Design and Testing of a Micro Reaction Calorimeter

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A micro reaction calorimeter has been designed and tested. The calorimeter is primarily intended for studies of biochemical reactions using small sample volumes. Electrical calibration experiments indicate an attainable precision of 0.05 % for comparatively large heat quantities and better than 1 % if 0.001 cal is evolved (fast processes). The calorimeter is useful for processes of long duration (hours). Measurements on the neutralization of tris(hydroxymethyl)aminomethane and on dilution of sucrose are reported and compared with literature values. Possible systematic errors involved in the present type of microcalorimetric measurements are discussed.

The microcalorimeter described in the present paper is primarily designed for measurements of heats of reaction in dilute solutions involving small sample volumes. The construction is primarily for studies on biochemical reactions which are usually performed in aqueous solution and in the region of room temperature.

The calorimeter is of a type usually called a heat conduction calorimeter. Heat evolved in the reaction vessel is conducted out to a comparatively large surrounding heatsink, and with an endothermal process heat will flow from the heatsink to the reaction vessel. The arrangement is such that essentially all heat exchange between the reaction vessel and the heatsink takes place through a thermopile, and heat evolved will be proportional to the voltage-time integral, *i.e.* the area below the voltage-time curve. As in most other microcalorimetric constructions the twin principle has been adopted.

The general calorimetric principle used in this work has been used earlier in other microcalorimetric constructions; notably the Tian-Calvet calorimeter [1] and the calorimeter designed by Benzinger and Kitzinger.[2]

DESIGN OF THE CALORIMETER

The principle arrangement of the apparatus is shown in Fig. 1. The reaction vessels are in good thermal contact with junctions of a large number of thermocouples where the opposite junctions are in contact with the surrounding heatsink. Thermocouples for each vessel are connected in series whereas the two thermopiles thus formed are connected in opposition. The differential voltage signal is amplified, recorded and integrated.
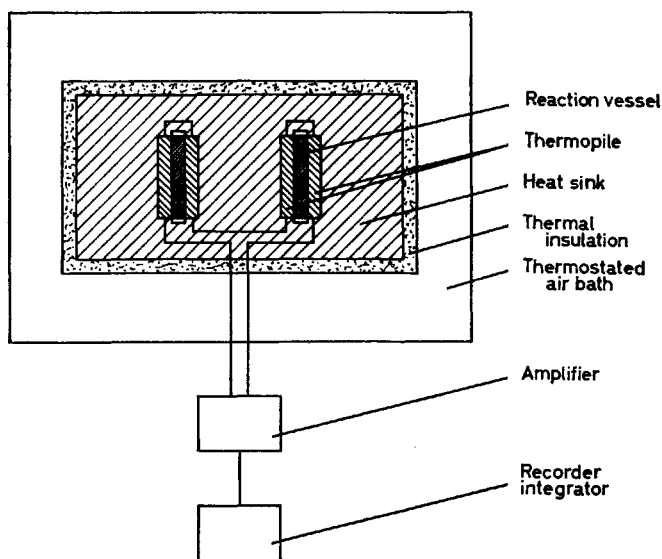

Fig. 1. Principle arrangement of the calorimeter.

Reaction vessels

In the present work experiments have been performed with different reaction vessels made from steel, gold or glass. They were all shaped as narrow rectangular or squared cans divided by a partition wall into two compartments (A, B; Fig. 2). The compartments were connected by an air space (C + D).

Steel vessels. The construction material was acid proof steel (Avesta 832 SK). The vessel was milled from one piece of steel and the lid which was made to give a close fit was sealed to the vessel from the outside by means of epoxy resin (Araldite AY 103). To the lid was fastened two glass filling tubes which could be closed by silicon rubber caps. The glass tubes were sealed to the lid by epoxy resin and care was taken that no resin was introduced inside the reaction vessel. The partition wall had a 2×30 mm bore containing a 50 ohm manganine heater used for electrical calibration. The size of the vessel was made to match the surface area of the thermopile; in the present case the dimensions were $45 \times 32 \times 10$ mm. Wall thickness towards the thermocouples was 1 mm; in other parts of the vessel it was slightly larger. Volumes A and B were 3 and 2 ml respectively. Suitable liquid volumes were 2.5 and 1.8 ml or less.

Gold vessels. The vessel was made from 18 carat gold.* Wall thickness was 0.6 mm and the outside dimensions were $40 \times 40 \times 10$ mm. The partition wall was a 0.6 mm

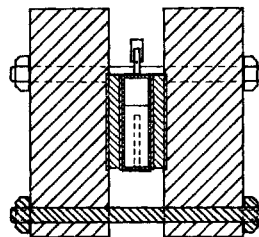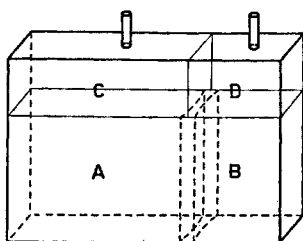---

* 75.0 % Au, 16.6 % Cu, 8.4 % Ag.

Fig. 2. Schematic view of reaction vessel.

Fig. 3. Section through the "calorimetric unit".

plate. The calibration heater was contained in a 3 mm tube which extended 30 mm into the vessel from the center of the bottom plate. The vessels were usually charged with approximately 5 + 2.5 ml liquid.

Glass vessels. The vessels were made from Pyrex glass and had a wall thickness of about 1 mm. Outside dimensions were the same as for the gold vessels. The partition wall was hollow and contained the calibration heater. The vessels were usually charged with approximately 4 + 2 ml. Aqueous solutions showed some tendency to creep up the partition wall which could cause some mixing prior to the experiment. This effect was overcome by making the glass surface hydrophobic by baking it with a film of silicone oil MS 200 at 140°C.

Thermopiles. In the initial phase of this work thermocouples were made by electrolytic copper plating of one side of a flat constantan spiral (with a Mylar ribbon as a core). From the thermocouple ribbon was made a thermopile having the shape of a disc contain-ing 5 000 — 10 000 junctions. Such thermopiles gave a satisfactory performance (*cf.* Refs. 2, 3) but during the course of this work it was found that commercially available thermoelectric coolers made from semiconducting material were more suitable because of their low resistance which facilitates amplification of the voltage signal. In the work reported here Thermagotrons TL 0812 (MCP Electronics Ltd., Wembley, England) were used in connection with the steel cells. Four such units, each containing 48 junctions, were connected in series and placed between epoxy insulated aluminium plates and moulded with epoxy resin to form a rectangular plate (45 × 32 × 6 mm). Together with the gold and glass vessels Thermoelectric Modules 3951 — 1 (Cambion, Cambridge, Mass.) were used (40 × 40 × 7 mm).

"Calorimetric unit". Fig. 3 shows a section through the "calorimetric unit". At the center of this sandwich construction is the reaction vessel surrounded by two thermo-couple plates. The external sides of thermopile are in thermal contact with aluminium bolts (75 mm in diameter, 25 mm thickness) which act as primary heatsinks. On the lid of the reaction vessel is fastened an epoxy coated 0.5 mm fabric bakelite plate which forms a thermal insulation and also acts as a mechanical support for the reaction vessel. The calorimetric unit is joined together by three 6 mm screw bolts. Contact surfaces are greased with silicone to increase the thermal conductivity.

Main heatsink. The main heatsink is an aluminium cylinder of two parts (diameter 150 mm, length 140 mm) having a 75 mm central bore and 5 mm end walls. In the bore are contained the two calorimetric units. The upper and smaller part of the block is used as a lid and can be fastened to the main part by bolts. The aluminium cylinder is suspended by horizontal steel shafts between ball bearings positioned on the inner walls of the surrounding thermostated air bath. The shafts are connected to each end of the cylinder through vertical aluminium discs which are joined to the end-walls of the cylinder by 4 mm steel pins. The metal block is covered with a 20 mm layer of styrofoam.

The temperature difference between the metal block and the air bath is indicated by a 200 junction copper-constantan thermopile (made by electroplating a 0.8 mm constantan wire wound on a mica strip). A 20 ohm electrical heater winding is also attached to the metal block. Electrical windings from the calorimetric units and from the block are

taken out through the end walls and several turns are wound on the shafts before taken to contacts on the inner wall of the air bath.

Thermostated air bath. The thermostated air bath consists of a 50 l aluminium box which is insulated on the outside by a 50 mm layer of styrofoam. Fifty mm PVC tubes are used to circulate air between the bath and another air container. The temperature was regulated by a LKB proportional controller 7602 A connected to a thermistor in the thermostated bath and a heater of bare resistance wires positioned close to a fan in the outside air container. Cooling water was circulated through a copper spiral also positioned in the outer container. When the room temperature was controlled within $\pm$ 0.5°C the temperature in the thermostated air bath varied by less than $\pm$ 0.02°C, during a 24 h period.

Amplification and recording of the voltage signal. The differential voltage signal from the two calorimetric units was amplified by a Hewlett Packard DC Null Voltmeter 419 A or by a Keithley 150 B Microvolt Ammeter. The amplified signal was recorded by a Sargent SR recorder fitted with a ball and disc integrator.

Electrical calibration circuit. A conventional electrical calibration circuit with constant voltage source (Oltronix B 40) and an electronic timer ($\pm$ 0.01 sec) was used. A 100 ohm standard resistance was connected in series with the 50 ohm calibration heater or with a 50 ohm dummy heater. Potential across the standard resistance (and thus the current) was measured during the heat input by means of a Cambridge Vernier potentiometer. From values for time, heater resistance and current electrical energy supplied was calculated.

Operational procedure

In an experiment one of the reaction vessels is charged with the reactant solutions by means of glass syringes fitted with Teflon tubings. Amount of reactant solution is determined by differential weighing of the syringe. The reference reaction vessel should be charged with approximately the same amount of pure solvent or with proper solutions for a blank experiment.

After the block has been assembled it is heated to the thermostat temperature ($\pm$ 0.02°C) and the apparatus is left to equilibrate for an hour or more.

The steel shafts attached to the metal block extend outside the air bath. Manual rotation of one of these shafts caused the reactants to be mixed. When the reaction vessels have been rotated 90° (anticlockwise) essentially all the liquid phase will be in the volume (A + C) and the two reactants partly mixed. On continued rotation the liquid phase will flow to volume D + B, but will be met by airbubbles excerting an efficient mixing effect. For most reactants complete mixing was achieved by rotating the vessel one turn and back. However, as a standard procedure for the experiments reported here this process was made twice. After the reaction had taken place additional rotations were usually made in order to determine the actual correction for the differential heat of friction during the mixing process.

The heat effect connected with the mixing procedure (one turn and back) was in the order of 4×10^{-4} cal. The differential heat effect was close to zero and usually reproducible to within 2×10^{-5} cal.

Fig. 4 shows a record of the thermopile signal from an acid-base neutralization experiment. Gold vessels were used. The decay half time for the signal is approximately 70 sec, and the after period baseline is established after 20 min. For the steel and glass vessels the decay half time is slightly longer (80 sec). Additional rotations were made and a small positive differential
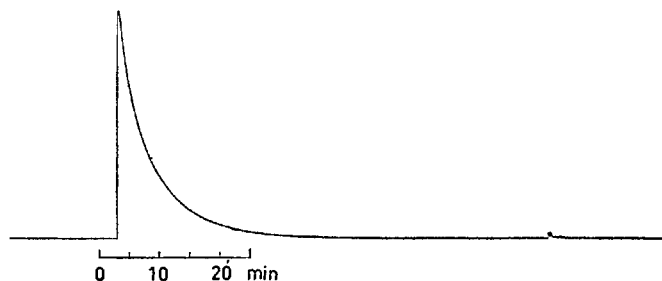
Fig. 4. Thermopile signal from an acid-base experiment using gold vessels. Heat evolution = 0.014 cal.

heat of friction was observed. The small peaks shown on the graph are characteristic, they occur synchronously with the rotations and are believed to be caused by a reversible mechanical effect on the thermopile.

TESTING OF THE CALORIMETER
Electrical calibration experiments

Ideally a given amount of heat evolved in the reaction vessel should at a given degree of amplification give rise to the same surface area under the voltage-time curve. The calibration constant should not be affected by heat capacity or heat conductivity of the reaction vessel or its content, the shape of the heat effect-time curve, or the amount of heat evolved. The following series of experiments were undertaken to establish a useful procedure for electrical calibration of the calorimeter. Calibration constants (ε) are expressed as calories per arbitrary integrator unit. For the different series of experiments where a Hewlett Packard null detector was used as amplifier several slightly different settings of the power output to the recorder was used. Hence, ε-values for the different types of experiments are not comparable. All uncertainties are expressed as standard deviations of the mean.

Position of the calibration heater. Experience has shown that the position of the calibration heater can be very critical in reaction calorimetry. The following experiments illustrate the property of the present calorimeter in this respect. Electrical calibration experiments were made where approximately 10 millicalories were evolved in the calorimeter heater and in a heater inserted in the larger compartment of the same reaction vessel. The insertion heater was made from enamelled manganin wire which had been further insulated by a thin layer of epoxy resin. The reaction vessel was charged with water and the heater together with about 5 mm of the epoxy insulated copper leads was kept under the water surface.

Experiments were performed both with steel vessels (Hewlett Packard amplifier) and with glass vessels (Keithley amplifier). For the steel vessels electrical energy was introduced without concommittant rotation of the

Table 1. Calibration constants obtained from experiments with the inbuilt heater and with an insertion heater. Heat input 0.01 cal.

Calorimetric vessel	No rotation		Rotation	
	Inbuilt heater	Insertion heater	Inbuilt heater	Insertion heater
Steel vessel	3748 ± 6	3753 ± 10		
Glass vessel	2505 ± 10	2494 ± 12	2536 ± 17	2520 ± 12

calorimeter. With the glass vessels, experiments were also made during which the calorimeter was rotated as in a mixing procedure. Each series consisted of 5—7 experiments. Results of the experiments are shown in Table 1.

Inspection of the table shows that there is no significant difference between calibration constants obtained with the inbuilt heater and with the insertion heater. Results thus indicate that for the present calorimeter position of the calibration heater is not very critical.

When the glass calorimeter was rotated during the heat input slightly but not significantly higher ε-values were obtained as compared with results from the static experiments. In separate experiments with steel and with gold vessels no such difference was observed.

Experiments with empty and charged vessels. In experiments with steel vessels approximately 10 millicalories were evolved during 40 sec in one of the reaction vessels while both vessels where charged with 3 ml of water and when both were empty. (No rotation of the calorimeter.) The shape of the reaction curve was markedly different but ε-values were, within uncertainty limits, the same. Mean values from the two series of experiments (6 experiments each) were obtained, $\varepsilon = 3850 \pm 8$ and $\varepsilon = 3868 \pm 20$. Neither heat capacity nor heat conductivity within the cell will thus affect the calibration constant.

Variation in heat quantity and length of experiment. In Table 2 results are given for several series of electrical calibration experiments where a number of factors have been varied: total amount of heat evolved, length of experiment and amplification. Experiments were performed with steel vessels and Hewlett Packard amplifier (output to recorder was kept constant). Electrical heat input was made without rotation of the calorimeter.

Table 2. Results from some electrical calibration experiments.

Heat input (millicalories)	Time for heat input (sec)	Amplification	Number of experiments	ε
113	400	$1/3 \times 10^3$	5	2650 ± 1
10	25	10^3	7	2697 ± 7
15	3600	10^4	6	2673 ± 20
0.9	20	$1/3 \times 10^4$	7	2670 ± 20

Inspection of Table 2 shows that if slightly more than 0.1 cal is evolved during a few minutes the reproducibility will be better than 0.05 %. If a fast heat evolution amounts to 0.01 cal precision is about 0.3 % whereas the precision will be 0.8 % if only 0.9 millicalorie is evolved. The same precision was obtained when 0.015 cal was evolved during 1 h. The small difference in ε-values between each series are within limits of expected amplification and recording error.

In other experiments (steel vessels, Keithley amplifier) 0.01 cal was introduced during as short a period of time as 2 sec, the electrical energy being supplied from a LKB 8700 Precision Calorimeter. Calibration constants did not differ significantly from those obtained from experiments where approximately the same amount of energy was supplied during 30 sec. (The calorimeter was rotated during these experiments.)

Results from the electrical calibration experiments strongly indicate that an electrical calibration procedure is suitable for the present type of calorimeter. In order to minimize errors from amplification and recording units the thermopile signal should preferably have a similar voltage-time curve in calibration and chemical reaction experiments although this is by no means critical. To get a close comparison between calibration and reaction experiments the calorimeter should be rotated also during the supply of the electrical energy.

Reaction and dilution experiments

Protonation of THAM. The solution of tris(hydroxy methyl)aminomethane ("THAM") in dilute aqueous hydrochloric acid has been found to be a suitable test reaction for reaction calorimeters employing ampoule technique.[4] Here several series of measurements on the protonation of aqueous THAM solution by dilute HCl have been performed.

Steel vessels. Some details of one series of measurements using the steel vessels will be given. Water used in preparing the solution was glass distilled and boiled to remove CO_2. THAM was purified according to Ref. 4. The larger compartment in the reaction vessel contained 2.5 ml of a THAM buffer solution (4×10^{-3} M THAM which had been neutralized by HCl to 25 %). The smaller compartment was charged with 1.5 ml of a 10^{-3} M HCl solution. The reference vessel was charged with 2.5 ml of the THAM buffer $+$ 1.5 ml of water. The pH value for the THAM buffer was about 8.6 before the experiments and the pH of the reaction solution was 8.2. A small amount of CO_2 present is thus not expected to interfere with the experiments in this pH-range. Measurements were performed at 25.0°C. Heat evolution in these experiments was about 17 millicalories. The mean value for 7 experiments was $\Delta H = -11.01 \pm 0.05$ kcal/mole (uncertainty value is the standard deviation of the mean).

Heat of dilution of HCl should in the present case be insignificant [5] and this was verified experimentally. The ΔH-value determined should thus refer to the heat of protonation of THAM in an aqueous solution of low ionic strength (10^{-3} M). As there is no charge generation in the process it may be expected that the measured value should be equal to that for infinite dilute solution. Other series of experiments were performed under slightly different

conditions where all solutions were 10^{-2} M with respect to NaCl, but essentially the same values were obtained.

Gold vessels. Several series of measurements similar to those described for the steel vessels were performed but different concentrations of HCl and buffer solutions were used.

From 12 experiments where the HCl concentration varied from 4×10^{-4} to 4×10^{-3} moles/l (corresponding heat evolution ranging from 11 to 110 millicalories) a mean value equal to -11.08 ± 0.05 kcal/mole was obtained for the protonation reaction. No correlation was found between HCl concentration and ΔH-value obtained. However, 3 experiments performed with a HCl concentration as high as 10^{-2} M gave a mean value of 11.32 (± 0.06, average deviation of the mean) kcal/mole.

Glass vessels. In the experiments with glass vessels two series of measurements were made. First a half neutralized 10^{-2} M solution of THAM was reacted with HCl solutions ranging in concentration from 4×10^{-4} to 4×10^{-3} M. (Corresponding heat evolution ranging from 8 to 80 millicalories.) The reference cell was charged with water. Heat of dilution of the THAM buffer was determined in separate experiments and corrected for. Results were very similar to those obtained with the gold vessels using moderate concentrations. As a mean value from 12 experiments $\Delta H = -11.08 \pm 0.05$ kcal/mole was obtained.

In another series of measurements a half neutralized 0.12 M THAM solution was reacted with 0.04 M HCl (heat evolution was 0.8 cal). Here a significantly larger value was obtained. $\Delta H = -11.25 \pm 0.05$ kcal/mole. (6 experiments). Electrical calibration constants were closely the same for the two series of experiments. The electrical heat input at the calibration experiments was similar to the amount of heat evolved in respective chemical reactions.

In Table 3 results are summarized from the present measurements on THAM together with results from other calorimetric investigations. Sturtevant [6] performed the measurements with an adiabatic microcalorimeter whereas the values by Nelander [7] and by Öjelund and Wadsö [8] were determined by an

Table 3. Heat of protonation of THAM in aqueous solution at 25°C.

Vessel material	Heat liberated, cal/l of calorimetric liquid	Ionic strength, moles/l	ΔH, kcal/mole	Reference
Tantalum	1—6	10^{-2}	-10.93 ± 0.10	Sturtevant [6]
Steel	4	10^{-3}	-11.01 ± 0.05	This work
Gold	1.5—15	10^{-2}	-11.08 ± 0.05	» »
Glass	1.3—13	*ca.* 5×10^{-3}	-11.08 ± 0.05	» »
Gold	40	10^{-2}	$-11.32(\pm 0.06)$	» »
Glass	140	5×10^{-2}	-11.25 ± 0.05	» »
Glass	120	10^{-1}	-11.36 ± 0.04	Nelander [7]
Glass	240	5×10^{-2}	-11.35 ± 0.01	Öjelund and Wadsö [8]

accurate "macrocalorimetric" technique (100 ml glass vessels; isothermal jacked calorimeters).

From the table it is seen that the results fall into two groups. Those which were determined at low heat evolution (1—13 cal/l) give low values, $\Delta H = -10.9$ to -11.1 kcal/mole. In experiments with a considerably larger heat evolution, ΔH-values are around -11.3 kcal/mole for the present microcalorimeter and -11.35 when the well established macrocalorimetric technique was used. These values are in good agreement with the values (referring to infinite dilution) which have been derived from accurate potentiometric measurements, 11.38 kcal/mole [9] and 11.33 kcal/mole.[10]

No explanation for the discrepancy between the two groups of results can be offered at the present time. It seems unlikely that systematic errors are involved in the actual heat measurements as entirely different calorimetric techniques have been used within both groups. Further, for the present calorimeter there was no significant difference in electrical calibration constant for the two groups of experimental conditions.

Neither does it seem to be likely that surface adsorption effects are involved as for the present calorimeter similar results are obtained with reaction vessels made from different materials. (*Cf.* the variation in experimental conditions with the steel cells.)

Dilution of sucrose solution. As another test reaction the heat of dilution of aqueous sucrose solution was determined. In the experiments a 0.1903 molal sucrose solution was mixed with approximately twice its weight of water. Experiments were performed at 25.6°C. Glass vessels were used.

Table 4. Heat of dilution of aqueous sucrose solution at 25.6°C (millicalories).

Amount of sucrose, mmole	Final concentration, mole/kg	Q_{exp}	Q_{calc}	Difference
0.3687	0.05752	6.62	6.54	+ 0.08
0.3702	0.05793	6.74	6.54	+ 0.20
0.3718	0.05814	6.47	6.56	−0.09
0.3704	0.05790	6.68	6.55	+ 0.13
0.3706	0.05787	6.58	6.55	+ 0.03
0.3697	0.05784	6.74	6.54	+ 0.20
			Mean	+ 0.09

Experimental results are summarized in Table 4 and heat values determined (Q_{exp}) are compared with those which may be calculated by the data given by Gucker *et al.*[11] (Q_{calc}). The present results are on the average 10^{-4} cal or 1.4 % higher than the calculated values, which is judged to be well within combined uncertainty limits for the two sets of data. (*Cf.* discussion concerning errors due to change in gas phase composition.) If the calculated values are increased by 1.4 % the precision for the present series of measurements may be calculated to be $\pm 5 \times 10^{-5}$ cal $[\pm \sqrt{\Delta^2/n(n-1)}]$.

DISCUSSION CONCERNING SOME POSSIBLE SYSTEMATIC ERRORS

Distillation effects. If the two compartments of the reaction vessel contain liquids with different vapor pressures there will be some distillation during the equilibration period. For aqueous solutions this will not be expected to cause any significant change in composition for the two liquids, but heat effects connected with the vaporization-condensation process might be appreciable. However, when a steady-state has been reached there should be very nearly the same cooling effect at the evaporation site as the heating effect in the region where condensation occurs. (The only difference being the heat of dilution effect; *cf.* above.) The electrical calibration experiments with different heaters and heater positions seem to rule out the possibility that such a zero net heat effect will give rise to a net voltage signal.

Change in gas phase composition. The present design of reaction vessel requires a comparatively large gaseous phase. It is thus not suitable for measurements on processes where there is a large change in the gas phase composition like that which accompanies mixing of volatile compounds (*cf.*, *e.g.*, Ref. 11). For experiments on aqueous solutions in the room temperature region the change in gas phase composition will be very small and usually insignificant. However, with dilution experiments some care should be exercised. As an example one might consider an experiment where a 1 M aqueous solution is mixed with two parts of water. The gas phase composition prior to the mixing is not well defined and therefore no accurate calculation can be made. However, the most unfavourable situation would be if the vapor phase before the mixing is nearly in equilibrium with the pure water (distillation will occur from the solvent compartment to the solution). The maximum decrease in vapor pressure at mixing can be estimated from Raoults law to be approximately 0.15 mm Hg. If the vapor space is 3 ml this change in vapor pressure corresponds to a condensation of 2.5×10^{-8} mole of water or a heat effect equal to 3×10^{-4} cal.

Baseline stability. In a few experiments a small but significant baseline shift accompanying the heat effect was observed. This disturbance occurred irregularly and could be positive or negative. It was found with both electrical calibrations and chemical experiments. The magnitude of the shift varied but it was rarely more than 1 % of the peak value. There was usually no sign of baseline drift accompanying the effect but the shift seemed to take place abruptly. When results were calculated the value for the after period baseline was used. It was observed that if a mean value between the two baselines were used a slightly lower precision was obtained. As the occurrence of the shift was random and was found in both calibration and reaction experiments it should not give rise to any systematic error.

There were usually no problems with baseline drift. At times with appreciable room temperature fluctuation ($> 1°C$) a slight baseline drift could be observed. For experiments run under such conditions a mean value between fore and after period baselines were used in the calculations. If a baseline shift occurred under such conditions results were discarded.

Adsorption effects. In a calorimetric experiment involving very dilute solutions the possibility for adsorption effects should be considered. No such

effect has yet unequivocally been observed in experiments with the present calorimeter but it has been reported for acid-base neutralization reactions.[2]

Note added in proof. A flow version of this calorimeter is described in a forthcoming paper. (Monk, P. and Wadsö, I. *Acta Chem. Scand.* **22** (1968)).

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