VOL. XIX. [JUNE, 1897.] NO. 6.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 27.]

ON THE EXPERIMENTAL DETERMINATION OF THE HYDROTHERMAL VALUE OF A BOMB CALORIMETER.

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Received March 29, 1897.

FOUR methods of determining the water equivalent of a bomb calorimeter and its accessories may be employed.

In the first place, a definite weight of a body whose thermal value is established may be burned in the system in the usual way, and the increase of temperature of the ambient water, the weight of which is also known, be determined. The difficulty attending this method is, in the first place, that the heat of combustion of the body employed rests upon experimental data, which themselves may be misleading.

In the second place, without a tedious and accurate chemical examination the experimenter cannot be assured of the purity of his materials.

This method may be varied by the successive combustions of double or triple the weight of the same body, and thus a factor be secured from which the water value of the metal parts of the system can be accurately calculated.

The second method of operation is one which is employed by Berthelot and Vieille. It consists in measuring the heat disengaged in mixing exact weights of water and sulphuric acid. The operation is carried on first in an ordinary calorimeter without the bomb, and afterwards the mixture is made in the interior of the bomb placed in position. The experiment being made upon absolute or relative weights permits of a comparison of the quantities of heat produced in the two conditions. This method of procedure, exact as it is in theory, is somewhat difficult in practice, because of the slowness with which the thermal equilibrium is established between two masses of liquid separated by a metallic wall.

The third method of estimating the hydrothermal value of the calorimeter system consists in calculating it directly from the specific heats of the various materials composing it.[1] This is by far the most convenient method of proceeding, and where the exact weights of the different constituents are known it leaves little to be desired. The specific heats of all the various metals composing the calorimetric system have been very carefully determined. It is only in the case of alloys of rather uncertain composition that errors may result. Most of the alloys, however, which are employed have a definite composition, or nearly so, and since the specific heats of metals are so low, the slight variations from the standard which may occur do not produce any appreciable errors. In all cases the hydrothermal value of the system should be calculated from the weights of its various components, and the manufacturers should always be asked to furnish the exact weights of each metal or alloy in the apparatus.

The fourth method of determining the hydrothermal value of the system is the direct experimental one of mixtures, the same in principle as the processes which have been used for the determination of the specific heats of various bodies. In the method which is to be described the steps will be set forth which are necessary in the determination of the hydrothermal value by the method of mixtures when the difference in temperature between the two bodies of water is not very pronounced. In all the methods of mixture which have heretofore been employed a relatively small volume of water at a relatively high temperature has been mixed with a large volume at ordinary temperature. In order to secure this mixture it has been customary to have the added water contained in a platinum capsule and placed as quickly as possible in the water in the calorimeter which has been kept at a definite temperature. After thorough mixing the in-

[1] Principles and Practice of Agricultural Analysis, 3, 575.

crease of temperature furnishes the basis of the calculations. In this case it is necessary to put the containing platinum capsule also in the mixture, and its hydrothermal value must be previously calculated by the usual factors. Thermometers which extend over large intervals of degrees are necessarily less exact and less easily read than those in which the scales mark only a few degrees. We therefore determined to attempt to ascertain the hydrothermal value of the calorimetric system by measuring the changes of temperature by means of the Beckmann thermometer employed for determining molecular weights. The scales of these thermometers usually extend over a little more than 5°, and are divided so as to read to hundredths, and, by means of a cathetometer, to thousandths of a degree. By using two of these thermometers it is possible to work with masses which have a difference in temperature of a little over 10°. Before the thermometers are used they must be calibrated against each other in order to be certain that they register exactly the same differences of temperature as marked upon the scales. This having been accomplished, the two thermometers are placed in water at room temperature, and when equilibrium has been perfectly established the two scales are read. The thermometers are set in such a way that when this comparison is made the column of mercury in one shall be near the top of the scale, and in the other one near the zero point. The difference in readings in the two thermometers is thus directly established, and this having been done, the two can be used as a single thermometer.

Following are the analytical data obtained in ascertaining by direct mixture the hydrothermal value of a bomb calorimeter made for this division by O. S. Blakeslee, of Middletown, Conn.:

Thermometers.—The two thermometers employed were made by F. O. R. Goetze, of Jena glass. The dimensions of the thermometers are as follows: No. 1 (Tl), distance from zero to bottom of bulb, twenty-five centimeters; length of scale, twenty-five centimeters; range of scale, zero to 5.6°. No. 2 (Ts), distance from zero to bottom of bulb, 17.5 centimeters; length of scale, twenty-two centimeters; range of scale, zero to 5.7°.

Immersed in water, at a temperature of 17.15°, the readings of the two thermometers were as follows:

No. 1, 0.030°; No. 2, 4.540°; difference, 4.510°.

Method of Using the Thermometers.—In order to secure as wide a range of temperature as possible with the two thermometers set as above, No. 2 was used for fixing the initial temperature of the water in contact with the bomb, and No. 1 for fixing the initial temperature of the water added to the bomb system. By this method of use a difference in initial temperatures of approximately 9° was easily obtained.

Method of Operation.—It is useless to attempt to determine the hydrothermal value of the bomb system immersed in air alone. The excessive slowness with which changes of temperature take place between polished metal and air is sufficient to prevent any accurate results from being obtained in an experimental way. Even after standing for several hours in air, a piece of polished metal may have a temperature which differs from that of the ambient air by as much as one degree or more. It is therefore necessary, at the very commencement, to add to the bomb system a sufficient quantity of water to secure without any great delay a uniform temperature in all its parts. In the apparatus employed the vessel containing the bomb holds approximately 1700 cc. of water when the bomb is in place. It is important that the range of temperature on mixing be as great as possible, as very small differences in temperature make a marked difference in the computations. Theoretically to get the best results the water which is added to the bomb at a higher temperature should be equivalent in weight to the water surrounding the bomb before mixture plus the hydrothermal equivalent of the calorimeter. The temperature of the bomb system, therefore, on mixing will rise to the same degree that the temperature of the added water falls. If, however, this arrangement should be followed, the quantity of water in contact with the bomb would not be sufficient to secure promptly the equilibrium of temperature between the water and the metallic parts of the calorimeter. To avoid any confusion of ideas, it may be stated that in the following experiments the added water was always at the higher temperature and the bomb system at the lower. After a large number of trials it was found that the best results, in the case under consideration, were secured by adding about 1000 cc. of water to the bomb in order to fix its initial temperature, and about 700 cc. at a higher temperature at the time of the determination. It was found that with 1000 cc. of water only a portion of the upper part of the bomb remained uncovered. Theoretically, the best adaptation of the system would be such that a sufficient quantity of water might be introduced to cover the whole of the bomb and the containing vessel still be large enough to hold the rest of the water added at the time of the determination. Practically, the small portion of the metal covering of the bomb which remained uncovered by the water in the experiments indicated below, by reason of its high conductivity, speedily acquired the temperature of the mixture.

Manipulation.—It is advisable to select a day for the experiments which is cloudy, and in which the changes in temperature are very slight. We were fortunate, after all the preliminary work necessary to the determination had been done, to secure such a day for the actual fixing of the hydrothermal value of the system. The changes in temperature during the day in which the experiments were made, *viz.*, March 9, 1897, were very slight, and in the room in which the experiments were carried on the whole change during the working day did not exceed 3°.

It is convenient to have the thermometer so set that the initial temperature of the bomb system is slightly below the temperature of the room. In this case the initial temperature of the added water is considerably above the room temperature, and hence the rate of cooling is a more important factor in this instance than in the other. The first point to be determined is the rate and direction of change of temperature of the water and the whole calorimetric system. The stirrer of the apparatus having been set in motion, the whole is allowed to stand for about half an hour. The reading of the thermometer immersed in the water is then commenced, and continued for about ten minutes, the thermometer being read at each minute during this time. These successive readings fix the rate of change of temperature. At the moment the readings cease the exact time is noted, in order that the whole amount of change before the mixing takes place may be computed. The next point to be determined is the rate of change of temperature in the water which is to be added. This is determined in exactly the same way, but, as a rule, five observations are sufficient to fix this point. At the moment of ceasing the readings, the time is also noted. The rates of change having been thus fixed, the thermometer is removed from the calorimeter system, and a funnel, which has been immersed in the water to be added, and is therefore at exactly the same temperature, and which has been used as the stirrer for this water, is inserted in the place of the thermometer, and the water poured into the calorimeter. The beaker and appurtenances having been previously weighed, a reweighing of the empty beaker permits of the exact determination of the weight of the water added. A large balance, capable of carrying heavy weights on each arm, and yet reading accurately to 10 milligrams, is necessary in weighing these large bodies. In order to secure as even a temperature as possible for the added water, the following device is employed: The water is contained in a lip beaker. This beaker is set in a tin can, which is insulated on the outside by a non-conducting covering of felt or cotton. The beaker rests upon three corks in the bottom of the can, and is separated from the sides by four corks inserted in such a way as to hold it firmly in place. The insulating covering is pushed down at the top between the tin can and the beaker, so that the air enclosed in the interior space is prevented from circulation with the exterior air. By this device the added water, which in these experiments was always several degrees higher in temperature than the ambient air, was protected as much as possible from rapid cooling. The time which is consumed in pouring the water, replacing the thermometer, and adjusting other parts of the apparatus, is noted, and from these data the initial temperatures of the bomb system and of the added water are calculated for the moments in which the last of the water is added. The thermometer at first indicates a rapid rise of temperature, which is observed through a reading glass, until it reaches its maximum. As a rule, it will be found that the added water causes the thermometer to rise to a slightly higher point than is indicated by the final equilibrium of temperature due to the fact that the mixture of the water affects the mercury in the thermometer with a slightly greater ease than it secures an equilibrium in the metal system. The difference, however, between the maximum reading of the thermometer in any case, and the final equilibrium is never more than a few thousandths. The temperature of the mixture is now read as before, at intervals of a minute, until two successive readings are practically identical. The readings are then continued for a few minutes until the temperature begins to fall, and the rate of fall is established. The correct temperature of the mixture is determined by taking the mean of the two readings which are nearest together after the slight fall from the maximum temperature, produced on the addition of the water, and correcting this reading as described below. From the data thus obtained the hydrothermal value of the system is calculated. As an illustration of the methods of calculation, the following data of four determinations made on the 9th of March, 1897, are given:

RECORD OF DETERMINATIONS, MARCH 9, 1897.

Weight of water in contact with the bomb, 997.1 grams.

Commencement of readings, 9 o'clock, 58 minutes.

Readings of thermometer (Ts) at intervals of one minute, 1.471°, 1.468°, 1.468°, 1.468°, 1.467°, 1.465°, 1.462°, 1.460°, 1.460°, 1.460°.

Ending of readings, 10 o'clock, 7 minutes.

Corrected temperature of water added, 5.360°, thermometer (Tl).

Commencement of reading of water added, 10 o'clock, 8 minutes.

Readings at intervals of one minute, 5.594°, 5.560°, 5.525°, 5.485°, 5.450°, 5.420°.

End of reading, 10 o'clock, 13 minutes.

Time of pouring, etc., 2 minutes.

Reading of thermometer after mixture (Ts), 4.285°.

Other readings not entered.

Calculation.—The readings show that the temperature of the calorimetric system at the time of mixture was the same as that of the external air, so that no correction for changing temperature is to be applied. The temperatures of the added water show a change at the rate of 0.030° per minute. The time elapsed from the last reading until the pouring was complete was two minutes; hence the initial temperature of the added water was (Tl) 5.360°.

The weight of the added water was 710 grams. We then have the following data:

SUMMARY OF DATA.

Initial temperature of bomb and water (Ts)	1.460°
Initial temperature of added water (Tl) 5.360°, (Ts)	9.870°
Weight of added water	710 grams
Final temperature of mixture (Ts)	4.285°
Rise of temperature of calorimeter	2.825°
Fall of temperature of added water	5.585°

Then $710 \times 5.585 = x \times 2.825$ in grams of water.

Whence $x = 1403.7$, and $1403.7 - 997.1 = 406.6 =$ hydrothermal value of the calorimetric apparatus in grams of water.

The method of correcting the reading of the thermometer for the influence of the environment after mixture is given is the next determination.

Second Determination.

Weight of water in contact with the bomb, 1034.2 grams.

Commencement of reading, 10 o'clock, 45 minutes.

Readings of thermometer at intervals of one minute, (Ts), 0.608°, 0.610°, 0.613°, 0.618°, 0.620°, 0.623°, 0.626°, 0.629°, 0.632°, 0.635°, 0.638°.

Ending of readings, 10 o'clock, 55 minutes.

First temperature of added water (Tl), 5.585°.

Commencement of readings, 10 o'clock, 58 minutes.

Readings at intervals of one minute, 5.550°, 5.505°, 5.465°, 5.420°, 5.375° (Tl).

End of readings, 11 o'clock, 3 minutes.

Time of pouring, 2 minutes.

The total time elapsed from the last reading of Ts, 0.638°, in the calorimeter until the pouring was complete, was ten minutes. The temperature of the calorimeter system was increasing at the rate of 0.003° per minute. The total increase during this time was therefore 0.030°, and the initial temperature of the bomb and water at the moment the pouring was complete was therefore $0.638° + 0.030° = 0.668°$. In the two minutes intervening between the completion of the pouring and the maximum reading of the thermometer, the change in temperature due to the environment is to be calculated from the observations of change after mixture, allowing for a temporary excess due to the time required for the metallic parts to assume the temperature of the ambient water. The rate of cooling, as determined by the final series of observations, was 0.004° per minute. The maximum temperature was observed at the end of two minutes, and the equilibrium of temperature was secured at the end of the third minute, when the observed temperature was (Ts) 3.620°. The loss of temperature for the three minutes which had elapsed since the completion of the mixture was therefore 0.012°, and this is to be added to the observed stable temperature (Ts) 3.620°. The final temperature of the mixture was therefore (Ts) $3.620° + 0.012° = 3.632°$.

SUMMARY OF DATA.

Reading of thermometer after mixture (Ts), 3.625°.

Time, 2 minutes.

Readings at intervals of one minute (Ts), 3.620°, 3.620°, 3.618°, 3.614°, 3.610°.

Initial temperature of bomb and water (Ts)	0.668°
Initial temperature of added water (Tl), 5.285°; (Ts) .	9.795°
Weight of added water	693.3 grams
Final temperature of mixture (Ts)	3.632°
Rise of temperature of calorimeter	2.964°
Fall of temperature of added water	6.163°

Then $6.163 \times 693.3 = x \times 2.964$.

Whence $x = 1441.6$, and $1441.6 - 1034.2 = 407.4$ = hydrothermal value of apparatus in grams of water.

THIRD DETERMINATION.

Weight of water in contact with the bomb, 1006.4 grams.

Commencement of reading, 11 o'clock, 50 minutes.

Readings of the thermometer (Ts) at intervals of one minute, 0.835°, 0.840°, 0.845°, 0.850°, 0.857°, 0.865°, 0.870°, 0.875°, 0.880°, 0.885°.

Ending of readings, 12 o'clock.

First temperature of added water (Tl), 5.585°.

Readings of thermometer (Tl) at intervals of one minute, 5.555°, 5.525°, 5.490°, 5.450°, 5.415°.

Ending of readings, 12 o'clock, 10 minutes.

Time of pouring, 2 minutes.

Reading of thermometer (Ts) after mixture, 3.914° (maximum).

Time, 1 minute.

Readings of thermometer (Ts) in mixture at intervals of one minute, 3.912°, 3.911°, 3.910°, 3.908°, 3.903°.

Interval from last reading of bomb until pouring was complete, 12 minutes.

Rate of change in temperature, 0.005° +.

Temperature of bomb, etc., at completion of pouring, 0.0885° + 60.

(Ts) = 0.945°.

Last reading of temperature of added water (Tl), 5.415°.

Rate of change per minute, 0.035° —.

Time of pouring, 2 minutes.

Final temperature of added water at time pouring ceased (Tl), 5.415° — 0.070° = 5.345°.

The rate of change in the temperature of the mixture was 0.003° per minute.

Time from end of pouring to concordant reading of the thermometer, 3 minutes.

Correction to be applied to concordant reading, 3.911° (Ts), $0.003 \times 3 = 0.009$.

Corrected reading of temperature of mixture 3.911°+0.009°=3.920° (Ts).

Summary of Data.

Initial temperature of bomb and water (Ts)	0.945°
Initial temperature of added water (Tl), 5.345°; (Ts)	9.855°
Final temperature of mixture (Ts)	3.920°
Weight of water added	704 grams.
Rise of temperature of calorimeter	2.975°
Fall of temperature of added water	5.935°

Then $5.935 \times 704 = x \times 2.975$.

Whence $x = 1404.5$, and $1404.5 - 1006.4 = 398.1$ = hydrothermal value of the calorimetric apparatus in grams of water.

Fourth Determination.

Weight of water in contact with the bomb, 999.5 grams.

Commencement of readings, 2 o'clock, 8 minutes.

Reading of temperature of bomb (thermometer Ts) at intervals of one minute, 0.695°, 0.700°, 0.710°, 0.723°, 0.730°, 0.740°, 0.755°.

Ending of readings, 2 o'clock, 16 minutes.

First temperature of added water (Tl), 5.585°.

Commencement of readings, 2 o'clock, 17 minutes.

Readings of thermometer at intervals of one minute, 5.560°, 5.530°, 5.505°, 5.470°, 5.450.

Ending of readings, 2 o'clock, 23 minutes.

Time of pouring, 2 minutes.

Reading of thermometer (Ts) after end of pouring, 3.870°.

Readings of thermometer (Ts) in mixture at intervals of one minute, 3.875°, 3.875°, 3.875°, 3.875°.

Summary of Data.

Initial temperature of bomb and water (Ts)	0.845°
Initial temperature of added water (Tl), 5.390°; (Ts)	9.900°
Final temperature of the mixture (Ts)	3.875°
Weight of water added	709.0 grams
Rise of temperature of calorimeter	3.030°
Fall of temperature of added water	6.025°

Then $709 \times 6.025 = x \times 3.03$.

Whence $x = 1409.8$, and $1409.8 - 999.5 = 410.3$ hydrothermal value of calorimetric apparatus in grams of water.

MEAN HYDROTHERMAL VALUE OF THE CALORIMETRIC SYSTEM.

From the data giving the hydrothermal values of the calorimeter, as determined in the foregoing experiments, we have the following table:

	Grams of water.
Hydrothermal value, first determination	406.6
" " second "	407.4
" " third "	398.1
" " fourth "	410.3
Mean hydrothermal value	405.6

COMPARISON OF HYDROTHERMAL VALUE OBTAINED EXPERIMENTALLY WITH THAT SECURED BY CALCULATION.

The specific heats of the various parts of the calorimetric system, as computed from the standard specific heats of the materials composing them, are given in the following table :

Material.	Specific heat.
Brass	0.093
Steel	0.1097
Platinum	0.0324
Copper	0.09245
Lead	0.0315
Oxygen	0.2389
Glass	0.190
Mercury	0.0332
Hard rubber	0.33125
Tin	0.0548
Antimony	0.0523

HYDROTHERMAL VALUE OF THE BOMB CALORIMETER.

The hydrothermal value of the bomb calorimeter is calculated from the following data :

Material.	Weight. Grams.		Specific heat.		Hydrothermal value. Grams of water.
Platinum	160.00	×	0.0324	=	5.1840
Steel	3,228.10	×	0.1097	=	354.1226
Lead	46.00	×	0.0315	=	1.4490
Brass	65.39	×	0.0930	=	6.0813
Brittania metal { tin	687.69	×	0.0548	=	37.6854
Brittania metal { antimony	53.49	×	0.0523	=	2.7974
Brittania metal { copper	22.92	×	0.09245	=	2.1192
Mercury (estimated)	21.76	×	0.0332	=	0.7224
Glass (estimated)	2.24	×	0.1900	=	0.4256
Total hydrothermal value					410.5869

The two values, as obtained by direct determination and by calculation, are very near together. In the calculation above given it should be borne in mind that it is difficult to determine the exact quantity of mercury in the thermometers without knowing the thickness of the sides of the bulb. It is also difficult to make the proper allowance for the glass part of the thermometer, inasmuch as it is not always immersed to exactly the same depth in the liquid, and further, the exact weight of the part immersed is not known, but can only be obtained approximately by calculation. Further, the tips of the wires, by which the firing of the bomb takes place, dip into the water, together with a portion of their caoutchouc covering. Further, the small piece of hard rubber by which one of the wires is insulated from the cover is not considered in the calculation. The hydrothermal value of these last-named bodies being slightly higher than metals, would have an appreciable influence upon the determination. The last thing to be mentioned in this connection is that while the specific heat of iron is pretty well established, it is known to vary slightly for the samples made in different localities and from different ores, and therefore the exact specific heat of steel, which composes the largest part of the calorimetric system, may be subject to slight variations. In view of this fact, it has been determined to use the mean of the two determinations as the correct expression for the hydrothermal value of the calorimeter in question, *viz.*, $(405.6 + 410.6) \div 2 = 408.1$.

CALCULATION BY THE FORMULA OF REGNAULT-PFAUNDLER.

The conditions of warming and cooling in the method of mixtures just described, are not precisely those which occur during the determination of the calorific power of a substance in the apparatus. The calculation of the influence of the ambient atmosphere upon the hydrothermal readings may, however, be conducted according to the formula of Regnault-Pfaundler.[1]

The calculation of the hydrothermal value in the case of the third determination given above, after correcting the end temperature according to the formula mentioned, is as follows:

Water value of the bomb, etc., x.

Weight of water added to the bomb, 1006.4 grams.

Preliminary thermometric readings, $t_1 = 0.835$, $t_2 = 0.840$, $t_3 = 0.845$, $t_4 = 0.850$, $t_5 = 0.857$, $t_6 = 0.865$, $t_7 = 0.870$, $t_8 = 0.875$, $t_9 = 0.880$, $t_{10} = 0.885$, $t_{n_1} = 0.945$. $(n_1 = 22)$.

[1] Principles and Practice of Agricultural Analysis, 3, 572, 574.

Thermometric readings after pouring, $\theta_1 = 0.945$, $\theta_2 = 3.914$, $\theta_3 = 3.912$, $\theta_n = 3.911$. ($n = 4$).

Final thermometric readings, $t'_1 = 3.911$, $t'_2 = 3.910$, $t'_3 = 3.908$, $t'_{n_2} = 3.903$.

From the formulas given above the following numerical values are computed :

$$v = \frac{t_{n_1} - t_1}{n_1 - 1} = 0.005.$$

$$v' = \frac{t'_{n_2} - t'_1}{n_2 - 1} = -0.003.$$

$$t = \frac{t_1 + t_2 + t_3 \cdots\cdots t_n}{n_1} = 0.891.$$

$$t' = \frac{t'_1 + t'_2 + t \cdots\cdots t'_{n_2}}{n_2} = 3.908.$$

$$\sum_{1}^{n-1} \theta r = \theta_1 + \theta_2 + \theta_3 + \frac{\theta_2 - \theta_1}{9} = 9.108.$$

Substituting these values in the Regnault–Pfaundler formula, the correction for the influence of the external air is

$$\Sigma \Delta t = \frac{0.005 - (-0.003)}{3.903 - 0.891}\left(9.10 + \frac{3.911 + 0.945}{2} - (4 \times 0.891)\right)$$

$- (3 \times 0.005) = 0.006$, which is added to the end temperature ($\theta_n = 3.911$).

The computation is then made from the following data:

Corrected end temperature ($\theta_n + 0.006$)	3.917°
Beginning temperature (θ_1)	0.945°
Increase in temperature of bomb, etc.................	2.972°
Total calories	x 2.972°
Weight of added water..........................	704.0 grams
Temperature of added water..........................	9.855°
Fall of temperature of added water...................	5.938°

Then $5.938 \times 704 = x \times 2.972$. Whence $x = 1406.6$, and $1406.6 - 1006.4 = 400.2$ = water value of calorimeter.

Calculated directly by the methods first given, the hydrothermal value in the third determination is found to be 398.1. After correcting for the end temperature by the Regnault–Pfaundler formula, and applying the calculation the hydrothermal value is found to be 400.2. It is thus seen that the two methods give almost the same results. For all practical purposes, therefore, it is not necessary to undertake the complicated computations required by the Regnault–Pfaundler formula, but the data may be calculated directly by the methods first given.