# Improvement of data logging for an LKB 8700 calorimeter

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(Received 12 July 1991)

**Abstract**

The goal of the present work is to present the automation of data logging (resistance versus time) from an LKB 8700 calorimeter, with a minimum of cost and modification of the original design. The proposed method was tested against the standard thermal reaction of solid tris(hydroxymethyl)aminomethane (THAM) with 0.1 M aqueous HCl and against the enthalpy of immersion of $CaF_2$ in water. The results obtained are in good agreement with previously published data.

INTRODUCTION

Despite considerable progress in the development of highly automated commercial calorimeters, many researchers use apparatus designed and constructed in their own laboratories. One reason is the high price of commercial designs, and another is the technical simplicity of the thermometric measurements.

The method most commonly used to measure the change in temperature in a typical experiment carried out in an adiabatic or isoperibolic calorimeter is by determining the variation with time of the resistance $R_t$ of a thermistor forming part of one of the arms of a Wheatstone bridge. Because the $R_t$ value is obtained by balancing the bridge with a variable resistance, the accuracy in its determination will depend only on the exactness of the variable arm of the bridge and on the sensitivity of the zero-current galvanometer. In practice, this form of operating is so tedious that it has led to several recent publications dealing with the automatic recording of the time variation of the temperature using either commercial [1–3] or home-made [4] designs.

There is an alternative technique of measuring with the Wheatstone bridge, consisting in registering the time variations of the potential difference between the points 1 and 2 (Fig. 1(a)), usually by means of a chart

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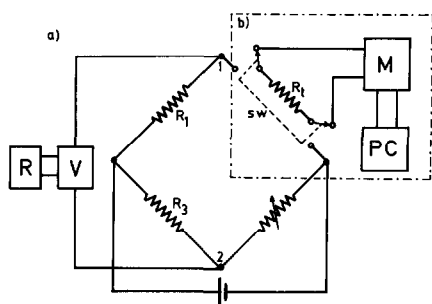
Fig. 1. (a) Wheatstone bridge and indirect measurement of the time variations in the potential difference between points 1 and 2. (b) Wheatstone bridge and direct measurement with a multimeter. R, chart recorder; V, voltmeter; M, multimeter; PC, personal computer; SW, switch.

recorder [5–7]. Nevertheless, we have opted for the direct measurement of $R_t$ (Fig. 1(b)) [8] with a multimeter controlled by a computer program which allows the operator to pre-set the rate of reading. We tested this method of measurement by determining the enthalpy of solution of tris(hydroxymethyl)aminomethane (THAM) in 0.1 M hydrochloric acid, and the enthalpy of immersion of fluorite in water, both at 25.00°C.

## MATERIALS

The N.B.S. reference material "Standard Solution Calorimetry" tris(hydroxymethyl)aminomethane was used directly. The 0.1 M HCl was prepared using Merck (Tritisol) HCl and deionized distilled water. Two different samples of fluorite were employed. A mineral sample (a) was obtained from Cerro Muriano (Córdoba, Spain). The crystals, translucent and with a greenish tint, were selected by hand, crushed in an agate mortar, and the 40–80 $\mu$m fraction was collected. Spectrographic analysis indicated only the presence of ppm levels of yttrium and strontium, so that the purity of the fluorite was better than 99.8%. Sample (b) was reagent grade calcium fluoride Suprapur obtained from Merck, and Soxhlet-washed with deionized distilled water for 24 h before use. The specific surface area of the samples (see Table 2, below) was determined by nitrogen adsorption using the BET method.

The calorimetric measurements were done in the usual way for the LKB 8700 calorimeter [9] except for data logging. When determining the enthalpy of solution of THAM, the calorimetric vessel (25 cm$^3$) was filled with 0.1 M HCl and the ampoule was filled with $\approx$ 1 g of THAM. For the experiments dealing with the heat of immersion of fluorite, the vessel was filled with a saturated solution of calcium fluoride (Merck) to eliminate any contribution from the process of solution, and the ampoule was filled with $\approx$ 1 g of the solid. The thermal capacity of the system was determined

electrically after each experiment. The heat of breaking in water of the LKB ampoules filled with water was undetectable, therefore no correction was made for this.


EXPERIMENTAL DESIGN


The calorimeter was a commercial precision calorimetry system LKB 8700 which is described in detail elsewhere [9]. The multimeter was a Keithley Multimeter (Model 196) with a 10 mOhm resolution on a range of 30 kOhm. Under these conditions the maximum measured current is 160 $\mu$A, with which for a 2 kOhm resistance the dissipated power is only 51.2 $\mu$W, a value far below the recommended upper limit above which the fluctuations in temperature through self-heating may mask the temperature changes in the medium.

The original design of the calorimeter was modified by disconnecting the thermistor from the Wheatstone bridge and connecting it to the Keithley multimeter in a four-terminal mode. A switch was introduced to allow the calorimeter to operate in this mode or in the conventional one without further manipulations.

The multimeter was connected to an IBM-PC computer via an IEEE-488 interface. A BASIC program, compiled for speed, controlled the whole measurement process.

The computer program (available on request) carries out, through the IEEE-488 interface, the sampling of the resistance shown by the multimeter at a rate (readings/second) pre-set by the operator from the initial menu, and timed by the internal clock of the computer. The values of the resistance and time are plotted onto the screen of the monitor, allowing the progress of the experiment to be followed in real time (Figs. 2 and 3).
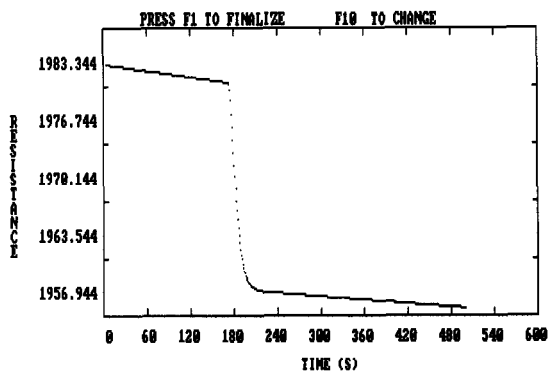


Fig. 2. Screen display from the computer program for an experiment measuring THAM enthalpy of solution in 0.1 M HCl.
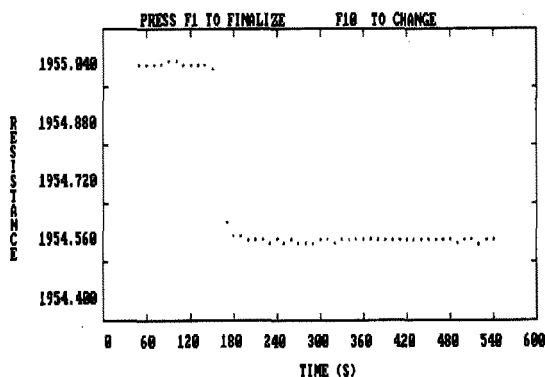
Fig. 3. Screen display from the computer program for an experiment measuring CaF$_2$ heats of immersion.

When the experiment is over, the data are saved for their later treatment in a way that is typical for the isoperibolic calorimeter [9,10].

RESULTS AND DISCUSSION

The average value obtained for the enthalpy of solution of THAM in hydrochloric acid after 10 experiments and its standard deviation is shown in Table 1, together with published values from other workers. As can be seen, our result agrees with the published data. This shows that the proposed modification for the calorimeter leads to satisfactory results with a minimum of change in the original design.

Table 2 lists the values obtained for the heat of immersion in water for the two samples of fluorite used, and those found in the literature for the same system.

The enthalpy of immersion of a solid in water is a quantity whose value is strongly influenced by the state of its surface, which can be altered, for instance, by the treatment of the sample during its preparation; its dependence on thermal treatment is well known [6,16]. But it is even possible to

TABLE 1

Enthalpy of solution of THAM in 0.1 M HCl

| $-H$ (kJ/mol$^{-1}$) | $-H$ (kcal/mol$^{-1}$) | Reference |
|---|---|---|
| $29.844 \pm 0.012$ | 7.140 | 11 |
| 29.720 | $7.110 \pm 0.003$ | 12 |
| 29.74 | $7.115 \pm 0.001$ | 13 |
| $29.69 \pm ?$ | 7.10 | 14 |
| $29.763 \pm 0.003$ | 7.120 | 15 |
| $29.735 \pm 0.003$ | $7.114 \pm 0.004$ | this work |

TABLE 2

Heats of immersion of $CaF_2$ in water at 298.15 K

| Surface area ($m^2 g^{-1}$) | Thermal treatment | | $H_{wet}$ ($J g^{-1}$) | $H_{spec}$ ($mJ m^2$) | Reference |
|---|---|---|---|---|---|
| | T (°C) | P (Pa) | | | |
| 10.2 | 250 | 0.1–1 | 5.16 | $506 \pm 68$ | 16 |
| 2.1 | 250 | 0.1–1 | 0.9 | $433 \pm 37$ | 16 |
| – | 200 | $1.33 \times 10^{-2}$ | – | $463 \pm 10$ | 17 |
| 14.89 | – | – | 1.88 | 126 | 6 |
| 4.65 [a] | – | – | $0.225 \pm 0.005$ | $202 \pm 5$ | This work |
| 0.520 [b] | – | – | $0.345 \pm 0.007$ | $663 \pm 14$ | This work |

[a] Calcium fluoride, Suprapur Merck.
[b] Mineral sample.

obtain different values for mineral samples from different sources subjected to the same treatment, because the state of the surface is also affected by the geological conditions under which the mineral was formed. Considering this, our values can be seen to be satisfactory. Also, it should be noted that our results for the specific heat of immersion have a smaller standard deviation than those obtained by other workers for similar values of this magnitude. This seems to confirm the soundness of our modification to the original design of the calorimeter.

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