# II. *Continuous Electrical Calorimetry.*

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## PART I.—INTRODUCTION.

### (1.) *General Account of the Origin and Progress of the Investigation.*

THE method of Continuous Electrical Calorimetry, described in the following paper, was originally devised as part of a Fellowship Dissertation on applications of the platinum thermometer, at Trinity College, Cambridge, in the year 1886, but, on account of unforeseen difficulties, the experiments did not at that time get beyond the preliminary stage. In the first rough apparatus, a steady flow of water, passing through a tube about 30 centims. long and 3 millims. in diameter, was heated by an electric current in a fine spiral of platinum wire of about 5 ohms resistance, nearly fitting the tube. The steady difference of temperature between the inflow and the outflow was measured by a pair of delicate mercury thermometers, which it was of course intended to replace in the final apparatus by a differential pair of platinum thermometers. The electrical energy supplied was measured by the potentiometer method in terms of a set of 5 Clark cells and a large German-silver resistance of 5 ohms in series with the platinum spiral. The potentiometer was specially made for the work, and consisted of a metre slide-wire, and ten resistances, each equal to the slide-wire, for extending the scale so as to secure sufficient accuracy of reading. This potentiometer was still in existence at the Cavendish Laboratory in 1893. The set of 5 Clark cells were tested by GLAZEBROOK and SKINNER ('Phil. Trans.,' A, 1892), and were still in good condition at a later date. The external heat-loss in these experiments was found to be much larger than had been anticipated, and so variable that the results were of little or no value. In order to remedy this defect, I designed the vacuum-jacket, which was suggested by some experiments of Sir WILLIAM CROOKES ('Roy. Soc. Proc.,' vol. 31, 1881, p. 239), which appeared to indicate that the rate of cooling of a mercury thermometer in a very good vacuum was ten to twenty times less than in air. I therefore regarded the vacuum-jacket as a most essential part of the experiment, and expected a great improvement to result from its use. Unfortunately I failed to make the jacket for want of sufficient skill in glass-work, and abandoned the experiment for the time, until my appointment as Professor of Physics at McGill College, Montreal, gave me greater facilities for carrying out the work. Eventually it proved that the effect of the vacuum-jacket in diminishing the external loss of heat was not nearly so great as I had been led to imagine, but it possessed several advantages as a heat insulator over such materials as cotton wool or flannel. The thermal capacity of a vacuum being negligible, the time required for attaining a steady state was much shortened. Moreover there was no risk of error from damp, which is the worst drawback of ordinary lagging.

I had not originally intended to employ the electrical method for determining the *variation* of the specific heat of water, but only for comparing the electrical and thermal units at ordinary temperatures. In the meantime the work of GRIFFITHS, with which I was intimately acquainted, had shown that the electrical units were probably in error, and appeared to indicate a smaller rate of variation of the specific heat than that given by ROWLAND. In reconsidering the problem, in 1893, I therefore determined to attempt the absolute measurement of the ohm and the Clark cell, in addition to the variation of the specific heat of water over as wide a range as possible. The method of steady-flow calorimetry appeared to be particularly adapted to the latter object, as it afforded much greater facility than that of GRIFFITHS or ROWLAND in varying the conditions of experiment over a wide range. For the absolute measurement of the ohm, I immediately obtained estimates for a Lorenz apparatus of Professor V. JONES' pattern, which was eventually ordered in October, 1894, and is briefly described in Section 6 of this paper. For the absolute measurement of the Clark cell in terms of the ohm, after spending some time in designing various forms of electrodynamometer, I decided to employ the British Association pattern, with certain modifications, which are explained below, Sections 10 to 16. At the same time I commenced a series of investigations into the defects of the form of Clark cell described in the Board of Trade Memorandum, in which I was assisted by Mr. H. T. BARNES. This work included an accurate determination of the variation of the E.M.F. with temperature and with strength of solution, in addition to measurements of the solubility of zinc sulphate and of the density of its solutions. It extended further than I had at first anticipated, and was not completed till the summer of 1896. The results were published in the 'Proceedings of the Royal Society,' vol. 62, pp. 117–152.

In the meantime I had been engaged, during the winter of 1895 and the summer of 1896, in testing various methods of temperature regulation, and in studying the theory of the flow of water in fine tubes under the conditions presented by the proposed method of calorimetry. This was a most important part of the work, as the determination of the variation of the specific heat over a large range of temperature exacted great accuracy of regulation, and close attention to details of design. The method of regulation and circulation finally adopted may appear very simple and obvious, but it was not reached without considerable expenditure of time and thought. The experiments on the flow of water heated by an electric current (Section 33) threw some light on the causes of failure of the rough preliminary experiments, and supplied the data necessary for the design of the glass-work of the calorimeter and vacuum-jacket, which was ordered of Messrs. MÜLLER, in Bonn, early in October, 1896.

At this stage of the investigation, finding that I should not have sufficient leisure during the work of the session to carry out the research single-handed, as I had at first intended, I secured the assistance of Mr. BARNES, who had already proved his ability in the making and testing of Clark cells. Our first experiments were made on mercury, which, being itself a conductor of electricity, presented fewer difficulties than water. The water apparatus was fitted up and tested shortly before the meeting of the British Association, in 1897, but it was at that time incomplete in certain important details, and only three sets of observations, at 5°, 25°, and 45°, were obtained. At the commencement of the next session I secured the services of Mr. STOVEL, the most promising of the electrical students of the previous session, to assist Mr. BARNES in setting up the apparatus and taking the observations. I spent a good deal of my leisure at this time in the adaptation of the method to the determination of the specific heat of steam, but continued to give the closest personal supervision to the work on the specific heat of water, and made several tests of the apparatus in the vacations when I had more leisure. A great part of the work during this session consisted in perfecting the mechanical details of the apparatus, which is always a most important and laborious process in an investigation of this character. The last work in which I personally assisted before leaving Montreal was the drawing and annealing of the platinum-silver wire for the Mica Current-Standards referred to in Section 7. By this time the fundamental portions of the apparatus had been practically perfected, but the observations, though very numerous, did not extend beyond the range 0° to 55°, and they had for the most part been taken for the purpose of testing improvements which from time to time were introduced, and could not be regarded as parts of a regular series.

When I left Montreal about the end of May, 1898, it was arranged that Mr. BARNES should continue the experiments throughout the summer, and should follow me to England with the apparatus as soon as I could make preparations for carrying on the work in my new laboratory. Unfortunately this plan proved to be impracticable, which caused some delay in the work, as I was unable to render him any material assistance by correspondence at such a distance, owing to the impossibility of detecting sources of error in any particular case without seeing the apparatus or the observations. But by the end of the McGill College session in April 1899, he had succeeded so well in overcoming his difficulties, and the work appeared to be progressing so favourably, that it seemed inadvisable to disturb the apparatus. I therefore reluctantly consented to abandon any further share in the observations. It had originally been intended that I should write the paper describing the theory and results of the investigation; but as, in the end, Mr. BARNES was solely responsible for the final series of observations, it seemed more appropriate that he should write the account of that part of the work.

The primary object of my own contribution is to supplement his account of the final observations by a general discussion of the theory of the experiment, and a description of the difficulties encountered in the earlier stages. He was unable to speak with authority on these points, as a good deal of this work was done before he joined the investigation, and I had not thought it necessary to give him a detailed account of it, since it was originally intended that we should finish the work together. A similar partition of authorship has already been sanctioned in a similar case in the work of REYNOLDS and MOORBY, and possesses undoubted advantages in presenting the results from two distinct and independent points of view. It was the more necessary in the present instance owing to the comparative independence of our several shares in the work, and to the impossibility of satisfactory collaboration at such a distance. I had hoped at one time that it might be possible by some rearrangement of the matter to weld the separately written portions into a continuous whole, but as the part written by Dr. BARNES had already been accepted by the Royal Society, and the Abstract had been already published, it appeared desirable that it should be printed without alteration as nearly as possible as it was received, subject only to a rearrangement of the Tables of Results, and the addition of one or two samples of the original observations.

The delay in publication has been partly due to the necessity of this rearrangement, and partly to the difficulty of obtaining satisfactory determinations of the resistance of the manganin standard ohm, on which the absolute values of the results depended. I have taken advantage of this delay to verify the calculations as far as possible, and to subject the whole work to as complete and careful a revision as the time at my disposal would allow. The final results do not materially differ from those previously published in the 'Report of the British Association, Dover,' 1899, and in the 'Physical Review.' There was, therefore, no need for haste so far as the numerical results of the work were concerned, but it was important in an investigation of this character that all the details of the apparatus, and the theoretical and practical difficulties of the work should be adequately explained and illustrated.

[*Added March 11th*, 1902.—Frequent references are made in the following pages to the paper by Dr. BARNES, *infra*, pp. 149–263, describing his experimental results. These references are generally indicated by the name (BARNES) in brackets, with the addition of the page, table, or section referred to.

It is hardly necessary that I should say anything here in praise of the conscientious accuracy with which Dr. BARNES has carried out his share of the work. In re-arranging the tabular summary of observations (BARNES, Table XVIII., p. 243), I have endeavoured to indicate clearly the order of accuracy attained, and it must be evident to anyone who studies the paper, that it would be difficult to make any improvement in this respect.]

## PART II. ELECTRICAL MEASUREMENTS.—(A.) POTENTIAL.

### (2.) *Advantages of the Potentiometer Method.*

The simplest method of observing the electrical energy expended in the calorimeter would be to measure the current C, and to assume the value of the resistance R to be that corresponding to the observed mean temperature of the calorimeter. The watts expended would then be given by the formula, $W = C^2R$. This method was adopted by the majority of the earlier experimentalists. An equally simple method, but more seldom practised, would be to observe the difference of potential E on the conductor, assuming the resistance as before. The advantage of assuming the resistance is that one reading only is required, but, as **Rowland** pointed out, the temperature of the resistance, when the heating current is passing through it, must be considerably higher than that of the calorimeter. This would introduce a serious error, unless it were possible to use a wire of some material like manganin, in which the variation of resistance with temperature could be neglected.

**Griffiths** ('Phil. Trans.,' A, 1893) adopted the method of balancing the potential difference on the conductor against a number of Clark cells in series, and deduced the expenditure of energy in watts from the formula $W = E^2/R$, by assuming the value of the resistance. He tried manganin to avoid the error of super-heating, but found that it was not sufficiently constant. In the end he found himself compelled to use platinum for the conductor, but avoided the error due to super-heating by measuring the actual excess-temperature of the wire as nearly as possible under the conditions of the experiment.

**Schuster** ('Phil. Trans.,' A, 1895) adopted the same method of balancing the P.D. on the conductor, but did not assume the value of the resistance. Instead of this, he measured the time integral of the current with a silver voltameter. This is a theoretically perfect and most appropriate method of procedure, but it introduces an additional measurement, and limits the accuracy to that attainable with the silver voltameter.

For our method of experiment there were several objections to the use of the silver voltameter, which put it practically out of the question. As is well known, when the current is first turned through the voltameter, the resistance changes considerably for some time. This makes it difficult to keep the P.D. on the conductor accurately balanced against the Clark cells unless the whole resistance in circuit is large. A change of this kind in the current at the moment of starting the experiment would be a fatal defect in the steady-flow method of calorimetry, as it would disturb all the temperature conditions, which must be perfectly steady and constant before observations are commenced. Moreover, it happened to be most convenient for our purpose to employ currents from 5 to 10 amperes, which would require very large voltameters, and could not be *continuously* regulated without constructing special rheostats. In any case regulation by hand would involve some discontinuity in the heat-flow, which it was desirable to avoid. We found it best not to make any attempt to control the current artificially, but to employ very large and constant storage cells, and to compensate the slow rate of running down of the current by the running down of the head of water, so that the temperature-difference might remain practically constant throughout the experiment.

Besides the above special objections to the use of the silver voltameter, there are the general objections : (1) that the voltameter method gives only the time-integral of the current, and does not permit the course of variation of the current to be accurately followed throughout an experiment; (2) that with Clark or cadmium cells of a suitable pattern it is possible to attain an order of accuracy in the *relative* values of the readings about ten times as good as that attainable with a silver voltameter. It was most important for our purpose to obtain accurate relative values, and whatever might be the doubt as to the absolute values of the E.M.F. of the cells, there could be none as to their constancy, which was easily tested over considerable periods of time.

It therefore appeared most satisfactory to measure the current by passing it through a suitable resistance, and observing the P.D. on the terminals with a potentiometer in the usual manner. The introduction of the potentiometer may appear at first sight to be an additional complication and source of error; but it really made the observations much simpler, and I satisfied myself by careful tests of the instrument that an accuracy of 1 in 100,000 was readily attainable so far as the potentiometer readings were concerned. Besides, it was unnecessary, with the potentiometer, to keep the P.D. on the conductor balanced against an *integral* number of cells, and it was, therefore, possible to adjust the electric current to give the same rise of temperature with different values of the flow of liquid. This most essential adjustment could not be so conveniently or quickly effected by varying the flow of liquid as by regulating the electric current with a low-resistance rheostat. It also proved in practice to be much more convenient to take all the electrical readings on a single instrument, instead of having the silver voltameter as well as the potential balance to attend to.

It will be seen that our method is independent of any assumption with regard to the electrochemical equivalent of silver, although the contrary is apparently assumed in discussing our result both by AMES ('Report to the Paris Congress of 1900 on the Mechanical Equivalent of Heat'), and by GRIFFITHS ('Thermal Measurement of Energy,' p. 93). The method of measurement is ultimately equivalent to that of GRIFFITHS, as it makes the result depend on the International Ohm, and the Clark cell. The measurement of the current by observing the P.D. on a known resistance, when combined with the observation of the P.D. on the heating conductor itself, is in effect equivalent to the measurement of the resistance of the heating conductor under the actual conditions of the experiment, in the most direct manner possible. The watts expended are derived from the formula $E^2/R$, so that an error in the absolute value assumed for the standard cell is twice as important as an error in the value of the ohm.

If $x_0$ is the balance-reading of the potentiometer when the standard cells are connected, and $e$ the E.M.F. of the standard cells, and if $x'$, $x''$ are the readings corresponding to the P.D. on the heating conductor and the standard resistance S respectively, the expression for the heat-supply in watts is evidently

$$EC = e^2 x' x''/x_0^2 S.$$

The accuracy of the reading $x_0$ for the cells, which enters by its square, is twice as important as that of $x'$ or $x''$, but it was also more easy to obtain with certainty, since the cells were kept at a constant temperature, and the reading $x_0$ seldom changed by more than 1 in 50,000 in the course of an experiment. It will be seen that, for the determination of the variation of the specific heat, the most important point in the electrical measurements is the question of the accuracy of calibration of the potentiometer, which is described in the following sections. The absolute values of the units are less important, but I have added a brief account of experiments on the absolute value of the Clark cells, and of the tests of the standard resistances, as they possess an interest of their own, even apart from the question of the absolute value of the "mechanical equivalent."

### (3.) *Description of the Potentiometer.*

The form of potentiometer selected as being most convenient for the purpose was the well-known Thomson-Varley Slide-Box, which is described and figured in many electrical works (*e.g.*, MUNRO and JAMIESON'S "Pocket-Book," p. 150). The annexed figure shows the arrangement of the connections, and will be useful for reference in explaining the details of the calibration.

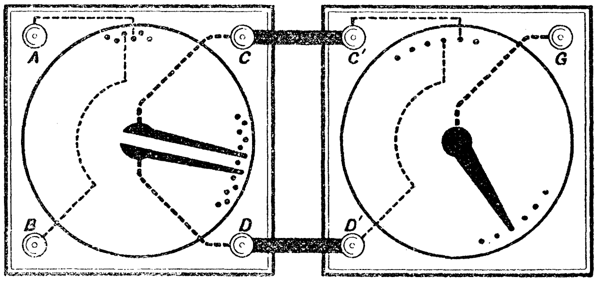

Fig. 1. Diagram of Thomson-Varley Slide-Box.

The main dial ABCD contains 101 coils, each of 1000 ohms resistance, connected in series, the ends of the series being connected to the terminals AB. The ends of each coil are connected to platinized studs, which are indicated by the black dots in the diagram. A pair of revolving contact springs, fixed to an ebonite handle, travel round the dial. These springs are severally connected to the terminals C and D, and the distance between them is adjusted so that they bridge over *two* of the 1000-ohm coils of the main dial.

The second, or "Vernier" dial, C′D′G, consists of a series of 100 coils of 20 ohms each, the ends of which are connected to C′ and D′, and are thus, by way of C and D and the double revolving contact of the main dial, in parallel with two of the 1000-ohm coils of the main dial. Since two coils of the main dial are always shunted in this manner by the vernier dial, the effective resistance between C and D is reduced to 1000 ohms, and the whole resistance of the potentiometer between the terminals A and B, to 100,000 ohms. The ends of each of the 20-ohm coils of the vernier dial are connected to platinized studs arranged in a circle, which make contact one at a time with a single revolving contact spring, connected to the galvanometer terminal G. This arrangement of main and vernier dials permits the sub-division of each hundredth part of the whole resistance into one hundred parts, so that the reading of the two dials gives the P.D. to be measured directly to one part in ten thousand of the P.D. on the terminals AB.

The advantages of this form of potentiometer, in addition to its high resistance, were (1) the great facility and rapidity of reading and manipulation, and (2) the symmetry of construction, which permitted a very high order of accuracy of calibration to be attained, and greatly facilitated the application of corrections, as compared with the usual type of instrument in which a bridge-wire is employed for the finer sub-divisions.

In the use of this instrument in our experiments the P.D. to be measured seldom exceeded 4 volts. The terminals AB were permanently connected to three Leclanché cells, which gave a very steady current through so high a resistance. The reading of the two Clark cells employed as a standard varied by a few parts in 10,000 only from week to week, and generally remained constant to 1 in 100,000 for the short interval of 15 minutes corresponding to any single experiment.

The galvanometer employed with this potentiometer had a resistance of 110,000 ohms. The astaticism of the needles was adjusted as carefully as possible, so that the effect of disturbance of earth-currents due to the electric railway might be negligible. The suspended system was fitted with a very perfect mirror and a damper to make it practically dead-beat. The sensitiveness was adjusted by control magnets to give a deflection of approximately 10 scale-divisions for one division of the vernier dial (1 in 10,000). The perfection and steadiness of the image was such as to permit reading to a small fraction of a scale-division. The first four figures of the reading were given by the setting of the dial contacts. It was easy to estimate the fifth figure at any moment by inspection of the galvanometer deflection. The temperature conditions were generally so steady in the course of an experiment, and the diminution of the electric current and the water-flow so gradual and regular, that it was possible, as a rule, to predict the reading of the P.D., either on the standard resistance or on the heating conductor, to 1 in 100,000 for at least five minutes ahead.

As there were no observational difficulties to contend with in the electrical readings, the relative order of accuracy of the results would be limited only by the constancy of the Clark cells and the current standards, and by the order of accuracy attainable in the calibration of the potentiometer and in the permanence of the relative values of the coils. The coils of the main dial, which were the most important, were all precisely similar, wound with the same wire and carefully protected from sudden or unequal changes of temperature. The ratio of the resistances of the two halves of the dial was frequently checked with consistent results, as a precaution to give warning of any accidental flaw. This precaution was by no means superfluous, for on one occasion in November, 1897, a fault, amounting very nearly to complete rupture of the wire, was discovered by Mr. KING in this manner. It was however easily located and rectified without altering the relative values of the coils.

### (4.) *Method of Testing.*

The method of testing the ratio of the two halves of the slide-box was as follows:—The slide-box was connected by the terminals AB in parallel with a 100,000-ohm box consisting of ten coils of 10,000 ohms each. The battery was connected as usual at A and B, one terminal of the galvanometer to G, and the other to the middle of the 100,000-ohm box. The slide-box contacts were set at 50,000 ohms. To take one particular experiment as an example, the deflection of the galvanometer observed on reversing the battery was 77 scale-divisions. When the contact was set at 50,010 ohms, the deflection was 215 scale-divisions in the same direction, showing a sensitiveness of 138 scale-divisions on reversal for a change of 1 in 5000 in the reading. The contact was then set back to 50,000, and the two halves of the box were interchanged with respect to the rest of the circuit by interchanging the connections at A and B. The deflection observed was increased from 77 to 181 scale-divisions in the same direction as before. The effect of interchanging the two halves is the same as if the slider were shifted through a resistance equal to their difference. Hence the difference of the two halves is to 10 ohms as 104 is to 138. The first half of the box is evidently the smaller, as the effect of interchanging is the same as that of increasing the reading. The correction to be applied to the reading, to reduce to mean ohms of the box, is half the difference of the two halves, and is negative, since the first half is the smaller. We have, therefore,

$$\text{Correction at reading } 50{,}000 \text{ ohms} = -10 \times 104/2 \times 138 = -3{\cdot}8 \text{ ohms.}$$

The galvanometer deflections in each case were observed several times and the mean taken. The details were also varied by using different resistances for the ratio arms in the comparison and different galvanometers. Observations were taken by different observers at various temperatures on several occasions, at intervals during five years. The greatest divergence of the results from the mean value is less than 1 part in 100,000 (·4 ohm in 50,000 ohms), which is strong evidence that the relative values of the corrections at any part of the box could be relied on at any time to a similar order of accuracy.

The following is a summary of the results of all the tests of which full details have been preserved, but several other tests were made from time to time as a precaution:—

TABLE I.—Verification of Correction at Middle Point of Slide-Box.

| Date. | Observers. | Correction (ohms in 50,000). |
|---|---|---|
| February, 1894 . . . . | CALLENDAR. | $-3\cdot8$ |
| December 20th, 1894. . . | CALLENDAR. | $-3\cdot96$ |
| January 29th, 1895 . . . | KING. | $-3\cdot77$ |
| November 24th, 1896. . . | THOMSON and STOVEL. | $-4\cdot2$ |
| February 2nd, 1897 . . . | BLAIR and MACDONALD. | $-3\cdot72$ |
| March 4th, 1897 . . . . | PITCHER and EDWARDS. | $-3\cdot50$ |
| April 22nd, 1898 . . . . | STOVEL. | $-3\cdot43$ |
| January 27th, 1899 . . . | BARNES. | $-3\cdot95$ |

Some of the above observations were taken by fourth-year students in the course of their work, but in the majority of cases I personally verified the readings and results at the time of entry.

## (5.) *Method of Calibration.*

In the calibration of the slide-box, the point of most importance was to determine the correction for each reading of the main dial, *i.e.*, at 100 equidistant points of the whole range. The vernier dial was so small in comparison that the errors of its individual coils were negligible in their effect on the whole reading, although it was necessary at each point to take account of the difference of resistance of the whole vernier dial and the pair of coils shunted by it in any position of the slider.

After several trials of various methods extending over nearly a month, I came to the conclusion that the most convenient and accurate method of performing the calibration was to determine the relative values of the coils of the main dial in pairs by comparison with the 2000 ohms of the vernier dial. The flexible copper cable connecting the terminals D and D′ was disconnected, and the terminals were connected to a galvanometer and to a pair of exactly similar resistances of 2000 ohms each forming the ratio arms P and Q of a Wheatstone bridge, the other two arms of which were the vernier dial S and any pair of consecutive coils $R_n$ and $R_{n+1}$ of the main dial. A battery of two storage cells, selected for constancy, was connected to the point between the ratio arms and to the terminals CC′. The deflection $d_n$ of the galvanometer corresponding to any setting of the slider was proportional to the difference of the sum of the corresponding pair of coils $R_n$ and $R_{n+1}$ of the main dial from a unit SP/Q, which was approximately 2000 ohms, and remained constant throughout the comparisons. The value of this deflection was reduced to ohms by observing the change of galvanometer deflection $s$ produced by a change of 1 ohm in one of the arms. This observation was repeated at intervals during the calibration.

The advantage of this particular arrangement was partly that of expedition and convenience, partly that of avoiding systematic errors due to changes of condition or temperature while the calibration was proceeding. The construction of the vernier dial, 100 coils of 20 ohms each, made it a good standard of comparison, as there was no risk of appreciable heating from the current employed, although it was necessarily kept on for more than an hour. Moreover, as it was constructed of similar wire and enclosed in a similar box to the main dial, it was probable that any change of the surrounding conditions of temperature would affect the two similarly. The heating effect of the current on P and Q would be sufficiently eliminated by their similarity of construction.

Readings taken in this manner, with the slider set in each position of the main dial, gave 100 equations of the following form :—

$$R_n + R_{n+1} = SP/Q + d_n/s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

To determine the correction at each point of the main dial, and the relative values of the 101 resistances and the vernier dial, it was also necessary to determine the ratio of any two of the coils to each other, and the ratio of the two together to the vernier dial. This was effected by the method of interchanging, as already described for determining the ratio of the two halves of the slide-box.

The ratio of coils $R_1$ and $R_2$ to the vernier dial S was found to be

$$(R_1 + R_2)/S = 1{\cdot}000039.$$

The ratio of coils $R_1$ and $R_2$ to each other was found to be

$$R_1/R_2 = 1{\cdot}000400.$$

In the latter case the galvanometer contact was made by means of a copper wire to the stud between 1 and 2, the glass cover being removed for the purpose of this test.

The observation of the values of the deflections $d$ for the 100 equations of the type (1), was repeated on two separate occasions. On the first occasion the 110,000-ohm galvanometer was employed, but it was found that when the galvanometer was adjusted to a suitable degree of sensitiveness for the experiment, its time period was too slow, and its zero not sufficiently constant to give the best results. It took upwards of an hour to obtain the first fifty observations. This series was not therefore continued throughout the box, but the observations were reduced to mean ohms of the box by reference to the value of the correction at the middle point of the box obtained from a separate observation. On the second occasion the 110,000-ohm galvanometer was replaced by one of 2000 ohms resistance, which was better suited for this particular experiment, though not so well adapted for observations in which the whole box was employed. The sensitiveness of this galvanometer was adjusted to give a deflection of 167 scale-divisions on reversal for a change of 1 ohm in 2000 with a time period of 5 seconds, and remained constant to less than one scale-division throughout the test of the whole box, which occupied only an hour and a halt.

The observations and results of the two calibrations for the first half of the slide-box are compared in the following table. The first column contains the reading of the slider on the main dial. The second column the observed deflection of the galvanometer $d$ in equation (1) reduced to ohms by dividing by $s$. Since $s = 167$ in the second series, one unit in the second decimal place of $d/s$ corresponds to nearly 2 scale-divisions deflection observed. The observations were taken to half a scale-division, but owing to slight variations of sensitiveness and zero it was not considered worth while to work the values of $d/s$ beyond the nearest hundredth of an ohm. The next column gives the error $d\mathrm{R}$ in ohms of each separate resistance of the main dial in terms of the mean of the whole, deduced from equations (1) by the aid of (2) and (3). The fourth column gives the correction $dn$ in ohms to the reading at each point. This correction is equal to the sum of the errors of all the coils up to the point considered, subject only to a small correction, called the "vernier-correction," to allow for the fact that the next two coils are shunted by the vernier dial. The value of the vernier-correction is given by the following expression—

$$\text{Vernier-correction to reading } n = -n\,(\cdot 38 - 3d\mathrm{R}_{n+1} - 3d\mathrm{R}_{n+2})/400.$$

This correction is often negligible when $n$ is small, but sometimes reaches ·5 or ·6 of an ohm near the higher readings. The next three columns in the table give the corresponding values of the same quantities $d/s$, $d\mathrm{R}$, and $dn$, deduced from the readings taken during the second calibration. Comparing the two sets it will be observed that the discrepancy very rarely exceeds half an ohm, which is only one part in 200,000 of the whole resistance.

TABLE II.—Calibration of 100,000-ohm Slide-Box. Corrections in ohms.

| Reading, of main dial *n*. | Observations, Series I. November 24, 1894, at 15°·5 C. | | | Observations, Series II. December 20, 1894, at 20°·2 C. | | | Difference of Series I–II. |
|---|---|---|---|---|---|---|---|
| | *d/s*. | *d*R. | Correction. | *d/s*. | *d*R. | Correction. | |
| 0 | +1·04 | – | 0 | +1·26 | – | 0 | 0 |
| 1 | +0·52 | +0·43 | +0·43 | +0·55 | +0·45 | +0·45 | −0·02 |
| 2 | +0·26 | +0·05 | +0·45 | +0·20 | +0·05 | +0·49 | −0·04 |
| 3 | +0·64 | −0·10 | +0·36 | +0·77 | −0·26 | +0·24 | +0·12 |
| 4 | +0·92 | −0·34 | +0·03 | +1·11 | −0·30 | −0·07 | +0·10 |
| 5 | +0·40 | +0·39 | +0·40 | +0·54 | +0·31 | +0·24 | +0·16 |
| 6 | +1·00 | −0·06 | +0·36 | +1·21 | +0·04 | +0·30 | +0·06 |
| 7 | +1·42 | −0·13 | +0·26 | +1·53 | −0·25 | +0·07 | +0·19 |
| 8 | +0·68 | +0·54 | +0·76 | +0·74 | +0·71 | +0·74 | +0·02 |
| 9 | +0·40 | +0·29 | +1·03 | +0·51 | +0·06 | +0·78 | +0·25 |
| 10 | +0·52 | −0·20 | +0·83 | +0·62 | −0·08 | +0·71 | +0·12 |
| 11 | +0·50 | +0·01 | +0·84 | +0·58 | −0·17 | +0·53 | +0·31 |
| 12 | +1·56 | −0·08 | +0·86 | +1·70 | +0·03 | +0·66 | +0·20 |
| 13 | +1·50 | −0·01 | +0·85 | +1·72 | −0·21 | +0·46 | +0·39 |
| 14 | +0·46 | +0·98 | +1·72 | +0·51 | +1·16 | +1·50 | +0·22 |
| 15 | +0·44 | −0·07 | +1·65 | +0·52 | −0·19 | +1·30 | +0·35 |
| 16 | +0·26 | −0·06 | +1·57 | +0·37 | −0·06 | +1·22 | +0·33 |
| 17 | +0·32 | −0·09 | +1·48 | +0·40 | −0·18 | +1·04 | +0·44 |
| 18 | +0·22 | −0·24 | +1·22 | +0·31 | −0·21 | +0·82 | +0·40 |
| 19 | +0·04 | −0·03 | +1·16 | +0·15 | −0·15 | +0·64 | +0·52 |
| 20 | +0·62 | −0·34 | +0·91 | +0·84 | −0·30 | +0·44 | +0·47 |
| 21 | +0·90 | −0·21 | +0·74 | +1·11 | −0·30 | +0·18 | +0·56 |
| 22 | +0·68 | +0·24 | +0·94 | +0·94 | +0·39 | +0·54 | +0·40 |
| 23 | +0·32 | +0·07 | +0·95 | +0·52 | −0·04 | +0·43 | +0·52 |
| 24 | +0·14 | +0·02 | +0·94 | +0·26 | +0·22 | +0·60 | +0·34 |
| 25 | +0·16 | −0·29 | +0·65 | +0·30 | −0·46 | +0·14 | +0·56 |
| 26 | +0·26 | −0·16 | +0·50 | +0·45 | −0·04 | +0·13 | +0·37 |
| 27 | +0·30 | −0·27 | +0·24 | +0·58 | −0·42 | −0·27 | +0·51 |
| 28 | −1·04 | −0·06 | −0·11 | −0·84 | +0·12 | −0·45 | +0·34 |
| 29 | −0·96 | −0·23 | −0·34 | −0·74 | −0·29 | −0·73 | +0·39 |
| 30 | +0·42 | −1·40 | −1·44 | +0·71 | −1·31 | −1·72 | +0·28 |
| 31 | +0·30 | −0·15 | −1·62 | +0·52 | −0·19 | −1·96 | +0·34 |
| 32 | +0·28 | −0·02 | −1·65 | +0·35 | +0·14 | −1·86 | +0·21 |
| 33 | +0·16 | −0·27 | −1·95 | +0·29 | −0·38 | −2·26 | +0·31 |
| 34 | +0·46 | −0·04 | −1·92 | +0·67 | −0·03 | −2·20 | +0·28 |
| 35 | +0·36 | −0·39 | −2·34 | +0·62 | −0·43 | −2·64 | +0·30 |
| 36 | +0·20 | +0·26 | −2·12 | +0·41 | +0·35 | −2·35 | +0·23 |
| 37 | +0·12 | −0·49 | −2·63 | +0·32 | −0·49 | −2·87 | +0·24 |
| 38 | +0·06 | +0·10 | −2·56 | +0·27 | +0·14 | −2·75 | +0·19 |
| 39 | +0·80 | −0·57 | −2·92 | +0·99 | −0·58 | −3·12 | +0·20 |
| 40 | +0·92 | +0·04 | −2·84 | +1·07 | +0·09 | −3·00 | +0·16 |
| 41 | +0·82 | +0·17 | −2·70 | +0·98 | +0·14 | −2·89 | +0·19 |
| 42 | +1·20 | +0·16 | −2·42 | +1·38 | +0·18 | −2·58 | +0·16 |
| 43 | +0·54 | +0·07 | −2·56 | +0·69 | +0·05 | −2·75 | +0·19 |
| 44 | +0·08 | +0·54 | −2·17 | +0·24 | +0·57 | −2·33 | +0·16 |
| 45 | +0·16 | −0·59 | −2·74 | +0·29 | −0·64 | −2·96 | +0·22 |
| 46 | +0·22 | +0·08 | −2·64 | +0·41 | +0·12 | −2·80 | +0·16 |
| 47 | +0·64 | −0·51 | −3·01 | +0·84 | −0·59 | −3·25 | +0·24 |
| 48 | +0·00 | +0·14 | −3·10 | +0·13 | +0·24 | −3·26 | +0·16 |
| 49 | −0·20 | −0·09 | −3·37 | −0·07 | −0·15 | −3·49 | +0·12 |
| 50 | −0·24 | −0·50 | −3·79 | −0·06 | −0·47 | −3·96 | +0·17 |

The following table gives the corrections found for the second half of the slide-box on the second occasion, December 20th, 1894.

TABLE III.—Calibration Corrections of Second half of Slide-Box.

| Reading of main dial. | Correction in ohms. | Reading of main dial. | Correction in ohms. | Reading of main dial. | Correction in ohms. | Reading of main dial. | Correction in ohms. | Reading of main dial. | Correction in ohms. |
|---|---|---|---|---|---|---|---|---|---|
| 50 | −3·96 | 60 | −4·58 | 70 | −3·13 | 80 | −1·33 | 90 | −0·92 |
| 51 | −4·42 | 61 | −4·68 | 71 | −3·32 | 81 | −1·21 | 91 | −0·96 |
| 52 | −4·57 | 62 | −4·07 | 72 | −3·19 | 82 | −1·11 | 92 | −0·45 |
| 53 | −5·09 | 63 | −4·04 | 73 | −3·03 | 83 | −1·24 | 93 | −0·70 |
| 54 | −4·88 | 64 | −3·69 | 74 | −3·03 | 84 | −1·38 | 94 | −0·63 |
| 55 | −5·15 | 65 | −3·60 | 75 | −2·47 | 85 | −1·70 | 95 | −0·82 |
| 56 | −5·26 | 66 | −3·62 | 76 | −2·16 | 86 | −1·83 | 96 | −0·94 |
| 57 | −5·31 | 67 | −3·68 | 77 | −1·92 | 87 | −1·64 | 97 | −0·22 |
| 58 | −5·19 | 68 | −3·45 | 78 | −1·61 | 88 | −1·71 | 98 | −0·23 |
| 59 | −5·23 | 69 | −3·51 | 79 | −1·64 | 89 | −1·24 | 99 | −0·06 |

In comparing the differences between the two calibrations given in the last column of Table II., it will be noticed that there is a cumulative divergence amounting to about half an ohm at the middle of the range. This is the kind of error to be expected in this method of calibration. It might be explained by the considerable difference in temperature of the box on the two occasions, but it is within the limits of error of the first series. The galvanometer was not sufficiently steady on that occasion, and the temperature rose nearly half a degree in the course of the observations. The observations serve, however, as a satisfactory verification of those of Series II.

It will be observed that the correction does not amount to so much as 1 part in 10,000 of the reading at any point of the slide-box, except quite near the beginning, a part which was never used in accurate comparisons. Also that the change of the correction in passing from one point to the next, never exceeds 1 part in 100,000 of the reading in the second half of the box, although the errors of two or three of the individual 1000-ohm coils exceeded 1 ohm. This is due to the levelling effect of the vernier.

It must be remembered that the corrections were never required beyond the nearest ohm, so that a difference of less than ·5 could be neglected.

It might be supposed that greater accuracy of calibration would have been attained by dividing up the box into subsidiary intervals of 10,000 ohms, and comparing each of these intervals with an auxiliary resistance, on the analogy of the method usually employed in the calibration of a mercury thermometer. I did not find, however, that any advantage was obtained by this procedure, and it is evident, on reflection, that the two cases are not precisely analogous. The advantage of employing longer columns in the case of a mercury thermometer is that the errors of estimation become of relatively less importance. It is practically possible to measure both the long and short columns to the same fraction of a degree, and an error of ·001° in a column of 20° is of much less relative importance than in a column of 2°. In the case of the resistance box, on the other hand, the relative accuracy of measurement is undoubtedly *greater* in the case of the smaller resistances. A 10,000-ohm coil cannot be measured with the same order of accuracy as one of 1000 ohms. This is partly due to difficulties of insulation in the winding of the coils themselves, and partly to the fact that wire finer than 2 or 3 millims. cannot be drawn and covered satisfactorily. As a consequence, high-resistance galvanometers are necessarily less efficient than low-resistance instruments of similar construction. The best high-resistance coils are constructed of a number of lower resistance coils in series, as in the Thomson-Varley slide-box, which permits a higher order of insulation than winding in a single coil.

## (B.) Resistance.

### (6.) *The Lorenz Apparatus.*

Although this apparatus was not actually applied to the direct determination of the resistances employed in this investigation, owing to delay in delivery, it was originally ordered with this object, and the preliminary experiments which were made by Professors Ayrton and Jones in testing the apparatus before it was sent out, are of so great value as bearing on the absolute value of the ohm that they cannot be passed over without mention. The null method of Lorenz, in which a resistance is directly determined in terms of the speed of rotation of a disc spinning in the field of a co-axial coil of known dimensions, is generally admitted to be the most accurate for the absolute measurement of resistance. The McGill College apparatus was constructed by Messrs. Nalder Bros. to my order, under the direct supervision of Professor Viriamu Jones, and embodied all the improvements introduced into the method by himself and by Lord Rayleigh. The most important new feature of the design was the winding of the coil on a heavy cylinder of marble, instead of metal as employed in Professor Jones' original apparatus. This material possesses the advantage of high insulating properties, great rigidity, and small thermal expansion. The employment of a marble cylinder made it possible to wind the coil with uncovered wire with the object of obtaining the most exact measurement of the dimensions, but on account of some difficulties of insulation, the original winding of bare wire was eventually replaced by one of silk-covered wire coated with paraffin and shellac varnish.

The results of the tests made by Professors Ayrton and Jones with this coil, at the laboratory of the Central Institution, during 1896 and 1897, have been published in the Reports of the British Association for 1897 and 1898, and in the 'Electrician.' They give a value for the Board of Trade standard ohm nearly 3 parts in 10,000 greater than $10^9$ C.G.S. units. This divergence might be explained as due to imperfect insulation if the precautions taken had not been so great, but it more probably represents the order of accuracy at present attainable in the absolute measurement of resistance by this or any other method. It is hardly possible that it could be entirely accounted for by errors of measurement of the diameter of the coil and the disc, although a discrepancy of 1 in 10,000 was actually found between the calculated and measured diameters of the coil ('B.A. Rep.,' 1897, p. 217), which points to some uncertainty in this direction.

At the time when I first examined the coil of the Lorenz apparatus, some time after its arrival in Montreal, while it was being set up, it seemed to me that the wire had worked a little loose on the marble, owing to some effect of the drying of the insulating tape and varnish, or to straining of the soft insulated wire due to contraction on exposure to cold. This would necessarily occur owing to the great difference in the coefficients of expansion of the wire and the marble, and the very small limits of elasticity of the soft annealed wire. Professor V. JONES himself, with whom I discussed the question in September, 1897, shortly after the arrival of the apparatus in Montreal, considered that the diameter could not be satisfactorily measured with a silk-covered wire, and strongly recommended the re-winding of the coil with bare wire. Accordingly, I procured for this purpose a sample of highly elastic silicium-bronze wire of high conductivity. I satisfied myself that the limits of elasticity of this wire would be ample, if it were wound on under suitable tension at a suitable temperature, to keep it perfectly tight on the marble cylinder for any range of temperature to which it was likely to be exposed. The tightness of the wire in practice is most important, from the point of view of insulation as well as from that of accurate measurement of the diameter. If the diameter of the wire is nearly equal (as it must necessarily be) to the pitch of the screw thread, a very slight defect in tightness or straightness will produce a short circuit. It is quite a difficult matter to wind a perfect coil of 200 turns of this size, unless the wire is highly elastic and quite free from kinks.

Owing to the great importance of securing perfect insulation, I proposed to adopt the method which I had already put in practice in the case of the electro-dynamometer, namely, to wind the coil in a double screw thread with two separate wires, in order to have a check on the perfection of the insulation, which could be applied at any time after the coil had been wound, or at any moment during the actual experiments.

In consequence of the delay caused by the failure of insulation of the first coil, the apparatus did not arrive in Montreal until the beginning of September, 1897. Some time was occupied in the course of the winter in building a suitable pier, and setting up the apparatus. But when I was about to commence observations, I received news of my appointment to the Chair of Physics at University College, London, which made it necessary for me to abandon the work.

### (7.) *Values of the Resistance Standards.*

The currents employed in this investigation were measured on the Thomson-Varley potentiometer by comparing the difference of potential on the terminals of a specially constructed resistance, called the Current-Standard, with that of a pair of hermetically sealed Clark cells. This current-standard consisted of a single 1-ohm coil, or of two 1-ohm coils in parallel, immersed in a well-stirred oil-bath. The resistance coils employed for this purpose in the earlier experiments were made of thick manganin wire of the best quality procured from Germany. The diameter of the wire was 1 millim., and the maximum current carried by each single wire was 2 amperes. The wire was not materially heated above the temperature of the oil, but, as no cooler was used in the earlier experiments, the temperature of the oil generally rose some 8 or 10° in the course of an hour. This was considered to be of no consequence with the manganin coils, as they had a temperature coefficient of only + ·000020 for rapid changes. On re-testing these coils after some months' work, it was found that their resistance had increased by two or three parts in 10,000, and that they continued to show small variations of this order. It was possible that these changes might have been due to the solder junctions, which would have explained certain anomalies observed in the earlier experimental results. It is equally likely, however, that they were caused by hysteresis in the wire as explained below.

Although the variations of the manganin coils did not exceed a few parts in 10,000, it was felt that they were quite inadmissible, as the potential readings were taken to 1 in 100,000. For this reason it was decided to make a pair of platinum-silver ohms wound on mica and annealed at a dull red heat *after winding*. These will be called the "Mica Current-Standards." They are fully described and illustrated by Dr. Barnes, p. 173. The method of construction was modelled on that of a platinum resistance thermometer, and had already been adopted for some years by the Instrument Company, Cambridge, for the manufacture of standard resistance coils. Standards constructed on this model possess great constancy, and their temperature can be determined with accuracy by immersion of the naked wire in an oil-bath. As compared with manganin coils, they have the disadvantage of a larger temperature coefficient, but the construction permits the determination of this coefficient with the greatest certainty, so that it is really no objection to their use for scientific purposes, for which constancy is the primary desideratum. The adoption of platinum-silver necessitated the addition to the oil-bath of a cooling coil of composition tubing, with a water circulation to keep the temperature steady.

For the determination of the variation of the specific heat of water, the absolute value of the current-standard was of no moment, but its constancy was of primary importance. It was also essential to be able to determine the temperature coefficient accurately, in order to reduce the observations at different temperatures in winter and summer to the same standard. This was determined under the actual conditions of observation with stirrer and cooler (BARNES, p. 174), by comparison with a manganin standard ohm, No. 4086, which was kept at a steady temperature. The value of the temperature coefficient of the mica current-standards is, therefore, independent of any assumption with regard to the temperature coefficients of the other standards employed. The low value ·000248 of the coefficient found is explained by the perfect annealing of the wire.

The absolute values of the mica current-standards were referred to the manganin standard No. 4086. The comparisons of this coil with the mica standards, which extended over two years, are given in Table IX. (BARNES), and do not show any relative changes of importance. The observations were taken on twelve different dates at temperatures varying from 15° to 21° C., the mean temperature of all the comparisons being 18°·36 C.

The temperature coefficient of the manganin standard No. 4086 was assumed to be ·000018 in the reduction of these observations. This value was determined by observing the change of resistance due to changes of temperature of the oil-bath in which the coil was immersed, the changes of temperature being effected at the rate of 10° C. in two or three hours. The results in Table IX. (BARNES) are reduced to a temperature of 20° C. If, however, we reduce the results to 18°·4 C., the mean temperature of the comparisons, we shall be independent of any assumption with regard to the temperature coefficients. We thus obtain the values :—

Mica current-standard, No. I. at 18°·27 = No. 4086 + ·00091 at 18°·4 C.
,, ,, ,, ,, II. ,, 18°·46 = ,, ,, − ·00035 ,, ,,
No. I. and No. II. in parallel at 18°·36 C. = Half No. 4086 + ·00014 . . (1).

The manganin standard No. 4086 had a Cambridge certificate No. 378 dated 1893, which stated its value to be ·99978 of a true ohm at 15·9° C. The preliminary results for the value of the calorie in terms of the electrical units, communicated to the British Association in September, 1899, were expressed in terms of this certificated value as correct. A comparison was subsequently made at McGill College of No. 4086 with a set of 10 platinum-silver standard ohms of the old pattern, the coils of which were embedded in paraffin wax. These 10 coils all possessed Cambridge certificates, and their relative values when tested agreed fairly with those obtained several years previously, showing no certain indication of change. The mean of the certificates of these 10 coils gives the value :—

Mean of 10 Pt-Ag standard ohms = ·99962 at 16°·5 C. . . . (2).

The details of the comparison of No. 4086 by Dr. BARNES* with 9 of these

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* The standard No. 3566 omitted by BARNES happens to be so near the mean of the 10 as to make no material difference in the result.

standards are given in Table VII. (BARNES). The mean of the results may be stated as follows :—

No. 4086 at 21°·74 C. = Mean of 10 Pt-Ag ohms − ·00054 at 21°·59 C. . (3).

The coils were also compared about the same time by Mr. FRASER at a lower temperature. The value of No. 4086 in terms of the mean deduced from this second comparison is :—

No. 4086 at 14°·8 C. = Mean of 10 Pt-Ag ohms + ·00153 at 13°·6 C. . (4).

The details of this comparison are given in Table VIII. (BARNES).

If the mean values of the 10 Pt-Ag ohms at 21°·6 and 13°·6 C., respectively, are deduced from the certificated value of the mean at 16°·5 C., adopting ·000254, the value taken by BARNES as the temperature coefficient, we obtain the following values for No. 4086 :—

No. 4086 at 21°·74 C. = 1·00037 ohms (from standards at 21°·6 C.) . (5).
,, ,, ,, 14°·8 C. = 1·00041 ,, ,, ,, 13°·6 C.) . (6).

These results are evidently inconsistent with the value + ·000018 for the temperature coefficient of No. 4086. The individual observations, however, are too consistent to admit of the supposition of an error of the order of two parts in 10,000 in the mean of the comparisons. It seems more likely that the value ·000254 assumed for the temperature coefficient of the Pt-Ag standards is too small. In any case, if we take the mean of the two comparisons, we shall obtain a result which is nearly independent of the value assumed for the temperature coefficient. We thus obtain :—

No. 4086 at 18°·4 C. = 1·00039 ohms (Pt-Ag standards at 17°·6 C.) . (7).

It happens that the temperature 18°·4 C. is precisely that at which the value of No. 4086 is required for the comparisons with the mica current-standards.

### (8.) *Comparisons at the National Physical Laboratory.*

It appeared practically certain from these comparisons that the value of No. 4086 had increased since the date of the original certificate by nearly ·00060 ohm. For further verification No. 4086 was sent over in a box from Montreal to Cambridge, and thence to Kew, to be compared with the original standards. Mr. GLAZEBROOK very kindly undertook the comparison himself, with the following results :—

VALUE of No. 4086 from Observations at the National Physical Laboratory.

| Date. | Temperature. | Value from 3715. | Temperature. | Value from "Flat."* |
|---|---|---|---|---|
| | ° | | ° | |
| July 20 . . . . . | 25·0 | 1·00067 | 24·9 | 1·00067 |
| " 26 . . . . . | 24·4 | 1·00072 | 24·4 | 1·00059 |
| " 28 . . . . . | 21·4 | 1·00063 | 21·3 | 1·00059 |
| " 28 . . . . . | 21·6 | 1·00062 | — | — |
| " 30 . . . . . | 18·9 | 1·00057 | — | — |
| August 1 . . . . . | 16·0 | 1·00045 | — | — |

These observations give a mean value of 1·00061 ohms at a temperature of 21°·96 C., and indicate a temperature coefficient of about ·000027 for changes taking place in a few days. This result is inconsistent with the value (5) 1·00037 at 21°·74 C. found by BARNES, unless we suppose the temperature-coefficient employed by BARNES for the Pt-Ag coils to be a little too small, or unless No. 4086 had *increased* in value on its journey from Canada. Mr. GLAZEBROOK was not perfectly satisfied with these observations, as the temperature was too high and variable, and the difference to be measured on the Pt-Ir bridge-wire, as well as the temperature correction of the standards, was rather large. He therefore repeated the observations in December, at a lower temperature, under much steadier conditions, with the following results:—

VALUE of No. 4086 from National Physical Laboratory Standards.

| Date. | Temperature. | Value from 3715. | Temperature. | Value from "Flat." |
|---|---|---|---|---|
| | ° | | ° | |
| December 13, 1900 . . | 12·1 | 1·00018 | 11·9 | 1·00020 |
| " 18 and 19 . | 13·2 | 1·00016 | 13·0 | 1·00018 |
| " 20 . . . . | 11·3 | 1·00016 | 11·5 | 1·00015 |
| " 21 . . . . | 12·1 | 1·00017 | 12·1 | 1·00015 |
| " 28 . . . . | 10·3 | 1·00010 | — | — |

The results of these observations give a mean value of 1·00016 at a temperature of 12°·0 C. This appeared inconsistent with the July observations. It was also much lower than the value (6) 1·00041 at 14°·8 found by FRASER, unless we suppose either that the coefficient ·000254 applied by BARNES to the platinum-silver coils was too small, or that No. 4086 had *fallen* in value in the interval.

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* "Flat" is one of the original B.A. unit standard coils belonging to the British Association, the temperature coefficient of which is taken to be ·000277, as determined by FLEMING in 1876. 1 ohm is assumed to be 1·01358 B.A. unit. No. 3715 is a more recent standard ohm.

In order to throw further light on the question, Mr. GLAZEBROOK undertook a determination of the temperature-coefficient of No. 4086 by heating it up to 20° C. and allowing it to cool slowly, the case being full of oil. Taking only the morning observations, which Mr. GLAZEBROOK considers the most reliable, we obtain the following mean results on the two days :—

TEMPERATURE-COEFFICIENT of No. 4086 at the National Physical Laboratory.

| Date. | Mean temperature. | Mean value from 3715. |
|---|---|---|
| January 4, 1901 . . | ° 17·2 | 1·00024 |
| " 5 " . . | 9·4 | 1·00005 |

These observations give a mean value of 1·00015 at 13°·3 C., which agrees very closely with the December comparisons, but is slightly lower, as though the diminution of resistance were still in progress. The value of the temperature-coefficient deduced is + ·000024, which is a very probable value for this kind of manganin for temperature changes of 10° in one day.

### (9.) *Hysteresis in Manganin Coils.*

From my own experience of the behaviour of manganin, I am inclined to explain these discrepancies as follows :—The temperature-coefficient of a manganin coil frequently depends to some extent on the past history and on the rate of heating or cooling. It may exhibit a kind of lag or hysteresis, the resistance continuing to increase gradually for some time after a rise of temperature, so that the value of the coefficient found by short-period observations is often smaller than the value which applies to changes of long period. Taking the July and December observations at the National Physical Laboratory as being correct, we find a long-period temperature-coefficient for No. 4086 of +·000047, which is about twice as large as the short-period coefficients ·000027 and ·000024, deduced from the observations from day to day. It was for this reason that I discontinued the use of manganin for accurate work in platinum thermometry some years ago, preferring to use platinum-silver coils annealed at a red heat and compensated for temperature by means of platinum similarly annealed. The defect is of a kind that would escape notice except in very accurate work over long periods with coils exposed to considerable changes of temperature. It also appears to depend on the manner in which the wire has been annealed.

It is worthy of notice, as a confirmation of this view, that a small effect of this nature was observed by HARKER and CHAPPUIS in their platinum thermometry

('Phil. Trans.,' A, 1900, vol. 194, p. 59), though they do not appear to have appreciated its full significance. In order to reduce the temperature correction, they selected a resistance box with manganin coils made by Messrs. CROMPTON in preference to one with platinum-silver coils annealed at a red heat after the pattern made by the Cambridge Instrument Company. In attempting to determine the temperature-coefficient of their box by raising the temperature for a short period, they noticed that the resistances did not return at once to their original values on cooling. They also observed a considerable increase of resistance in all the coils, which was most rapid at the outset, and which they attributed to the effect of recovery from the soldering. We have seen that No. 4086 underwent a similar increase of resistance at the outset. Messrs. HARKER and CHAPPUIS do not seem to have observed the long-period effect of hysteresis, which is more insidious. The correction for this cannot be accurately applied, but it appears that it might explain some of their errors of observation.

In order to reconcile the observations of BARNES and FRASER with each other and with those of GLAZEBROOK, it is necessary to suppose that the value of the temperature coefficient ·000254 assumed by BARNES for the McGill Pt-Ag standard ohms is a little too small. According to my own experiments with these particular standards, in 1893 and 1894, made by heating the coils in a water-bath, the value should be ·000275. I tested only two of the coils, but it is clear from the agreement of the relative differences observed by BARNES and FRASER that the temperature coefficients of all the coils are nearly the same. The changes in the relative differences observed by them are in no case greater than can be explained by the uncertainty of temperature, as the coils were not immersed in a water-bath in their comparisons.

Adopting the value ·000275 for the temperature coefficient of the 10 Pt-Ag standard ohms, we find the following corrected results in place of (5) and (6),

BARNES, No. 4086 at 21°·74 C. = 1·00048 ohms . . . . (8).
FRASER ,, ,, ,, 14°·8 C. = 1·00035 ohms . . . . (9).

The difference between these two values gives a temperature coefficient for No. 4086 of ·000020, which agrees with their other results supposing that FRASER's observations were taken in the basement within a few days of those of BARNES. In comparing these results with those of GLAZEBROOK, it must be remembered that owing to the solidity of the construction and the perfection of the heating arrangements in the Physics Building at McGill College, the temperature of the Heat Laboratory very rarely fell below 15° in winter (except in a few corners near the windows), or rose above 22° in summer. No. 4086 was never exposed at Montreal to so great changes of temperature as it experienced in the temporary observing room at Kew. The results of the comparisons as regards the absolute values of the current-standards at McGill College are, therefore, deserving of greater weight than might be supposed at first sight.

Taking the mean of the observations of BARNES and FRASER as fairly applying to the mean temperature of the Heat Laboratory at the time, we obtain

No. 4086 at 18°·4 C. = 1·00042 ohms in terms of ten McGill standards . (10).

Taking the long-period coefficient ·000047 as appropriate for deducing the value of No. 4086 at the same temperature, from GLAZEBROOK'S observations we find

No. 4086 at 18°·4 C. = 1·00046 ohms in terms of original B.A. standards (11).

This agreement is as close as could reasonably be expected, and we may conclude that the value of No. 4086 is known from the comparisons to at least 1 part in 20,000. Adopting the latter value for 4086, we obtain finally for the value of the mica current-standards,

Mica current-standards in parallel at 18°·36 C. = ·50037 ohm . . (12).

Assuming the temperature coefficient ·000248 for the mica current-standards, we find for the values at 5°, 10°, 15°, and 20°, respectively,

VALUES of Mica Current-standards in Parallel.

| Temp. Cent. . . . . . | 5° | 10° | 15° | 20° |
|---|---|---|---|---|
| Value . . . . . . . . | ·49871 | ·49933 | ·49995 | ·50057 |

These values are in practical agreement with those obtained by BARNES from the McGill comparisons alone, but he does not make any attempt to explain the apparent discrepancies. They are probably correct in terms of the International Standard Ohm to 1 part in 20,000, but the uncertainty of the absolute value of the International Ohm itself may amount to 2 or 3 parts in 10,000. If the Board of Trade Ohm really exceeds the C.G.S. Ohm by nearly 3 parts in 10,000, according to the result of the measurements of Professors JONES and AYRTON with the McGill College apparatus, the electrical watts supplied in the calorimeter have been over-estimated to that extent, so that the absolute value of the equivalent of the calorie in terms of electrical energy as deduced from this investigation would require to be reduced by about 1 part in 4,000.

It should be observed that the absolute values of the current-standards are of comparatively little importance for the present investigation, as they do not at all affect the question of the variation of the specific heat. I have thought it worth while, however, to discuss the question somewhat fully for two reasons. In the first place, the comparisons illustrate a possible objection to the use of manganin coils for accurate work, which is not I think sufficiently appreciated. In the second place, it is possible that at some future time the absolute values of the electrical standards may be more accurately determined, in which case it is desirable that the apparent discrepancies in the comparisons of the standards employed in the present investigation should be clearly explained, in order that the correction may be suitably applied.

The above explanation of the discrepancies observed in the comparisons of the manganin standard No. 4086, was submitted to Mr. GLAZEBROOK for his approval in January, 1901. He considered, however, that the measurements in his possession at that time were not conclusive evidence of hysteresis, as four other manganin coils of German make, which had been tested at the same time, had shown similar though not identical variations. He was himself inclined to explain these irregularities by uncertainties of temperature or of temperature-coefficient of the Pt-Ag standards, especially at the higher temperature in the July observations. The large value of the coefficient ·000047 for the manganin coil, deduced from the July and December observations, might be explained by supposing that the value of the coefficient assumed for the Pt-Ag coils was too large. This, however, would not explain the smaller values of the coefficient for the manganin coil deduced from the observations from day to day, in which the same value of the Pt-Ag coefficient was assumed.

In order to settle the question, a further series of comparisons of No. 4086 was made in June and July, 1901, at the National Physical Laboratory, which completely confirmed the observations made in the previous July, showing that they were not merely accidental results due to erratic change of No. 4086 or to uncertainty in the temperature conditions prevailing at that time in the observing room.

As a further test of the possibility of hysteresis theory already advanced, a special comparison was made, in which No. 4086 was heated through a small range of temperature and allowed to cool slowly, being tested against a *manganin* standard kept at a steady temperature throughout the comparison. This test gave a very small coefficient, but the curve representing the observations gave unmistakable indications of hysteresis. It was confirmed by a second test, in which No. 4086 was cooled, and allowed to warm up slowly. The curve representing the observations in this case had the opposite curvature. The two curves combined gave a figure similar to one of the familiar cycles of magnetic hysteresis. These effects could not be explained as due to a real lag of temperature, since the rate of change of temperature was very slow, and the case was filled with oil in direct contact with the wire and also with the thin metal tube on which the wire was wound. With this direct evidence of the existence of hysteresis over short periods and small ranges of temperature, it becomes easier to admit the possibility of larger variations of long period, such as those indicated by the July and December comparisons with the platinum-silver standards.

My assistant, Mr. EUMORFOPOULOS, is now engaged in testing the conditions of existence of the long-period effect, by a differential method designed for the purpose.

## (C.) CURRENT.

### (10.) *The Electrodynamometer.*

For the absolute measurement of the E.M.F. of the Clark cells employed in this investigation in terms of the standard ohm, I proposed to employ an electrodynamometer of the pattern constructed by LATIMER CLARK for the Electrical Committee of the British Association. This instrument is described and figured in MAXWELL'S "Electricity and Magnetism," vol. 2, p. 339. The moment of the couple due to the current is measured by means of a bifilar suspension, the constant of which is determined by observations of the time of oscillation. It has been usual of recent years to prefer the current-weighing method, in which the force due to the current is directly balanced by weights, to methods depending on the observation of an angular deflection; but it appeared to me that the British Association apparatus, with certain modifications of detail, would escape most of the errors generally urged against the deflection method, and that it possessed important advantages in other respects.

The electro-dynamometer in the possession of McGill College, as originally constructed by Messrs. NALDER, was intended to be an exact duplicate of the apparatus in the Cavendish Laboratory at Cambridge. The coils of the Cambridge apparatus were wound under the supervision of MAXWELL, whose measurements of the large coils were assumed by LORD RAYLEIGH in his determination of the electrochemical equivalent of silver. As a preliminary step, the apparatus was set up and tested in October, 1894, with the assistance of Mr. R. O. KING, then a fourth-year student. The defects of the electrodynamometer, in its original form, were found to be so serious that it was necessary to re-wind the coils, and make other extensive alterations. This involved considerable delay, while the necessary materials were being obtained and preparations made; and the apparatus was not set up in its final form until the return of Mr. KING from Harvard in September, 1897.

The principal defects of the original apparatus were found to be as follows:—(1) The framework of the large coils, and the pulley arrangement for equalising the tensions of the bifilar suspension were not sufficiently rigid. It was not possible to obtain the desired order of accuracy in the observation of the times of oscillation, or in the deflections. (2) The most serious defect was the uncertainty of the insulation between adjacent layers of the windings of the coils. This could not be directly tested, but was inferred from a comparison of the mean radii of the coils determined by electrical methods with the values calculated from the measurements. The difference could only be attributed to defective insulation, as the number of turns and the measurements were verified by unwinding the coils. The error amounted to nearly 1 part in 500 for the large coils (324 turns each), and about

1 in 300 for the small coils (576 turns each). The insulation between the coils and the metal frame-work was in all cases perfect, as the channels were lined with paraffined paper. The wire itself proved to be very carefully wound, and the double silk covering throughout was uninjured. The defects could not be attributed to excessive damp, as the winter climate of Montreal is extremely dry, and the laboratory was most efficiently heated. Having regard to the perfect condition of the wire, it seemed unlikely that absolute security of insulation could be attained with silk-covered wire, however carefully wound.

Owing to the extreme importance of securing perfect insulation, and of being able to test the insulation at any time, the small pair of coils were immediately re-wound with a double winding of two wires side by side throughout, with paper between each layer. They were then boiled in paraffin wax, and the insulation has since proved to be practically perfect. At the same time it was decided to re-wind the large coils with a double-winding of copper tape, of the same width as the channel, insulated with paraffined paper or silk between the layers. But as there was some delay in securing the requisite material, the experiment had to be postponed for the time. I took advantage of this delay to work out the details of the following improvements, which were introduced into the method on resuming the work in October, 1897, with Mr. KING's assistance.

### (11.) *Duplex Scale Reading.*

For greater accuracy in observing the deflections and measuring the scale distance, which is generally one of the weakest points in a deflection method, a duplex system of reading was adopted. The apparatus was erected on a suitable pier, which had been provided for it in a basement room, with copper fittings and heaters, where the temperature was very steady and the ground free from vibration. A plane parallel mirror, $\frac{1}{8}$ inch thick, and 2 inches in diameter, silvered on *both* faces, was fitted to the suspended coils. A pair of metre scales, accurately divided on plane milk-glass, were mounted with suitable adjustments on a rigid frame of copper tubes at a distance of 3 metres apart, 150 centims. east and west of the mirror respectively. A circulation of water was maintained through the copper tubes. The distance between the scales and the thickness of the mirror could be measured with great accuracy. The deflections were observed simultaneously from either side with a pair of very perfect reading telescopes of 2 inches aperture, and about 2 feet long. These were fitted with filar micrometers, and adjusted so that one turn of the micrometer screw was very nearly equal to 1 millim. on the scale. The mirror and telescopes were specially made by BRASHEAR for this work. The coils and suspension were completely enclosed to screen them from draughts, and observations were taken through a pair of thin mica windows. With this arrangement, it was optically possible to read with certainty to a fiftieth of a millimetre on a steady deflection of 50 centims. on either side of the zero. This method of reading eliminates a number of small uncertainties, and makes it possible to approach an order of accuracy of 1 part in 100,000 in the deflection measurements.

### (12.) *The Bifilar Suspension.*

In order to minimise the effect of imperfect elasticity, the wires of the suspension were made of hard drawn copper of high conductivity, as fine as was consistent with constancy of length (safety factor 5), and were rigidly clamped at a distance of 3·2 centims. apart, after the tensions had been adjusted to equality. The length of the suspension was 80 centims., and the effect of torsion of the wires was comparatively small. The directive force of the bifilar depended almost entirely on gravity, and remained constant to 1 in 20,000 for several months. The effect of current heating of the suspension was tested by observing the time of oscillation with the working current of ·5 ampere flowing in opposite directions in the two windings of the small coils, and was found to be less than 1 part in 20,000.

To determine the moment of inertia, the small coils were fitted with a co-axial brass tube about 2·5 centims. in diameter, and 50 centims. long, containing a pair of cylindrical inertia weights, 150 grammes each, which could be clamped at the centre of the tube, or at the ends. The distance between the weights in their extreme position is the most important measurement. This was determined by a very accurate pair of steel callipers by Brown and Sharpe, reading to ·01 millim., with a range of 50 centims. This gave sufficient accuracy for the preliminary measurements, but it was intended to employ a Whitworth measuring machine for the final series. In observing the oscillations, the times of passage were recorded on an electric chronograph with a standard clock rated from the observatory. The periods o oscillation, with the ends of the weights flush with the ends of the tube, and with the weights in contact at the centre of the tube, were 11·5385 and 6·7857 seconds respectively, and the observations on different days, when corrected for temperature, did not vary by more than two or three in the last figure.

### (13.) *Mean Radius of the Large Coils.*

The mean radius of the pair of large coils was determined from the length of the copper tape with which they were wound. This method is not satisfactory with soft annealed copper wire owing to stretching, but the hard rolled copper tape could be wound without any tension, and did not undergo any change of length. This was verified by graduating the tape itself on a 50-foot comparator, the errors of which were known; then winding the coil for trial, and unwinding and measuring the tape again, which was found not to have changed in length by more than a tenth of a millimetre in each 50 feet. The tape was supported horizontally on the polished surface of the comparator, and measured under a tension of 6 kilogs. Young's modulus was determined for each section. The tape was wound on each coil in two lengths of 19 turns each, starting at opposite ends of a diameter, with two thicknesses of paraffined paper between each turn, so that the insulation could be tested with absolute certainty at any time. There were 38 complete turns, and nearly 6000 centims. of tape, on each coil. The probable error of the measurement was less than 1 millim. on the whole length, *i.e.*, less than 1 part in 100,000. The coils could not be boiled in paraffin after winding, as this would subject the tape to uncertain strains owing to the contraction of the wax. It was found necessary to re-wind the coils two or three times with minor improvements before the insulation proved to be perfect. Finally, silk ribbon was adopted in place of paper.

### (14.) *Distance between Mean Planes of Large Coils.*

The coils were fitted to the frame at a distance between their mean planes equal to the mean radius of either coil. For this purpose, the original frame, which was insufficiently rigid, was strengthened with heavy rings of brass turned to fit the coils, and carefully tested for non-magnetic quality. The distance between the mean planes, though four times less important than the mean radius, must be known with considerable accuracy. This was effected by making the coils reversible and measuring their thickness. Each coil when in position rested against the points ot three screws, which were adjusted to the right distance apart, and clamped in position. The distances between the points of opposite screws were measured with the callipers, and also the thickness of the coils themselves at the points of contact. The coils were connected to their respective terminals by eight pairs of flexible conductors, twisted together in pairs so as accurately to compensate, and arranged so that the coils could be rapidly removed, reversed and replaced at any moment. This appears to be the only satisfactory method of determining the distance between the mean planes, as the winding of the coils and the distribution of the current in the tape cannot be assumed to be perfectly symmetrical with respect to the channels.

### (15.) *Area of the Small Coils.*

The most difficult part of the work was the determination of the area of the small coils by comparison with the large coils. A thick brass tube, carrying a delicately suspended magnet and mirror at its centre, was rigidly fixed to the framework so as to be co-axial with the large coils. The small coils could be mounted co-axially on this tube at a mean distance of 30 centims. on either side of the centre. Currents were passed in opposite directions through the large coils and small coils in parallel, and the resistances of the circuits were adjusted until the magnetometer showed no deflection. The ratio of the resistances was then immediately determined in a manner similar to that employed by Lord RAYLEIGH in measuring the mean radius of the small coil in his current balance. The chief difficulties were due to change of resistance of the coils with change of temperature. These changes were considerably reduced by employing copper resistances for the adjustment, and by arranging the details so as to secure the greatest rapidity of observation. Readings were taken in each position with the large and small coils severally reversed, and interchanged, and replaced, the complete series each night including 36 independent readings of the ratio. The distance between the two positions of the small coils on either side of the centre is the most important measurement. This was determined by two shoulders turned on the thick brass tube, the distance between which was measured with the callipers. It was necessary to make all these comparisons at night between the hours of 2 and 5 A.M. in order to avoid disturbance from the electrical railway, two lines of which passed within about a quarter of a mile of the building. The values of the ratio obtained from observations on three different nights, when there was no magnetic disturbance and the conditions were otherwise satisfactory, showed extreme differences, amounting to nearly 1 part in 5,000. These may have been partly due to temperature, as the small coils had been boiled in paraffin, which must have affected the expansion.

### (16.) *Ratio of the Currents in the Coils.*

In the usual method of employing the electrodynamometer, the same current is passed through the large coils and small coils in series. This method has the advantage of simplicity, but it is essential, in order to obtain steady deflections and secure the maximum accuracy of reading, that there should be no appreciable heating of the small coils by the current. The latter condition, however, cannot be satisfied if the currents are equal, unless the large coils are wound with very fine wire, which is for many reasons objectionable. In the present case, the windings were designed to secure approximately equal current heating when the currents are in the ratio of 1 to 10 in the small and large coils respectively. The ratio of the currents was adjusted to this value at each observation by having a standard ohm in series with the small coils, and a standard tenth-ohm in series with the large coils. The whole arrangement formed a Wheatstone bridge, the balance of which was adjusted by means of some copper coils and a high-resistance shunt in series with the small coils. The standard coils were of manganin immersed in oil, and the ratio remained extremely constant, owing to the equality and smallness of the current heating, and the perfection of the insulation. Thus, although the division of the current involved an additional adjustment of the ratio of the resistances, no appreciable error was thereby introduced, and great advantages were secured by the equable distribution of the heat developed, and the steadiness of the observed deflections.

### (17.) *Electromotive Force of the Clark Cells.*

The electromotive force of the Clark cells was determined by simultaneous observations with the potentiometer of the difference of potential on either of the standard manganin resistances while the currents were being measured by the electrodynamometer. This observation depended to some extent on the accuracy of calibration of the potentiometer, but this was repeatedly tested with results consistent to 1 part in 50,000. Owing to the great steadiness of the current, there being no silver voltameter in circuit, the potentiometer readings could easily be taken to this order of accuracy. The Clark cells were of the hermetically sealed type described in the 'Proceedings of the Royal Society' for October, 1897, and were kept in a well-stirred water-bath at a constant temperature.

The results of the first series of observations on the absolute value of the E.M.F. of the Clark cell in terms of the ohm, taken with this apparatus during the spring and summer of 1898, were sent in by Mr. R. O. KING as the report of his third year's work as 1851 Exhibition Scholar. When certain minor corrections are applied for the values of the resistance coils and for the higher harmonics in the series representing the force between the fixed and suspended coils, the result found for the E.M.F. of the Clark cell at 15° C is,

$$\text{Clark cell} = 1{\cdot}4334 \text{ volts},$$

the volt being defined as the potential difference due to a current of one-tenth of a C.G.S. unit through a standard ohm. This result was not immediately published, because Mr. KING hoped to be able to secure an order of agreement higher than 1 part in 10,000 in the comparison of the small coils with the large coils, which was much the most difficult part of the measurements. But it may be questioned whether a higher order of accuracy could reasonably be expected in this determination, and although the value above given was not at the time intended to be final, I feel that it may be regarded with considerable confidence on account of the high order of accuracy of the individual measurements, and the many new devices which were introduced into the design of the apparatus.

The work of setting up the apparatus and taking the observations was performed almost exclusively by Mr. KING under my supervision, with occasional assistance from other students in taking readings. I was able to assist him personally during the vacations in some of the more important measurements, such as the graduation of the copper tape on the comparator, the first winding of the large coils, and the first comparison of the small coils. I also verified the accuracy of most of the adjustments, and the perfection of the insulation, and am satisfied that the whole work was most carefully and systematically carried out. Mr. KING has since left McGill College, but I hope that he may yet find time to work out and publish in detail the final results of his observations, which should form a valuable contribution to absolute electrical measurement. It should be noticed that the result above deduced from the first series of observations by Mr. KING agrees with that deduced from the observations with the electrical calorimeter by comparison with ROWLAND and with REYNOLDS and MOORBY, namely, 1·4332, within the limits of probable error of the several methods.*

## PART III.—THERMOMETRY.

### (18.) *The Compensated Resistance Box.*

Nearly all the temperature measurements in this investigation were made with a special form of resistance box, which contains some devices which have not as yet been adopted in any other instrument of its class, or described in any scientific periodical. The most important feature in its construction was the system adopted for compensating the resistances to eliminate the effect of change of temperature. In the usual form of box the temperature of the coils is taken by means of a mercury thermometer, and the correction for change of temperature applied from a knowledge of the temperature-coefficient. The principal objection to this method is that the mercury thermometer cannot follow the temperature changes of the coils with sufficient exactness, and that the temperature is generally far from uniform throughout the box. In the method of compensation which I patented in 1887 (Complete Specification No. 14,509) the temperature correction is automatically eliminated by combining with each of the resistance coils proper, which are made of platinum-silver or some other alloy possessing a small temperature-coefficient, a compensating coil of copper or platinum having a large coefficient. The resistance of the compensating coil is adjusted so that its change of resistance per degree is equal to that of the coil it is intended to compensate, while its actual resistance at any temperature is much smaller, the ratio of the resistances being inversely as the temperature-coefficients. Each compensator is placed in the box in close proximity to the coil it is intended to compensate, so as to be always at the same temperature, but coil and compensator are connected on opposite sides of the bridge-wire, so that the balance depends only on their difference, which remains constant for any change of temperature, provided that the adjustment has been properly effected. The advantage of the method lies in the fact that this adjustment can be made with extreme accuracy, by testing coil and compensator together over the required range of temperature before they are connected in their places in the box. But the method has not come into general use, partly on account of the labour involved in the adjustment of the coils, and also in part owing to the discovery shortly afterwards of manganin and other alloys of small temperature-coefficient, which are fairly satisfactory for ordinary work though inferior, in my opinion, to the compensation method for work of precision The objections to manganin, for instance, are—(1) That it cannot be perfectly

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* The details of the construction and comparison of the Clark and cadmium cells employed are sufficiently described in the 'Proc. Roy. Soc.,' 1897, vol. 62, p. 117, and by Dr. BARNES, Section 3A, p. 159.

annealed after winding, and that its resistance is consequently liable to change for some time. (2) That the temperature-coefficients of different specimens are often different, and vary for different sizes according to the method of annealing, so that it is desirable to test the temperature-coefficient of each coil in the box, and to apply the corrections separately in the most accurate work. (3) That the temperature correction cannot be satisfactorily applied, as there is generally some hysteresis in the change of resistance with temperature, and the values of the resistances depend to some extent on previously existing conditions of temperature. (4) That it cannot be hard soldered without burning, and that soft solder connections to manganin are frequently found to be defective, unless they have been most carefully made. (5) That it is liable to corrosion if exposed to damp or gas fumes, although the usual coating of shellac is sufficient protection in most cases. These defects have been noted by other observers, notably by HARKER and CHAPPUIS, who employed a box with manganin coils in their recent comparison of the platinum and gas-thermometers The majority of other alloys of this class are inferior to manganin in constancy; they are also frequently objectionable (*e.g.*, "constantan") on account of their great thermoelectric power, which produces inconvenient disturbances if the temperature of the box is not uniform. The advantage of platinum-silver lies in the perfection with which it may be annealed, and in the absence of lag or change when properly annealed.

If *uncompensated* coils of platinum-silver are used, it is necessary to keep them in an oil-bath to secure sufficient certainty of temperature. It is also desirable to employ a thermostat for regulating the temperature of the oil-bath, and a stirrer for keeping the temperature uniform throughout. This adds considerably to the cumbersomeness and expense of the apparatus, and to the difficulty of using it. It is really simpler in the end to use compensated coils, as the individual temperature-coefficients of the coils must otherwise be determined and corrected separately, at least for work of the highest accuracy.

The first apparatus constructed on this principle was made in 1887, shortly before applying for the patent, and was figured in the specification. All the parts of this apparatus were made interchangeable in pairs, by an extension of the CAREY-FOSTER principle, with a view to facilitate testing and calibration. There were two exactly similar bridge-wires, each a metre long, and three pairs of compensated coils, which could be inserted singly or in series, with resistances on the binary scale equal to 1, 2, and 4 times that of either bridge-wire. The platinum-thermometers were also made in pairs, after the pattern described and figured in the 'Phil. Trans.,' A, 1890, but were generally contained in separate tubes, which greatly facilitated construction, and permitted them to be used differentially by a simple change in the connections of the bridge. In the instrument used for the boiling-point of sulphur (*loc. cit.*) it was necessary to have both thermometers in the same tube. This construction was also adopted in 1887 for comparison coils in which it was necessary that both wires should be accurately at the same mean temperature. The necessary changes of connection were effected by means of mercury cups and thick copper connectors, similar to those employed for standard resistance coils. The mercury cups were made by boring suitable holes in a flat plate of ebonite, to the under side of which thick copper plates were screwed, the joint being made mercury tight with a thin sheet of rubber.

The apparatus above referred to was first used for some determinations of the linear expansion of standard yards at the Standards' Office in 1887. It was subsequently employed by Dr. A. S. LEA, F.R.S., and Dr. W. H. GASKELL, F.R.S., and later by Dr. ROLLESTON, in some physiological experiments on the heat produced in muscle and nerve by electrical and other stimuli. For this purpose a very delicate pair of differential thermometers were constructed of ·001-inch wire wound on mica, weighing a few milligrammes each, and sensitive to the ten-thousandth of a degree C. One of these thermometers was described and figured in the specification (No. 14,509, 1887). This apparatus is still in the possession of the Physiological Laboratory, Cambridge.

The chief defect of the original form of apparatus was the uncertainty of the temperature correction of the platinum-silver bridge-wire owing to its length. In making a new form of apparatus in October, 1890, bridge-wires of manganin were employed, annealed at a red heat in coal gas. The pair of bridge-wires could be very accurately calibrated throughout their length by the Carey-Foster method, but owing to the trouble of determining and applying the bridge-wire correction, it was eventually decided to use a bridge-wire of low resistance in conjunction with a larger number of resistance coils. It also proved to be unnecessary in practice to make all the coils interchangeable in pairs, provided that the ratio coils were tested for equality of temperature-coefficient. In this case, it was sufficient to calibrate the bridge-wire and resistances by a method of substitution, which was much simpler than the Carey-Foster method. Apparatus constructed on this principle was described in the 'Phil. Mag.,' July, 1891, and figured in the patent specification (No. 5342, 1891). As the resistance coils were no longer required to be interchanged, they were permanently connected to the copper plates in a single box instead of being connected to copper rods in separate boxes like standard coils. The mercury cups, however, were still retained, in preference to plugs for short circuiting the resistance coils in accurate work, and were constructed precisely as originally described. The simplification consisted in connecting the resistance coils permanently in series, and using simple bridges of thick copper connected in pairs for short-circuiting each resistance coil and its compensator simultaneously.

The particular resistance box employed in this investigation is shown in the accompanying fig. 2. It was made to my designs by the Instrument Company, Cambridge, at the beginning of 1893, but I had personally to undertake the delicate work of compensating and adjusting the resistance coils. It contained 9 resistance coils, A, B, C, D, &c., on the binary scale, ranging from 2560 to 10 units, constructed of platinum-silver annealed at a red heat, and compensated with similarly annealed platinum. The box measured 15″ × 6·5″ × 3·5″. The bridge-wire was of platinum-silver, nearly 34 centims. long, but only 5 centims. on either side of the middle were actually used in the measurements. The scale was of brass, divided by Troughton and Simms to half millimetres, with a vernier reading to a hundredth of a millimetre. To secure this order of accuracy in the readings, the contact piece, consisting of a short length of the same platinum-silver wire with a nearly sharp edge, was rigidly fixed to the sliding piece carrying the vernier. The bridge-wire was stretched at such a height as to clear the contact edge by about ·01 inch, and contact was effected by pressing down the bridge-wire on to the contact wire by means of an india-rubber finger. This finger was provided with a screw adjustment, so that the contact could be set and held at any desired point. To keep the tension of the bridge-wire constant, which is most important in accurate work, the wire was stretched between parallel bars of brass and iron in an intermediate position corresponding approximately to its coefficient of expansion. Connection was made to the galvanometer through a similar wire stretched parallel to the bridge-wire, in order to eliminate thermal effects at the sliding contact. All the connecting wires throughout the box were accurately paired and compensated, and the thermometer connections were made by means of mercury cups at PP′ CC′. Screw terminals were used in the galvanometer and battery circuits only, where changes of resistance are immaterial. The ratio coils were adjusted to equality by the method of interchanging, and were tested and compensated for equality of temperature-coefficient before being fixed in their places in the box. They were *not* wound up together, as is usual in apparatus of this class, but were merely fixed side by side, as it is most important to secure the most perfect insulation of the ratio coils for delicate differential work.

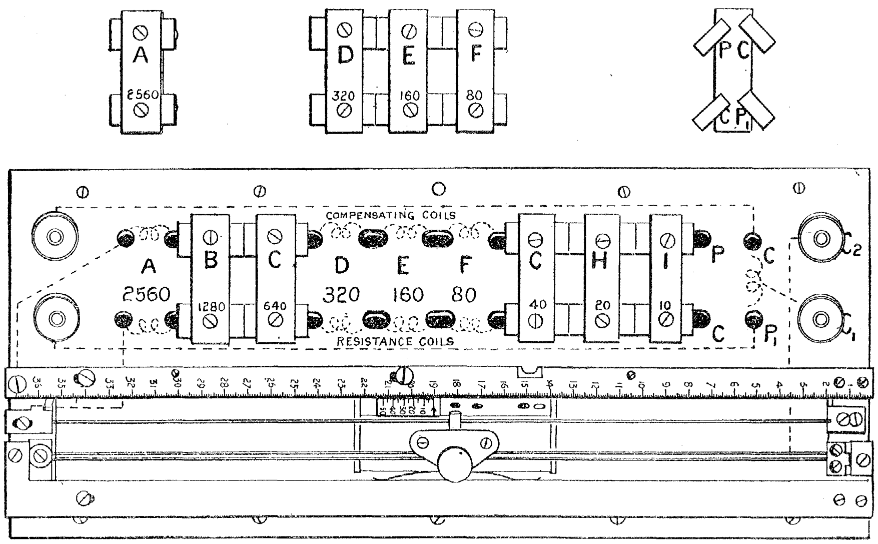

Fig. 2. Compensated Resistance Box.

The box was originally intended for working chiefly with thermometers of pure platinum having a zero resistance equal to the largest coil, *i.e.*, 2560 box-units, and a fundamental interval of 1000 box-units, or nearly 10 ohms. This gave a very convenient scale of 10 centims. of the bridge-wire to the degree, and made it possible to take readings to the ten-thousandth part of a degree. Thermometers of double the resistance, having a scale of 20 centims. to the degree, were employed for some differential work, *e.g.*, for demonstrating the lowering of the melting point of ice due to one atmosphere of pressure (·0075° C.) at the May Soirée of the Royal Society in 1893, where this box was first exhibited. But for ordinary temperature measurements, unless the insulation were extremely perfect, it was found that very little could be gained in point of accuracy by going beyond 10 ohms for the fundamental interval. For the boiling-point of sulphur, a fundamental interval of 5 ohms was found to be preferable; and 1 or 2 ohms for higher temperatures where the insulation was necessarily less perfect and the conditions less steady. As the portion of the bridge-wire actually utilised never exceeded 5 centims., and averaged only 2·5 centims., or $\frac{1}{4}$ of a degree, it was seldom necessary to take any account of the calibration correction of the bridge-wire, the errors of which proved to be less than one part in 500, or one two-thousandth part of a degree, without correction. In the best mercury thermometers it is unusual to calibrate closer than 2° intervals, and the corrections are necessarily uncertain to two or three thousandths, even if the interpolation formulæ can be trusted to one part in a thousand, which is very doubtful. It is easy to see how great is the advantage of the platinum-thermometer in point of ease and accuracy of calibration.

The comparison of the 9 coils of the resistance box, which were arranged on the binary scale, could be carried out and the relative values calculated in less than an hour. The peculiar advantages of the binary scale for this purpose are frequently misunderstood or misrepresented. The most important of these advantages are: (1) That a given resistance can be represented only by one particular combination of coils, so that there can never be any doubt as to which combination was employed for any given reading; (2) That the least possible number of separate coils are required, and that the complete calibration requires the least possible number of readings, and can be effected in the least possible time. It is often urged as an advantage of less simple and symmetrical arrangements, that each resistance can be made up in a great variety of ways, which act as checks in case of doubt; and that the relative values of the coils can be compared in a number of different combinations, so that several equations can be obtained for evaluating each resistance. This is, no doubt, an advantage in cases where the accuracy of calibration depends on micrometric *estimation*, as in calibrating a mercury-thermometer. But, if a good galvanometer is available, the accuracy of comparison of resistances is not limited in this way. We may, therefore, fairly consider the disadvantage of the excessive expenditure of time in the observations and calculations; moreover, the risk of error due to changes of condition or temperature, which is the really important point to be considered in work of this kind, is increased by the greater complexity and want of symmetry of the system of comparison. Examples of the calibration of this box on the binary method are given by BARNES, p. 187.

### (19.) *Heating of the Thermometers by the Measuring Current.*

It is generally assumed in the construction and use of apparatus for comparing standard resistance coils, that the conditions of greatest sensitiveness are obtained when the resistance of the ratio arms is equal to that of the resistances to be compared. This, however, is certainly not the case in platinum-thermometry, and seldom in other cases, unless the heating of the resistances by the measuring current can be safely neglected. In platinum-thermometry the heating of the thermometer by the current is the limiting consideration which determines the amount of power available for the test. For a given rise of temperature with a given thermometer the current must not exceed a certain value, *e.g.*, about a hundredth of an ampere for a rise of temperature of a hundredth of a degree, with an average platinum-thermometer of ·006″ wire ('Phil. Trans.,' A, 1887, p. 184). With this limiting condition it is easy to see (1) that if the ratio coils are in parallel with the thermometer, the sensitiveness is doubled by making the ratio coils very small; (2) that if the ratio coils are in series with the thermometer, the sensitiveness is doubled by making the ratio coils as large as possible. In every case it is necessary, in order to secure accurate compensation for the variation of the leads, that the ratio coils should be equal, and that the bridge-wire should be inserted in the circuit between the thermometer and the adjustable balancing coils. The arrangement (2) with the ratio coils in series with the thermometer, involves leading the battery current in through the bridge-wire sliding contact, which is generally unadvisable on account of possible disturbance produced by variation of resistance at the contact, or by breaking the circuit to readjust. The first arrangement is therefore generally adopted, and some advantage is gained in this case by making the resistance of the ratio coils considerably *smaller* than that of the thermometers, provided that they are not made so small as to be appreciably heated when the working current is passed through the thermometer. In this particular box the ratio coils had a resistance of 6·4 ohms, or about a quarter of the normal thermometer at 0° C. They were each constructed of two ·008″ platinum-silver wires in parallel, and adjusted for equality of temperature-coefficient. With a working current of ·002 ampere through a 25·6 ohm. thermometer constructed of ·004″ wire, the heating effect in the thermometer would be nearly a thousandth of a degree, and the current through the ratio coils would be nearly one-hundredth of an ampere, which would not produce any material rise of temperature.

In differential work it is seldom necessary to take any account of current heating of the thermometers, unless the difference of temperature is considerable, or the thermometers are very differently situated. With a single thermometer, it is desirable to measure the heating effect occasionally, especially if a galvanometer of suitable sensibility is not available, or an excessive current is employed for any other reason. The simplest method of determining the rise of temperature due to the current in any case is to use two similar cells of low resistance, preferably storage cells, which can be connected in series or parallel by changing a switch. The normal measurements are effected with the cells in parallel. On putting the cells in series, the current through the thermometer is very nearly doubled, and the heating effect is nearly quadrupled, provided that it is small. The correction for current heating is obtained by subtracting from the first reading one-third of the difference between the two readings. I have used this method in all accurate work for the last ten years, and it appears to be worth recording, as there is some conflict of opinion with regard to the proper method of procedure. Harker and Chappuis measured the heating effect of the current on one of their thermometers at 0° C., and, assuming that the effect would vary as the watts expended on the coil, they adjusted the external resistance in the battery circuit so as to give always *the same watts* in the coil at different temperatures. This is not quite correct, since the cooling effect of conduction and convection-currents of air in the tube increases nearly in proportion to the absolute temperature. The effect of radiation also becomes important at high temperatures, and the cooling is then more rapid. If, therefore, the watts are kept constant, the heating effect will diminish as the temperature rises, and a small systematic error will be produced. Assuming that the rate of cooling increases as the absolute temperature $\theta$, and that the watts are kept constant, the heating effect at any temperature $\theta$ is $273h/\theta$, where $h$ is the heating effect in degrees of temperature at 0° C. It is easy to see that the corresponding systematic error in the temperature $t$ on the centigrade scale, would be approximately $ht(t-100)/373(t+273)$. In the case described by Harker and Chappuis ('Phil. Trans.,' A, 1900, p. 62), the heating at 0° C. was ·014° C. The systematic error at 50° C. would be only ·0003°, and at 445° C. only ·008°.

A better rule is to keep the *current* through the thermometer constant. In this case the heating effect is nearly constant, since the resistance of the thermometer increases very nearly as fast as the rate of cooling, *i.e.*, a little faster than the absolute temperature. In this case it is evident that the error would be negligible, even if the heating effect at 0° C. were as large as a hundredth of a degree. In any case, provided that a galvanometer of suitable sensibility is used, the error due to the heating effect will be practically negligible, even if no account is taken of it, *i.e.*, if the resistance in the external battery circuit is kept constant. It is assumed, of course, that the current is kept flowing through the thermometer continuously, so that the heating effect is steady. Some writers have advised keeping the circuit closed for the shortest possible time. This method should never be used in accurate work. Other writers have apparently found more serious difficulties, and appear to have considered that the heating effect was fatal to accurate work. This view has arisen merely from the use of unsuitable apparatus or faulty arrangements.

### (20.) *Ice-point Apparatus.*

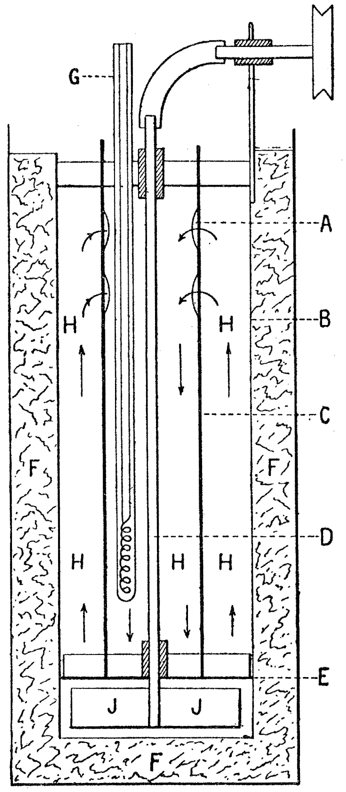

Fig. 3. Ice-point Apparatus.

A, gauze-covered apertures; B, outer vessel; C, inner vessel; D, shaft of stirrer; E, gauze strainer; F, lagging; G, thermometer; H, ice; J, stirrer blades.

In accurate work the heating effect should never exceed a hundredth of a degree, and the correction can be readily applied if required, in case the current through the thermometer is not kept constant. It is possible, however, to obtain consistent results, even if the heating effect amounts to several tenths of a degree, provided that the conditions are steady, and that the heat generated is not allowed to accumulate. This condition is generally satisfied in a bath of saturated steam or vapour, or in a well-stirred bath of liquid, but not at the freezing or melting point of a bad conductor. Errors due to variation of the heating effect are most common in observing the ice-point. The density of the water at this point is nearly constant, so that the convection currents are feeble, and the thermometer, if the current is excessive, or if there is considerable conduction of heat along the stem, as in the case of thick porcelain tubes, may become surrounded by a layer of water at a temperature appreciably above the freezing-point. Some advantage is gained in this case by employing a stirrer to make the water circulate vigorously through the ice. For this purpose I devised the following apparatus, which proved very useful for investigating the heating effects of large currents at the freezing-point, where accurate results could not be obtained by merely surrounding the thermometer with ice. The apparatus consists of two concentric cylindrical vessels. The thermometers are placed in the inner vessel. The whole apparatus is filled with melting ice, with enough water from previously melted ice to fill up the interspaces. The bottom and top of the inner vessel are fitted with gauze strainers to prevent circulation of the ice. The water is caused to circulate through the ice by means of a centrifugal stirrer below the middle of the inner vessel, worked by a shaft passing up through the centre of the apparatus. The thermometers should be deeply immersed, if they have thick tubes, or copper or silver leads, in order to minimise the effect of conduction along the stem. It is probable that a similar method would give the most accurate results in all cases, but if the current heating is small its variation may generally be neglected, so that no special apparatus is required.

### (21.) *Insulation of Thermometers.*

Defective insulation due to moisture condensed in the tubes is sometimes a source of error in accurate work at the ice-point with thermometers of high resistance, if the tubes are not sealed. To avoid this, the instruments may be fitted with a small inner tube leading to the bottom, through which dry air may be forced occasionally. A better plan, which I first adopted in 1893, for accurate work at low temperatures, is to seal the platinum leads through the glass so that the whole thermometer is air-tight. In this case the platinum leads may conveniently terminate in glass cups, and may be connected to the external leads by mercury or by fusible alloy,* as indicated in fig. 4. If the tubes are made of lead-glass, there is no difficulty in fusing the four leads through the tube. The joint will even stand sudden exposure to high-pressure steam without cracking, if properly annealed. All the thermometers employed in my experiments on the temperatures of steam in the cylinder of a steam-engine ('Proc. Inst. C.E.,' November, 1897), were made in this manner in order to make the joint perfectly steam-tight at high pressures. The method cannot be applied to porcelain tube pyrometers, but in this case the employment of a high resistance is out of the question for other reasons. I recommended hermetic sealing for the Kew thermometers ('Nature,' October, 1895), but it was not adopted, as the instruments were of low resistance, intended primarily for high temperature work. With such an instrument it is easy, as the recent report of the Kew Observatory shows ('Proc. Roy. Soc.,' November, 1900), to obtain an order of accuracy of a hundredth of a degree on the fundamental interval, which is all that is required for work at high temperatures; but it would be unreasonable to expect to be able to work to the thousandth of a degree, except under the best conditions, with the most perfect apparatus and the most skilful observers.

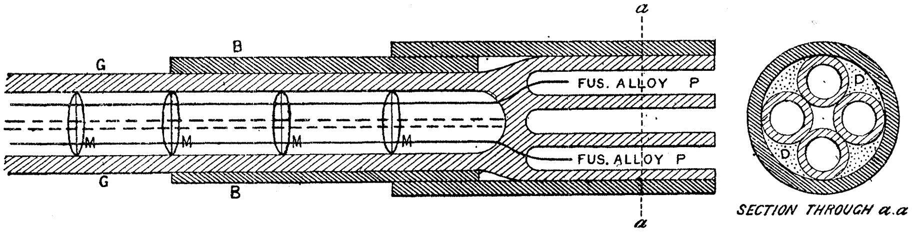

Fig. 4. Hermetically-sealed Thermometers.

B, brass tube; C, compensator; D, plaster of Paris; G, glass tube; M, mica discs; P, pyrometer leads.

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* I originally employed common solder, but the fusible alloy, first suggested by GRIFFITHS, appears to make a good connection and is more easily managed, though it could not be used in the steam-engine experiments.

### (22.) *Differential Measurements.*

The only thermometric measurement requiring the highest accuracy in the present investigation was the difference of temperature between the inflowing and outflowing water at the two ends of the calorimeter. As this difference was obtained by a single reading of a pair of differential thermometers, all the minor errors and corrections were practically eliminated. Further, as there was no particular advantage to be gained by observing the fundamental interval with greater proportionate accuracy than the differential measurement, many special precautions, such as measuring the current heating, or keeping the current constant, were rendered superfluous. For the same reason it was unnecessary to secure the highest possible accuracy in the comparison of the coils of the box (as only a few of the smallest were used for the differential measurement), and no attempt was made to keep the temperature of the box approximately constant (to minimise possible errors due to imperfect compensation, or variation of temperature), although such precautions would naturally be adopted in many other investigations. It was sufficient to make sure that the vernier was correctly set and read, and that the sensitiveness of the galvanometer was suitable for the differential measurement.

The galvanometer employed in this investigation was specially made for the work by Messrs. NALDER BROS., to my order, in 1896. It was an astatic instrument, with four small coils of 5 ohms each. It had a fairly small and light magnet system, and a light plane mirror about 4 millims. in diameter, and was fitted with a long silk suspension, and a symmetrical system of control magnets above and below. The suspension might have been more delicate, and the magnet and mirror system lighter, with a smaller moment of inertia, but as the sensitiveness proved to be ample for the purpose, no alterations were made. The most important point for our work was the astaticism of the magnets. It was quite impossible to work with a sensitive non-astatic galvanometer owing to disturbance from the electric railway. But the astatic instruments, if properly adjusted, were very little affected. It was necessary to keep the time of swing short to secure sufficient rapidity of observation, but even with this restriction there was no difficulty in adjusting the galvanometer to give a deflection of four or five scale-divisions for a thousandth of a degree with a current of about one two-hundredth of an ampere through the thermometers. The deflections were observed with a microscope carrying a fine scale and a micrometer eye-piece. No attempt was made to adjust the contact to the exact balance point. It was merely set to the nearest millimetre division of the bridge-wire, and the galvanometer deflection observed on reversing the battery current. The exact balance reading could be easily calculated from this by observing the deflection per millimetre of the bridge-wire, which remained fairly constant. The mean temperature difference was worked out to the ten-thousandth of a degree. It appears probable from the observations that the error very rarely amounted to as much as one two-thousandth of 1° on a rise of temperature of 8°.

### (23.) *Reduction of Results to the Hydrogen Scale.*

A most important factor in the variation of the specific heat of water, as ROWLAND was the first to point out, is the correction to the absolute scale of the readings of the particular thermometer employed in the research. In the present case, the temperature observations were taken with platinum-thermometers of standard wire, and were approximately reduced to the absolute scale by the difference-formula,

$$t - pt = dt\,(t - 100)/10{,}000 \;.\;.\;.\;.\;.\;.\;.\;.\;.\quad (1).$$

The recent observations of Messrs. HARKER and CHAPPUIS ('Phil. Trans.,' A, 1900) with a constant-volume nitrogen thermometer have confirmed my conclusion that a formula of this type represents the deviation of the platinum-thermometer from the absolute scale within the limits of error of observation over the range 0° to 600° C. A similar conclusion follows from the comparison by GRIFFITHS ('Phil. Trans.,' 1893) and by WAIDNER and MALLORY ('Phil. Mag.,' July, 1899) of mercury-thermometers standardized at the International Bureau with platinum-thermometers from 0° to 25°, and from 0° to 50°.

The value of the difference-coefficient $d$ in this formula was assumed to be 1·50 from the mean of a number of observations taken at different times with different samples of the wire. The thermometers themselves were not directly tested, as the variation of the difference-coefficient for different specimens of the pure wire is in nearly all cases less than the probable error of a single determination. The particular sample of wire employed for thermometers E, on which most of the results depend, was tested by Mr. TORY ('Phil. Mag.,' 1900) by comparison with the original standard wire from which it was drawn, and found to be identical.

The limits of variation of the difference-coefficient for pure platinum wire, as tested by competent observers, assuming the normal boiling-point of sulphur to be 444°·53 C., on the scale of the constant-pressure air-thermometer, is only 1·49 to 1·51. The greater part of this variation is probably due to errors of observation and differences of annealing. A variation of 0·01 in the value of $d$ would affect the specific heat of water by only 1 part in 10,000 at 0° or at 100° C., and by much less at intermediate points of the range. If we had assumed the boiling-point of sulphur to be 445°·27 C.,* as found by HARKER and CHAPPUIS with a constant-volume nitrogen-thermometer, the value of $d$ would have to be increased to 1·54, which would increase the values of the specific heat of water by only 4 parts in 10,000 at 0° C., and by 2 in 10,000 at 25° C. The difference in the above values of the boiling-point of sulphur may possibly be explained as due to a real difference in

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* CHAPPUIS has recently ('Phil. Mag.,' 1902) accepted the results of HOLBORN and DAY for the expansion of Berlin porcelain, which reduce his value for the boiling-point of sulphur to 444°·7 C.—*Added March* 11, 1902.

the scales of the constant-volume and constant-pressure thermometers, as we have little direct experimental knowledge of the relation of the scales at these temperatures. It may be equally due to systematic differences of reduction of the observations, as for instance in the application of the correction for the expansion of the envelope of the gas-thermometer. The correction applied by CHAPPUIS,* obtained by extrapolation of a formula deduced from observations over the range 0° to 100° C., is much larger than similar corrections found by CALLENDAR and BEDFORD for hard glass and porcelain from observations over the range 0° to 600° C. The lower value of the boiling-point of sulphur obtained by CALLENDAR and GRIFFITHS in 1890 was confirmed by CALLENDAR with a different instrument in 1893, and later by EUMORFOPOULOS. Since the uncertainty of the correction for the expansion of the envelope is so great (CALLENDAR, 'Phil. Mag.,' December, 1899), it was decided to adopt the older value, which has been in use for 10 years, rather than to attempt a special correction based on the probable scale difference of the constant-pressure and constant-volume thermometers.

The uncertainty of this correction is mainly due to the difficulties of gas thermometry. The scale of a platinum-thermometer constructed of pure wire is so easily and so accurately reproducible, that it appears practically certain, as I have already explained at some length in a previous paper ('Phil. Mag.,' December, 1899), that it would afford a more convenient standard of reference than the hydrogen thermometer for scientific purposes. By employing a standard difference-formula, such as (1) for reduction of platinum temperatures to the absolute scale, we should obtain results in sufficiently close agreement with the thermodynamical scale for all practical purposes, and we should be saved the trouble and confusion incidental to small uncertain corrections. From this point of view it would be more scientific to omit any further reduction to the hydrogen scale, but it may be of interest to indicate the nature and the probable magnitude of the correction.

Since the parabolic difference-formula (1) was established and verified by means of observations with air- or nitrogen-thermometers, it would be most natural to assume that the scale obtained by its application coincided very closely with that of the nitrogen-thermometer, and to reduce the results to the hydrogen scale by the application of the table of corrections given by CHAPPUIS, deduced from the following formula for the difference,

$$t_n - t_h = t\,(t - 100)\,(+\,6{\cdot}318 + {\cdot}00889t - {\cdot}001323t^2) \times 10^{-6} \quad . \quad . \quad (2).$$

This formula has been applied to our results by GRIFFITHS ('Thermal Measurement of Energy,' Cambridge, 1901), who gives a table of the corrected values. But there

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* CHAPPUIS has recently ('Phil. Mag.,' 1902) accepted the results of HOLBORN and DAY for the expansion of Berlin porcelain, which reduce his value for the boiling-point of sulphur to 444°·7 C.—*Added March* 11, 1902.

are some objections to be considered. CHAPPUIS' formula (2) refers to the constant-volume nitrogen-thermometer at 100 centims. of mercury initial pressure, whereas the difference-formula (1) was obtained with a constant-pressure air-thermometer at 76 centims. pressure. Moreover, formula (2) makes the difference negative between 73° and 100°, as shown in the second column of Table IV., so that the correction to the specific heat would change from $-2$ in 10,000 at 80° to $+6$ in 10,000 at 100°. The negative differences are of the same order as the probable errors of the observations. CHAPPUIS himself considered them to be impossible, and gave a revised formula for the mean coefficient of expansion of nitrogen, from which the "corrected" values in the third column have been calculated. He has since recalculated the values on a slightly different assumption, namely that the pressure-coefficient $(dp/dt)/p_0$ of nitrogen at an initial pressure $p_0 = 100$ centims., reaches a minimum value ·0036738 at 80° C., and then remains constant at all higher temperatures. Taking the fundamental coefficient (0° – 100°) as being ·00367466, the difference of the scales above 100° C. would be linear, and would amount to ·023° per 100°. The effect of this assumption between 0° and 100° does not differ materially from M. CHAPPUIS' first "corrected" results.

It is interesting to compare CHAPPUIS' results with those calculated from the observations of JOULE and THOMSON. In order to represent the results of these observers more accurately, especially in the case of hydrogen, I have added a term $b$ to their formula, to represent the "co-volume," as in the later equations of HIRN and VAN DER WAALS. The equation of JOULE and THOMSON then becomes

$$v - b = \mathrm{R}\theta/p - \mathrm{A}/\theta^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which is practically equivalent for moderate pressures to the formula devised by CLAUSIUS to represent the divergences of $CO_2$ from VAN DER WAALS' formula. The differences calculated from this formula for nitrogen and hydrogen at constant-volume and 100 centims. initial pressure, are of the same order of magnitude, but not quite so large, as the "corrected" differences of CHAPPUIS. On the whole the agreement appears very satisfactory. It would have been still closer if the nitrogen-differences observed by CHAPPUIS in the second series of his observations between 0° and 25° had not been raised by ·007° in order to make the curve pass through the zero point. (See CALLENDAR, 'Proc. Phys. Soc.,' March, 1902, where the subject is more fully discussed.) It should be remarked, on the other hand, that the observations of JOULE and THOMSON can be represented well within the limits of experimental error by the formula of VAN DER WAALS. According to the latter formula the pressure at constant-volume is a linear function of the temperature, and the differences between the scales of all constant-volume thermometers should be identically zero. The evidence of the experiments of JOULE and THOMSON taken alone is therefore inconclusive, but it may be stated that the observations of AMAGAT, WITKOWSKI, and others on the compressibility of gases over considerable ranges of temperature and pressure, indicate a real difference between the scales, similar to that calculated from the observations of JOULE and THOMSON by the modified equation (3).

The differences between the nitrogen and hydrogen scales at a constant pressure of 1 atmosphere calculated from the observations of JOULE and THOMSON by the same equation are given in the same table. In each case the difference between the hydrogen scale, $t_h$, and the absolute scale, $\theta$, is added. In the case of the constant-pressure thermometer the correction is larger than at constant-volume, but there is less uncertainty in its value, as the results calculated by different formulæ (*e.g.*, VAN DER WAALS and CLAUSIUS) are very nearly the same.

TABLE IV.—Difference between Scales of Nitrogen and Hydrogen Gas-Thermometers.

| Temperature, Centigrade. | CHAPPUIS, formula (2). | CHAPPUIS, corrected. | JOULE-THOMSON, constant-volume, 100 centims. | | JOULE-THOMSON, constant-pressure, 76 centims. | |
|---|---|---|---|---|---|---|
| | $t_n - t_h$. | $t_n - t_h$. | $t_n - t_h$. | $t_h - \theta$. | $t_n - t_h$. | $t_h - \theta$. |
| 10° | + ·0057 | + ·0053 | + ·0030 | + ·0005 | + ·0062 | + ·0011 |
| 20 | + ·0095 | + ·0087 | + ·0050 | + ·0009 | + ·0103 | + ·0019 |
| 30 | + ·0113 | + ·0105 | + ·0065 | + ·0012 | + ·0131 | + ·0024 |
| 40 | + ·0110 | + ·0110 | + ·0073 | + ·0013 | + ·0143 | + ·0026 |
| 50 | + ·0086 | + ·0103 | + ·0073 | + ·0013 | + ·0144 | + ·0026 |
| 60 | + ·0049 | + ·0090 | + ·0066 | + ·0013 | + ·0130 | + ·0025 |
| 70 | + ·0010 | + ·0069 | + ·0055 | + ·0011 | + ·0112 | + ·0020 |
| 80 | − ·0023 | + ·0045 | + ·0044 | + ·0008 | + ·0083 | + ·0015 |
| 90 | − ·0032 | + ·0022 | + ·0025 | + ·0004 | + ·0044 | + ·0008 |

In order to reduce the value of the specific heat of water expressed in terms of any scale of temperature $t'$ to the corresponding value expressed in terms of any other scale of temperature $t''$, it is only necessary to multiply by the factor $dt'/dt''$. This factor is readily obtained if the formula giving the relation between $t'$ and $t''$ is known. For instance, in order to reduce from the platinum scale by means of the difference-formula, we obtain at once by differentiation of the formula the factor

$$dpt/dt = 1 + (100 - 2t)\,d/10{,}000 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4).$$

Since the specific heat of water varies so little from unity, the correction to be added at any point may be taken as being practically equal to the excess of the correction factor above unity. The corrections from the nitrogen to the hydrogen scale, obtained by differentiation from the table of differences above, are very uncertain, and are for this reason given only to the nearest part in 10,000. The platinum-scale correction is given for comparison in the last line of the table.

TABLE V.—Corrections (Parts in 10,000) to be added to reduce the Value of the Specific Heat of Water from the Nitrogen to the Hydrogen Scale.

| Temperature, Centigrade | 0° | 10° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° | 100° |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CHAPPUIS, formula (2) | +6 | +5 | +3 | +1 | −1 | −3 | −4 | −4 | −2 | +1 | +6 |
| ,, corrected | +6 | +4 | +3 | +1 | +0 | −1 | −2 | −2 | −2 | −2 | −2 |
| JOULE-THOMSON, constant-volume, 100 centims. | +4 | +3 | +2 | +1 | +0 | −0 | −1 | −1 | −2 | −2 | −3 |
| JOULE-THOMSON, constant-pressure, 76 centims. | +7 | +5 | +3 | +2 | +1 | −1 | −2 | −2 | −3 | −4 | −5 |
| Platinum scale correction by difference-formula (1) | +150 | +120 | +90 | +60 | +30 | 0 | −30 | −60 | −90 | −120 | −150 |

It will be observed that the correction in any case is very small, and that the uncertainty of the correction is nearly as large as the correction itself. A change of nearly 1 in 1000 in the correction at 100° is produced, if we adopt the "corrected" results of CHAPPUIS instead of the table taken by GRIFFITHS. On the whole, as the difference-formula (1) was obtained by comparison with a constant-pressure air-thermometer at 76 centims., we shall probably be most nearly correct if we apply the corrections calculated from the observations of JOULE and THOMSON for air under the same conditions. The corrections thus obtained do not differ materially from those applied by GRIFFITHS (they agree to 1 in 5000), except at 90° and 100°, where they differ by 5 and 11 in 10,000 respectively. I have therefore assumed the corrections calculated from JOULE and THOMSON in reducing the results to the hydrogen scale in Table XII., Section 37.

The value 1·54 for the difference-coefficient already referred to was obtained by HARKER and CHAPPUIS with a constant-volume nitrogen-thermometer at 56 centims. initial pressure. The corrections for this case can be calculated from the observations of JOULE and THOMSON by reducing those for the constant-volume thermometer given in Table IV. in proportion to the initial pressure, namely, in the ratio 56 to 100. It happens that if our results are reduced by employing CHAPPUIS and HARKER'S value of the difference-coefficient, 1·54, and are then corrected to the hydrogen scale by applying the correction for the constant-volume nitrogen-thermometer at 56 centims., the results are identical with those obtained by using the difference-coefficient, 1·50, and then applying the correction for the constant-pressure air-thermometer. This agreement, however, is not really so satisfactory as it appears at first sight, because, according to the theory on which it is based, the correction to the hydrogen scale does not follow the same function as the difference-formula, and the difference in the values of the coefficients assumed, namely, 1·50 and 1·54, cannot be entirely explained by the difference of the scales at the boiling-point of sulphur.*

## Part IV.—Calorimetry.

### (24.) *Temperature Regulation.*

The question of temperature regulation was particularly important in this method of calorimetry. It also presented exceptional difficulties on account of the form of the calorimeter, and the large range of temperature to be covered. The apparatus employed for this purpose was made in the summer of 1895, and I spent a good deal of my leisure time during the session 1895–96 experimenting with various forms of regulator before I was able to obtain a satisfactory arrangement.

On account of the extreme length of the calorimeter (over 1 metre), and since it was necessary to have both the ends accessible for inserting leads and thermometers, I decided to employ a tube form of water-jacket open at both ends in place of the more usual bath and stirrer. The most convenient method of maintaining such a jacket at a constant temperature appeared to be by means of a vigorous water circulation maintained by a centrifugal pump. The apparatus constructed for this purpose is shown diagrammatically in fig. 5. It was intended to serve as heater, regulator and circulating pump simultaneously. The annular bulb AB was filled with oil, the expansion of which actuated a gas regulator in the usual manner. The revolving blades CC of the centrifugal pump were connected through the gland D with a water motor by means of a short piece of stiff rubber tubing. The circulating

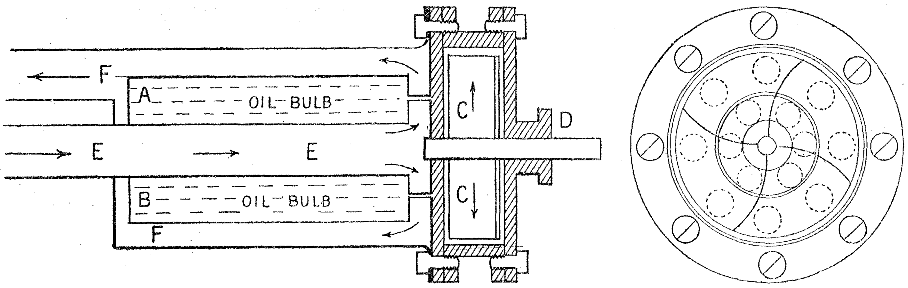

Fig. 5. Heater, Circulator, and Regulator.

AB, oil bulb; C, stirrer blades; D, gland; E, inflow; F, F, outflow.

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* The Joule-Thomson equation, extrapolated to 445°, would make the constant-volume thermometer read two or three-tenths of a degree higher than the constant-pressure thermometer, which would account for the difference between Chappuis' corrected result, 444°·7 C., for the sulphur boiling-point, and the value, 444°·53 C., obtained by Callendar and Griffiths.—*Added March* 11, 1902.

water was sucked in through the central tube E, 1 inch in diameter, and ejected through the annular space surrounding the bulb of the regulator by the tube F. The whole was mounted on a large gas burner, and shielded with an asbestos screen.

The object of placing the regulator bulb *inside the heater*, and in close proximity to the pump, was to secure quickness of action in response to any change in the gas-pressure. The violent stirring, and the comparatively small capacity of the heater in proportion to the bulb favoured this result. It was most important that the regulator should be very sensitive, and that there should be no forced oscillations of temperature, because the jacket-temperature determined that of the inflowing water-supply to the calorimeter, and did not merely affect the external heat-loss. Any temperature oscillation would produce a serious effect on the results, especially on the smaller flows, in which the total mass of water passing, about 250 grammes in 15 minutes, was not very large compared with the effective thermal capacity of the calorimeter, which was about 50 grammes.

When the regulator was made sufficiently sensitive to cut off the gas for a very small change of temperature, I found it necessary at the higher points of the range, where a large supply of gas was required, to adjust the by-pass so that, if the regulator were cut off, the temperature would very nearly reach the required point. Forced oscillations could only be avoided if the regulator controlled a very small fraction of the heat supply, acting merely as a fine adjustment on the temperature of the system. Under these conditions, however, when the total gas-supply was large, any small accidental change in the gas-pressure might exceed the limits of control of the regulator. A rapid change in the quality of the gas produced similar effects. It was therefore absolutely necessary at the higher temperatures to keep the gas-pressure very constant. The best forms of gas-governor were tried, but did not prove sufficiently delicate. I therefore fitted up a large copper gas-holder, delicately suspended and counterpoised by means of a steel tape passing over a wheel with ball bearings so as to move with very little friction. This arrangement proved to be capable of regulating the pressure to within a tenth of a millimetre of water. The large capacity of the gas-holder tended also to minimize the effect of sudden small variations of quality of the gas, such as might be produced by air in the pipes, &c.

The action of this constant-pressure gas-supply was so perfect that for many purposes no other temperature-regulator was required, and as a matter of fact none was used in many of the preliminary experiments. Since variations of gas-pressure were practically eliminated, it was found to be unnecessary to have the regulator bulb inside the heater, and the fine adjustment-regulator was placed in the tank C, (BARNES, figs. 14 and 15, pp. 211, 213). This regulator was employed to operate an electric heating arrangement, as described by Dr. BARNES in Section 4, in which slow period oscillations were prevented by the device of the reciprocating contact suggested by GOUY ('Journ. de Phys.,' 1897, p. 479). I found it necessary to introduce a few modifications into the arrangement as described by Gouy, the most important of which was to make the relay put another lamp in series, instead of breaking the circuit. This prevented the destructive sparking at the break, which was a serious matter with a 100 candle-power lamp. Of course, the greater part of the work still fell on the constant-pressure gas-supply, which was mainly responsible for the excellence of the results at high temperatures.

### (25.) *Preliminary Experiments on the Specific Heat of Mercury.*

Our first experiments by the steady-flow electric method of calorimetry were made on the specific heat of mercury, as it presented fewer experimental difficulties than water. Since mercury is itself a conductor of suitable specific resistance, it was unnecessary to insert a heating conductor in the fine flow-tube, which greatly simplified the fitting together of the apparatus. The conducting properties of mercury were also utilised in the design of an electrical device for maintaining a constant head so as to secure uniformity of flow. The level of the mercury in the reservoir was regulated by a platinum wire contact which actuated an electro-magnet compressing a small rubber tube which supplied mercury to the reservoir. As soon as the level fell below the platinum point, the contact was broken, the armature released, and more mercury supplied. The inflow was arranged to keep the mercury near the platinum point in perpetual agitation, so that there was no sticking or hunting of the regulator. The whole arrangement was fitted to a wooden bracket belonging to a Geissler pump, which could be hung up on the wall at different levels when it was required to alter the flow of mercury in a given ratio. The flow was regulated and steadied by passing the mercury through fine glass tubes immersed in a tank of water before entering the calorimeter. In measuring the flow of mercury, the time of switching over was automatically recorded on an electric chronograph by the momentary contact of the mercury thread with an edge of platinum foil, which diverted the flow from one beaker to another.

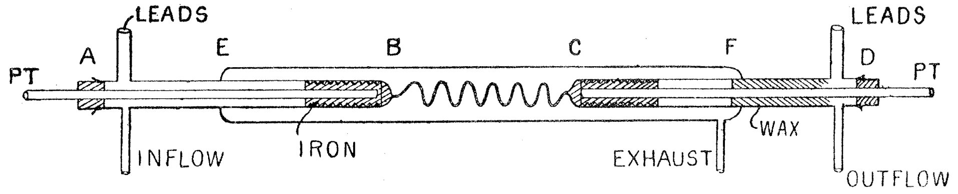

Fig. 6. Diagram of Mercury Calorimeter.

The design of the calorimeter itself will be readily understood from the accompanying diagram (fig. 6). The inflow and outflow tubes AB and CD are exactly similar, about 2 centims. internal diameter and 25 centims. long. They are connected by the fine flow-tube BC, of 1 millim. bore and 1 metre long, coiled in a short spiral of about 2·5 centims. diameter. The vacuum jacket EF extends about 13 centims. along the inflow and outflow tubes, and is provided with a side tube for exhausting. The inflow and outflow tubes are provided with two side openings, the smaller of which was intended for the inflow or outflow of mercury, and the larger for the leads conveying the electric current. In some of the earlier experiments the larger tubes were fitted with a pair of delicate mercury-thermometers for watching the progress of the experiment, and observing when the conditions became steady. But these mercury-thermometers were found to be of little or no use, and the large side-tubes were subsequently removed to facilitate the fitting of the calorimeter in a tubular form of water-jacket.

### (26.) *Method of Determining the True Mean Temperature of Outflow.*

By far the most important point in this method of calorimetry is the device adopted for obtaining the true mean temperature of the outflowing liquid, and securing a definite measurement of the electrical watts expended in heating it. If a thermometer were merely inserted in the outflow-tube, leaving a free space all round for the circulation of the liquid, it is evident that the heated liquid would tend to flow in a stream along the top of the outflow-tube, and that the thermometer might indicate a temperature which had little or no relation to the mean temperature of the stream. It is easy to make an error of 20 per cent. in this manner, as I found in my preliminary experiments in the summer of 1896. A fairly uniform distribution of the flow might be secured by making the space between the thermometer and the outflow-tube very narrow. But this leads to another difficulty in the case of mercury. As the space is narrowed, the electrical resistance is increased, and an appreciable quantity of heat, which cannot be accurately estimated, is generated in the vicinity of the thermometers.

Both the difficulties above mentioned were overcome in the mercury experiment by fitting the inflow and outflow tubes with soft iron cylinders, 6 centims. long, turned to fit the tubes, and bored to fit the thermometers. The soft iron had a conductivity about ten times that of mercury for both heat and electricity. The heat generated by the current in the immediate vicinity of the thermometer bulbs was so small that the watts might fairly be calculated from the difference of potential between the iron blocks at the middle points of the bulbs. The mercury stream was forced to circulate in a spiral screw thread of suitable dimensions cut in the outer surface of the blocks, which prevented the formation of stream-lines along one side of the tube, and secured uniformity of temperature throughout the cross section of the outflow-tube. The high conductivity of the iron also assisted in securing the same result.

A precisely analogous device for averaging the outflow temperature was applied in the water calorimeter. The bulb of the thermometer was fitted with a copper sleeve of high conductivity, on the outside of which a rubber spiral was wound to fit the outflow-tube as closely as possible. The accuracy of fit was found to be much more important in the case of water than in the case of mercury. The reason of this is that, the thermal conductivity of water being 10 or 15 times less than that of mercury, the accurate averaging of the outflow temperature is more dependent on the uniformity of the spiral circulation and the complete elimination of asymmetric stream-lines.

In order to obtain a perfect fit for the sleeves with their spiral screws, it was necessary that the bore of the outflow-tube should be as nearly uniform as possible, and accurately straight. It was most essential that there should be no constriction at the points of junction E and F with the vacuum-jacket, and that the external portions of the tubes AE, FD should not be of smaller bore than the portions inside the vacuum-jacket, though it would not matter much if they were a little larger. These details of the design, which determined the choice of the dimensions of the tubes, had all been carefully worked out before the ordering of the first six calorimeters with vacuum-jackets in October, 1896, and the importance of the straightness and uniformity of the tubes was clearly explained in the specification. There was some difficulty in making the calorimeters accurately to specification, and when they arrived about three months later, it was found that this particular detail had been somewhat overlooked. It was consequently a difficult matter, even with a soft rubber spiral, to secure sufficient perfection of fit, and the accuracy of many of the earlier experiments was seriously impaired.

The effect of an imperfect fit was to permit part of the heated stream to escape directly past the thermometer, so that the temperature indicated by the outflow thermometer was lower than the true mean of the flow. This defect was less apparent with a large flow or a large rise of temperature, either of which conditions tend to promote mixing of the liquid and the attainment of a proportionately greater uniformity of temperature. A good illustration of this is afforded by the results quoted by Dr. BARNES in Section 7 of his paper, p. 237, which were obtained with one of the first three calorimeters in which the bore was undoubtedly defective. The apparent diminution of the heat-loss per degree rise with increase in the rise of temperature is probably due in part to the more perfect mixing of the stream caused by the greater differences of temperature, which promote instability of flow and increase the formation of eddies. I may add that I have repeatedly observed the same effect in my experiments on steam by a similar method. With steam it is much more difficult than with water to secure a true average of the outflow temperature. Any imperfection of fit or circulation immediately produces the observed effect in an exaggerated form.

The greater irregularity of the results (BARNES, Section 7) for the small flows is probably in part accidental, but is also characteristic of imperfect fitting of the rubber spiral in the outflow-tube, which is obviously more detrimental in the case of the smaller flows. As a consequence of this irregularity of the small flows, I do not think these results can be fairly treated by the somewhat artificial method adopted by Dr. BARNES. The extrapolation of the heat-loss per degree for zero rise of temperature is too uncertain in the case of the small flow. The natural method of treatment would be to take the difference between the sum of the electrical watts $\Sigma EC$, and the sum of the heat-watts $\Sigma JQd\theta$, and divide by the sum of the temperature differences $\Sigma d\theta$, to find D for each flow. Combining the two flows in the usual manner, without any arbitrary assumptions, we thus obtain practically the same result as that deduced by Dr. BARNES.

### (27.) *Design of the Water Calorimeter.*

The design of the water calorimeter presented certain points of difficulty which were not settled without some preliminary experiments on the conditions of flow in fine tubes. The greater part of these experiments were carried out in the summer of 1896, in the Thermodynamical Laboratory of the Engineering Building of McGill College, with the kind permission of Professor NICOLSON, who erected for this purpose a large supply-tank of water on an upper floor in a room at a very constant temperature. The results of some of these experiments were mentioned in a paper on the 'Law of Condensation of Steam,' which was communicated to the Institution of Civil Engineers in September, 1896, and read in the following year.

Since water is practically a non-conductor of electricity, it was necessary either to make the fine flow-tube of platinum instead of glass, or else to thread a conducting wire or strip of platinum through it. A fine bore *metallic* flow-tube would have presented some advantages in point of smallness of radiation loss, but in the end I decided to use a glass flow-tube and a central conductor, chiefly on account of the importance of securing the greatest possible constancy and perfection in the vacuum-jacket. This could be most easily and certainly attained by making the vacuum-jacket entirely of glass.

The glass-work of the water calorimeter differed from that of the mercury calorimeter (fig. 6) only in having a straight flow-tube 50 centims. long and 2 millims. bore, instead of a spiral flow-tube 100 centims. long and 1 millim. bore. It was necessary to make the flow-tube straight on account of the difficulty of threading the conductor through it as well as the connecting wires to which it was attached. This operation would have been facilitated by using a larger tube, but, apart from this necessity, it was desirable to have the flow-tube as fine as possible to secure uniformity of temperature of cross-section and other advantages. From one point of view, it was desirable to make it as short as possible, in order to minimise the heat-loss, which depended chiefly on the surface of the flow-tube; but on the other hand it was necessary to have sufficient length to eliminate leakage of the current through the water, and to secure a suitable resistance for the conductor, and sufficient surface to prevent excessive superheating by the current. It was found that the dimensions above given satisfied the required conditions very fairly, and although there were a few minor details which could not be satisfactorily settled until the complete apparatus had been fitted up, it was not found necessary to make any changes in the essential features of the design. The three calorimeters ordered two years later by Dr. BARNES were of the same design in all important points, except that two of them had 3 millims. bore flow-tubes; but these were found to be less suitable, and were employed in very few of the tests.

### (28.) *Improvements in the Design of the Calorimeter.*

Although Dr. BARNES was naturally unwilling to introduce any radical changes in the original pattern, which had proved to be capable of giving very good results, there can be no doubt that it was capable of improvement, and I had in fact already noted several points in which alterations were desirable.

The importance of uniformity of bore in the flow-tube, and particularly in the outflow-tube, has already been referred to (§ 26). This was remedied in the later apparatus. Two of the side tubes were also removed, and the other two bent parallel to the flow-tube, to facilitate insertion in the cylindrical form of jacket. These modifications were of small importance, and were made in the first calorimeters after the apparatus was received. A more important improvement in the same direction would be to have the tube for exhausting the vacuum-jacket inserted at F, fig. 6, in a direction *parallel* to the flow-tube, which would permit the water-jacket to be made much smaller, thus securing a more vigorous and uniform circulation.

It would be most important for future work to endeavour to reduce (1) the risk of error from conduction at the outflow end of the calorimeter at high temperatures; (2) the correction for the heat-loss, which amounted to 4 per cent. at the higher points of the range.

The conduction error might be reduced by including a greater length of the outflow-tube in the vacuum-jacket. This would be much more effective than lagging the exposed parts with flannel, since the flannel lagging is exposed to the temperature of the laboratory, which is much lower than that of the jacket. Besides, the lagging is apt to become damp, and takes a long time to reach a steady state. The length of outflow-tube inside the vacuum-jacket might easily be increased to 25 centims. instead of 12, with 5 centims. outside. This would greatly diminish the possible uncertainty of the conduction loss.

The heat-loss depends chiefly on the extent of surface of the flow-tube and thermometer bulb. The thermometer bulb could not be made much smaller, but the greater part of the loss arises from the flow-tube, which might be reduced to about half the external diameter, although the bore could not conveniently be made less than 1·5 millims. This would also be an advantage as diminishing both the heat capacity of the tube and the difference of temperature between the inside and outside of the glass. In heating the apparatus during exhaustion, there is some risk of breaking the flow-tube, as it heats and cools very slowly in a good vacuum. The difference of temperature between the thick flow-tube and the jacket in some cases caused the tube to bend so as nearly to touch the sides of the jacket. This effect would be reduced by making the tube thinner.

It does not appear that very much could be gained by taking excessive precautions to improve the vacuum. With a less perfect vacuum there would probably be less variation of the heat-loss, due to the evolution of minute traces of gas during exposure to a high temperature. The greater certainty of the correction in that case might compensate for its larger magnitude. The first three calorimeters, one for mercury and two for water, were exhausted in the laboratory on a five-fall Sprengel pump which I had set up some time previously for experiments on radiation and on X-ray tubes. This pump gave a very perfect vacuum, but the tubes were merely heated by hand with a bunsen burner during the process. They showed, however, approximately the same rate of heat-loss as the best of the calorimeters which were subsequently exhausted by Messrs. EIMER and AMEND in an asbestos oven. The vacuum in one of the calorimeters exhausted in the laboratory was also tested by means of a powerful oscillating discharge from a battery of Leyden jars passed through a coil surrounding the tube. This failed to induce a ring discharge inside the vacuum-jacket, although the same test would produce a brilliant discharge in the majority of commercial vacuum vessels for liquid air.

Probably the most effective method of reducing the heat-loss would be to silver the inside of the vacuum-jacket. I have tried this method in my experiments on the specific heat of steam by the electrical method with a vacuum-jacket calorimeter, and have found it very advantageous, owing to the low radiative power of the silver. The vacuum-jacket in this case requires very careful evacuating on account of the difficulty of drying the silver film.

With these improvements, the heat-loss could probably be reduced to about one-quarter of its value in the existing apparatus, and the uncertainty of the correction would be greatly diminished, though perhaps not quite in the same proportion. In any case the results obtained with a calorimeter having a very different value of the heat-loss could not fail to be a valuable confirmation of the previous work.

### (29.) *Effect of Variation of Viscosity.*

The rise of temperature of the water due to friction in its passage through the tube, can be easily estimated from the observed difference of head at the inflow and outflow. I made this observation for each of the conductors mentioned on p. 117, with a flow of half a gramme per second in a tube very slightly less than 2 millims. diameter and 50 centims. long. The difference of head was found to vary from

20 to 30 centims. of water at 20° C., for different arrangements of the conductor, and different conditions of flow, being greater when the flow was non-linear. Since 1° C. corresponds to a fall of 42,700 centims. under gravity, the rise of temperature due to the friction would be less than a thousandth of a degree. This is a quantity which ought not to be neglected in working to a ten-thousandth of a degree, but the effect was practically eliminated by the method of observing the difference of temperature, which was expressly intended to eliminate small residual sources of error of this character. For each value of the flow, the difference of temperature was observed "cold" before turning on the electric current, and the "cold reading" was subtracted from the difference observed with the current passing. We are therefore concerned only with the change in the head due to diminution of viscosity with rise of temperature when the current is turned on. I found by calculation from the known variation of the viscosity, and also verified by direct observation in each case, that this amounted to only 10 per cent. of the head for a rise of 8° C. at 20° C. This would be equivalent to 2 or 3 centims. fall, or less than a ten-thousandth of a degree, a quantity which might safely be neglected. The correction would be much smaller at higher temperatures, owing to the great diminution in the viscosity.

In the final apparatus, as employed by Dr. BARNES, the difference of head would be somewhat greater owing to the rubber spirals on the copper sleeves, and the rubber cord on the central conductor. The question was raised at the Dover meeting of the British Association, and I wrote to Dr. BARNES asking him to measure the head under the actual conditions of experiment, but the apparatus happened to be dismounted at the time. We may safely conclude, however, that the difference of head could not have exceeded 1 metre of water, in which case the correction would be less than 1 in 40,000 at 20° C., and might be fairly neglected. This correction corresponds with that for the heat generated by stirring in the GRIFFITHS and SCHUSTER methods of calorimetry. It amounted in GRIFFITHS' apparatus to about 10 per cent. of the heat-supply, but was apparently negligible in SCHUSTER'S experiments.

### (30.) *Radial Distribution of Temperature in the Fine Flow-Tube.*

We assume in the elementary theory of the experiment that the temperature is uniform across the section of the flow-tube at any point. It is important to consider how far and under what conditions this is true. Given the rate of external heat-loss at any point it is easy to calculate the difference of temperature between the inside and outside surfaces of the glass tube, but the distribution of temperature in the liquid can only be calculated if we assume the flow to be in straight lines parallel to the axis of the tube, and the conductor to be circular in section and concentric with the tube. Even in this simple case the solution cannot be made complete, owing to the variations of viscosity and conductivity with temperature;

but it is possible to estimate the order of magnitude of the differences involved, which is all that is really required for our purpose.

Assuming that the internal and external diameters of the flow-tube are 2 and 6 millims. respectively, and length 50 centims., and that the conductivity of the glass is ·0020 cal. C.G.S., it is easy to calculate that the mean difference of temperature between the internal and external surfaces would be of the order of one-tenth of a degree only when the final rise of temperature is 8°, and the heat loss ·050 watt per degree, as in the majority of our experiments. It will therefore evidently be unnecessary to take account of this in any of the calculations.

To find the radial distribution of temperature in the liquid, assuming the flow to be linear, I will take first the case of the metallic flow-tube, which is much the simplest. The differential equation of the radial distribution of temperature, neglecting the minute effect of longitudinal conduction, is

$$d\,(kr\,d\theta/dr)/dr = +\,vcr\,d\theta/dx \quad \ldots\ldots\ldots \quad (1),$$

in which $k$ is the thermal conductivity of the liquid, and $c$ the specific heat per unit volume, $v$ the velocity of the stream, $\theta$ the temperature, $r$ the distance from the axis, and $x$ the distance along the tube. The velocity $v$ is a function of $r$, which can be easily calculated if the viscosity is assumed constant. As a matter of fact, both the viscosity and the conductivity vary rapidly with change of temperature. The viscosity at 100° is nearly six times less than at 0° C., and its variation is accurately known. But if we assume both conductivity and viscosity constant (as we are practically compelled to do, since the variation of conductivity with temperature is quite uncertain) we shall obtain a solution which is sufficiently simple to be useful, and which can be strictly applied to small changes of temperature.

To simplify the solution still further, I shall assume the longitudinal temperature gradient $d\theta/dx$ constant over the cross-section of the tube at any point, and equal to $\theta'/l$, where $\theta'$ is the rise of temperature observed in a length $l$. This will not be true near the inflow end of the tube, where the radial distribution of temperature is rapidly changing, but it will very fairly represent the *limiting state*, which is attained when the liquid has flowed along the tube for some distance.

If the flow is linear, and the viscosity constant, the velocity at any point of the cross-section is given in terms of $r$ by the equation

$$v = 2\mathrm{V}\,(1 - (r/r_0)^2) = 2\mathrm{Q}\,(1 - (r/r_0)^2)/\pi r_0^2 \quad \ldots\ldots \quad (2),$$

where V is the mean velocity, Q the flow in cub. centims. per second, and $r_0$ the internal radius of the flow-tube.

Making this substitution in (1) and integrating, we obtain

$$k\,r\,d\theta/dr = \frac{\mathrm{Q}\theta'}{\pi l}\left(\frac{r^2}{r_0^2} - \frac{r^4}{2r_0^4}\right) + \mathrm{B} \quad \ldots\ldots\ldots \quad (3).$$

The constant of integration B is determined by the consideration that the temperature-gradient vanishes at the centre of the tube. Putting this condition in (3), we find $B = 0$, which materially simplifies the solution of the equation. Integrating from the temperature $\theta_0$ of the surface of the tube, we find

$$\theta_0 - \theta = Q\theta' \left(r^4/4r_0^4 - (r/r_0)^2 - \tfrac{3}{4}\right)/2\pi lk \quad . \quad . \quad . \quad . \quad . \quad (4).$$

The temperature $\theta_1$ at the axis of the tube where $r = 0$, is given by

$$\theta_0 - \theta_1 = 3Q\theta'/8\pi lk \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

The mean temperature $\theta_2$ of the flow, allowing for variation of velocity over the cross-section, is given by the expression

$$\theta_0 - \theta_2 = 11Q\theta'/48\pi lk \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

### (31.) *Electrical Method of Measuring the Thermal Conductivity of a Liquid.*

The remarkable simplicity of this expression induced me to attempt a method of measuring the conductivity of a liquid, based on the observation of the difference of temperature $\theta_0 - \theta_2$ between the tube and the mean of the flow at any point; the temperature $\theta_0$ of the tube and the gradient $\theta'/l$ being deduced from observations of the changes of resistance of the flow-tube itself. Although this may appear at first sight a difficult and out of the way method, it possessed special attractions for me as an application of the electrical resistance method of measuring temperature, and it really offers several advantages which more than counterbalance the difficulty of the electrical measurements. The longitudinal distribution of temperature in the flow-tube was deduced from observations of the resistance of consecutive sections by the same method which I had already applied in 1886 to the determination of the conductivity of platinum. The difficulty of this part of the work was therefore largely discounted by previous experience. The advantage of the method is that the tube is its own thermometer; the temperature measured is that of the tube itself, and not that of a thermo-couple or water-bath assumed to be at the same temperature as the tube. This avoids the most common and insidious source of error in all conductivity measurements.

As compared with the plate-method of measuring the conductivity of liquids, which has been practised by WEBER and many other observers in different forms, the tube-method possesses several important advantages. (*a*) It avoids the difficulty of measuring accurately the small distance between the bounding surfaces of the liquid, or the thickness of the sheet, since the expressions (5) and (6) already given are independent of the radius of the tube, and contain only lengths and differences of temperature which are easily observed. (*b*) All uncertainties with regard to the area from which the heat is conducted, and all difficulties of boundary conditions, which cannot satisfactorily be eliminated in the plate-method, even by the employment of a guard-ring, are easily avoided in the tube-method by making the tube small in proportion to its length. (*c*) The error of the plate-method due to direct radiation through the liquid, which is quite important with a thin transparent stratum, is completely eliminated, since all the heat which is lost by the inner surface of the tube must be absorbed by the liquid itself.

GRAETZ, ('Wied. Ann.,' vol. 18, p. 79) has applied a non-electrical steady-flow method to the determination of the conductivity of a liquid, which bears a close superficial resemblance to that above described, but in reality differs from it in several fundamental points. In his method a stream of liquid at a temperature between 30° and 40° C. flows through a thin capillary tube, 10 centims. long, and 0·6 millim. bore, immersed in a water-bath at a temperature of 7° C. to 10° C. The mean outflow temperature is observed, and is also calculated in terms of the conductivity on the assumption that the flow is linear. The temperature of the external surface of the tube is *assumed* to be the same as that of the water-bath. This is the most obvious defect of his method, as the assumption could not be even approximately true unless the current of liquid through the tube were extremely slow. Unfortunately in that case the difference of temperature between the outflow and the bath, on which the measurement depends, tends to vanish ; it is also more difficult to obtain the true mean temperature of a small stream owing to defective mixing in the outflow tube, and accidental sources of error due to end-effects are exaggerated. These defects might be avoided in various ways. The true mean temperature of the tube itself might be determined by making the tube very thin, and observing its expansion, or preferably its electrical resistance. Or the temperature of the outside surface might be indefinitely approximated to that of the bath by making the tube very thick, and supplying a vigorous circulation around it. The true mean temperature of the outflow might also be determined for small flows by adopting a spiral circulation similar to that employed in the present investigation. There would remain, however, a most essential point of distinction between the two methods.

In the electrical method, heat is continuously supplied by the current at a nearly constant rate as the liquid flows along the tube. The observation depends on the *limiting* difference of temperature at the end of a long tube when a *steady* radial distribution has been reached. The advantage of this is that the solution is independent of the initial or variable state, the calculation of the effect of which is much less certain on account of the steep gradients and excessive differences of temperature involved, which tend to produce disturbances in the flow. In GRAETZ' method the initial differences, amounting to 20° or 30° C., were much larger than in the electrical method, and the result entirely depends on the correctness of the assumptions made in the solution of the initial state. The final or limiting state in his method is one of uniform temperature, and cannot be utilized at all.

In carrying out the electrical method, advantage was taken of the increase of resistance of the tube with temperature in order to secure a constant temperature gradient in the latter part of the flow-tube by suitably adjusting the current, as explained below in § 34. The results were not quite as good and consistent as I had hoped to obtain, on account of want of uniformity in the platinum-tube employed. I therefore thought it best to defer publication till I could find time to repeat the observations under better conditions, but the preliminary work was distinctly encouraging, and was particularly valuable as an indication of effects to be expected in steady-flow electrical calorimetry.

### (32.) *Superheating of the Central Conductor.*

The case of a glass flow-tube with a concentric conductor, which more nearly approaches the arrangement actually employed in the present investigation, leads to nearly the same differential equation, but the solution is much less simple. In the course of designing the experiment, I worked out the complete solution for this case also, including the initial state, on similar assumptions of constant viscosity and conductivity. But since the conductor cannot be held exactly central in practice, and the other theoretical conditions cannot be realized, the method cannot conveniently be applied with a central conductor to the measurement of the conductivity of liquids. For the purposes of the present investigation, moreover, since we are only concerned with the approximate estimation of a small correction, a less elaborate calculation will be more appropriate. In order not to overburden the paper with purely mathematical difficulties, it will suffice to give the solution of the limiting state for the simpler case in which the velocity of flow is assumed to be constant over the cross-section of the tube and equal to its mean value. This simplification does not materially alter the general character of the solution, and the numerical results which it gives for the calorimeters actually employed are within a few parts per cent. of those obtained when allowance is made for the variation of the velocity.

If we integrate the differential equation (1) on the assumption of a constant velocity $V = Q/(r_1^2 - r_0^2)$, where $r_1$ is the radius of the glass-tube, and $r_0$ the radius of the conductor, writing A for $Vc\theta'/2lk$, we obtain the solution

$$d\theta/dr = Ar - Ar_1^2/r \quad \ldots \ldots \quad (7),$$

$$\theta_0 - \theta = Ar_1^2 \log_e (r/r_0) - A(r^2 - r_0^2)/2 \quad \ldots \ldots \quad (8),$$

in which the constant is determined by the condition that, neglecting external heat-loss, the gradient is zero at the surface of the glass. This gives for the difference of temperature between the surface of the wire and the surface of the glass,

$$\theta_0 - \theta_1 = Ar_1^2 \log_e (r_1/r_0) - A(r_1^2 - r_0^2)/2 \quad \ldots \ldots \quad (9).$$

The mean temperature $\theta_2$ of the outflow deduced from (8) is given by

$$\theta_0 - \theta_2 = \mathrm{A}r_1^4 \log_e (r_1/r_0)/\mathrm{S} - \mathrm{A}r_1^2/2 - \mathrm{AS}/4 \quad . \quad . \quad . \quad . \quad (10),$$

where S is the sectional area $\pi (r_1^2 - r_0^2)$ of the flow, and $\mathrm{A} = \mathrm{Q}\theta'/2\pi lk\mathrm{S}$. Equation (10) gives the superheating of the conductor above the mean temperature of the outflow. The difference (9)–(10) gives the error of the assumption that the glass is at the same temperature as the mean of the outflow at the outflow point. The limiting value of the latter error, if $r_0^2$ is negligible in comparison with $r_1^2$ (the most unfavourable case), is $\theta_2 - \theta_1 = \mathrm{AS}/4 = \mathrm{Q}\theta'/8\pi lk$.

Although the above formulæ cannot be directly applied to the experiments on the specific heat of water, it is interesting to make an estimate of the superheating of the conductor, and of the difference of temperature between the glass and the water under the assumed conditions of linear flow and concentric conductor. It is obvious from the formulæ already given, that the differences of temperature in each case are directly proportional to the heat supplied by the electric current, and inversely proportional to the length of the tube and the conductivity of the liquid. To estimate the effects numerically, we may take the rate of heat supply as $\mathrm{Q}\theta' = 5$ calories per second, or 21 watts, for the larger flows. The conductivity $k$ of water at 25° C. may be taken as ·0016 C.G.S., but is much too uncertain to permit the estimate to be extended to other temperatures. Since $l = 50$ centims., we have $4\pi lk = 1{\cdot}00$ very nearly.

For the metallic flow-tube from equation (6) the superheating of the tube above the mean temperature of the flow in the limiting state would be about 5° C., and would be independent of the diameter. For the glass flow-tube, from equations (9) and (10), the temperature of the glass would be from 1°·5 to 2°·0 below the mean of the outflow for tubes of the dimensions employed, increasing to 2°·5 as a limit for a very large flow-tube with a very small conductor. In spite of its higher temperature the metallic flow-tube would have the advantage of a smaller heat-loss, owing to its smaller surface (1 millim. diameter instead of 6 millims.), and far lower radiative power. It would also be possible to measure the actual temperature of the metallic flow-tube at any time from its resistance, without any knowledge of the conductivity of the liquid, and without assuming the flow to be linear.

The superheating of the conductor in the glass flow-tube would naturally depend on the size of the conductor as well as that of the tube, as given by equation (10). With a wire ·8 millim. in diameter, and the flow-tube 2 millims., the superheating of the wire would be about 4°·5 for a heat supply of 21 watts. With a wire ·4 millim. diameter, and a 3 millims. flow-tube, the superheating would be about 13°·2. This illustrates the importance of having a large surface for the wire and a small flow-tube. It is probable, however, that the superheating would not directly affect the radiation loss, as platinum is a bad radiator, and water is very opaque to heat-rays from heated water.

### (33.) *Methods of Eliminating Stream-Line Motion.*

It was evident from the equations above given that, since the conditions of linear flow gave rise to a systematic variation of the temperature of the flow-tube, which was directly proportional to the flow for a constant rise of temperature, it would be necessary to adopt some device for mixing the water in its passage through the tube so as to produce a nearly uniform distribution of temperature over the cross-section of the tube. The obvious method of securing this result was to employ a *stranded conductor*. This would diminish the superheating by increasing the available surface of the conductor, and would distribute the heat evenly over the cross-section of the tube, provided that the strands were separated and arranged in such a manner as to break up the stream-lines.

In order to verify the theory and observe the nature of the effects to be expected, I made some rough preliminary experiments on the superheating of various conductors in a 2 millim. tube with a steady flow of water. The general character of the flow, and the degree of mixing attained, were observed by the introduction of a colour-band of blue ink, after the method employed by OSBORNE REYNOLDS, and generally practised in hydraulic laboratories in studying the flow of liquids. The most instructive results were obtained with a stranded conductor consisting of 5 strands of ·006″ pure platinum wire. My reason for selecting this particular size of wire was that I happened to possess a considerable quantity of it, and that its temperature-coefficient was accurately known, as it was regularly employed for making thermometers.

The resistance of the stranded platinum conductor, when carrying the heating current, was measured by the Wheatstone-bridge method, by comparison with a specially constructed platinoid resistance connected in series with it. The two were connected in parallel with a post-office box, by means of which the ratio of the resistances was observed. The resistance in the arm connected to the platinoid strip was 2000 ohms, the resistance in the adjustable arm corresponding to the platinum conductor was about 6000 ohms. As the platinoid strip remained practically constant, the resistance of the platinum could be taken as proportional to the resistance in the adjustable arm. The watts on the conductor were observed by means of a Weston ammeter and voltmeter of suitable ranges.

The platinoid strip resistance, which was subsequently utilised for regulating the current, is shown very clearly at L in the bird's-eye view (BARNES, fig. 15, p. 213). It consisted of a number of strips of platinoid about 1 foot long, one-half inch broad, and $\frac{1}{32}$ inch thick, having a resistance of nearly $\frac{1}{50}$th of an ohm each. The ends of the strips were bent at right angles and amalgamated. They could be connected in series or parallel in a great number of different combinations by means of the mercury cups and copper connectors shown in the plate. For this particular experiment they were arranged two in parallel, and 19 in series, giving a resistance of nearly $\frac{1}{5}$th of an ohm, capable of carrying a current of upwards of 60 amperes without excessive heating. The maximum currents used in this experiment were about 8 amperes.

The rise of temperature of the platinum conductor in each case was found to be nearly proportional to the watts expended. This was verified by varying the number of cells employed, and keeping the water-flow constant, for each arrangement of the conductor to be tested. The superheating of the conductor was estimated by deducting from the observed rise of temperature half the calculated rise of temperature of the water, making a suitable allowance for the heat-loss. The value of the water-flow was nearly half a gramme per second in all cases, and the results were reduced to a value of $Q\theta' = 5$ calories per second to render the experiments with the different conductors strictly comparable. The actual heat-loss from the flow-tube could not be measured by this comparatively rough method, but I made some attempts to obtain comparative estimates of the temperatures of the outside of the flow-tube by winding a platinum wire round it, covering the spiral with flannel, and observing its resistance. These measurements could not lay claim to any accuracy, but were useful as an indication of effects to be expected.

TABLE VI.—Superheating of Stranded Conductor.

| Form of Conductor employed. | Conditions of Flow. | Superheating. |
|---|---|---|
| | | ° |
| Five strands, irregular . . . . . . . . | Mixed | 2·8 |
| Same, annealed and straightened . . . | Linear | 6·5 |
| ,, twisted into a rope . . . . . . . | Linear | 8·5 |
| ,, spiral fitting tube . . . . . . . | Mixed | 3·0 |

In the first case the wire was taken as it came from the reel. The strands were well separated, and crossed each other irregularly, so that the colour-band was completely broken up and mixed to a uniform tint in a space of 10 or 15 centims. The flow was not precisely turbulent or eddying, but the stream-lines were so quickly sub-divided and mixed that the same effect was produced. When the wire was annealed and straightened,* the colour-band remained practically unbroken from end to end of the tube, but as the strands were still separate, the heat was more or less distributed over the cross-section. The twisting of the wire into a rope in the third experiment diminished the effective surface and increased the superheating, the value of which closely approached that calculated for a central conductor in a 2 millim. tube assuming the conductivity of water ·0016 C.G.S. The great diminution of the superheating in the fourth case, in which the wire was wound into

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* It is probable that the failure of Dr. BARNES to obtain consistent results with a stranded conductor may have been due to the use of annealed wire, which would inevitably become straightened in fitting up the apparatus unless special care were exercised. I was not aware of this mistake at the time.

a spiral of about 1 centim. pitch, closely fitting the tube, was chiefly due to the breaking up of the stream-lines. The colour-band rapidly became mixed to a uniform tint as in the first experiment. I found, however, from the indications of the platinum thermometer wound round the outside of the tube, that the glass was considerably heated by the close contact of the spiral. The simpler arrangement of the loose stranded conductor was equally effective in mixing the stream-lines, and appeared to be free from this defect.

An excellent illustration of the possible effects of a faulty arrangement of the conductor is given by Dr. BARNES in § 6, p. 234. In this case it is possible to calculate the actual heat-loss from a knowledge of the correct value of J for the temperature of the experiment.* The conditions were purposely chosen to exaggerate the errors as much as possible, and it must not be imagined that such large differences could be obtained without special pains in the arrangement of the heating conductor. The normal heat-loss for this calorimeter at a temperature of 26° with a constant gradient of temperature along the flow-tube was approximately ·070 watt per degree rise. Starting from this value, it is possible to calculate the limiting values of the heat-loss for either condition of flow, that of the metallic tube or the small concentric conductor, by drawing the curves representing the actual distribution of temperature in either case, and making a suitable allowance for the loss of heat from the thermometer. Dr. BARNES has given a pair of imaginary curves for these two cases in § 2, p. 152, but it should be observed that these curves are not drawn to scale, being merely intended to illustrate the general nature of the difference, which is considerably exaggerated in order to make it clearer.

TABLE VII.—Superheating of Straight Conductor in 3 millim. Flow-Tube.

| Number of experiment. | Position of conductor. | Flow, Q. | Watts, EC. | Superheat of wire. | Heat-loss, observed. | Limit, calculated. |
|---|---|---|---|---|---|---|
| (1) | At side of tube | ·600 | 21·7 | 8°·0 | ·1108 | ·1140 |
| (2) | | ·277 | 10·4 | 4·1 | ·0909 | ·0920 |
| (3) | In middle of tube | ·600 | 21·7 | 12·8 | ·0482 | ·0530 |
| (4) | | ·271 | 10·7 | 7·0 | ·0773 | ·0610 |

The observed values of the superheat and of the heat-loss agree in a general manner with those calculated by the theory given in § 32, but there are some difficulties. The limit in the last column of lines (1) and (2) is estimated for a *metallic* flow-tube, and it is difficult to see how the heat-loss for a *glass* flow-tube could approach this value so closely when the conductor is in imperfect contact with the glass over a small fraction of its surface. The superheat 12°·8 in line (3) agrees

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* In discussing these observations Dr. BARNES takes (EC − 4·2 Q $d\theta$) in place of the actual heat-loss, which unduly exaggerates the difference. The conductor had evidently been *annealed*, otherwise it would have filled the tube instead of resting along the side.

very closely with the value 13°·3, calculated for a similar case in § 32, but the heat-loss is *less* than the limit for a small conductor in a large tube. On the other hand, the observed heat-loss in line (4) is greater than the normal value ·0700 instead of being less, as theory requires. It is possible that there may have been some other source of error in this experiment due to shifting the thermometer in the outflow-tube or similar causes.

When the first apparatus was set up with the vacuum-jacket in June, 1897, only three strands of ·006″ wire were employed, as it was necessary that the resistance of the heating conductor should be of the same order as that of the manganin current-standard. The latter had been made of 1 ohm resistance to suit the mercury experiment, and there was not time to make another, as the experiment had to be tried before the meeting of the British Association at Toronto. In order partially to compensate for this defect, I took pains to exaggerate the irregularity of the wire by bending it into a zigzag before pulling it through the tube, but the superheating of the wire (4° at 14 watts) proved to be somewhat excessive. In spite of this the readings were extremely steady, and could be taken easily to 2 or 3 parts in 100,000. The accuracy of this preliminary series of experiments was seriously impaired by the bad fitting of the thermometers in the inflow- and outflow-tubes, but the results showed that the method was capable, under suitable conditions, of attaining a very high order of precision on account of the great steadiness of the readings, which was much more perfect than anyone could have anticipated without actual trial.

Shortly after the British Association meeting, another manganin current-standard of 1 ohm resistance was made, and placed in parallel with the first. The platinum conductor was composed of 6 strands of ·006″ wire, which gave a much better distribution of the heat. After numerous preliminary difficulties of temperature regulation, of leakage, and of bad fitting and connections had been overcome, the results, though often very consistent, still showed occasional discrepancies, especially after refitting. I was inclined to attribute these difficulties at the time either to bad fitting of the thermometer in the outflow-tube as previously explained, § 26, or to variable contact between the conductor and the walls of the glass tube, or possibly to bad solder joins on the manganin current-standards, one of which had actually broken away on one occasion.

With the view of preventing the uncertainty of contact with the walls of the glass tube, I thought at one time of trying a conductor in the form of a twisted strip, which I had employed some years previously in experiments on the viscosity of liquids by the Wheatstone-bridge method, for which I required a continuously variable resistance analogous to a slide-wire in the electrical method. I found that a round wire sliding in a tube would not do for this purpose owing to the impossibility of centering. A twisted strip, sliding in a tube which it closely fitted, evaded this difficulty, but led to further anomalies, which proved, on investigation by the colour-band method, to be due to the fact that the motion of the liquid became turbulent if the pitch of the twist was too steep. This change in the character of the flow was a serious defect in the viscosity experiment, but was exactly what was required for the calorimeter. As the calorimeters were already made, and I could not choose the flow-tube to fit the strip, I procured a special pair of rolls about the end of 1897 for rolling a wire to fit the flow-tube as closely as possible. But after carefully rolling a wire to fit one of the calorimeters at one end, I found that it would not go through the tube, on account of want of uniformity of diameter, and in particular on account of a join near one end which unduly constricted the bore. I accordingly abandoned the attempt at the time, as I did not feel at all certain of the necessity of making any change in the form of the conductor. But the twisted strip was subsequently employed by Dr. BARNES at my suggestion with great success in two other calorimeters, the tubes of which were probably more uniform.

The method independently devised by Dr. BARNES for eliminating the effect of the stream-lines, and at the same time preventing all contact between the conductor and the glass, was to wind a rubber cord round the conductor so as nearly to fit the tube, after a similar manner to that employed in fitting the copper sleeve of the outflow thermometer. This is undoubtedly a very simple and effective method, and unlikely to get out of order. It is quite possible that some of the discrepancies in the earlier experiments may have arisen from the accidental disarrangement of the stranded conductor, which might be pulled tight along the side or middle of the tube in refitting the apparatus, either of which contingencies would lead to serious errors. There were many other sources of error and difficulties in the earlier experiments which might have accounted for the effects observed, but Dr. BARNES' opinion on this point is entitled to the greatest weight, as he was personally responsible for the greater part of the fitting-up of the apparatus. With proper care I have no doubt that it would be possible to obtain as accurate results with the stranded conductor as by any other method, but I should be inclined to prefer the rubber-spiral method as being safer and more certain.

A possible objection to the rubber-spiral is that, since the wire is held central and considerably superheated, the temperature of the surface of the glass must necessarily be less than the mean of the flow, in spite of the mixing of the stream-lines. This would not matter if the difference of temperature were independent of the flow. Since it is impossible to calculate what the effect would be in the case of turbulent flow, the question can be answered only by trial. The experiments with the twisted strip, which was partly in contact with the glass and gave a higher heat-loss, were undertaken, at my suggestion, with the object of testing this important point. The extremely close agreement of the results with those obtained with the rubber-spiral at 30° C. are sufficient proof that the error, if any, must be extremely small. It is unlikely that it could amount to more than two or three parts in 10,000 at 30°, and there is no reason to think that this type of error should increase largely at higher temperatures, where the viscosity of water is much smaller and the conductivity probably much larger.

### (34.) *Correction for Variation of the Temperature-Gradient in the Flow-Tube.*

The elementary theory of the elimination of the heat-loss in the steady-flow method of calorimetry assumes that, if the electric current and the flow of liquid be simultaneously varied in such a manner as to keep the rise of temperature the same, the heat-loss by radiation, &c., will remain constant. Dr. BARNES (p. 225) has quoted experiments to show that this condition is very closely satisfied in the present method, and has calculated all the results of the investigation on this assumption. It will be noticed, however, that there are small systematic divergences in the experimental verification for the small flows, which, though amounting only to a few parts in 10,000, require careful examination as possible indications of constant errors.

So long as the distribution of temperature throughout the apparatus is accurately the same for the same rise of temperature, whatever the flow, the heat-loss must also be identical. But if there is any systematic change in the temperature distribution with change of flow, then there must be a corresponding systematic difference in the heat-loss, which will lead to constant errors in the calculation if no account is taken of it. A possible source of error of this type is loss of heat by conduction along the outflow-tube. When the flow is large, the heated liquid passing along the tube will keep it nearly at a uniform temperature, so that the gradient in the outflow-tube will be small, and the conduction loss correspondingly minute. As the flow is diminished, supposing the temperature of the outflow to remain the same, the gradient in the outflow-tube must increase in proportion to the reciprocal of the flow, since the radiation-loss remains nearly the same. The conduction-loss will vary directly as the gradient, or inversely as the flow, for a given rise of temperature.

A small error of this kind, due to conduction, was detected at an early stage in the mercury-calorimeter, owing to the large mass of mercury in the flow-tube, the small rate of flow, and the relatively high thermal conductivity of the liquid. It was practically eliminated by filling the greater part of the outflow-tube from the end of the vacuum-jacket with paraffin wax, leaving only a small passage for the outflow of mercury. This made the conduction-loss very small, and nearly independent of the flow. In the water experiment it is easy to see that the conduction loss must be practically negligible in any case, but special pains were taken to make it as small as possible, and to verify its non-existence.

A more important correction of this type is that due to variation of temperature gradient in the fine flow-tube, which can be estimated with considerable precision. As the liquid flows along the tube it is receiving heat at a nearly uniform rate from the electric current, but it is also losing heat more and more rapidly by radiation as its temperature rises. As a result, the mean temperature of the fine flow-tube, upon which the radiation-loss chiefly depends, usually exceeds the mean between the initial and final temperature by an amount which varies, to a first approximation, inversely as the flow.

In order to calculate the value of this correction in terms of the heat-loss and the flow, it is necessary to consider the differential equation of the distribution of temperature in the flow-tube. We assume, as a first approximation, that the temperature of the surface of the flow-tube, on which the loss of heat depends, is at each point nearly the same as that of the liquid flowing through it. This is very nearly true in the case of mercury, and to a sufficient approximation in the case of water under suitable conditions.

The rate of evolution of heat by a current C amperes in a length $dx$ of the tube is $C^2r\,dx$ watts, where $r$ is the resistance in ohms per centim. The rate of loss of heat is $f\theta p\,dx$, where $p$ is the perimeter of the flow-tube in centims., and $f$ the emissivity in watts per sq. centim. per degree of temperature excess $\theta$. The rate of gain of heat by the liquid is $JsQ\,d\theta$, where J is the number of joules in one calorie; $s$ the specific heat of the liquid in calories per gramme degree C; Q the flow of liquid in grammes per second; and $d\theta$ the rise of temperature in a length $dx$. Since it is necessary to take account of the change of resistance with temperature, we must substitute for $r$ the value $r_0(1 + a\theta)$, where $a$ is the temperature-coefficient of the increase of resistance, and $r_0$ the value of $r$ when $\theta = 0$. We thus obtain the linear differential equation

$$JsQ\,d\theta/dx + (fp - C^2ar_0)\,\theta = C^2r_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

Writing for brevity, $A = (fp - C^2ar_0)/JsQ$, and $B = C^2r_0/JsQ$, and observing that $\theta = 0$ when $x = 0$, since the liquid flows into the tube at the jacket-temperature, the solution of this equation is

$$\theta = (1 - e^{-Ax})\,B/A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

Since A is very small compared with B in the actual experiment, we may obtain a sufficient approximation for our purpose by expanding the exponential and neglecting the terms beyond $A^2$, which gives

$$\theta_x = Bx\,(1 - Ax/2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

If the whole length of the fine flow-tube is $l$, the temperature at the end of the flow-tube will be approximately

$$\theta_l = Bl\,(1 - Al/2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4),$$

and the mean temperature $\theta_m$ from 0 to $l$, will be

$$\theta_m = Bl\,(1 - Al/3)/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

It will be observed that the value of A is zero, and that the gradient is constant throughout the tube for a particular value of the current, $C^2 = fp/ar_0$, which may be called the critical value of the current. In this case the radiation-loss along the flow-tube is exactly compensated by the increase of resistance of the conductor with rise of temperature. I made use of this relation in some experiments on conduction of heat in metals by an electrical method with Mr. KING in 1895, and also in some experiments on the conduction of heat in liquids, § 31, in which the elimination of the heat-loss was a matter of some importance as simplifying the differential equation. In the calorimetric experiment, the constancy of the gradient along the tube was not a matter of primary importance, provided that the temperature distribution was approximately the same for different flows. Moreover, the relation could not apply accurately to both the flows required in the experiment. Nevertheless, I thought it worth while, in designing the dimensions of the calorimeter and the details of the experiment, to arrange that the compensation might hold for a value of the flow between ·5 and 1·0 gramme per second in the water experiment, as nearly as it could be estimated beforehand. The gradient would then be nearly constant, and the mean temperature of the flow-tube nearly half the rise of temperature observed with the differential-thermometers.

### (35.) *Application to the Mercury Experiments.*

Neglecting for the present that part of the heat-loss which occurs in the outflow-tube before the liquid reaches the middle of the thermometer bulb where its temperature is measured (which loss is a comparatively small fraction of the whole in the mercury experiment), the systematic error of the elementary theory given by Dr. BARNES, p. 152, consists in assuming that the mean temperature of the flow-tube is always the same for the same rise, or that the gradient is independent of the flow. This is equivalent to assuming the mean temperature of the flow-tube equal to $\theta_l/2$ instead of $\theta_m$. The error of this assumption may be approximately estimated from equations (4) and (5) above, which give

$$\theta_m = (1 + \mathrm{A}l/6)\,\theta_l/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

If we write (as in BARNES, p. 242) $d\theta$ for the whole rise of temperature observed by the differential thermometers, and $h\,d\theta$ for the heat-loss, we must then regard $h$ as variable with the flow, since the heat-loss is really $fpl\theta_m$. We thus arrive at the expression,

$$\text{Heat-loss} = fpl\theta_m = fpl\,(1 + \mathrm{A}l/6)\,\theta_l/2 = h_0\,(1 + \mathrm{A}l/6)\,d\theta \quad . \quad . \quad . \quad (7),$$

in which $d\theta$ is written for $\theta_l$, and $\mathrm{h}_0$ is the value of the heat-loss per degree rise when the gradient is constant ($\mathrm{A} = 0$), namely $fpl/2$. We have also, to the same order of approximation,

$$\mathrm{A}l = 2h_0/\mathrm{J}s\mathrm{Q} - a\,d\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8).$$

Hence, the complete equation of the method, when corrected for the effect of the variation of the temperature gradient in the fine flow-tube, becomes

$$EC = JsQ\, d\theta + h_0 (1 + h_0/3JsQ - a\, d\theta/6)\, d\theta \quad . \quad . \quad . \quad . \quad . \quad (9).$$

If we divide through the equation by $d\theta$, and write $s = s_0 (1 + d)$, since our object is to determine the variations of $s$, we obtain

$$EC/d\theta - Js_0Q = D = Js_0Qd + h_0 (1 - a\, d\theta/6) + h_0^2/3JsQ \quad . \quad . \quad (10),$$

in which D is employed as an abbreviation for the expression on the left-hand side, which it is most convenient to calculate as the first stage in the reduction of the observations.

By combining the observations for two different flows, $Q'$ and $Q''$, for which the current is adjusted to give approximately the same rise of temperature, $d\theta$, if $D'$ and $D''$ are the corresponding values of the difference observed, we obtain

$$(D' - D'')/(Q' - Q'') = Js_0d - h_0^2/3JsQ'\,Q'' \quad . \quad . \quad . \quad . \quad . \quad (11).$$

Since the last term, which represents the effect of the correction sought on the variations of the specific heat, is generally very small, the equation may be readily solved by approximation, employing the value of $h$ found in the first instance by neglecting the term involving $h^2$.

As an example of the order of magnitude of the correction, and of the method of application, we may take the following experimental results, which were given as an illustration of the method at the meeting of the British Association in 1897, and were quoted in the 'Electrician' of that date. In all the earlier series of observations, three independent flows were taken, with the same rise of temperature at each point, with the object of verifying the theory of the method, and detecting possible sources of error. If the values calculated from the largest and smallest flow disagreed with the observation on the intermediate flow, it was a sure sign of some error or defect in the work. I thought at first that it might be possible to determine the conduction error experimentally in this manner, but the effect proved to be too small.

TABLE VIII.—Example of Calculation of Specific Heat of Mercury.*

| | Flow, Q. | Rise, $d\theta$. | Watts, EC. | $EC/d\theta$. | ·1400Q. | D. | $h^2/3JsQ$. | Results, corrected. |
|---|---|---|---|---|---|---|---|---|
| (1) | 8·753 | 11°·764 | 14·862 | 1·2632 | 1·2255 | ·0377 | ·0008 | $h =$ ·0546 |
| (2) | 6·740 | 11·8720 | 11·696 | ·9851 | ·9435 | ·0416 | ·0010 | $Jsd = -$ ·00202 |
| (3) | 4·594 | 12·301 | 8·488 | ·6901 | ·6433 | ·0468 | ·0015 | $Js =$ ·13798 |

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* These results are given merely as an illustration of the method; they were not corrected for the absolute values of the resistances and other minor sources of error.

In working out these results, the standard value of the specific heat was taken as $Js_0 = \cdot1400$ joule per gramme degree, since the specific heat of mercury is approximately $\frac{1}{30}$th of that of water. If we take only the values of the difference D corresponding to the first and third flows, and calculate the values of $h$ and $Jsd$, according to the elementary theory, neglecting the correction term $h^2/3JsQ$, we find

$$Jsd = (D' - D'')/(Q' - Q'') = - \cdot0091/4\cdot159 = - \cdot00219,$$

$$\text{whence, } h = \cdot0568, \ Js = \cdot1400 - \cdot00219 = \cdot13781 \text{ joule per gramme degree.}$$

As a verification, we may calculate the value of D for the intermediate flow (2). We find $D_2 = \cdot0420$, in place of the observed value ·0416. The difference is only four parts in 10,000, on $EC/d\theta$, and might well be attributed to errors of observation in these preliminary experiments.

Inserting the correction for the variation of the temperature gradient in the flow-tube, by subtracting $h^2/3JsQ$ from each of the corresponding values of D, and then calculating as before, we find the corrected results given in the last column, which exceed those calculated on the elementary theory by nearly one part in 700. It should be remarked that this correction can be deduced with certainty from (1) and (3) without reference to (2). It cannot be calculated satisfactorily from three flows, as it depends on small differences.

### (36.) *Correction of Results with Water Calorimeter.*

In applying the correction to the water calorimeter, it is necessary to take some account of the heat-loss from the outflow-tube round the thermometer bulb, as well as that from the fine flow-tube. This changes the numerical factors, which depend to some extent on the dimensions of the tubes, but the theory of the correction is otherwise unchanged. Assuming the heat-loss from the thermometer bulb to be two-fifths of the whole, which is sufficiently exact, since the whole correction is very small and a change of one-tenth in the ratio would not alter the result by more than 2 or 3 per cent. of itself, equation (10) becomes

$$EC/d\theta - Js_0Q = D = Js_0Qd + h_0(1 - ad\theta/10) + h_0^2\, 11/25JsQ \quad . \quad . \quad (12),$$

and the correction to be added on this account to the value of the specific heat in joules, as calculated by Dr. BARNES, is given by the expression

$$\text{Correction for Variation of Gradient with Flow} = + 11h_0^2/25JsQ'Q'' \quad . \quad (13)$$

In calculating this correction it is desirable to use the corrected value of $h_0$, which is obtained from that of $h$ as given by Dr. BARNES by adding the terms

$$\text{Correction to value of } h = + ah\,d\theta/10 - (11h^2/25Js)(1/Q' + 1/Q'') \quad . \quad (14).$$

The standard value of $Js_0$ assumed in reducing the tables in the case of water for calculating the value of D, was the British Association unit of 4·200 joules. Inserting this value, and putting $a = \cdot 0039$, we have the numerical formulæ

$$\text{Correction to } h = + \cdot 00039 h \, d\theta - \cdot 105 h^2/Q' - \cdot 105 h^2/Q''.$$
$$\text{Correction to } J = + \cdot 105 h_0^2/Q'Q'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15).$$

These formulæ are to be employed in correcting the results for the specific heat of water given in the summarized tables (BARNES, p. 243).

In cases where more than two flows are available at the same time and under the same conditions, it is naturally possible to obtain a more reliable value for the result by utilising all the flows, so as to minimize the effect of accidental errors. The accuracy of the work may then be verified by comparing the observed values of D for each flow with those calculated by equation (12). As an illustration we may take observations I. and II. with calorimeter D (BARNES, p. 243), which are also selected by Dr. BARNES as an experimental verification of the elementary theory.

TABLE IX.—Correction for Variation of Gradient in Flow-Tube.
Specific Heat of Water. Observations I. and II. (BARNES, Table XVIII., p. 243),
Calorimeter, D.

| Number of flow | (1) | (2) | (3) | (4) | (5) | Mean of 2, 3, 4 |
|---|---|---|---|---|---|---|
| Flow, Q, gramme per second | ·6741 | ·3993 | ·3902 | ·4967 | ·2482 | ·4287 |
| $h_0$, watts per degree | ·06975 | ·06975 | ·06975 | ·06975 | ·06975 | ·06975 |
| $\cdot 0039 h_0 \, d\theta/10$ | − ·00021 | − ·00022 | − ·00022 | − ·00022 | − ·00022 | − ·00022 |
| $\cdot 105 h_0^2/Q$ | + ·00076 | + ·00128 | + ·00132 | + ·00103 | + ·00207 | + ·00120 |
| $- \cdot 0190Q$ | − ·01281 | − ·00758 | − ·00741 | − ·00944 | − ·00471 | − ·00815 |
| D, calculated | (·05749)* | ·06323 | ·06344 | ·06112 | ·06689 | (·06258)* |
| D, observed | ·05749 | ·06317 | ·06318 | ·06135 | ·06691 | ·06257 |
| $\cdot 07145 - \cdot 00207Q$ | (·05749)* | ·06318 | ·06337 | ·06117 | ·06631 | (·06257)* |

The last column gives the mean of the three intermediate flows, which has been combined with the first flow in the calculation of the results. The second line gives the approximate values of the flows, which are required in working out the results.

The next four lines give the values of the several terms in equation (12) for the calculation of D. The two unknown quantities $h_0$ and $Jsd$ are calculated by assuming the values of D enclosed in brackets for (1) and the mean of (2, 3, and 4).

The values of D "calculated" are obtained by adding the numbers in the four lines above, and are corrected for the effect of variation of the gradient in the fine flow-tube. The values D "observed," given in the next line, are taken from the tables, and are found by subtracting 4·2Q from $EC/d\theta$.

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* Assumed in the calculation of $h_0$ and $d$.

The last line contains the values of D calculated on the elementary theory, neglecting the variation of the gradient, assuming the same two values (1) and (2, 3, 4), and taking the heat-loss per degree constant. This assumption gives $h = \cdot07145$ for the heat-loss, and $Jsd = - \cdot00207$ joule per gramme degree for the defect of the specific heat from 4·200.

Comparing the observed and calculated values of D on the two assumptions, we see that the relatively large discrepancy of ·00060 on the elementary theory in the value calculated for the small flow (5), is exactly accounted for by the correction for variation of the gradient in the flow-tube.

The effect of applying the correction in this particular case is to increase the value of the specific heat from 4·1793 to 4·1810, *i.e.*, by 4 parts in 10,000. This correction is very small, but it cannot be neglected, because it is systematic. Besides, it is much larger than the errors of observation, which rarely amount to so much as 1 in 10,000 on a single flow with a rise of 8°.

In the discussion of these observations, Dr. BARNES (§ 5, p. 226) concludes, from the close agreement of the observed and calculated values of the heat-loss for the larger flows, that the elementary theory is valid and requires no correction, provided that the flow exceeds a certain limit, about ·35 gm./sec. But the agreement for the larger flows results merely from his method of calculation, and is no evidence that the correction is negligible. The need for the correction could not arise *per saltum* below a certain limit, as he suggests.

The existence of the correction is obviously required by theory, and it is a remarkable verification of the accuracy of his observations that the small apparent discrepancy on the smaller flows, which he was prepared to attribute to some unknown source of error, should be so nearly accounted for by the variation of temperature distribution with flow, which is a necessary consequence of the method adopted.

In going through the summary of observations (BARNES, Table XVIII.), it may be noticed that there is generally a small systematic error of this nature in the results, as calculated on the elementary theory, tending to make the value of the specific heat smaller, the smaller the flows from which it is calculated. It would not, however, be worth while to recalculate the whole in detail as above illustrated, because the correction is so small that it may reasonably be applied to the observations as a whole.

In any particular case, for a pair of flows, the correction can most easily be applied by means of the numerical formulæ (15) already given. This will not give the best results, if more than two flows are available, but the residual errors will then be accidental, so far as this particular correction is concerned. A few examples of this method of correction, taken from the first few experiments at 29°·10 C. with calorimeter C, are given in the following table. The heat-loss in this calorimeter was much smaller than in calorimeter D, owing to a better vacuum and a smaller flow-tube. The correction is consequently smaller, and its effect is more obscured by accidental errors, but so far as it goes, it tends to bring the observations into better agreement.

TABLE X.—Correction for Variation of Gradient in Flow-Tube, Calorimeter C.

| Number of Experiment. | Values of Flow. | | Heat-Loss $h$ per 1°. | | Specific Heat in Joules. | |
|---|---|---|---|---|---|---|
| | Q′. | Q″. | Table. | Reduced. | Table. | Corrected. |
| III. | ·665 | ·399 | ·04944 | ·04859 | 4·1803 | 4·1813 |
| IV. | ·501 | ·258 | ·05123 | ·04989 | 4·1771 | 4·1791 |
| V. | ·660 | ·392 | ·04937 | ·04859 | 4·1795 | 4·1805 |
| VI. | ·590 | ·375 | ·04965 | ·04882 | 4·1790 | 4·1802 |

The general effect of the correction here is to raise the values by about 1 in 4000 for the larger pairs of flows. The discrepancy between Experiments III. and IV. is mainly due, as the values of D show, to accidental errors of the small flows in opposite directions. The mean value 4·1803 agrees very well, allowing for the difference of temperature, with the value 4·1810 deduced from observations I. and II. with calorimeter D at 28°·0 C., which would give 4·1805 at 29°·10 C.

### (37.) *Variation of the Gradient-Correction with Temperature.*

The importance of this correction arises chiefly from the fact that the value of the heat-loss increases with rise of temperature for any calorimeter. As a result, the correction, which depends on the square of the heat-loss, is considerably larger at higher temperatures, and thus affects the curve of variation of the specific heat as well as the absolute values. If the correction were constant, it would affect only the absolute values, which would matter little owing to the uncertainty of the electrical units.

As an illustration of the greater importance of this correction at higher temperatures, the last four observations (BARNES, Series 8, Table XVIII.) are given in the next table, reduced and corrected in a similar manner. Although these observations do not include any exceptionally small values of the flow, the correction at the higher points nearly reaches 1 in 1000 owing to the larger value of the heat-loss.

TABLE XI.—Correction for Variation of Gradient in Flow-Tube, Calorimeter C, Series 8.

| Number of Experiment. | Temperature, Centigrade. | Values of Flow. | | Heat-Loss per 1°. | | Specific Heat in Joules. | |
|---|---|---|---|---|---|---|---|
| | | $Q'$. | $Q''$. | Table. | Reduced. | Table. | Corrected. |
| | ° | | | | | | |
| LII. | 74·05 | ·621 | ·384 | ·08469 | ·08198 | 4·1920 | 4·1950 |
| LIII. | 91·55 | ·644 | ·402 | ·10011 | ·09643 | 4·2017 | 4·2055 |
| LIV. | 80·38 | ·617 | ·388 | ·09218 | ·08891 | 4·1951 | 4·1986 |
| LV. | 68·21 | ·603 | ·388 | ·08283 | ·08011 | 4·1890 | 4·1919 |

The effect of the correction on the curve of variation of specific heat is most readily appreciated by taking the approximate formula for the variation of the heat-loss with temperature, given by Dr. BARNES, p. 253, which, when slightly reduced to allow for the correction of the value of $h$ given in equation (15), becomes

$$h = \cdot 0300 + \cdot 00070t \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (16).$$

This formula represents the experimental results very fairly, except for the lower temperatures in the neighbourhood of 0° C. It leads to the following values of the corrections for the specific heat in joules and calories.

TABLE XII.—Variation of Gradient-correction with Temperature, and Corrected Values of Specific Heat of Water.

| Temperature, Centigrade. | Heat-Loss. | | Correction $\cdot 105\ h_0^2/Q'Q''$. | | Results, 1900, Corrected. | Reduced to H scale. |
|---|---|---|---|---|---|---|
| | Formula (16). | $E\theta^4$. | Joules. | Calories. | | |
| ° | | | | | | |
| 0 | ·0300 | ·033 | ·00038 | ·00009 | 1·0080 | 1·0084 |
| 10 | ·0370 | ·039 | ·00058 | ·00014 | 1·0029 | 1·0031 |
| 20 | ·0440 | ·045 | ·00082 | ·00019 | 1·0000 | 1·0000 |
| 30 | ·0510 | ·051 | ·00109 | ·00026 | 0·9987 | 0·9986 |
| 40 | ·0580 | ·058 | ·00141 | ·00034 | 0·9986 | 0·9984 |
| 50 | ·0650 | ·066 | ·00177 | ·00042 | 0·9993 | 0·9989 |
| 60 | ·0720 | ·074 | ·00218 | ·00052 | 1·0005 | 1·0000 |
| 70 | ·0790 | ·083 | ·00263 | ·00063 | 1·0018 | 1·0013 |
| 80 | ·0860 | ·094 | ·00312 | ·00074 | 1·0033 | 1·0027 |
| 90 | ·0930 | ·105 | ·00364 | ·00087 | 1·0048 | 1·0041 |
| 100 | ·1000 | ·117 | ·00420 | ·00100 | 1·0062 | 1·0055 |

In calculating the correction, the value of the product $Q'Q''$ is taken as $\cdot 64 \times \cdot 39 = \cdot 25$, which represents fairly the values of the larger pair of flows on which the results mainly depend. The corrections calculated from the actual numbers in the tables are, as a rule, slightly larger than those calculated from the formula for the heat-loss, but the latter are usually within 1 in 10,000 of those observed.

It may be interesting to remark that formula (16) gives a mean rate of increase of the heat-loss which is proportional to the fourth power of the absolute temperature over the range 0° to 80°. The fourth power law is well known to represent heat-loss by radiation with considerable accuracy over a moderate range at ordinary temperatures under conditions similar to those of this experiment. Values of the heat-loss calculated according to the fourth power law starting from the same value at 30° C., are given, for comparison, in the third column, headed $E\theta^4$. They represent the experimental numbers rather better than the linear formula (16) at temperatures below 30°, but give results which are a little too high at 80° and 90°. The corrections in the table have been calculated from the linear formula, but the difference would be very slight over the greater part of the range.

The values of the specific heat given in the column headed "Results, 1900, Corrected," are obtained from those calculated by the formulæ given by BARNES, 'Proc. Roy. Soc.,' 1900, p. 242, by adding the correction in calories given in the previous column, and expressing the results in terms of a unit at 20° C., instead of the unit at 16° employed by BARNES. Although the values of the corrections are worked to the next figure, I have not considered it desirable to give the values of the specific heat beyond 1 part in 10,000.

It happens, by a curious coincidence, that the correction for the variation of the temperature gradient is very nearly equal and opposite to the correction required to reduce the results to the hydrogen scale, if calculated, as previously explained in Section 23, from the observations of JOULE and THOMSON for air at a constant pressure of 76 centims. The values given in the last column, reduced to the hydrogen scale, are practically identical with those calculated directly from BARNES' formulæ without correction, except that they are expressed in terms of a unit at 20° C., and are corrected for an obvious misfit of the formulæ at 55° C. (see §46).

## PART V.—DISCUSSION OF RESULTS.

### (38.) *Meaning of the Term "Specific Heat."*

The term "specific heat" is here employed as an abbreviation for the phrase "specific capacity for heat," or "thermal capacity of unit mass," *i.e.*, the quantity of heat per unit mass per degree required to raise the temperature of a substance. In a similar manner, "specific electrical resistance" or "resistivity" of a substance is understood to mean the resistance of the material per unit area of section per unit length. On this understanding, specific heat may be measured in terms of any convenient unit, either in joules per gramme per degree Centigrade, or in foot-pounds per pound per degree Fahrenheit, without any implied reference to the properties of water. On the other hand, it is not unusual in elementary text-books to define specific heat as the *ratio* of the thermal capacity of a given mass of the substance considered to that of an equal mass of *water* at a standard temperature. The two definitions lead to the same numerical results, provided that the unit of heat is the thermal capacity of unit mass of water at the standard temperature. But there is nothing in the derivation of the term "specific heat" to imply that it denotes a ratio with respect to water at a standard temperature, and I think that this definition unduly restricts the meaning, and has given rise indirectly to a good deal of confusion.

### (39.) *Choice of a Standard Temperature for the Thermal Unit.*

In addition to the absolute unit of heat, which is naturally the same as the unit of mechanical energy, it is necessary for practical calorimetry to adopt as a standard of reference a thermal unit equal to the quantity of heat required to raise unit mass of water one degree at a standard temperature. For purely academic purposes, it would suffice to adopt either of the time-honoured standards at 0° C. or 4° C., which have been frequently proposed, and are still to be found in the majority of text-books. But it has been conclusively shown that the specific heat of water at these low temperatures is considerably higher than over the range which is commonly employed for calorimetric determinations. The units at 0° and 4° would be practically inconvenient on this account. A still more serious objection is that the specific heat at these temperatures cannot readily be determined with the same order of accuracy as at ordinary temperatures. The unit of 4·200 joules proposed by the British Association Committee, which was supposed at that time to represent the specific heat of water in joules per gramme degree at 10° C., is open to the additional objection that it is really an absolute unit in disguise, and that, as such, it is superfluous, and does not satisfy the requirement of a thermal unit defined in terms of the specific heat of water at a definite temperature.

For practical purposes, it is evidently necessary to define the thermal unit in terms of the mean specific heat *over a range* of temperature rather than at a definite point. The range of 1°, which is generally taken in definitions, is evidently too small for the accurate measurement of the rise of temperature in terms of the fundamental interval. These very small ranges of temperature have frequently been employed in calorimetry, as in JOULE's earlier experiments, for the purpose of reducing the uncertain correction for external heat-loss; but with modern appliances for accurate thermal regulation, and provided that the duration of the experiment is not unduly prolonged, it is quite possible to employ a rise of 10° or more without the uncertainty of the heat-loss exceeding the probable theormometric error.

So far as the thermometric error alone is concerned, the obvious interval to select is the fundamental interval itself. For this reason, the "mean calorie," which is equal to one-hundredth part of the quantity of heat required to raise the temperature of a gramme of water from 0° to 100° C., has been often proposed as the most suitable thermal unit. But in this case the calorimetric difficulties due to the large range of temperature are so exaggerated that the relation of the mean calorie to the practical unit employed in calorimetry cannot be determined with the same order of accuracy as the practical unit itself can be realized. This point is further illustrated in Section 45 below. An equivalent proposition is to select as the standard temperature for the definition of the thermal unit that temperature at which the specific heat is equal to its mean value over the fundamental interval. The objection to this is that it leaves the standard temperature uncertain. If, however, a definite temperature of either 15° or 20° C. were selected, we should have a definite unit, which would probably be within one part in a thousand of the mean calorie, or near enough for all practical purposes.

On the whole, a range of 10° appears to be the most appropriate to adopt for the practical definition of the thermal unit. ROWLAND'S results for the specific heat were calculated in this manner by taking the mean value over each interval of ten degrees. GRIFFITHS also adopted a range of ten degrees, 15° to 25°, in his experiments, and his results may be held to refer to the mean of this range, which is also very close to the mean of the range, 18° to 20°, of SCHUSTER and GANNON'S experiments. For this reason, I have been in the habit for some years of expressing results in terms of the mean specific heat of water over the range 15° to 25° C., which is, within 1 part in 20,000, the same as the value *at* 20° C. The mean thermal unit over this range may conveniently be called the "calorie *at* 20° C.," although of course it cannot be practically realized except as the mean over a range.

The preliminary results for the variation of the specific heat of water communicated to the British Association at the Dover meeting in 1899, were expressed in terms of the calorie at 20° C. I have thought it important to retain this unit in the present paper to avoid confusion, although Dr. BARNES and Mr. GRIFFITHS* have since proposed units at 16° and 15° respectively, as being probably closer in magnitude to the mean calorie between 0° and 100° C. From a scientific point of view there is little to choose between these units, and the relation between them is known with a high degree of accuracy; but as a question of practical calorimetry, I think the unit at 20° is undoubtedly superior. In all accurate calorimetric work it is necessary to employ thermal regulators, and there can be no doubt that from this point of view the range 10° to 20°, corresponding to the unit at 15° C., is too low. The range 20° to 30° would be better for temperature regulation than 15° to 25°, but I adopted the latter as corresponding to the mean of ROWLAND'S, and GRIFFITHS', and SCHUSTER'S experiments, and as agreeing more nearly with the mean range of an ordinary

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* More recently, GRIFFITHS ('Thermal Measurement of Energy,' Cambridge, 1901) has proposed to adopt the calorie at 17·5° C., or the mean value over the range 15°–20° C.

calorimetric experiment without a thermal regulator. It might be objected that SCHUSTER (range 18° to 20°) and LÜDIN (range 11° to 18°) found it necessary to keep the calorimeter always *below* the temperature of its surroundings, in order to avoid readings on a stationary or falling temperature, which are quite unreliable with a mercury-thermometer, owing to capillary friction. But even in this case it would be better to use a regulator at 25°, to avoid any risk of cooling the calorimeter below the dew-point, if a range of 10° is required.

### (40.) *Choice of a Standard Scale of Temperature.*

An equally important question in the definition of the practical thermal unit is the choice of the scale of temperature to which it should be referred. There would probably be little hesitation in selecting the scale of the constant-volume hydrogen-thermometer at 1 metre initial pressure; but this necessitates the further consideration of the secondary standard by which the practical unit is to be realized, as it would of course be quite impossible to employ the hydrogen-thermometer at constant-volume *directly* in a calorimetric experiment. The mercury-thermometer, which is regarded at present as the representative of the normal scale, is a most unsatisfactory instrument for accurate calorimetric work. Some of its defects in this respect have already been incidentally mentioned, and it is impossible to regard with confidence results obtained by its use under conditions so different from those of the comparison with the ultimate standard. The only satisfactory method of standardizing a mercury-thermometer under the conditions of experiment, is by comparison with a platinum-thermometer. In the great majority of cases it would be far less trouble to discard the mercury-thermometer in accurate work and employ the platinum-thermometer itself. The results could be nominally reduced to the hydrogen scale in the manner described in the present paper, with an accuracy which is limited only by the gas-thermometer. But though nominally expressed in terms of the hydrogen scale, and subject to all the uncertainties of gas-thermometry, the results would have the advantage of being really referred to a practical scale which could be reproduced at any time with an accuracy depending only on that of the original observations.

Although it is very generally admitted that the platinum-thermometer is the most accurate instrument for scientific work, it is also commonly assumed that the mercury-thermometer is much easier to work with. This is quite a mistake if an accuracy of the order of ·001° C. is aimed at. If anyone wishes to realize the incalculable simplification introduced into accurate work by the employment of platinum-thermometers instead of mercury, even over the range 0° to 100° C., he should try to perform an experiment like the present. After endless labour spent in calibrating and standardizing a suitable series of limited scale-thermometers, he would probably find all his observations spoilt by uncertainties of stem exposure and capillary friction, and more particularly by unknown changes of zero at the higher points of the range.

It is no exaggeration to say that this investigation could not have been carried out successfully without the direct employment of platinum-thermometers.

### (41.) *The Work of* REGNAULT.

The work of REGNAULT ('Mémoires de l'Institut,' Paris, 1847) on the specific heat of water by the method of mixture at temperatures between 110° C. and 190° C., represents the only evidence at present available on the variation of the specific heat at high temperatures. It was carried out on a large scale with his usual experimental skill, and is undoubtedly entitled to great weight; but there are large discrepancies in several cases between the recorded data and the calculated results, and very little is known of the scale of the thermometers employed in the work.

The total capacity of the calorimeter employed was about 110 kilogs. At each experiment 10 kilogs. of cold water was drawn off, and the same amount of hot water, at a known temperature, was introduced from a high-pressure boiler. The rise of temperature varied from 8° to 15°, according to the initial temperature of the hot water, and was read to the hundredth of a degree. The discrepancies in the observations taken at any one point under similar conditions are of the order of ·5 per cent. The results have been recalculated from the data columns by J. M. GRAY ('Proc. Inst. Mech. Eng.,' 1889), who finds in several cases disagreements amounting to from 2 to 4 per cent. In all these cases it appears that the total recorded quantity of water considerably exceeded the capacity of the calorimeter. As the result of a careful enquiry, GRAY concludes that REGNAULT'S calculations are probably right, and that the apparent discrepancies in the data arise from deficient information or erroneous entries.

It would appear to be hopeless at the present time to make any corrections to the readings of the thermometers employed for observing the temperature of the hot water, beyond those which REGNAULT himself applied. The principal source of uncertainty lies with the calorimetric-thermometers, as REGNAULT was unable to obtain any consistent evidence of deviation from the scale of the air-thermometer between 0° and 100° C., and did not apply any correction from the mercurial to the absolute scale. Moreover, no allowance was made for the temporary depression of zero to which French "*cristal*" thermometers appear to be particulary liable. Some thermometers of this class show a depression of as much as half a degree after heating to 100° C. If such a thermometer is suddenly immersed in steam, its reading rapidly rises to a maximum, and then slowly falls for half an hour or so towards its steady reading. In using a mercury-thermometer in a calorimeter, where it is exposed to a sudden rise of temperature, the effect of this phenomenon is to make the observed rise of temperature too large. The maximum reading is always taken, with additive corrections to represent the subsequently observed rate of cooling. At the time of reading the maximum, the zero depression has not had time to produce its full effect, owing to the suddenness of the rise, and it therefore tends to increase slightly the subsequent rate of fall. In graduating the thermometer, or comparing it with an air-thermometer, the readings are taken at steady temperatures, so that the zero depression has time to produce its full effect. These steady readings will be systematically lower than the instantaneous readings obtained on suddenly heating the thermometer. Unless the method of variable zero is employed in taking the observations, it is quite impossible to apply an accurate correction, since the depression in any given case depends so much on the past treatment of the thermometer, especially in the case of French "*cristal*" glass. It is possible, however, to assert that the probable effect would be to produce an error in the observed rise of temperature approximately proportional to the rise, and therefore nearly proportional to the excess of temperature of the hot water, since the same weight of water was employed in all the experiments. The corresponding error in the value of the mean specific heat deduced would therefore be nearly constant on the average, although no doubt the variations of the zero depressions in consecutive experiments may be responsible for some of the individual discrepancies. The possible limit of error from this source would be about 5 parts in 1000, allowing for the effect of the zero depression in accelerating the apparent rate of cooling, which would tend to increase the error. The *probable* effect would be to make the specific heat, as calculated by REGNAULT, about 2 or 3 parts in 1000 too large.

The correction of REGNAULT'S thermometers to the hydrogen scale cannot be applied with any certainty without recovering the original instruments, as different thermometers of the same glass often differ considerably, and so much depends on the exact method of treatment. But if we assume GUILLAUME'S tables for modern thermometers of similar glass, the correction to the values of the specific heat would be of the order of 3 parts in 1000 in the direction of reducing REGNAULT'S results, and would be nearly constant for the different observations.

Including both sources of error, we should infer that REGNAULT'S values for the mean specific heat may require to be reduced by a constant correction of 5 or 6 parts in 1000.

Although it is evident that some correction is necessary, I should hesitate to assume the above estimate without experimental corroboration. I find, however, as explained in the 'Brit. Assoc. Rep.,' 1899, that a correction of precisely this order of magnitude is required to make REGNAULT'S observations of the mean specific heat between 20° and 110° C., agree with those of REYNOLDS and MOORBY, between 0° and 100°, and with those of BARNES, between 40° and 90° C. The correction also makes REGNAULT'S observations at 110° agree much better with his own observations at higher temperatures. It has the further advantage of being the simplest, as well as the most probable kind of correction to apply. I therefore proposed in 1899 to adopt REGNAULT'S formula provisionally for the higher temperatures, merely subtracting the constant quantity ·0056 from his values of the specific heat, in order to make them agree with the curve of variation deduced from the present investigation at a temperature of 60° C. Thus modified, the formula for the specific heat $s$ at a temperature $t$ is as follows :—

$$\text{From } 60^\circ \text{ to } 200^\circ\text{ C. } s = {\cdot}9944 + {\cdot}00004t + {\cdot}000{,}000{,}9t^2 \quad . \;\; . \;\; . \quad (1).$$

Regnault's formula for the *mean* specific heat would require further modification, as it is of course quite erroneous between 0° and 60°. But it is really of comparatively little use to tabulate the mean specific heat. The quantity most often required is the total heat $h$ from 0° to $t$. If we adopt as unit the specific heat of water at 20° C., the total heat from 0° to 60° is 60·020. The value of the total heat $h$ above 60° is then represented by the formula,

$$(\text{Above } 60^\circ)\ h = +\ {\cdot}220 + {\cdot}9944t + {\cdot}000{,}02t^2 + {\cdot}000{,}000{,}3t^3 \quad . \;\; . \quad (2),$$

which differs from Regnault's formula only in the first two terms, and is deduced from the formula (1) for the specific heat at $t$ by integration, and addition of a suitable constant to make the value right at 60° C.

To find the mean specific heat between any two arbitrarily selected temperatures, which is often required in reducing calorimetric observations, the simplest method of procedure is usually to take the difference between the values of $h$ corresponding to the integral values nearest to the extremes of the range, and divide by the whole number of degrees between the values taken. This will generally give a result which is accurate to 1 in 10,000. If the range is less than 10° the order of accuracy will be proportionately less; but this is immaterial, as the same will probably be true of the observations themselves with which the comparison is required.

The work of Pfaundler and Platter, of Hirn, of Jamin and Amaury, and of many other experimentalists who succeeded Regnault, appeared to indicate much larger rates of increase than he had found; but there can be little doubt that the discrepancies of their results, which often exceeded 5 per cent., were due to lack of appreciation of the difficulties of the problem. Before the time of Rowland's experiments in 1879, sufficient attention had not been paid to the thermometry, and the results were of comparatively little value.

### (42.) *The Work of* Rowland.

It is unnecessary to give any description or criticism of Rowland's work, which is generally recognised as being the most accurate determination of the mechanical equivalent of the thermal unit at ordinary temperatures. Rowland himself considered that his results were probably correct to at least 1 in 500, and that the greatest uncertainty lay in the comparison of the scale of his mercury-thermometers with the air-thermometer, which was the most difficult part of the work. His thermometers have recently been compared with a mercury-thermometer standardized at Paris, and with a platinum-thermometer standardized by GRIFFITHS. The result has been to reduce the rate of change of specific heat shown by his original calculations by nearly one-half, but the absolute value of the specific heat about the middle of the range remains almost unchanged. The accuracy of his results in terms of the hydrogen scale has probably been raised to 1 in 2000 on the average by this correction; but it must be remembered that the thermometers were compared at steady temperatures, and not under the actual conditions of the experiment on a steadily rising temperature. This may affect the validity of some of the conclusions.

In ROWLAND'S experiments, the most striking difference from ours is the sharp minimum at 30° followed by a rapid rise. ROWLAND himself considered that at 30°, owing to the increasing magnitude and uncertainty of the radiation correction, "there might be a small error in the direction of making the equivalent too great, and the specific heat might go on decreasing to even 40°." It should be remembered that his method gives directly the total heat reckoned from the start of each experiment, and that the values of the specific heat over shorter ranges would be more affected by thermometric errors, especially near the ends of the range. If our results are compared with his by means of the *total heat* starting from the same value at 5° C., it will be seen that, in spite of the apparent dissimilarity in the forms of our curves for the specific heat, our values of the total heat do not differ from those of ROWLAND by more than 1 in 5000 over the whole range of his experiments. This is shown in the following table :—

TABLE XIII.—Values of Total Heat of Water compared with ROWLAND.

| Temperature, Centigrade. | Total Heat, CALLENDAR and BARNES. | Total Heat, ROWLAND. |
|---|---|---|
| ° 5 | 5·037 | 5·037 |
| 10 | 10·056 | 10·058 |
| 15 | 15·065 | 15·068 |
| 20 | 20·068 | 20·071 |
| 25 | 25·065 | 25·067 |
| 30 | 30·060 | 30·057 |
| 35 | 35·052 | 35·053 |

### (43.) *The Method of Mixture.* LÜDIN.

The experiments of BARTOLI and STRACCIATI ('Boll. Mens. dell' Acc. Gioenia,' 18, Ap., 1891), by the method of mixture between 0° and 30°, gave a curve very similar to ROWLAND'S, but with a minimum at 20° C. This excessive lowering of the minimum may probably be attributed to constant errors inherent in their methods of experiment.

The later work of LÜDIN (Zurich, 1895), under the direction of Professor PERNET, extending from 0° to 100° C., requires further notice on account of the wider range of the experiments, and the great attention paid to the thermometry. He employed mercurial thermometers of the Paris type, with all the usual precautions. He adopted the method of mixture, adjusting the quantity of hot water in each case to give the same rise of temperature, from 11° to 18°, in the calorimeter. The discrepancies of individual measurements at any one point do not exceed ·3 per cent., but he did not vary the conditions of experiment materially, and it may be questioned whether the well-known constant errors of the method could have been eliminated by the devices which he adopted. His results (see Table XIV., p. 144) give a minimum at 25° and a maximum at 87° C., the values being ·9935 and 1·0075 respectively, in terms of the mean specific heat between 0° and 100°. The rapid rise from 25° to 75° may possibly have been due to radiation error from the hot water supply; and the subsequent fall between 90° and 100° to the inevitable loss of heat by evaporation of the nearly boiling water on its way to the calorimeter. His values, reduced to a unit at 20° C., are given for comparison in Table XIV. The agreement with our values is remarkably close at the lower temperatures; but the difference at 80° amounts to nearly 1 per cent. In addition to the fact that his curve cannot easily be reconciled with REGNAULT, there is this theoretical difficulty in accepting his values at higher temperatures. The quantity which he actually observed was the *mean* specific heat between the higher temperature and the final temperature of his calorimeter. His values of the specific heat itself were obtained by differentiating the curve, and really depend on small differences at the higher points between observations which are themselves difficult and uncertain. His values for the *mean* specific heat differ much less from ours. The peculiar advantage of the method we adopted is that the specific heat itself is determined over a range of 8° to 10° at each point by adding accurately measured quantities of energy to the water at the desired temperature. There is no possibility of evaporation or heat-loss in transference as in the method of mixture, and the protection from external radiation is much more perfect.

### (44.) *The Work of* MICULESCU.

The work of MICULESCU ('Ann. Chim. Phys.,' XXVII., p. 202, 1892), though not directly affecting the question of the variation of the specific heat, is interesting as an example of a steady-flow method of calorimetry. The apparatus consisted of a Joule calorimeter mounted horizontally, with the paddles directly driven by an electric motor, the torque being observed by the "cradle-method" of DÉSPRETZ and BRACKETT. The heat generated was measured by passing a steady current of water round the calorimeter, and observing with a platinum-iron thermocouple the rise of temperature of the stream. The rate of heating was about 50 calories per second, the rise of temperature 2°, and the capacity of the calorimeter about 3 litres. The work has been criticised by SCHUSTER, and also by AMES ('Paris Congress Reports,' 1900) on the ground that the length of the lever by which the torque was measured was apparently taken as 28 centims. without verification. M. GUILLAUME replies in a footnote that the length would probably in any case be accurate to a tenth of a millim., or 1 in 2800 (which is about the limit of accuracy claimed for the best absolute measurements of the mechanical equivalent), but regrets that the original lever cannot be found for the purpose of verification. It appears, however, from the description given by MICULESCU, and also from the wood-cut of the apparatus, that the weight was not supported on a knife-edge but suspended from *a round hook* clamped to the lever with a screw, so that it would be a matter of some difficulty to estimate the effective length. Moreover, it would be very difficult with a platinum-iron couple to measure so small a difference as 2° with a degree of accuracy higher than ·01°, and MICULESCU does not mention some of the necessary precautions. In addition, the correction for the external loss of heat from the calorimeter by radiation and conduction was regarded as being negligible in comparison with the heat-supply, and no correction was applied for it. It is easy to estimate, however, from the dimensions of the apparatus, that it could not have been much less than 0·5 per cent., and that it was probably larger on account of the smallness of the interval between the calorimeter and the jacket, which would considerably increase the heat-loss by conduction and convection through the air space. There are several other indications in the paper that the author did not really aim at a higher order of accuracy than 1 per cent., which is about the limit usually reached in engineering experiments, and that the work should be regarded rather as an illustration of a method than as a serious absolute determination.

### (45.) *The Work of* REYNOLDS *and* MOORBY.

The work of REYNOLDS and MOORBY ('Phil. Trans.,' A, 1897), on the mean specific heat between 0° and 100° C. in absolute measure, stands in the same category as that of ROWLAND as an accurate determination of the mechanical equivalent. The two are not directly comparable, but if we assume the rate of variation of specific heat found in our experiments as the medium of comparison, the result of REYNOLDS and MOORBY would give 4·179 for the number of joules in one calorie at 20° C., at which point ROWLAND'S corrected results give 4·181. If we took LÜDIN'S table, we should find 4·157. The formula of WINKELMANN* gives 4·133, and that of REGNAULT 4·167. The comparison of REYNOLDS and MOORBY with ROWLAND is therefore a confirmation to some extent of the accuracy of the present experiments, as compared with LÜDIN'S, or with formulæ proposed by other writers. On the strength of this comparison, I have generally adopted the mean value 4·180 joules per calorie at 20° C. as the most probable estimate of the "Mechanical Equivalent," assuming that the absolute value cannot be certain to a higher order of accuracy than 1 in 2000.

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* WINKELMANN, 'Handbuch der Physik,' Band 2, Abth. 2, p. 338.

It might, however, be claimed that either or both of the absolute determinations above cited were more accurate than this, and that the error lay with our comparison. It is a nice question whether the mean specific heat, which is practically independent of the scale of the thermometer employed, should be chosen as the standard of reference, rather than the specific heat at a particular temperature such as 20° C. on the scale of a particular thermometer. My own opinion is that the latter unit is the more practical, and the most accurately reproducible. It is not very difficult in a thermochemical experiment to measure a quantity of heat to 1 in 1000 with a suitable rise of temperature and a good thermometer with known scale errors. But it is quite impossible to realize the mean thermal unit to this order of accuracy without the most elaborate apparatus on a scale approaching that adopted by REYNOLDS and MOORBY.

The fundamental difficulty in the determination of the mean specific heat between 0° and 100° C. lies in the great range of temperature to be covered, and the consequent risk of excessive or uncertain loss of heat. REYNOLDS and MOORBY endeavoured to meet this objection by working on a very large scale, and succeeded in reducing the heat-loss to 5 per cent., even without the use of lagging. But in working on this scale they encountered peculiar difficulties, which were not overcome without great pains and ingenuity, and which must in any case have materially affected the order of accuracy attainable by their method. Owing to the employment of a steam-engine as motor, it was difficult to secure a high degree of steadiness in the conditions of running, and the outflow-thermometer could not be read more closely than a tenth of a degree owing to its incessant oscillations. The largest variation recorded in the two trials of which full details are given, was 4·9° F. in two minutes on the outflow temperature, and four or five revolutions per minute in 300 on the speed. The greater part of these variations being accidental would disappear in the mean, but it is probable that there would be systematic errors of the same order as the limit of accuracy of the instantaneous readings. In using so large a quantity of water, it was impracticable to deprive it entirely of air, which caused considerable trouble, owing to loss of heat by generation of steam in the air bubbles. Again it was naturally impossible to enclose the brake in a vacuum-jacket, or shield it from draughts and extraneous disturbances by means of an isothermal enclosure. The greatest uncertainty appears to have arisen from damp in the lagging, which caused the rejection of a number of trials. The correction for conduction along the 4-inch shaft was of much smaller magnitude, though probably more uncertain on account of the impossibility of determining the actual gradient in the shaft itself. The extreme limits of variation of the recorded results were from 776·63 to 779·46 foot-pounds, but considering that the main sources of error above mentioned were accidental, it is probable that the accuracy of the mean would be of a higher order than might be inferred from the separate experiments.

### (46.) *Empirical Formulæ.*

The usual method of representing the results of a series of observations like the present is to adopt an empirical formula of the type,

$$s = 1 + at + bt^2 + ct^3 + dt^4 + \&c., \quad . \; . \; . \; . \; . \; . \; . \quad (3),$$

and to calculate the values of the coefficients $a$, $b$, $c$, $d$, &c., by the method of least squares. This was, in fact, the method adopted by LÜDIN. It has the advantage of providing a simple and ready rule, which is very generally recognized and applied; but it appears to me that it is in reality liable to several objections. Too much weight is given to the observations at higher temperatures, which are necessarily less accurate than the rest. The results obtained are in a great measure dependent on the particular type of formula assumed, which is frequently inadequate to represent the phenomenon, and is generally quite unsuitable for extrapolation. Moreover, the method gives a fictitious appearance of completeness and accuracy, which is quite misleading, as the calculated values of the probable errors contain no reference to possible sources of *constant* error. It also generally happens that the terms of the empirical formula are large and of alternate sign, so that the small variation required is given as the difference between large quantities, which must be calculated to several figures in applying the formula. The following formula of LÜDIN supplies a good illustration of some of these points:—

$$\left.\begin{array}{llll} s = 1 - \cdot 00076668t & + \cdot 000019598t^2 & - \cdot 000{,}000{,}1162t^3 \\ \quad\;\; \pm \cdot 0000025 & \pm \cdot 000004 & \pm \cdot 000{,}000{,}03 \end{array}\right\} \; . \; . \; . \quad (4).$$

The probable errors of the several coefficients, as calculated by LÜDIN, are given in the second line below the coefficients to which they apply. The value of the specific heat at 100° C. on LÜDIN'S formula is made up as follows:—

$$\begin{array}{rll} s = 1 & - \cdot 076668 & \pm \cdot 00025 \\ & + \cdot 19598 & \pm \cdot 040 \\ & - \cdot 1162 & \pm \cdot 030 \\ \hline & 1 + \cdot 0031 & \end{array}$$

It is at once obvious that a formula of this type is quite unsuitable for the representation of the variation of the specific heat over the whole range 0° to 100° C. Moreover, since the maximum divergence of the specific heat from its mean value over the range 10° to 70° is only 2 parts in 1000, according to the present series of experiments, it is evidently desirable from a practical point of view to employ the simplest possible formulæ for its representation. The variation from unity over this range cannot be determined more closely than 2 or 3 parts in 10,000 (*i.e.*, 10 per cent. of the variation itself), so that it would appear ridiculous to employ coefficients with five significant figures in the formulæ.

For the above reasons, in the 'British Association Report,' 1899, the following simple formula was given as representing the results between 10° and 60° within the limits of accuracy of the observations, in terms of a unit at 20° C.—

$$s = \cdot 9982 + \cdot 000{,}0045\,(t - 40)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

It was stated that the variation of the specific heat near the freezing-point was apparently more rapid than the formula indicated, and could be approximately represented by the addition of the constant quantity ·020 calorie to the total heat. This correction to the formula has since been further verified, and may be represented by the addition of a small cubic term below 20°.

$$\text{Below } 20^\circ\text{ C. add to (5)} + \cdot 000{,}000{,}5\,(20 - t)^3 \quad . \quad . \quad . \quad . \quad (6).$$

At that time the observations had not been extended above 60°, and the formula of REGNAULT, emended as already described, was therefore adopted for the higher temperatures, namely,

$$\text{Above } 60^\circ \text{ to } 200^\circ\text{ C.} \quad s = \cdot 9944 + \cdot 000{,}04t + \cdot 000{,}000{,}9t^2 . \quad . \quad . \quad (7).$$

Shortly afterwards, Dr. BARNES succeeded in obtaining six observations at higher temperatures. One of these was vitiated by dissolved air, and another was incomplete. There remain four good observations, which could be represented within 1 part in 10,000 by the linear formula,

$$\text{From } 68^\circ \text{ to } 92^\circ. \quad s = 1 + \cdot 000{,}14\,(t - 60) \quad . \quad . \quad . \quad . \quad (8).$$

This formula gives a value nearly 1 part in 1000 lower than (7) at 90°, and it cannot be satisfactorily fitted on to REGNAULT's observations at higher temperatures. I think on the whole it would be better to retain REGNAULT's formula as previously emended, until further observations are available. Although the agreement of the four observations is so perfect among themselves, it is possible that they may be affected by a constant error of this order of magnitude, if all the difficulties of the work are rightly considered. Besides, the linear formula cannot represent the probable increase in the rate of variation of the specific heat at higher temperatures, which is theoretically required to account for the vanishing of the latent heat at 360° C., the critical temperature.

It would of course be easy to represent the observations a little more accurately in any particular part of the curve by using more complicated formulæ, but it is doubtful whether the advantage gained would be worth the extra complication, and the possible confusion caused by changing a formula already published and widely distributed.

Dr. BARNES ('Roy. Soc. Proc.,' vol. 67, p. 242) has proposed the following:—

From 5° to 37°·5,

$$s = {}^{\cdot}99733 + {}^{\cdot}000{,}0035\,(37{\cdot}5 - t)^2 + {}^{\cdot}000{,}000{,}10\,(37{\cdot}5 - t)^3 \quad . \quad . \quad (9).$$

From 37°·5 to 55°,

$$s = {}^{\cdot}99733 + {}^{\cdot}000{,}0035\,(37{\cdot}5 - t)^2 - {}^{\cdot}000{,}000{,}10\,(37{\cdot}5 - t)^3 \quad . \quad . \quad (10).$$

From 55° to 100°,

$$s = {}^{\cdot}99850 + {}^{\cdot}000{,}120\,(t - 55) + {}^{\cdot}000{,}000{,}25\,(t - 55)^2 \quad . \quad . \quad . \quad . \quad (11).$$

The first two formulæ differ only in the sign of the third term. They are not quite so simple and convenient for calculation as (5) above. The first formula does not represent the observations below 10° quite so accurately as formula (6), but both are probably within the possible limits of error. The mean divergence of the observations between 37°·55 and 5° from the second formula is about 3 parts in 10,000, and is rather greater than the mean divergence of the observations from the old formula (5). The agreement with the latter would be greatly improved if we reject the discordant observation No. XXII., in series 2 at 54°·61 (BARNES, p. 244), giving greater weight to the later observations, No. XXXII. in series 3 at 54°·57, and No. XLVIII., in series 6 at 51°·02. On the whole, the balance of probability appears to me to be in favour of retaining the older and simpler formula in preference to that since proposed by Dr. BARNES.

The third of the above formulæ, from 55° to 100°, does not fit with the second at 55°, the respective values being, (10) ·99893, and (11) ·99850. This is shown by the difference in Table XIV. between the values at 55° and 60° in the column headed "BARNES, Roy. Soc., 1900," which is only ·00016. The corresponding differences for five degrees on either side are 50° to 55°, ·00087; 60° to 65°, ·00061. There is also a considerable change of slope from ·000216 to ·000120 at 55°. It is, of course, necessary that the values should fit accurately at the point where the formulæ meet, and it is further desirable that there should *not* be a sudden change of slope. The first condition is accurately and the second very approximately satisfied by the old formulæ (5) and (7) at 60°.

The following table contains a comparison of the formula of LÜDIN and those of BARNES, with those previously published in the B.A. Report, 1899.

TABLE XIV.—Comparison of Formulæ.

| Temperature, Centigrade. | LÜDIN, 1895. | BARNES, Roy. Soc., 1900. | B.A. Report, 1899. | Values of J. |
|---|---|---|---|---|
| 0° | 1·0084 | 1·0084 | 1·0094 | 4·219 |
| 5 | 1·0051 | 1·0055 | 1·0054 | 4·203 |
| 10 | 1·0026 | 1·0031 | 1·0027 | 4·191 |
| 15 | 1·0009 | 1·0012 | 1·0011 | 4·185 |
| 20 | 1·0000 | 1·0000 | 1·0000 | 4·180 |
| 25 | 0·9998 | 0·9991 | 0·9992 | 4·177 |
| 30 | 0·9999 | 0·9986 | 0·9987 | 4·175 |
| 35 | 1·0006 | 0·9984 | 0·9983 | 4·173 |
| 40 | 1·0017 | 0·9984 | 0·9982 | 4·173 |
| 45 | 1·0030 | 0·9986 | 0·9983 | 4·173 |
| 50 | 1·0046 | 0·9991 | 0·9987 | 4·175 |
| 55 | 1·0063 | 0·9999 | 0·9992 | 4·177 |
| 60 | 1·0079 | 1·0001 | 1·0000 | 4·180 |
| 65 | 1·0094 | 1·0006 | 1·0008 | 4·183 |
| 70 | 1·0109 | 1·0013 | 1·0016 | 4·187 |
| 75 | 1·0123 | 1·0020 | 1·0024 | 4·190 |
| 80 | 1·0131 | 1·0027 | 1·0033 | 4·194 |
| 85 | 1·0137 | 1·0034 | 1·0043 | 4·198 |
| 90 | 1·0136 | 1·0041 | 1·0053 | 4·202 |
| 95 | 1·0129 | 1·0048 | 1·0063 | 4·206 |
| 100 | 1·0117 | 1·0055 | 1·0074 | 4·211 |

For the reasons already stated, the values in the above table are all expressed in terms of a unit at 20° C. for comparison, and are given to 1 part in 10,000 only. I am inclined to regard the values and formulæ corresponding to the column headed "B.A. Report, 1899," as being the most probable. The corresponding values of J, the number of joules per calorie, are calculated assuming the value 4·180 at 20° C.

### (47.) *Theoretical Discussion of the Variation of the Specific Heat.*

CLAUSIUS ('Mechanical Theory of Heat,' p. 180, translation, 1879) has calculated the specific heat of water at constant volume $C_v$ from that at constant pressure $C_p$ by means of the well-known equation,

$$C_v = C_p - T(dv/dT)_p\,(dp/dT)_v = C_p - T(dv/dT)_p^2/(dv/dp)_T \quad . \quad . \quad (12).$$

Taking REGNAULT'S values of $C_p$, KOPP'S values of the coefficients of expansion, and GRASSI'S values of the compressibility, CLAUSIUS finds the values,

| Temperature . . . . . . . | 0° | 25° | 50° |
|---|---|---|---|
| $C_p$, at constant pressure . . | 1·0000 | 1·0016 | 1·0042 |
| $C_v$, at constant volume . . . | 0·9995 | 0·9918 | 0·9684 |

DIETERICI ('WIEDEMANN'S Annalen,' vol. 57, p. 333) has repeated the calculation, employing ROWLAND'S values of the specific heat at constant pressure. He seems to argue that the variation of the specific heat at constant pressure as discovered by ROWLAND is of the character to be expected from the large variation of the specific heat at constant volume. I do not think, however, that we can fairly infer anything with regard to the variation of the specific heat at constant pressure from that at constant volume. The value of the latter can only be deduced by the aid of very uncertain data, and we have as yet no sure theoretical guide as to the way in which it ought to vary, apart from experiments on the specific heat at constant pressure.

The most remarkable facts about the specific heat of water are its great constancy over a considerable range, and its high value as compared with that of the solid or the vapour. The specific heat of liquid mercury is nearly the same as that of the solid, and both are about double that of the vapour at constant volume. The specific heat of water is double that of ice, and nearly three times that of steam at constant volume. If we adopt RANKINE'S hypothesis of a constant "absolute" specific heat for each kind of matter, we must admit that this absolute specific heat has a different value in different states.

J. MACFARLANE GRAY ('Proc. Inst. Mech. Eng.,' 1889), adopting RANKINE'S idea of a constant specific heat for "ideal" water, gives, without proof, the following formula for the total heat $h$ of water reckoned from 0° C.,

$$h = 1\cdot0106\ (\theta - 273) + \theta v\ dp/d\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (13),$$

in which the constant is the ideal specific heat, and $dp/d\theta$ is the rate of increase of the steam-pressure with temperature. The term $\theta v\ dp/d\theta$ is evidently intended to represent the latent heat of expansion of the liquid from the ideal state against the steam-pressure. The value of $v$, however, is not the apparent expansion from 0° C., but is the "actual volume of unit mass of water less its absolute matter-volume, the pressure during the heating being that due to the higher temperature. Absolute matter is no doubt much more dense than platinum; and the reduction from the apparent volume, being very small, may therefore be disregarded." The value of $v$ is therefore taken as the observed volume at the temperature $\theta$ of unit mass of water. The justification of this argument is not very clear, but the values calculated by the formula on this assumption agree fairly with the observations of REGNAULT on the specific heat between 110° and 190° C.*

W. SUTHERLAND, in a recent paper "On the Molecular Constitution of Water," ('Phil. Mag.,' vol. 50, p. 460, 1900), has endeavoured to explain the properties of water on the assumption that it is a mixture of two kinds of molecules in varying proportions, "trihydrol," $3H_2O$, which is identical with ice, and "dihydrol," $2H_2O$, which constitutes the greater part of liquid water at higher temperatures. He

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* In a recent paper ('Proc. Inst. Civil Engn.,' vol. 147, 1902), GRAY gives a further elucidation of this formula, and a detailed comparison with our experimental results.—*Added March* 11, 1902.

calculates the densities and proportions of the two ingredients on the assumption that each constituent follows the MENDELÉEFF law of expansion, or that the density is a linear function of the temperature. He thus finds that 1 gramme of water at 0° C. consists of liquid $3H_2O$, density ·88, ·375 gramme; liquid $2H_2O$, density 1·09, ·625 gramme. The latent heat of fusion of trihydrol, 16 calories, is calculated on the assumption that it would expand ·0366 on fusing, which is the mean expansion on fusion deduced from a number of metals. The remainder of the latent heat of fusion of ice is supposed to be made up of the heat of dissociation of ·625 trihydrol into dihydrol, and the solution of the remaining fraction ·375 in the dihydrol. As a starting-point for the explanation of the variation of the specific heat, he assumes that the specific heat of dihydrol is 1·00 at 200° C., at which temperature water contains ·167 of trihydrol. Taking "the usual rate of variation of the specific heat of a liquid as ·1 per cent. per degree," he finds ·83 for the specific heat of pure dihydrol at 0° C. He takes that of trihydrol to be ·6 with a similar rate of increase, and explains the remainder of the specific heat of water as due to the heat of dissociation of trihydrol and of solution in dihydrol, which he calculates on the above assumed values of the specific heats.

It is more natural to regard the high specific heat of water as due to internal work done against molecular forces, and as being closely related to the decrease of the latent heat of vaporization with rise of temperature. Whatever assumptions are made with regard to the molecular constitution of water, it was proved by RANKINE (in a slightly different form), in 1849, that the rate of decrease of the latent heat $dL/d\theta$ was equal to the difference between the specific heat of water $s_w$, and that of steam $S_s$ at constant pressure.

$$dL/d\theta = S_s - s_w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14).$$

This is accurately and necessarily true if we assume that steam may be regarded as an ideal gas of constant specific heat, which is probably justifiable at low pressures. At higher pressures, it is necessary to make allowance for the co-aggregation of the steam molecules, which may be effected to a high degree of approximation by the method which I have explained ('Roy. Soc. Proc.,' Nov., 1900). If we write $h$ for the total heat of water from 0° C. (without assuming the specific heat to be constant), we obtain the relation,

$$L - L_0 = S_0(\theta - \theta_0) - (n + 1)(cp - c_0p_0) - h \quad . \quad . \quad . \quad . \quad (15),$$

where $S_0$ is the limiting value of $S_s$ at zero pressure, and $c$ represents the defect of the actual volume of the steam from the ideal volume $R\theta/p$. This defect of volume is independent of the pressure $p$, but varies inversely as the $n$th power of the absolute temperature $\theta$. It is clear that the rate of diminution of the latent heat is not constant, but increases at higher temperatures, on account of the co-aggregation of the molecules, as represented by the increase of the product $cp$, where $p$ is the saturation-pressure.

Similarly, we might suppose that the rate of variation of the total heat $h$ of the liquid would be constant for ideal water, but increases at higher temperatures for actual water on account of the existence of molecules of vapour in the liquid. The two phases in equilibrium at saturation-pressure may be regarded as a saturated solution of water in steam (the dissolved water being represented by the proportion of co-aggregated molecules $cp/\mathrm{R}\theta$), the liquid phase conversely as a saturated solution of steam in water. On the one hand, the total heat of the steam is reduced below its ideal value by the amount $(n + 1)\,cp$, owing to the presence of dissolved molecules of water causing a diminution of volume $c$ per unit mass of the solution; on the other hand, the total heat of the liquid is increased by the presence of a certain proportion of dissolved molecules of steam, which may doubtless account for part of the thermal expansion of the liquid. When the temperature is raised, the properties of the two phases continue to approach each other, as the proportion of water in the steam and of steam in the water increases At the critical temperature the two solutions mix in all proportions.

It is possible to estimate more or less perfectly the number of co-aggregated molecules present in steam at any temperature by observing the defect of volume from the ideal state; or to deduce the value theoretically on certain assumptions from experiments by the JOULE-THOMSON method on the cooling effect of expansion through a porous plug or throttling aperture ('Roy. Soc. Proc.,' 1900, vol. 67, p. 270). It is probable that the proportion of steam molecules present in the liquid is similarly related to its expansion, but there is no certain theoretical guide to the relation. The simplest hypothesis to make would be that the number of vapour molecules per unit volume of the liquid is the same as the number of molecules per unit volume of the saturated vapour at the same temperature. If we suppose the formation of vapour molecules in the interior of the liquid (specific volume $w$) to require the addition to the liquid of the latent heat corresponding to the same quantity of vapour (specific volume $v$) when formed outside the liquid (*i.e.*, if we neglect the heat of solution of the vapour in the liquid), the total heat $h$ of the liquid would require to be increased by an amount $w/(v - w)$ of L to allow for the latent heat of the dissolved steam. It happens that this result, though obtained by a quite different line of reasoning, agrees with the expression given by GRAY, and approximately represents the experiments of REGNAULT at high temperatures. We thus obtain the simple formula,

$$h = s_0 t + w\mathrm{L}/(v - w). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16).$$

On similar grounds it would be natural to suppose that the increase of the specific heat, as we approach the freezing-point, was due to the presence of a certain proportion of dissolved ice molecules, which are also required to account for the anomalous expansion. But here there is no obvious guide to the proportion required, or to the latent heat of solution to be assumed. The basis adopted by SUTHERLAND appears to be too empirical, and the results to which it leads are too vague and inexact to permit of a profitable comparison with experiment. In order to place any such hypothesis as that represented by formula (16) on a sound experimental basis, it would be necessary to determine the variation of specific heat of several typical liquids with great accuracy over a wide range. The required data are not at present obtainable, but the suggestion appears to be worth recording as a possible physical interpretation of the variation of specific heat.