XCVII.—*An Adiabatic Calorimeter.*

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For thermochemical work, Richards and Burgess (*J. Amer. Chem. Soc.*, 1910, **32**, 431) devised an adiabatic mantle, in which the heating was effected by chemical means, and Benedict and Higgins (*ibid.*, 461) designed one in which the heating was electrical, and the cooling was effected by means of a stream of cold water. In the adiabatic mantle described here, the heating and cooling are both effected by a stream of water in a flexible copper tube

immersed in the mantle water, which, however, itself remains in the mantle throughout the experiment.

The outer can, *T*, is connected by means of the tubes *B*, *B* (1.27 cm. diameter) with the tube *A*, in which rotates a turbine stirrer. This stirrer may be driven by a small 2 to 4 volts motor, and produces very efficient mixing. *R* is a tube fixed on to *T* opposite a slit, and serves to hold a Beckmann thermometer. To *T* are attached the blocks *L* and *L*, to which are hinged the levers *K* and *K*; these are movable downwards from the horizontal position, but not upwards. There are three such levers placed

symmetrically. Pressing up against K and K are the corks C and C , up against which the lid E of the submerged can D is pressed by the upward thrust of the mantle water. When a very large calorimeter has to be placed inside, it may be necessary to support D below by means of small corks. To ensure that the lid E is watertight, the rim may be smeared with a little vaselin. Access to the inside of D is obtained by means of the tubes G (1.27 cm. diameter) and H (1.9 cm. diameter). H is for a thermometer and G for a stirrer. It is convenient to have a third tube also (1.9 cm. diameter). D is surrounded by water on all sides. For many purposes, there may be substituted a can screened on all sides except the top, and reaching up to K and K , which hold it in position without corks.

A flexible copper tube of 0.63 cm. internal diameter and about 240 cm. long is soldered at the ends to short brass tubes (1.11 cm. external diameter). The flexible tube itself does not make a watertight joint with rubber tubing. Short brass tubes (1.11 cm. external diameter) are soldered in through the wall of T at S and S . These are connected by means of rubber tubes with the brass ends of the flexible F , which coils down from one S round the mantle, and rises from the bottom almost straight up to the other S .

The stream of water in the flexible tube is controlled by two T-tubes and the taps M , N , O , and P . M , N , and O are glass taps with bore of about 3 mm., and for P a fixed metal water-tap may be used, provided it has no leather washer. To obtain a stream of cold water, the taps M and O are closed, and P (the water-tap) and N are opened, the stream being regulated with the taps. To obtain a stream of hot water, N and P are closed, and M and O are opened as far as required. The stream of hot water is pumped with a Luther pump from a hot-water bath, which may be conveniently heated by means of an asbestos woven wire net placed between the bath and a layer of bricks. A net of Standard Wire Gauge 33½, of about 220 ohms resistance for use with 220 volts, will usually suit. Frequently, about 5 to 6 litres of water maintained at about 45° will serve as a hot bath.

It is advisable that all the metallic parts of the apparatus except the flexible tube should be made of nickel-plated brass. The flexible tube, however, should be of copper.

To screen the top, a lid containing water is sometimes used, but as the regulation of the mantle and the lid simultaneously is rather inconvenient, the submerged tin is to be preferred.

The can D can be easily removed when required, and the flexible tube also; thus the apparatus can be used for a variety of experiments other than thermochemical.

If it is desired to maintain the calorimeter at a temperature higher than that of the room, it will be necessary to keep the temperature of the mantle higher than that of the calorimeter, on account of radiation through the thermometer, etc., from the calorimeter to the room.

In measuring heat evolved within the calorimeter, it is the aim to maintain the temperature steady when it reaches its maximum point. It is difficult, however, to prevent a slight fall from the maximum when the original rise to the maximum is rapid and large, as in the cases of heat of neutralisation quoted below. These examples put the apparatus to a very severe test. It is fortunate, therefore, that the need for an adiabatic mantle is most urgent in cases of slow change of heat, where, on the other hand, the control is easiest.

Below are given three sets of simultaneous calorimeter and mantle temperatures. In the first experiment, the calorimeter was about 3 cm. from the inner can, and the response to the mantle control was improved upon in the second and third experiments, when the bottom of the calorimeter was only 0.5 cm. from the bottom of the inner can.

The first and third experiments are on heat of neutralisation. The second experiment shows how the same bulk of calorimeter water as in the other experiments could be kept at a constant temperature higher than that of the room by mantle-control. From this can be seen how the mantle would be used in a case of slow change of heat.

First experiment.—Room temperature, 15°. Bath, 5 litres at 44°. The hot current was passed for one and a-half minutes. Two hundred c.c. of 0.25*N*-hydrochloric acid at 14.865° were added to 200 c.c. of 0.25*N*-sodium hydroxide at 14.765° two and a-half minutes from the beginning or one minute after stopping the hot current. The temperatures were read, when possible, at intervals of fifteen seconds. The maximum was almost reached in thirty seconds, and reached in forty-five seconds, and maintained steady for forty-five seconds, after which the fall was very slow.

	Started hot current.					Stopped current.				
Time in min- utes	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	2	$\frac{1}{4}$
Mantle	14.865°	14.87	14.88	14.96	15.22	15.67	16.17	16.52	16.87	17.11
Calorimeter. .	14.765°	—	—	—	—	—	—	—	—	—
Added acid.										
Time	2 $\frac{1}{2}$	$\frac{3}{4}$	3	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	4	$\frac{1}{4}$		
Mantle	17.17	17.19	17.20	17.22	17.24	17.25	17.26	17.26		
Calorimeter ...	14.765	16.30	16.50	16.52	16.52	16.52	16.52	16.518		

Time	4½	¾	5	¼	½	¾	6	¼
Mantle	17-26	17-261	17-264	17-264	17-263	17-263	17-263	17-264
Calorimeter.....	16-515	16-515	16-514	16-512	16-511	16-510	16-509	16-508

Time	6½	¾	7	¼	½	¾	8
Mantle	17-263	17-262	17-259	17-256	17-254	17-251	17-250
Calorimeter ...	16-507	16-506	16-505	16-505	16-505	16-503	16-503

Second experiment.—Room temperature, 14·8°. Bath, 5 litres at 44°. The asterisk indicates that at that point the hot current was passed for five seconds to maintain the temperature.

Time	0	½	1	¾*	2	3	¼
Mantle	16-97	16-967	16-965	16-96	16-958	16-98	16-988
Calorimeter.....	16-839	—	16-839	—	16-838	—	—

Time	3½	3¾	4	5	5½	6½*
Mantle.....	—	16-985	—	16-969	—	16-965
Calorimeter ...	16-838	16-838	16-838	—	16-839	16-838

Time	7½	8	8½	8¾	9¼	9¾*
Mantle.....	16-955	16-97	16-99	16-982	16-975	—
Calorimeter ...	—	16-838	—	16-838	16-837	16-837

Time	11	12	12½	13½	15*
Mantle.....	17-00	17-01	17-015	17-015	17-008
Calorimeter.....	16-838	16-838	16-838	16-838	16-838

Time	15½	16	16½	17	17½	18	19
Mantle	17-008	17-005	17-015	17-02	17-02	17-02	17-02
Calorimeter ...	—	16-838	—	16-838	16-838	16-838	16-838

Third experiment.—Room temperature, 14·6°. Bath, 5 litres at 44°. The hot current was passed for one minute, and afterwards was occasionally passed for five seconds. Two hundred c.c. of 0·25*N*-hydrochloric acid at 14·4° were added to 200 c.c. of 0·25*N*-sodium hydroxide at 14·205° two and a-half minutes from the start, or one and a-half minutes after the hot current was stopped.

	Started hot current.				Stopped current.			
Time in min- utes	0	¼	½	¾	1	¼	½	¾
Mantle	14-40	14-40	14-402	14-42	14-77	15-20	15-39	15-45
Calorimeter...	14-2	—	—	—	—	—	—	—

	Added acid.					
Time	2	¼	½	¾	3	¼
Mantle.....	15-50	15-51	15-53	15-58	15-60	15-61
Calorimeter ...	14-205	—	14-205	—	16-01	16-02

Time	3½	¾	4	¼	½	¾
Mantle.....	15-64	15-67	15-70	15-71	15-73	15-75
Calorimeter ...	16-022	16-022	16-022	16-022	16-018	16-018

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Time	5	$\frac{1}{4}$	$\frac{1}{2}$	6	$\frac{1}{4}$	$\frac{1}{2}$
Mantle.....	15.80	16.07	16.25	16.45	16.46	16.46
Calorimeter	16.018	16.017	16.016	16.015	—	—

Time	$6\frac{3}{4}$	7	$\frac{1}{4}$	$\frac{1}{2}$
Mantle.....	16.45	16.49	16.50	16.50
Calorimeter.....	16.015	16.015	16.015	16.015

After six minutes, the calorimeter reached 16.015° , at which it remained steadily for at least six minutes.

It may be mentioned that the heat of neutralisation as obtained from the above agrees fairly well with the values obtained by Wörmann (1905).

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