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The Use of APPLE II Microcomputer as Kinetic Laboratory Data Acquisition System**

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A laboratory microcomputer system based on an APPLE II microcomputer is presented. Data transfer from a temperature jump equipment or a stopped flow apparatus can be performed via a serial interface, the data can be stored on a memory expansion card or on the disk drives. Data transfer to a central host computer can also be done. Application of the laboratory data system on kinetic and spectroscopic measurements are shown.

(Keywords: Microcomputer; Microprocessor 6502; Data acquisition system; Pyridine carbaldehyde; Alkylaminonaphthols)

APPLE II Mikrocomputer als Übertragungssystem kinetischer Laboratoriumsdaten

Ein Labormikrocomputersystem, basierend auf einem APPLE II Mikrocomputer, wird vorgestellt. Daten können von einer Temperatursprung- oder einer Stopped-Flow-Anlage übertragen und auf einer Speichererweiterungsplatine oder einer Diskettenstation gespeichert werden. Ein Datentransfer an einen Großrechner kann ebenfalls durchgeführt werden. Die Anwendung auf kinetische und spektroskopische Messungen wird beschrieben.

Introduction

The use of computerized data acquisition is rapidly becoming an integral part of many laboratory equipments. Instrumental control, data acquisition and reduction, data processing and storage together with final

** Dedicated to Prof. Dr. *K. L. Komarek* on the occasion of his 60th birthday.

data analysis and display are the most important applications of microprocessor technology in chemical laboratories. Low cost systems with high flexibility have been introduced to many different experimental equipments. Especially in kinetic or spectroscopic laboratories a large amount of data have to be collected, stored and processed, sometimes e.g. like in relaxation kinetic experiments in a very short period. Due to various experimental methods data collection has to be performed in different ways from different equipments on the same microprocessor system.

We will describe here a microcomputer system based on an APPLE II-6502 microprocessor for collecting kinetic data from relaxation kinetic and stopped flow experiments, for processing these kinetic data together with data from thermodynamic measurements by electron absorption spectroscopy and reduction and transfer of data to batch data processing by a central host-computer if necessary.

The application of this data acquisition system on some selected chemical reactions will be described.

Results and Discussion

Equipment

Fig. 1 shows a block scheme of a laboratory data system, based on a 6502 microcomputer (APPLE II+ or APPLE II+ compatible

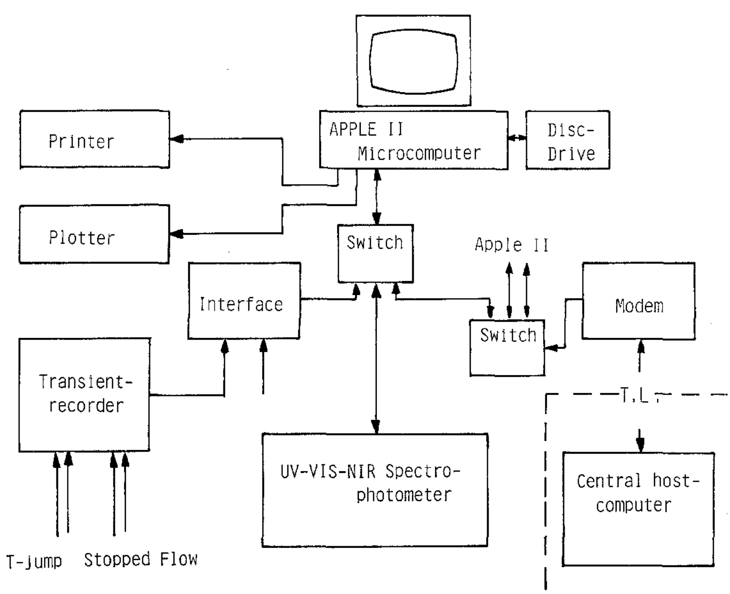


Fig. 1. Block scheme of a laboratory data system (T.L. = telefon line)

microcomputer). The main computer, equipped with a video monitor, includes a 6502 microprocessor, 48 kbyte dynamic RAM and 12 kbyte ROM. System programs and data can be stored on $5^1/_2$ inch softsectored floppy disk interfaced by a standard controller. The computer is connected to a matrix printer (Epson FX 80 or MX 82) and to a plotter (Hewlett-Packard 7475 A Plotter) for final data display. With additional peripherals the computer communicates via various interfaces and switches. Data can be received from a transient recorder, which collects analog signals from a temperature jump machine or from a stopped flow apparatus. A bidirectional data transfer can be performed to and from a UV-VIS-spectrophotometer or to a modem for on line communication with a central host computer.

To use different application program packages and for an effective data display various expansion plug-in cards at the computer are necessary. The eight ports of the APPLE microcomputer can be used for these expansion cards as it is described in Fig. 2. In slot number 0 a

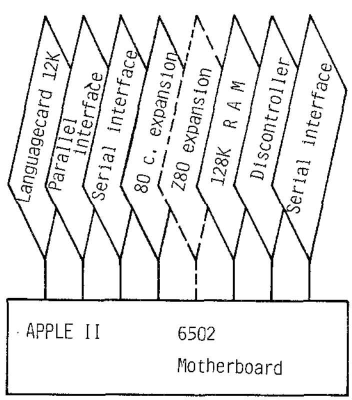


Fig. 2. Expansion card of an APPLE II microcomputer system used in a laboratory data system

16 kbyte memory board is located, also named as language card, which is required from software languages like INTEGER BASIC or PASCAL for operation. Slot 1 contains the parallel interface to the matrix printer. In slot number 2 as well as in slot number 7 serial interface cards are placed, necessary for the communication with the peripherals (transientrecorder, spectrophotometer, plotter and modem). The 80 column display card in slot 3 provides a much more dense data display at the video monitor, it is also essential for many software packages. Different other processors can be used additionally to the 6502 processor either as supporting arithmetic

processors or as independent processors operating with own software. Beyond 6809 and 68000 processors the Z80 microprocessor is mainly used. This Z80 plug-in expansion card has been designed to use CP/M software on an APPLE II microcomputer. This expansion card is placed in slot number 4, in some APPLE compatible microcomputers the Z80 processor is located on the main board already—in this case port 4 is not available. Slot number 5 contains a 128 kbyte RAM board designed to provide an extra 128 kbyte of random access memory for the APPLE system. The expansion card emulates a disk drive under DOS, PASCAL and CP/M. Application programs which use APPLE-DOS for saving and loading programs and data with therefore see the RAM board as an additional disk drive. Data can also be stored by machine language routines. The disk controller for one or two disk drives is located in slot number 6. Language card, parallel interface, 80 column display card, Z80 processor expansion card as well as the disk drive controller are more or less standard firmware, an extensive description must not be given here. The RAM card and the serial interface card will be characterized in a short way:

128 kbyte RAM Board

As a 6502 microprocessor addresses directly only 64 kbyte memory and some utility and system programs occupy a large amount of that limited memory space an additional possibility for data storage is desirable. Therefore a 128 kbyte RAM expansion card has been designed, which makes it possible to store additional data and programs in a simple way. The 128 kbyte RAM board is organized in 16 × 64 kbit dynamic random access memory (type 4164) in two banks with hidden refresh. 256 bytes (corresponding to one sector on a floppy disk) are memory mapped onto the peripheral card memory space of the APPLE II at locations hexadecimal $C500 to $C5FF (if the 128 kbyte RAM board is placed in APPLE's slot number 5). Addressing of the 256 byte window of the expansion cards memory can be done at APPLE peripheral card device select addresses at locations $C0D0 (RAM-page, 1–64) and $C0D1 (RAM-bank, 1–64 or 65–128). Setting these two locations allows data I/O successively to or from the 128 kbyte memory from a machine language or a BASIC program. Moreover the RAM board emulates an additional disk drive, that means that program and data transfer can be performed with APPLE-DOS or CP/M. It should be mentioned that the program or data transfer succeeds in a parallel way in comparison to the serial transfer of the disk drive. Additional the memory access is much faster than the average access to any data sector of the floppy disk. Therefore the data and program transfer rate is much higher than the read-write procedure on the disk drive.

ACIA RS 232 C

For data transfer from the microprocessor to peripherals, like data acquisition systems or other equipments serial interfaces are used. They are based on an asynchronous communication interface adapter of type 6850. By this unit data of the parallel data bus system are serially transmitted and received with its proper format, it includes also various handshake possibilities and parity generation. During system initialization data format, parity type, format of the stop bit and clock division ratios are programmed via the data bus. The XTAL clock is modified by a baud rate generator using dip switches selecting different baud rates. The internal prescaler of the 6850 unit allows a two stage software selection of the ACIA baud rate. Therefore it is possible to use the serial interface at two different baud rates without modification of the dip switches. The EPROM on the plug-in card contains firmware for control and communication with the APPLE's microprocessors. The EPROM program space is mapped into APPLE's memory address hexadecimal C200 to C2FF (if the card is located in slot number 2). Communication and control of the ACIA is done by the two device select addresses hexadecimal C0A0 and C0A1. These addresses contain four different registers: status register, control register, receive data and transmit data registers. The status register allows to check the condition of the receive and transmit shifters as well as the detection of parity and frame errors. The control register is used to select handshake and baud rate via the on-chip prescaler. Additional during initialization the data format is selected too by means of that register. The data transfer itself is performed by the receive and transmit registers of the ACIA.

The Microcomputer—Host-Computer "Network"

The serial interface card makes it possible to transfer data or programs from the 6502 or Z 80 microprocessor to the central main frame. Two different possibilities of the communication of some laboratory microcomputers with the host-computer via phone line are shown in Fig. 3. The connection of one microcomputer to a modem allows the transfer of data with a baud rate of 300 baud; the application of a multiplexer (type Infotron SM 388) increases the data transfer rate to 1 200 baud, additional up to 8 microcomputers can be connected to one phone line at the same time. Data transfer between the different microcomputers succeeds via serial interfaces by use of opto couplers and current loop (Fig. 3).

The interactive software for data processing from the transient recorder which is connected to the temperature jump equipment or to the stopped flow machine is written in BASIC. Only the Biomation transient

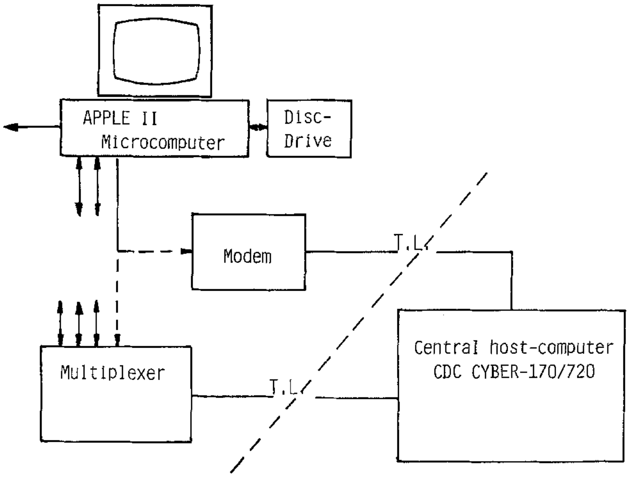


Fig. 3. Block scheme of the connection of a laboratory data system to a central host computer

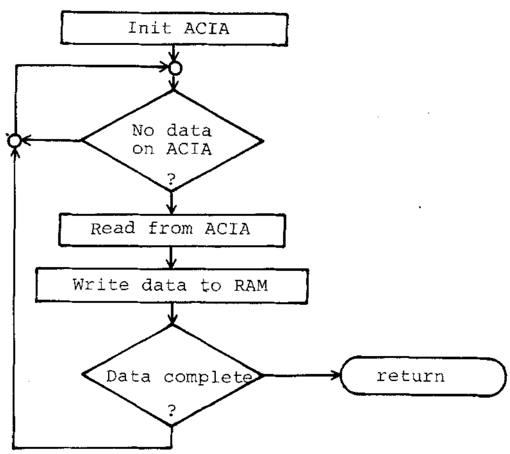


Fig. 4. Flow chart of the data transfer routine transient recorder—APPLE II via ACIA 6850

recorder data transfer routine is written in assembler. This machine routine (flow chart given in Fig. 4) includes the initialization of the ACIA and the data transfer from the interface of the transient recorder. The data, accepted via the 6850 are stored on the RAM pseudo disk. In the BASIC routine the data are transferred onto floppy disks and stored together with additional informations like parameters of the time base of

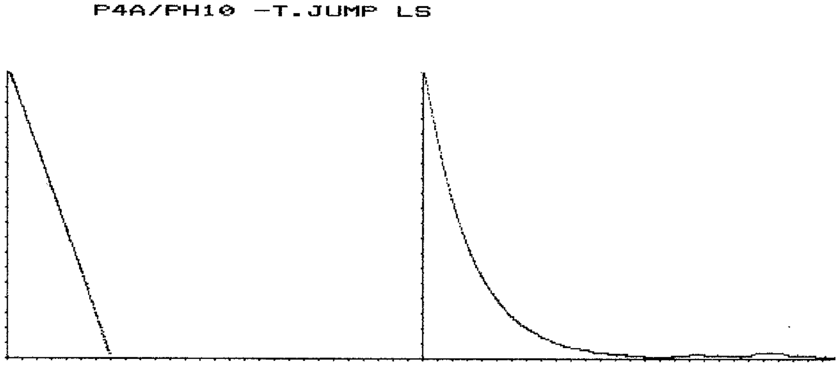


Fig. 5. Temperature jump experiment performed via laboratory data system. The extinction of pyridine-4-carbaldehyde is monitored at 295 nm ($pH = 10.0$). 1 024 points are taken at intervals of 2.10^{-4} s. Right picture: extinction decay, left picture: linearized decay. Resulting relaxation time $\tau = 10.96$ ms (correlation coefficients $R = 0.99$)

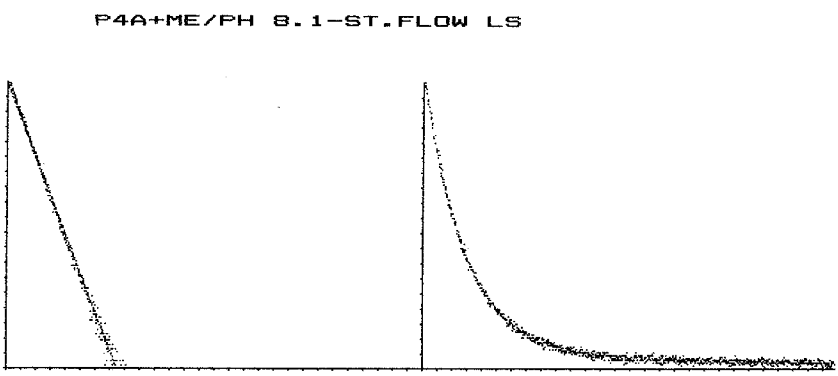


Fig. 6. Stopped flow experiment using laboratory data system. The extinction of pyridine-4-carbaldehyde is monitored at 295 nm. The reaction with mercaptoethanol at $pH = 8.1$ is followed. 1 024 points are taken at time intervals of 1.10^{-2} s. Resulting relaxation time $\tau = 0.60$ s ($R = 0.98$)

the transient recorder. A nonlinear least square fitting procedure of the first order rate constants can be performed by standard methods. The accepted data together with the fitted values can be printed or plotted as desired, with printout of the calculated coefficients and standard error data. Fig. 5 shows an example of a temperature jump experiment. The hydration of pyridine-4-carbaldehyde is acid and base catalysed [1–3].

The reaction itself cannot be followed by classical kinetic methods, because the relaxation time is between 10^{-5} seconds (at high and low *pH* values) and a few seconds at neutral *pH*. For such reactions the reversible chemical equilibrium is disturbed by the change of an external parameter (e.g. the temperature) and the relaxation of the system to the new equilibrium is monitored. From the theory of relaxation kinetics follows that a single step reaction mechanism leads to a monoexponential relaxation decay. In cases of multistep chemical reactions higher than monoexponential relaxation curves can be observed. To prove such a possibility the relaxation time analysis can be done for various smaller pieces of the whole experimental decay curve.

In Fig. 6 a typical stopped flow experiment is shown. The evaluation of the kinetic parameters with the present program is possible for reactions first or pseudo first order. In all other cases the data have to be stored and analysed by other proper programs, e.g. on a large computer. Fig. 6 shows as an example the reaction of mercaptoethanol with pyridine-4-carbaldehyde. This nucleophilic reaction is only base catalysed, it succeeds at low *pH* value within a few seconds and can therefore be followed by the stopped flow method, where both reaction solutions are mixed rapidly

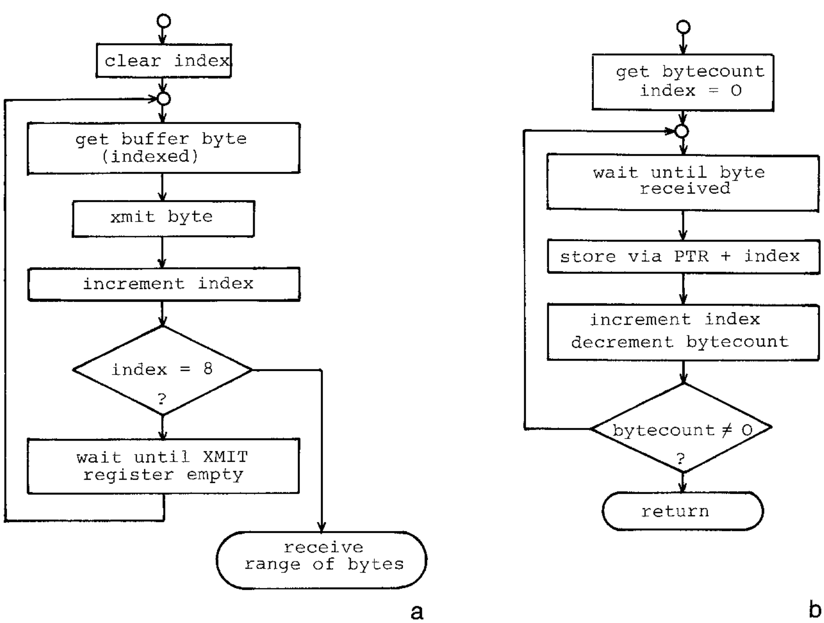
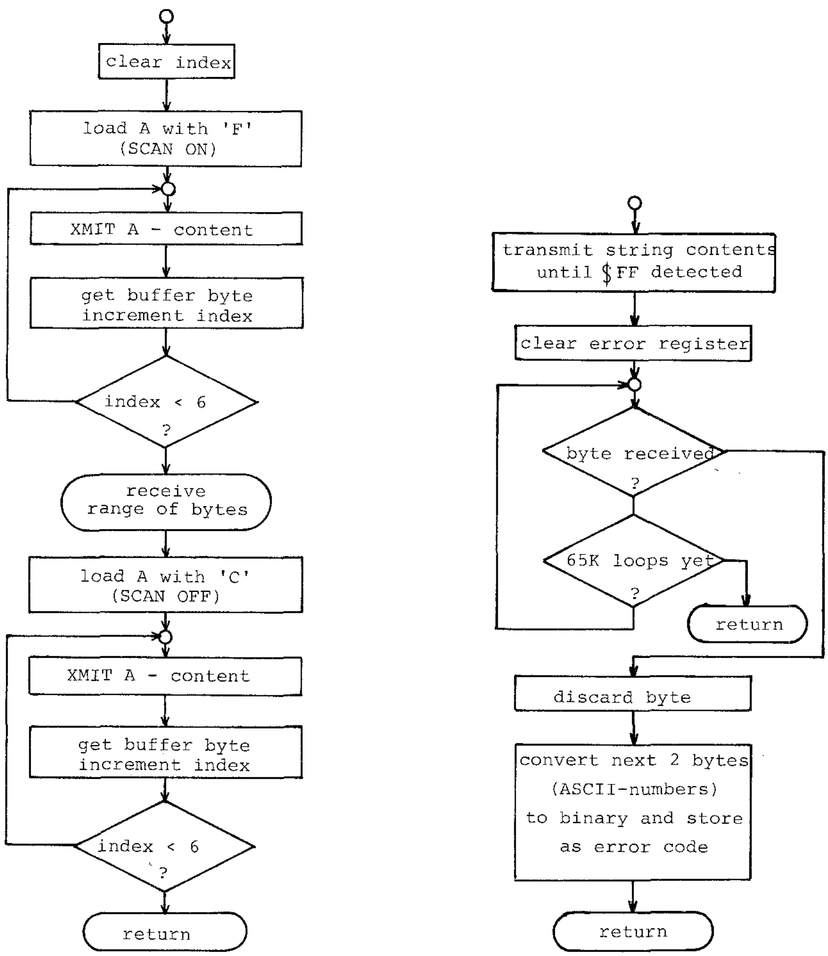


Fig. 7. Flow chart of the four machine routines of the UV-VIS-NIR spectrophotometer manipulation program

(within 2 ms) and the change of optical density is registered. An extensive treatment of the system pyridine-4-carbaldehyde in water with mercaptoethanol will be given elsewhere [4].

The manipulation program of the UV-VIS-spectrophotometer (Perkin Elmer 330) is also written in BASIC with a machine routine handling the data and command exchange between the serial interface of the spectrophotometer and the APPLE II. A flow chart diagram of the machine routine is given in Fig. 7.

The main part of the BASIC program includes the "MENU" for the operation of the keyboard functions of the spectrophotometer. All



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keyboard functions can be chosen via the program, additional functions like spectra manipulation or plotting routines are provided. Spectra can be recorded and stored on floppy disk. In Fig. 8 an experiment for the estimation of the equilibrium constant of a single step reaction is given. Aminomethylnaphthol reacts with methoxide in methanol producing its anion. Such a reaction can be followed by the change of the UV-spectrum of the naphthol ($\lambda = 283$ nm) to the spectrum of the naphtholate anion ($\lambda = 342$ nm). The equilibrium constant $K = 670$ can be calculated following the method of *Hildebrand* and *Benesi* [5] at several wavelengths. The results of these thermodynamic investigations will be published elsewhere [6].

The communication program for data and program transfer from the APPLE II microprocessor to a central host computer is mainly written in assembler. Only a small BASIC program for starting the machine

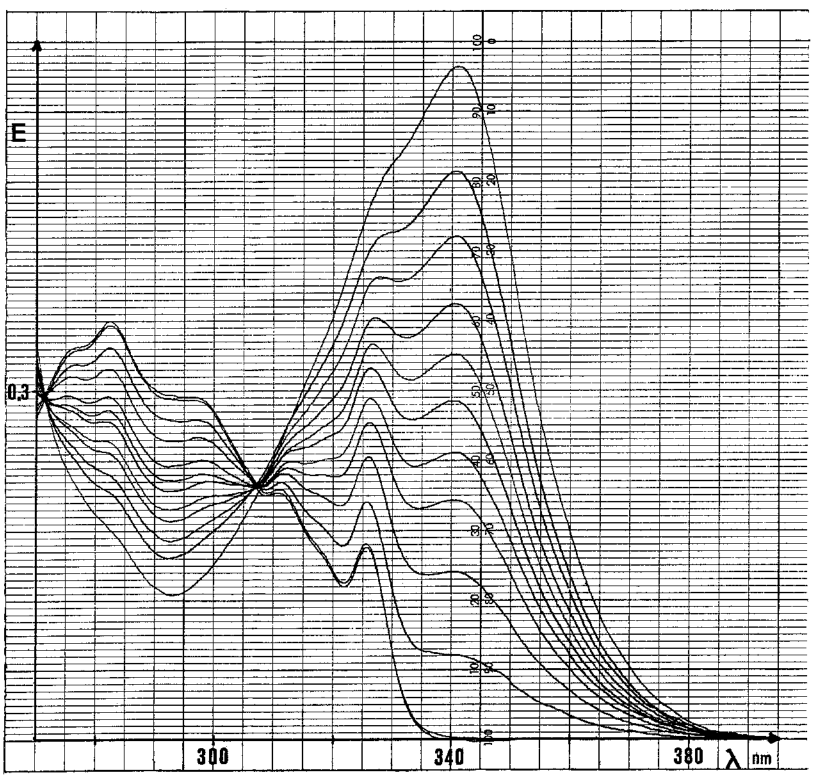

Fig. 8. UV-VIS spectrum of a substituted alkylaminonaphthol with several concentrations of methoxide (concentration of the naphthol derivative: $c = 1.10^{-4}$ mol/l, base concentrations: $6.7 \cdot 10^{-5}$, $3.8 \cdot 10^{-4}$, $5.1 \cdot 10^{-4}$, $7.6 \cdot 10^{-4}$, $1.0 \cdot 10^{-3}$, $1.3 \cdot 10^{-3}$, $1.5 \cdot 10^{-3}$, $2.0 \cdot 10^{-3}$, $3.0 \cdot 10^{-3}$, $5.0 \cdot 10^{-3}$ and 0.031 mol/l)

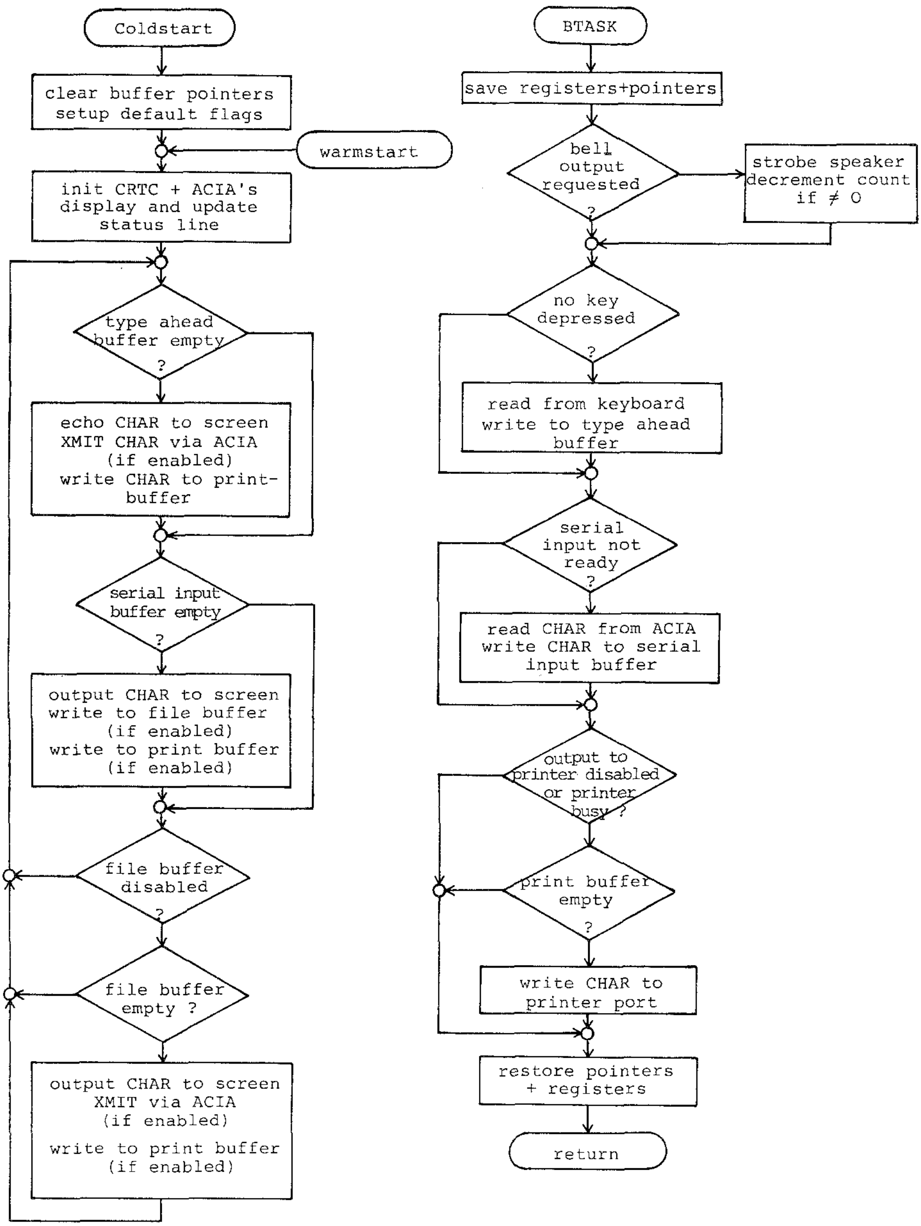

Fig. 9. Flow chart of the "terminal program" for communication of the APPLE II laboratory data system with a large computer connected via telefon line

program choosing different options is requested. A flow chart diagram of the most important program parts is given in Fig. 9. The terminal program configures the APPLE as a terminal with enhanced features:

(1) There is buffer space provided to save relatively large textfiles (64 *K*) immediately without slowing down the system by use of handshake methods. About one half of the RAM disk is used for this purpose.

(2) The other half of the RAM disk acts as a printer buffer and store to allow spooling. It is possible to receive characters in the printer buffer and store them in parallel to the file buffer too.

(3) Two relatively short parts of the RAM disk memory have the functions of a type ahead buffer and a serial input buffer.

(4) The use of this buffer system is open to the user. It is possible to disable some of the functions by simply type the appropriate control character on the keyboard.

(5) Buffer contents could be recovered if desirable (e.g. to send the textfile to the printer, producing a second copy).

(6) Flags and the amount of buffered characters are displayed at any time in the status line.

A second program called BTASK is a subroutine and assists the terminal program in various ways. First of all it should be mentioned that the operating system DOS 3.3 does not allow the use of interrupts. Therefore BTASK mainly checks the keyboard for characters or the break command. It handles the printer system and buffers characters which are received by the ACIA. In addition to this it produces a second output to provide for the bell character.

The terminal program uses its own driver routines for screen, printer and serial interface, which is necessary for operating the system at higher baud rates. It is possible to leave the terminal program at any time and to return to it without destroying any buffer contents. At reentry all of the peripheral devices are reinitialized to allow proper function of the system.

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References

[1] *Jencks WP* (1972) Chem Rev 72: 705
[2] *Pocker Y, Meany JE* (1968) J Phys Chem 72: 655
[3] *Kalchhauser H, Wolschann P* (1986) Monatsh Chem 117: 841
[4] *Földesi P, Kainradl R, Schuster P, Wolschann P* (in preparation)
[5] *Benesi HA, Hildebrand JH* (1949) J Am Chem Soc 71: 2703
[6] *Schlederer M, Wolschann P* (in preparation)