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Thermochimica Acta 271 (1996) 189–194

thermochimica
acta

Note

Application of an adiabatic calorimeter with safety concept[1]

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Received 11 May 1995; accepted 12 June 1995

Abstract

A new adiabatic calorimeter ACTRON 5 is described, in which the adiabatic conditions are realized due to change the temperature in the thermostat. For example, it was used to carry out the titration of boric acid with sodium hydroxide and for the kinetic investigation of thiosulfate reaction with hydroperoxide. Relative measurements of heat capacities are also directly possible. At last hazardous reaction can be observed on its way to point of no return.

Keywords: Adiabatic calorimeter; Safety; Thiosulphate; Hydrogen peroxide; Heat capacity

Compared with the isothermic and isoperibolic calorimetry, adiabatic calorimetry has several advantages [1]. Due to the specific conditions of heat transfer, the heat of an exothermic process is totally retained. Therefore the flow part of the TIAN-equation can be neglected for the evaluation. If the heat capacity of the filled reactor is known, the heat of process can be determined directly.

The adiabatic calorimeter we used is a further development of the precision calorimeter ACTRON [2–4].

To guarantee the high stability and constant temperature of the thermostat in non-air-conditioned laboratories also, the calorimeter was equipped with two thermostats (see Fig. 1). The outer thermostat was a controlled air thermostat, which maintained a constant ambient temperature for the inside thermostat (liquid bath). A homogeneous temperature was ensured by special mixing pumps in the liquid bath.

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[1] Presented at the 11th Ulm Conference, Freiberg, Germany, 29–31 March, 1995.

SSDI 0040-6031 (95) 02578-2

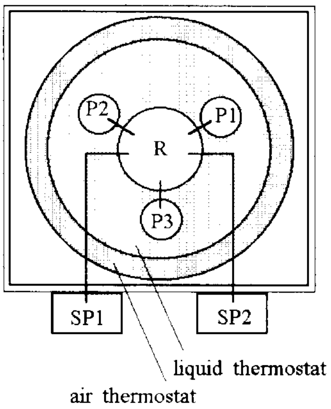

Fig. 1. Schematic design of the ACTRON 5: P1–P3, programmable precision pumps; R, reactor; SP1 and SP2, safety pumps.

The adiabatic conditions of the system were obtained by adapting the temperature of the inner and the outer systems. Changes of temperature in the reactor were quickly realized in the bath by a 1 kW heater. The highest rate amounted to 3 K min^{-1} with a resolution of 10^{-4} K.

There were two cooling circuits, one at each thermostat. It was possible to switch over

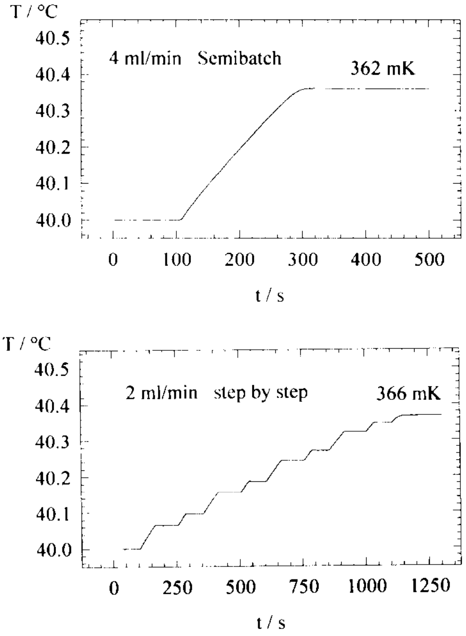

Fig. 2. Comparison of addition modes for the adiabatically guided titration of boric acid by sodium hydroxide.

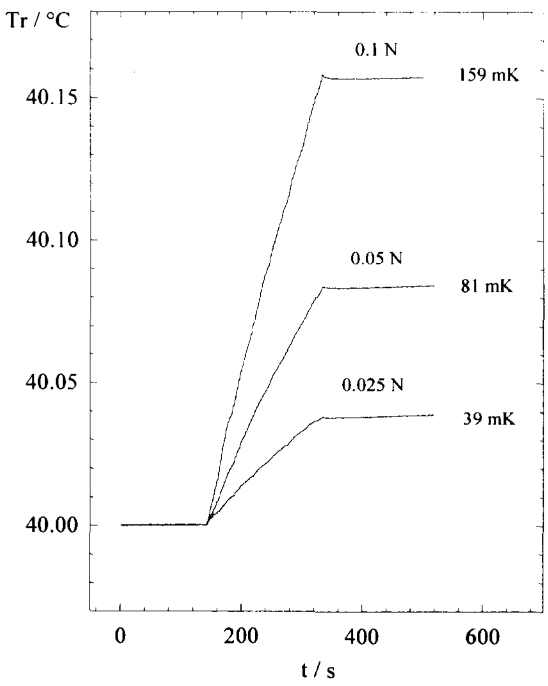

Fig. 3. Dependence of the final temperature on the initial concentration of the reaction of boric acid.

between them by means of a solenoid valve. The circuit of the air thermostat enabled the setting of an ambient temperature below room temperature, so that a working temperature down to 1°C was possible. To cool down the liquid bath quickly, the inside thermostat was also equipped with a cooling circuit, which permitted the adiabatic pursuit of exothermic and endothermic reactions.

Using a PTFE-reactor, a relative high thermal isolation was assured which prevented heat flow out of the reactor in the liquid bath due to the finite heating rate. The reactor volume amounted to 40–60 ml. It was equipped with a stirrer, sensor and calibration heater, as well as tubes to change the atmosphere in the reactor.

Contrary to a former model, the ACTRON 5 calorimeter has only one reactor, but three precision burette pumps. All pumps were built up in the thermostat and connected

Table 1

Results of calibration by varying the heating time

P/mW	120	120	120	120
t (heating)/s	200	400	800	1600
dT/dt/mK s^{-1}	0.486	0.485	0.484	0.485
C_p/J K^{-1}	246.71	247.17	247.68	247.22

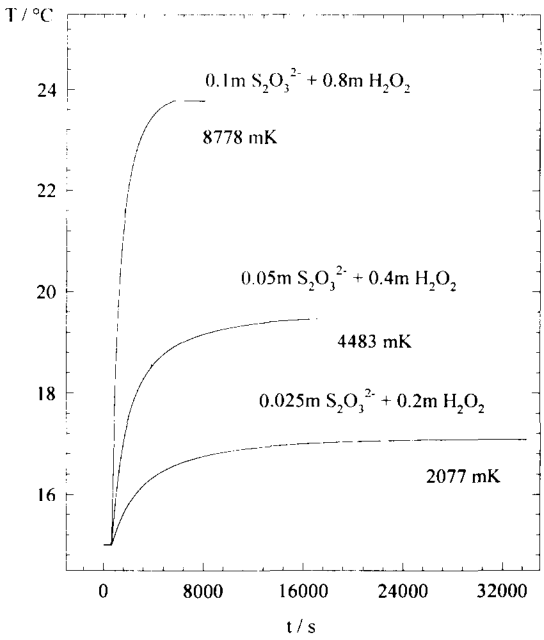

Fig. 4. Dependence of the reaction rate and the final temperature difference on the initial concentration of thiosulfate and hydrogen peroxide.

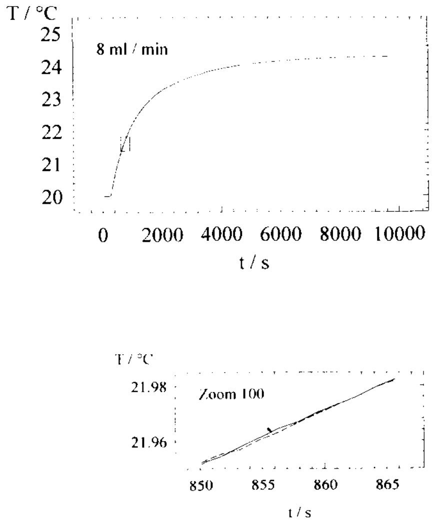

Fig. 5. Deviation of temperature between reactor and liquid thermostat by zooming on the thiosulphate reaction curve.

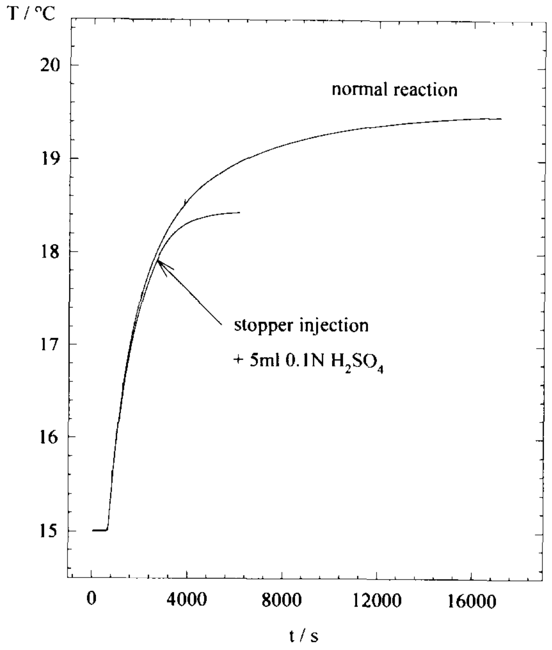

Fig. 6. Effect of sulphuric acid as a stopper during thiosulphate/hydroperoxide reaction.

to the reactor. Therefore many kinds of addition modes for the reaction components were possible.

Fig. 2 shows a comparison of two adiabatically recorded reactions of boric acid with sodium hydroxide. The kind of addition was varied. In the upper part the titration mode has been chosen whilst Fig. 2b demonstrates the step by step addition mode. This proves explicitly that the various addition modes attain finally equal temperature differences. The dependence of temperature differences on initial concentration is shown in Fig. 3.

This calorimeter permits the direct determination of the reaction heat without correction of temperature data. In the same way C_p values of the filled reactor can be measured. To demonstrate this possibility, we carried out some calibrations of the reactor filled with 50 g of water, varying the power and heating time. The values determined for the slopes dT/dt and C_p values are given in Table 1. The comparison of these values with data from the literature shows a difference of 38.2 J K^{-1}. The difference corresponds to the C_p value of the reactor cell. Thus the estimation of C_p values of unknown substances is possible.

The oxidation of thiosulfate with hydrogen peroxide is described in the literature as a possible means of preparing trithionate [5]. This conversion will be carried out below room temperature and follows a rate law of second order. Fig. 4 indicates the calorimetric curves varying the initial concentration at a start temperature of 15°C. The concentrations are halved stepwise. It can be pointed out that the reaction rate increases with increasing concentration.

In addition to the reactor temperature, we recorded the temperature of the adiabatic liquid bath. In this presentation a difference between both temperature courses cannot be noted. Therefore we have zoomed a small area in the rising part of the curves by factor of 100 (see Fig. 5). Only in the last case are both curves discernible. The deviation between them is less than 1 mK.

The ACTRON 5 is provided to follow reactions accompanied by security risks and hazards. The pumps connected to the reactor can automatically be started to inject an inhibitor or stopper. So in dangerous situations the reaction can be interrupted. An example is given in Fig. 6. To stop the reaction, 5 ml of 0.1 N sulphuric acid were added while the titration with hydrogen peroxide was running. This figure shows the reaction with and without stopper. The sulphuric acid decomposed the thiosulfate producing sulphur and sulphur dioxide.

The calorimeter is optionally equipped with two special safety pumps. In the case of a high danger level, they are switched on. The first exhausts the reactor in three seconds and the other can be used to purge the reactor with cool solvent. This provides a way to avoid damage to precious equipment when working near the range of “point of no return”.

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