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CONSTRUCTION AND SOFTWARE DESIGN FOR A MICROCOMPUTER CONTROLLED pH/ION TITRATOR

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ABSTRACT

The construction of an automated titration device is described. The major components include an Apple II+ Microcomputer and 8-bit parallel interface, Fisher Accumet, Model 520 Digital pH/Ion Meter, Gilmont Micrometer Buret of 2.5 mL capacity, Sigma stepper motor, power supply and driver to operate the buret, and a constant temperature bath of ± 0.005 °C stability.

The limitations of the system are 0.001 pH/0.1 mv for the pH/ion sensing system, and 0.125 μL per step for the buret. The system as described is designed to determine equilibrium constants for metal ion-amino acid complexes. By changing the software a variety of different pH and redox titration experiments may be performed.

A computer program used to operate the stepper motor driven syringe buret and record the pH from a digital pH meter is described. The program uses both Apple BASIC and assembly language. This is a closed loop operation in which the data from the pH meter is used to control the amount of reagent delivered by the buret.

The results are displayed graphically as the titration proceeds. The variance of the pH readings are calculated using an assembly language subroutine and the calculations are done with zero round-off error.

INTRODUCTION

In the process of our research it became necessary to determine acid-base equilibrium constants for a variety of coordination compounds. Of course these values have to be accurate, precise and reproducible. Furthermore, the equilibrium constants are to be determined over the temperature interval of 5 to 40 celsius. This is to allow evaluation of the Gibbs free energy, entropy, enthalpy and heat capacity through the following relationships:

$$\Delta G^\circ = -RT\ln K$$

$$\Delta S^\circ = -(\partial \Delta G^\circ/\partial T)_p$$
$$\Delta H^\circ = -[\partial(\Delta G^\circ/T)/\partial(1/T)_p]$$
$$\Delta C_p^\circ = (\partial \Delta H^\circ/\partial T)_p$$

Because of the great amount of time and patience which must be devoted to gathering such data it was decided to construct an apparatus that could perform these experiments with a minimum of human intervention. Also, the design was to be flexible enough so that, once assembled, the apparatus could perform other related tasks by changing only the software. The apparatus to be described was built and programmed specifically to determine equilibrium constants. However, plans are being implemented to program and use it as an end-point titrator for pH or redox systems as well as a pH stat for biochemical and kinetic studies.

CONSTRUCTION DETAILS

Figure 1 is a block diagram of the system. It is a closed-loop system in that, once initiated, the microcomputer controls the course of the experiment. The major components of the system are the microcomputer, peripheral interface adapter, pH meter, BCD to binary converter, automated buret assembly, titration cell and thermostated water bath.

Microcomputer

The microcomputer system consists of an Apple II+, 64K, microcomputer, two 5½ inch mini floppy disk drives, a CRT monitor and dot matrix printer.

Peripheral Interface Adapter (PIA)

The peripheral interface adapter, PIA, is a Motorola MC-6821P, which is compatible with the Apple's 6502 microprocessor. The 6821 PIA uses TTL logic which requires a +5 volt power supply. Figure 2 gives the wiring diagram for the interface circuit. The components of the interface are mounted on an Apple prototype board (CSI Part No. 07500-002A) which plugs into the expansion slots on the back of the Apple's main circuit board. Wire wrap staking pins and DIP sockets are secured to the board by soldering. The two 741 operational amplifiers are inserted side by side onto a single 16 pin wire wrap DIP socket. All four resistors in the circuit are 8.2 kohm, ¼ watt resistors. The circuit is assembled by wire wrapping with 30 AWG color coded insulated wire. The 18 AWG, 3 wire, cable to the stepper motor power supply is connected by soldering to staking pins. It is mechanically secured by means of a tight fitting cable hanger attached to the interface board by means of a screw, lockwasher and nut.

pH Meter

The pH meter used is the Fisher Accumet, Model 520 Digital pH/Ion Meter. The read-out is 4½ digits. The meter is advertised as having a repeatability of ± 0.001 pH/± 0.1 MV and accuracy of ± 0.002 pH/± 0.2 MV. Also, the meter has an input impedance of greater than 10^{12} ohms and a drift of less than 0.003 pH/0.18 MV drift per 24 hours. The most attractive feature of the pH meter is the digital printer output. The digital printer output information is available by means of a 30 pin edge-connector at the back of the instrument. The output is TTL logic (2.4 volt minimum impulse for digital "1" and 0.4 volt maximum for digital "0"). Each of the 4 full digits of the meter is accessed through this connector by means of binary coded decimal, or BCD, format. The ½ digit, or carry, strobe, pH, +MV, −MV indicators and common connection is also available at this connector.

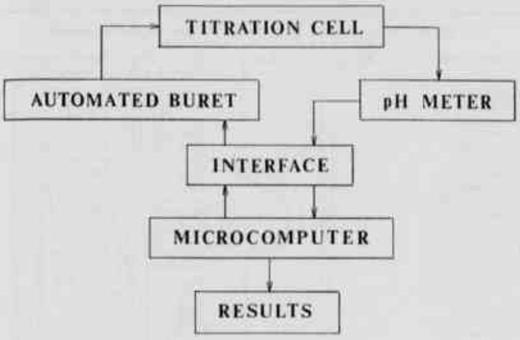


Figure 1. Block diagram of automated titration/pH stat system.

BCD to Binary Converter

The information produced by the pH meter is converted to a form usable to the computer by means of the circuit given in Figure 3. The components are mounted by means of DIP IC wire-wrap sockets glued to perf-board with super glue. The perf-board used measures 6½ x 3 x 1/16 inches with holes on 1/10 inch centers. There is a large amount of empty space in the pH meter. Therefore, the BCD to binary circuit is mounted inside the pH meter case by means of angle brackets affixed to the perf-board and back cover of the meter. Circuit connections are made by wire wrapping with 30 AWG, color-coded, insulated wires. A stranded, rainbow color coded, 28 AWG, flat ribbon cable with 24 conductors is used to connect the pH meter's 30 card edge connector to the BCD to binary circuit. The cable is 6 inches long with a 24 pin DIP male connector on one end and a 30 connection card edge female connector on the other. Heat-shrink tubing is used to insure good insulation on the card edge connector end after soldering the cable wires to the connector plug. A similar cable that is 24 inches long and with a 16 pin DIP male connector at each end is used to connect the BCD to binary circuit to the PIA circuit inside the microcomputer. Table 1 gives the cable connections for the two cables. The BCD to binary circuit is powered by the +5 volt line taken from the Apple II+ power supply via the connecting cable.

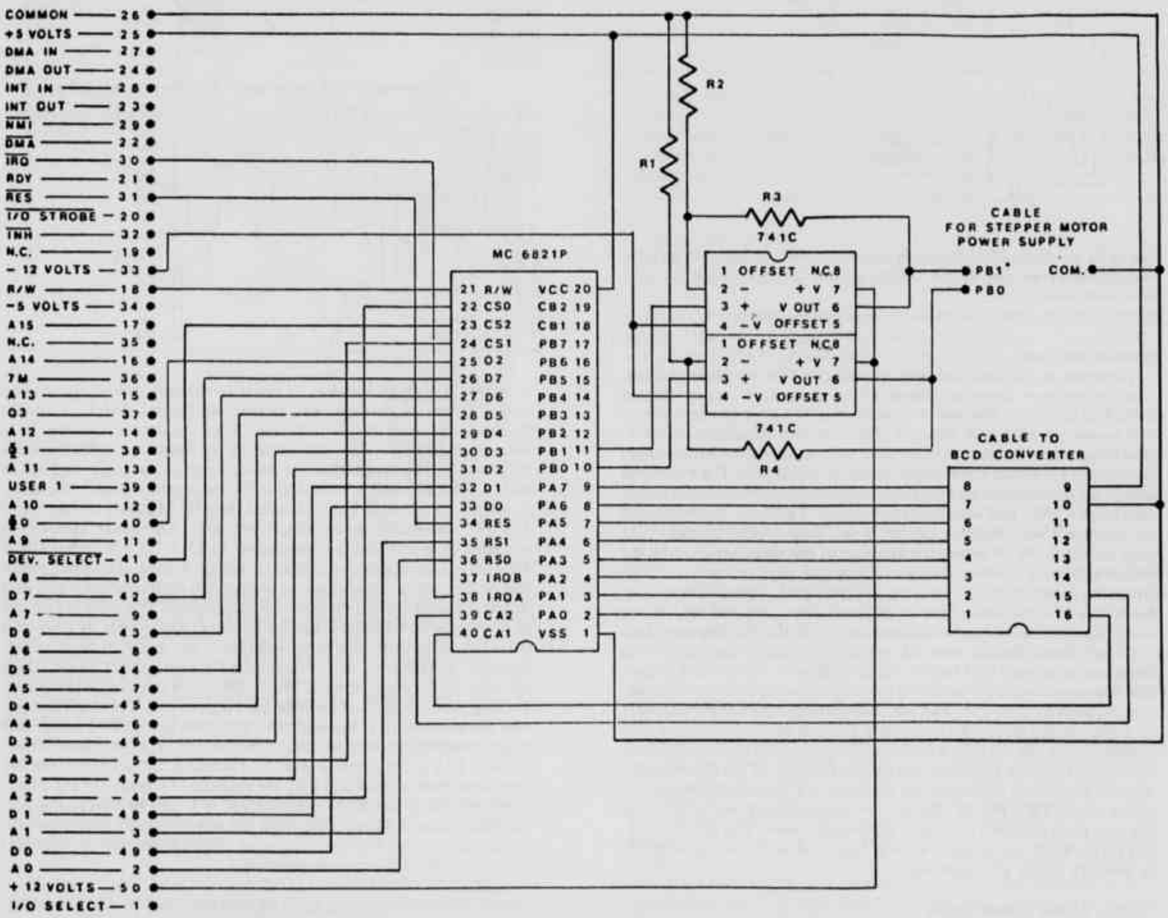


Figure 2. Peripheral interface adapter circuit utilizing the Motorola MC-6821P Peripheral Interface Adapter (PIA). All resistors are 8.2 kohm, ¼ watt.

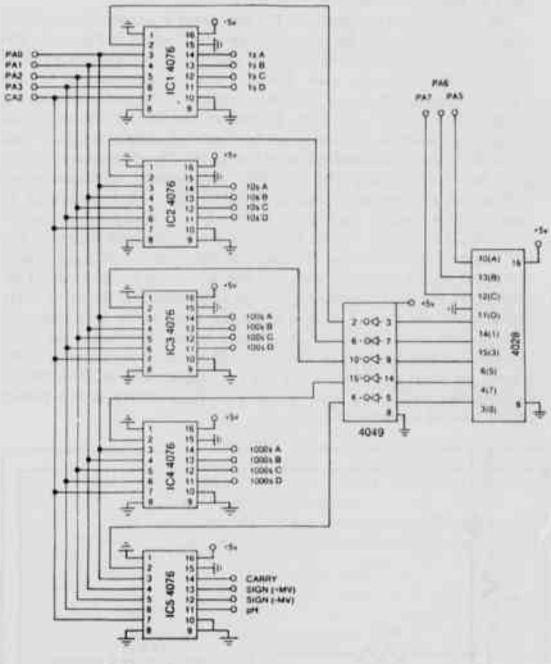


Figure 3. 4½ Digit BCD to binary converter used to read pH meter's information from its 30 pin digital printer output connector into microcomputer.

Table 1. Cable Connections

BCD to Binary Circuit to pH Meter Digital Printer Connector

pH Meter End	BCD to Binary End	BCD to Binary Board Connections from 24 pin DIP Connector
A Ones (D)	1	Ones (D) IC1, pin 11
B Ones (B)	2	Ones (B) IC1, pin 13
C Ones (C)	3	Ones (C) IC1, pin 12
D Tens (A)	4	Tens (A) IC2, pin 11
E Tens (D)	5	Tens (D) IC2, pin 13
F Tens (B)	6	Tens (B) IC2, pin 12
H Tens (C)	7	Tens (C) IC2, pin 14
J Hundreds (A)	8	Hundreds (A) IC3, pin 14
K Hundreds (D)	9	Hundreds (D) IC3, pin 11
L Hundreds (B)	10	Hundreds (B) IC3, pin 13
M Hundreds (C)	11	Hundreds (C) IC3, pin 12
N Thousands (A)	12	Thousands (A) IC4, pin 14
P Thousands (D)	15	Thousands (D) IC4, pin 11
R Thousands (B)	14	Thousands (B) IC4, pin 13
S Thousands (C)	13	Thousands (C) IC4, pin 12
1 − MV indicator	24	− MV indicator, IC5, pin 12
2 Ones (A)	23	Ones (A) IC1, pin 14
3 + MV indicator	22	+ MV indicator, IC5, pin 13
4 pH indicator	21	pH indicator, IC5, pin 11
5 N.C.		
6 N.C.		
7 Ten Thousands (A)	18	Ten Thousands, IC5, pin 14
8 N.C.		
9 N.C.		
10 N.C.		
11 Strobe	17	Strobe, pin 16 of cable below
12 Common	16	Common, Ground
13 Common	19	N.C.
14 Common	20	N.C.
15 Common		

BCD to Binary Circuit to Peripheral Interface Adapter Board

BCD to Binary Circuit, 16 Pin DIP Connector	PIA, 16 Pin DIP Connector
1 Pin 3, 4076	1 PA0
2 Pin 4, 4076	2 PA1
3 Pin 5, 4076	3 PA2
4 Pin 6, 4076	4 PA3
5 Common	5 PA4
6 Pin 10, 4028 (A)	6 PA5
7 Pin 13, 4028 (B)	7 PA6
8 Pin 12, 4028 (C)	8 PA7
9 N.C.	9 +5 Volts
10 N.C.	10 Common
11 N.C.	11 N.C.
12 N.C.	12 N.C.
13 N.C.	13 N.C.
14 N.C.	14 N.C.
15 Pin 7, 4076	15 CA2
16 Pin 16, Strobe	16 CA1

Automated Buret

The buret is a 2.5 mL Gilmont Micrometer Syringe Buret (S3200). The micrometer drive is connected to a stepper motor (Sigma 20-2235D200-E17). The motor is wired to give half-step operation of 0.9 degree per half-step. Figure 4 illustrates the important construction features of the buret assembly. The base plate of the buret assembly measures 13.5 x 3.25 x 0.5 inches and is of aluminum. The buret and motor are secured by 1 inch thick aluminum blocks of base 3.25 inches and height 2.625 and 4 inches, respectively. The holes for buret and motor were drilled slightly oversize. A slot in each block allows a 0.25 inch diameter bolt to reduce the diameter of the hole thus securing the motor and buret in place. A 0.25 x 2.75 inch aluminum disc is attached to the micrometer part of the buret as shown in the figure. This is done by means of a 0.25 inch wide shoulder machined on one side of the disc. Again a slot and screw arrangement locks the disc in place. Two 0.25 inch holes, slightly oversize, are drilled through the disc. These holes accept the two 0.25 inch diameter steel drive shafts which impart the rotational motion from the motor and allow the translational motion required by the buret. The two steel shafts are affixed permanently to a disc on the motor shaft that is 0.5 inches thick. The motor disc is mounted on the shaft by a 0.25 inch thick shoulder machined on the disc and a set screw tightened against the flat part of the motor shaft. The six wires from the motor are attached to a 6-terminal barrier terminal block (TRW 6-140). The barrier terminal block was attached to the base plate with two 8-32 steel, allen-head screws. The male luer fitting on the buret was mated to a 3-way Hamilton valve (Hamilton 86728) to simplify filling and emptying.

Stepper Motor Power Supply

The stepper motor requires an unregulated DC power supply of twice the motor's phase current of 2.3 amps. The power supply constructed is shown in Figures 5 and 6. In order to simplify motor operation a motor driver logic card was purchased (Sigma 29A47 Unipolar Resistance Limited Driver). The logic card required a regulated +12 volt power supply. This was achieved by means of a 7812 voltage regulator also powered from the motor supply. The logic card has to have forced air cooling to maintain its temperature below 50 celcius. A 4.5 x 4.5 x 1.5 inch fan is installed (Muffin MU2A1) on the 7 x 11 x 2 inch aluminum chassis (BUD AC-407). The entire assembly is mounted in a steel cabinet measuring 13.25 x 7.5 x 9 inches (BUD SB-2141). A six conductor cable, 18 AWG, is used to connect motor and power supply. Spade lugs are soldered to each conductor and heat shrink is placed around the soldered connections. The cable is fastened at both ends by 6-terminal barrier blocks (TRW 6-140). A resistor is placed in series with each phase winding of the motor to limit current through the motor to the recommended current of 2.3 amps. These resistors are 7.5 ohm, 50 watt, 1%. A 4066 quad bilateral switch is used to bring pins 11 and 16 of the logic card high or low. Pin 11 is the direction pin and pin 16 is the step pin. The 4066 is a CMOS device and requires amplification to 10 volts of the 5 volt TTL logic available from the 6821 PIA in the Apple (Figure 2). Therefore, the voltage of the two lines from Port B, PB0 and PB1 are amplified by means of the 74IC's to bring them up to CMOS specification. A 3-wire 18 AWG cable provides common, PB0 and PB1 from the Apple's PIA. The rest of the connections to the 4066 are connected to either ground or +12 volts to prevent the chip from overheating.

SOFTWARE DESCRIPTION

The computer software is designed with a closed loop operation in

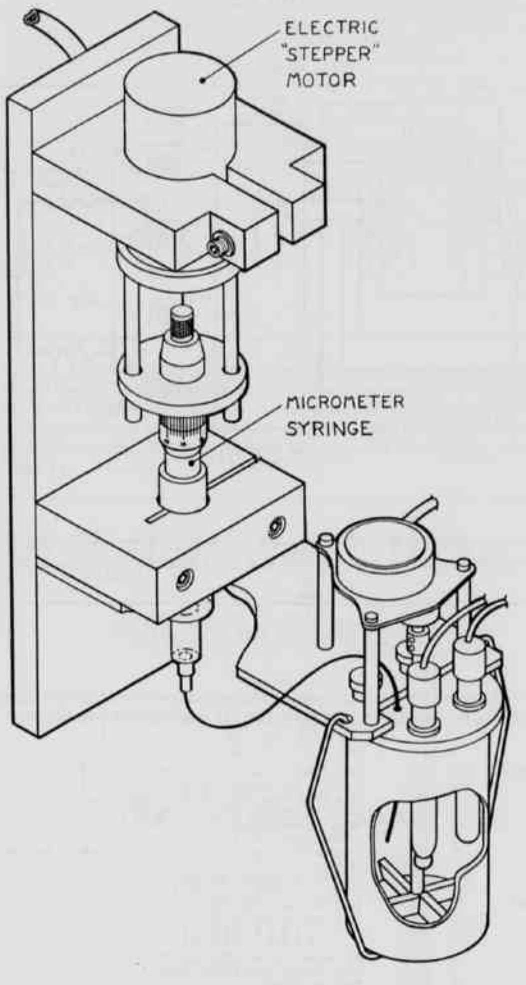


Figure 4. Isometric rendering of automated buret in its normal vertical position. The glass part of the buret and the titration cell are designed to be submerged in a thermostated bath during actual use. The titration cell has a total volume of 200 mL and is polypropylene. It is equipped with a 150 rpm glass stirrer and has provision for nitrogen gas purge. The three way Hamilton valve has been omitted from the drawing for clarity.

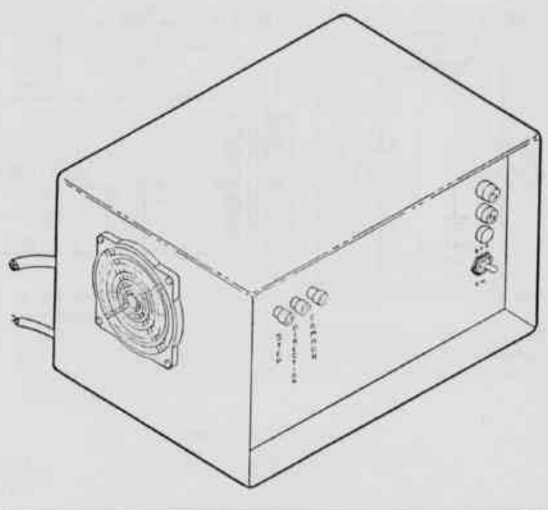


Figure 5. Sketch of stepper motor power supply and logic circuit. Two fuse holders and indicator light are on upper right hand side of panel. One of the two cables on the back is for 115 VAC power; the other is the 6-conductor cable to the stepper motor. The control cable from the computer is connected on the top left of the front panel.

mind. The program controls the operation of the automated buret either at a constant increment for pH determination or variable increment for endpoint determination.

The software is designed to utilize the MC6821 peripheral interface adapter (PIA). This versatile circuit allows memory locations, internal to the computer, to be used as input or output to two ports; A and B. See Figure 7. Device A is the pH meter; device B is the stepper motor.

Additional circuitry is needed to read the pH from the pH meter. The meter outputs the pH as binary coded decimal (BCD). BCD output is illustrated in Figure 8. A 4076 tri-state quad storage register is utilized for each of the 5 digits. Each 4076 is capable of storing 4 bits of data, the amount needed for a single decimal digit. Five 4076 IC's are utilized in the hardware configuration, one for each digit. The 4076's are accessed, one at a time, when the pH is read into memory.

The 6821 uses two memory locations for each port. One of these is the Control Register. The Control Register allows the microprocessor to control two things, the operation of the interrupt and handshaking lines (CA1, CA2, CB1, CB2) and access to the other memory location. If bit two of the Control Register is set then the other memory location is used to define which of the Port A (or Port B) lines will be input and which will be output. Since the memory location has eight bits, corresponding to eight data lines, each line can be programmed as input or output. Thus, the second memory location is called the Data Direction Register when bit 2 of the control register is set. We write a "1" in the lines of the Data Direction Register we wish to become outputs, and a "0" into those lines to be designated inputs. When bit 2 of the Control Register is not set, i.e. zero, then the second memory location becomes an output register, and the microprocessor can read the data on those lines that have been designated as input, and write data on those lines designated as output.

Since port A is connected to the pH meter, 4 lines are designated as input (required for BCD input) and 3 lines as output (for control over reading the digits). Line PA4 is not needed. It is grounded, and therefore always at logic level zero. As can be seen from Figure 3, lines PA5, PA6, and PA7 are connected to the 4028 BCD to Decimal Decoder. Only one pin of the 4028 goes high based on the conditions of lines PA5, PA6, and PA7. See Figure 9. This causes a single pin on the 4049 hex inverting buffer to go low. There are lines that go from the 4049 to pin 2 of each 4076 IC. When pin 2 of the 4076 IC goes low, the outputs (pins 3-6) can be read. These outputs are connected to PA0-PA3.

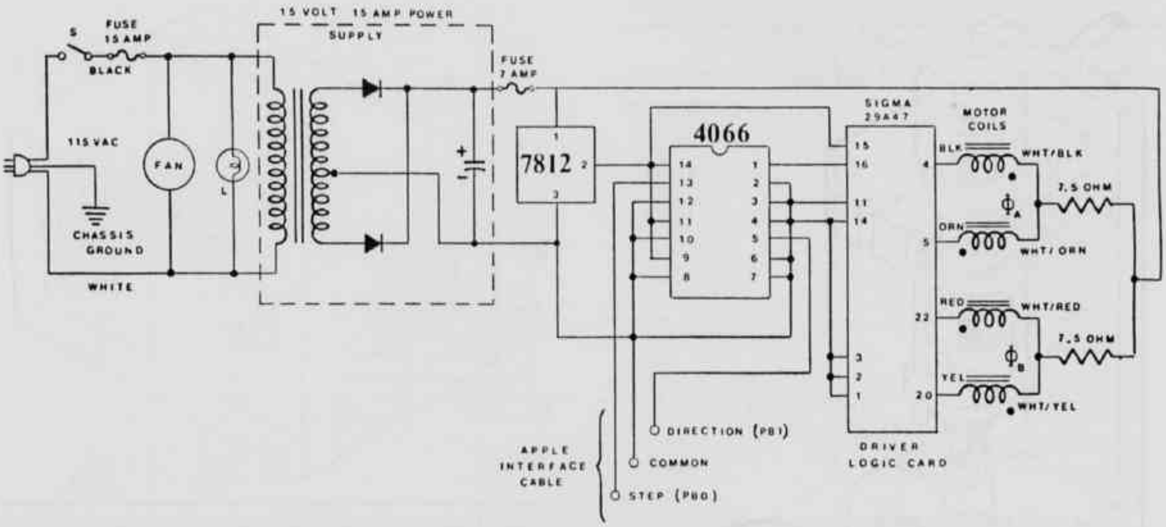


Figure 6. Schematic of stepper motor power supply and logic. The 7812 is a +12 volt regulator and the 4066 is a quad bilateral switch. L is an indicator lamp. The two 7.5 ohm resistors are 50 watt, 1%.

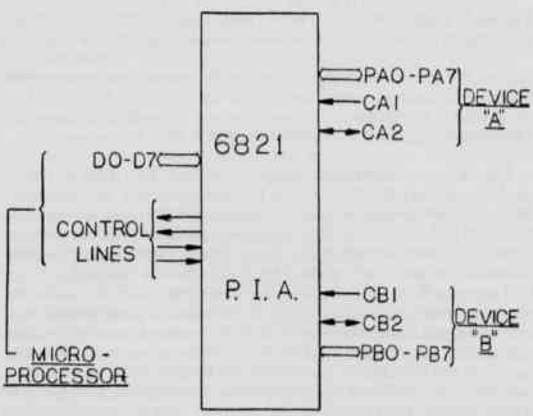


Figure 7. Simplified schematic of MC6821 Peripheral Interface Adapter.

Pin 7 of each 4076 is connected to CA2, an handshake line that is controlled via the Control Register of the PIA. This line is sent low, and then high. The 4076 IC is configured in such a manner that this procedure causes the data it "sees" on its input pins (11-14) to be latched. When pin 2 goes low, the data is placed on the data bus.

The strobe of the pH meter is connected to CA1, the interrupt line of the PIA. This line is the most significant bit (bit 7) of the Control Register. Thus, the program constantly poles the pH meter strobe that indicates a pH value is ready to be read.

The assembly language routine that sets direction of the data lines, checks for the strobe, and takes the pH reading is shown below.

```
READ    LDA   $00      Select Data Direction Register (bit 2 = 0)
        STA   $COCD    $COCD is the Control Register
        LDA   $$E0     Make lines PA5, PA6, and PA7 outputs
        STA   $COCC    $COCC is the Data Direction Register
CLEAR   LDA   $$06     SELECT OUTPUT REG.; Make an active
        STA   $COCD    transition of CA1 a positive transition.
        LDA   $COCC    Reading this clears CA1 (bit 7 of the Control Register)
TEST    BIT   $COCD    Wait for a strobe
        BMI   DOIT     Is bit 7 of Control Register set?
        JMP   TEST     If not, no strobe, try again
DOIT    LDA   $$34     Send CA2 low, then high
        STA   $COCD    This locks a reading in
        LDA   $$3C
        STA   $COCD
        LDA   $$00     Put zeroes in PA5, PA6, and PA7
        STA   $COCC    This selects the 10,000's place
        LDA   $COCC    Read the value
        AND   $$01     Mask unnecessary bits
        STA   $7000    Store it
        LDA   $$E0     Put ones in PA5, PA6, and PA7
        STA   $COCC    Select 1000's place
        LDA   $COCC    Read the value
        AND   $$0F     Mask unnecessary bits
        STA   $7001    Store it
        LDA   $$A0     Similarly for 100's place
        STA   $COCC
        LDA   $COCC
        AND   $$0F
        STA   $7002
```

When this routine is finished, the pH value is stored in five memory locations ($7000-$7004). This BCD value is then converted to a hex number requiring two bytes for storage.

The routine that operates the stepper motor is fairly simple. Only two lines are needed to control the motor, one which specifies the direction, and one which, when pulsed, directs the motor to take a step. The motor is connected to port B of the PIA. PB0 is connected to the line that directs the motor to take a step. PB1 is connected to the line that controls the direction of the motor (high = CW; low = CCW). When PB0 is low, pin 16 of the driver card is high. The motor takes

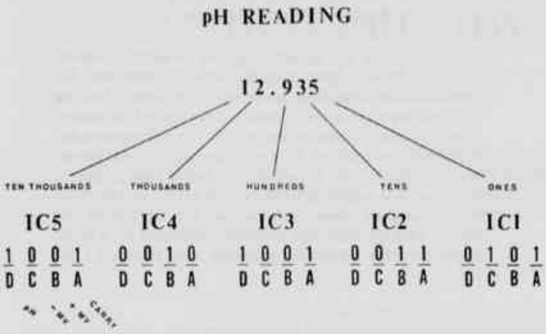
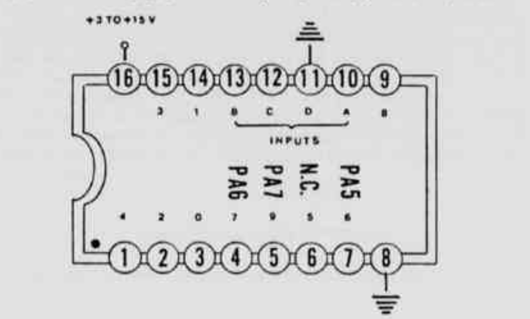


Figure 8. Diagram representing the breakdown of pH reading into five Binary Coded Decimal (BCD) numbers. Each decimal digit is latched into a 4071 quad storage register as four bits. The "A" bit is the least significant bit and is related to pins 3 (output) and 14 (input) of the 4076 IC while the "D" bit is the most significant bit and involves pins 6 and 11.

BCD TO DECIMAL (1-OF-10) DECODER



LOGIC TABLE

HEXADECIMAL NUMBER	INPUT PINS ACTIVATED A PA5	B PA6	C PA7			OUTPUT PIN ACTIVATED	IC 4076 ADDRESSED
0	0	0	0	=	0	3	5
20	1	0	0	=	1	14	1
	0	1	0	=	2		
	0	0	1	=	4		
60	1	1	0	=	3	15	2
A0	1	0	1	=	5	6	3
	0	1	1	=	6		
E0	1	1	1	=	7	4	4

Figure 9. This device converts any 3-bit code into 1-of-8 outputs. The BCD code is input on terminals 10 through 13, with the least-significant or $2^0 = 1$ bit on "A", the $2^1 = 2$ bit on "B", the $2^2 = 4$ bit on "C", and the $2^3 = 8$ bit on "D". Positive logic with a "1" positive and a zero grounded is used.

```
LDA   $$60     Similarly for 10's place
STA   $COCC
LDA   $COCC
AND   $$0F
STA   $7003
LDA   $$20     Similarly for 1's place
STA   $COCC
LDA   $COCC
AND   $$0F
STA   $7004
```

a step when the signal on pin 16 drops below 2 volts. The signal must stay below 1 volt for 20 μsecs.

A BASIC routine determines the number of steps to be taken. Each step of the motor is 0.9 degrees. The syringe buret to which it is attached, delivers 0.05 ml for each revolution. Thus, the resolution is 0.000125 ml per step.

BURET STEPPING RESOLUTION

$$\frac{\text{360 DEGREES}}{\text{0.05 mL}} \times \frac{\text{STEPPER MOTOR STEP}}{\text{0.9 DEGREES}} = \frac{\text{8000 STEPS}}{\text{mL}}$$

OR

0.000125 mL PER STEP

The BASIC program calls an assembly language routine via a FOR-NEXT loop for the number of steps needed. The assembly language routine is shown below.

```
BEGIN   LDA  $$00    Select Data Direction Register by making
        STA  $COCF   Bit 2 of Control Register B($COCF) a zero.
        LDA  $$FF    Make all lines, PBO-PB7 outputs
        STA  $COCE   $COCE is Data Direction Register B
        LDA  $$04    Bit 2 of Control Register B set
        STA  $COCF
        LDA  $7340   This location contains the direction (CW or CCW) given
        STA  $COCE   by the BASIC routine.
        LDA  $$20
        JSR  $FCAB   Short delay loop
        INC  $COCE   Make PBO=1; Pin 16 of driver card low; take a step
        LDA  $$10    Short delay loop; keeps pin 16 low
        JSR  $FCAB
        RTS          Return to BASIC program
```

A BASIC driver program is used to carry out a titration. At present the program inputs 60 pH values from the meter and calculates the variance (the square of the standard deviation). Sixty values are taken to allow about 30 seconds for the pH readings to stabilize. The calculation of the variance is done entirely in assembly language. Assembly language is faster than BASIC and calculations can be carried out with no round-off error. The variance is then compared to a user-set value (usually 0.001 pH). If the variance is greater than the test value, this indicates that the pH readings have not yet stabilized. In this case, another reading is taken and the first value is discarded. Then, the variance calculation is repeated on the last 60 values. When the pH has stabilized, the mean of the pH values is stored, and the program directs the stepper motor to deliver some titrant.

Table 2. Automated Buret Calibration

Apparent Vol. Delivered (mL)	True Vol. Delivered (mL)
0 to 0.5	0.5001 ± 0.0001
0 to 1.0	1.0004 ± 0.0001
0 to 1.5	1.5005 ± 0.0000
0 to 2.0	1.9999 + 0.0002
0 to 2.5	2.5001 + 0.0002

CALIBRATION OF BURET

The ability of the buret to deliver specified volumes of titrant was tested by weighing the water it dispensed at specified intervals over its range. The results are given in Table 2. As can be seen the results are excellent. The highest standard deviation in the table was 0.0002 mL which corresponds to a relative standard deviation of 0.01 percent.

CONCLUSION

We have been using this apparatus for several months now and have found it to be an accurate and reliable aid in carrying out pH titrations and in evaluating equilibrium constants.

ACKNOWLEDGEMENTS

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