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COMPUTER PROGRAM OF CALCULATION METHOD FOR A CONSTANT-ENVIRONMENT CALORIMETER

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ABSTRACT

A computer program (in BASIC) for the determination of heats of solution and reaction in a constant-environment calorimeter has been developed. Particular attention was paid to the choice of parameters such as K/C and the endpoint of a generic calorimetric reaction in solution. The result derived from the program, for the standard thermochemical test reaction of solid tris(hydroxymethyl)aminomethane (THAM) with aqueous HCl 0.1 M, is in good agreement with that reported in literature using a graphical procedure.

INTRODUCTION

The recently developed commercial calorimeters (Perkin-Elmer model DSC 4; Mettler TA 300 System) for solid-state thermal analysis investigations are completely computerized and complete evaluation software is also included. For solution and titration calorimeters this generally does not occur and therefore a considerable number of computer programs of calculation methods for the various calorimetric techniques has lately been released [1–7]. It is our opinion that a computer program must enable a flexible choice and explanation a posteriori for some parameter values as the end-point of the reaction, the heat capacity of the system and the calorimeter leakage constant in the experimental conditions. This fact is clearly related to the quite different reactions which may occur in solution calorimetry and thus a "fast" reaction cannot be read in the same way as a "slow" one.

A method of calculation for the determination of solution and reaction heats in a constant-environment calorimeter has been the subject of a recent paper [8]. In the present work a computer program for the method is

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supplied and discussed. The goal of this work is to obtain a flexible and personal calculation program.

EXPERIMENTAL

Since there are many types of constant-environment temperature calorimeters, we have considered a "home-made" isothermal-jacket calorimeter. The calorimeter cell was a rapid-response glass cell of volume 100 cm^3. The thermostat was maintained at 298.15 ± 0.001 K by using a LKB (model 8700) precision temperature controller. To measure the temperature change a thermistor with a value of 1981 Ω at 25 °C was used. Its experimental calibration indicates that it follows the equation $R\ (\Omega) = A \exp B/T$ where $A = 0.017082\ (\Omega)$ and $B = 3476.9$ K.

The temperature scale of the calorimetric curves was modified by varying the attenuation of the strip chart recorder (Speedomax L&N) model. A scale of 1 mV = 0.136 °C was normally used. The temperature change of the reaction or of the electrical calibration gives rise to a corresponding voltage change in the Wheatstone bridge circuit. The main components of the bridge and heater apparatus are indicated in Figs. 1 and 2(a, b).

Figure 1 shows the heating apparatus where A is a HP 6133 A constant voltage supply, B a Keithley 175 A multimeter, C a Keithley 195 A multimeter, R_H ($\doteq$ 50 Ω) is the precision heater resistance of the cell and S is a switch. Figure 2(a) represents the thermistor bridge where A_1 is a HP 6133 A constant voltage supply, R_1 (100.17 Ω), R_2 (10.07 Ω), R_3 (40.00 kΩ) are constant resistance values of the Wheatstone bridge, R_v (2500 Ω) is a box of variable resistances, R is the thermistor resistance value, R_c is the resistance value between the leads connecting the box of variable resistances to the thermistor and R_{tot} (total resistance) is the sum of R_v, R and R_c, V_a (4.555 V) is the potential of A_1, R_G (4,000,000) and V are the resistance and the potential between the strip-chart recorder terminals respectively.

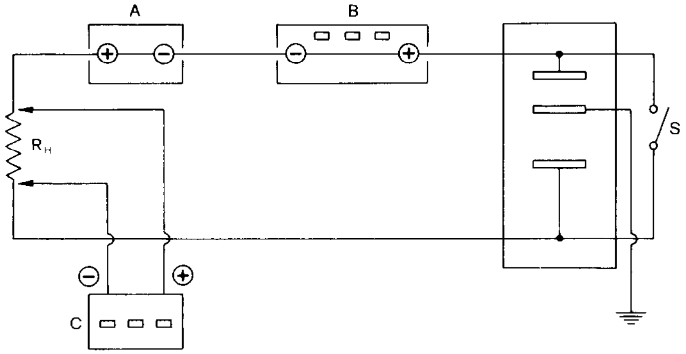

Fig. 1. Calibration heating circuit.

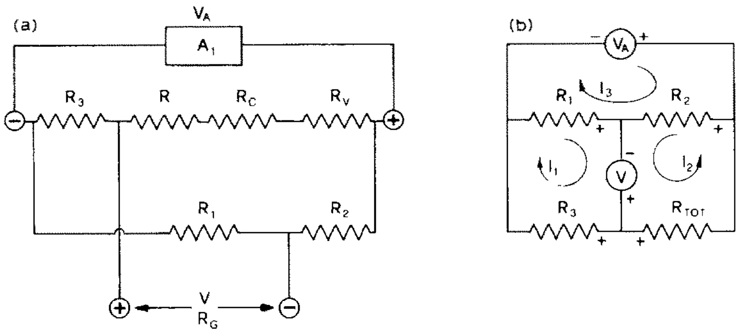

Fig. 2. (a) Thermistor bridge circuit. (b) Application of Kirchoff laws to the thermistor bridge.

The microprocessor used was a PC IBM model 5150 with a RAM of 512 kbyte. The printer used was an Epson RX80. The language used was BASIC.

The instantaneous power is measured by reading the calibration current I (by means of B) and the potential drop V (by means of C) of the calibration resistance R_H.

The Kirchoff laws allow us to write the following equations for the thermistor bridge (Fig. 2(b))

$$I_1 = (V + (I_3 \times R_1))/(R_3 + R_1) \tag{1}$$

$$I_2 = -(I_1 + (V/R_G)) \tag{2}$$

$$I_3 = V_a/(R_2 + R_1) \tag{3}$$

$$R_{tot} = (V + (I_3 \times R_2) - (I_2 \times R_2))/I_2 \tag{4}$$

$$R = R_{tot} - R_c - R_v \tag{5}$$

$$T_A = B/\lg(R/A) \tag{6}$$

$$T = T_A - 273.15 \tag{7}$$

In this way the voltage change between the terminals of the recorder is converted into the corresponding temperature change of the chemical reaction or electrical calibration expressed in degrees Celsius. This part is a subroutine of the program. T_E is the equilibrium temperature, i.e. the constant temperature T_∞, to which the calorimeter vessel will eventually approach [8].

PROGRAM DESCRIPTION

Refinement of the Wheatstone bridge parameters

In this part of the program the hypothesized conditions of perfect thermal equilibrium for the Wheatstone bridge $V = 0$ V and $R_v = 2500\ \Omega$ can be modified as a function of the experimental conditions.

Calibration curve

This allows us to calculate the temperature rise as a function of the time, dT/dt, during the electrical calibration. Although 100 voltage (V)–time (t) pairs can be taken, six points every 30 s are sufficient. However, it is necessary to choose these points after the transition period of heat conduction is completed. The time values increase with a quadratic function.

Curve of cooling (for electrical calibration and for exothermic reactions)

In this part of the program the K/C coefficent is calculated; a set of points taken during the cooling process can be interpolated with a least-squares analysis for the expression

$$T - T_\infty = (T_0 - T_\infty)e^{-(K/C)/(t-t_0)} \tag{8}$$

where K/C is the exponential coefficient [8]. From eqn. (8) the K/C term can be obtained as

$$K/C = -\ln[(T - T_\infty)/(T_0 - T_\infty)]/(t - t_0) \tag{9}$$

In eqn. (9) interpolation may be avoided and only two points considered. These, however, must be very precise. At least five pairs of V, t (following each other) every six minutes were taken (after the electrical calibration or the reaction effects were over). It is convenient to choose the K/C value related to the farthest pair of values. One hundred points can be obtained.

Reaction curve

This part carries out the following steps.

(a) The calculation of the temperature correction term $\Delta T = K/C\int_{t_0}^{t}(Tt - T_\infty)\,dt$ which holds because during the reaction the vessel temperature changes by virtue of the heat exchange with the surroundings [8].

(b) The calculation of the heat capacity using the expression $C = P_{cal}/[(dT/dt) + (K/C(T - T_\infty)]$ where P_{cal} is the instantaneous power (V_I).

(c) The calculation of the heat of reaction $Q = C(\Delta T_{obs} + \Delta T_{corr})$, the enthalpy of molar reaction, the enthalpy of molar reaction increase and the portion of the enthalpy of molar reaction increase due to the temperature correction term. The enthalpy of molar increase is a very useful parameter to identify the endpoint of the reaction. Up to 100 points for the pairs V, t can be taken.

THE PROGRAM

Instantaneous power

It is well-known that the method commonly used for determining the heat capacity is based on the supply of a known amount of energy during time t

across the heater resistance R_H. However, this method has two drawbacks.
(a) The energy supplied during t is not constant because the resistance values are a function of time.
(b) The transition periods of the heat conduction must be completed before measuring the temperature change ΔT. This requires longer measuring times, which, in turn, requires calculation of (by means of the integral) the heat dissipated. As previously shown, instantaneous power was used for the electrical calibration in this work. It is also convenient to use power ($V = 2.2$ V, $I = 0.040$ A) such that the temperature rise dT/dt may have a value of about 45 ° C. In this way it is possible to read the points with more precision.

Choice of K/C *value*

The correct choice of K/C values is necessary for correct calculation of the temperature correction term. As previously shown [8], it is possible to calculate two values for the K/C coefficient: one for the calibration cooling curve and another for the exothermic reaction cooling curve. These values are closely connected. We have observed [8] that for a "fast" reaction it is convenient to use the K/C value of the cooling calibration curve, while for a "slow" exothermic reaction that of the reaction cooling curve is more useful. We think that the two values of K/C should differ by no more than 4–5%. This usually occurs when the system reaches a perfect thermal equilibrium and if the reaction is sufficiently "fast"; hence speed of stirring plays a fundamental role.

Endpoint of reaction

The endpoint of the reaction is characterized by the change in sign for the values of the molar enthalpy of reaction increase. This point is easily read

TABLE 1

Molar enthalpy of reaction (ΔH) between solid tris(hydroxymethyl)aminomethane(tris) and 0.1 M HCl(sol) in water at 25 ° C

tris (mg)	$-\Delta H$ (kJ mol^{-1})
52.5	29.690
52.7	29.700
98.0	29.700
98.4	29.700
106.1	29.720
110.0	29.730
121.4	29.730
126.0	29.730
136.0	29.740
140.0	29.740
180.0	29.741
Mean	29.720 ± 0.006

for a "fast" reaction but is very difficult to read for a very "slow" reaction. Indeed, for the farthest points, the mathematical errors in the temperature correction term are larger than the corresponding heats. Furthermore, over a long period the conditions for thermal equilibrium would be changed so that the relation $K/C\int_{t_\infty}^{t}(T-T_\infty)\mathrm{d}t = -\Delta T_{\mathrm{obs}}$ would not apply [8]. For these reasons in the very "slow" reaction curves, misleading values for the endpoint may be obtained.

Reaction enthalpy program test

This reaction enthalpy program was tested by using a standard thermochemical reaction between solid tris(hydroxymethyl)aminomethane and 0.1 M HCl(sol) at 25 ° C in water. The value obtained (Table 1), 29.720 ± 0.006 kJ, was compared with that reported in the literature [9] (29.744 ± 0.003 kJ using a graphical procedure. The average deviation of the former relative to the latter is 0.08%.

CONCLUSIONS

One of the purposes of this work was to develop a program which allowed us to choose the "best" values of parameters such as K/C and the endpoint for a generic calorimetric reaction in solution. Such results are achieved if the system has reached a perfect thermal equilibrium.

APPENDIX

A BASIC computer program for calculating the heats of solution and reaction in a constant-environment calorimeter

```
7 N% = 100
8 DIM V#(N%),S#(N%),T#(N%)
9 CLS
12 REM *Values for parameter of thermistor circuit*
15 R1#=100.19:R2#=10.07:R3#=400111':RC#=.5:RV#=2500:VA#=4.555:RG#=4000000':A#=.01
7082:B#=3476.9
18 PRINT : PRINT
70 PRINT : PRINT TAB(10);"1 - calibration for the parameters of bridge"
130 PRINT : PRINT TAB(10);"2 - curve of calibration"
150 PRINT : PRINT TAB(10);"3 - curve of cooling"
160 PRINT : PRINT TAB(10);"4 - curve of reaction"
165 PRINT : PRINT TAB(10);"5 - end " : PRINT
170 LOCATE 23,16 :INPUT;"option(1-5)";OP%
180 IF OP% 1 OR OP% 5 THEN LOCATE 1,16  : PRINT CHR$(7);:GOTO 170
190 IF OP%=5 THEN CLS : END
200 ON OP% GOSUB 2000,3000,4000,5000
210 CLS:GOTO 70
2000 CLS
2010 LINE1$=" CR - acceptance of inserted parameter  "
2020 LINE2$=" D - to the previous question "
2030 GOSUB 30000
2035 PRINT :PRINT :PRINT
2040 PRINT "                PARAMETERS MODIFICATION "
2050 PRINT
2060 PRINT "  variable box resistance ";RV#;:INPUT A1N$ : GOSUB 50000
```

```
2072 ON SW GOTO 2090,15,2074
2074 RV#=VAL(AIN$)
2090 AIN$="" : PRINT "voltage of bridge at constant temperature";VC#;:INPUT AIN$
 : GOSUB 50000
2100 ON SW GOTO 2120,2060,2110
2110 VC#=VAL(AIN$)
2120 SCREEN 2 : RETURN
3000 PRINT :CLS:MV#=VC#
3010 GOSUB 15000
3020 TE#=T#
3030 GOSUB 20000
3040 FOR F%=1 TO I%
3050 MV#=V#(F%):GOSUB 15000:T#(F%)=T#-TE#
3060 NEXT
3070 SX#=0#:SX2#=0#:SXY#=0#:SY#=0#
3072 LPRINT "a=";A#,"b=";B#
3075 LPRINT"VOLT";TAB(20);"SECONDS";TAB(40);"TEMPERATURE"
3080 FOR F%=1 TO I%
3090 LPRINT V#(F%);TAB(20) S#(F%);TAB(40);:LPRINT USING"##.########";T#(F%)
3100 SX#=SX#+S#(F%)
3110 SX2#=SX2#+S#(F%) 2#
3120 SXY#=SXY#+S#(F%)*T#(F%)
3130 SY#=SY#+T#(F%)
3140 NEXT F%
3150 A1#=(I%*SXY#-SX#*SY#)/(I%*SX2#-SX# 2)
3160 LPRINT
3170 LPRINT "dT/dt =";A1#
3173 TT#=SY#/I%
3175 LPRINT "temperature average of the calibration =";TT#
3180 RETURN
4000 PRINT : CLS
4010 MV#=VC
4020 GOSUB 15000
4030 TE#=T#
4040 GOSUB 20000
4045 LPRINT "temp at const. =";TE#,"var res =";RV#,"bridge volt. =";VC#
4047 LPRINT "pair";TAB(10);"volt";TAB(30);"seconds";TAB(50)"delta T":LPRINT
4050 FOR F%=1 TO I%
4060 MV#=V#(F%):GOSUB 15000:T#(F%)=T#-TE#
4070 LPRINT F%;TAB(10);V#(F%);TAB(30);S#(F%);TAB(50);:LPRINT USING "##.########"
;T#(F%)
4080 NEXT
4090 LPRINT :LPRINT "pair";TAB(20);"F/C":LPRINT
4100 SUM#=0#:ACCOUNT%=0
4110 FOR F%=1 TO I%-1
4120 FOR L%=F%+1 TO I%
4130 FSC#=1#/(S#(F%)-S#(L%))*LOG(T#(L%)/T#(F%))
4140 LPRINT F%;" -";L%;TAB(20);:LPRINT USING "##.###########";FSC#
4150 SUM#=SUM#+FSC#:ACCOUNT%=ACCOUNT%+1
4160 NEXT
4170 NEXT
4180 LPRINT :LPRINT "F/C mean =";SUM#/ACCOUNT%:LPRINT
4190 RETURN
5000 PRINT : CLS
5010 MV#=VC#
5020 GOSUB 15000
5030 TE#=T#
5040 GOSUB 20000
5050 INPUT "F/C =";FSUC#
5052 INPUT "number of mol. =";MOLI#
5053 INPUT "calibration current (mA)=";CURRTAR#
5054 INPUT "calibration voltage (volt) =";VOLTTAR#
5055 POT#=VOLTTAR#*CURRTAR#/1000#
5056 C#=POT#/(A1#+FSUC#*TT#)
5058 LPRINT "temp at const  =";TE#,"var res =";RV#,"bridge volt. =";VC#,"F/C =";
FSUC#:LPRINT "thermic capacity =";C#,"calibration val. =";VOLTTAR#,"calibration
curr.=";CURRTAR#,"moli";MOLI#
5059 LPRINT :LPRINT
5060 LPRINT "pair";TAB(10);"volt";TAB(30);"seconds";TAB(50)"delta T ":LPRINT
5070 FOR F%=1 TO I%
5080 MV#=V#(F%):GOSUB 15000:T#(F%)=T#-TE#
5090 LPRINT F%;TAB(10);V#(F%);TAB(30);S#(F%);TAB(50);:LPRINT USING "##.########"
;T#(F%)
5100 NEXT
5110 INTEGRAL#=0#
5112 VDH#=0#
5115 LPRINT :LPRINT "from point 1 to....";TAB(28);"DELTA H";TAB(60);"DELTA H inc
r.";TAB(100)"(DELTA H CORRECTIVE INCR.)":LPRINT
```

```
5120 FOR K%=2 TO I%
5130 INCRINT#=(S#(K%)-S#(K%-1))*((T#(K%)+T#(K%-1))/2#)
5131 INTEGRAL#=INTEGRAL#+INCRINT#
5132 DELTAT#=T#(K%)-T#(1)
5133 DH#=(DELTAT#+FSUC#*INTEGRAL#)*(C#/(MOLI#*1000#))
5134 IDH#=DH#-VDH#
5135 VDH#=DH#
5136 IDHC#=FSUC#*INCRINT#*C#/(MOLI#*1000#)
5140 LPRINT TAB(8) K%;TAB(20);:LPRINT USING "########.########";DH#;
5145 LPRINT TAB(60);:LPRINT USING "#####.########";IDH#;
5150 LPRINT TAB(100);:LPRINT USING "#####.########";IDHC#
5160 NEXT
5170 PRINT :INPUT "do you want repeat the calculus by changing the parameters
            (y/n)";SI$
5180 IF SI$="Y" OR SI$="y" GOTO 5050
5190 IF SI$  "N" AND SI$  "n" GOTO 5170
5200 RETURN
15000 REM * conversion MV# to T# *
15010 V#=MV#/100000#
15020 I3#=VA#/(R2#-R1#)
15030 I1#=(V#+I3#*R1#)/(R3#+R1#)
15040 I2#=-I1#-V#/R0#
15050 RTOT#=(V#-I3#*R2#-I2#*R2#)/I2#
15060 R#=RTOT#-RC#-RV#
15070 TA#=B#/(LOG(R#/A#))
15080 T#=TA#-273.15#
15090 RETURN
20000 CLS
20030 LINE1$=" D - return to the previous question":LINE2$=" F - introduction en
d":GOSUB 30000
20035 PRINT :PRINT
20040 PRINT "VOLT-TIME PAIRS INTRODUCTION (MAX"N%" PAIRS)":PRINT
20050 I%=0
20060 I%=I%+1
20070 PRINT "voltage (hundredths of mv) number";I%;:INPUT AIN$ : GOSUB 40000
20080 ON SW GOTO 20090,20100,20110,20120
20090 I%=I%-1 : IF I%=0 THEN 20060 : GOTO 20130
20100 I%=I%-1 : GOTO 20154
20110 PRINT CHR$(7) : GOTO 20070
20120 V#(I%)=VAL(AIN$)
20130 AIN$="" : PRINT"time(seconds)                   number";I%;:INPUT AIN$ : PRINT : G
OSUB 40000
20135 ON SW GOTO 20070,20140,20140,20150
20140 PRINT CHR$(7) : GOTO 20130
20150 S#(I%)=VAL(AIN$)
20152 IF I% N% THEN 20060
20153 SCREEN 2
20154 CLS
20158 PRINT : PRINT
20160 PRINT " 1 - data print "
20170 PRINT " 2 - data modification "
20190 PRINT " 3 - data introduction finish "
20210 PRINT
20220 INPUT "option (1-3)";OP%
20230 IF OP% 1 OR OP% 3 THEN GOTO 20220
20240 IF OP%=3 THEN RETURN
20250 ON OP% GOSUB 20270,20320
20260 GOTO 20154
20270 LPRINT "pair" TAB(20)"voltage"TAB(40)"time":LPRINT
20280 FOR K%=1 TO I%
20290 LPRINT K%;TAB(20)V#(K%);TAB(40) S#(K%)
20300 NEXT
20310 RETURN
20320 CLS
20330 LINE1$="CR - acceptance of the inserted parameters":LINE2$=" R - return t
o previous menu'":GOSUB 30000
20335 PRINT :PRINT
20340 PRINT "                 DATA MODIFICATION".PRINT
20350 INPUT "pair which must be modified";C%
20360 IF C% I% OR C% 1 GOTO 20350
20380 PRINT "pair voltage";C%;" =";V#(C%);:INPUT AIN$ : GOSUB 60000
20390 ON SW GOTO 20410,20154,20400
20400 V#(C%)=VAL(AIN$)
20410 PRINT "pair time";C%;" =";S#(C%);:INPUT AIN$ : GOSUB 60000
20420 ON SW GOTO 20350,20154,20430
20430 S#(C%)=VAL(AIN$)
20440 PRINT :GOTO 20350
30000 REM **************************************************
```

```
30010 REM the subroutine open a window of three lines in the
30020 REM lower video (64x16) place and print upon the
30030 REM contents of LINE1$ and LINE2$
30040 REM ************************************************
30060 SCREEN 2:CLS
30070 PRINT
30080 PRINT TAB(3) LINE1$ : PRINT TAB(3) LINE2$
30090 LINE(0,0)-(552,30),,B
30100 RETURN
30110 SCREEN 2
40000 SW=0 : IF AIN$="D" THEN SW=1 : RETURN
40005 IF AIN$="F" THEN SW=2 : RETURN
40010 IF AIN$="" THEN SW=3 : RETURN
40015 SW=4 : RETURN
50000 SW=0 : IF AIN$="" THEN SW=1 : RETURN
50010 IF AIN$="D" THEN SW=2 : RETURN
50020 SW=3 : RETURN
60000 SW=0 : IF AIN$="" THEN SW=1 : RETURN
60010 IF AIN$="R" THEN SW=2 : RETURN
60020 SW=3 : RETURN
```

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