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ACQUISITION AND NUMERICAL ANALYSIS OF THERMOANALYTICAL DATA BY MICROCOMPUTER, APPLIED TO AN EXISTING FLOW MICROCALORIMETER

W.G. JONES, A.C. NORRIS and M.I. POPE

Department of Chemistry, Portsmouth Polytechnic, St Michael's Building, White Swan Road, Portsmouth, Hants PO1 2DT (Gt. Britain)

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ABSTRACT

Many scientists will possess accurate and reliable thermoanalytical instruments which, while perfectly satisfactory, lack the means of data acquisition and numerical analysis made possible by modern microcomputers. Often the cost of updating such apparatus to the latest standard by means of manufacturers dedicated modules is prohibitive, relative to the modest price of microcomputers now available.

This paper describes the application of a microcomputer to a flow microcalorimeter. However, essentially the same approach can readily be modified for use with other thermochemical techniques, or indeed any instrumentation producing its output in the form of a peak.

INTRODUCTION

Many modern scientific instruments produce their data in analogue form, appearing as a curve or peak on a potentiometric chart recorder. Here we are concerned primarily with flow microcalorimetry (FMC), where appearance of a peak confirms that some thermal effect has occurred in the "reaction cell". In order to obtain useful information from the recorded data, various characteristics of the peak need to be evaluated; these may include position of the peak, peak height, area, slope of the leading edge, retention times, etc.

In the past such measurements have been made manually, but the advent of modern automatic integrators, etc., has rendered this approach obsolescent. Today, evaluation of experimental data is generally carried out by computer. The application of computers in this way is by no means new, the major fields of use being chromatography [1] and spectroscopy [1,2], where the concepts of data acquisition and peak detection, etc., are well established.

In order to use computers for analysis of the data produced by the instrumentation in question, it has firstly got to be transferred from the

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instrument to the computer. This can be achieved directly by use of data transmission lines, or the information can be stored on paper, magnetic tape, or a disc, before subsequently being read back into the computer. A third and least satisfactory method is to type in data from the chart recorder, using the computer keyboard. Problems in applying the first two approaches may arise through:

(a) additional specialised equipment may be required, even if direct transfer of data is feasible, and
(b) all transferred or stored data are susceptible to corruption, which may mean that the data are irretrievably lost.

While the third method does not suffer from either of the foregoing problems, it is still prone to operator error and is time-consuming to perform.

Today, with the advent of desk-top microcomputers and the wide range of transducers that can be interfaced with them, it is possible to read the signal produced by experimental apparatus, carry out all data manipulation, such as integration, etc., and analyse the data within the confines of one machine. The software required to do this, if not readily available, can be developed to meet the precise needs of the user. Conversion to such a system carries a number of advantages for the user, viz:

(a) modern methods of data acquisition and analysis are more sensitive, better defined and certainly more accurate than those used previously;
(b) the process of transferring the data prior to analysis and actual analysis of the data can be carried out immediately, avoiding the need to transfer data to another machine;
(c) since the results are available immediately, the experiment can be monitored while in progress and the experimental procedure modified as desired, in the light of information already obtained.

The combined effect of these advantages is to present the user with more reliable and precise data, in a shorter time. Any need for further numerical analysis may be avoided, leaving the scientist free to devote his time to evaluating the significance of the results obtained.

The major disincentives to carrying out such a conversion lie in:

(a) problems associated with the interfacing of the computer to the instrument, and
(b) producing and testing the relevent software required to obtain and process the data output of the instrument.

These problems occur at the outset of the conversion process and tend to act as a barrier to computerisation of the procedures for gathering and manipulation of experimental data. Another barrier can be the initial cost of either buying new digital versions of the instrument in question, or up-grading the existing equipment with the manufacturers dedicated and often expensive modules, assuming of course that such options exist.

This paper describes the interfacing of a flow microcalorimeter (FMC) to a computer via an analogue-to-digital converter (A/DC), and the development of the software required to transform the acquired data into conventional physicochemical parameters, from which the computer can construct either:

(a) the differential heat of adsorption isotherms, or
(b) the conventional adsorption isotherm,

as well as giving information on the reversibility of the adsorption/desorption processes.

The software was developed "in house", resulting in two major advantages compared with either replacement, or upgrading, of the equipment. Firstly, the data can be manipulated so as to produce precisely the information required; secondly, the results can be output in the format desired by the user.

One problem with replacement or upgrading is that the extent of data analysis may prove insufficient, thereby necessitating further computation, probably on a different machine. In addition, the format in which the data are presented may not be ideally suited to the particular needs of the user, and may well prove difficult to modify.

CALCULATION OF PEAK AREA BY ON-LINE INTEGRATION AND DETERMINATION OF RETENTION TIMES

Essentially only one type of measurement can be made with a calorimeter, that of the evolution or absorption of heat. This is also true of the FMC, but because it uses a flow system, the instrument can be operated in a way similar to that of a gas chromatograph, thereby allowing retention times to be determined.

Now, the output of the calorimeter is recorded in the form of a peak on the chart recorder; the properties of the peak required for making measurements of the heat evolved/absorbed and retention times are the peak area and the time taken from introduction of an adsorbate into the system to peak onset, respectively.

In order to use a computer to obtain these figures, three pieces of information are required; they are the time of:

(i) peak onset,
(ii) peak termination, and
(iii) instructions for calculating the peak area from incoming data.

BASELINE ANALYSIS, PEAK ONSET AND TERMINATION DETECTION

A peak is a controlled deviation away from a pre-determined standard position which eventually returns to that standard position. Therefore in

```
SR = 0
SS = 0
TINC = TIME INCREMENT CALCULATED FROM SAMPLE RATE
TIME = 0
FOR $i = 1$ TO $n$ DO
   TIME = TIME + TINC
   CHECK IF TIME FOR NEXT READING IF NOT THEN WAIT
   READ SIGNAL VALUE $r_i$
   SUM SIGNAL VALUES SR = SR + $r_i$
   IF $i > 1$ THEN
      CALCULATE SLOPE OF LINE AND SUM VALUES SS = SS + $(r_i - r_{i-1})/3$
   END IF
END FOR $i$
CALCULATE AVERAGE SLOPE $\bar{s}$ = SS/$(n-1)$
CHECK VALUE OF $\bar{s}$ ACCEPTABLE ($|\bar{s}| \leqslant 0.05$) IF NOT THEN REPEAT CALCULATIONS
CALCULATE AVERAGE BASELINE $\bar{b}$ = SR/$n$
```

Scheme 1. Calculation of average baseline and slope algorithm.

order to detect a peak a standard point of reference is required; in experimental work this is defined to be the "baseline".

In the present work the average value of the baseline and its average slope are calculated from fifty readings *, taken at constant time intervals, from the FMC output signal using the following equations:

$$\bar{b} = \left(\sum_{i=1}^{n} r_i \right) / n \tag{1}$$

$$\bar{s} = \left[\sum_{i=2}^{n} (r_i - r_{i-1})/3 \right] / (n-1) \tag{2}$$

where $\bar{b}$ is the value of the average baseline, $\bar{s}$ the average slope of the line, r_i the current input value and n is the number of readings taken (in our case fifty). The complete algorithm is shown in Scheme 1.

The average value of the baseline, $\bar{b}$, is accepted providing that the average slope of the base line, $\bar{s}$, is within the acceptable threshold limits, i.e. $-0.05 \leqslant \bar{s} \leqslant 0.05$; if it falls outside these limits then the whole process is repeated. The threshold value of 0.05 was determined experimentally, its purpose being to ensure that the baseline is "flat" and contains minimum drift, thereby allowing a fairly consistent standard point of reference for use in peak detection, etc.

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* The number of points read is a function of the data acquisition rate given by $n = 25d_a$, where d_a is the data acquisition rate in Hz.

Having obtained a standard reference point, all readings taken from then on are referenced to zero by subtracting the value for the average baseline from the value read in.

The process of peak onset detection involves monitoring the change in the slope of the baseline between consecutive points. If three consecutive values of this slope are greater than the threshold value of 0.05 then the onset of a peak has been detected. This is acceptable providing that the baseline is effectively noise-free and there is no possibility of a slight negative deflection prior to the main peak. To cater for either eventuality, two additional criteria are used in testing for peak onset; they are that the deflection must be in a positive direction and that the deflection must exceed an experimentally determined value, known as the critical peak height (a value between 5 and 10 mV in a full scale deflection of ±10 V has been found satisfactory in our present work).

So overall, in order for peak onset to be established the following criteria have to be satisfied:

(a) the values of three consecutive slopes must exceed the experimentally determined threshold value of 0.05;
(b) the deflection from the baseline must be greater than the critical peak height; and
(c) the deflection must be in the positive direction.

The peak integration routine is initiated only when all three criteria are satisfied, confirming that peak onset has occurred.

The criteria used for peak termination detection are the converse of those given in (a) and (b) above, i.e. that:

(a) the values of three consecutive slopes must not exceed the threshold value of 0.05; and
(b) the deflection from the baseline must not exceed the critical peak height.

DETERMINATION OF RETENTION TIMES

Retention time is a term more generally associated with chromatography and related techniques; here retention time is taken as being a measure of the time difference between the start of the run and the point where a perpendicular, dropped from the apex of the peak, intersects the baseline.

In the case of FMC, however, the above method for determination of retention times is not applicable because of the experimental procedure used. Instead the retention time is taken as being the time period between the start of the run and peak onset. Therefore unlike the process of peak integration, where both peak onset and peak termination must be detected, only peak onset detection is required for the determination of retention time.

As described earlier, data are read from the FMC at regular fixed time intervals; therefore in order to determine the retention time, all that has to be done is to record the time of the last datum point read, after satisfying the criteria for peak onset detection. However, because of the way in which the peak onset detection algorithm works, the time recorded will be four time intervals after the actual time of peak onset. The reason for this is that three consecutive values of the slope must be greater than the threshold value in order to satisfy one of the criteria for peak onset detection, the slopes being calculated in the following way:

$$S_1 = (r_{i-3} - r_{i-4})/3 \qquad (3a)$$

$$S_2 = (r_{i-2} - r_{i-3})/3 \qquad (3b)$$

$$S_3 = (r_{i-1} - r_{i-2})/3 \qquad (3c)$$

S_1, S_2 and S_3 are the three consecutive slopes greater than the threshold value and the r_{i-1} to r_{i-4} are the last four data points read, so the peak actually started when point r_{i-4} was read, four time intervals behind the current value being read (r_i). The calculated retention time, t_r, is therefore given by:

$$t_r = t - (4t_i) \qquad (4)$$

where t is the time of peak onset detection and t_i the time increment between readings. The timing function itself is derived from the internal clock of the computer.

ON-LINE NUMERICAL INTEGRATION OF PEAK AREA

There are several methods of calculating the area under a peak, or curve, numerically, a discussion of which can be found elsewhere, e.g. in the books by Phillips and Taylor [3] and by Rice [4].

One of the methods available for integration is Simpson's rule, given by the general equation:

$$A = h/3 \ \ y_0 + y_n + 4\sum_{i=1}^{n-1} y_i + 2\sum_{j=2}^{n-2} y_j \qquad (5)$$

where A is the area calculated over $n+1$ data points (y_0 through y_n), h is the incremental step between data points and the increment steps for the indices i and j are both 2. This equation was chosen for its high degree of accuracy and its ease of coding, as can be seen by expanding the above equation into the form normally used numerically.

$$A = h/3(y_0 + 4y_1 + y_2) + h/3(y_2 + 4y_3 + y_4) + \ldots$$
$$+ h/3(y_{n-2} + 4y_{n-1} + y_n) \qquad (6)$$

```
        SET SLOPES 1, 2 AND 3 TO ZERO $S_1 = 0$ $S_2 = 0$ $S_3 = 0$
        SET PEAK TERMINATION FLAG FL = 3
        SET LOOP COUNTER TO ZERO $n = 0$
        SET PEAK DETECTED FLAGS TO ZERO PEAK = 0 PEAK2 = 0
        SET TIME INCREMENT BETWEEN READING $T_i$ AND TIME OF NEXT READING $T$ TO ZERO
        $T_i = 0$ $T = 0$
        RESET CLOCK TO ZERO TIME = 0
1       INCREMENT LOOP COUNTER $n = n + 1$
        CALCULATE TIME OF NEXT READING $T = T + T_i$

2       CHECK IF TIME FOR NEXT READING IF NOT THEN WAIT IF TIME $< T$ THEN GOTO 2
        READ SIGNAL $r_n$
        REFERENCE SIGNAL TO ZERO BY SUBTRACTING AVERAGE BASELINE VALUE $r_n = r_n - \bar{b}$
        CALCULATE SLOPE $S_3 = (r_n - r_{n-1})/3$

        CHECK IF PEAK HAS ALREADY BEEN DETECTED IF PEAK = PEAK2+1 THEN GOTO 3

        CHECK FOR NEGATIVE DEFLECTION IF $r_n < 0$ THEN GOTO 6
        CHECK IF DEFLECTION GREATER THAN CRITICAL PEAK HEIGHT $C_p$ IF $r_n < C_p$ THEN GOTO 6
        CHECK FOR THREE SLOPES GREATER THAN THRESHOLD VALUE TH
        IF $S_3 <$ TH THEN GOTO 6
        IF $S_2 <$ TH THEN GOTO 6
        IF $S_1 <$ TH THEN GOTO 6
        PEAK DETECTED, INCREMENT PEAK PEAK = PEAK+1
        INCREMENT NUMBER OF PEAKS NP = NP+1
        BRANCH ON EXPERIMENT TYPE IF TYPE < > 3 THEN GOTO 3
*       STOP CLOCK AND CALCULATE RETENTION TIME $T_r$
        $T_r = T - 4 \times T_i$
        GOTO 4

3 **    CALCULATE PEAK AREA $A = A + T_i/3 \times (r_{n-6} + 4 \times r_{n-5} + r_{n-4})$

        CHECK IF DEFLECTION LESS THAN CRITICAL PEAK HEIGHT $C_p$ IF $r_n > C_p$ THEN GOTO 5
        CHECK FOR THREE SLOPES LESS THAN THRESHOLD VALUE TH
        IF $S_3 >$ TH THEN GOTO 5
        IF $S_2 >$ TH THEN GOTO 5
        IF $S_1 >$ TH THEN GOTO 5

4       FL = 1
***     CHECK FOR DESORPTION PEAK IF EXPECTED
        IF TYPE < > 4 THEN GOTO 3
        CHECK IF ALREADY IN DESORPTION PEAK
        IF PEAK2 = 1 THEN GOTO 5
        START OF DESORPTION PEAK SET UP PARAMETERS
        PRESERVE AREA OF ADSORPTION PEAK A1 = $A$
        INCREMENT PEAK AND PEAK2 PEAK = PEAK+1 : PEAK2 = 1
        CHANGE PEAK TERMINATION FLAG FL = 2
```

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5    TERMINATE PEAK IF FL = 1 IF FL = 1 GOTO 7

6    UPDATE SLOPES $S_1 = S_2 : S_2 = S_3$
     NEXT LOOP GOTO 1

7    CALCULATION OF DATA REQUIRED FOR REPORT ON EACH PEAK
```

NOTE and SEE LATER:

EXPERIMENTAL TYPE
1 CALIBRATION OF INSTRUMENT
2 MEASUREMENT OF DIFFERENTIAL HEAT OF ADSORPTION ISOTHERM
3 MEASUREMENT OF STANDARD ADSORPTION ISOTHERM
4 COMPARISON OF ADSORPTION/DESORPTION PROCESSES

* Only required for experiments concerned with measurement of adsorption isotherms by retention time, i.e. TYPE 3.

** Required by all experiments measuring quantity of heat released or absorbed, i.e. TYPE 1, 2 and 4.

*** Allows for continuous integration of the combined adsorption/desorption peaks produced by TYPE 4 experiments.

Scheme 2. Algorithm for peak detection and integration.

It is this form of the equation that is implemented within the integration routine given here. The actual equation used is:

$$A = \text{“}A\text{”} + t/3(r_{n-6} + 4r_{n-5} + r_{n-4}) \tag{7}$$

where the initial value of A is zero, r_n is the current FMC reading and t is the time interval between readings.

The complete algorithm for peak onset detection, peak termination detection, retention time determination and peak area integration is given in Scheme 2.

MEASUREMENT OF THE DIFFERENTIAL HEAT OF ADSORPTION AND ADSORPTION ISOTHERMS, TOGETHER WITH COMPARISON OF THE ADSORPTION/DESORPTION PROCESSES

The differential heat of adsorption isotherm and the actual isotherms are produced from data related to the peak areas and retention times, respectively. Before such data can be calculated for the differential heat of adsorption isotherm, it is necessary to calibrate the calorimeter, in order to convert the proportionality between peak area (A) and heat released (H) during the adsorption process into an

$$A \propto H \tag{8}$$

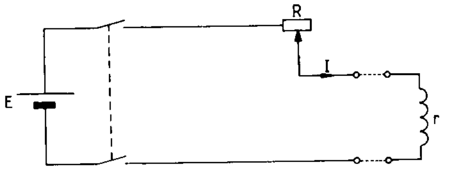

Fig. 1. Calorimeter calibration circuit.

equality. In theory a first order linear relationship passing through the origin should exist between A and H i.e.

$$A = kH \tag{9}$$

no intercept term is included because if no heat is evolved then a peak will not be produced.

Hence we may evaluate k using the following equation [5]:

$$k = \sum_{i=1}^{n} AH \Big/ \sum_{i=1}^{n} H^2 \tag{10}$$

where n is the number of data sets. The term k is the calibration constant for the instrument and allows the area under the peaks on the chart recorder to be converted to quantities of heat evolved or absorbed within the measurement cell.

The heat used to produce the calibration curve for the calorimeter is generated by passing a current I though a calibration coil of resistance r situated in the cell, at a potential E supplied by a dry cell battery. The magnitude of the current flowing can be adjusted by a variable resistor of resistance R. The battery, variable resistor and calibration coil constitute the calibration circuit of the calorimeter (see Fig. 1).

From Ohm's Law the current flowing, I, is given by

$$I = E/R' \tag{11}$$

where R' is the total resistance of the circuit $(R + r)$. Therefore the quantity of heat liberated per second via the calibration coil is w watts (or Js); given by

$$w = I^2 r \tag{12}$$

substituting for I from eqn. (11) gives

$$w = E^2/(R')^2 \times r \tag{13}$$

Energising the coil for t seconds liberates H joules given by

$$H = wt = E^2/(R')^2 \times rt \tag{14}$$

and converting the units of H to millijoules gives

$$H = 1000 \times trE^2/(R')^2 \tag{15}$$

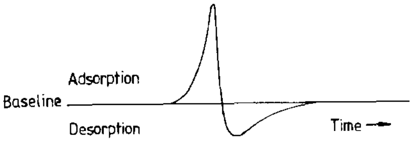

Fig. 2. A typical peak produced in the pulse mode of operation.

Known quantities of heat can therefore be liberated in the cell by varying the time, t, for which the circuit is energised, giving rise to a set of data consisting of measured peak areas and known quantities of heat, from which k (eqn. 10) can be determined.

MODES OF OPERATION

The calorimeter can be operated in either of two modes, the first referred to as PULSE ADSORPTION and the second EQUILIBRIUM ADSORPTION, a variation of which is used for determination of retention times.

In the pulse mode, known volumes of solution are injected into the flowing carrier fluid and the heats evolved and absorbed during the adsorption/desorption process are recorded, the peak format being similar to that shown in Fig. 2.

Operation of the instrument in the equilibrium mode involves passing solutions of increasing concentration over the adsorbent and determining the additional heat evolved with every increase in concentration of the adsorbate, thereby producing a series of peaks of the form shown in Fig. 3.

Retention times are determined by the same method, except that adsorption occurs in a cell external to the instrument, the instrument being used as a very sensitive detector. An adsorbent of low surface area (less than 0.05 m^2 g^{-1}) is used in the FMC cell to determine the time, t_0.

CALCULATIONS BASED ON DATA OBTAINED FROM EQUILIBRIUM ADSORPTION EXPERIMENTS

The differential heat of adsorption isotherm can be constructed by plotting the integral heat of adsorption I_h, at solution concentration c,

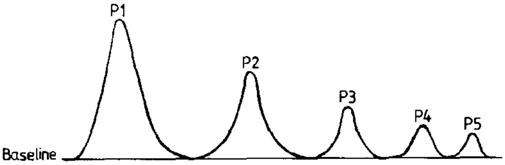

Fig. 3. A typical series of peaks produced in the equilibrium mode of operation.

against the solution concentration. The value of I_h for the nth solution of concentration $c(n)$ is calculated using the following expression

$$I_h(n) = \sum_{i=1}^{n} H(i) \tag{16}$$

where $H(i)$ is the heat evolved during adsorption from the ith solution of concentration $c(i)$.

In our work with the FMC it was found that the isotherm obtained by this method corresponded to type L2 of the Giles' classification [6], i.e. a Langmuir isotherm, the general equation for which is

$$\theta = bc/1 + bc \tag{17}$$

where θ represents the fraction of the total amount of heat liberated by monolayer formation, at concentration c, i.e. $\theta = H/H_m$. H_m is the heat of monolayer formation and b a constant. Substitution for θ therefore gives

$$\frac{H}{H_m} = \frac{bc}{1 + bc} \tag{18}$$

Rearrangement produces the following equation and provides a means for calculating the value of H_m [7–9]

$$c/H = c/H_m + 1/bH_m \tag{19}$$

A plot of c/H against c should therefore give a straight line graph of slope $1/H_m$ and intercept $1/bH_m$ on the ordinate, so that the heat of monolayer formation can be calculated.

CALCULATIONS BASED ON DATA OBTAINED FROM RETENTION TIME DETERMINATIONS

The data available from such determinations consist of solution concentrations c and corresponding retention times t_r. Using these two pieces of information and the following equation allows the mass of adsorbate taken up to be calculated.

$$x = t_r \times F \times c/m \tag{20}$$

where F is the flow rate of the solution (cm^3 min^{-1}) and m is the mass of adsorbent (g) in the external cell.

Analysis of these data via an equation of the same form as (19) i.e.

$$c/x = c/x_m + 1/ax_m \tag{21}$$

allows x_m, the mass of adsorbate required for monolayer formation, per gram of adsorbent, to be calculated. By plotting the integral mass of adsorbate taken up against solution concentration $c_1 - c_n$ the adsorption isotherm can be constructed.

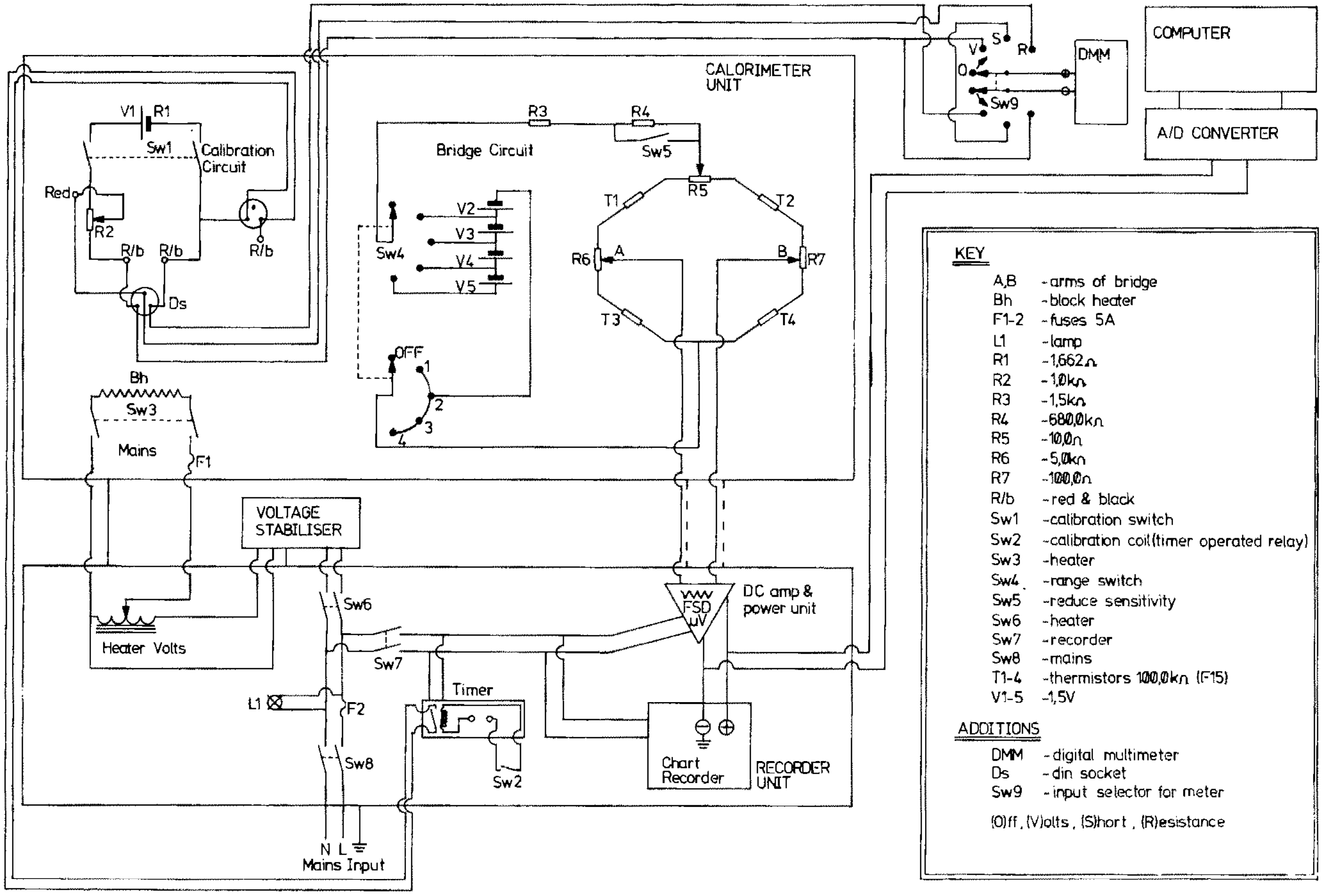

Fig. 4. Circuit diagram of calorimeter with interfaced computer and digital timer.

CALCULATIONS BASED ON DATA OBTAINED FROM PULSE ADSORPTION EXPERIMENTS

The area under the adsorption peak is due to the preferential adsorption of the adsorbate onto the adsorbent surface by displacing the carrier fluid already present. Hence the peak area provides a direct measure of the heat of preferential adsorption.

The only calculation that can be made on-line is the difference between the quantities of heat evolved and absorbed during the adsorption/desorption process, thereby giving an indication of sorption reversibility.

However, it is possible to calculate thermodynamic data from the results of pulse adsorption experiments, as described by Groszek [10] in his paper "Heat of preferential adsorption from liquid mixtures". While it is not impossible to carry out such calculations in on-line mode, they are better suited to manual evaluation after all the experimental data have been accumulated.

THE APPARATUS USED

A schematic diagram of the major components of the system is shown in Fig. 4. These comprise:

(i) The flow microcalorimeter and its built in recorder/amplifier; the calorimeter is a Microscal Mark II model supplied by Microscal Ltd., London.

(ii) The analogue-to-digital converter; this is a 'PUPI' A-D converter supplied by CIL Microsystems Ltd., Worthing, Sussex.

(iii) The computer, a Commodore 4000 series PET, actually a 4016 machine with 16k bytes of RAM. The computer is also linked to an SFD1001 single disc drive, C2N cassette recorder and a 4023 dot matrix printer, all by Commodore.

The other items required by the system are:

(i) a digital multimeter, and

(ii) a universal digital timer.

The latter are used during the calibration of the calorimeter to ensure the required accuracy in measurement of cell voltage (E), coil resistance (r) and current control resistance (R); also to enable the circuit to be energised for a known and reproducible period of time.

CONCLUSION

This paper explains how a relatively cheap microcomputer can be linked to existing apparatus which provides its output in analogue form on a potentiometric chart recorder. The algorithms used to enable on-line calculation of the position of peak onset, peak termination, peak areas and retention times are described. Although our work is primarily concerned with flow microcalorimetry, the principles used could readily be applied to other thermoanalytical techniques, such as DTA.

Further details of the software used in this work can be obtained from Mr. W.G. Jones.

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