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Automation of a Titration Calorimeter System

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The automation of a titration calorimeter system by means of a personal computer is described. Minor modifications compared with the previous described calorimeter are reported. The enthalpy of ionization of water which has been determined by the system was found to be -55.90 ± 0.05 kJ mol^{-1}.

The titration calorimeter of the isothermal jacket type described by Grenthe *et al.*[1] and by Ots[2] has been computerized by means of an ABC80 personal computer.[3] Minor modifications on the calorimeter made during recent years are reported. The main principles of the previous calorimeter construction have been retained, but the measuring and cooling units and procedures have been changed. The accuracy of the automated system has been tested by measuring the enthalpy of ionization of water.

The automation of the titration system has been made in order to increase the efficiency of the calorimeter measurements and to decrease the time necessary to spend at the instrument.

Description of the system. The system consists of a calorimeter and an ABC80 personal computer which controls cooling, titration, calibration and measuring units. The system is schematically shown in Fig. 1.

The calorimeter. Three modifications are made and can be summarized as follows:

(a) The previous gold tube for inert gas inlet or solution outlet has been exchanged for a gold tube loop for cooling by liquid. The previous method for cooling the solution in the reaction vessel by blowing cool air through the stirrer is no longer used. The calorimeter with the modified details is shown in Fig. 2. The thermistor and the heater which are placed in front of and behind the stirrer are not shown.

(b) The rubber sealing ring on the top of the reaction vessel is sometimes exchanged for a teflon ring. Rubber expands very much when organic solvents as amines and sulfides come into contact with it. This means that it can be extremely difficult to disconnect the reaction vessel from the calorimeter after an experiment.

(c) The reaction vessel was previously attached into the calorimeter. This system is changed to a hanging system; there the reaction vessel hangs on two pins, which can be moved up and down. With this system the reaction vessel can be fairly easily disconnected even if the sealing ring has expanded.

The measuring unit. The Wheatstone bridge has been changed to a digital voltmeter, Fluke 8502 A, and a mercury cell supplying a constant current of about 30 μA through the thermistors. This current will not heat on the thermistors, but if it is increased to 40 μA or

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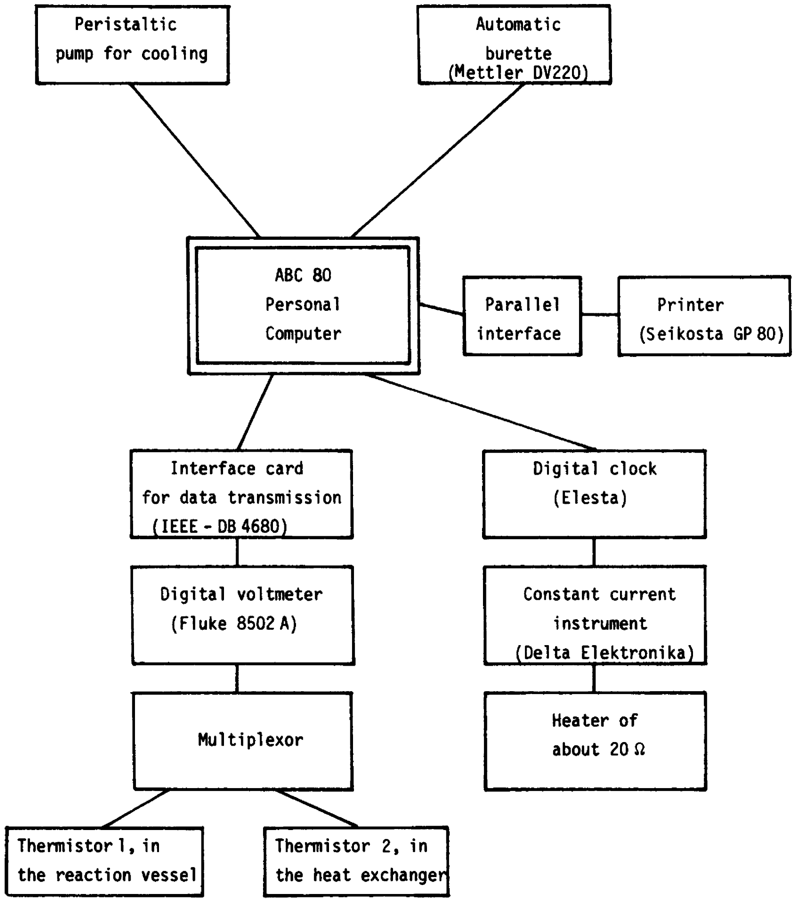

Fig. 1. A block scheme of the computerized titration calorimeter system.

more, then it will heat the thermistor. The potential across a thermistor, with a resistance of about 2000 Ω, is determined by the voltmeter and the data is sent to the computer via a DB4680 IEEE Interface, where it is stored. As before, there are two thermistors, one in the reaction vessel and one in connection with the gold spiral where the titration solution is thermostated before addition. The choice of thermistor is made with a multiplexor, which is controlled by the computer.

The titration unit. The titration solution is added portionwise by an automatic burette, Mettler DV220, which is controlled by the computer. The titration solution is added at a rate of 1.00 ml per minute, regardless of the volume added.

The cooling unit. This system is built around a peristaltic pump, which is pumping ice cooled water, stored in a Joha vessel, through a 1.0 mm gold tube loop inside the reaction vessel. The starting and stopping of the pump is controlled by the computer.

The calibration unit. The calibration unit consists of a heater, a constant current instrument, Delta Elektronika, and a digital clock, Elesta CPT, equipped with a quartz oscillator. The heater is a wire, with a resistance of about 20 Ω, placed on the walls in a gold

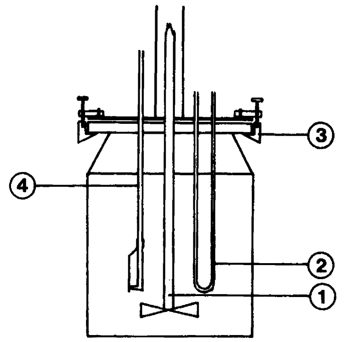

Fig. 2. The reaction vessel of the calorimeter seen from one side. The heater and thermistor 1 are excluded for clarity. The parts marked with figures are: 1. Stirrer. 2. Gold tube loop for cooling. 3. New arrangement for holding the reaction vessel consisting of a ring with two pins, which can be moved up and down. 4. Spring-loaded valve.

tube in the reaction vessel. A constant current in the range 30–80 mA passes through the heater for 50 or 60 seconds. The time is controlled by the clock. The computer starts the clock. If it is necessary to heat the solution in the reaction vessel, the calibration unit is used.

The calorimeter is thermostated to 25.000±0.002 °C by an LKB ultrathermostat.

DESCRIPTION OF THE OPERATING PROCEDURE

Measuring of an experimental point. The titrand solution must be added when the temperature of the solution in the reaction vessel has reached the very same temperature as the titrand solution has. The difference in potential at a certain temperature across the thermistor in the reaction vessel, thermistor 1, and across the thermistor in the heat exchanger, thermistor 2, must therefore be determined in advance. An experimental point starts by determing the potential across thermistor 2. From this value, a potential across thermistor 1 is calculated, when the temperature in the reaction vessel becomes the same as in the heat exchanger. The addition takes place when the calculated potential across thermistor 1 is reached. The titrand is added at a rate of 1.00 ml/min. The potential across thermistor 1 is registered and stored in the computer memory every 15 s from last cooling or heating until the addition takes place, the preperiod, and 5 min after completed addition, the afterperiod. By linear regression from both the preperiod and the afterperiod the potentials at the mid point of the addition are calculated. The heat evolved in the experiments is the difference between the calculated potentials, expressed in volts. The difference in resistance is then calculated by Ohms law and correlated to energy in J via the calibrations. A schematic picture of temperature (potential)-time relationship during a measuring loop is shown in Fig. 3.

Measuring of a calibration point. The calibration is made in the same way as described above, but instead of adding a solution a well-known amount of electric energy is added through the heater. A current of 30–80 mA passes the calibrated heater resistance of about 20 Ω for 50 seconds and the resistance change in thermistor 1 is registered as described above. How the resistance depends upon the volume has been discussed previously.[1]

Calibration. The calibration constant ε_V has been determined in the same way as reported by Ots.[2] It was found that the calibration constant can be fitted very well to a straight line $\varepsilon_V = a + bV$, in the volume range 80–100 ml where V is the total volume in ml in the reaction vessel. A least squares refinement of the calibration experiments gives $a = 0.2770 \pm 0.0072$ J^{-1} and $b = (5.188 \pm 0.078) \cdot 10^{-2}$ J^{-1}ml^{-1}.

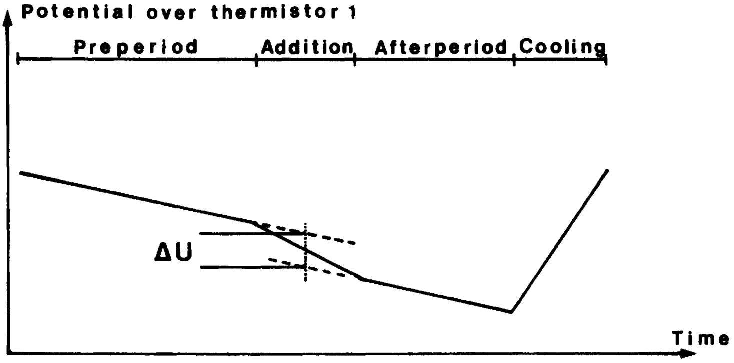

Fig. 3. The diagram shows how the temperature in the reaction vessel/the potential across thermistor 1 varies during an experimental or a calibration cycle.

DETERMINATION OF THE ACCURACY OF THE SYSTEM

The enthalpy of ionization of water has been chosen as a test system to check the accuracy of the calorimeter system. 79.60 ml 100.02 mM sodium hydroxide solution was pipetted into the reaction vessel. 20.00 ml 100.01 mM hydrochloric acid was added portionwise to the hydroxide solution giving a total of 17 experimental points. Five titration series were carried out. In addition, similar series for determination of heats of dilution were performed twice.

The computer program KALORI[4] were used for the calculation of the enthalpy. The enthalpy of ionization of water was found to be -55.90 ± 0.05 kJ mol^{-1}, which agrees very well with what other authors have reported.[5]

A more detailed description of the system and the computer programs for calibrations and measurements is available from the author.

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