*Thermochimica Acta*, 71 (1983) 25–41
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# DATA ANALYSIS IN THERMOMETRIC TITRIMETRY

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(Received 1 June 1983)

## ABSTRACT

The application of a microprocessor and a high level programming language (BASIC) is described for data acquisition and data analysis in thermometric titrimetry The results derived by the microprocessor for the standard thermochemical test reactions THAM/HCl, $NaOH/HClO_4$ and $NaOH/H_2SO_4$ are in excellent agreement with those obtained using a classical graphical data analysis procedure

## INTRODUCTION

The methodology associated with data analysis in thermometric titrimetry continues to be modified as the range of applications of this technique expands. Christensen and co-workers [1–3] have provided a definitive theoretical treatment of thermometric titrimetry and previous data analysis procedures [4] for this technique are based on this work. Data analysis procedures for the closely related technique of solution calorimetry are also well-known [5,6]. However, as thermometric titrimetry is associated with an ever-increasing variety of applications and a wide diversity of calorimetric equipment, it is difficult to apply or adapt general data analysis procedures to the particular system under study.

This paper reports the software interfacing of a microprocessor to the data acquisition system of a conventional titration calorimeter. Several computer programs in BASIC have been developed to effect data analysis in terms of generating the molar reaction enthalpy. The software was tested by employing several standard thermochemical test reactions and enthalpy data derived by microprocessor were compared to similar data derived by Dickinson's graphical method [5,6].

## EXPERIMENTAL

### *Calorimeter and accessories*

The Tronac (model 450) thermometric titrimetric system was used. The calorimeter was a rapid-response, glass vacuum Dewar of 100 $cm^3$ maximum capacity. The burette capacity was 6 $cm^3$ and the measured titrant delivery rate was $1.0355 \pm 0.0011$ $cm^3$ $min^{-1}$. The thermostat was maintained at $298.0 \pm 0.001$ K by employing a Tronac (model 1040) precision temperature controller. Potential vs. time measurements were made using a Systron Donner (model 7005A) digital voltmeter (DVM), which was interfaced with a microprocessor. The overall sensitivity with respect to energy measurement was 2600 mV $K^{-1}$. Such sensitivity was achieved by amplifying the thermistor bridge output by a factor of 100 using a low-level, chopper-stabilised, differential amplifier (Utah Electronics).

The microprocessor used was a Rockwell R6500 Advanced Interactive Microprocessor (AIM 65) with the optional 8K BASIC Interpreter. The on-board RAM was expanded up to 4K and the off-board RAM was also expanded up to 65K address limit of the R6502. The hardware interfacing between the DVM and the microprocessor was accomplished via the input/output signal Binary Coded Decimal (BCD) option 05 of the DVM and the Versatile Interface Adapter (VIA) input/output of the DRAM AIM 65. Table 1 indicates the detailed pin-connections of the itnerfacing procedure.

### *Materials*

*Test reaction THAM/HCl.* The N.B.S. Reference Material 724, "Solution Calorimetry Standard", tris(hydroxymethyl)aminomethane (THAM) was used directly. 1.19568 g of THAM were dissolved and made up to 100 $cm^3$ with deionized distilled water. 0.1 M HCl was prepared by diluting 200 $\mu l$ of Aristar grade HCl to 25 $cm^3$ with deionized distilled water.

*Test reaction $NaOH/HClO_4$.* 20 g of AnalaR grade sodium hydroxide pellets were washed quickly with deionized distilled water to remove traces of carbonates, dissolved and made up to 500 $cm^3$ with deionized distilled water. The solution was standardized by pH titration with May and Baker Standard Concentrate 0.1 M HCl. 0.015 M $HClO_4$ was prepared by diluting AnalaR grade perchloric acid with deionized distilled water. The solution was standardized by pH titration with the standard sodium hydroxide solution prepared previously.

*Test reaction $H_2SO_4/NaOH$.* 0.2 M $H_2SO_4$ and 0.1 M NaOH aqueous solutions were prepared directly from the appropriate May and Baker Volucon Standard Volumetric Concentrates with deionized distilled water.

TABLE 1

The DVM–AIM 65 hardware interface

| Digital voltmeter | | | Dram AIM 65 | | |
|---|---|---|---|---|---|
| Output | BCD | Pin no. | VIA input | Pin no | Addresses (Hex.) |
| 100,000's | 1 | 13 | PA 4 | 8 | |
| 10,000's | 1 | 11 | PA 0 | 4 | |
| | 2 | 12 | PA 1 | 5 | |
| | 4 | 36 | PA 2 | 6 | $9801 |
| | 8 | 37 | PA 3 | 7 | |
| 1,000's | 1 | 9 | PB 4 | T | |
| | 2 | 10 | PB 5 | U | |
| | 4 | 34 | PB 6 | V | |
| | 8 | 35 | PB 7 | W | |
| | | | | | $9000 |
| 100's | 1 | 7 | PB 0 | N | |
| | 2 | 8 | PB 1 | P | |
| | 4 | 32 | PB 2 | R | |
| | 8 | 33 | PB 3 | S | |
| 10's | 1 | 5 | PA 4 | J | |
| | 2 | 6 | PA 5 | K | |
| | 4 | 30 | PA 6 | L | |
| | 8 | 31 | PA 7 | M | |
| | | | | | $9001 |
| 1's | 1 | 3 | PA 0 | D | |
| | 2 | 4 | PA 1 | E | |
| | 4 | 28 | PA 2 | F | |
| | 8 | 29 | PA 3 | H | |
| Polarity | | | | | |
| "+" = 0 | 1 | 19 | PB 1 | 13 | $9800 |
| "−" = 1 | | | | | |
| Overload | | | | | |
| "O/L" = 1 | 2 | 16 | PA 7 | 11 | $9801 |
| "NO O/L" = 0 | | | | | |
| Print | | | CA 1 | 2 | |
| Command | | 23 | CA 1 | B | |
| Inhibit | | 22 | CA 2 | 3 | $980C |
| | | 50 | | | |
| | | 40 | | | |
| GND | | 44 | GND | 1 | |
| | | etc. | | | |
| +5 VOLT | | | | | |
| Supply for open collectors | | 41 | 5 VOLT | A | |

## *The thermometric titration procedure*

The usual and well-documented thermometric titration procedure was adopted. Heat capacities were determined before and after each titration.

The deionized water used in the experiments was purged with high purity nitrogen prior to transfer to the reaction vessel. Sufficient water was added to the reaction vessel to make up the final volume to 90 $cm^3$ of titrant. Known amounts of the titrant stock solution, 200, 400, 600, 800 and 1,000 $\mu$l, measured with a micropipette with disposable tips were then added. The solution in the reaction vessel was kept constantly under a nitrogen blanket.

## *Program development*

Three programs were developed, a data acquisition program, a calibration/heat capacity program and a reaction enthalpy program. As the data acquisition program is essentially required to collect and store milli-volt readings from the DVM as a function of time, this program was therefore incorporated into each of the other two programs.

### *(a) Data acquisition program*

A choice of computer language exists: ASSEMBLY, which has the advantage of speed, or BASIC, which is a very powerful and widely applicable programming language. By comparison with ASSEMBLY, BASIC is slow in operation. However, the speed of BASIC is compatible with the generation of data from the DVM which has a rate of about 200 ms [7]. Other factors, which favour the use of BASIC, include simplicity, diminishing memory storage space with increasing program length and operator control over data storage files [8].

The use of BASIC for collecting data generated by DVM is effected by the PEEK (I) function, which returns the contents of the memory address I [9]. A precise knowledge of particular addresses corresponding to the hardware interfacing is, therefore, necessary (Table 1). The DVM generates a maximum of six digital numbers in BCD with the sixth digit being either 0 or 1. The program immediately assigns the digits to $D_1$ to $D_6$, respectively, corresponding to the 1st to 6th digits. The reconstruction of the number is accomplished by allocating the decimal point and assigning the polarity corresponding to that displayed by the DVM.

Assuming that the program execution time for collection and reconstruction of a single data point generated by the DVM is shorter than the DVM print command pulse rate, the next execution must be delayed until a new number arrives.

### *(b) Calibration/heat capacity program*

A typical calibration/heat capacity thermogram is shown in Fig. 1 and consists of three linear segments, the initial rating period (IRP), the heating period and the final rating period (FRP). It was necessary to take into account that, with the Tronac 450 calorimeter, voltage spikes occur, when the calibration heater is turned on or off.

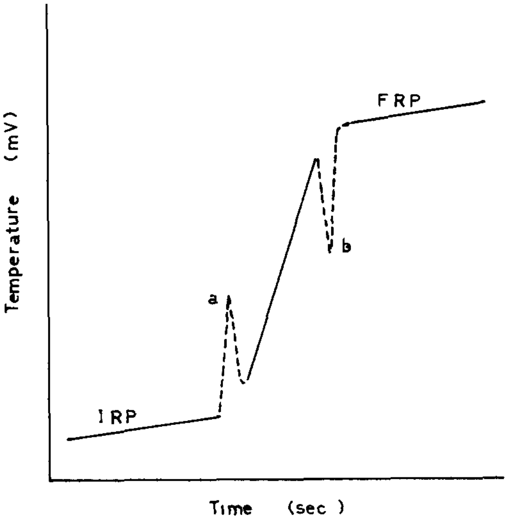

Fig 1. A typical calibration (heat capacity) thermogram a and b are voltage indicator spikes a, heater on, b, heater off.

Calculation of the corrected temperature rise essentially involves the principles listed.

(i) 600 data points are acquired. The first 100 data points are taken to represent the IRP. The following 150 data points are rejected, since these correspond to the voltage spike obtained when the heater is turned on. Data points 250 to 350 are taken to represent the heating period, while the subsequent 150 data points are rejected because they correspond to the voltage spike obtained when the heater is turned off. Finally, data points 500 to 600 are taken to represent the FRP.

(ii) The three data groups, IRP, heating period and FRP were subjected to least-squares fit equations and the corrected temperature rise was evaluated in accordance with the application of Dickinson's method [6].

### *(c) Reaction enthalpy program*

For convenience, the program was developed for exothermic reactions with large single K values. If necessary, the program can be modified for other types of reaction. Such simple reactions normally produce a thermogram of the type shown in Fig. 2 which consists of two linear portions for IRP and FRP, respectively, and a non-linear reaction period. The extremities of the reaction period are indicated by the deviations from linearity of the IRP and FRP, respectively. However, the real time of commencement and termination of the reaction are unknown. For a classical thermogram, the commencement of the reaction is not the time when the burette is turned on, as a small air space is usually left at the tip of the titrant delivery tube to prevent pre-mixing of titrant with titrate [2]. It is, therefore, necessary for the

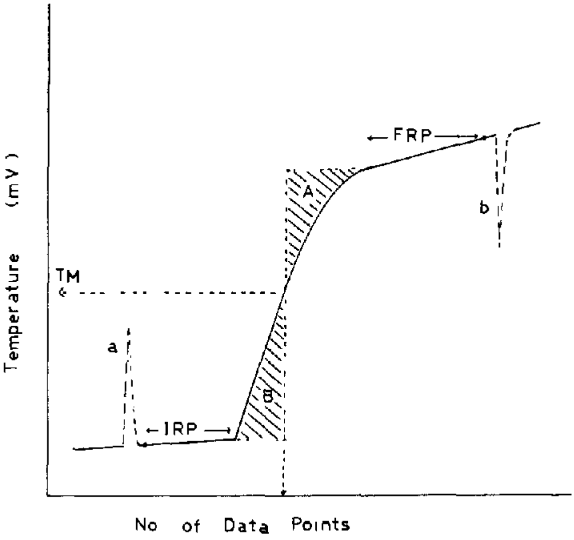

Fig. 2 An idealized reaction thermogram a and b are voltage indicator spikes· a, burette on, b, burette off

program to establish the times corresponding to commencement and termination of the reaction.

With the Tronac 450 calorimetric system, a voltage spike occurs when the burette is turned on or off. Such effects constitute a source of error in the study of reactions associated with a small enthalpy change. The reaction period is therefore established, after the initial voltage spike by extending the air space at the tip of the titrant delivery tube so as to extend the initial time of mixing of titrant and the titrate beyond that of generation of the voltage indicator spike for commencement of the titration.

Data processing to obtain the corrected total temperature rise for the reaction is perforemd according to the Dickinson method [5,6] and involves the steps listed.

(i) The slope $S_i$ at all data points $i = 3$ to $i = (N - 2)$ is given by

$$S_i = \mathrm{ABS}\left[\frac{(Y_{i+2} - Y_{i-2})}{(i + 2) - (i - 2)}\right] \tag{1}$$

where $Y_i$ = the DVM reading at the $i$th point. The point $P_1$ corresponding to the time at which the burette is turned on is obtained, when the slope at the $i$th point is greater than $1 \times 10^{-3}$. This number was arbitrarily chosen after determination of the slope changes resulting from the corresponding voltage spike. All data points from $i = 1$ to $i = P_1 + 50$ are rejected since these are directly associated with the voltage spike. The remaining data points are subjected to five cycle data smoothing, which involves the derivation of a five point quadratic equation.

(ii) The slope at each point from $i = P_2 + M$, where $P_2 = P_1 + 50$ and $M$ is an integer, to $i = n - 2 \times M$ is calculated according to eqn. (1). Slopes are successively compared and a point is considered to have deviated from linearity, when two successive comparisons are greater than $6 \times 10^{-6}$. This number was chosen after determination of the slope variations of the linear segments produced by the calorimeter under equilibrium conditions. Accordingly, the point $P_3$, corresponding to the end of the IRP or to the beginning of the reaction period is established. The data points between $P_2$ and $P_3$ are subjected to a least-squares calculation to obtain the gradient, intercept and linear correlation coefficient of the IRP.

(iii) The slope comparison routine now commences using the last data point backwards and involves a procedure similar to that described in (ii) until the point $P_6$, which corresponds to the end of the reaction period or to the beginning of the FRP is established.

(iv) The mid-point TM is then calculated by successive calculations and comparison of the areas marked A and B of the thermogram shown in Fig. 2. TM is established, when these two areas are equal. The corrected temperature rise may then be calculated by the standard extrapolation method

The three programs are given in Appendices I and II.

## RESULTS AND DISCUSSION

Each of the three programs were tested and, in the case of heat capacity and reaction enthalpy determinations, the corrected temperature changes

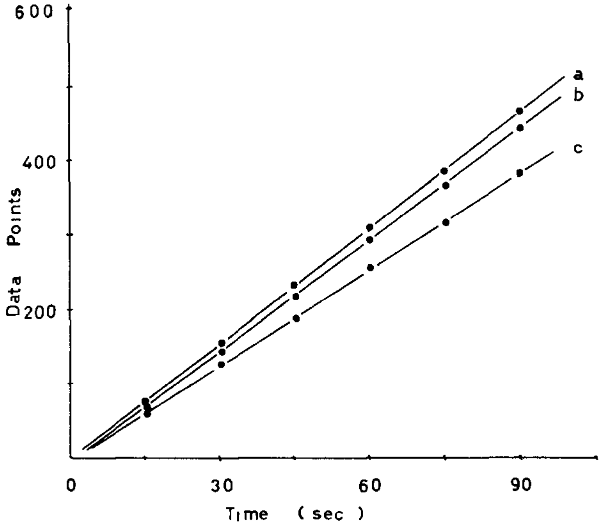

Fig 3 The effect of the DVM range on the rate of data acquisition for DVM ranges of a, 100; b, 10, c, 1

derived by microprocessor were compared with those derived by the graphical procedure.

*(a) Data acquisition program*

As the BASIC program is relatively slow, the program execution time was tested by utilizing the AIM 65 internal clock. The time taken for the program to acquire a data point generated by the DVM was less than 100 ms. Hence, the data acquisition speed depends only on the DVM print command pulse rate which was found to vary with the DVM range. Hence, it was necessary to calibrate the data acquisition speed by counting the number of data points acquired after a predetermined time period. The program was executed for the DVM ranges 1, 10 and 100 and periods ranging from 15 to 90 s. The calibration profiles are shown in Fig. 3. It is apparent that the data acquisition rate decreases as the DVM sensitivity range increases. Such calibration profiles are useful in assessing the compatibility of the time period allocation with the numbers of data points taken to represent the IRP heating period and FRP in the heat capacity determination.

*(b) Calibration / heat capacity program*

The calibration/heat capacity program was tested using water as the calorimetric solvent (90 cm$^3$). The actual heat capacity determination run was accomplished within 120 s, of which 30 s are for collecting data to represent the initial rating period (IRP), 60 s to the heating period and the last 30 s corresponds to the final rating period (FRP). A heating rate of 50 mcal sec$^{-1}$ was employed. Table 2 shows the comparison of the corrected temperature rise and heat capacity, respectively, obtained by the graphical

TABLE 2

Heat capacity determination

| $\Delta T_{corr}$(mV) | | Deviations | | Heat capacities (kJ mV$^{-1}$) | |
|---|---|---|---|---|---|
| By graph | By AIM-65 | mV | % | By graph | By AIM-65 |
| 0.0549 | 0.0551 | +0.0002 | +0.36 | 0.2310 | 0.2314 |
| 0.0545 | 0.0545 | 0.000 | 0.00 | 0.2319 | 0.2322 |
| 0.0552 | 0.0553 | +0.0001 | +0.18 | 0.2327 | 0.2316 |
| 0.0555 | 0.0554 | −0.0001 | −0.18 | 0.2329 | 0.2331 |
| 0.0558 | 0.0557 | −0.0001 | −0.18 | 0.2310 | 0.2317 |
| 0.0558 | 0.0558 | 0.0000 | 0.00 | 0.2280 | 0.2295 |
| 0.0555 | 0.0556 | +0.0001 | +0.18 | 0.2300 | 0.2316 |
| 0.0561 | 0.0561 | 0.0000 | 0.00 | 0.2290 | 0.2290 |
| | | | | Mean 0.2308 ± 0.0017 | 0.2313 ± 0.0014 |

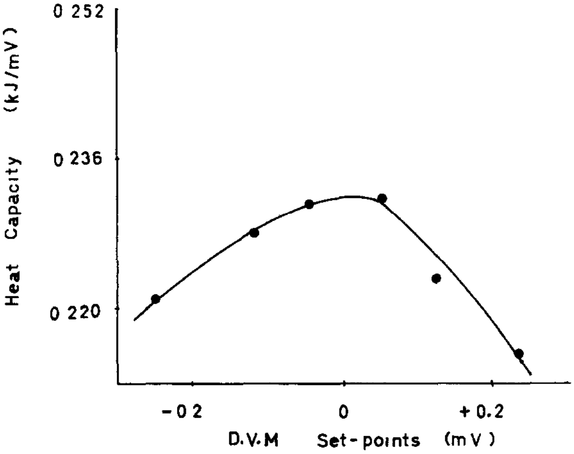

Fig 4. The effect of the DVM set-point on heat capacity determination.

method and that obtained by the microprocessor. A deviation of less than 0.5% between methods is generally within the range of acceptability for thermochemical data. It is significant to note that the heat capacity value varies according to the initial DVM set-point and is at a maximum when the set-point is zero (Fig. 4). Hence the DVM set-point is determined prior to commencement of the thermometric titration.

### *(c) Reaction enthalpy program*

The reaction enthalpy program was tested using three standard thermochemical test reactions. Reaction molar enthalpies for the reactions between $THAM_{(aq)}$ and 0.1 M $HCl_{(aq)}$, $NaOH_{(aq)}$ and 0.015 M $HClO_{4(aq)}$ and between $H_2SO_{4(aq)}$ and 0.1 M $NaOH_{(aq)}$ calculated by the microprocessor

TABLE 3

Standard test reaction, THAM + 0.1 M HCl

| THAM × $10^{-5}$ (mole/90 $cm^3$) | $-\Delta H$ (kJ mole$^{-1}$ THAM) | |
|---|---|---|
| | Graphical method | AIM-65 |
| 2.8468 | 47.36 | 47.16 |
| 3.5957 | 48.19 | 47.97 |
| 3.9482 | 47.19 | 46.75 |
| 5.9223 | 47.56 | 47.32 |
| 7.8964 | 47.83 | 47.76 |
| 9.8705 | 48.50 | 47.93 |
| Average | 47.77 ± 0.50 | 47.48 ± 0.48 |
| Average percentage deviation (−) 0.61% | | |

TABLE 4

Standard test reaction, NaOH + 0.015 M $HClO_4$

| NaOH (mole $l^{-1}$) | $-\Delta H$ (kJ $mole^{-1}$ NaOH) | |
|---|---|---|
| | Graphical method | AIM-65 |
| 0.0025 | 55.85 | 55.58 |
| 0.0025 | 56.08 | 55.93 |
| 0.0020 | 55.65 | 56.01 |
| 0.0020 | 55.84 | 55.82 |
| 0.0015 | 55.80 | 54.86 |
| 0.0015 | 56.07 | 56.08 |
| 0.0010 | 55.85 | 56.31 |
| 0.0010 | 54.23 | 54.32 |
| Average | 55.54 ± 0.67 | 55.61 ± 0.68 |
| Average percentage deviation (+) 0.13% | | |

were compared to those obtained by the graphical method [5,6].

The enthalpy of protonation of $THAM_{(aq)}$ obtained via the graphical method is $-47.77 \pm 0.50$ kJ $mole^{-1}$ compared to the value calculated by the microprocessor of $-47.48 \pm 0.48$ kJ $mole^{-1}$ (Table 3). The average percentage deviation of the values calculated by the microprocessor relative to the graphical method is 0.61%. The enthalpy values obtained by both methods are in good agreement with literature values. Hansen and Lewis [10] reported the protonation enthalpy of THAM as $-47.36$ kJ $mole^{-1}$ obtained by titration of $THAM_{(aq)}$ with 0.5139 M $HClO_4$. Hill et al. [11] reported a value of $-47.50$ kJ $mole^{-1}$ by subtracting the enthalpy of solution of $THAM_{(s)}$ in water from the enthalpy of solution in 0.1 M HCl.

The enthalpy of water formation using the reaction of $NaOH_{(aq)}$ with

TABLE 5

Standard test reaction, $H_2SO_4$ + 0.1 M NaOH

| $H_2SO_4 \times 10^{-3}$ (mole/90 $cm^3$) | $-\Delta H$ (kJ $mole^{-1}$ $H_2SO_4$) | |
|---|---|---|
| | Graphical method | AIM-65 |
| 0.04 | 58.49 | 58.20 |
| 0.04 | 57.76 | 57.95 |
| 0.05 | 58.18 | 58.15 |
| 0.05 | 56.84 | 56.17 |
| 0.03 | 58.33 | 58.16 |
| 0.03 | 56.83 | 56.65 |
| Average | 57.74 ± 0.75 | 57.55 ± 0.89 |
| Average percentage deviation (−) 0.34% | | |

0.051 M $HClO_{4(aq)}$ calculated by the microprocessor was $-55.6 \pm 0.68$ kJ mole$^{-1}$ compared to the graphical value $-55.54 \pm 0.67$ kJ mole$^{-1}$ (Table 4). These data are slightly lower than those reported by Christensen et al. [12] ($-55.81$ kJ mole$^{-1}$), Eatough et al. [13] ($-55.75$ kJ mole$^{-1}$) and Hansen and Lewis [10] ($-55.78$ kJ mole$^{-1}$). The average percentage deviation of the enthalpy of formation of water calculated by the microprocessor relative to that obtained by the graphical method is 0.13%.

The enthalpy of formation of water obtained from the reaction between dilute solutions (3.3 to $5.6 \times 10^{-4}$ mole $l^{-1}$) of $H_2SO_{4(aq)}$ and 0.01 M $NaOH_{(aq)}$, calculated by the microprocessor was $-57.55 \pm 0.89$ kJ mole$^{-1}$ and that obtained graphically was $-57.74 \pm 0.75$ kJ mole$^{-1}$ (Table 5). However, the enthalpy of reaction between $H_2SO_{4(aq)}$ and $NaOH_{(aq)}$ reported here cannot be compared to that reported in the literature [14], as these data were obtained under different conditions, in particular at different dilutions. The average percentage deviation of the values calculated by the microprocessor was 0.34% relative to those values obtained by the graphical method.

There are two possible sources of the discrepancy in the two sets of data generated [15]. The first source arises from the two different methods of establishing the initial and final rating period gradients which may result in different corrected temperature changes. The second source arises from the different methodology associated with the two different approaches to the application of the Dickinson method for derivation of corrected temperature change. The microprocessor method transforms the reaction period into a series of linear segments whereas the graphical method assumes that the same reaction period is a smooth curve.

## CONCLUSIONS

The principal aim of the present work was to interface a microprocessor with a conventional thermometric titrimetry system and to create programs to generate enthalpy data to the same degree of precision as conventional graphical procedures. Such aims are achieved if special features of the thermometric titrimetry system, such as voltage indicator spikes and reference temperature set-point, are considered in the data analysis procedures.

## ACKNOWLEDGEMENTS

We gratefully acknowledge Mr. I. Shaw for the technical interfacing of calorimeter and microprocessor and Dr. J. Traeger for invaluable assistance with computer programming.

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## APPENDIX I. HCC4. HEAT CAPACITY DETERMINATION PROGRAM

```
 1 PRINT"HCC4:HEAT C
APACITY/"
 2 PRINT"     :CALIBR
ATION"
 3 PRINT"N=600:D.V.M
  DISPLAY:-0.03000"
 4 PRINT"I.R.P.:30 S
EC."
 5 PRINT"HEATING: ST
RICTLY 60 SEC."
 6 PRINT"F.R.P.: 30
SEC."
 7 DIM R$(4),S$(4)
 8 R$(1)="DATE":R$(2
)="EXP.:":R$(3)="RUN
 NO:":R$(4)="READY ?
"
 9 FORI=1TO4:PRINTR$
(I):INPUTS$(I):NEXT
 10 N=600:DIMP(N)
 20 M6=100000:M5=100
00:M4=1000:M3=100:M2
=10
 30 I=0:A=2:A1=15:A2
=16:A3=240:A4=127
 40 L1=36864:L2=3686
5:L3=38912:L4=38913
 50 L7=38924:F=36877
 60 D=10^(-INT(PEEK(
L3)AND60)/4)
 70 POKEL7,13
 80 J=PEEK(L2)
 90 WAITF,A
 100 J=PEEK(L2)
 110 D1=JANDA1
 120 D2=(JANDA3)/A2
 130 J=PEEK(L1)
 140 D3=JANDA1
 150 D4=(JANDA3)/A2
 160 J=PEEK(L4)
 170 D5=JANDA1
 180 D6=(JANDA2)/A2
 190 IFJ>A4THEN270
 200 P=D6*M6+D5*M5+D
4*M4+D3*M3+D2*M2+D1
 210 P=P*D
 220 J=PEEK(L3)
 230 IFJANDATHENP=-P
 240 I=I+1:P(I)=P
 250 IFI=NTHEN285
 260 GOTO90
 270 PRINT"OVERLOAD"
:GOTO90
 285 J=1:M=100:GOSUB
570
 320 IG=GK:PRINT"INI
T. GRAD."IG
 330 IC=CK:PRINT"INI
T. INT."IC
 340 PRINT"LIN. COR.
 COEF."R
 350 J=250:M=350:GOS
UB570
 390 HG=GK:PRINT"HEA
TING GRAD."HG
 400 HC=CK:PRINT"HEA
TING INT."HC
 410 PRINT"LIN. COR.
 COEF."R
 420 J=500:M=N:GOSUB
570
 430 FG=GK:PRINT"FIN
AL GRAD."FG
 440 FC=CK:PRINT"FIN
AL INT."FC
 450 PRINT"LIN. COR.
 COEF."R
 460 TI=(HC-IC)/(IG-
HG)
 470 TF=(FC-HC)/(HG-
FG)
 480 TM=(TI+TF)/2
 490 VI=IG*TM+IC
 500 VF=FG*TM+FC
```

```
 510 TR=VF-VI:PRINT"
TEMP. RISE="TR"MV."
 520 TIME=60
 521 PRINT"HEATING P
ERIOD="TIME"SEC."
 530 PRINT"INPUT HTR
I":INPUTHI
 531 PRINT"INPUT HTR
V":INPUT HV
 540 HEAT=(HI*HV*TIM
E)/(101.5*TR)
 550 PRINT"HEAT CAPA
CITY="HEAT"J/MV."
 553 PRINT"D.V.M. DI
SPLAY:"
 554 PRINT"STARTS AT
:"P(1)
 555 PRINT"STOPS AT:
"P(N)
 556 STOP
 560 GOTO660
 570 S1=0:S2=0:S3=0:
S4=0:S5=0:K=0
 580 FORI=JTOM:S1=S1
+I:S2=S2+I*I
 590 S3=S3+P(I):S4=S
4+P(I)*P(I):S5=S5+I*
P(I):K=K+1:NEXT
 600 DK=K*S2-S1*S1
 610 GK=(K*S5-S1*S3)
/DK
 620 CK=(S3*S2-S1*S5
)/DK
 630 R=K*S5-S1*S3
 640 R=R/SQR((K*S2-S
1*S1)*(K*S4-S3*S3))
 650 RETURN
```

## APPENDIX II. DATR2. DATA ACQUISITION AND $\Delta T_{corr}$ CALCULATION PROGRAM

```
 2 PRINT"DATR2:REACT
ION EXP."
 4 PRINT"TOTAL HEAT
EFFECT"
 10 PRINT"N-DATA POI
NTS=":INPUTN
 20 DIMP(N),R$(4),S$
(4)
 30 R$(1)="DATE":R$(
2)="EXP.:"
 40 R$(3)="RUN NO.:"
:R$(4)="READY ?"
 50 M6=100000:M5=100
00:M4=1000:M3=100:M2
=10
 60 A=2:A1=15:A2=16:
A3=240.A4=127
 70 L1=36864:L2=3686
5:L3=38912:L4=38913:
L5=36877:M=30100 .
 90 DEC=10^(-INT(PEE
K(L3)AND60)/4)
 100 POKE38924,13
 110 FORI=1TO4:PRINT
R$(I):INPUTS$(I):NEX
T
 115 I=0
 120 J=PEEK(L2)
 130 WAITL5,A
 140 J=PEEK(L2)
 150 D1=JANDA1
 160 D2=(JANDA3)/A2
 170 J=PEEK(L1)
 180 D3=JANDA1
 190 D4=(JANDA3)/A2
 200 J=PEEK(L4)
 210 D5=JANDA1
 220 D6=(JANDA2)/A2
 230 IFJ>A4THEN290
 240 P=D6*M6+D5*M5+D
4*M4+D3*M3+D2*M2+D1
 250 P=P*DEC:J=PEEK(
L3)
 260 IFJANDATHENP=-P
 270 I=I+1:P(I)=P:IF
I=NTHEN300
 280 GOTO130
 290 PRINT"OVERLOAD"
:GOTO130
 300 PRINT"OFF THE B
URETTE NOW"
 301 FORI=1TO3:PRINT
I,P(I):NEXT
 302 FORI=250TO255:P
RINTI,P(I):NEXT
 303 FORI=(N-5)TON:P
RINTI,P(I):NEXT
 305 FORI=1TO4:L1=LE
N(S$(I))
 310 POKEM,L1:M=M+1
 320 FORJ=1TOL1:J$=M
ID$(S$(I),J,1)
 330 POKEM,ASC(J$):M
=M+1:NEXTJ:NEXTI
 340 L1=LEN(STR$(N))
:POKEM,L1:M=M+1
 350 FORI=1TOL1:J$=M
ID$(STR$(N),I,1)
 360 POKEM,ASC(J$):M
=M+1:NEXT
 370 A1=65535:A2=256
:I=0
 380 MAX=-1.0E38:MIN
=1.0E38
 390 I=I+1:IFP(I)>MA
X THEN MAX=P(I)
 400 IFP(I)<MIN THEN
 MIN=P(I)
 410 IFI=NTHEN430
 420 GOTO390
 430 L1=LEN(STR$(MAX
)):POKEM,L1:M=M+1
 440 FORI=1TOL1:J$=M
ID$(STR$(MAX),I,1)
 450 POKEM,ASC(J$):M
=M+1:NEXT
 455 L1=LEN(STR$(MIN
)):POKEM,L1:M=M+1
 460 FORI=1TOL1:J$=M
ID$(STR$(MIN),I,1)
```

```
 470 POKEM,ASC(J$):M
=M+1:NEXT
 480 FORI=1TON
 490 A=INT((P(I)-MIN
)*A1/(MAX-MIN))
 500 J=INT(A/A2):POK
EM,J:M=M+1
 510 POKEM,(A-J*A2):
M=M+1:NEXT
 514 PRINT"LAST MEM=
"M
 515 MA=INT(M/16)
 516 MB=M-MA*16:PRIN
TMB
 517 IFMA<16THEN519
 518 M=MA:GOTO515
 519 PRINTMA
 522 PRINT"TEMP. RIS
E CALCTN"
 600 DIMS(N)
 610 I=3
 620 S(I)=ABS((P(I+2
)-P(I-2))/((I+2)-(I-
2)))
 630 I=I+1:IFI<N-2TH
EN620
 640 I=3
 650 IFS(I)>1.0E-03T
HEN670
 660 I=I+1:IFI<N-2TH
EN650
 670 P1=I-1:PRINT"BU
RETTE ON:P1="P1
 680 P2=P1+50:PRINT"
I.R.P. STARTS:P2="P2
 690 PRINT"DATA SMOO
THING: RMSD"
 700 D=5:I=P2-1:J=0
 710 I=I+1:J=J+1:S(J
)=P(I):IFI<NTHEN710
 720 NA=N:N=J
 730 FORI=1TON:P(I)=
S(I):NEXT
 740 C1=3/35:C2=1/7
 750 D1=S(4)-3*S(3)+
3*S(2)-S(1)
 760 D2=S(5)-4*S(4)+
6*S(3)-4*S(2)+S(1)
 770 D4=S(N)-3*S(N-1
)+3*S(N-2)-S(N-3)
 780 D5=S(N)-4*S(N-1
)+6*S(N-2)-4*S(N-3)+
S(N-4)
 790 S1=S(1)+.2*D1+C
1*D2
 800 S2=S(2)-.4*D1-C
2*D2
 810 N1=N-1:N2=N-2
 820 FORK=3TON2
 830 D3=S(K+2)-4*S(K
+1)+6*S(K)-4*S(K-1)+
S(K-2)
 840 S(K-2)=S(K)-C1*
D3
 850 NEXT
 860 FORK=3TON2:N1=N
1-1:S(N1)=S(N1-2):NE
XT
 870 S(1)=S1:S(2)=S2
 880 S(N-1)=S(N-1)+.
4*D4-C1*D5
 890 S(N)=S(N)-.2*D4
+C2*D5
 900 R=0
 910 FORI=1TON:Q=P(I
)-S(I):R=R+Q*Q:NEXT
 920 R=SQR(R/N):PRIN
TR
 930 D=D-1:IFD<>0THE
N720
 940 J=0
 950 FORI=P2TONA:J=J
+1:P(I)=S(J):NEXT
 960 M=10:T3=7.0E-06
 970 I=P2
 980 I=I+M:S(I)=(P(I
+M)-P(I-M))/((I+M)-(
I-M))
```

```
 1000 IFI<(NA-2*M)TH
EN390
 1010 I=P2
 1020 I=I+M:IF(S(I+M
)-S(I))<T9THEN1020
 1030 I=I+M:IF(S(I+M
)-S(I))<T9THEN1020
 1050 P3=I-2*M:PRINT
"I.R.P. ENDS:P3="P3
 1060 MIN=P2:MAX=P3:
GOSUB1360
 1070 GIRP=G:PRINT"I
RP GRAD="GIRP
 1080 CIRP=C:PRINT"I
NT="CIRP
 1090 PRINT"LCC="R
 1092 I=NA
 1093 I=I-M:IF(S(I-M
)-S(I))<T9THEN1093
 1094 I=I-M:IF(S(I-M
)-S(I))<T9THEN1093
 1096 P6=I+1+2*M:PRI
NT"F.R.P. STARTS P6=
"P6
 1100 MIN=P6:MAX=NA:
GOSUB1360
 1110 GFRP=G:PRINT"F
RP GRAD="GFRP
 1120 CFRP=C:PRINT"I
NT="CFRP
 1130 PRINT"LCC="R
 1140 PRINT"TM CALCU
LATION"
 1170 SA=0:FA=0:I=P3
:J=P6
 1180 IFJ<=ITHEN1280
 1190 I=I+1
 1200 S(I)=P(I)-P(P3
)
 1210 SA=SA+S(I)
 1220 IFSA<FATHEN118
0
 1230 IFJ<=ITHEN1280
 1240 J=J-1
 1250 S(J)=P(P6)-P(J
)
 1260 FA=FA+S(J)
 1270 GOTO1220
 1280 IM=I:PRINT"SA=
"SA"AT"IM,P(IM)
 1290 JM=J:PRINT"FA=
"FA"AT"JM,P(JM)
 1300 TM=(JM+IM)/2:P
RINT"TM="TM
 1310 PRINT"AREA DIF
F="ABS((FA-SA)*100/S
A)"%"
 1320 T1=TM*GIRP+CIR
P:PRINT"INIT. TEMP.=
"T1"MV"
 1330 T2=TM*GFRP+CFR
P:PRINT"FINAL TEMP.=
"T2"MV"
 1340 T=T2-T1:PRINT"
TEMP. RISE="T"MV."
 1350 STOP
 1360 S1=0:S2=0:S3=0
:S4=0:S5=0:K=0
 1370 FORI=MIN TO MA
X
 1380 S1=S1+I:S2=S2+
I*I
 1390 S3=S3+P(I):S4=
S4+P(I)*P(I)
 1400 S5=S5+I*P(I):K
=K+1:NEXT
 1410 D=K*S2-S1*S1
 1420 G=(K*S5-S1*S3)
/D
 1430 C=(S3*S2-S1*S5
)/D
 1440 R=K*S5-S1*S3
 1450 R=R/SQR((K*S2-
S1*S1)*(K*S4-S3*S3))
 1460 RETURN
```