AN ADIABATIC CALORIMETER FOR USE WITH THE CALORIMETRIC BOMB.

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The calorimeters generally used with the calorimetric bomb are subject to error due to thermometer lag and exchange of heat with the surrounding media. The thermometer lag is seldom taken into consideration, although Richards[1] shows it is likely to be the cause of a considerable error. The exchange of heat with the surrounding media involves the use of an elaborate, time-consuming, cooling correction, which can hardly gauge the loss of heat with any great accuracy. If, however, the calorimeter is rendered adiabatic by keeping the media surrounding it always at the same temperature as the calorimeter itself, both of these errors are avoided.

In 1895, in applying calorimetry to experiments on man, Rosa[2] constructed a large chamber which was made adiabatic by arbitrarily cooling and heating an outer zinc wall to correspond with the fluctuations in temperature of the copper wall of the calorimeter proper. By this method any interchange of heat was avoided and the principle has been found very satisfactory in respiration calorimeters. In connection with the respiration calorimeter at Wesleyan University, considerable work was done with the calorimetric bomb, including the production of a modification of the Berthelot bomb.[3] Experiments were also made there by one of us in an attempt to apply adiabatic conditions to the bomb calorimeter. To this end, special forms of apparatus for heating electrically a surrounding water jacket were employed, but owing to the difficulty in properly insulating the heating wires, the experiments proved unsuccessful. Meanwhile the excellent apparatus of Richards, Henderson and Frevert[4] appeared, an adiabatic calorimeter which is admirably designed for the special purposes for which it has been used in Richards' laboratory and which leaves nothing to be desired in regard to accuracy. For practical purposes, however, it is somewhat cumbersome and involves the use of rather large amounts of strong alkali and acid.

On installing a calorimetric bomb at the Nutrition Laboratory for use in measuring the potential energy of food, feces, and urine, experiments were continued to obtain a practical form of adiabatic calorimeter in which the temperature of an outer water jacket should be controlled by electric heating, and the apparatus here described was devised.

Description of Apparatus.—The calorimeter system, the rise in tem-

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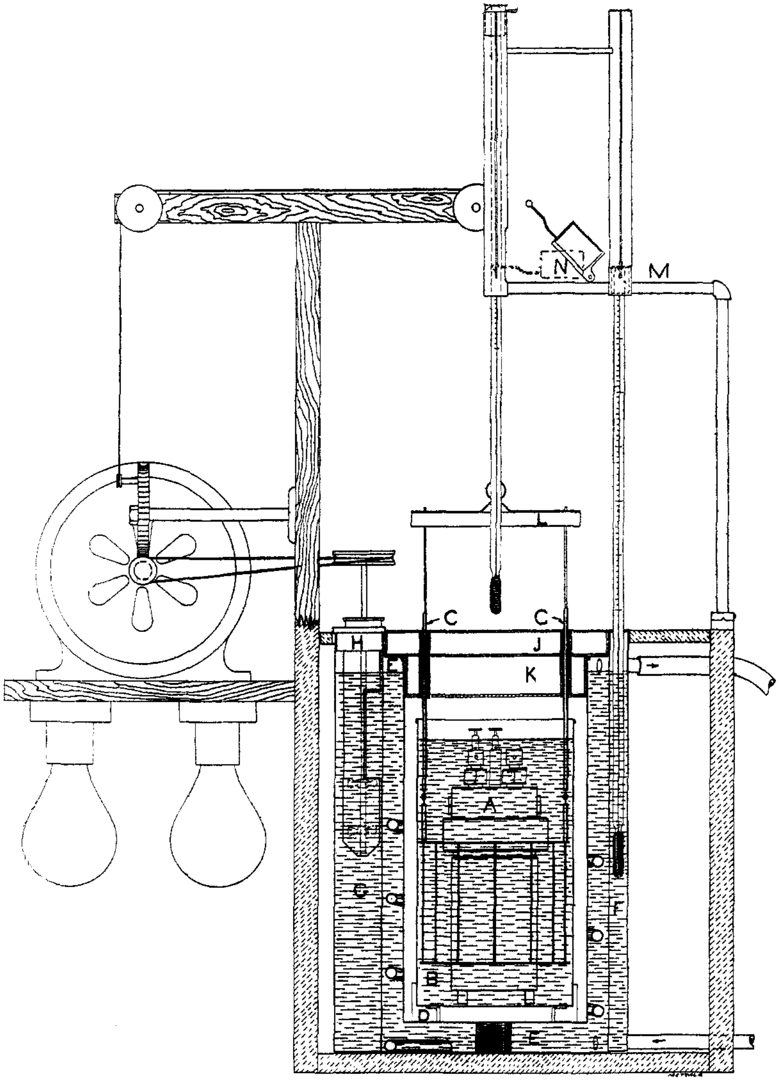
[1] Richards, Henderson and Forbes, *Proc. Amer. Acad. Arts and Sci.*, **41**, No. 1 (May, 1905).

[2] Atwater and Rosa, *Physical Rev.*, **9**, Nos. 3 and 4 (1899).

[3] Atwater and Snell, THIS JOURNAL, **25**, 659 (1903).

[4] Richards, Henderson and Frevert, *Proc. Amer. Acad.*, **42**, No. 21 (March, 1907).

perature of which gives the data for computing the number of Calories produced during a combustion, is shown in the figure and consists of the bomb A, the calorimeter can B, and the water it contains, the stirrer, and the immersed portion of the thermometer. In our development of the calorimeter, we have used for the most part a Kröker bomb, but the calorimeter is applicable to any type of bomb with which we are familiar. The calorimeter can is of nickel-plated brass (24 cm. high and 13 cm. in diameter), being 13 mm. higher than the bomb. The stirrer consists



of two flat brass rings, encircling the bomb, perforated by a number of holes, and held together by several small brass rods 10 cm. long. This stirrer is connected with the mechanism for raising and lowering it by two rods, C C, which are made of hard rubber to prevent conduction of heat from the calorimeter. On both of these rods, brass eye-joints are used which allow the stirrer flexibility of motion and prevent it from binding. The calorimeter can rests on three hard rubber guides and knife edges, D, within a second can, about 13 mm. of air space surrounding the calorimeter can on all sides.

To prevent the calorimeter system from exchanging heat with the surrounding media, it is placed inside of a water jacket, E, which is always maintained at the same temperature as the calorimeter. This jacket consists of two nickel-plated brass cans, the smaller one (30.5 cm. high and 15.3 cm. in diameter) so fitting into the larger one (35 cm. high and 19 cm. in diameter) that there is an annular space about 17 mm. wide between the two cans. Two slits are cut in opposite sides of the outer can and two small brass tubes with corresponding slits are soldered to the can so as to provide on the one side, F, for the immersion of a Beckmann thermometer and on the other, G, for a turbine stirrer, H. This annular space, with its two cylindrical enlargements, is filled with about 3500 cc. of water. The water is heated or cooled to correspond with the temperature of the calorimeter water; to heat it, a Simplex electric heating coil (6.8 amp., 750 watts), helical in shape, which is immersed in the water, is used; for cooling, cold water from the city mains is admitted through a small pipe at the bottom of the outer can, the excess of water in the jacket passing out through an overflow. A 2° rise in temperature can be obtained in three minutes by passing the current through the heater for 50 seconds; the cooling is much more rapid.

The calorimeter is protected from exchange of heat at the top by means of a cover, which fits snugly in the top of the water jacket and reaches to 13 mm. from the top of the calorimeter can. This cover consists of two dead-air compartments, J and K, separated by an asbestos plate. The side of the lower dead-air compartment, K, is of metal to allow contact with the outer water jacket and so cause this compartment to take the temperature of the water jacket (and consequently that of the calorimeter) in preference to the temperature of the room air. The other parts of the cover are of non-conductible material—fiber and asbestos—, the top consisting of a larger sheet of fiber for convenience in handling. Soft rubber packing is on the bottom of the cover. Three hard rubber tubes pass through the cover, two for the stirrer rods and one for the thermometer, and the ignition wires pass through a small groove on one side.

Auxiliary Apparatus.—The cans are encased in a wooden box, which serves as a support and also protects them from undue local heating or cooling. A door in front opens to a pet-cock on the water jacket for emptying the latter if desired.

A motor, resting on a shelf back of the box, actuates the two stirrers. The outer stirrer is connected directly to the motor shaft by a cord, and rotates about 750 times a minute. The inner stirrer is raised and lowered 44 times per minute, a distance of 6.5 cm., by means of a worm gear fastened directly to the armature shaft of the motor. This worm gear is connected to the stirrer by a cord passing over pulleys on the back of the box to a cross bar with spring, L, which grips the tops of the stirrer rods.

The ignition of the substance in the bomb is accomplished by a 110-volt current passing through three 32 c. p. lamps in parallel; these lamps are placed in receptacles beneath the shelf upon which the motor rests. The wires are attached to the bomb before lowering it into place in the calorimeter, and later attached to a plug outside which connects it to the switch used for ignition; this avoids handling the wires under water after the bomb is immersed.

The electric switches have been placed on the front of the case. One controls the 110-volt circuit, and there is one each for the motor, the electric heater, and the ignition. Two push buttons for the thermometer tappers are also placed on the front of the case.

The thermometers are held by a special form of support, M, consisting of two brass tubes, one for each thermometer. Attached to the top of each thermometer is a collar with a handle, which fits into a slit in the wall of the tube support. When lowered, the collar handle rests on the bottom of the slit; when raised, the handle is turned 90° and thus rests in a notch in the top of the support. When the thermometers are not being used, the whole support is swung to one side out of the way; when they are to be used, the support is swung back into position and automatically centers itself so that both thermometers are directly above the corresponding openings in the cover. We have been using two Beckmann thermometers, readable to 0.001°, although a cheaper thermometer could doubtless be used for the water jacket. For tapping the thermometer, we use the hammer of a small electric bell, N, attached to the thermometer support.

Method of Making a Combustion.—In a combustion, the substance to be burned is prepared, weighed, and put in the bomb and the bomb charged to 25 atmospheres with oxygen. The calorimeter water is brought to a temperature of about 2° lower than that of the room, as it is generally planned to have a 2° rise in the combustion and it has been found advantageous to have the final temperature of the calorimeter about the same as the room temperature. The calorimeter water is then weighed. The system is assembled; the calorimeter can, with water and stirrer, is lowered into the jacket, and then the bomb, connected with the ignition wires, is in turn lowered into the calorimeter can; the cover is put in place, the thermometers adjusted, and the stirrers connected and started. By means of the electric heating coil and the cold water, the temperature of the water jacket is adjusted to about 0.1° lower than that of the calorimeter system and a temperature constant to within 0.001° is readily obtained in the calorimeter system for several minutes. It has been found that the water jacket should be slightly colder than the water in the calorimeter to compensate for the small amount of heat entering from the warmer room, probably through the tubes in the cover.

After the temperature of the calorimeter water has remained constant for several minutes, showing no interchange of heat, the switch for heating the water jacket is closed. The current is then passed through the heater for such a length of time as will be necessary to raise the outer water to the temperature it is expected the inner water will reach after the substance in the bomb is burned. The length of time required for this is calculated from the known fact that the heater gives a 1° rise for every 25 seconds the current is on. Forty-five seconds after the current is turned on, another reading of the calorimeter thermometer is taken, and the substance is ignited. The heating of the water jacket is begun before ignition, as the electric heater is somewhat sluggish. During the 45 seconds the current is on before ignition, the rise in temperature of the outer water indicates on the thermometer about 0.2°, showing that there is very little, if any, interchange of heat, but the rise of temperature becomes considerably more rapid after one minute, and the temperatures of the calorimeter and the water jacket are found to rise at about the same rate. After the ignition, the two thermometers are watched very carefully and if the temperature of the water jacket does not follow very closely the temperature of the calorimeter water, it is heated by the electric heater or cooled by cold water, as may be necessary to keep the two temperatures the same. Generally, however, little or no adjustment of the temperature of the outer water is necessary, as a careful timing of the heating of the jacket at the start will regulate the temperature. Readings of the thermometers are recorded every minute, and three or four minutes after ignition, the thermometer in the calorimeter water is found to attain a maximum reading which will remain constant practically as long as desired. The combustion now being completed, the thermometers are removed, the bomb opened and rinsed with water, and the rinsings titrated for nitric acid, using methyl orange as an indicator.

Calculation of Results.—The initial constant reading of the temperature of the calorimeter system subtracted from the final constant reading after the burning of the substance gives, after applying thermometer corrections, the total rise in temperature of the system. This rise multiplied by the weight of water (plus the hydrothermal equivalent of the apparatus) gives the total number of Calories liberated. From this is subtracted the heat resulting from the ignition (electrical energy and combustion of kindling material, such as cotton thread or iron wire) and from the formation of nitric acid. The result, divided by the weight of the substance, gives the number of Calories per gram of substance.

The water equivalent of the calorimeter system was determined by us by burning known amounts of cane sugar (rock candy), the heat of combustion of sugar being taken as 3957 Calories per gram.[1] The amount of water used in our calorimeter has, for convenience in calculating, been such that the weight of water plus the hydrothermal equivalent is equivalent to 2500 grams of water.

SPECIMEN COMBUSTION.

		Grams.
Cane sugar:	Weight of substance taken..................	1.2905
	Weight of water in calorimeter..............	2125.8
	Hydrothermal equivalent....................	374.2
		2500 0

Time.	Temperature of calorimeter water.	Temperature of water jacket.	
3.30	18.430°	18.36°	
3.31	18.430	18.38	
3.32	18.430	18.38	Electric heater on for 55 seconds at 3.32.15.
3.33	18.430	18.66	Ignition at 3.33.
3.34	19.200	19.60	
3.35	20.420	20.33	
3.36	20.478	20.45	
3.37	20.479	20.46	Room temperature, 20.7°.
3.38	20.479	20.49	

20.479°
—18.430

2.049°

Thermometer correction. +0.008

Total rise............... 2.057°

Ignition heat = 27.5 cal.
HNO_3 = 7.5 cal.

2.057° × 2500 g. = 5143 cal.
5143 — 35 = 5108 cal.
5108 ÷ 1.2905 = 3958 cal. per gram.

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[1] This value is that found by Fischer and Wrede, *Sitzungsberichte d. Koniglich. Preuss. Akad. d. Wissenschaften*, **5**, 129 (January, 1908). If later investigation gives another more accurate result, the results obtained assuming 3957 as correct may be revised by proportion.

The apparatus here described has proved very efficient, and we are able to obtain very satisfactory duplicate results in two combustions of the same substance. Practically no trouble is experienced in obtaining a constant temperature of the calorimeter system either at the beginning or end of a combustion; in fact, with the room temperature even 5° higher than that of the calorimeter water, constant readings have been obtained. With this calorimeter, the time required for a combustion is much less than usual, inasmuch as long preliminary and final periods are avoided and the calculation is materially simplified.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS.]

A SIMPLE SYSTEM OF THERMODYNAMIC CHEMISTRY BASED UPON A MODIFICATION OF THE METHOD OF CARNOT.

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CONTENTS.

1. Introduction.

In order to determine the maximum amount of work which can be obtained from a given amount of heat by a fall in temperature, Carnot, in 1824, performed an "imaginary experiment," the Carnot Cycle. In performing this "experiment" Carnot made use of the simplest and most familiar example of a mechanism for obtaining work from heat, the cylinder and piston of the steam engine. He realized clearly that in order to obtain the desired relation he had only to *imagine* a mechanism which could operate under the most ideal conditions, one which represented the limit approached by all actual machines of the same class, as the losses due to friction, heat radiation and conduction, incomplete external compensation, etc., became indefinitely small. The reversible cyclical process thus invented by Carnot and later slightly modified by the work of Clapeyron and of Clausius, constitutes to-day the basis for the derivation of the mathematical formulation of the Second Law of Thermodynamics. Resting upon this law, the whole structure of thermodynamics has since been built up.

In the process of constructing our systems of thermodynamic chemistry, two general methods may be distinguished. The first of these, the analytic method, starts with Clausius' formulation of the Second Law in terms