

ART. VIII.—*On the Variation of the Specific Heat of Water*; by G. A. LIEBIG, Student of Physics in the Johns Hopkins University.

UNTIL the year 1877 it was generally believed by physicists that the specific heat of water increased regularly from  $0^{\circ}$  to  $100^{\circ}$ . During that year, however, Professor Rowland proved by his researches on the mechanical equivalent of heat\* and by separate experiments, using the method of mixture, that the specific heat of water did not increase regularly with increase of temperature, but decreased from  $0^{\circ}$  to a minimum at about  $30^{\circ}$ . In 1882, F. Neesen,† of Berlin, investigated the subject, deducing the variation of the specific heat of water from the specific heat of platinum, which he had previously determined; and although his results are not quantitatively the same as Rowland's they are so qualitatively, i. e. they show that the specific heat of water decreases from  $0^{\circ}$  to a minimum somewhere near  $30^{\circ}$ . Owing to the general interest and importance of these conclusions, I have, at the instance of Professor Rowland, undertaken during the last few months a new series of experiments. The apparatus used was that devised and employed by him in his researches, and the method of procedure was also as nearly as possible identical with his.

The two thermometers (Nos. 108,947 and 108,954) necessary for the work were made by Hicks, and graduated in millimeters. They were carefully calibrated and compared with the University Standards,‡ after which a table of temperatures was constructed for each. They were found to agree very closely with the air thermometer, verifying the conclusions reached in the article before referred to, that thermometers made of English glass are characterized by this property.

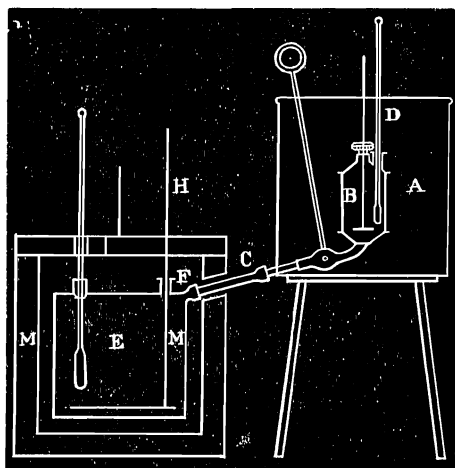
Some idea of the form of the apparatus used can be had from an inspection of the accompanying figure (taken from Professor Rowland's paper). It consisted of three essential parts; a reservoir A which was filled with broken ice, or warm water according as the experiment was to be made at low or high temperatures, connecting by means of a three-way stop-cock with an interior vessel B and with the vulcanite spout C; the calorimeter E, into an orifice in which the vulcanite spout fitted closely; and a water jacket M entirely surrounding the calorimeter. The reservoir and spout—which was very short—were wrapped with a cloth to obviate change of temperature,

\* Mech. Equiv. of Heat, Proc. Am. Academy Sciences, 1880.

† Ann. Physik u. Chemie, neue Folge, vol. xviii, 1883.

‡ These—Nos. 6,163 and 7,832—were made by Baudin, and had frequently been compared with the air thermometer. No. 6,163 was used by Professor Rowland in his before-mentioned research.

and the calorimeter was held in place by three vulcanite strips to prevent conduction to the jacket. Although when experimenting at low temperatures the vessel B was useless, still it was often kept in place and the water from the melting ice allowed to flow through it before entering the calorimeter. In no case did the temperature of the water from the ice, when in



the vessel B, differ appreciably from zero. The opening into the stop-cock was always covered with fine wire gauze to prevent particles of ice from being carried into the calorimeter with the flowing water. The calorimeter was made of very thin copper and lightly plated with nickel; three orifices on the top permitted the insertion of the vulcanite spout and the two thermometers. The weight of the calorimeter was 388.5 grams and its calorific capacity 35.4 grams. During the course of the investigation, the stirrer H having been broken, it was necessary, in order to repair it, to unsolder and afterwards resolder the top of the calorimeter. In this way the weight of the calorimeter increased four grams. But as the increase was due entirely to solder, nothing else having been removed or added, the new capacity was readily determined. Thus, assuming solder to be composed of equal parts of tin and lead, its specific heat between 0° and 40° would be about .043, therefore

$$.043 \times 4 = .172$$

or .2 must be added to the former value of the capacity, making 35.6 and the weight 392.5 grams.

The method of experimenting was as follows: the vessel A having been filled with broken ice, the thermometers were immersed therein and after about ten or twelve minutes their zero

readings taken. The calorimeter was, in the mean time, filled about two-thirds with water, weighed and placed in position within the jacket; one thermometer was then removed from the ice and immersed in the water in it. After a sufficient lapse of time, readings were taken every minute for six or seven minutes, to determine the time correction for radiation. The stop-cock was then turned, water flowed from A into the calorimeter, and the other thermometer having been placed in the latter, the flow of water was discontinued, and readings of both thermometers taken every minute as before. In this way the final temperature of the mixture was given as the mean of the readings of the two thermometers, one of which approached it from above, the other from below. The mean must therefore have been very nearly correct, even if thermometers, as is supposed, lag behind the true temperature. Corrections for the calorific capacity of the thermometers (equal to about 1.1 gram for each) and for protruding stem were always applied, as well as a time correction for radiation. The temperature of the jacket was always noted, but, because it never differed more than one or two degrees from that of the surrounding air, and owing to the before-mentioned corrections, it has not been thought necessary to give it. As an example, the following experiment is given in detail:

Let  $W$  be the weight of the calorimeter alone.

Let  $W_i$  be the weight of the calorimeter + water before adding water from vessel A.

Let  $W_{ii}$  be the weight of the calorimeter + water after adding water from vessel A.

$t$  = temperature of calorimeter before,  $t_i$  = temperature of mixture.  
 $t_{ii}$  = temperature of water in vessel A.

Then with the proper corrections

$$\frac{(W_i - W)(t_i - t) \times \text{sp. heat between } t \text{ and } t_i}{(W_{ii} - W_{ii})(t_{ii} - t_i) \times \text{sp. heat between } t_{ii} \text{ and } t_i} = \text{constant, then}$$

$$\frac{\text{sp. heat between } t_{ii} \text{ and } t_i}{\text{sp. heat between } t_i \text{ and } t} = \frac{(W_i - W)(t_i - t)}{(W_{ii} - W_{ii})(t_{ii} - t_i)}.$$

$W$  = with added solder 392.5;  $W_i$  = 1574.8;  $W_{ii}$  = 2419.9.

Zero readings of thermometer 108,947 were .35 .38 .38

Zero readings of thermometer 108,954 were .00 .00 .00

Time.	Readings on Thermometer.	
	108,947 In calorimeter.	108,954 In vessel A.
42	243.39	0.00
43	242.95	0.00
44	242.50	0.00
45	242.05	0.00
		In calorimeter.
46 $\frac{2}{3}$	143.50	140.60
47 $\frac{2}{3}$	143.60	140.68
48 $\frac{2}{3}$	143.70	140.74

Water running from time 45 $\frac{2}{3}$  to 46 $\frac{1}{4}$ , therefore temperature of water in calorimeter at the instant of mixing is that at time 45 $\frac{2}{3}$  or 241.75 and the temperature of mixture the mean of 140.53 and 143.40, now

$$\begin{array}{l}
 241.75 \text{ corrected } +.019 \text{ for zero and } +.046 \text{ for stem} = 33.507 \\
 143.40 \text{ corrected } +.019 \text{ for zero and } -.004 \text{ for stem} = 19.741 \\
 140.53 \text{ corrected } 0.00 \text{ for zero and } -.004 \text{ for stem} = 19.729 \} \\
 W' - W = 1574.8 - 392.5 + 35.4 + 1.1 \quad | \quad t' - t = 33.507 - 19.735 \\
 W'' - W' = 2419.9 - 1574.8 + 1.1 \quad | \quad t'' - t' = 19.735 - 0
 \end{array}$$

hence

$$\frac{\text{sp. heat } 0^\circ - 19^\circ}{\text{sp. heat } 19^\circ - 33^\circ} = \frac{(1574.8 - 392.5 + 35.6 + 1.1)(33.507 - 19.735)}{(2419.9 - 1574.8 + 1.1)19.735} = 1.0034$$

The temperatures throughout are on the absolute scale. The results are given in a more concise form in Table I. In this table the first two columns give the weight of the calorimeter and contained water before and after the addition of water from the reservoir A. The next eight, of which four are devoted to thermometer 108,947 and four to 108,954, are occupied by the readings, temperature of surrounding air, correction for protruding stem and reduced temperature (absolute scale). In each experiment the initial temperatures are placed on the upper row and the final temperatures, i. e. those of the mixture, occupy the lower row. The ratios of the specific heats between the assigned limits will be found in the last two columns, one of which is taken up by Rowland's figures. Although it was attempted to make the limits coincide with Rowland's, still in many cases this was impracticable and blanks have in consequence been left in three or four places. Where the temperature intervals are comparable it will be seen that there is great similarity in the results.

It may be interesting to further compare these values with those which can be computed from the tables given in Professor Rowland's paper on the mechanical equivalent of heat. The specific heat varies directly as the mechanical equivalent; it is therefore only necessary to plot a curve with the

TABLE I.

Weight of Calorimeter.		Thermometer 108.947 in calorimeter.				Thermometer 106.354, first in vessel A, afterwards in calorimeter.				Reduced ratios of the specific heats.	
Before.	After.	Reading.	Correction.	Temp'ture.	Air.	Reading.	Correction.	Temp'ture.	Air.	Liebig.	Rowland.
1609.3	1897.9	Initial Final	123.25 100.26	—006 —007	16.937 13.755	21°0	0.00 97.98	0.00 13.768	21°0	0.13 = 1.0032 13.17 = 1.0032	—
2017.6	2528.6	Initial Final	216.43 166.04	+029 000	29.952 22.893	22°0	0.00 162.96	0.00 22.878	22°0	0.22 = 1.0044 22.30 = 1.0044	—
2129.6	2576.4	Initial Final	159.75 127.89	+002 —006	22.014 17.578	21°0	0.00 —	0.00 —	21°0	0.17 = 1.0015 17.22 = 1.0015	0.17 17.25 = 1.0027
1827.2	2358.3	Initial Final	206.20 152.00	+017 —004	28.509 20.935	23°0	0.00 149.11	0.00 20.931	23°0	0.21 = 1.0030 21.28 = 1.0030	0.21 21.28 = 1.0023
1921.3	2654.4	Initial Final	183.00 197.25	+009 +016	25.267 27.261	22°0	224.75 —	31.521 —	22°0	25.27 = .9995 27.31 = .9995	—
1774.5	2515.1	Initial Final	153.00 177.00	—004 +004	21.078 24.427	23°0	216.40 174.00	30.852 24.432	23°0	21.24 = .9989 24.31 = .9989	20.24 24.29 = .9983
1971.1	2957.1	Initial Final	152.00 175.00	—004 +004	20.939 24.148	24°0	209.60 172.00	29.406 24.151	24°0	21.24 = .9980 24.29 = .9980	21.29 29.36 = .9954
1574.8	2419.9	Initial Final	241.75 143.40	+046 —004	33.507 19.741	22°0	0.00 140.53	0.00 19.729	22°0	0.20 = 1.0053 20.33 = 1.0053	0.21 21.34 = 1.0062
1824.8	2234.1	Initial Final	220.50 172.81	+034 +010	30.536 23.854	22°0	0.00 169.75	0.00 23.841	22°0	0.24 = 1.0040 24.30 = 1.0040	—
1677.3	2341.5	Initial Final	224.63 149.98	+032 —003	31.102 20.657	23°0	0.00 147.08	0.00 20.648	23°0	0.21 = 1.0050 21.31 = 1.0050	0.18 18.30 = 1.0067
1616.5	2357.5	Initial Final	217.25 137.20	+027 —007	30.067 18.876	23°0	0.00 134.60	0.00 18.896	23°0	0.19 = 1.0057 19.30 = 1.0057	—
1488.1	2130.6	Initial Final	262.23 168.10	+064 +002	36.397 23.183	22°0	0.00 165.05	0.00 23.173	22°0	0.23 = 1.0034 23.36 = 1.0034	0.21 21.34 = 1.0062

values of the mechanical equivalent (given in table LIII) at different temperatures as ordinates and temperatures as abscissæ. Then measuring off ordinates as averages between the required limits, and dividing one by the other, the ratios of the specific heats between the same degrees of temperature will be obtained.

TABLE II.

Temperature intervals.	Mech. equivalent value.	Rowland.	Neesen.	Liebig.
0—14				
14—17	1·0046	----	----	1·0030
0—17				
17—22	1·0056	1·0027	----	1·0015
0—17				
17—29	1·0067	1·0024	1·0079	----
0—18				
18—27	1·0063	1·0025	1·0099	----
0—19				
19—30	1·0065	1·0067	1·0111	1·0057
0—19				
19—33	1·0066	1·0062	----	1·0053
0—20				
20—31	1·0064	----	----	1·0051
0—21				
21—28	1·0060	1·0045	1·0358	1·0032
0—23				
23—30	1·0059	----	----	1·0043
0—23				
23—36	1·0068	----	----	1·0034
0—24				
24—29	1·0058	----	----	1·0045
20—24				
24—29	1·0013	·9983	·9794	·9980
21—24				
24—31	1·0012	----	----	·9989
21—29				
29—36	1·0007	·9954	----	----
25—27				
27—31	1·0004	----	----	·9995
29—32				
32—38	·9996	----	----	----

A glance at table II will show how these compare with the results of other determinations. It will be remarked that, although in no case do the figures (with the exception of Neesen's) differ very greatly among themselves, still there is a remarkable discrepancy in the indications of the position of the minimum. The values deduced from the mechanical equivalent certainly place the minimum at about 30°, while those obtained from direct experiment as surely place it at about

23°. There can be no doubt that experiments on the mechanical equivalent can be made with far greater accuracy than those on the specific heat by the method of mixture, and the total variation between 0° and 30° is only about one per cent; nevertheless it does appear surprising that three independent series of results (two by one method and one by another) all agreeing so closely on this point, should differ from the original value given by the mechanical equivalent. I have in vain sought its cause in any constant error which I could detect inherent in either method, and have now no explanation to offer of this minor discrepancy, but reaffirm as the result of direct experiment that the specific heat of water decreases from zero to a point between twenty and thirty degrees centigrade.

Baltimore, May 16, 1883.