

VALTER-II: A PROGRAM FOR AUTOMATIC SOLUTION CALORIMETRY INCLUDING HEAT-LEAK CORRECTIONS

G. RAMIS

Department of Analytical Chemistry, University of Valencia, E-46100 Burjassot, Valencia (Spain)

M.T. OMS and V. CERDÁ

Department of Chemistry, University of The Balearic Islands, E-07071 Palma de Mallorca (Spain)

(Received 26 July 1988)

ABSTRACT

VALTER-II, an expanded version of a previously published program for control, data acquisition and treatment in automatic solution calorimetry is presented. The possibility of correcting heat exchanges with the surroundings as well as some new operation modes such as automatic electrical calibration, thermokinetic measurements and titrations for enthalpy determinations have been introduced. The performance of the program is discussed and checked by using a metallic cell in an air-bath isoperibol calorimeter.

INTRODUCTION

Analytical solution calorimetry can benefit remarkably from automation. Automatic control of the calorimeter allows the practical use of long stabilization periods and, in addition, the number of data which can be handled increases dramatically when direct input to a computer is available. This is important in improving the accuracy and precision of many calorimetric determinations and provides a convenient way of correcting heat losses. The calculation of heat-transfer constants in isoperibol calorimeters requires the measurement of small temperature differences along the cooling curve in the after-period, which cannot be done manually.

The reconstruction of the ideal adiabatic thermometric curve by calculating the heat losses has been attempted in a number of different ways [1–6]. Heat losses are important in microcalorimeters, where the ratio between the surface in contact with the surroundings and the heat capacity of the system (cell and contents) is large [3]. However, microcalorimeters permit the extension of these techniques to rare or expensive materials and small samples [7,8]. Corrections are particularly important in enthalpy determina-

tions [9] and in the thermometric monitoring of a slow reaction for kinetic determinations.

In a previous paper [10], a simple modular automatic system for thermometric titrations, supported by the program VALTER was described. In this paper, VALTER-II*, an expanded version of the program, is presented. The possibility of correcting heat exchanges with the surroundings as well as some new operation modes such as automatic electrical calibration, thermokinetic measurements and titrations for enthalpy determinations have been introduced. The performance of the program is checked and discussed by using a metallic and a polypropylene cell in an air-bath isoperibol calorimeter.

EXPERIMENTAL

The modular automatic calorimeter, controlled by an IBM PC computer interfaced with the thermistor probe and an autoburette, has been described elsewhere [11–13], therefore only the modifications introduced in the cell design and the program will be discussed here.

The mathematical model adopted for heat-leak corrections includes a single massive long-term heat sink, which limits the application of the program to cells which would reasonably fit this simple model. Dewar vessels surrounded by water baths present at least two significant heat sinks: a short-term sink mainly associated with the massive glass walls and a long-term sink which is the isothermic bath [1]. Single-sink systems cannot be built using Dewar vessels because a minimum wall thickness of about 0.6 mm is required to support the pressure coming from the internal vacuum. Thin-wall plastic or metallic cells surrounded by air baths can approach this model much better.

In addition, most cells give rise to a small spike or overshoot immediately after a period of rapid heat generation. This effect is due to the presence of very short-term heat sinks associated with the materials directly in contact with the solution, being smaller with plastic and metallic cells than with Dewar vessels.

A cell made of aluminum was used in this work. The cylindrical 10-ml capacity cell had a wall thickness of 0.25 mm and was covered internally with a PVC thin film to increase chemical resistance. The cell cover holds a glass-coated thermistor probe, a mechanical stirrer made of thin plastic sheet and a bar, and a standard resistor for calibration. The cell is suspended in a

* The program VALTER-II for IBM PC or compatible computers can be obtained from the SCIWARE, Department of Chemistry, University of The Balearic Islands, E-07071, Palma de Mallorca, Spain.

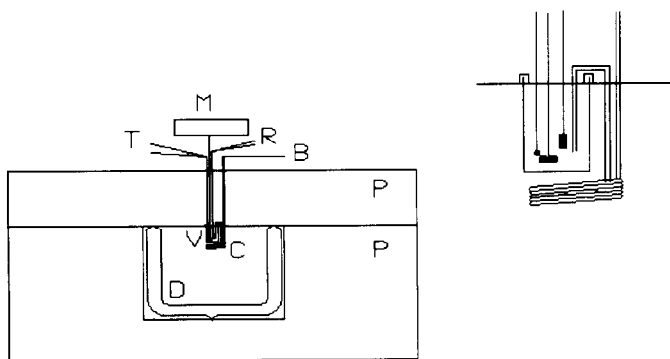


Fig. 1. Calorimetric system and cell details: T, thermistor; M, synchronous motor; R, resistor; B, connection for burette or syringe; P, porexpan block; V, reaction vessel; C, reagent coil; D, Dewar.

large Dewar flask. Inside the Dewar, a hanging tygon coil contains the titrant. The Dewar is surrounded by a porexpan block (Fig. 1), and the whole system operates in a $25.0 \pm 0.1^\circ\text{C}$ thermostatted room.

DESCRIPTION OF THE MODEL

A typical thermogram is shown in Fig. 2, where the AB section is the baseline, BC represents the main period and CS is the after-period. Since temperature differences are always referred to the baseline extrapolation, the obtention of accurate data requires the establishment of a good, reliable baseline. In the program VALTER-II, the establishment of a satisfactory baseline with a small constant slope is required before starting the reaction or electrical calibration step at B. It can be assumed that a reasonably horizontal stable baseline is reached when the heat generated by the thermistor (Joule heating) and the stirrer (frictional heating), and the heat exchanged to the air bath are in dynamic equilibrium. Thus, as it is depicted in

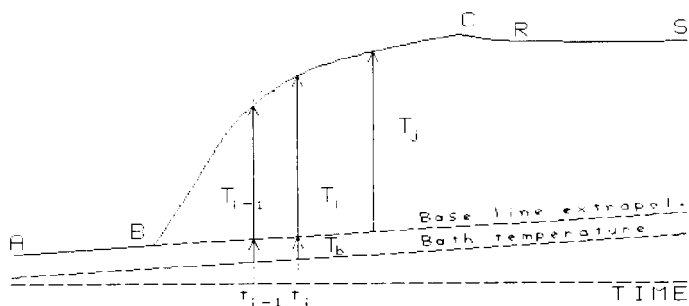


Fig. 2. Thermometric curve for symbols and heat-exchanged integration.

Fig. 2, at the beginning of the reaction or electrical heating period, an initial temperature mismatch, ΔT_b , exists between the bath and the cell.

At any time along a titration, t_j , when a volume of the titrant, v_j has been added, the heat balance is

$$\Delta T_j (C_p + v_j) = Q_{g,j} + Q_{d,j} - Q_{p,j} \quad (1)$$

where ΔT_j is the difference between the cell temperature and the baseline extrapolation and C_p is the heat capacity of the system when loaded with the initial volume of sample. On the other hand, $Q_{g,j}$ is the heat generated by the reaction, $Q_{p,j}$ the heat exchanged with the surroundings from the beginning of the titration, and $Q_{d,j}$ a function of v_j which takes into account the heat of dilution of the titrant and the effect of the temperature mismatch between the titrant and the sample. The product of the density of the titrant and its specific heat is assumed to be the unity.

Equation (1) also applies to other types of experiments with a few modifications. Thus, for electrical calibration, the value of v_j has been approximated as half the total titrant volume used in the titrations, v_T . For kinetic measurements, v_j is eliminated, and the total volume of reagent injected to start the reaction is added to the initial volume of sample to determine C_p .

The amount of heat exchanged to the surroundings can be established by applying Newton's cooling law to the after-period. In the program VALTER-II, the measurements on this section begin at an arbitrary point, R, which is located 3 s after point C. In this way, the possible overshoot is avoided and those elements which constitute the associated very short-term heat sinks are included in the system. Newton's law applied to any point of the RS curve, $(t_i, \Delta T_i)$ will be

$$dQ_{p,i} = \frac{C_p + v_T}{\tau} (\Delta T_i + \Delta T_b) dt \quad (2)$$

and finally

$$\frac{d\Delta T_{p,i}}{dt} = \frac{\Delta T_i + \Delta T_b}{\tau} \quad (3)$$

where τ is the time constant of the system (ratio of heat capacity to overall heat transfer coefficient). Equation (3) can be integrated between any two points, i and $i+k$, along the cooling curve, in the form:

$$\frac{\Delta T_i + \Delta T_b}{\Delta T_{i+k} + \Delta T_b} = \exp\left(\frac{t_{i+k} - t_i}{\tau}\right) \quad (4)$$

This expression was used in an attempt to determine the two unknowns τ and ΔT_b by using a simplex procedure. Two initial values for ΔT_b were assumed and the simplex moved until the best standard deviation of τ for all pairs of points was found. However, because erratic and absurd values

were obtained, it was decided to neglect ΔT_b and use eqn. (4) to determine only the parameter τ .

As illustrated in Fig. 2, if a linear change in ΔT_j within any small time interval, $t_i - t_{i-1}$, is assumed, the value of $Q_{p,j}$ can be obtained by integrating eqn. (2) in the form

$$Q_{p,j} = \frac{C_p + v_j}{2\tau} \sum_{i=1}^j (t_i - t_{i-1})(\Delta T_i + \Delta T_{i-1}) \quad (5)$$

where the term $2\Delta T_b$ has been neglected and removed from the last set of parentheses. A corrected thermometric curve can be obtained from eqns. (1) and (5)

$$\Delta T_{c,j} = \Delta T_j + \frac{1}{2} \sum_{i=1}^j (t_i - t_{i-1})(\Delta T_i + \Delta T_{i-1}) \quad (6)$$

In analytical thermometric titrimetry, the determination of C_p and $Q_{d,j}$ is not necessary, and eqn. (6) can be applied directly just to obtain a better linearity before and after the equivalence point and, hence, to improve accuracy. On the other hand, when the data are used for enthalpy determinations, the values of C_p and $Q_{d,j}$ must be previously established.

The determination of C_p can be carried out by generating a known amount of heat by means of a standard resistor, R_s . When the cell contains a volume of sample, $v_s + v_T/2$, the heat balance [eqn. (1)] will be

$$\Delta T_j(C_p + v_T/2) = i^2 R_s t_j - Q_{p,j} \quad (7)$$

and by substituting eqn. (5) in eqn. (7)

$$C_p = \frac{i^2 R_s t_j}{\Delta T_{c,j}} \frac{v_T}{2} \quad (8)$$

For the determination of $Q_{d,j}$ we have adopted the simple linear model

$$Q_{d,j} = Dv_j \quad (9)$$

where D is a constant which is calculated from a blank titration as

$$D = \frac{2}{N} \sum_{j=N/2}^N \frac{(C_p + v_j)\Delta T_{c,j}}{v_j} \quad (10)$$

If relatively high concentrations of substrate are used for the determination of reaction enthalpies, the ΔT_j values would be much larger than the corresponding values obtained for the blank titration, thus making the simple model represented by eqn. (10) adequate.

Finally, combining eqns. (1), (5), (6) and (10) gives

$$Q_{g,j} = (C_p + v_j)\Delta T_{c,j} - Dv_j \quad (11)$$

Reaction enthalpies can be calculated by using eqn. (11) after substitution of $Q_{g,j}$ by the appropriate expression which will depend upon the reaction being studied.

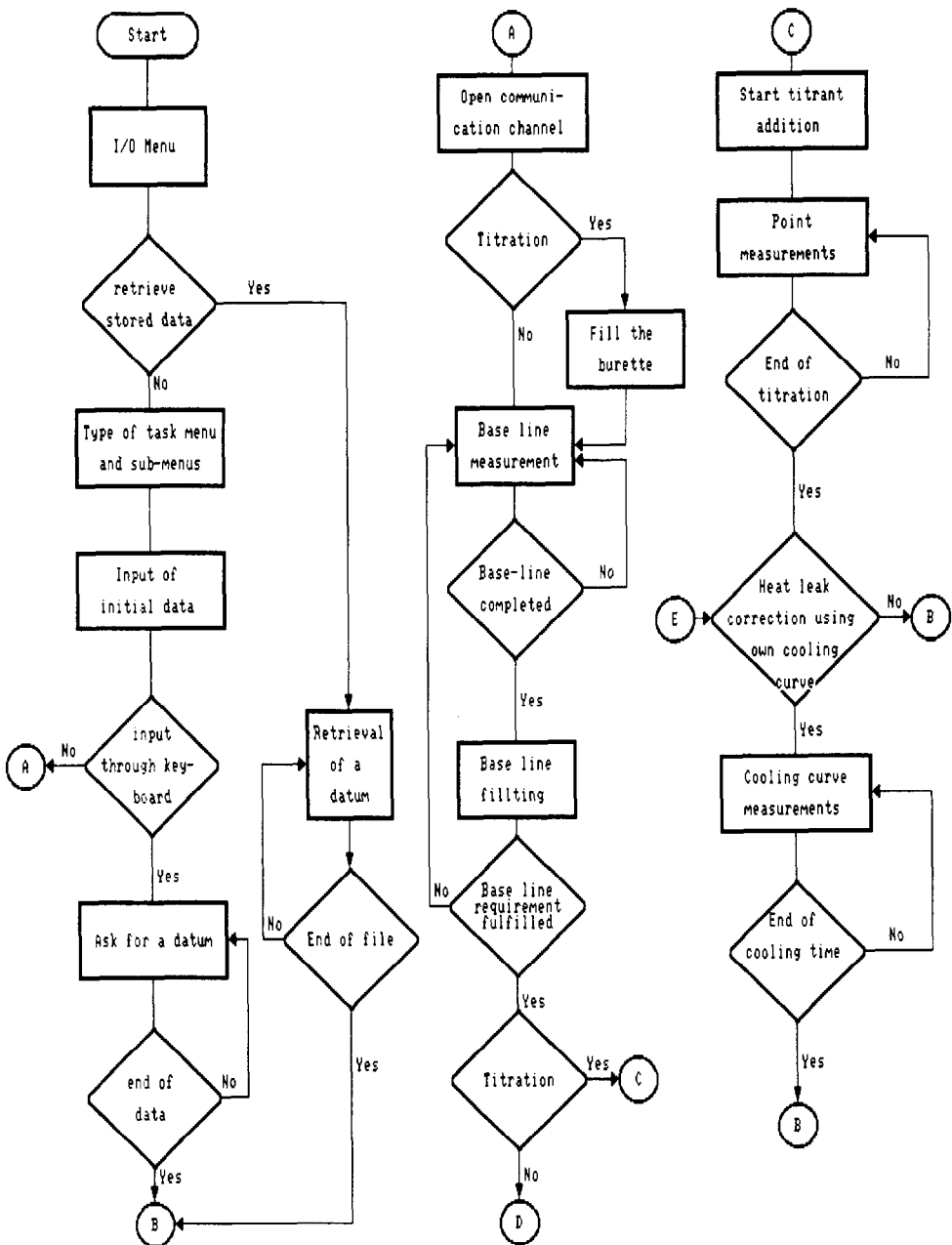


Fig. 3. Flow chart of VALTER-II.

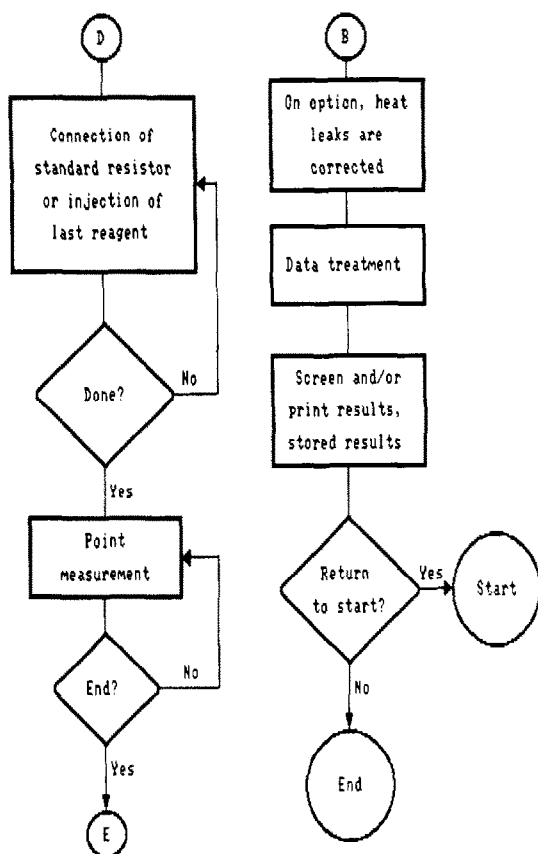


Fig. 3 (continued).

DESCRIPTION OF THE PROGRAM

The program VALTER-II was written in BASIC and compiled for rapid execution of experimental tasks. A flow chart is shown in Fig. 3. The program is driven by two menus which contain the following options. (i) Three data input modes: experimental, manual and from diskette; the three output modes are screening, printing and diskette storage. (ii) Five types of tasks: analytical titration, electrical calibration, kinetic monitoring of slow reactions, titration for enthalpy determination and blank titration for the determination of the parameter D ; sub-menus contain other options mainly related to baseline requirements and heat-leak corrections.

The baseline is constructed by a moving box-car technique. The length of the box (number of points and time) as well as the maximum slope allowed are selected by the user. Once the box is completed, linear-regression analysis is applied and the box moves by taking a new point and dropping off the first. Titrations begin automatically when the specified requirements have been reached.

Similarly, for electrical calibration and kinetic monitoring, the computer shows a message and beeps periodically to indicate that the calibration resistance can be connected, or the last reagent injected, at any time. This operation must be carried out manually. Simultaneously, any key must be pressed, to indicate to the computer that the reaction or electrical calibration period begins. On pressing any key again, the computer understands that this period is finished. If an electrical calibration is being executed, the resistance must be simultaneously shut off. When the experiment is finished (point S in Fig. 2), the baseline is extrapolated to compute the ΔT_j differences.

In addition, heat-leak corrections can be made for all types of tasks. On option, the value of τ can be determined by using the cooling curve of the running experiment. In this case, the user establishes a maximum time for the cooling curve. The program takes points every second, and τ is calculated as the average of the values given by all the pairs of points separated by 10 s after elimination of outliers. On the other hand, previously established values of τ can be used, which save time in routine or preliminary experiments. Moreover, only this procedure is adequate when a slow reaction is monitored. In this case, the cooling curve can only be obtained if an adequate means for stopping the reaction, such as the total consumption of a limiting reagent or the injection of an inhibitor, is provided.

Additional output options include the uncorrected and corrected thermograms, or both superimposed, with or without the cooling curve. All curves can be obtained in graphical or numerical (table) form.

The type of task "analytical titration" also includes automatic calculation of the equivalence point. A given number of points at the beginning and end of the titration are selected, fitted by least-squares analysis and the intersection of both straight lines calculated. The titration starting point (null volume) is also calculated as the intersection of the baseline and the first of the straight lines fitted. However, the equivalence point obtained by this procedure must be considered approximative due to the difficulty in establishing the best sets of points for the fittings.

RESULTS AND DISCUSSION

The experimental results for an electrical calibration are shown in Table 1. First, experimental conditions, as have been settled by the user, are printed. Next, 20 points separated by 2-s intervals constitute the baseline. In this example, the main period began when the baseline reached a slope smaller than 2 mV min^{-1} ($0.002^\circ \text{C min}^{-1}$). However, baseline points were still taken, until the standard resistor was connected.

TABLE 1

Experimental results of an electrical calibration

| Type of job: electric calibration | | | | | |
|---|----------|------------|---------------|---------------------|----------|
| Experiment number: 4 | | | | | |
| Remarks: electrical calibration no. 4 | | | | | |
| Sample, water. Sample volume, 10 ml | | | | | |
| Electrical sensitivity, 1000 mV °C ⁻¹ | | | | | |
| Electrical heating rate, 0.06 cal min ⁻¹ | | | | | |
| Baseline points: time (s) and temperature (mV) | | | | | |
| 28.34 | 81 | | 48.71 | | 89.2 |
| 30.37 | 79.3 | | 50.75 | | 87.7 |
| 32.4 | 91.9 | | 52.78 | | 84.6 |
| 34.49 | 90.4 | | 54.87 | | 83.1 |
| 36.52 | 90.1 | | 56.9 | | 84.1 |
| 38.55 | 85.5 | | 58.93 | | 85 |
| 40.58 | 85.3 | | 60.96 | | 87.1 |
| 42.62 | 80.7 | | 62.99 | | 87.7 |
| 44.65 | 81.9 | | 65.03 | | 84.7 |
| 46.68 | 83.9 | | 74.53 | | 80.1 |
| N | Time (s) | Temp. (mV) | Corr. t. (mV) | Corr. t. incr. (mC) | CP (cal) |
| 21 | 75.24 | 72 | 71.99 | -12.2 | 0 |
| 22 | 77.28 | 69.5 | 69.48 | -14.6 | 0 |
| 23 | 79.64 | 85.6 | 85.58 | 1.6 | 0.21 |
| 24 | 81.67 | 98.4 | 98.38 | 14.5 | 0.03 |
| 25 | 84.03 | 113.6 | 113.60 | 29.8 | 0.02 |
| 26 | 86.11 | 121.3 | 121.32 | 37.6 | 0.01 |
| 27 | 88.47 | 132.2 | 132.26 | 48.6 | 0.01 |
| 28 | 90.50 | 151.2 | 151.29 | 67.7 | 0.01 |
| 29 | 92.86 | 170.3 | 170.45 | 86.9 | 0.01 |
| 30 | 95.28 | 172.8 | 173.02 | 89.6 | 0.01 |
| 31 | 97.32 | 175.5 | 175.78 | 92.4 | 0.01 |
| 32 | 99.68 | 182.2 | 182.55 | 99.3 | 0.01 |
| 33 | 101.72 | 188.5 | 188.91 | 105.7 | 0.01 |
| 34 | 104.08 | 192.8 | 193.29 | 110.2 | 0.01 |
| 35 | 106.5 | 201.9 | 202.48 | 119.5 | 0.01 |
| 36 | 108.53 | 206.7 | 207.36 | 124.4 | 0.01 |
| 37 | 110.89 | 219.2 | 219.95 | 137.1 | 0.01 |
| 38 | 113.25 | 219.9 | 220.76 | 138 | 0.01 |
| 39 | 115.34 | 232.4 | 233.35 | 150.7 | 0.01 |
| 40 | 117.81 | 246.8 | 247.87 | 165.3 | 0.01 |
| 41 | 119.73 | 258.6 | 259.78 | 177.3 | 0.01 |
| 42 | 122.09 | 270.1 | 271.41 | 189 | 0.01 |
| 43 | 124.51 | 280.4 | 281.86 | 199.5 | 0.01 |
| 44 | 126.54 | 291 | 292.59 | 210.3 | 0.01 |
| 45 | 128.91 | 314 | 315.75 | 233.6 | 0.01 |
| 46 | 131.27 | 330 | 331.93 | 249.8 | 0.01 |
| 47 | 133.35 | 331 | 333.10 | 251.1 | 0.01 |
| 48 | 135.72 | 350.4 | 352.69 | 270.8 | 0.01 |

TABLE 1 (continued)

| <i>N</i> | Time (s) | Temp. (mV) | Corr. t. (mV) | Corr. t. incr. (mC) | CP (cal) |
|----------|-------------|---------------|------------------|------------------------|-------------|
| 49 | 137.75 | 360.2 | 362.67 | 280.8 | 0.01 |
| 50 | 140.11 | 376.6 | 379.28 | 297.5 | 0.01 |
| 51 | 142.53 | 390 | 392.91 | 311.2 | 0.01 |
| 52 | 144.5 | 410.6 | 413.71 | 332.1 | 0.01 |
| 53 | 146.92 | 412 | 415.36 | 333.8 | 0.01 |
| 54 | 149.28 | 416.2 | 419.81 | 338.4 | 0.01 |
| 55 | 151.37 | 425.3 | 429.13 | 347.8 | 0.01 |
| 56 | 153.73 | 436.3 | 440.39 | 359.1 | 0.01 |
| 57 | 156.09 | 439.4 | 443.76 | 362.6 | 0.01 |
| 58 | 158.13 | 438.7 | 443.29 | 362.2 | 0.01 |

Cooling curve

| <i>N</i> | Time (s) | Temp. (mV) | Temp. incr. (mC) |
|----------|-------------|---------------|---------------------|
| 59; 1 | 161.53 | 463.9 | 382 |
| 60; 2 | 166.97 | 463.2 | 382 |
| 61; 3 | 172.41 | 445.8 | 365 |
| 62; 4 | 177.84 | 453.3 | 372 |
| 63; 5 | 183.28 | 459.6 | 379 |
| 64; 6 | 188.72 | 462.9 | 382 |
| 65; 7 | 194.16 | 449.7 | 369 |
| 66; 8 | 199.59 | 448.9 | 369 |
| 67; 9 | 205.03 | 438.1 | 358 |
| 68; 10 | 210.47 | 439.1 | 359 |
| 69; 11 | 215.91 | 434.7 | 355 |
| 70; 12 | 221.34 | 442.3 | 363 |
| 71; 13 | 226.78 | 435.2 | 356 |
| 72; 14 | 232.22 | 425.4 | 347 |
| 73; 15 | 237.66 | 429.2 | 351 |
| 74; 16 | 243.1 | 431.3 | 353 |
| 75; 17 | 248.53 | 417.3 | 339 |
| 76; 18 | 253.97 | 422.2 | 344 |
| 77; 19 | 259.41 | 417.5 | 340 |
| 78; 20 | 264.85 | 427.5 | 350 |
| 79; 21 | 270.28 | 414.1 | 337 |
| 80; 22 | 275.72 | 414.3 | 337 |
| 81; 23 | 281.16 | 414.7 | 338 |
| 82; 24 | 286.6 | 421.1 | 344 |
| 83; 25 | 292.03 | 413.5 | 337 |
| 84; 26 | 297.47 | 409.2 | 333 |
| 85; 27 | 302.91 | 394.8 | 319 |
| 86; 28 | 308.35 | 416 | 340 |
| 87; 29 | 313.78 | 414.7 | 339 |
| 88; 30 | 319.22 | 399 | 323 |
| 89; 31 | 324.66 | 405.7 | 330 |
| 90; 32 | 330.1 | 391.4 | 316 |
| 91; 33 | 335.53 | 370.3 | 295 |

TABLE 1 (continued)

Cooling curve

| <i>N</i> | Time (s) | Temp. (mV) | Temp. incr. (mC) |
|----------|-------------|---------------|---------------------|
| 92; 34 | 340.97 | 378.9 | 304 |
| 93; 35 | 346.41 | 372.3 | 298 |
| 94; 36 | 351.85 | 380.1 | 306 |
| 95; 37 | 357.29 | 392 | 318 |
| 96; 38 | 362.72 | 420.4 | 346 |
| 97; 39 | 368.16 | 438.7 | 365 |
| 98; 40 | 373.6 | 445.1 | 372 |
| 99; 41 | 379.04 | 427.6 | 354 |
| 100; 42 | 384.47 | 415.4 | 342 |
| 101; 43 | 389.91 | 430.4 | 357 |
| 102; 44 | 395.35 | 421 | 348 |

Time constant, 52 min.

Cell calorific capacity including 10 ml of water, 10.014.

After shutting off the resistor and after 4 min, cooling curve data were taken at 5-s intervals. A time constant of 52 min was calculated and used to correct the main period temperatures. Calorific capacity was calculated for each point and the results averaged after eliminating the first five values. From the large value of τ it can be deduced that the 10-ml cell studied here still has an adiabatic-like behaviour and, therefore, temperature corrections are negligible. Much larger corrections can be expected using microcells (5 ml).

On the other hand, the program can be used to study how well the system approaches the heat-leak model. Thus, a single heat-sink behaviour would give the same value of the time constant along all the cooling curve. However, when the time constant is very large, small random deviations in the temperature readings lead to large fluctuations of τ , it being difficult to calculate its value along a small time period with a satisfactory accuracy. However, in all the experiments performed, no overshoot was observed, and the values of τ were within the 40–60 min interval with 0.5–5 min cooling curves. Furthermore, similar experiments performed with a 25-ml polypropylene cell gave time constants which increased quickly in the first minute showing that, in contrast with the metallic cell, more than one heat sink was significant.

ACKNOWLEDGEMENT

Financial support from the DGICYT (Grant PA86-0033) is gratefully acknowledged.

REFERENCES

- 1 C.J. Martin, B.R. Sreenathan and M.A. Marini, *Biopolymers*, 19 (1980) 2047.
- 2 D.J. Eatough, J.J. Christensen and R.M. Izatt, *Thermochim. Acta*, 3 (1972) 219.
- 3 L.D. Hansen, T.E. Jensen, S. Mayne, D.J. Eatough, R.M. Izatt and J.J. Christensen, *J. Chem. Thermodyn.*, 7 (1975) 919.
- 4 G. Ramis Ramos, R. Ibáñez Tomás, M.C. García Álvarez-Coque and C. Mongay Fernández, *Thermochim. Acta*, 98 (1986) 213.
- 5 P.W. Carr, *Thermochim. Acta*, 3 (1972) 427.
- 6 C.E. Vanderzee, *J. Chem. Thermodynamics*, 13 (1981) 1139.
- 7 L.D. Hansen, R.M. Izatt, D.J. Eatough, T.E. Jensen and J.J. Christensen, in *Analytical Calorimetry*, R.S. Porter and J. Johnson (Eds.), Plenum Press, New York, 1974, p. 7.
- 8 R.M. Izatt, L.D. Hansen, D.J. Eatough, T.E. Jensen and J.J. Christensen, in *Analytical Calorimetry*, R.S. Porter and J. Johnson (Eds.), Plenum Press, New York, 1974, p. 237.
- 9 M.V. Kilday, *J. Res. NBS*, 85 (1980) 449.
- 10 V. Cerdá, M.T. Oms, A. Alvarez-Ossorio, X. Lumbarres, R. Forteza and G. Ramis, *Thermochim. Acta*, 128 (1988) 9.
- 11 J. Maimó, M. Far, J.M. Estela and V. Cerdá, *Quím, Anal.*, 5 (1986) 245.
- 12 J. Lumbarres, C. Mongay and V. Cerdá, *Analisis*, 8 (1980), 62.
- 13 J. Lumbarres, C. Mongay and V. Cerdá, *J. Therm. Anal.*, 22 (1981) 275.