1	741·1	741·1	740·8
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.

TABLE XL.—(continued).

Series II.

	Group A. W = 139·776.					Group C. W = 199·674.				Group D. W = 259·500.			
No of cells.	3	4	5			4	5			5	6		
No. of experiments performed.	1	3	2			2	2			4	1		
Temperature.				Mean.	From curve.			Mean.	From curve.			Mean.	From curve.
14·477	458·7	458·7	458·3	458·7	458·8	580·5	580·8	580·7	580·9	702·8	701·9	702·7	702·9
15·581	458·7	459·0	459·4	459·1	458·9	581·2	580·8	581·0	581·0	703·2	703·5	703·3	703·0
16·682	459·0	458·8	459·4	459·1	459·0	581·2	581·0	581·1	581·1	703·0	703·2	703·0	703·0
17·683	459·2	459·0	458·9	459·0	459·1	581·9	580·8	581·3	581·1	703·0	703·2	703·1	703·0
18·688	459·9	459·4	459·1	459·4	459·2	581·7	581·0	581·3	581·2	703·1	703·0	703·1	703·0
19·835	459·4	459·4	459·1	459·3	459·3	582·0	581·8	581·9	581·3	703·7	703·1	703·6	703·1
21·115	459·4	459·7	459·0	459·4	459·5	581·1	581·1	581·1	581·4	703·5	702·5	703·3	703·1
22·409	459·3	459·9	459·6	459·7	459·6	581·7	581·6	581·6	581·4	703·0	702·5	702·9	703·1
23·862	459·6	459·4	460·0	459·7	459·7	581·0	581·1	581·1	581·5	702·4	702·9	702·7	703·2
25·006	459·9	459·8	460·1	459·9	459·8	581·6	581·4	581·5	581·6	703·2	704·0	703·4	703·2
I.	XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	XXIII.

Remarks on Table XL.

The column headed "Mean" was obtained by multiplying the numbers in the preceding columns of each section by the number of experiments from which they were deduced, and dividing the sum of the products by the total number of experiments. The "means" were plotted on a scale such that $\frac{1}{10}$ inch of ordinate represented a difference of ·1 second in T, and the smooth curve in each case so drawn that the sum of the positive and negative areas included between it and the experimental curve was zero. The curvature is so slight over our range that by assuming T to be a linear function of θ_1, our "curve numbers" are not affected when written to four figures.

It will be found that our results (obtained from the "smooth curve" values of T) are in much closer agreement than might be expected from a study of Table XL. This indicates that the irregularities are due to some (or all) of the following causes.

(1.) Errors in the comparative values of the ranges. The effect of such errors would be common to all the experiments, and there is evidence that the sixth range is too small, the value of T over that range being nearly always too large; the error, however, does not amount to 0°·001. Again, the ninth range is evidently too great. These errors do not affect the result when the values of T over two or three consecutive ranges are meaned (as is done by the smooth curve), the excess in one case is then compensated by the deficiency in another.

(2.) The *irregular* (as apart from the strictly recurrent) "stickings" of the thermometer; these, as previously mentioned, must mean out when sufficient observations are taken over the same range.

(3.) Irregularities in the temperature of the water ejected through the opening in the cylinder on to the thermometer bulb, water from cooler parts of the calorimeter being followed by a gush of warmer water brought direct from the hot wire. This, no doubt, is a fruitful cause of alternate lag and acceleration, but again, it is evidently an irregularity which would but slightly affect the results of many experiments continued through a sufficient number of intervals of time. We have previously pointed out that the "throw" was irregular throughout Groups B and E, and the effect on the individual experiments is very marked; nevertheless the values of T derived from the fifteen experiments in those groups are in practical agreement with the values deduced from the experiments in Series II.

(4.) Personal errors of observation which, from their very nature, are unlikely to recur at regular intervals or over identical ranges. These, no doubt, are the origin of many discrepancies, the strain on the observer during these experiments being great.

The cumulative effect of all the above causes of irregularity may at times be large. In Series I. differences of 1 in 500 occasionally present themselves, although, in Series II., there is only one case in which the difference between the mean and the curve-numbers exceeds 1 in 1000, and only two others in which it exceeds 1 in 2000.

The values of J deduced from the different groups (using the numbers given by the respective smooth curves) are, however, in much closer agreement, the extreme divergence being less than 1 in 4000 (see Table XLIII.).

It is worth mentioning that in previous years we found the agreement between individual experiments in the same group (having the same E.M.F.) was closer than that shown in the above Table; but, on the other hand, the values of J and of the water equivalent given by different groups (or by members of the same group when the number of cells was changed), differed hopelessly, in some cases by more than 1 per cent., showing that constant causes of error had not been eliminated. We attribute the improvement (1) to the alteration in the form of stirrer, for the mechanical work done in previous years varied capriciously, although no doubt the thermometer bulb was more thoroughly "washed" than before the alteration; (2) to the correction (now introduced for the first time) for the difference between the temperature of the wire and that indicated by the thermometer.

As it is more convenient to examine the values of T for integral values of the temperature, we have read off from the smooth curves the values of T for every two degrees covered by our range, and also the values at 15° C. and 25° C. These are given in the following table.

Table XLI.—Values of T from Smoothed Curve.

Temperature.	Series I.		Series II.		
	Group B. W = 188·065.	Group E. W = 277·931.	Group A. W = 139·776.	Group C. W = 199·674.	Group D. W = 259·500.
14·000	557·04	740·44	458·77	580·90	702·88
15	557·14	740·46	458·87	580·95	702·91
16	557·24	740·48	458·97	581·01	702·95
18	557·43	740·55	459·16	581·13	703·00
20	557·62	740·60	459·35	581·25	703·05
22	557·80	740·66	459·53	581·37	703·11
24	557·99	740·72	459·72	581·49	703·17
25	558·09	740·75	459·81	581·55	703·20
26	558·18	740·77	459·92	581·61	703·22
1	2	3	4	5	6

Taking the data given in Columns 4 and 6 of the above table, we give an example of the final calculation of our results.

Using the notation of pp. 478–481, we have the following values

$W_1 = 139{\cdot}776$ $W_2 = 259{\cdot}500$ $\theta_0 = 15°$ C.
$T_{1,0} = 458{\cdot}87$ $T_{2,0} = 702{\cdot}91$ $\theta_1 = 25°$ C.
$T_{1,2} = 459{\cdot}81$ $T_{2,2} = 703{\cdot}20$ $E = 1{\cdot}4344$* volts.

Substituting these values in equation (15) and dividing, we obtain

$$\frac{1 + 15f}{1 + 25f} = \frac{243{\cdot}39}{244{\cdot}04} = {\cdot}99734.$$

As the difference in weight of water here amounts to nearly 120 grms., it is probable that the value obtained in this case is the most reliable.

In the same manner using the values of W and T given in Columns 4 and 5, we get

$$\frac{1 + 15f}{1 + 25f} = \frac{121{\cdot}74}{122{\cdot}08} = {\cdot}99722.$$

And again from Columns 5 and 6,

$$\frac{1 + 15f}{1 + 25f} = \frac{121{\cdot}65}{121{\cdot}96} = {\cdot}99746.$$

Hence mean value of $\frac{1 + 15f}{1 + 25f}$ deduced from Series II. = ·99734.†

Hence, adopting 15° C. as the standard temperature, the

Specific Heat of Water = 1 − ·000266 (θ_1 − 15).‡

Also by means of equation (15) we get the following values of J,

Columns 4 and 6 . . . . $J = 4{\cdot}1939 \times 10^7$
„ 4 „ 5 . . . . $J = 4{\cdot}1940 \times 10^7$
„ 5 „ 6 . . . . $J = 4{\cdot}1940 \times 10^7$

Mean . . . . **$4{\cdot}1940 \times 10^7$.**

This value of J, as pointed out on p. 481, is entirely *independent of the value assigned to the water equivalent of the calorimeter.*

Performing the operations of equation 16, we find that the water equivalent at

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* See p. 388, *supra*.

† If we mean the results from Columns 4 and 5 and 5 and 6, we must of course obtain the same result as that given by Columns 4 and 6. We have however given the numbers in the above form as they show the nature of the agreement between the different groups.

‡ Over the range 14° to 26° C.

15° C. in terms of water at 15° C. = 85·340 grms.; and from the operations indicated in equation (17), we get water equivalent at 25° C. in terms of water at 15° C. = 86·174 grms. Hence

$$\textbf{Water equivalent} = 85·340\,\{1 + ·000977\,(\theta_1 - 15)\}.^*$$

We are now in a position to find the value of $M(1 + l\,\overline{\theta_1 - \theta})$ for any weight of water at any temperature, and the value of J can then be found by equation (18).

The following Table gives the value of $M(1 + l\,\overline{\theta_1 - \theta})$ for each weight of water at temperatures 15°, 20°, and 25° C.

TABLE XLII.—Value of $M(1 + l\,\overline{\theta_1 - \theta})$ at 15°, 20°, and 25°.

Group.	W.	15°.	20°.	25°.
A	139·776	225·116	225·347	225·578
B	188·065	273·405	273·572	273·739
C	199·674	285·014	285·165	285·317
D	259·500	344·840	344·912	344·984
E	277·931	363·271	363·318	363·366

Substituting the values of T (Table XLI.) and $M(1 + l\,\overline{\theta_1 - \theta})$ in equation (18), we get the following values of J. The first column shows the group of experiments from which each value is derived.

TABLE XLIII.—Values of J given by each Group at different Temperatures.

Group.	15°.	20°.	25°.	Mean.
A	4·1940 × 10^7	4·1940 × 10^7	4·1939 × 10^7	4·1940
B	4·1930 ,,	4·1941 ,,	4·1949 ,,	4·1940
C	4·1939 ,,	4·1938 ,,	4·1937 ,,	4·1938
D	4·1940 ,,	4·1939 ,,	4·1940 ,,	4·1940
E	4·1938 ,,	4·1940 ,,	4·1943 ,,	4·1940
				4·1940

We have in the above Table given the values resulting from the calculation at different temperatures since the limit of our experimental errors is thus clearly indicated; for the values of J ought (in the absence of experimental errors) to be identical at all temperatures. The close agreement between the values from different groups, and from the same group at different temperatures, is a satisfactory proof of

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* Over the range 14° to 26° C.

the accuracy of our determination of the water equivalent of the calorimeter, and or the changes in it and in the capacity for heat of the water. If we reject Group B (and we have already shown that it has little value) the results are practically identical.

Hence if we assume—

(1.) The unit of resistance as defined in the 'B.A. Report,' 1892.

(2.) That the E.M.F. of the Cavendish standard Clark cell at 15° C. = 1·4342 volts.*

(3.) That the thermal unit = quantity of heat required to raise 1 grm. of water through 1° C. at 15° C.

The most probable value of

$$\mathbf{J = 4{\cdot}1940 \times 10^7}.^{\dagger}$$

This, by reduction, gives the following:—

$J = 427{\cdot}45$ kilogrammetres in latitude of Greenwich ($g = 981{\cdot}17$).
$J = 1402{\cdot}2$ ft.-lbs. per thermal unit C in latitude of Greenwich ($g = 981{\cdot}17$).
$J = 778{\cdot}99$ „ „ F „ „ „ „

SECTION XV.—DISCUSSION OF THE RESULTS.

As stated in the Introduction, we proposed to determine the value of J in terms of the thermal unit there defined, viz., the quantity of heat required to raise unit mass of water through 1° C. at 15° C. ROWLAND has preferred to tabulate his results by giving the changes in the numerical value of J caused by changes in the capacity for heat of water. We can, however, deduce from his table the expression for the change in the specific heat of water over our range.

Expressed in the same form as above, it becomes

$$1 - {\cdot}000400\,(\theta_1 - 15).$$

The difference between our results on this point is marked, and it is evident that further investigation is required. ROWLAND finds that the minimum value lies between 30° and 35° C.; we hope to carry the investigation beyond that temperature, and some explanation of the difference in our results may then present itself. The whole question is probably one of thermometry, and possibly our revision of this part of the subject may bring our results into closer agreement. ROWLAND himself (p. 198) points out that the whole matter depends on a small difference which he

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* If we assume the E.M.F. of our Clark cells to be the same as that of the Cavendish standard (and we are inclined to think we have over-estimated the difference), we get $J = 4{\cdot}1930 \times 10^7$.

† The value obtained by us in 1891 = $(4{\cdot}192 +) \times 10^7$; *supra*, p. 365.

denotes by the letter m. This quantity appears to be of the same nature as that which we term $d\,(= \theta - pt)$ in the platinum-thermometer formulæ. This quantity m had to be determined from a difference of the order of 0°·05 C. between the air- and mercury-thermometers. The method adopted for finding the value of the analogous quantity d would appear much less liable to error.

Rowland himself was evidently anxious to throw more light on this portion of his investigation, for he performed, with great care, a series of experiments by the method of mixtures. These are given on pp. 125 to 130; he has not, however, tabulated his results. We give, with one exception (No. 10), the results of all these experiments which did not involve temperatures above 30° C.

Table XLIV.—Specific Heat of Water by the method of Mixture (Rowland).

Experiment.	Rowland's result.	Mean coefficient of decrease.
1	$\frac{\text{Mean sp. heat } 0^\circ-18^\circ}{\text{,, ,, } 18^\circ-27^\circ} = 1\cdot0025$	·000185
2	Above our range	—
3	$\frac{\text{Mean sp. heat } 0^\circ-17^\circ}{\text{,, ,, } 17^\circ-29^\circ} = 1\cdot0024$	·000165
4	Rejected by Rowland	—
5	$\frac{\text{Mean sp. heat } 0^\circ-18^\circ}{\text{,, ,, } 18^\circ-30^\circ} = 1\cdot0067$	·000447
6	Rejected by Rowland	—
7	$\frac{\text{Mean sp. heat } 0^\circ-16^\circ}{\text{,, ,, } 16^\circ-24^\circ} = 1\cdot0010$	·000083
8	$\frac{\text{Mean sp. heat } 0^\circ-17^\circ}{\text{,, ,, } 17^\circ-25^\circ} = 1\cdot0027$	·000216
9	$\frac{\text{Mean sp. heat } 0^\circ-21^\circ}{\text{,, ,, } 21^\circ-28^\circ} = 1\cdot0045$	·000321
10	Requires explanation, as it gives an increasing specific heat. Also the difference between the mean temperatures (2°·5 C.) is too small to enable us to expect an accurate result. The remaining experiments are above our range	—
	Mean	·000236

It is thus apparent that the results of Rowland's investigation by this method are in closer agreement with our conclusions than they are with his own.[*] We do not, however, attach much importance to this point, since—as he justly remarks—the method by the mechanical equivalent is of far greater value.

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[*] Our value ·000266.

The values of J deduced from the two groups of Series I. and the middle group of Series II. are dependent upon the value of the water equivalent deduced from the highest and lowest weights of Series II. The agreement in the results is a sufficient proof of the accuracy of the value assigned to that equivalent.

The coefficient of increase in the specific heat of the calorimeter may appear large. TOMLINSON ('Roy. Soc. Proc.,' 1885), gives the following as the specific heat of copper and zinc :—

$$\begin{aligned} \text{Specific heat of copper}^{*} &= \cdot 09008 + \cdot 000065\ \theta_1, \\ \text{,,} \quad \text{,,} \quad \text{zinc} &= \cdot 09009 + \cdot 000075\ \theta_1, \end{aligned}$$

and he quotes the values given by BÈDE as

$$\begin{aligned} \text{Copper} &= \cdot 0892 + \cdot 000065\ \theta_1, \\ \text{Zinc} &= \cdot 0859 + \cdot 000084\ \theta_1. \end{aligned}$$

Expressing the mean of these results in the same form as that given to the expression for the water equivalent, we get

$$\begin{aligned} \text{Specific heat of copper} &= \cdot 0896\ (1 + \cdot 00071\ \theta_1), \\ \text{,,} \quad \text{,,} \quad \text{zinc} &= \cdot 0876\ (1 + \cdot 00091\ \theta_1). \end{aligned}$$

TOMLINSON states that when reducing his observations, he used REGNAULT'S expression for the capacity for heat of water, viz., $1 + \cdot 00004\ \theta_1 + \cdot 0000009\ \theta_1^2$.

Unfortunately the account of these experiments given in the 'Proceedings' does not supply us with sufficient data to estimate the changes in the coefficient of θ_1 that would be caused by assuming our expression for the specific heat of water. We are, therefore, unable to say how far our rate of increase in the water equivalent agrees with the above determinations. We are, however, enabled to state that the values of the specific heats at 0° C. would be reduced by about 6 parts in 1000, on the assumption that our formula holds over so large a range.

Our calorimeter may be regarded as a mixture of copper, zinc, gold, glass, and mercury, and the coefficient of increase of such a mixture can only be obtained by direct experiment.

ROWLAND, in order to compare his results with those of JOULE, expressed both in kilogrammetres at Baltimore ($g = 980 \cdot 05$), and gave the numerical value of J in terms of water at differing temperatures, assuming his own value of the specific heat of water. In order to make a similar comparison we give our results in the same form. The following Table is extracted from the Appendix to ROWLAND'S paper, with the exception of the last column, which we have added.

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* TOMLINSON'S paper (Table II., p. 497) contains an obvious misprint in the coefficient of θ_1.

TABLE XLV.—Comparative values of J given by JOULE, ROWLAND, and GRIFFITHS.

Date.	JOULE'S method.	Temperature of water.	JOULE'S value in the metric system. Reduced to ROWLAND'S air-thermometer.	ROWLAND, 1880.	GRIFFITHS, 1892.
		° C.			
1847	Friction of water . . .	15	442·8	427·4	427·9
1850	,, ,, . . .	14	426·8	427·7	428·1
1850	Friction of mercury . .	9	427·5	428·8	428·6
1850	,, ,, . .	9	428·7	428·8	428·6
1850	Friction of iron. . . .	9	429·1	428·8	428·6
1850	,, ,, ...	9	428·0	428·8	428·6
1867	Electric heating . . .	18·6	428·0*	426·7	427·6
1878	Friction of water . . .	14·7	425·8	427·6	427·9
1878	,, ,, . . .	12·7	427·1	428·0	428·2
1878	,, ,, . . .	15·5	426·0	427·3	427·9
1878	,, ,, . . .	14·5	422·7	427·5	428·0
1878	,, ,, . . .	17·3	426·3	426·9	427·7

ROWLAND remarks as follows : "JOULE rejected quite a number of his results, but I have thought it best to include them, giving them small weight however. In this way we obtain a value of JOULE'S experiments of 426·75 at 14°·6 C., my value at this point being 427·52 ; the difference amounts to 1 in 550 only."

Adopting this method of comparison we get (at 14°·6 C., and expressed in kilogrammetres at Baltimore) :

JOULE.	ROWLAND.	GRIFFITHS.
426·75	427·52	427·98

Thus our difference from JOULE amounts to 1 in 350,† and our difference from ROWLAND amounts to 1 in 930.‡

The difference between ROWLAND'S determinations of the changes in the specific heat of water and ours, would cause the values of J to be identical if expressed in terms of a thermal unit at 11°·5 C., and below that temperature ROWLAND'S value would be the greater.

[Notes by E. H. G., added April, 1893.

1. No change in the value of the various units, or constants, involved in our

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* Value deduced by ROWLAND by assuming his own value of the ohm.

† If we attach equal weight to the different values given by JOULE (ROWLAND in obtaining the above numbers attached arbitrary values to different experiments and methods) we obtain J = 428·23 as the mean value at 13°·2 C., *i.e.*, J = 428·08 at 14°·6 C. This *exceeds* our value by 1 in 4281.

‡ If we assume the E.M.F. of our cells to be that of the Cavendish standard, our value would be 427·86 and these differences would become 1 in 386 and 1 in 1260 respectively.

investigation could bring our results into absolute agreement with those obtained by ROWLAND, since, owing to the difference in the expressions for the temperature coefficients of the specific heat of water, it is inevitable that our conclusions should agree at some one temperature, but must necessarily differ when expressed in terms of a thermal unit at any other temperature, and, thus, changes in the values of the units would only alter the temperature of agreement. For example, Dr. GUILLAUME has pointed out to me that the experiments of Commandant DEFFORGES lead to the conclusion that the value of g, at Greenwich, should be increased from 981·17 centims. to 981·24 centims. A similar correction would slightly increase ROWLAND'S value of J, and thus cause our point of agreement to be about 12° C. instead of $11^\circ{\cdot}5$ C. Again, the value of g, assumed by Lord RAYLEIGH ('Phil. Trans.,' A., 1884, p. 427), would have to be slightly increased, and the resulting values of the electro-chemical equivalent of silver, and of the absolute electromotive force of a Clark cell, would require modification, but the only result of any such change would, as before, be to shift the temperature of agreement.

It is, therefore, evident that the difference is chiefly due to errors in thermometry. An error of $0^\circ{\cdot}01$ C., in the value of the range 14° to 25° C., would suffice to explain the discrepancy between the results, and the close agreement in the range value, as obtained from our standard and the Paris nitrogen standard (see p. 430, *supra*), appears to me to warrant a brief criticism of ROWLAND'S methods and conclusions.

The science of exact thermometry has made great strides during the past fourteen years, and, no doubt, much of this progress is due to ROWLAND'S initiative, for his work undoubtedly marks a distinct advance in this subject. Great, however, as his services have been, he would, I feel sure, be the first to admit that his investigations of 1878–79, by no means exhaust the possibilities of further progress in the science of thermometry. In his paper, he constantly indicates possible causes of error, and, in some cases, makes valuable suggestions as to methods by which they may be eliminated.

In a previous paper ('Phil. Trans.,' A., 1891, p. 155) it was pointed out by Mr. CALLENDAR and myself that "the indications of the air-thermometer cannot be relied on beyond $0^\circ{\cdot}01$ C.... the limit of accuracy of a single reading of the barometer."

On p. 95 of his paper, ROWLAND gives the data on which the following statements are based. A difference of ·03 millim. in the reading of his barometer gave a difference of $0^\circ{\cdot}01$ C. in the air-temperature, and an error of $0^\circ{\cdot}3$ C. in the estimation of the temperature of his barometer-column would produce the same effect. From his remarks, it is evident that he regarded his possible error from this cause alone as $\pm\ 0^\circ{\cdot}01$ C.

Again, his temperatures depended on the direct observation of the height of a mercury manometer column by means of a cathetometer, and everyone who has worked with such an instrument knows the difficulty of obtaining measurements accurate to ± ·02 millim. (It is true that *small* differences can be read to a much closer degree of accuracy by means of a microscope fitted with a micrometer scale, but this method is not applicable when large differences have to be read, nor does it appear to have been adopted by ROWLAND.) On p. 94, ROWLAND remarks that on repeating the observations upon an accurate scale, they "agreed with the scale to within two or three hundredths of a millimetre, which was as near as I could read on such an object," and 0·03 millim. appears to have been equivalent to 0°·01 C. Also, the temperature of the manometer column was only ascertained by means of a thermometer placed alongside it, and the uncertainty thus introduced might nearly double the resulting error.

A study of ROWLAND'S Tables, XI. to XV., leads to the conclusion that the discrepancy between individual observations, due to the above and other causes, in some cases amounted to as much as 0°·03 to 0°·04 C.

The following extract will, I think, show that ROWLAND did not rely upon his observations to ± 0°·01 C. In his concluding remarks he says: "I now believe that, with the improvement to the air-thermometer of an artificial atmosphere of constant pressure, we could be reasonably certain of obtaining the temperature at any point up to 50° C., within 0°·01 C. from the mean of two or three observations. I believe that my own thermometers scarcely differ much more than that from the absolute scale at any point up to 40° C., but they represent the mean of eight observations. However, there is an uncertainty of 0°·01 C. at the 20° C. point, owing to uncertainty in the value of m. But, taking $m = \cdot 00015$, I hardly think that the point is uncertain to more than that amount for the thermometers Nos. 6163, 6165, and 6166."

The causes of error above enumerated do not affect the platinum thermometer determinations to the same extent. It is true that the values of d (which corresponds to ROWLAND'S quantity, m), are dependent upon the boiling-points of water and sulphur, which are again dependent on barometer readings, but, on the other hand, an error of as much as 0°·1 C., at those points, would produce so little change in d as to leave the value of our range unaltered, although it would slightly affect the actual elevation; more especially, it should be noticed that any small changes of pressure which may take place *during the comparison of the platinum thermometer with other thermometers* do not affect the results.

The above considerations appear to me to justify the conclusion that the value of ROWLAND'S temperature range, 14° to 25° C., may be in error by as much as 0°·011 C., and, if this is the case, the values of the C.G.S. unit of heat, and of the temperature coefficients of the specific heat of water, as deduced from his experiments, may be identical with ours.

2. I have, since the publication of an abstract of this paper, received several communications criticising our statement (see p. 496, *supra*), that we differ from the results obtained by JOULE, by "1 part in 350," and my correspondents have pointed out that the ratio, 772·55 to 778·99, is very different from that of 349 to 350. It would, therefore, appear necessary that I should indicate, more fully than I have

done, the ground upon which we based the above statement. Joule himself, in 1879, made a careful comparison of his thermometer with one which had been standardized by Rowland (Baudin's Therm., No. 6166). The results were published as an appendix to Rowland's paper in the 'Proceedings of the American Academy' for March, 1880. A considerable correction in the values obtained by Joule was then found to be necessary. Again, Joule had assumed Regnault's expression for the specific heat of water, and a correction for the capacity for heat of the calorimeter was also rendered necessary by the changes in the thermometry. As the appendix above referred to appears to be but little known in this country, I give one example (p. 44, *ibid.*) to indicate the nature of the various corrections.

Joule's result in 1878 (friction of water)		774·6
Correction for thermometer	+	3·7
" " capacity for heat	+	·2
" " latitude (to Baltimore)	+	·9
" " vacuum	—	·9
Corrected value (at 12°·7 C.) . . .		778·5

As these corrections were published in 1880, it appears probable that, had they not met with Joule's approval, he would have signified his dissent, but I can find no record of any such expression of opinion on his part.

As previously stated, Rowland attached what appear to me to be curiously arbitrary values to certain of Joule's experiments. If we accept his verdict as to their respective merits, the mean of the selected experiments, as corrected by Rowland (but reduced by me to temperature 15°, and to latitude Greenwich), is 776·75 ft.-lbs.; but if we assign equal value to all Joule's published results, the corrected mean becomes 779·17 ft.-lbs., and it was on these numbers that our statement was based.

It is extraordinary that, although these results (or rather the corrections by which they are deduced) were published as far back as 1880, we still find that our modern books of reference continue to give 772·55 as the number resulting from Joule's own experiments.]

APPENDIX I.

Determination of the "Null Point" and an alternative Method of calculating the Results.

As stated in the introduction we append a full analysis of the "null point," *i.e.*, the point at which the radiation is self-eliminated.

Using a similar notation to that on p. 478, we have as the equation of condition

$$\mathrm{M}\frac{d\theta}{dt} = a - \rho\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

where the temperatures are measured from that of the surrounding envelope.

For the sake of simplicity we can assume that the values of a and M remain constant.

Integrating and putting $\lambda = \rho/\mathrm{M}$, $\mu = a/\mathrm{M}$, and determining the constant from the fact that when $t = 0$, $\theta = -\theta_0$, we obtain the equation

$$e^{\lambda t} = \frac{\frac{\mu}{\lambda} + \theta_0}{\frac{\mu}{\lambda} - \theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

If there had been no radiation, $\rho = 0$, and the equation of condition would have been $d\theta/dt = \mu$.

Integrating, and using the same constant as before

$$\theta = \mu t - \theta_0 \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

If we find the points of intersection of (2) and (3) one point $(-\theta_0, 0)$ is that at which the experiment commenced, the other (Θ, T) is the point on (2) at which the radiation is eliminated.

It is more convenient, for experimental work, to obtain an expression involving T rather than Θ; substituting therefore the value of θ given by (3) in (2), we obtain

$$e^{\lambda \mathrm{T}} - \frac{\frac{\mu}{\lambda} + \theta_0}{\mu} \, \frac{e^{\lambda \mathrm{T}} - 1}{\mathrm{T}} = 0 \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

This equation can be solved for T when the values of λ, μ, θ_0 are known.

In order to obtain λ, μ, we can take the following observations: Commence an experiment at $-\theta_0$, note the time t when $\theta = 0$, and again note the time t_2, when $\theta = +\theta_0$.

Then equation (2) gives the relations

$$e^{\lambda t_1} = \frac{\frac{\mu}{\lambda} + \theta_0}{\frac{\mu}{\lambda}} \quad \ldots\ldots\ldots\ldots \quad (5),$$

and

$$e^{\lambda t_2} = \frac{\frac{\mu}{\lambda} + \theta_0}{\frac{\mu}{\lambda} - \theta_0} \quad \ldots\ldots\ldots\ldots \quad (6).^*$$

From this pair of equations we can eliminate $\lambda\theta_0/\mu$ and obtain

$$2\{e^{\lambda(t_2 - t_1)} - 1\} - \{e^{\lambda t_2} - 1\} = 0 \quad \ldots\ldots\ldots \quad (7),$$

which is the equation from which to determine λ.

So far as we are aware, the solution of these equations cannot be expressed as an algebraical expansion, except on the assumption that λt_1, λt_2, $\lambda \mathrm{T}$ are small. Making this assumption, and writing $x = t_2 - 2t_1$, successive approximation leads to

$$\mathrm{T} = 2t_1 + \tfrac{1}{3}x - \tfrac{2}{9}\frac{x^2}{t_1} + \frac{787}{200}\frac{x^3}{t_1^2} \quad \ldots\ldots\ldots \quad (8).$$

The method which we have found best adapted to the numerical solution of such equations amounts practically to tracing their graph, using, for instance, in equation (7), λ and $f(\lambda)$ as abscissa and ordinate. A rough approximation to the value of λ is soon obtained, and afterwards by means of a table of logarithms as close an approximation as is necessary can be found.

Since μ does not occur as an exponential, its value is at once found from (5) or (6).

Equation (4) can be solved for T in a similar manner to equation (7), using T and $f(\mathrm{T})$ as abscissa and ordinate. A rough approximation to the value of T is given by equation (8),

$$\mathrm{T} = 2t_1 + \tfrac{1}{3}(t_2 - 2t_1).$$

The forms given to equations (4) and (7) are those which we have found most convenient from which to calculate the values of $f(\lambda)$ and $f(\mathrm{T})$.

Besides being thus able to eliminate radiation, we can at the same time eliminate the change in all those quantities whose rate of variation can be expressed as a linear function of the temperature. Thus, on p. 477, we have shown that when the variations in M and a are considered, their full values are

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* Equation (6) shows that θ_0 is not altogether at our disposal, but must be less than μ/λ. For, otherwise, the calorimeter would reach its final state, where the loss by radiation balances the supply of heat, and could never attain the temperature $+ \theta_0$.

$$a' = a\{1 - k(\theta + \beta)\}$$
$$M' = M\{1 + l\theta\},$$

and, hence, equation (1) becomes

$$M(1 + l\theta)\frac{d\theta}{dt} = a\{1 - k(\theta + \beta)\} - \rho\theta. \quad . \quad . \quad . \quad . \quad . \quad (9).^*$$

By neglecting squares and products of small quantities (9) can be written in the same form as (1), thus,

$$M\frac{d\theta}{dt} = a(1 - k\beta) - \{\rho + a(k + l)\}\theta,$$

and the values of λ and μ become

$$\lambda = \frac{l + a(k + l)}{M}, \quad \mu = \frac{a(1 - k\beta)}{M}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10),$$

where $a = n^2E^2/JR$.

Let λ_{11}, μ_{11} denote the values of λ and μ when a weight of water W_1 and an E.M.F. of n_1 Clark cells are used, the first suffix referring to the weight, the second to the number of Clark cells; further, as before, let W_x be the water equivalent.

Then

$$\mu_{11} = \frac{n_1{}^2E^2\{1 - k\beta_1\}}{JR(W_1 + W_x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

(β_1 is written for β as its value is dependent on n).

Similarly

$$\mu_{21} = \frac{n_1{}^2E^2\{1 - k\beta_1\}}{JR(W_2 + W_x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).$$

Hence, by division of (11) and (12),

$$\frac{\mu_{11}}{\mu_{21}} = \frac{W_2 + W_x}{W_1 + W_x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13).$$

Equation (13) gives the means of calculating the water equivalent.

Writing M_1, M_2 for $W_1 + W_x$ and $W_2 + W_x$ respectively, we have

$$\mu_{12} = \frac{n_2{}^2E^2\{1 - k\beta_2\}}{J.R.M_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14),$$

which, with (11), gives

$$\frac{\mu_{12}}{\mu_{11}} = \frac{n_2{}^2}{n_1{}^2}\cdot\frac{1 - k\beta_2}{1 - k\beta_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15).$$

---

* This does not introduce σ, the heat developed by the stirrer, but this can be found by preliminary experiments and due allowance made for it.

If k, the temperature coefficient of the resistance of the wire, is determined by preliminary observations, and we assume $\beta = p\mathrm{E}^2$ where p is a constant (p. 400), we have with (15) sufficient data to determine the values of β_1, β_2. Equation (11) then gives

$$\mathrm{J} = \frac{n_1{}^2\mathrm{E}^2 \{1 - k\beta_1\}}{\mathrm{M}_1.\mathrm{R}.\mu_{11}} \quad \ldots\ldots\ldots \quad (16).$$

Again equation (10) gives

$$\lambda_{11} = \frac{\rho}{\mathrm{M}_1} + \frac{n_1{}^2\mathrm{E}^2 (k + l_1)}{\mathrm{J.R.M}_1} \quad \ldots\ldots\ldots \quad (17),$$

and

$$\lambda_{12} = \frac{\rho}{\mathrm{M}_2} + \frac{n_2{}^2\mathrm{E}^2 (k + l_1)}{\mathrm{J.R.M}_1} \quad \ldots\ldots\ldots \quad (18),$$

which are two equations to give ρ and l_1.

Similarly, by performing the operations λ_{21} and λ_{22}, we could determine the value of l_2; and since (p. 480)

$$l_1 = \frac{f\mathrm{W}_1 + g\mathrm{W}_x}{\mathrm{W}_1 + \mathrm{W}_x} \quad \text{and} \quad l_2 = \frac{f\mathrm{W}_2 + g\mathrm{W}_x}{\mathrm{W}_1 + \mathrm{W}_x},$$

we can find both f and g, the coefficients of increase in specific heat of water and of the calorimeter.

APPENDIX II.

The Regulator for Maintaining the Laboratory at a Constant Temperature.

A narrow glass tube, several feet in length, was fixed in a horizontal position on one of the walls.* This tube contained chloride of silver, and a stream of dry ammonia gas at a low temperature was passed through it until the compound $\mathrm{AgCl,3NH_3}$ was formed.† This compound, as pointed out by ISAMBERT, dissociates at ordinary temperatures, the pressure of the vapour at about 15° C. altering by more than 12 millims. per degree. Care had to be taken to completely saturate the AgCl, for the pressure of the vapour $\mathrm{AgCl,2NH_3}$ changes at ordinary temperatures by a much smaller amount. The horizontal tube communicated with a gas regulator of the ordinary pattern, except that the diameter of the regulator tube could be made of any size, since we are dealing with the pressure of a saturated vapour, not with that of a gas, and thus the changes in *volume* caused by a movement of the mercury column could be disregarded, the diameter of the smallest pipe in our

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* The exterior of this tube was blackened.

† This substance was suggested by Mr. C. T. HEYCOCK.

regulator exceeding 1 centim. In order to diminish the effect of changes in the atmospheric pressure, some air was allowed to remain in the horizontal tube. As the column of mercury communicating with the regulator was about 800 millims. in height, this residual air was under a pressure of two atmospheres, and, its volume being very small, and the diameter of the mercury tube large, a small movement sufficed to compensate changes in atmospheric pressure. Thus, an alteration of 20 millims. in the barometer produced a change of only a fraction of a degree in the resulting laboratory temperature. The gas, after passing through the regulator, communicated with a large Doulton ware stove, in which small pilot lights were always kept burning by means of an independent supply. An entrance and an exit tube, closed by glass taps, were so fixed in the vertical tube containing the mercury that, by their means, the instrument could be adjusted.

The action of the apparatus is, in many ways, interesting. On a day when the gas would be burning, if the room was unoccupied, the presence of one person in the room would diminish the supply, whereas the presence of two or three would cause it to be entirely cut off. We were surprised to learn, by this means, the amount of heat communicated to a room by the presence of a human being.

Fig. 1.

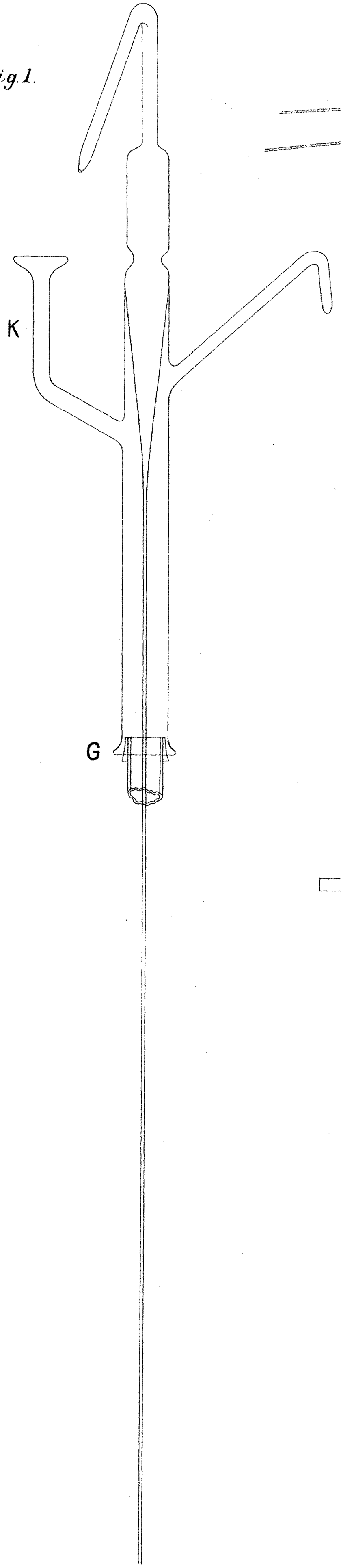
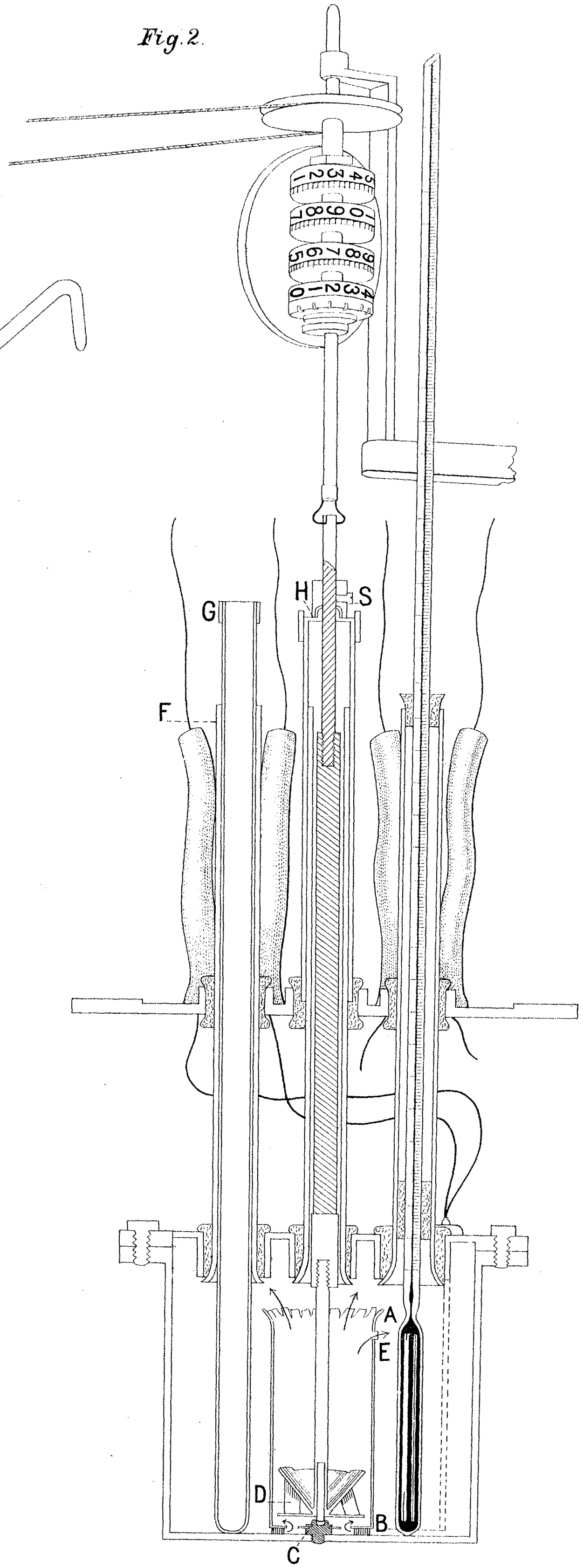
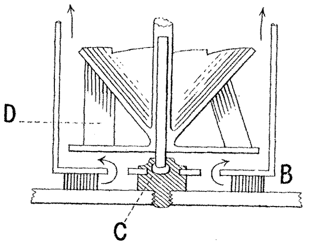


Fig. 2.

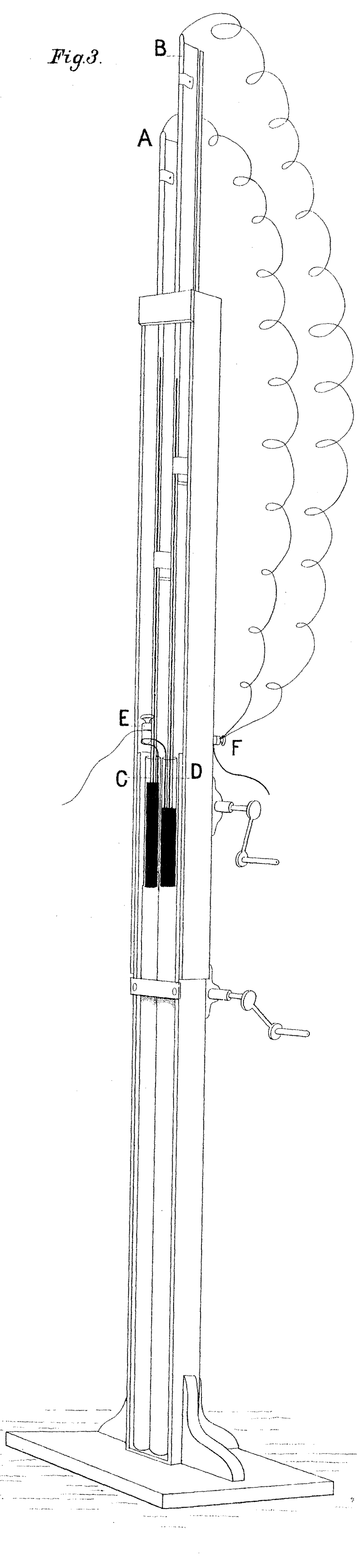


Half size

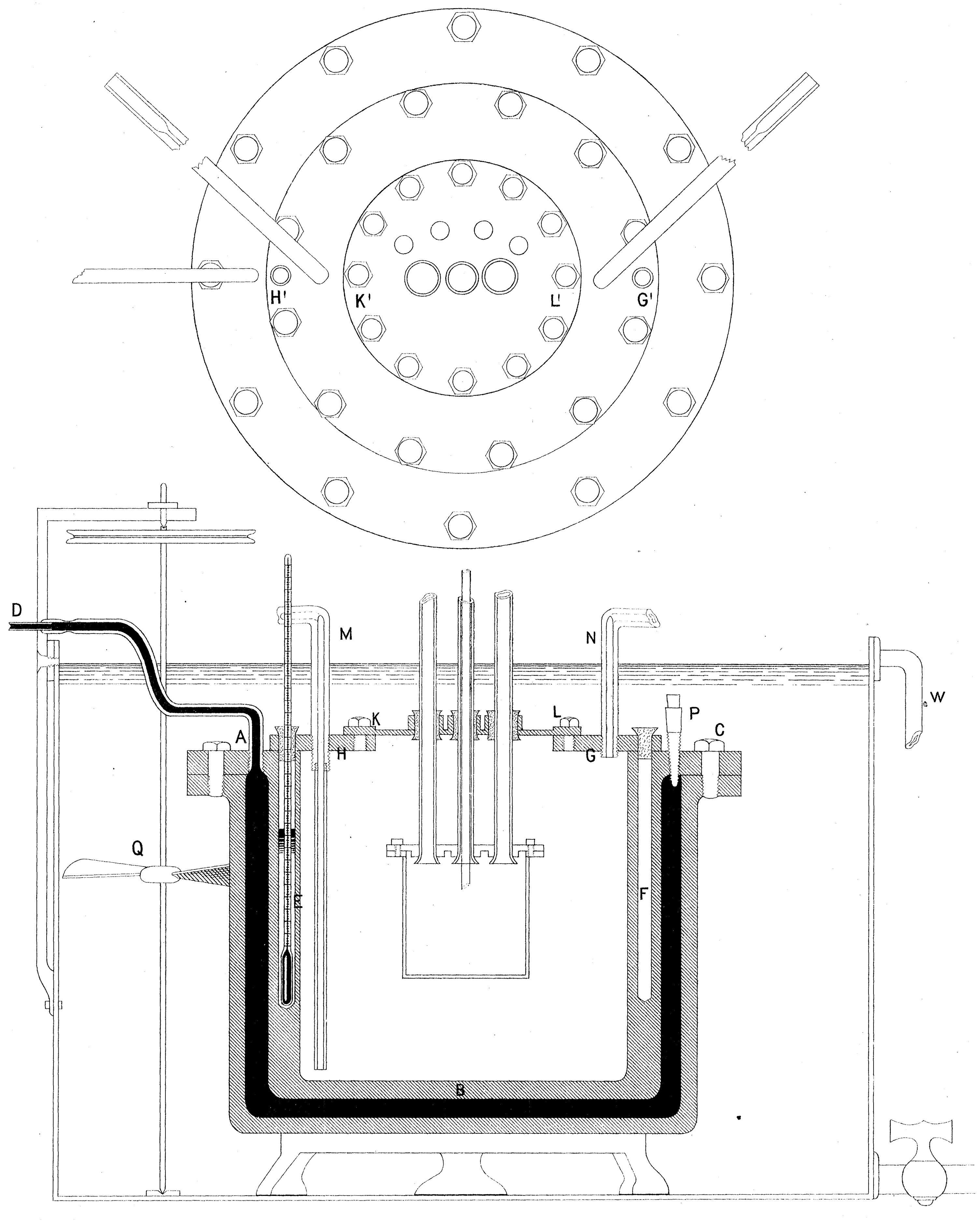


Full size

Fig. 3.



Edwin Wilson, Cambridge.



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Edwin Wilson, Cambridge.

Fig. 1.

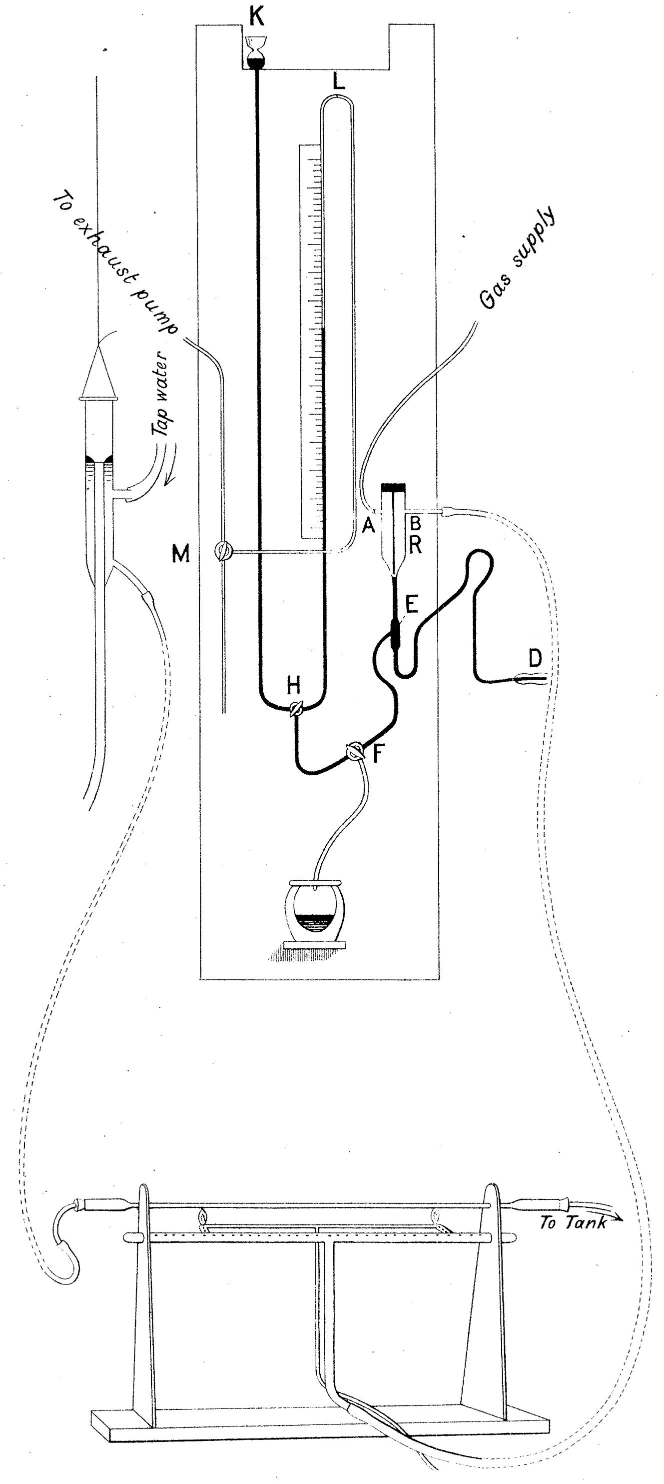
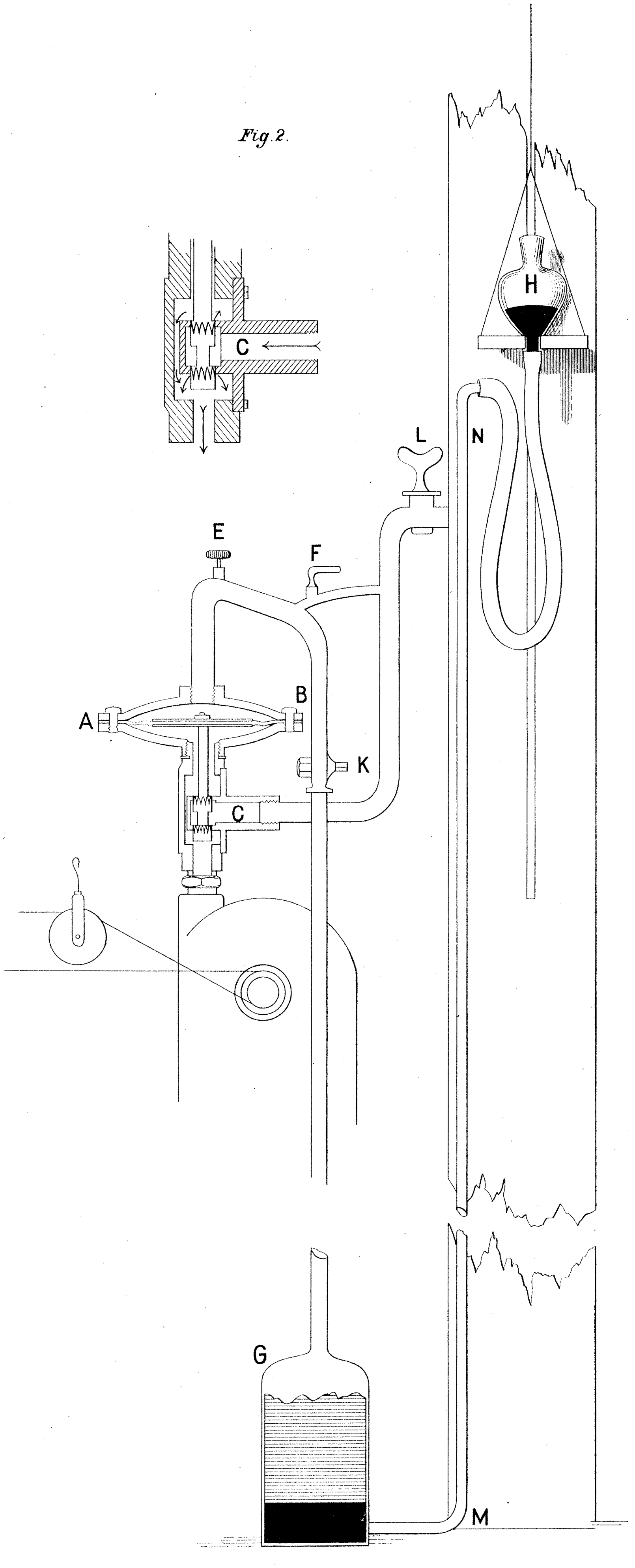


Fig. 2.



Edwin Wilson, Cambridge.