NOTE ON THE VARIATION OF THE SPECIFIC HEAT OF WATER BETWEEN 0° AND 100°C.

BY H. L. CALLENDAR AND H. T. BARNES.

THE present note which it is thought would be of interest to many of the readers of the PHYSICAL REVIEW is, with a few changes made to introduce later results, almost a reprint of the report communicated by the authors at the meeting of the British Association at Dover (Sept., 1899). In 1897, during the Toronto meeting, a preliminary note was communicated to the same society, in which the authors described briefly a new method for determining the specific heat of a liquid in terms of the international electrical units. At that time the method had only been roughly applied to the cases of water and mercury. The preliminary apparatus, however, was exhibited to several members of Section A on the occasion of their visit to McGill University. One of the main objects of the work was the determination of the variation of the specific heat of water over the range 0° to 100°C. for which the method is peculiarly suited. Shortly after the commencement of the work one of the authors (H. L. C.) was called to London to fill the Quain Chair of Physics in University College, leaving the work in the sole charge of H. T. B.

The general principle of the method, and the construction of the apparatus will be readily understood by reference to the diagram of the continuous-flow electric calorimeter given in Fig. 1. A steady current of water flowing through a fine tube, AB, is heated by a steady electric current in a central conductor of platinum. The steady difference of temperature between the inflowing and outflowing water is observed by means of a differential pair of platinum thermometers at either end. The bulbs of these thermometers are surrounded by thick copper tubes, which by their conductivity serve to equalize the temperature, and to prevent the generation of heat by the current in the neighborhood of the bulbs of the ther-

mometers. The leads CC serve for the introduction of the current, and the leads PP, which are carefully insulated, serve for the measurement of the difference of potential on the central conductor. The flow tube is constructed of glass, and is sealed at
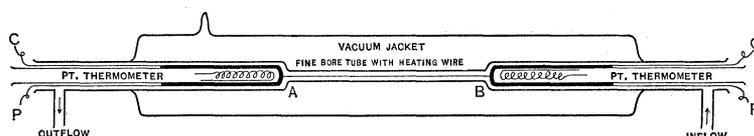

Fig. 1.

either end, at some distance beyond the bulbs of the thermometers, into a glass vacuum jacket, the function of which is to diminish as much as possible the external heat loss. The whole is enclosed in an external copper jacket (not shown), containing water in rapid circulation at a constant temperature maintained by means of a very delicate electric regulator.

The general equation of the method may be stated in the following form :

$$JMd\theta + H = ECt.$$

The difference of potential E on the conductor is measured in terms of the Clark cell by means of a Thomson-Varley slide potentiometer, very accurately constructed and calibrated. The current C is also measured by observing the difference of potential on a standardized resistance R included in the circuit.

The Clark cells employed in this work were " crystal " cells [1] of the B. O. T. pattern and hermetically sealed cells. They were kept immersed in a regulated water bath at a constant temperature, near 15° C., and have maintained their relative differences constant to a few parts in 100,000 since they were made in 1895.

The resistance R consists of two one-ohm coils in parallel, each made of four bare platinum-silver wires in parallel wound on mica frames and immersed in paraffin oil at a constant temperature. The coils were annealed at a red heat after winding on the mica frames, and are not appreciably heated by the passage of the electric currents employed in the work. The two one ohms are repeatedly

[1] H. L. Callendar and H. T. Barnes, Proc. Roy. Soc., 62, 117 (1897).

standardized by comparison with an oil immersed certified one ohm manganin standard of the English Electrical Standards Committee, and have not changed their resistance since being made by as much as 5 parts in 100,000.

The time of flow t of the mass of water, M, was generally about fifteen minutes, and was recorded automatically on an electric chronograph reading to .01 second, on which the seconds were marked by a standardized clock.

The letter J stands for the number of joules in one calorie at a temperature which is the mean of the range $d\theta$, through which the water is heated.

The mass of water, M, was generally from 400 to 600 grammes. After passing through a cooler, it was collected and weighed in a tared flask in such a manner as to obviate all possible loss by evaporation.

The range of temperature was generally about 8° in the series of experiments on the variation of J, but other ranges from 1° to 12° were tried to test the theory of the method. The thermometers were read to the ten-thousandth part of a degree, and the difference was probably in all cases accurate to .001° C. This order of accuracy could not have been possible with mercury thermometers under the conditions of the experiments.

The external loss of heat, H, was very small, owing to the perfection and constancy of the vacuum attainable in the sealed glass jacket. It was determined and eliminated by adjusting the electric current so as to secure the same rise of temperature, $d\theta$, for widely different values of the water-flow.

The great value of the continuous-flow method as compared with the more common method in which a constant mass of water at a uniform temperature is heated in a calorimeter, the temperature of which is changing continuously, is that in this method there is practically no change of temperature in any part of the apparatus during the experiment. There is no correction required for the thermal capacity of the calorimeter; the external heat loss is more regular and certain, and there is no error due to the lag of the thermometers. Another distinct advantage is that the steadiness of the conditions permits the attainment of the highest degree of accuracy in the instrumental readings.

In work of this nature it is recognized as being of the utmost importance to be able to detect and eliminate constant errors by varying the conditions through as wide a range as possible. In addition to varying the electric current, the water-flow, and the range of temperature, it is possible with comparatively little trouble to alter the form and resistance of the central heating conductor, and to change the glass calorimeter for one with a different degree of vacuum, or a different bore for the flow tube. Several different calorimeters were thus employed, and the agreement of the results, on reduction, affords a very satisfactory test of the accuracy of the method.
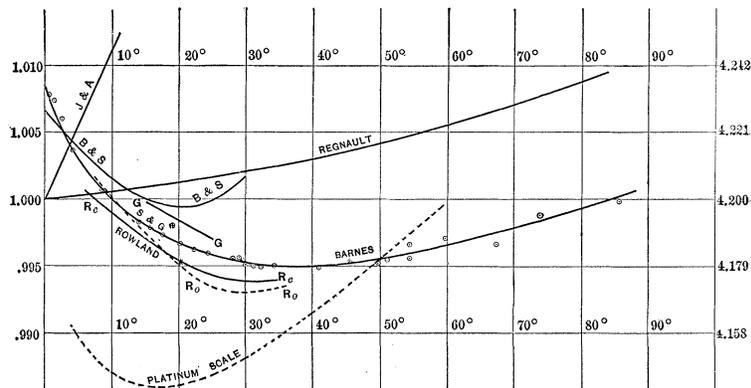

Fig. 2.

Variation of the Specific Heat of Water between 0° and 100° C.

J. & A.   Jamin and Amaury, 1870.
B. & S.   Bartoli and Stracciati, 1891.
R_0.   Rowland's Original Values, 1880.
R_c.   Rowland's Corrected Values, 1898.
G.   Griffiths, 1893.   ⎫
S. & G.   Shuster and Gannon, 1893.   ⎬   Lord Rayleigh's Value for the Clark Cell, Assumed.
⊙   Authors' Values, 1899.   ⎭

*   Authors' at 20.°2 C.   ⎫   Kahle's and Carhart's Identical Clark Cell Values, Assumed.
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The general results of the investigation, so far as it is possible to give them for publication at present, may be seen by reference to the plot given in Fig. 2, which includes also the results of other ob-

servers, to the same scale. The curve marked Regnault represents the well-known formula of Regnault which has been adopted as the basis of much calorimetric work. This formula was confessedly approximate, and was deduced from experiments on mixing water at high temperatures with water at $15°$ C. The method could not be expected to give any information with regard to the variation of the specific heat at ordinary temperatures. The experiments of Jamin and Amaury (J. and A.), by the method of electric heating, gave a very rapid increase of the specific heat at low temperatures, but the science of electrical measurement, and the difficulties of the electrical method, were not at that date sufficiently known to render the results of any value.

Rowland's original curve (R_o) is shown by the dotted line, and with it his corrected values[1] (R_c) are given by the smooth line. His original results, obtained by Joule's method, were expressed in terms of his own air thermometer, and showed, for the first time, how rapidly the specific heat of water diminishes as the temperature rises from $0°$ to $30°$ C. The corrected values are those obtained by reducing his thermometers to the Paris scale. The effect of this correction is to lower the temperature at which the specific heat is 4.200 joules from $10°$ to $7°$ C. and to diminish the temperature coefficient. In the plot in Fig. 2 the right hand margin gives the scale of joules in absolute measure.

The experiments of Bartoli and Stracciati (B. and S.) were made by the method of mixtures, and are expressed in terms of a thermal unit at $15°$ C. Their curve bears a general resemblance to that of Rowland, but shows a minimum point at $20°$ C. The errors and limitations of this method are well known, and it is difficult to suppose it capable of any high degree of accuracy, or to think otherwise than that the excessive lowering of the minimum point is due to some error not eradicated by mere repetition of similar experiments.

The experiments of Griffiths (G.) between $15°$ and $25°$ were made by observing the rate of rise of temperature of a mass of water heated by an electric current. His work threw a flood of light on the difficulties of electric calorimetry, and explained the failure of

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[1] William S. Day, PHYSICAL REVIEW, 7, 193 (1898).

previous observers to obtain satisfactory results by this method. Over the range of his experiments he found approximately the same rate of diminution of the specific heat as that given by Rowland.

The curve marked by circled dots in the figure, extending from 0° to 86° C. represents the results so far obtained in the present investigation. The points represented are samples of single observations with different calorimeters, and give an idea of the order of accuracy attainable by this method. The accuracy of course diminishes as the temperature rises, owing to the greater difficulty of obtaining satisfactory regulation in the water-jacket at the higher points.

The curve shows clearly that the minimum point occurs at 40° instead of 30°. The experiments of Rowland did not extend sufficiently beyond his minimum point to obtain a satisfactory determination. The value of the specific heat could not be determined by his method with the same accuracy at the extremities of the range as in the middle, and all the probable errors of the method would be greatly increased as the temperature of the calorimeter was raised above its surroundings. In particular, the corrections and changes of zero of the mercury thermometers, and the rate of external heat loss, would be excessive at the higher points. In the present work, however, there are no thermometric difficulties of this nature, owing to the use of platinum thermometers, and the external heat loss increases very little as the temperature is raised, because the external water-jacket is always at the same temperature as the inflowing water, so that the mean excess of temperature is always nearly the same. Another indication that the temperature of minimum specific heat is not far below the middle of the range is given by the experiments of Regnault, and more recently by those of Reynolds and Moorby, on the mean specific of water between 0° and 100° C. Their results by entirely different methods agree in showing that the mean specific heat over the whole range does not greatly exceed the value at 20° C.

The present work shows that the specific heat of water approaches an exceedingly high value at 0°. The observations at 0.6°, 1.5°, 2° and 4° were obtained by using rises of temperature of

1°, 3°, 4° and 8° with the inflow water nearly at 0°.   This rapid in-
crease, shown by these points, was foreseen by Rowland, but not
shown in his work.

It is interesting to compare the absolute values of the specific
heat deduced by the electrical method with those of Rowland by
the mechanical method.   For this purpose the authors' results, and
those of Griffiths (G.), and of Shuster and Gannon (S. and G.), have
been reduced to joules on the assumption that the absolute value
of the E. M. F. of the Clark cell is that found by Glazebrook and
Skinner, assuming Lord Rayleigh's value of the electro-chemical
equivalent of silver, and taking the international ohm as correct.   It
has been pointed out that the results of Griffiths would be brought
into harmony with those of Rowland by supposing that the true
E. M. F. of the Clark cells employed was about 2 millivolts lower,
or one part in 700.   The authors' results, however, lie about mid-
way between those of Rowland and Griffiths, and would require a
correction of only 1 millivolt, if the whole of the difference were to
be ascribed to the Clark cell.   It is not at all likely that the cells
used in this work can have exceeded the B. O. T. standard by so
much as 1 millivolt, or that the resistance standards can have been
incorrect by as much as one part in 700.   It is most likely that
both the Clark cells and the resistance standards agreed with those
used by Griffiths to within one or two parts in 10,000 and that the
difference of the results is mainly to be attributed to the radical dif-
ference in the methods of calorimetry.   In view of the recent deter-
minations of the absolute value of the Clark cell made by Kahle
and later by Carhart and Guthe, the authors' value at 20° C. is re-
duced assuming the new value of the Clark cell, *i. e.*, 1.4330 volts.
This has the effect of lowering the specific heat and causing it to al-
most exactly coincide with Rowland's corrected value at the same
temperature.   The complete variation curve would then be lowered
the same amount had the new Clark cell value been used in its de-
duction.

These and similar questions relating to the absolute values of the
standards used do not affect the accuracy of the relative results as
regards the variation of the specific heat of water with temperature.
The relative results are regarded by the authors as being as accu-

rate as the present apparatus is capable of affording. By far the most important consideration affecting the form of the curve is the particular thermometric scale to which the results are reduced. If, for instance, the results were expressed in terms of the platinum scale, which differs from the absolute scale by only 0.38° C. at 50° C., when the divergence is a maximum, the curve would be that represented by the dotted line in the figure. The authors' variation curve is deduced from this by the usual parabolic formula, which gives results in practical agreement with the Paris scale.

Since the discussion of the thermal unit introduced by Griffiths at the British Association meeting of 1895, and partly in consequence of the general interest excited by that discussion, so many new facts have been brought out, and so much experience has been gained of the practical effect of the proposals then made, that it appears desirable to discuss more fully the bearing of the present work on the general question of the relation between the various thermal units.

Dieterici[1] made a determination of the mean specific heat in terms of the electrical units by means of a Bunsen ice-calorimeter. His result gives 4.233 joules as the value of the mean specific heat of water in absolute measure between 0° and 100° C.

Winkelmann[2] endeavored to connect this result with Rowland's at low temperatures by assuming a parabolic formula for the mode of variation, and taking the minimum value at 30.6° C. to be 0.9898 of the value at 0° C. This formula makes the ratio of the mean specific heat between 0° and 100° C. to the specific heat at 20° C. to be 1.0120. According to Regnault's formula the same ratio would be 1.0038. If we take Rowland's corrected value at 20° C. as 4.181 joules, the mean value between 0° and 100° would be 4.197 joules according to Regnault, but 4.233 joules according to Winkelmann. The latter gives a remarkable coincidence with Dieterici, in consequence of which the formula of Winkelmann has been frequently quoted and employed in physical investigation. It must be remarked, however, that Rowland's curve is not even approximately parabolic and that the range covered by his observations is hardly

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[1] Wied. Ann., 33, 417 (1888).
[2] Handbook of Physics, Vol. II., Pt. 2, p. 338.

sufficient to justify this method of treatment. It must also be observed that the values given by Winkelmann's formula for the specific heat in the neighborhood of 100°, and still more at higher temperatures, are so large that they cannot possibly be reconciled with the experiments of Regnault and other good observers.

Griffiths[1] came to the conclusion from a comparison of his experiments on the latent heat of evaporation of water at 30° C. and 40° C. with those of Dieterici at 0° C. expressed in terms of the mean specific heat, and with those of Regnault on the total heat or steam at 100° C. that the mean specific heat must be very nearly identical with the specific heat at 15° C., although Regnault's direct experiments made the ratio from 0.5 per cent. to 1 per cent. larger. At his suggestion Prof. Joly performed the inverse experiment of determining the mean specific heat between 12° and 100° with his steam calorimeter in terms of the latent heat of steam at 100° taken as 536.63 times the thermal unit at 15° C. The result of this experiment was to make the mean specific heat appear nearly 0.5 per cent. smaller than the specific heat at 15° C. If we suppose that the inversion of the experiment would tend to reverse the error of the original determination of the latent heat, the result would appear to be strongly in support of Griffith's contention.

Peabody, in the preface of his " Tables of the Properties of Saturated Steam " (1896), as a result of a careful discussion of Rowland's and Regnault's experiments, adopts Rowland's values from 0° to 40°, and expresses his results in terms of the mean specific heat between 15° and 20°. He finds that Regnault's experiments may be sufficiently represented in terms of this unit by assuming the specific heat to be constant and equal to 1.008 between the limits 45° and 155°, and constant and equal to 1.046 between the limits 155° and 200° C. This assumption would make the mean specific heat between 0° and 100° have the value 1.0044 in terms of the specific heat at 17.5° C., or the value 1.0056 in terms of the specific heat at 20° C., assuming Rowland's coefficient of diminution. The general effect of these changes is to make the tables agree fairly well throughout with Regnault's experiments, but the method can only be justified on the ground of expediency, and can hardly be

[1] Phil. Trans., 7, 318 (1895).

regarded as a satisfactory reconciliation of conflicting evidence on account of the assumed discontinuities in the specific heat.

Shaw[1] gives a similar reduction of Regnault's experiments by means of Rowland's original table, but tabulates only the total heat in joules at each point between 100° and 180° C. His reduction shows a similar flattening of the curve between 100° and 150°, as compared with Regnault's formula. This may be a physical fact, but might also be explained by supposing that the earlier experiments at 108° to 120° were about 0.4 per cent. too high. Shaw's reduction expressed in terms of a thermal unit at 20° C. is given for comparison in the table.

Recently a direct determination of the mean specific heat in terms of the mechanical units has been made by Reynolds and Moorby on a large scale with Reynolds' break and a steam engine. Their results expressed in absolute measure is 4.1832 joules, and is entitled to very great weight on account of the minute accuracy of the measurements, and the full discussion of possible sources of error. It exceeds the value found by Rowland at 20°C. by only one part in two thousand, but is no less than 1.20 per cent. smaller than the mean value found by Dieterici. This is a discrepancy far too large to be explained by any uncertainty in the values of the electrical units.

Accepting the trustworthy measurements of Reynolds and Moorby it is clear that the minima of specific heat at 20° and 30° indicated by the work of Bartoli and Stracciati and of Rowland respectively, must be due to some source of error in their methods, and that all formulæ hitherto proposed for the mode of variation of the specific heat between 0° and 100° must be abandoned.

It is possible, however, to deduce a more satisfactory comparison of the results of Rowland with those of Reynolds and Moorby by means of the present series of experiments, on account of their great range, and the close agreement of the individual observations. Neglecting for the present the rapid change of the specific heat in the immediate neighborhood of 0° C., it may be observed that all the authors' observations between 10° and 60° (with the exception of one at 55°) are represented to about one part in 5,000 (*i. e.*,

[1] B. A. Report, 1896, p. 162.

within the limits of agreement of the observations with different calorimeters at any one point) in terms of the minimum value S_{40} at $40°$ C., by the simple formula

$$S_t = S_{40} (1 + .0000045(t - 40°)^2).$$

which gives for the mean specific heat between $0°$ and $t°$ the formula

$$S_0^t = S_{40}(1.0072 - .00018t + .0000015t^2).$$

If this formula could be assumed to hold beyond these limits over the whole range $0°$ to 100, the ratio of the mean specific heat between $0°$ and $100°$ to the specific heat at $20°$ would be 1.0024. Assuming Rowland's 4.181 joules at $20°$, this ratio would give the value 4.191 joules for the mean specific heat, a result obviously in excess of Reynolds' and Moorby's 4.183 joules.

It is evident from the observations at higher temperatures that the variation curve is not symmetrical, but flatter between $60°$ and $100°$. The rate of change of the specific heat at $100°$ as given by the above formula, if extrapolated, is more than twice as great as that given by Regnault, and at $200°$ about four times as great. The experiments of Regnault apply particularly to this portion of the range, for which they have remained the standard, and have been so universally adopted. It would be desirable to retain his formula for the present, with such change as would make it fit the present experiments. It will be readily seen by reference to the figure that Regnault's curve is very nearly parallel to the authors' curve between $40°$ C. and $86°$ C. The two curves can then be very accurately fitted over this range by simply subtracting a constant quantity from the values given by Regnault's formula. This method leads to results, which require the simplest modification of existing tables.

Adopting the authors' formula between $10°$ and $60°$, and the corrected formula of Regnault from $60°$ to $100°$, the ratio of the mean specific heat between $0°$ and $100°$ to the specific heat at $20°$ is 1.0014. Taking Rowland's value as 4.181 joules at $20°$, this ratio would give 4.1868 for the mean specific heat, which exceeds the value found by Reynolds and Moorby by less than one part in a thousand—a discrepancy so small as to be within the limits of

TABLE OF THE SPECIFIC HEAT OF WATER.

RANGE 0° TO 60°C.

FORMULA.

$$S_t = 0.9982 + 0.0000045 (t - 40°)^2.$$

t°C.	Joules.	S_t	S_{40}^t	h Authors' Formula.	Rowland (reduced).
0	4.203	1.0054	—	—	—
5	4.196	1.0037	1.0045	5.023	5.023
10	4.190	1.0022	1.0037	10.037	10.044
15	4.185	1.0010	1.0030	15.045	15.054
20	4.181	1.0000	1.0024	20.048	20.057
25	4.178	0.9992	1.0018	25.045	25.053
30	4.176	0.9987	1.0013	30.039	30.043
35	4.174	0.9983	1.0009	35.032	35.039
40	4.174	0.9982	1.0006	40.024	40.024
45	4.174	0.9983	1.0003	45.016	Peabody 45.000
50	4.176	0.9987	1.0001	50.008	50.008
55	4.178	0.9992	1.0000	55.002	55.080
60	4.181	1.0000	1.0000	60.000	60.120
60	4.181	1.0000	1.0000	60.000	60.12
65	4.184	1.0008	1.0000	65.002	65.16
70	4.188	1.0016	1.0001	70.008	70.20
75	4.191	1.0024	1.0002	75.018	75.24
80	4.195	1.0033	1.0004	80.032	80.28
85	4.199	1.0043	1.0006	85.051	85.32
90	4.203	1.0053	1.0008	90.075	90.36
95	4.207	1.0063	1.0011	95.105	95.40
100	4.212	1.0074	1.0014	100.138	100.44
110	4.222	1.0097	1.0020	110.22	110.67
120	4.232	1.0121	1.0028	120.33	120.73
130	4.243	1.0148	1.0036	130.47	130.80
140	4.255	1.0176	1.0045	140.63	140.88
150	4.267	1.0206	1.0055	150.82	151.01
160	4.281	1.0238	1.0066	161.05	161.20
170	4.295	1.0272	1.0077	171.31	171.61
180	4.310	1.0308	1.0089	181.60	182.14
190	4.326	1.0345	1.0102	191.94	—
200	4.342	1.0384	1.0115	202.31	—
210	4.359	1.0425	1.0130	212.72	—
220	4.377	1.0467	1.0145	223.18	—

(Shaw. — bracketed in Rowland column for 160°–180°.)

Range 60° to 220°C.   Regnault (Corrected).

Formula $S_t = 0.944 + 0.00004t + 0.0000009t^2$.

possible error even in the case of these two extremely accurate de-
terminations.

The annexed table has been constructed on the basis of the above
considerations and represents, by the authors' formula combined
with the corrected formula ot Regnault, the variation of the specific
heat of water between 0° and 220° C. The absolute measure at
20° C. given by Rowland, *i. e.*, 4.181 joules, is taken as the basis
of column 2. The values of the specific heat are worked out assum-
ing a unit at 20° C. and neglecting the rapid increase below 10° C.
The general effect of this table is to diminish the extent of the varia-
tion hitherto assumed, but it is believed that the results here tabu-
lated are within the limits of error of all the best determinations.
The order of agreement may be inferred from a comparison of the
values of h, the total heat of the liquid, given in the last two columns.
The agreement with Rowland is within 1 in 3,000, between 10° and
40°, and with Regnault within 1 in 1,000 at 160° C. The varia-
tions of Regnault's individual observations exceed 5 parts in 1,000.

The values of the total heat h are obtained by integrating the
specific heat from 0° to $t°$ by the formula. By adding below 10°
the constant quantity .020 to the value of h as given in the table,
account is taken of the rapid increase at the freezing point.

In conclusion it may be stated that the work is being rapidly con-
tinued to verify the points obtained above 60° C. The observations
at the higher points are exceedingly difficult and tedious to obtain
but with the present arrangements designed especially with this
object in view observations as high as 95° C., will probably be ob-
tained.