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Various applications of the new solution calorimeter ACTRON 4.2 [1]

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Abstract

Application of the ACTRON 4.2 calorimeter shows that several types of measurement can be made satisfactorily. After a short review of the automatic device for the range 15–180°C with a resolution of 0.05 mK, five types of experiments are described to demonstrate its versatility. The measurement of mixing enthalpy by step-wise injection of propanol pinpoints the position of a maximum at 5.67 mol% *n*-propanol in water. Titrations of solutions of ammonia and boric acid, respectively, yield results of good accuracy in the mmol/l range.

INTRODUCTION

The investigations were made using the ACTRON 4.2 twin calorimeter which is suitable for studying various kinds of reactions in organic and inorganic chemistry. The device has all the components necessary for measuring under homogeneous conditions, selecting the desired concentrations and temperature. All the functions are controlled by a personal computer which makes this well-designed device very convenient to use.

The instrument (Fig. 1) consists of an outer air thermostat AT, an inner liquid thermostat LT and a block with two symmetrical cells: a measuring cell MC and a reference cell RC. With regard to the volume of these cells, a choice between 400, 100 and 200 ml is possible. Each cell contains a temperature sensor S, a calibration heater H, a mixing turbine MT, and various tubes for the final reaction component and for gas inlet/outlet or purging.

The essential constituents of the device are the two precision burette pumps with volumes of 3–10 or 3–30 ml. The computer program permits

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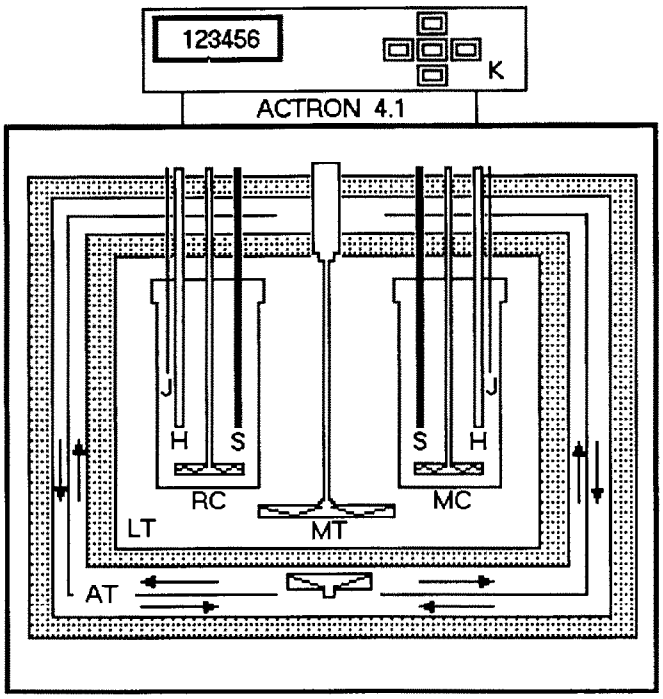

Fig. 1. Cross-section of the automatic twin calorimeter; for an explanation, see the text.

three types of operation: batch (5 ml s^{-1}), semi-batch (0.05–0.5 ml s^{-1}) and titration (0.002–0.05 ml s^{-1}). The starting and finishing mark of the pump are fixed using the computer.

While the air thermostat is controlled to within 0.1 K, the liquid thermostat is constant to within 0.15 mK. The temperatures can be set to exactly one mK in the range from 15 to 180°C. The measurement of temperature takes place independently in both cells, MC and RC, using platin resistance thermometers with a resolution of 0.05 mK. The difference between them is immediately displayed by the PC.

The flow of the thermostat liquid, water or oil, is effectively directed by the advantageous construction of the bath so that in spite of a very homogeneous temperature, the input power of the mixing turbine is relatively low. All the mechanical parts are protected against corrosion.

This calorimeter has proved suitable in the following applications: chemical reactions in a liquid phase in the batch or semi-batch operation; titrations with very different titrants, including reactions with low enthalpies; mixing and solving reactions; biochemical reactions and biotechnological modelling; and determination of the heat capacities of liquid media.

For all operations, suitable software has been developed so that data acquisition and the evaluation of parameters are easy to perform.

APPLICATIONS

The following results were obtained using 100-ml stainless steel cells, with a wall thickness of 1 mm. We first investigated the heat of mixing in the system water–propanol at 40°C in the region of 0–8 mol% of propanol. In this region, there is an exothermic maximum of the integral mixing enthalpy [1]. It is well known that the measurement of mixing heat is particularly difficult near 0 and 100 mol.%. Our aim was to determine the exact position of the maximum enthalpy. Figures 2 and 3 show typical results. On one side we injected propanol in 1 ml steps into 60 ml of water, and on the other, after adding 12 ml of propanol to the water, we injected decreasing volumes down to 0.2 ml. Especially from Fig. 3, we can derive the position of the maximum as the point at which the tangent is horizontal, i.e. 15.05 ml, which indicates a mixture of 5.67 mol% of propanol, which is most satisfactory.

Figure 4 shows the titration of a solution of ammonia of 0.00227 mol l^{-1} with 0.2 N sulphuric acid, using a pumping rate of 9 ml min^{-1} at 35°C. The evaluation of this curve shows that its peak after 47 s exactly represents the equivalence point. The shape of the titration curve may be very different with different pumping rates and cell parameters.

To test this equipment in the case of a very difficult titration, we applied

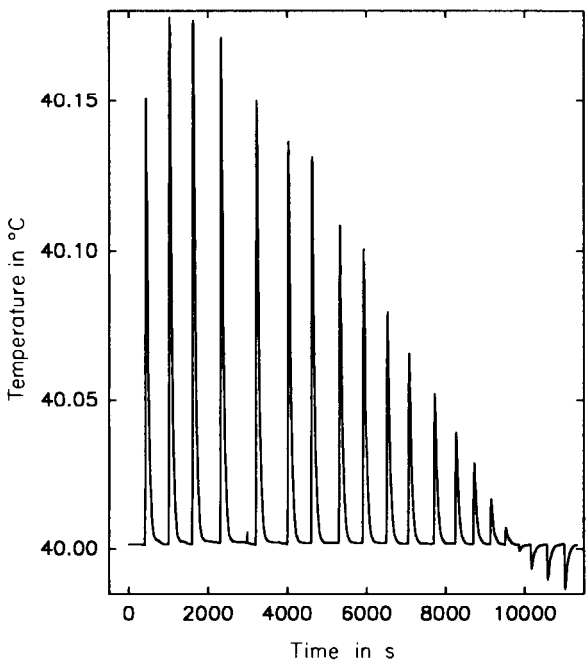

Fig. 2. Heat of mixing in the system of 60 ml water + *n*-propanol added in steps of 1 ml, starting with pure water.

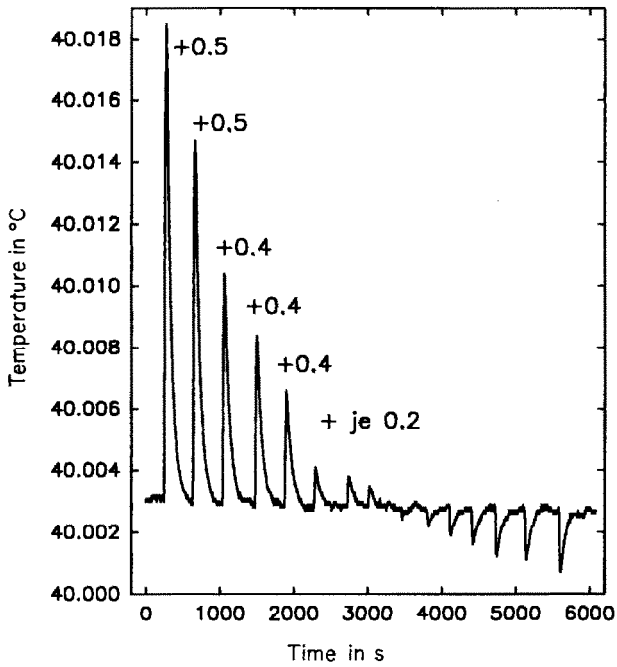

Fig. 3. Heat of mixing in the system of 60 ml water + 12 ml *n*-propanol with additions of *n*-propanol in decreasing steps from 0.5 ml to 0.2 ml. Inversion point at 15.05 ml *n*-propanol ≡ 5.67 mol%.

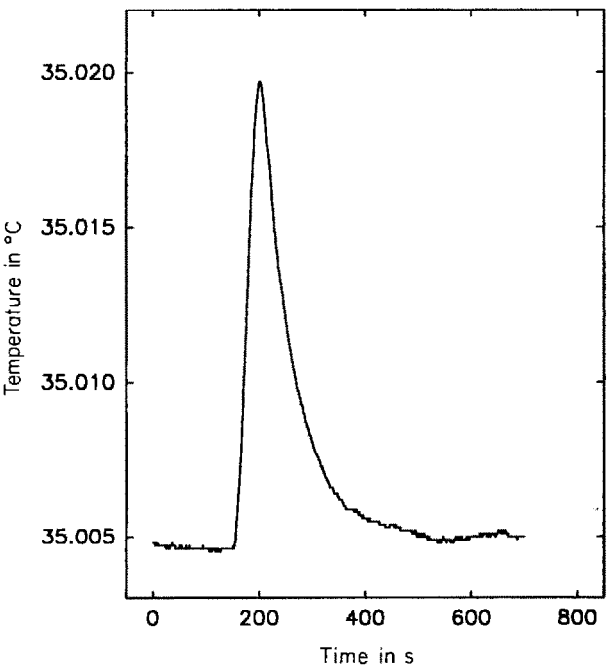

Fig. 4. Calorimetric titration of 60 ml of 0.00227 N NH_3 solution with 20 ml of 0.02 N H_2SO_4; rate of titration, 9 ml min^{-1}.

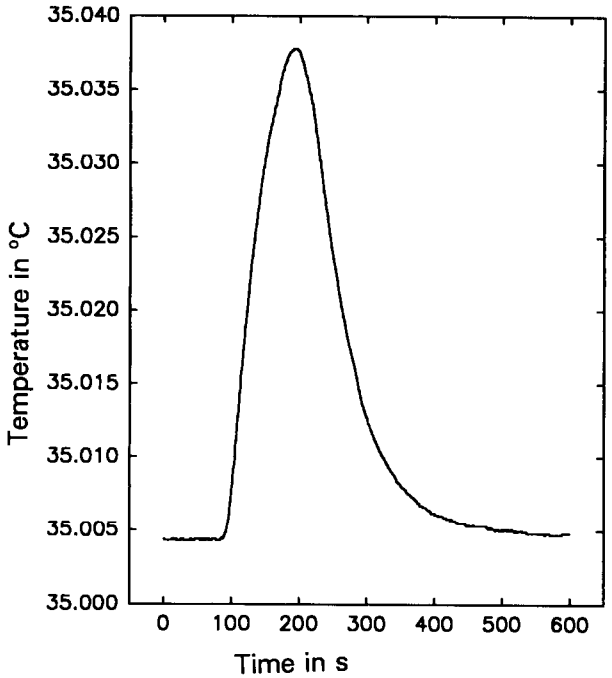

Fig. 5. Calorimetric titration of 60 ml of 0.01 N boric acid with 20 ml of 0.04 N sodium hydroxide; rate of titration, 9 ml min^{-1}.

it to the analytical determination of boric acid and phosphoric acid. Figure 5 demonstrates the reaction between 0.01 M boric acid and 0.04 M sodium hydroxide. The position of the peak after 101 s is, according to the theoretical value of 100 s, surprisingly good. Because of the sensitivity of this instrument, it is possible to apply this method to solutions of boric acid of 0.001 mol l^{-1} with a resultant accuracy of 4%. Using Teflon titrations cells, the concentration may be decreased to 0.0005 mol per l H_3BO_3.

These examples speak for the quality of this device and its versatility with regard to substrates and types of operation. Further applications will be described in a forthcoming paper.

REFERENCE

1 F. Frignet, M. Ratouis and M. Dode, Bull. Soc. Chim. Fr., 7 (1967) 2458.