THE
PHYSICAL REVIEW.

THE SPECIFIC HEAT OF SOLUTIONS. III. A FORM
OF THE PFAUNDLER CALORIMETER.

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1. In the course of my investigation of the specific heat of solutions¹ the calorimeter which was employed in the earlier work has been considerably modified and improved. As I expect to use the instrument in its present form in the future, it may not be superfluous for me to present a brief description of it, with an account of the method of using it and of the results which can be obtained with it. In the somewhat tedious course of experimentation by which this form of the instrument was worked out, I have been greatly indebted to Mr. Frederick Fisher, the mechanician of the John C. Green School of Science, who has aided me by his practical skill, and has furnished many valuable suggestions.

2. *The Calorimetric Method.*—The general plan of the instrument is that first proposed by Pfaundler.² The liquid to be examined and the standard liquid are contained in two similar vessels, and are heated by the same electric current in two coils of equal resistance. The specific heat is then determined from the observation of the rise of temperature in each vessel. In the study of solutions, the solvent is made the standard liquid. It is then possible to use such amounts of the solution and of the standard that the rise of temperature shall be nearly the same in each vessel. When this is the case the two most important corrections in most calorimetric work, that involving the water equivalent of the calorimeter and that

¹ This REVIEW, Vol. IX., No. 2, Aug., 1899; Vol. XIII., No. 2, Aug., 1901.

² Wien. Acad. Bericht, Vol. LIX., 1869.

depending on radiation, are practically eliminated, if only the two vessels are alike in mass, in shape, and in character of surface.¹

3. *The Calorimeter.*—The calorimeter vessel is a cylindrical cup, 6 inches high and 4 inches in diameter, made of thin sheet silver. It is furnished with a cover of fairly thick sheet brass, that fits snugly with an exterior flange over the top of the cup. Through the center of the cover passes a brass tube, projecting three fourths of an inch above the cover and $1\frac{1}{2}$ inches below it. Within this is fitted a glass tube, the ends of which were shrunk a little in the flame of a Bunsen burner, and then ground and polished on the interior so as to furnish the bearings for the shaft of the stirrer. This shaft is a silver rod, provided above the upper bearing with a small pulley, and projecting below the cover $5\frac{1}{2}$ inches. On the lower end is forced a cubical block of silver. Into slots cut diagonally in the surfaces of this block are forced rectangular silver plates $1\frac{1}{8}$ inches long and $\frac{5}{8}$ inch wide. The paddle or stirrer thus formed is held in place by the pulley above and by a collar below its bearings. When it is turned at the usual rate it rotates about four times a second, and stirs the liquid vigorously.

In a line $\frac{1}{2}$ inch from the center of the cover are placed three short brass tubes. The two end ones are $1\frac{1}{2}$ inches apart, corresponding to the distance between the mercury cups of my Carey Foster bridge. They are fitted with rubber bushings through which pass stout copper wires, the upper ends of which carry removable binding screws. These wires within the cup are bent out and down again, so that in the cup they are $2\frac{3}{4}$ inches apart. They terminate 3 inches below the cover, where they are attached to the ends of the heating coil. This is a spiral $\frac{5}{8}$ inch in diameter of about 40 turns of a special German Silver wire, furnished me by Mr. Edward Weston. It has a resistance of 4 ohms, and is characterized by its small or negligible temperature coefficient. This spiral is opened in the middle and held down nearly to the stirrer by a glass tube fitted in the middle one of the three brass tubes in the cover. The most convenient way to arrange this tube is to heat the lower end,

³ These features of the instrument have been recognized by Stroud and Gee, who have described a method which is essentially the same as the one here described. *El. Rev.*, 21, p. 262; *Nature*, Vol. XXXVI., p. 483. 1887.

pinch it flat, and make a small notch in the flat end. The wire is caught in this notch, and may be held there by the insulating coating.

It may be worth mentioning that it is convenient to drill the holes in the ends of the copper wires, in which the heating coil is soldered, diagonally through, so that the adjustment of the coils to equal resistance may be made without cutting the wire.

Two other tubes, $1\frac{1}{4}$ inches long, and of such a diameter that they will admit the thermometers used, are placed in line with the center of the cover and the tube carrying the glass rod. Their centers are $\frac{3}{4}$ inch from the edge of the cover. The thermometer is ordinarily borne in the one that is more distant from the heating coil, and the other one, which is generally stopped with a cork, is used for filling the cup, though it also receives a thermometer when the two thermometers are to be compared with each other.

The heating coils and the copper wires are coated first with asphalt varnish and then with ozokerite. Neither of these insulators could be used alone, and rubber and gutta-percha were tried also without success. The inner side of the cover and those portions of the brass tubes which project below it are coated with a thin sheathing of rubber dissolved in naphtha, to prevent possible conduction across the cover when it is covered with moisture by condensation.

Each of the cups thus constructed is set upon a network of fine cord within a cylindrical vessel of brass, 8 inches high and 6 inches in diameter, and is centered by three adjustable wooden pegs. These brass vessels or shields are placed about 4 inches from each other within a wooden box, with a cover made in two parts and cut so that the thermometers can project through it; the parts of the lid can be removed and replaced without disturbing the instrument. The conductors for the electric current enter through holes in the ends of the box. I am not sure that it would not be better to dispense with the box, when the temperature of the room can be kept constant. Thomsen¹ found it to be so; but the temperature of my work-room is so changeable that it is probably safer to protect the cups from outside changes of temperature, and to expose them only to those changes which they cause themselves. These at least are regular and similar in all observations.

¹ Pogg. Ann., Vol. 92, p. 34; Thermochem. Untersuchungen, Vol. I., p. 22.

On either side of the box rises a wooden upright sustaining a crosspiece, on which are fastened small wooden blocks, grooved to receive the upper ends of the thermometers. When the cups are in position, the thermometers are held in place in these grooves by stout brass springs. In appropriate positions are fastened to the crosspiece the magnets and circuit-breakers of two small electric bells, the hammers of which have been replaced by longer handles carrying on their ends small corks. The magnets are actuated by a pair of Edison-Lalande cell, and when in action the cork hammers keep up a lively tapping on the tops of the thermometers. The contact-maker used with this circuit is fixed in a convenient place on the side of the box.

The paddles are turned by a belt passing over both of their pulleys and over a 4-inch pulley carried on an offset in front of the box. The belt enters the box through two notches in the front, into which it falls when the front part of the cover is not in place. To admit of this the front part of the cover is made removable and is not hinged like the back part. The belt is a rubber cord about $\frac{1}{8}$ inch thick.

4. *The Cooling Vessels.*—Before beginning an observation it is necessary to cool off the cups to some temperature below that of the room. This is done in cylindrical vessels $8\frac{1}{2}$ inches in diameter and 6 inches high. Within these are placed cylinders of coarse wire netting, held in place in the vessels by three projecting arms. They are just large enough to admit the cups, which rest on cross-pieces of wood about an inch from the bottom. The space outside these cylinders is packed with broken ice or with snow, and the vessels are filled about half full of water. When the charged cups are placed in position in these coolers, the paddles may be turned with the fingers sufficiently to bring about a regular fall of the thermometers, and after a little experience the cups can be removed so that the temperatures indicated after the cups have been wiped dry do not differ by more than two or three hundredths of a degree. If they differ by more than that, it is easy to equalize them by warming one of the cups with the hand.

5. *The Current.*—The current for the heating coils is furnished by a dynamo machine or a storage battery. It is led into the box

by stout copper wires, which are sufficiently flexible to admit of being pushed aside when the cups are to be removed. The connection between the cups is made by a straight piece of the same wire. The circuit contains an ammeter, a variable resistance of coarse wire, and a snap switch, placed conveniently on the front of the box. Ordinarily a current of 5 ampères is used.

6. *The Thermometers.*—The thermometers were made by Fuess. They are of Jena glass, No. 59, III., and are similar in size and shape. The graduation extends from 12° to 33° in the one and 36° in the other. A degree covers about 2 cm. and is divided directly into fiftieths. The graduation is marked in beautifully fine and even lines on a scale of opaque glass placed just behind the thermometer tube. By the help of the reading microscopes, which are arranged to slide on the external protecting tubes, an estimate of the temperature can be made to thousandths of a degree with considerable accuracy. The bulbs are long and narrow. A short piece of rubber tubing is slipped over each thermometer and supports it at the proper height in the cup. The bottom of the bulb is brought as close as is safe to the paddle, and the upper end of it is below the surface of the liquid in the cup by $\frac{3}{8}$ inch when 700 grams of water are used.

It is a feature of this method that the corrections of the thermometers to a standard need not be accurately known. All that is necessary is to have a comparison of one with the other. To obtain this, both thermometers were placed in the same cup, and compared at different temperatures. The curves of comparison obtained from three independent sets of observations nowhere differed from each other by more than $\frac{3}{1000}$ degree. From them a mean curve was constructed from which to correct the readings of one thermometer to the scale of the other. Since the comparison is made under the conditions of service, the corrections for stem exposure and lag are included in the results.

7. *Method of Observation.*—The course of an observation is as follows: After the cups are filled, usually with 700 grams of water and with the appropriate amount of the solution, they are placed in the coolers until the temperature falls about 5° below the room temperature (say to 15°). They are then wiped dry, the tempera-

tures being adjusted if necessary to be nearly equal, and are placed in position. At the beginning of a minute the tappers are set going, and the stirring is begun. Stirring is kept up in one sense for twenty seconds and then in the reverse sense for twenty seconds. The tappers are allowed to run five seconds longer, are then stopped, and the readings are made. This process is repeated usually twice and oftener if the differences of reading of the two thermometers show signs of a progressive change. At the beginning of a minute, after the last reading has been made, the current is thrown into the heating coils and is maintained usually for six minutes; with the current used the rise of temperature is then about 10° . During this period the stirring is continued, being changed in sense at the end of each minute. At the end of six minutes the current is cut off, the tappers set going, and readings are made as before. Nothing remains but to determine from the average temperature differences the most probable value of the rise of temperature in each cup, and to calculate the specific heat s' of the solution directly from the formula, $s' = \frac{ms\vartheta}{m'\vartheta'}$. The cups may be cooled off again and another observation made. Such an observation can be made in twenty minutes or a little over.

As an illustration we may take an observation on a $\frac{1}{200}$ milk-sugar solution. The mass of water in cup *A* was 700 grams, of solution in cup *B* was 736.57 grams. The thermometer corrections fall on the temperature in *B*; those due to errors in reading on that in *A*.

Readings.	A		Diff.	B	
		Corr. Reading.			Corr. Reading.
Before heating.	15.110		14	15.124	
	15.130	15.130	14	15.144	15.115
After heating.	25.324	25.324	-5	25.319	25.309
	25.296		-4	25.292	
	25.272		-5	25.267	
Rise of temp.		$\vartheta, 10.294$			$\vartheta', 10.294$

$$\frac{\vartheta}{\vartheta'} = 1.0000, \quad s' = 0.9504$$

Heat capacity of 200 mols. water + 1 mol. milk-sugar or of 3942 grs. solution, 3746.4.
Apparent molecular heat of milk-sugar in solution, 146.4.

8. *Correction for Evaporation.*—The most important change which has been made in the construction of this instrument from that previously described¹ consists in the use of covered calorimeter cups instead of open ones. In the 25 minutes required in the earlier work for an observation, 500 mg. of water were lost from each cup by evaporation. This not only made it necessary to weigh and refill the cups after each observation, but introduced an element of uncertainty in the work that is at least partially avoided by the use of covered cups, in that any inequality in the amount of evaporation from the cups involved a considerable inequality in the amount of heat lost by evaporation. This possible difference in the amount of heat lost was included in the probable error, but it no doubt contributed to increase the magnitude of that error. Even with the covers, the evaporation is not wholly checked, as the temperature of the liquid changes, and is different from that of the cover, but it is at least rendered more uniform. In working with alcohol as a solvent or in determining the calorimeter constant with water, the first observations were always more divergent than the later ones from the mean, unless the precaution was taken to carry the temperature through its ordinary range before beginning the observations.

9. *Correction for Radiation.*—When the cups are so charged that the rise of temperature is about the same in each, the correction for radiation is negligible. This can be seen from the uniformity with which the temperatures in the cups rise or fall while the readings are being made. When the temperature changes in the cups are quite different, as in the observations for the calorimeter constant, the radiation has to be determined and allowed for. This may be done completely by determining the rate of loss of heat at different temperatures; but it is generally sufficient to judge from the differences in the temperature changes observed during the preliminary and final readings as to how much more heat one of the cups loses than the other, and to express this in terms of temperature change. This method is not suitable when the temperature changes differ greatly.

10. *Corrections for Errors in Stirring.*—In the ordinary case, the

¹ This REVIEW, Vol. IX., No. 2, August, 1899.

errors which are most difficult to control are connected with the stirring of the liquids. It is necessary to make the pulleys that turn the paddles exactly of the same diameter, and to make the paddles themselves geometrically similar; and even when they are as similar as they can be made, it is advisable to turn them in opposite senses for equal times. Even with the utmost regularity, it is not possible to be certain that the liquids are thoroughly and equally mixed, and I believe that the remaining error is more largely due to unequal mixing than to any other cause. The condition, which is important, that the paddles should extend as near the sides of the cup as possible, introduces an occasional difficulty, when the paddles, owing to imperfect fitting of the cover or to too great a strain on the belt, touch the sides of the cup. Fortunately when this happens it can usually be detected by the ear. An observation in which such a condition has existed is worthless, the heat developed by the contact being always sufficient to cause too great a rise of temperature in the cup in which it occurs.

11. *Correction for Calorimeter Constant.*—A difference in the water equivalents of the two cups may exist which must be examined and allowed for. This can scarcely be due to differences in the cups themselves, if they are carefully constructed, but may be introduced by the use of thermometers which are not sufficiently alike. The amount of this difference may be determined by a series of observations with equal quantities of water in the cups. If we represent by φ the heat capacity of the water used, by ϑ_1 the rise of temperature in cup No. 1, by C_1 the water equivalent of that cup, and use similar symbols with the subscript 2 for the quantities pertaining to cup No. 2, and remember that the same quantity of heat is contributed to each cup, we have,

$$\varphi\vartheta_1 + C_1\vartheta_1 = \varphi\vartheta_2 + C_2\vartheta_2;$$

whence

$$\varphi - \varphi \frac{\vartheta_2}{\vartheta_1} = \frac{C_2\vartheta_2}{\vartheta_1} - C_1.$$

Since ϑ_1 is nearly equal to ϑ_2 , and C_1 and C_2 are small in comparison with φ , this equation gives approximately

$$\varphi \left(1 - \frac{\vartheta_2}{\vartheta_1} \right) = C_2 - C_1,$$

from which by the observations just mentioned $C_2 - C_1$ may be determined. This difference is all that is needed for correction, when the temperature change is nearly the same in each cup.

The value of the water equivalent, when it is the same for each cup, is got by using different quantities of water, so that φ_1 and φ_2 are not the same. We then have

$$C = \frac{\varphi_1 \vartheta_1 - \varphi_2 \vartheta_2}{\vartheta_2 - \vartheta_1}.$$

Even if the water equivalents differ, this equation will determine a value that is correct enough for use when the temperature changes are different, and the difference between the water equivalents may be got as before.

12. *Effect of Condensation.*—In the damp summer weather, the moisture which condensed on the outside of the cups, when they were cooled below the room temperature, affected the changes of temperature during the period of the initial readings, so that they were very irregular and uncertain. Successful observations could not be made at such a time.

13. *Test with Water.*—It is an advantage of this form of calorimeter that its performance can be tested by the use of equal quantities of water in the two cups. If the water equivalents and the radiation losses are the same for each, the mean ratio of the observed temperature changes should equal 1. The first set of results which follows was obtained for this case on October 10, 1901, before the laboratory was heated, and while there was a slight condensation on the cups of moisture from the atmosphere. The second set was obtained on November 9, 1901, when the laboratory was heated. The numbers given are the ratios of the temperature changes in cups *A* and *B*.

0.99987	1.00005
0.99974	1.00004
1.00004	0.99995
1.00030	1.00002
0.99963	1.00030
0.99991	
Mean, 0.99992	1.00007

The mean of both sets is 0.99999 and indicates that the correction for difference of water equivalent is negligible. In these observations the rise of temperature was over 10° . Another set of observations, in which the rise of temperature was about 3.5° , gave the following results :

1.0003
0.9996
1.00025
Mean, 1.00005

Although the variations are no larger than in the other sets of measurements, and although there are good reasons for restricting the temperature change within as narrow limits as possible, yet in view of the larger effect of errors in reading the thermometers, I do not think it best to use so small a temperature change.

14. *The Calorimeter Constant.*—The water equivalent or constant of the calorimeter was determined as the mean of the following results : 700 grams of water were used in one cup, and 800 grams or 850 grams in the other.

22.6	1.0002
24.1	0.9998
24.3	1.0002
21.7	0.9997
23.4	1.0000
Mean, 23.2	

The numbers in the second column represent the specific heat of water, calculated from the observations with the mean value of the constant, and indicate the range of error when the constant is known and the difference of the temperature changes is about 1° in 10° .

15. *Examples.*—The following numbers under I. are the ratios and the molecular heats obtained from observations on a $\frac{1}{200}$ gram-molecular solution of an anhydrous form of milk-sugar. The amount of water used was 700 grams, of the milk-sugar solution 735 grams. Under II. are given the corresponding numbers for a similar solution of another form of milk-sugar. The amount of solution used in that case was 736.57 grams.

I.		II.	
0.9978	146	0.9998	145
0.9979	146	0.9999	146
0.9986	149	1.0000	146
0.9982	147	0.9997	145
0.9978	146	0.9995	144
0.9981	147	0.9999	146
0.9983	148	1.0003	147
		1.0003	147
		1.0000	146
Means, 0.9981	147	Means, 0.9999	146

The water equivalent of the calorimeter applied to such cases as those under I., where the difference between the temperature changes was about 0.02° , does not appreciably modify the results.

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