*Volume XVI.* *February, 1903.* *Number 2.*

THE

PHYSICAL REVIEW.

# NOTE ON THE VARIATION OF THE SPECIFIC HEAT OF MERCURY WITH TEMPERATURE. EXPERIMENTS BY THE CONTINUOUS-FLOW METHOD OF CALORIMETRY.[1]

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SINCE the communication to the Royal Society in 1900, of the work of one of the authors on the specific heat of water, it has been possible to continue the experiments by the continuous-flow method of calorimetry to the case of mercury. These measurements, which include an interval of temperature between 0° and 90° C., have been carried out with essentially the same apparatus as previously used for water, and with the same electrical standards. The first determinations which were made by mercury by this method were made by Professor Callendar and one of the authors during the summer of 1897, just previous to the Toronto meeting of the British Association. The results then obtained with our preliminary apparatus were entirely revised and recalculated three years later. It was the intention of one of the authors to include them in his paper on the specific heat of water since they afforded a most satisfactory verification of the theory of the method. Deeming it advisable, however, to redetermine the value of the specific heat and to extend the experiments over as large a range of temperature as possible with more refined apparatus, it was decided to reserve the publication until later. These results, which were ob-

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[1] Paper read before the British Association, Belfast, 1902.

tained from our preliminary experiments, stand in close agreement with the authors later results, the error being less than 1 part in 1,000, although carried out with different electrical standards, and a calorimeter differing materially in design from the one recently employed.

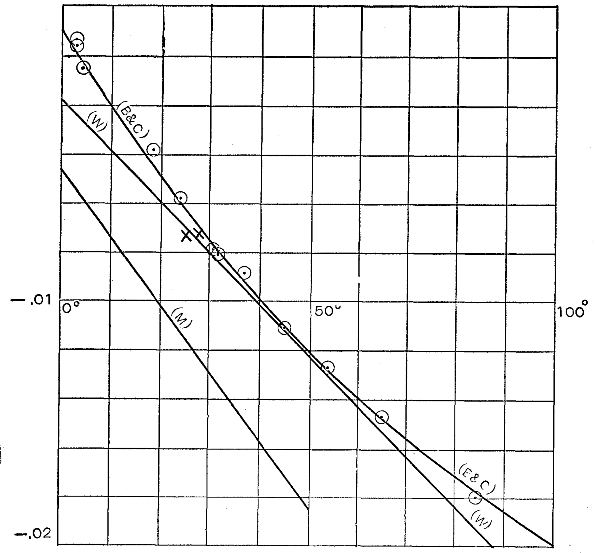

Fig. 1.

⊙. Observations of Barnes and Cooke, 1892. ×. Observations of Callendar and Barnes, 1897. *B. & C.* Formula proposed by Barnes and Cooke. *W.* Formula proposed by Winkelmann. *M.* Formula proposed by Milthaler.

The present series of experiments was made with a calorimeter in every way similar to the " water " calorimeter described by Professor Callendar and one of the authors (B. A. report, 1898) with the exception that the flow tube was smaller in bore. The rest of the apparatus was essentially the same, with a few minor changes.

## Preliminary Results.

These results obtained in 1897, we reproduce here through the courtesy of Professor Callendar who was one of the observers at that time. They were obtained with jacket circulation system, without temperature regulator, so that observations taken at the temperature of the laboratory only could be successfully carried out. The calorimeter employed had a flow tube 1 meter long and 1 mm. in diameter coiled in a spiral as described by Professor Callendar (Phil. Trans., Vol. 199, 1902). The thermometers were pair *A* described by one of the authors (Phil. Trans., Vol. 199, 182, 1902, Sec. 3c). The Clark cells were $S_1$ and $S_5$ and the resistance standard was one of the manganin coils described in Section 3b, *supra.*

The only three determinations made at room temperature are as follows:

| Date. | Mean Temperature. | *Js* | *s* |
|---|---|---|---|
| July 9, 1897 | 25.0 | .13898 | .033174 |
| " 14 " | 27.4 | .13899 | .033177 |
| " 19 " | 28.0 | .13900 | .033179 |

## Recent Results.

The later results were obtained with improved apparatus. The calorimeter had a flow tube about 1 mm. in diameter and 45 cm. long. The thermometers were pair *E.*

The mica-frame resistance standards and Clark cells $X_2$ and $X_{11}$ were used. Redeterminations were made of the value of the resistances in terms of the standard platinum-silver coils in the possession of the laboratory, which showed that they had remained unchanged to 1 in 100,000 since the series of tests taken for the measurements for water, and already described. The Clark cells were found to have lowered a little in value since 1900, and a correction was necessary in order to reduce to the mean of a number of new cells. The history of these original crystal cells, made in 1895, to which $X_2$ and $X_{11}$ belong, shows that from comparisons with new cells made from time to time, they have steadily lowered in value. A new comparison was also made to several Weston cadmium cells. There is no reason to doubt that the values assumed for the electrical standards are the same as those assumed in the measurement of the specific heat of water, to much better than 1 in 10,000. The thermometers were also recalibrated several times, as well as further determinations made of the box coil corrections. Hence, even assuming that any error exists for the values assigned to the units used in the calculations for water, the specific heat of mercury may be expressed from these measurements in terms of water, and any possible error eliminated from the relative value. Since also the same apparatus has been used, and as far as possible the same experimental arrangements systematic sources of error in the method are to a large extent avoided.

The absolute values of the thermal capacity of mercury are given in the following table for different temperatures, calculated by the method already described by one of the authors.

The results are in terms of the nitrogen thermometer and are uncorrected as yet for the temperature gradient in the flow tube as described by Professor Callendar.

Since this correction is small, and is nearly balanced by the correction to the standard hydrogen scale, the results will not be changed much by its application, and the variation with temperature will remain practically unaffected.

| Mean Temp. | $Js$ | $S(J=4.1891)$. | Formula. |
|---|---|---|---|
| 2.85 | .140056 | .033435 | .14003 |
| 2.93 | .140085 | .033440 | .14002 |
| 4.42 | .139927 | .033405 | .13996 |
| 18.37 | .139459 | .033291 | .13939 |
| 24.52 | .139182 | .033224 | .13915 |
| 31.68 | .138890 | .033156 | .13889 |
| 32.14 | .138873 | .033151 | .13888 |
| 32.41 | .138846 | .033141 | .13887 |
| 36.59 | .138753 | .033121 | .13873 |
| 45.00 | .138447 | .033050 | .13847 |
| 53.39 | .138225 | .032997 | .13822 |
| 65.22 | .137942 | .032929 | .13791 |
| 83.89 | .137479 | .032818 | .13752 |

In Fig. 1 is given a plot of the observations the vertical scale being the value $\frac{Js - 0.140}{0.140}$. The preliminary results are also included.

It will be seen that the specific heat decreases with rise in temperature, suggesting that portion of the curve for water between 10° and 20°.

Results over a wider interval of temperature could not be conveniently taken with the present apparatus. We purpose continuing the work to much higher temperatures immediately, in order to trace the course of the curve as the boiling point of the mercury is reached.

The equation representing the change of $Js$ and shown by the curve in Fig. 1, reads:

$$Js_t = Js_0 - 4.462 \times 10^{-5}t + .0157 \times 10^{-5}t^2$$

where

$$Js_0 = .140154.$$

The value of the specific heat in terms of water has been calculated, taking the value of $J$ equal to 4.1891 for a thermal unit at 15.5°, which was the temperature recommended by Griffiths at the Paris Congress in 1900 as being suitable for the selection of the thermal unit.

The temperature expression of the specific heat reads:

$$S_t = S_0 - 1.074 \times 10^{-5}t + .00385 \times 10^{-5}t^2,$$

or

$$\frac{S_t - S_0}{S_0} = -.000321t + .00000115t^2$$

where

$$S_0 = .033458.$$

This gives for the temperature coefficient at any temperature $t$ the expression,

$$\frac{d}{dt}\left(\frac{S_t}{S_0}\right) = -.000321 + .00000230t,$$

and for the average change per degree at 50°, the value $-.0000069$.

## Comparison to the Work of other Observers.

The value of the specific heat obtained by Regnault[1] and so universally adopted, *i. e.*, .03332 is found to be in agreement with our determination at 13.3° and very close to the value at the ordinary temperature of laboratory work. The value was obtained over a range 10° to 100° in terms of a thermal unit at 10°, and is considerably in excess of our value for the same mean temperature.

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[1] Pogg. Ann., 51, 44, 1840; 51, 238, 1840.

Experiments to determine the variation with temperature indicated an increase in specific heat with increasing temperature.

Winkelmann[1] carried out an extensive series of experiments by the method of mixture, to determine the temperature coefficient and was the first to show that the specific heat decreased as the temperature increased. This result being so exceptional at the time and so contrary to the results for other liquids, the author was inclined to regard it as doubtful until he finally verified the first experiments by a second series, in which he eliminated certain sources of error. Two ranges of temperature were taken, the first between 20° and 50° C. and the second between 26° and 142° C. The average variation from these measurements was found to be .0000069. No absolute measurements were made, but the value obtained by Regnault was assumed.

The formula proposed by Winkelmann is shown in Fig. 1; this reads:

$$S_t = S_0 - .0000069t.$$

The remarkable agreement with the average change from our determinations is shown very clearly in the figure, a total decrease of 2 per cent. between 0° and 100° being given both by Winkelmann's results and our own.

The position of the curve in the figure shows that the temperature at which Winkelmann assumed Regnault's value, which in one case was the mean from 16° to 20° and in the second case from 13° to 25° is very nearly equal to the temperature at which our value is exactly equal to Regnault's, *i. e.*, 13.3° C.

Pettersson and Hedelius[2] obtained .033266 between 0° and 5°, .033262 between 5° and 16°, .033300 between 5° and 26° and .033299 between 5° and 36° C. These results were all expressed in terms of a thermal unit for water at 0°.

The measurements were repeated more accurately by J. Milthaler[3] who used a similar method to the previous investigators, *i. e.*, the method of mixture. This author verified Winkelmann's results and

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[1] Pogg. Ann., 159, 152, 1876.

[2] Jour. für Prak. Chem., 24, 136, 1881.

[3] Wied. Ann., 36, 897, 1889.

showed that the specific heat apparently decreased with rise of temperature, the average decrease from his measurements being .0000092, which is somewhat greater than Winkelmann obtained.

The formula proposed by Milthaler is shown in the figure ($M$). The slope of the curve is about the same as the slope of our curve at the low temperature, but since Milthaler supposed this formula to apply as high as 200° its agreement for the low temperatures is more a matter of coincidence. The position of the line in the figure shows that the value of Pettersson and Hedelius which he assumed, is too small at 0° compared to our values, but this value will be increased when corrected to a thermal unit for water at 15.5° instead of 0° and will then be brought into much closer agreement.

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