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Note

A PROGRAMMABLE, PORTABLE, LOW-COST MICROCOMPUTER DATA ACQUISITION SYSTEM FOR A CALORIMETER [1]

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The manual analysis of the thermogram obtained from a titration calorimeter such as a Tronac 450 is tedious and subject to human error. These disadvantages can be eliminated or significantly reduced with the use of a computer data acquisition system. An economical approach to computer data acquisition has been provided through the development of microprocessors and associated integrated circuits. A microcomputer data acquisition system is discussed for use with a titration calorimeter but it can be adapted to any experimental system where there is a variation of voltage as a function of time. The data acquisition system collects data from the experiment, then stores the data in the computer memory. After the experiment is complete the data is exported to a mainframe computer for processing by FORTRAN language programs.

EXPERIMENTAL DESIGN

In the design of the data acquisition system several general guidelines were considered. It was desirable to (1) make maximum use of existing equipment, (2) keep computer hardware development time to a minimum, (3) maximize the use of any purchased computer hardware, (4) eliminate interfacing to the computer bus, if possible, and (5) provide a data acquisition system flexible enough to be interfaced to other instrumentation. There were some specific design considerations. These were to (1) store the data in memory as it was collected, (2) export the data to a time-sharing system via phone lines, and (3) structure the software such that the non-computer oriented user would be prompted at each appropriate step.

The existing equipment was a Tronac model 450 calorimeter, a Hewlett—Packard (HP) model 3490A digital multimeter (DMM), and a Rolla Engineering and Development (R.E.A.D.) model 400 digital clock. The clock and DMM have transistor—transistor logic (TTL)-level input lines for instrument control and TTL-level parallel binary coded decimal (BCD) outputs. This provided for rapid interface to a computer system that has TTL-level parallel input/output (I/O) capability. Although we used the above clock and DMM, any digital clock and digital voltmeter can be used as long as it has the appropriate TTL-level input and output signals.

In order to meet the above guidelines with respect to the data acquisition system, an Intel SBC 80/10 microcomputer prototype system and SBC 116 memory-I/O expansion board were chosen. These boards provided the necessary parallel I/O lines (96 total) for interfacing the clock, DMM and interface board. These boards also provided the necessary memory to store the programs and the data. The SBC 116 board provided an interval timer which was used to determine the approximate time interval between each point to be taken. Because the buret and heater on/off events are asynchronous, it is not possible to use the interval timer as a clock. The SBC 116 board also provided a serial I/O port that was connected to a mainframe via a modem-phone line combination. The cost for the SBC 80/10 prototype system and SBC 116 was under $ 2000.

As anticipated, a significant part of the development time was spent in writing the necessary assembly language software for the microcomputer system. The software development was greatly facilitated by the SBC 80/10 prototype system monitor and cross-assembler *.

A block diagram of the data acquisition system is shown in Fig. 1. Switches on the front panel provide for (1) resetting of the computer, (2) determining if the start/hold sequence for the clock is to be controlled by the microcomputer or the switches on the calorimeter, and (3) starting and stopping of the data collection. The calorimeter provides information to the interface on the status of the buret and heater on/off switches. Also, the calorimeter provides an analog signal (which is proportional to temperature in the reaction vessel) to the DMM. The interface routes the signal (buret or heater on/off) and provides this information to the clock or the microcomputer as determined by a switch on the front panel. With the appropriate initialization of the front panel switches and the data collection program, the microcomputer causes the DMM to sample the calorimeter bridge voltage. After the analog-to-digital conversion is complete, the digital clock is sampled. This digital information is stored in the microcomputer memory. The sampling process is repeated at time intervals specified by the user. At each event of the buret or heater being turned on or turned off, the microcomputer samples the clock and this information with an appropriate flag is also stored in memory. After the experiment is completed, a second program is initialized which dumps the data to a mainframe for processing by two FORTRAN programs.

The typical titration calorimetry experiment involves one or more initial energy equivalent determinations by electrical calibration. The energy equivalent experiment requires the microcomputer to record voltage—time data only for the lead and trail periods of the operation. The numerical values of the slope and intercept for the lead and trail are computed from the voltage—time data by the first FORTRAN program using a method of linear

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* A cross-assembler as well as an 8080 simulator and a PL/M-80 cross-compiler-assembler, all written in FORTRAN, are available (to colleges and universities) from Intel Corporation for a nominal charge (currently $ 20.00 each). Contact: Intel Corporation, 2625 Walsh Avenue, Santa Clara, Calif. 95051, Attention: University Relations Program/Mail Stop 4-483.

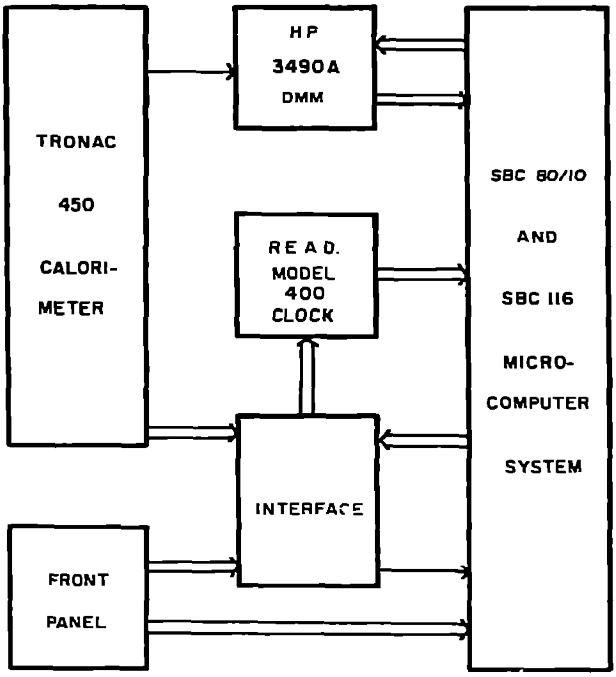

Fig. 1. Block diagram of a microcomputer data acquisition system for a calorimeter.

least-squares. The voltages at the time the heater is turned on and off are calculated from the linear equation of the lead and trail, respectively. The printout displays the values for the slopes and intercepts, the linear least-squares statistics, the total temperature change, the temperature change which is corrected for the heat of stirring—heat-leak effect, the time when the heater was turned on and turned off, and the energy equivalent value. After energy equivalent determinations have been made, the microcomputer collects voltage—time data for the buret addition part of the experiment. This involves collecting data during the lead and trail periods as well as when the buret is delivering titrant. The printout displays the values for the slopes and intercepts which are calculated by a linear least-squares method. The time and voltage is displayed when the buret is turned on and turned off. The total temperature change, the corrected temperature change, and the volume of titrant delivered to the Dewar vessel is also displayed. The first FORTRAN program then asks the user for information that will be used in creating a data file for use by the next FORTRAN program. The voltage—time data are corrected for the heat of stirring—heat-leak effect and the heat effects due to any temperature difference between titrant and titrate at the beginning of the titration.

The second FORTRAN program [2] uses the voltage—time data file to calculate the value of ΔH and $\log \beta$ using an iterative technique. Both of these programs are based upon the algorithms that are presented in the laboratory manual by Eatough et al. [2].

Detailed hardware schematics and software (programs) are available from the authors.

TABLE 1

Thermodynamics of ionization of the bisulfate ion

pK	$-\Delta H^0$ (kcal mol^{-1})	$-\Delta S^0$ (e.u.)	Ref.
1.98 ± 0.02	4.80 ± 0.10	25.2 ± 0.3	This work
1.97 ± 0.03	4.86 ± 0.2	25.4 ± 0.6	6

RESULTS

The determination of the thermodynamics of ionization of the bisulfate ion was chosen to test the data acquisition system and associated FORTRAN programs. The procedure involved titrating 3—4 ml of 0.5115 M $HClO_4$ into 50 ml of 0.04924 M $(NH_4)_2SO_4$ after first determining the initial energy equivalent of the calorimeter by electrical calibration. The data was processed with a computer program [2] to yield pβ and ΔH. This program [2] uses an iterative technique to find the value of the equilibrium quotient β that produces a minimum in the error-square sum. The data points so treated were taken at 58 sec intervals during the buret addition. A mean of 11 runs gave a pβ value of 1.57 ± 0.02, a ΔH value of —4.53 ± 0.10 kcal mol^{-1}, and a normalized error-square sum of 3.05×10^{-4}. The ionic strength of these runs was 0.137 M at the end of the titration.

The pβ value was converted to that of the standard state by means of the Davies equation [3].

$$-\log f_i = AZ_i^2\left[\frac{I^{1/2}}{1 + \mathring{a}BI^{1/2}} - 0.2I\right] \tag{1}$$

with the modification that $\mathring{a} = 5$ Å for the sulfate ion instead of 3 Å as used earlier [4]. The enthalpy value was converted to that of the standard state by using the relationship [5].

$$\Delta H^0 = \Delta H - (\nu/2)|z_+z_-|\,\delta_H I^{1/2}\alpha \tag{2}$$

where δ_H represents the theoretical Debye—Hückel limiting enthalpy slope at 25°C. These values appear in Table 1 along with those of Izatt et al. [6], which the authors consider to be highly reliable.

Our results are in excellent agreement with this earlier work [6], and demonstrate the reliability of the data acquisition system and the algorithms used in the two FORTRAN programs.

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REFERENCES

1 H.R. Pinnick, Jr., R.L. Smith and K. Kornstett, 33rd Calorimetry Conference, Logan, Utah, July, 1978, p. 71.
2 D.J. Eatough, J.J. Christensen and R.M. Izatt, Experiments in Thermometric Titrimetry and Titration-Calorimetry, Brigham Young University Press, Provo, Utah, 1974, Appendix 3.
3 C.W. Davies, J. Chem. Soc., (1938) 2093.
4 G.H. Nancollas, Interactions in Electrolyte Solutions, Elsevier, New York, 1966, p. 83.
5 C.M. Criss and J.W. Cobble, J. Am. Chem. Soc., 83 (1961) 3223.
6 R.M. Izatt, D. Eatough, J.J. Christensen and E.H. Bartholomew, J. Chem. Soc. A, (1969) 45.