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Bakerian Lecture: On the Variation of the Specific Heat of Water, with Experiments by a New Method

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PHILOSOPHICAL TRANSACTIONS.

I. BAKERIAN LECTURE.—*On the Variation of the Specific Heat of Water, with Experiments by a New Method.*

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THE question of the mode of variation of the specific heat of water is so fundamental in calorimetry, there are so few experiments between 50° C. and 100° C., and the results in this region obtained by different observers are so discordant, that no apology is needed for the publication of new experimental work tending to throw light on the subject. But in order to elucidate the points at issue, it will first be necessary to review briefly the experimental evidence already in existence, and to exhibit the results graphically as an indication of the order of accuracy of the various methods.

A minor difficulty in comparing the results of different observers arises from the fact that they are expressed in terms of different thermometric scales and units, and that the reduction to a uniform standard of comparison cannot always be effected with certainty. Throughout the present paper, for reasons which have been fully explained elsewhere, all heat quantities are expressed in terms of the specific heat of water at 20° C. taken as unity. The scale of temperature, t, adopted is that deduced from the temperature pt by platinum resistance thermometer by means of the difference formula,*

$$t - pt = 1{\cdot}50\, t\,(t-100)\times 10^{-4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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* Many computers have corrected this formula by assuming values from 444°·8 C. to 445°·0 C., or even 445°·5 C., for the sulphur boiling-point on the perfect-gas scale. But the recent experiments of HOLBORN and HENNING ('Ann. Phys.,' 35, pp. 761–794, 1911) with a quartz-glass bulb give the value 444°·51 C. on the perfect-gas scale. They assume the linear expansion coefficient of quartz-glass constant and equal to $0{\cdot}54\times 10^{-6}$, which makes the cubical coefficient $1{\cdot}62\times 10^{-6}$. But it appears that the linear coefficient vanishes at −100° C., and is likely to be smaller between 0° C. and 100° C. than at higher temperatures. In any case it is unsatisfactory to deduce the cubical coefficient from the linear, because the latter is difficult to measure accurately, and may well be different in different directions for a drawn bulb, especially as quartz-glass cannot be annealed owing to its rapid devitrification at temperatures in the neighbourhood of 1,000° C. Direct measurements of the cubical coefficient of a quartz-glass bulb, by E. J. HARLOW ('Proc. Phys. Soc.,' Lond., Nov., 1911), employing the method of the mercury weight

which was proposed at the British Association meeting in 1899 as an easily reproducible scale of reference for the experimentalist. The correction of the practical scale, as above defined, to the absolute scale is so small and uncertain, and has so often been applied incorrectly, that its application appears more likely to lead to confusion than to improved agreement in experimental work.

The specific heat of water at 15° C. has often been adopted as the standard. It exceeds that at 20° C. by little more than 1 in 1,000. The reduction from 15° C. to 20° C. can be effected with comparative certainty, but does not materially affect the question of the variation of the specific heat, since all the values are altered nearly in the same proportion, and few results are accurate to 1 in 1,000.

REGNAULT'S *Experiments*, 100° C. to 200° C.

REGNAULT operated by mixing 10 litres of water from a boiler at various temperatures between 107° C. and 187° C. with 100 litres of water in a calorimeter at the atmospheric temperature. His observations gave directly the mean specific heat* of water from the temperature and pressure of the boiler to the final temperature of the calorimeter at atmospheric pressure in terms of the mean specific heat between the initial and final temperatures of the calorimeter. The results did not give any direct evidence with regard to the variation of specific heat between 0° C. and 100° C., but were fairly consistent over the range 100° C. to 200° C. with the assumption of his well-known parabolic formula

$$s_0{}^t = 1 + 0{\cdot}002\,(t/100) + 0{\cdot}003\,(t/100)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for the mean specific heat between 0° C. and t° C.

ROWLAND'S discovery, in 1879, that the specific heat of water diminished by about 1 per cent. between 0° C. and 30° C., showed that REGNAULT'S formula could not possibly be correct at low temperatures, and necessitated a recalculation of his

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thermometer, and assuming the absolute expansion of mercury from the observations of CALLENDAR and MOSS ('Phil. Trans. Roy. Soc.,' A, vol. 211, pp. 1-32) give a value $1{\cdot}00 \times 10^{-6}$ between 0° C. and 100° C., increasing to $1{\cdot}50 \times 10^{-6}$ between 0° C. and 184° C. If this should be correct, the result of HOLBORN and HENNING would require to be raised by 0°·10 C., giving 444°·61 C. on the absolute scale. It is hoped that experiments now in progress by N. EUMORFOPOULOS by the constant-pressure method, with a quartz-glass thermometer of the Callendar type, will throw further light on this important point. It would appear in any case that formula (1) gives a better approximation to the absolute scale of temperature than has previously been supposed. It has been possible for the last twenty years to obtain platinum for thermometric purposes of the same unvarying degree of purity, giving a temperature coefficient approximating to 0·00390, and a practically constant difference-coefficient. It seems, therefore, preferable to eliminate errors of observation of the sulphur boiling-point, and differences of opinion as to its absolute value, by assuming a standard value $1{\cdot}50 \times 10^{-4}$ for the difference-coefficient in the definition of the practical scale.

* More accurately, the change of total heat $E + pv$.

experimental results. This was undertaken by J. M. Gray ('Proc. Inst. Mech. Eng.,' 1899) who found that the data given by Regnault did not in all cases agree with his calculated results, the discrepancies occasionally reaching 2 or 3 per cent. It appeared, from measurements of the original apparatus, that in all these cases the recorded quantity of water exceeded the total capacity of the calorimeter. Gray concluded that Regnault's calculations were probably correct, and that the discrepancies arose from deficient information or erroneous entries in the data columns. Adopting this assumption, it is possible to recalculate Regnault's observations, allowing for the known variation of the specific heat from 0° C. to 30° C., and to express his results for the mean specific heat from 0° C. to t° C. in terms of the specific heat at 20° C. The separate observations, reduced in this manner, are represented by the small crosses in fig. 1. The large crosses surrounded by circles indicate the means of each group. The general effect of this reduction is to bring the results on the average about 2 parts in 1,000 below Regnault's original formula. The correction is fairly certain, and is less than the discrepancies between the observations in any one group.

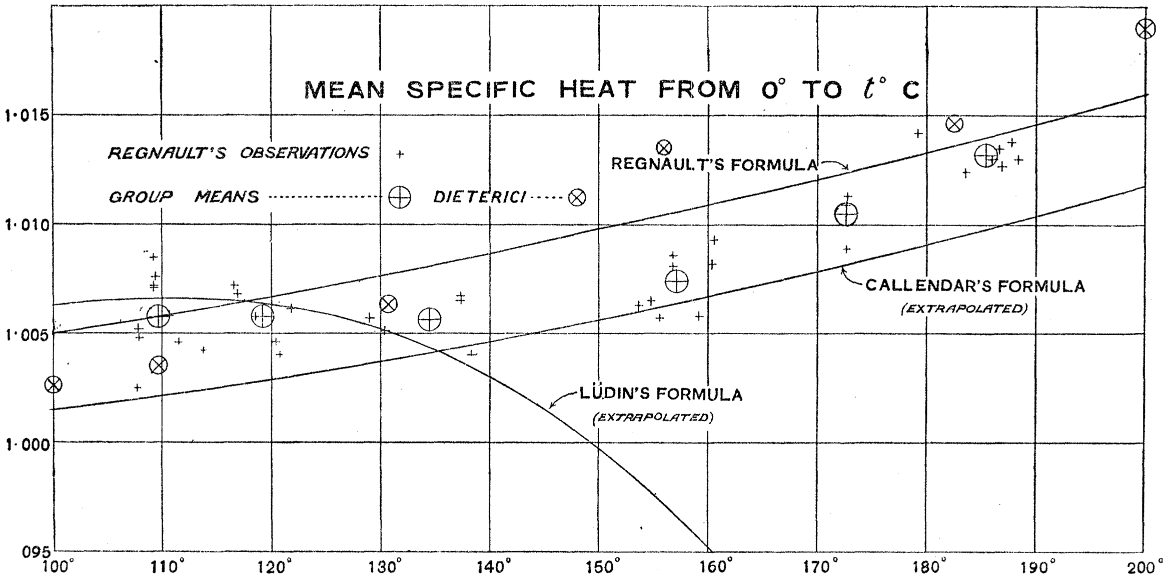

Fig. 1.

The probable errors of Regnault's thermometers remain to be considered. These have not been included in the reduction, as being much less certain, because the original thermometers cannot now be recovered and tested. It appears from recent observations on the absolute expansion of mercury, and on the pressures of steam between 100° C. and 200° C. that Regnault's temperature scale over this range did not differ materially from that given by formula (1). It is certain, however, that Regnault was ignorant of the phenomenon of the temporary depression of zero of a mercury thermometer when heated, and that he was unable to detect any systematic difference between the mercury and gas scales of temperature over the range 0° C. to 100° C., both of which facts would appreciably affect the reduction of the readings of the thermometers employed for observing the rise of temperature in the calorimeter. The correction for these two sources of error combined might *reduce* REGNAULT's values by 5 or 6 parts in 1,000 if the thermometers he employed were of French "*cristal*" glass. In any case the reduction could hardly be less than 2 or 3 parts in 1,000. This would bring the observations into fairly good agreement with my extrapolated formula, indicated by the lower curve in fig. 1, but the corrections involved are so hypothetical that no great stress can be laid on them. The only satisfactory solution is to repeat the observations, for which I have already made such preparations as my scant intervals of leisure will permit. In the meantime we may regard REGNAULT's observations as giving, with some degree of probability, *the rate of increase* of the mean specific heat between 100° C. and 200° C., although the absolute values given by his formula probably require reduction by about 0·4 per cent. It should be observed that, even if all the corrections could be applied with certainty, the order of accuracy of his final results could not be expected to exceed 1 or 2 parts in 1,000, because the calorimetric thermometers were read to 0°·01 C. only on a rise of temperature of 8° C. to 15° C., and the individual observations in each group show corresponding discrepancies from the means. REGNAULT himself did not claim any higher order of accuracy, and endeavoured to indicate this by the values of the coefficients given in his formula.

Range 0° C. *to* 100° C. (LÜDIN).

Many of the investigations by able experimentalists extending over the range 0° C. to 100° C. have given rates of variation exceeding 10 per cent. per 100° C., which were doubtless due to defective experimental methods and insufficient appreciation of the real difficulties of the problem. Such results are of no value except as an indication that the problem is not quite so simple as it appears at first sight. The first investigation in which sufficient attention was given to the well-known difficulties of mercurial thermometry, was that of E. LÜDIN ('Die Abhängigkeit der specifischen Wärme des Wassers von der Temperatur,' Inaug. Diss. Zurich, 1895), carried out by the method of mixtures under the direction of Prof. PERNET. His observations gave directly the mean specific heat over eight different ranges of temperature above 18° C., and two different ranges below 11° C., in terms of the mean specific heat over the range 11° C. to 18° C. The variation of the actual specific heat was deduced by assuming a formula of the type

$$s = 1 + at + bt^2 + ct^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and calculating the values of the coefficients by the method of least squares to agree with the observed ratios of the mean specific heats over the various ranges. This method is somewhat indirect, and makes the result depend to some extent on the particular type of empirical formula chosen. The formula given by LÜDIN for the actual specific heat s was as follows* :—

$$s = 1 - 0{\cdot}00076668t + 0{\cdot}000019598t^2 - 0{\cdot}0000001162t^3 \quad . \quad . \quad . \quad . \quad (4)$$
$$\pm 0{\cdot}0000025 \quad \pm 0{\cdot}0000040 \quad \pm 0{\cdot}000000030.$$

The probable errors of the several coefficients, as calculated by LÜDIN, are given in the second line below the coefficients to which they apply. It would appear that this type of formula is unsuitable for representing the variation of specific heat of water from 0° C. to 100° C., because the coefficients come out relatively large and of opposite signs. For instance, the value of the specific heat at 100° C. is made up as follows, according to LÜDIN's formula :—

$$\begin{array}{rll} s = & 1 - 0{\cdot}076668 & \pm 0{\cdot}00025 \\ & + 0{\cdot}19598 & \pm 0{\cdot}040 \\ & - 0{\cdot}1162 & \pm 0{\cdot}030 \\ \hline \text{Sum} = & 1 + 0{\cdot}0031 & \pm\ ? \\ \hline\hline \end{array}$$

The small difference 0·0031, representing the required variation of the specific heat, is less than 1 per cent. of the sum 0·388848 (taken without regard to sign) of the terms by which it is represented, and is only a tenth of the probable error of either of the last two terms. It is obvious *à priori* that a measurement of the mean specific heat between 18° C. and 89° C., combined with a measurement between 18° C. and

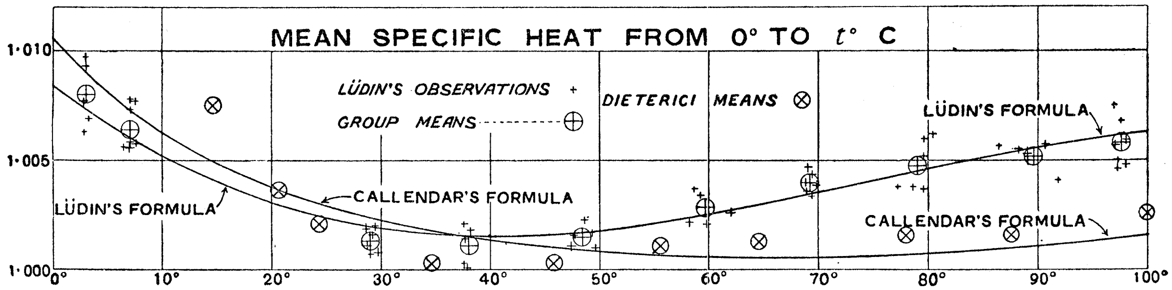

Fig. 2.

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* LÜDIN'S results have since been corrected by reference to a comparison made by THIESEN, SCHEEL, and SELL between the French "*Verre Dur*" and the Jena 16$^{\text{III}}$ glass thermometers. This reduction is somewhat uncertain, and does not affect his values materially except in the neighbourhood of 0° C. His original formula has been retained for purposes of discussion, because it is more nearly correct between 0° C. and 20° C., and because it was employed by Messrs. BOUSFIELD in their comparisons. There is an obvious misprint in LÜDIN'S corrected formula as quoted in the 'Fortschritte der Physik,' 1900, II., p. 304, but the tables appear to be correct. LÜDIN'S ratio of the mean specific heat from 0° C. to 100° C. to the specific heat at 20° C. is reduced from 1·0063 to 1·0058. His value for the specific heat at 90° C. is reduced from 1·0136 to 1·0127 in terms of the specific heat at 20° C.

97° C., could not give very certain information with regard to the actual specific heat between 89° C. and 97° C. The observations themselves, giving the ratios of the mean specific heats over different ranges, cannot be represented graphically in relation to the curve of actual specific heat represented by formula (4), which is shown by the dotted line in fig. 3. It is easy, however, to deduce the corresponding formula for

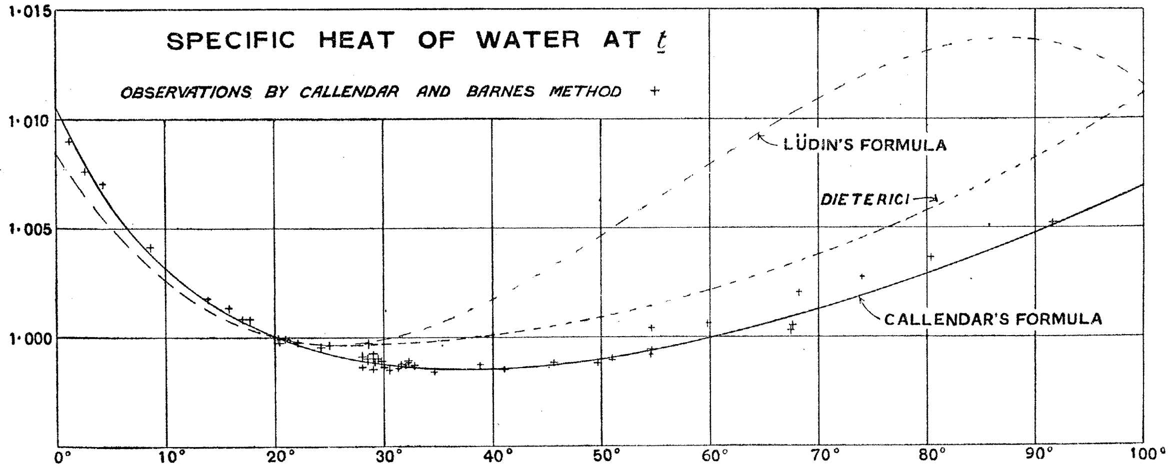

Fig. 3.

the mean specific heat from 0° C. to t° C., shown in fig. 2, in relation to which the observations may be represented by a slight reduction (as in the case of Regnault's observations) which does not materially affect their relative errors. The individual observations at each point are shown by the small crosses. The large crosses surrounded by circles represent the means of each group. The full curve, marked Lüdin's formula, represents the equation

$$s_0^t = 1·0084 - 0·00038656t + 0·000006588t^2 - 0·00000002929t^3 \quad . \quad . \quad . \quad (5)$$

which gives the mean specific heat from 0° C. to t° C. by Lüdin's formula in terms of the specific heat at 20° C. taken as unity. The group means are seen to differ by less than 1 in 1,000 from Lüdin's curve. It must be remembered, however, that the observations in each group were all taken consecutively under the same conditions with the same calorimeter and thermometers, and would give no indication of possible constant errors. Thus in Lüdin's method of operation it was necessary to vary the quantity of hot water introduced into the calorimeter from 460 gr. at 30° C. to 102 gr. at 90° C., with a corresponding variation in the initial water content of the calorimeter, and in the temperature of the walls above the water level. In spite of the great care taken in reading the thermometers and applying all corrections to 0°·001 C., the results of consecutive observations under the same conditions often differ by 2 or 3 parts in 1,000, especially near the ends of the range. This is probably due to the uncertainty of heat loss or gain during the transference of the hot water to the calorimeter, of which no account could be taken. Such gain or loss would vary, on the whole, systematically with the temperature of the hot water, and would inevitably lead to constant errors.

It will be observed, on reference to fig. 1, that LÜDIN'S formula for the mean specific heat, when extrapolated, gives results agreeing closely with REGNAULT'S observations up to 130° C. But this is really without significance, because REGNAULT'S results, as plotted, are not corrected for the probable errors of his calorimetric thermometers, and would certainly require to be further reduced. LÜDIN'S curve, if extrapolated to 200° C., would give results about 10 per cent. too low, and is obviously of a type which cannot be trusted for extrapolation. It is almost inconceivable on any theoretical grounds that the specific heat of water, after reaching a maximum at 87° C., should then diminish and increase again. LÜDIN'S method, as already explained, could not be trusted to give certain results with regard to the variation of the specific heat near the ends of his range. The experimental evidence for the drop in the curve near 100° C. is very weak, and, such as it is, may be most readily explained by a slight loss of heat due to evaporation of the nearly boiling water on its way to the calorimeter. It would appear almost hopeless to obtain reliable results by the method of mixtures with an *open* calorimeter. REGNAULT'S method, employing a nearly closed calorimeter of large volume, permanently connected to the heater by a tube for introducing the water, appears to be the only satisfactory means of avoiding the uncertainty of heat loss in transference if the ordinary method of mixtures is employed.

Continuous-Electric Method (CALLENDAR *and* BARNES).

The continuous-electric method, in which a steady current of water at any desired temperature is heated through a small range of temperature by a steady electric current, has the great advantage that it gives directly the actual specific heat over a small range at the desired point in place of the mean specific heat over a large range, and appears for this reason peculiarly suited for determining the *variation* of the specific heat. The method has been very fully described and discussed in previous papers (CALLENDAR, 'Phil. Trans.,' A, 1902, vol. 199, pp. 55–148; BARNES, *loc. cit.*, pp. 149–263), but it appears desirable to enumerate briefly its principal features. The form of the calorimeter, being merely a fine-bore tube about half a metre long with enlargements at either end for the thermometers, gives a very small water equivalent and radiating surface, and permits complete enclosure in a hermetically sealed vacuum-jacket, which reduces the external heat-loss to a minimum. The vacuum-jacket is surrounded by a water-jacket maintained at a steady temperature. The water current is brought to the same temperature as the jacket before passing the inflow thermometer. The rise of temperature of the water passing through the tube is obtained by a single reading on a pair of differential platinum thermometers, sensitive to 0°·0001 C., and probably in all cases accurate to 0°·001 C., thus avoiding nearly all the difficulties of mercurial thermometry. The electric heating current passes through a conductor of bare platinum wire, extending throughout the length of the fine-flow tube, and connected at either end to massive terminals of negligible resistance in the form of thick copper tubes enclosing the thermometers. These terminals serve to define accurately the resistance of the heater, and also to equalise the temperature along the length of the bulbs of the thermometers. The fineness of the flow tube renders any insulation of the conductor unnecessary. Sufficient stirring is obtained by causing the water to flow spirally round the thermometer bulbs and along the fine tube, or by subdividing the heating conductor. The heat generated by the friction of the water current in passing through the tube could be accurately measured by observing the difference of pressure between the ends of the tube, but its effect on the results was in all cases less than 1 part in 40,000. The electric current of 4 to 6 amperes was maintained steady by a battery of very large cells (300 ampere rate of discharge) because this permitted an order of accuracy of 1 or 2 parts in 100,000 in the electrical readings and appeared preferable to discontinuous hand regulation. For this and other reasons the potential difference on the heating conductor was not directly balanced against an integral number of Clark cells, but was measured on a carefully calibrated potentiometer, together with the potential difference due to the same current passing through a specially designed standard resistance of platinum-silver maintained at a constant temperature in an oil-bath.

As is usual in calorimetric experiments, the accuracy obtainable was limited chiefly by the determination of the heat-loss, which was deduced from experiments in which the electric and water currents were varied in such a way as to maintain the same rise of temperature. The heat-loss for the same rise of temperature was found to be not quite independent of the flow. It was also found to vary slightly owing to slight changes in the vacuum, when the apparatus was maintained for some time at a high temperature. It was inferred, however, that the uncertainty from all causes combined could not have exceeded 1 in 1,000 even at the limit of the range, and was probably much less at lower temperatures.

The experiments have been criticised chiefly on the ground of the uncertainty of the absolute values of the electrical units ten years ago, but this would not affect the question of the *variation* of the specific heat with temperature, as there was no question of the *constancy* of the standards employed. It is true that it was not at that time possible to secure a direct comparison of the Clark cells with the international standards which have since been established. In default of this I made, with the assistance of Mr. King, an absolute determination of the E.M.F. of the cells at that time in use in the laboratory, by means of an electro-dynamometer specially designed to read to 1 or 2 parts in 100,000. I was confident that the result of this determination, namely, 1·4334 volts for this type of cell at 15° C., would prove accurate to at least 1 in 10,000. This has since been verified independently by WOLFF and WATERS (‘Bull. American Bureau of Standards,’ vol. 4, p. 64, 1907), who give the value 1·43330 volts at 15° C., in terms of modern standards, for Clark cells constructed with washed mercurous sulphate according to the specification then adopted.

The idea that the absolute values of the mechanical equivalent deduced from the continuous-electric method were uncertain to the extent of more than 1 in 1,000, and had recently required correction, appears to have arisen from the fact that some of the results were originally expressed in terms of the conventional, or legal, value, 1·4342 volts at 15° C., of the Clark cell, adopted twenty years ago. This value was known at the time to be inaccurate, and was employed merely for the purpose of comparing results with those of other observers who had also assumed the conventional value.

The resistance of the standard platinum-silver coil employed in the current measurements was probably known to 1 in 10,000 in terms of then existing standards, but it has been suggested that some uncertainty existed with regard to the heating effect of the current. The coil was designed with eight wires in parallel, so that its rise of temperature in a well-stirred oil-bath when carrying 8 amperes (4 watts in each wire), should not exceed 1° C., or 1 in 4,000 increase of resistance. The currents actually employed in the specific-heat determinations gave about 2·5 watts in each wire. It is, therefore, unlikely that the increase of resistance could have been greater than 1 in 5,000, even if allowance is made for slight differences between the experimental coil on which the design was based and the actual standard.

The experiments, made by Profs. VIRIAMU JONES and W. E. AYRTON, with the Lorenz apparatus, which I ordered for McGill College in 1895, had shown (CALLENDAR, *loc. cit.*, p. 71) that the Board of Trade Standard Ohm was probably 2 or 3 parts in 10,000 larger than 10^9 C.G.S. Since the absolute values of the Clark cells as well as the platinum-silver resistance were determined with reference to this standard, the absolute values of the mechanical equivalent would require to be raised on this account by 2 or 3 parts in 10,000. Correction for the heating effect of the current would require the results to be lowered to nearly the same extent. Since these corrections were nearly equal and of opposite sign, and since both were so small and uncertain, it did not appear desirable at the time to correct for either.

Formula for the Variation from 0° C. *to* 200° C.

When the preliminary results of the continuous-electric method were first announced at the meeting of the British Association at Dover in 1899, I suggested two simple formulæ to represent the variation empirically, one covering the range of minimum specific heat from 20° C. to 60° C., and the other, a simple modification of REGNAULT's, fitting the first at 60° C. and representing REGNAULT's corrected and reduced results up to 200° C. The first formula was subsequently modified by the addition of a small term below 20° C. to represent more accurately the rapid increase of specific heat as the freezing-point was approached. It is for many purposes inconvenient to have to deal with different formula covering limited ranges, however carefully they may have been fitted together. I have, therefore, devoted some attention to devising a single formula of a suitable type to cover the whole range. Of the many possible types of formula which might be devised for the purpose, the following has appeared to me, after exhaustive trials of many types from different points of view, to be the simplest and the most generally convenient :—

$$s = 0{\cdot}98536 + 0{\cdot}504/(t+20) + 0{\cdot}0084\,(t/100) + 0{\cdot}009\,(t/100)^2. \quad . \quad . \quad . \quad (6)$$

This formula was obtained by combining a formula with REGNAULT's coefficients to represent the variation from 100° C. to 200° C., with a formula containing a reciprocal term to represent the rapid fall in the neighbourhood of 0° C. The value of the constant term 0·98536 is adjusted to make $s = 1$ when $t = 20°$ C., which is the most convenient temperature in practice to use as a standard of reference. The other terms are all small and positive, and can be calculated with sufficient accuracy for all possible purposes by means of a 10-inch slide-rule, which is far from being the case if a formula of the LÜDIN type is employed.

This formula is represented by the full line in fig. 3. The observations of BARNES, represented by the crosses, have been reduced to a unit at 20° C., and corrected for the variation of the temperature-gradient in the flow-tube, as explained in my paper (*loc. cit.*, p. 129). The results are plotted in terms of the temperature scale defined by formula (1), and are not reduced to the hydrogen scale on account of the smallness and uncertainty of this correction, as previously stated. It may be observed that the agreement of the observations with the curve would be slightly improved if the mean of the large group of observations near 30° C. had been taken as the basis of reduction in place of the few observations near 20° C. This would have the effect of depressing all the points by 0·00014, but would not alter the form of the curve. It happens that the absolute value of the specific heat can be most easily determined by the continuous-electric method in the neighbourhood of 30° C., which would naturally be selected as the standard temperature if this method were the only one to be considered. None of the observations deviate from the curve by more than 1 in 1,000, and only seven by more than 1 in 2,000. The agreement is very good considering that the observations were taken with several different calorimeters and thermometers at dates extending over more than a year. Taking account of all the changes of condition which were made in testing the method, it seems hardly likely that the variation of the specific heat given by the formula (6) can be in error by so much as 1 in 1,000 even at 80° C.

0° C. *to* 300° C. (DIETERICI).

The earlier experiments of DIETERICI ('WIED. Ann.,' 33, p. 417, 1888), in which he determined the absolute value of the mean calorie (0° C. to 100° C.) by passing a current of 0·5 ampere to 0·7 ampere, measured with a silver voltameter, through a resistance of 1·71 ohms in a Bunsen ice-calorimeter, gave a result 4·2436 ± 0·0017 joules per gr. ° C., assuming the constant of the calorimeter as 15·44 mgr. of mercury per mean calorie from the mean of the values given by BUNSEN 15·41, SCHULLER and WARTHA 15·44, and VELTEN 15·47. Taking ROWLAND'S values for the mechanical equivalent from 0° C. to 30° C., and assuming a linear increase from 30° C. to 100° C. to fit with his own value for the mean calorie, DIETERICI deduced a table (*loc. cit.*, p. 441) for the variation of the specific heat from 0° C. to 100° C., which has been frequently quoted and employed for reducing observations. According to this table, the mean calorie exceeded that at 20° C. by 1·5 per cent. The specific heat at 90° C. was 3 per cent. greater than the value subsequently found by the continuous-electric method, but appeared to be in fair agreement with older observations.

DIETERICI'S later determinations of the mean calorie ('Ann. Phys.,' 16, p. 593, 1905) by a similar method, in which the current was reduced to 0·05 ampere and the resistance increased to 40 ohms in order to diminish errors due to conduction and generation of heat in the leading wires, gave a result 4·1925 joules per gr. ° C., exceeding the value 4·187 given by the continuous-electric method by only 1·4 in 1,000, which is almost, if not quite, within the possible limits of error of the ice-calorimeter. Accepting DIETERICI'S value of the specific heat at 20° C., namely, 0·9974 in terms of the mean calorie, his value for the mechanical equivalent at 20° C. would be 4·1815, which agrees to 1 in 3,000 with the continuous-electric method. DIETERICI'S value of the calorie at 20° C. has accordingly been taken in place of the mean calorie in reducing his results for comparison with those of other observers. It should be remarked, however, that the rate of heat supply in his experiments with the ice-calorimeter was 300 times smaller than in the continuous-electric method, and that, in order to obtain equally good results with the ice-calorimeter, it would be necessary that the uncertainty of the heat-loss should also be 300 times smaller, the probability of which is open to doubt.

DIETERICI also redetermined the constant of the ice-calorimeter by an improved method, employing sealed tubes of quartz-glass to contain the water at 100° C. The value thus found was 15·491 mgr. per mean calorie, exceeding the value previously employed by 1 in 300. His results by the same method for the mean specific heat from 0° C. to t° C., reduced to his calorie at 20° C. as unit, are indicated by the diagonal crosses in figs. 1 and 2. Between 0° C. and 100° C., his results, as shown in fig. 2, agree to 1 in 1,000 with my formula, except for one observation at 14°·6 C., where, as he admits, an inferior degree of accuracy was to be expected. For temperatures above 35° C. he represents his results for the mean specific heat from 0° C. to t° C. in terms of the mean calorie by the formula

$$s_{0,t} = 0{\cdot}99827 - 0{\cdot}005184\,(t/100) + 0{\cdot}006912\,(t/100)^2$$

which gives a minimum at 35° C., agreeing with his observations. He points out that the corresponding formula for the specific heat at t,

$$s_t = 0{\cdot}99827 - 0{\cdot}010368\,(t/100) + 0{\cdot}020736\,(t/100)^2,$$

being obtained by differentiation, has an inferior degree of accuracy, which he sets at 0·3 per cent. in the neighbourhood of 100° C. The curve marked DIETERICI, in fig. 3, represents this formula reduced to a unit at 20° C. by dividing by the factor 0·9974, representing his value at 20° C. DIETERICI employs this formula for the actual specific heat, s_t, in calculating the values given in his table down to a temperature of 25° C., although it does not strictly apply below 35° C. Below 25° C. his values for the specific heat are calculated in a different way, but agree so closely with my formula that his curve could not be shown separately. This agreement is very satisfactory, but gives rise to a somewhat sharp change of curvature at 25° C., which is repeated at 35° C. in his formula for the mean specific heat, and introduces some uncertainty in the interpretation or application of the tabulated results. Below 35° C. his table of mean specific heat appears to represent his experimental results between 35° C. and 20° C. (neglecting the discordant observation at 14°·6 C.) with an almost linear extrapolation which follows my curve very closely from 20° C. down to 0° C. Values of the actual specific heat calculated from this table show a rapid fall from 1·0075 at 0° C. to 0·9912 at 30° C., and a sudden jump from below 0·9900 up to the value 0·9973 at 35° C. If, on the other hand, his table of actual specific heat is taken as the basis of calculation, the value of the mean specific heat from 0° C. to 40° C. comes out 0·9992 in place of 0·9973, given in his other table. The observations themselves do not afford any valid evidence for the existence of these discontinuities, which might prove very troublesome in the practical application of his tables. A single continuous formula, such as (6), presents many advantages in this respect, especially for representing observations on the mean specific heat, which ought not to show sudden changes of curvature. The deduction of the true specific heat at any temperature from the mean specific heat is most uncertain in any case, and the observations cannot be said to support the minimum at 25° C., shown in DIETERICI's curve for the actual specific heat. The uncertainty in the reduction of the results from 0° C. to 35° C. must affect the whole form of the curve, and even the apparent discrepancy of 0·4 per cent. at 100° C., shown in fig. 3, does not exceed the limits of possible error in the calculation.

Apart from variations in the fundamental constant (depending possibly on the quality of the ice formed), and uncertainty of the correction for creep of zero, which might give rise to accidental errors, the main source of systematic error in DIETERICI's method would lie in the correction for the water equivalent of the quartz-glass bulbs, and in loss or gain of heat during transference from the heater to the calorimeter. The water equivalent of each bulb was calculated from its mass by means of a formula for the variation of the specific heat of quartz, which is appropriate if there is no heat-loss in transference. It appears probable, however, that bulbs of different form and thickness would experience different losses in transference. In fact, a small systematic error of this kind is indicated by the observations themselves, and might produce appreciable errors at the higher temperatures.

Below 100° C. the uncertainty would probably not exceed 1 in 1,000, as the thermal capacity of the bulbs employed was only a quarter of that of the contained water. From 130° C. to 220° C. all the observations, except one at 130° C., were made with bulbs having a thermal capacity nearly equal to that of the contained water. In the observations at 100° C., 109° C., and 130° C., where both thick and thin bulbs were employed, the results deduced from the thick bulbs, assuming the same formula for the specific heat of quartz-glass, were systematically higher by 0·12, 0·17, and 0·23 per cent. respectively than those deduced from the thin bulbs. The point shown at 156° C. in fig. 1, which is the lowest depending entirely on observations with the thick bulbs, shows so great an increase, when compared with REGNAULT'S observations, as to suggest a systematic error of this kind. Assuming that the error might amount to 0·1 per cent. in the mean specific heat at 100° C. with the thin bulbs, and that it would probably increase in proportion to the temperature and to the relative thermal capacity of the bulbs, it would amount to 0·8 per cent. at 200° C., which would be more than sufficient to bring the results of DIETERICI into agreement with the most probable reduction of REGNAULT'S observations as indicated by my formula. A similar uncertainty would apply with greater force to the experiments at higher temperatures where the thermal capacity of the quartz-glass bulbs amounted to four times that of the contained water. The heat-loss in transference might have been in part eliminated from the results for water by using *the same bulbs* full and empty at each temperature, but even in this case the accuracy of the results for water would have been reduced to about a fifth with the thickest bulbs.

The large correction for the water equivalent of the bulbs, which could not easily be reduced, is a serious objection to DIETERICI'S method as compared with REGNAULT'S at the higher temperatures. Below 100° C. this source of error is unimportant as compared with evaporation losses incurred in transferring hot water when exposed to evaporation, as in LÜDIN'S method. On this account there would probably be little hesitation in preferring DIETERICI'S results to LÜDIN'S between 0° C. and 100° C., if it were not that, within the last year, Messrs. W. R. and W. E. BOUSFIELD ('Phil. Trans. Roy. Soc.,' A, 1911, vol. 211, pp. 199–251) have succeeded in reproducing LÜDIN'S results with remarkable fidelity by a method of electric heating with a vacuum-jacket calorimeter, which presents many ingenious and novel features. Owing to the uncertainty in the reduction of DIETERICI'S results for the specific heat at 20° C., it might naturally be argued that his curve for the mean specific heat should be fitted to LÜDIN'S at a higher temperature, such as 60° C. or 70° C. This could easily be done by raising all the points representing DIETERICI'S observations in fig. 2 by only 0·25 per cent., in which case they would nearly all agree with LÜDIN'S curve to 1 in 1,000 except those below 30° C., where DIETERICI admits a larger possible error. It would then appear that Messrs. BOUSFIELD, LÜDIN, and DIETERICI were in fair agreement in assigning a much higher value to the mean specific heat from 0° C. to 80° C. than that assigned by the continuous-electric method, and that the error probably lay with the latter. It is usual to take the curves for the actual specific heat in making these comparisons, but these do not represent the observations themselves, except in the case of the continuous-electric method, and little can fairly be deduced from such a comparison (though DIETERICI, LÜDIN, BOUSFIELD, and many others have adopted this method), owing to the great uncertainty involved in deducing the actual from the mean specific heat. There is no similar uncertainty in deducing the mean from the actual specific heat, so that the method adopted in fig. 2 is the more appropriate. Since the evidence for the slow rate of increase of the specific heat between 60° C. and 100° C., in the continuous-electric method, rested chiefly on half-a-dozen observations taken under conditions of exceptional difficulty, it appeared desirable to confirm them, if possible, over this range by an entirely different method, at least equal in accuracy.

Continuous-Mixture Method.

If two steady currents of fluid at different temperatures are passed through an arrangement of concentric tubes called a "heat exchanger," it is clear that, neglecting external heat-loss or gain, the loss of total heat by the hot current will be equal to the gain of total heat by the cold current. By measuring the currents and the temperatures of inflow and outflow, we have all the data required for determining the ratio of the mean specific heats over the respective ranges. This method does not appear to have been applied to any extent in accurate calorimetry, on account of the experimental difficulties involved in regulating and measuring the currents and the temperatures simultaneously to a sufficient order of accuracy. As applied to the variation of the specific heat of a single fluid, the method permits of a most important simplification which does not appear to have been hitherto noticed. In place of employing two separate currents, each of which must be measured and regulated to the limit of accuracy, *the same current* is passed twice through the heat exchanger, first as a hot current, and then, after suitable cooling, as a cold current, or *vice versâ*. If there is no leakage the ratio of the currents is always one of equality, and a comparatively rough determination of the absolute value of the current suffices for the application of small corrections. The experimental problem is reduced to the regulation and measurement of the temperatures, which, taken by itself, is comparatively easy. The method possesses the advantage, common to all continuous-flow methods, that a knowledge of the water equivalent of the calorimeter and of its variation with temperature is not required provided that the conditions are fairly steady. There is no uncertainty of heat-loss in transference, or by evaporation, as with an open calorimeter. It is also easy, by a suitable arrangement of the flow-tubes, to reduce the external heat-loss almost to a vanishing quantity without the employment of vacuum-jackets or elaborate precautions in lagging. The method requires considerable variation in detail to suit different ranges of temperature, and is in some ways less direct than the electric method, but it is peculiarly suitable as a means of independent verification.

General Arrangement of the Apparatus.

The continuous-mixture method was primarily designed for determining the variation of the total heat of water at temperatures above 100° C., where the continuous-electric method appeared to present greater difficulties. But, as the arrangements for this were not complete, it was decided to apply the method in the first instance as an independent test of the accuracy of formula (6) over the range 60° C. to 100° C., where it differed most widely from those of Lüdin and Bousfield. The arrangement adopted for this purpose will be readily understood from the diagrammatic scheme in fig. 4.

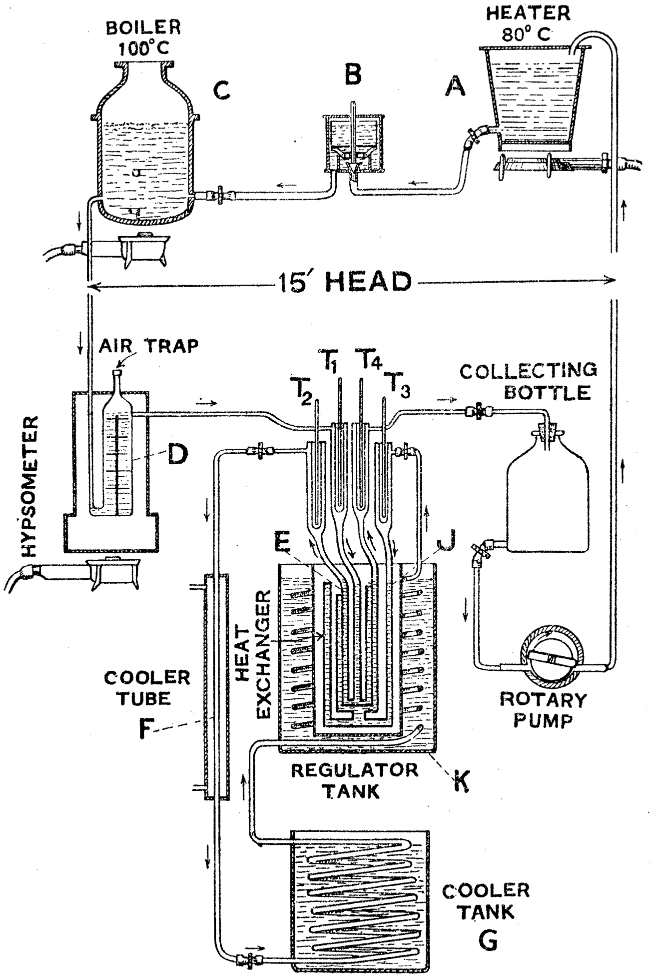

Fig. 4.

The current of air-free distilled water is supplied from a boiler C in which the level is kept constant by means of a float-feed B, from an auxiliary tank A, maintained at a temperature of about 80° C. From the boiler the current passes with a fall of about 15 feet to a reservoir D_1 surrounded by a steam-jacket, in which it is again raised to the boiling-point before entering the exchanger E. There is an air-trap at the top of the reservoir D, and similarly at each of the highest points of the circulating system, to facilitate filling the apparatus completely with water before starting the flow. Just before entering the exchanger E, the current passes through thermometer-pocket T_1, the construction of which is shown on a larger scale in the section of the exchanger, fig. 5. In order to protect the thermometer-pocket itself from loss of heat, the current is made to circulate upwards through a jacket-tube surrounding the thermometer-pocket before circulating downwards past the thermometer. Any small loss of heat which may occur before reaching the thermometer is immaterial. The thermometer-pockets and other tubes throughout the exchanger are made of thick copper, with deep screw-threads carefully fitted to produce a spiral circulation of the current. After passing thermometer T_1 the current flows downwards through the central tube to the bottom of the exchanger and thence upwards through a concentric tube, where it loses heat to the cold current. Its temperature on first leaving the exchanger is taken by a thermometer T_2 in a pocket constructed similarly to T_1, but not shown in fig. 5, in order to avoid confusion. The thermometer-pockets are all connected to the exchanger by thin tubes about 2 cm. to 3 cm. long and 0·5 cm. bore. These connections are exaggerated in the diagram, fig. 4, so as to permit the general course of the circulation to be more easily followed. After leaving T_2 at a temperature between 60° C. and 70° C., the current passes through a cooling-tube F surrounded by an easily regulated jacket of cooling water; thence through a long tin spiral immersed in a large cooling tank G to steady the temperature, before reaching a similar spiral in the regulator tank K, where its temperature is reduced precisely to that required for the cold current. From the regulator tank the current passes directly through the thermometer-pocket T_3 before entering the exchanger again as a cold current. In order to prevent loss of heat from the exchanger to the regulator tank in which it is immersed, the current, at very

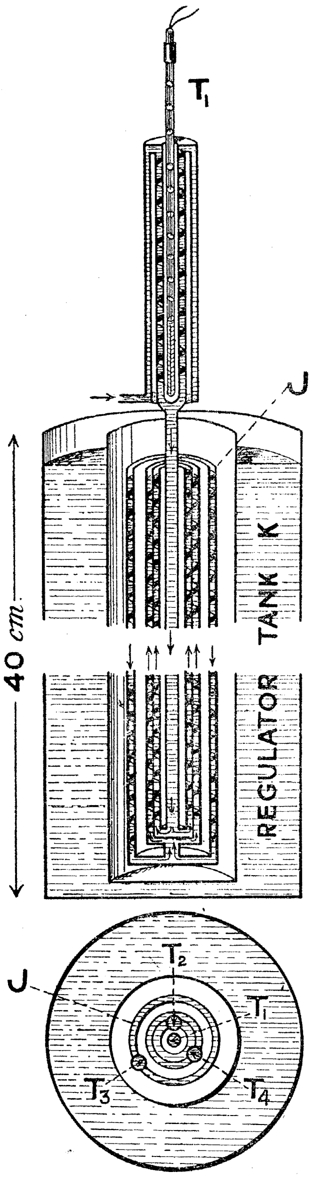

Fig. 5.

nearly the same temperature as the regulator tank, first circulates downwards through the outer jacket J and then upwards through the next inner tube, where it comes in contact with the hot current, emerging finally through the thermometer-pocket T_4, whence it passes to the collecting bottle, where the flow is measured from time to time. The head being maintained constant, steady currents of suitable values are obtained by fitting exit tubes of various bores between T_4 and the collecting bottle. From the collecting bottle the water is continuously returned to the heater on the floor above by means of a small rotary pump. With the exception of the heat exchanger itself, the details require considerable modification for different ranges of temperature. But the arrangement above described has been found to work very well for comparing the mean specific heat from 70° C. to 100° C. with the mean specific heat from 30° C. to 60° C., and will sufficiently illustrate the general nature of the method.

With a flow of 10 c.c. per second the heat-exchange amounts to about 300 calories per second, and the external heat-loss with the arrangement above described can be reduced to less than a tenth of a calorie per second, or about 1 in 3,000 of the total quantity measured. Owing to the relatively small thermal capacity of the exchanger, and to the fact that the distribution of temperature is nearly independent of the flow, the conditions become steady to 0°·002 C. in a few minutes when the flow is changed. The accuracy attainable depends chiefly on the limit of accuracy in reading the thermometers.

The Platinum Thermometers.

The thermometers employed were of my usual pattern in glass tubes, with leads partly of silver and partly of platinum, insulated by mica discs, spaced at intervals of 2 cm. throughout the length of the tube by means of mica crosses. Spacing the discs by means of mica crosses appears preferable to spacing the discs by long thin tubes of biscuit porcelain, as commonly practised by many makers, because the porcelain tubes are more hygroscopic than the mica. They also make the compensation less sensitive by shielding the leads. The thermometer coils were of pure standard wire, 0·01 cm. diameter (0″·004), and the ends of the compensating leads were connected by fusing on a short piece of the same wire to eliminate any conduction effects which might exist. Thick platinum leads extended for a distance of 7 cm. from the coil, where they were fused to silver leads. The object of this is partly to avoid possible contamination* of the fine wire with silver and partly to diminish conduction along the tube near the bulb. The immersion of the thermometers in the apparatus was

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* From the first I have always adopted this method of construction in my own thermometers for accurate work at high temperatures. It seems likely that many of the small variations of zero and difference-coefficient, found by careful observers, are due to contamination of the fine wire with gold or silver solder at its junction with the copper or silver leads. HOLBORN and HENNING, in their recent paper (*loc. cit.*), attribute some of the small variations of their platinum thermometers to this cause.

15 cm. At the head of each thermometer the silver leads were soldered to flexible copper leads, 3 m. long, with amalgamated copper terminals fitting the mercury cups of the compensated box described in a previous paper (CALLENDAR, *loc. cit.*, p. 90). This was essential to permit of rapid interchange of the thermometers in taking readings.

The ice- and steam-points were observed on several occasions. The sulphur-point was also observed on one occasion, when the following readings were taken:—

Thermometer.	T_1.	T_2.	T_3.	T_4.
Steam at 100°·262 C.	1785·39	1783·70	1785·38	1782·39
Ice at 0° C.	1284·07	1282·84	1284·11	1281·85
Fundamental interval	500·03	499·57	499·98	499·25
Sulphur reading	3394·67	3391·26	3394·38	3389·10
pt_s deduced	422·09	422·05	422·07	422·08
t_s from barometer	445·22	445·19	445·21	445·21
$t_s - pt_s$	23·13	23·14	23·14	23·13
Difference-coefficient × 10^4	1·505	1·506	1·506	1·505

Readings at the fixed points were taken and corrected for box-temperature and coil-errors to one figure beyond that given in the above table (corresponding to 0°·0002 C.), but the last figure has been rejected as not being fully significant even at the fixed points, and as being beyond the limit of accuracy at the sulphur-point. The fundamental intervals of the thermometers were approximately 5 ohms each, or 500 cm. of the bridge-wire. Thermometers T_1 and T_3 had been made at the same time, by my assistant Mr. W. J. COLEBROOK, for use as a differential pair, and had been adjusted with special care so that their uncorrected readings agreed to 1 in 10,000 throughout the scale. T_2 and T_4 were precisely similar thermometers made at different times, with resistances adjusted to about 1 in 1,000. The readings at the sulphur-point were taken in succession on the same day, when the barometer was falling slightly, in the order T_1, T_3, T_4, T_2. The corresponding temperatures, t_s, on the gas-scale are calculated from the observed barometer readings by assuming the normal boiling-point to be 444°·53 C., and the pressure variation to be 0°·090 C. per mm., as found by CHREE. The results show that all four thermometers agreed in their temperature scales to 0°·01 C. at the sulphur-point, which is nearly the limit of error of the readings. An iron-tube apparatus was employed for boiling the sulphur and the thermometers were fitted with a single screen. Experience has shown that this apparatus gives consistently a temperature nearly 0°·10 C. lower than the glass-tube apparatus with two screens, as originally described. Allowing for this, the difference coefficients of all four thermometers would be within 1 in 1,500 of the standard value, $1·50 \times 10^{-4}$, for pure platinum when the S.B.P. is taken as 444°·53 C. In any case, this correction (from 1·506 to 1·500) would not affect the scale of the thermometers by so much as 0°·002 C. at 50° C. In my experience, platinum thermometers, when carefully constructed of suitable wire, always agree so closely with this scale that it is seldom worth while to make a special determination of the difference-coefficient by reference to the sulphur boiling-point. It was, however, considered desirable to make the test in the present instance because the apparent variation of the specific heat of water depends in a great measure on the thermometric scale employed. The thermometers were also compared differentially between 0° C. and 100° C. and were found to agree so closely that no differences in their scales could be detected.

Method of Reading the Thermometers.

The galvanometer employed was of the moving coil type, with a resistance of about 13 ohms. Readings were generally taken by the constant-current method which I first introduced in 1891. In this method the platinum thermometer is connected on the compensator side of the box in series with the box coils, and is balanced against a compensated resistance,* equal to, or greater than, the resistance of the thermometer at the highest point of the range it is desired to cover, in this case 17·84 ohms. With this arrangement the current through the thermometer is nearly the same at all temperatures, since the resistances on both sides of the bridge are kept nearly constant. The current through the thermometer was approximately 0·005 ampere, and was adjusted so that the deflection of the galvanometer was 1 mm. at 1 metre on reversal for a change of temperature of 0°·001 C. Readings were taken by setting the contact-point on the bridge-wire as exactly as possible with a lens to the nearest millimetre, and then observing the small deflection of the galvanometer on reversing the battery. The definition was so perfect that it was possible to read to 0·1 mm. of the scale, or 0°·0001 C., by the galvanometer deflection when the temperature was steady. But this was the case only at the fixed points. No attempt was made to read nearer than 0°·001 C. at other temperatures, but the provision of ample sensitiveness greatly facilitated quickness and certainty of reading. The constant-current arrangement of the measuring apparatus possessed special advantages for the continuous-mixture method, because it was necessary to read four

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* These compensated resistances are very useful in accurate resistance measurements or platinum thermometry. They are best constructed of platinum-silver, wound on mica and annealed *in situ* at a dull red heat, compensated by a small resistance of pure platinum, having an equal temperature increment, and connected in the opposite arm of the bridge (CALLENDAR, 'Brit. Patent,' No. 14,509, 1887). The two coils may conveniently be enclosed in a glass tube with compensated leads like a platinum thermometer, and the point of zero temperature-coefficient may easily be adjusted as near to 20° C. as desired. In this case the whole change of resistance of the combination between 0° C. and 40° C. is less than 1 in 100,000, and the change between 15° C. and 25° C. is only 1 in 2,000,000. The best specimens of manganin generally have a temperature-coefficient of 2 or 3 in 100,000 per 1° C. at 20° C., which is more than 100 times as great; but even if the point of zero-coefficient for manganin could be adjusted to 20° C., the changes in the neighbourhood of 20° C. would be more than 10 times as great as with the platinum-silver coil compensated with platinum. For a further discussion of this point see CALLENDAR, 'Phil. Trans.,' A, vol. 199, p. 89, 1902.

thermometers at different temperatures in rapid succession. It was important that the sensitiveness of the galvanometer should be the same for each, and it was desirable that the rise of temperature produced by the measuring current should be nearly the same for each thermometer. This last condition is approximately secured by keeping the current constant. CHAPPUIS and HARKER ('Phil. Trans.,' A, 1900, p. 62; CALLENDAR, *loc. cit.*, p. 93) proposed to do this by keeping the watts C^2R constant, adjusting the current C to suit the value of R. But the emissivity of the wire increases somewhat more rapidly than R, so that the rise of temperature due to C at different points of the scale is nearly proportional to C^2. The rise of temperature produced by a current of 0·005 ampere at 30° C. was measured and found to be 0°·0066 C. The rise at 100° C. was found to be 0°·0063 C. Assuming that the variation between these limits was regular, it was evident that it could not produce a systematic error of the temperature scale greater than 0°·0001 C. between the limits 0° C. and 100° C. In measuring the mean specific heat over a range of 30° C., a limit of accuracy of 0°·001 C. in the thermometric readings appeared to be ample, because this would amount to only 1 in 30,000 of the heat measured, and it was hardly to be expected that the external heat-loss could be determined with a much higher order of accuracy than 1 in 10,000.

Theory of the Continuous-Mixture Method.

If X is the external heat-loss in calories per second, and Q the water current in grammes per second, the equation connecting the mean specific heats $s_{1,2}$, $s_{4,3}$ over the ranges t_1 to t_2 and t_4 to t_3 for a single value of the flow Q is evidently

$$s_{1,2}(t_1-t_2) = s_{4,3}(t_4-t_3) + X/Q. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If the heat-loss X could be neglected by sufficiently increasing the flow, this equation would give the required ratio of the specific heats directly, being simply the inverse ratio of the temperature ranges. In any case, if X is small and Q large (say 10 to 20 gr./sec.), this would give a good first approximation, better than 1 in 1,000 if X is less than 1 in 1,000 of the whole heat exchange. Assuming that the temperature distribution in the exchanger, and consequently the heat-loss X, does not vary appreciably when the flow is changed within reasonable limits, a second approximation could easily be secured by employing the first approximation to evaluate the heat-loss for a small flow, say 1 gr./sec., and employing the value so obtained for the large flow; or the heat-loss X might be directly eliminated by subtracting one equation from the other if the temperature ranges were so nearly the same that the values of the mean specific heats could be assumed to be the same for the small flow without sensible error. This method of reduction would undoubtedly give good results if the losses were small. In practice, however, it is impossible to secure *exact* similarity in the temperature distribution for flows varying in the ratio of 10 to 1, and it is, therefore, preferable to adopt a method of reduction depending on some assumed variation of the total heat. This appears at first sight a less direct method, but is peculiarly appropriate when the primary object of the experiment is to verify formulæ already obtained by different methods.

Variation of the Total Heat.

The variation of the total heat is not so familiar as the variation of the specific heat, but since the change of total heat between given limits is the quantity actually measured in a calorimetric experiment, the total heat is generally the most useful quantity to tabulate for experimental purposes. The numerical value of the total heat h from 0° C. to t° C. in terms of a unit at 20° C. differs but little from t over the range 0° C. to 100° C. It is, therefore, convenient to write

$$h = t + dh, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where dh is the small excess of h over t at any temperature, which may appropriately be called "the variation of the total heat."

The value of dh given by LÜDIN's formula (5) is

$$dh = 0{\cdot}84\,\frac{t}{100} - 3{\cdot}8656\left(\frac{t}{100}\right)^2 + 6{\cdot}588\left(\frac{t}{100}\right)^3 - 2{\cdot}929\left(\frac{t}{100}\right)^4, \quad . \quad . \quad . \quad (9)$$

whence the value at 100° C. is $0{\cdot}84+6{\cdot}588-3{\cdot}8656-2{\cdot}929 = +0{\cdot}633$.

The corresponding formula for dh deduced from my formula (6) representing the results of the continuous-electric method is

$$dh = 1{\cdot}1605\,\log_{10}\frac{t+20}{20} - 1{\cdot}464\,\frac{t}{100} + 0{\cdot}42\left(\frac{t}{100}\right)^2 + 0{\cdot}30\left(\frac{t}{100}\right)^3, \quad . \quad . \quad (10)$$

whence the value at 100° C. is $0{\cdot}903-1{\cdot}464+0{\cdot}420+0{\cdot}300 = +0{\cdot}159$, differing from LÜDIN's formula by nearly 0·5 per cent.

These two formulæ are represented by the curves in fig. 6. In order to save space,

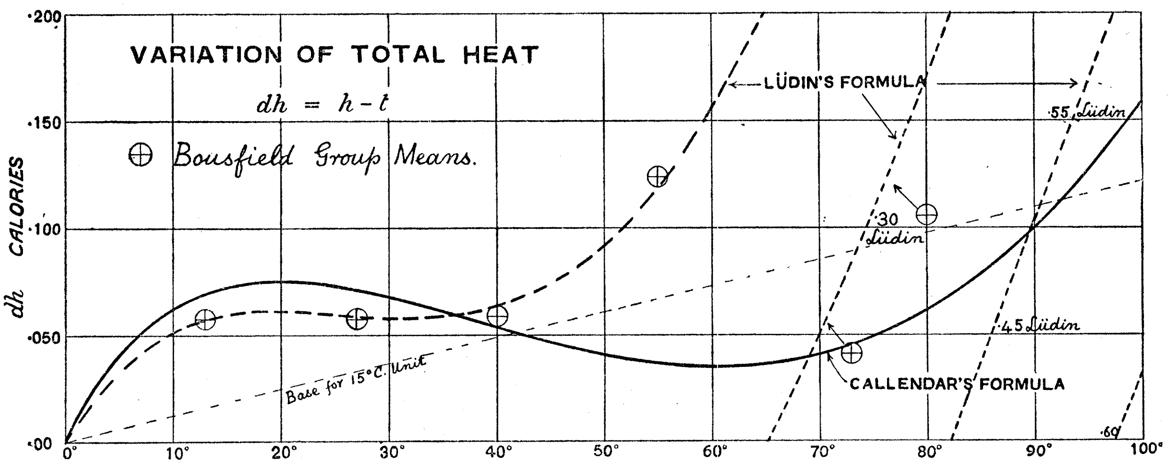

Fig. 6.

LÜDIN's curve from 65° C. to 100° C. is represented in three pieces, the curve being shifted downwards through 0·200 when it reaches the upper limit of the diagram. ROWLAND's observations on the mechanical equivalent from 5° C. to 35° C., if plotted on the same scale, would agree to 0·003 throughout his range with formula (10), the full curve. His experiments do not, as generally stated, afford any conclusive evidence of a minimum at 30° C. in the specific heat. ROWLAND himself considered that, owing to the increasing magnitude and uncertainty of the radiation correction beyond 30° C., "there might be a small error in the direction of making the mechanical equivalent too great at that point (30° C.), and the specific heat might keep on decreasing to even 40° C." The discrepancy from LÜDIN's curve in this region is less than 1 in 1,000 of the total heat, and is within the limits of error of LÜDIN's experiments. Formula (6) gives a minimum at 37°·63 C. LÜDIN's formula gives a minimum at 25°·22 C., which cannot be reconciled with ROWLAND's observations.

The point at which the specific heat in absolute units can be most accurately inferred from ROWLAND's experiments is 20° C., at the middle of his temperature range. The value at this point is probably within 1 in 2,000 of 4·180 joules per gr.-deg. C. on the scale defined by formula (1). ROWLAND himself gave the value 4·179 on the air scale; DAY's reduction of ROWLAND's thermometers gave 4·181 on the hydrogen scale. The results of REYNOLDS and MOORBY, when corrected to cover the range 0° C. to 100° C., give 4·184 joules for the mean calorie. Combining these two results we find 4·184/4·180, = 1·0010, for the ratio of the mean calorie to the calorie at 20° C. My formula (10) would make the ratio 1·0016, which is fairly good agreement. But LÜDIN's formula gives the ratio 1·0063, showing a discrepancy of 0·53 per cent., which would appear to be beyond the possible limits of error of REYNOLDS and MOORBY's experiments, since the extreme variations of their results did not exceed 0·36 per cent., and the mean would probably be correct to 1 in 1,000.

The evidence to be deduced from the observations of W. R. BOUSFIELD and W. E. BOUSFIELD (*loc. cit.*) with regard to the variation of the total heat rests on their "point-to-point" experiments over the following ranges:—

Range of temperature .	0–13° C.	13–27° C.	27–40° C.	40–55° C.	55–73° C.	55–80° C.
Mean value of J . . .	4·1937	4·1752	4·1756	4·1935	4·2024	4·2056
dh deduced	0·058	0·058	0·059	0·124	0·242	0·306
dh LÜDIN	0·057	0·059	0·064	0·119	0·285	0·371

The values of the variation *dh* at the points 13° C., 27° C., 40° C., 55° C., 73° C., and 80° C. are deduced from Messrs. BOUSFIELD's observations by taking their value 4·1752 for the unit at 20° C. and adding up their values of the total heat for the separate ranges. Up to 55° C. they agree very closely with LÜDIN's curve, as indicated by the crosses in fig. 6. Their values at 73° C. and 80° C. are somewhat lower than LÜDIN'S, but the discrepancy here is only from 0°·043 C. to 0°·065 C. They considered that the measurements could not be carried beyond this point with an open calorimeter owing to the rapidly increasing uncertainty of the heat-loss due to evaporation, "obturator" heating, &c. The general agreement with LÜDIN'S curve is so striking that it would seem at first sight as though it could hardly be due to chance. Their methods had no points in common, except that they both used mercury thermometers and open calorimeters.

Reduction of Observations by the Total-Heat Method.

The curves of variation of total-heat above described and explained, when plotted on a scale of 1 mm. to 0°·001 C. for dh, afforded the most accurate and expeditious method of reducing the observations by the continuous-mixture method, since it was easy to take exact account in this way of small differences of range with different flows. If h_1, h_2, h_3, h_4 are the total heats from 0° C. corresponding to the observed temperatures t_1, t_2, t_3, t_4, equation (7), when expressed in terms of the total heat, becomes

$$h_1 - h_2 = h_4 - h_3 + \mathrm{X}/\mathrm{Q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Substituting $h = t + dh$, and writing Σt for the sum $t_1 - t_2 + t_3 - t_4$, and Σdh for the sum $dh_1 - dh_2 + dh_3 - dh_4$, this equation may be written

$$\mathrm{Q}\,(\Sigma t + \Sigma dh) = \mathrm{X}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

If the formula assumed for dh is correct, the values of the heat-loss X deduced from different flows should be nearly the same for the same temperature range, or should vary in relation to the mean excess-temperature of the calorimeter above its surroundings. If the formula employed for dh is incorrect, the calculated values of the heat-loss X will vary with the flow, and will bear no consistent relation to the external conditions.

As there was some delay in procuring the requisite sizes of solid-drawn copper tube for the high-pressure apparatus designed for work at temperatures up to 230° C., the apparatus was in the first instance constructed of ordinary brass tubing with solder joints for work below 100° C. The soft-solder joints would not stand high temperatures, but had the advantage that the apparatus could be taken to pieces readily and remade in different forms, to test the effect of variations in the external conditions on the heat-loss observed. Thus in order to test for possible errors due to conduction of heat along the thin tubes, 2 to 3 cm. long, 5 mm. bore, and 0·5 mm. thick, connecting the thermometer-pockets to the exchanger, the connecting tubes were replaced by short thick brass cylinders 1 cm. long by 2 cm. in diameter. This produced an appreciable effect on the thermometer readings only with the smallest flow of 1·25 gr./sec. It was inferred that the conduction error with the thin tubes actually employed would be inappreciable even with the smallest flow.

A possible source of error to be carefully avoided in the continuous-mixture method is leakage of fluid at any point of the circuit between the first and last thermometers. Precautions against this were taken in designing the apparatus by making the cooling coils and other inaccessible parts of the apparatus of continuous lengths of solid-drawn tubing, and arranging all joints and connections as far as possible so as to be easily accessible and at all times open to inspection.

In addition to this, a leakage test was regularly applied each day before starting observations, when the apparatus was at a nearly uniform temperature. The boiler was disconnected, and a glass tube of small bore was attached to the inflow at the top, to serve as an index. Any possible leaks were thus subjected to the full head of 15 feet. A special test was also made for leakage between the hot and cold tubes in the exchanger. A small continuous leak due to strain, amounting to about 1 c.c. per hour, was detected on one occasion, and immediately rectified. But, as a rule, the movements of the sensitive index were negligibly small, being due merely to slight changes of temperature, and more often positive than negative.

The apparatus was also tested with and without the jacket-tube J, figs. 4 and 5, between the exchanger and the regulator tank in which it was immersed. The loss from the thermometer-pockets, when unjacketed, was found to be from 1·2 to 1·4 calories per second, according to the conditions of the experiment, and to be nearly independent of the flow, since the mean excess-temperature of the thermometer-pockets above the regulator tank, namely $(t_1+t_2+t_4-3t_3)/4$, varied but slightly with the flow. The loss from the inner tubes of the exchanger itself, *when unjacketed*, was nearly 2 calories per second, but varied by nearly 20 per cent. of itself when the flow was changed in the ratio of 1 to 10. This could easily be foreseen, because the cold current was raised to a higher temperature when the flow was small. The actual distribution of temperature in the outer tube of the exchanger was observed by means of thermocouples, and found to correspond with theory and with the observed changes in the heat-loss with flow. The jacket-tube J was designed to intercept this variable heat-loss and reduce it to about a tenth for the smallest flow. The mean rise of temperature of the jacket-tube for the smallest flow was found to be of the order of 1° C. The mean difference of temperature between the jacket-tube and the regulator was always measured and allowed for in estimating the mean excess-temperature, but it was generally less than 0°·2 C. for the largest flow, corresponding to a heat-loss of about 1 in 10,000, which was about the limit of agreement of the temperature measurements. It was ultimately decided to do without jackets for the thermometer-pockets at temperatures below 100° C., because the heat-loss from the thermometer-pockets at these low temperatures was fairly small and nearly independent of the flow. The omission of these jackets considerably simplified the construction and connection of the apparatus. The main jacket J for the exchanger was employed in nearly all the experiments, because it made the heat-loss so nearly independent of the flow, and made the reduction of the observations comparatively simple and certain.

For regulating the temperature of the cold current, an electric temperature regulator was employed of the same type as that used in the continuous-electric method, which had been specially designed to prevent hunting. With a 32 c.p. lamp, and suitable adjustment of the cooling water, currents up to 20 gr./sec. could be kept steady to a few thousandths of 1° C. for considerable periods, over a range from 20° C. to 35° C. But this was not such an easy matter as might be imagined, owing to variations of temperature of the cooling water.

During the months of May, June, and July, 1911, upwards of 150 complete sets of readings were taken, each for a single flow. The upper limit of temperature was always nearly 100° C., but the lower limit was varied from 25° C. to 35° C. The flow was varied from 1 c.c./sec. to 20 c.c./sec. It is a great advantage of the method that it permits the flow to be so widely varied without introducing any serious experimental difficulties, but the largest flows were somewhat difficult to regulate, and there was no material gain in accuracy beyond about 10 c.c./sec., at which point the limit of accuracy of the thermometric readings corresponded with the limit of reading the total heat curves. Many variations were tried in the disposition of the apparatus, with corresponding variations in the heat-loss, which, even without jackets or lagging, seldom exceeded 1 per cent. of the heat-exchange for the largest flow. The results of all these experiments were so nearly similar that it will suffice to give one example of the detailed readings. The following readings were taken with the jacket-tube J surrounding the exchanger, but without lagging or jackets on the thermometer-pockets :—

OBSERVATIONS of July 3, 1911.

Flow gr./sec. Q . .	10·44	10·47	7·43	4·08	2·55	1·240
Thermometer t_1 . .	+99·980	99·972	99·901	99·702	99·451	98·762
„ t_2 . .	−68·979	68·989	67·107	64·383	62·996	61·763
„ t_3 . .	+25·442	25·445	25·466	25·524	25·548	25·587
„ t_4 . .	−56·452	56·436	58·205	60·628	61·567	61·486
Sum Σt	− 0·009	− 0·008	+ 0·055	+ 0·215	+ 0·436	+ 1·100
Σdh from curve . .	+ 0·152	+ 0·152	+ 0·153	+ 0·154	+ 0·152	+ 0·148
Heat-loss X	1·49	1·50	1·54	1·51	1·50	1·55

The above table includes observations for five different values of the flow. Each flow was maintained steady for about half-an-hour, during which time two measurements of the flow were taken, and four sets of readings of the thermometers. The flows generally agreed to 1 in 500, and the thermometers seldom varied more than 0°·01 C. in half-an-hour. In the above example the readings for the maximum flow were continued for over an hour. Such changes in the thermometer readings as occurred during each flow were due partly to change in the barometer and partly to change in the temperature of the cooling water, which also made it necessary to reset the regulator between each flow, as indicated by the readings of the thermometer t_3.

It was found on reducing the above observations that insufficient time had been allowed for the conditions to become steady after changing the flow from 10·47 to 7·43 gr./sec. A change of 0°·016 C. occurred in t_3 after the first pair of readings at Q = 7·43. All the readings have been included in the mean, but, if the first pair had been rejected, the heat-loss would have been 1·50 for this flow. The signs attached to the temperatures are those taken in finding the sum Σt. The values of Σdh were taken from the curve given in fig. 6, representing my formula (10). The values of the heat-loss X deduced are nearly the same for all the flows. It should be observed that the heat-loss, 1·50 cal./sec., is less than 0·5 per cent. of the heat-exchange, 325 cal./sec., for the large flow, and that the flow could easily be varied in the ratio of 1 to 8. In the continuous-electric method with a vacuum-jacket, the heat-loss at 92° C. amounted to 4 per cent. of the maximum watts, or 10 per cent. of the difference between the flows, on which the result depends. In REYNOLDS and MOORBY's experiments the heat-loss amounted to 5 or 10 per cent. (with or without lagging) of the difference of the loads in the heavy and light trials. In neither case could the flow be varied satisfactorily in a ratio greater than about 1 to 2. The continuous-mixture method is undoubtedly preferable to either in this respect, since it permits a wider range of variation of the flow, and a greater reduction in the heat-loss. The agreement of the values of the heat-loss deduced from the different flows by means of formula (10) is closer than might have been expected, because 1 in the last figure of the heat-loss corresponds to 0°·001 C., or 1 in 30,000 of the heat-exchange for the large flow. It may be said that formula (10) is verified to at least 1 in 5,000 for the ratio of the mean specific heat from 69° C. to 100° C., where it differs most widely from LÜDIN's, to the mean specific heat from 25° C. to 56° C. Formula (10) gives 1·0050 for the ratio. LÜDIN's formula gives 1·0104, differing by 0·54 per cent. If LÜDIN's formula had been employed for the reduction, the heat-loss, instead of being nearly the same for the different flows, would have appeared to vary from 3·38 for the largest flow to 1·79 for the smallest flow. The heat-loss should, as a matter of fact, have been slightly less for the large flows than for the small, because the rise of temperature of the jacket J with the smallest flow was rather more than sufficient to compensate for the fall of mean temperature of the thermometer-pockets.

Seeing that the results of the continuous-electric method have now been so closely verified by the continuous-mixture method, which is independent of electrical energy measurements, it would appear to follow that the discrepancy of 1 per cent. at 80° C. between these methods and those of Messrs. BOUSFIELD and LÜDIN is to be attributed mainly to fundamental differences in the thermometric and calorimetric methods employed. In my continuous-flow methods the troublesome and uncertain corrections of mercurial thermometry at temperatures between 40° C. and 100° C. have been avoided, and a higher order of accuracy in the temperature measurements has been secured by the direct employment of platinum thermometers. Errors due to lag, or to uncertainty of the water-equivalent of the calorimeter and its variation with temperature, have been practically eliminated by keeping all the conditions steady, so that the observations could be pushed to the limit of accuracy of temperature measurement. Errors due to dissolved air and to evaporation, which are quite appreciable at 40° C., and begin to be serious at 50° C., with an open calorimeter, have been minimised by keeping the water free from air up to the moment of its passage into the calorimeter, where it is completely enclosed and protected from evaporation. Without presuming to criticise in detail the work of Messrs. BOUSFIELD, I maintain that these difficulties have not been adequately met in their investigations, and would inevitably give rise to constant errors, which could not be detected without fundamental variations in the conditions of experiment. While their method may undoubtedly be suitable for the purpose for which it was originally devised, namely, that of comparing the specific heats of similar solutions over the same range of temperature, I cannot admit that it affords any promise of exceptional accuracy in the determination of the variation of the specific heat *over different ranges* of temperature, which is a much more difficult problem. According to my own work and that of Dr. BARNES, the whole variation of the specific heat of water between 10° C. and 80° C. is less than one-half of 1 per cent., and demands the most accurate methods of investigation. The occurrence of so high a maximum as LÜDIN'S experiments show in the neighbourhood of 80° C. is theoretically inadmissible, and cannot be reconciled with the work of REYNOLDS and MOORBY, or with the corrected results of REGNAULT, which are satisfactorily represented by my formula.

Variation of Specific Heat with Pressure.

The continuous-electric and continuous-mixture methods both compare the variations of the total heat of the fluid, $h = E + pv$, under the condition of practically constant pressure, or give ratios of the values of the mean specific heat at constant pressure over different ranges of temperature. Below 100° C. the pressure is always atmospheric, and the variation of the specific heat with pressure does not exceed 1 in 10,000 per atmosphere. At higher pressures and temperatures it would be necessary to take account of the variation of the specific heat with pressure in comparing observations taken at different pressures, since the pressure in the apparatus must always exceed the saturation pressure at the highest temperature observed. This reduction can be effected with sufficient approximation by means of the thermodynamical relation,

$$(ds/dp)_\theta = -\theta\,(d^2v/d\theta^2)_p.$$

The variation amounts to nearly 2 in 10,000 per atmosphere at 200° C. The quantity of heat supplied to water in a boiler, maintained at constant pressure and temperature, per unit mass of water pumped into it at the same pressure but at a lower temperature, is the change of total heat at constant pressure, and is a quantity of the same kind as that measured in the continuous-mixture method. The work $(p-p_0)v_0$, which is generally included in tabulated values of the total heat, is supplied as work by the feed-pump, and not as heat in the boiler. It would amount to only 1 in 500 of the total heat at 200° C., and might be neglected except in the most accurate calorimetric work.

The quantity measured in REGNAULT'S method was the change of total heat from boiler pressure and temperature down to the final temperature of the calorimeter at atmospheric pressure, which may be denoted by the expression $(\mathrm{E}+pv)-(\mathrm{E}_1+p_1v_1)$, where the suffix 1 denotes atmospheric pressure at the final temperature of the calorimeter. The differential of this is the rate of change of the total heat of water under saturation pressure, and exceeds the specific heat at a constant pressure equal to that of saturation by the expression $[v-\theta(dv/d\theta)_p](dp/d\theta)_{\text{sat}}$, which amounts to nearly 0·3 per cent. at 200° C. The specific heat at constant pressure exceeds the so-called "saturation" specific heat at the same pressure and temperature by the expression $\theta(dv/d\theta)_p(dp/d\theta)_{\text{sat}}$, which amounts to 0·6 per cent. at 200° C. The values of the total heat and the specific heat from 100° C. to 200° C. given in the following tables, in so far as they represent a reduction of REGNAULT'S observations, must be taken as representing the total heat of water and its rate of variation under saturation pressure, and not under constant pressure; but the uncertainty of the reduction probably exceeds the difference in question.

The quantity measured by DIETERICI was the change of intrinsic energy E of water from saturation pressure and temperature in the heater to saturation pressure at 0° C., which may be denoted by $\mathrm{E}-\mathrm{E}_0$. Neglecting the small change of intrinsic energy due to 1 atmosphere at 0° C., the quantity measured by DIETERICI is less than that measured by REGNAULT by the expression $(pv-p_1v_0)$, which amounts to 0·43 calorie at 200° C., or 0·2 per cent. on the mean specific heat. His tabulated values of the mean specific heat at 200° C., when reduced to a unit at 20° C., are already 0·8 per cent. higher than my reduction of REGNAULT'S observations, so that the discrepancy is increased to 1 per cent. at this point if allowance is made for the difference in the quantities measured. The actual specific heat at t tabulated by DIETERICI is the rate of increase of the intrinsic energy under saturation pressure, which is less than that of the total heat $\mathrm{E}+pv$ under the same conditions by the expression $[d(pv)/d\theta]_{\text{sat}}$, which amounts to nearly 1 per cent. at 200° C. The specific heat tabulated by DIETERICI already exceeds that deduced from REGNAULT by 2 per cent. at 200° C., so that the discrepancy is increased to 3 per cent. in the value of the actual specific heat at this point. The discrepancy is of the same order as the whole variation of the specific heat, and is not unimportant from a theoretical standpoint. Accurate experiments at these temperatures are very difficult, but it is clear that further experiments are desirable, if any theory of the variation of specific heat is to be framed or tested.

Explanation of the Tables.

The most useful table in practice is that of the variation of the total heat, which also permits the mean specific heat between any limits to be readily calculated. The corresponding curve, representing the variation between 0° C. and 100° C., has been given in fig. 6, but the scale of fig. 6 does not permit the values to be read with sufficient accuracy from the curve as reproduced. It should be observed that it is important to tabulate the variation in terms of the specific heat at 20° C. taken as unity, and not in terms of the specific heat at 15° C., which is so often taken as the standard, because in the latter case the values of dh from 42° C. to 92° C. would all be negative, which would be inconvenient in using the table. If, on the other hand, the minimum value of s, or the value at 30° C., were taken as the standard, the values of dh would be inconveniently large.

The table gives the values of dh for each degree, and a column of differences is added to facilitate interpolation if desired, but the differences are so small for the greater part of the range 0° C. to 100° C. that this is seldom required. Above 100° C. the differences are larger, but the values are here so uncertain that it could seldom be worth while to interpolate. The method of using the table is fairly obvious, but the following examples may make it clearer.

To find the total heat h from 0° C. to any point t; add to the exact value of t, expressed to $0^\circ\cdot001$ C., the corresponding value of dh for the nearest whole degree taken from the table, interpolating for fractions of a degree if great accuracy is required in a problem depending on small differences. Unless t is known to $0^\circ\cdot001$ C., interpolation is unnecessary.

To find the change of total heat between t_1 and t_2; find from the table the corresponding values of dh, namely, dh_1 and dh_2, and add the difference $dh_2 - dh_1$ to the difference $t_2 - t_1$, with due regard to sign.

To find the mean specific heat from 0° C. to t; divide the corresponding value of dh by t and add unity.

To find the mean specific heat between t_1 and t_2; find the difference $dh_2 - dh_1$, divide by the difference $t_2 - t_1$, and add unity. Thus, if the given values are $t_1 = 25^\circ\cdot442$ C., $t_2 = 56^\circ\cdot452$ C., we find $dh_1 = 0\cdot073$, $dh_2 = 0\cdot037$, whence $dh_2 - dh_1 = -0\cdot036$, $s_{1,2} = 1 - 0\cdot036/31\cdot0 = 1 - 0\cdot00116 = 0\cdot99884$. The result will be correct to 1 in 10,000, if $t_2 - t_1$ is not less than 10° C. If the range is less than 10° C., the specific heat at the mean point of the range, taken from the table of specific heat at t, is a sufficiently close approximation in most cases.

The values of the entropy of water ϕ reckoned from 0° C. are sometimes required, and are generally given in steam-tables. Assuming that 0° C. is $273^\circ\cdot10$ C. from the absolute zero, the formula for the entropy obtained by integrating from 0° C. to t formula (6) for the specific heat divided by $t + 273\cdot1$ is as follows:

$$\phi = 2\cdot36602 \log_{10} (t+273\cdot1)/273\cdot1 + 0\cdot004586 \log_{10} (t+20)/20 \\ - 0\cdot01618\,(t/100) + 0\cdot0045\,(t/100)^2.$$

TABLE of the Specific Heat of Water, $s = dh/dt$ at t° C., for each degree from 0° C. to 200° C., in terms of the specific heat at 20° C. taken as unity, according to formula (6), p. 10, above, namely,

$$s = 0{\cdot}98536 + \frac{0{\cdot}504}{t+20} + 0{\cdot}0084\,\frac{t}{100} + 0{\cdot}0090\left(\frac{t}{100}\right)^2, \quad \ldots \quad (6)$$

referred to the standard scale of temperature t, deduced from the platinum scale pt by the difference formula (1), p. 1, above, namely,

$$t - pt = 1{\cdot}50\,t\,(t-100)\times 10^{-4}. \quad \ldots \quad (1)$$

t.	0° C.	1° C.	2° C.	3° C.	4° C.	5° C.	6° C.	7° C.	8° C.	9° C.	Differences.
° C.											
0	1·01056	1·00944	1·00844	1·00753	1·00671	1·00596	1·00528	1·00466	1·00410	1·00358	112 to 48
10	1·00310	1·00266	1·00225	1·00188	1·00154	1·00122	1·00093	1·00066	1·00042	1·00020	44 ,, 20
20	1·00000	0·99982	0·99964	0·99948	0·99934	0·99922	0·99911	0·99901	0·99892	0·99884	18 ,, 8
30	0·99877	0·99870	0·99865	0·99861	0·99858	0·99856	0·99855	0·99854	0·99854	0·99855	−7 ,, +1
40	0·99856	0·99858	0·99861	0·99864	0·99867	0·99871	0·99875	0·99881	0·99887	0·99894	+2 ,, +7
50	0·99901	0·99909	0·99917	0·99925	0·99933	0·99942	0·99952	0·99962	0·99972	0·99983	8 to 11
60	0·99994	1·00005	1·00017	1·00029	1·00042	1·00055	1·00079	1·00083	1·00097	1·00111	11 ,, 14
70	1·00125	1·00140	1·00155	1·00170	1·00185	1·00201	1·00217	1·00234	1·00251	1·00269	15 ,, 18
80	1·00288	1·00306	1·00324	1·00342	1·00361	1·00380	1·00399	1·00419	1·00439	1·00459	18 ,, 20
90	1·00479	1·00499	1·00520	1·00541	1·00562	1·00583	1·00605	1·00627	1·00650	1·00673	20 ,, 23
100	1·00696	1·00719	1·00742	1·00766	1·00790	1·00814	1·00838	1·00862	1·00887	1·00912	23 to 25
110	1·00937	1·00962	1·00988	1·01014	1·01040	1·01066	1·01092	1·01119	1·01146	1·01173	26 ,, 27
120	1·01200	1·01228	1·01256	1·01284	1·01312	1·01340	1·01368	1·01397	1·01426	1·01455	28 ,, 29
130	1·01484	1·01514	1·01544	1·01574	1·01604	1·01634	1·01665	1·01696	1·01727	1·01758	30 ,, 31
140	1·01790	1·01822	1·01854	1·01886	1·01919	1·01952	1·01985	1·02018	1·02051	1·02084	32 ,, 34
150	1·02118	1·02152	1·02186	1·02220	1·02254	1·02289	1·02324	1·02359	1·02394	1·02429	34 to 35
160	1·02464	1·02500	1·02536	1·02572	1·02608	1·02645	1·02682	1·02719	1·02756	1·02793	36 ,, 37
170	1·02830	1·02868	1·02906	1·02944	1·02982	1·03021	1·03060	1·03099	1·03138	1·03177	38 ,, 39
180	1·03216	1·03256	1·03296	1·03336	1·03376	1·03416	1·03457	1·03498	1·03539	1·03580	40 ,, 41
190	1·03621	1·03663	1·03705	1·03747	1·03789	1·03831	1·03873	1·03916	1·03959	1·04002	42 ,, 43

200 1·04045 REGNAULT (uncorrected) 1·0440 at 200° C.

The values are calculated from the formula to the fifth place, which is useful for small differences, and as serving to fix the value in the fourth place. The Mechanical Equivalent J may be taken as equal to 4·180 s joules/gr.-deg. C.

VARIATION of the Total Heat of Water, $h = t + dh$, reckoned from 0° C. Table of Values of dh for each degree from 0° C. to 200° C., in terms of the specific heat at 20° C. taken as unity, according to formula (10), p. 21,

$$dh = 1{\cdot}1605 \log_{10} \frac{t+20}{20} - 1{\cdot}464 \frac{t}{100} + 0{\cdot}42 \left(\frac{t}{100}\right)^2 + 0{\cdot}30 \left(\frac{t}{100}\right)^3 . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

referred to the standard scale of temperature t defined by the formula (1), p. 1, above, namely,

$$t - pt = 1{\cdot}50\, t\, (t - 100) \times 10^{-4} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

t.	0° C.	1° C.	2° C.	3° C.	4° C.	5° C.	6° C.	7° C.	8° C.	9° C.	Difference per 1° C.
° C.											
0	0·000	0·010	0·019	0·027	0·034	0·040	0·046	0·051	0·055	0·059	10 to 4
10	0·062	0·065	0·068	0·070	0·071	0·072	0·073	0·074	0·075	0·075	3 ,, 0
20	0·075	0·075	0·075	0·075	0·074	0·073	0·073	0·072	0·071	0·069	0 ,, −1
30	0·068	0·067	0·066	0·064	0·063	0·062	0·060	0·058	0·057	0·056	−1
40	0·054	0·053	0·051	0·050	0·048	0·047	0·046	0·045	0·044	0·043	−1
50	0·042	0·041	0·040	0·039	0·038	0·038	0·037	0·037	0·037	0·036	−1 to 0
60	0·036	0·036	0·036	0·037	0·037	0·037	0·038	0·039	0·040	0·041	0 ,, +1
70	0·042	0·043	0·045	0·046	0·048	0·050	0·052	0·054	0·057	0·059	1 ,, 2
80	0·062	0·065	0·068	0·072	0·075	0·079	0·083	0·087	0·091	0·095	3 ,, 4
90	0·100	0·105	0·110	0·115	0·121	0·127	0·133	0·139	0·145	0·152	5 ,, 7
100	0·159	0·166	0·173	0·181	0·189	0·197	0·205	0·213	0·222	0·231	7 to 9
110	0·240	0·250	0·260	0·270	0·280	0·290	0·301	0·312	0·323	0·335	10 ,, 12
120	0·347	0·359	0·372	0·385	0·398	0·411	0·424	0·438	0·452	0·466	12 ,, 14
130	0·481	0·496	0·511	0·527	0·543	0·559	0·575	0·592	0·609	0·626	15 ,, 17
140	0·644	0·662	0·680	0·699	0·718	0·737	0·757	0·777	0·798	0·819	18 ,, 21
150	0·840	0·861	0·883	0·905	0·927	0·950	0·973	0·996	1·020	1·044	21 to 24
160	1·069	1·093	1·118	1·143	1·169	1·195	1·223	1·250	1·278	1·306	24 ,, 28
170	1·334	1·362	1·391	1·420	1·450	1·480	1·511	1·542	1·573	1·605	28 ,, 32
180	1·637	1·669	1·702	1·735	1·768	1·802	1·836	1·870	1·905	1·941	32 ,, 36
190	1·977	2·013	2·050	2·087	2·125	2·163	2·202	2·241	2·280	2·320	36 ,, 40

200 2·361 REGNAULT (uncorrected) $h = 203{\cdot}20$ at 200° C.

If the specific heat were constant and equal to unity the value of ϕ would be

$$2{\cdot}30259 \log_{10} (t+273{\cdot}1)/273{\cdot}1.$$

The values of the specific heat, total heat, and entropy between 0° C. and 100° C. are for a constant pressure of 1 atmosphere. The values above 100° C. are for water under saturation pressure. The difference between saturation pressure and 1 atmosphere would not affect the values by 1 in 10,000 below 100° C.

In conclusion, my best thanks are due to Mr. W. J. Colebrook, Superintendent of the Physics Workshop of the Imperial College, and to other members of the staff under his direction, for the great care and skill displayed in making and adjusting the platinum thermometers and other apparatus required for this investigation.