The Specific Heat of Water and the Mechanical Equivalent of the Calorie at Temperatures from O degrees C. to 80 degrees C.

W. R. Bousfield and W. Eric Bousfield

Email alerting service	Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click **here**

[199]

V. *The Specific Heat of Water and the Mechanical Equivalent of the Calorie at Temperatures from 0° C. to 80° C.*

By W. R. Bousfield, *M.A., K.C., and* W. Eric Bousfield, *B.A.*

Communicated by Sir Joseph Larmor, *Sec. R.S.*

Contents.

1. *Introduction.*—The work described in this paper started from the researches upon the properties of aqueous solutions, which have occupied one of us for some years past.* In the course of this work it had been found that the measurement of various physical properties of solutions, including density, conductivity, and viscosity, at various temperatures and various concentrations, threw considerable light, not only on the constitution of solutions, but upon that of water itself and upon the amounts

---

* See Bousfield and Lowry, 'Phil. Trans.,' A, vol. 204, p. 253, 1905; Bousfield, 'Zeit. für Phys. Chem.,' vol. 53, p. 257, 1905; Bousfield, 'Phil. Trans.,' A, vol. 206, p. 101, 1906; Bousfield and Lowry, 'Trans. Farad. Soc.,' vol. 3, p. 123, 1907; Bousfield and Lowry, 'Trans. Farad. Soc.,' vol. 6, p. 85, 1910.

of water combined with a solute at various temperatures and concentrations. It seemed probable that similar series of observations upon the specific heat of solutions over considerable ranges of concentration and temperature would throw further light upon these matters, and the apparatus described in this paper was therefore primarily designed for the observation of the specific heat of solutions with the desired degree of accuracy, and with the facility and ease of manipulation which are essential when it is required to amass a large body of data in a reasonable time.

At an early stage it became apparent that the temperature-specific heat curve of water was entirely altered in character by the introduction of a small amount of solute. With a half-normal solution of KCl the more or less parabolic curve for water becomes nearly a straight line, and even with fairly dilute solutions the water curve is greatly modified. The appreciation of this modification necessarily involved as a starting-point the consideration of the curve for pure water, as to the form of which different observers have come to widely different conclusions. A reference to fig. 10 (Section 14 *post*), where the curves given by different observers are plotted, shows that the latest form of the curve, which is the result of the researches of CALLENDAR and BARNES, differs widely from the curves given by REGNAULT and by LÜDIN.* At 80° C. the values of the specific heat of water in terms of the 15° calorie are—

$$
\begin{aligned}
&\text{BARNES} &. &. &. &. &. &. &\quad 1\cdot 0014, \\
&\text{REGNAULT} &. &. &. &. &. &\quad 1\cdot 0081, \\
&\text{LÜDIN} &. &. &. &. &. &. &\quad 1\cdot 0113,
\end{aligned}
$$

showing a difference of 1 per cent., which was of the same order as the differences we were expecting to find between dilute solutions and water. We were therefore led first of all to use the apparatus to endeavour to verify the specific heat curve for water. Moreover, it seemed likely that differences in the value (in joules) of the 15° calorie might underlie the large differences which appeared at the upper end of the temperature scale. The lowest value of the 15° calorie is that which is given by the determination by JOULE in 1878,† which works out at about 4·174 joules, whilst the highest is that given by GRIFFITHS,‡ which is 4·198, BARNES' latest value§ being 4·184. Hence it seemed desirable to endeavour to verify not only the relative values required for the specific heat curve, but also the absolute value of the mechanical equivalent. By slight modifications of our apparatus we were able to adapt it to this purpose. The method of electrical heating being that adopted, we were able to use it for continuous-flow experiments of the general type of those of CALLENDAR and BARNES. The investigation upon which we were thus launched proved sufficiently

---

* See the 'Landolt-Börnstein Tables,' ed. 1905, p. 393, where the results of previous observers are set out in parallel columns.

† JOULE, 'Phil. Trans.,' 1878, vol. 169, p. 365.

‡ GRIFFITHS, 'Phil. Trans.,' A, 1893, vol. 184, p. 361.

§ BARNES, 'Roy. Soc. Proc.,' A, vol. 82, p. 394, 1909.

lengthy without proceeding to the ultimate goal of a comparison of the specific heat curves of solutions with that of water, and the present paper deals only with the results of our apparatus as applied to water.

It is unnecessary to go into the history of previous researches, since this was carefully and compendiously reviewed by CALLENDAR and BARNES,* and we are not aware that any further work of importance has been done since. The Callendar-Barnes method was based on the electrical heating of a stream of water flowing through a small tube, the flow-tube being surrounded by a vacuum vessel, and the temperatures of inflow and outflow being measured by platinum thermometry.

One of the difficulties with which CALLENDAR and BARNES had to grapple arose from the uncertainty in the electrical units and, in particular, in the value of the Clark cell. BARNES' last correction on this score (April, 1909) involved an alteration of about 1 part in 1000 on the 1902 results. At the present time the international electrical units, in terms of which our results are given, are so closely ascertained that any uncertainty in their value does not affect the third place of decimals in the value of J. But other difficulties remain of a serious character, one of which in particular does not appear heretofore to have received sufficient attention. Measurements of the electrical energy developed in a heater usually depend in one way or another upon the value in actual use of the resistance of a standard resistance carrying the heavy heating current (in our case a current of 5 amperes). The resistance of a standard carrying only the small current required for bridge measurements may easily be determined with an accuracy much greater than 1 in 10,000 at the various temperatures of the bath in which it is immersed. But the resistance of the standard at the same temperatures of the bath when a heavy current is passing may be quite different. It has long been known that a hysteresis effect may be produced by the passage of a heavy current, that is to say, a change in the resistance which persists for a time and may afterwards disappear with a well-annealed resistance. We have found reason to believe that, in addition to this, there is another effect which we may call a thermoid effect, that is to say, a change in resistance which is of the same kind as would be produced by a considerable heating of the resistance, the greater part of which change *exists only whilst the current is passing*, the hysteresis effect being merely the small residual effect which persists when the current ceases. We cannot find that the possibility of such an effect has been guarded against in previous electrical determinations of the mechanical equivalent of heat. It might differ according to the particular alloy used for the standard resistance and the current density used in each experiment, and we suggest that it may help to account for discrepancies such as those to which we have called attention.

In order to meet this difficulty we abandoned the use of a standard resistance made

---

* See CALLENDAR, "On Continuous Electrical Calorimetry," 'Phil. Trans.,' A, vol. 199, p. 55, 1902; and BARNES, "On the Capacity for Heat of Water, &c.," same vol., p. 149.

of an alloy and adopted a mercury resistance of a novel type. It consists of a long spiral glass tube containing mercury, into the ends of which are sealed platinum wire electrodes. This spiral tube is connected with a thermometer tube provided with a scale. The spiral resistance thus forms the bulb of a thermometer and a calibration of resistance in relation to scale-reading enables the resistance to be accurately ascertained from the scale-reading even when a heavy current is passing. Two such thermometer-resistances are used in our apparatus, one as the heater, the other as a standard resistance for ascertaining the current with the aid of a battery of standard cadmium cells.

The following are the principal points of the method used by us :—

(*a*) A considerable bulk of liquid is used (about 3 litres) which is contained in a Dewar vessel and constantly stirred.

(*b*) The Dewar vessel is placed in a water-bath of plate glass. The temperature of the contents of the calorimeter is indicated by mercury thermometers which can be read through the glass walls, and for all experiments, whether involving steady or rising temperature, the temperature of the external bath is kept the same as that of the contents of the calorimeter.

(*c*) The mouth of the Dewar vessel is closed by means of a loosely fitting obturator, consisting of a circular platinum box, containing water which can be heated to the temperature desired by an electric heater. The obturator is kept at the fixed temperature of 20° C. when the contents of the calorimeter are below 10° C., and when the contents of the calorimeter are at any temperature above 10° C. the obturator is kept 10° C. higher. The obturator contains suitable open vertical tubes through which stirrer, shaft, thermometers, &c., can be passed. The heating effect due to obturator, stirring, &c., amounts to less than one-half per cent. of the electrical heating, and was determined by a separate series of experiments.

(*d*) The contents of the calorimeter are heated electrically by means of a mercury thermometer-resistance of 9 to 10 ohms furnished with a graduated scale, by means of which the resistance of the mercury, when a current is passing, is accurately known.

(*e*) The whole current is also passed through a second mercury thermometer-resistance of about 2 ohms resistance, which is in shunt with 9 cadmium cells and a galvanometer and key. The current is regulated by means of a resistance in the main circuit so as always to balance the standard cells. By this means the current is accurately known, and was kept approximately constant.

(*f*) There is also in the main current circuit a Kelvin ampere balance which served as a useful check in regulating the current, and whose corrected readings agreed within about 1 part in 5000 with the current deduced from the standard cells and thermometer-resistance.

(*g*) The current used (about 5 amperes) was obtained from a dynamo driven from power mains by an alternating current motor. The poles of the dynamo were

bridged by thirty secondary cells in series, which were not themselves capable of giving out a continuous current of more than 4 amperes, but served to take off the small variations of the dynamo current and rendered the regulation of the current more easy.

(*h*) For continuous-flow experiments water from the water-mains was used (which we may shortly designate as "tap-water"). The volume of water required in these experiments, which involved a flow of many litres of water per hour for several hours for one experiment, rendered the use of distilled water inconvenient. The water was passed through a large thermostat, and the regulation was such that it was easy to keep the temperature constant within 0°·01 C. The relative value of the specific heats of distilled water and tap-water was subsequently determined.

The fundamental experiment was the determination of the mean value of J by the method of steady flow and steady heating, and its accuracy depended on maintaining all the conditions steady for a sufficient time. The temperatures at the points of inflow and outflow could be read by means of mercury thermometers to 0°·005 C. This involved a possible error on the temperature interval of 0°·01 C. To obtain the order of accuracy at which we were aiming, it was therefore necessary to have a temperature interval of about 40° C., so that an error of 0°·01 C. would not vitiate our results by more than 1 part in 4000. For convenience the temperature of inflow was fixed at 13° C., as during the portion of the year in which the continuous-flow experiments were made, water could always be obtained from the mains below that temperature. The temperature of outflow was in the neighbourhood of 54°·5 C. This temperature range had many conveniences. The liberation of air was negligible up to about 55° C., and with a heating effect of about 240 watts the weight of water and the time of flow were such as to be easily ascertainable with an accuracy equal to that required. Moreover, the necessary corrections could be more accurately determined below this temperature than for higher temperatures.

The result of these experiments was to give the mean value of J for tap-water over the interval from 13° C. to 54°·5 C. as

$$4\cdot179.$$

The second set of experiments was to determine with the aid of the figure 4·179 the mean capacity of the calorimeter. For this purpose a weighed quantity of tap-water at the temperature of 13° C. was placed in the calorimeter and heated through the same interval. The result was to give the mean capacity of the calorimeter from 13° C. to 54°·5 C. as 595·5 joules per degree.

The third set of experiments was similar to the last, except that distilled water was used. The result of these experiments, in conjunction with the capacity figure previously obtained, was to show that the mean value of J for distilled water over the interval of 13° C. to 54°·5 C. was slightly higher, that is to say,

$$4\cdot182.$$

In order to determine the variations in the value of J from point to point it was necessary to know what, if any, variation of capacity there might be in the calorimeter. For this purpose we made a separate series of experiments on the specific heat of glass. They showed a considerable rise in the specific heat of glass in the range from 0° C. to 80° C., the expression for the mean specific heat of glass from 0 to θ being

$$S_0{}^{\theta} = 0\cdot1949 + 0\cdot000009\theta.$$

From this we were able to deduce the mean heat capacity of the calorimeter at various parts of the scale, which was requisite for the next experiments.

The fifth set of experiments was designed to determine the variation of the specific heat of water from point to point between 0° C. and 80° C.

It has been already observed that the apparatus was primarily designed so as to be specially convenient for making, with reasonable rapidity, a large number of observations on salt solutions. This involved the use of the open-mouthed Dewar vessel loosely closed by an obturator. From 80° C. to 100° C. the rise in the vapour pressure brings in corrections of too great magnitude for work of the order of accuracy required, and hence our experiments have been limited to the range from 0° C. to 80° C.

In these experiments a known weight of water was placed in the calorimeter and heated from 0° C. to 80° C. with various breaks. It has been already observed that any temperature interval, small or great, may have a possible error of 0°·01 C. in its estimation. For this reason we took a 40° C. interval for our fundamental experiment, involving a possible error in any individual result of 1 part in 4000. With shorter intervals of only 12 or 15 degrees, we now have possible errors due to this cause of 1 part in 1200, but, by taking the average of repeated observations, the probable error due to this cause is again reduced to errors of the order of 1 part in 4000. These experiments were conducted in the same manner as the third series of observations above described. The results are as follows :—

Temperature interval. ° C.	Mean value of J.
0 to 13	4·1937.
13 „ 27	4·1752.
27 „ 40	4·1756.
40 „ 55	4·1935.
55 „ 73	4·2024.
55 „ 80	4·2056.

No value is to be attached to the fourth place of decimals, except for the purpose of fixing the value in the third place. But it may be noted that whilst the result of the third series of experiments was to give

$$J_{13}{}^{55} = 4\cdot1821,$$

the result of the above entirely independent series on the shorter periods gives

$$J_{13}^{55} = 4\cdot1819.$$

Thus the temperature errors on short periods with mercury thermometers seem to disappear in the average in a satisfactory manner. The most recent figures previous to our own (BARNES, 'Roy. Soc. Proc.,' A, vol. 82, 1909, p. 390) yield a lower value for this interval, viz.,

$$J_{13}^{55} = 4\cdot175.$$

From the above values for the periods we obtain for the average values of J from $0°$ C. to any temperature θ the expression

$$J_0^\theta = 4\cdot2085 - 0\cdot0015111\theta + 0\cdot00002611\theta^2 - 0\cdot00000001225\theta^3.$$

This expression gives values which agree with the observed values within 1 part in 4000.

To obtain the series of values of J at various points from the above expression we have

$$J = \frac{d}{d\theta}(\theta J_0^\theta).$$

This gives the value of the $15°$ C. calorie as

$$4\cdot179.$$

BARNES' most recent value for the $15°$ C. calorie is

$$4\cdot184,$$

and, indeed, the only value lower than ours which has been obtained by previous workers is the figure

$$4\cdot174,$$

which results from the mechanical method employed by JOULE in 1878. We are inclined to attribute these differences from BARNES and other observers who have employed the electrical method in part to the thermoid effect, to which reference has already been made, and which appears to have been hitherto unnoticed.

We regard our fundamental figure, that is to say,

$$J_{13}^{55} = 4\cdot182,$$

for the mean value of J from $13°$ C. to $55°$ C. as being probably correct within $\pm 0\cdot001$.

2. *Description of the Calorimeter.*—In fig. 1 is shown the general arrangement of the calorimeter, with the inflow and outflow arrangements installed which were necessary for the continuous flow series of experiments. A is a Dewar vessel of clear
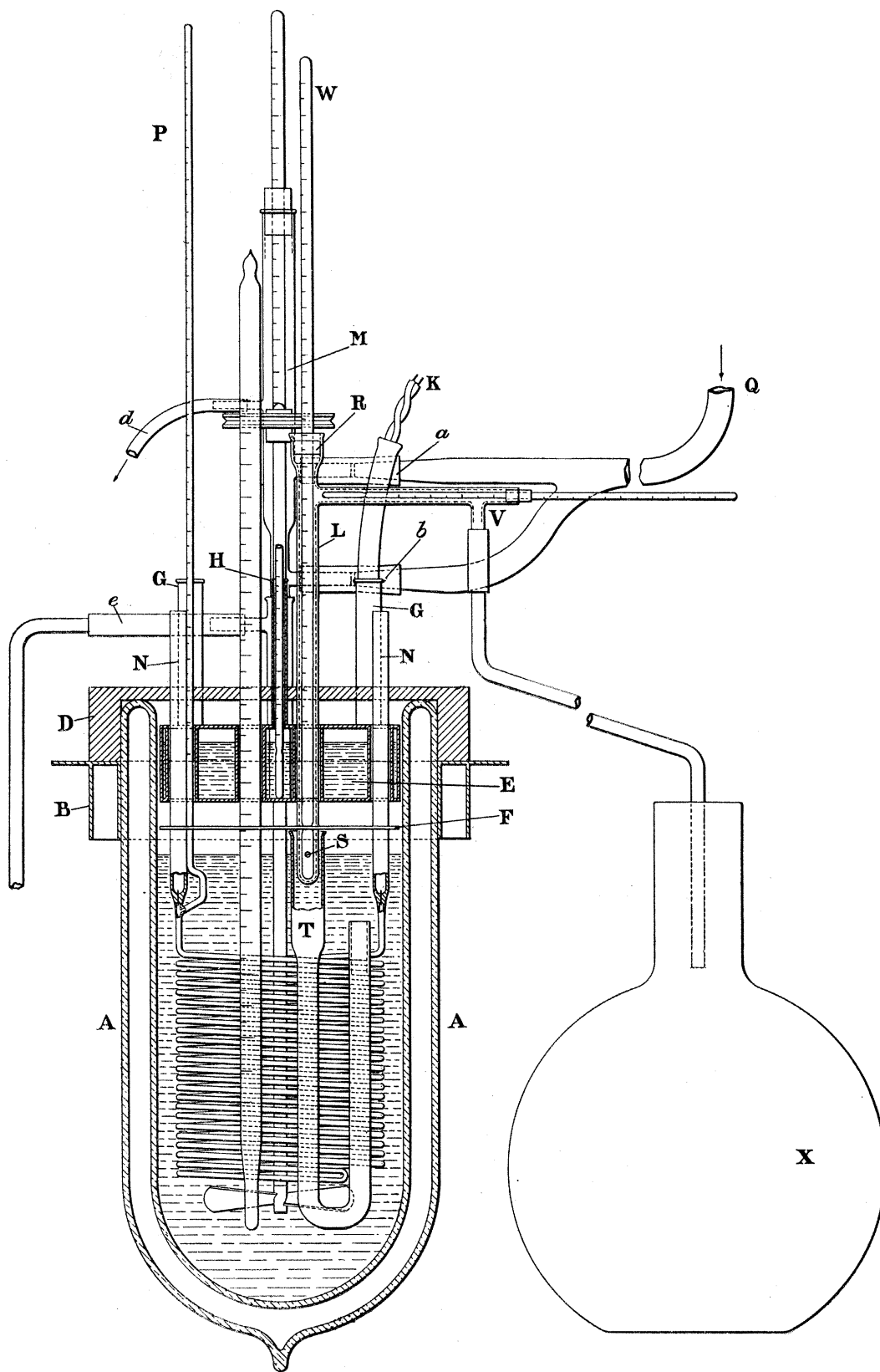
Fig. 1.

glass having a capacity of about three and a half litres. The Dewar vessel is held by means of a copper clip B in a bath with plate-glass sides (not shown), which is filled with water nearly up to the top of the clip. The Dewar vessel is closed by a wooden lid D which carries the obturator E (separately shown in fig. 2), which is suspended from the lid by means of the three tubes G, G, H, which communicate with the interior of the obturator. The obturator contains water which is introduced through one of the tubes G and is heated by an electric heater of wire (not shown) to which leads K pass through the other tube. A thermometer inserted in the tube H shows the temperature of the water in the obturator. A baffle plate F is attached to the underside of the obturator. The obturator is furnished with six tubular openings and the baffle plate is pierced with holes to correspond. Through the centre hole passes a glass rod which carries at the lower end a stirrer and at the upper end a pulley, by means of which the stirrer is constantly rotated at a speed
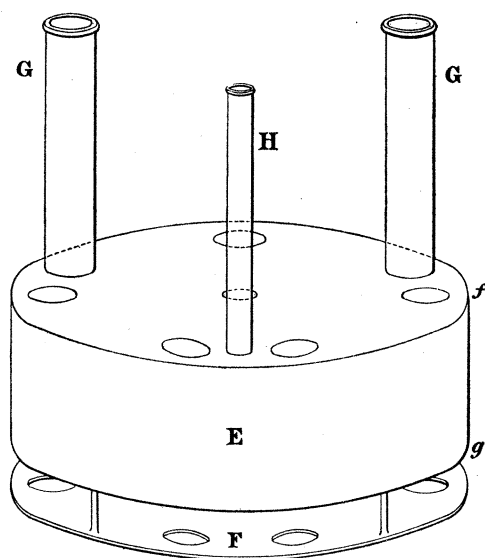
Fig. 2.
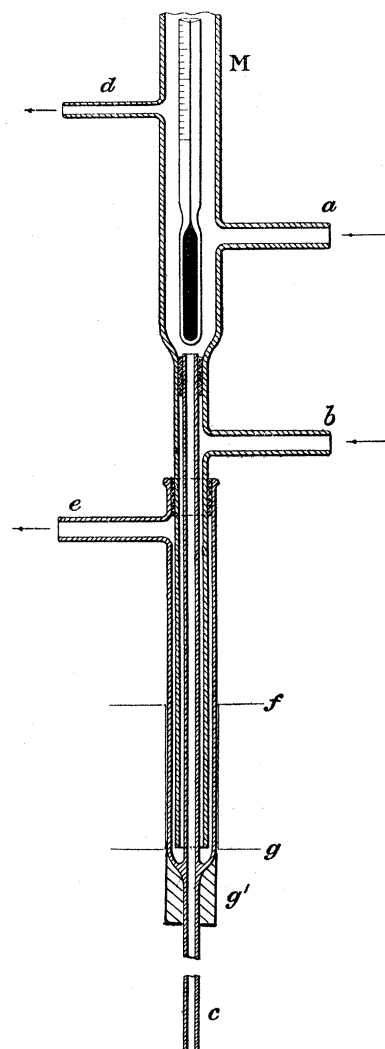
Fig. 3.

of 340 revolutions per minute. The front pair of tubes served for the insertion of two standard thermometers in the point-to-point experiments, but in the continuous flow experiments the outflow pipe LL passed through one of the front tubes, whilst the inflow pipe M (which is shown separately in fig. 3) passed through the back tube of the obturator. The other tubes served for passage of the tubular glass leads NN of the mercury thermometer-resistance, which is shown clearly in fig. 1, and forms the electrical heater of the contents of the calorimeter. This thermometer-resistance

consists of a long spiral of glass tube which is fused at each end to the tubular leads NN, there being at the points of fusion a short piece of platinum wire fused in which makes electrical connection between the mercury with which the tubular leads are filled and the mercury contained in the glass spiral. A thermometer tube P furnished with a scale communicates with the spiral glass tube, and the mercury in the spiral rises to a convenient height in the thermometer tube, so that the spiral heater forms in effect the bulb of a thermometer, the indications of which can be read off on the scale of the tube P. Thick wire leads dipping into the mercury in the tubes N served to connect the heater electrically with the dynamo.

The resistance of the heater was from 9 to 10 ohms, so that with a current of about 5 amperes a heating effect equal to 230 to 250 watts was obtained. The bore of the lead tubes NN was made of such a size (6 mm. diameter) that when using a current of about 5 amperes, which would raise the contents of the calorimeter (3 litres of water) at the rate of about 1° C. per minute, the heating effect of the current on the mercury leads in the tubes should be approximately such as to raise their temperature at the same rate. The portion of the mercury leads below the baffle plate F was taken as forming part of the heater (see Section 5).

Another mercury thermometer-resistance similar to the above, but of 2 mm. internal diameter and only 2 ohms resistance, was used to determine the current in conjunction with the standard cells. This is shown diagrammatically as M_1 in fig. 4, but does not require further description.

For the continuous flow experiments a large volume of water was required which was brought into a large thermostat raised above the level of the calorimeter. A large toluene mercury regulator of a modified Lowry type was used, and with this it was easy to maintain the inflow water during a run of some hours at a practically constant temperature (within $\pm 0°\cdot005$ C.). This cistern, in which a constant level of water was maintained, was connected with the calorimeter by a tube Q which bifurcated into two branches a and b. As the obturator was maintained at a temperature 10° C. above that of the calorimeter, it was necessary to provide for the inflow water being passed through the obturator without sensible change of temperature. The arrangement of the inflow by which this was secured is shown in detail in fig. 3. The inflow water comes in through the tube a, round the thermo-meter which indicates the inflow temperature, and passes down through the tube c into the calorimeter and mixes with the water there, after passing through a bent prolongation of the tube c, which is immersed in the calorimeter water so as to bring it up to nearly the temperature of the contents of the calorimeter before mixture therewith. The inflow water rises up to the level of tube d, and a slight excess overflows through that tube. In this way a sufficiently constant level and flow was obtained. The volume of water which passes through the tube Q and thence through tube a is only about a tenth of that which passes from the tube Q through the tube b. This latter water passes down through the jacket-tube surrounding the tube c and

thence up outside the jacket-tube and out by the exit tube *e*. By this means the inflow water is effectively shielded from heating by the obturator. The level of the top and bottom of the obturator in relation to the inflow is indicated by *f* and *g* in fig. 3.

For the outflow there is provided a tube L furnished with a side branch V. The tube L is closed at the bottom, except for a small hole S, and has an opening at the top which is closed by a cork R, through which passes the thermometer W, which indicates the outflow temperature. The bulb of this thermometer is adjacent to the orifice S through which the water passes to the outflow. Instead of taking the outflow through S direct from the main body of water in the calorimeter, it is taken through a bent tube T immersed in the water for two reasons. In the first place, the surface of the water is a good deal agitated by the stirrer, so that the tube T provides a small space in which an undisturbed surface can be maintained. In the second place, by causing the outflow to travel through the tube T a steady outflow temperature is more easy to maintain. It should be noted that the tube L jackets the lower part of the thermometer where it passes through the obturator and into the air, so that the thermometer could be read in the condition of being immersed to the level of the cork R. The reading point on the scale of the thermometer was just above the top of tube R. This arrangement secured true readings of this ther-

Fig. 4.

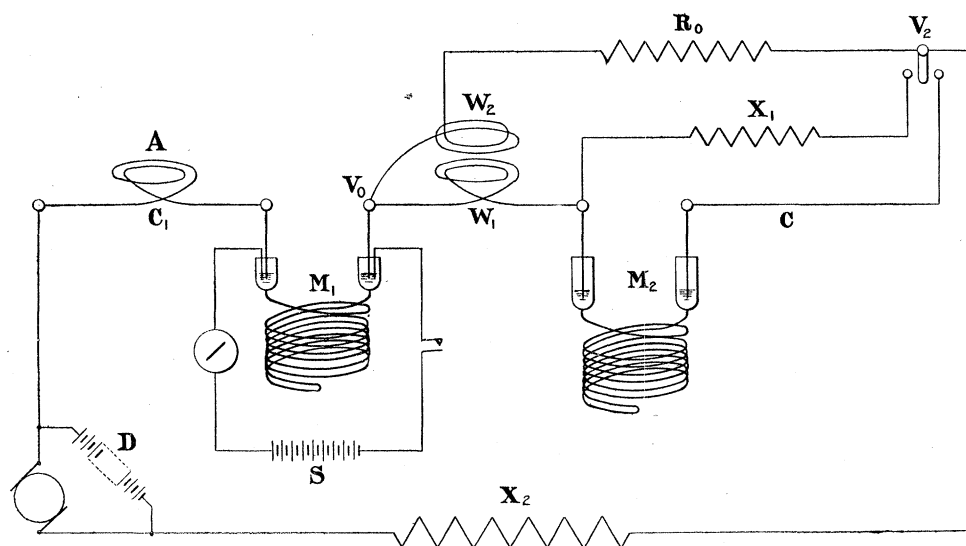mometer from calibration when immersed to the same level. A thermometer placed in the side branch V showed that the temperature of the water after it had passed through the tube L was practically the same as at the outflow point S.

From the tube V the outflow water passed by gravity through a tube of convenient length to the weighing flask X, which was placed upon a block on an adjacent table.

3. *The Electrical Arrangements.*—These are shown diagrammatically in fig. 4. M_2 is the mercury thermometer-resistance heater. M_1 is the 2-ohm resistance of similar construction. The spirals of the resistance M_1 were immersed in a current of water, so as to keep its temperature as steady as possible. A represents an ampere balance, W_1 the series coils of a watt balance, W_2 the shunt coils of this balance, in circuit with R_0, the watt balance resistance. Where used quantitatively R_0 indicates the total shunt resistance from V_0 to V_2, amounting to about 500 ohms, and M_2 indicates the total series resistance from V_0 to V_2, for observations in which the watt balance was used, so that the resistance W_1 and the leads and part of the mercury leads had to be deducted to give the net resistance R of the heater. The resistance R_0 was carefully calibrated for different temperatures and was checked from time to time. The main current passed from the point V_0 through the series coils of the watt balance W_1 and the heater to the point V_2.

At V_2 is placed a switch by means of which the current could be shunted from the heater M_2 through an equivalent idle resistance X_1. This shunt was arranged so as to be able to turn on the current in the heater at the required instant without disturbing the readings of the ampere and watt balances.

The ends of the resistance M_1 were connected up through a key and galvanometer to a battery of nine standard cadmium cells S. By means of an adjustable resistance X_2 in the main circuit the current was regulated by hand so as to keep the galvanometer always at zero. The resistance of M_1 being nearly constant and always accurately known, the total current C_1 passing in the circuit was thus kept nearly constant and always accurately known. A series of thirty secondary cells D across the poles of the dynamo served to steady the dynamo current. The current C passing through the heater is given by the expression $C = C_1 R_0 / (R_0 + M_2)$. Whilst the watt balance was in circuit, the temperature of R_0 was noted from time to time and R_0 was thus accurately known.

It was finally found that the watt balance was not sufficiently accurate, and its use was discontinued. The shunt circuit $V_0 W_2 R_0 V_2$ was then disconnected and the coils W_1 were cut out, leaving everything else the same. The whole current C_1 then passed through the mercury heater. In the later experiments without the watt balance M_2 where used quantitatively indicates the resistance of the mercury thermometer-resistance only, including the long tubular mercury leads, part of which had to be deducted from M_2 to give the net resistance R of the heater. The ampere balance was always very useful, as its indications were found to keep accurate to 1 in 5000, even in a long run, and though the actual regulation of the current by the resistance X_2 was determined by the standard cells and galvanometer, any fluctuation of the current showed itself at once on the ampere balance and gave warning of the necessity for regulation.

4. *The Primary Standards.* *Time.*—The timing of all observations was made by a Dent's ship's chronometer. This was compared at frequent intervals, and found to

gain less than 30 seconds between 7th January and 9th August, 1910, or less than 1 part in 70,000. The correction was therefore inappreciable.

Mass.—The weights used were kindly calibrated under the direction of Major MacMahon, F.R.S., at the Standards Department of the Board of Trade. The errors were of the order of 3 or 4 parts in 1,000,000. All weighings were corrected for air displacement.

Temperature.—Four mercury thermometers, each having a range of 50° C., were used for determining the temperature of the contents of the calorimeter, and for calibrating the other thermometers used. These four standards were specially calibrated at the National Physical Laboratory, and corrections (to the nearest 0°·005 C.) were given for every five degrees to reduce the readings to the hydrogen-thermometer scale. Two of these thermometers had been previously calibrated in 1903 at the Reichsanstalt at Charlottenburg. The two sets of calibrations did not differ, except at one point, by more than 0°·01 C. All these four standards had freezing-points marked, which were checked from time to time. The two chief standards (from 0° C. to 50° C. and from 50° C. to 100° C.) experienced a change of only 0°·01 C. in the freezing-point between the years 1903 and 1910. The two other standards (from 25° C. to 75° C. and from 75° C. to 125° C.) were calibrated at the National Physical Laboratory in July, 1910, and the first of these (owing to some suspicious readings) was carefully re-calibrated at the National Physical Laboratory in December, 1910.

These thermometers were of boro-silicate glass, and the depressions of the freezing-point, after heating them to 100° C., ranged from 0·025 to 0·045, and some days were required before the normal condition was again restored after heating. The thermometers were not heated beyond 80° C., and generally not beyond 73° C. The two lower-range thermometers were not heated beyond 55° C. The outflow thermometer for the continuous-flow experiments was always used at a steady temperature of about 55° C., so that no question of zero depression arose upon it. The inflow thermometer was never heated above laboratory temperature. The outflow and inflow thermometers, each of which only required to be read at one point, were repeatedly compared with the standards under the conditions of actual use. All thermometers were always used in the vertical position.*

Electrical Standards.—The electrical calibrations necessary for this investigation were originally founded upon a cadmium cell (N.P.L. 5179) and a 1-ohm manganin resistance (N.P.L. 5180). Special care was kindly given to the comparison of these standards with those of the National Physical Laboratory. The international ohm is based upon the resistance of a column of mercury 106·3 cm. in length. The international volt is such as to give the normal Weston cell, set up in accordance with the standard specification, a value of 1·0184 volts at 20° C. Dr. Glazebrook

---

* No tapping of the thermometers in use was required, as the apparatus had a stirrer always rotating at a speed of 340 revolutions a minute, the vibrations of which were more effective than tapping.

tells us that the values realised for the international volt and ohm at the National Physical Laboratory as from the 1st January, 1909, cannot differ from the absolute values by more than 2 parts in 10,000, and hence, within the limits of accuracy of the experimental work of this investigation, the values of the international volt and ohm may be taken as identical with the absolute values.

The cadmium cell (N.P.L. 5179) was tested at the National Physical Laboratory in June, 1908, and, after the preliminary work of this investigation was finished, it was again tested in December, 1909. It was found to have fallen in value in the interval by about 15 parts in 100,000. A battery of nine cadmium cells was used in our actual experiments. Each of these cells was calibrated from the standard, and the value so derived for the nine cells was 9·167 international volts at 16°·7 C.

In December, 1910, when most of the work was finished, the standard 1-ohm resistance was again sent to the National Physical Laboratory. It was found that this resistance had gone up by about 2 parts in 10,000. A re-calibration of the bridge, on which the accuracy of the working standards depended, showed that the change in the bridge resistances during this time was of the order of only 4 parts in 100,000.

The battery of nine cadmium cells was sent to the National Physical Laboratory at the same time, and its value was found to be 9·167 volts at 17° C., so that it had undergone no sensible change.

Our best thanks are due to Dr. GLAZEBROOK, F.R.S., and to his assistants, Mr. F. E. SMITH and Dr. J. A. HARKER, F.R.S., for the trouble which they so kindly gave to the calibration of the thermometers and electric standards, and for the detailed information with reference to them which they furnished from time to time.

5. *Calibration of the Mercury Thermometer-resistances.*—For this purpose a large bridge was used which, as subsequently appears, was in good working order throughout the range of comparison coils used (from 10,000 ohms to 0·1 ohm). By means of this bridge resistances could be obtained in "bridge ohms," and in order to eliminate errors in the ratio coils, and to obtain results in international ohms, corrective factors were obtained at different temperatures for resistances of the approximate value of the resistances which were being calibrated. Thus, in measuring resistances of the value of 1 to 2 ohms, the corrective factor for reducing bridge ohms to international ohms was found to vary from 0·99985, at a temperature of 10° C., to 1·00000 at 19° C. In measuring resistances of 9 to 10 ohms it was found to vary from 1·00010 at 11° C. to 1·00021 at 18° C.

To obtain these factors the large 10-ohm manganin standard, to which reference is subsequently made, which contains coils of 1, 2, 2 and 5 ohms, was calibrated from the 1-ohm primary standard by the method of substitution, and the value of each coil at 20° C. was thus found in international ohms within 1 or 2 parts in 100,000 by reference to the primary standard. Measurements of these coils on the bridge at various bridge temperatures gave the required corrective factors.

This method eliminated errors in the ratio coils, and temperature errors in the bridge, leaving only the possibility of casual errors in the range of comparison coils of the bridge. The result of the series of values obtained in the calibration of the mercury thermometer-resistance, where the maximum error found was less than 1 part in 20,000 (which error included errors in reading the thermometer graduations of the resistances), was taken as showing that the bridge itself was in sufficiently good working order, and needed only the application of the proper corrective factors to reduce bridge ohms to international ohms.

The Mercury Thermometer-resistance M_1.—When in use, this resistance had a stream of cold water flowing over the spiral, so that its temperature range was small. Within this range it was found that the temperature-resistance curve could be taken as a straight line. One calibration is given below:—

TABLE I.—Calibration of Thermometer-resistance M_1. Experiment 35B.

Temperature.	Graduation, m_1.	R, observed.	R, calculated.	Difference.
° C. 8·74	12·82	1·83742	1·83746	+ 4
	16·97	1·84452	1·84452	
13·25	17·38	1·84522	1·84522	
	20·12	1·84985	1·84987	+ 2
15·89	20·15	1·84988	1·84993	+ 5
	22·17	1·85340	1·85336	− 4

The calculated values are from the expression

$$R = 1\text{·}81567 + 0\text{·}0017 m_1.$$

The bridge factor was about unity, so that the result is in international ohms. The differences between observed and calculated values show that the resistance can be calculated from the graduations of the mercury thermometer tube with an accuracy of within about 1 in 40,000. But for practical purposes the constant was calculated only to the fourth decimal place, giving a possible error of the order of 1 in 18,000.

The Mercury Thermometer-resistance M_2.—This served as the electrical heater in the calorimeter, and was calibrated under the actual conditions of subsequent use, that is to say, the whole apparatus was installed as for a specific heat observation, the calorimeter contained the requisite amount of water, the heater was itself used to raise the temperature step by step from 0° C. to 80° C., and the obturator (through which pass the large mercury leads of the heater) was kept at 20° C. whilst the temperature of the calorimeter rose from 0° C. to 10° C., and was thenceforward kept at 10° C. above the temperature of the calorimeter. In Table II. the

Table II.—Calibration of Thermometer-resistance M_2. Experiment 34.

Calorimeter temperature.	Graduation, m_2.	M_2, observed.	M_2, calculated.	Difference.
° C.				
2·82	4·98	9·5115	9·5114	+ 1
2·92	5·00	9·5123	9·5120	+ 3
3·10	5·06	9·5138	9·5138	±
3·32	5·12	9·5156	9·5155	+ 1
10·20	7·04	9·5725	9·5721	+ 4
10·38	7·09	9·5740	9·5736	+ 4
20·43	9·96	9·6601	9·6600	+ 1
20·50	9·99	9·6606	9·6609	− 3
29·92	12·65	9·7429	9·7431	− 2
29·97	12·66	9·7433	9·7434	− 1
40·17	15·52	9·8342	9·8339	+ 3
40·20	15·54	9·8344	9·8345	− 1
50·17	18·37	9·9261	9·9262	− 1
50·19	18·39	9·9264	9·9268	− 4
60·17	21·13	10·0180	10·0177	+ 3
60·18	21·14	10·0181	10·0180	+ 1
70·17	23·90	10·1115	10·1117	− 2
70·17	23·89	10·1115	10·1113	+ 2
80·10	26·64	10·2068	10·2067	+ 1
80·10	26·64	10·2068	10·2067	+ 1

figures in the first column give the temperature of the contents of the calorimeter, those in the second give the values of m_2, that is to say, the readings of the scale of the thermometer tube of the resistance. The readings in the third column give the resistance (including the leads amounting to about 0·14) as measured in "bridge ohms" on the bridge, and those in the fourth column give the resistance in "bridge ohms" calculated from the formula

$$M_2 = 9·3696 + 0·02781 m_2 + 0·0001355 m_2^2.$$

The fifth column shows the difference between observed and calculated values. This difference covers both errors of observation of the thermometer scale and casual errors from point to point in the bridge coils. The maximum single error is of the order of 1 in 20,000, whilst the mean error is less than 1 in 50,000. The result shows that the bridge was in sufficiently good working order, and that the resistance of M_2 could be deduced from the graduation readings by means of the formula with the order of accuracy required. The corrective factor to reduce "bridge ohms" to international ohms was found to be on this occasion in measuring 9 ohms 1·00013 and for 10 ohms 1·00015. Taking the factor as 1·00014, this gives by multiplication the value of M_2 in international ohms as

$$M_2 = 9·3709 + 0·02781 m_2 + 0·0001355 m_2^2.$$

The constant in this formula includes the wire leads to the bridge and also the large mercury leads of the heater.

In the above formulæ for M_1 and M_2 the coefficients of m_1 and of m_2 and $m_2{}^2$ remained constant over a long period of time, but small changes in the constant terms took place owing, perhaps, partly to contraction of the glass and partly to the working out of minute bubbles of air. In order to avoid errors arising from these causes the resistances were constantly re-calibrated at points in the neighbourhood of those at which the resistances were actually in use. This re-calibration was usually carried out immediately after the conclusion of an experiment in which the resistances were used, which had the additional advantage of eliminating any correction for the effect of changes of laboratory temperature on the exposed stem of the thermometer tube of the resistance. Examples of such re-calibration may be seen in the details of experiments set out in Appendices A and B.

Definition of the Mercury Heater.—One of the difficulties involved in any system of calorimetry by electric heating is the definition of the limits of the heater. The heater necessarily is connected with leads which are also heated by the passage of the current, and as the leads conduct heat as well as electricity, it is always difficult to say at what precise point the resistance is to be reckoned as belonging to the leads and not to the heater. There must always be a certain debatable portion at the junction of leads and heater, and the endeavour must be to make the resistance of the debatable portion negligible in relation to that of the heater within the limits of accuracy desired.

For the purpose of heating from one temperature to another the problem is slightly different from that of heating for continuous flow. For instance, in the design of the present heater the diameter of the mercury leads was chosen so that with a current sufficient to heat the contents of the calorimeter at the rate of 1° C. per minute the heat developed in the mercury leads should be about sufficient to raise the temperature of the leads at the same rate. The resistance of a portion of the leads could be then included or not in the resistance of the heater, the only effect being to alter the capacity of the calorimeter.

But for the purpose of continuous-flow experiments the leads remaining at a steady temperature might still serve as a source of heat to the contents of the calorimeter. Referring to fig. 1, showing the position of the obturator and the water level in continuous flow, it was decided to include the portions of the mercury leads above the water and up to the baffle plate F (each portion being about 1 cm. in length) as part of the heater. The heat generated in this portion and the portion next above it would be disposed of partly in the air space and partly by conduction to the water. As the resistance of the mercury leads was only 0·00025 per centimetre of length, and as the total length of the portions of the leads above the water and up to the baffle plate was about 2 cm., their total resistance would be about 0·0005 on a total of about 10 ohms. We estimate that the possible error due to the inclusion or exclusion of the debatable portion cannot exceed 1 in 10,000. It may be noted in passing that the element of heating due to conduction of heat from the obturator along the

mercury leads to the water is included in the heating effects, the determination of which is described in Section 7.

The total resistance of the two mercury leads from the level of the baffle plate upwards in the earlier range of experiments was 0·0045, and this was subtracted from the total resistance of the thermometer-resistance M_2 in order to obtain the net resistance of the heater for calculating the electrical energy.

6. *Considerations in Reference to Working Standards of Resistance for Carrying Heavy Currents.*—We must now turn aside for a moment in order to explain the reasons which led us to abandon the use of manganin or other alloys, and to design a type of calorimeter in which the mercury thermometer-resistances could be conveniently employed. For quantitative measurements of electrical heating, unless one could rely on absolute measurements of current used, it is necessary to work from a standard resistance of known magnitude which carries the heavy current used for heating. At an early stage of these experiments a standard 10-ohm manganin resistance was procured which was made by the Cambridge Scientific Instrument Company and designed to carry 5 amperes. It was intended to use this resistance in conjunction with standard cells to determine the current. This resistance consisted of two sets of coils of manganin wire in parallel. The diameter of the wire was 1·2 mm. and the length per ohm of the two wires was 1065 cm. This gave a total cooling surface per ohm of about 400 cm.², so that with a current of 5 amperes through the resistance, developing 25 watts per ohm, the cooling surface was 16 cm.² per watt. The wire was wound on brass tubes of about 3 cm. diameter, and the whole resistance was immersed in a large bath of paraffin oil provided with an efficient stirrer.

The standard resistance used by BARNES[*] consisted of eight wires of platinum-silver in parallel of 0·4 mm. in diameter, and each 1 m. in length, immersed in oil. Four watts were developed in each wire, so that the cooling surface was 3·2 cm.² per watt. He observes that "it was impossible to imagine that the temperature of the wire could have been sufficiently different to that of the oil to appreciably affect the resistance." BARNES' wires were bare. Ours had a thin coating of insulating material, but a cooling surface per watt five times greater than his. We were at first under the belief that the possible difference of temperature between the wire and the bath might be a serious source of error in inferring the resistance under a heavy working current from the temperature of the bath. This suspicion originally led to the device of the mercury thermometer-resistance, the calibration of which has been just described. When this had been installed, it became possible to use it in order to test the value of the manganin resistance during the passage of a heavy current so as to put our suspicions to the proof. We found, not the temperature difference which we had suspected, but a result of a different kind.

In fig. 5 the curve A is the temperature-resistance curve of the manganin standard

[*] 'Phil. Trans.,' A, vol. 199, p. 180, 1902.

as supplied by the makers, which was, of course, ascertained by bridge measurements with a small current only.

Curve B, in fig. 5, shows the result of an experiment in which the bath was gradually heated by passing a current of about 5 amperes through the resistance, by which means the bath was heated by steps from about 13° C. to 50° C. The current was turned off every five or ten degrees, and the resistance measured on the bridge with a small current. These resistances, *plotted on temperatures*, gave the curve B.
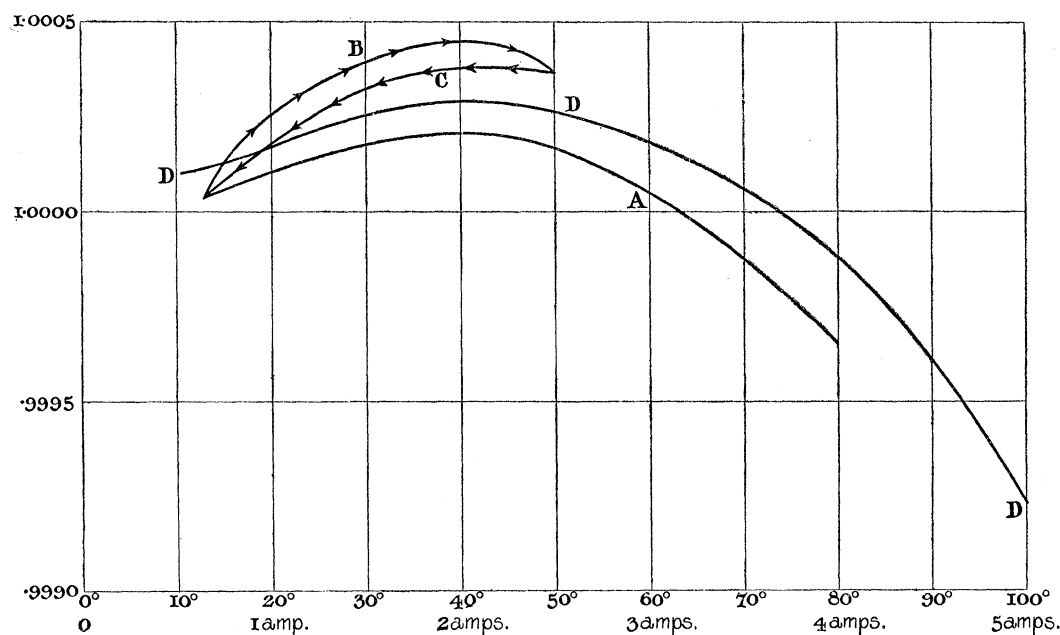
Fig. 5.

The bath was then allowed to cool, and the resistances measured from point to point are set out on the curve C, the arrow heads indicating the direction in which the temperature was moving. It will be observed that the passage of a current of 5 amperes produced a raising of the resistance above the value due to the temperature of the bath with the hysteresis effect which had been previously noted by other observers (see CALLENDAR, "On Continuous Electrical Calorimetry," 'Phil. Trans.,' A, vol. 199, p. 77, 1902).

In the foregoing experiment the resistance measured is that *which persists after the heavy current has ceased*. In curve D is given the result of an experiment to determine the variation of resistance *during the passage of a heavy current*. The manganin resistance was arranged for an ordinary bridge measurement, as shown in fig. 6, in which R is the manganin resistance of 10 ohms, and M a mercury thermometer-resistance of about 5·6 ohms, ρ being a fixed resistance of 130,000 ohms, and ρ' an adjustable resistance of about 73,000 ohms. The bridge current was varied step
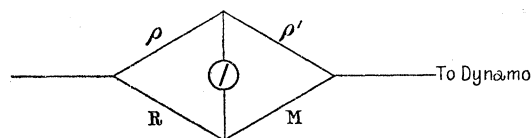
Fig. 6.

by step from 0·5 to 5 amperes, and the resistances measured thereby. Special insulation precautions were taken. The oil-bath of the manganin resistance was kept constantly stirred, and the temperature of the bath during the experiment only rose from 17°·9 C. at the start to 20°·1 C. at the end, the change of resistance due to this slight change of bath temperature being for our present purpose negligible.

In curve D the results of this experiment are set out, the ordinates representing resistances as before, but the *abscissæ now representing amperes*. It will be noted that the form of the *resistance-current* curve closely follows that of the *resistance-temperature* curve, and it might be supposed for a moment that the resistance might be taken as an index of the actual internal temperature of the wire when the current is passing, as in platinum thermometry. Thus when 4·4 amperes are flowing the resistance is that corresponding to a temperature of 80° C. on curve A. It is, however, clear on consideration that the temperature of the wire could not be 60° C. above the temperature of the bath. With a mercury thermometer-resistance in a glass tube of about 1 mm. internal diameter, the rise of the mercury on passing a current of 5 amperes indicates a temperature only of five or six degrees above the bath, although the heat generated has all to escape through the glass walls of the tube. An increase of temperature of 60° C. in the case of the 1·2 mm. wire with 4 to 5 amperes was clearly out of the question, and we think that such increase could not have exceeded 2° C. or 3° C. with a cooling surface of 16 cm.² per watt. We infer, therefore, that the passage of a heavy current through an alloy such as manganin produces an effect on the molecular structure of the wire whilst the current is passing, which affects the resistance in the same way as heating the wire would do, but to a much greater extent. Thus the passage of a current of 4·4 amperes through our manganin wire has about the same effect on the resistance as would be produced by raising the temperature of the bath to 80° C. We propose to designate this effect of the passage of a current through an alloy as a *thermoid* effect, since, although it is not a thermal effect depending on increase of temperature of the wire, the resulting change in the resistance appears to be of the same kind as that produced by heating the wire. The ordinary hysteresis effect we regard as a comparatively small residuum from the thermoid effect. It would naturally follow that if the passage of the current produced a molecular strain there would be a residual effect after the cesser of the current, though the greater part of the thermoid effect might quickly disappear.

The above test was founded on the assumption that there was no thermoid effect in the mercury thermometer-resistance, so that the scale readings would give accurate indications of the resistance even when a heavy current was passing. *A priori* this is probably true, since a hysteresis effect indicates a state of strain which is gradually disappearing, and no hysteresis effect is observable with a resistance of liquid mercury.

It is not an easy matter to devise a test. If a very heavy standard resistance were available having so large a cross-section that the current density due to a

current of 5 amperes was very small, the test could be made. Not having available such a heavy standard, the comparison was made with the resistances M_1, M_2, the calibration of which was described in the last section. M_1 having a bore of 2 mm. and M_2 a bore of only 1 mm., the current density in M_2 was four times as great as in M_1. The constant terms were ascertained at the date of the test, and in M_2 all the mercury in the leads above the level of the baffle plate was removed, the coefficients of M_2 and M_2^2 being thus slightly altered. The values of the resistances were :—

$$M_1 = 1\cdot8118 + 0\cdot0017 m_1,$$

$$M_2 = 9\cdot2159 + 0\cdot0278 m_2 + 0\cdot0001354 m_2^2.$$

The resistances were arranged in bridge, as shown in fig. 7, the resistance R (about 19,000 ohms) being adjusted to obtain equilibrium with different values of current. A stream of water was kept flowing around the glass spirals containing the resistances, but, as the current was kept on continuously, the temperature rose slowly, and gave some trouble in getting the required simultaneous scale readings. In the accompanying table, the current used is placed in the first column, the next two columns give the thermometer-resistance scale readings, the next two the
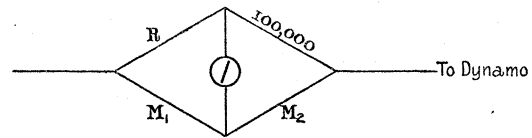
Fig. 7.

TABLE III.—Test of Thermometer-resistances under Various Currents.
Experiment 147.

Current.	m_1.	m_2.	M_1.	M_2.	M_1/M_2.	R.	Difference.
0·5	11·81	6·51	1·8319	9·4026	0·19483	19485	− 2
1	11·88	6·62	1·8320	9·4058	0·19477	19478	− 1
1·5	11·99	6·90	1·8322	9·4141	0·19462	19461	+ 1
2	12·15	7·23	1·8325	9·4240	0·19445	19445	±
2·5	12·31	7·57	1·8327	9·4341	0·19426	19430	− 4
3	12·52	8·00	1·8331	9·4470	0·19404	19404	±
3	12·55	8·18	1·8331	9·4524	0·19393	19395	− 2
3·5	12·77	8·60	1·8335	9·4650	0·19371	19372	− 1
3·5	12·80	8·80	1·8336	9·4710	0·19360	19360	±
4	13·08	9·42	1·8340	9·4898	0·19326	19324	+ 2
4	13·00	10·11	1·8339	9·5108	0·19282	19282	±
4·5	13·20	10·85	1·8342	9·5334	0·19240	19239	+ 1
4·5	13·20	11·37	1·8342	9·5495	0·19207	19207	±
5	13·40	12·11	1·8346	9·5724	0·19166	19163	+ 3
5	13·58	12·89	1·8349	9·5967	0·19120	19118	+ 2

resistances calculated from the formulæ by means of the readings, the next the ratio M_1/M_2, the next the value of the resistance R when adjusted for equilibrium. The value of R divided by 100,000 is the ratio which should be equal to M_1/M_2, the

differences from which are set out in the last column. Most of these differences must be set down to experimental inaccuracies, resulting from the difficulty due to the slight rise of temperature in the short interval which is necessary to get the readings when a balance is obtained. There appears, however, to be a slight difference in the ratios as between no current and the full current of 5 amperes of the order of about 2 parts in 10,000. Even this error is possibly not genuine, but due to a slight thermoid effect in the resistances of 100,000 and 19,000 which were used in the other arms of the bridge. But in the case of the manganin resistance, the curve D (fig. 5, p. 217), shows an error of 10 parts in 10,000 for a similar range of current. There is, therefore, no doubt that the mercury resistance is much better adapted as a standard to carry heavy currents than the manganin resistance.*

7. *Heating due to Obturator, Stirring, &c.*—The obturator, situated about 3 cm. above the level of the liquid in the calorimeter, and kept at a temperature of 10° C. above that of the liquid, constitutes a source of heat which it was necessary to determine accurately. This determination also includes various sources of heat gain or loss which must be enumerated :—

(*a*) *Radiation from obturator*, which is the main effect.

(*b*) *Conduction from the obturator through the mercury* leads of the heater. The portion of the leads passing through the obturator, being 10° C. higher than the contents of the calorimeter, thus constituted a source of heat by conduction.

(*c*) *Stirring.*—The stirrer was driven from an alternating-current motor running at a constant speed. The rate of revolution was frequently counted and found to be practically constant at about 340 revolutions per minute. The heat due to stirring is included in the determinations.

(*d*) *Evaporation.*—Any escape of vapour would of course constitute a heat loss which might be considerable. It was the function of the obturator, kept at 10° C. above the temperature of the water, to minimise this. In a preliminary series of experiments, in which only 2 litres of liquid were placed in the calorimeter, thus leaving an air space of over a litre above the surface of the water, it was found that the heat loss due to this cause became sensible at 60° C. and considerable at 80° C. Hence the volume of water used in the experiments described in this paper was increased to nearly 3 litres, and the obturator was lowered so as to reduce the air space to the smallest dimensions consistent with allowing for the expansion of the contents on heating. With this alteration the observations show that this element of heat loss introduces no uncertainty until a temperature of about 75° C. is reached.

Determination of Heat Gain and Loss.—The joint effect of all these elements was determined in a series of about 30 experiments in which all the conditions were the same as during a run, except that there was no electrical heating of the contents of

---

* A short note of further experiments on the thermoid effect is added at the end of this paper (p. 242), but the matter is being made the subject of further investigation, the results of which we hope to communicate.

the calorimeter. That is to say, the contents of the external bath were kept at the same temperature as the contents of the calorimeter, the obturator was kept 10° C. higher and the stirrer was kept rotating at 340 revolutions per minute. Each experiment lasted from 60 to 90 minutes, and the results are tabulated in the following table as degrees per hour rise in temperature of the contents of the calorimeter (2950 gr. of water) :—

TABLE IV.

Calorimeter temperature.	Rise of temperature per hour.	Calorimeter temperature.	Rise of temperature per hour.	Calorimeter temperature.	Rise of temperature per hour.
° C.	° C.	° C.	° C.	° C.	° C.
1·2	0·335	50·3	0·22	73·6	0·22
5·1	0·29	55·2	0·21	75·1	0·155
10·0	0·225	60·2	0·215	75·2	0·24
10·0	0·22	62·2	0·195	75·4	0·24
10·4	0·21	65·3	0·19	76·2	0·21
20·3	0·21	67·9	0·22	77·1	0·19
21·1	0·20	68·2	0·20	77·5	0·19
28·4	0·22	70·2	0·19	79·0	0·15
39·9	0·21	70·2	0·21	80·1	0·09
40·1	0·21	73·3	0·22		

These results are set out in fig. 8, from which it will be seen that from 10° C. to 70° C. the rate of rise owing to obturating heating, &c., is 0°·21 C. per hour. From 0° C. to 10° C., during which interval the obturator is kept at a steady temperature
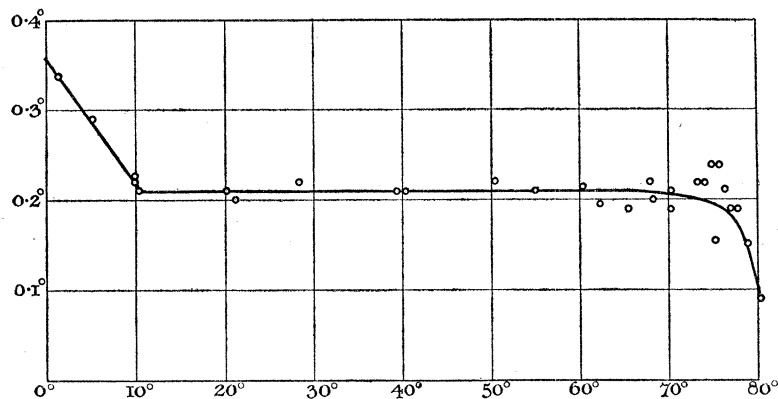
Fig. 8.

of 20° C., the rise per hour follows a straight line law. From 10° C. to 60° C. the steadiness of the heating shows that there is no sensible uncertainty introduced by evaporation. Between 70° C. and 80° C. there appears to be considerable uncertainty, especially from 75° C. to 80° C. This may be partly owing to differences in the amount of air contained in the water, which tends to come off at about this temperature; but is probably chiefly due to some variability in the amount of escape

of moisture through the holes in the obturator as the vapour pressure rises. This uncertainty seemed to show that the method, involving as it does a free surface of water, is not likely to yield accurate results beyond 80° C. In a point-to-point experiment the rise of temperature from 75° C. to 80° C. takes 5 minutes, so that, assuming an uncertainty of 0°·05 C. in the rate of rise of temperature per hour there would thence arise an uncertainty of 0°·005 C. in the temperature interval from 55° C. to 80° C., *i.e.*, an uncertainty of 1 in 5000.

Obturator Heating in Continuous-flow Experiments.—In the continuous-flow experiments a further element comes into play. In order that the cold water (at 13° C.) might flow through the obturator without sensible heating, the flow tube was jacketed, as previously described, with a larger tube through which flowed water at the same temperature in much larger volume. This cold-water jacket terminated at a point near *g* (see fig. 3, p. 207) on a level with the bottom of the obturator, and formed a small cold area on which steam condensed. To determine the total effect of obturator heating with this new element, experiments were made at a temperature of about 54°·5 C., similar to those before described, but with the new element of a flow of cold water through the water jacket. Most of these experiments were made after the two first series of continuous-flow experiments were concluded, as it was not discovered till later that a deposition of moisture had taken place which varied in each experiment. The earlier results were consequently erratic, and it was not till a much later period that the cause was traced to the fact that the lower surface of the obturator was so much cooled in the neighbourhood of the cold-water jacket as to permit of the condensation of water upon it, the evaporation or fall of which produced irregular results.

It was therefore decided to make a third series of continuous-flow experiments. In these the end of the inflow water-casing was surrounded by a short piece of rubber tubing *g*[1], which was shaped to fit it and which was cemented into the end of the opening through the obturator with rubber solution. The under surface of the obturator, just round the opening *g*, was also painted with a coat of rubber solution. It was found that these precautions entirely prevented the deposition of moisture on the obturator, and reduced the whole correction to so small an amount that variations in its amount were of small importance.

Experience showed that the circumstances which determined the amount of the correction differed in different experiments from some obscure cause. In the third series of continuous-flow experiments the determination was therefore made at the conclusion of each run, so that the apparatus was in the same condition in all respects as during the run.

As regards the first and second series of continuous-flow experiments, there were fortunately two determinations of the correction which were also made at the end of runs. The other determinations, which were made under conditions in which there had been no accumulation of moisture on the obturator, were rejected. These two

experiments (Nos. 67 and 68) gave respectively $0°\cdot0018$ C. and $0°\cdot0022$ C. rise of temperature per minute, which, on the weight of water contained in the calorimeter, is equivalent to a mean heating effect of $0\cdot43$ watts—a very high figure, which would import a possible error of 1 in 2000 into the results of the first two series of experiments.

In the third series of continuous-flow experiments the amount of the correction is reduced to about $0\cdot15$ watts, and the resulting uncertainty is of an order of less than 1 in 4000. The correction for each experiment was obtained by observing the rise of temperature during 60 minutes after the conclusion of the main run, and the results are given in the third table in Appendix C in joules per minute. The figures of one experiment are given in Appendix B.

8. *Continuous-flow Experiments.*—The special arrangement of the calorimeter for these experiments has been already described with reference to figs. 1, 2, and 3. There were three series of these experiments. In the first two the watt balance as well as the ampere balance was in series with the calorimeter, the resistance of the watt balance being in parallel with the calorimeter heater as shown in fig. 4. Before the third series of experiments the watt balance had been disconnected, it having been found that whilst the corrected readings of the ampere balance could be relied on as a check to an accuracy of 1 part in 5000 the accuracy of the watt balance was considerably less. The abandonment of the watt balance simplified the arrangement and the calculations.

In Appendix A (p. 244) are set out the notes of one experiment in the first two series of experiments, and in Appendix B the notes of one of the third series. We will describe the course of a continuous-flow experiment by reference to the notes in Appendix B, which only differs from the earlier ones in the absence of the watt balance and the introduction of the rubber-cap g_1 over the end of the inflow tube as shown in fig. 3. In this experiment (No. 164) the continuous-flow run lasted only three hours, as steady conditions were practically attained soon after the end of the first hour.

Water from the mains flowed continuously into a cistern, where it was brought to the required temperature (as described in Section 2), and thence flowed through the pipe Q to the calorimeter.

The outflow water passed into the flask X which stood upon a block, upon the removal of which the flask could be lowered and withdrawn laterally. By inclining two flasks until the mouths touched, it was easy to substitute one flask for another by a lateral tipping at the exact instant indicated by the chronometer ticks without loss of any water. The space between the tube and the neck of the flask X was filled by a cotton wool plug. Careful experiments showed that there was no appreciable loss of water owing to vaporization with this method of stoppering. The plug was weighed with the bottle and dried after each use before being used again.

The flasks for receiving the outflow water were introduced one after another at intervals of half an hour. The weighings are given in the last three columns of the table, and are set opposite the middle of each period of 30 minutes. For the purpose of the calculation the last four results are taken, the mean of which is a flow of 86·04 gr. of water per minute.

The current from the dynamo was maintained throughout so as to balance the E.M.F. of the nine cadmium cells on the resistance M_1 as indicated in fig. 4.

Readings were recorded every quarter of an hour, the time being shown in the first column of the table. Thermometer readings are recorded uncorrected, except that the bath thermometer is corrected so as to read with the outflow thermometer, in order to show the difference of temperature between the bath and the interior of the Dewar vessel. It will be observed that the slight variations of the temperature of the supply cistern (which are shown in the second column) do not affect the temperature of the inflow water (shown in the third column). To secure this result a bottle containing about 8 litres was sunk in the cistern and the inflow water was taken from near the bottom of this bottle, the temperature of which was practically constant.

At 3 o'clock the conditions had been steady for over an hour and the main run then ceased, and the subordinate observations were made to check the resistances and determine the heating effect of the obturator, &c. The flow of electricity and of water through the interior of the calorimeter was stopped, everything else being continued as before, including the flow of water through the pipe b (see figs. 1 and 3) into the water jacket of the inflow and out by the pipe e. A very slow rise of temperature took place under these circumstances, the record of which for an hour is shown in the notes (Appendix B). The total rise of temperature during the hour was 0°·04 C. The water contents of the calorimeter together with its water equivalent amounted to 3170 gr., giving a total heating effect of 0·15 watt, or 9 joules per minute.

The measurements of the resistances M_1 and M_2 are also recorded in the notes (Appendix B). The formulæ for those resistances are those given before in Section 5 except for the constant terms. These are obtained as shown in bridge ohms and converted into international ohms by the appropriate factors. For the third series of experiments the resistance of the mercury leads of the heater was re-measured and found then to be 0·0055.

With the exception of the complication introduced by the watt balance the notes of Experiment 66 recorded in Appendix A are of the same character and seem to require no further explanation.

In order that the inflow water might be brought to a temperature near to that of the contents of the calorimeter before mixing therewith, it was carried through a zig-zag tube of a length of about 4 feet immersed in the calorimeter. The resistance thus offered to the passage of the water produced a heating effect which was ascer-

tained by a separate experiment (No. 171). This experiment was conducted in the same way as the other continuous-flow experiments, except that there was no electrical heating, no heating of the obturator, and no stirring. Under these circumstances water flowing in at 13°·00 C. flowed out at 0°·02 C. to 0°·025 C. higher. In the actual experiments, owing to the heating of this tube by the contents of the calorimeter, the viscosity of the entering water and its consequent rise of temperature would be diminished. We have taken the lower figure 0°·02 C. as representing this frictional heating, and this is deducted from $\Delta\theta$ in order to get the rise of temperature due to electrical heating only.

The data furnished by these three series of experiments are summarised in Appendix C.

The first series embraces eight experiments, the second six, and the third five. The headings of the columns are in most cases self-explanatory. The temperatures are given corrected. For the first two series the correction for heating by obturator, stirrer, &c., is taken as 0·43 watt for all the experiments of both series and the total heating is given in the column headed "$C^2R + 0·43$." Also M_2 in the first two series includes the resistance of the primary leads of the watt balance as well as that of the mercury leads of M_2. The leads are deducted to obtain the figure entered in the column headed "Resistance of heater." C_1 (see fig. 4) is the total current through M_1 and $C = C_1R_0/(R_0 + M_2)$ is the current through the heater. For the third series the correction for heating by obturator, stirring, &c., is given for each experiment in the column "Obturator, &c."

Looking at the columns headed "Difference from mean," it will be seen that there is an ascending degree of accuracy as between individual experiments in the three series. This is due in the second series to the fact that the runs were longer than in the first, and in the third to the additional fact that the correction for heating by obturator, stirring, &c., had been reduced to a much smaller amount. When corrected to correspond with the exact period from 13° C. to 55° C. the result of the first two series is to give the mean value of J for tap-water from 13° C. to 55° C. as 4·177 and that of the third series 4·179. Owing to the largeness of the correction for heating by obturator, &c., in the first two series we do not bring the results into the average, but take the exact corrected figure yielded by the third series as the basis of our calculations, that is·to say, for "tap-water" the mean value of J for the interval from 13° C. to 54°·25 C. is 4·1785, or corrected to the interval from 13° C. to 55° C. we have

$$J_{13}^{55} = 4·1788.$$

This figure is also entitled to special weight owing to the fact that the thermometer and the standard resistance and battery of nine standard cells had all been sent again to the National Physical Laboratory to be re-calibrated, and had been returned only a few days before this third series of continuous-flow experiments was made, and that the bridge and mercury thermometer-resistances were also re-calibrated from

the standard for the purpose of this series. In the third series the mean error of a single observation is $\pm 0\cdot0006$, and the probable error in the result, so far as it depends on casual experimental errors, is only $\pm 0\cdot0002$.

9. *Point-to-Point Experiments. General Description.*—For experiments subsequent to the continuous-flow experiments the inflow and outflow tubes shown in fig. 1 were removed, the inflow aperture through the obturator being stopped and the outflow aperture used for a second thermometer. The general course of a point-to-point experiment may now be described. A quantity of water was weighed into the calorimeter sufficient to fill it to within about half an inch of the baffle plate F. The wooden lid D carrying the obturator, heater, thermometer, &c., was then put in place and the requisite connections made. The current was turned on by the switch V_2 (see fig. 4) through the by-pass X_1, and adjustments of the resistance X_1X_2 were made so that on turning the current by the switch V_2 to pass through the heater M_2 the current at the commencement should be such as to balance the cells S. The reading of the ampere balance A enabled this to be done with sufficient accuracy. The timing was done with the help of the chronometer beating half seconds, the switch being thrown over usually at the exact minute or half minute so as to turn the current through the heater M_2 or to switch it off. It was then the business of one observer to regulate the temperatures of the bath and obturator, so as to keep pace with the temperature rise in the calorimeter, which averaged about $1°$ C. rise per minute. The bath was kept at the same temperature as the contents of the calorimeter; the obturator was kept $10°$ C. higher, except that whilst the contents of the calorimeter were below $10°$ C. the obturator was kept at a constant temperature of $20°$ C. This observer noted down at frequent intervals the excess or defect of temperature of bath and obturator, and also noted down the readings given by the other observer.

As an illustration the notes of Experiment 125 are given in full in Appendix D. The excess or defect of obturator and bath temperatures is noted in the fourth and fifth columns in tenths of a degree. The other observer was occupied in regulating the current by means of the adjustable resistance X_2 so as to keep the galvanometer at zero. He had also to read the graduations of the thermometer tubes of the resistances M_1 and M_2, which are noted in the second and third columns under m and m_2. He read also from time to time the temperature of the watt balance resistance R_0, so long as the watt balance was kept in the circuit (but it had been abandoned before Experiment 125). In the final column are given the uncorrected readings of the temperature of the contents of the calorimeter. At each stop three readings are given which indicate a lag of about $0°\cdot005$ C.

Four standard thermometers were in use in this experiment, two being in use simultaneously throughout the experiment. For the range from $0°$ C. to $27°$ C. a thermometer was used whose zero depression after heating to $50°$ C. is only $0°\cdot01$ C. No correction is made for this, but, assuming that the whole of it persisted at the

commencement of this experiment, its effect would only be to increase each of the temperature intervals by $0°\cdot0025$ C., which would be insensible. The first $40°$ C. point is read on the second range thermometer. The third range thermometer was then substituted for the first and the $40°$ C. to $55°$ C. interval determined by this third thermometer. At $55°$ C. the fourth range thermometer was substituted for the second. In each case the error due to a possible zero depression, which had not entirely disappeared at the time of the experiment, would not produce an error of greater magnitude than 1 in 4000 on the interval.

At the close of the experiment the constants of the resistances M_1M_2 were obtained in the manner previously described, the data being shown on the notes (Appendix D).

The allowance for heating by obturator and stirring is obtained from the curve described in Section 7. It amounts in the middle range of temperatures to $0°\cdot21$ C. rise per hour. The correction for this, in the point-to-point experiments, is made by deducting this rise from the temperature interval. Thus in Experiment 125 (see Summary, Appendix D) there is a rise in the second period of $14\cdot235$ in 13 minutes. Of this $\dfrac{13 \times 0\cdot21}{60} = 0°\cdot045$ C. is due to obturator heating, stirring, &c. This is deducted from the total temperature interval to give the interval $\Delta\theta$, which is the rise of temperature due to electrical heating.

With regard to small defects or excess of temperature of bath or obturator during a run, the effort of the observer was to make these balance as far as possible. With practice it was found fairly easy to regulate the rise of temperature in the bath, so that no correction for temperature difference between the inside and outside of the calorimeter was required. But it was deemed advisable to ascertain the effect of any such difference, and an experiment (No. 51) was made for this purpose. It was found that, with about 2950 gr. of water in the calorimeter, if δ represents the difference of temperature between the bath and the contents of the calorimeter, the change in temperature of the contents of the calorimeter was

$$0\cdot00322\delta$$

degree per minute. This amounts to a heating (or cooling) effect of $0\cdot66\delta$ watt. The electrical heating employed being of the order of 230 watts, an excess of temperature of one-tenth of a degree maintained throughout the whole of any interval would have involved a correction of the order of 1 in 3000 on the result. It was not, however, difficult to regulate the temperature so as to make excess and defect of temperature substantially balance, and experiments where the regulation went wrong were not corrected, but rejected. The only exception to this was in two or three cases where towards the end of a run there was for the last few minutes a drop in bath temperature owing to the gas pressure being insufficient. In such cases the temperature difference could be represented as $\delta = \alpha t$, and the necessary correction could be obtained from the formula $\Delta\theta = 0\cdot00161\alpha t^2$. Two or three corrections of the order of $0°\cdot01$ C. were made in this way.

10. *Determination of Mean Capacity of Calorimeter.*—The continuous - flow experiments gave us the mean value of J for tap water between 13° C. and 54°·5 C. as J' = 4·1786. With the aid of this figure the next step was to determine the mean capacity of the calorimeter between the same limits. For this purpose the calorimeter was filled with about 3 litres of tap water at a temperature of about 13° C., which was heated for a period of 39 minutes with a current of about 5 amperes, thereby raising its temperature to about 54°·5 C. The method of the experiment is that described in the last preceding section, and the notes of Experiment 125 in Appendix D will serve to show the course of these experiments, the only difference being that there was one unbroken run of 39 minutes instead of the shorter periods. The result of eight experiments is set out in Table V. The corrected $\Delta\theta$ due to electrical heating is given in the second column, the weight of water employed in the experiment in the third column, and the number of joules employed to produce the rise of temperature $\Delta\theta$ in both the water and the calorimeter in the fourth column.

TABLE V.—Capacity of Calorimeter.

Experiment.	$\Delta\theta$.	W = weight of water.	Electrical joules.	$W\Delta\theta \times J'$.	Joules for calorimeter.	Joules per degree.	Difference from mean.
56	41·65	2950·9	538,157	513,571	24,586	590·3	− 5·2
61	41·90	2931·3	538,169	513,220	24,949	595·4	− 0·1
63	41·605	2951·1	537,716	513,053	24,663	592·8	− 2·7
71	41·575	2951·7	537,378	512,786	24,592	591·5	− 4·0
72	41·495	2950·9	536,519	511,662	24,857	599·1	+ 3·6
73	41·415	2950·8	535,559	510,656	24,903	601·3	+ 5·8
82a	41·365	2950·8	534,669	510,042	24,627	595·4	− 0·1
82b	41·37	2950·4	534,784	510,033	24,751	598·2	+ 2·7
				Mean value =		595·5	

In the fifth column is given the number of joules required to heat the water alone through $\Delta\theta$, which is obtained by multiplying $W\Delta\theta$ by J', where J' = 4·1786, the value which we obtained as the mean value of J for tap-water over this range of temperature. The difference set out in the next column is therefore the joules required to heat the calorimeter alone through the interval $\Delta\theta$. This difference divided by $\Delta\theta$ is the mean capacity of the calorimeter per degree expressed in joules, which works out at 595·5 joules. The mean error of the single observations works out at 3·1 joules, or about $\frac{1}{2}$ per cent., but it must be remembered that it is the difference of two large quantities. The mean probable error of the result works out at 1 joule. With 2950 gr. water (which is the amount with which we work) an error of 1 joule in the capacity of the calorimeter involves an error of less than 1 part in 10,000 in the value of J.

11. *Value of J_{13}^{55} for Distilled Water.*—The value of $J_{13}^{54 \cdot 5}$ having been determined for "tap water" and the capacity of the calorimeter having been thence deduced, the next step was to determine what correction of the value was required for distilled water. The experiments for this purpose followed precisely the same course as the "tap-water" series described in Section 10. The distilled water used had a conductivity of about 1×10^{-6} at laboratory temperature. Experiments were made to determine whether the air contained in the distilled water affected the specific heat, but the results were inconclusive, as the differences which appeared were of the same order of magnitude as the possible experimental errors.

But in nearly all the experiments made with distilled water, the water used was substantially air-freed. This precaution was necessary in later experiments in which the water was heated up to 70° C. or 80° C., as at these temperatures dissolved gas would otherwise come off freely, probably in sufficient quantity to render the results inaccurate. For this reason we adopted the plan of keeping the water in bottles of a capacity of 8 litres from which the air was exhausted. In Appendix E are set out the data obtained from 15 experiments, the result of which is to show that the mean value of J over this interval for distilled water exceeds that for tap water by about 0·003. The table sufficiently explains itself. In the table in Appendix E the rise of temperature due to obturator, stirring, &c., is deducted from the final temperature before entering in the table. The joules required for heating the calorimeter are obtained by the multiplication of $\Delta\theta$ by the mean capacity per degree of the calorimeter, as determined in the preceding section. The average initial temperature of the 15 experiments is 13°·11 C., and the average final temperature 54°·51 C. Making a small correction to reduce to round temperature figures, we obtain as the value of the mean calorie, from 13° C. to 55° C., 4·1821, or in round figures

$$J_{13}^{55} = 4 \cdot 182.$$

This may be regarded as our fundamental figure, and we believe it to be accurate within $\pm 0 \cdot 001$. The deduction of the value for distilled water from that for tap water is based on the mean of 15 experiments, of which the mean error of individual observations is about 1 in 2600, whilst the mean probable error in the result is 0·0005, so far as it depends on casual errors of experiment.

In confirmation of the result at which we arrive, regard may be had to the results of the experiments for shorter intervals described later in Section 13, which were made to determine the variation in the value of J from point to point for smaller intervals. From the mean values of J for the intervals 13° C. to 27° C., 27° C. to 40° C., and 40° C. to 55° C., we can deduce the mean value for the interval 13° C. to 55° C. The value so deduced is

$$J_{13}^{55} = 4 \cdot 1819,$$

which is in close agreement with the figure to which the experiments already described lead.

12. *Specific Heat of Glass.*—In the continuous-flow experiments the heat capacity of the calorimeter does not come into the account, but in the experiments from point to point of the range it is necessary to know the capacity. This has been found to have a mean value of 595·5 joules per degree, between 13° C. and 55° C.

The assumption that this capacity would be substantially constant for the range from 0° C. to 80° C. seemed hardly justifiable, and a rough experiment showed a probable variation of 3 or 4 per cent. within these limits. It was therefore decided to make a more careful determination of the specific heat of the glass. For this purpose the broken remains of a similar Dewar vessel (one of the same batch) were taken and the fragments were enclosed in a string bag. The weight of glass taken was 1000 gr. The weight of the string bag was 14 gr., the effect of which was neglected. A small glass tube was inserted into the mass of glass fragments, so that a thermometer could be readily inserted into the interior.

The observations were made by observing the change produced in the temperature of a given weight of water by the introduction of the mass of glass. The glass was placed overnight, before each experiment, in a suitable Dewar vessel which was kept in an air thermostat regulated at a temperature about a degree above laboratory temperature. This was deemed necessary in order to secure that the temperature of the glass should be uniform throughout. About $2\frac{1}{2}$ litres of water was placed in a Dewar vessel, which was closed by an obturator consisting of a copper box for holding water at a suitable temperature. The construction of this obturator was very similar to that of the platinum obturator described in Section 11. For the experiments at the higher temperatures an electric heater was used in the obturator so as to maintain the temperature of the obturator at about 10° C. above that of the water in the Dewar in order to prevent deposition of moisture. The Dewar vessel was immersed in a water-bath, the temperature of which could be regulated so that (in conjunction with the obturator) steady conditions of temperature could be maintained in the interior of the Dewar vessel. Temperatures were taken every minute, so that accurate allowance could be made for any small steady variation. At the higher temperatures the time required for lifting the obturator, inserting the mass of glass, and replacing the obturator, was from 15 to 20 seconds. This exposure of the contents of the calorimeter involved a small reduction of temperature, which was accurately ascertained, and a proper correction was made therefor. The glass being in all cases at about laboratory temperature (15° C.) no correction was considered to be necessary for the exposure of the glass in transferring it from one Dewar vessel to the other.

Four experiments were made with the water only slightly above the freezing-point. These, together with the experiments at higher temperatures, are included in Table VI., in which the first column gives the reference number of the experiment; the second and third columns the temperatures of the glass before and after the experiment; the fourth column gives, under the heading $\Delta_1\theta$, the difference produced

in the temperature of the water; the fifth column, under the heading $\Delta_2\theta$, the difference produced in the temperature of the glass; the sixth column gives the weight of the water in the calorimeter, to which is added the approximate water equivalent of the calorimeter (137 gr.); the seventh column gives the mean specific heat of glass for the temperature interval indicated, taking the specific heat of water as unity in all cases.

TABLE VI.

Reference number.	Glass temperature.		$\Delta_1\theta$.	$\Delta_2\theta$.	Weight of water + 137.	Mean values.
	Before.	After.				
	° C.	° C.				
139a	15·56	1·655	1·035	13·905	2624·6	0·1954
139b	17·62	1·678	1·178	15·942	2637·2	0·1949
140b	16·492	1·617	1·106	14·875	2638·5	0·1962
141a	16·514	1·857	1·087	14·657	2631·7	0·1952
137b	15·95	39·62	1·78	23·67	2636·3	0·1984
134a	17·84	46·47	2·176	28·63	2634·8	0·2003
142	16·23	59·59	3·28	43·36	2635·7	0·1994
144	15·13	70·05	4·18	54·92	2640·6	0·2010
145	15·22	74·14	4·495	58·92	2638·2	0·2013

Since the changes of water temperature took place at different points of the temperature range, they require to be multiplied by the values of the specific heat of water at the various points. These values were obtained from the preliminary rough curve of the values of J, the values used being set out in Table VII. This

TABLE VII.

Reference number.	θ.	S_{16}^θ taking water = 1.	Water factor.	S_{16}^θ in 15° calories.	S_0^θ.	S_0^θ calculated.	Difference.
139 to 141	0	0·1953	1·006	0·1965	—	—	—
137b	40	0·1984	1·003	0·1990	0·1980	0·1984	+ 4
134a	46	0·2002	1·004	0·2010	0·1994	0·1990	− 4
142	60	0·1994	1·008	0·2010	0·1998	0·2003	+ 5
144	70	0·2010	1·009	0·2028	0·2014	0·2014	− 2
145	74	0·2013	1·010	0·2033	0·2018	0·2018	− 2

table gives the values for the mean specific heats in 15° calories, corrected for the temperature of the water, and also reduced to exact temperature figures, from which are calculated the mean values of the specific heat from 0° to θ. In the table S_{16}^θ indicates the mean value of S between 16° C. and the temperature in the second column, whilst S_0^θ indicates the mean value from 0° to θ. The mean of the first four

observations in Table VI. gives the value $S_0^{16} = 0\cdot1965$. This value is used to obtain the values of S_0^θ from the values S_{16}^θ. The last columns of the table show the values of S_0^θ calculated from the formula $S_0^\theta = 0\cdot1949 + 0\cdot00009\theta$, and also the differences between observed and calculated values.

The experimental values of S_0^θ are set out in fig. 9.

The mean capacity of the calorimeter employed for the main research was found to be $595\cdot5$ joules between $13°$ C. and $54°\cdot5$ C. To apply the above result to this we must note that this capacity includes not only the glass, but also about 170 gr. of
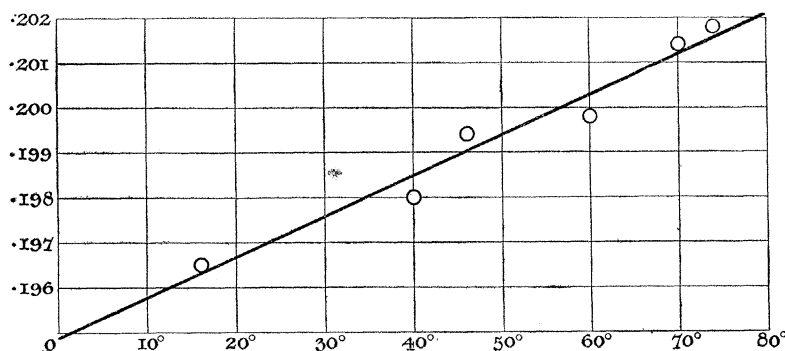
Fig. 9.

mercury. The specific heat of mercury diminishes with rise of temperature from $0\cdot0335$ at $0°$ C. to $0\cdot0328$ at $80°$ C. by a straight-line law. Taking this into account, the expression

$$C_\theta^{\theta'} = 578\cdot3 + 0\cdot255\,(\theta + \theta')$$

gives the mean capacity in joules per degree of the calorimeter between any two temperatures θ, θ'. It will be found that between the limits $13°$ C. and $54°\cdot5$ C. the value given by the formula is the experimentally found value $595\cdot5$, while for the end values of the capacity at $0°$ C. and $80°$ C. the ratio of the values agrees with those derived from our experimental values for glass and from the figures quoted for mercury.

Subjoined are the resulting values of the mean-heat capacity of the calorimeter for the various intervals which are hereafter dealt with :—

Interval. ° C.	Mean capacity in joules per degree.
0 to 13	581·6.
13 „ 27	588·5.
27 „ 40	595·4.
40 „ 55	602·5.
13 „ 55	595·6.
55 „ 73	610·9.
55 „ 80	612·7.

13. *Determination of Mean Values of* J *for Various Intervals.*—In the determination of the value of J at any point most experimenters have determined the value for a small range of temperature, and have taken the mean value of J for the interval as the value at the middle point of the interval. Where the slope of the J curve is substantially constant during the interval this gives a correct result; where, however, this is not the case, the curve obtained for the values of J must be slightly distorted. We have endeavoured to obtain the mean value of J for consecutive intervals, and by the aid of the values so obtained to construct a curve which should represent the values of J_0^θ, *i.e.*, the mean value of J from zero to any temperature θ. The values of J are then given by the expression $J = \dfrac{d}{d\theta}(\theta J_0^\theta)$.

The course of these experiments has been already described in Section 9 by reference to the notes of Experiment 125, which are given in Appendix D. We will briefly indicate the method of calculation of the results also by reference to the notes of this experiment. A graph was first plotted of the values of m_1 and m_2 to help in getting the mean values for each of the five intervals into which this experiment is divided. The mean values of m_1 could be got with sufficient accuracy from the curve, and the values of M_1 were then obtainable from the formula $M_1 = 1\cdot8117 + 0\cdot0017m_1$. The value of m_2 was obtained from the observed values by calculation. Thus, for the third interval of 12 minutes (see Appendix D, from 10.58 to 11.10 a.m.), the observed values of m_2 give

$$m_2 = 13\cdot65 + 0\cdot306t,$$

where t is time in minutes from beginning of interval. This gives for the middle of the interval $m_2 = 15\cdot49$. From this figure the value of M_2 is calculated from the formula

$$M_2 = 9\cdot2208 + 0\cdot02781m_2 + 0\cdot0001355m_2^2.$$

This gives for the total value of the mean resistance of the heater, including the mercury leads, the figure $9\cdot6839$. From this has to be deducted the resistance of the mercury leads above the obturator baffle-plate (which was $0\cdot0045$), giving for the mean resistance of the heater during this interval the net figure $9\cdot6794$, which is entered in the appropriate place in the column of the summary in Appendix D, C_1 being the current passing through the heater, C_1^2R multiplied by time in seconds gives the electrical joules expended in heating the water and calorimeter through $\Delta\theta$. To calculate the joules for heating the calorimeter the appropriate capacity figure for the interval is taken as worked out in Section 12. The summary of the experiment in Appendix D shows how the results are worked out. It should be noted that in this summary the corrected temperatures a and b for the beginning and end of an interval are given, and that the rise of temperature, due to heating by obturator, stirring, &c., is deducted from the total temperature rise so as to give the value of $\Delta\theta$, which is due to electrical heating only. The results of Experiment 125, so far as regards the interval from 0° C. to 13° C., are set out in Appendix F.

As the object of the point-to-point experiments was to determine the series of

values of J_0^θ, special care was given to the determination of the first interval from 0° C. to 13° C. In Appendix F are given the data obtained from 17 experiments, like that above described, in which this interval was measured. The table shows the initial and final temperatures a and b, the final temperature b being diminished by the rise of temperature due to obturator and stirrer-heating. In the fourth column is given the difference, $\Delta\theta$, which is rise of temperature due to electrical heating only. The total joules expended are placed in the next column, the joules required for heating the calorimeter in the next, and the difference, *i.e.*, the joules expended in heating the water, in the next. The weight of water, multiplied by $\Delta\theta$, which gives the mean calories for the interval due to electrical heating, is placed in the next column, and the ratio joules/calories, which gives the mean value of J for the interval, in the next.

Taking the means, we get for the mean interval 1°·30 C. to 13°·09 C., the mean value for J, which is 4·1921.

In the last column are shown the differences of the individual experiments from the mean. We may correct for the interval from 0° C. to 1°·3 C. without sensible error by taking the approximate value for J as 4·2. The value at which we thus arrive is

$$J_0^{13} \quad . \quad . \quad . \quad . \quad . \quad . \quad 4\text{·}1937.$$

The mean error in individual values works out at about 1 in 2000. We estimate that in reading any interval, long or short, by means of thermometers such as we were using, there may be a casual error of 0°·01 C., so that on an interval of 12° C., the mean error of 1 in 2000 on individual values is about what we might have expected. The mean probable error in the result is less than 1 in 6000, so far as it depends on casual errors of observation.

In Appendix G are set out shortly the results of the other point-to-point experiments, which cover the intervals 13° C. to 27° C., 27° C. to 40° C., 40° C. to 55° C., 55° C. to 73° C., and 55° C. to 80° C. These results are calculated in the same way as for the interval 0° C. to 13° C. When these results are corrected for small differences of temperature at the beginning and end of the intervals, we obtain for the mean value of J in each interval the figures set out in Table VIII.

TABLE VIII.—Mean Values of J for Intervals.

Interval.		
$a.$	$b.$	$J_a^b.$
° C.	° C.	
0	13	4·1937
13	27	4·1752
27	40	4·1756
40	55	4·1935
55	73	4·2024
55	80	4·2056

From these figures we obtain for the mean value of J from 0° C. to any temperature θ the values set out in Table IX.

TABLE IX.—Values of J from 0° C. to θ.

θ. °C.	J_0^θ.
13	4·1937
27	4·1841
40	4·1813
55	4·1848
73	4·1892
80	4·1913

An important test of our methods of working and of computing the results is obtained by working out the figures for the mean value of J for the interval from 13° C. to 55° C. from the figures for the intervals from 13° C. to 27° C., 27° C. to 40° C., and 40° C. to 55° C. now obtained. By this process we arrive at the result

$$J_{13}^{55} = 4·1819.$$

The figure, at which we arrived by the series of direct experiments over the complete interval, without any breaks, was

$$J_{13}^{55} = 4·1821.$$

The two sets of experiments were entirely independent, and the close agreement indicates that the various small errors of observation which occur in obtaining the time and temperature values at the beginning and end of short intervals, and the small errors of computation, which result from taking the mean values for current and resistance as the values at the middle points of the intervals, all average out in such a way as not seriously to impair the accuracy of the results.

14. *Deduction of Values of J for Various Temperatures.*—The values of J probably require a curve of the fourth degree for their accurate expression, or even of the fifth degree over the range of 0° C. to 100° C. This would be in accord with the expression required for the density of water from 0° C. to 100° C., which can be accurately represented by an expression of the fifth degree. It is probable that liquid water is a mixture of three species of molecules, to which SUTHERLAND has given the useful names hydrol (H_2O, or steam molecules), dihydrol (H_4O_2), and trihydrol (H_6O_3, or ice-molecules) (see "Liquid Water a Ternary Mixture," BOUSFIELD and LOWRY, 'Trans. Faraday Soc.,' vol. 6). It is further probable that both the specific heat and the density of liquid water would depend additively upon the specific heat and density of their components, and hence that if an equation of the fifth degree represented the density of water, an equation of the same degree would be required for the specific

heat. But within the range of 0° C. to 80° C. an equation of the third degree represents the experimental values of J within the limits of accuracy of 1 part in 4000, which is quite within the limits of experimental accuracy. The following expression accords with the experimental values within these limits, the differences between observed and calculated values being shown in the table :—

$$J_0^{\theta} = 4\cdot2085 - 0\cdot0015110\theta + 0\cdot000026110\theta^2 - 0\cdot0000001225\theta^3.$$

TABLE X.

θ.	J_0^{θ} observed.	J_0^{θ} calculated.	Difference.
13	4·1937	4·1930	−7
27	4·1841	4·1843	+2
40	4·1813	4·1820	+7
55	4·1848	4·1840	−8
73	4·1892	4·1897	+5
80	4·1913	4·1920	+7

We give the values to four places of decimals, but no value is to be attached to the fourth place except so far as it may serve to determine more accurately the third place.

To obtain the values of J_θ we have

$$J_\theta = \frac{d}{d\theta}(\theta J_0^{\theta}),$$

which gives

$$J_\theta = 4\cdot2085 - 0\cdot0030220\theta + 0\cdot000078833\theta^2 - 0\cdot00000049\theta^3.$$

From this expression we obtain the following values for J :—

TABLE XI.—Values of J.

θ.	J.	θ.	J.	θ.	J.
0	4·2085	30	4·1751	60	4·2033
5	4·1953	35	4·1777	65	4·2084
10	4·1856	40	4·1816	70	4·2127
15	4·1791	45	4·1865	75	4·2157
20	4·1755	50	4·1920	80	4·2172
25	4·1743	55	4·1977		

The temperature curve for the value of J which results from these figures (together with the curves of other observers, to which reference is made in the next section) is shown in figs. 10 and 11. Our relative value at 80° C. compared with that of 70° C. has some uncertainty, but we think that some drop in the curve as this temperature is approached is a genuine phenomenon, though probably not quite so marked a drop

as that which a formula of the third degree gives. Any formula of the third degree which fits the curve from 0° C. to 70° C. tends to give too much drop in the values in the neighbourhood of 80° C., as may be well seen with the curve which we have calculated for BARNES' figures, and which is given in the next section.
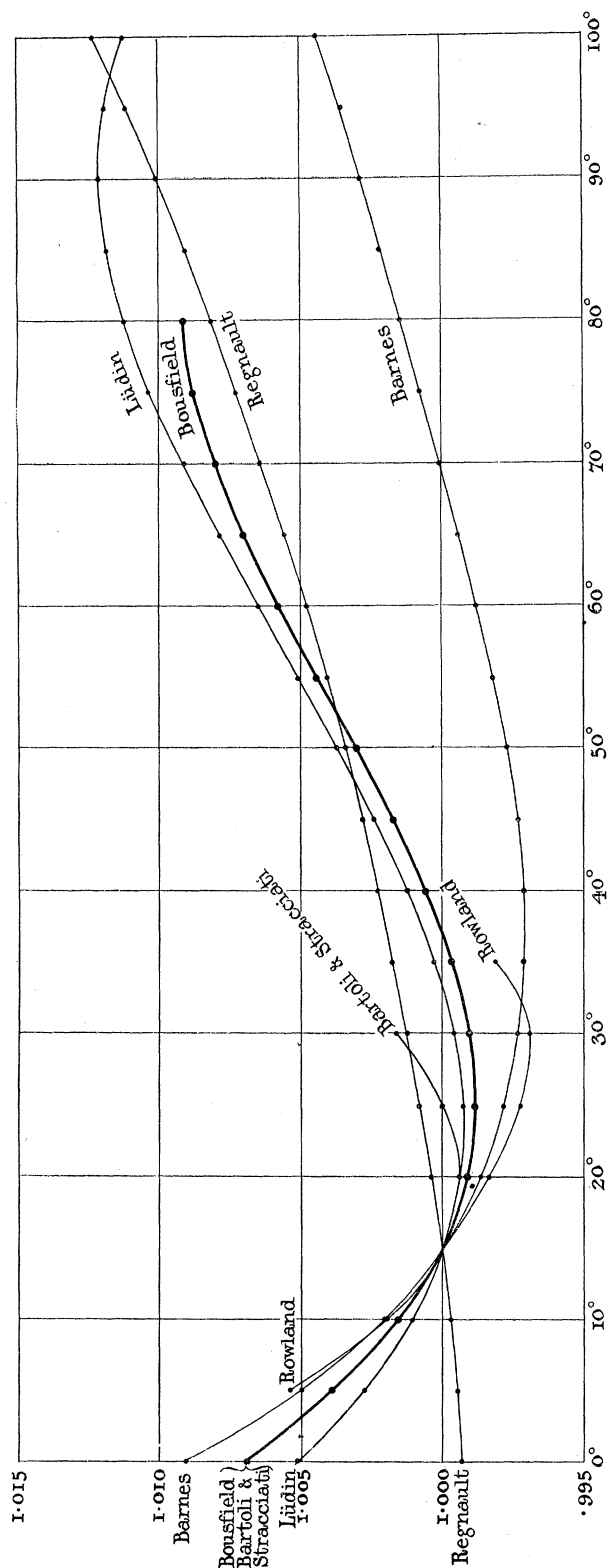
15. *Comparison of Results with Former Determinations.*—Some of the results of former observers are given only relatively, and others in absolute values. Relative figures for the specific heat of water at various temperatures referred to the value at 15° C. as unity, and taken with reference to the scale of the hydrogen thermometer, are set out in the 'Landolt-Börnstein Tables' (ed. 1905, p. 393). BARNES' latest absolute values corrected for the later value of the Clark cell were not published till July, 1909 ('Roy. Soc. Proc.,' Ser. A, vol. 82, p. 390), but the relative values remain the same as given in the above tables in 1905. In Table XII. all these figures are set out, together with our own figures obtained by dividing our absolute values by our absolute value for the 15° calorie. The differences between our own figures and the others are also shown in the table. In fig. 10 all these results are set out, together also with REGNAULT's figures, which, though calculated for the air thermometer scale and therefore not entirely comparable, still afford a useful basis for comparison when

Fig. 10.

such large divergencies exist. As regards the general course of the curve, it will

238   MESSRS. W. R. BOUSFIELD AND W. ERIC BOUSFIELD

be seen that ours corresponds much more nearly with the curves of LÜDIN and REGNAULT than with BARNES' curve, except from 0° C. to 15° C. In this portion of the range our curve is very near the mean of the observers since REGNAULT, and is almost identical with that of BARTOLI and STRACCIATI.

TABLE XII.—Comparative Values of Specific Heat of Water, taking the 15° Calorie as Unity.

Temperature.	Bousfield.	Lüdin.	Barnes.	Rowland.	Bartoli and Stracciati.	Differences.			
						Lüdin.	Barnes.	Rowland.	Bartoli and Stracciati.
°C.									
0	1·0070	1·0051			1·0070	− 19			±
5	1·0039	1·0027	1·0050	1·0054	1·0041	− 12	+ 11	+ 15	+ 2
10	1·0016	1·0010	1·0020	1·0019	1·0017	− 6	+ 4	+ 3	+ 1
15	1·0000	1·0000	1·0000	1·0000	1·0000	±	±	±	±
20	0·9991	0·9994	0·9986	0·9979	0·9994	+ 3	− 5	− 12	+ 3
25	0·9989	0·9993	0·9978	0·9972	1·0000	+ 4	− 11	− 17	+ 11
30	0·9990	0·9996	0·9973	0·9969	1·0016	+ 6	− 17	− 21	+ 26
35	0·9997	1·0003	0·9971	0·9981		+ 6	− 26	− 16	
40	1·0006	1·0013	0·9971			+ 7	− 35		
45	1·0018	1·0024	0·9973			+ 6	− 45		
50	1·0031	1·0037	0·9977			+ 6	− 54		
55	1·0045	1·0051	0·9982			+ 6	− 63		
60	1·0058	1·0065	0·9988			+ 7	− 70		
65	1·0070	1·0079	0·9994			+ 9	− 76		
70	1·0080	1·0092	1·0001			+ 12	− 79		
75	1·0088	1·0104	1·0007			+ 16	− 81		
80	1·0091	1·0113	1·0014			+ 22	− 77		

As regards the absolute values of the mechanical equivalent of the water calorie at various temperatures, the only figures available for a complete comparison over the range of 0° to 80° are those resulting from the researches of CALLENDAR and BARNES. In addition to these there are others for a portion of the range or for single points, the evaluation of which is rendered difficult for comparative purposes by an incomplete knowledge of the electrical units and of the exact point in the scale at which the mean calorie from 0° to 100° is equivalent to other calories. Assuming, however, that the mean calorie is approximately equal to the 15° calorie, and giving the results in terms which take the E.M.F. of the standard Clark cell as being about 1·433 volt at 15°, we have the following data :—*

* The different values for the mechanical equivalent are considered and evaluated for purposes of comparison in the following publications, where all the references to the original papers are to be found :— 'Jahrbuch der Elektrochemie,' vol. 12, p. 6, 1909; 'Verh. der Deut. Phys. Ges.,' vol. 6, p. 589, 1908; BARNES, 'Phil. Trans.,' Series A, vol. 199, p. 257, 1902; BARNES, 'Roy. Soc. Proc.,' Series A, vol. 82, p. 393, 1909.

Mechanical Methods. °C.

JOULE	4·173	at	16·5
ROWLAND	4·187	„	15
REYNOLDS and MOORBY	4·183	„	15

Electrical Methods. °C.

GRIFFITHS	4·193	at	15
MICULESCU	4·185	„	11·5
SCHUSTER and GANNON	4·193	„	15
CALLENDAR and BARNES	4·184	„	15
JÄGER and STEINWEHR	4·19	„	15

The different absolute values are set out in fig. 11.

Looking first at the general course of the curves as shown in fig. 10, we note that our curve is in comparatively close accord with the others, whilst BARNES' curve
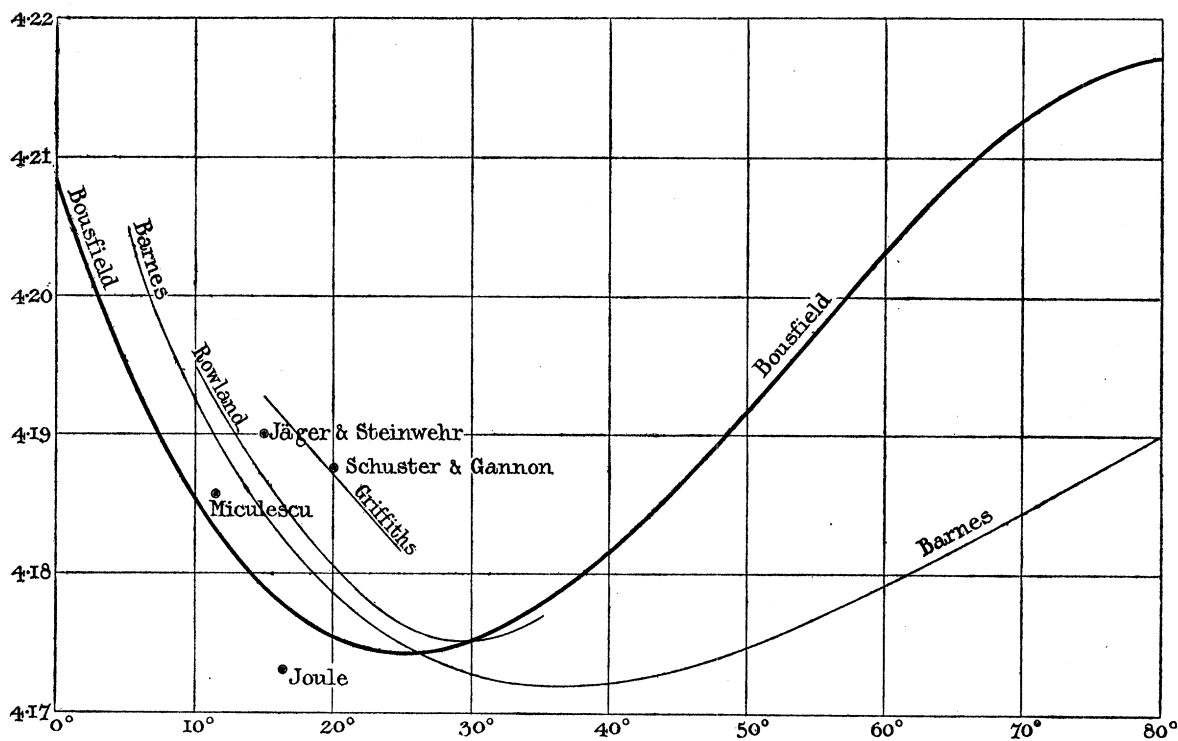
Fig. 11.

differs from them all in being flatter and with the minimum carried further to the right. The minima, according to different observers, are as follows:—

	°C.		°C.
BARTOLI and STRACCIATI	20	ROWLAND	30
LÜDIN	25	BARNES	38
BOUSFIELD	25		

Hence the preponderance of the results by various methods is in favour of the lower minimum. We are confirmed in the view that the minimum is in fact at about 25° C. by an entirely different set of experiments which were made by us by heating with a constant power of about 250 watts regulated by a watt-balance, so that determinations of current and resistance were unnecessary. This set of experiments also gave the minimum value at about 25° C. We have not here set out the details of these experiments, as they could not be relied on for absolute values, and would have lengthened this communication without corresponding advantages. But for relative values, which alone are required for determining the minimum, such measurements are better adapted than any others for determining the comparative rise of temperature at different points of the scale for the same heating, and they strengthen our view as to the probability that the minimum is in fact in the neighbourhood of 25° C.

On the other hand, as regards the absolute value of the 15° calorie which we place at 4·179, the preponderance of the results is against this low figure and in favour of the value of 4·184, at which it is placed by BARNES. JOULE's determination, which works out at 4·173 at 16°·5 C., or about 4·174 at 15° C., is the only one which is lower than our own (JOULE, 'Phil. Trans.,' vol. 169, p. 365, 1878). All the electrical determinations give higher values than ours.

For the purpose of further comparing our figures with the most recent figures given by BARNES, we have worked out a formula for BARNES' figures and have found that BARNES' values from 0° C. to 80° C. may be represented with sufficient accuracy by the equation

$$J = 4\cdot2146 - 0\cdot00269\theta + 0\cdot000051\theta^2 - 0\cdot0000002065\theta^3.$$

In the subjoined Table XIII. BARNES' values for J are given and the values calculated from the above expression, and also the differences.

TABLE XIII.

	BARNES' J.	J calculated.	Difference.
0	----	4·2146	——
10	4·1926	4·1925	− 1
20	4·1785	4·1781	− 4
30	4·1727	4·1726	− 1
40	4·1720	4·1717	− 3
50	4·1745	4·1746	+ 1
60	4·1792	4·1796	+ 4
70	4·1845	4·1849	+ 4
80	4·1901	4·1901	±
90	4·1957	4·1924	− 33

It will be seen that from 0° C. to 80° C. the agreement is well within the limits of experimental error. Beyond this point there is a serious divergence for any curve

of the third degree, which is, however, of no importance for the present purpose. To get the mean value for any period we have

$$\mathrm{J}_0{}^\theta = \frac{1}{\theta}\int_0^\theta \mathrm{J}\, d\theta = 4{\cdot}2146 - 0{\cdot}001345\theta + 0{\cdot}0000017\theta^2 - 0{\cdot}0000000066\theta^3,$$

from which we get from BARNES' figures for the mean calorie from 13° C. to 55° C. the result

$$\mathrm{J}_{13}{}^{15} = 4{\cdot}175.$$

Our own result is

$$\mathrm{J}_{13}{}^{55} = 4{\cdot}182,$$

which is higher than the Callendar-Barnes value by 0·007. On the other hand, our value for the 15° calorie is less than that of BARNES' by 0·005, whilst the values for the 26° calorie are identical, and the values for the 80° calorie differ by nearly 2 per cent. Our value for the 30° calorie is identical with that obtained by ROWLAND for 30° with the mechanical method.

It is difficult to explain these discrepancies, which clearly result from differences of method involving defects which are more or less concealed. We are inclined to attribute them to some extent to the thermoid effect described above in Section 6.

Another point which might lead to discrepancies between different observers is one necessarily incidental to electric calorimetry, and which has been already discussed in Section 6, *i.e.* the difficulty of exactly defining where the leads to the heating resistance end and the heating resistance begins. Owing to the large scale of our apparatus, it was possible to reduce the debatable portion to an amount of not more than 1/10,000 of the heating resistance. We do not find sufficient data to enable us to say how this matter was dealt with by former observers.

It is obvious that both the above matters might affect not only the absolute values, but also the relative values obtained at different parts of the temperature scale. Whether these causes in fact account for the differences in the values obtained for the 15° calorie, and in the still larger differences beyond 35° C., it is impossible to say with certainty.

It is particularly unfortunate that such differences should exist with reference to so widely accepted a standard as the 15° calorie. But it is clear that, apart from the points above mentioned, there is a general consensus of observers that the value of J for 15° C. comes on a very sloping portion of the curve and may therefore be affected by small temperature differences. It is curious that the result of all observers who have given a range of absolute values of J (*i.e.*, ROWLAND, GRIFFITHS, BARNES, and ourselves) is to give the value of the 30° calorie as 4·174 within ±0·001. This may be seen by reference to fig. 11, and may be connected with the fact that at 30° C. the value of J comes on what is generally recognised to be the flat portion of the curve near the minimum value. But it would be much better were the standard value chosen over a longer range on the flat portion of the curve, and in such a way

as to be easily reproducible in any well-equipped physical laboratory. The present mean calorie from 0° C. to 100° C., which is sometimes used, cannot be accurately determined without extraordinary precautions. If the mean calorie from 15° C. to 55° C. were taken as the standard practical unit, it would have the following practical advantages :—

1. The lower limit of 15° C. would enable the unit to be readily realised with convenience at any time of the year.

2. The upper limit of 55° C. is so low that no trouble would arise from dissolved air, and the vapour-pressure of the water would be so small that effective precautions against error on this score could be easily taken.

3. The range of 40° C. would embrace the flat portion of the curve, and allow the temperature interval to be easily ascertained with mercury thermometers with an error not greater than 0°·01 C., or 1 part in 4000.

4. The value of the mean calorie from 13° C. to 55° C. is nearly the same as the value of the 15° calorie. When the data are ascertained with sufficient accuracy, it would be easy to adjust the interval so as to make the mean calorie over the interval exactly equal to the 15° calorie.

Received January 30, 1911.—*Additional Note on the Thermoid Effect.*

Further investigation appears to indicate that the thermoid effect is not dependent upon the conductor being made of an alloy, but that it occurs with pure metals. Where the temperature coefficient of a resistance is positive, so is the coefficient of the thermoid effect ; and where negative, negative.

Sir J. LARMOR suggested to us that the effect might be due to strains in the wire caused by the steep temperature gradient from the centre line of the wire to its outer surface. To test this we have taken three wires of pure platinum of different diameters and measured the coefficients. Platinum was chosen because the hysteresis effect with platinum is very small, and one has therefore to deal with a simpler case than manganin. For currents not so heavy as to strain the wire unduly, we have found that, if R_0 is the resistance in ohms of the wire at a given temperature, and R the resistance of the wire at the same temperature whilst a current of C amperes is passing through the wire, we have

$$R = R_0 (1 + \alpha C^2).$$

Further, if we take as the unit of current density that which exists when a current of one ampere is passing in a wire of one square millimetre section, then, if r = radius of wire in centimetres and D = current density,

$$D = C/100\pi r^2,$$

and we have

$$R = R_0 (1 + \beta D^2).$$

It is clear that the thermoid effect must be considered in relation to current density. We may therefore call β in this last expression the thermoid coefficient for wire of a given material and size.

In the following table are given the particulars of the three platinum wires above mentioned, and the values of α and β which result from our experiments. These were of the same nature as mentioned in Section 6 of the paper, *i.e.*, the wire was

THERMOID Effect in Pure Platinum Wires.

Radius of wire in cm.	Area in cm.²	Temperature coefficient.	α.	β.
0·0254	0·002029	0·00366	0·00140	0·0000578
0·01526	0·000732	0·00371	0·00466	0·0000250
0·00892	0·0002495	0·00387	0·02394	0·0000134

measured in a bridge arrangement against a mercury resistance, the current being varied from zero to about five amperes for the largest wire and two for the smallest, and the bath kept at a nearly uniform temperature. The thermoid effect, as expressed in the coefficient β, is seen to be roughly proportional to the radius of the wire or more nearly proportional to $r^{4/3}$. It may also be expressed approximately as

$$\beta = 0{\cdot}0007r + 0{\cdot}063r^2.$$

These comparative results for β are only approximate as the drawing of the wire affects its structure so that the results in the different wires are not exactly comparable. The ordinary temperature coefficient of each wire was observed and is placed in the third column of the table. It appears that each successive drawing of the wire affects its structure in such a way as to send up its temperature coefficient. Probably the heat conductivity would also be affected by the successive drawings.

APPENDIX A.—NOTES OF EXPERIMENT, No. 66.

April 19, 1910. Tap-water—continuous flow—20-minute periods. Nine Standard Cells at 17°·4 C. Laboratory at 15° C.

Time.	Cistern.	Inflow.	Outflow.	Bath.	Obturator.	m_1.	m_2.	Watt resistance.	Weight of flask.	Weight of flask and water.	Water flow in 20 minutes.
2.0 p.m.	13·07	13·17	54·455	54·76	63·6	20·01	21·16	22·8	250·35	1875·27	1624·92
2.10 „	·06	·16	·455	·57	64·7	·03	·17	23·0			
2.20 „	·07	·16	·455	·45	·9	·05	·17	·1	273·27	1897·70	1624·43
2.30 „	·07	·16	·445	·50	·6	·05	·17				
2.40 „	·07	·16	·435	·45	·2	·02	·17	·2	250·64	1875·73	1625·09
2.50 „	·07	·16	·425	·22	·6	·02	·16	·3			
3.0 „	·07	·16	·415	·33	·5	·01	·16		274·15	1899·9	1625·75
3.10 „	·07	·16	·41	·46	·5	·00	·15	·4			
3.20 „	·07	·16	·41	·49	·2	·00	·15		250·61	1874·51	1623·9
3.30 „	·07	·16	·415	·47	·4	·00	·16				
3.40 „	·07	·16	·415	·44	·8	·00	·16	·5	273·24	1898·35	1625·11
3.50 „	·08	·16	·415	·41	·4	·01	·15				
4.0 „	·08	·16	·405	·37	·3	·00	·16	·6	250·73	1874·95	1624·22
4.10 „	·08	·16	·405	·45	·3	·01	·15				
4.20 „	·09	·16	·405	·43	·0	·00	·15		273·37	1898·07	1624·70
4.30 „	·08	·16	·405	·40	·3	·01	·15	·7			
4.40 „	·08	·16	·41	·38	·3	·00	·17		251·50	1875·63	1624·13
4.50 „	·09	·16	·41	·45	·3	·00	·16				
5.0 „	·08	·16	·405	·40	·5	·00	·16	·8	273·23	1897·00	1623·77
5.10 „	·06	·16	·405	·39	·3	·00	·16				
5.20 „	·07	·16	·405	·39	·4	19·98	·15		250·63	1874·96	1624·33
5.30 „	·07	·16	·41	·44	·2	·96	·16				
5.40 „	·08	·16	·41	·41	·2	·95	·15		273·17	1896·35	1623·18
5.50 „	·07	·16	·41	·43	·4	·96	·15				
6.0 „	·06	·16	·41	·39	·1	·95	·16	·8	250·82	1875·44	1624·62
6.10 „	·06	·15	·41			·95					
6.20 „	·08	·155	·40								

Test of Watt Balance Resistance. Bridge, 15°·5 C.

At 23°·5 C. R_0 + leads . . . . . = 500·41
Leads . . . . = 0·07
R_0 . . . . = 500·34

Test of Mercury Heater (at $m_2 = 19·56$).

M_2 + leads . . . . = 9·9616
Leads . . . . = 0·07055
$f(m_2)$ . . . . = 9·89105
  0·5958
Gives constant in bridge ohms . . = 9·29525

Constant in international ohms . . = 9·2966
Gives for $m_2 = 21·16 M_2$ . . . = 9·9458
Deduct leads of watt balance and mercury leads. 0·0816
R of heater . . . . = 9·8642

Test of Mercury Resistance M_1. Bridge, 15°·5 C.

M_1 (at 19·05) + leads. . . . = 1·8465
Leads . . . . = 0·00205
M_1 . . . . = 1·84445
$0·0017 m_1$ . . . . = 0·03239
Constant . . . . = 1·8121

Another Test.

M_1 (at 20·23) + leads . . . = 1·8485
Leads . . . . = 0·00205
M_1 . . . . = 1·84645
$0·0017 m_1$ . . . . = 0·03439
Constant . . . . = 1·8121
Constant in international ohms. = 1·8120
Gives for $m_1 = 19·96 M_1$ . . = 1·8461

From 3.20 to 6.20 p.m.

Temperatures.

Mean outflow . . . . . 54·41
Correction . . . . . -0·005
  54·405

Mean inflow . . . . . 13·16
Correction . . . . . -0·15
  13·01

Mean water outflow in 20 minutes from } 1624·2 gr.
3.20 to 6.20 p.m.
Air correction . . . . 1·7 „
Corrected outflow } 1625·9 „
≡ 81·30 gr. per } minute . . . .

APPENDIX B.—NOTES OF EXPERIMENT No. 164.

26th December, 1910.   Laboratory at 13°·2 C.   Nine cells at 17°·5 C.

E.M.F. 9.   1669 volts.

Time.	Cistern.	Inflow.	Outflow.	Bath.	Obturator.	m_2.	m_1.	Flask.	Flask and water.	Flow per minute.
12.0	13·05	13·13	54·27	54·36	59·0	21·17	13·77			
12.15 p.m.	·04	·14	·21	·22	64·0	·18	·77	337·25	2917·9	86·11
12.30 ,,	·03	·13	·20	·20	·2	·18	·78			
12.45 ,,	·03	·14	·195	·16	62·3	·18	·76	287·5	2865·45	86·02
1.0 ,,	·03	·13	·20	·18	64·1	·16	·81			
1.15 ,,	·04	·14	·20	·20	·0	·17	·46	337·45	2913·6	85·96
1.30 ,,	·04	·14	·21	·21	·2	·18	·45			
1.45 ,,	·04	·14	·205	·24	63·4	·18	·44	287·25	2866·4	86·06
2.0 ,,	·03	·14	·21	·21	64·3	·19	·40			
2.15 ,,	·06	·14	·21	·22	·0	·19	·40	337·3	2917·0	86·08
2.30 ,,	·03	·14	·21	·21	·1	·19	·40			
2.45 ,,	·04	·14	·21	·22	·2	·19	·41	287·2	2866·0	86·05
3.0 ,,	·04	·14	·21	·21	·2	·19	·41			

Experiment to determine heating effect of obturator, stirring, &c., with water at 13° C. through inflow jacket.			
Time.	Dewar.	Bath.	Obturator.
4.5	54·27	54·29	63·7
4.10	·27	·26	64·5
4.15	·275	·28	·3
4.23	·28	·27	·3
4.28	·285	·28	·3
4.35	·29	·30	·3
4.40	·295	·30	·4
4.45	·295	·29	·3
4.51	·30	·29	·3
4.58	·305	·31	·3
5.5	·31	·31	·3

$\equiv 0°·04$ C. per hour.

Correction for inflow thermometer, $-0·16$.

,,   ,, outflow   ,, $-0·07$.

Test of Mercury Resistances.

Bridge, 12°·2 C.

M_1 + leads	= 1·8397
$m_1 = 15·25$, leads	= ·00205
	1·83765
$f(m_1)$	= ·02593
Constant in bridge ohms	= 1·8117
Constant in international ohms	= 1·8115
For $m_1 = 13·40$, M_1	= 1·8343
M_2 + leads	= 9·9021
$m_2 = 20·05$, leads	= ·0701
	9·8320
$f(m_2)$	= ·6121
Constant in bridge ohms	= 9·2199
Constant in international ohms	= 9·2216
Resistance of mercury leads	= ·0055
	9·2161
For $m = 21·19$, resistance of heater . .	= 9·8662

APPENDIX C.—Summary of Continuous-flow Experiments.

First Series.

No.	Outflow.	Inflow.	$\Delta\theta - 0.02$.	$W = $ flow per minute.	M_1.	$R = $ resistance of heater.	R_0.	$C_1 = \dfrac{9.167}{M_1}$.	$C = \dfrac{C_1 R_0}{R_0 + M_2}$.	$C^2R + 0.43$.	Mean calories per second. $\dfrac{W\Delta\theta}{60}$.	$J = \dfrac{C^2R + 0.43}{\text{mean calories}}$.	Difference from mean.
40	54·485	12·95	41·515	81·14	1·8459	9·8682	500·15	4·966	4·869	234·38	56·14	4·175	− 1
45	54·395	12·95	41·425	81·27	1·8461	9·8675	500·00	4·9656	4·8687*	234·33	56·11	4·176	± 1
47	54·36	12·95	41·39	81·30	1·8461	9·8671	500·07	4·9656	4·8687	234·32	56·08	4·178	+ 2
48	54·46	12·955	41·485	81·12	1·8463	9·8695	500·11	4·9651	4·8682	234·33	56·09	4·178	+ 2
49	54·49	12·98	41·49	81·08	1·8465	9·8686	500·03	4·9644	4·8675	234·24	56·07	4·177	+ 1
55	54·99	12·935	42·035	80·07	1·8460	9·8732	500·09	4·9659	4·8690	234·50	56·10	4·180	+ 4
58	54·485	12·955	41·51	81·20	1·8460	9·8688	500·12	4·9659	4·8690	234·39	56·17	4·172	− 4
59	54·36	12·95	41·39	81·38	1·8460	9·8674	500·00	4·9659	4·8690	234·36	56·14	4·174	− 2

Mean . . . 4·1763

Second Series.

No.	Outflow.	Inflow.	$\Delta\theta - 0.02$.	$W = $ flow per minute.	M_1.	$R = $ resistance of heater.	R_0.	$C_1 = \dfrac{9.167}{M_1}$.	$C = \dfrac{C_1 R_0}{R_0 + M_2}$.	$C^2R + 0.43$.	Mean calories per second. $\dfrac{W\Delta\theta}{60}$.	$J = \dfrac{C^2R + 0.43}{\text{mean calories}}$.	Difference from mean.
61	54·405	12·95	41·435	81·27	1·8460	9·8674	500·02	4·9659	4·8690	234·36	56·13	4·175	− 1
63	54·53	12·955	41·555	81·03	1·8456	9·8646	500·11	4·9669	4·8700	234·39	56·12	4·176	± 1
64	54·575	12·94	41·615	80·90	1·8458	9·8653	500·14	4·9664	4·8695	234·36	56·11	4·177	± 1
66	54·405	13·01	41·375	81·30	1·8461	9·8641	500·35	4·9656	4·8688	234·26	56·07	4·178	+ 2
67	54·495	13·00	41·475	81·19	1·8459	9·8649	500·20	4·9661	4·8692	234·32	56·12	4·175	− 1
68	54·565	13·025	41·52	81·07	1·8456	9·8655	500·20	4·9669	4·8700	234·41	56·11	4·178	+ 2

Mean . . . 4·1765

Third Series.

No.	Outflow.	Inflow.	$\Delta\theta - 0.02$.	Flow per minute.	M_1.	$R = $ resistance of heater.	C.	C^2R.	Joules per minute. Electrical.	Joules per minute. Obturator, &c.	Mean calories per minute.	$J = \dfrac{\text{joules}}{\text{mean calories}}$.	Difference from mean.
161	53·932	13·003	40·91	86·46	1·8349	9·8632	4·9959	246·18	14,771	+ 8	3537·1	4·1783	− 2
162	54·88	12·978	41·88	84·54	1·8351	9·8738	4·9953	246·38	14,783	+ 9	3540·5	4·1779	− 6
164	54·14	12·98	41·14	86·06	1·8343	9·8662	4·9975	246·41	14,785	+ 9	3540·5	4·1785	± 1
165	54·16	12·973	41·167	86·00	1·8339	9·8675	4·9986	246·55	14,793	+ 4	3540·4	4·1795	+ 10
166	54·137	12·99	41·127	86·075	1·8343	9·8693	4·9975	246·49	14,789	+ 3	3540·0	4·1785	± 1

Mean value of J from 13° C. to 54°·25 C. . . . = 4·1785

APPENDIX D.—Point-to-Point Experiment, No. 125.

August 6, 1910.   Distilled water—air freed.   Nine cells, 17°·8 C.
W = weight of water = 2950·6 gr.

Time.	m_1.	m_2.	Obturator.	Bath.	Calorimeter.
10.30	start		+ 3	− 1	1·165
10.31	21·90	6·61	+ 2	±	
10.33			±	+ 1	
10.35	21·98	7·81	±	+ 1	
10.36	21·88	8·12	±		
10.39			− 5	+ 1	
10.40	21·89	9·36	− 2	+ 1	
10.41	stop				
10.41½					13·15
10.42					13·155
10.43	start		±	− 1	13·155
10.44	21·89	9·98	− 1	±	
10.46			− 2	±	
10.47		.	+ 1	+ 1	
10.48			+ 2	±	
10.49	21·94	11·50	+ 1	±	
10.51	21·98	12·11	±	− 1	
10.54			− 2	±	
10.55	21·89	13·31	±	±	
10.56	stop				
10.56½					27·33
10.57					27·335
10.58	start		±	− 1	27·335
10.59	21·88	13·95	±	− 1	
11.3	21·90	15·17	− 1	±	
11.5			±	±	
11.7	21·92	16·40	±	±	
11.9	21·90	17·01			
11.10	stop				
11.10½					40·565
11.11					40·57
11.11½	Changed thermometers				40·57
11.16	start		− 2	− 1	40·56
11.17	21·84	17·63	− 2	− 1	
11.21			±	+ 2	
11.22	21·88	19·20	±	+ 1	
11.23	21·89	19·50	±	±	
11.25			+ 2	+ 2	
11.26			±	+ 2	
11.28	21·88	21·85	− 2	±	
11.29	stop				
11.29½					54·995
11.30					55·00
11.30½	Changed thermometers				55·00
11.37	start			− 1	54·975
11.38	21·84	22·63		− 1	
11.39	21·90	21·95	±	±	
11.47			±	+ 2	
11.49	21·92	25·10		+ 3	
11.50			− 2	+ 1	
11.52	21·90	26·03	− 3	±	
11.55	21·97	26·98	+ 2	− 2	

APPENDIX D.—Point-to-Point Experiment, No. 125 (continued).

Time.	m_1.	m_2.	Obturator.	Bath.	Calorimeter.
11.57			±	− 2	
11.58			− 2	− 2	
11.59	21·89	28·21	− 5	− 3	
11.59½	stop				
12.0					80·605
12.0½					80·61
12.1					80·61

Test of Resistances.

Bridge 17° C.

M_2 + leads . . . . = 10·1320 $m_2 = 26·78$
Leads . . . . = 0·0710

                                            10·0610
$f(m_2)$ . . . .   0·8420

Constant in bridge ohms . . . . . . = 9·2190
Bridge factor . . . . = 1·00020
Constant in international ohms . . . = 9·2208

M_1 + leads . . . . = 1·8499 $m_1 = 21·26$
Leads . . . . = 0·0021

                                            1·8478
$f(m_1)$ . . . .   = 0·0361

Constant in international ohms . . . = 1·8117
Bridge factor . . . . = 1·000

SUMMARY.

	1st.	2nd.	3rd.	4th.	5th.
Duration of period	11 minutes.	13 minutes.	12 minutes.	13 minutes.	22½ minutes.
Corrected tem- { start (a) . .	1·095	12·980	27·215	40·51	55·025
peratures { end (b). . .	12·980	27·215	40·52	55·05	80·563
Difference	11·885	14·235	13·305	14·54	25·538
Obturator, &c., heating . . .	0·047	0·045	0·042	0·045	0·075
$\Delta\theta$ due to electrical heating .	11·838	14·19	13·263	14·495	25·463
Average values m_1	21·93	21·92	21·90	21·87	21·91
Average values M_1	1·8488			1·8487	
$C_1 = 9·1666/M_1$	4·9581			4·9584	
Mean values m_2	7·97	11·65	15·49	19·34	24·85
Mean values R = M_2 − 0·0045	9·4465	9·5586	9·6794	9·8046	9·9906
$C_1^2 R$	232·22	234·98	237·97	241·05	245·62
Joules expended	153,265	183,281	171,343	188,021	331,587
Joules for calorimeter . . .	6,885	8,351	7,897	8,733	15,604
Joules for water	146,380	174,930	163,446	179,288	315,983
Calories = W × $\Delta\theta$	34,929	41,869	39,134	42,769	75,131
J_a^b	4·1906	4·1780	4·1766	4·1920	4·2058

APPENDIX E.

$J_{13}^{54\cdot5}$ Distilled Water.

Reference number.	Initial temperature. °C.	Final temperature. °C.	$\Delta\theta$.	Joules.	Joules for calorimeter. Capacity = 595·5 per 1°.	Joules for water.	Calories = $\Delta\theta$ × weight of water.	Joules/calories.	Difference from mean.
74	13·66	55·04	41·38	535,278	24,642	510,636	122,104	4·1820	+ 1
75	13·00	54·445	41·445	536,308	24,680	511,628	122,288	4·1838	+ 19
76	14·03	54·515	40·485	523,569	24,109	499,460	119,431	4·1820	+ 1
77a	13·01	54·485	41·475	536,765	24,698	512,067	122,376	4·1844	+ 25
77b	13·035	54·55	41·515	536,940	24,722	512,218	122,494	4·1816	− 3
79	12·95	54·415	41·465	536,554	24,692	511,862	122,363	4·1831	+ 12
80	13·02	54·36	41·34	534,576	24,618	509,958	121,974	4·1809	− 10
81a	13·00	54·335	41·335	534,530	24,615	509,915	121,967	4·1808	− 11
81b	13·02	54·385	41·365	534,951	24,633	510,318	122,056	4·1810	− 9
85	12·94	54·325	41·385	535,478	24,645	510,833	122,044	4·1856	+ 37
86a	13·025	54·43	41·405	535,411	24,657	510,754	122,186	4·1801	− 18
86b	13·025	54·385	41·36	534,740	24,630	510,110	122,037	4·1800	− 19
92	13·105	55·015	41·91	542,077	24,957	517,120	123,651	4·1821	+ 2
93	13·36	54·75	41·39	534,912	24,648	510,264	122,096	4·1792	− 27
94	13·295	54·155	40·86	528,513	24,332	504,181	120,562	4·1819	±1
Mean value . . .								4·1819	

APPENDIX F.

Mean Values of **J** from 0° C. to 13° C.

Number.	Corrected temperatures.		Corrected Δθ.	Joules.	$\Delta\theta \times 582 \cdot 0$ joules for calorimeter.	Joules for water.	Calories.	J_a^b.	Difference from mean.
	a.	b.							
	°C.	°C.							
92	1·205	13·033	11·828	153,186	6,884	146,302	34,897	4·1924	+ 3
93	1·47	13·313	11·843	153,311	6,892	146,419	34,936	4·1911	− 10
94	1·40	13·248	11·848	153,509	6,895	146,614	34,959	4·1939	+18
99	1·735	13·060	11·325	146,739	6,591	140,148	33,413	4·1944	+23
100	1·43	13·298	11·868	153,687	6,907	146,780	35,017	4·1917	− 4
102	0·71	13·105	12·395	160,597	7,214	153,383	36,565	4·1948	+27
103	1·00	13·132	12·132	157,085	7,061	150,024	35,795	4·1912	− 9
104	1·00	13·127	12·127	157,038	7,058	149,980	35,780	4·1917	− 4
107	2·33	13·093	10·763	139,573	6,264	133,309	31,758	4·1976	+55
114	1·16	13·003	11·843	153,384	6,892	146,492	34,937	4·1930	+ 9
115	1·16	13·013	11·853	153,476	6,898	146,578	34,969	4·1917	− 4
121	1·18	13·033	11·853	153,370	6,898	146,472	34,965	4·1891	− 30
122	1·20	13·043	11·843	153,384	6,892	146,472	34,936	4·1931	+10
123	1·33	13·178	11·848	153,265	6,895	146,370	34,960	4·1868	− 53
124	0·81	13·19	12·38	160,231	7,205	153,026	36,525	4·1896	− 25
125	1·095	12·933	11·838	153,265	6,890	146,375	34,929	4·1906	− 15
126	0·945	12·783	11·838	153,337	6,890	146,447	34,926	4·1931	+10
Means	1·30	13·09					Mean J_0^{13}	4·1921 = 4·1937	

Mean Gives J_0^{13}

APPENDIX G.

Mean Values of J for Intervals.

No.	Temperature range. a.	Temperature range. b.	J_a^b.	No.	Temperature range. a.	Temperature range. b.	J_a^b.
	° C.	° C.			° C.	° C.	
99	13·105	25·147	4·1711	100	39·820	54·903	4·1893
102	13·155	27·410	4·1719	102	40·245	54·725	4·1986
103	13·18	27·405	4·1770	114	40·315	54·810	4·1940
104	13·17	27·405	4·1720	115	40·35	54·855	4·1915
107	13·135	26·796	4·1729	121	40·545	55·030	4·1982
114	13·045	26·975	4·1771	122	40·655	55·15	4·1949
115	13·055	26·995	4·1757	123	40·755	55·245	4·1924
121	13·09	26·751	4·1732	124	40·245	54·73	4·1936
122	13·095	27·30	4·1767	125	40·51	55·005	4·1920
123	13·23	27·425	4·1760				
124	13·24	27·445	4·1748				
125	12·98	27·17	4·1780	Means . . .	40·38	54·94	4·1938
126	12·835	27·02	4·1813				
				94	54·285	70·071	4·2014
				100	54·945	73·036	4·2023
Means . . .	13·10	27·02	4·1752	114	54·85	72·91	4·2043
				115	54·905	72·984	4·2025
				121	55·09	73·169	4·2013
				122	55·20	73·269	4·2034
102	27·455	40·20	4·1741	123	55·295	73·349	4·2026
114	27·02	40·28	4·1792	124	54·78	73·124	4·2015
115	27·04	40·318	4·1745				
121	26·805	40·078	4·1743	Means . . .	54·92	72·74	4·2024
122	27·35	40·623	4·1757				
123	27·475	40·733	4·1768				
124	27·49	40·215	4·1712	125	55·025	80·488	4·2058
125	27·215	40·478	4·1766	126	54·855	80·33	4·2056
126	27·07	40·328	4·1794				
Means . . .	27·21	40·36	4·1758	Means . . .	54·94	80·41	4·2057