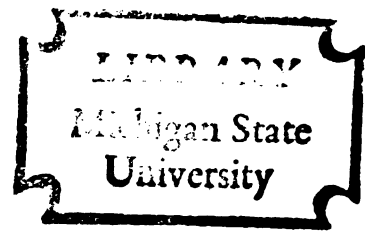
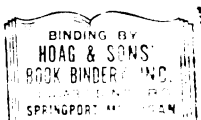


A COMPUTER-INTERACTIVE
BIPOLAR PULSE CONDUCTANCE SYSTEM

Dissertation for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
KEITH JOSEPH CASERTA
1974



1-30
7-21



ABSTRACT

A COMPUTER-INTERACTIVE BIPOLAR PULSE CONDUCTANCE SYSTEM

By

Keith Joseph Caserta

A computer-interactive conductance measurement system has been developed which utilizes the bipolar voltage pulse technique for conductance determination. The entire measurement system is controlled by a dedicated minicomputer. Within the system the computer exercises control over the pulse width, the pulse height, the amount of offset current applied, and the tracking amplifier gain. The computer also controls the triggering of the bipolar pulse perturbation and the pulse repetition frequency. It monitors the conductance signal produced by the sum of the cell and offset currents, and stores and analyzes this data. Discrete conductance measurements may be made as often as every thirty microseconds. The dynamic range of measurable conductances extends from 0.22 to $1.8 \times 10^{-7} \Omega^{-1}$.

Signal-to-noise ratios for this instrumental system vary from 6.40×10^2 to 6.70×10^3 over the operating range, for single bipolar pulse perturbations. Averaging up to 2000 perturbations per point increases these values to 1.18×10^3 to 6.40×10^5 over the operating range. The conductance measurement is unaffected by parallel cell capacitances at least as high as 1000 pF. Accuracy within the operating

59510
range has been found to vary from 0.38 to 0.0037 percent for a series capacitance of 10 μ F. Increased accuracy is obtained at larger series capacitance values.

The conductance system is capable of measuring temperature simultaneously by means of a separate analog temperature monitor and digital conversion circuit. Software has been written which utilizes this measured temperature for correction of conductance data for temperature fluctuations. This is done by curve-fitting a temperature-conductance profile obtained by changing the temperature of the system to be studied over the temperature range of interest, while acquiring conductance and temperature data. The coefficients of the fitted curve are used to calculate temperature-corrected conductance within various data analysis routines. In addition to the correction features, a record of the temperature-conductance behavior of a particular system may be obtained. This behavior has been investigated for several electrolytes in aqueous media, and several in non-aqueous media. The curves thus obtained have indicated that the temperature coefficient of conductance will often change sign over a few degrees temperature change. This preliminary work has indicated that such profiles may be both qualitatively and quantitatively useful.

Other programs within the computer-interactive conductance system software set enable the system to acquire and analyze data for conductometric titrations, stopped flow kinetic experiments, dissociation constant determinations, absolute conductance measurements, chromatography monitoring, instrumental performance characterization, and instrumental self-testing. In addition, a computer-interactive instructional package has been developed for teaching operation of the system. It includes

text messages, interactive dialog, and graphic displays. This facility provides the novice operator with most of the information required to operate and understand the system. It also provides a continual reference source for the more experienced user.

A number of aqueous and non-aqueous titrations have been investigated with the system. The chemiluminescence reaction of luminol with base in DMSO and 1:1 DMSO-EtOH has also been studied with the system by monitoring the conductance, temperature, and chemiluminescence changes.

The computer-interactive conductance system has been shown to be a versatile and powerful measurement tool which is capable of monitoring those conductance changes which are too small for, too fast for, or beyond the operating range of conventional instruments.

A COMPUTER-INTERACTIVE
BIPOLAR PULSE CONDUCTANCE SYSTEM

By

Keith Joseph Caserta

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1974

I dedicate this Dissertation to my sons, Keith and Kevin.

May they love to learn, be strong but gentle,
and be free to dream and create and be happy.

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to Professor C. G. Enke for his help and guidance during the entire project presented in this Dissertation. Professor Enke succeeded not only in providing technical aid when it was needed but, equally importantly, helped me develop an appreciation of the broader perspective of analytical measurement and scientific technique.

I wish to thank the fellow members of Professor Enke's research group for the interaction and comradeship which developed between us during my studies at Michigan State. I especially want to thank Brian Hahn and Tim Nieman for their friendship, interest, and help during the past three years. I wish to express appreciation to Professor S. R. Crouch for his aid during the project, and the other members of my Guidance Committee for their comments and interest. Professor R. N. Hammer deserves special thanks for his contributions to my overall graduate education.

I want to thank my parents and grandparents who continuously provided the guidance and encouragement which lead to whatever successes I've enjoyed in my studies and research. Special thanks go to my father who has supported me in everything I've done, all my life, and who probably knows me best of all.

Most importantly, I want to express my deepest thanks to my beautiful wife, Connie. She has stood with me throughout these last four years of study, during days when my work has kept me at the laboratory and left her alone with the children for long hours at a time. She has been a daily inspiration to me to pursue my work with determination. And, finally, she

typed the initial draft of this entire Dissertation while taking care of our two sons and our apartment, and preparing our meals and our move to a new city and a new life.

TABLE OF CONTENTS

	Page
LIST OF TABLES	ix
LIST OF FIGURES	x
INTRODUCTION	1
A. User-Oriented Laboratory Instrumentation	1
B. Expanding the Application of Classical Measurement Techniques Through Laboratory Automation	3
CHAPTER 1. General Description of the Computerized Conductance System	6
A. Philosophical Overview	6
B. The Computer-Interactive Conductance System	7
C. The Computerized System Employed in the Computerized Conductance System	8
D. The Computer-Interactive Conductance System Block Diagram	10
E. The Computerized Conductance System Software Library	13
CHAPTER 2. The Analog Measurement of Conductance	20
A. Early use of the AC Bridge Technique	20
B. Later Improvements in the AC Bridge Technique	23
C. The Bipolar Pulse Technique	26
D. The Analog Circuits of the Computerized Conductance System	32
E. The Power Supplies of the Computerized Conductance System	40
CHAPTER 3. Implementation of a Dedicated Computer for Total Digitization of the Conductance Measurement Sequence	43

Chapter		Page
	A. Interfacing the Digital Computer for Chemical Applications	43
	B. Digital Conversion and Control of Analog Signals	49
	C. Digital Sequencing of the Bipolar Pulse Measurement	55
CHAPTER 4.	Programming the Computerized Conductance System for Optimized Measurement	63
	A. Creating a Software Library for Laboratory Instrumentation	63
	B. Laboratory Computer Languages	64
	C. Programming with Commonly Provided Languages	67
	D. The DEC OS/8 Operating System	68
	E. Creating an Experimentally Flexible Software Set	73
	F. Determination of the Optimum Measurement Parameters for the Computerized Conductance Instrument	74
	G. The Preliminary Scan Routine	75
	H. The Averaging Routine	80
	I. The Timed Data Acquisition Routine	82
CHAPTER 5.	Performance Characteristics and Self Testing Ability of the Computerized Conductance System	91
	A. Performance Characterization Via the System Software	91
	B. Determination of System S/N, Precision, and Resolution	91
	C. Determination of System Accuracy	98
	D. Optimum Pulse Width Selection	105
	E. Scale Change Corrections in the Computerized Conductance System	108
	F. Linearity, Range and Speed Characteristics	110

Chapter		Page
	G. System Diagnostic and Exerciser Facility	111
CHAPTER 6.	Temperature Measurement and Compensation in the Computerized Conductance System	119
	A. The Temperature Monitor	119
	B. The Software set for the Determination of the Thermistor Response Coefficients of Conductance	126
	C. Conductance Data Enhancement Through Temperature Variation Correction	139
	D. Some Comments on the Shape of Conductance-Temperature Profiles	148
CHAPTER 7.	Application of the Computerized Conductance System to Titration Monitoring and Analysis	152
	A. Specific Software and Hardware for Titration Experiments	152
	B. Titration Data Analysis and Display Software	156
	C. Early Studies with the Computerized Conductance System: Precipitation Titration of Ag^+ with KCl	161
	D. Some Observations Concerning the End Point Phenomenon Associated with Certain EDTA Titrations	163
	E. Determination of Small Amounts of NaOH in the Presence of Large Quantities of Sodium Phenolate	174
	F. Titration of Phthalic Acid in 1:1 DMSO-EtOH	180
CHAPTER 8.	Application of the Computerized Conductance System to Kinetic Studies: Preliminary Investigation of the Luminol Reaction	184
	A. Specific Software for Kinetic Experiments	184
	B. Specific Hardware for Kinetic Experiments	187
	C. Previous Investigation of the Luminol Reaction	191

Chapter		Page
	D. Stopped-flow Study of the Luminol Reaction	195
	E. Conclusions from the Preliminary Investigation of the Luminol Reaction	208
CHAPTER 9.	CBHELP: The System Instructional Package	212
	A. Use of the Computerized Conductance System by Future Workers	212
	B. Creating the CBHELP Program	213
	C. Using the CBHELP Program	224
CONCLUSION		230
REFERENCES		231
APPENDIX	Selected Program Listings	234
	A. CBTSLS	234
	B. CBPSLT	250
	C. CBTCLH	262
	D. CBTALR	274
	E. CCLALF	282
	F. CDTALC	287
	G. CFPTLI	290
	H. CCLMLT	291
	I. CDPMLT	297
	J. FILEII	305
	K. CBHELP	310

LIST OF TABLES

Table		Page
1.	Computerized conductance system instruction set.	48
2.	Performance characteristics.	99
3.	Accuracy for various conductance-series capacitance combinations	104

LIST OF FIGURES

Figure		Page
1	Computer System Block Diagram	9
2	Computerized Conductance System Block Diagram	11
3	Computerized Conductance System Software Set Flowchart	14
4	AC Conductance Bridge Circuit	21
5	DC Coupled Lock-in Detector Conductance Measurement Circuit	25
6	Bipolar Pulse Conductance Device	27
7	Schematic Diagram of the Computerized Conductance System Analog Circuits	33
8	Photograph of the Analog Circuits	39
9	Photograph of the Conductance Instrument Power Supply	41
10	Schematic Diagram of the +24 Volt Relay Power Supply	42
11	PDP/8 Computer Functions Available with the Heath EU-801E Interface System	47
12	Signal Sampler and Converter Schematic Diagram	51
13	Control Circuits Schematic Diagram	54
14	Measurement Sequencer Schematic Diagram	57
15	Photograph of the Digital Circuits Compartment	60
16	Photograph of the Control Circuits for Offset and Gain	61
17	Photograph of the Control Circuits for Pulse Height and the Analog Temperature Monitor Circuit	62
18	Simplified Preliminary Scan Flowchart	77

Figure		Page
19	Preliminary Scan Routine Output	79
20	Averaging Routine Flowchart	81
21	Averaging Routine Output	83
22	Timed Data Acquisition Routine Output	84
23	Simplified Timed Data Acquisition Routine Flowchart	85
24	Simplified Reset Routine 1 Flowchart	88
25	Simplified Reset Routine 2 Flowchart	90
26	Random System Noise Profile (Plot)	94
27	Reduction of System Noise to Quantization Level (Plot)	95
28	Ensemble Averaging Improvement in S/N and Resolution (Plot)	97
29	CBPSLT Program Flowchart	101
30	Percent Relative Error vs. Log (R) for a Series Capacitance of 5.0 μ F (Plot)	107
31	Conductance-Time Profile for Cooling of a Sulfuric Acid-Water System, Raw and Scale Change Corrected Data (Plot)	109
32	CBTCLH Program Flowchart	113
33	Test Probe Schematic Diagram	114
34	Temperature Monitor Schematic Diagram	122
35	Temperature Monitor Response vs. Thermistor Conductance (Plot)	125
36	Thermistor Response - Conductance Profiles for Luminol, Potassium Tertiary Butoxide, and Reaction Products in DMSO (Plot)	128
37	CBTALR Array Arranger Program Flowchart	130
38	Array Arranged Data from Figure 36 (Plot)	133
39	CCLALF Program Flowchart	134

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

Figure		Page
40	Curve Fitting Program Flowchart	136
41	CFPTLI Program Flowchart	138
42	Temperature - Conductance Profile and Cubic Fitted Curve for a Sulfuric Acid-Water System (Plot)	140
43	Conductance - Time Profile for Cooling a Sulfuric Acid - Water System, Raw, Scale Change and Temperature Corrected Data (Plot)	141 141
44	Conductance Profile for Addition of Concentrated Sulfuric Acid to Water. Raw and Temperature Corrected Data (Plot)	144
45	Temperature Change When DMSO and EtOH are Mixed in the Stopped Flow. Temperature Change During a Reaction of Luminol in DMSO and KOH in EtOH (Plot)	145
46	Stopped-Flow Study of the Luminol System. Raw and Temperature Corrected Conductance vs. Time (Plot)	147
47	Automatic Burette Interface Schematic Diagram	154
48	Simplified CCLMLT Program Flowchart	157
49	Simplified CDPMLT Program Flowchart	160
50	Conductometric Titration of Ag^+ with KCl (Plot)	162
51	Conductometric Titration of Ca^{++} with EDTA in $\text{NH}_3/\text{NH}_4^+$ Buffer Showing End Point Anomaly (Plot)	165
52	Conductometric Titration of $2.3 \times 10^{-5} \text{M}$ Ca^{++} with $2.0 \times 10^{-4} \text{M}$ EDTA in $\text{NH}_3/\text{NH}_4^+$ Buffer (Plot)	169
53	Induced Conducticator Effect for Titration of Ca^{++} with EDTA in $\text{NH}_3/\text{NH}_4^+$ Buffer Before and After Scrubbing the Cell (Plot)	172

Figure		Page
54	Conductometric Titration of NaOH with Phenol in the Presence of Sodium Phenolate (Plot)	177
55	Conductometric Titration of NaOH with HCl in the Presence of Sodium Phenolate (Plot)	179
56	Conductometric Titration of Phthalic Acid with KOH in 1:1 DMSO-EtOH (Plot)	181
57	Photograph of the Early Hacker Stopped-Flow Apparatus	186
58	Luminescence Data Monitor	190
59	Conductance Curve of the Luminol-Potassium Tertiary Butoxide Reaction in DMSO (Plot)	196
60	Temperature Profile Due to Mixing two DMSO Solutions of Luminol and Potassium Tertiary Butoxide in an Unthermostated Cell (Plot)	197
61	Conductance Change with Increasing Concentration of KOH in 1:1 DMSO-EtOH (Plot)	201
62	Equivalent Conductance vs. (Concentration) ^{1/2} for KOH in 1:1 DMSO-EtOH (Plot)	202
63	Conductance and Chemiluminescence Curves for a Reaction of Luminol in DMSO with KOH in EtOH (Plot)	206
64	Conductance Change for the Reaction of Luminol in DMSO with KOH in EtOH Corrected for Background Effects (Plot)	207
65	FILEII Program Flowchart	218
66	Photograph of CBHELP-Generated Scope Display of the System Block Diagram	221
67	X-Y Plotting of a CBHELP-Generated Graphic Display Depicting Pulse Width Selection Curves	222
68	Program Set Selection Options in the CBHELP Program	226

Figure		Page
69	CBHELP-Generated Program Flowchart for Temperature-Conductance Profile Measurement and Analysis	227

INTRODUCTION

A. USER-ORIENTED LABORATORY INSTRUMENTATION

A significant portion of the research effort in analytical and physical chemistry, in recent times, has been directed toward development of instrumentation and instrumental techniques for chemical analysis and basic physical measurement. This research has not only resulted in faster, more accurate, and more precise measurements, but also in the ability to perform measurements which were not previously possible.

Perhaps the greatest problem associated with the use of this new and sophisticated instrumentation is that most of these measurement systems require equally sophisticated operators to insure that they will be utilized to the fullest extent. This situation has resulted in the emergence of specialists in NMR, far IR, interferometric, ESR, and ESCA spectroscopic techniques, as well as in mass spectrometry, conventional voltametry, coulometrics, and so forth. These groups of specialists have been needed in order to operate these instruments in the various modes which have been designed into them and to interpret the extraordinary amounts of data, which these techniques produce. The conventional laboratory chemist does not usually possess the time or the inclination to familiarize himself with the details of operation and data interpretation for more than a few of these methods. Thus, the caliber of the experimentation, which he is able to realize through the use of these techniques, is very much dependent upon his ability to communicate his desires and goals to the specialists. Unfortunately, the necessary "meeting of minds" often fails to occur, resulting in a

poorly designed experiment and only minimal utilization of the power of a particular measurement technique.

Problems associated with optimum utilization of an analytical method are not confined to those techniques which have a significant group of specialists dedicated to them. In addition to these, there are numerous other techniques which are commonly used by the laboratory chemist to solve analytical problems. These techniques are rarely utilized to their maximum capabilities because there seldom is an individual present who possesses the necessary expertise to take full advantage of the method. What appears to be needed in the case of the specialized instruments and the less complex but more commonly used techniques is a system through which any operator, with a reasonable technical background, can realize the best measurement possible with a particular analytical technique, for each experiment which he designs and executes himself.

Fortunately, the introduction of monitoring and control computers into laboratory instrumentation in the past eight years does, at least, hold the promise of not only greatly enhancing the sophistication of instrumental techniques, but also adapting easily to operators who are relatively unfamiliar with the intricacies of these methods. Nevertheless, this goal can be accomplished only if the computer interaction is properly implemented, not only from a hardware standpoint, but also from a philosophical one. Since computer-interactive instrumentation has the ability to perform both unique and delicate experiments as well as to produce voluminous amounts of data, there exists a very real danger of building such instrumentation in a manner in which the overall instrumental system (instrument, computer, peripherals, etc.)

as (read)

2000 85

for a

relative

transmission

used for

interaction

reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

the reaction

has a greatly increased "apparent" complexity (as it appears to the operator) as opposed to more conventional systems.

From a chemist's viewpoint, then, the goal in designing computer-interactive instrumentation should be to permit maximum utilization of a technique. This should be done regardless of the complexity required for any component of the system. However, an equally important consideration is that which requires the measurement system-operator interaction to be such that the experiment performed with the system will appear to be only as complex as the chemistry involved. Furthermore, the final form of the data produced by such a system should make interpretation as simple as possible. If any analytical technique is incorporated into such a system, the result will be a user-oriented laboratory measurement device which is not dependent upon operation by a specialist. If properly designed, the device will be sufficiently flexible to move from one analysis problem to another totally different one with little modification beyond that of changing the operating program. The instrument can then be "time shared" among many different users, much as the computer itself can be utilized in the time sharing mode.

B. EXPANDING THE APPLICATION OF CLASSICAL MEASUREMENT TECHNIQUES THROUGH LABORATORY AUTOMATION

Recently, there has been a renewed interest in those measurement techniques which monitor the bulk properties of solutions. These techniques do not differentiate between chemical species but are responsive to some overall physical property. Conductance measurement, with which this thesis is concerned, is, of course, one of these

classical bulk property techniques. It has traditionally been utilized for titration monitoring, where a specific chemical reaction between analyte and titrant is chosen such that a chemically specific analysis method need not be used. Chromatographic monitoring is another area in which conductance instruments are being used as detectors. Finally, as will be demonstrated later in this manuscript, reaction mechanisms can be studied with conductance techniques alone, or by coupling these measurements with other, more chemically specific, methods.

Conductance methods, although certainly in widespread use, have been generally ignored by analysts. This is due both to the lack of understanding of interferences present in real systems when these measurements are made and to the application problems associated with the use of classical conductance instruments. The problems include the necessity of platinizing electrodes, delicately balancing bridge and grounding circuits, gross dependence of the property measured on temperature, and the calculations necessary for correction of conductance data for interferences, for analysis of chemical systems, and for plotting meaningful data. The measurement of conductance, although often utilized in laboratories concerned with widely diverse studies, has usually not been performed in an optimum manner, and has seldom been exploited for its maximum capabilities. This is the direct result of the problems mentioned above, as well as the lack of measurement speed from which the technique has traditionally suffered. Thus, conductance techniques fit easily into the category of research techniques which lack a widespread group of routine applications specialists to oversee the modernization of the technique.

It is the purpose of this thesis to demonstrate how the application

of a dedicated computer to the monitoring and control of the entire conductance measurement process results in a dynamic laboratory measurement system which overcomes most of the problems associated with the conventional application of the conductance technique. In addition, the use of the computer-interactive system expands the application possibilities of conductance measurement into areas where it has not previously been used at all, or only used conservatively. Finally, the system described here enables an unsophisticated operator to perform experiments which make the maximum use of conductance measurement and produce the maximum useful data automatically, without regard to the operator's degree of understanding of the intricacies of the measurement being performed.

CHAPTER 1

GENERAL DESCRIPTION OF THE COMPUTERIZED CONDUCTANCE SYSTEM

A. PHILOSOPHICAL OVERVIEW

The thoughts presented in the Introduction to this manuscript could certainly serve as a basis for design of any computerized measurement system. The fact that they were, as will be seen, important considerations in the design of the computerized conductance system does demonstrate that they are definite principles which can be implemented in the design of user-oriented laboratory measuring apparatus. However, these principles are, in themselves, of little value to the researcher unless he is directed toward the chemical problems which this approach to instrumentation is strategically designed to solve. To one who would be a chemist, the development of instrumentation performing no unique chemical measurement would appear to be a foolish pursuit. The author feels certain that this is the case.

The author wishes to stress, at the beginning of the discussion of the actual research presented in this thesis, that the work to be presented here did not involve the building of a unified conductance instrument. The group of circuits which perform conductance measurement per se do not constitute an independent instrument. Except for an on-off switch they possess no dials or dial settings and no switches or indicators which would enable them to be operated in the way that any other instrument might be. They constitute several functional blocks out of many separate blocks which, when properly combined in implementation, are the viable chemical measurement tool referred to

here as the computer-interactive conductance system. Other functional blocks, such as the temperature monitor, real-time clock, and display devices, are of nearly equal importance when the overall operation of the system in a chemical measurement application is considered. The entire system is welded into a functional unit through a series of interfaces and a collection of flexible software, all of which are rendered interactive through the power of the controlling computer. The author can assume considerable responsibility for the design, construction, and ultimate operation of many of these functional blocks but not, by any means, all of them. However, the unique manner in which these blocks are combined to create a laboratory measurement system which is user-oriented, and the chemical measurements which have been made with this system to the present time, are the direct subject of this thesis and the author's contribution to chemical research.

B. THE COMPUTER-INTERACTIVE CONDUCTANCE SYSTEM

The computerized conductance system itself is constituted from three interacting elements, the computer and its peripherals, the conductance instrument (referring, now, to the group of circuits which, when placed in the system, perform conductance measurement), and the software. The computer intimately takes part in the operation of the conductance instrument through the logical flow of the programs. The experiment, monitored most directly by the conductance instrument itself, is under the supervision of the measurement system at all times. This four-way involvement, software-computer-instrument-experiment, results in experiments which are modified during their execution by the

measurement system in such a way that the best measurement attainable for that particular chemical process is obtained. Furthermore, the operator, having set up the experiment, need have no further knowledge of the intricacies of the bipolar pulse measurement technique because the system does possess that "knowledge" through the logical sequencing and decision processes performed by both the hardware and the software throughout the experiment and subsequent data analysis. Finally, the computerized conductance system itself, has become capable of supplying the operator with much desired information concerning the theory, operation, adjustment, and trouble-shooting of, as well as program selection for the computerized conductance system (Chapter 9).

C. THE COMPUTER SYSTEM EMPLOYED IN THE COMPUTERIZED CONDUCTANCE SYSTEM

The computer system which was available for use with the computerized conductance system is shown in Figure 1. It has proven to be an extremely powerful system for laboratory use. This arises from both the standard peripherals it includes and the specialized peripherals interfaced in this laboratory.

The computer is a Digital Equipment Corporation (DEC) PDP-8/I minicomputer with 12K of memory. 8K of this memory is standard core memory and 4K is a solid state memory block manufactured by Calcomp Galaxies Inc. The standard computer peripherals include an extended arithmetic element (EAE) for fast, hardware multiplication and division, dual magnetic tape units (DECTAPE), a high speed paper tape reader and punch (all made by Digital Equipment Corporation) and an ASR 35

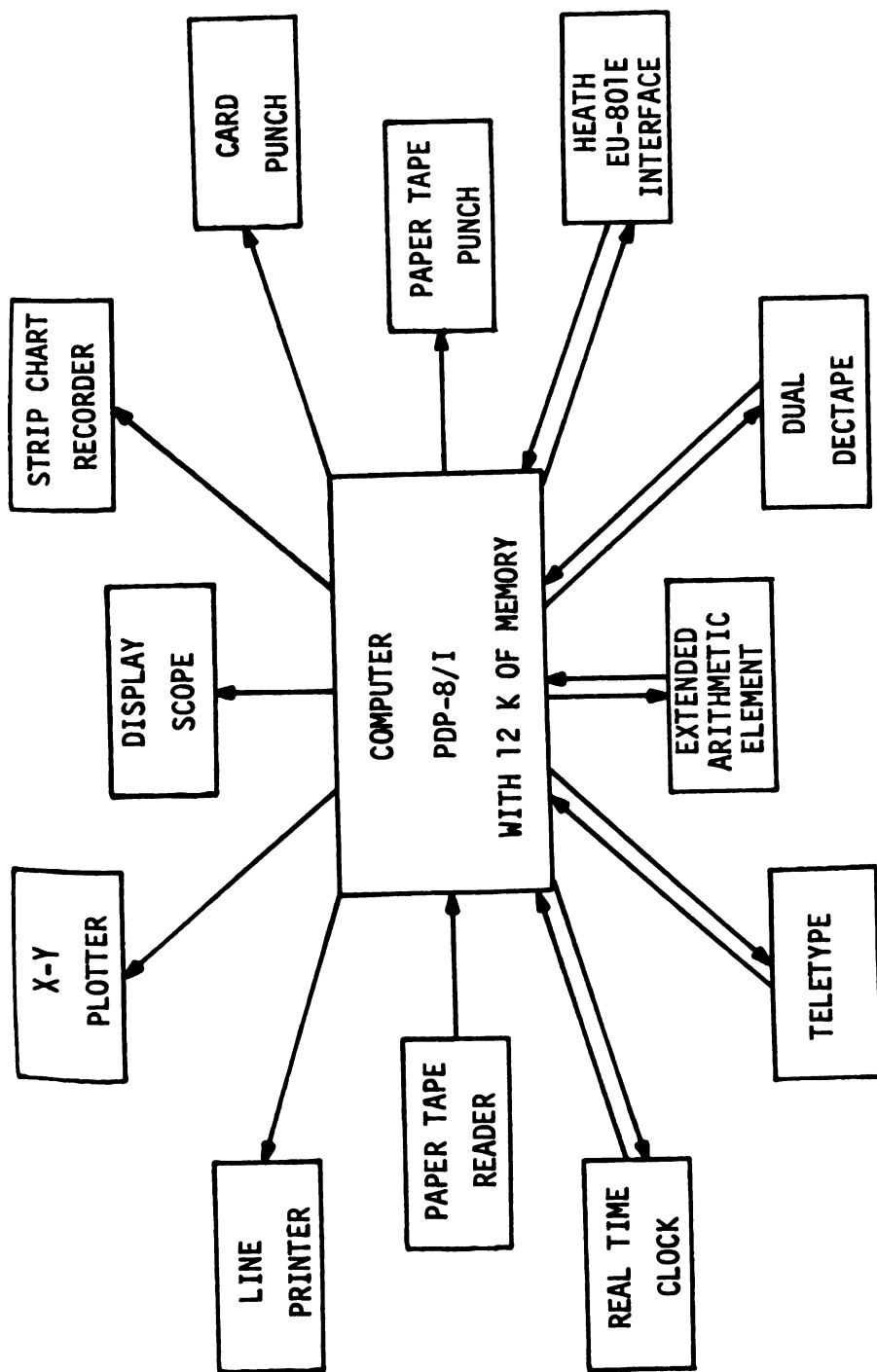


Figure 1. Computer System Block Diagram.

teletype. In addition, several non-DEC peripherals have been interfaced to the PDP-8/I in this laboratory. These include an RCA-301 line printer (1), a card punch (2), a Varian F-80 X-Y plotter and a Tektronix 535A display scope (3) with a character generating capability (4), and a Heath EU-205-11 strip chart recorder (3). Finally, there is an extremely versatile mainframe real-time clock, as described by Hahn and Enke (5).

The Heath EU-801E interface system (6) (described in detail in Chapter 3) was used for interfacing the above peripherals as well as all components of the conductance instrument itself. The bipolar pulse conductance instrument, which was made functional through this computer system, was structured to take advantage of the interactions available with it.

D. THE COMPUTER-INTERACTIVE CONDUCTANCE SYSTEM BLOCK DIAGRAM

The bipolar pulse conductance measurement technique will be examined in detail in Chapter 2. Briefly, it involves the application, to a cell, of two voltage pulses of equal magnitude and duration but opposite polarity, followed by instantaneous measurement of the cell current at the exact end of the second pulse. Measurement in this way has the effect of eliminating the capacitive interferences associated with real cells, as will be seen, resulting in a much more accurate determination of the true cell conductivity than possible with more classical techniques.

The specific modules which constitute the conductance instrument are shown in the overall conductance system block diagram of Figure 2. The instrument is controlled by data transferred from the computer to

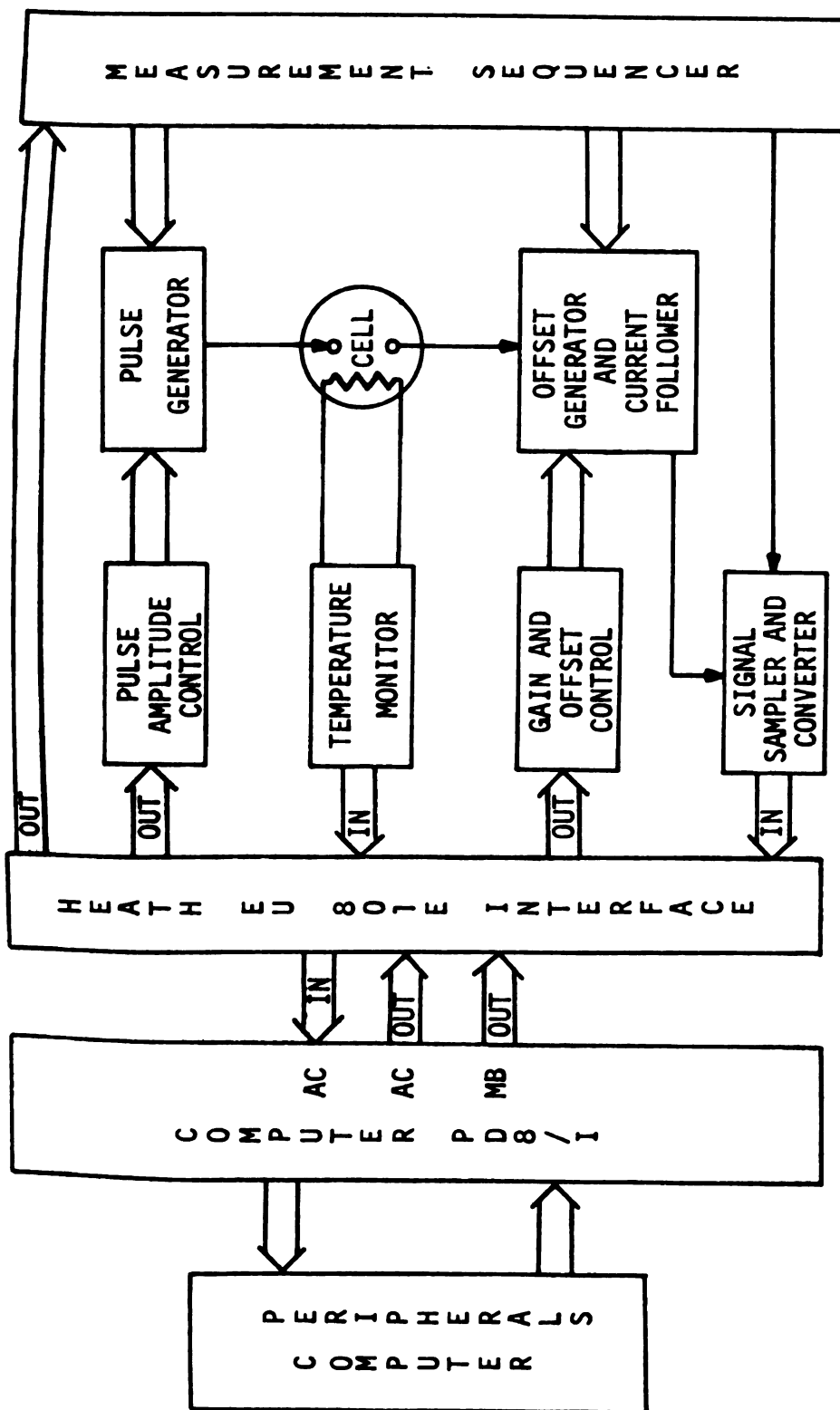


Figure 2. The Computerized Conductance System Block Diagram.

the control circuits and the measurement sequencer (both discussed in detail in Chapter 3) through the Heath interface. The computer also supplies the triggering signal to the measurement sequencer which initiates pulsing. The pulse amplitude control receives data which determines the pulse height. It provides the correct positive and negative voltage levels to the pulse generator (Chapter 2). The gain and offset control is set to determine the amplification of the signal produced by pulsing the cell and the amount of that signal offset before amplification (Chapter 2). The measurement sequencer, which supplies the signals that determine the length of the pulses and the timing of the measurement, contains a time base also controlled by the computer. The analog signal produced by combination of the cell and offset currents is tracked, held, and converted (Chapter 3) under control of the measurement sequencer. Finally, the digital signal is driven into the computer upon request and stored for later analysis.

Cell temperature may be simultaneously followed by the temperature monitor which contains its own digital conversion system (discussed in Chapter 6). The temperature measurement is triggered and the data acquired by the computer. This data can be used by the computerized conductance system to correct conductance data for temperature fluctuations in the chemical system under study as well as to provide interesting information on the temperature-conductance behavior of solutions (chapter 6).

E. THE COMPUTERIZED CONDUCTANCE SYSTEM SOFTWARE LIBRARY

The flexibility of the computerized conductance system is realized through the software library which has been developed for it. A flow-chart-style listing of this library appears in Figure 3. All of the programs which perform data acquisition or analysis of directly acquired data are given a six-letter name which codes the operation and use of the program. The six-letters are decoded in the following manner:

Letter 1) A "C" in this position indicates that this program is a conductance system data acquisition, analysis, or test program. All other letters represent plotting or file generation routines.

Letter 2) This letter indicates the program sequence position in a group of programs performing acquisition and analysis of the same type of data. The letters run from B to F. The exception to this sequencing is CBTALR, which must follow CBTSLR. However, since CBTALR, as will be seen, creates a "new" data set, it was given a "B" sequence symbol.

Letter 3) This letter indicates the output devices used by the program. A "T" implies use of the teletype only. An "L" implies the use of the line printer and possibly the plotters and teletype also. A "P" implies the use of plotters and the teletype.

Letters 4 and 6) These are codes which designate the particular task which the program performs (discussed below).

Letter 5) This letter indicates the memory requirements for the particular program. An "L" indicates an 8K program, a "C" indicates a 12K program. The exception to this nomenclature, CBHELP, is coded to immediately inform the novice operator of

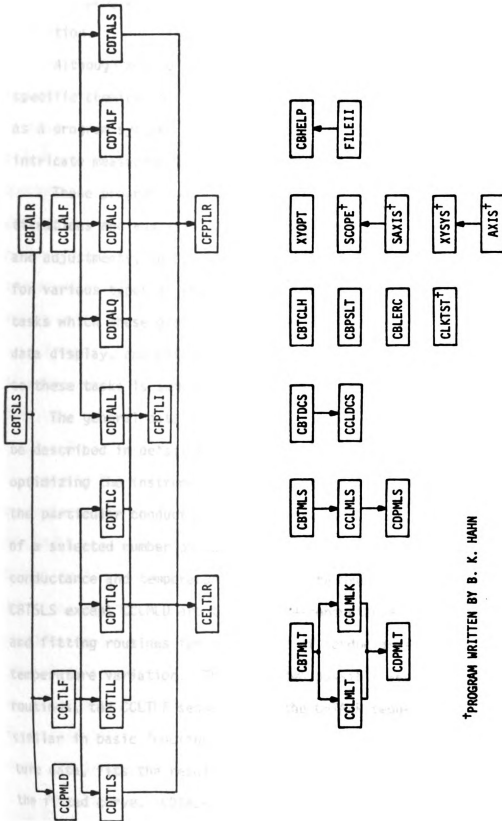


Figure 3. Computerized Conductance System Software Set Flowchart.

the program to call in order to solve problems in system operation.

Although most of these programs were originally written to perform specific chemical or instrumental measurements, when they are considered as a program system, they can accomplish an astounding variety of intricate measurements.

These programs may be divided into six basic groups including titrations and analysis, kinetics and analysis, instrumental tests and adjustments, temperature-conductance profiles and analysis, plotting for various types of analysis, and aid in using the system. The basic tasks which these groups perform are data acquisition, data analysis, data display, and reference. Each group and its particular approach to these tasks is summarized below:

The general data acquisition program for the system CBTSLS will be described in detail in Chapter 4. It includes routines for initially optimizing the instrument with respect to accuracy and resolution for the particular conductance measurement to be made, ensemble averaging of a selected number of points, and timed data acquisition of both conductance and temperature. All of the programs flowcharted from CBTSLS except CCLMLD are temperature-conductance profile analysis and fitting routines for correction of conductance measurements for temperature variation. There are two possible sequences within these routines, the CCLTLF sequence and the CBTALR sequence. They are very similar in basic function, each of them plots conductance vs. temperature data, fits the resulting curve, and outputs the data and plots the fitted curve. CBTALR is, however, a pre-analysis data arranging program (explained in detail in Chapter 6) which enables data to be

fitted without accidental weighting due to a non-linear rate of temperature variation during the measurement of the temperature-conductance profile. Program CCL(T or A)LF outputs the raw or arranged data respectively prior to fitting and sets up the fitting parameters. Program CDT(T or A)LS performs a fit to a function of the form $AX + BX^{1/2} + C$. Program CDT(T or A)L(L,Q, or C) performs fits to linear, quadratic, or cubic equations respectively. Program CDTALF can fit data to a fifth order equation. Raw data, fitted data from any program, and residuals may be output on the line printer with CELTLR. Fitted curves of any integer power may be plotted by the faster CFPTLI. This entire group is discussed in detail in Chapter 6.

Program CCPMLD is a data analysis routine for use with CBTSLS. It calculates standard deviation and S/N, as well as plotting raw data, for determination of instrumental performance, as presented in Chapter 5.

The CBTMLT sequence is used in titrations (Chapter 7) and dissociation studies (Chapter 8). Program CBTMLT is a simple modification of CBTSLS which contains instructions for titrator control. Program CCLMLT performs analysis of titration data including scale change, dilution, and temperature correction of such data. Program CCLMLK provides equivalent conductance and concentration data for determination of dissociation constants. Program CDPMLT plots conductance data vs. time (which corresponds to volume of titrant added for a timed data acquisition) for raw data and scale change, dilution, temperature, and dilution-temperature corrected data.

The CBTMLS sequence is used in kinetic studies. Program CBTMLS is a simple modification of CBTSLS which contains the instructions

for the stopped flow apparatus triggering of data acquisition. Programs CCLMLS and CDPMLS are similar to CCLMLT and CDPMLT, but do not include dilution correction provisions.

Programs CBTDCS and CCLDCS are designed to acquire and analyze not only conductance and temperature data but also data from some auxiliary source, such as a spectrophotometer, for kinetic studies. Program CCLDCS is capable of analyzing all three types of data and outputting their values on the line printer. In addition, it can fast plot on the display scope or slow plot on the X-Y plotter all three of these types of data plus the integral of the auxiliary data. These routines are described in detail in Chapter 8.

Programs CBTCLH is the general system exerciser and diagnostic program. It is used for troubleshooting, testing, or adjusting the conductance and temperature monitors. It outputs error messages which help to pinpoint instrument failure. The other testing programs for the conductance monitor are CBPSLT and CBTELC. Program CBPSLT is designed to test the system for accuracy, for use in not only characterizing the system but also in determining the optimum pulsing parameters to be used in a particular conductance region, and in instrument adjustment. Program CBLERC is another random exerciser for the conductance circuits which is no longer often used since CBTCLH has proven to be a more powerful diagnostic tool.

A real time clock testing and exerciser program, CLKTST (7) is included in the computerized conductance system to assure that critical timing of data acquisition will proceed smoothly.

A general utility plotting program, XYOPT, has proven to be a useful routine for plotting data for any calculation purposes. It

accepts scope and plotter scaling parameters and X and Y values input from the teletype. It may then plot those values on the display scope and X-Y plotter as Y vs. X or Y vs. $1/X$. It is also capable of plotting axes on the resulting plot.

Four other plotting routines (7) are used for data display in many of the analysis routines described above. Program SCOPE enables fast plotting of data on the display scope. It can be used to point plot or plot straight lines between points. Program SAXIS is used to plot axes on the display scope plots. Programs XYSYS and AXIS are X-Y plotter (and thus, slower) equivalents of SCOPE and SAXIS.

There are three other programs which are not currently functional but may be of use to future workers. Program CBTFLS takes temperature data simultaneously with (not immediately after) conductance data. It results in a savings in time when long pulses must be used. Program CBTFLA was designed to take data in the fastest possible manner, even where the range of data required one or more scale changes, for use in kinetic studies. It hasn't been completed since scale changes appear to be rare for the cell and flow system which have been used. Thus, CBTMLS has proven sufficient. Program CBLCLQ was designed for continuous analysis of slow data, such as slow chromatographic data. It prints out such data as they are acquired and plots them on the strip chart recorder. However, since no such systems have been investigated in the studies done to the present time, this program has not been updated for the latest computerized conductance system changes.

The final operating program in the computerized conductance system library is CBHELP. Program CBHELP is a rather elaborate attempt

to bridge the gap between experimenter and instrumentalist. It is an operator-interactive program designed to input to the novice user that information which he must know in order to use the computerized conductance system. It can lead an operator from a very shallow understanding of the measurement system to a detailed comprehension of the total operation and theory of the technique. It does this by explanations, questions, graphic displays, and user interactions. These text messages and graphic displays are generated by the FILEII program for use in CBHELP. CBHELP includes virtually all information which an experimenter would need in order to understand, operate, troubleshoot, and maintain the system. Furthermore, a very real effort was made, in writing CBHELP, to make it an enjoyable means of learning the system operation. This was done to enable an operator with no instrumentation or computer orientation to get a "hands on" feel for the computer and the computerized conductance system, thus relieving the often inherent fear of such systems. The author considers CBHELP to be so important to the accomplishment of the overall aim of the work presented here that the entire last chapter will be devoted to discussion of CBHELP goals and implementation.

CHAPTER 2

THE ANALOG MEASUREMENT OF CONDUCTANCE

A. EARLY USE OF THE AC BRIDGE TECHNIQUE

As early as 1926, Morgan and Lammert (8) had stated that, "The present status of our knowledge of methods for measuring the electrolytic conductance of solutions and liquids is such that it is quite necessary for a conscientious investigator, who wishes to make even a small number of determinations with any degree of precision, to have at his disposal a generous supply of both time and equipment." Now, forty-eight years later, conductance measurements are still not a bulk property analysis technique which can be quickly applied to a short-term chemical problem by the casually interested. Conductance has, instead, become the concern of specialists or those willing to invest the time required to master the technique, set up the apparatus, the cell, and the experiment, and perform the measurement. The increased complexity required for the technique to remain "competitive" with new "simpler-to-use" methods has resulted in the disuse of the technique. Many other electrochemical techniques have met similar fates with time.

Conductance measurements were then, as they still are, most often made by the use of a bridge circuit to which an oscillating field is applied to prevent electrode polarization. This technique was first made popular by Kohlrausch (9). Such a bridge circuit is shown in Figure 4 where the conductance cell occupies one arm of the bridge. Kohlrausch was the first investigator to place a capacitor, C_S in

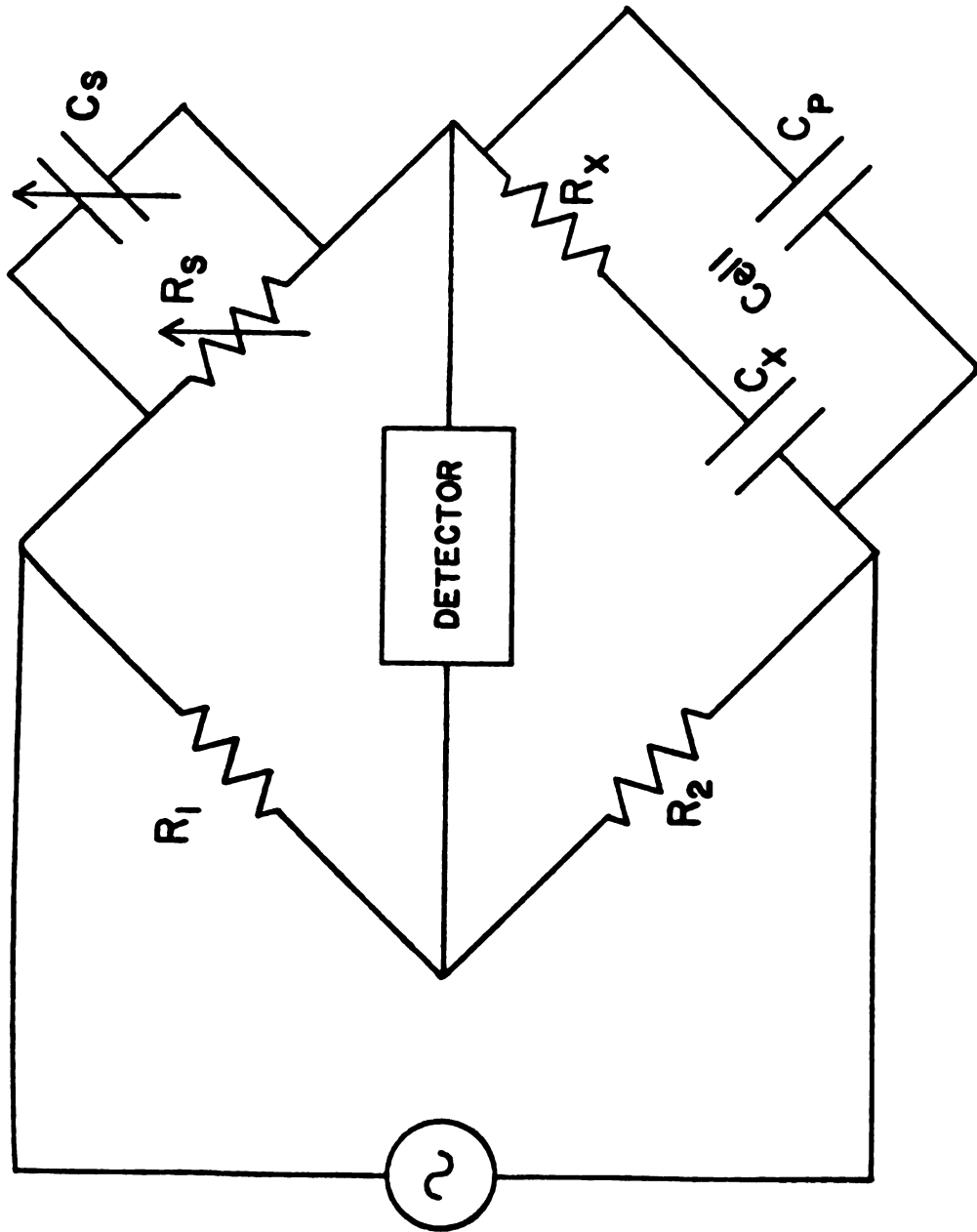


Figure 4. AC Conductance Bridge Circuit.

Figure 4, in parallel with the standard resistance, R_S , to compensate for the reactance caused by the double layer capacitance, the major source of C_X . He did not recognize the parallel cell capacitance, C_P , which results from several cell parameters including the dielectric properties of the solution between the electrode plates and the capacitance associated with the cell leads and their contact with the electrodes.

The relative error associated with measuring conductance in this way (disregarding the peculiarities of the instrument employed) results from the effects of the impedances of C_X and C_P . For a capacitor, the frequency dependent impedance, X_C , is given by:

$$X_C = \frac{1}{2\pi f C}$$

where $2\pi f$ is the angular frequency
 C is the capacitance in farads

Johnson and Enke (10) have shown that the magnitude of this relative error, for a perfectly balanced bridge obtained by adjusting R_S and C_S in Figure 4, is $(2R_X C_X \pi f)^{-2}$. The measurement may be compensated for this term if C_X and f are known. However, as they pointed out, the correction term should be kept small. In order to minimize this correction term in performing a conductance measurement using the AC-bridge technique, one generally tries to make the frequency of the applied field, and the magnitude of the series capacitance, C_X , both high enough that X_{C_X} is small compared to R_X . Likewise, R_X measured must be kept large enough that X_{C_X} is insignificant. This places a lower limit on the resistances measurable. On the other hand, as f increases, X_{C_P} also decreases. For large R_X , significant current may be diverted through

C_p , causing error and placing an upper limit on the value of f employed and the maximum measurable resistance.

B. LATER IMPROVEMENTS IN THE AC BRIDGE TECHNIQUE

Kohlrausch's initial design of the AC conductance apparatus, as well as the design of conductance cells, were improved by later workers. Jones and Bollinger (11) were the first to realize the presence of C_p . Their solution to the problem of the lead and contact capacitance and resistance was to design a cell in which close proximity of parts of opposite polarity is avoided.

Washburn and Bell (12) improved the Kohlrausch bridge by using a stable signal source of 1 KHz with a stable power supply and a tuned "telephone" as the null detector. Washburn (13) did recognize that at high frequencies, C_p contributes significantly to the error in the measurement. Jones and Josephs (14) used a modified Wagner ground which enabled them to measure smaller signals and thus extend the operating range upwards to about 60 K ohms. They also indicated the importance of balancing the reactance in each arm of the bridge to bring the current and voltage into phase in any two adjacent arms. At about the same time, Shedlovsky (15) used a screened bridge to increase the resolution to 1 part in 10^5 .

Various modifications for special tasks were designed into the same basic bridge circuit over the next forty years. The improvement in electronic circuitry has yielded oscillators of increased stability, more sensitive and useful detectors (especially the phase angle voltmeter as discussed by Schmidt (16)), and components with generally improved long term stabilities.

Quite recently Bentz, Sandifer, and Buck (17) introduced a DC coupled lock-in detector for extension of the dynamic operating range of the bridge to cover nine orders of magnitude (10^2 to $10^{11}\Omega$). Their measurement circuit is shown in Figure 5. The differential input of the operational amplifier serves as a null detector and keeps the circuit in balance regardless of changes in the cell impedance. The current-voltage phase relationship in the cell can be obtained by resolution of the amplifier output into in-phase (resistive) and quadrature (reactive) components with respect to the signal source. They resolved these components by correlating the amplifier response with square waves that were in phase and 90° out of phase with the perturbation signal. By interchanging R_M and the cell they were able to measure admittance rather than impedance. They performed their measurements in the admittance mode. They were able to resolve the quadrature admittance in either quadrature to 1% when it was 100 times smaller than the real admittance. They could then resolve the admittance to 1 part in 10^4 . However, the in-phase admittance, which approximates the conductance at high frequencies, could still only be resolved to 1%.

They were able to operate with frequencies on the order of 1000 Hz for conductance determination where the real admittance expression simplified to $1/R_X$. They claimed an accuracy of 1% from 10^2 to $10^8\Omega$ and 3% from 10^8 to $10^{11}\Omega$.

It can be seen that a number of workers made significant contributions to the enhancement of conductance measurement by modification of the AC bridge. Nevertheless, these applications of the traditional AC techniques all suffered from the complication of the instrument as it appeared to the experimenter, the confusing criteria developed for

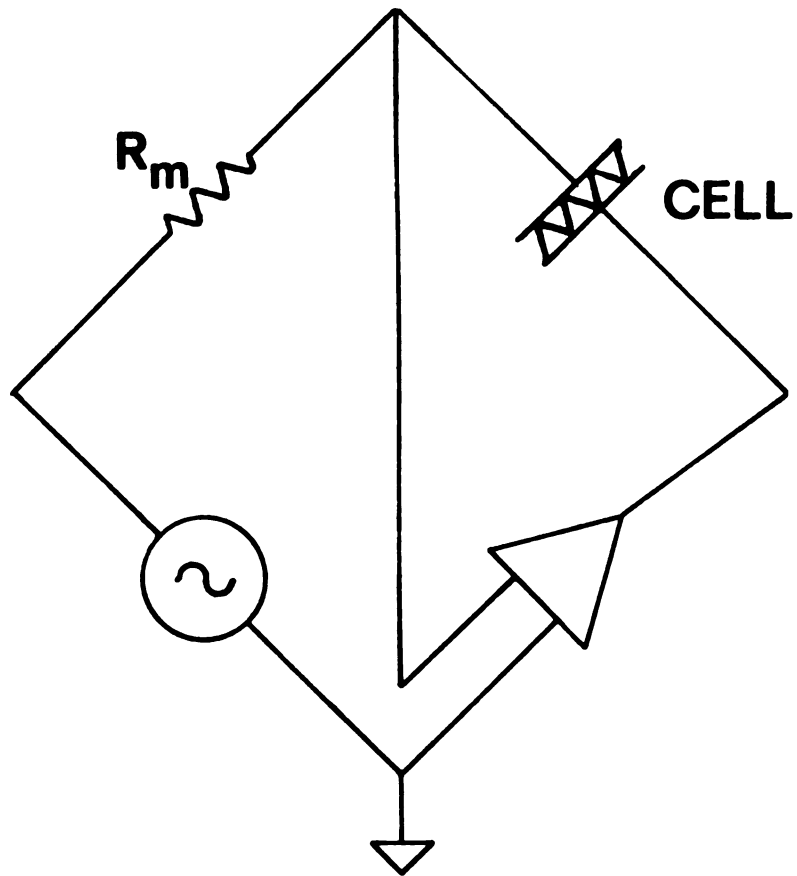


Figure 5. DC Coupled Lock-In Detector Conductance Measurement Circuit.

cell design, the necessity of platinizing the electrodes to increase C_X and the amount of time required for the actual measurement. Furthermore, the chemist's attention began to be drawn toward specific rather than bulk property techniques. It has only been in the past few years that more specific chemical reactions or separations, such as those employed in chromatographic analysis, have given rise to a rebirth of interest in bulk property detection techniques such as conductance. The first real breakthrough in fast and accurate conductance measurements, in which the AC bridge was finally put aside altogether, occurred in 1970.

C. THE BIPOLAR PULSE TECHNIQUE

In 1970 Johnson and Enke (10) introduced the bipolar pulse technique for rapid and accurate measurement of conductance. The technique involves the sequential application of two voltage pulses of equal magnitude and duration but opposite polarity to a cell, followed by measurement of the instantaneous cell current at the exact end of the second pulse. The effects of the capacitances are minimal at this time because the voltage across the series capacitance of the cell electrodes is nearly zero and the parallel capacitances associated with the conductivity cell and connections are drawing essentially no current. A determination of the cell current/voltage ratio at this time, therefore, allows an accurate measurement of the cell resistance. The sequence of events, illustrated in Figure 6 (10) proceeds as follows:

At the instant the first pulse is applied to the cell, C_p , being small, will charge quickly to the first potential, E_1 , causing a spike in the cell current. T , the length of one pulse, must be chosen such

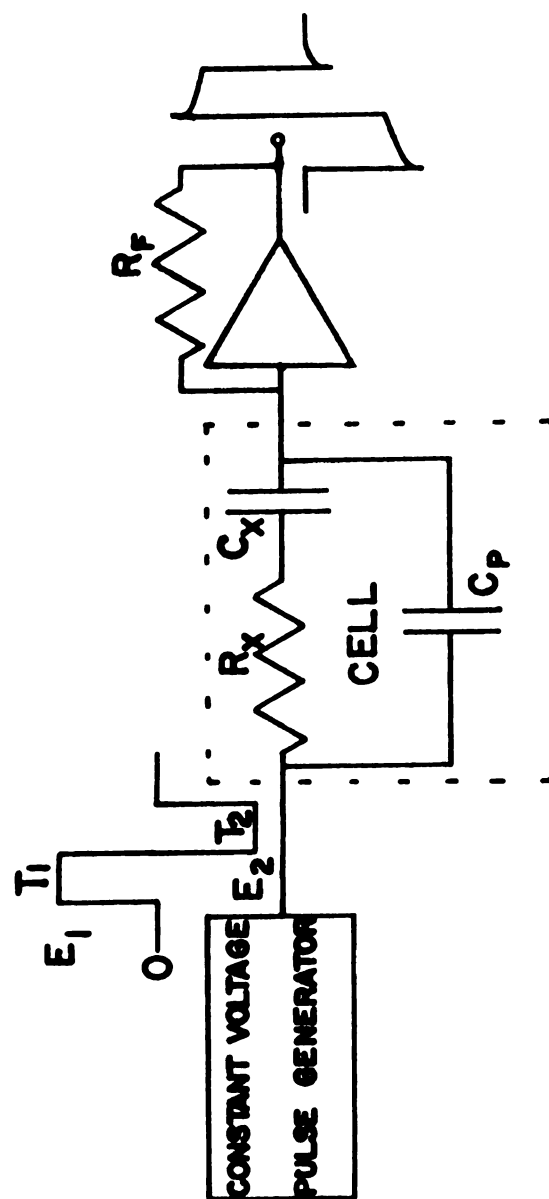


Figure 6. A Bipolar Pulse Conductance Device.

that $R_X C_X \gg T \gg R_0 C_P$ where R_0 is the output impedance of the pulse generator. If this is true, C_X will develop only small polarization during the pulse and will charge approximately linearly with time. Thus at the end of the first pulse, C_P is fully charged to E_1 and is drawing no current, and C_X is charged to some potential less than E_1 . When the polarity reverses, C_P will again quickly charge to the new potential, E_2 ($-E_1$). C_X will begin to discharge approximately the same number of coulombs that it charged during the first pulse. At the exact end of the second pulse, the voltage across C_X is nearly zero and C_P is again drawing no current. Thus the instantaneous current measured at this time is only that current due to the voltage drop across R_X . The effects of C_X and C_P are not just reduced but are virtually eliminated when pulses of the appropriate duration are chosen. The measurement itself is therefore subject only to the limitations of the particular instrument and not to the cell design, chemical application, or solvent system employed.

Johnson and Enke showed that the theoretical relative error, Q , for this measurement technique is given by:

$$Q = b(a - 1) - b^2[a(d + 2) - 1]/2 + b^3[a(d^2 + 3d + 3) - 1]/6 - \dots$$

where $a = -E_1 T_1 / E_2 T_2$

$$b = T_2 / R_X C_X$$

and $d = T_1 / T_2$

If the pulses are truly symmetrical ($E_1 = -E_2$ and $T_1 = T_2$), $Q \sim -b^2$.

Since pulses as short as 10 μ seconds can be easily utilized with state-of-the-art electronic circuitry, even for $R_X = 100$ ohms and $C_X = 10$ μ F, $Q \approx 10^{-4}$ or 0.01% relative error. There is no theoretical dependence on C_P as long as $C_P R_0$ (R_0 is the output impedance of the pulse generator) $< 5T_2$.

for

ment

the

the

the

the

the

the

the

the

the

the

the

the

the

the

the

the

the

the

the

the

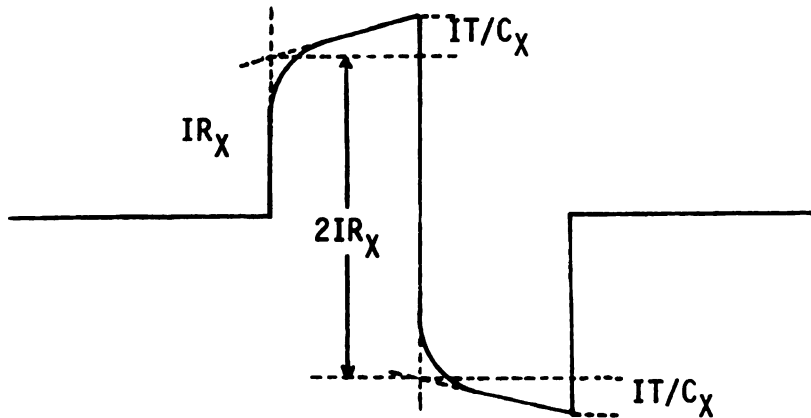
the

the

For their prototype instrument, Johnson and Enke reported 0.01% linearity, no dependence on C_p ($<0.0004\%$), the predictable dependence on C_x which was always less than that obtained using the conventional bridge, and a dynamic range also superior to that of the bridge. For a later instrument, with analog interactions similar to the instrument which will be reported here, Johnson (18) claimed accuracies of up to 0.01% and sensitivities of up to 1 part per million over a dynamic range extending from $0.1\Omega^{-1}$ to $10^{-7}\Omega^{-1}$.

Recently, Daum and Nelson (19) announced an interesting variation on the Johnson-Enke bipolar pulse technique. They claimed to have overcome the problem of series capacitance effects, to which the Johnson-Enke method is still susceptible at low resistances, by controlling the current in the cell through the application of bipolar current pulses. The resistance of the cell can then be determined in either of two ways. The cell voltage at the end of the second pulse (equal to the product of R_x and the current supplied) can be sampled, or the cell voltage during both pulses can be rectified and integrated. They showed that for the second method, the integral was proportional to R_x . They chose this method of analysis for its expected improvement in signal-to-noise ratio. They claimed excellent results in the area of conductance greater than $10^{-2}\Omega^{-1}$, where the bipolar voltage pulse technique encounters its most serious series capacitance effects. They felt they could obtain accuracies of 10% for conductances as high as $10\Omega^{-1}$.

The potential of the cell during the current pulse is shown in the following waveform:



At the beginning of the current pulses, the potential across the cell will rise very rapidly, but not instantly, due to the current required to charge C_p to the voltage IR_X . Later in the pulse, the voltage increases due to the charging of the series capacitance C_X . The charging of C_p is a function of the $R_X C_p$ time constant which is, of course, smaller for small R_X . If the polarity of the current pulse should be reversed before C_p is significantly charged, the IR_X drop and the amount of charging of C_X will diminish and the voltage at the end of the second pulse will be somewhat less than it should be. The current pulse must, therefore, last long enough to cause the potential change in the cell to be predominately a function of IR_X and the charging of $C_X (IT/C_X)$. Longer current pulses are required as R_X increases due to the slower charging of C_p through larger R_X .

As mentioned previously, the bipolar voltage pulse technique requires that as the series resistance and capacitance get smaller, the pulse width must decrease to prevent significant charging of C_X from affecting the measurement. This results from the predominant term, b , in the error equation. A decrease in R_X causes b to increase. This increase must be offset by a decrease in pulse width, T , to maintain an accurate

measurement. There is virtually no effect of the parallel cell capacitance on the measurement.

Thus, it can be seen that the bipolar current technique essentially exchanges the C_X dependence of the bipolar voltage technique for a C_P dependence. Better results at low R_X are obtained at the expense of measurement speed at high R_X . Both techniques have distinct advantages in particular conductance regions. However, for solutions normally encountered in conductometric studies, the cell resistance rarely is below 100Ω . One possible exception to this might be highly buffered solutions required in biological studies. Nevertheless, the bipolar voltage pulse technique appears to provide the most useful operating region as well as the theoretical ability to measure more rapidly throughout this region as compared to the bipolar current technique.

The difficulties in the application of conductance measurement to real chemical problems, which the non-expert finds discouraging, are largely eliminated through the use of the bipolar voltage pulse technique. The cell design becomes relatively unimportant due to the expanded dynamic range of operation. Since C_X is no longer an interferent, platinization of the electrodes is not necessary. By clever use of a four cell lead system, Johnson and Enke reduced the effect of contact resistance, making cell connections less critical. However, selection of the various measurement parameters incorporated in the new instrument (18) was certainly time consuming and required significant expertise. Training was required in both the use of the instrument and its application to solving particular chemical measurement problems. Conductance determination, as a step toward chemical determination, had been brought closer to the experimenter. Nevertheless, the interaction between the

system

the com

the A

The

the app

the inst

to it

result

x disc

Fig

the p

the

the

the

the

the

the

the

the

the

the

the

the

the

the

the

experimenter, the instrument, and the chemical process might still be quite complex.

D. THE ANALOG CIRCUITS OF THE COMPUTERIZED CONDUCTANCE SYSTEM

The computerized conductance system has been developed to overcome these application problems and the others previously discussed. Since the instrument was specifically designed for computer control and monitoring, it was possible to simplify the analog circuits by use of digital circuit adjustment techniques and a digital data acquisition system to be discussed in Chapter 3.

Figure 7 is a schematic diagram of the analog circuits. It consists of the precision power supplies, the pulse generator, the offset generator, and the current follower. Because the pulses must be exactly equal in magnitude for the technique to be free of dependence on the series capacitance and because reproducibility is a function of the long term stability of these signals, the sources of the positive and negative voltages were chosen with care. The precision +5 volt signal is produced by a Signetics S5723L regulator. This signal is inverted by operational amplifier A_1 , an ultra low drift amplifier set to give a gain of -1. The precision +5 and -5 volt signals are fed to the two voltage divider circuits of the pulse amplitude control. The computer selects the pulse height to be either ± 5 , ± 0.5 , or ± 0.05 volts by switching one of the three DPDT reed relays at the outputs of the divider. The pulse generator, operational amplifier A_3 connected as a fast voltage follower, applies the chosen positive and negative pulses to the cell. Pulsing occurs during the timing sequence A-B-C, shown on the waveforms in Figure 7.

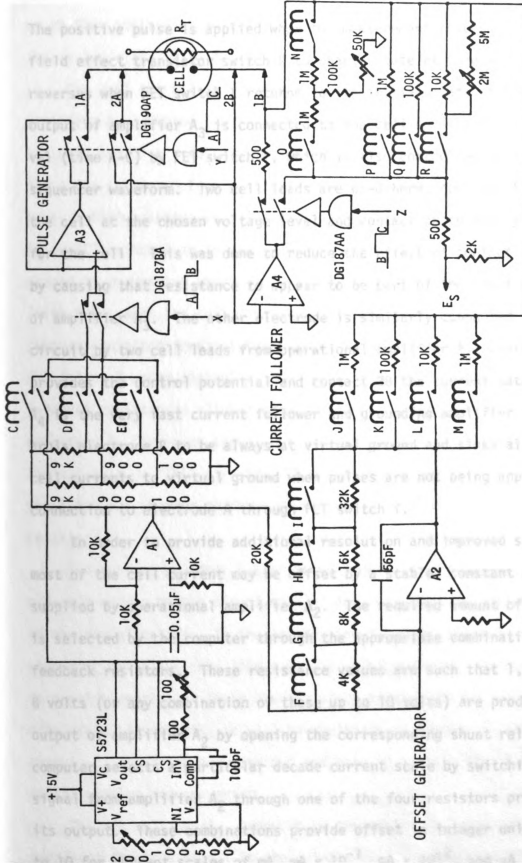


Figure 7. Schematic Diagram of the Computerized Conductance System Analog Circuits.

The positive pulse is applied when the measurement sequencer causes field effect transistor switch X to change state at time A. The polarity reverses when FET switch X returns to its initial state at time B. The output of amplifier A_3 is connected to the cell during the pulsing interval (time A-C) by FET switch Y, which is also controlled by a measurement sequencer waveform. Two cell leads are used here, contact 1A to maintain the cell at the chosen voltage level and contact 2A to supply current for the cell. This was done to reduce the effect of contact resistance by causing that resistance to appear to be part of the input impedance of amplifier A_3 . The other electrode is similarly connected to the circuit by two cell leads from operational amplifier A_4 ; contact 1B provides the control potential and contact 2B the current path. Amplifier A_4 is the very fast current follower and grounding amplifier. It controls electrode B to be always at virtual ground and sinks all spurious cell currents to virtual ground when pulses are not being applied by its connection to electrode A through FET switch Y.

In order to provide additional resolution and improved sensitivity, most of the cell current may be offset by a stable, constant current supplied by operational amplifier A_2 . The required amount of offset is selected by the computer through the appropriate combinations of feedback resistors. These resistance values are such that 1, 2, 4, and 8 volts (or any combination of these up to 10 volts) are produced at the output of amplifier A_2 by opening the corresponding shunt relays. The computer selects a particular decade current scale by switching the signal from amplifier A_2 through one of the four resistors provided at its output. These combinations provide offset in integer units from 0 to 10 for current scales of mA, $\text{mA} \times 10^{-1}$, $\text{mA} \times 10^{-2}$, and μA . Thus

up to four additional most-significant bits of resolution are added, by the analog circuit, to the 12 bits of the conductance A/D converter.

The cell and offset currents are summed at the inverting input of amplifier A_4 . During the positive pulse, the cell and offset currents are both positive resulting in a large positive current at amplifier A_4 . Since the current output of the cell is not being monitored at that time, a 500Ω resistor is switched into the feedback loop of amplifier A_4 by FET switch Z to insure that the inverting input will be at virtual ground by preventing amplifier saturation. During the negative pulse (time B-C), when the cell current is being sampled, the appropriate computer-selected feedback resistance is switched into the circuit by FET switch Z under control of the measurement sequencer. The available feedback resistances allow a 10 volt output signal to be produced by amplifier A_4 for input signals of 1mA, 100 μ A, 10 μ A, and 1 μ A. For the highest gain, a "TEE" circuit (20) equivalent to $10M\Omega$ is used for greater precision and shorter response time than could be obtained from a $10M\Omega$ resistor.

The current follower output is divided to give a signal to the sample-and-hold module of the signal sampler and converter, E_S , which is 4/5 of the actual output. To the analog circuit, then, the 0-10 volt A/D converter actually looks like a 0-12.5 volt converter. This was done to provide overlap at scale changes which eliminates the need for precise scale adjustments, as will be explained in Chapter 5. The voltage output, E_S , is tracked during B-C and held at exactly time C by the signal sampler and converter.

The net voltage, E_S , produced by the analog circuits can only represent the true signal to the extent which the various components

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

of the circuit approach their ideal true values. The choice of components is critical to the production of an accurate, sensitive, fast instrument. Some comments about the components used in the analog circuits are necessary for an understanding of how these goals are successfully accomplished.

The precision positive voltage is regulated to 0.01% by the S5723L regulator which will drift a maximum of 0.01% per 1000 hours of operation. Amplifier A_1 , which produces the precision negative voltage, does not have to be fast, but it must be constant and steady. The amplifier chosen (Analog Devices 184J) has an initial offset not greater than $\pm 50 \mu$ Volts and will drift a maximum of $\pm 3 \mu$ V/month and $\pm 1.5 \mu$ V/ $^{\circ}$ C. Amplifier A_2 must be somewhat fast since the offset may be expected to change quickly and settle quickly during an experimental run. It must also be stable as any error produced by drift will directly affect the measured conductance. The amplifier which was chosen (Analog Devices 148B) will slew at 50 V/ μ sec and settle to within 0.01% of the true value in 1 μ second. It can be trimmed to zero initial offset voltage and has a maximum drift of $\pm 50 \mu$ V/day and $\pm 20 \mu$ V/ $^{\circ}$ C.

The pulsing amplifier, A_3 , must be stable in order to provide the true voltage signals to the cell. It must have minimal offset voltage as this would result in asymmetrical pulses and subject the measurement to series capacitance effects. It must also be fast in order that it be able to switch between positive and negative input signals and settle to its new value quickly. Finally, it must provide sufficient current when cell conductivity is high. At the time the instrument was built, the Analog Devices 149B had the best of these characteristics with a slew rate of 100V/ μ sec, settling to within 0.01% of true value in 1.5 μ sec.

Its offset can be trimmed to zero and its maximum drift is $\pm 50 \mu\text{V}/\text{day}$ and $\pm 15 \mu\text{V}/^\circ\text{C}$. It can supply up to 20 mA at ± 10 Volts output. Amplifiers which are still better suited to this use are available now. However, no serious problems have been encountered with the use of this amplifier which would warrant its replacement.

Some problems were encountered with the use of this same type of amplifier as the current follower. The current follower is probably the most critical component in the analog circuit. It must not only supply the final composite signal to the signal sampler and converter, but also provide a controlled, stable cell ground. In addition it must track the signal in the time periods of the shortest pulse widths, sometimes being slowed by large feedback resistors. It must also quickly sink all spurious cell currents to ground in the brief interval (as short as 10 $\mu\text{seconds}$) between discrete pulsing sequences to prevent a build-up of charge in the cell which would result in gross nonlinearity and measurement error. Therefore, a very new, fast amplifier (Analog Devices 50K) slewing at 500 V/ μsec and settling to 0.1% in 200 nseconds was substituted for the 149B. It can be trimmed to zero initial offset voltage and has a maximum drift of $\pm 500 \mu\text{V}/\text{month}$ and $\pm 25 \mu\text{V}/^\circ\text{C}$.

Relays C, D, and E are DPDT reed relays (Electrol RA 30212241) which were fastest available (150 μsec on plus 150 μsec bounce, 20 μsec off) with low contact resistance (0.1Ω). Relays were chosen over FET switches for these applications because the significantly larger contact resistance of FET switches would cause serious measurement errors which could only be eliminated by trimming the circuit at each control point. The "on" resistance of FET switch Z, in series with the selected feedback resistance of amplifier A_4 , is significant for the 10 K Ω

feedback resistor. Therefore, provisions are made for trimming the circuit at this point. Relays F-R are SPST reed relays (Electrol RA 30211241), which have specifications identical to relays C-E.

All resistors less than $1\text{M}\Omega$ in the pulse generator, offset generator and current follower are fast response, 0.01% Vishay metal film resistor (S102 or S106). All $1\text{M}\Omega$ resistors are General Resistance fast, wire-wound, 0.01% "Nanistors". All FET switches are monolithic N-channel junction FETS with TTL compatible drivers made by Siliconix. In the application where FET switch Z is used, small leakage currents could cause significant errors for measurements of low conductivities. Therefore a special military-grade switch was used with a maximum leakage current of less than 1 nA.

For the purpose of noise reduction through shielding, the instrument itself and its power supplies were built in two separate modules. Within the instrument module, two compartments are arranged, one on top of the other. Most of the digital circuits and the interface, which will be described in Chapter 3, are located in the large compartment. The smaller compartment below it is divided into three sections. The outer sections contain the control circuits and relays which are shielded from the other circuits. The center section, shown in the photograph of Figure 8, contains the analog circuits described above. These circuits are mounted directly above the signal sampler and converter, in the large compartment on the other side. In this way the signal, E_S , from the current follower must be sent only a very short distance to the sampler. The circuits in each section receive the signals from other circuits by wires which run through the aluminum shielding walls of each section.

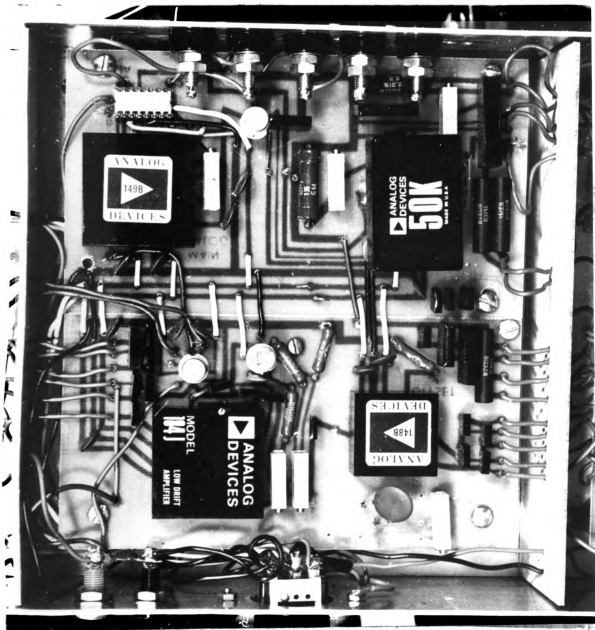


Figure 8. Photograph of the Analog Circuits.

The connection of the instrument to the cell is made by four leads from the analog circuits to gold plated banana jacks on the chassis. A gold-plated "Kelvin Klip" probe assembly (made by ESI) plugs directly into these jacks. This probe clips directly onto the cell leads to complete the circuit.

E. THE POWER SUPPLIES OF THE COMPUTERIZED CONDUCTANCE SYSTEM

An early production model Heath 181-75 ± 15 volt power supply card is used to provide ± 15 volt signals to various parts of all circuits. The +5 volt signal for the digital circuitry is produced by a prototype Heath 181-74 +5 volt power supply card. A Heath 54-206 transformer was used to supply both of these cards. The entire assembly is mounted in the power supply module shown in the photograph of Figure 9.

The +24 volt relay power supply is also mounted in this module. A schematic diagram of this circuit appears in Figure 10. It consists of a second Heath 54-206 transformer, a rectifier, and the two transistors which constitute the 24 volt regulator. It can supply up to 1A at 24 volts. It would, however, not have to supply more than 320 mA to the relays at any given time.

The power supplies, circuit common, and chassis ground are all connected to the instrument through shielded cable which is grounded at the power supply end only, for noise reduction. In addition, a separate high quality ground line is provided for directly connecting the ground for the precision signals in the measurement to the power supply. Using this technique, noise signals generated on the ground which parallels the power supply lines for the various components has only minimal effect on the precision signals.

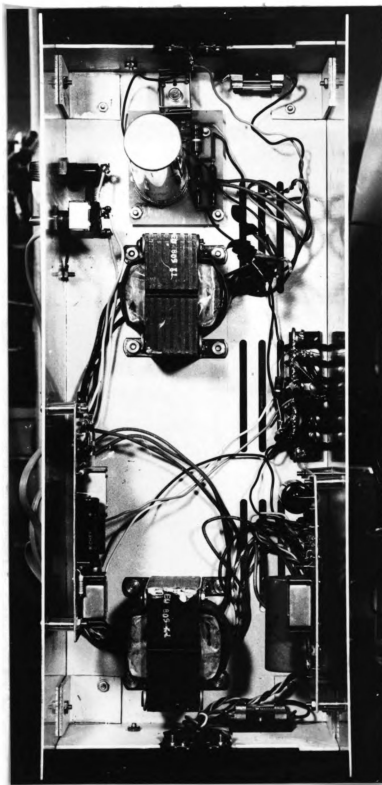


Figure 9. Photograph of the Conductance Instrument Power Supply.

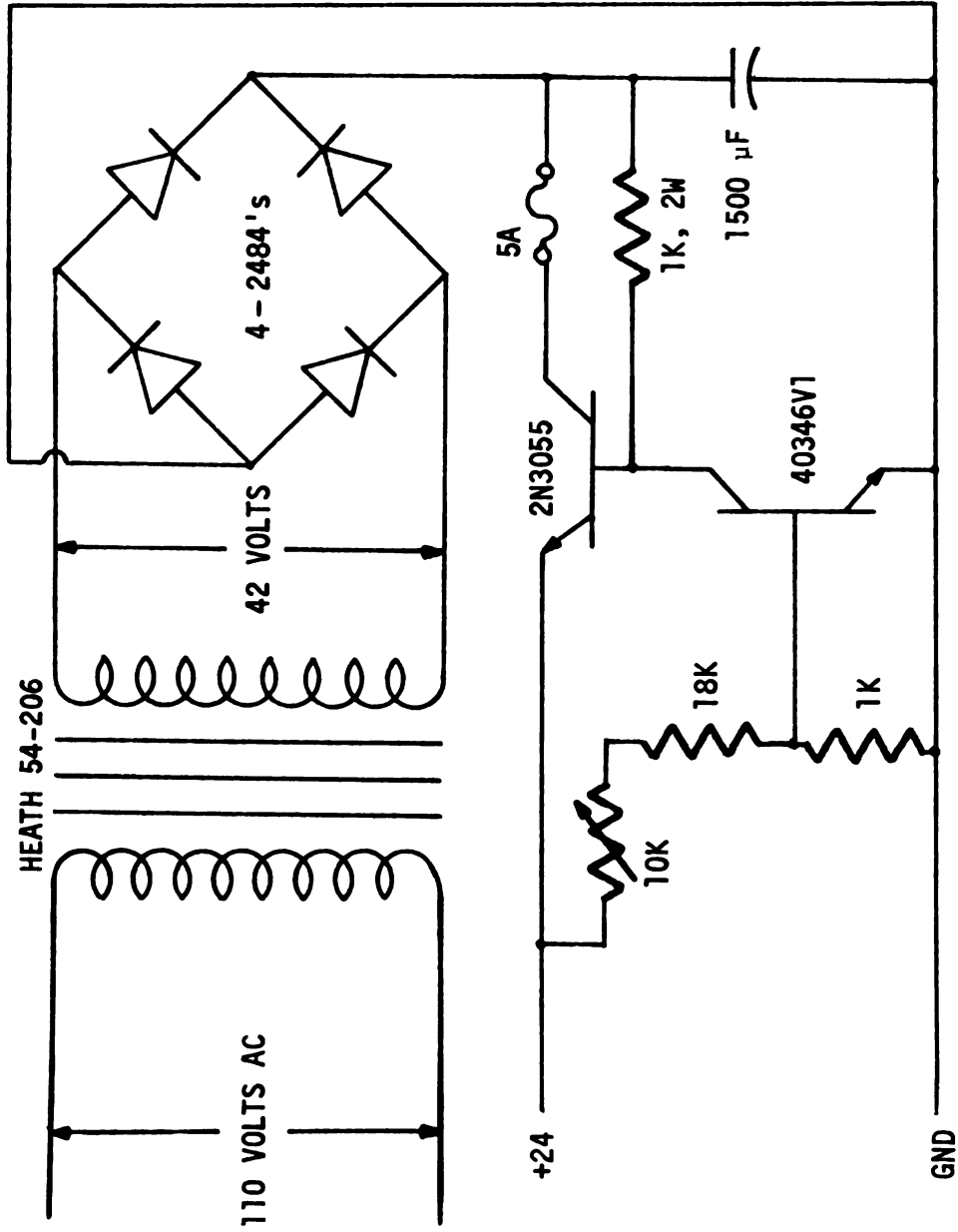


Figure 10. +24 Volt Relay Power Supply Schematic Diagram.

CHAPTER 3

IMPLEMENTATION OF A DEDICATED COMPUTER FOR TOTAL DIGITIZATION OF THE CONDUCTANCE MEASUREMENT SEQUENCE

A. INTERFACING THE DIGITAL COMPUTER FOR CHEMICAL APPLICATIONS

During the past ten years the digital computer has become an increasingly important tool in performing chemical analysis. Looking back over this period, it is possible to identify at least five steps through which computer-instrumentation interaction has passed. These interactions became increasingly intimate as the computer assumed greater responsibilities for control of the measurement process. They might be summarized as follows:

- 1) Analysis of experimental data by a computer isolated from the data source, after the data has been produced.
- 2) Direct acquisition of experimental data by a computer at the instrumental site, during run time, followed by analysis.
- 3) On-line acquisition and analysis of experimental data during run time with the computer exercising control of the measurement parameters as a result of the quality of that data.
- 4) In addition to on-line analysis and parameter control, initiation and control of the entire measurement sequence by the computer.
- 5) Computer generation of the perturbation signal in addition to control of the measurement sequence and parameters.

In his review article on computer applications in the chemistry laboratory, Perone (21) has pointed out that the earliest laboratory

uses of digital computers involved the collection and analysis of the extraordinary amounts of data produced by mass spectrometry. The earliest examples of computer control over instrumental parameters and generation of the perturbing waveform came in the area of electroanalytical chemistry.

Eventually chemists became aware that new or previously impractical chemical measurement techniques could now easily be implemented in the laboratory through computer-interactive instrumentation. Unfortunately, the programmers who set up the experimental software and the electronic specialists who designed the instrumental systems had little chemical intuition which would have enabled them to provide the optimum chemical measurement system. Thus, the chemist was forced to become active in these fields. Frazier (22) argued that it was important for the chemist to be involved in actually programming the experiment if he wished to realize the maximum benefit and flexibility of his computer system. He indicated that if there is anything more difficult than interfacing a computer and an instrument, it is interfacing the chemist with the programmer, who has no knowledge of experimental laboratory operations.

Probably the greatest problem of using the computer in the laboratory in the early years was the enormous cost of custom built interfaces supplied by computer manufacturers for chemical systems as indicated by Venkataraghvan, Klimowski, and McLafferty (23) at the time. They also felt that these costs could be brought under control by having the chemist himself assume a greater responsibility in development of interfacing techniques.

Discussion of programming, digital circuitry, and interfacing techniques began to appear in chemical journals. An article by Dessy and Titus (24) was one attempt to familiarize the chemist with the

fundamental building blocks of interfacing systems. They explained standard logic circuits, A/D and D/A converters, multiplexers, clocks, and general computer functions. Their discussion was intended for the chemist interested in becoming involved in computer applications with little background in these techniques. In their later article (25) they presented a system through which laboratory automation could be achieved in a minimum amount of time.

Other systems have been developed in the last few years in an attempt to bring the computer into operation in the laboratory with the same ease with which oscilloscopes have been used for some time. Ramaley and Wilson (26) interfaced an H-P 2115A computer using Raytheon hardware. Their setup consisted of a real time clock, two D/A converters, a data storage register and a sequencer. A fast A/D converter was supplied through an eight channel analog multiplexer. Two of these channels contained sample and hold amplifiers to take X-Y data with no time skew. They claimed their system could be used as a "black box" and programmed by those with no experience in electronic design.

Parker and Pardue (27) have gone as far as developing an in-house micro-computer using a Texas Instruments 74181 arithmetic logic unit as the central processor and equipping it with various external peripherals. These include an A/D converter, a logarithmic amplifier module with temperature compensation, a sample-and-hold amplifier, and display facilities. This micro system was used with considerable success for single component analysis, two component analysis and simulated response. They estimated that it could be duplicated for \$300.

DeVoe, et al. (28) used a parallel data bus to provide a computer utility to a series of labs by connection to a medium size UNIVAC

computer. They stressed the ease with which the chemist in the laboratory could connect his instruments to the system, interact with his own programs, and receive his analysis and data display in his own lab.

One of the most flexible interfacing systems, with respect to laboratory applications, which has been developed at this time is the Heath EU-801E interface for the PDP-8 computers, diagramed in Figure 11 (6). This interface provides 12 input lines to the single 12-bit accumulator (AC) of the PDP-8, 12 buffered AC out lines, and 12 buffered memory buffer (BMB) lines. It also permits control of external sequences and gating of data transfer by means of device select (DS) lines, input-output transfer pulses (IOP), and skip (SKP), program interrupt (PI), initialize (INIT) and run lines. Access to these functions is made by connection of an interface buffer box to the computer bus. Connections of the Heath EU-801-21 I/O cards (29) to this buffer box bring the signals, in parallel, to the instrument. Since the system was partially developed in this laboratory, it was available for incorporation into the computerized conductance system from the earliest design stages.

The computerized conductance system requires two I/O cards, one providing AC in and the operating controller functions, one providing AC out and these same functions. The I/O cards also provide BMB bits 3-8 which form the device select code. These bits are decoded in the instrument by a prototype of the Heath EU-800SA dual octal decoder card (29) and a series of NOR gates to give device select codes 32, 33, 34, 35, and 36. These are combined with IOP pulses 1, 2, and 4 to perform the various instrumental functions shown in Table 1. These functions will appear on the diagrams which follow.

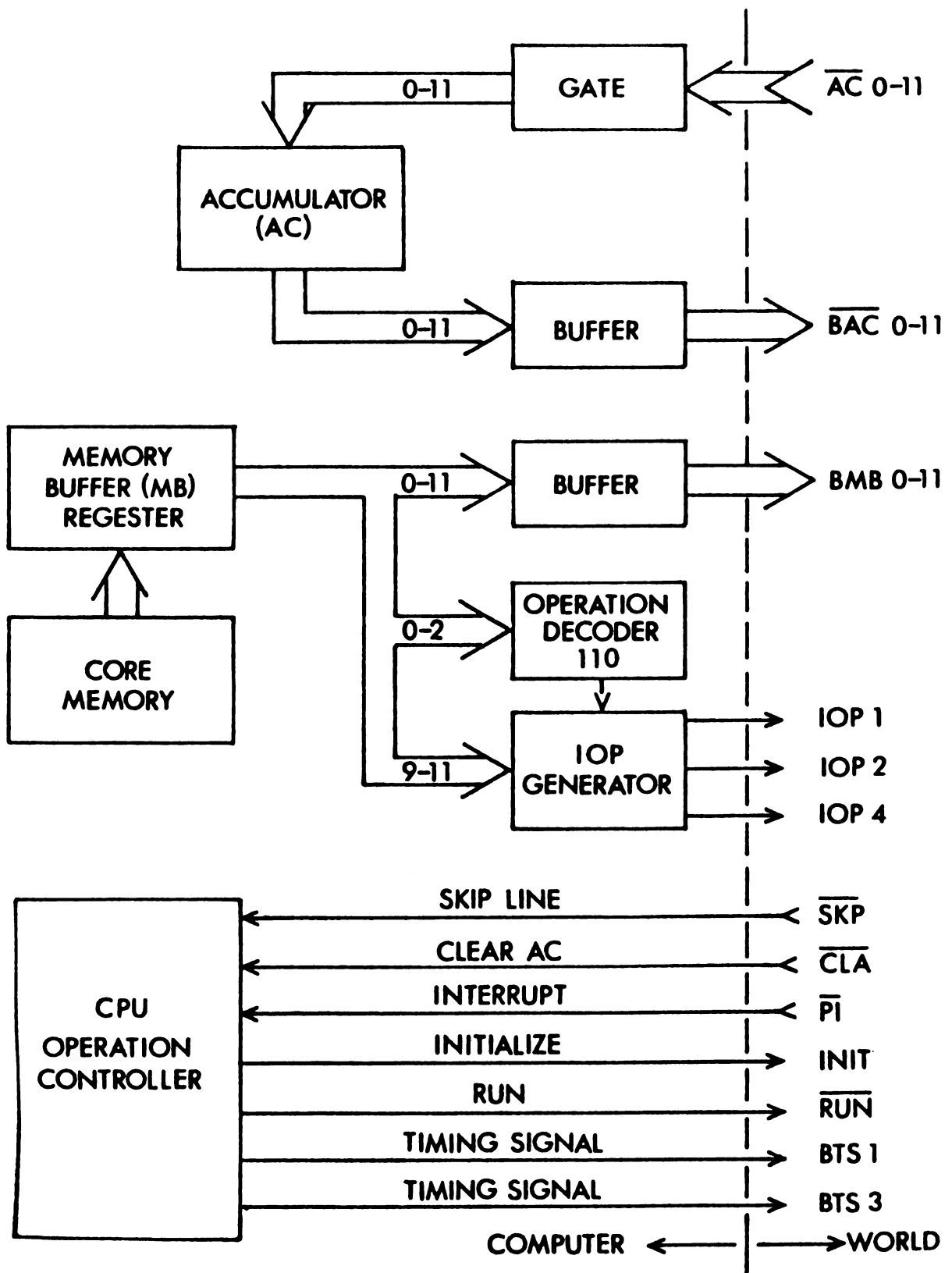


Figure 11. PDP-8 Computer Functions Available with the Heath EU-801E Interface System.

Table 1. Computerized conductance system instruction set.

Device Select (DS)	IOP Pulse	Function
32	1	Clear conductance circuit flag; clear conductance program interrupt ability
32	2	Gate conductance circuit driver
32	4	Enable conductance circuit program interrupt
33	1	Test conductance circuit flag
33	2	Turn off pulse sequence
33	4	Trigger pulse sequence
34	1	Test temperature circuit flag
34	2	Latch accumulator into relays F - Q
34	4	Latch accumulator into relays C - E, Time base
35	1	Enable temperature circuit program interrupt
35	2	Clear temperature circuit flag; clear temperature program interrupt ability; gate temperature driver
35	4	Trigger temperature A/D conversion
36	1,2,4	Available to control peripheral devices such as titrators, flow systems, etc.

B. DIGITAL CONVERSION AND CONTROL OF ANALOG SIGNALS

One of the first examples of an attempt to create a general purpose laboratory data acquisition and control system was that described by Lauer and Osteryoung (30), for the PDP-8 computer. Their system consisted of an A/D converter, three D/A converters, a real time clock, a relay controller, a solenoid controller, four solid state switches, an interrupt control, and a plotter. They used the system for electrochemical studies, producing the waveform, triggering the measurement sequence, and tracking, analyzing and outputting the data through the computer. Perone, Jones, and Gutknecht (31) used another system built around an H-P 2115A computer to optimize the measurement parameters in another electrochemical system during actual run time. Keller and Osteryoung (32) were able to perform measurements which would otherwise have been impossible by use of a computerized electrochemical system for pulse polarography.

Daum and Nelson (19) demonstrated the only previous use of digital conversion techniques in conductance measurement systems. Since they had chosen to integrate over the entire pulsing period, they were able to use digital counters at the integrator output to provide automatic A/D conversion of this signal. Their data could then be displayed directly as a 3 digit BCD nixie tube display or stored as BCD data in MOS-LSI shift registers. This provided them with a digital means of storing data from rapid changes in conductance such as kinetic studies. A D/A converter was also provided in order that the data could be read out of memory and recorded in analog form on a slow time scale.

The analog circuits of Chapter 2 were designed for use with computer control and monitoring only. No other means of external

control or measurement were provided. In developing an instrument with this type of computer dedication, circuitry which would be found in conventional instruments to provide repeatable pulsing, analog temperatures compensation, signal conditioning for output to plotters, integration, etc., could be eliminated since the computer, coupled with several digital circuits, could assume these tasks. Another major advantage of the computerized system is its ability to make a discrete measurement at the completion of each pulsing sequence (each "scan"). Each data point can then be ensemble averaged with any number of subsequent scans for signal improvement, or stored separately to provide a picture of a rapidly changing conductance pattern. In order to provide measurements at this rate, the signal sampler and converter of Figure 12 was designed.

The signal, E_S , from the divider at the current follower output, is sent, along with the quality analog ground, to the sample-and-hold module of Figure 12. The tracking/holding sequence of this module is controlled by measurement sequencer waveform Z. Thus, at the beginning of the second pulse (time B), the module is placed in the tracking mode and follows the signal produced by the analog circuits. At the exact end of the second pulse (time C), waveform Z returns to zero, causing the module to hold the signal which existed at that time, as required by the bipolar pulse technique.

The falling edge of waveform Z also triggers a 1.5 μ second monostable. The monostable pulse, initiated at time C, resets the A/D converter on its rising edge and causes conversion to begin on its falling edge at time D. When conversion begins, the A/D status output goes high and remains high until conversion is complete at time E.

The A/D converter performs the conversion on the analog signal held by

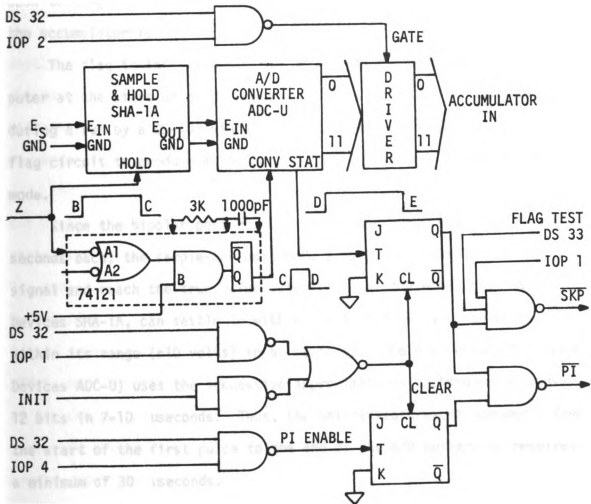


Figure 12. Signal Sampler and Converter.

the sample and hold module. When the status output returns to zero upon completion of conversion, it sets a flag and may cause a program interrupt if this function had been previously enabled. The computer, upon testing the flag, will gate the information at the A/D output into the accumulator for storage and analysis.

The flag is initially cleared by an INIT pulse issued by the computer at the start of each program. It is cleared by the computer during a run by a DS-IOP signal. The computer can also enable the flag circuit to produce an interrupt if it is desired to run in this mode.

Since the bipolar perturbation pulses can be as short as 10 μ seconds each, the sample-and-hold module must be able to track the signal and reach the true value quickly. The module chosen, Analog Devices SHA-1A, can settle to within 0.01% of true value anywhere within its range (± 10 volts) in 5 μ seconds. The A/D converter (Analog Devices ADC-U) uses the successive approximations technique to convert 12 bits in 7-10 μ seconds. Thus, the entire measurement sequence, from the start of the first pulse to the end of the A/D conversion requires a minimum of 30 μ seconds.

The gated driver is a prototype of the Heath EU-800-JL gated driver card (29). It contains 12 open collector buffers which are gated to provide input to the accumulator of the information from the A/D conversion.

In order to overcome the time delay involved in setting the measurement timing and the analog circuit parameters, the computer has been given complete control over the 3888 possible combinations of pulse width, pulse height, offset, and current follower gain. Since many of

these combinations are redundant with respect to the output voltage, E_S , which they produce, the computer is also allowed to make the decision as to which circuit setting provides the optimum resolution and accuracy. In this way the system relieves the operator of the task of setting up the measurement system parameters, and does so more quickly and correctly than the operator could himself. The computer can then check the data which it receives during a run to assure that the optimum measurement continues to be made. If a change of circuit parameters is required at this time, the computer can effect such a change quickly.

The analog circuit parameters of pulse height, offset, and gain are set by the state of the relays of Figure 6. The relays, in turn, are controlled by the series of latches, drivers, and gates of Figure 13. The proper logic level for each controlling bit is set in the accumulator by the program. Two words, one of 12 bits and one of 6 bits, are required. The 12 bit word controls offset unit steps (0-10), decade steps, and current follower gain. It is transferred to three latches of the control circuit by a DS-IOP combination. The six bit word is similarly transferred by a separate DS-IOP signal, controlling the pulse height and width. The latches turn drivers on (logic "0") or off (logic "1"), which in turn open or close the relays respectively. The other latch controls the time base of the measurement sequencer through a multiplexer described in the next section.

The latches used are 7475 TTL quad latches. The three latches which control offset and gain had a tendency to unlatch when computer generated noise appeared on the I/O lines. This problem was minimized by use of a 7437 NAND buffer, with greater fan out than the 7400, for the gate and by a small, 220pF capacitor connected between the IOP

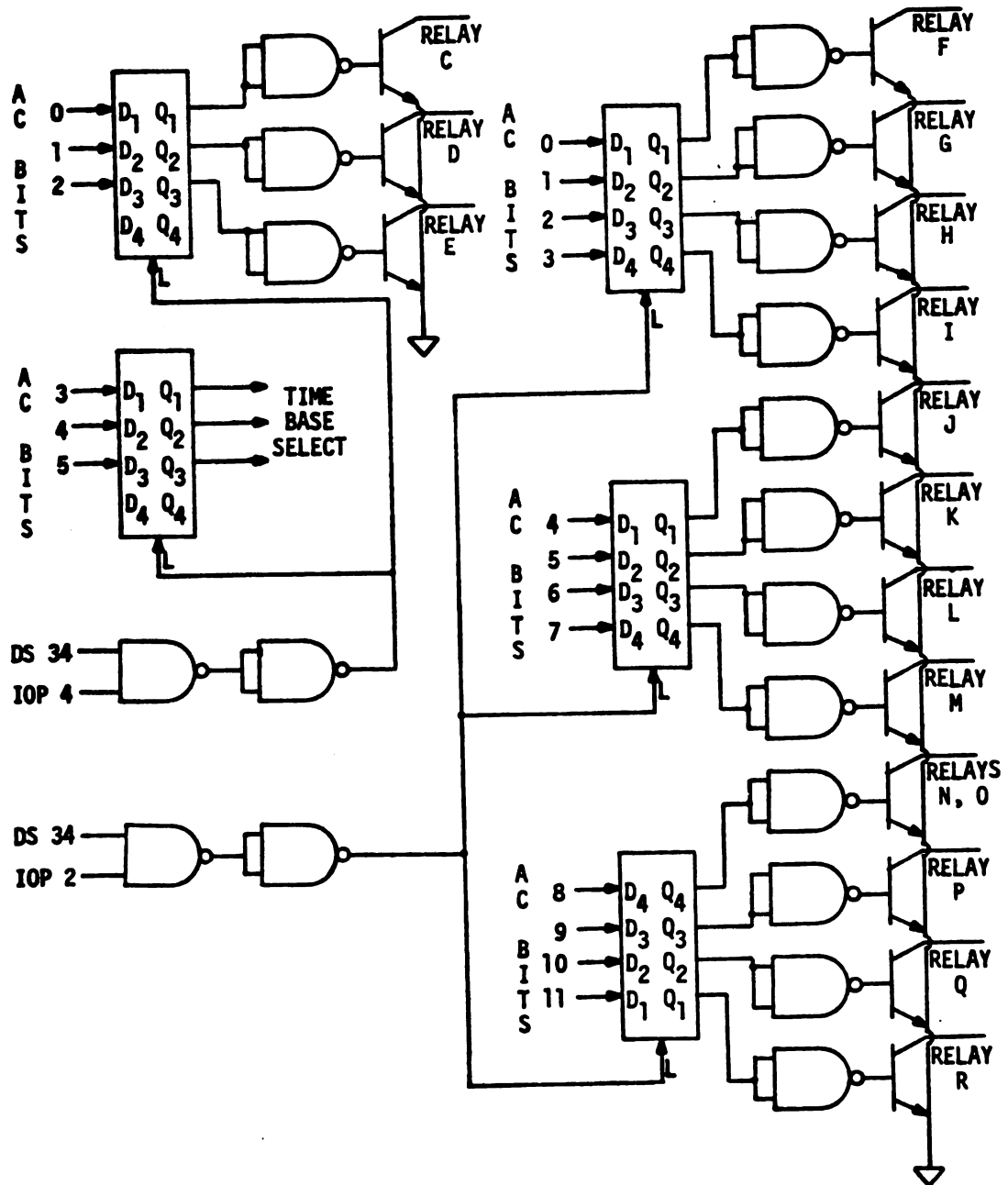


Figure 13. Control Circuits Schematic Diagram.

pulse line and ground to absorb short noise pulses. The problem still occurs, although never during a run, when a peripheral device which uses the conductance instrument interface is being set up.

The relay drivers are 75451 dual positive AND drivers. They can switch up to 35 volts and continuously dissipate up to 300 mA of current. When the signal from the latch connected to a driver goes high, the driver base voltage goes low causing the 24 volts at the collector to be applied to the relay coil, closing the relay. Inversely, a low signal from the latch causes the driver transistor to turn on, the 24 volts at the collector is dropped across the transistor and not the relay coil, and the relay is opened.

C. DIGITAL SEQUENCING OF THE BIPOLAR PULSE MEASUREMENT

In their earliest bipolar conductance instrument, Johnson and Enke (10) utilized a series of monostables to produce the switching waveforms which control the critical timing of the bipolar pulse measurement. Their trigger for the sequence could be an internal unijunction oscillator, line frequency via this oscillator, or some external trigger source. Because the timing of pulses is most critical to the successful application of the bipolar technique, Johnson (18) used a more precise timing circuit in his later instrument. He used a crystal oscillator to provide the time base and a set of flip flops and logic gates to produce the switching waveforms. Pulses could also be repeatedly triggered by this circuit at precise intervals which could be varied. Pulsing could also be initiated by an external trigger. Daum and Nelson (19) used a similar circuit to generate the switching waveforms and repetition frequency signal for their bipolar current instrument.

During the early design stages of the computerized conductance instrument, two different means of timing the measurement were considered. The first, which initially seemed the most attractive, was to program the computer to produce the switching waveforms by DS-IOP signals to external counters. The computer would also provide the voltage levels for the pulses by control of a fast D/A converter. The second method was to produce the timing signals and bipolar perturbation pulses within the instrument itself. The first method would have resulted in extremely flexible measurement timing as well as pulse heights which were variable in small steps over the operating range. Unfortunately, this method had to be discarded because of the timing errors it introduced.

The PDP-8/I has inherent cycle time uncertainties which would have caused these errors. Furthermore, there is a variable delay of up to 6 μ seconds from the time the computer responds to a flag to the time it issues a DS-IOP signal to an external device. This same delay would have affected transfer of data from the computer to a D/A converter producing the pulses. Even if the mainframe real time clock (as described by Hahn and Enke (5)) had been equipped with Schmidt triggers for direct external triggering, an uncertainty of up to ± 1 μ second would have existed in the pulse width for each pulse. This would have yielded a pulse assymetry of up to 20% for the 10 μ second pulse. It was thus decided to take the second approach, which avoids the large error in pulse width but allows a small error in repetition rate as will be seen below. The computer is still able to provide control and increased flexibility compared to previous sequencing circuits. The measurement sequencer, shown in Figure 14

Figure 14. Measurement Sequencer Schematic Diagram.

was thus built into the instrument. Its functions are described below:

The time base for the measurement sequencer consists of the 1 MHz oscillator and its 7 decade scaler on a Heath EU-800KC time base card (29). The output of the card is set by the computer through latch 5 of the control circuit (Figure 13). The timing circuit is arranged such that the pulse applied to the cell will be ten times this output. This permits pulse widths in decade steps from 10 μ seconds to 100 seconds. Only the four shortest are used by the system. The time base output is connected to a 7490 decade counter, wired to give a gated divide-by-five output. Initially, flip flop A is cleared by an INIT pulse at the start of the program. Flip flops B-G are cleared by their connection to Q_A . The signal at Q_A is set to "1" which inhibits the clocking of the $\div 5$ counter by the chosen time base.

When the computer issues the DS-IOP trigger pulse, flip flop A is set, releasing flip flops B-G. The signal, Q_A , becomes "0" which enables the counter to be clocked by the chosen time base. The counter output, in turn, clocks flip flops B-G. Flip flops B, C, and D form a synchronous three-bit binary counter. Their outputs are used to inhibit the J and K inputs of flip flops E, F, and G which produce the switching waveforms X, Y, and Z discussed previously. The Q outputs of flip flops B and D are also gated to trigger flip flop A on the fifth count (time C). This signal returns the sequencer to its initial state. Provision is also made for the computer to terminate pulsing by a DS-IOP command at any time. The computer thus retains control over the pulse width and the triggering of the measurement sequence. The only uncertainty in the pulse width comes from the negligible (<40 nsec). propagation delay through the flip flops. There is a delay of up to

4.5 μ seconds in triggering the sequences due to the DS-IOP signal interval. Also, since the $\div 5$ counter will only clock on a $1 \rightarrow 0$ transition at its input from the time base, an additional triggering delay error which can be as large as one time base cycle is added. This results from the uncertainty in the state of the time base output at the instant of triggering.

When the measurement sequencer was originally designed, the outputs of the synchronous counter were simply gated to produce the necessary waveforms. This approach was found to be unsatisfactory. The response of the gates was sufficiently faster than the propagation time of flip flops B, C, and D that the waveforms produced by the gates contained glitches at the transition times of these flip flops. These glitches caused the FET switches of the analog circuit to momentarily change state, greatly disturbing the pulsing and signal tracking. Bypass capacitors failed to remedy the situation. The circuit was reconstructed as described above. No significant glitches are present in it.

The computer interface, the signal sampler and converter, the two latches which control pulse width and pulse height, and the measurement sequencer are contained on Heath compatible circuit cards in the large compartment of the instrument module. They are shown in the photograph of Figure 15. These cards all plug into the main digital board which provides the interconnections between them. Thus they can easily be removed for inspection. The other section of the control circuits, shown in the photographs of Figures 16 and 17, are mounted, with the relays they control, in the two end sections of the other compartment of the module. They also lift up for easy inspection.

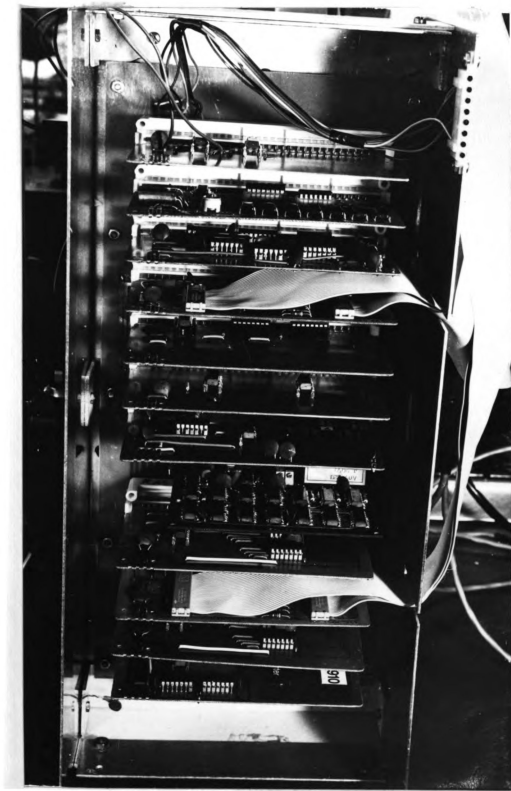


Figure 15. Photograph of the Digital Circuits Compartment.

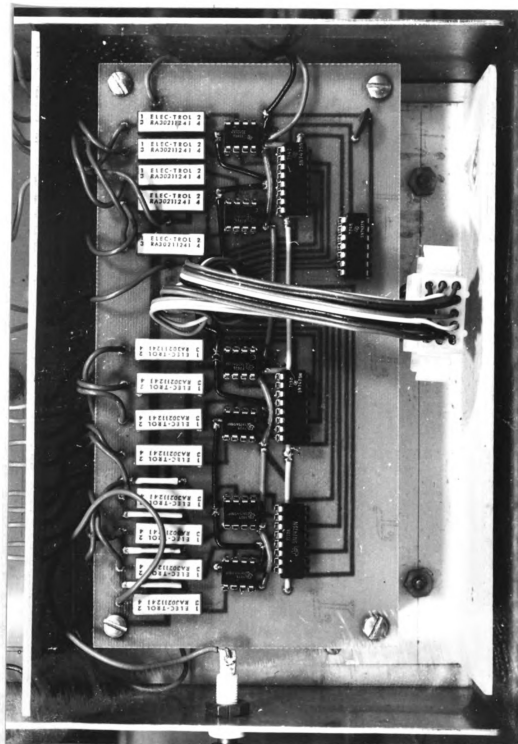


Figure 16. Photograph of the Control Circuits for Offset and Gain.

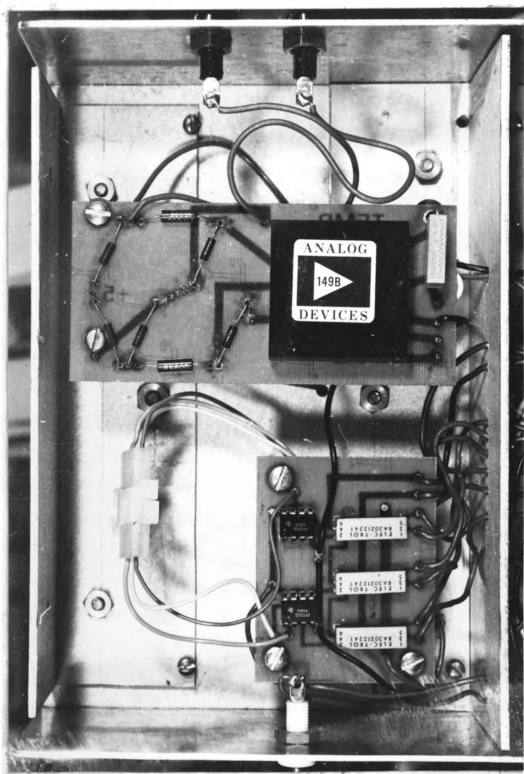


Figure 17. Photograph of the Control Circuits for Pulse Height and the Analog Temperature Monitor Circuit.

CHAPTER 4

PROGRAMMING THE COMPUTERIZED CONDUCTANCE SYSTEM FOR OPTIMIZED MEASUREMENT

A. CREATING A SOFTWARE LIBRARY FOR LABORATORY INSTRUMENTATION

From the references discussed in Chapter 3 it is evident that considerable work has been done by chemists interested in simplifying applications of computer interfacing hardware in the chemical laboratory. This work has resulted in increased availability of standard, inexpensive interfaces and digital hardware for laboratory uses. Unfortunately, at the present time only a small amount of work has been done to relieve similar problems in programming the systems which have been interfaced. Consequently the experimenter often spends an amount of time programming which is equal to or exceeds the time spent designing and building the instrument. This situation affected the rate of the implementation of the computerized conductance system as is described below.

There are three approaches to solving the problem of creating a flexible software set for a particular instrumental system. The first is for the chemist to hire a programmer to perform the task for him. The danger in this approach was mentioned in Chapter 3. It is often more difficult for the chemist to communicate his exact wishes concerning experimental operation and data analysis to the programmer than it would be for him to do the programming himself. Furthermore, should the necessity of altering the program arise after the programmer is gone, the chemist is faced with the double task of decoding the original program and rewriting it to suit his new idea. Nevertheless, this method is definitely attractive, especially for those systems where

changes are to be infrequent.

The second, and most gallant, attempt to solve the programming problem involves the creation of a computer language or subroutine set which is specifically oriented toward laboratory operations. Very few workers have implemented this approach (three references are presented below). Their systems are not yet capable of solving sophisticated research problems, but they do indicate a direction in which computer application programming must proceed if the researcher is to realize the maximum experimentation possible from the time he is willing to devote to measurement system development. The third approach to programming, which will be discussed later, involves the chemist intimately in the software development.

B. LABORATORY COMPUTER LANGUAGES

The earliest of the attempts to create a laboratory-specific computer language involved a scheme to introduce digital computer applications into undergraduate laboratories. Perone and Eagleston (33) wished to effect this introduction without significant alteration of the sophistication of the experiments which might result if the students were also required to spend large amounts of time programming. They therefore developed a series of data acquisition and control subroutines for use with the BASIC language. They chose BASIC because it is easy to learn, is an algebraically-oriented conversational language, and because it is interactive, interpreting and executing programs line-by-line. It is also available on most computers, providing more widespread use. Their new subroutines performed data acquisition, experimental control, and timing through control of such peripherals

as D/A and A/D converters, clocks, and trigger lines. The interactions between experimenter and instrument, through the development of software, were thus greatly simplified. However, their routines did nothing to simplify programming for data analysis or manipulation which is usually a much more complex task. The BASIC language itself does, to some extent, simplify data analysis. However, because it is an interpretive language, available core space in a minicomputer using BASIC is limited. BASIC therefore lacks the power and speed to perform data analysis of the complex systems often encountered in research.

The next attempt involved the development of an interpretive laboratory computer language, LABTRAN, by Toren, Carey, Sherry and Davis (34). LABTRAN was designed for use with the ELLA system (35) for clinical analysis. LABTRAN consists of nine statements, each of which causes performance of a specific task such as pipetting, measuring reaction rate, pausing, and so forth. The commands are decoded by the computer into a series of instructions which performs these tasks. The only instruction which required the computer to make a decision was the instruction to compare analyses to determine whether or not to terminate the run. The comparison criteria were input by the experimenter. The net result was a neat system of performing routine analysis. An experiment could be designed by a person with no programming background at all. The experimenter would simply list the tasks (not the decisions!) he would perform if he were doing the experiment himself. The computer acted as an elaborate sequencer. The use of the computer's decision making abilities was neglected as LABTRAN contained no provisions for branching, altering tasks, etc. The research applications of LABTRAN could only include those types of measurements and analyses which

must be mechanically duplicated often for bulk data compilation.

The most sophisticated laboratory-oriented language which has yet been developed is the MIRACL language presented by Keller, Courtois, and Keller (36). MIRACL (Macro Implimented Real-time Analytical Chemistry Language) is a macro assembler built around a modified PAL-11 assembler for use on a PDP-11 computer with a floating point processor and 8K of memory. It makes use of macros, coded statements which usually are designed for a specific task, in performing laboratory operations. When a macro statement is encountered by the assembler, the statement is translated into a pre-arranged set of machine language instructions and a set of constants corresponding to the argument of the macro. Examples of nine macro statements which MIRACL uses were presented. They included branching macros with arguments which could be data tests, printing macros, assignment macros, etc. An interesting macro was the AT TIME statement which initiated a block of statements to be executed whenever the clock time was equal to the time variable argument of the macro. Complex timing algorithms could thus be created by nesting such statements.

The authors indicated three basic defects in the use of MIRACL in research. These were the slowness of their floating point processor (all MIRACL functions were performed in floating point arithmetic), limitation by available core space to 36 variables, and lack of a plotting facility and corresponding macros. These problems were to be remedied in a later version of MIRACL.

It became evident throughout the article that the MIRACL system suffered from lack of computer power. Looking ahead toward future developments one might envision a multi-level system, both in software

and hardware. Laboratory job descriptions of a series of tasks, including branching and decisions jobs, could constitute a super-compiler laboratory language. Once the order of such tasks had been determined by the experimenter, a large batch processor would translate the jobs, compile the resulting program, and assemble a machine language program suitable for operation on the particular laboratory mini or micro computer which was to be used for actual operation of the experiment. The assembled program could also be optimized for core space and run time by the large processor. Programming could thus be done in the same modular way in which interfacing is done in the Heath system described in Chapter 3. The amount of time which the experimenter would save as a result would be comparable to the savings realized by using a modular interface as opposed to designing and building an interface each time a different experiment was performed. Such a system does not yet exist but its creation would seem inevitable.

C. PROGRAMMING WITH COMMONLY PROVIDED LANGUAGES

The third approach to programming is, of course, for the chemist to do it himself. This is the approach which was taken with the computerized conductance system. The basic problem is obvious; the experimenter's time is channeled toward software development rather than experiment design. It should, however, be noted that such programming can be greatly simplified by use of a higher level language, such as FORTRAN, wherever possible. Furthermore, after the initial time spent learning software techniques and writing the first programs, it was found that the experimenter became sufficiently "fluent" in the language

employed that the time required to create new programs or alter old ones decreased considerably. For example, all operating programs for the computerized conductance system presented in this thesis, with the exception of the data treatment program for determination of S/N discussed in Chapter 5, were completely written or derived from extensively modified programs in only four months. This was, of course, the direct result of over a year's previous exposure to programming the system, which constituted the necessary learning experience. As a consequence one of the most sophisticated and intricate program sets in the computerized conductance system was created by extensive modification of existing programs in a single day. This was the program set written for simultaneous acquisition and analysis of conductance, temperature, and luminescence data, discussed in Chapter 8. This indicates that once the chemist masters the intricacies of programming, the subsequent time devoted to programming becomes reasonable compared to the experimental time, when a sufficiently powerful, general-purpose compiler system (such as the DEC OS/8 system described below) is available.

D. THE DEC OS/8 OPERATING SYSTEM

All programs for the computerized conductance system were written using the Digital Equipment Corporation OS/8 operating system (37). This system is based on a Keyboard Monitor which allows the user to control the flow of programs. A Symbolic Editor (EDIT) is provided for creation or modification of source files. A Peripheral Interchange Program (PIP) enables the user to transfer files between system devices. An absolute assembler (PAL-8) and loader as well as a relocatable

assembler (SABR) and loader are included. FORTRAN II is available. The FORTRAN compiler translates FORTRAN source files into SABR, permitting mixing of these two languages. This enables the programmer to write the necessary instrumental control and monitoring routines in assembler language, while performing data manipulation and system device I/O in FORTRAN. This combination of FORTRAN and SABR is exclusively used in the computerized conductance system programs presented in this thesis.

The OS/8 system does contain several idiosyncracies which were discovered during development of these programs. The more important of these are discussed below to prevent future workers desiring to expand this program set from repeating mistakes or encountering problems which have previously been resolved.

Because of the limited core space available in the 12K PDP-8/I it is impossible for both data acquisition and analysis routines to be resident in memory at the same time, except for the few very simple programs. It is, therefore usually necessary to write the data obtained during an acquisition onto tape at the completion of a run, for later analysis. Initially, it had been decided to write file-structured data blocks on tape by use of the device independent I/O command OOPEN in FORTRAN (38). The acquisition program would then use the CHAIN command (38) to call the first analysis program. For some reason, however, these routines failed to work with the programs which had been written for the computerized conductance system. Consultation with DEC software specialists failed to resolve the problem. Fortunately, the eventual solution provided a better means of bulk data storage than that first sought.

It was found that the best method for transfer of data from memory to DECTAPE and vice versa was to use the non-file structured I/O commands WTAPE and RTAPE in FORTRAN (39). With these routines the absolute block number on the DECTAPE where data transfer is to begin is input to the routine as an argument. The computer proceeds immediately to that location and transfers the data. No consultation with the DECTAPE directory is necessary, as in the case of OOPEN and IOPEN, resulting in considerably faster data transfer.

It is now suspected that the problem with OOPEN and CHAIN arose from the use of certain page zero locations (74 to 103) by the computerized conductance system programs. It was discovered (40) that these locations are used by the PS/8 operating system (which preceeded OS/8) for device independent I/O pointers. OS/8 was to have been configured in such a way that these locations would be freed. However, it is suspected that this has not been the case. In any event, there is no desire to return to the use of these device independent I/O routines because of the higher speed at which WTAPE and RTAPE operate. It should be noted, however, that WTAPE and RTAPE can only be used with the TC08 direct memory access (data break) tape controller. These routines will not function with a tape controller, such as the TD8E, which does not transfer data by direct memory access. Transfer of the computerized conductance system to a computer system with such a controller would necessitate use of OOPEN and IOPEN for data transfer.

One feature which the FORTRAN II compiler supplied with the OS/8 system lacks and which would prove extremely useful is the ability to use the extended arithmetic element (EAE) in its math routines. This FORTRAN package performs all mathematic operations by means of software,

even where an EAE is available. A considerable improvement in speed would result from use of the EAE instead, for fast hardware multiply, divide, and shift functions. Unfortunately, since a SABR listing of the FORTRAN II compiler was not available, it has not been possible to incorporate the EAE into the FORTRAN package.

The SABR language allows the programmer to be rather careless in core location assignment and paging, by supplying indirect statements and page pointers, where needed, itself. However, this convenience can inhibit smooth operation in some applications. For example, SABR inserts a CDF 0 (change to data field zero) instruction each time it encounters an instruction which uses the indirect addressing mode. This not only results in loss of core space and time but can be catastrophic in a program sending information into other data fields under command of the source program. This problem is circumvented in the computerized conductance system in two ways. One is to define an absolute address pointer on page zero. This pointer is then loaded with the address to or from which data is to be transferred. The actual octal instruction is then used in the program to reference indirectly the page zero location. The assembler is "fooled" without further incident.

Another method, employed only in the timed data acquisition routine, is that suggested by DEC concerning optimization of SABR code (41). This is to define a series of indirect statements (e.g. OPDEF TADI 1400) which are equivalent to the PDP-8 memory reference instructions but contain an indirect bit. These statements will work, if used sparingly, but they do precipitate an (illegal character) error message from the assembler. When such an error occurs in

assembly, the assembler will not call the LINKING LOADER to load the program but will return control to the Keyboard Monitor when assembly is complete. Therefore it is necessary to have saved the relocatable file generated by SABR so that the LINKING LOADER may be called by the user to load the program. Once this is done, the program will run properly, ignoring the error statements.

The final problem with the use of the OS/8 system, which has not been overcome, is that one cannot make use of the program interrupt facility with it. This appears to result from part of the system subroutine calls occupying the first few locations on page zero, including location zero. Location zero is the address to which the PDP-8 computers jump for the interrupt service routine pointers when an interrupt is sensed. According to the DEC literature (42), locations 0 to 6 on page zero in each field are available to the user. However, it has been found in operation that this is not the situation. Thus the computerized conductance system has never been operated in the interrupt mode although its hardware is capable of doing this.

Despite these few defects, the OS/8 system has enabled the sophisticated programming of the computerized conductance system, for both data acquisition and analysis, to be completed and implemented with relative ease. It seems most instructive to discuss the particulars of each of these programs in the chapters that present the chemical measurements which these programs perform and analyze (Chapters 5-8). However, three routines which appear often in the data acquisition programs are sufficiently important and general to be discussed separately. These programs are presented in the following sections. They are all contained in the example system program CBTSLS in the Appendix.

E. CREATING AN EXPERIMENTALLY FLEXIBLE SOFTWARE SET

The component circuits of the instrument provide the sequence of events necessary to perform a bipolar pulse measurement of conductance. These blocks are hardware combined only to the extent required by these sequences. This was done with the intention of producing an instrument with the highest degree of internal flexibility, both in combination of functions and in timing these functions. The use of digital measurement and timing techniques places the computer's decision-making abilities within the instrumental framework. This encourages the use of "intelligent" rather than fixed interactions between the various separate circuits. In this way, the experiment itself may be "designed" during run time such that the data received as a result of the software-instrument-chemistry correlation are the optimum data attainable by the technique.

If these design philosophies are properly implemented, a system which is user-oriented results. Any experiment, even one designed by the most novice operator, will yield the maximum amount of information because the computer will be programmed to automatically optimize the entire measurement sequence. Thus, if a chemist designs a significant "chemical" experiment, even though he has no knowledge of the intricacies of measurement which the computerized conductance system employs, he is guaranteed to receive data which is of a quality commensurate with the quality of the chemistry involved. The only assumption is that the experimenter have sufficient knowledge of the parameter he wishes to measure to enable him to decide that a conductance measurement is suitable. It will be seen in Chapter 9 that the computerized conductance system is even capable of providing this information.

F. DETERMINATION OF THE OPTIMUM MEASUREMENT PARAMETERS FOR THE COMPUTERIZED CONDUCTANCE INSTRUMENT

For the circuit presented in Figure 6 the cell conductance, G_{CELL} , in MHOS, is given by:

$$G_{\text{CELL}} = \frac{R_T}{R_D} \left(\frac{R_F}{R_{\text{IN}} R_I} - \frac{E_S}{E_{\text{IN}} R_V} \right)$$

where R_T is the total divider resistance (10000 Ω), R_D is the divider resistance to ground, R_F is the offset amplifier feedback resistance, R_{IN} is the offset amplifier input resistance (20000 Ω), R_I is the offset current producing resistance, R_V is the current follower feedback resistance, E_{IN} is the precision -5 volt power supply level (-5.000 Volts), and E_S is the sampled voltage (on a scale of 0 to 12.5 volts).

It was indicated in Chapter 3 that certain arrangements of the circuit settings (for a given conductance measurement) will produce values of the output signal, E_S , equivalent in magnitude. It was desirable to design the software in such a way that each time the computer set the circuit, the minimum instrumental error and noise level and the maximum resolution resulted. Since the tolerance for each component, C_i , of the above equation is known, the maximum error in G_{CELL} (corresponding to all component deviations being in the same direction), dG_{CELL} , is given by:

$$dG_{\text{CELL}} = \sum_{i=1}^8 \left| \left(\frac{\delta G_{\text{CELL}}}{\delta C_i} \right) \right| dC_i + \text{QUANTIZING ERROR}$$

The quantizing error is the error due to digitization of the signal as a result of the A/D conversion, as discussed by Kelly and Horlick (43). It is the resolution limit of the instrument for a single measurement, equal to or less than $\pm 1/2$ of the least significant bit (LSB) of conversion. For one discrete A/D conversion of 12 bits with no offset applied, the maximum quantizing error of G_{CELL} is the product of cell current and R_V divided by 8192 ($1/2$ digital value of LSB). A program was written to solve for the error fraction, $dG_{\text{CELL}}/G_{\text{CELL}}$, for all circuit settings and various sampled voltages, E_S . It was found that maximum accuracy was obtained at maximum pulse height, minimum current follower feedback resistance, and maximum offset. The error also decreased as E_S increased. Since maximum offset also corresponds to maximum resolution, no trade-off between accuracy and resolution was necessary.

In summary, then, the sequence of events for the computer to follow in setting the circuit for optimized measurement is:

- 1) Maximize the pulse height to make $E_S > 12.5$ volts if possible.
- 2) If necessary, increase R_V to make $E_S > 12.5$ volts.
- 3) Apply the maximum offset possible to bring E_S within the range of 0 to 12.5 volts.

G. THE PRELIMINARY SCAN ROUTINE

In order to set up the system for data acquisition, it is necessary for the computer to determine the conductivity region in which the measurement is to occur and to establish the optimum circuit settings for measurement in that region. To accomplish this, all data acquisition routines in the computerized conductance system utilize

the preliminary scan routine for measurement initialization. This routine is flowcharted in Figure 18. A complete listing of the routine appears in the CBTSLS program in the Appendix.

The preliminary scan sequence begins when a "G" is entered on the teletype. The computer initially selects the 10 μ second pulse width. It sets the circuit in its widest possible range. This corresponds to minimum pulse height ($R_D = 100$), minimum current follower gain ($R_V = 10^4$), and no applied offset current ($R_I = 0$, $R_F = 4000$). These values are latched into the control circuit. The computer waits for the relays to close, then measures. The measurement is tested to determine if the A/D converter is reading full scale. If it is not, the pulse height is increased (R_D increased ten-fold) until the converter reads full scale or the maximum pulse height is reached. If the A/D converter still does not read full scale, the gain of the current follower is increased (R_V increased ten-fold) until it does or until the maximum gain is reached. If, at maximum gain, the A/D converter still does not read full scale, the computer outputs a resolution error, stores the scale settings and takes and outputs the measurement, and proceeds to the next pulse width. The resolution error indicates to the operator that the conductance was too small to permit offset to be applied, thus eliminating the extra bits of resolution which the offset provides.

As soon as the A/D converter output becomes equal to full scale, the computer begins to apply offset to bring the signal within the 0 to 12.5 volt range of the converter. The computer sets the proper decade scale of offset ($R_I = R_V/10$), latches in one offset unit on this scale, and measures. The computer continues to apply offset until the A/D converter reads less than full scale. At this time the computer

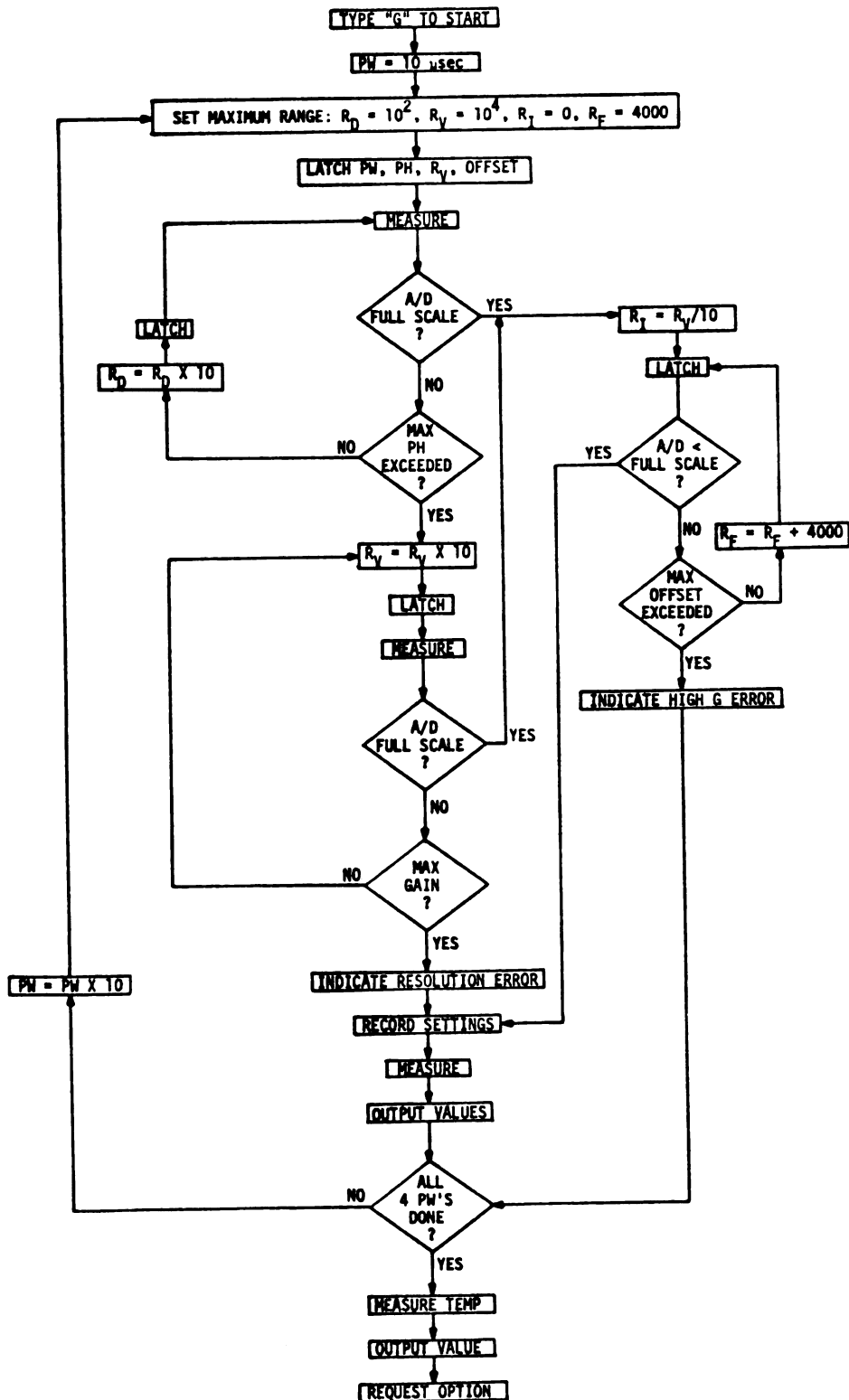


Figure 18. Simplified Preliminary Scan Routine Flowchart.

records the settings, measures, outputs the measurement parameters, and goes on to the next pulse width.

If, on the initial measurement of the sequence, the A/D converter had read full scale and the computer could not apply sufficient offset to bring it on scale, the computer outputs a high conductance error, which indicates that the conductance is greater than $0.22\Omega^{-1}$ and, thus, beyond the operating range of this instrument. The measurement is skipped and the computer proceeds to the next pulse width.

Typical computer output from the preliminary scan routine is shown in Figure 19. After the parameters for the first pulse width measurement are determined, the computer, having measured the conductance at these circuit settings, outputs the chosen pulse height (PH), pulse width (PW), offset units applied (UNITS), and the current follower feedback resistance (RV). The computer also outputs the magnitude of the voltage signal from the current follower (ES), the calculated cell resistance (RCELL), and conductance (CCELL).

When the sequence has been repeated for the next three pulse widths, the computer measures the response of the temperature sensor, as will be discussed in Chapter 6, and outputs the value. Finally, the computer prints the available measurement options and waits for selection of one of them.

The circuit parameters determined by the preliminary scan routine are stored in two ways. The instruction words, which, when output to the instrument, cause the circuit to be set in that particular optimum mode, are stored intact, one set for each pulse width. These are later used to set the circuit in the correct initial state when an option routine is called. In addition, a single parameter word is


```

TYPE "G" TO START
G
PH = 0.5000E+01 VOLTS
PW = 0.1000E-01 MSEC
UNITS = 0.9000E+01
RV = 0.1000E+06
SAMPLED V = 0.729980E+01
RCELL = 0.513876E+04 OHMS
CELL = 0.194600E-03 MHOS

PH = 0.5000E+01 VOLTS
PW = 0.1000E+00 MSEC
UNITS = 0.9000E+01
RV = 0.1000E+06
SAMPLED V = 0.741272E+01
RCELL = 0.513280E+04 OHMS
CELL = 0.194825E-03 MHOS

PH = 0.5000E+01 VOLTS
PW = 0.1000E+01 MSEC
UNITS = 0.9000E+01
RV = 0.1000E+06
SAMPLED V = 0.721130E+01
RCELL = 0.514343E+04 OHMS
CELL = 0.194423E-03 MHOS

PH = 0.5000E+01 VOLTS
PW = 0.1000E+02 MSEC
UNITS = 0.9000E+01
RV = 0.1000E+06
SAMPLED V = 0.685425E+01
RCELL = 0.516240E+04 OHMS
CELL = 0.193708E-03 MHOS

TEMP RESPONSE = 0.156494E+01

OPTIONS: 1)AVERAGE
         2)RESTART
         3)TDA
         4)CALL EXIT

```

Figure 19. Preliminary Scan Routine Output.

stored which contains the information as to how the circuit was set. This word is decoded by a special subroutine (DCODE in CBTSLS) where the conductance is calculated from the circuit equation.

In executing the preliminary scan routine, the computer has optimized the circuit setting according to the sequence described above. If the computer should be unable to perform this optimization, appropriate messages inform the operator. Thus, at the end of this routine, the operator may be assured that the measurement of conductance for that particular system has been initially optimized.

H. THE AVERAGING ROUTINE

One of the option routines which the operator may always select is the option to average a specified number of scans (discrete measurements) for a more precise determination of the measured conductance. This routine is flowcharted in Figure 20. A listing of this routine also appears in CBTSLS in the Appendix.

In order to utilize the averaging routine the operator must input the pulse width to be used in the measurement (which is chosen by the criteria presented in Chapter 5), the number of scans, from 1 to 2047, to average, and whether or not double precision data is to be taken. (Double precision data arises from the additional bits of resolution resulting from averaging, as discussed in Chapter 5.) The computer then looks up the instruction words corresponding to the chosen pulse width, sets the circuit, and measures. The measurements are summed as they are taken and stored in two words. When all scans have been taken, the sum is loaded into the EAE and divided. This provides fast, hardware calculation of the average ES. The DCODE subroutine is called

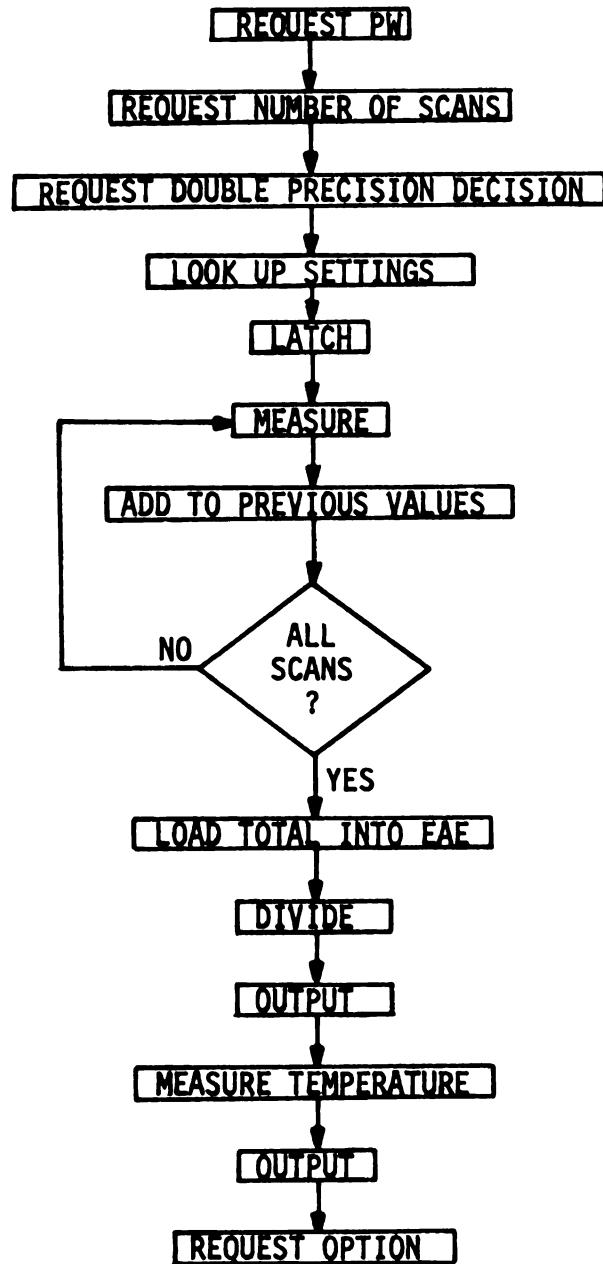


Figure 20. Averaging Routine Flowchart.

to calculate the conductance. The average ES, RCELL, and CCELL are output, the temperature response is measured again and output, and the program returns to the option selection. The printout generated by this routine is shown in Figure 21.

I. THE TIMED DATA ACQUISITION ROUTINE

Most chemical measurements involve the acquisition of data at regular intervals. The timed data acquisition routine (TDA) provides the computerized conductance system with a flexible means of sequencing this experimental interaction, both for conductance monitoring and for control of other peripheral devices used in the experiment. This routine is found in most of the conductance system programs for chemical analysis. It is also listed in the sample program, CBTSLS, in the Appendix.

The computer dialog for this routine is shown in Figure 22; the flowchart appears in Figure 23. Initially, the computer requests the total number of data points to be taken. Up to 500 points may be taken with this routine if temperature and double precision data are taken, up to 1000 points if they are not. Next, the time interval between points is requested. This can be any time from 130 μ seconds to 40000 seconds. The computer then requests the number of temperature measurements to average. If zero is input, the temperature measurement is skipped. The computer then outputs the approximate length of time the experiment will require and requests the address of the first tape block on which to write the data accumulated during the run. The operator inputs the pulse width, the number of conductance scans to average (up to 2047) for each point, and whether or not double precision data are to be

OPTIONS: 1)AVERAGE
2)RESTART
3)TDA
4)CALL EXIT

1

AT WHAT PW? (MSEC): .1
NUMBER OF G SCANS TO AVERAGE: 100.
DOUBLE PRECISION? (1=Y,0=N):1
TYPE EXPERIMENTAL INFO (CNTRL G TO END):

CONDUCTANCE MEASUREMENT OF A 0.0001 M
SOLUTION OF HCL
3/25/74

AVERAGE OF 100. SCANS: SAMPLED V =	0.60561523E+01 VOLTS
RCELL =	0.52052886E+04 OHMS
CCELL =	0.19211230E-03 MHOS

TEMP RESPONSE = 0.168457E+01

Figure 21. Averaging Routine Output.

OPTIONS: 1)AVERAGE
2)RESTART
3)TDA
4)CALL EXIT

3

TOTAL NUMBER OF POINTS:100.
TIME BETWEEN POINTS (SECS):5.
NUMBER OF T SCANS TO AVERAGE:25.
THIS WILL REQUIRE ABOUT 0.8333E+01 MIN
FIRST BLOCK TO WRITE: 200.
AT WHAT PW? (MSEC): .1
NUMBER OF G SCANS TO AVERAGE: 100.
DOUBLE PRECISION? (1=Y,0=N):1
TYPE EXPERIMENTAL INFO (CNTRL G TO END):

TITRATION OF 50.0 MLS OF 0.002 M
HCL WITH 0.01 M NAOH
CELL THERMOSTATED AT 24.0 C
3/25/74

TYPE "G" TO START

G

.

Figure 22. Timed Data Acquisition Routine Output.

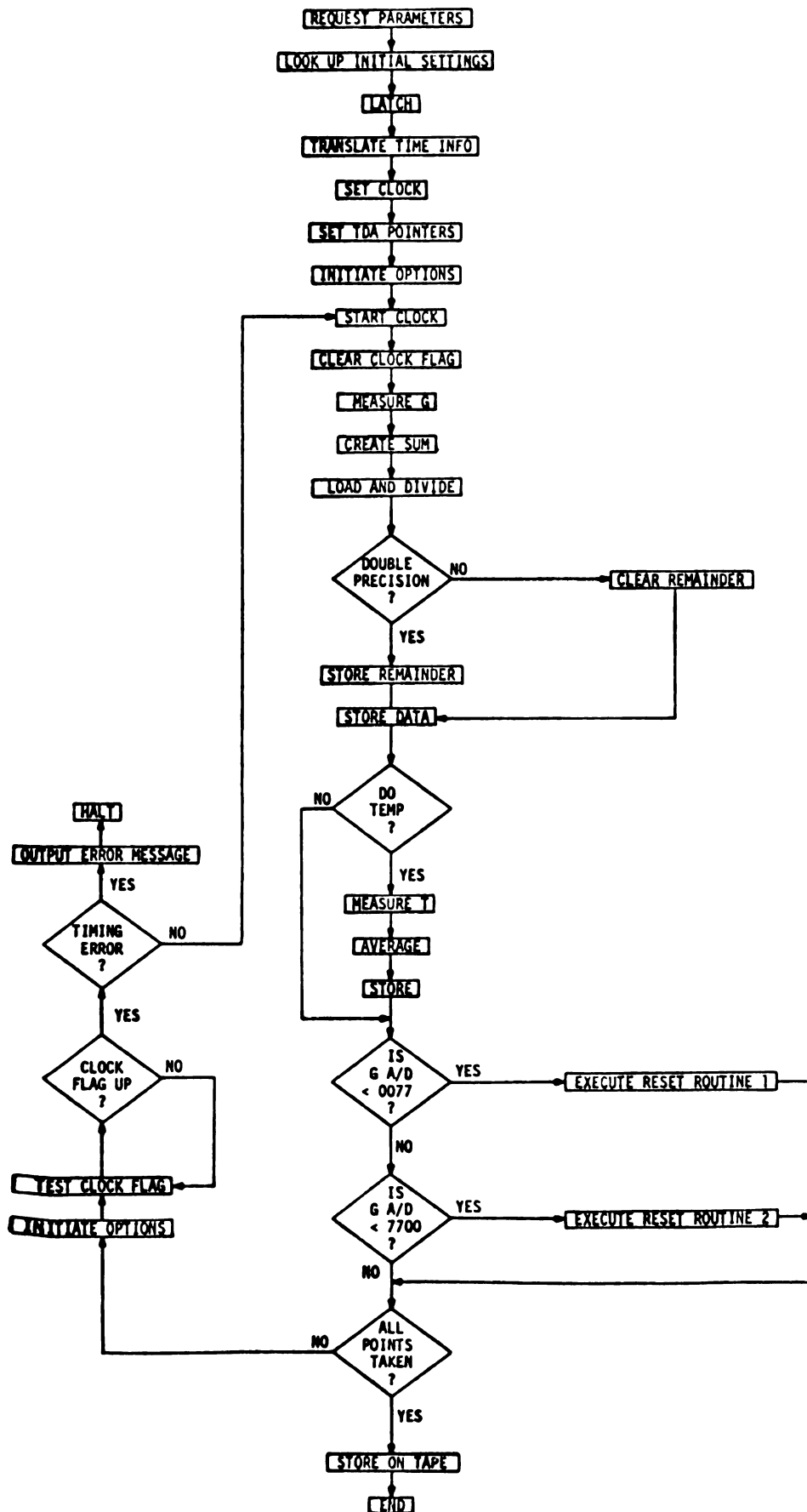


Figure 23. Simplified Timed Data Acquisition Routine Flowchart.

taken. The operator may finally record information about the particular experiment, for future reference, on that printout.

When a "CNTRL G" is entered on the teletype, the computer looks up the initial settings from the preliminary scan and sets the circuit (refer to the flowchart, Figure 23). It translates the timing information, sets the clock, and sets up the software pointers utilized during the run. It then waits for a "G" to be typed before beginning the actual acquisition. Once a "G" is typed, the computer may initiate operation of a peripheral device, such as the triggering of a stopped flow apparatus. It then starts the clock and begins to measure. Averaging is performed as in the averaging routine discussed previously. If double precision data are to be taken, the remainder from the EAE division is saved, to be later re-divided by the analysis routine in floating point format. If double precision data are not requested, the remainder is cleared, increasing storage capacity. In addition, the 12 bit dividend and the parameter word which contains the circuit setting information are stored.

If temperature information is to be taken, it is measured, averaged, and stored in the same manner as the conductance data. No provision for double precision is required as will be seen in Chapter 6.

The conductance measurement which the computer has just acquired is tested to determine if the sampled signal, E_S , is within the proper limits. The criteria for these limits were determined by the hysteresis necessary for scale overlap which will be discussed in detail in Chapter 5. If the A/D converter reads less than or equal to 0077, the computer will execute reset routine 1 to insure that the next measurement will be on scale. If the converter reads greater than or equal to 7700,

reset routine 2 is executed in a similar manner.

If all points are not yet taken the computer may again initiate operation of a peripheral device, such as the addition of the next increment of titrant in a conductometric titration. The computer then waits for the clock to signal time for data to be taken again and proceeds to measure as before. If more than twice the amount of time allowed between points has elapsed, due to a clock error or the time involved in a reset routine, the computer signals that the measurement timing has been destroyed and halts. If all data points have been acquired, the program transfers the data to DECTAPE and returns control to the Keyboard Monitor.

If the conductance has decreased such that the digital value of conversion is equal to or less than 0077, the circuit must be reset according to the optimization rules already discussed. This adjustment is performed in the fastest possible manner by reset routine 1, flow-charted in Figure 24. This routine will cause the offset to be decreased so that the signal to the A/D converter is increased to compensate for decreased cell conductance. If the offset is already 1 unit, the pulse height is increased to enhance the signal. If the pulse height is already at maximum, the current follower gain is increased. Once either the pulse height or gain have been increased, the offset is set to 10 units which will cause the next measurement to be properly on scale. If the circuit had already been set at maximum gain and 1 offset unit, the offset is turned off altogether. Finally, the parameter word is reset for the new values of the circuit settings, these values are latched in, and control returns to the main program. Reset routine 2, for resetting the circuit to compensate for increased conductance,

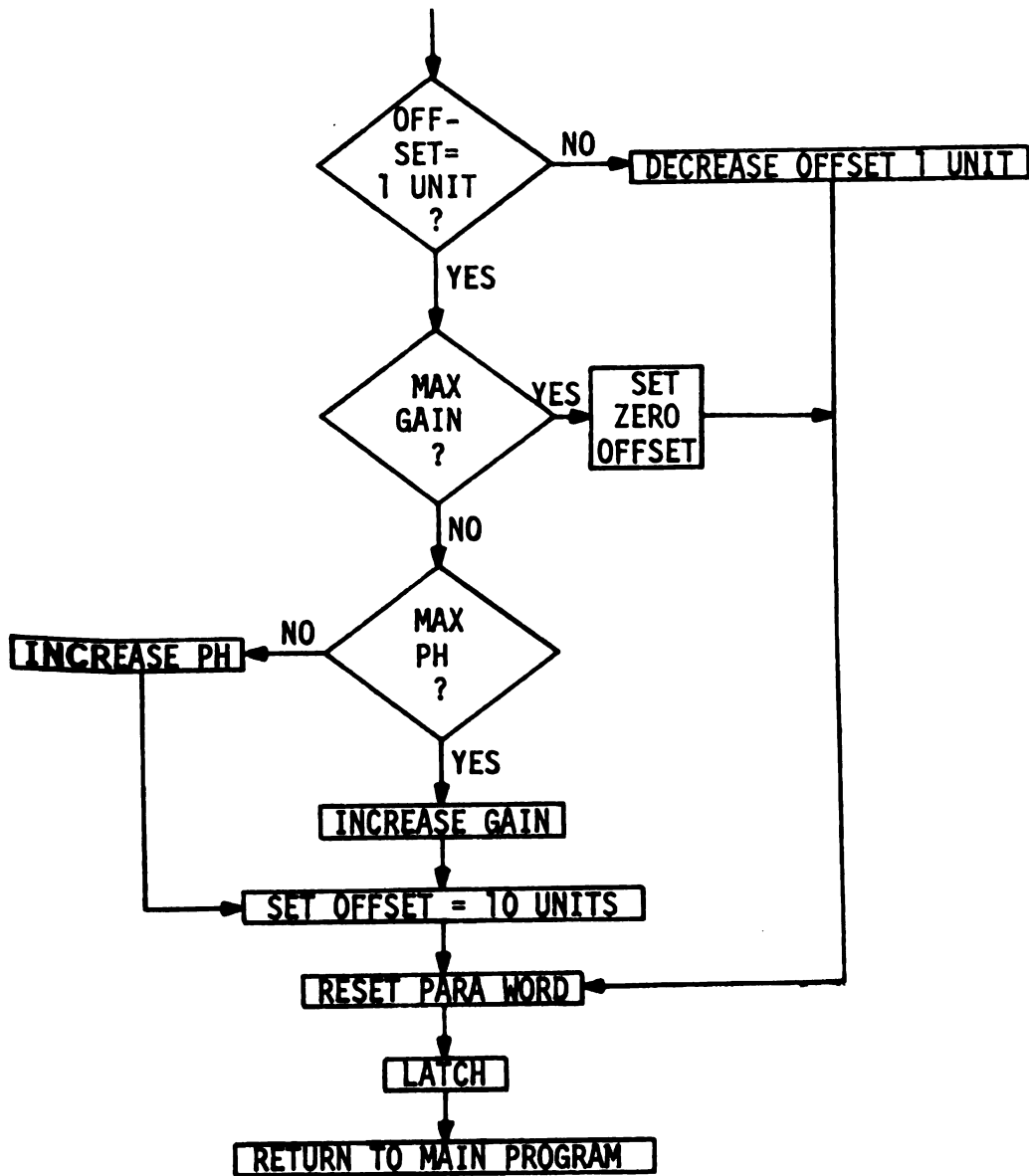


Figure 24. Reset Routine 1. (Simplified)

works similarly. It is flowcharted in Figure 25. These routines insure that the optimum measurement will continue to be made during the entire TDA run.

At the shortest pulse width, the TDA routine allows individual conductance scans to be made every 30 μ seconds. Approximately 100 μ seconds are required to calculate the average and store and test the data between points, if no resetting is required. Reset routines require 300 μ seconds to become "effective" due to the relay closing time. Simultaneous temperature measurement requires the additional time of 6 mseconds per scan.

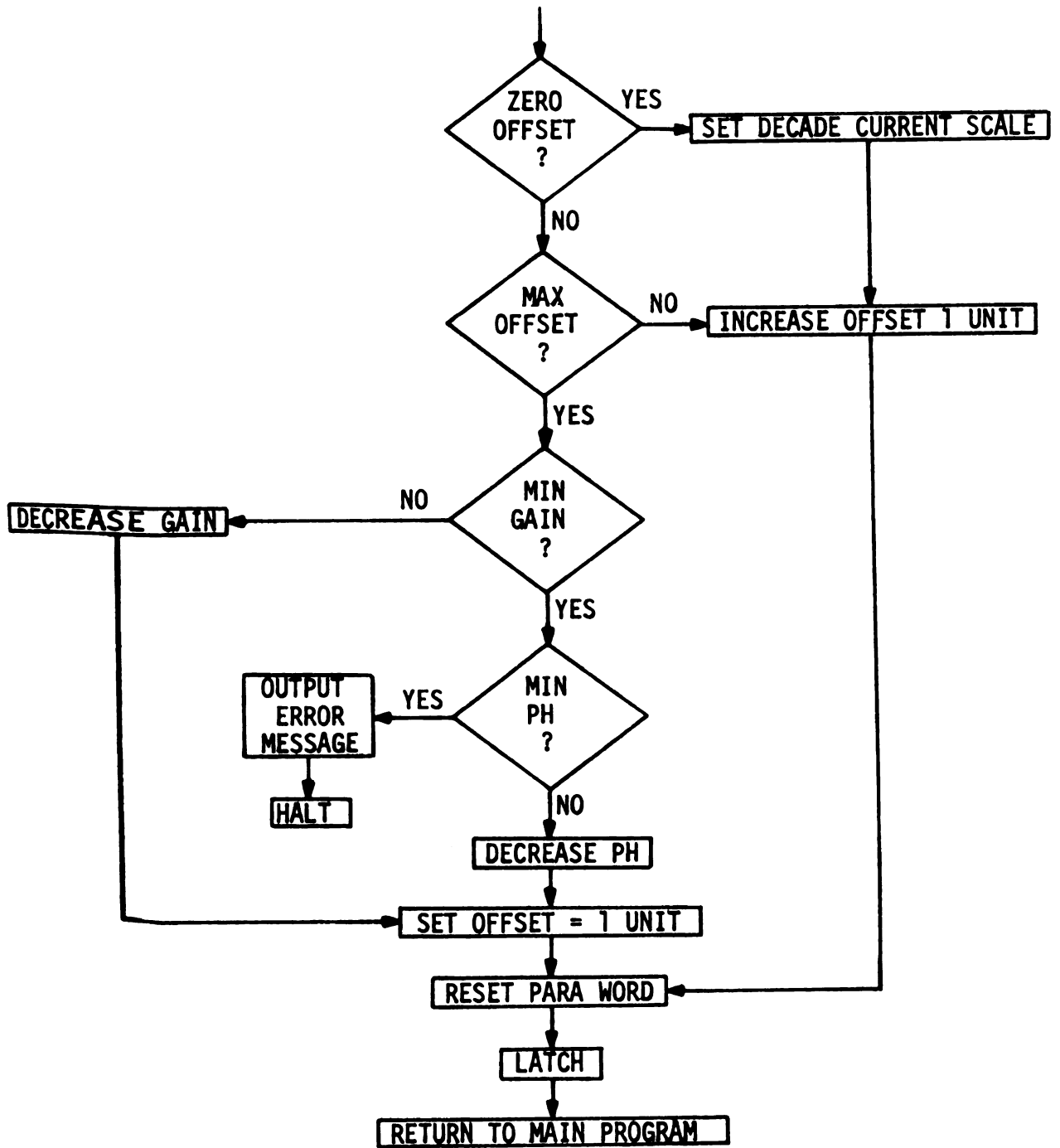


Figure 25. Reset Routine 2. (Simplified)

CHAPTER 5
PERFORMANCE CHARACTERISTICS AND SELF TESTING ABILITY
OF THE COMPUTERIZED CONDUCTANCE SYSTEM

A. PERFORMANCE CHARACTERIZATION VIA THE SYSTEM SOFTWARE

An instrumental system, such as the computerized conductance system, in which the computer has complete control over the measurement process and circuit setting is, in itself, the most powerful tool in the determination of its own performance abilities. It is possible, through appropriate software, to determine these characteristics with considerable efficiency and precision. Accuracy, resolution, and precision can thus be measured relatively easily over the entire eight orders of magnitude within the operating range of the computerized conductance system. In addition, the computer may assume the responsibility for making optimum measurements with respect to any of these characteristics for any particular region within this range. The trial and error tedium associated with manually setting a conventional instrument for determination of its optimum measuring abilities is therefore largely eliminated. Finally, performance characteristics which may only be discussed in relatively qualitative terms for many instruments may be quantitatively determined with high precision in the computerized conductance system.

B. DETERMINATION OF SYSTEM S/N, PRECISION, AND RESOLUTION

The first performance characteristic which was determined for the computerized conductance system was the signal-to-noise ratio, S/N,

in various parts of the operating range. From these measurements, information concerning precision and resolution were derived.

To determine the S/N the instrument was connected to a standard resistance with, usually, 1 ppm/°C temperature stability (e.g. Vishay metal film resistors type S106 or S102). A TDA routine, such as CBTSLS discussed previously, was utilized to make 500 measurements of this standard at discrete intervals. Each measurement could be a single scan or the average of up to 2047 scans. Standards were used which covered the entire operating range of the instrument. A special data treatment routine, CCPMLD, was written to analyze the data and plot it on the X-Y plotter and the display scope.

The program computes and outputs the maximum and minimum conductances measured during the run. It also calculates the standard deviation, σ , as given by:

$$\sigma = \left(\frac{\sum_{i=1}^n (\bar{G} - G_i)^2}{n} \right)^{1/2}$$

where n = the number of points, $\bar{G}$ = the average conductance, and G_i is the measured conductance at point i . Finally, the S/N is calculated from:

$$S/N = \bar{G}/\sigma$$

The program is also capable of calculating G_{MAX} , G_{MIN} , $\bar{G}$, σ , and S/N for any continuous group of points in the data set. The operator may then select to plot any or all of these points. Such a plot is

shown in Figure 26. This plot represents a worst-case situation for precision in the computerized conductance system. This occurs in the region near the highest measurable conductance, corresponding to the lowest pulse height utilized for bipolar perturbation. The data consist of single scans taken per measurement (i.e. no ensemble averaging). The standard deviation calculated for this situation was $4.6 \times 10^{-5} \Omega^{-1}$. The S/N ratio was 1180. The obtainable resolution, in this region, with no ensemble averaging is limited by noise and not by the 12 bit (1 part in 4096) resolution of the A/D converter.

During the initial stages of these resolution determinations, the method used for ensemble averaging was the same as that described in Chapter 4 with the exception that the remainder generated from the EAE division was always discarded; only the 12 most significant bits of the dividend were stored for later treatment. At this time, it was suspected that the attainable resolution would always be limited, by noise, to less than the 12 bits of the A/D converter plus any additional most-significant bits supplied by the offset generator. This quickly proved not to be the case as can be seen in Figure 27. This plot clearly shows the measured signal oscillating between two least-significant bit positions for only 16 averages per point in the conductance region around $3 \times 10^{-4} \Omega^{-1}$. The resolution has clearly been limited by the 12 bits of the averaging which have been kept for analysis. Increasing the number of averages could do nothing to improve the signal. However, Malmstadt, Enke, Crouch, and Horlick (44) have shown that a level of system noise greater than 1/2 of the quantization level randomizes the quantization error, making S/N enhancement by ensemble averaging possible. Furthermore, once the

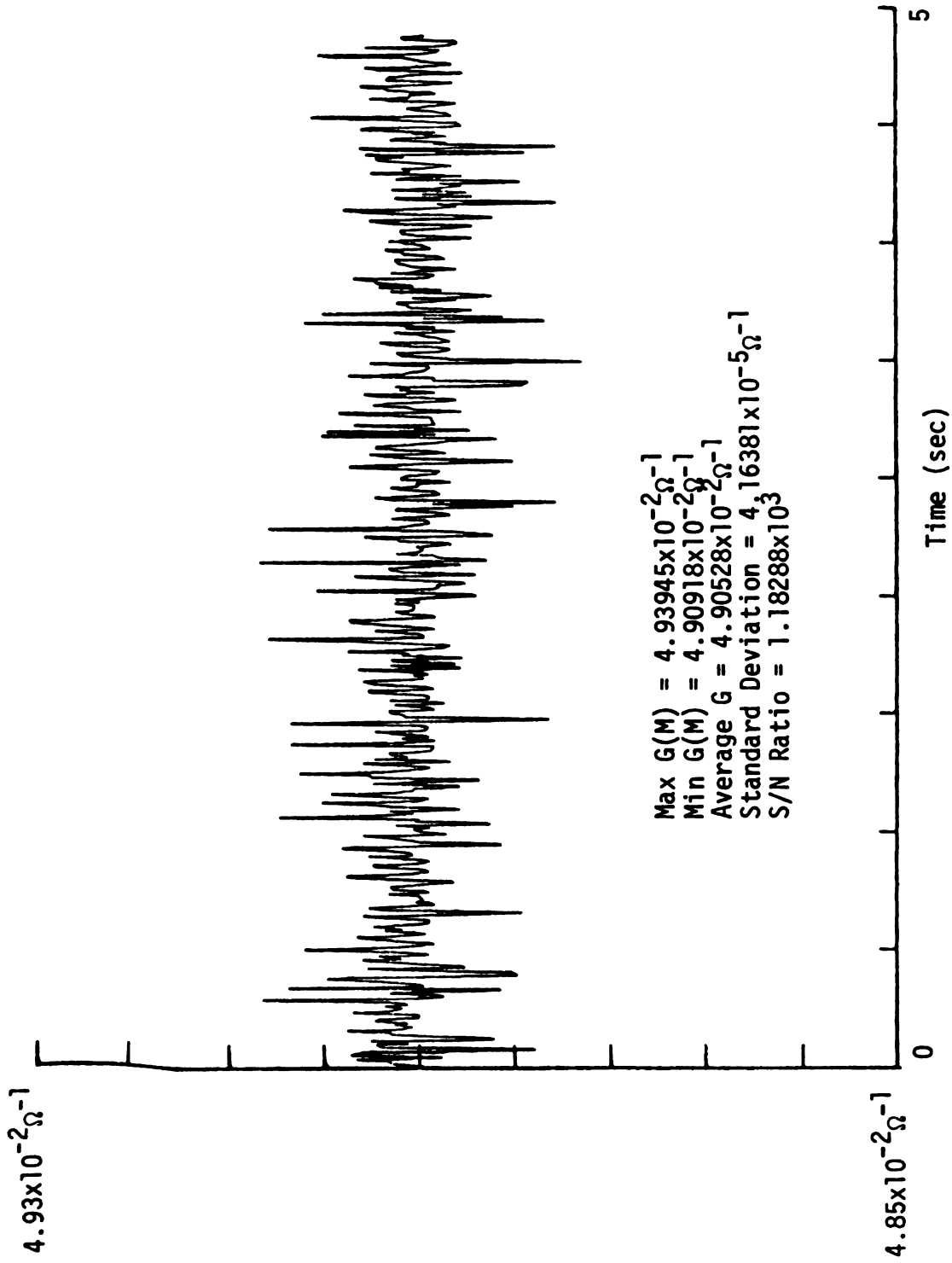


Figure 26. Random System Noise Profile. (101373-9)

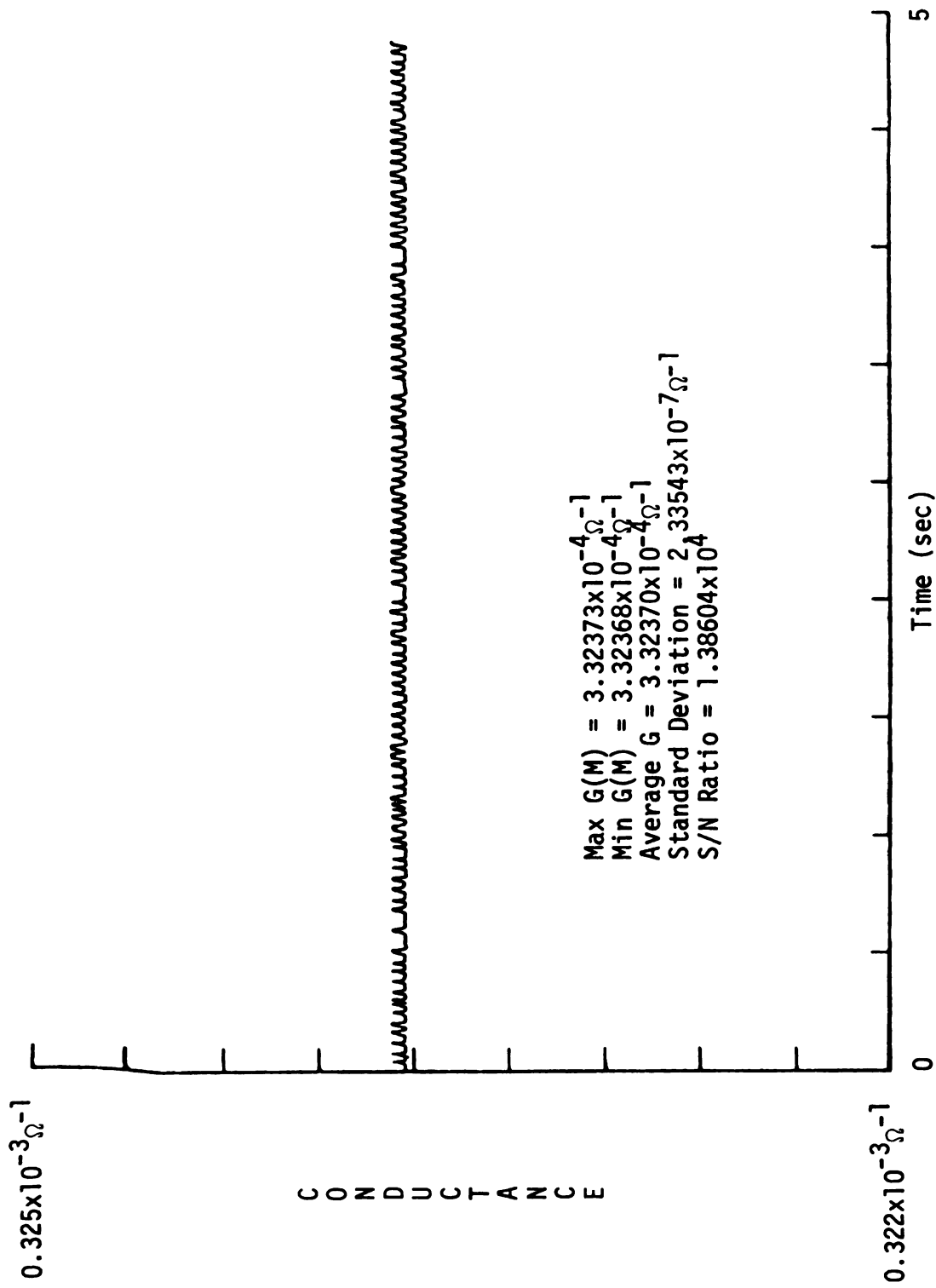


Figure 27. Reduction of System Noise to Quantization Level. (101373-5)

number of averages decreases the system noise to $1/2$ of the quantization level, increased resolution beyond the number of bits of the A/D converter will result. For example, if 16 12-bit A/D conversions are totaled, a 16 bit word will result. If the noise on the signal was not greater than $1/2$ the value of the least-significant bit when the data were taken, two of the four bits beyond the initial 12 are significant, providing a 14-bit conversion and increasing the resolution by a factor of 4.

It was therefore decided to store the remainder from the EAE division during the TDA run (essentially "double precision") and re-divide it by software during the data analysis routine. In this way the predicted improvement in S/N and in resolution could be realized. The effect of this technique is demonstrated rather dramatically in Figure 28.

Figure 28 shows a TDA monitoring of a standard resistance in the region of $1000\Omega(10^{-3}\Omega^{-1})$. Double precision data have been taken (i.e. the remainder is saved and re-divided during analysis) for an average of 2000 scans per point. The two irregularities in the curve were found to be a disturbance caused by the temperature bath heater switching on for 10 seconds, every 35 seconds or so. Although the standard resistor was attached to an aluminum plate with heat sinking grease, a small amount of initial heating can be observed during the first 10-15 points. After this time, the heating by pulsing and cooling by air reach a steady state. Neglecting these recognized interferences, for points 250-400 (2000 scans/point), the standard deviation was found to be $1.58 \times 10^{-9}\Omega^{-1}$ yielding a S/N of 624,000. Thus the option to take double precision data has henceforth been incorporated

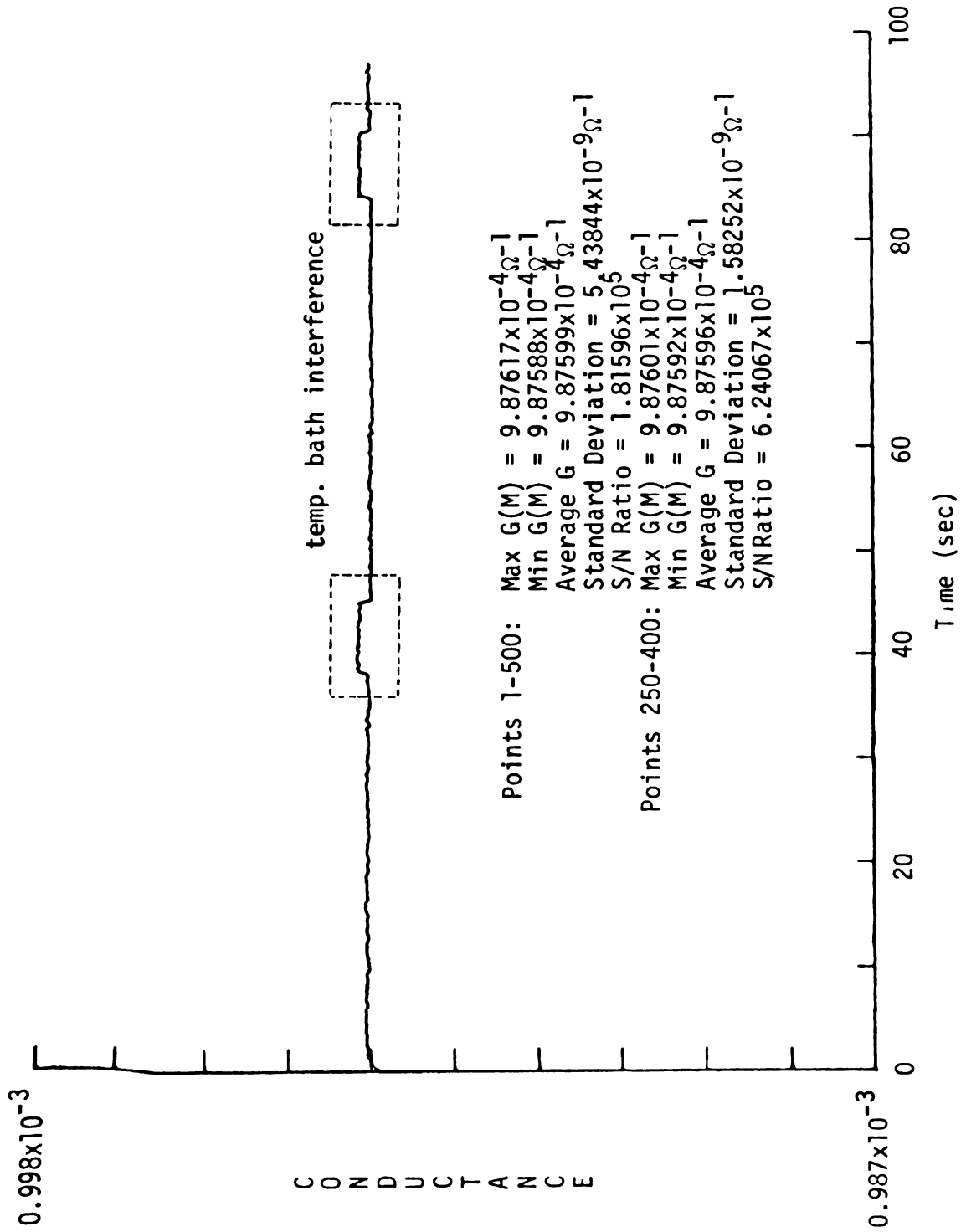


Figure 28. Ensemble Averaging Improvement in S/N and Resolution. (102373-8)

into all data acquisition and analysis programs.

As shown in Table 2, this region of conductance proved to be the most precise for measurement by the computerized conductance system. For an average of 2000 scans, the noise on the signal totaled only about 1.6 parts per million. In the region of highest conductivity, the S/N was limited by the number of averages which could be performed in a reasonable amount of time. The greater noise is most probably the effect of the relatively higher noise levels on the 0.05 volt pulsing signal employed here. In the region of lowest conductivity the results obtained during these measurements are somewhat limited by the stability of the standards which were available for use. In addition, at the very low signal levels being detected for these conductances, spurious currents through the glass epoxy printed circuit board become significant compared to the measured signal. Had this problem been anticipated in the design stages, its effect could have been minimized by placing ground loop foil patterns around the cell contacts on the analog printed circuit board. Since few measurements are made on solutions with a conductivity this low, rebuilding the board to correct this problem has not appeared necessary.

Finally, increasingly long pulse widths must be employed, as will be discussed later, at low conductivities, limiting the number of averages which can be made in a reasonable amount of time.

C. DETERMINATION OF SYSTEM ACCURACY

The response of the computerized conductance system was found to be linear for any particular scale setting. Discontinuities, which were encountered at scale changes (which will be discussed later),

TABLE 2. Performance characteristics.

Conductance	Number of Averages	Standard Deviation	Signal-to- Noise Ratio	Limited By
4.9×10^{-2}	1	4.16×10^{-5}	1.18×10^3	Noise
4.9×10^{-2}	2000	2.17×10^{-6}	2.26×10^4	Limit of Averaging
9.4×10^{-3}	1	1.41×10^{-6}	6.70×10^3	Noise
9.4×10^{-3}	2000	3.23×10^{-8}	2.92×10^5	Limit of Averaging
9.9×10^{-4}	1	1.50×10^{-7}	6.60×10^3	Noise
9.9×10^{-4}	2000	1.54×10^{-9}	6.40×10^5	Stability of Standard
3.2×10^{-4}	1	7.45×10^{-8}	4.34×10^3	Noise
3.2×10^{-4}	2000	1.52×10^{-9}	2.13×10^5	Stability of Standard
9.9×10^{-5}	1	6.29×10^{-8}	1.43×10^3	Noise
9.9×10^{-5}	2000	2.30×10^{-10}	4.20×10^5	Limit of Averaging
9.9×10^{-6}	1	6.74×10^{-9}	1.47×10^3	Noise
9.9×10^{-6}	2000	3.60×10^{-11}	2.74×10^5	Limit of Averaging
8.2×10^{-7}	1	1.27×10^{-9}	6.40×10^2	Noise
8.2×10^{-7}	2000	1.05×10^{-11}	7.77×10^4	Stability of Standard
9.0×10^{-8}	1000	9.96×10^{-12}	9.01×10^3	Stability of Standard, Time Scale of Experiment

had no effect on the linearity of measurements made at the same scale setting. Thus, in making absolute conductance measurements, a standard resistance is measured which requires the same instrumental scale settings as the unknown conductance to be determined. Once the computer is given the true value of the standard, it can software-correct any conductance measured at that scale setting since the net error will be constant over that interval. Instrumental drift was found to be an insignificant problem (less than 0.005% per day) over most of the operating range. Accuracy was, rather, found to be predominately a function of the series capacitance associated with the cell.

In order to facilitate the determination of maximum accuracy associated with each conductance region within the operating range of the system, the CBPSLT program, flowcharted in Figure 29 and listed in the Appendix, was developed. CBPSLT provides four option routines. Two of these routines are data analysis and plotting subprograms (options 1 and 2 respectively). The other two are both data acquisition routines, one for accuracy determination (option 4), and one for pulse width optimization (option 3) which will be discussed in the next section.

The data acquisition routine in option 4 is designed to eliminate or minimize the effects of extraneous signals on the accuracy determination. These effects are most often caused by a build up of charge on the series capacitance due to pulse asymmetry or the short range temperature characteristics of the standard. Option 4 overcomes these effects by allowing the operator to vary the relaxation time between single conductance scans as is necessary. The routine functions as follows:

After selection of a pulse width by the operator the computer

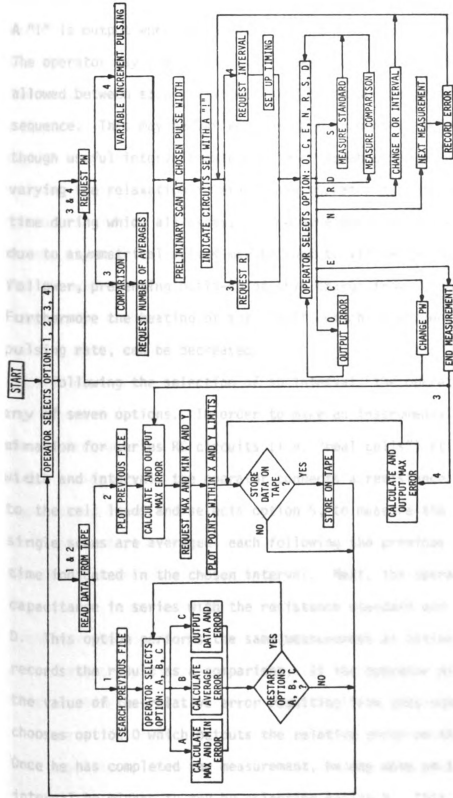


Figure 29. CBPSLT Program Flowchart. (Simplified)

executes a preliminary scan of the system at that pulse width only. A "!" is output when the preliminary scan is successfully completed. The operator may then choose the relaxation interval which is to be allowed between each individual bipolar pulse perturbation-measurement sequence. This may be varied from 10 μ seconds to 40000 seconds (although useful intervals extend only up to about 50 m seconds). By varying the relaxation interval, the operator is able to establish a time during which all excess charge developed on the series capacitance due to asymmetrical pulses may be sunk to virtual ground by the current follower, preventing build-up of this charge from affecting accuracy. Furthermore the heating of the "cell", which is a function of the pulsing rate, can be decreased.

Following the selection of an interval, the operator may choose any of seven options. In order to make an instrumental accuracy determination for series RC circuits (i.e. "real cells") at the chosen pulse width and interval, the operator connects a resistance standard alone to the cell leads and selects option S, to measure the standard. 1000 single scans are averaged, each following the previous scan by the time indicated in the chosen interval. Next, the operator places a capacitance in series with the resistance standard and selects option D. This option performs the same measurement as option S above but records the result as a comparison. If the operator wishes to know the value of the relative error resulting from this comparison, he chooses option O which outputs the relative error on the teletype. Once he has completed the measurement, he may move on to the next interval he wishes to try by selecting option N. This causes the data just taken to be entered in the program output buffer for later plotting

and analysis. If he desires to change an interval or pulse width before the data are entered he may select option R or C respectively. Once all data have been taken, the user selects option E which closes the output buffer. The buffer is subsequently searched and the computer calculates and outputs the maximum relative error. Finally, the data may be stored on tape for more detailed analysis and/or plotting at a later time. This more detailed analysis is performed by CBPSLT option 1. It can include calculation of maximum and minimum relative error, average error for the entire data set, and output of the data set (% relative error and pulsing interval) on the line printer. The data may be plotted by CBPSLT, option 2. The operator inputs the desired X and Y plotting limits. The computer uses this information to generate a point plot of % relative error vs. log (pulsing interval).

These accuracy determinations were made for conductances covering the entire operating range with series capacitance of 10, 5, and 1 μ F. These series capacitance values were equal to or less than the series capacitance of most real conductivity cells (i.e. worst case values for implementation of the bipolar voltage pulse technique). The results of these measurements are summarized in Table 3. The presence of effects due to series capacitance, in regions where the bipolar pulse technique should be relatively immune to these effects, arises from pulse height asymmetry due to finite FET switching and amplifier settling times as well as the stability of the ground supplied by the current follower. This stability decreases as the amount of current supplied to the current follower summing point increases. The current reaches a maximum at the highest offset currents, corresponding to conductances of $2 \times 10^{-3} \Omega^{-1}$, $2 \times 10^{-4} \Omega^{-1}$, etc. This accounts for

TABLE 3. Accuracy (in percent) for various conductance - series capacitance combinations. Allowed relaxation time is 30 μ seconds unless otherwise indicated.

$G(\Omega^{-1})$	$C(\mu F)$		
	10	5	1
10^{-1}	0.17	4.4	19
2×10^{-2}	0.0053	0.82	0.057
10^{-2}	0.0071	0.40	1.4
2×10^{-3}	0.12	0.21	0.38
10^{-3}	0.026	0.059	0.13
2×10^{-4}	0.074	0.38	0.15
10^{-4}	0.0069	0.0045	0.23
$2 \times 10^{-5}^{\dagger}$	0.0073	0.0051	0.018
10^{-5}	0.0037	0.0012	0.28
$2 \times 10^{-6}^{\ddagger}$	0.049	0.072	0.095
10^{-6}	0.024	0.054	0.18
2×10^{-7}	0.25	0.52	0.99
10^{-7}	0.38	0.45	0.76

† 9 msec between pulses.

‡ 30 msec between pulses.

the relatively poorer accuracies in these areas.

All values in Table 3 represent 30 μ seconds allowed relaxation time between pulses except at $2 \times 10^{-5} \Omega^{-1}$ and $2 \times 10^{-6} \Omega^{-1}$ where longer relaxation times were found to increase accuracy. It can be seen that over much of the operating region, accuracies of close to 0.02% or better can be obtained for series capacitances of 10 μ F. At lower capacitances, the effects of pulse asymmetry are greater as can be seen. Correspondingly, at the higher series capacitances of many real conductance cells (20 μ F), the accuracy would be even closer to that obtained with the resistance standard alone.

Finally, no measurable effect on accuracy by parallel cell capacitances less than 1000pF has been observed. Since real cells normally fall well within this region, any effect of such capacitance has been discounted.

D. OPTIMUM PULSE WIDTH SELECTION

Two factors must be considered in the selection of a particular pulse width for use in a given conductance region. First, the pulse width must be short compared to the time constant for the series RC circuit formed by the conductance cell as discussed in Chapter 2. Secondly, the pulse width must be long enough to allow the current follower to settle to its true output at the end of pulsing. For low conductances the gain of the current follower must be increased, slowing the response of the amplifier. Thus longer pulse widths must be used at lower conductances.

CBPSLT provides, through option 3, a means to determine exactly

the optimum pulse width for use in a particular conductance region. In using this option, the operator inputs the chosen pulse width and the number of individual conductance scans to average per measurement. A preliminary scan is conducted as with option 4. The operator then inputs the true value of the resistance which is being measured. Using the same measurement options which are available in option 4, the operator first measures the standard resistance, then the RC network, and stores the true resistance and the relative error as an X-Y pair. After each measurement is stored, the value of the next resistance is input and the sequence repeated. When the E option is finally selected, the maximum error is calculated and output. The operator then selects the plotting scale and the data is point plotted as relative error vs. $\log$ (true resistance). The data may then be stored on tape for the more detailed analysis provided by option 1 or replotted by option 2.

A composite plot of data obtained in this way for each of the four shortest pulse widths, over the entire operating range of the instrument, appears in Figure 30. This particular plot corresponds to a series capacitance of $5 \mu\text{F}$. The two factors which contribute to the error, a pulse length that is significant compared to RC and the current follower settling time, are manifest in the rapid increase in error at either end of a particular pulse width region. It can be seen from the plot that, for the best accuracy, the pulse width should be chosen as follows: Above $10^{-4} \Omega^{-1}$ ($< 10 \text{ K}\Omega$) the shortest pulse width (0.01 msec) is used, between $10^{-4} \Omega^{-1}$ and $1.4 \times 10^{-5} \Omega^{-1}$ ($10 \text{ K} - 70 \text{ K}\Omega$) the pulse width = 0.1 msec, between $1.4 \times 10^{-5} \Omega^{-1}$ and $1.4 \times 10^{-6} \Omega^{-1}$ ($70 \text{ K} - 700 \text{ K}\Omega$) the pulse width = 1.0 msec, and between $1.4 \times 10^{-6} \Omega^{-1}$ and the lower

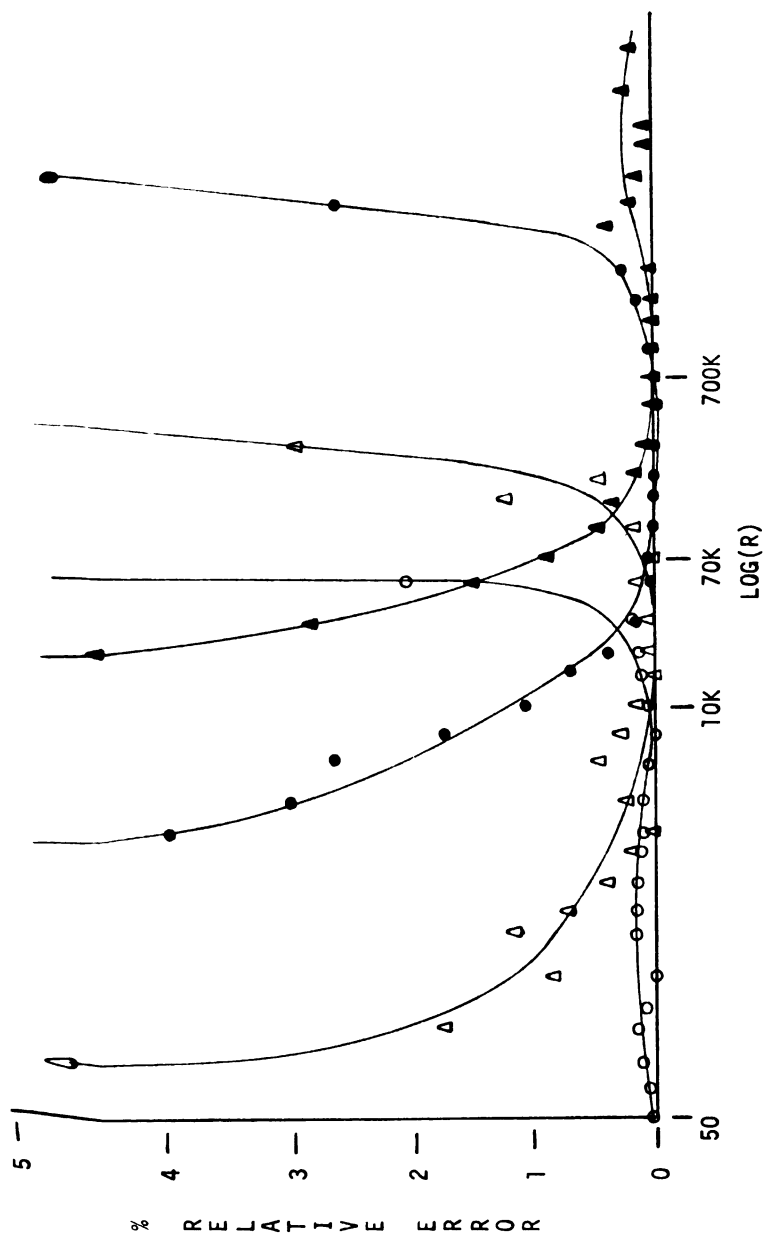


Figure 30. % Relative Error vs. Log(R) for a Series Capacitance of 5.0 μ F.

$\circ$ PW = 0.01 msec, Δ PW = 0.1 msec, $\bullet$ PW = 1.0 msec, $\blacktriangle$ PW = 10.0 msec

conductance end of the scale (700 K - 80 M Ω), the pulse width = 10.0 msec. A series of such plots were prepared for various other series capacitances. They are all in approximate agreement with Figure 30 concerning which pulse width to select for a particular conductance region.

E. SCALE CHANGE CORRECTIONS IN THE COMPUTERIZED CONDUCTANCE SYSTEM

The instrument, as initially designed, performed well over its entire range except in the regions of scale changes. It was found to be impossible to perfectly align the pulse height, current follower gain, and offset such that there was no overlap or underlap of scales. The problem of underlap was most severe as it resulted in a "dead zone" in which data points were lost altogether, as the computer caused the instrument to oscillate between the lower offset, gain, or pulse height setting full scale conversion and the higher offset, gain, or pulse height setting zero conversion because of the area where the scales failed to meet. All data taken during the underlap interval were lost. In addition, some non-linearity occurred at low voltage level outputs of the current follower, apparently due to pulse asymmetry with insufficient allowed relaxation time. Both problems were solved by providing overlap of the scales through the divider at the current follower output. Hysteresis was provided at both ends of the scale by not permitting an A/D conversion above 7700₈ or below 0077₈ without a scale change. Any discontinuity occurring at the scale change point (see raw data, Figure 31) was eliminated by programming the computer

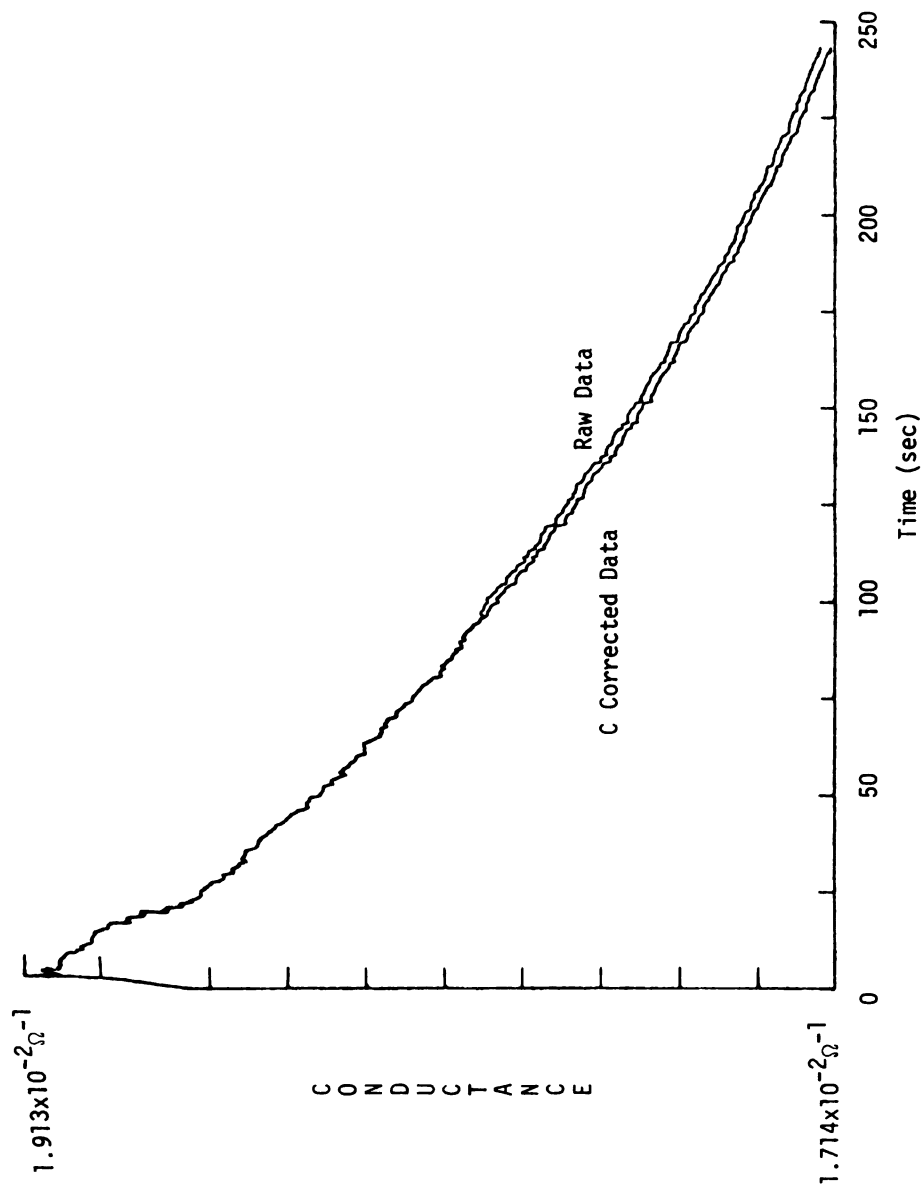


Figure 31. Conductance - Time Profile for Cooling of a Sulfuric Acid - Water System 15°C with no Bulk Ionic Change (38-23°C) (11974-2)

to adjust mathematically the data at those points (see scale change corrected data, Figure 31. The computer performs this correction by calculating the best straight line through the last three points measured on the previous scale setting and from this calculation, predicting the position of the next point. The offset between the predicted position and the actual position of the first point at the new scale setting is used to correct all subsequent data. If fewer than three points are taken at a particular scale setting, as may be the case for very rapid conductance changes, scale change correction is not performed by the computer.

After implementation of the hysteresis and scale change correction provisions, it was found that instrumental adjustment was virtually unnecessary. Only infrequent trimming of the current follower, to prevent non-linear response due to pulse asymmetry, power supply adjustment, and adjustments for extremely accurate absolute conductance determinations are performed.

F. LINEARITY, RANGE, AND SPEED CHARACTERISTICS

Many of the operational amplifiers in the analog circuit have very fast response times and, thus, a tendency to oscillate. A 56 pF capacitor in the feedback loop prevents oscillation of the offset amplifier but would cause the current follower response to become non-linear if used. The resulting small 10 MHz oscillations of the current follower are transparent to the measurement and are allowed to occur since the noise bandwidth of the instrument is upper-limited by the

frequency response of the sample and hold module (500 KHz).

The instrument was found to be linear over its entire operating range, which extends from 0.22 to $1.3 \times 10^{-8} \Omega^{-1}$. Above $0.22 \Omega^{-1}$, the conductivity is so high that maximum offset is insufficient to put the conversion system on scale. Below $1.3 \times 10^{-8} \Omega^{-1}$, as previously mentioned, conduction between the copper foil pattern through the glass epoxy printed circuit board becomes significant compared to the measured conductance.

Finally, the instrument can be completely reset by the computer and settle to its new settings in 300 μ seconds, limited by the relay closing time. Discrete conductance measurements may be made in 30 μ seconds (20 μ seconds for pulsing and 10 μ seconds for relaxation during which A/D conversion takes place) at the maximum rate.

G. SYSTEM DIAGNOSTIC AND EXERCISER FACILITY

Even during the earliest stages of development of computers and computer systems, software sets were designed specifically for exercising these systems and indicating malfunctions within them. It was found that if such tests were conducted routinely, the system gained a high degree of reliability. This is because many malfunctions can be detected before they become sufficiently serious to effect operation of the entire system. Furthermore, computer systems can become so complex that they are literally impossible to troubleshoot in any other way. Thus, when a computer system is developed, appropriate testing software should also be written. Such software is standard for the computer part of the PDP-8/I system described in Chapter 1. It includes central processor

tests, magnetic tape transfer and transport tests, extended memory test, and EAE tests (45).

This same mode of testing may be extended to non-standard peripherals such as those developed in a chemical laboratory. The computerized conductance system is, of course, such a peripheral. In the interest of a smoothly running system, then, it was desirable to take advantage of the power inherent in software instrument tests. In this way, again, an operator lacking a feel for instrumentation would be able to implement a software test which would pinpoint a particular hardware malfunction. Often, the problem may be solved simply by tightening a circuit card connection or replacing an integrated circuit chip. The software diagnostics can lead the inexperienced operator to these causes. If the problem is more complex, the system can inform the user to seek outside help. The manner in which the operator is taught the use and interpretation of these system tests is described in Chapter 9. The program which performs these tests, CBTCLH, is flowcharted in Figure 32 and listed in the Appendix. Its function is described below:

In order to use CBTCLH to perform instrument tests, the test probe shown in Figure 33 is normally plugged into the instrument cell lead connections. This probe provides series resistances and series and parallel cell capacitances for use in the system tests. These components are available through switches on the probe itself. A BNC connection for oscilloscopic monitoring of the pulses is also provided. For most instrument tests, the 1000 Ω resistance standard with no series or parallel capacitance is chosen. The program is entered by the operator in the normal manner. The operator is asked to choose a pulse width. He normally will select one of the shortest which provides the greatest

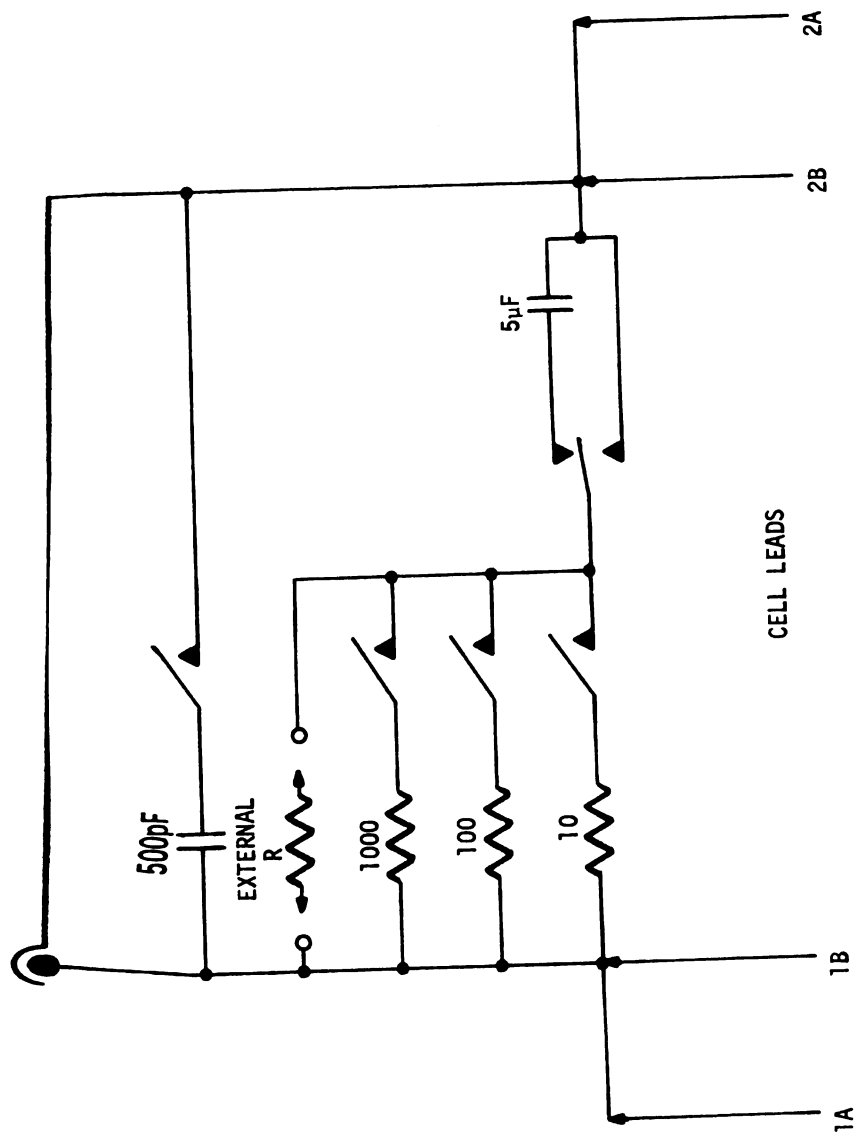


Figure 33. Test Probe Schematic Diagram.

number of tests in the shortest time. A preliminary scan of the resistance standard "cell" begins at the chosen pulse width. If either the conductance or the temperature flag (to be discussed in Chapter 6) fails to appear in the proper amount of time, the appropriate error message (ERROR 3 or ERROR 6 respectively) is given as output. The program will then move to a routine which continuously triggers conductance pulse sequences and temperature measurements, testing for proper flag response at the appropriate time. Error messages will continue to be given for flag failures until the operator is able to correct this problem or until he halts the program manually. If the user is unable to correct the problem, CBHELP (discussed in detail in Chapter 9) will instruct him in the proper troubleshooting procedure to follow.

If A/D conversion problems arise during the preliminary scan, error messages are also given. If the scan is completed successfully, the operator may select any of seven option test routines. Two of these routines involve averaging of measurements; option 1 for 100 conductance scans and option 6 for 25 temperature points. It was found that these routines proved especially useful for testing experimental measurements prior to an actual run or for general tests of reproducibility where an actual quantitative measurement of deviation is unnecessary.

Option 2 allows the operator to restart the program. The other four options actually exercise and test the hardware functions of the instrument. Option 3 causes the conductance circuit to continuously pulse the cell at a rate equal to ten times the chosen pulse width. No error checks are made which would cause the timing to be disturbed. This permits the operator to use an oscilloscope to check the generation of measurement sequencer waveforms, proper amplifier switching, sample

and hold tracking/holding sequence, the A/D triggering monostable signal, the conductance A/D converter status output, and finally, the bipolar perturbation pulses themselves. This routine proved to be invaluable when the hardware was initially being debugged. It is still used when instrument performance indicates failure of a circuit producing one of the above signals.

Option 4 causes the conductance conversion system to be tested. It assumes that a stable resistance has been placed in the cell position (as in the test probe) and that a zero or full scale A/D conversion is not required to measure that particular resistance. The bipolar perturbation pulses are applied at intervals equal to ten times the chosen pulse width. If the conductance flag fails to raise within this period, the computer outputs an error message (ERROR 3). If the conductance A/D converter returns a zero or full scale conversion, the computer outputs ERROR 4 or ERROR 5 respectively. The probable causes of these errors are explained by CBHELP (Chapter 9). These causes would include failure of the A/D triggering monostable, momentary failure of the latches to hold circuit settings, or failure of the A/D converter itself, the gated driver, or one of the analog components. CBHELP informs the user of the components to check for the particular failure circumstances encountered.

The temperature conversion circuit may be exercised and tested in a similar manner by option 7. Flag, zero conversion, and full scale conversion error messages (ERRORS 6, 8, and 9 respectively) are given. CBHELP also aids in interpretation of these failures.

Options 4 and 7 are combined into one routine by option 5. This permits tests of the entire computerized conductance instrument at one

time.

In designing the exerciser routines for the computerized conductance system, no new hardware, specific for testing purposes, was built into the instrument. The only additional implement is the test probe which merely substitutes for the cell. It did not appear desirable to introduce extraneous circuits into the instrument which might possibly interfere with the testing and operation of the instrument in determining its characteristics and in performing chemical measurements, which is the basis of this thesis. However, expanded testing capabilities and increasingly detailed diagnostics could be obtained by the inclusion of several other circuits of varying complexity. These might include:

- 1) Read-out read-in latches. This circuit would enable the computer to test the state of the latches at any time by reading their real settings back into the accumulator and comparing these with the intended settings.
- 2) IOP and DS test circuit. A flag which the computer could set and clear itself could be used to determine if the device select and input-output transfer pulses were, indeed, reaching the instrument and being decoded properly.
- 3) Measurement sequencer test circuit. The waveforms generated by the measurement sequencer could be digitally sampled and measured through reference to the computer mainframe clock. Problems with the circuits which produce each of these signals could then be isolated.
- 4) Pulse generator monitor. The bipolar perturbation pulses themselves could be sampled and measured for determination of their magnitude, symmetry, etc.

- 5) Gated Driver I/O test circuit. The gated driver inputs could be multiplexed between the A/D converter and a set of computer-controlled latches. The computer could read out to these latches and back in through the driver to determine data transfer errors.
- 6) Power supply level test circuit. The power supply voltage levels could be analog multiplexed and read by an A/D converter to see if they required adjustment.

Inclusion of all of the above circuits (and probably others) would add considerably to the real complexity of the instrument. One could probably argue that failures increase as complexity does. However, the counter argument is that these circuits would make the "apparent" complexity of the instrument considerably less than it currently is by pinpointing errors more exactly. Development of self-testing instrumentation certainly has been the subject of an entire thesis itself (probably not a chemical thesis!). The degree of self testing in the computerized conductance system was thus purposefully limited to those interactions which the measuring circuits themselves already provided.

Finally, it should be mentioned that the computerized conductance system utilizes the real time clock diagnostics written by B. K. Hahn (46) for detection of circuit malfunctions in the computer mainframe real time clock.

CHAPTER 6

TEMPERATURE MEASUREMENT AND COMPENSATION IN THE COMPUTERIZED CONDUCTANCE SYSTEM

A. THE TEMPERATURE MONITOR

The performance characteristics presented in Chapter 5 indicate that the computerized conductance system is essentially unaffected by instrumental drift or parallel cell capacitance and only slightly affected by the series cell capacitance. The single remaining effect which will most influence the quality of data obtained from a computerized conductance system measurement is that of temperature changes in the chemical system under study.

Very little work has been done at this time in providing automatic correction of conductance measurements for temperature fluctuations. Most workers have been extremely careful to maintain a constant temperature (within 0.01 to 0.001°C) for the duration of a particular conductance measurement process. In order to maintain these temperature stabilities, conductance-based studies of chemical systems with inherent temperature variations had to be avoided. These included reactions which are significantly exothermic or endothermic, solvent systems which have large enthalpy changes associated with mixing, and mixing systems themselves which caused more than a few hundredths of a degree Centigrade temperature change when used. One of the few attempts to compensate conductance measurements automatically for temperature changes was the circuit employed in Johnson's later bipolar pulse instrument (18).

Johnson assumed that over a narrow temperature range, the conductance of a thermistor and the conductance of the chemical system being

studied vary approximately linearly with temperature. He used this assumption in providing automatic signal feedback compensation in his analog conductance circuit. In this way he was able to boost a conductance signal produced after a drop in temperature proportionately and, likewise, scale a conductance signal obtained after an increase in conductance accordingly. Johnson showed that temperature compensation was possible for his circuit provided that either the temperature coefficients of the thermistor temperature sensor and the chemical system are constant or that they vary in exactly the same way. He assumed that they would be nearly constant over a 1°C temperature change. Since he realized that it is extremely difficult to make a prediction of the temperature coefficient of the chemical system, the circuit settings for temperature compensation for that particular system were determined by varying the temperature over the 1°C range in which the conductance measurement was to be made. The accuracy of the conductance determinations made with this type of correction was improved by one or two significant figures. Johnson claimed excellent results for 1°C negative temperature deviation correction but positive deviation corrections were not suitable beyond 0.25°C .

In designing the computerized conductance instrument, it was desirable to keep the analog conductance circuit as simple as possible, not encumbering it with those amplifiers and multipliers which were necessary to compensate for temperature variation in Johnson's instrument. In addition, situations could be envisioned in which a record of the actual temperature change itself would be useful. Reaction studies in which heating due to a reaction or mixing would affect the system chemistry is one such example. In order to accomplish both of these

goals, it was decided to include in the computerized conductance system a separate analog temperature measuring and digital conversion circuit for fast monitoring of temperature simultaneously with, but not affecting, the measurement of the conductance signal. The temperature monitor designed for these measurements is shown in the schematic diagram of Figure 34.

The temperature monitor consists of an analog bridge circuit and difference detector to follow the conductance of a thermistor, R_T , and an A/D conversion system with a flag. The precision 5 volt signal produced by the S5723L regulator of Figure 6 is used to provide the stable signal for the bridge. The bridge is designed in such a way that a 10 K Ω thermistor will produce a potential difference between points A and B of about 1 volt. The voltage level at B is subtracted from the level at A by operational amplifier A_5 which also supplies a gain of 5.11 to this difference. The output of amplifier A_5 is connected directly, along with the quality analog ground signal discussed in Chapter 2, to a dual-slope, integrating A/D converter. The A/D converter is triggered directly by a DS-IOP signal from the computer, resetting on the rising edge and initiating conversion on the falling edge. Upon triggering, the STATUS output goes high. When STATUS returns to low, it triggers a flag and possibly a program interrupt. The flag circuit is identical to the conductance flag circuit discussed in Chapter 3. After testing the flag and finding it raised, the computer will gate the driver and transfer the data to the accumulator.

The analog section of the temperature monitor appears in the photograph of Figure 17. It is mounted directly over the temperature monitor A/D converter which is located in the digital circuit compartment, photographed in Figure 15.

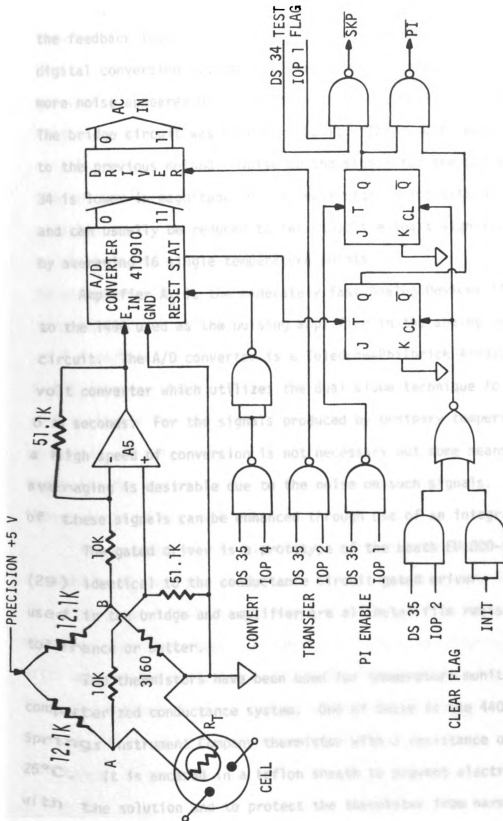


Figure 34. Temperature Monitor Schematic Diagram.

Originally, a temperature sensor which consisted of a thermistor in the feedback loop of an operational amplifier was used with the same digital conversion system. It was found, however, that considerably more noise appeared on the signal for this circuit than could be tolerated. The bridge circuit was therefore built. The results were far superior to the previous method. Noise on the signal for the circuit of Figure 34 is lower in magnitude than 3 least significant bits of conversion and can usually be reduced to less than the least significant bit level by averaging 16 single temperature points.

Amplifier A_5 is the moderately fast Analog Devices 149B, identical to the 149B used as the pulsing amplifier in the analog conductance circuit. The A/D converter is a Teledyne-Philbrick 410910, a 0 to + 10 volt converter which utilizes the dual slope technique to convert in 6 m seconds. For the signals produced by ordinary temperature sensors, a high speed of conversion is not necessary but some means of signal averaging is desirable due to the noise on such signals. The resolution of these signals can be enhanced through use of an integrating converter.

The gated driver is a prototype of the Heath EU-800-JL gated driver (29) identical to the conductance circuit gated driver. The resistors used in the bridge and amplifier are all metal film resistors of 0.1% tolerance or better.

Two thermistors have been used for temperature monitoring in the computerized conductance system. One of these is the 44006 Yellow Springs Instrument Company thermistor with a resistance of 10 K Ω at 25°C. It is encased in a teflon sheath to prevent electrical contact with the solution and to protect the thermistor from harmful solvents. This thermistor has a time constant of 25 seconds in still air and 2.5

seconds in a "well stirred" oil bath. (The time constant is the time required for a thermistor to indicate 63% of a new impressed temperature). The resistance change for the 44006 thermistor is 4%/°C. It was used for most studies in slowly mixing solutions where response speed was not critical, but mechanical strength was.

For very fast applications, such as temperature monitoring in stopped flow kinetic systems (to be discussed in Chapter 8), the fastest possible thermistor probe was desired. The fastest probe which could be obtained proved to be the 41A40 Victory Engineering Corporation bead-in-glass-probe thermistor. This thermistor is extremely fast due to its tiny size (0.02" outside diameter). It has a time constant in still air of 1.4 seconds, in a still oil bath 0.11 seconds, and in still water 0.055 seconds. Its resistance change is 3.9%/°C. Faster thermistors are available from the same company (up to a time constant of 300 μ seconds in still air), but they are not available in a configuration suitable for use as a probe and would be too fragile for use in a liquid flow stream of high velocity.

The response of the temperature monitor, the voltage output of amplifier A_5 , vs. the conductance of the thermistor, is shown in Figure 35. This curve includes the range from 17 to 43 °C for the two thermistors described above. It can be seen that the response is not linear with thermistor conductance, which is proportional to the temperature. This is the result of the design of the monitor analog circuit. The output of this circuit, which is the signal, E_{IN} , which the A/D converter receives, is given by:

$$E_{IN} = \frac{25.55R_T}{12100 + R_T} - 1.062$$

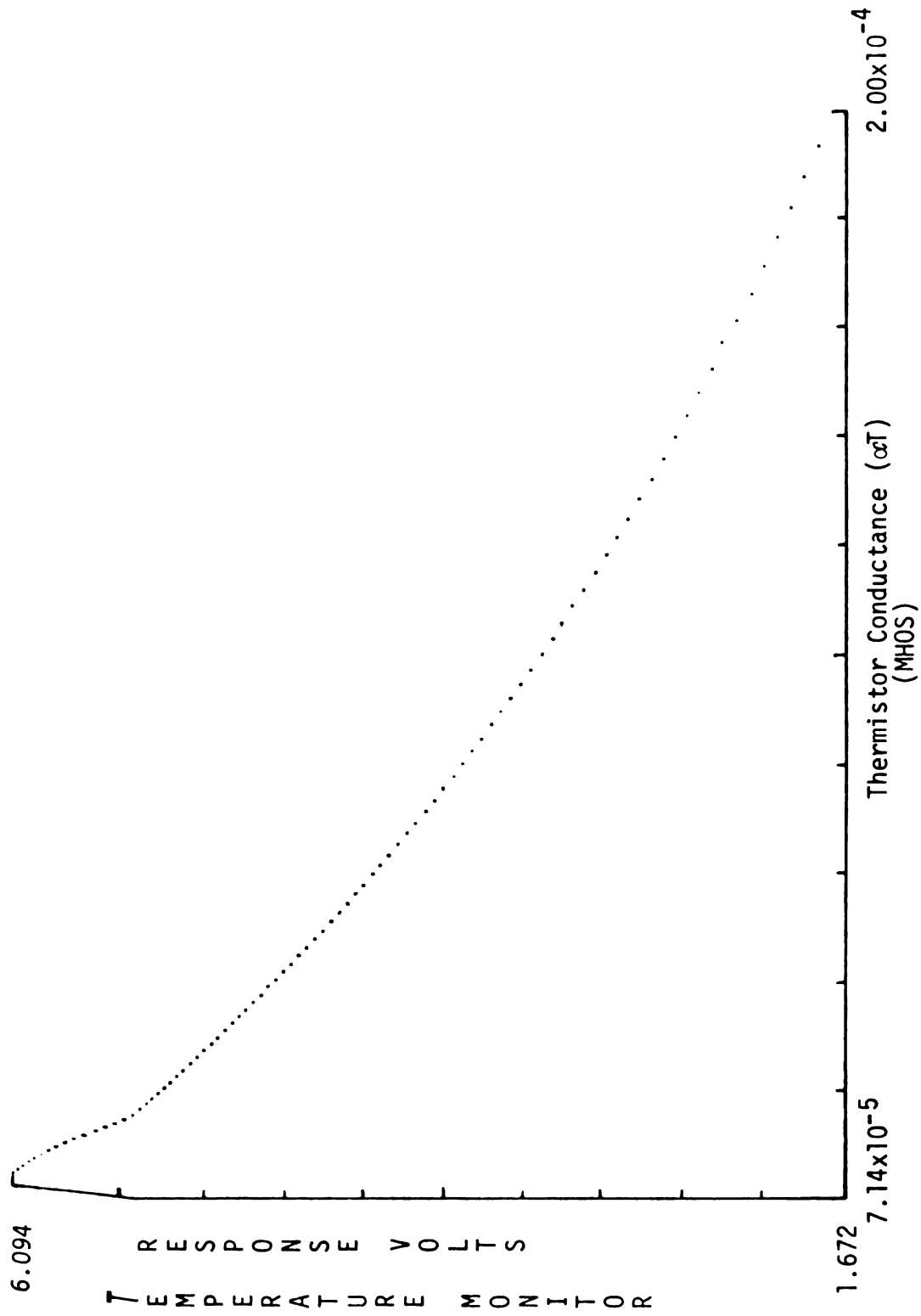


Figure 35. Temperature Monitor Response vs. Thermistor Conductance.

The voltage, E_{IN} , can also be seen to be inversely proportional to temperature. This non-linearity and inverse proportionality have no effect on the implementation of temperature correction in the computerized conductance system. This is because the variation in conductance, as a function of thermistor response (which is the "monitored" function of temperature), is fitted to an equation suitable for describing its behavior. The coefficients of thermistor response are then used in data analysis routines to provide the necessary temperature variation correction of the measured conductance. The details of this correction technique are given below.

B. THE SOFTWARE SET FOR THE DETERMINATION OF THE THERMISTOR RESPONSE COEFFICIENTS OF CONDUCTANCE

In order to perform corrections of measured conductance for changes in temperature in the computerized conductance system, the actual variation of the conductance of a system with temperature variation must be measured in the absence of other effects, such as changes in the ionic character or dielectric properties of the solution. If these other effects should occur the resulting correction parameters will be formed to include them. Implementation of these parameters will eliminate the other effects as well as temperature effects. Since changes in ionic character or dielectric properties are most often the effect which the operator desires to follow, such a "correction" for them would destroy the measurement.

To construct a temperature-conductance profile, the temperature of the chemical system under study is varied over at least the temperature range which would occur during a measurement run. While the

temperature variation is occurring, a TDA routine such as CBTSLS, described previously, is used to monitor both conductance and temperature. The raw data from such a run may be plotted as conductance vs. thermistor response (E_{TN}) by the CCLTLF program which will not be described here. Such raw data is shown in Figure 36 a, b, and c for three systems in dimethyl sulfoxide (DMSO); $4 \times 10^{-4}M$ lumino1 (36a), $10^{-3}M$ potassium tertiary butoxide (36b), and the products of the reaction between these species (36c) which will be discussed in Chapter 8. These curves cover a temperature range of 5.4 °C, from 29.9 to 24.5 °C. They have been included in this manuscript because they demonstrate several interesting qualitative aspects of the work done with temperature-conductance profiles which will be discussed later in this chapter.

It can be seen that the temperature change which occurred during the runs in which the data of Figure 36 were obtained was, itself, non-linear. This is evidenced by the accumulation of an increased density of data points near the 24.5°C region of the curve (lower right). The cause of this effect is the way in which the data was generated, by first heating the solutions in the conductivity cell and then plunging the cell into a constant temperature bath at 24.5°C when the data acquisition began. The cooling was, of course, much faster in the early stages of the run. In general, it is common for temperature to change non-uniformly in an experiment. This presents an interesting problem in curve fitting which is the method employed to construct temperature correction parameters for the conductance of a particular system. If there are more points in one section of a curve than another, the method of least squares will effectively weight that portion of the curve most heavily at the expense of the rest of the curve (unless the

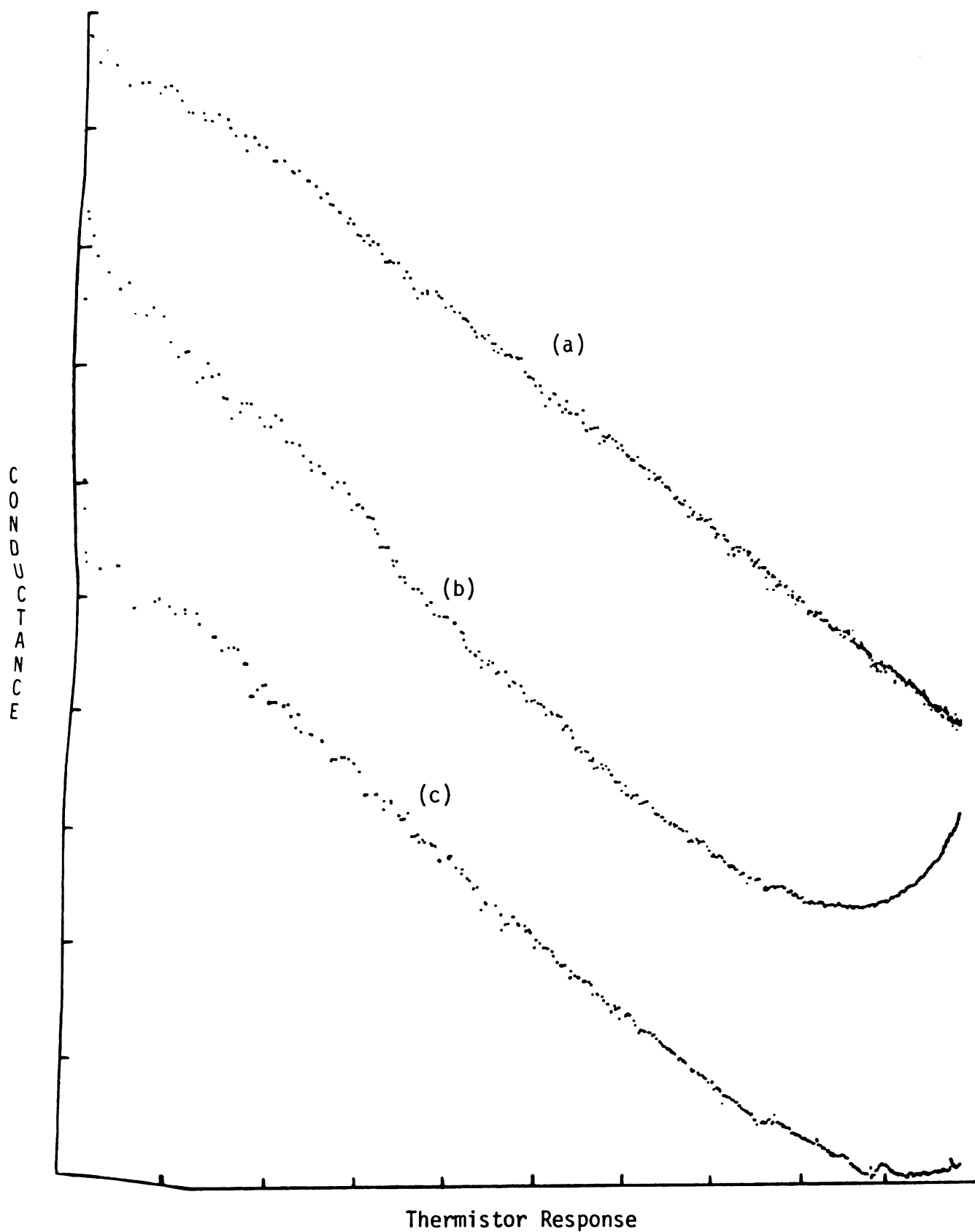


Figure 36. Termistor Response-Conductance Profiles for (a) Luminol, (b) Potassium Tertiary Butoxide, (c) Products of Reaction of (a) and (b) all in DMSO.

curve is perfectly linear).

There are two possible solutions to the problem. One is to program the computer to store measured temperature-conductance data only when the temperature is at a certain value, set up by the initial measurement and a running increment. This method leaves some doubt as to the length of a particular run, what increment to set up, how many points to take, etc. It has the advantage of automatically constructing a data set with points linear in thermistor response.

The other approach was chosen for the computerized conductance system. It involves arranging the raw data set in monotonically decreasing order with respect to thermistor response. Intervals within the array were created by software. Each interval contains a single thermistor response-conductance point which would be the average of all measured points which fell within that interval. The program which performs this "array arranging", CBTALR, is flowcharted in Figure 37 and is listed in the Appendix.

(It should be noted, to avoid confusion for the reader who is also referring to the CBTALR Appendix listing, that the flowchart in Figure 37 is considerably simplified. Many of the operations of CBTALR which are explained in FORTRAN terms in the flowchart are actually manipulations which are done in assembly language in CBTALR for reasons of speed and necessity. These include magnitude comparisons, data switches, array addressing, averaging of thermistor response measurements, and so forth).

CBTALR begins by requesting the first block on the DECTAPE where the data from the TDA routine was written, reads the file, and sets up the necessary software pointers. The raw data array must consist of a

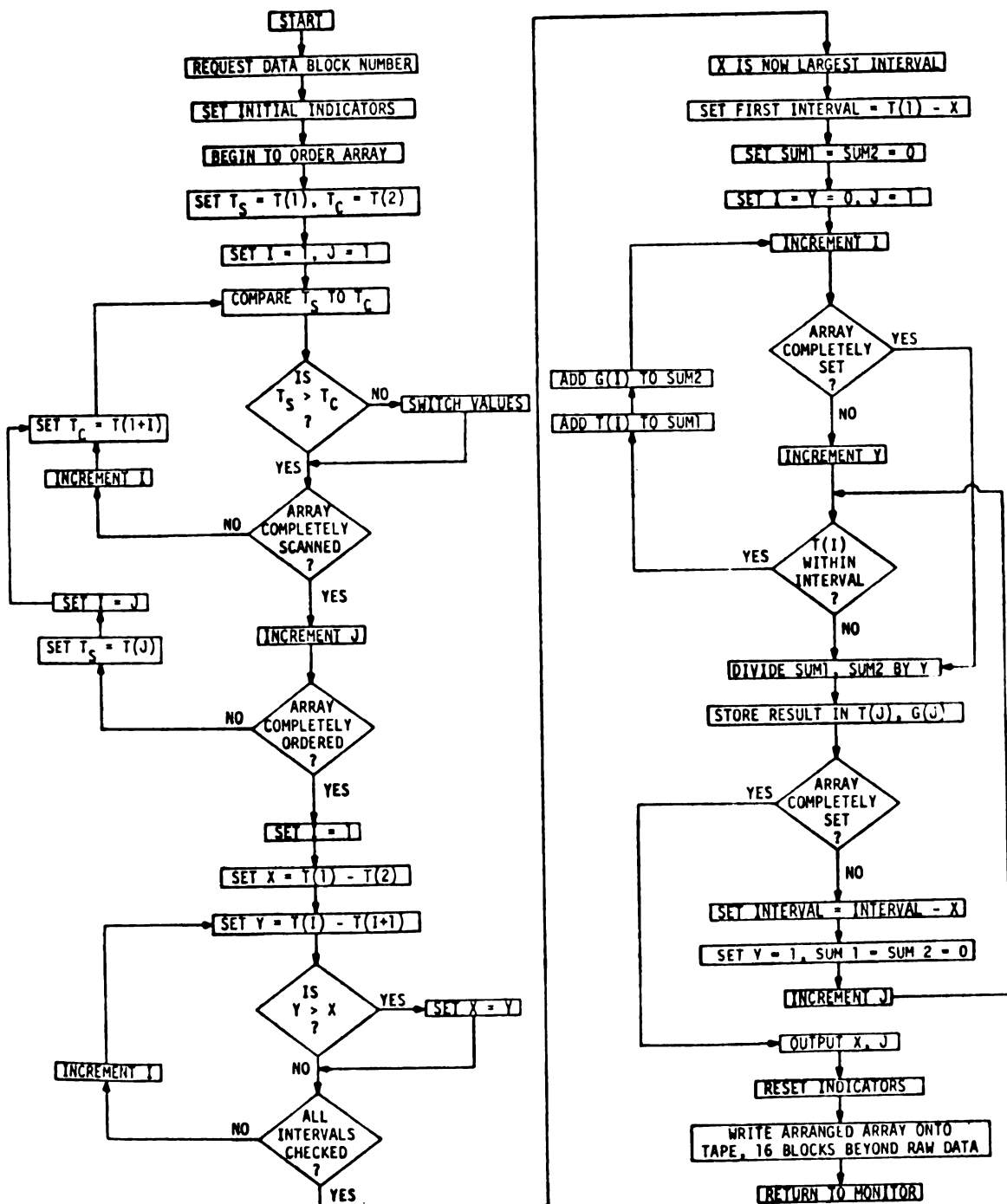


Figure 37. CBTALR, Array Arranger, Program Flowchart. (Simplified)

won

nas

con

(sc

won

va

men

If

th

po

th

va

co

th

co

ar

th

in

th

an

wh

an

tn

cu

th

12 bit conductance word, the 12 bit division remainder, the parameter word, and the 12 bit, averaged thermistor response word. After CBTALR has completed the array arranging process, the data in the array will consist of the 3-word FORTRAN floating point values of the conductance (scale change corrected) and the 12 bit, averaged thermistor response words. The array arranger begins ordering the array in decreasing value of thermistor response by comparing the first temperature measurement ($T(1)$ in Figure 37) with all other temperature elements in the array. If a thermistor response is encountered which is larger than $T(1)$, the two measurements are switched in location along with their corresponding conductance values. In this way, at the end of the first pass through the array, the largest thermistor response is in $T(1)$; the other values are in indeterminate order. The second pass through the array compares all remaining values to $T(2)$ so that at the end of this pass the second largest thermistor response is in $T(2)$ and its corresponding conductance value is in $G(2)$. The process is repeated until the entire array is ordered in decreasing thermistor response.

The array arranger next begins to scan the array to determine what the largest interval between thermistor response points (X in Figure 37) in the data set is. Once it has determined this interval it sets up the first boundary in which to average the data by starting at $T(1)$ and going to the value of T given by $T(1) - X$. It zeros SUM1 and SUM2 which will contain the running summations of thermistor response data and conductance data respectively, within a given interval. CBTALR then checks each thermistor response word to see if it is within the current interval. It continues to sum these T and G values until a thermistor response value is encountered which is outside this interval.

At this point the sums are divided by the number of measurements totaled (Y in Figure 37). The averages are stored back in the array beginning at the location which had corresponded to the first element and continuing to as many locations as needed (given by T(J) and G(J) in Figure 37). CBTALR then moves the boundary downward by X, resets SUM1 and SUM 2 to zero, and repeats the process beginning with the first point to fall outside the previous interval. When the arranging is complete, there are J points left in the array. Only one point may exist per interval, thus eliminating the apparent "weighting" of points toward one region of the curve. Some points will, of course, be more precise than others. The computer outputs the chosen interval and number of final points in the array, and the new array is stored on tape 16 blocks beyond the raw data array. Arrangement of a 500 point array requires approximately 145 seconds.

The effect of CBTALR on the data of Figure 36 is shown in Figure 38 a, b, and c. The shape of the curves is unaltered. Some of the noise has been reduced by averaging of discrete points. The data are properly suited for fitting by the least squares technique.

The data of Figure 38 were plotted by CCLALF. This is the second analysis program in the temperature-conductance coefficient determining routines which use the array arranger. A series of programs was required due to limited core space in the PDP-8/I. CCLALF is flowcharted in Figure 39 and listed in the Appendix. CCLALF reads the arranged data from tape, outputs it on the line printer if the operator desires, and plots the data on the X-Y plotter and/or the display scope. Plotting options include plotting axes or the data set. The operator may request that any continuous group of points within the data set be plotted.

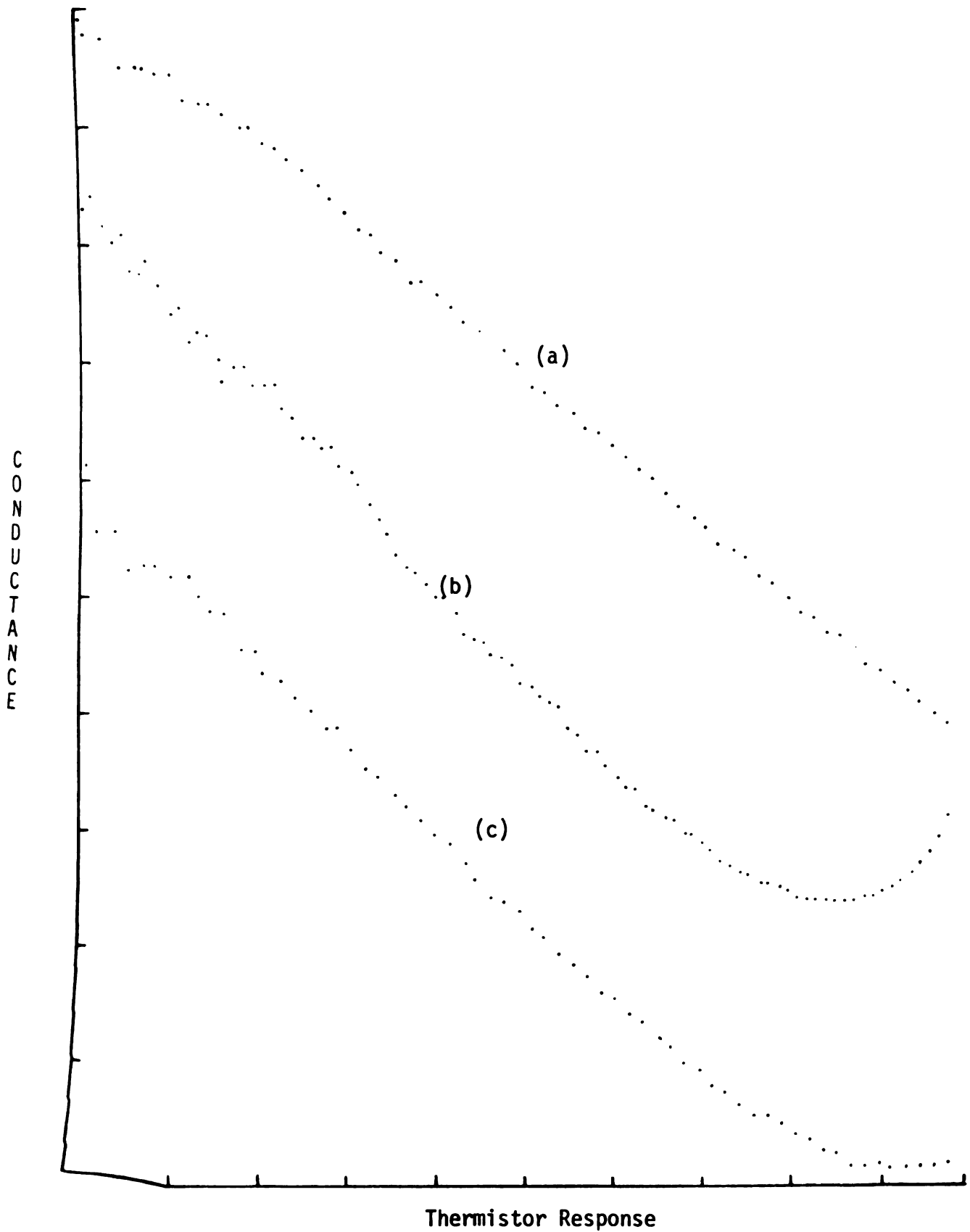


Figure 38. Array-Arranged Data From Figure (6-3) (a) Luminol, (b) Potassium Tertiary Butoxide, (c) Products of Reaction of (a) and (b) all in DMSO.

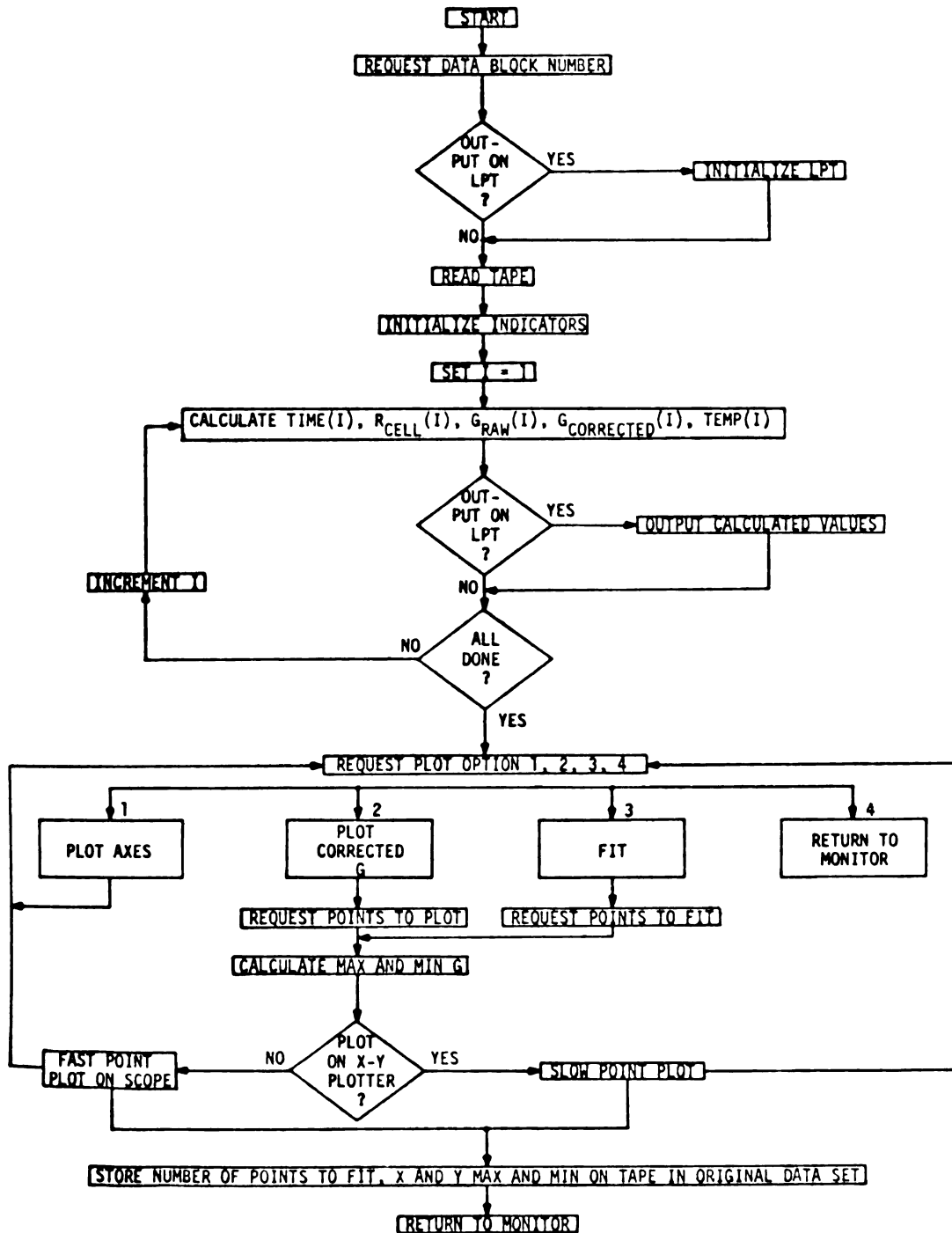


Figure 39. CCLALF Program Flowchart. (Simplified)

In plotting, the program searches the array for the maximum and minimum conductance and thermistor response for that group of points and uses this information to automatically scale the data for output to the plotter and scope. If the operator does not require hard copy of the data, he may fast point-plot it in a second or two on the display scope. Point-plotting on the X-Y plotter requires as much as 20 minutes for 500 points.

When the operator selects the FIT option, he may fit any continuous block of points within the data set. The maximum and minimum conductance and temperature are calculated for the selected group of points and they are plotted. The program then stores, in the indication portion of the data array, the values of the first and last points to be fitted and the calculated plotter scaling parameters. The entire array is retransferred to tape with these new indicators included.

The operator may, at this time, select any of five fitting programs which generate least squares fits to functions of the following forms:

$$G = aT + b$$

$$G = aT + bT^{1/2} + c$$

$$G = aT^2 + bT + c$$

$$G = aT^3 + bT^2 + cT + d$$

$$G = aT^5 + bT^4 + cT^3 + dT^2 + eT + f$$

The general form of these fitting programs appears in the flow-chart of Figure 40. The cubic fitting program, CDTALC, is listed in the Appendix. The chosen fitting program reads the array written onto tape by CBTALR and CCLALF, initializes software pointers, and proceeds

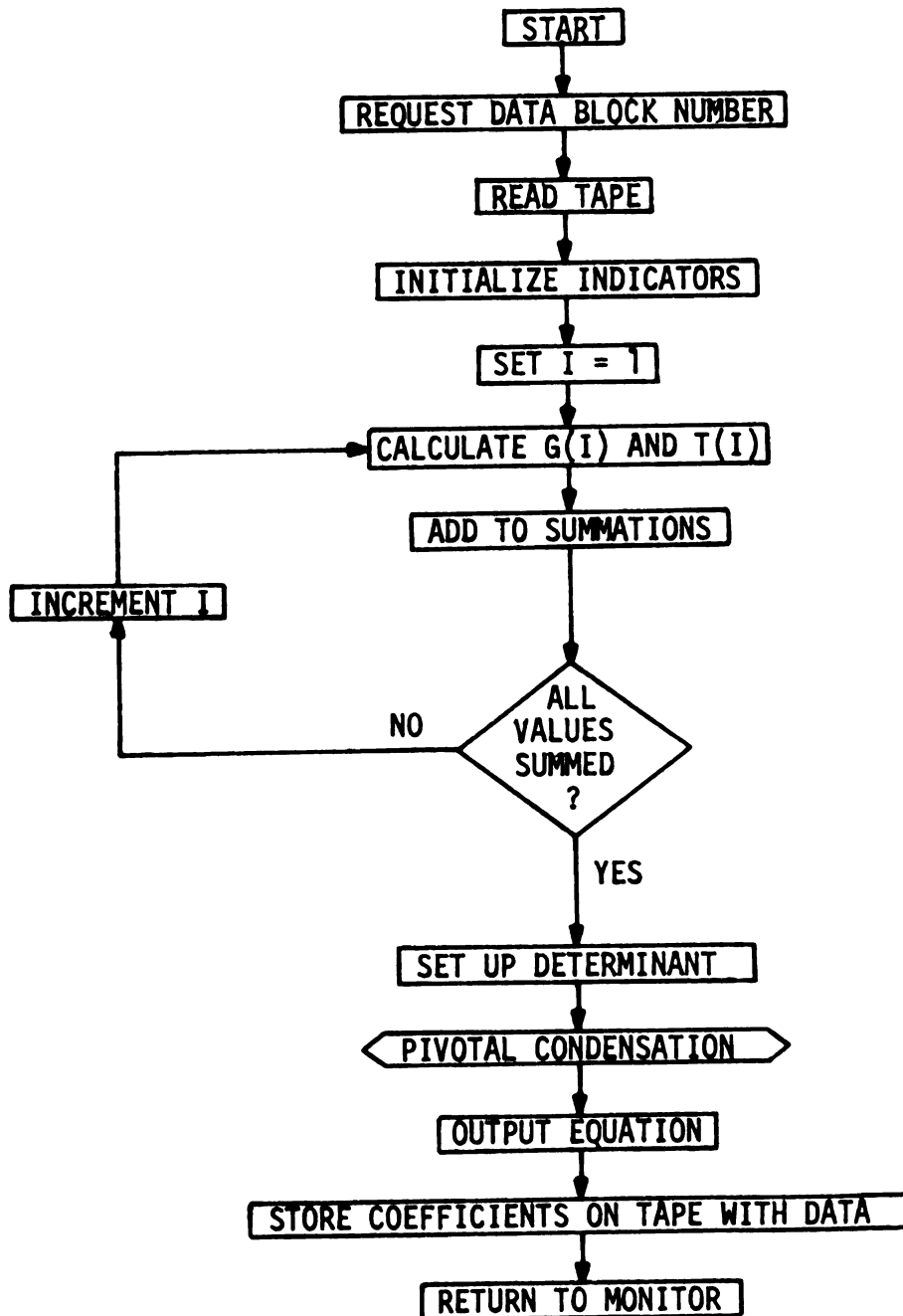


Figure 40. Curve Fitting Program Flowchart.

to cal
partic
the pr
a, b,
by a
funct
from
the d
tion
of th
the c
A 100
prin
from
inte
char
coet
sca
num
and
equ
to
fit
It
If
the

to calculate the summations required for the least squares fit to the particular order of equation chosen. Once the summations are complete, the program sets up the determinant to be solved for the coefficients a , b , c , etc. of the chosen fitting equation. The determinant is solved by a pivotal condensation (47), to help reduce roundoff errors, for all functional forms except the linear function which is solved directly from the least squares formulae for slope (a) and intercept (b). Once the determinant is solved, the equation giving conductance as a function of thermistor response is printed on the teletype. The coefficients of thermistor response are stored on tape within the data array to enable the operator to obtain comparison of the real data and the fitted curve. A 100 point cubic fit requires about 9 seconds of PDP-8 run time.

The fitted data, real data, and residuals may be listed on the line printer by CELTLR (not included in the Appendix). The fitted curve from any function may be plotted by CFPTLR. Any function with only integer powers of T may also be plotted by the faster CFPTLI, flow-charted in Figure 41 and listed in the Appendix. CFPTLI reads the T - G coefficients determined by the fitting routine and sets up the plotter scaling parameters determined by CCLALF. It calculates one five-hundredth of the measured thermistor response range for that data set and plots the first point as the conductance calculated from the fitted equation vs. the smallest thermistor response measured. It then proceeds to plot the entire measured thermistor response range according to the fitted equation by incrementing T by $1/500$ for each successive point. It plots straight lines between points, producing a continuous curve. If the plot of raw data generated by CCLALF or CCLTLF has been saved on the scope or X-Y plotter, it will, by plotting the fitted curve on the

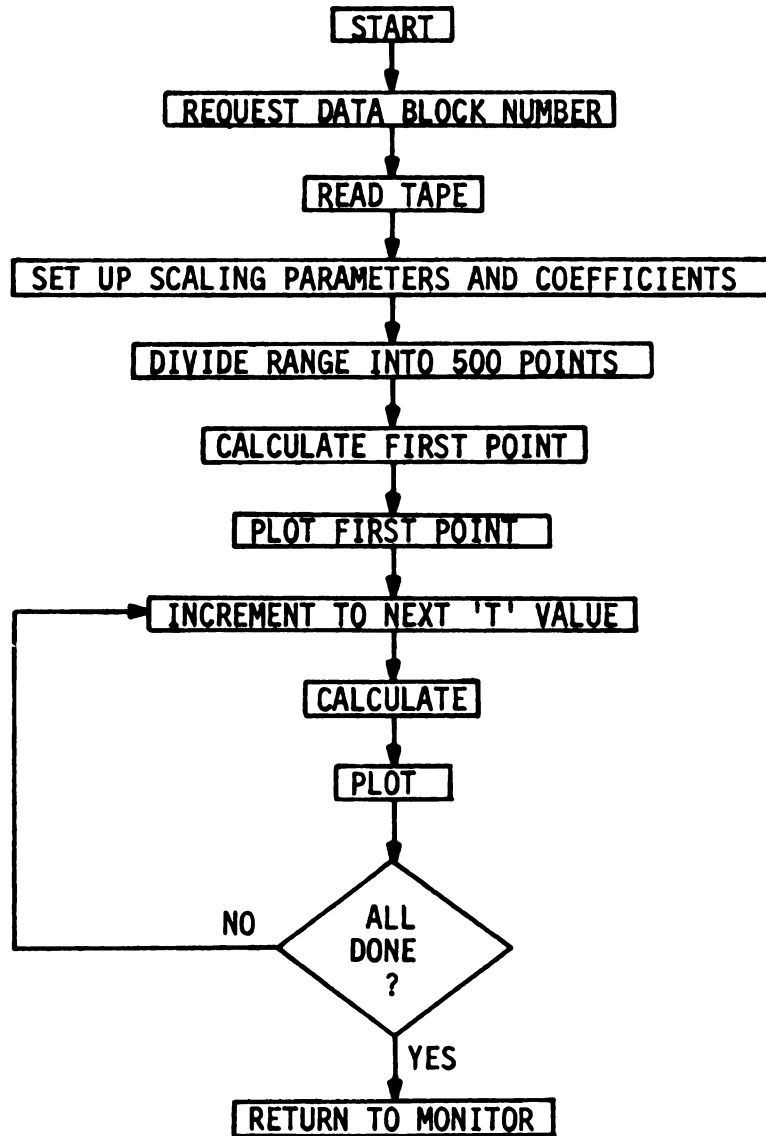


Figure 41. CFPTLI Program Flowchart.

same scale on top of the raw data, allow the user to qualitatively examine the fit. When the entire curve is plotted, the program terminates and returns computer control to the Keyboard Monitor.

It should be noted here that there is an entire series of T-G data analysis routines and fitting programs which run without using the array arranger. These routines were written for the computerized conductance system prior to the implementation of the array arranger. They are essentially analogs of the programs discussed above. They are still useful where temperature variation can be relatively linear although they are seldom used due to the simplicity and speed with which the array arranged data can be manipulated.

C. CONDUCTANCE DATA ENHANCEMENT THROUGH TEMPERATURE VARIATION CORRECTION

Figure 42 shows a raw data set with its corresponding fitted curve as discussed above. The raw data displayed in Figure 42 is the data in the form in which it was acquired by CBTSLs, before array arranging. The fitted curve was calculated for the arranged data. In this case the data was nearly linear, but sufficiently curved so that all terms in the cubic fitting equation were of nearly equal size when the magnitude of T is considered. This particular fit was used to correct the data of Figure 43 for temperature variation. This run was performed to demonstrate the power of this temperature correction technique. The TDA run involved varying the temperature of a dilute sulfuric acid solution 15 °C while no bulk ionic change occurred. Thus, the only conductance change (about $2 \times 10^{-3} \Omega^{-1}$) which takes place is that due to the temperature change of the system. The data of Figure 43 are

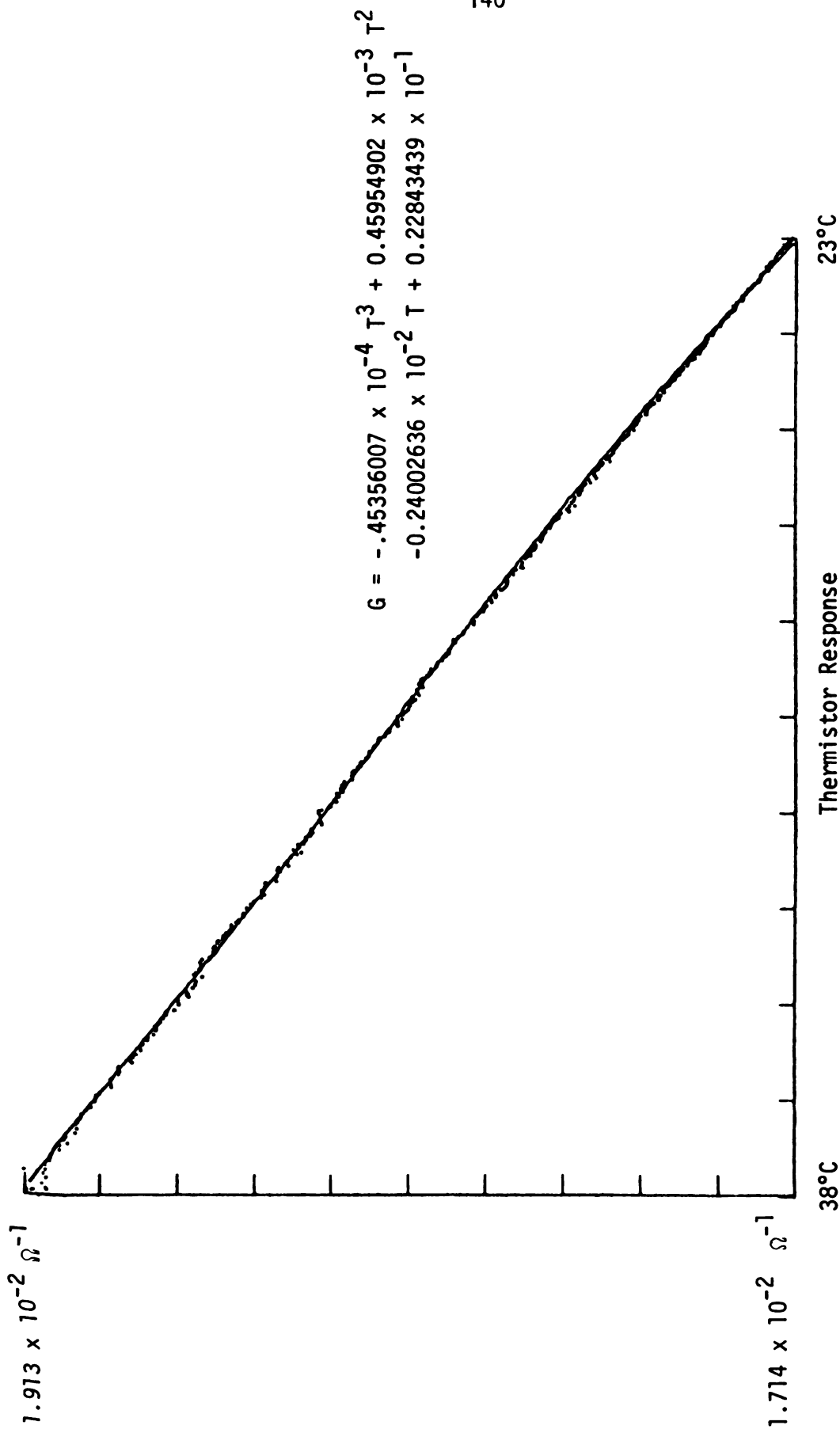


Figure 42. Temperature - Conductance Profile and Cubic Fit for a 15°C Temperature Change for a Predissolved Sulfuric Acid - Water System (38 - 23°C). (11974-3)

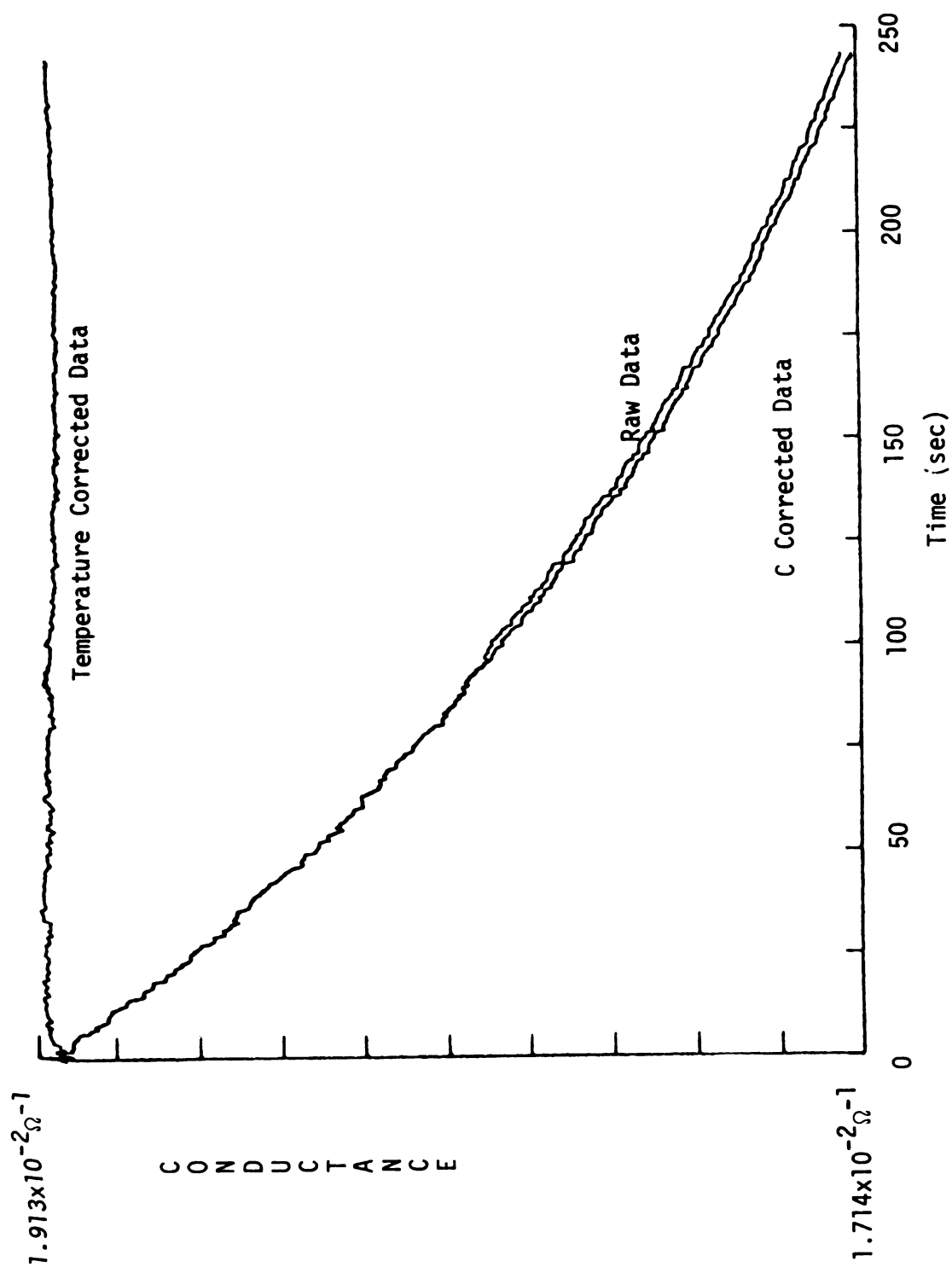


Figure 43. Conductance - Time Profile for Cooling of a Sulfuric Acid - Water System 15°C with no Bulk Ionic Change (38-23°C) (11974-2)

corrected for temperature change by inputting the thermistor response coefficients from the fitted equation of Figure 42 to the data analysis routine used to construct the curves of Figure 43. Notice that the effects of temperature (except for the first 9 points out of 500 which were rather random and not well fitted) have been virtually eliminated, even over a 15°C change. The variation of conductance data has been reduced from $1.99 \times 10^{-3} \Omega^{-1}$ (10.9% of the signal) to $6.6 \times 10^{-5} \Omega^{-1}$ (0.358% of the signal). The noise on the signal is on the order of $2 \times 10^{-5} \Omega^{-1}$ which indicates that the temperature correction for this system was good to about 0.15% over the 15°C temperature change.

Fitted curves have been consistently good to 0.1 - 0.01% over as much as a 50°C temperature change. Temperature changes of this magnitude would, of course, not be encountered in normal operation but the shapes of some of these curves have been interesting in themselves. An attempt was made to fit the curves of Figures 36 and 38 b and c with third, fifth, and seventh order equations. The third order equation failed to fit even approximately the rather sharp curvature of the lower end of these curves or the smooth curve in the center of the plot. The fifth order equation fit the data properly except at the end of the sharp curve at temperatures around 24.5°C. The seventh order fitting routine failed altogether. This was apparently because the summations became so large (up to T^{14}) that significant round-off error was introduced into the determinant coefficients due to the limited precision of the PDP-8 FORTRAN word size. It is suspected that the fifth order equation may also be somewhat affected by round-off error since it had been expected to fit Figures 36 and 38 b respectively easily. Nevertheless, if the entire temperature range represented by these curves was to be used in data

analysis from an actual experiment, the T-G data could be fit in two parts, to two separate equations with no difficulty. The data analysis would also be done in two parts.

The conductance change of a chemical system in which a bulk ionic change is occurring along with a temperature change is shown in Figure 44. The experiment consisted of injection of concentrated sulfuric acid into a solution of dilute sulfuric acid which was being continuously stirred in a conductance cell suspended in a constant temperature bath. A very sharp rise in conductance occurs at the instant sulfuric acid is injected into the solution, due to autoionization of the acid. This dissociation is well known to be exothermic so that the overall curve obtained (see raw data, Figure 44) reflects not only the increase in bulk ionic character but also the conductance change due to an increase in temperature. A temperature profile and cubic fit were performed on the resulting solution and the thermistor response coefficients input to the data analysis program which produced Figure 44. It can be seen that the conductance change due to heating of the solution has been eliminated from the temperature corrected data. The result is a truer picture of the conductance change due only to the change in ionic character of the system.

The author wishes to present one other example of temperature correction on a real system. The preliminary kinetic studies of the liminol reaction, which will be presented in Chapter 8, produced some interesting temperature curves. These curves were encountered during the search for the most suitable solvent for these studies. Figure 45 shows the temperature changes which occurred in the observation cell of the stopped flow apparatus used in these studies when dimethyl sulfoxide (DMSO) and ethanol (EtOH) were mixed, both with and without reactants

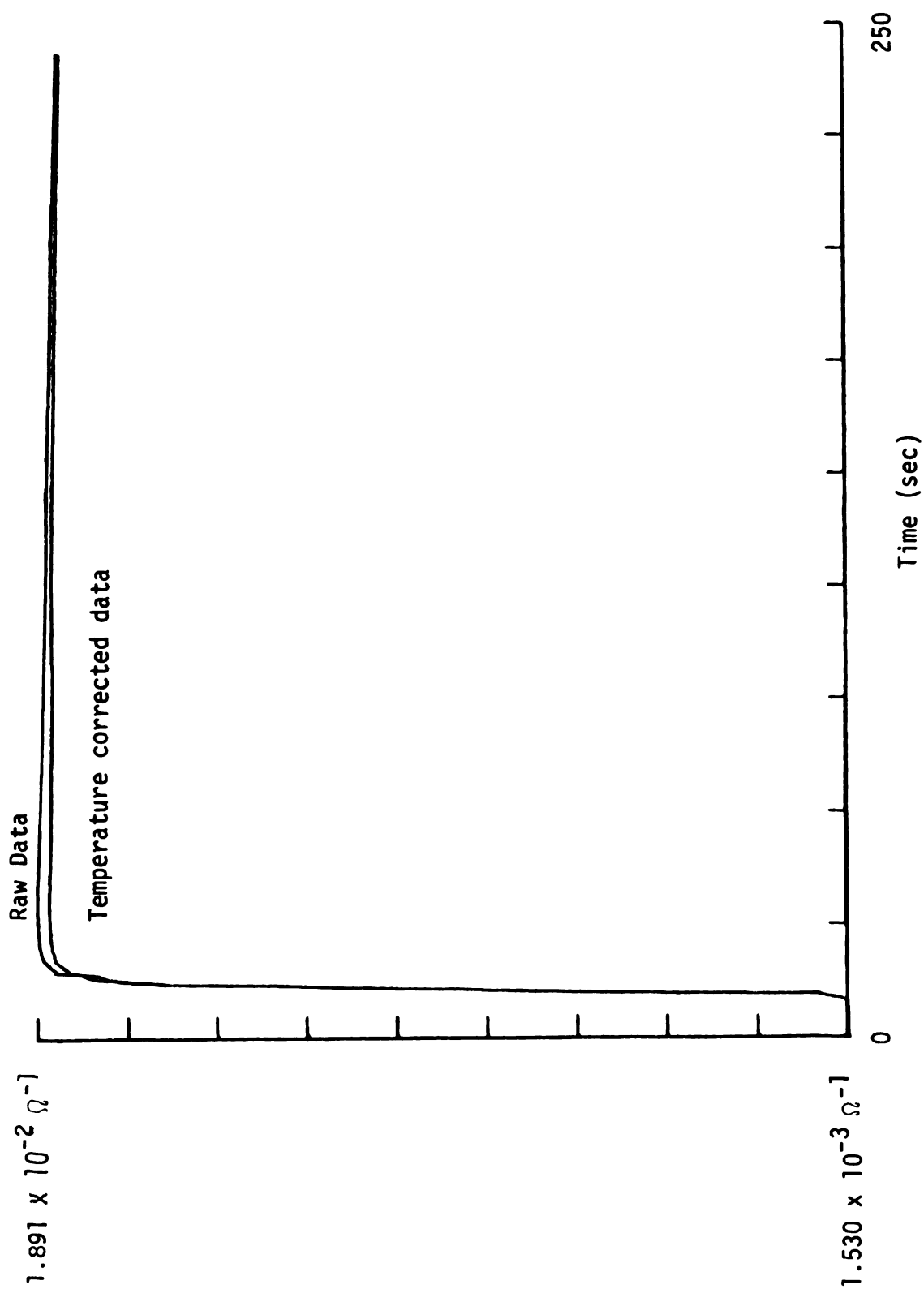


Figure 44. Addition of Concentrated Sulfuric Acid to Dilute Sulfuric Acid to Dilute Sulfuric Acid, Conductance Profile. (100973-2 Cubic)

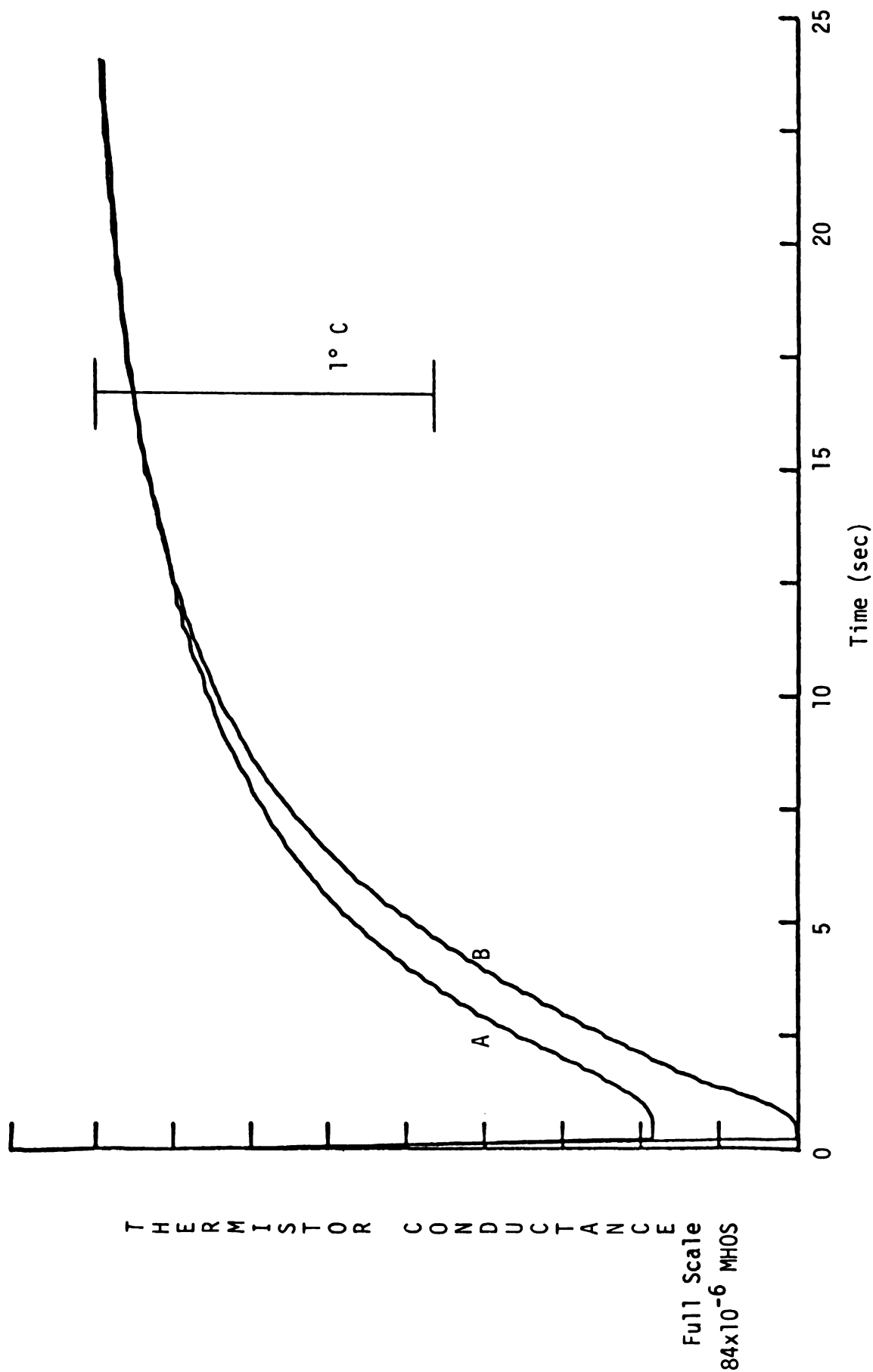


Figure 45. A = Temperature Change When DMSO and EtOH are Mixed in Stopped-flow. B = Temperature change when 0.5 M KOH in EtOH and 0.05 Lumino1 in DMSO are Mixed in Stopped Flow. Cell Thermostated at 23.5°C

pre

ins

des

ce?

ci

be

wh

te

ca

an

D

t

w

-

s

present. The conductance monitor in the computerized conductance instrument was used to follow the conductance of the fast thermistor described earlier, which was embedded in the wall of the observation cell extending into the flow stream. The cell was thermostated with circulating water from a constant temperature bath at 23.5°C. It can be seen (curve A) that the conductance of the thermistor drops significantly when these solvents are mixed, corresponding to a decrease in cell temperature due to a positive enthalpy of mixing. The temperature change can be seen to be about 1.5°C. The reaction occurring between luminol and KOH is shown by curve B to also be endothermic, causing an additional 0.5°C temperature decrease.

A temperature conductance profile and cubic fit were performed on the products of the reaction. The temperature response coefficients were utilized in the data analysis routine which produced Figure 46. This figure corresponds to a stopped flow run of the luminol-KOH reaction monitored by the conductance change associated with it. The raw data does not reflect the true change of conductance due to the reaction because of the attendant cooling of the system due to mixing and reaction enthalpy changes. The temperature corrected data can be seen to provide the necessary correction in conductance change at the beginning of the reaction, where the temperature effects most strongly influence the measured signal. The two curves approach each other at later stages of the reaction where thermal equilibrium becomes established again.

The solvent system investigated in these figures was used for some of the luminol studies discussed in Chapter 8. However it should be noted that although the conductance curves could be corrected for the

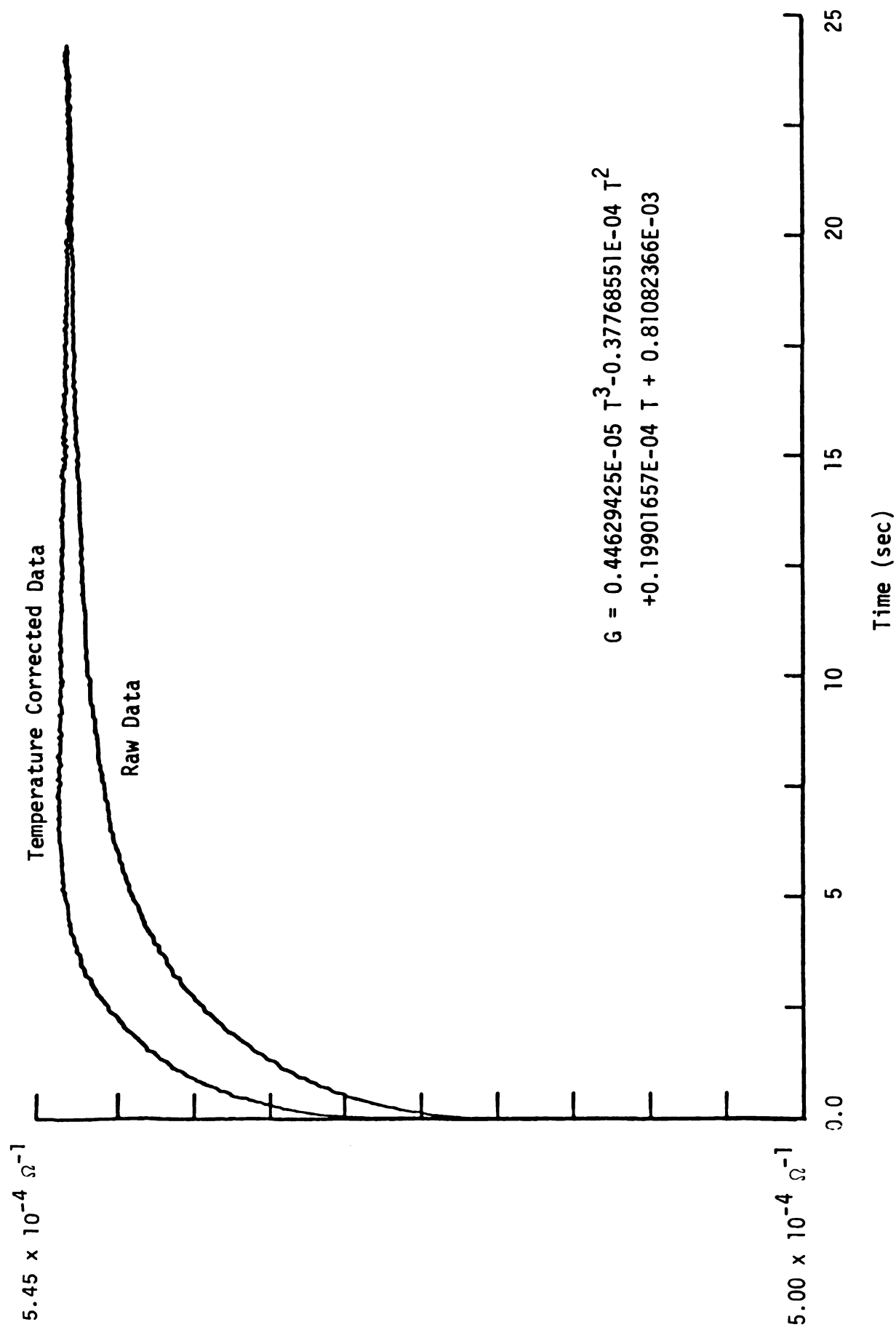


Figure 46. Stopped flow Study of Lumino1 System $5.00 \times 10^{-2} \text{M}$ Lumino1 in DMSO $5.00 \times 10^{-2} \text{M}$ KOH in EtOH Cell Thermostated at 23.5°C . (20274-5)

conductance change due to cooling, little could be done to correct rate constants calculated from the data obtained during these temperature changes. Nevertheless, the power of the conductance correction for temperature changes by the technique presented here can be clearly seen.

D. SOME COMMENTS ON THE SHAPE OF CONDUCTANCE-TEMPERATURE PROFILES

At the time the initial temperature-conductance measurements were made using the computerized conductance system, it was assumed that the curves obtained would be approximately linear over the few degrees of temperature change investigated. Most of the curvature expected was to be that curving due to the slightly non-linear response of the temperature monitor. It was thought that the real temperature coefficients of conductance (approximately proportional to (thermistor response)⁻¹) would always be positive, even where they were not constant. It can be seen from the curves of Figure 36 b and c (and others which could have been presented here) that neither of these expectations proved to be totally correct. In Figure 36 b the temperature coefficient of conductance actually changed sign in the area around 25°C. This behavior was found to be by no means unique. Curves which were approximately sinusoidal were obtained for certain concentrations of sulfuric acid. Curves with plateaus were observed for solutions of $\text{NH}_3 \text{NH}_4^+$ buffer at pH 10 when Ca^{++} was present. Other curves measured were nearly linear or curved slightly upward or downward.

Franklin (48) was one of the earliest workers to discover chemical systems which possessed a negative temperature coefficient of conductance.

These included various solutions of an iodide salt in liquid sulfur dioxide. For tetramethylammonium iodide, he discovered a positive temperature coefficient at high and low concentrations and a negative one at intermediate concentrations. Armitage and French (49) also reported negative temperature coefficients of conductance for cupric perchlorate dihydrate in ethyl methyl ketone and in n-propyl ketone over certain ranges of concentration. They believed that the occurrence of this type of phenomena might be more general than had previously been assumed.

Some explanation of these effects and the effects encountered with computerized conductance system measurements might be found in the studies done by Falkenhagen (50). In an attempt to analyze the variation of conductance with temperature for electrolytes, he differentiated the Onsager conductance equation with respect to temperature. He obtained an expression for the equivalent conductance which is the difference between two terms. The first term increases with temperature owing to a decrease in viscosity. The second term, which contains the square root of concentration and the reciprocal of the solvent dielectric constant, also increases with temperature since dielectric constants decrease with increased temperature. Falkenhagen suggested that the measured equivalent conductance will pass through a maximum at a certain temperature. This maximum will be lower for solvents with lower dielectric constants and for higher solute concentrations. For a particular concentration these two terms may balance each other; for higher concentrations, then, the second term will predominate and the temperature coefficient of conductance will become negative. The theory does predict a maximum but no minimum. However, Armitage and French (49)

have pointed out that the presence of the solute itself will offset the dielectric constant of the system. It seems reasonable, therefore, to assume that a point may be reached in a given solution when the effect of an increase in system dielectric constant, due to the presence of solute, outweighs the effect of increased concentration from Falkenhagen's second term. The equivalent conductance might again increase with increasing temperature, causing a minimum in the curve. It is possible that such effects are being observed in the case of the solutes in DMSO of Figures 36 and 38.

A qualitative examination of the curves in Figures 36 and 38 seems to indicate that the T-G curve for the products of the reaction between luminol and potassium tertiary butoxide is the sum of the curves for the reactants. This would appear to be a reasonable assumption, since conductances are approximately additive in dilute solutions, provided that the ionic character of the products in the reaction is similar to that of the reactants. It was previously mentioned that attempts to fit these curves were not entirely successful. However from the equations obtained, the predominating coefficients (which corresponded to the coefficients of the higher order terms) for the two reactants do roughly add to produce the coefficients of the fitting equation for the product. In any event, these results lend some credence to the method of performing the T-G profile run and fit on the products of the reaction in order to compensate for temperature variations which occur during the reaction. In practice, no other approach is possible short of developing correction software which employs differential fitting equations which are, in themselves, functions of the changing ionic character which results from a reaction in progress.

Finally, as a result of the preliminary work presented here, the author is able to state that the T-G profiles appear to be both qualitatively and quantitatively useful. Variation in the fitting functions occurs with both changes in concentration and in the chemical systems investigated. It appears that a significant amount of work could still be done in this area for further elucidation of the mechanism by which these profiles are formed as well as their applicability as an analytical tool. It is possible that the fitting functions of T-G profiles will be shown to be sufficiently diverse to be used for identification of the concentration of solute, the particular solute, and the particular solvent in a chemical system.

CHAPTER 7
APPLICATION OF THE COMPUTERIZED CONDUCTANCE SYSTEM
TO TITRATION MONITORING AND ANALYSIS

A. SPECIFIC SOFTWARE AND HARDWARE FOR TITRATION EXPERIMENTS

One of the most popular uses of conductance as a detector for chemical processes has been the determination of titration endpoints. This is the result of titrations, in themselves, being specific chemical techniques where the analyte and titrant are engaged in a specific chemical reaction. If an interferent is present, the endpoint will usually be uncertain regardless of the detection method since the chemistry involved will no longer be specific. Thus, equally pertinent results are obtained for detectors which are monitoring a particular change in the system (such as the change in the absorption at a particular wavelength) as well as detectors which examine the overall bulk properties of the solution, assuming both methods can detect the change. Often, a general, bulk property detection technique, such as conductance, is much more suitable as a detector for a wider variety of analysis-by-titration problems.

Endpoint detection in titrations was the first chemical problem investigated with the computerized conductance system. There are, at the present time, three programs in the system software set specifically designed or modified for use with titrations. Two of these are analysis programs discussed in Chapter 7B. The other program is a data acquisition program, CBTMLT. The program CBTMLT is a modification of the standard acquisition program, CBTSLS, discussed in Chapter 4. Program CBTMLT contains instructions for control of

an E298 Metrohm Motor Burette which has been interfaced to the computer through the peripheral control facility in the computerized conductance system.

During the titration CBTMLT will cause the computer to measure the conductance, measure the thermistor response if the operator desires, and test to see if the conductance system is on scale. If it is not, the instrument will be reset and the measurement for that titrant volume retaken. (This can be done in titrations where measurement timing is not critical). When an on-scale measurement has been made, the computer will immediately signal the titrator to add the next volume of titrant. The computer will then wait for the clock to signal the time for the next data acquisition. During this waiting period, the cell solution will be continuously stirred to assure mixing by the time the next measurement is made. When the computer has completed the titration, data is transferred to tape in the usual manner.

A schematic diagram of the burette interface appears in Figure 47. A DS-IOP command from the computer is gated through 1/2 of a 75451 driver, pulled up to +5 volts, to trigger a 1.5 second monostable. When the monostable is triggered, $\bar{Q}$ goes low, turning "on" the other half of the 75451 driver. This causes the relay to change state, switching the 120 volts AC to the motor driver of the burette. The 1.5 second pulse causes the burette to add 0.2 ml of titrant to the cell when it is in the 1/100 volume increment mode. It will exactly pipette 1/100 of its total volume ($1/100 \times 20 \text{ ml} = 0.2 \text{ ml}$) for each computer command signal. The titrator interface may be plugged directly into the conductance instrument module which has provisions

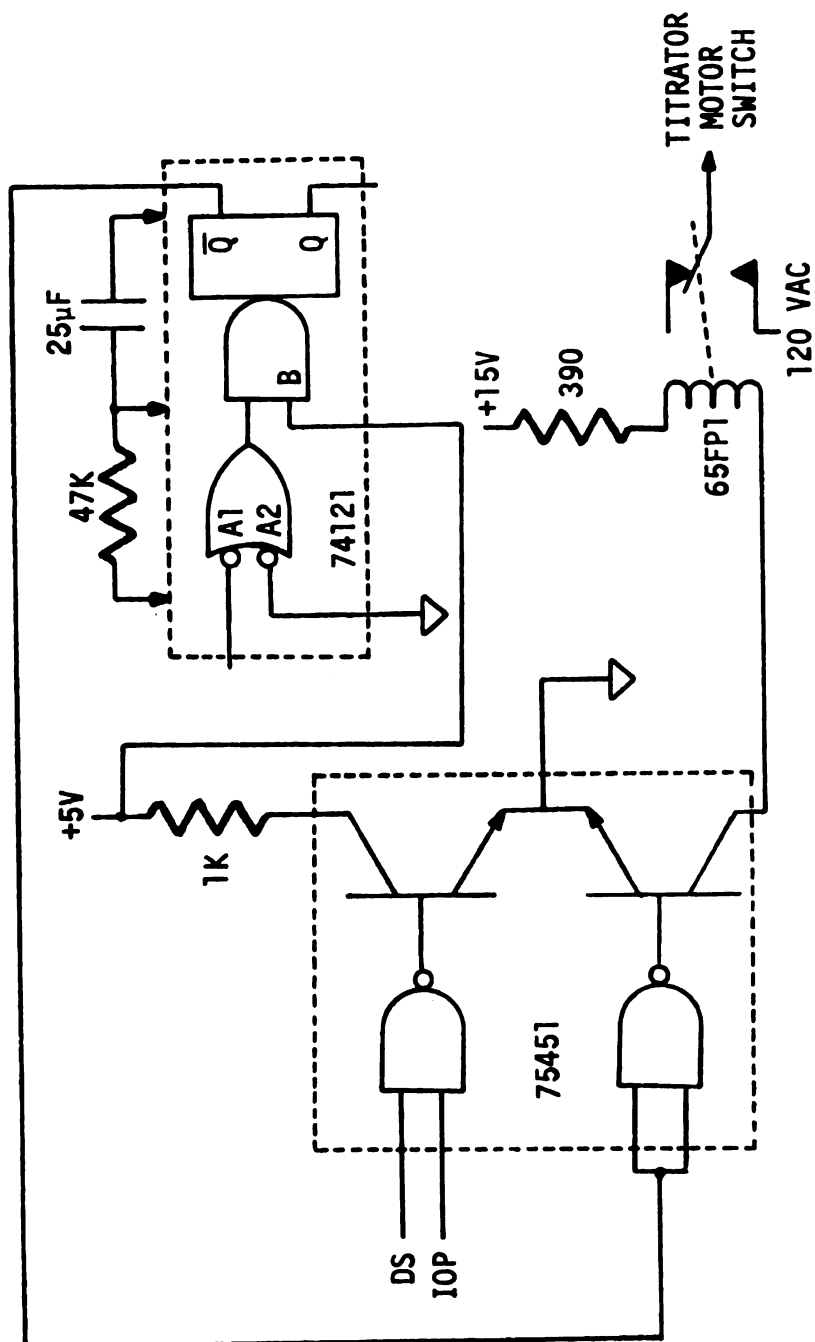


Figure 47. Automatic Burette Interface.

for supplying DS-IOP signals (DS 36, IOP, 1, 2, and 4) to external devices used with the computerized conductance system.

The cell which was used for most of the titrations investigated with the computerized conductance system was constructed from a 100 ml three-neck, round-bottom flask with two platinum wire electrodes mounted in the side, facing each other end to end. There are no platinum discs on the ends of the wires and the wires themselves are not platinized. The side of the flask was indented above the electrodes to provide a "shelf" which shields the electrodes from waves formed on the surface of the solution by the action of stirring. Stirring is accomplished by a 3/4" glass propeller placed in the center of the cell through the central opening of the flask and connected to an overhead stirrer. A glass bushing is provided around the propeller shaft to hold it in place. The burette delivery tip and the thermistor probe are each mounted in ground-glass joint plugs which can be inserted into the other two openings of the cell and held firmly in place. Most of the cell is immersed in a constant temperature bath. The measured cell constant, k , is defined as

$$k = \kappa R$$

where κ is the specific conductance of a particular solution in $\Omega^{-1} \text{ cm}^{-1}$ and R is the measured resistance. The constant, k , for this cell was found to be $1.889 \pm 0.002 \text{ cm}^{-1}$.

B. TITRATION DATA ANALYSIS AND DISPLAY SOFTWARE

Once the computer has completed a titration and written the data onto DECTAPE, the operator will call CCLMLT, the first of two analysis routines for titration data. Program CCLMLT is flowcharted in Figure 48 and listed in the Appendix. It begins by asking the operator for the first block on tape which contains the data to be analyzed and then reads that data. It determines, from the parameters written into the data set, whether or not temperature and double precision data were taken. If it finds that temperature data were taken, the computer asks the operator to input the coefficients from the temperature-conductance profile fit for that system. (The operator may input zeros for these coefficients if the temperature-conductance run has not yet been performed). Finally, the computer asks for the initial volume in the cell before the titration began so that the data may be corrected for dilution effects, and whether or not the operator wishes to have the data listed on the line printer. If a line printer listing is to be made, the computer will set up the line printer and data table headings. A set of maximum and minimum pointers, for all types of raw and corrected data, equal to the first points in the data set, will be established and the analysis begun. The sampled voltage, ES , the raw conductance measured, $G(M)$, the conductance corrected for scale changes, $G(C)$, and the dilution corrected conductance, $G(D)$, will all be calculated. The quantity $G(D)$ is calculated according to

$$G(D) = (V_i + V_{tit})(G(C))/V_i$$

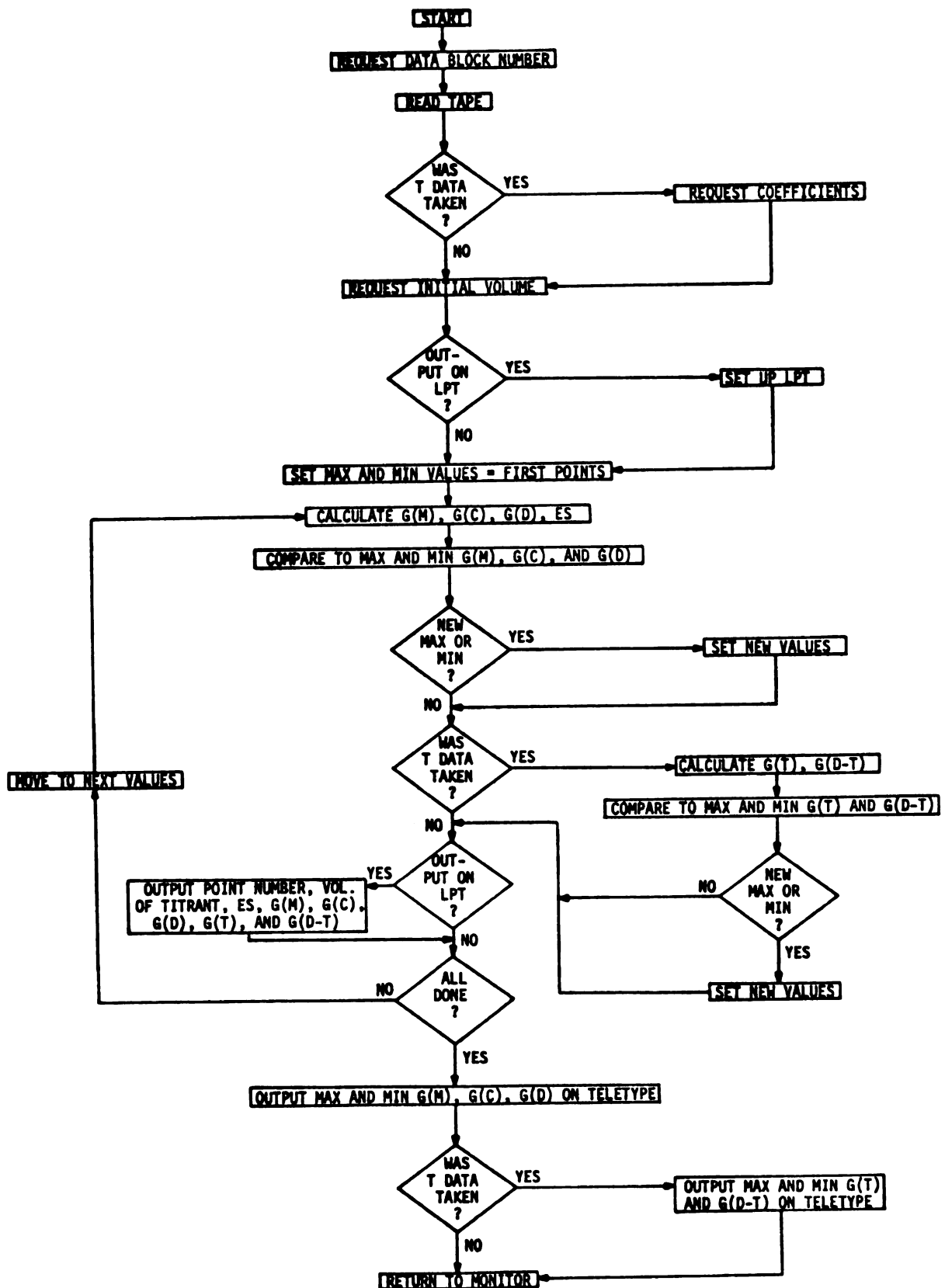


Figure 48. CCLMLT Program Flowchart. (Simplified)

where V_i is the initial volume (input by the operator) and V_{tit} is the volume of titrant added.

The computer will compare each calculated conductance to the corresponding maximum and minimum in the set and reset these limits if a new maximum or minimum is encountered. If temperature data have been taken, the conductance corrected for temperature fluctuations $G(T)$, will be calculated from:

$$G(T) = G(C) + (A_n)(T_s^{n-1} - T^{n-1}) + (A_{n-1})(T_s^{n-2} - T^{n-2}) + \dots$$

where A_n is the coefficient of the $n-1$ power of the thermistor response, T , from the fitted equation (input by the operator) and T_s is a standard reference thermistor response, measured at the beginning of a run, before any temperature change has occurred.

Conductance corrected for dilution and temperature, $G(D-T)$ will be calculated from an expression identical to that for $G(D)$ with $G(T)$ substituted for $G(C)$. Maxima and minima are also calculated for the $G(T)$ and $G(D-T)$ data sets.

If the data are to be listed on the line printer, the computer will output the conductances for each point, $G(M)$, $G(C)$, $G(D)$, $G(T)$ and $G(D-T)$ as they are calculated along with the point number, the volume of titrant added to that point, and the sampled voltage, E_s . Thus, in the few minutes following the actual titration, the computerized conductance system has completed calculations which would require many man-hours of tedious work if the data were taken by conventional means and treated in a conventional manner. Finally, when all the data have been scanned, the maximum and minimum values for all conductances calculated are listed on the teletype for use in setting up the scope

and X-Y plotter boundaries for data display. Computer control returns to the Keyboard Monitor.

The plotting routine for titration analysis, CDPMLT, is flow-charted in Figure 49 and listed in the Appendix. It begins by requesting the first tape block to read, reads the file, requests correction coefficients if temperature data were taken, requests the initial volume, and allows the operator to plot axes, $G(M)$, $G(C)$, $G(D)$, $G(T)$, or $G(T-D)$ vs. volume of titrant, or return to monitor. When the operator selects an option to plot one of the calculated conductances, the program allows him to select the points to be plotted and the upper and lower conductances to be the limits of the plot. The computer then calculates the chosen conductance data point-by-point, scales it for plotting, and plots it on the X-Y plotter and/or display scope, drawing straight lines between points. When the plot has been completed, the routine returns to await the selection of the next option.

It has not yet been necessary to provide a fitting routine to calculate the endpoint of a conductometric titration analyzed by these programs since the endpoints for most of the systems investigated to date have been quite distinct. Furthermore, the conductance change during these titrations is being continuously monitored within the quantization level provided by the titrator (0.2 ml/20 ml). Having 100 connected points to define a curve largely eliminates the uncertainty in the endpoint which some workers have experienced using conductance detection. These persons only obtained a few measurements on either side of the endpoint and draw straight lines through them, taking their intersection as the true endpoint. In fact, one of the most interesting phenomena presented in this chapter (section D)

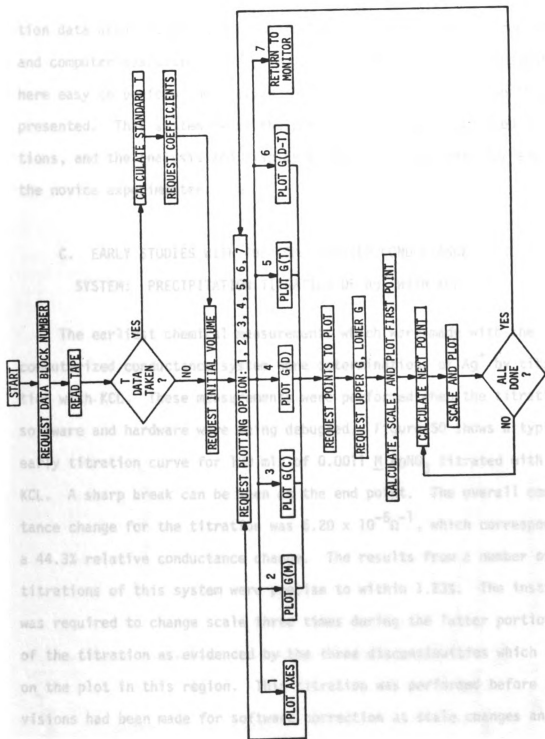


Figure 49. CDPMLT Program Flowchart. (Simplified)

would have been completely unobserved if continuous monitoring of the titrations had not been employed. The use of a TDA routine for titration data acquisition, an automatic titrator under computer control, and computer evaluation of data made all of the titrations presented here easy to perform and analyze for the chemical information they presented. This system makes the performance of sophisticated titrations, and the analysis and display of the data, possible for even the novice experimenter.

C. EARLY STUDIES WITH THE COMPUTERIZED CONDUCTANCE

SYSTEM: PRECIPITATION TITRATION OF Ag^+ WITH KCL

The earliest chemical measurements which were made with the computerized conductance system were determinations of Ag^+ by titration with KCL. These measurements were performed when the titration software and hardware were being debugged. Figure 50 shows a typical early titration curve for 100 mls of 0.0011 M AgNO_3 titrated with 0.010 M KCL. A sharp break can be seen at the end point. The overall conductance change for the titration was $5.20 \times 10^{-5} \Omega^{-1}$, which corresponds to a 44.3% relative conductance change. The results from a number of titrations of this system were precise to within 1.23%. The instrument was required to change scale three times during the latter portion of the titration as evidenced by the three discontinuities which appear on the plot in this region. This titration was performed before provisions had been made for software correction at scale changes and overlap of adjacent scales. These discontinuities indicated the need for such corrections which were later implemented. The computerized

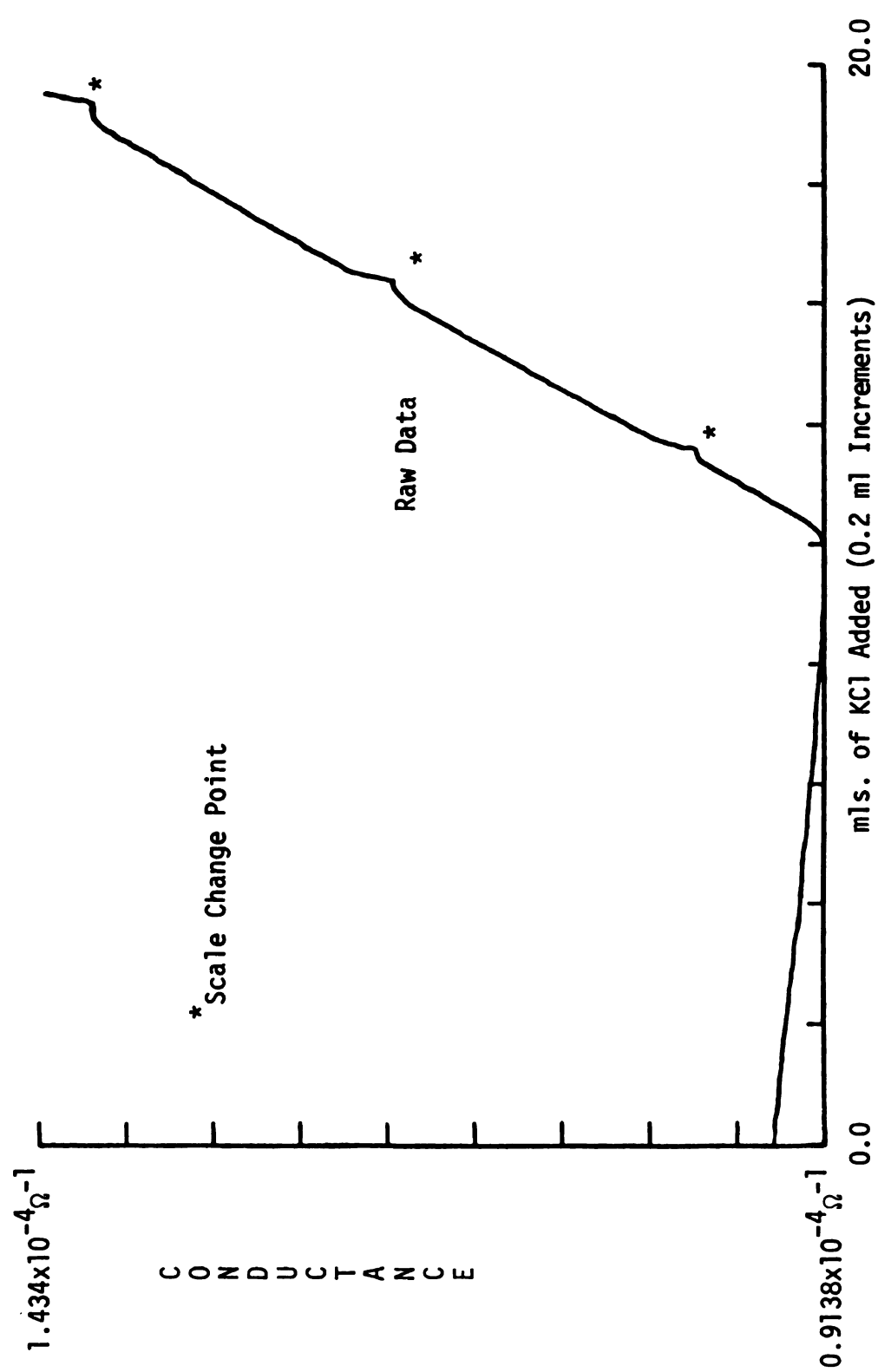


Figure 50. Conductometric Titration of 0.00011 Moles of Ag^+ with 0.010 M KCl . (60173-1)

conductance system did, however, demonstrate its ability to measure conductance changes in chemical systems where precipitation occurred. No effects due to silver chloride formation on the electrodes were observed. Concentrations of Ag^+ as low as 10^{-4} M were successfully titrated.

D. SOME OBSERVATIONS CONCERNING THE END POINT PHENOMENON ASSOCIATED WITH CERTAIN EDTA TITRATIONS

During the early chemical measurements with the computerized conductance system, what was assumed to be another "simple" titration was examined, largely to determine titration sensitivity in the presence of a strong background electrolyte. This system was the titration of Ca^{++} with EDTA in ammonia ammonium chloride buffer at pH 10. These titrations were performed at four separate times, in June and August of 1973, and in January and March of 1974. The first two studies were performed to assess the performance of the computerized conductance system in buffered solutions, where there is a large conductance background due to the buffer ions. The later two studies were attempts to investigate and duplicate the end point anomaly observed during the August, 1973 study.

The initial set of titrations, performed in June, 1973, were observed to be normal conductometric titrations with normal end points. During this study, Ca^{++} concentrations as low as 1.25×10^{-4} M were determined by titration with EDTA. The buffer present in the calcium solution had an ionic strength of about 0.05. The end points were distinct and the accuracy, 0.625%, was limited by the solutions prepared. The precision was excellent, duplicate experiments

agreeing to within 0.020%. Further titration studies were, however, delayed for about two months while the temperature monitor circuit and software were assembled and integrated into the computerized conductance system.

In August, 1973, the chemical tests were resumed with further investigation of the Ca^{++} - EDTA titration among the experiments to be performed. The results of this series of Ca^{++} - EDTA titrations were totally different from those observed in June. Instead of the normal titration curves previously observed, the region around the endpoint of these new titration curves was significantly altered. One of these curves appears in Figure 51. Two breaks near the endpoint occur where only one existed previously. The instrument was thoroughly checked and the cell thoroughly cleaned but the phenomenon failed to disappear during the entire five days when these runs were made. The phenomenon was found not to be a function of buffer strength, concentrations of Ca^{++} , concentration of EDTA, any tested ratio of these concentrations, or any particular instrumental settings. It was found that the true Ca^{++} endpoint was obtained by graphically finding the point half way between both breaks as shown in Figure 51.

It was discovered, at the time, that a number of previous workers had noted similar effects for Ca^{++} , Zn^{++} , Cu^{++} , and other divalent metals with EDTA titrations in buffered solutions. The earliest of these was in the pioneering work of Hall, Gibson, Wilkinson, and Philips (51) who were the first to use conductometric methods for determination of endpoints in EDTA titrations. They noted curvature in most of their titration curves which could not be explained by dilution effects. This curvature was not, however, as dramatic as

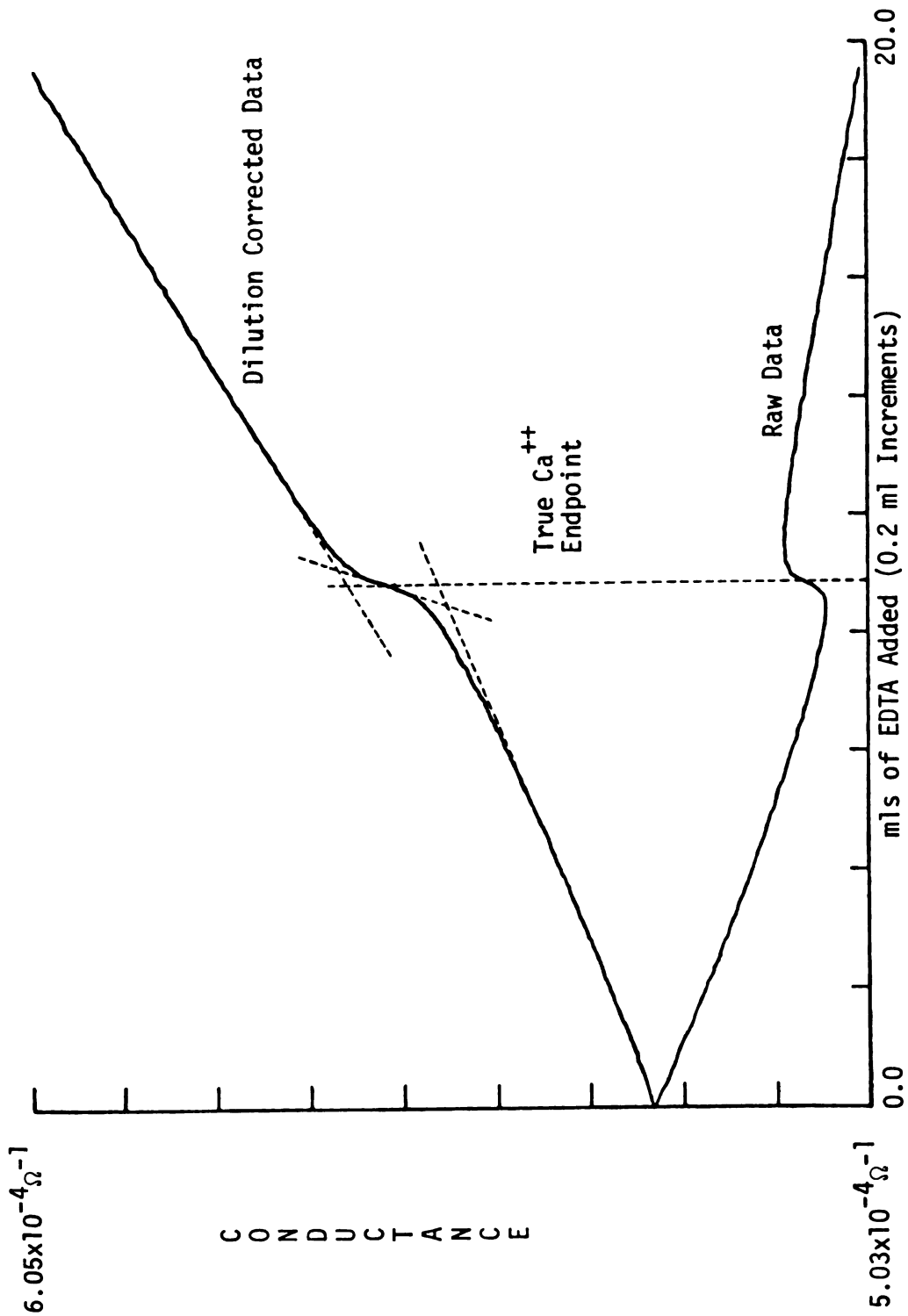


Figure 51. Titration of 10 mls of 0.0002M Ca⁺⁺ with 0.0020M EDTA in NH₃ - NH₄⁺ Buffer at pH 10.0

that of Figure 51. Hall et al. discounted this effect which they believed was due to "incomplete buffer action".

Farrow and Hill (52) discovered two endpoints while following titrations of zinc, lead, cadmium, bismuth, manganese, magnesium or calcium with EDTA by potentiometric means. They investigated these effects and claimed the anomaly resulted from the presence of nitrilotriacetic acid (NTA) impurity in the EDTA. They said that the first endpoint they observed was due to EDTA and the second endpoint due to NTA. In the case of Ca^{++} , Solochrome black T indicator detected the first endpoint; in the titration of Zn^{++} , the second endpoint, corresponding to the NTA endpoint, was detected by Solochrome black T. They showed that commercially available EDTA still contained enough NTA to produce the effect.

Levine and Golden (53) titrated zinc in the presence of manganese using Eriochrome black T as the indicator and photometric endpoint detection. They titrated manganese directly by reducing it with ascorbic acid in ammonical tartrate solution and masking the zinc with KCN. The zinc could then be demasked by addition of formaldehyde and titrated with EDTA. They observed two "endpoints" near the real zinc endpoint (after manganese had been titrated). They assumed the first break corresponded to the beginning of the indicator reaction and the second break to the completion of this reaction.

During the August, 1973 titrations, the author discovered that Johnson and Enke (10) had observed the same phenomenon which these titrations were presenting, during measurements with their earlier bipolar pulse instrument of the titrations of Ca^{++} and Zn^{++} in $\text{NH}_3 / \text{NH}_4^+$ buffer at pH 10 with EDTA. They found that the first break

was proportional to the amount of Ca^{++} or Zn^{++} present while the second break was not. They found the first break to agree to within 0.2% of the Eriochrome black T endpoint. They also noted a sharp conductance increase which leveled off to a more moderate increase even when no Zn^{++} was present, for addition of EDTA to buffer. Johnson (18) proposed the formation of a complex between EDTA and NH_4^+ after the EDTA concentration built up to significant levels following the Zn^{++} endpoint.

Further work by Bauer (54) with Johnson and Enke's same bipolar pulse instrument, in the same laboratory, verified these results. He found that the anomaly occurred for every titration of zinc or calcium with EDTA in $\text{NH}_3/\text{NH}_4^+$ buffer at pH 10 except for the first time the electrodes were used after having been unused for several months (the electrodes were not platinized). Bauer claimed that the second break in the curve was a function of the rate of addition of EDTA (he was continuously adding titrant while following the conductance change on a recorder). He also observed other breaks in the titration curve, much less significant than the second break at the endpoint. He believed that he was observing a non-equilibrium situation. Finally, he proposed further investigation with platinized electrodes to see if the anomaly was a surface phenomenon.

It should be noted that this author observed the anomaly with or without Eriochrome black T as did Johnson and Enke and Bauer. During the studies by Johnson, Enke, and Bauer, other research was being done in the same laboratory which involved the use of cyanide complexes. This is a possible connection here with the observations of Levine and Golden about the effect of the presence of KCN in the solution

during titration.

In addition to the normal curiosity concerning an unexplained phenomenon, this author was interested in this particular anomaly because it resulted in considerably more distinct endpoints than those which occurred when the anomaly was not present due to the sudden "burst" of conductance at or near the expected endpoint. Thus, the computerized conductance system was able to determine very low concentrations of calcium with relative ease as can be seen in Figure 52. In this titration, a distinct endpoint is observed for the titration of $2.3 \times 10^{-5} \text{ M Ca}^{++}$ with $2 \times 10^{-4} \text{ M EDTA}$ in $\text{NH}_3/\text{NH}_4^+$ buffer at pH 10. The lowest previous concentration of Ca^{++} determined by conductance was that reported by Hall et al. (51) of $10^{-4} \text{ M Ca}^{++}$ after dilution in the titration vessel. It is obvious, from Figure 52 that much lower Ca^{++} concentrations could be determined with the anomaly present.

Investigation of the anomaly was resumed in January, 1974. Every curve obtained was found to be a normal titration curve with only the single break at the endpoint. The calcium and EDTA solutions had been prepared from the same bottles of stock chemicals as the two previous titration series, discounting the effects of NTA in this case. The ammonium chloride used to prepare the buffer was the same although the ammonium hydroxide solution was not. The results of this series did show, however, that the effect was due to an interferent and not an NH_4^+ - EDTA complex as Johnson (18) had proposed. This was done by comparing the ratio of the slopes before and after the two "endpoints" and before and between the two "endpoints" with the ratio of the slopes of a normal curve before and after the endpoint. If the second break corresponded to the beginning of the formation of an

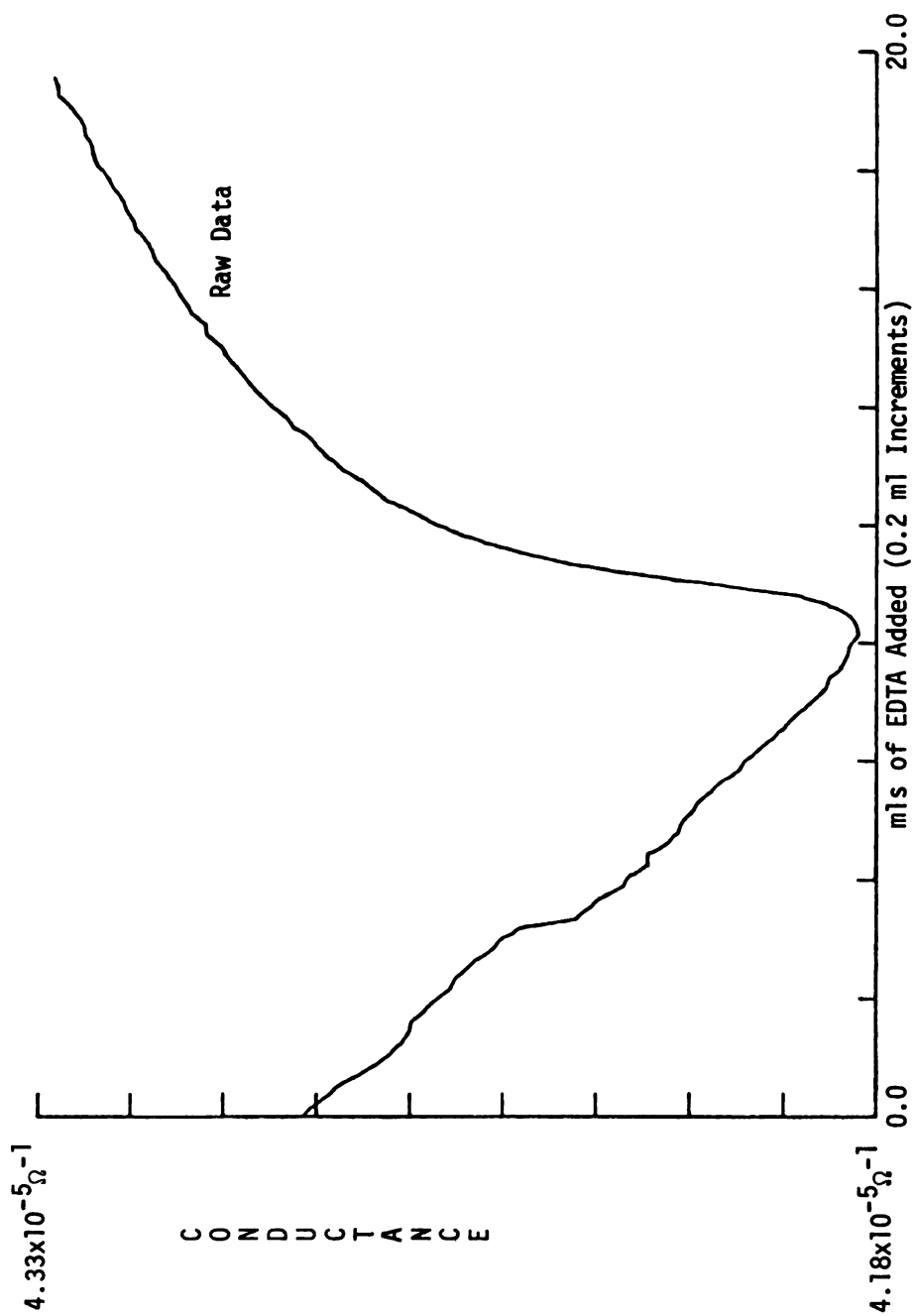
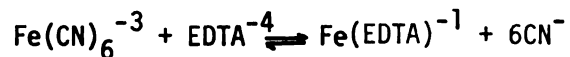


Figure 52. Titration of 10 mls of 0.000023M Ca^{++} with 0.0002M EDTA in $\text{NH}_3 - \text{NH}_4^+$ Buffer at pH 10.0. (82173-1)

NH_4^+ - EDTA complex, the ratio of the slopes before and between the two endpoints should be the same as the ratio of slopes in the normal curve. If the ratio of slopes before and after the two "endpoints" were the same as the normal curve slope ratio, this would indicate an interferent being titrated between breaks and that the conductance is proceeding to change in a normal manner after this interferent was titrated, due to addition of ionized EDTA. It was found that the ratio of slopes before and after the two breaks in the curve was identical to the ratio of slopes of a normal curve to within 6%. The 6% difference could be explained by slight variation in ionic strength between the anomalous and normal runs. The ratio of slopes before and between the two breaks had no relationship to the ratio of slopes for the normal curve. Therefore, the region between the first and second breaks in the abnormal curve was the result of a release of ions by some interferent which occurred when significant uncomplexed EDTA was present near and after the Ca^{++} endpoint. The interferent had the effect of a "conducticator", a conductance-specific indicator which produced a burst of ions (as opposed to a burst of color for a normal indicator) at the Ca^{++} endpoint. The species which produced these effects had not been isolated but the effect itself appeared to be a useful one. Therefore, an attempt was made to reproduce it in a controlled manner.

Since CN^- was present in several of the situations where abnormal curves were observed, it was thought that a complex of CN^- and another metal might be responsible. If this complex could be broken up at the calcium endpoint by EDTA, the result would be to release four to six highly mobile ions to the solution per complex, which should

cause a significant increase in conductivity. A reaction of the type:



seemed reasonable. The complexation constant of Fe(CN)_6^{-3} is 10^{42} whereas that of Fe(EDTA)^{-1} is $10^{25.1}$. However, both complexation constants would be affected by the presence of NH_3 . In addition, there would be no excess CN^{-} present and significant amounts of free EDTA at the Ca^{++} endpoint which should cause the above equilibrium to shift to the right.

The amount of Fe(CN)_6^{-3} to be added to try to obtain the conducticator effect was determined by calculation of the approximate amount of interferent present in the anomalous curves. This concentration was calculated to be on the order of 10^{-5} M. A solution of $\text{K}_3\text{Fe(CN)}_6$ was prepared and the proper amount added to the titration cell to make the concentration 2×10^{-5} M. The curve obtained from this titration is shown in Figure 53a. The conducticator effect is clearly present although not as strong as that observed accidentally. In order to try to increase the effect, the concentration of Fe(CN)_6^{-3} was tripled for the next titration. The effect vanished and no endpoint was observed at all. Further titrations at the initial or lower concentrations did contain the conducticator phenomenon. It was found, however, that rinsing the cell with distilled water in order that a standard run without Fe(CN)_6^{-3} present could be obtained was not sufficient to remove the effect. Indeed, the effect was still present after cleaning the cell, the pipettes used, the titrator, and the stirrer with HCl and HF three times and using fresh solutions of Ca^{++} , EDTA, and buffer which

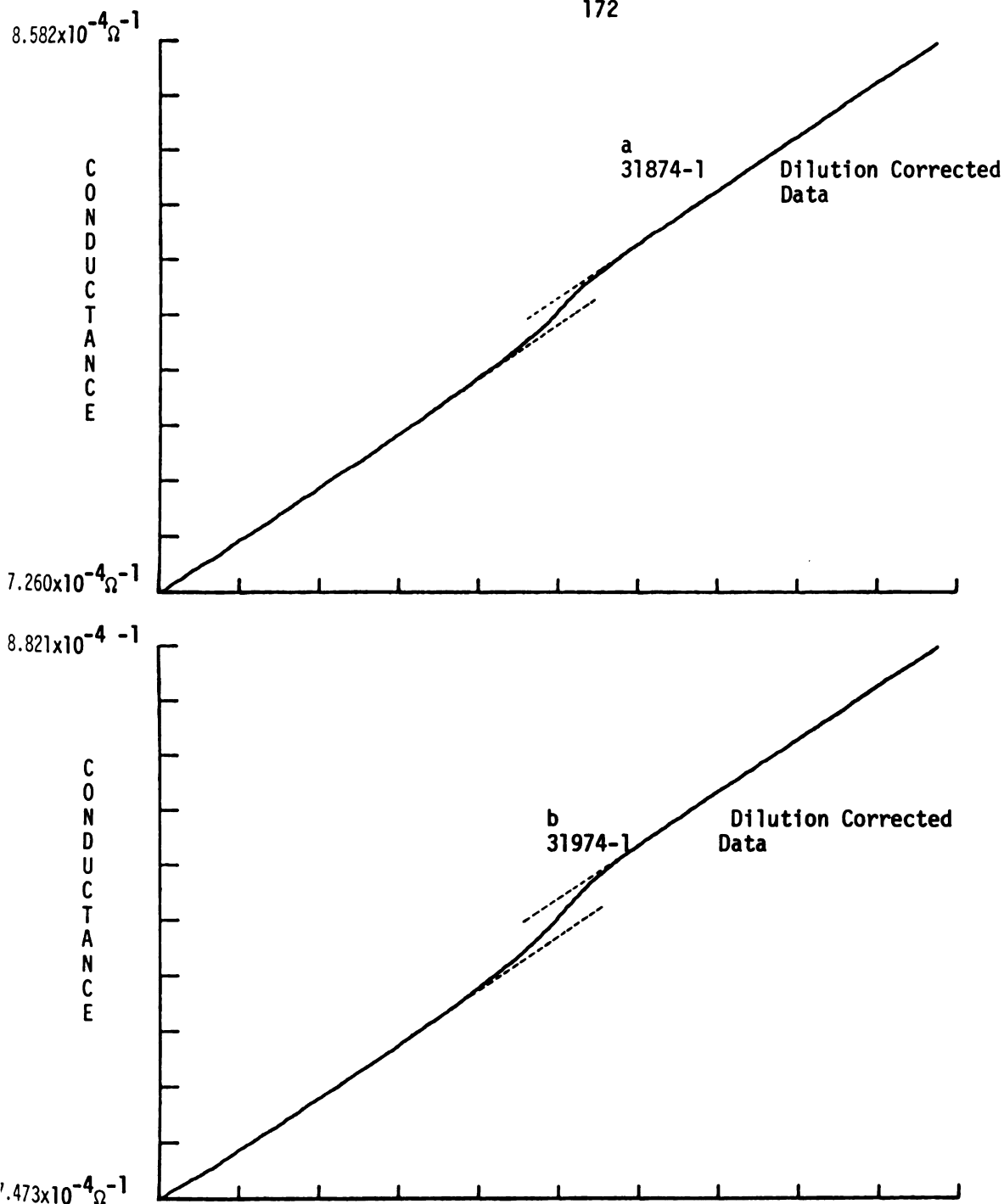


Figure 53. a) Conductator effect for $4 \times 10^{-4} \text{ M Ca}^{++}$ Titrated with 0.002 M EDTA in the presence of $2 \times 10^{-5} \text{ M K}_3\text{Fe}(\text{CN})_6$ and $0.01 \text{ M NH}_3 \text{ NH}_4^+$ Buffer at pH 10, (b) Same as (a) but no $\text{K}_3\text{Fe}(\text{CN})_6$ Present, Cell has been Scrubbed three Times with HF and HCl.

were prepared in previously unused glassware. This is reflected in Figure 53b which represents the titration made following the above cleaning. The conducticator effect now appeared to be a surface phenomenon within the titration cell, either on the glass or the platinum electrodes.

The effect was finally eliminated by cleaning the cell with concentrated nitric acid. It was then expected that the effect could be recreated by addition of fresh $\text{Fe}(\text{CN})_6^{-3}$ as in the first experiment. However, the effect could not be recreated although the exact experimental conditions and the conditions preceeding them were carefully duplicated. Treating the surface of the cell with HF to remove the outer monolayer of glass, exposing a fresh surface, produced no effect. Treating the cell with concentrated NaOH to restore the Na^+ balance on the glass (since an ion exchange with the glass surface seemed a reasonable mechanism for the conducticator effect) had no effect. Finally, having the cell re-anealed had no effect. Since other studies with the computerized conductance system had been undertaken at this time, and because of the lack of further results, the investigation was halted.

Several conclusions can be made at this time which might be of use to later workers investigating this effect. They are:

- 1) The conducticator phenomenon is real, having been observed by a number of workers with different instruments under different environments.
- 2) The effect could prove to be valuable in determination of lower concentrations of analyte by conductance than previously possible. However, if the effect is due to complex equilibrium

between the conducticator ligand and conducticator-EDTA the chance of finding such a species which could be used in numerous systems, where complexation constants can be quite different, seems to be rather small.

- 3) The effect is due to an interfering species and not to the formation of an EDTA-buffer complex.
- 4) The conducticator phenomenon appears most likely to be a surface effect, possibly an ion-exchange on the glass surface of the cell, rather than an effect resulting from the presence of a species in solution, since careful cleaning of the cell failed to remove the effect.
- 5) CN^- in some form seems to be a species which will trigger such an effect.
- 6) The equivalent conductance of the ions released to the solution when the phenomenon occurred, per mole of EDTA added (calculated from data in Figure 53b was $579.9 \Omega^{-1} \text{ cm}^2/\text{mole EDTA}$. This almost exactly corresponds to three OH^- species (total equivalent conductance, $576.0 \Omega^{-1} \text{ cm}^2$).

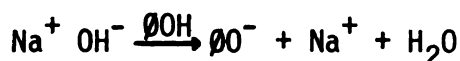
E. DETERMINATION OF SMALL AMOUNTS OF NaOH IN THE PRESENCE OF LARGE QUANTITIES OF SODIUM PHENOLATE

The author became aware of an analysis problem which a chemical company was experiencing while attempting to determine small amounts (<0.5%) of sodium hydroxide in a solution which was 60% sodium phenolate and approximately 40% water. They wished to maintain an excess of NaOH which would insure complete reaction of phenol ($\text{C}_6\text{H}_5\text{OH}$) to sodium phenolate (NaOC_6H_5). However, since the process was being performed as one step

in a large batch operation of several steps, they did not want the NaOH concentration to rise above 0.5% because it would not only interfere with later processes, but waste raw materials. The method which they had employed for the determination of the NaOH present was to titrate first the total base (NaOH plus NaO ϕ) with strong acid. The phenol formed in this reaction was then extracted into another solvent and brominated to form the tribromophenol. The excess bromine was then titrated with iodate. The net result was two rather imprecise large numbers representing total base and that part of the base which was phenolate. These two numbers were then subtracted to yield a small number representing the NaOH concentration. The results they reported were of poor accuracy.

The project seemed to be an ideal one for the computerized conductance system which, because of its excellent resolution, should be able to sense even small endpoint changes. The conductometric method seemed able to provide a direct means of endpoint detection for a direct titration of NaOH where no other indicator was available.

The chemists involved with the analysis believed that sodium phenolate and sodium hydroxide were both nearly equal in strength in this semi-aqueous solution. This would make it impossible to distinguish the NaOH and NaO ϕ endpoints for a titration with a strong acid. Therefore, the first attempt to titrate NaOH alone was done using phenol as the titrant. It was expected that an endpoint could be observed which corresponded to the reaction:



Please note: the convention which has been chosen to represent titrations in this manuscript involves placing the titrant over the arrow for the reaction. In this way, the ionic character of the solution before and after titrant is added can easily be represented by the left and right sides of the equation respectively.)

If this reaction occurred with the ionic forms as written above, a decrease in conductance would be expected before the endpoint since O^- is being exchanged for the somewhat more mobile OH^- (after dilution effects on the conductance are corrected for). After the endpoint the conductance should begin to increase slowly due to very slightly ionized O^-H , assuming dilution effects are eliminated.

A solution of O^-H , NaOH , and water was prepared such that the final weight percents of the reaction products would be 60% NaO^- , around 40% water, and less than 0.5% excess NaOH . The solution was prepared in a round-bottom flask which was placed in a heating mantle to maintain the temperature of the contents above 60°C at all times to prevent solidification of the solution. Seven mls. of the solution were pipetted (with some difficulty due to solidification during pipetting) into the titration cell and diluted to 50 mls with distilled water. The resulting solution was about 8.4% NaO^- (0.8M) before dilution by the titrant (0.035M O^-H).

The dilution-corrected titration curve is shown in Figure 54. A small change in slope is observed at the endpoint. The expected decrease in conductance before the endpoint was not observed. Rather, the conductance increased before the endpoint and less slowly afterward. This seemed to indicate that NaO^- was not as strong an electrolyte as the chemists involved with the project had thought. The conductance

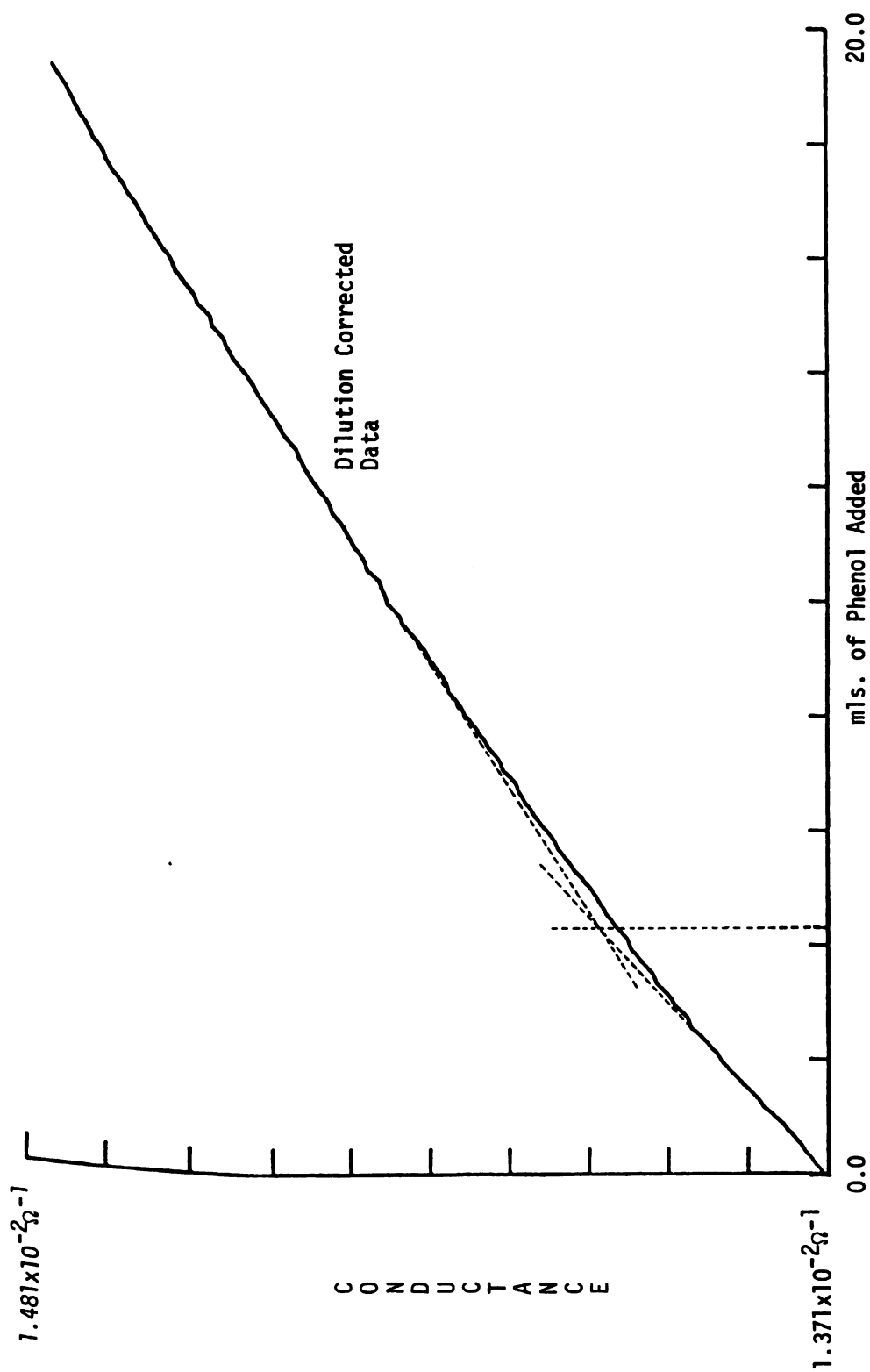
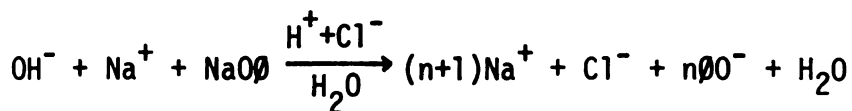


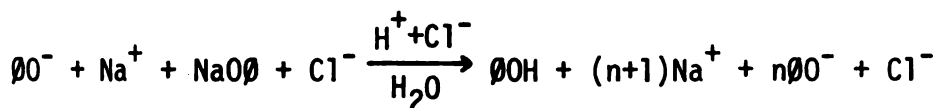
Figure 54. Conductometric Titration of 7 mls of a solution which is 60% Sodium Phenolate, 40% Water, and less than 0.5% NaOH in 43.0 mls of water with 0.035 M Phenol. Cell Thermostated at 23.5°C. (30674-2)

anges which occurred appeared to be not only decreasing conductance due to loss of OH^- in the reaction but also, and predominately, an increase in conductance by the release of Na^+ and O^- ions due to the dissociation of NaOO which was a weak electrolyte, plus the introduction of free O^- from the titration reaction. After the endpoint, only additional Na^+ and O^- are formed through increased dilution (since H is a weak electrolyte) so that the increase in conductivity is lower.

Since this titration indicated that OONa was a significantly weaker base than NaOH , it was expected that NaOH could be titrated first, with a strong acid such as HCl , which should produce a sharper endpoint. The resulting curve from this titration appears in Figure 5. A sharp endpoint is visible for the titration of the NaOH present in 8 mls of analyte solution, diluted to 50 mls with distilled water, and titrated with 0.0192 M HCl . The curvature of the line is possibly due to ion-pairing effects which become less prominent as the solution is diluted. The reactions which are occurring are:



before endpoint and



after the endpoint, where n is the amount of additional NaOO which dissociates due to dilution. The amount of NaOH present in the 8 ml sample of analyte was 6.07×10^{-3} g (3.00×10^{-3} M before dilution),

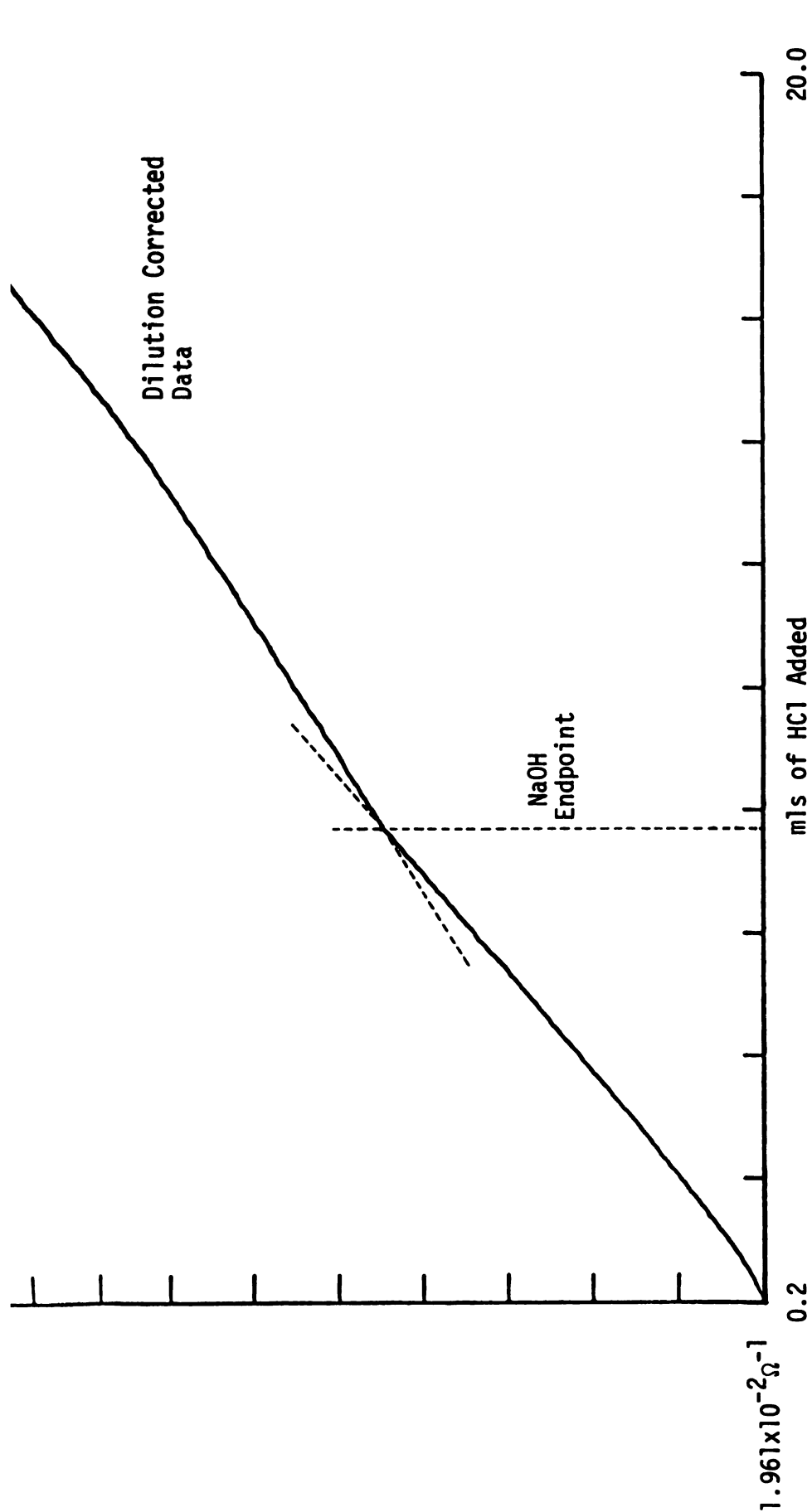


Figure 55. Conductometric Titration of 8 mls of a Solution which is 60% Sodium Phenolate, 40% Water, and less than 0.5% NaOH in 42.0 mls of Water with 0.0192 M HCl. Cell Temperature stated at 23.5°C. (30874-1)

h corresponded to a weight percent of 0.061%.

It was hoped that an actual sample of the solution from the chemical plant could be obtained for analysis and comparison with their multi-step analytical method. However, due to unforeseen circumstances, this was not possible at the time. It is evident, however, that the single step method presented here is far superior to the multi-step method employed previously, not only in accuracy, but especially in speed and ease of application.

F. TITRATION OF PHTHALIC ACID IN 1:1 DMSO-ETOH

The author would like to mention one non-aqueous titration which was performed during the studies of the luminol system to be discussed in Chapter 8. At one point in these studies, some information concerning the behavior of phthalic acid protons in 1:1 DMSO-ETOH, and the relative conductivity of phthalic acid single and di-anions with respect to hydroxide ion in the same solvent, was desired. It is known that non-aqueous titrations can present complex endpoint detection problems to conductance methods due to the low dielectric constant of the medium, low double layer capacitance, and so forth. Nevertheless, by using the computerized conductance system, it was possible to set up, run, and analyze a titration of 50.0 mls. of 0.0015 M phthalic acid (PH_2) with 0.01003 M KOH in 1:1 DMSO-EtOH in about an hour. Much of this time was involved in preparation of standards and in mixing time during the titration. The resulting titration curve appears in Figure 56.

It can be seen that endpoints for both protons are obtained. The

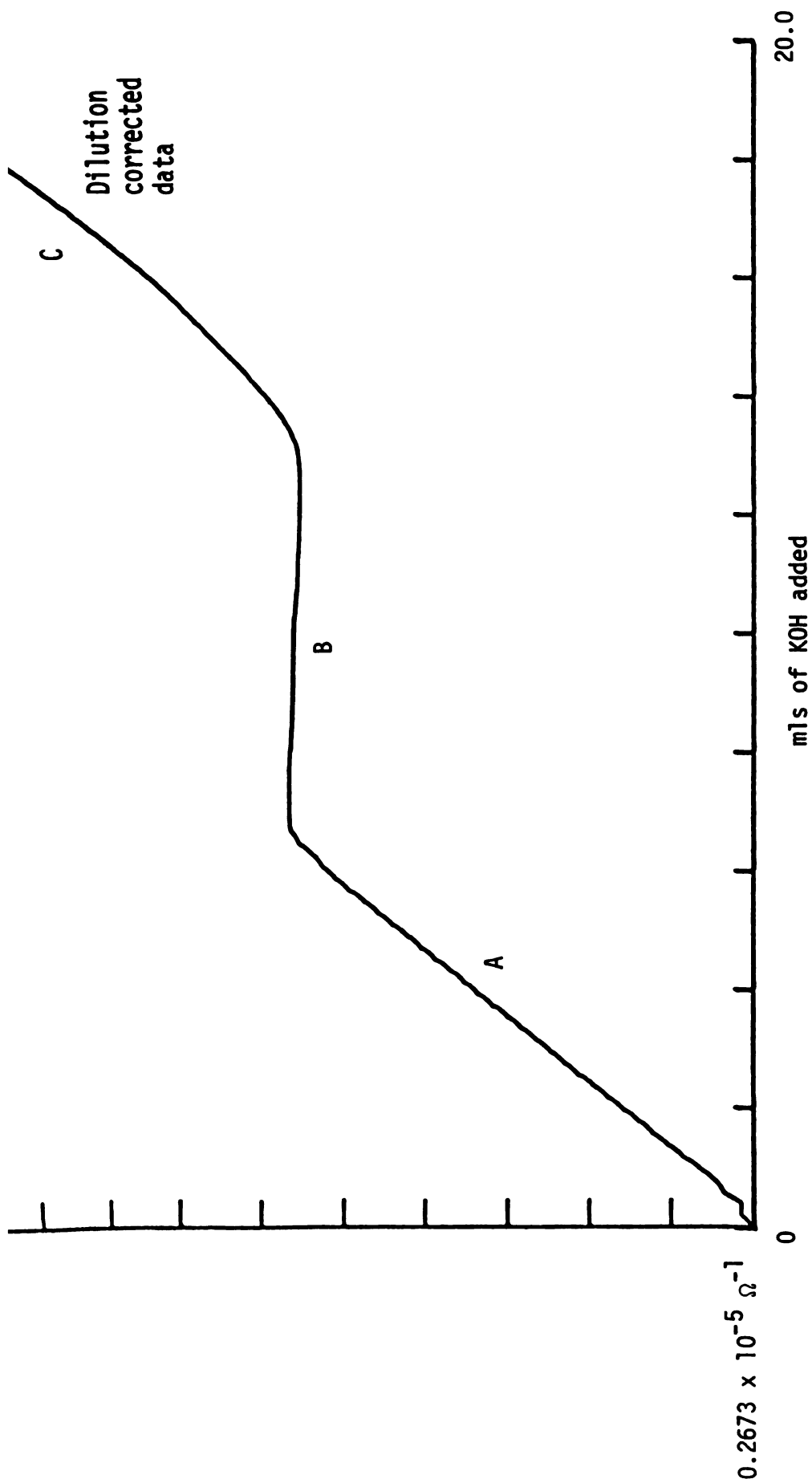
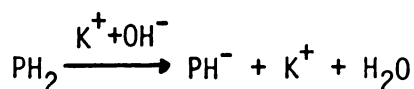


Figure 56. Conductometric Titration of 50.0 mls of 0.0015 M phthalic acid with 0.01003 M KOH Cell Thermostated at 24.5°C. Solvent System: 1:1 DMSO-EtOH. (51774-1)

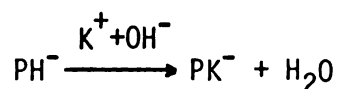
phenomenon associated with each portion of the curve (A, B, and C in Figure 56 is given below:

Region A: The increase in conductance in this region is due to the reaction:



where two ions not previously present (PH^- and K^+) are being formed.

Region B: The conductance in this region of the curve decreases very slightly. The increase in conductance due to the addition of K^+ (with OH^- reacting with the second phthalic proton to yield H_2O) is not seen. In addition, the product formed is of slightly lower conductivity than the PH^- species. The reaction which is occurring here should correspond to:



where λ_{PK^-} is slightly less than λ_{PH^-} .

Region C: The conductance increase here is due to addition of K^+ and OH^- . Notice that the conductivity increase is not as rapid as that for the formation of K^+ and PH^- in Region A. Two possible conclusions can be drawn. Either $\lambda_{\text{OH}^-} < \lambda_{\text{PH}^-}$ or some PK_2 forms when excess K^+ is present after the second endpoint. It is quite possible that the first conclusion may be correct due to higher solvation of OH^- by the bulky DMSO molecules present because of its higher charge-to-mass ratio with respect to PH^- .

This titration, along with the others presented in this chapter, demonstrates the versatility of the software and hardware in the computerized conductance system, and the power of its instrumental sensitivity and automatic data analysis, for applications in titration studies. These titration abilities may now be implemented by other workers, who desire to use conductometric monitoring techniques, with a minimum of effort and the anticipated maximum data attainable by the conductance method.

CHAPTER 8

APPLICATION OF THE COMPUTERIZED CONDUCTANCE SYSTEM TO KINETIC STUDIES: PRELIMINARY INVESTIGATION OF THE LUMINOL REACTION

Acknowledgment: All of the actual experimental work and much of the implementation of specialized hardware presented in this chapter was done in conjunction with Timothy A. Nieman to whom the author wishes to express his gratitude.

A. SPECIFIC SOFTWARE FOR KINETIC EXPERIMENTS

One of the greatest differences between the computerized conductance system and conventional conductance instruments is the speed with which data may be acquired and analyzed. At its maximum rate the system can acquire over 33,000 measurements of conductance per second. It was shown in Chapter 5 that these measurements were of good precision and low noise level. If the timing of an experiment permits, ensemble averaging can increase this precision and lower the noise level accordingly. Thus, the system is ideally suited for and, indeed, was intended to be used in, kinetic studies of slow to moderately fast reactions in which an overall ionic change is occurring.

In order to permit use of the system in reaction mechanism and rate studies, some modification of the basic software was required. As a result, there are currently two sequences of kinetic study programs in use in the system. One of these sequences performs acquisition and analysis of conductance and temperature data (the CBTMLS sequence). The other sequence (the CBTDCS sequence) is also capable of acquiring and analyzing data from another data source, in addition to acquisition

and expanded analysis of temperature and conductance data.

The program CBTMLS is a simple modification of the basic acquisition program, CBTSLS, discussed in Chapter 4. It contains stopped-flow flag check instructions to permit data acquisition triggering from the stopped-flow apparatus employed in most of the kinetic studies performed to this time. Analysis of the data acquired by CBTMLS is accomplished by CCLMLS. Program CCLMLS is identical to the CCTMLT program used in titration analysis, but does not contain provisions for dilution correction of data. The plotting routine in this sequence, CDPMLS, is identical to CDPMLT used for titration curve plotting with the exception that it lacks provisions for plotting dilution corrected data.

The other kinetic program sequence contains two computerized conductance system programs which require 12 K of memory for operation. Program CBTDCS is a modification of CBTSLS which is capable of acquiring conductance, temperature, auxiliary data, and a baseline for the auxiliary data. It contains additional storage space which enables it to acquire up to 500 points from spectroscopic, electrochemical, or other data sources. It has instructions to trigger the auxiliary A/D converter on the same signal (DS 33, IOP 4) as the bipolar pulsing trigger. It uses DS 36, IOP 2 for a flag check of the stopped-flow apparatus and DS 36, IOP 4 for the data transfer. Data are analyzed and plotted by the 12 K CCLDCS program. This program is an extensive modification and combination of CCLMLS and CDPMLS. In addition to listing the calculated data on the line printer, calculating maxima and minima, and slow plotting raw, scale change corrected and temperature corrected conductances, it will fast plot all of these values on

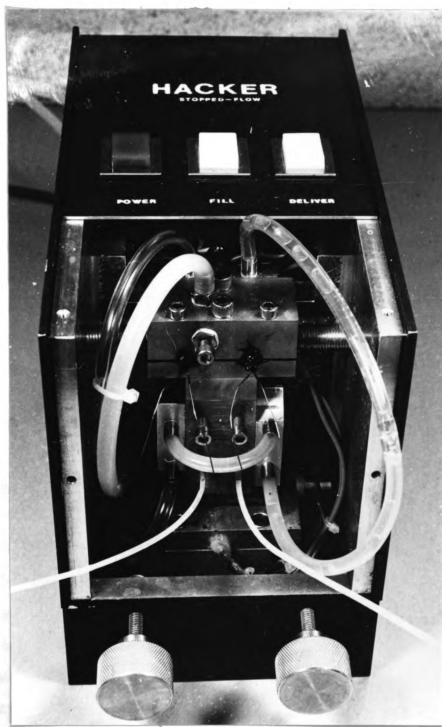


Figure 57. Photograph of the Early Hacker Stopped-Flow Apparatus.

the display scope, list them on the lineprinter, and slow or fast plot thermistor response, auxiliary data, and the integral of the auxiliary data (baseline corrected). The fast plotting option permits an operator to observe his data on the display scope within about a minute of the completion of a run. The only waiting period necessary between completion of data acquisition and plotting (about 45 seconds for a 500 point data set) is that required for the computer to calculate the set of maxima and minima used for scaling of the data on the scope. Plotting of data requires two-to-ten seconds for 500 points. If an operator desires a hard copy, data may be slow-plotted on the X-Y plotter in the normal manner.

B. SPECIFIC HARDWARE FOR KINETIC EXPERIMENTS

The stopped-flow apparatus which was used for the studies to be discussed later in this chapter is shown in the photograph of Figure 57. It is an early version of a custom stopped-flow device built by the Hacker Machine Company. It utilizes compressed air-driven syringes which inject a total volume of about 1.2 ml per trigger. It has been fitted with a combination conductance-temperature-spectroscopy observation cell. The cell has quartz windows at either end to permit monitoring of spectroscopic data. The flow pathway in the cell was bored through four platinum disc electrodes which are sandwiched in Kel-F. The electrodes are spaced such that, by choosing appropriate pairs of electrodes, the distance between conductance monitoring points can be selected as 2, 3, 5, 7, 8, or 10 cm. In addition, all four electrodes could be used at one time with the four-lead computerized conductance system. A thermistor is imbedded in the cell wall, touching

the flow stream, to permit the cell temperature to be monitored. To minimize temperature changes, provisions are made for thermostating the cell directly or in combination with the rest of the apparatus.

At the time of its use in this study, this apparatus had three problems associated with it which adversely affected its use in kinetic studies. The first was a rather long dead time of about 40 mseconds which prevented its use in initial rate studies of fast reactions. The second problem was that more heating was generated by mixing than would normally be desirable (the exact temperature change depends on the viscosity of the solvent, but is on the order of 0.1 to 0.3°C even with thermostating). Finally, the solution was in electrical contact with the chassis of the instrument at the outlet of the cell. For solutions of high conductance, this causes the measured conductance signal to be intolerably noisy. The noise can only be eliminated by unplugging the apparatus which, of course, rendered it useless since the activation switches are electrical. Grounding the two electrodes closest to the outlet (the left electrodes in Figure 57) did diminish the noise somewhat. Nevertheless, in its condition at the time, the device could not be used for kinetic studies by conductance where the measured resistance between the two right electrodes is less than 20 K Ω . It is hoped that fitting the newer Hacker stopped flow apparatus with a conductance cell will enable these problems to be overcome. However, for the studies presented here, which involved a relatively slow reaction and solutions of low conductivity, the earlier apparatus proved suitable.

In many of the experiments which were performed with the luminol reaction, it was desirable to obtain light data from the

chemiluminescence (CL) of the reaction as well as conductance and temperature data. To implement this measurement, an auxiliary data acquisition system was added to the computerized conductance system as shown in Figure 58. The CL from the reaction was followed by positioning a Heath EU-701-30 photomultiplier module containing a 1P28A photomultiplier tube at the observation cell window. Since only the total light intensity was followed, no monochromator was needed. The current output of the photomultiplier module was amplified and converted to a voltage signal by a Heath EU-701-31 Photometric Readout Module. A supplementary amplifier, A_6 (Analog Devices 142B) was used to amplify the Photometric Readout Module output to levels near full scale for a 0 to +10 volt A/D converter. The output of amplifier A_6 is sampled by an Intronic FS 201 sample-and-hold module. When the computer outputs a convert command to the A/D converter, the STATUS output of the A/D converter goes high, causing the sample-and-hold module to hold the data until conversion is complete (when STATUS returns to low). The A/D converter, an Analog Devices ADC-12QU, was set in the 0 to +10 volt conversion range. It can perform a 12 bit conversion in 15 μ seconds. Since it is being triggered by the same signal which initiates the bipolar pulsing sequence, which requires a minimum of 30 μ seconds, no provisions for a flag for this circuit were necessary. The A/D output is transferred to the accumulator through a Heath EU-800-JL gated driver, in the same manner as the conductance data discussed in Chapter 3.

A flag is provided for triggering the timed data acquisition sequence by the stopped-flow apparatus itself. The stopped-flow device contains a relay which closes when the drive syringes close

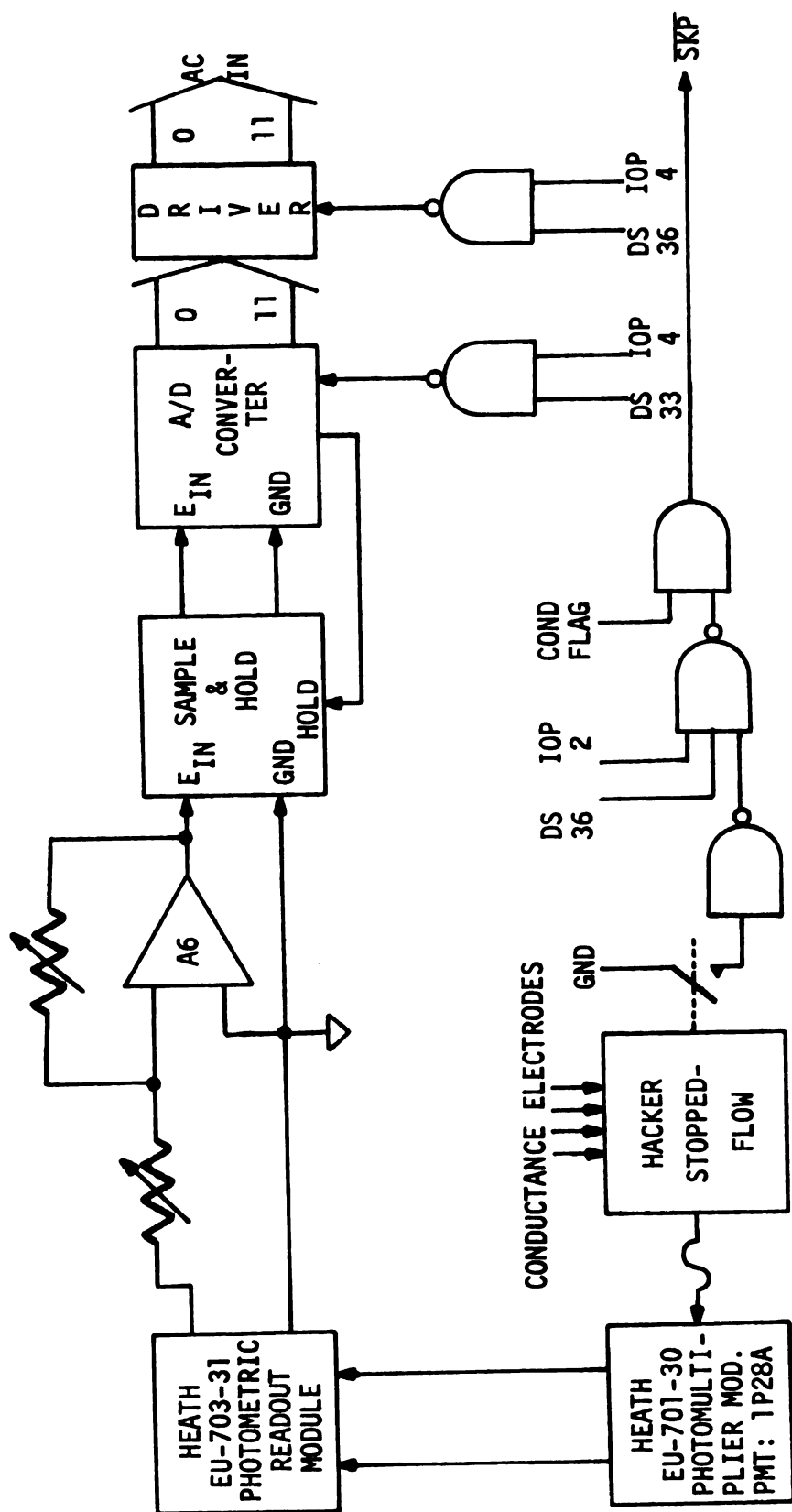


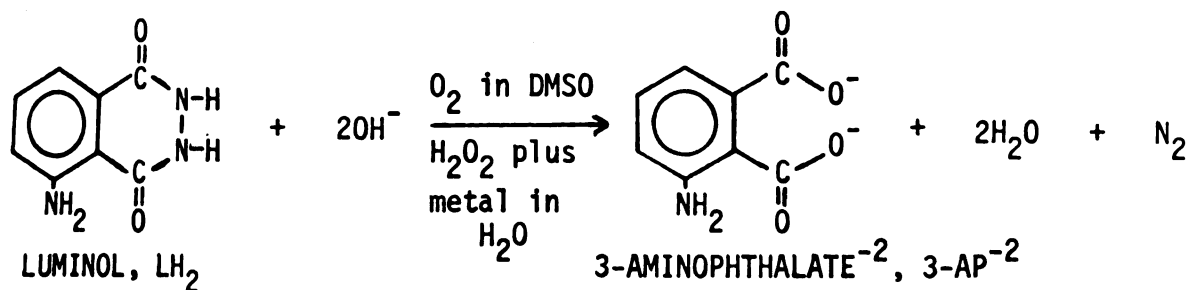
Figure 58. Luminescence Data Monitor.

and which can be used to switch a signal to some external circuitry. The card containing the logic gates of the flag circuit of Figure 58 was placed in a peripheral control slot available in the digital circuit compartment of the conductance instrument module. When the drive syringes close, the relay closes, which grounds the input to the first NAND gate and places a "1" at the input to the second NAND gate. A DS-IOP signal will cause the output of this gate to go low, which causes a skip and allows the computer to begin data acquisition. It was necessary to combine this inverse function ($\overline{SKP}$) by a logical AND with the corresponding output of the conductance flag circuit in order that one of the I/O cards already within the instrument module could be utilized with the stopped-flow flag. Later workers using the auxiliary acquisition hardware of the computerized conductance system should be able to acquire data other than simple light data with only minor modifications to the conversion system itself.

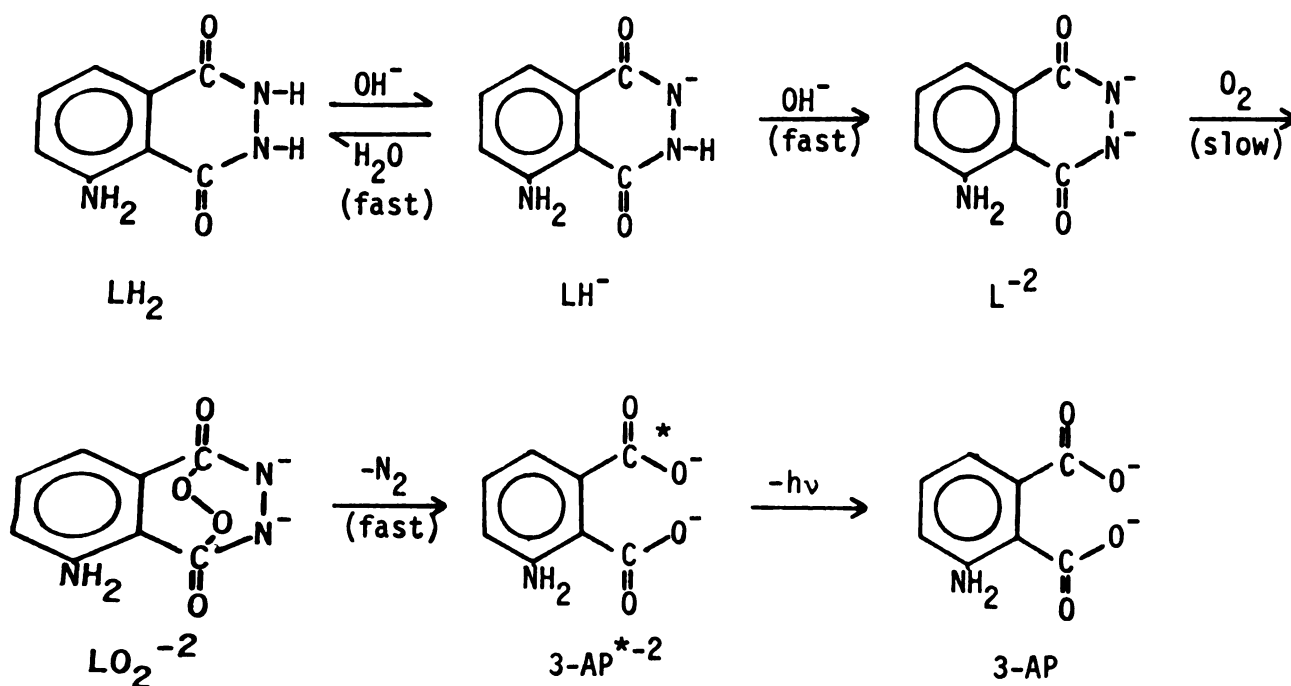
C. PREVIOUS INVESTIGATION OF THE LUMINOL REACTION

The chemiluminescence reaction of luminol with base was first observed by Albrecht (55) in 1928. Albrecht studied the aqueous reaction of luminol in alkaline solution with hydrogen peroxide in the presence of a catalyst such as potassium ferricyanide. The reaction, in both aqueous and aprotic solvent systems has the highest quantum yield (about 5%) of any non-biological CL reaction studied to date. Although many workers have investigated the CL and fluorescence spectra of this reaction system since Albrecht's initial study of it, little work has been done to define the complete reaction mechanism.

White and his co-workers (56,57) have shown that the overall reaction appears to be:



They studied the reaction in DMSO containing 30 mole percent water. The products of the reactions in aqueous, semi-aqueous, and non-aqueous media appear to be the same although the reaction in DMSO is somewhat simplified. In DMSO the reaction takes place with no stronger oxidizing agent than molecular oxygen present; no metal catalyst is required in these solutions at all. White et al. proposed the only complete reaction mechanism which has been suggested to this time for the luminol CL reaction:



They felt that the initial proton transfer occurred in two steps since, when no excess base was present to remove the second proton, no CL occurred. Thus, the LH^- species reacts only very slowly or not at all with O_2 . They were convinced that 3-AP^{-2} in an excited state was the luminescing species since they found that the CL spectrum of the reaction matched the fluorescence of 3-AP which they were also able to isolate as the almost exclusive product of the reaction. The reaction they studied was found to be first order in luminol, base, and O_2 . The CL from the reaction in DMSO is dampened by the presence of water. McCapra (58) reports the maximum of this CL to be at 425 $\text{m}\mu$ in water and 485 $\text{m}\mu$ in DMSO.

Other workers (59,60,61) have investigated the spectral characteristics of the emitter in the luminol CL reaction. The result of this work has largely been to support the mechanism of the reaction as proposed by White et al. and to reinforce the belief that 3-AP^{-2} in an excited state is the emitting species. Drew and Garwood (62) claimed to isolate a compound from the reaction mixture which contained two oxygen atoms bridged between the two nitrogens of luminol. This lead them to believe that the reaction intermediate formed after the reaction between L^{-2} and O_2 might be a bridged species. Other workers have stated their belief in this form of an intermediate, although there is some possibility that the species observed by Drew and Garwood is a simple luminol salt, solvated by peroxide. No other intermediates have been proposed.

Gorsuch and Hercules (60) have performed the only stopped-flow studies of the luminol reaction published at this time. The system they studied was the reaction between luminol and potassium tertiary

butoxide (PTB) in DMSO with 0 to 40% water present. They found the decay of 3-AP^{*-2} to be very fast and the rate of the CL decay to be determined by either the overall proton transfers, the L^{-2} reaction with O_2 , or the rearrangement of LO_2^{-2} to form 3AP^{*-2} . They assumed that for low concentrations of luminol and excess base and O_2 , the proton transfer would be very fast and, thus, not the rate determining step. Since their CL decay curves for low PTB base concentrations became first order after reaching a CL maximum, they were convinced that the rearrangement of LO_2^{-2} was controlling the reaction rate after the CL maximum. Finally, the rate constant which they proposed for this reaction in pure DMSO was $1.2 \pm 0.3 \times 10^{-1} \text{ sec}^{-1}$.

Besides the interesting phenomenon associated with the luminol CL, the reaction itself has proven to be a useful analytical tool as indicated by Seitz and Neary (63). The reaction has been used for detection of trace amounts of metal catalysts and oxidants which react with luminol to produce CL. Concentrations of Co (II) as low as 10^{-11} M , Cu (II), Ni (II), Cr (III), Fe (II), and Mn (II) from 10^{-8} to 10^{-10} M , and OCl^- , I_2 , MnO_4^- , and H_2O_2 from 10^{-9} to 10^{-10} M are detectable in the luminol CL reaction. Furthermore, these responses are, in most cases, linear over three to four orders of magnitude.

Because of its analytical usefulness and the lack of substantiating evidence concerning many of the proposed reaction mechanism steps or rates, it was thought that a study of this CL reaction by other than spectroscopic means could provide additional information unavailable to previous workers. Thus, the luminol reaction was investigated with the computerized conductance system.

STOPPED-FLOW STUDY OF THE LUMINOL REACTION BY MONITORING CONDUCTANCE, TEMPERATURE, AND CHEMILUMINESCENCE CHANGES

The first investigations of the luminol reaction with the computerized conductance system were performed with the CBTMLS program sequence. The basic aim of these early experiments was to determine if a conductance change which corresponded to the reaction could be observed. Potassium tertiary butoxide (PTB) was the chosen base. Both luminol and PTB were prepared in pure DMSO. Karl Fisher titration of DMSO showed the water content to be always less than 260 PPM.

One of the earliest reaction curves obtained from the conductance measurement is shown in Figure 59. This curve resulted from the reaction of $2.52 \times 10^{-5} \text{ M}$ luminol with 1.37×10^{-2} PTB in DMSO. (The concentration of the base was somewhat difficult to determine since there often appeared to be a residue of base remaining after attempts to dissolve it in DMSO. Furthermore, the PTB-DMSO solution would deteriorate as PTB reacted with oxygen present in solvent over the period of about an hour as also observed by Gorsuch and Hercules (60). Figure 59 shows a rapid and smooth conductance change upon mixing the reactants. 1000 points were taken, each every 0.025 seconds, for this run. When the curve is expanded by plotting only the first 100 points, most of the conductance change can be seen to occur during the first 0.25 seconds. This particular run was performed at room temperature (about 19°C) without thermostating the cell. The results appear encouraging, but it was necessary to prove that the curve was not a result of temperature changes or base or solvent dilution effects on the conductance of the species involved in the reaction.

Figure 60 shows the change in conductance of a thermistor in the

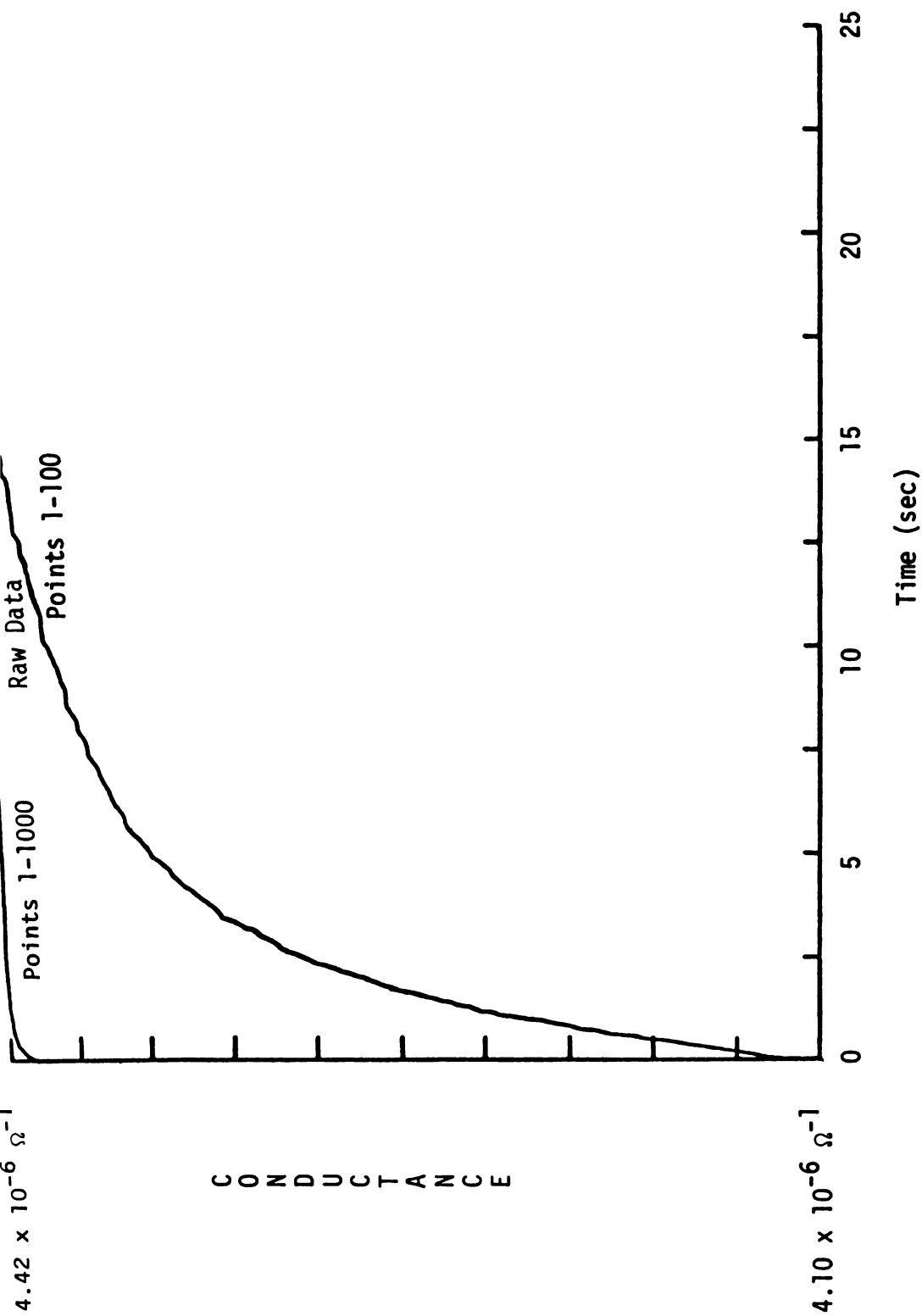


Figure 59. Stopped-flow Study of the Lumino1 System 2.52×10^{-3} M Lumino1 in DMSO 1.37×10^{-2} M K-t-BuO in DMSO Run at Room Temperature (About 19°C)

THERMISTOR CONDUCTANCE

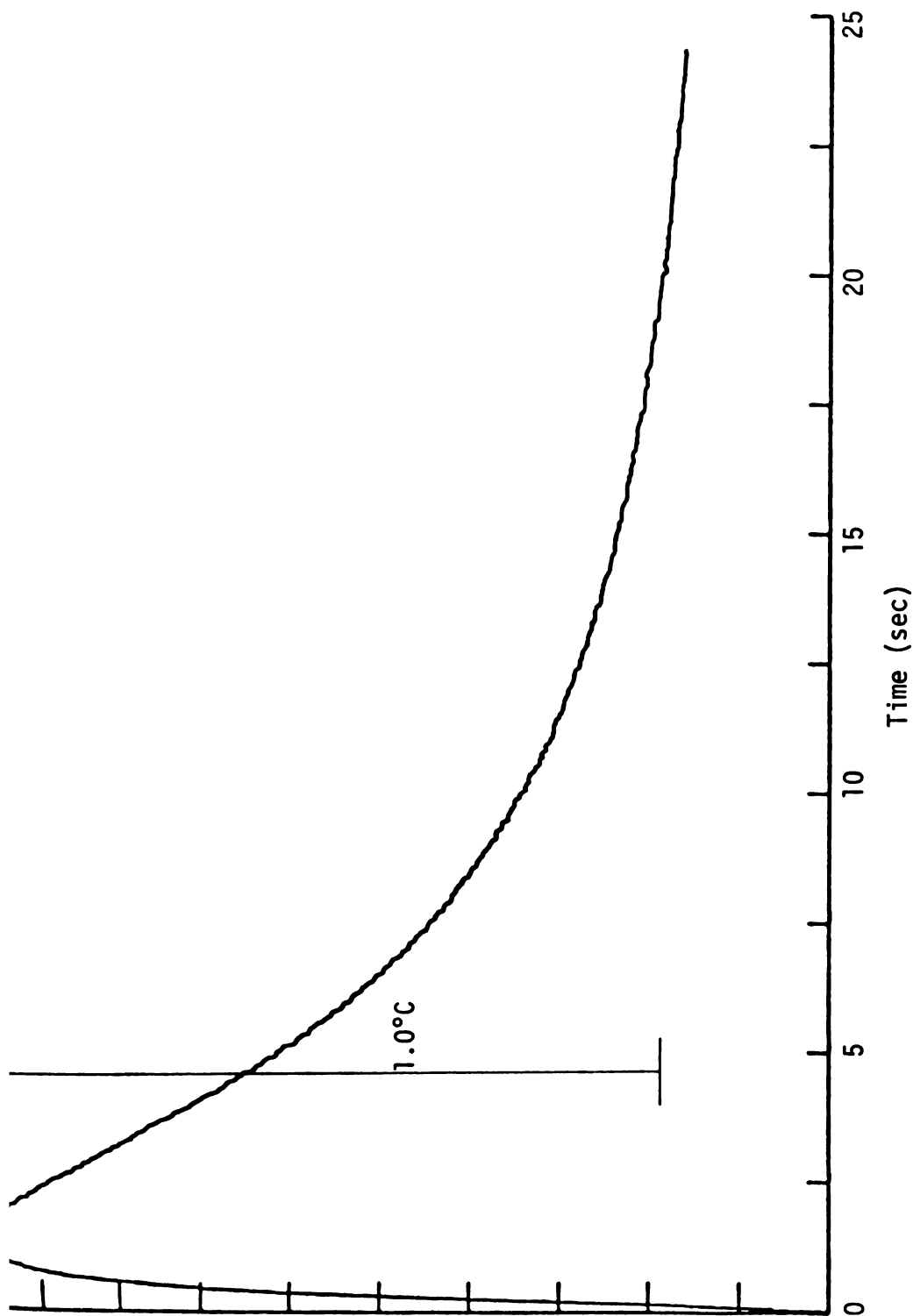


Figure 60. Temperature Change Due to Mixing DMSO Solutions of Lumino1 and K-t-BuO in Stopped Flow Apparatus. Unthermostated. Run at Room Temperature (About 19°C). (12574-2)

stopped flow cell during a reaction of two DMSO solutions of luminol and PTB in an unthermostated cell. The overall thermistor conductance change corresponded to an increase in temperature of about 0.9°C . For this run the conductance monitor and not the thermistor monitor was used to follow the change in thermistor conductance.

The overall conductance change for the reaction which occurred during the temperature change shown in Figure 60 was 14.04%. A temperature-conductance profile of the products of that reaction was measured. It was found that the conductance of these species changed $1.34\%/^{\circ}\text{C}$. Since the overall change in temperature for the reaction corresponded to 0.915°C , the conductance should change only 1.23% if the total conductance change is due to temperature changes only. Therefore, of the 14.04% observed conductance change, 87.6% of that change (or a total conductance change of 12.8%) was due to effects other than temperature effects. To eliminate the possibility that solution or mixing effects might have caused the observed conductance change, both syringes were filled with DMSO and the conductance change during stopped flow mixing was followed. No change in conductance was noted. Injecting PTB or luminol into pure DMSO with the cell thermostated produced no significant conductance change. Therefore, the conductance curve which was observed for luminol and PTB in DMSO reflected the conductance change due to the reaction.

At this point in the experimentation, it was decided to thermostat the cell separately from the rest of the stopped-flow apparatus at all times to maintain a cell temperature as constant as possible during a reaction. For the luminol-PTB system, thermostating the cell reduced the temperature change during the reaction from 0.9 to about 0.3°C .

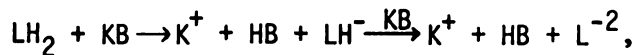
Essentially all of this temperature change was due to the exothermic reaction. This was shown by placing water in both syringes and triggering the stopped-flow apparatus. The temperature change noted was less than 0.05°C .

The experimental effort was now directed toward a determination of the particular reaction step which was responsible for the observed conductance change. A decision was made to use KOH in ethanol and luminol in DMSO as the reactants rather than PTB and luminol in DMSO for two reasons. There was some doubt concerning the concentration of the PTB since it did not appear to dissolve quantitatively in DMSO. Secondly, the base would deteriorate to one-half to one hour due to reaction with O_2 in the solvent. KOH is essentially insoluble in pure DMSO. An attempt to use KOH and luminol in 1:1 DMSO-EtOH failed to produce a reaction curve for either conductance or light. The cause of this phenomenon has not been explained. However, what appeared to be a completely suitable reaction curve (with the exception of temperature effects which could be corrected for as demonstrated in Chapter 6) was observed for KOH in EtOH and luminol in DMSO. Although considerable problems with this choice of reactants were eventually realized, the cause of the conductance curve was finally discovered during the work with this system.

The luminol-KOH reaction was endothermic as mentioned in Chapter 6. However, after temperature correction of data, a strong conductance change which was not due to temperature effects was still observed. It was therefore assumed that the system would be a reasonable one for the purpose of this study.

The possibility that the observed conductance increase resulted

from the initial proton transfer was considered. The hypothesis involved the reaction of a relatively weak base, KB (either PTB or KOH in their respective solvent systems), with luminol according to



where the conductance increase which was being observed was due to the liberation of free K^+ and L^{-2} in the solution where no B^- or K^+ was present to contribute to the conductance before reaction. Since little was known about the base strength of KOH in 1:1 DMSO-EtOH (the final solvent system after mixing), the computerized conductance system was used to investigate it. Figure 61 shows the dilution-corrected conductance curve obtained when 0.1003 M KOH in 1:1 DMSO-EtOH is added to 50 mls of 1:1 DMSO-EtOH. (Dilution correction of the data has the effect of making the X-axis on this plot, which actually corresponds to mls. of KOH added, linear in increasing concentration). The concentration range represented here runs from 0 to 0.01866 M. There is no noticeable curvature in the plot at higher concentrations which would occur if KOH were a weak electrolyte. Figure 62 shows a plot of conductance/concentration, G/C (the equivalent conductance, not corrected for cell constant) vs. $C^{1/2}$. For a 1:1 electrolyte such as KOH, the conductance should increase slowly at lower concentrations and intercept the G/C axis if the electrolyte is strong. If the electrolyte is weak, the value of G/C will increase sharply as C gets very small due to increased ionization at low concentrations. No such increase is evident on this plot for concentrations as low as 4×10^{-4} M. Other such curves were prepared for concentrations as low as 8×10^{-8} M. No rapid increase in conductance occurred as infinite

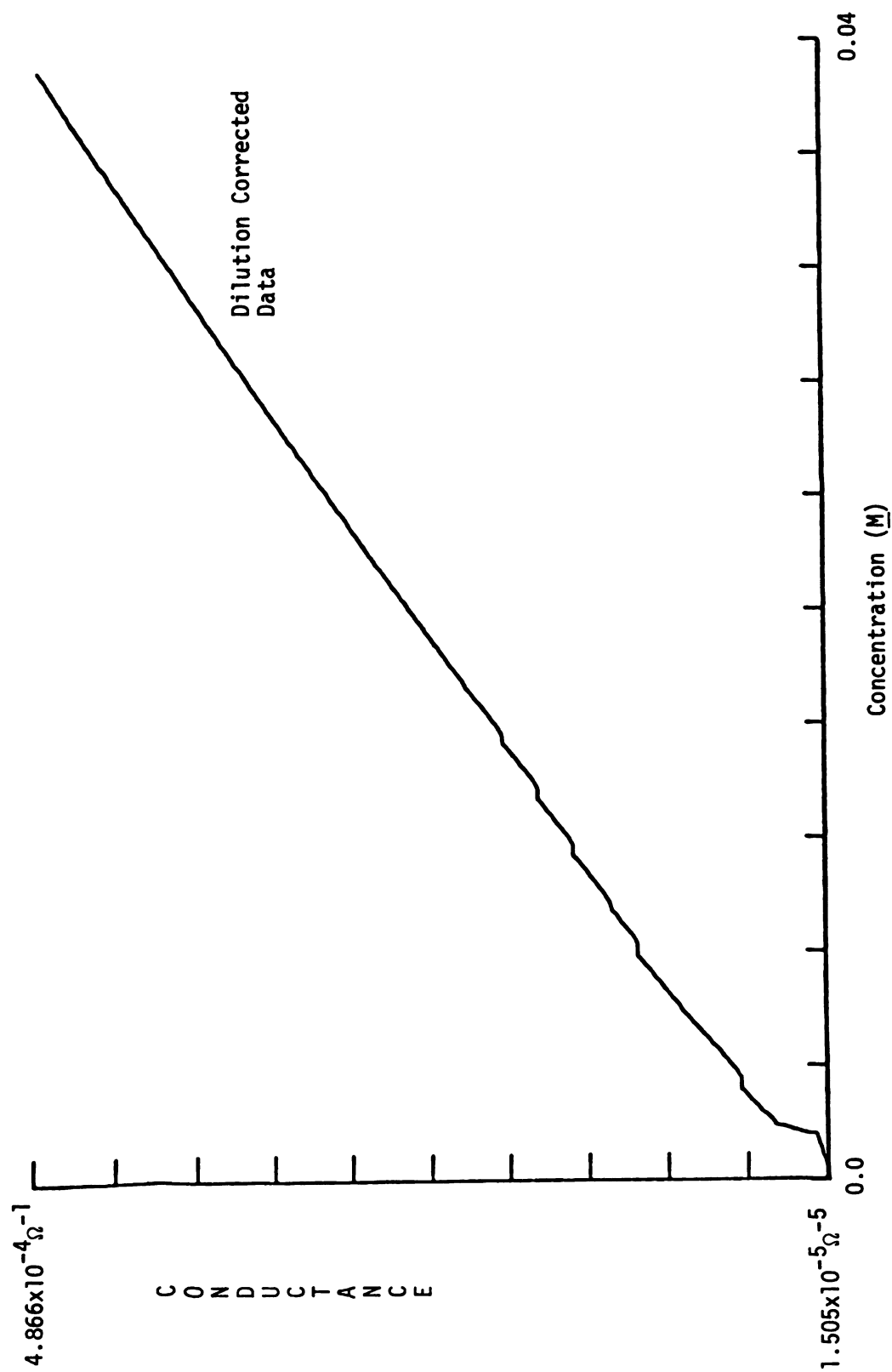


Figure 61. Conductance Change with Increasing Concentration of KOH in 1:1 DMSO-EtOH at 25.0°C.

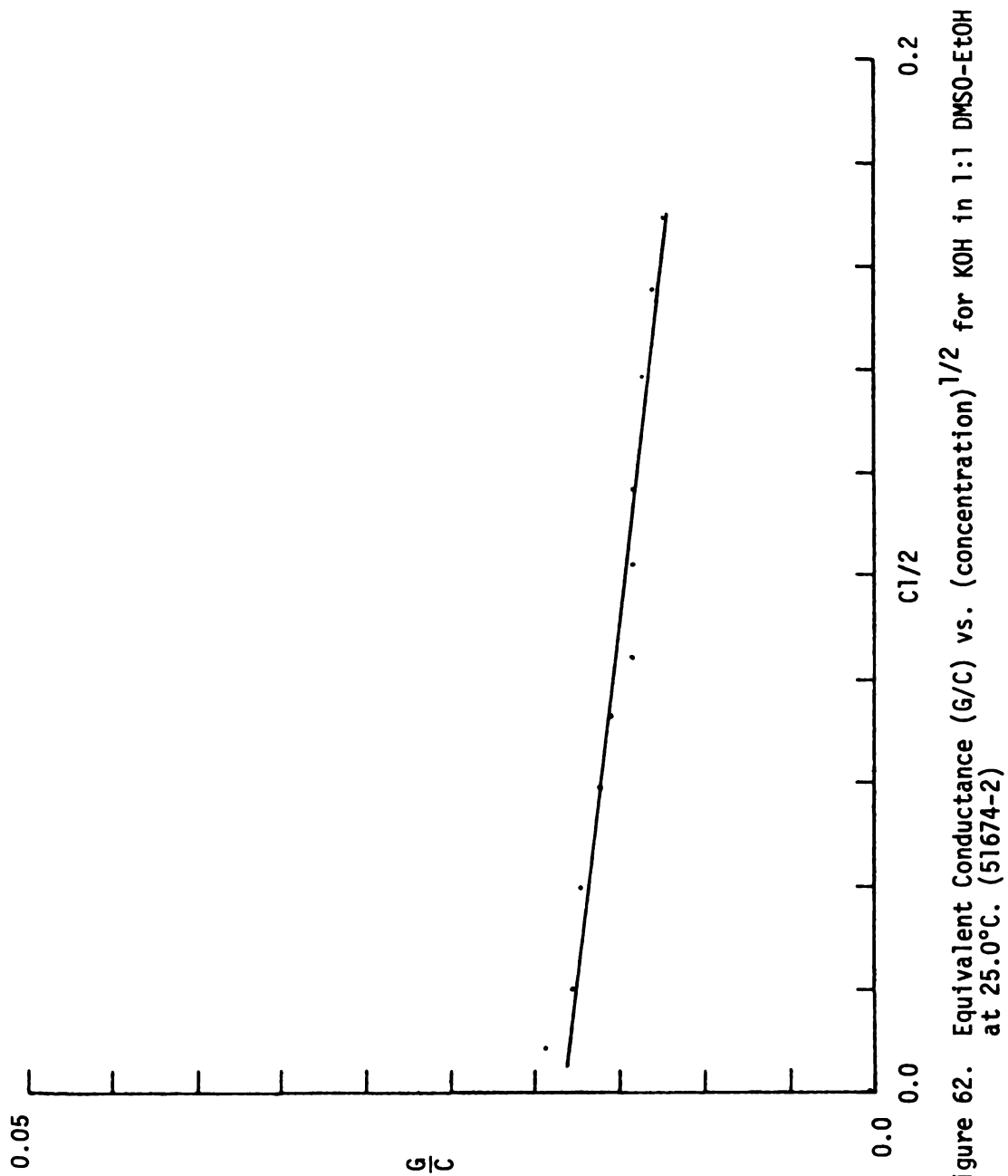


Figure 62. Equivalent Conductance (G/C) vs. $(\text{concentration})^{1/2}$ for KOH in 1:1 DMSO-EtOH at 25.0°C. (51674-2)

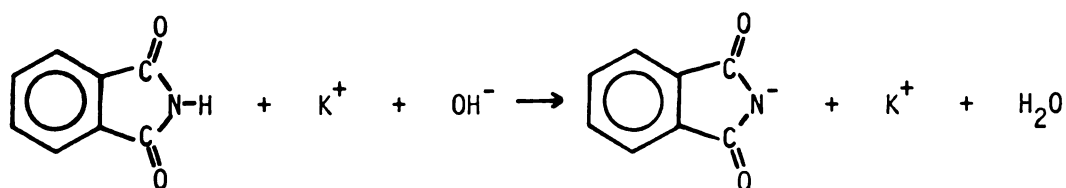
dilution was approached.

One final experiment was performed to assure the workers that KOH was indeed a strong electrolyte. A solution of KOH was prepared and its conductance measured. A quantity of dicyclohexyl-18-crown-6 sufficient to complex all of the potassium ion present was added. This crown- K^+ complex is known to be highly preferred in solution and has approximately the same conductivity as K^+ . If KOH were a weak electrolyte, there would be a significant increase in conductivity, due to ionization, when the crown ligand was put into the solution. If the KOH were already completely ionized, addition of crown ligand would, at most, cause a slight decrease in conductance by replacing the solvent modules surrounding K^+ by the somewhat larger crown ligand. The latter effect was observed experimentally, further indicating KOH to be a strong electrolyte in 1:1 DMSO-EtOH. This disproved the hypothesis that the observed conductance change was due to formation of free K^+ .

Stopped-flow studies of the reaction of phthalic acid and phthalamide with KOH were performed. In these reactions, the only species available to react are protons. In both reactions, an immediate increase in conductivity resulted, which could not be followed using this stopped-flow system. In the case of phthalic acid, both proton transfers occurred in less than 100 mseconds. For the single proton transfer from phthalamide (chemically similar to luminol but with no NH_2 group on the aromatic ring and only a single nitrogen in the heterocyclic ring), the reaction is complete in at least 100 mseconds also. Thus, it appeared certain that the conductance curve being observed for the luminol reaction was not due to proton transfer which was found to be

very fast for species which were chemically similar to luminol, compared to the rate determining step being monitored.

The stopped-flow reaction study performed with phthalamide and KOH indicated that the products of that reaction were more highly conductive than the reactants. This was demonstrated by a definite and immediate conductance increase upon mixing. Since the reaction is given by



the phthalamide anion must be of higher conductance than OH^- . This is possible due to association of the relatively heavy solvent molecules present with OH^- which has a relatively higher charge-to-mass ratio than phthalamide anion. In addition, the charge on OH^- is localized, whereas in phthalamide anion, the charge is very likely delocalized, causing phthalamide anion to be even less affected by solvent interaction. If this is the case, it could be expected that the particular form of 3-AP produced in the luminol reaction will be of higher conductivity than the reactants and that this species gives rise to the observed conductance curves.

In order to show that the major portion of the conductance curve for the luminol reaction might correspond to the production of some form of 3-AP, it was desirable to compare the time at which the conductance curve reached its maximum with the time of disappearance of the

CL. Since the CL has been convincingly shown to correspond to the formation of 3-AP*, these two curves should, in time, reflect the same formation.

Figure 63 shows the time relationship between the CL curve and the conductance curve obtained for the reaction of luminol with alcoholic KOH. The CL curve reaches its maximum in about one second and decays to near the baseline in about 2.5 seconds. The conductance curve does not level off until almost 15 seconds has elapsed. These curves were typical of the curves obtained for luminol-KOH reactions. Even with temperature correction, the conductance curve required almost 5 seconds to reach its maximum (see Figure 46, Chapter 6). Furthermore, the overall conductance change for the reaction of luminol and KOH was much greater than that for comparable concentrations of luminol and PTB, and much greater than could be explained by the conductivity differences between the reactants and the 3-AP species formed.

The cause of this phenomenon became apparent when alcoholic KOH was injected into pure DMSO in the stopped-flow apparatus. A conductivity curve similar to the one presented in Figure 63 was obtained, even when no luminol was present. This indicated that, in addition to the recognized temperature effects, there were long-range solution effects which influenced the conductivity of KOH. Subtracting the curve obtained from the run in which no luminol was present during injection from a run in which a reaction occurred produced the curve shown in Figure 64. It can be seen that the overall conductance change (from 8.8 to $9.8 \times 10^{-6} \Omega^{-1}$) is much closer to that observed for comparable concentrations of luminol and PTB. Furthermore, the conductance change levels off in about 7 seconds. Temperature correction

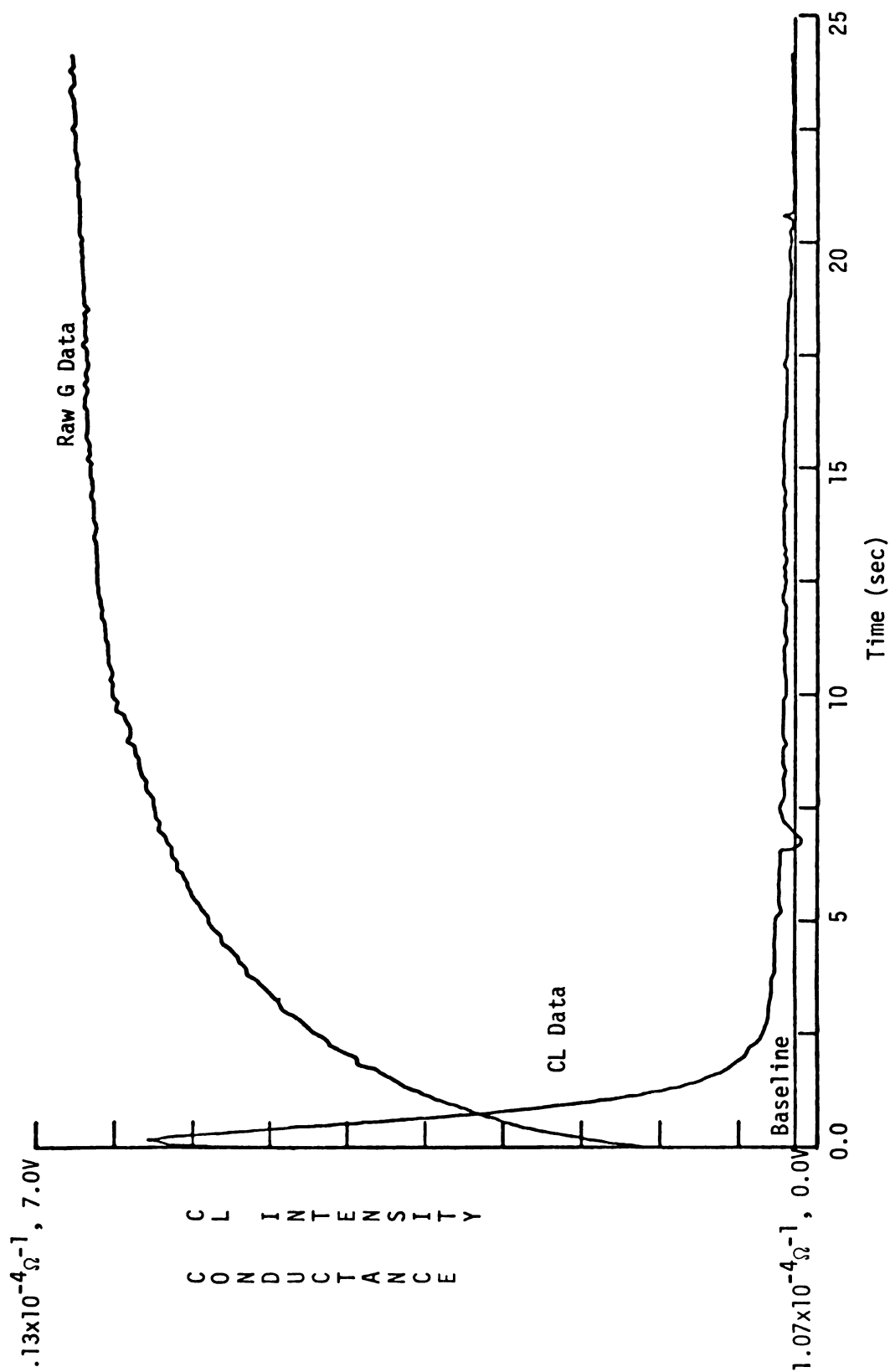


Figure 63. Conductance Curve and CL Curve Produced from the Reaction of 0.0250M Lumino1 in DMSO and 0.08814M KOH in EtOH. Cell Thermostated at 25.0°C. (52874-12)

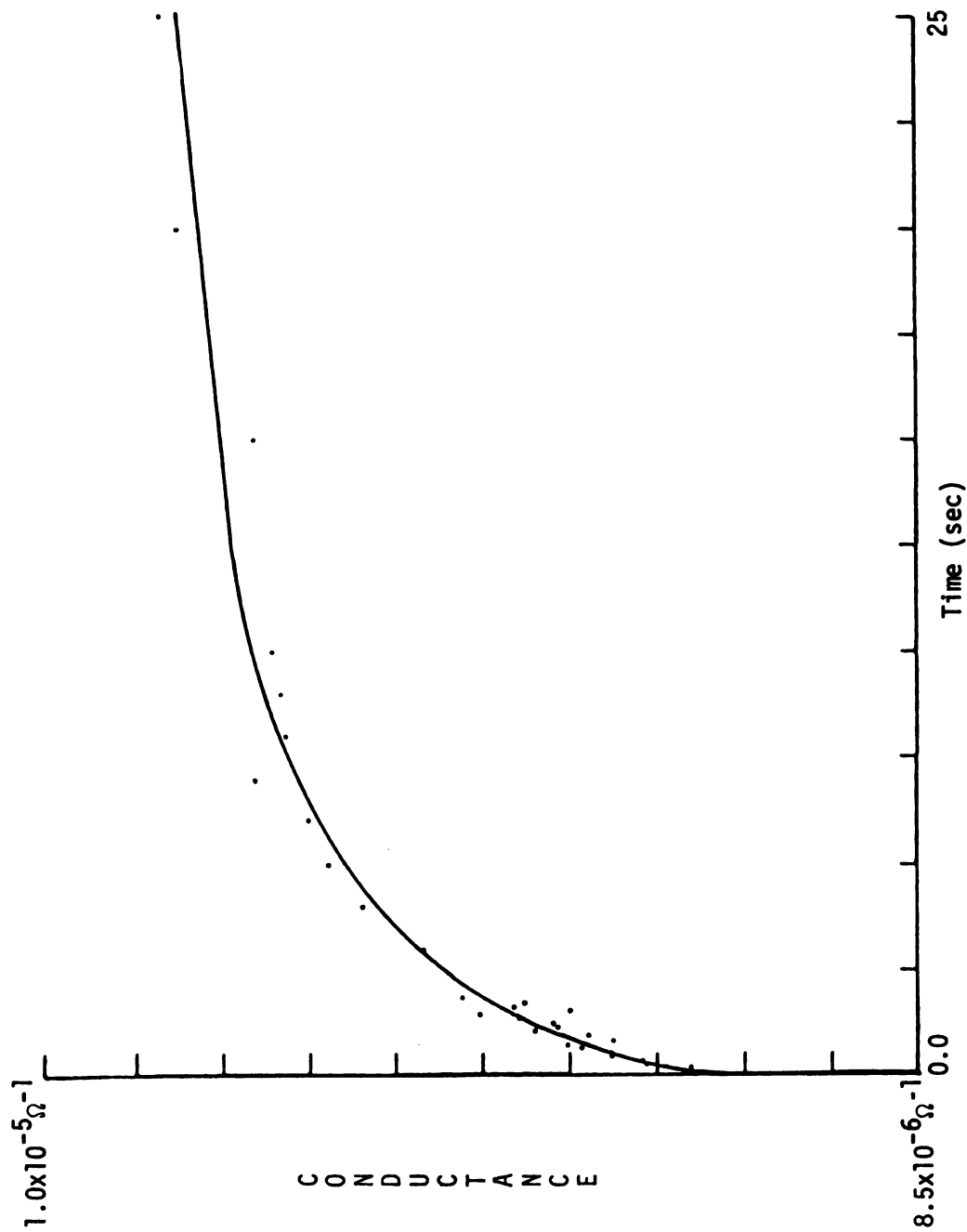


Figure 64. Conductance Change for the Reaction of 0.0250M Lumino1 in DMSO with 0.08814M KOH in Ethanol. Background Conductance due to KOH Solution Effects has been Subtracted.

causes the conductance to reach its maximum value in about 3 seconds, which corresponds to the complete decay of the CL observed for this run. Thus, what is shown in Figure 64 is the true reaction (plus temperature effects), which is unobservable on the background of the conductance effects of mixing KOH in ethanol with DMSO. For the luminol-PTB reaction, both reactants were dissolved in DMSO. Thus, the mixing effects do not occur and only the conductance change due to the reaction (plus any temperature effects) is observed. In addition, the "true" conductance reaction curve for luminol-KOH or luminol-PTB reaches a maximum at the same time that the CL is completed, substantiating the hypothesis that the conductance curve follows the production of 3-AP in some ionized form.

E. CONCLUSIONS FROM THE PRELIMINARY INVESTIGATION OF THE LUMINOL REACTION

In Section D all of the work which has been done to the present time for the investigation of the luminol reaction with the computerized conductance system was presented. From these investigations, a number of statements may be made concerning the interpretation of the data compiled during these experiments. These conclusions are listed below:

- 1) The computerized conductance system is capable of directly following a true reaction curve for the luminol-PTB reaction in DMSO. Temperature correction of data is all that is necessary to provide a true picture of the conductance change due to the reaction.
- 2) In order for studies to be pursued using PTB as the base, the solutions would have to be prepared, titrated to determine

true base concentration, and run within one-half to one hour of preparation.

- 3) The signal monitored directly by the computerized conductance system in the luminol-KOH reaction, with luminol in DMSO and KOH in EtOH, is a combination of dissolution effects, reaction effects, and temperature effects with dissolution effects predominating.
- 4) It is possible to examine the true reaction curve for the luminol-KOH reaction by subtracting the KOH dissolution curve from the overall conductance curve. However, some difficulty is encountered in performing this subtraction because of the relatively high noise levels on these two signals. These noise levels are the result of the noise imposed by the stopped-flow apparatus on conductance signals from solutions of relatively high conductivity (such as the KOH solutions used) as discussed earlier. Since the result of this subtraction is a curve two orders of magnitude smaller than either observed curve, this noise can have a significant effect on the reliability of data obtained in this way. However, the computerized conductance system has shown itself capable of resolving these differences easily. Therefore, if a new stopped-flow apparatus, which does not have these inherent noise problems becomes available, this particular reaction system and method of correction might prove to be an especially satisfactory one. This is because there is no problem associated with the quantitative preparation or short-term stability of alcoholic KOH.

- 5) The conductance curve follows the formation of 3-amino-phthalate in some form.
- 6) From the titration curve shown in Figure 56 (Chapter 7), it can be seen that phthalic acid, in the presence of excess KOH, will exist as the mono-potassium anion rather than the dianion. Since the only difference between phthalic acid and 3-AP is the NH_2 substitution on the aromatic ring, it is quite possible that the species formed in the luminol reaction is 3APK^{-1} and not 3-AP^{-2} . Furthermore, the emitting species might also be 3-APK^{*-1} and the intermediate may exist as the mono-potassium anion rather than as the dianion. Indeed, the L^{-2} species may not exist but, rather, the reactive form of luminol may be the LK^{-1} complex.
- 7) The work presented here substantiates the hypothesis of Gorsuch and Hercules (60) which states that the two protons transfers from luminol are fast compared to the rate determining step.
- 8) The conductance curve reaches a steady maximum and does not decay after the maximum, which would reflect the presence of an intermediate in the rate determining step. Thus the data produced in this study substantiate the claim of Gorsuch and Hercules that the formation of 3-AP in some excited state form is the rate determining step.
- 9) Finally, the computerized conductance system has shown that it is quite capable of following moderately fast reactions in non-aqueous media. It is expected that future workers using this system will be able to investigate even faster reactions in both aqueous and non-aqueous media with few modifications

to the software and hardware already developed. In addition, the other support software and hardware, for titration, temperature-conductance profiles, and absolute conductance measurements can all be utilized in the space of few minutes to help solve a difficult measurement or data interpretation problem.

CHAPTER 9

CBHELP: THE SYSTEM INSTRUCTIONAL PACKAGE

A. USE OF THE COMPUTERIZED CONDUCTANCE SYSTEM BY FUTURE WORKERS

The preceding eight chapters have discussed the hardware and software design of the computerized conductance system and its application in a number of chemical measurement situations. The system has been shown to be a viable analytical tool, not through its hardware, software, or performance characteristics alone, but also through its successful implementation in these chemical applications. It was stated in Chapter 1 that the computerized conductance system was not developed as a project in itself but, rather, as a means of solving certain chemical problems which included a reasonably wide range of applications. It is certainly true that the largest fraction of the time and effort which was involved in the work presented here was channeled toward development of the system and not the measurement applications discussed in the three later chapters. However, it is felt that these measurement applications were of some significance and that they indicate possible areas of further investigation by later workers. The last task which the author undertook was to insure that such investigation can proceed in a manner which expands upon the work done to this time and avoids the struggles which have already been overcome. The basic premise of this thesis has been not only the development and use of a novel measurement system, but also the creation of a system which can be utilized by both the sophisticated analytical instrumentalist and the person with little or no innovative

instrumentation experience. To insure this continuity and expanded use of the computerized conductance system, the CBHELP program was written.

The CBHELP program is an operator-interactive teaching program which describes both the theoretical and practical considerations that are important in using the computerized conductance system. It attempts to take the operating instructions and basic theory out of equipment manuals, textbooks, and journals and present it to the interested user as he asks for it. It utilizes the power of computerized conductance system display and output devices to make learning the system operation interesting and enjoyable to the student, while giving him a feel for computer-based data systems. Even if he has had no such previous experience, the CBHELP program can guide him through operation of the computerized conductance system, and the background knowledge necessary to make that operation meaningful. Furthermore, he is able to view and interact with much of the computer system while using CBHELP.

It is difficult to convey the impact of such a program, which tries to cover all facets of operation of the computerized conductance system, without actually running it for the reader. However, a valuable insight into its goals, and methods of attaining them, can be obtained by examining the design of the CBHELP program itself, discussed below.

B. CREATING THE CBHELP PROGRAM

There were several real goals to be accomplished in the implementation of the CBHELP program. These were to provide the user with virtually all of the information he would need; a) to operate the computerized

conductance system, b) to troubleshoot and routinely adjust it, c) to understand its operation, and d) to understand its theory if he were so inclined. It was hoped that in using the CBHELP program, the operator would get a feel for the computer and some of the peripheral devices associated with it. In this way the user who lacks previous experience with minicomputer systems could get over any apprehension he might have concerning such systems while his mind was diverted by the learning experience to which he was being exposed.

The possibility of constructing a program which would simply produce reams of text upon command was rejected altogether. The basic aim in using computer-assisted instructional methods is to utilize as much of the power and as many of the features of such a device as possible, in order that this teaching technique realize its maximum potential. Reading text as it is disgorged by a computer is only marginally more interesting than picking up an operation manual and reading it - and considerably more trouble to the occasional user. Because of this, a real attempt was made to allow the user to select his motion through the material by interactive dialog with the computer. He is able to branch to any subject within the knowledge bank of the program with ease. For those subjects which are discussed in several stages of detail, he is able to select the amount of detail to which he desires to expose himself at that particular time. Finally, by equipping CBHELP with a graphics facility and diagrammatical output on both the plotter and scope, and a text output on the lineprinter and teletype, the user benefits from having a diagram, flowchart, or sample data to refer to while reading a particular explanation. Thus, he is able to become more involved in the operation of other system

peripheral devices.

There were three problems to be overcome or minimized in developing the CBHELP software. These problems were: generating and editing large text files on a minicomputer system, generating and editing files which create graphical displays, and making the delay involved in accessing any given piece of information as short as possible. The solutions to these problems are discussed below:

Generating and editing large text files on the PDP-8 system:

From the very inception of the CBHELP program idea, it was known that the entire program would have to be written, debugged, and implemented with only a relatively small expenditure of the time normally devoted to chemical research. Therefore, the author was aware of the necessity of using the basic system software available to him, rather than constructing a complex set of special routines to produce the text messages and graphical displays. It is, of course, quite easy to generate small amounts of text in this computer system, either from assembly language routines or from FORTRAN READ and WRITE statements. However, these routines and statements require the data to be resident in memory when the program is compiled, assembled, and executed. Since the CBHELP program possesses over 60 line printer pages of text messages and ten graphical displays, it would have been impossible to store the total knowledge bank of the program in the computer memory from an assembled program. Thus, it was decided that the program would call text files and plotting files from some bulk storage device (DECTAPE in the system at the present time although a DISC would work just as easily and much faster) for use during the actual program operation. Routines to read data from a teletype keyboard and store

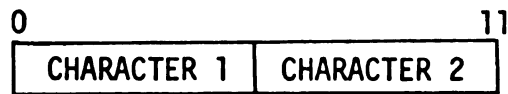
them on tape are usually easy to write since they are often a part of a language's MACROS (e.g. the TEXT command in SABR or MACRO-8) or library programs (such as the READ command for teletype input or the WTAPE and OOPEN commands for writing onto tape in FORTRAN). Unfortunately, using these does not provide the programmer with any editing facilities. If one should make a mistake while inputting characters to a text array, there would be no means of correcting that error without the user himself writing an editor into his text generation program. Writing such an editor is no simple task at all. There was no desire on the part of the author to attempt it.

However, since the OS/8 system possesses a powerful EDITOR itself, the use of this editor seemed the simplest way of generating text files for CBHELP. The original approach to using the EDITOR in this manner was to give the files EDITOR generated the ".DA" extension, used in the FORTRAN device-independent I/O routines OOPEN and IOPEN. The IOPEN routine would then simply be used to read the EDITOR-generated file as though it were an OOPEN file. It was discovered, however, that there is a basic incompatibility between the way in which the OS/8 EDITOR transfers data onto and off of DECTAPE and the way in which such data is transferred by OOPEN and IOPEN. EDITOR transfers 8-bit ASCII characters onto DECTAPE in the format shown below (64):

0		11
CH 3 MSBS		CHARACTER 1
CH 3 LSBS		Character 2

Three 8-bit characters are packed into two DECTAPE locations. On the other hand, OOPEN transfers packed ASCII characters to tape as

shown by:



if A2 format is used with a FORTRAN WRITE statement (65). Two 6-bit packed ASCII characters are generated from the input 8-bit characters. Correspondingly, when files are read with IOPEN, it assumes that it is reading packed ASCII coded as above and attempts to decode it to produce the two extra bits needed for teletype or line printer control. Using IOPEN to directly read EDITOR-generated files proved to be disastrous as IOPEN interpreted the EDITOR files incorrectly, getting illegal characters, and storing blanks in the data array. The text message was lost entirely.

It was not desirable to spend time writing a program to read directly EDITOR files using the USR routines with OS/8. Furthermore, the use of RTAPE to read EDITOR files in the CBHELP program itself was precluded since it was necessary to maintain CBHELP working files, and the program itself, in file-structured form on a single tape. If RTAPE were directly used by CBHELP, any time a text file was modified, CBHELP would have to be altered to account for the file's new location on tape.

The problem was finally solved through the use of a small but clever routine which is part of the FILEII program developed to create CBHELP. FILEII is flowcharted in Figure 65 and listed in the Appendix. The routine to create a text file from an EDITOR-generated file is option 1 of FILEII. In order to use this option, the programmer first writes a text message using the OS/8 EDITOR and stores the message on

Figure 65. FILEII Program Flowchart.

tape. The programmer must know the absolute block number on tape where the text was stored by EDITOR and the total number of OS/8 blocks (each equal to two DECTAPE blocks) that the text occupies. This information can easily be obtained by using PIP to generate a directory listing (/E option). If the particular tape has an OS/8 System Area on it, the first program will begin at absolute block 112 (decimal). The next program will begin a number of blocks equal to twice the number of OS/8 blocks beyond it, etc. If no OS/8 System Area is present on the tape, programs begin at block 14 (decimal). The user gives the block number information to FILEII along with the desired name of the text file. FILEII uses RTAPE to read the absolute blocks, which comprise the file stored by EDITOR on tape, into memory, one 128 word block at a time. It then outputs each block back onto tape, as a file-structured text message, using OOPEN. Thus, the problem of easily generating text from existing software was solved.

Generating and editing graphics files on the PDP-8 system: The author wished to be able to create graphic displays for use with CBHELP in an easy manner, similar to the generation of text files. Since plotting programs were already available which would draw straight lines between points (66), the best approach seemed to be to input the coordinates of all points for a given figure (X and Y values) to a program which would then generate a graphics file using OOPEN. The routine which performs this task is shown as option 2B with the FILEII program of Figure 65. The routine requests the desired file name and the X and Y scaling factors. The scaling factors enable the graphics designer to construct his display on a convenient sized grid and then scale it up or down to fill the scope screen. The

operator then begins to input the coordinates of all points in his figure. The plotting program accepts all positive integers from 0 to 2047 as valid grid points for the figure. Only two control numbers are needed. An $X = -1$ serves as a line segment delimiter and $X = -2$ indicates the end of a file. When a -2 is typed for the X coordinate of an X-Y pair, the program moves the output buffer onto tape. The current size of the buffer in use in FILEII and, consequently, in CBHELP is 300 points. More complex figures may be drawn using more than one file for a given display. Examples of the computer-generated graphics used with CBHELP are shown in Figures 66 and 67.

Figure 66 is a display scope photograph of the computer-generated version of the computerized conductance system block diagram shown in Figure 2 in this manuscript. It is used for a system description explanation in CBHELP much as it was used in Chapter 1. Figure 67 is a computer rendition of the pulse width selection curves appearing in Figure 30 of this thesis, as plotted by the X-Y plotter. Unfortunately, this plotter leaves something to be desired as far as pen response and position reproducibility are concerned. Nevertheless, it shows how curved lines were generated by approximation with straight lines. In addition, Figure 67 was graphically derived from Figure 30. Use of the scaling ability of FILEII enabled it to be scaled to fit the scope or plotter grid size.

Because of the large number of points which must be input to FILEII for creation of figures (Figure 66 required more than 450 points, Figure 67 more than 200 points) a simple editor facility had to be included in it. This was done with relative ease since numbers are more easily manipulated than text. As shown in Figure 65, the

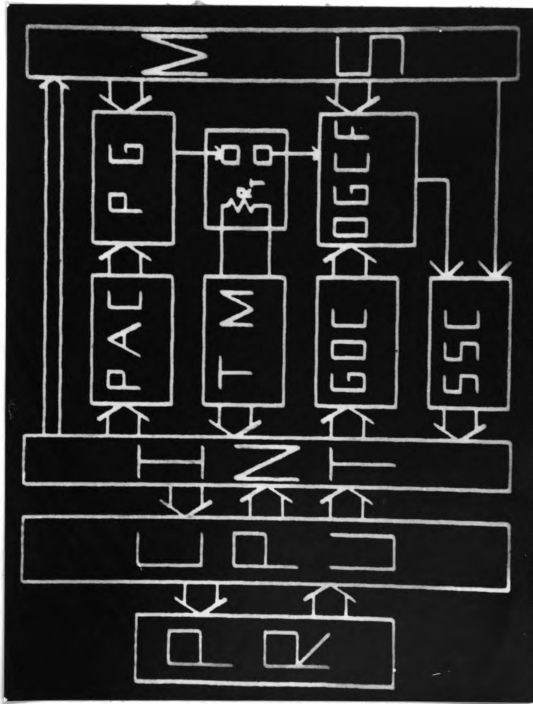


Figure 66. Photograph of CBHELP-Generated Scope Display of the System Block Diagram.

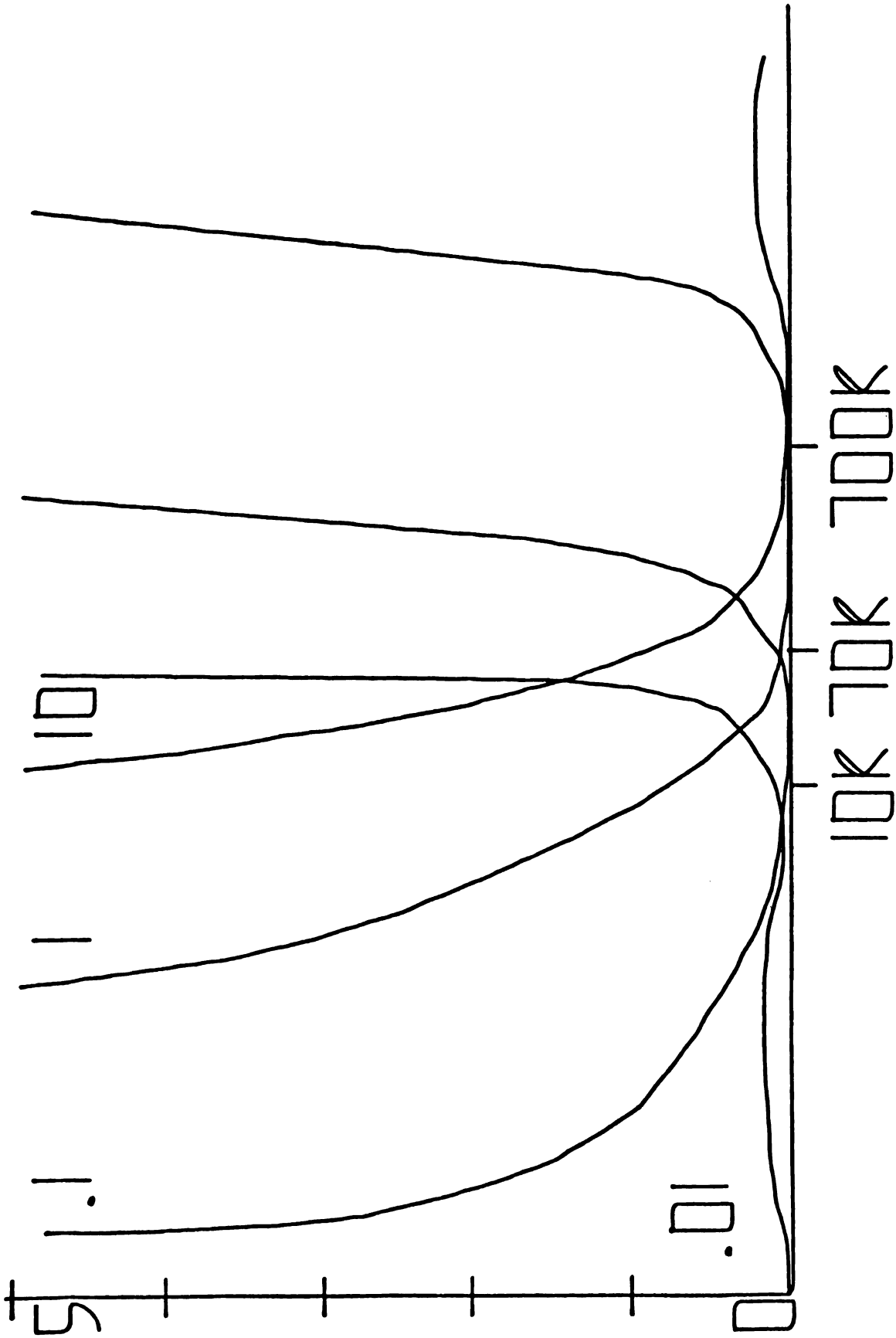


Figure 67. CBHELP Version of Pulse Width Selection Curves.

graphics editor contains provisions for searching the buffer for a given X or Y and outputting any point number where this value is encountered. In addition, editing options for changing points and scaling factors, and inserting or deleting points, are provided. Finally, the graphics files created with FILEII may be test plotted by FILEII option 3.

All of the text and graphics files used in CBHELP were generated with FILEII. There are currently 59 text messages and 10 figures used with CBHELP which were produced and incorporated into CBHELP itself with only the addition of three lines of programming to CBHELP (and, of course, recompilation).

Turn-around time in the use of CBHELP: Because file-structured data sets were used with CBHELP, and because those files are accessed via DECTAPE, the time involved between the selection of an option and its actual appearance to the user can be as long as 20-25 seconds. This lack of high-speed acquisition of files is probably the singular non-pleasing aspect of CBHELP. Faster acquisition could have been achieved with the use of RTAPE, which does not need to consult the directory before reading the tape, but, as mentioned above, this speed would have been achieved at the expense of flexibility and expandibility of the program. This problem will be completely overcome if the program is ever transferred to a disc-based system.

Core requirements: Both FILEII and CBHELP require 12 K of memory for operation.

C. USING THE CBHELP PROGRAM

It is not practical to present a flowchart of the operation of the CBHELP program in this manuscript because of the very large number of cross-interactions and branches available within it. A listing of the CBHELP program itself appears in the Appendix, however, the text messages and graphic displays, because of their large number, have not been included.

CBHELP can probably best be illustrated by guiding the reader partially through the program so that he might develop an insight into its operation.

The canister in which the CBHELP tape is contained holds instructions which should guide even the novice operator through loading the tape and calling the program. When CBHELP first responds, it asks the operator if he would like a list of instructions to follow in using the program. These instructions include turning on the scope, plotter, and line printer, how to type answers to questions, choosing an option within CBHELP, etc. If the operator wishes to view such instructions, he types "YES" and they are given to him. CBHELP follows with an initial dialog, that can be listed on the teletype, line printer, or display scope, or skipped if the operator is already familiar with the program. Next, the major options available with CBHELP are printed and the operator is asked to select one. This dialog is shown below:

PLEASE TYPE THE NUMBER OF THE OPTION YOU WISH TO SELECT:

- 1) GENERAL SYSTEM DESCRIPTION
- 2) DESCRIPTION OF THE INSTRUMENT
- 3) DISCUSSION OF CONDUCTANCE MEASUREMENT

- 4) DISCUSSION OF THE BIPOLAR PULSE TECHNIQUE
- 5) INSTRUCTIONS FOR ROUTINE OPERATION
- 6) INSTRUCTIONS FOR PULSE WIDTH SELECTION
- 7) INSTRUCTIONS FOR ROUTINE ADJUSTMENT
- 8) ERROR MESSAGE SUMMARY AND TROUBLESHOOTING
- 9) SELECTION OF A PROGRAM SET FOR SPECIFIC EXPERIMENTS
- 10) CREATING OR CHANGING A CBHELP FILE
- 11) TERMINATION OF THIS PROGRAM

:9

When the operator types a particular option number, the program branches to that subject and calls the proper files from the knowledge banks on tape for graphics displays and text messages. For example, if the operator selected option 9, because he wishes to utilize the computerized conductance system and its program set to perform a specific experiment, the computer would respond with:

```
:9
THE NAMES OF THE PROGRAMS IN THE COMPUTERIZED
CONDUCTANCE SYSTEM ARE CODED FOR
EASY RECOGNITION. WOULD YOU LIKE
AN EXPLANATION OF THIS CODE? YES
OUTPUT ON LPT=1, ON TTY=0:1
```

If the operator types "YES" an explanation of the program nomenclature is generated. If he types "NO", the program moves immediately to output the list of available program sets, shown in Figure 68. If the operator were to select, for example, program set 3, CBHELP produces the temperature-conductance program flow chart shown in FIGURE 69. The operator is then asked:

WOULD YOU LIKE AN EXPLANATION OF THE PROGRAM SET?

If the operator answers "YES" such an explanation is produced for him. It is in this way that multi-level explanations are built into CBHELP.

- 1)A TITRATION
- 2)A DETERMINATION OF DISSOCIATION CONSTANTS, EQUIVALENT IONIC CONDUCTIVITIES, OR THE RELATIVE STRENGTH OF AN ELECTROLYTE
- 3)A TEMPERATURE-CONDUCTANCE PROFILE FOR DETERMINATION OF CORRECTION PARAMETERS TO BE USED WITH VARIOUS DATA ANALYSIS ROUTINES, OR FOR A QUALITATIVE OR QUANTITATIVE EXAMINATION OF THE CONDUCTANCE BEHAVIOR OF AN ELECTROLYTE WITH CHANGES IN TEMPERATURE. THIS SEQUENCE INCLUDES THE ARRAY ARRANGER ROUTINE FOR LINEARIZING A NON-LINEAR TEMPERATURE CHANGE TO PREVENT WEIGHTING OF DATA IN ANY PARTICULAR TEMPERATURE REGION.
- 4)A TEMPERATURE-CONDUCTANCE RUN AS IN (3) BUT WITHOUT ARRAY ARRANGING THE DATA (USED WHERE THE TEMPERATURE CHANGE HAS BEEN LINEAR).
- 5)A KINETICS RUN IN WHICH ONLY CONDUCTANCE AND TEMPERATURE ARE TO BE MONITORED AND IN WHICH ONLY CONDUCTANCE IS TO BE PLOTTED.
- 6)A KINETICS RUN IN WHICH AUXILLARY DATA, IN ADDITION TO CONDUCTANCE AND TEMPERATURE DATA, IS TO BE TAKEN, OR IN WHICH TEMPERATURE DATA WILL BE PLOTTED.
- 7)CHROMATOGRAPHIC MONITORING
- 8)INSTRUMENTAL NOISE DETERMINATION
- 9)INSTRUMENTAL ACCURACY DETERMINATION
- 10)AVERAGE OF N DISCRETE MEASUREMENTS
- 11)INSTRUMENTAL FUNCTION TEST

Figure 68. Program Set Selection Options in the CBHELP Program.

THIS IS THE PROGRAM FLOW CHART FOR THE TEMPERATURE-CONDUCTANCE DATA ACQUISITION AND ANALYSIS, WHICH USES THE ARRAY ARRANGER, CBTALR, TO PREVENT ACCIDENTAL WEIGHTING OF POINTS DURING THE CURVE FITTING.

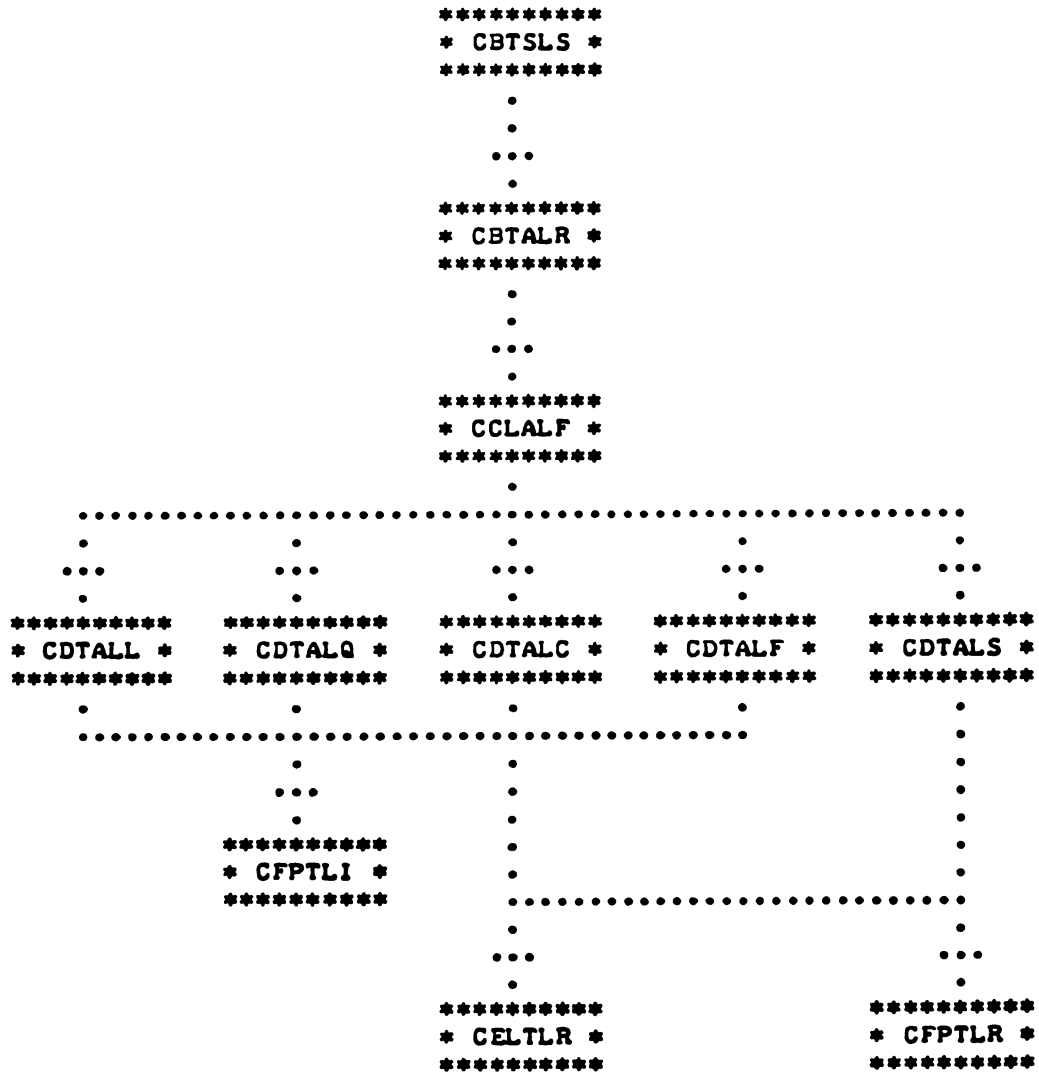


Figure 69. CBHELP-Generated Program Flowchart for Temperature-Conductance Profile Measurement and Analysis.

If the operator types "NO", he is able to select another of the 11 programming options or he may return to the selection of a different one of the major options. If he were to choose other options within the option 9 program selection routine, he might receive flowcharts and explanations for other types of experiments, and even graphic displays depicting a sample titration curve with explanation of its various regions, or a sample strong-weak electrolyte comparison curve and so forth. Any of the other major 11 options produce figures and text and interactive dialog as does option 9. CBHELP will even check to see if the line printer is turned on and tell the operator to activate it if he has requested output on it and has failed to turn it on previously.

It can be seen that most of the subjects which one would be interested in with respect to utilization of the computerized conductance system are included in CBHELP. Admittedly, CBHELP lacks much of the sophistication of many institutional computer-based teaching systems such as, for example, the Plato IV system at the University of Illinois (67). CBHELP does go much further in using the computer system to instruct an operator in the use of the instrumentation controlled and monitored by that computer system than any device which computer-based instrument manufacturers have provided with their systems. It serves an important function by largely assembling the theory and techniques of the computerized conductance system into one package to present to the prospective or veteran user. In addition to this major purpose, it is possible that CBHELP will point the way toward instrumentation systems which are still more interactive with the operator. There is much to be gained in continuity of instrument use,

a steady source of reference material, and user acclimation to a new system by permitting "smart" instrumentation systems to tell their own story to prospective "clients". It seems somewhat short-sighted to build an elaborate and useful computer-interactive laboratory measurement system and provide with it stacks of manuals in conventional form. Such systems are often so complex that it is impossible for a casual user to delve through these mounds of literature, or even for a dedicated user to troubleshoot or expand his use of the system efficiently. Thus, it is hoped that CBHELP will be viewed as movement toward more complete user-system interaction, where the system is capable of that level of interaction.

CONCLUSION

The capabilities of the computerized conductance system have been demonstrated in a significant number of diverse applications. It has proven to be a sufficiently powerful system to arouse the interest of other workers who will benefit from its continued usefulness as a dynamic measurement system. Because of the nature of the system itself, it is impossible to state that either the instrumental work is complete, or that all areas of possible application have been defined. Although the hardware portion of the system has remained relatively unchanged during these studies, it is possible that some modification of the circuitry will be undertaken by later workers to make it operate with other computer systems, expand its operating range, possibly incorporate bipolar current techniques for high conductance measurements and so forth. The author has shown that the system, as it developed over the past three and one-half years, included a number of innovations which give it the flexibility to perform meaningful measurements for operators of various backgrounds and interests. Finally, the success of the project serves to legitimize the pursuit of instrumentation research for chemists by showing that such research can produce devices which not only perform sophisticated measurements for the scientist with an instrumentation orientation, but continue to be of use to other workers as important laboratory tools after the instrumentation chemist has completed his work with that particular measurement system.

REFERENCES

REFERENCES

1. Controller design by Hahn, B. K., Interface design by Kelly, T.
2. Interface design by Rabb, M., and Hahn, B. K.
3. Interface design by Davis, R. and Hahn, B. K.
4. Designed by Last, T.
5. Hahn, B. K. and Enke, C. G., Anal. Chem. 45, 651A (1973).
6. Heath-Schlumberger product bulletin 595-1422. Computer Interface ADD (1972)
7. Program written by Hahn, B. K.
8. Livingston, J., Morgan, R., and Lammert, O. M., J. Am. Chem. Soc. 48, 1220 (1926).
9. Kohlrausch, F., Wied. Ann. 69, 249 (1893).
10. Johnson, D. E. and Enke, C. G., Anal. Chem. 42, 329 (1970).
11. Jones, G. and Bollinger, G., J. Am. Chem. Soc. 53, 411 (1931).
12. Washburn, E., and Bell, J., J. Am. Chem. Soc. 35, 177 (1913).
13. Washburn, E., J. Am. Chem. Soc. 38, 2431 (1916).
14. Jones, G. and Josephs, R., J. Am. Chem. Soc. 50, 1049 (1948).
15. Shedlovsky, T., J. Am. Chem. Soc. 52, 1793 (1930).
16. Schmidt, K., Rev. Sci. Instr. 47, 671 (1966).
17. Bentz, A. J., Sandifer, J. R., and Buck, R. P., Anal. Chem. 46, 543 (1974).
18. Johnson, Donald E., Ph.D. Thesis, Michigan State University (1970).
19. Daum, P. H. and Nelson, D. F., Anal. Chem. 45, 463 (1973).
20. Philbrick Researches, Inc. Applications Manual for Computing Amplifiers, Boston: Nimrod Press Inc., 1966. I.26.
21. Perone, S. P., Anal. Chem. 43, 1288 (1971).
22. Frazer, J. W., Anal. Chem. 40, 8, 27A (1968).
23. Venkataraghavan, R., Klimowski, R. J., and McLafferty, F. W., Accounts Chem. Res. 3, 158 (1970).

24. Dessy, R. E. and Titus, J. A., Anal. Chem. 45, 2, 124A (1973).
25. Dessy, R. E. and Titus, J. A., Anal. Chem. 46, 3, 294A (1974).
26. Ramaley, L. and Wilson, G. S., Anal. Chem. 42, 606 (1970).
27. Parker, R. A. and Pardue, H. L., Anal. Chem. 44, 1622 (1972).
28. DeVoe, J. R., Shideler, R. W., Ruegg, F. C., Aronson, J. P., and Shoenfeld, P. S., Anal. Chem. 46, 509 (1974).
29. Heath-Schlumberger equipment bulletin 595-1422, Computer Interface ADD, "Modular Component Cards" (1972).
30. Lauer, G., and Osteryoung, R. A., Anal. Chem. 40, 10, 30A (1968).
31. Perone, S. P., Jones, D. O., and Gutknecht, W. F., Anal. Chem. 41, 1154 (1969).
32. Keller, H. E. and Osteryoung, R. A., Anal. Chem. 43, 342 (1971).
33. Perone, S. P. and Eagleston, J. F., J. Chem. Ed. 48, 317 (1971).
34. Toren, E. C., Jr., Carey, R. N., Sherry, A. E., and Davis, J. E. Anal. Chem. 44, 339 (1972)
35. Hicks, G. P., Eggert, A. A., and Toren, E. C., Jr., Anal. Chem. 42, 729 (1970).
36. Keller, H. E., Courtois, G. E., and Keller, J. E., Chem. Instr. 4, 269 (1972).
37. Digital Equipment Corporation. Introduction to Programming, Maynard, Mass.: Digital Equipment Corporation, 1972, Ch. 9.
38. Digital Equipment Corporation. Programming Languages. Maynard, Mass.: Digital Equipment Corporation, 1972. pp. 13-37 to 13-39.
39. Ibid. pp. 13-39 to 13-42.
40. Ibid. p. 15-80.
41. Ibid. pp. 15-73 to 15-76.
42. Ibid. p. 15-80.
43. Kelly, P. C. and Horlick, Gary, Anal. Chem. 45, 518 (1973).
44. Malmstadt, H. V., Enke, C. G., Crouch, S. R., and Horlick, G. Optimization of Electronic Measurements, Module 4, Menlo Park, Calif., W. A. Benjamin, Inc., 1974.
45. Digital Equipment Corporation. "MAINDEC Test", 1968.

46. Hahn, B. K., unpublished program. 1972.
47. Hildebrand, F. B., Numerical Analysis, New York: McGraw-Hill Book Company (1974). pp. 549-559.
48. Franklin, E. C., J. Phys. Chem. 15, 675 (1911)
49. Armitage, P. T. and French, C. M., J. Chem. Soc., 743 (1963)
50. Falkenhagen, H., Electrolytes, London: Oxford University Press, (1934), pp. 200-201.
51. Hall, J. L., Gibson, J. A., Jr., Wilkinson, P. R., and Phillips, H. O., Anal. Chem. 26, 1484 (1954).
52. Farrow, R. N. P. and Hill, A. G., Analyst. 90, 210 (1965).
53. Levine, S. L. and Golden, H. J., Anal. Letters, 1, 39 (1967)
54. Bauer, W. E., private communication.
55. Albrecht, H. O., Z. Phys. Chem. 136, 321 (1928).
56. White, E. H. Zafirion, O., Kagi, H. H., and Hill, J. M., J. Am. Chem. Soc. 86, 940 (1964).
57. White, E. H. and Bursey, M. M., Ibid., p. 941.
58. McCapra, F., Quarterly Reviews, 485 (1966).
59. Beck, M. P. and Joo', F., Photochemistry and Photobiology, 16 491 (1972).
60. Gorauch, J. D. and Hercules, D. M., Photochemistry and Photobiology, 15, 567 (1972).
61. Lee, J. and Seliger, H. H., Photochemistry and Photobiology, 15, 227 (1972).
62. Drew, H. D. K. and Garwood, R. F., J. Chem. Soc., 791 (1938).
63. Seitz, W. R. and Neary, M. P., Anal. Chem. 46, 188A (1974).
64. Digital Equipment Corporation, OS/8 Software Support Manual, Maynard, Mass.: Digital Equipment Corporation, 1972. p. A-5.
65. Digital Equipment Corporation, Programming Languages, op. cit. pp. 13-18 to 13-20.
66. Hahn, B. K., XYSYS.SB and SCOPE.SB Plotting Routines, unpublished programs.
67. Smith, S. G. and Ghesquiere, J. R. Computer-Assisted Instruction in Chemistry, Part B: Applications, ed. Mattson, J. S., Mark, H. B., Jr., and MacDonald, H. C., Jr. New York: Marcel Dekker, Inc., 1974, Chapter 2.

CBTSLS
PROGRAM LISTING


```

S /PROGRAM NAME: C3TSLS.FT
S /FORTRAN-943R1 KEITH J. CASERTA 1974
S /THIS IS THE GENERAL FORM OF THE BASIC DATA ACQUISITION PROGRAM
S /FOR THE COMPUTERIZED CONDUCTANCE SYSTEM.
S /IT BEGINS WITH A PRELIMINARY SCAN OF THE CELL, DURING WHICH
S /THE OPTIMIZED CIRCUIT PARAMETERS FOR EACH OF FOUR PULSE
S /WIDTHS ARE DETERMINED AND STORED.
S /THESE VALUES ARE PRINTED. THE AVAILABLE OPTIONS AT THIS POINT:
S /1)AVERAGE OF AN INPUT NUMBER OF SCANS
S /2)RESTART
S /3)TIMED DATA ACQUISITION OF UP TO 500 POINTS OF UP TO
S / 2047 ACQUISITIONS PER POINT FOR BOTH COND AND TEMP
S / IF ZERO IS INPUT AS THE # OF TEMP POINTS, TEMP MEASUREMENT
S / IS SKIPPED DURING TDA
S /4)RETURN TO MONITOR
S /DATA IS FINALLY WRITTEN ONTO TAPE FOLLOWING TDA AND
S /MAY BE TREATED BY A VARIETY OF ANALYSIS ROUTINES.
S /
COMMON NARA
DIMENSION NARA(2046)
DIMENSION I PARA(4), I PH(4), I PWP(4), I IVP(4), I UNIT(4)
S JPDF CCFP 6321 /CLEAR COND FLAG, CLEAR PI ENABLE
S JPDF 3CDR 6322 /GATE CONDUCTANCE DRIVER
S JPDF CCFPD 6323 /CCFP + 3CDR
S JPDF ECPI 6324 /ENABLE COND PROGRAM INTERRUPT
S JPDF CCFGD 6327 /CCFP + 3CDR + ECPI
S SKPDF TCFL 6331 /TEST CONDUCTANCE FLAG
S JPDF TOST 6332 /TURN OFF SEQUENCE TRIGGER
S JPDF TRIG 6334 /TRIGGER SEQUENCE
S SKPDF TTFL 6341 /TEST TEMPERATURE FLAG
S JPDF LIVO 6342 /LATCH I/V, OFFSET
S JPDF LPHW 6344 /LATCH PH, PW
S JPDF ETP1 6351 /ENABLE TEMP PROGRAM INTERRUPT
S JPDF CTFPG 6352 /CLEAR TEMP FLAG, PI ENABLE, GATE DRIVER
S JPDF TTAD 6354 /TRIGGER TEMP A/D CONVERSION
S JPDF TFPQT 6356 /CTFPG + TTAD
S JPDF TIT 6361 /TITRATE
S SKPDF SKPSF 6362 /SKIP ON STOPPED FLOW SIGNAL
S JPDF LPSET 6121 /LOAD THE CLOCK PRESET REGISTER
S JPDF CLCL 6122 /CLEAR THE CLOCK
S JPDF ICNTR 6123 /INITIALIZE THE COUNTER
S JPDF CLCIC 6124 /CLEAR CLOCK AND INITIALIZE COUNTER
S JPDF LCNTR 6125 /LATCH THE COUNTER
S JPDF RCTRL 6126 /READ THE COUNTER LATCH
S JPDF RCNTR 6127 /READ THE COUNTER
S JPDF LCTRL 6131 /LOAD CONTROL REGISTER
S SKPDF SKPOF 6132 /SKIP ON OVERFLOW
S SKPDF SKPOE 6133 /SKIP ON OVERFLOW ERROR
S JPDF CLJFE 6134 /CLEAR OVERFLOW AND OVERFLOW ERROR FLAGS
S SKPDF SKPTR 6135 /SKIP ON TIME BASE FLAG
S SKPDF SKTBE 6136 /SKIP ON TIME BASE ERROR FLAG
S JPDF CLTBE 6137 /CLEAR T.B. AND T.B. ERROR FLAGS
S JPDF MUY 7405 /MULTIPLY
S JPDF DVI 7407 /DIVIDE
S JPDF VMI 7411 /NORMALIZE
S JPDF SHL 7413 /SHIFT LEFT
S JPDF ASR 7415 /ARITHMETIC SHIFT RIGHT
S JPDF LSR 7417 /LOGICAL SHIFT RIGHT
S JPDF MOL 7421 /LOAD MULTIPLIER QUOTIENT
S JPDF SCL 7403 /STEP COUNTER LOAD FROM MEMORY
S JPDF SCA 7441 /STEP COUNTER LOAD INTO AC

```

```

S      JPDEF  HQA      7301  /HQ LOAD INTO AC
S      JPDEF  ERASE    6034  /ERASE DISPLAY SCOPE
S      JPDEF  STORE    6037  /SET SCOPE IN STORE MODE
S      JPDEF  ANDI     0400  /INDIRECT AND
S      JPDEF  TADI     1400  /INDIRECT TAD
S      S<PDI  ISZI     2400  /INDIRECT ISZ
S      JPDEF  DCAI     3400  /INDIRECT DCA
S      JPDEF  JMSI     4400  /INDIRECT JMS
S      JPDEF  JMPI     5400  /INDIRECT JMP
S      ABSY4  AINC     0012  /AUTO INCREMENT REGISTER
S      ABSY4  PWP      0074  /PW POINTER
S      ABSY4  PWP      0075  /PW POINTER
S      ABSY4  IVP      0076  /I/V POINTER
S      ABSY4  JNITS    0077  /OFFSET JNITS POINTER
S      ABSY4  ASET     0100  /GENERAL POINTER
S      ABSY4  SPARA    0101  /PARAMETER POINTER
S      ABSY4  SPPU     0102  /INDIRECT ADDRESS IN FIELD 1 POINTER
S      ABSY4  SPPW     0103  /INDIRECT ADDRESS IN FIELD 1 POINTER

```

```

S /
S /
S /THE PRELIMINARY SCAN ROUTINE BEGINS HERE
S /
S /

```

```

100      JD=0
        LD=0
        XT=0.
        PW=.001
S      TAD ATHRE      /SET UP 4 PW'S POINTER
S      DCA I BTHRE
S      JMP AAYY
S      ATHRE,7774
S      BTHRE,T4RE
S      AAYY, JMS TYP3      /30 ASK FOR A "Q"
S      CLA CLL
S      TAD (0200          /SET UP PARAMETER POINTER
S      DCA SPARA
S      DCA PWP           /SET INITIAL PW
S      =2, CLA CLL
S      TAD (0400          /SET PW POINTER
S      DCA P4P
S      TAD (0401          /SET I/V POINTER
S      DCA IVP
S      TAD (7400          /SET UNITS POINTER
S      DCA JNITS
S      6211              /ZERO THE PARA WORD LOC FOR THIS RUN
S      3501
S      6201
S      50      JD=JD+1
        PW=PW+10.
S      AAJ, CLA CLL
S      IAC
S      LIVO          /OFFSET=0J I/V: 1MA=10V
S      WA, ISZ ASET    /LATCH OFFSET=0J I/V: 1MA=10V
S      JMP 4A          /WAIT FOR RELAYS TO SETTLE
S      WY, ISZ ASET
S      JMP 4Y
S      AD, CLA CLL
S      TAD P4P          /PW POINTER
S      RAL
S      SZL              /SET P4 INSTRUCTION
S                      /MAX PW YET,

```

```

S      JMP I QGAIN      /YES, INCREASE GAIN OF I/V
S      DCA PH           /NO, CONTINUE
S      IAC              /ADD 1
S      5211             /CHANGE TO DATA FIELD 1
S      1501             /ADD PH INFO TO PARAMETER WORD
S      3501
S      5201             /CHANGE TO DATA FIELD 0
S      TAD PH           /SET PH
S      TAD PH           /LATCH PH, PH
S      -PHW             /WAIT FOR RELAYS TO SETTLE
S  WB,  ISZ ASET
S      JMP 49
S  WZ,  ISZ ASET
S      JMP 4Z
S      CLA CLL
S      TRIG              /PULSE TRIGGER
S  AE,  TCFL             /TEST FLAG
S      JMP AE
S      CCFPD             /CLEAR FLAG, GATE DRIVER
S      IAC              /CHECK INPUT
S      SNA              /IS A/D NEARLY PEGGED.
S      JMP JFF           /YES, ADD OFFSET
S      JMP AD            /NO, INCREASE PH
S  QGAIN, JAIN           /ADDRESS OF ADD GAIN ROUTINE
S  /
S  /SUBPROGRAM GAIN
S  /THIS SUBPROGRAM INCREASES GAIN OF I/V AMP
S  /
S      PAGE
S  GAIN, CLA CLL
S      TAD IVP           /I/V POINTER
S      RAL              /SET I/V INSTRUCTION
S      SZL              /IS MAX GAIN APPLIED.
S      JMP I PTC         /YES, GO TELL
S      DCA IVP           /NO, CONTINUE
S  #52, TAD JAPT         /ADD 1 TO GAIN POINTER
S      5211             /CHANGE TO DATA FIELD 1
S      1501             /SET PARA WORD TO PROPER GAIN VALUE
S      3501
S      5201             /CHANGE TO DATA FIELD 0
S      TAD IVP           /ERASE DUMMY POINTER
S      AND 40077
S      LIVO             /LATCH, OFFSET=0 I/V
S  WC,  ISZ ASET         /WAIT FOR RELAYS TO SETTLE
S      JMP 4C
S  WX,  ISZ ASET
S      JMP 4X
S      CLA
S      TRIG              /PULSE TRIGGER
S  AF,  TCFL             /TEST FLAG
S      JMP AF
S      CCFPD             /CLEAR FLAG, GATE DRIVER
S      IAC              /CHECK INPUT
S      SNA              /IS A/D NEARLY PEGGED.
S  PTA, JMP JFF           /YES ADD OFFSET
S      JMP JAIN          /NO, INCREASE I/V GAIN
S  GAPT, J004            /JAIN POINTER TO PARA WORD
S  M0077, J077          /ASK
S  PTC,  FALT1          /ENDING ROUTINE 1

```

```

S /
S /SUBPROGRAM OFFSET
S /THIS SUBPROGRAM APPLIES OFFSET CURRENT
S /
S OFF,   CLA CLL
S        TAD AJ11           /SET UNITS INCREMENTER
S        DCA J11
S        TAD IVP           /BRING IN CURRENT SCALE
S        AND 40077         /MASK DUMMY POINTER
S        DCA IVP           /STORE
S        TAD IVP
S        RTL               /SET UP OFFSET CURRENT DECADE SCALE
S        RTL
S        TAD IVP           /SET I/V, OFFSET DECADE
S        DCA IVP           /STORE
S AG,    CLA CLL
S        ISZ J11           /IS MAXIMUM OFFSET APPLIED.
S        JMP AAI           /NO, CONTINUE
S        JMS I PTD         /YES, TELL DEFAULT
S        NOP
S        JMP AF2           /SKIP MEASUREMENT
S AAI,   TAD KUPT          /SET OFFSET POINTER TO PARA WORD
S        ISZ J11           /CHANGE TO DATA FIELD 1
S        ISZ J11           /ADD IN PARA WORD
S        ISZ J11
S        ISZ J11           /CHANGE TO DATA FIELD 0
S        TAD V7400         /SET OFFSET UNITS POINTER
S        TAD JNITS         /ADD PREVIOUS OFFSET
S        DCA JNITS
S        TAD IVP
S        TAD JNITS         /SET OFFSET, I/V WORD
S        JIVO             /LATCH OFFSET, I/V
S WD,    ISZ ASET          /WAIT FOR RELAYS TO SETTLE
S        JMP 4D
S WJ,    ISZ ASET
S        JMP 4J
S WU,    ISZ ASET
S        JMP 4U
S        CLA CLL
S        TRIG              /PULSE TRIGGER
S AH,    TCFL              /TEST FLAG
S        JMP 4H
S        CCFPD             /CLEAR FLAG, GATE DRIVER
S        IAC               /CHECK INPUT
S        SNA               /A/D PEGGED.
S        JMP AG            /YES, ADD MORE OFFSET
S /
S /BEGIN TO OUTPUT DATA FROM THE PRELIMINARY SCAN ROUTINE
S /
S AN,    CLA CLL
S        TAD 2HP
S        DCA 4NIH
S        TAD 2HP
S        DCA 4NIH
S        TAD IVP
S        DCA 4NII
S        TAD JNITS
S        DCA 4NIJ
S        IPMP(JP)=4NIH
S        IPMP(JP)=4NIW

```

```

      IIVP(JP)=NII
      IJNIT(JP)=NIU
S      CLA CLL
S      TRIG          /PULSE TRIGGER
S AP,   TCFL          /TEST FLAG
S      JMP AP
S      CCFPD          /CLEAR FLAG, GATE DRIVER
S      TAD 34000      /CHANGE TO 2'S COMPLEMENT
S      CLL
S      DCA =ITORE
      Z=FLJAT(ITORE)
S      6211          /CHANGE TO DATA FIELD 1
S      1501          /PUT PARA WORD IN AC
S      6201          /CHANGE TO DATA FIELD 0
S      JMS I ACODE    /GO TO DCODE ROUTINE WITH PARA WORD IN AC
S      CLA CLL
S      JMP I U71
S 84000, 4000        /CHANGE TO 2'S COMPLEMENT ADD IN
S XUPT, 0020         /OFFSET POINTER TO PARA WORD
S AU11, 7765         /-11
S U11, 0000          /UNITS INCREMENTER
S PTD, FALT2         /WARNING ROUTINE 2
S N0077, 0077        /DUMMY POINTER MASK
S V7400, 7400        /OFFSET UNITS POINTER
S U71, 071
S ACODE, DCODE       /PARA WORD DECODE SUBROUTINE
71  WRITE(1,3)PW,P4,XJVI,RV
   3  FORMAT(/,'PW = ',E10.4,' VOLTS',/, 'PW = ',E10.4,' MSEC',/, 'UNITS
      * = ',E10.4,/, 'RV = ',E10.4)
      WRITE(1,4)ES,RCELL,CCELL
   4  FORMAT('SAMPLED V = ',E12.6,/, 'RCELL = ',E12.6,' OHMS',/, 'CCELL
      * = ',E12.6,' MHOS',/)
S AF2,   CLA CLL
S      ISZ THRE       /ALL FOUR PW'S YET,
S      JMP AQ         /NO, CONTINUE
S      JMP INOR       /YES, GO TO NEXT ROUTINE
S AQ,    TAD PWP       /SET UP FOR NEXT PW
S      TAD PWCN       /PW INCREMENT
S      DCA PWP        /STORE IN PW POINTER LOC
S      ISZ SPARA      /SET UP ADDRESS OF NEXT PARA WORD
S      30 TO 2
S THRE, 0000         /3 PW'S POINTER
S PWCN, 0100         /PW INCREMENT
S /
S /THIS SECTION DETERMINES SELECTED OPTION
S /
S INOR,   CLA CLL
S      ITAD          /TRIGGER TEMP A/D
S CAP1,   ITFL        /TEST TEMP FLAG
S      JMP CAP1
S      CTFP3         /CLEAR TEMP FLAG, GATE DRIVER
S      TAD (4000     /CHANGE TO 2'S COMPLEMENT
S      CLL
S      DCA =ITORE
      Z=FLJAT(ITORE)
      ES=Z*(10./4096.)+3.
   5  WRITE(1,6)ES
   6  FORMAT(/,'TEMP RESPONSE = ',E14.6,/, 'OPTIONS: 1)AVERAGE',/,9X,'
      *2)RESTART',/,9X,'3)TDA',/,9X,'4)CALL EXIT',/)
S      CLA CLL

```

```

S TA1, <SF          /KEYBOARD STRUCK YET,
S      JMP TA1
S      <RB          /YES, READ CHARACTER
S      TLR          /ACKNOWLEDGE IT ON PRINTER
S      TAD V7517    /-261
S      SNA          /IS IT A "1".
S      JMP AJ       /YES, GO TO AVERAGE ROUTINE
S      TAD 37777    /NO, ADD -1
S      SNA          /IS IT A "2".
S      JMP I AT     /YES, RESTART
S      TAD 37777    /NO, ADD -1
S      SNA          /IS IT A "3".
S      JMP I CA     /YES, GO TO TDA ROUTINE
S      CALL EXIT
S V7517,7517        /-261
S 07777,7777        /-1
S AT,  #100         /RESTART ADDRESS
S CA,  TDA          /TDA ADDRESS
S /
S /
S /THIS ROUTINE PERFORMS AVERAGE OF INPUT NUMBER OF SCANS
S /
S /
S AU,  CLA CLL
      WRITE(1,51)
      FORMAT(/)
      JSTI<=0
      PAGE
S      JMS SETJP    /GO TO SETUP ROUTINE
S      CLA CLL
S      TAD #LD
S      SZA
S      JMP TAP
S      CLA CLL
S      TAD TAN
S      AND (0177
S      TAD (5200
S      DCA TAN
S TAP,  TAD #IPTS    /BRING IN NUMBER OF SCANS TO AVERAGE
S      DCA VBAR
S      TAD VBAR
S      CIA          /SET UP # PTS, POINTER
S      DCA #BAR
S      DCA VLS3     /CLEAR LSB WORD
S      DCA VMS3     /CLEAR MSB WORD
S AW,  CLA CLL
S      TRIG         /PULSE TRIGGER
S AX,  TCFL         /TEST FLAG
S      JMP AX
S      SCFPO        /CLEAR FLAG, GATE DRIVER
S      TAD VLS3     /ADD IN LSBS
S      DCA VLS3
S      RAL          /SET JP OVERFLOW
S      TAD VMS3     /ADD IN MSBS
S      DCA VMS3
S      ISZ #BAR
S      JMP AJ       /ALL DONE,
S      TAD VLS3     /NO, RETURN FOR NEXT SCAN
S      TAD VMS3     /YES, GET SET TO AVERAGE
S      TAD #0       /TAD #0 WITH LSB WORD
S

```

```

S      DVI          /DIVIDE
S NBAR, 0000       /THE DIVISOR
S TAN,  TAD (4000
S      DCA =JSTIK
S TAO,  CLA CLL
S      MDA          /LOAD DIVIDEND INTO AC
S      TAD (4000    /CHANGE TO 2'S COMPLIMENT
S      CLL
S      DCA =ISTIK
S      Z=FLJAT(ISTIK)
S      ZL=F_OAT(JSTIK)
S      CLA CLL
S      TAD SPPT      /SET UP PROPPER ADDRESS OF PARA WORD
S      TAD =JP
S      DCA SPPJ
S      6211          /CHANGE TO DATA FIELD 1
S      1502          /PUT PROPER PARA WORD INTO AC
S      6201          /CHANGE TO DATA FIELD 0
S      JMS I BCODE   /GO TO DECODE SUBROUTINE WITH PARA WORD IN AC
S      CLA CLL
S      JMP =72
S NLSB, 0000       /THE LEAST SIGNIFICANT BIT WORD
S NMSB, 0000       /THE MOST SIGNIFICANT BIT WORD
S PBAR, 0000       /AVERAGE NUMBER POINTER
S TAN,  TAO        /JUMP OVER DOUBLE PRECISION LOC
S SPPT, 0177
S BCODE, BCODE     /PARA WORD DECODE SUBROUTINE
72  WRITE(1,13)APTS,ES,RCCELL,CCELL
13  FORMAT(//,'AVERAGE OF ',F5.0,' SCANS: SAMPLED V = ',E16.8,' VOLT
    *S',/,29X,'RCCELL = ',E16.8,' OHMS',/,29X,'CCELL = ',E16.8,' MHOS',/
    */)
S      JMP INQR      /RETURN, TAKE TEMP POINT, GET OPTION
S /
S /
S /SUBPROGRAM TDAR
S /THIS PROGRAM CONTROLS TIMED DATA ACQUISITION
S /OVER AN INPUT PERIOD AT INPUT INTERVALS
S /
S /
S TDAR, CLA CLL
      WRITE(1,31)
      READ(1,200)TRVL,TIPT,TCTA
200  FORMAT('TOTAL NUMBER OF POINTS:',E16.8,/, 'TIME BETWEEN POINTS (S
    *ECS):',E16.8,/, 'NUMBER OF T SCANS TO AVERAGE:',E16.8)
      IF(TCTA)942,942,943
942  NT=0
      GO TO 945
943  NT=1
945  ES=(TRVL*TIPT)/60.
      WRITE(1,202)ES
202  FORMAT('THIS WILL REQUIRE ABOUT ',E10.4,' MIN')
      READ(1,946)BLK
946  FORMAT('FIRST BLOCK TO WRITE: ',E14.6)
      IBLK=IFIX(BLK)
S      JMS I QA01     /GO TO SETUP SUBROUTINE
S      JMP QA06
S QA01, SETUP      /ADDRESS OF SETUP SUBROUTINE

```

```

S /
S /THIS IS THE SET UP SECTION FOR CLOCK AND POINTERS OF TDA ROUTINE
S /
S QA06, CLA CLL
S 203 IF(TIBPT=.004)205,204,204
S #204, TAD TMB /CLOCK PRESET MODE INDICATOR
S TAD T1000 /CLOCK TB INCREMENTER
S DCA TMB
S TIBPT=TIBPT/10.
S ISZ QA07 /ALL DONE,
S JMP #203 /NO, RETURN
S JMP #205 /YES, CONTINUE
S TMB, J400 /PRESET MODE INDICATOR
S T1000,1000 /CLOCK TB INCREMENTER
S QA07, 7771
S 205 TIBPT=TIBPT*1000000.
S /
S /THIS IS THE SPECIAL FIX ROUTINE FOR CLOCK SETUP
S /
S CLA CLL
S TAD #TIBPT /BRING UP EXPONENT, UPPER MANTISSA
S DCA #OT1
S DCA #OT2 /ZERO MSB WORD
S TAD #OT1
S AND #3770 /MASK SIGN, MANTISSA
S RTR /RIGHT JUSTIFY EXPONENT
S RAR
S TAD #7600 /SET EXPONENT
S CLL #4 /SET SCALING POINTER
S DCA #PNT
S TAD #OT1
S AND #0007 /ERASE ALL BUT UPPER MANTISSA
S RTR /LEFT JUSTIFY
S RTR
S DCA #OT1
S TAD #TIBPT# /BRING IN FIRST COMPLETE MANTISSA WORD
S AND #7770 /MASK LOWER 3 BITS
S RTR /RIGHT JUSTIFY
S RAR
S IFA, TAD #OT1 /SET COMPLETE WORD
S ISZ #PNT /ALL SCALED,
S SKP /NO, SCALE
S JMP 3004 /YES, GO ON TO NEXT SECTION
S RAL /SCALE BY 2
S DCA #OT1
S TAD #OT2 /WILL CONTAIN COMPLETED VALUE
S RAL /SCALE BY 2
S DCA #OT2
S JMP IFA /RETURN FOR NEXT SCALING
S POT1, 0000
S POT2, 0000
S N3770,3770
S #7600,7600
S #PNT, 0000
S #0007,0007
S #7770,7770

```



```

S /SET UP CLOCK PARAMETERS
S GOUN, CLA CLL
S      TAD T4B           /SELECTED TO PRESET MODE
S      LCTR_            /LOAD CONTROL REGISTER
S      CLA CLL
S      TAD #OT2         /SETS UP EXACT INTERVAL
S      CIA
S      LPSSET           /LOAD PRESET REGISTER
S      CLA CLL
S /SET UP NUMBER OF POINTS POINTER
S      ITRV_#FIX(TRV_)
S      TAD #ITRVL
S      CIA              /SET UP # POINTS
S      DCA I SYDP
S /SET UP # OF 3 SCANS POINTER
S      TAD #PTS
S      DCA I SP40
S      TAD I SP40
S      CIA              /SET UP # SCANS
S      DCA I AY40
S /SET UP # OF 7 SCANS POINTER
S      TAD #4T          /CHECK TO SEE IF TEMP INFO IS DESIRED
S      SZA
S      JMP 3003
S      TAD STE44         /SET UP JMP OVER TEMP AQ INSTRUCTION
S      AND (0177
S      TAD (5200
S      DCA I STEM3
S      JMP STE46
S GOUN, CLA CLL
S      ITCT4#FIX(TCT4)
S      CLA CLL
S      TAD #ITCTA
S      DCA I STEM2
S      TAD I STEM2
S      CIA
S      DCA I STEM1
S /SET UP FOR DOJBLE PRECISION
S STEM6, CLA CLL
S      TAD #LD
S      SZA
S      JMP CEC
S      CLA CLL
S      TAD CED
S      AND (0177
S      TAD (5200
S      DCA CEE
S /SET UP PARAMETER WORD
S CEC, CLA CLL
S      TAD (0177        /SET PARA WORD ADDRESS
S      TAD #JP
S      DCA SPPJ
S      6211             /CHANGE TO DATA FIELD 1
S      1502             /BRING IN PROPER PARA WORD
S      6201             /CHANGE TO DATA FIELD 0
S      DCA S PARA       /STORE IN PARA WORD OF TDA ROUTINE

```

```

S /BEGIN DATA ACQUISITION SET
S /
S     JMS TYP3           /30 ASK FOR A "G"
S     TAD (0177         /SET UP ADDRESS OF FIRST DATA WORD
S     DCA AINC
S     JMP I SA09         /BEGIN TDA RUN
S ANAQ, VAO             /NUMBER OF SCANS POINTER TO TDA
S SA09, SA09            /STARTING ADDRESS OF TDA RUN
S SPAQ, PAQ             /DIVISOR FOR FLYING AVERAGE
S SNDF, NDP             /NUMBER OF POINTS POINTER
S STEM1, TEM1
S STEM2, TEM2
S STEM3, JLOC
S STEM4, STEM5
S CED, CEF              /DOUBLE PRECISION SKIP OVER LOC
S /
S /THIS IS THE TDA DATA ACQUISITION ROUTINE ITSELF
S /
S     PAGE
S     -AP
S /
S /A PERIPHERAL CONTROL INSTRUCTION MAY BE INSERTED INTO QA09
S QA09, NOP
S     NOP
S /
S QL09, CLCIC           /CLEAR CLOCK AND INITIALIZE COUNTER
S     TRIG              /INITIATE PULSING SEQUENCE
S     CLOFE             /CLEAR CLOCK AND OVERFLOW ERROR FLAGS
S     CCFP              /CLEAR COMBIP FLAG
S     CLA CLL
S     DCA TLSB           /ZERO LSB WORD
S     DCA TMSB           /ZERO MSB WORD
S     TAD VAO            /SET UP NUMBER OF SCANS POINTER FOR THIS RUN
S     DCA LVA2
S QA13, TCPL           /TEST COMBIP FLAG
S     JMP QA13
S     TRIG              /INITIATE PULSING SEQUENCE
S     CCFPD             /CLEAR FLAG, GATE DRIVER
S     TAD TLSB          /ADD IN PREVIOUS LSB VALUE
S     DCA TLSB
S     RAL               /SET LINK INTO LSB
S     TAD TMSB          /ADD IN MSB
S     DCA TMSB
S     ISZ LVA2           /ALL N ACQUISITIONS,
S     JMP QA13           /NO, RETURN FOR MORE
S     TAD TLSB          /YES, AVERAGE LAST SCAN IN COMBIP REGISTER
S     MQL               /LOAD AC INTO MQ
S     TAD TMSB          /SET UP TO DIVIDE WITH MSB IN AC
S     DVI               /DIVIDE
S PAQ, 0000            /THE DIVISOR, SET UP BY # ACQUISITIONS
S CEE, 5211            /COF 1
S     3412              /AUTO-INCREMENT AND STORE REMAINDER
S CEF, CLA CLL
S     MQA               /LOAD AVERAGE INTO AC
S     DCA CHECK         /STORE CURRENT DATA IN OVER/UNDER RANGE CHECK LOC
S     TAD CHECK
S     5211
S     3412              /AUTO-INCREMENT AND STORE DATA
S     TAD SPARA
S     3412              /AUTO-INCREMENT AND STORE PARA WORD
S     5201              /CHANGE TO DATA FIELD 0

```

```

S /CHECK FOR TEMPERATURE POINTS AND TAKE IF INDICATED
S JLOC, NOP /REPLACED BY JMP STEMS IF NO T DATA TO BE TAKEN
S TFPQT /CLEAR FLAG, GATE DRIVER, TRIGGER TEMP A/D
S CLA CLL /DISCARD PREVIOUS MEASUREMENT
S DCA TLSB /ZERO LSB WORD
S DCA TMSB /ZERO MSB WORD
S TAD TEM1 /NUMBER OF AVERAGES POINTER
S DCA LNAQ
S ELA, TTFL /TEST TEMP FLAG
S JMP ELA
S TFPQT /CLEAR FLAG, GATE DRIVER, TRIGGER TEMP A/D
S TAD TLSB
S DCA TLSB
S RAL /SET OVERFLOW INTO LSB
S TAD TMSB
S DCA TMSB
S ISZ LNAQ
S JMP ELA /NOT DONE, RETURN FOR MORE
S TAD TLSB /ALL DONE, AVERAGE
S MQL /AC LOAD INTO MQ
S TAD TMSB
S DVI /DIVIDE
S TEM2, J000 /THE DIVISOR, SET UP BY # OF SCANS
S CLA CLL
S MQA /AC LOAD FROM MQ
S B211
S B412 /AUTO-INCREMENT AND STORE T DATA
S B201
S /BEGIN CHECK ROUTINE FOR RANGE OVERFLOW
S STEMS, TAD CHECK /READ IN CURRENT MEASUREMENT
S SPA
S JMP SARA /AC NE3, GO CHECK FOR OVERRANGE
S TAD (7700 /TEST FOR AC>0077
S SPA
S JMPI PFIx1 /AC<0017, GO FIX
S JMP B417
S SARA, TAD (0100
S SQA /IS A/D NEAR FULL SCALE.
S JMPI PFIx2 /YES, GO FIX
S /
S /A PERIPHERAL CONTROL INSTRUCTION MAY BE INSERTED INTO QA17
S QA17, NOP
S /
S ISZ NOP /NO, ALL DATA POINTS YET.
S SKP /NO, CONTINUE
S JMPI QA19 /YES, OUTPUT
S GNE, SKPOF /SKIP ON CLOCK OVERFLOW
S JMP BVE
S SKPOE /SKIP ON OVERFLOW ERROR
S JMP BLO9 /NO ERROR, RETURN FOR NEXT POINT
S JMPI PA17 /DO INDICATE CLOCKING ERROR
S TLSB, J000 /LOC OF FLYING ADD LSB
S TMSB, J000 /LOC OF FLYING ADD MSB
S NAQ, J000 /NUMBER OF ACQUISITIONS POINTER
S LNAQ, J000 /BECOMES RESETTABLE # ACQUISITIONS POINTER
S NDP, J000 /NUMBER OF DATA POINTS POINTER
S QA19, DTOUT /OUTPUT ROUTINE ADDRESS
S CHECK, J000 /CURRENT MEASUREMENT TO BE CHECKED FOR OVER/UNDER RANGE
S PFIx1, PFIx1 /ADDRESS OF INCREASED RCELL COMPENSATOR ROUTINE
S PFIx2, PFIx2 /ADDRESS OF DECREASED RCELL COMPENSATOR ROUTINE
S TEM1, J000 /CONTAINS # OF TEMP POINTS POINTER
S PA17, PA17 /CLOCKING ERROR INDICATING ROUTINE LOC

```

```

S / THIS ROUTINE RESETS THE SYSTEM TO COMPENSATE FOR INCREASED RCELL
S /
S     PAGE
S     EAP
S OFIX1, CLA CLL
S     TAD JNITS
S     TAD 2F1000
S     SNA /MINIMUM OFFSET,
S     JMP 2F12 /YES, 30 RESET PH
S QPZ, TAD 27400 /NO, SET 1 LESS UNIT
S     DCA JNITS
S     CLA CLL
S     TAD 27760 /CUT 1 OFFSET UNIT VALUE
S     JMP 2A21
S OF12, CLA CLL
S     TAD IVP /CHECK FOR MAX GAIN SITUATION
S     TAD 17570 /RETURNS 0 AC AT MAX GAIN
S     SZA
S     JMP 20A /NOT AT MAX GAIN, CONTINUE
S     CLA CLL
S     TAD 14010 /NEW I/V IF MAX GAIN
S     DCA IVP
S     JMP 2PZ /REMOVE LAST OFFSET UNIT, SET PARA
S QQA, CLA CLL
S     TAD PHP
S     RAL
S     SZL /INCREASE PH IF POSSIBLE
S     JMP 2F14 /DONE TOO FAR,
S     DCA PHP /YES, CHECK GAIN
S     IAC /NO, PH SET, STORE
S     JMP 2A20 /ADD1
S OF14, CLA CLL
S     TAD IVP
S     RAL /INCREASE GAIN IF POSSIBLE
S     DCA IVP
S     TAD 20004 /INCREASE GAIN VALUE IN PARA WORD
S     JMP 2A20
S /
S / THIS ROUTINE RESETS THE SYSTEM TO COMPENSATE FOR DECREASED RCELL
S /
S OFIX2, CLA CLL
S     TAD IVP /CHECK FOR PREVIOUS 0 OFFSET
S     TAD 13770 /RETURNS 0 AC AT PREVIOUS 0 OFFSET
S     SZA
S     JMP 20B /NOT AT 0, CONTINUE
S     CLA CLL
S     TAD 10210 /NEW I/V SETTING
S     DCA IVP
S QQB, CLA CLL
S     TAD JNITS
S     TAD 45400
S     SNA /MAXIMUM OFFSET,
S     JMP 2F21 /YES, 30 RESET GAIN
S     TAD 22000 /NO, SET 1 MORE UNIT
S     DCA JNITS
S     CLA CLL
S     TAD 20020 /JNITS INCREMENTER FOR PARA WORD
S     JMP 2A21
S OF21, CLA CLL

```

```

S      TAD IVP
S      RAR                      /DECREASE GAIN IF POSSIBLE
S      SZL                      /DONE TO FAR.
S      JMP 3F22                 /YES, 30 LOWER PH IF POSSIBLE
S      DCA IVP                 /NO, STORE
S      TAD 37774
S      JMP 3A22
S 0F22, CLA CLL
S      TAD PHP
S      RAR                      /DECREASE PH IF POSSIBLE
S      DCA PHP
S      TAD PHP
S      TAD 37400
S      SNA                      /DONE TOO FAR,
S      JMS I 0F19              /30 TO SUBSCALE WARNING ROUTINE
S      SKP
S      HLT                      /YES, STOP
S      CLA CLL                  /NO, SET UP
S      CMA                      /-1
S      JMP 3A22
S /BEGIN RESET ROUTINES, EXECUTED AFTER RETURN FROM OFIX ROUTINE
S /ROUTINE TO RESET AFTER RETURN FROM OFIX1 FROM PH, GAIN CHANGES
S 0A20, TAD SPARA              /RESET PARA WORD ON RETURN FROM FIX
S      AND 32MSK              /RESET OFFSET UNITS IN PARA WORD
S      TAD 30240              /SET OFFSET UNITS = 10 IN PARA WORD
S      DCA SPARA
S      TAD 32400              /SET UNITS POINTER = 10 OFFSET UNITS
S      DCA JNITS
S      JMP 3A23              /30 LATCH CIRCUIT
S /THIS IS RETURN ROUTINE FOR RESET OF UNITS ONLY
S 0A21, TAD SPARA              /RESET PARA WORD
S      DCA SPARA
S      JMP 3A24              /30 LATCH UNITS
S /THIS IS THE RETURN ROUTINE FOR OFIX2 FROM PH, GAIN CHANGES
S 0A22, TAD SPARA              /RESET PARA WORD
S      AND 32MSK              /RESET OFFSET UNITS IN PARA WORD
S      TAD 30020              /SET OFFSET UNITS = 1 IN PARA WORD
S      DCA SPARA
S      TAD 37000              /SET OFFSET UNITS POINTER = 1 OFFSET UNIT
S      DCA JNITS
S /THIS ROUTINE RESETS COMPBIP FOR NEW PARAMETERS
S 0A23, CLA CLL
S      TAD PHP                /RESET PH, PW
S      TAD PHP
S      LPHW                    /LATCH PH, PW
S 0A24, CLA CLL
S      TAD IVP                /RESET UNITS, OFFSET DECADE, GAIN
S      TAD JNITS
S      LIVO                    /LATCH
S      CLA CLL
S 0A25, JMP I 3F16            /RETURN TO MAIN PROG
S 07000, 7000                /3IVES OFFSET UNITS = 1
S 02400, 2400                /10 OFFSET UNITS VALUE TO COMPBIP
S 00240, 240                /PARA WORD 10 OFFSET UNITS INDICATOR
S 02MSK, 7417                /PARA WORD OFFSET UNITS VALUE MASK
S L0020, 3020                /1 OFFSET UNIT VALUE TO COMPBIP
S 02000, 2000                /JNITS INCREMENTER
S 07760, 7740                /PARA WORD OFFSET UNITS DECREMENTER
S 00004, 3004                /PARA WORD GAIN INCREMENTER
S 07400, 7400                /PH UNDERRANGE CHECK

```

```

S M5400,3400          /OFFSET OVERRANGE CHECK
S Q0020,0020          /PARA WORD OFFSET INCREMENTER
S Q7774,7774          /PARA WORD GAIN DECREMETER
SQF1000,1000          /MIN OFFSET (*1) CHECK
S QF16, 0A17
S QF19, FALT2          /SUBSCALE WARNING ROUTINE
S /
S /SUBPROGRAM DTOUT
S /THIS SECTION SETS UP THE TRANSFER TO THE ANALYSIS ROUTINE
S /
S DTOUT,CLA CLL
      VARA(2043)=MT
      VARA(2044)=ITRVL
      VARA(2045)=LD
      VARA(2046)=IPTS
      CALL WTAPE(1,13L4,2046,NARA)
      CALL EXIT
S /
S /SUBPROGRAM FALT1
S /THIS SUBPROGRAM INDICATES THAT CELL COND IS VERY LOW
S /
S FALT1,CLA CLL
      WRITE(1,14)PW
14      FORMAT(/,'ERROR 1 AT PA = ',F6.3,' MSEC')
S      CLA CLL
S      JMP I PAF1
S PAF1, AN
S /
S /SUBROUTINE FALT2
S /THIS SUBROUTINE INDICATES CELL COND TOO HIGH
S /
S FALT2,0000
S      CLA CLL
      WRITE(1,15)PW
15      FORMAT(/,'ERROR 2 AT PA = ',F6.3,' MSEC')
S      CLA CLL
S      ISZ FALT2          /SET TO RETURN TO MAIN PRG + 1
S #17, JMP I FALT2
S /
S /SUBPROGRAM FALT7
S /THIS SUBPROGRAM INDICATES THAT ONE OVERFLOW OF CLOCK TIMING
S /
S /HAS OCCURRED DURING TOA - A FATAL ERROR WHICH HALTS THE PROGRAM
S FALT7,CLA CLL
      WRITE(1,117)
117      FORMAT(/,'ERROR 7')
S      HALT
S /
S /SUBROUTINE SETUP
S /THIS SUBROUTINE SETS NECESSARY PARAMETERS FOR AVERAGING
S /A SERIES OF SCANS AND SETS PROPER PW, AND INSTRUMENT PARAMETERS
S /
S SETUP,0000
      READ(1,7)APW,APTS,LD
      7      FORMAT('AT WHAT PA, (MSEC): ',E15.8,/, 'NUMBER OF G SCANS TO AVER
      +AGE: ',E16.8,/, 'DOUBLE PRECISION. (1=Y,0=N)','','I5)
      WRITE(1,309)
      309      FORMAT('TYPE EXPERIMENTAL INFO (CNTRL G TO END):',/)
S TE11, CLA CLL
S TE12, KSF          /KEYBOARD STRUCK YET,

```

```

S      JMP TE12          /NO CHECK AGAIN
S      <R8              /YES, READ CHARACTER
S      TLR              /ECHO IT ON PRINTER
S      TAD TE13         /-207
S      SZA              /IS IT AN ALT MODE,
S      JMP TE11         /NO, RETURN FOR MORE
S      JMP TE14         /YES, CONTINUE IN NEXT ROUTINE
S TE13, 7571           /-207
S TE14, CLA CLL
S      JP=1
S      XX=.301
S      9      XX=XX*10.
S      IF(A>W-XX)11,11,10
S      10     JP=JP+1
S      30 TO 9
S      11     IPTS=IFIX(APTS)
S      CLA CLL
S      VIM=IPHP(JP)
S      TAD =VIM         /LOAD PH
S      DCA PHP
S      VII=IIVP(JP)
S      TAD =VII         /LOAD I/V, OFFSET DECADE
S      DCA IVP
S      VIM=IPWP(JP)
S      TAD =VIM         /LOAD PH
S      DCA PHP
S      VIU=IUNIT(JP)
S      TAD =VIU         /LOAD OFFSET UNITS
S      DCA JNITS
S      TAD IVP
S      TAD JNITS
S      -IVO            /LATCH OFFSET, I/V
S WE, ISZ ASET         /WAIT FOR RELAYS TO SETTLE
S      JMP JE
S WF, ISZ ASET
S      JMP JF
S      CLA CLL
S      TAD PHP
S      TAD PHP
S      LPHW            /LATCH PH, PH
S WG, ISZ ASET         /WAIT FOR RELAYS TO SETTLE
S      JMP JG
S WH, ISZ ASET
S      JMP JH
S      CLA CLL
S      JMP I SETUP     /RETURN TO MAIN PROG
S /
S /SUBROUTINE TYPG
S /THIS SUBROUTINE READS ITY AND CHECKS FOR A "G"
S /
S TYPG, J000
S AA, CLA CLL
S      WRITE(1,1)
S      FORMAT('TYPE "3" TO START')
S AS, <SF             /KEYBOARD STRUCK YET,
S      JMP AS          /NO, CHECK AGAIN
S      <R8            /YES, READ CHARACTER
S      TLR            /ACKNOWLEDGE IT ON PRINTER
S      TAD V7471      /SUBTRACT 307
S      SZA            /IS IT A "G".
S      JMP AA          /NO, GO CHECK AGAIN
S      JMP I TYPG      /YES, RETURN TO MAIN PROGRAM
S V7471,7471          /-307

```

```

S /
S /SUBROUTINE DCODE
S /THIS SUBROUTINE DECODES PARAMETER WORDS AND COMPUTES
S /PH,RV,XUNI,ES,RCELL,AND CCELL. IT MUST BE ENTERED WITH PARA WORD IN AC
S /PARA WORD FORMAT: FIRST 4 BITS (MSB) ARE UNUSED
S / NEXT 4 BITS FOR UNITS VALUE (BINARY 1-10)
S / NEXT 2 BITS FOR GAIN INFO (BINARY VALUE 0-3)
S / NEXT 2 BITS FOR PH INFO (BINARY 1-3)
S /
S DCODE, J000
S DCA SPPJ /STORE PARA WORD
XUNI=0.
PH=.005
RV=10000.
S TAD SPPJ
S AND MSK1 /MASK ALL BUT PH BITS
S DC1, DCA SPPH
S TAD SPPH
S SNA /ALL SET.
S JMP DC2 /YES, CONTINUE
S CLA CLL /NO, ADJUST
PH=PH*10.
S SNA /ADD -1
S TAD SPPH /SET UP NEXT ITERATION
S JMP DC1
S MSK1, J003 /MASK ALL BUT PH BITS
S DC2, TAD SPPJ
S AND MSK2 /MASK ALL BUT GAIN BITS
S DC3, DCA SPPH
S TAD SPPH
S SNA /ALL SET.
S JMP DC4 /YES, CONTINUE
S CLA CLL /NO, ADJUST
RV=RV*10.
S TAD DC7774
S TAD SPPH /SET UP NEXT ITERATION
S JMP DC3
S MSK2, DC14 /MASK FOR ALL BUT GAIN BITS
SDC7774, 7774 /GAIN DEINCREMENTER
S DC4, TAD SPPJ
S AND MSK3 /MASK ALL BUT OFFSET UNITS BITS
S DC5, DCA SPPH
S TAD SPPH
S SNA /ALL SET.
S JMP DC6 /YES, CONTINUE
S CLA CLL /NO, ADJUST
XUNI=XUNI*1.
S TAD DC7750
S TAD SPPH /SET UP FOR NEXT ITERATION
S JMP DC5
S MSK3, DC60 /MASK FOR ALL BUT UNITS BITS
SDC7760, 7760 /UNITS DEINCREMENTER
S DC6, CLA CLL
80 ES=(Z*(12.5/4096.)*6.25)
IF(L0)312,312,311
311 ES=(ZL*(12.5/4096.)*6.25)/APTS
ES=ES+ES_
312 RCELL=PH/((ES/RV)+((10.*XUNI)/RV))
CCELL=.1./RCELL
S CLA CLL
S JMP I DCODE
END

```


CBPSLT
PROGRAM LISTING

```

S /PROGRAM NAME: C3PSLT.FY
S /FORTHAN-SABRI KEITH J. CASERTA 4/2/74
S /THIS PROGRAM RUNS WITH ANY ONE OF FOUR OPTIONS:
S / 1)SEARCH A PREVIOUS FILE GENERATED WITH THIS PROGRAM
S /      A)CALCULATE MAXIMUM AND MINIMUM ERROR
S /      B)CALCULATE AVERAGE ERROR
S /      C)OUTPUT THE DATA SET ON THE LPT
S / 2)PLOT A PREVIOUSLY GENERATED FILE
S /      A)CALCULATE AND OUTPUT MAXIMUM ERROR
S /      B)REQUEST SCOPE SCALING PARAMETERS
S /      C)PLOT POINTS WITHIN LIMITS
S / 3)COMPARISON RUN
S /      A)REQUEST NUMBER OF AVERAGES
S /      B)PERFORM PRELIMINARY SCAN, OUTPUTTING A ".", WHEN DONE
S /      C)REQUEST REAL R FOR X AXIS (AS LOG(R))
S /      D)OPERATOR SELECTS OPTION:
S /          S1 MEASURE AND AVERAGE INPUT SCANS OF THE STANDARD
S /          D1 MEASURE AND AVERAGE INPUT SCANS OF THE COMPARISON
S /          R1 RESET X AXIS VALUE
S /          N1 GO ON TO NEXT VALUE, STORING CURRENT DATA
S /          C1 CHANGE PD
S /          E1 END MEASUREMENT AND SELECT OPTION
S /          O1 OUTPUT ERROR
S / 4)VARIABLE INCREMENT PULSING
S /      A)PERFORM PRELIMINARY SCAN, OUTPUTTING A ".", WHEN DONE
S /      B)REQUEST INTERVAL, USED AS X AXIS (AS LOG(INTERVAL))
S /      C)OPERATOR SELECTS OPTION AS IN (D) ABOVE BUT DATA IS
S /          ACQUIRED AS 1000 SCANS AT THE CHOSEN INTERVAL
S /THIS PROGRAM IS BASICALLY DESIGNED FOR ACCURACY DETERMINATIONS
S /
COMMON DATA, PARA
DIMENSION DATA(2,30), PARA(2)
S      JDEF      CCFP      6321      /CLEAR COND FLAG, CLEAR PI ENABLE
S      JDEF      CCCR      6322      /GATE CONDUCTANCE DRIVER
S      JDEF      CCFPD      6323      /CCFP + CCCR
S      JDEF      ECPI      6324      /ENABLE COND PROGRAM INTERRUPT
S      JDEF      CCFGD      6327      /CCFP + CCCR + ECPI
S      SKPD      TCFL      6331      /TEST CONDUCTANCE FLAG
S      JDEF      TOST      6332      /TURN OFF SEQUENCE TRIGGER
S      JDEF      TRIG      6334      /TRIGGER SEQUENCE
S      SKPD      TTFL      6341      /TEST TEMPERATURE FLAG
S      JDEF      LVO      6342      /LATCH I/V, OFFSET
S      JDEF      PMW      6344      /LATCH PH, PW
S      JDEF      ETP1      6351      /ENABLE TEMP PROGRAM INTERRUPT
S      JDEF      CTFG      6352      /CLEAR TEMP FLAG, PI ENABLE, GATE DRIVER
S      JDEF      TTAD      6354      /TRIGGER TEMP A/D CONVERSION
S      JDEF      TFGT      6356      /CTFG + TTAD
S      JDEF      TIT      6361      /TITRATE
S      JDEF      LPSET      6121      /LOAD THE CLOCK PRESET REGISTER
S      JDEF      CLCL      6122      /CLEAR THE CLOCK
S      JDEF      ICNTR      6123      /INITIALIZE THE COUNTER
S      JDEF      CLCIC      6124      /CLEAR CLOCK AND INITIALIZE COUNTER
S      JDEF      LCNTR      6125      /LATCH THE COUNTER
S      JDEF      RCTRL      6126      /READ THE COUNTER LATCH
S      JDEF      RCNTR      6127      /READ THE COUNTER
S      JDEF      LCTRL      6131      /LOAD CONTROL REGISTER
S      SKPD      SKPOF      6132      /SKIP ON OVERFLOW
S      SKPD      SKPOE      6133      /SKIP ON OVERFLOW ERROR
S      JDEF      CLJFE      6134      /CLEAR OVERFLOW AND OVERFLOW ERROR FLAGS
S      SKPD      SKPTB      6135      /SKIP ON TIME BASE FLAG
S      SKPD      SKTBE      6136      /SKIP ON TIME BASE ERROR FLAG
S      JDEF      CLTBE      6137      /CLEAR T.B. AND T.B. ERROR FLAGS

```

```

S      CODE?  MUY      7405      /MULTIPLY
S      CODE?  DIV      7407      /DIVIDE
S      CODE?  NMI      7411      /NORMALIZE
S      CODE?  SHL      7413      /SHIFT LEFT
S      CODE?  ASR      7415      /ARITHMETIC SHIFT RIGHT
S      CODE?  LSR      7417      /LOGICAL SHIFT RIGHT
S      CODE?  MQL      7421      /LOAD MULTIPLIER QUOTIENT
S      CODE?  SCL      7403      /STEP COUNTER LOAD FROM MEMORY
S      CODE?  SCA      7441      /STEP COUNTER LOAD INTO AC
S      CODE?  MQA      7301      /MQ LOAD INTO AC
S      CODE?  SRASE     6034      /ERASE DISPLAY SCOPE
S      CODE?  STORE     6037      /SET SCOPE IN STORE MODE
S      ASSY4  PHD       0074      /PH POINTER
S      ASSY4  PHD       0075      /PH POINTER
S      ASSY4  IVP       0076      /I/V POINTER
S      ASSY4  JNITS     0077      /OFFSET UNITS POINTER
S      ASSY4  ASET      0100      /GENERAL POINTER
S      ASSY4  SPARA     0101      /PARAMETER POINTER
S      ASSY4  SPPU      0102      /INDIRECT ADDRESS IN FIELD 1 POINTER
S      ASSY4  SPPW      0103      /INDIRECT ADDRESS IN FIELD 1 POINTER
S /
S /
S /PROGRAM BEGINS WITH FIRST OPTION SELECTION
S /
S /
69      MT=0
172     WRITE(1,972)MT,
872     FORMAT(/,'SEARCH PREVIOUS FILE = 2',/, 'PLOT PREVIOUS FILE = 1',/
*, 'START COMPARISON = 0',/, 'VARIABLE INCREMENT PULSING = -1',10)
      READ(1,151)JQ
161     FORMAT(15)
      IF(JQ)150,160,159
159     READ(1,158)J
158     FORMAT('FIRST BLOCK:',15)
      CALL RTAPE(1,J,374,DARY)
      IF(NARA(2))380,391,381
380     WRITE(1,382)
382     FORMAT('THIS IS A COMPARISON FILE',/)
      DO TO 394
381     WRITE(1,383)
383     FORMAT('THIS IS A VARIABLE PULSING FILE',/)
384     I=NARA(1)
      IF(J2-2)519,502,512
619     J2=NARA(2)
S      CLA CLL
S      JMS ACUT
S      JMS TCUT
S      CLA CLL
      DO TO 69
160     CONTINUE
S /
S /BEGIN THE PRELIMINARY SCAN SEQUENCE
S /
S PNNY, CLA CLL
S      DCA PWP          /SET PW AT 0.01 MSEC
      READ(1,7)PW
7      FORMAT('PW (MSEC):',12.8)
      IF(J2)997,998,998
988     READ(1,999)X0
989     FORMAT('AVERAGE S1',15)
987     XX=X01
8      XX=XX+10,

```

```

IF(P4-XX)11,11,10
S =10. CLA CLL
S TAD PWP /SET P4 TO PROPER VALUE
S TAD (0100 /INCREMENT PW
S DCA PWP
S JMP #0
S =11. CLA CLL
S DCA SPARA
S TAD APH /SET P4 POINTER
S DCA PWP
S TAD AIV /SET I/V POINTER
S DCA IVP
S TAD AJNIT /SET UNITS POINTER
S DCA JNITS
S AAJ, IAC /JFFSET=0; I/V; 1MA=10V
S LIVO /LATCH OFFSET=0; I/V; 1 MA=10V
S MA, ISZ ASET /WAIT FOR RELAYS TO SETTLE
S JMP 4A
S MY, ISZ ASET
S JMP 4Y
S /
S /SET UP PROPER PULSE HEIGHT
S /
S AD, CLA CLL
S TAD PWP /PW POINTER
S RAL /SET P4 INSTRUCTION
S SZL /MAX P4 YET.
S JMP I GAIN /YES, INCREASE GAIN OF I/V
S DCA PWP /NO, CONTINUE
S IAC /ADD 1
S TAD SPARA /ADD P4 INFO TO PARA WORD
S DCA SPARA
S TAD PWP
S TAD PWP /SET P4
S LPHW /LATCH PW, PW
S MB, ISZ ASET /WAIT FOR RELAYS TO SETTLE
S JMP 43
S WZ, ISZ ASET
S JMP 4Z
S CLA CLL
S TRIG /PULSE TRIGGER
S AE, TCFL /TEST FLAG
S JMP 4E
S SCFPO /CLEAR FLAG, GATE DRIVER
S IAC /CHECK INPUT
S SVA /IS A/D NEARLY PEGGED.
S JMP OFF /YES, ADD OFFSET
S JMP AD /NO, INCREASE PW
S APWP, J400 /PW POINTER
S AIVP, J401 /I/V POINTER
S AUNIT, J400 /UNITS POINTER
S OGAIN, JAIN /ADDRESS OF ADD GAIN ROUTINE
S /
S /SUBPROGRAM GAIN
S /THIS SUBPROGRAM INCREASES GAIN OF I/V AMP
S /
S GAIN, CLA CLL
S TAD IVP /I/V POINTER
S RAL /SET I/V INSTRUCTION
S SZL /IS MAX GAIN APPLIED.
S JMP I PTC /YES, GO TELL
S DCA IVP /NO, CONTINUE

```

```

S 052, TAD 3APT /ADD .1 TO GAIN POINTER
S TAD 9PARA /SET PARA WORD TO PROPER GAIN VALUE
S DCA 9PARA
S TAD IVP
S AND 40077 /ERASE DUMMY POINTER
S JVO /LATCH OFFSET=0) I/V
S WC, ISZ ASET /WAIT FOR RELAYS TO SETTLE
S JMP 4C
S WX, ISZ ASET
S JMP 4X
S CLA
S TRIG /PULSE TRIGGER
S AF, TCFL /TEST FLAG
S JMP AF
S CCFPD /CLEAR FLAG, GATE DRIVER
S IAC /CHECK INPUT
S SNA /IS A/D NEARLY PEGGED.
S PTA, JMP OFF /YES ADD OFFSET
S JMP 3AIN /NO, INCREASE I/V GAIN
S GAPT, 0004 /3AIN POINTER TO PARA WORD
S 00077, 0077 /MASK
S PTC, FALT1 /WARNING ROUTINE 1
S /
S /SUBPROGRAM OFFSET
S /THIS SUBPROGRAM APPLIES OFFSET CURRENT
S /
S OFF, CLA CLL /SET UNITS INCREMENTER
S TAD 4J11
S DCA J11 /BRING IN CURRENT SCALE
S TAD IVP /MASK DUMMY POINTER
S AND 40077 /STORE
S DCA IVP
S TAD IVP
S RTL /SET UP OFFSET CURRENT DECADE SCALE
S RTL
S TAD IVP /SET I/V, OFFSET DECADE
S DCA IVP /STORE
S AG, CLA CLL /IS MAXIMUM OFFSET APPLIED.
S ISZ J11 /NO, CONTINUE
S JMP AA1 /YES, TELL DEFAULT
S AA1, TAD 4JPT /SET OFFSET POINTER TO PARA WORD
S TAD 9PARA /ADD IN PARA WORD
S DCA 9PARA
S TAD 47400 /SET OFFSET UNITS POINTER
S TAD 4NITS /ADD PREVIOUS OFFSET
S DCA 4NITS
S TAD IVP
S TAD 4NITS /SET OFFSET) I/V WORD
S JVO /LATCH OFFSET, I/V
S WD, ISZ ASET /WAIT FOR RELAYS TO SETTLE
S JMP 4D
S WJ, ISZ ASET
S JMP 4J
S WU, ISZ ASET
S JMP 4J
S CLA CLL
S TRIG /PULSE TRIGGER
S AH, TCFL /TEST FLAG
S JMP AH
S CCFPD /CLEAR FLAG, GATE DRIVER
S IAC /CHECK INPUT

```

```

S      SNA                      /A/D PEGGED.
S      JMP AQ                   /YES, ADD MORE OFFSET
S      JMP AV
S      XUPT, 0020                /OFFSET POINTER TO PARA WORD
S      AU11, 7765                /-11
S      U11, 0000                /UNITS INCREMENTER
S      PYD,  FALT2
S      N0077, 0077
S      V7400, 7400
S      AN,   CLA CLL
71      WRITE(1,48)
48      FORMAT(/,1,1)
        ISTI<=0
        JSTI<=0
614     IF(MT)728,68,233
68      DO 656 I=1,50
S      CLA CLL
S      JMS JPS4V
S      CLA CLL
666     CONTINUE
S      =674, CLA CLL
S      JMS AQUT
S      JMS TOUT
S      CLA CLL
        DO TO 162
162     READ(1,67)J
67      FORMAT('RESTART=0,RECORD=-11',15)
        IF(J)163,69,69
163     READ(1,154)J
164     FORMAT('FIRST BLOCK:',15)
        VARA(1)=I
        VARA(2)=JD
        CALL WTape(1,J,374,DARY)
        DO TO 69
S /
S /SUBROUTINE TOUT
S /THIS SUBROUTINE PLOTS DATA
S /
S TOUT, 0000
S      CLA CLL
        READ(1,1)UPD,R_,R4
1      FORMAT('YMAX:',E15.8,/, 'XMIN:',E16.8,/, 'YMAX:',E16.8)
        R4=ALOG(R4)/2.303
        RL=ALOG(RL)/2.303
432     YSCAL=2047./UPD
        XSCAL=2047./(R4-RL)
        DO 3 J=1,I
        X=DARY(1,J)
        Y=DARY(2,J)
        IF(Y-UPD)434,434,5
434     X=ALOG(X)/2.303
433     Y=Y-YSCAL
        X=(X-RL)*XSCAL
        IY=IX(Y)
        IX=IX(X)
        CALL XYST(IX,IY)
        CALL XEND
S      CONTINUE
S      CLA CLL
S      JMP I TOUT

```

```

S /
S /SUBROUTINE OPSHN
S /THIS SUBROUTINE ALLOWS THE SELECTION OF THE DATA OPTION
S /
S OPSHN, 0000
S      CLA CLL
233      WRITE(1,994)J
994      FORMAT(10)
        IF(J)664,665,666
664      READ(1,201)TI9PT
201      FORMAT('INTERVAL (MICROSECS):',E16.8)
        DARY(1,1)=TI9PT
        TI9PT=TI9PT/1.E6
S      CLA CLL
S      JMS STC<
S      CLA CLL
        30 TO 729
665      READ(1,51)DARY(1,1)
51      FORMAT('R = ',E16.8)
729      WRITE(1,729)J,
729      FORMAT('I',10)
S      CLA CLL
S KIM. 4SF
S      JMP KIM
S      CRB
S      TLS
S      CIA
S      OCA 4LD
S      TAD 4LD
S      TAD (0317      /O
S      SVA          /OUTPUT ERROR,
S      JMP 0JER      /YES, 30
S      CLA CLL
S      TAD 4LD
S      TAD (0303      /O
S      SVA          /CHANGE PH.
S      JMP 0PW       /YES, 30
S      CLA CLL
S      TAD 4LD
S      TAD (0305      /E
S      SZA
S      JMP KTS
S      CLA CLL
        IF(J)674,162,162
S KTS.  CLA CLL
S      TAD 4LD
S      TAD (0316      /N
S      SZA
S      JMP KTT
S      JMP 1 OPSHN
S KTT.  CLA CLL
S      TAD 4LD
S      TAD (0322      /R
S      SVA          /REREAD R,
S      JMP 233       /YES, 30
S      CLA CLL
S      TAD 4LD
S      TAD (0323      /S
S      SVA          /TAKE STANDARD,
S      JMP STNO      /YES, 30
S      CLA CLL      /NO, TAKE DATA
        IF(J)667,668,669

```

```

S #667, JMS AV10
S      CLA CLL
      30 TO 669
S #668, JMS AVER3
669    DARY(2,1)=498((S-RCCELL)/S)
      30 TO 729
S OVER, CLA CLL
      WRITE(1,477)DARY(2,1)
477    FORMAT(/,'ER = ',E16.8)
      30 TO 729
S CPW,  CLA CLL
      MT=1
S      CLA CLL
S      JMP #NNY
S STND, CLA CLL
      IF(J2)670,671,571
S #670, JMS AV10          /30 AVERAGE 1000 SINGLE SCANS
S      CLA CLL
      30 TO 672
S #671, JMS AVER3
672    S=RCCELL
      30 TO 729
S HLD,  0000
S /
S /SUBROJTIME ADJT
S /THIS SUBROJTIME JUST PICKS UP SOME VALUES
S /
S AOUT, J100
152    XMAX=DARY(2,1)
      DO 64 J=1,I
      IF(XMAX-DARY(2,J))55,64,64
65     XMAX=DARY(2,J)
64     CONTINUE
      WRITE(1,56)XMAX
66     FORMAT(/,'MAX ER = ',E16.8)
S      CLA CLL
S      JMP I ADJT
S /
S /SUBPROGRAM SETCLK
S /THIS PROGRAM SETS THE CLOCK FROM THE PERIOD INPUT FROM THE TTY
S /IT CONTAINS ITS OWN FIX ROUTINE TO INSURE AGAINST
S /FORTRAN FIX ERRORS
S /ANY TIME INTERVAL FROM 1 MICROSECOND TO 40000 SECONDS
S /MAY BE INPUT
S /
S STCK, J100
S      CLA CLL
S      TAD ATM3          /SET UP PRESET MODE INDICATOR
S      DCA T4B
S      TAD SCT2          /SET UP TB POINTER
S      DCA SCT3
202    IF(T1BPT=.004)204,203,203
S #203, TAD T4B          /CLOCK PRESET MODE INDICATOR
S      TAD T1000         /CLOCK TB INCREMENTER
S      DCA T4B
      T1BPT=T1BPT/10.
S      ISZ SCT3          /ALL DONE,
S      JMP #202          /NO, RETURN
204    T1BPT=T1BPT+1000000.

```



```

S /
S /SPECIAL FIX ROUTINE FOR CLOCK SETUP
S /
S      CLA CLL
S      TAD #T13PT      /BRING UP EXPONENT, UPPER MANTISSA
S      DCA #OT1
S      DCA #OT2      /ZERO 458 WORD
S      TAD #OT1
S      AND #3770      /MASK SIGN, MANTISSA
S      RTR      /RIGHT JUSTIFY EXPONENT
S      RAR
S      TAD #X7600      /SET EXPONENT
S      CLL #MA      /SET SCALING POINTER
S      DCA #PNT
S      TAD #OT1
S      AND #0007      /ERASE ALL BUT UPPER MANTISSA
S      RTR      /LEFT JUSTIFY
S      RTR
S      DCA #OT1
S      TAD #T13PT#      /BRING IN FIRST COMPLETE MANTISSA WORD
S      AND #7770      /MASK LOWER 3 BITS
S      RTR      /RIGHT JUSTIFY
S      RAR
S SCT4, TAD #OT1      /SET COMPLETE WORD
S      ISZ #PNT      /ALL SCALED,
S      SKP      /NO, SCALE
S      JMP SCT5      /YES, GO ON TO NEXT SECTION
S      RAL      /SCALE BY 2
S      DCA #OT1
S      TAD #OT2      /WILL CONTAIN COMPLETED VALUE
S      RAL      /SCALE BY 2
S      DCA #OT2
S      JMP SCT4      /RETURN FOR NEXT SCALING
S ATMB, #400      /PRESET MODE INDICATOR
S TMB, #000
S T1000, #000
S SCT2, #7771      /CLOCK TO INCREMENTER
S SCT3, #000      /TS POINTER
S POT1, #000
S POT2, #000
S N3770, #3770
S X7600, #7600
S XPNT, #000
S N0007, #0007
S N7770, #7770
S SCT5, CLA CLL
S      TAD TMB      /SELECTED TO: PRESET MODE
S      CTR      /LOAD CONTROL REGISTER
S      CLA CLL
S      TAD #OT2      /SETS JP EXACT INTERVAL
S      CIA
S      LPSET      /LOAD PRESET REGISTER
S      JMP I STCK
S /
S /THIS IS THE ROUTINE WHICH TAKES 1000 MEASUREMENTS AT AN INPUT
S /INTERVAL APART AND AVERAGES THEM
S /
S      PAGE
S AV10, #000
S      CLA CLL
S      DCA #LS3      /ZERO LEAST SIGNIFICANT BITS
S      DCA #MS3      /ZERO MOST SIGNIFICANT BITS

```

```

S      TAD (7000      /-512
S      DCA ASET
S XQ,   TRIG         /PULSE
S      CLOF2        /CLEAR CLOCK FLAG
S      SCFF         /CLEAR COMBIP FLAG
S XR,   TCFL        /TEST COMBIP FLAG
S      JMP XR
S      CLCIC        /CLEAR CLOCK, INITIALIZE COUNTER
S      SCFPD        /CLEAR COMBIP FLAG, GATE DRIVER
S      TAD T1S3
S      DCA T1S3
S      RAL
S      TAD TMS3
S      DCA TMS3
S      ISZ ASET
S      SKP
S      JMP XT
S XS,   SKPD?        /WAIT FOR CLOCK FLAG
S      JMP XS
S      JMP X2        /RETURN FOR MORE
S T1S3, J000
S TMS3, J000
S XT,   CLA CLL
S      TAD T1S3
S      MQL
S      TAD TMS3
S      DVI
S      1000         /THE DIVISOR, 512
S      TAD (4000
S      CLL
S      DCA =JSTIK
S      MCA
S      TAD (4000
S      DCA =ISTIK
S      Z=FLOAT(ISTIK)
S      Z2=FLOAT(JSTIK)
S      <D=512
S      TAD SPARA
S      JMS DCODE
S      CLA CLL
21      WRITE(1,21)RCEL
S      FORMAT(/,1R = ',E16.8,/)
S      DARY(2,1)=RCEL
S      CLA CLL
S      JMP I AV10
S /
S /THIS SECTION OUTPUTS THE DATA STORED ON TAPE
S /AND FINDS THE MAXIMUM, MINIMUM, AND AVERAGE ERRORS OF THAT DATA.
S /
502     READ(1,503)J
503     FORMAT('MAX-MIN=1,AVERAGE=0,OUTPUT=-11',15)
504     IF(J)504,505,509
504     DO 507 J=1,I
505     WRITE(3,505)DARY(1,J),DARY(2,J)
506     FORMAT(5X,'X = ',E16.8,5X,'ER = ',E16.8)
507     CONTINUE
508     DO 509 J=1,I
509     TOT=0
510     DO 506 J=1,I
511     TOT=TOT+DARY(2,J)
512     CONTINUE
513     TOT=TOT/FLOAT(I)

```

```

922  WRITE(1,522)TOT
      FORMAT(/,1AVERAGE = ',E16.8)
      DO TO 520
909  XMAX=OARY(2,1)
      XMIN=OARY(2,1)
      YMAX=OARY(1,1)
      YMIN=OARY(1,1)
910  DO 519 J=2,I
      IF(XMAX-OARY(2,J))511,512,512
911  XMAX=OARY(2,J)
      YMAX=OARY(1,J)
      DO TO 519
912  IF(OARY(2,J)-XMIN)513,519,519
913  XMIN=OARY(2,J)
      YMIN=OARY(1,J)
919  CONTINUE
      WRITE(1,514)XMAX,YMAX,XMIN,YMIN
914  FORMAT(/,1MAX ER = ',E16.8,' AT X = ',E16.8,/,1MIN ER = ',E16.8,
      *' AT X = ',E16.8)
920  READ(1,521)J
921  FORMAT('OPTIONS=1,RESTART=01',I5)
      IF(J)69,69,502

S /
S /THIS ROUTINE PERFORMS THE AVERAGE OF AN INPUT NUMBER OF SCANS
S /
S AVERG, 0000
S AU,      CLA CLL
           MT=-1
S          CLA CLL
           TAD #4D          /SET UP DIVISOR
S          DCA V9AR
           TAD #4D          /SET UP # OF POINTS POINTER
S          CIA
           DCA P9AR
S          DCA VLSB        /CLEAR LSB WORD
           DCA VMSB        /CLEAR MSB WORD
S AW,      CLA CLL
           TRIG             /PULSE TRIGGER
S AX,      TCFL            /TEST FLAG
S          JMP AX
           SCFPO            /CLEAR FLAG, GATE DRIVER
S          TAD VLSB        /ADD IN LSBs
           DCA VLSB
S          RAL             /SET UP OVERFLOW
           TAD VMSB        /ADD IN MSBs
           DCA VMSB
S          ISZ P9AR        /ALL DONE.
           JMP AD          /NO, RETURN FOR NEXT SCAN
S          TAD VLSB        /YES, SET SET TO AVERAGE
           MQL             /LOAD MQ WITH LSB WORD
S          TAD VMSB
           DVI             /DIVIDE
S NBAR,    0000           /THE DIVISOR
           TAD C4000
S          CLA
           DCA =JSTIK      /STORE REMAINDER
S          MDA             /LOAD DIVIDEND INTO AC
           SNA             /UNDERRANGED.
S          JMP I K11       /YES, RESET
S          DCA VALJ        /NO, STORE
S          TAD VALU
S          IAC

```

```

S SVA /OVERRANGED.
S JMP I K11 /YES, RESET
S CLA CLL /NO, CONTINUE
S TAD VALJ
S TAD C4000 /CHANGE TO 2'S COMPLIMENT
S CLL
S DCA #ISTIK
S Z=FLOAT(ISTIK)
S Z2=FLOAT(JSTIK)
S CLA CLL
S TAD SPARA /PUT PARA WORD IN AC
S JMS I BCODE /GO TO DECODE SUBROUTINE WITH PARA WORD IN AC
S CLA CLL
S JMP #72
S VALU, 0000
S K11, #11
S NLSB, 0000 /THE LEAST SIGNIFICANT BIT WORD
S NMSB, 0000 /THE MOST SIGNIFICANT BIT WORD
S PBAR, 0000 /AVERAGE NUMBER POINTER
S C4000, 4000
S BCODE, BCODE /PARA WORD DECODE SUBROUTINE
S 72 WRITE(1,13)ES,RCCLL
S 13 FORMAT(/, 'AVERAGE' = ' ', E12.6, /, 'X' = ' ', E12.6)
S JMP I AVERG
S /
S /SUBPROGRAM FALT1
S /THIS SUBPROGRAM INDICATES THAT CELL COND IS VERY LOW
S /
S FALT1, CLA CLL
S WRITE(1,14)
S 14 FORMAT('ERROR 1')
S JMP I PAF1
S PAF1, AV
S /
S /SUBPROGRAM FALT2
S /THIS SUBPROGRAM INDICATES CELL COND TOO HIGH
S /
S FALT2, CLA CLL
S WRITE(1,15)
S 15 FORMAT('ERROR 2')
S CLA CLL
S #17, JMP #614
S /
S /SUBROUTINE DCODE
S /THIS SUBROUTINE DECODES PARAMETER WORDS
S /COMPUTES PH, RV, XUNI, ES, RCCLL, CCELL
S /IT MUST BE ENTERED WITH PARA WORD IN AC
S /PARA WORD FORMAT:
S / FIRST 4 BITS (MSB) ARE FOR REMAINDER OF AVERAGE
S / NEXT 4 BITS FOR UNITS VALUE (BINARY 1-10)
S / NEXT 2 BITS FOR GAIN INFO (BINARY VALUE 0-3)
S / NEXT 2 BITS FOR PH INFO (BINARY 1-3)
S /
S DCODE, 0000
S DCA SPPJ /STORE PARA WORD
S XUNI=0.
S #4=.005
S RV=10000.
S TAD SPPJ
S AND #SK1 /MASK ALL BUT PH BITS
S DC1, DCA SPPJ
S TAD SPPJ

```

```

S      SNA                      /ALL SET.
S      JMP DC2                  /YES, CONTINUE
S      CLA CLL                  /NO, ADJUST
S      P4=P4*10.
S      SNA                      /ADD -1
S      TAD SPP4                 /SET UP NEXT ITERATION
S      JMP DC1
S MSK1, J003                    /MASK ALL BUT PH BITS
S DC2,  TAD SPPJ
S      AND MSK2                  /MASK ALL BUT GAIN BITS
S DC3,  DCA SPP4
S      TAD SPP4
S      SNA                      /ALL SET.
S      JMP DC4                  /YES, CONTINUE
S      CLA CLL                  /NO, ADJUST
S      RV=RV*10.
S      TAD DC7774
S      TAD SPP4                 /SET UP NEXT ITERATION
S      JMP DC3
S MSK2, J014                    /MASK FOR ALL BUT GAIN BITS
SDC7774, 7774                  /GAIN DEINCREMENTER
S DC4,  TAD SPPJ
S      AND MSK3                  /MASK ALL BUT OFFSET UNITS BITS
S DC5,  DCA SPP4
S      TAD SPP4
S      SNA                      /ALL SET.
S      JMP DC6                  /YES, CONTINUE
S      CLA CLL                  /NO, ADJUST
S      XUNI=XUNI+1.
S      TAD DC7760
S      TAD SPP4                 /SET UP FOR NEXT ITERATION
S      JMP DC5
S MSK3, J360                    /MASK FOR ALL BUT UNITS BITS
SDC7760, 7760                  /UNITS DEINCREMENTER
S DC6,  CLA CLL
S      ESL=(Z2*(12.5/4095.)*6.25)/FLOAT(KD)
S      ES=(Z*(12.5/4096.)*6.25)+ESL
S      RCEL=P4/((ES/RV)+((10.*XUNI)/RV))
S      CLA CLL
S      JMP I DCODE
S      END

```

CBTCLH
PROGRAM LISTING

```

S /PROGRAM NAME: C3TCLH.FT
S /FORTRAN-SABR: KEITH J. CASERTA 5/17/74
S /THIS IS THE TEST PROGRAM AND EXERCISER ROUTINE FOR THE ENTIRE
S /COMBIP SYSTEM. IT CONTAINS DIAGNOSTICS AND ERROR CODES TO
S /PERMIT DETERMINATION OF HARDWARE MALFUNCTIONS AS WELL AS
S /PERIODIC INSTRUMENTAL ADJUSTMENT.
S /IT BEGINS WITH AN INITIAL 3 SCAN OF THE SYSTEM AFTER THE CHOSEN
S /PULSE WIDTH IS INPUT. TEMPERATURE IS ALSO MEASURED. IF A FLAG
S /ERROR SHOULD OCCUR IN EITHER CIRCUIT DURING THE PRELIMINARY SCAN,
S /THE PROGRAM AUTOMATICALLY ENTERS A CONTINUOUS FLAG-CHECK ROUTINE.
S /IF THE PRELIMINARY SCAN IS COMPLETED SUCCESSFULLY, THE VALUES OF THE
S /CIRCUIT PARAMETERS ARE OUTPUT.
S /THE OPTIONS AVAILABLE AT THIS TIME:
S / 1)AVERAGE 100 CONDUCTANCE SCANS FOLLOWING EACH "G" TYPED
S / 2)RESTART THIS PROGRAM
S / 3)CONTINUOUSLY PULSE THE CELL AT PW X 10 INTERVALS
S / 4)TEST THE CONDUCTANCE CONVERSION SYSTEM
S / 5)TEST BOTH CONDUCTANCE AND TEMPERATURE CONVERSION SYSTEMS
S / 6)AVERAGE 25 TEMPERATURE POINTS FOLLOWING EACH "G" TYPED
S / 7)TEST THE TEMPERATURE CONVERSION SYSTEM
S /ERROR MESSAGES ARE OUTPUT WITH EACH FAILURE.
S /(1) AND (6) OUTPUT DATA TO THE TTY.
S /
S JPDF CCFP 6321 /CLEAR COND FLAG, CLEAR PI ENABLE
S JPDF GCDR 6322 /GATE CONDUCTANCE DRIVER
S JPDF CCFPD 6323 /CCFP + GCDR
S JPDF ECP1 6324 /ENABLE COND PROGRAM INTERRUPT
S JPDF CCFGD 6327 /CCFP + GCDR + ECP1
S SKPD TCFL 6331 /TEST CONDUCTANCE FLAG
S JPDF TOST 6332 /TURN OFF SEQUENCE TRIGGER
S JPDF TRIG 6334 /TRIGGER SEQUENCE
S SKPD TYFL 6341 /TEST TEMPERATURE FLAG
S JPDF LIVO 6342 /LATCH I/V. OFFSET
S JPDF LPWH 6344 /LATCH PI, PW
S JPDF ETP1 6351 /ENABLE TEMP PROGRAM INTERRUPT
S JPDF CTFG 6352 /CLEAR TEMP FLAG, PI ENABLE, GATE DRIVER
S JPDF TTAD 6354 /TRIGGER TEMP A/D CONVERSION
S JPDF TFGT 6356 /CTFG + TTAD
S JPDF TIT 6351 /TITRATE
S JPDF PSET 6121 /LOAD THE CLOCK PRESET REGISTER
S JPDF CLCL 6122 /CLEAR THE CLOCK
S JPDF ICNTR 6123 /INITIALIZE THE COUNTER
S JPDF CLCIC 6124 /CLEAR CLOCK AND INITIALIZE COUNTER
S JPDF LCNTR 6125 /LATCH THE COUNTER
S JPDF RCTRL 6126 /READ THE COUNTER LATCH
S JPDF RCNTR 6127 /READ THE COUNTER
S JPDF LCTRL 6131 /LOAD CONTROL REGISTER
S SKPD SKPDF 6132 /SKIP ON OVERFLOW
S SKPD SKPDE 6133 /SKIP ON OVERFLOW ERROR
S JPDF CL7FE 6134 /CLEAR OVERFLOW AND OVERFLOW ERROR FLAGS
S SKPD SKPT9 6135 /SKIP ON TIME BASE FLAG
S SKPD SKTBE 6136 /SKIP ON TIME BASE ERROR FLAG
S JPDF CLTBE 6137 /CLEAR T.B. AND T.B. ERROR FLAGS
S JPDF MUY 7405 /MULTIPLY
S JPDF DIV 7407 /DIVIDE
S JPDF NMI 7411 /NORMALIZE
S JPDF SHL 7413 /SHIFT LEFT
S JPDF ASR 7415 /ARITHMETIC SHIFT RIGHT
S JPDF LSR 7417 /LOGICAL SHIFT RIGHT
S JPDF MOL 7421 /LOAD MULTIPLIER QUOTIENT
S JPDF SCL 7403 /STEP COUNTER LOAD FROM MEMORY
S JPDF SCA 7441 /STEP COUNTER LOAD INTO AC

```

```

S      JODE?  MOA      7301      /MO LOAD INTO AC
S      JODE?  ERASE    6034      /ERASE DISPLAY SCOPE
S      JODE?  STORE    6057      /SET SCOPE IN STORE MODE
S      ABSY4   PWP      0074      /PW POINTER
S      ABSY4   PWP      0075      /PW POINTER
S      ABSY4   IVP      0076      /I/V POINTER
S      ABSY4   JNITS    0077      /OFFSET UNITS POINTER
S      ABSY4   ASET     0100      /GENERAL POINTER
S      ABSY4   SPARA    0101      /PARAMETER POINTER
S      ABSY4   SPOU     0102      /INDIRECT ADDRESS IN FIELD 1 POINTER
S      ABSY4   SPPW     0103      /INDIRECT ADDRESS IN FIELD 1 POINTER
S /
S /
S /THE PRELIMINARY SCAN BEGINS
S /
S /
S PNNY, CLA CLL
S      DCA PWP          /SET PW AT 0.01 MSEC
S      MT=0
S      READ(1,7)PW
7      FORMAT('AT WHAT PW. (MSEC): ',E12.8)
S      XX=.001
S      XX=XX*10.
S      IF(PW-XX)11,11,10
S #10, CLA CLL
S      TAD PWP          /SET PW TO PROPER VALUE
S      TAD (0100        /INCREMENT PW
S      DCA PWP
S      JMP #0
S #11, CLA CLL
S      DCA SPARA
S      TAD APWP        /SET PW POINTER
S      DCA PWP
S      TAD AIVP        /SET I/V POINTER
S      DCA IVP
S      TAD AJNIT        /SET UNITS POINTER
S      DCA JNITS
S      TAD PWP          /SET CLOCK FOR PW X 10 FOR FLAG CHECK
S      RTR
S      RTR
S      RTR
S      IAC
S      IAC
S      LCTR_          /LOAD THE CLOCK CONTROL REGISTER
S      CLA CLL
S      CCFP          /INITIALLY CLEAR THE CONDUCTANCE FLAG
S AAJ, IAC          /OFFSET=0 I/V 1MA=10V
S      LIVO          /ATCH OFFSET=0 I/V 1 MA=10V
S WA, ISZ ASET        /WAIT FOR RELAYS TO SETTLE
S      JMP WA
S WY, ISZ ASET
S      JMP WY
S AD, CLA CLL
S      TAD PWP          /PW POINTER
S      RAL            /SET PW INSTRUCTION
S      SZL            /MAX PW YET.
S      JMP I 034IV      /YES, INCREASE GAIN OF I/V
S      DCA PWP          /NO, CONTINUE
S      IAC            /ADD 1
S      TAD SPARA        /ADD PW INFO TO PARA WORD
S      DCA SPARA
S      TAD PWP

```



```

S      TAD PHP      /SET PH
S      LPHW      /LATCH PH,PH
S  WB,  ISZ ASET    /WAIT FOR RELAYS TO SETTLE
S      JMP J3
S  WZ,  ISZ ASET
S      JMP JZ
S      CLA CLL
S      CLCL      /CLEAR THE CLOCK
S      CLTB3     /CLEAR TIME BASE AND ERROR FLAGS
S      TRIG      /PULSE TRIGGER
S  AE,  TCFL      /TEST FLAG
S      SKP
S      JMP <TC1
S      SKPT3     /SKIP ON TIME BASE
S      JMP AE
S      JMS FALTS  /30 INDICATE FLAG ERROR
S      JMP SKTC   /30 TO CONTINUOUS FLAG CHECK ROUTINE
S  KTC1, CCPLD     /CLEAR FLAG,GATE DRIVER
S      IAC      /CHECK INPUT
S      SNA      /IS A/D NEARLY PEGGED.
S      JMP OFF   /YES, ADD OFFSET
S      JMP AD     /NO, INCREASE PH
S  APHP, J400      /PH POINTER
S  AIVP, J401      /I/V POINTER
S  AUNIT, J400     /UNITS POINTER
S  OGAIN, JAIN      /ADDRESS OF ADD GAIN ROUTINE
S  /
S  /SUBPROGRAM GAIN
S  /THIS SUBPROGRAM INCREASES GAIN OF I/V AMP
S  /
S  GAIN, CLA CLL
S      TAD IVP      /I/V POINTER
S      RAL      /SET I/V INSTRUCTION
S      SZL      /IS MAX GAIN APPLIED.
S      JMP I PTC    /YES,30 TELL
S      DCA IVP      /NO,CONTINUE
S  #52, TAD 3APT    /ADD 1 TO GAIN POINTER
S      TAD 3PARA    /SET PARA WORD TO PROPER GAIN VALUE
S      DCA 3PARA
S      TAD IVP
S      AND 40077    /ERASE DUMMY POINTER
S      LIVO      /LATCH, OFFSET=0) I/V
S  WC,  ISZ ASET    /WAIT FOR RELAYS TO SETTLE
S      JMP JC
S  WX,  ISZ ASET
S      JMP JX
S      CLA
S      CLCL      /CLEAR THE CLOCK
S      CLTB3     /CLEAR TIME BASE AND ERROR FLAGS
S      TRIG      /PULSE TRIGGER
S  AF,  TCFL      /TEST FLAG
S      SKP
S      JMP <TC2
S      SKPT3     /SKIP ON TIME BASE FLAG
S      JMP AF
S      JMS FALTS  /30 INDICATE FLAG ERROR
S      JMP SKTC   /30 TO CONTINUOUS FLAG CHECK ROUTINE
S  KTC2, CCPLD     /CLEAR FLAG,GATE DRIVER
S      IAC      /CHECK INPUT
S      SNA      /IS A/D NEARLY PEGGED.
S  PTA, JMP OFF     /YES ADD OFFSET
S      JMP JAIN   /NO, INCREASE I/V GAIN

```

```

S GAPT, 0004          /MAIN POINTER TO PARA WORD
S M0077, 0077        /MASK
S PTC,  FALT1        /WARNING ROUTINE 1
S /
S /SUBPROGRAM OFFSET
S /THIS SUBPROGRAM APPLIES OFFSET CURRENT
S /
S OFF,  CLA CLL
S          TAD (7769          /SET UNITS INCREMENTER
S          DCA J11
S          TAD IVP          /BRING IN CURRENT SCALE
S          AND (0077        /MASK DUMMY POINTER
S          DCA IVP          /STORE
S          TAD IVP
S          RTL              /SET UP OFFSET CURRENT DECADE SCALE
S          RTL
S          TAD IVP          /SET I/V, OFFSET DECADE
S          DCA IVP          /STORE
S AG,  CLA CLL
S          ISZ J11          /IS MAXIMUM OFFSET APPLIED.
S          JMP AAI          /NO, CONTINUE
S          JMP FALT2        /YES, TELL DEFAULT
S AAI,  TAD (0020          /SET OFFSET POINTER TO PARA WORD
S          TAD SPARA        /ADD IN PARA WORD
S          DCA SPARA
S          TAD (7400        /SET OFFSET UNITS POINTER
S          TAD JNITS        /ADD PREVIOUS OFFSET
S          DCA JNITS
S          TAD IVP
S          TAD JNITS        /SET OFFSET I/V WORD
S          LIVO            /LATCH OFFSET, I/V
S WD,  ISZ ASET          /WAIT FOR RELAYS TO SETTLE
S          JMP 40
S WJ,  ISZ ASET
S          JMP 4J
S WU,  ISZ ASET
S          JMP 4J
S          CLA CLL
S          C-CL           /CLEAR THE CLOCK
S          C-CL           /CLEAR TIME BASE AND ERROR FLAGS
S          TRIG           /PULSE TRIGGER
S AM,  TCFL              /TEST FLAG
S          SKP
S          JMP <TC3
S          SKPT3          /SKIP ON TIME BASE FLAG
S          JMP 44
S          JMS FALT3        /30 INDICATE A FLAG ERROR
S          JMP SKTC        /30 TO CONTINUOUS FLAG CHECK ROUTINE
S KTC3, CCFPD           /CLEAR FLAG, GATE DRIVER
S          IAC             /CHECK INPUT
S          SNA             /A/D PEGGED,
S          JMP 43          /YES, ADD MORE OFFSET
S          SKP
S U11,  0000            /JNITS INCREMENTER
S /
S /BEGIN TO OUTPUT THE DATA FROM THE PRELIMINARY SCAN
S /
S AN,  CLA CLL
S          CTFP3          /CLEAR TEMP FLAG INITIALLY
S          CLA CLL
S          DCA ASET        /ZERO T FLAG CHECK POINTER
S          ITAD           /TRIGGER TEMP A/D

```

```

S      CLCL          /CLEAR THE CLOCK
S      CLTB=         /CLEAR THE TIME BASE AND ERROR FLAGS
S      TRIG          /PULSE TRIGGER
S AP,   TCFL         /TEST FLAG
S      SKP
S      JMP <TC4
S      SKPT3         /SKIP ON TIME BASE FLAG
S      JMP AP
S      JMS FALTS     /33 INDICATE A FLAG ERROR
S      JMP SKTC      /33 TO CONTINUOUS FLAG CHECK ROUTINE
S KTC4, CCFP0        /CLEAR FLAG, GATE DRIVER
S      TAD (40C0)    /CHANGE TO 2'S COMPLEMENT
S      CLL
S      DCA =ITORE
S      Z=FLJAT(ITORE)
S      CLA CLL
S      TAD SPARA      /PUT PARA WORD IN AC
S      JMS DCODE      /33 TO DECODE ROUTINE WITH PARA WORD IN AC
S      CLA CLL
S XLZ,  TTFL         /TEST TEMP FLAG
S      SKP
S      JMP <TC5
S      ISZ ASET
S      JMP XLZ
S      JMS FALTS     /33 INDICATE A T FLAG ERROR
S      JMP SKTC      /33 TO CONTINUOUS FLAG CHECK ROUTINE
S KTC5, CTFP3        /CLEAR FLAG, GATE DRIVER
S      TAD (4033)
S      CLL
S      DCA =ITORE
S      Z=FLJAT(ITORE)
S      T=Z+(10./4096.)*3.
S /
S /OUTPUT CIRCUIT PARAMETERS
S /
71      WRITE(1,3)PH,XJN1,RV
3        FORMAT('PH = ',E10.4,/, 'UNITS = ',E10.4,/, 'RV = ',E10.4)
        WRITE(1,4)ES,RCELL,T
4        FORMAT('ES = ',E12.6,/, 'RCELL = ',E12.6,/, 'TEMP = ',E12.6,/)
614     IF(MT)730,728,730
S /
S /
S /OPTION ROUTINE TO SELECT TESTING OPTION
S /
S /
728     WRITE(1,729)
729     FORMAT(/,'OPTIONS: 1)AVERAGE 100 G SCANS',/,9X,'2)RESTART',/,9X,
+ '3)PULSE',/,9X,'4)3 CONV TEST',/,9X,'5)TEMP-COND TEST',/,9X,'6)AVE
+ 'RAGE 25 T POINTS',/,9X,'7)T CONV TEST',/)
S      CLA CLL
S KIM,  <SF
S      JMP <IM
S      <RR
S      T=5
S      TAD (7517)
S      SVA
S      JMP AJ
S      TAD (7777)
S      SVA
S      JMP >QNY
S      TAD (7777)
S      SVA

```

```

S      JMP CTPL3
S      TAD (7777)
S      SVA
S      JMP CONV
S      TAD (7777)
S      SVA
S      JMP TCTT
S      TAD (7777)
S      SVA
S      JMP JZ1
S      JMP TCONV
730    CONTINUE
S /
S /THIS ROUTINE PERFORMS AVERAGE OF 100 3 SCANS
S /
S AU,   CLA CLL
        MT=1
S      JMS TYP3           /30 WAIT FOR A "3"
S      CLA CLL
S      TAD (0144)         /SET UP DIVISOR OF 100 DECIMAL
S      DCA NBAR
S      TAD (7634)         /SET UP # OF POINTS POINTER
S      DCA PBAR
S      DCA VLSB           /CLEAR LSB WORD
S      DCA VMSB           /CLEAR MSB WORD
S AW,   CLA CLL
S      TRIG               /PULSE TRIGGER
S AX,   TCFL              /TEST FLAG
S      JMP AX
S      CCFPD              /CLEAR FLAG, GATE DRIVER
S      TAD VLSB           /ADD IN LSBs
S      DCA VLSB
S      RAL                /SET UP OVERFLOW
S      TAD VMSB           /ADD IN MSBs
S      DCA VMSB
S      ISZ PBAR           /ALL DONE.
S      JMP A4              /NO, RETURN FOR NEXT SCAN
S      TAD VLSB           /YES, SET SET TO AVERAGE
S      MCL                /LOAD MSB WITH LSB WORD
S      TAD VMSB
S      DVI                /DIVIDE
S NBAR, J100              /THE DIVISOR
S      CLA CLL           /ERASE REMAINDER
S      MCA                /LOAD DIVIDEND INTO AC
S      SVA                /UNDERRANGED.
S      JMP I K11          /YES, RESET
S      DCA VALJ           /NO, STORE
S      TAD VALJ
S      IAC
S      SVA                /OVERRANGED.
S      JMP I K11          /YES, RESET
S      CLA CLL           /NO, CONTINUE
S      TAD VALJ
S      TAD (4000)         /CHANGE TO 2'S COMPLIMENT
S      CLL
S      DCA #ISTIK
S      Z=FLCAT(ISTIK)
S      CLA CLL
S      TAD $PARA          /PUT PARA WORD IN AC
S      JMS I RCJDE        /30 TO DECODE SUBROUTINE WITH PARA WORD IN AC
S      CLA CLL
S      JMP #72

```

```

S K0144,J144          /100
S K7634,7634         /-100
S VALU, 0000
S K11, 011
S NLS0, 0100          /THE LEAST SIGNIFICANT BIT WORD
S NMS0, 0100          /THE MOST SIGNIFICANT BIT WORD
S PBAR, 000           /AVERAGE NUMBER POINTER
S C4000,4000
S BCODE,0CODE        /PARA WORD DECODE SUBROUTINE
    72 WRITE(1,13)ES,RCCL
    13 FORMAT(/,'AVI ES = ',E12.6,/,4X,'RCCL = ',E12.6)
S      JMP AJ          /RETURN FOR NEXT RUN
S /
S /SUBPROGRAM SKTC
S /THIS SUBPROGRAM CONTINUOUSLY CHECKS THE CONDUCTANCE AND
S /TEMPERATURE FLAGS. IT IS ENTERED AS THE RESULT OF A FLAG
S /ERROR DURING THE PRELIMINARY SCAN ROUTINE.
S /
S SKTC, STFP3         /CLEAR TEMP FLAG
S      CLA CLL
S      DCA ASET        /ZERO T FLAG TEST POINTER
S      CCFP           /CLEAR THE CONDUCTANCE FLAG
S      CLCL           /CLEAR THE CLOCK
S      CLTB           /CLEAR THE TIME BASE AND ERROR FLAGS
S      TRIG           /TRIGGER PULSES
S KTC6, TCFL          /TEST CONDUCTANCE FLAG
S      SKP
S      JMP <TC7
S      SKPT3          /SKIP ON TIME BASE FLAG
S      JMP <TC6
S      JMS FALTS      /30 INDICATE G FLAG ERROR
S KTC7, TTAD          /TRIGGER TEMP A/D
S KTC8, TTFL          /TEST THE TEMP FLAG
S      SKP
S      JMP SKTC
S      ISZ ASET
S      JMP <TC8
S      JMS FALTS      /30 INDICATE T FLAG ERROR
S      JMP SKTC
S /
S /SUBPROGRAM CTPLS
S /THIS SUBPROGRAM ALLOWS CONTINUOUS PULSING OF THE COMPUTERIZED
S /CONDUCTANCE SYSTEM AT A PERIOD EQUAL TO 10 X PH
S /
S CTPLS,CLA CLL
S      TAD PH
S      RTR            /SET TIME BASE TO BE CHOSEN PULSE
S      RTR            /X 10
S      RTR
S      IAC
S      IAC
S      LCTR           /LOAD THE CONTROL REGISTER
S      CLA CLL
S CTP1, CLCL          /CLEAR THE CLOCK
S      CLTB           /CLEAR T.B. AND T.B. ERROR FLAGS
S      TRIG           /PULSE
S CTP2, SKPT3         /SKIP ON T.B. FLAG
S      JMP CTP2
S      JMP CTP1

```

```

S /
S /SUBPROGRAM CONV
S /THIS SUBPROGRAM ALLOWS CONTINUOUS PULSING AND CONVERSION
S /AND CHECKS FOR FLAG OR ZERO CONVERSION ERRORS IN THE G CIRCUIT
S /
S CONV, CLA CLL
S      TAD RWP
S      RTR
S      RTR
S      RTR
S      IAC
S      IAC
S      LCTR
S CNV1, CLA CLL
S CNV2, CLCL
S      CLTBZ
S      TRIG
S CNV3, TCFL
S      SKP
S      JMP CNV4
S      SKPT3
S      JMP CNV3
S      JMS FALT3
S      JMP CNV1
S CNV4, CCFPD
S      SZA
S      JMP CNV5
S      JMS FALT4
S      JMP CNV1
S CNV5, IAC
S      SZA
S      JMP CNV1
S      JMS FALT5
S      JMP CNV1
S /
S /SUBPROGRAM TCTT
S /THIS SUBPROGRAM CHECKS BOTH T AND G CONVERSION AND FLAG CIRCUITS
S /
S TCTT, CLA CLL
S      TAD RWP
S      RTR
S      RTR
S      RTR
S      IAC
S      IAC
S      LCTR
S TCC1, CLA CLL
S      DCA ASET          /ZERO TIME INDICATOR
S TCC2, CLCL
S      CLTBZ
S      CCFPD            /INITIALLY CLEAR G FLAG
S      TRIG
S TCC3, TCFL
S      SKP
S      JMP TCC4
S      SKPT3
S      JMP TCC3
S      JMS FALT3
S      JMP TCC1
S TCC4, CCFPD
S      SZA
S      JMP TCC5

```

```

S      JMS FALT4
S      JMP TCC6
S TCC5, IAC
S      SZA
S      JMP TCC6
S      JMS FALT5
S TCC6, CTFP3      /INITIALLY CLEAR T FLAG
S      CLA CLL
S      TTAD
S TCC7, TTFL
S      SKP
S      JMP TCC8
S      ISZ ASET
S      JMP TCC7
S      JMS FALT6
S TCC8, CTFP3
S      SZA
S      JMP TCC9
S      JMS FALT8
S      JMP TC10
S TCC9, IAC
S      SZA
S      JMP TC10
S      JMS FALT9
S TC10, CLA CLL
S      JMP TCC1
S /
S /THIS ROUTINE PERFORMS THE AVERAGE OF 25 T POINTS
S /
S 021, CLA CLL
S      TAD (7747      /-25
S      DCA ASET
S      DCA TLS3
S      DCA TMS3
S      JMS TYP3
S 023, CTFP3      /CLEAR TEMP FLAG
S      CLA CLL
S      TTAD      /TRIGGER TEMP A/D
S 022, TTFL      /TEST FLAG
S      JMP 222
S      CTFP3      /CLEAR FLAG, GATE DRIVER
S      TAD TLS3
S      DCA TLS3
S      RAL
S      TAD TMS3
S      DCA TMS3
S      ISZ ASET
S      JMP 223
S      TAD TLS3
S      MQL
S      TAD TMS3
S      DVI
S      J031
S      CLA CLL
S      MDA
S      TAD (4000
S      DCA #IPDT
S      Z=FLJAT(IPDT)
S      ES=(Z*(10./4095.))+5.)
S      WRITE(1,900)ES
900   FORMAT('TEMP = ',E12.6)
S      JMP 221

```

```

S TLSB, J000
S TMSB, U000
S /
S /SUBPROGRAM TONV
S /THIS ROUTINE CHECKS THE TEMPERATURE CONVERSION SYSTEM
S /FOR CONVERSION AND FLAG ERRORS
S /
S TONV, STFP3           /INITIALLY CLEAR T FLAG
S MN1,  CLA CLL
S          DCA ASET       /CLEAR INITIAL TIMING POINTER
S          TTAD           /TRIGGER TEMP A/D CONVERSION
S MN2,  TTFL           /TEST TEMP FLAG
S          SKP
S          JMP M43
S          ISZ ASET
S          JMP M42
S          JMS FALT6
S MN3,  STFP3           /CLEAR T FLAG, GATE DRIVER
S          SZA
S          JMP M44
S          JMS FALT5
S          JMP M45
S MN4,  IAC
S          SZA
S          JMP M45
S          JMS FALT5
S MN5,  CLA CLL
S          JMP M41
S /
S /SUBPROGRAM FALT1
S /THIS SUBPROGRAM INDICATES THAT CELL COND IS VERY LOW
S /
S FALT1, CLA CLL
          WRITE(1,14)
14      FORMAT('ERROR 1')
S          JMP I PAF1
S PAF1, 4V
S /
S /SUBPROGRAM FALT2
S /THIS SUBPROGRAM INDICATES CELL COND TOO HIGH
S /
S FALT2, CLA CLL
          WRITE(1,15)
15      FORMAT('ERROR 2')
S          CLA CLL
S M17,  JMP M614
S /
S /SUBROUTINE FALT3
S /THIS SUBPROGRAM INDICATES FLAG ERROR
S /
S FALT3, J000
S          CLA CLL
          WRITE(1,740)
740     FORMAT('ERROR 3')
S          CLA CLL
S          JMP I FALT3
S /
S /SUBROUTINE FALT4
S /THIS SUBPROGRAM INDICATES A ZERO CONVERSION ERROR
S /
S FALT4, J000

```



```

S      CLA CLL
      WRITE(1,741)
741    FORMAT('ERROR 4')
S      CLA CLL
S      JMP I FALT4
S /
S /SUBROUTINE FALT5
S /THIS SUBPROGRAM INDICATES 3 FULL SCALE CONVERSION ERROR
S /
S FALT5,J000
S      CLA CLL
      WRITE(1,742)
742    FORMAT('ERROR 5')
S      CLA CLL
S      JMP I FALT5
S /
S /SUBROUTINE FALT6
S /THIS SUBROUTINE INDICATES TEMP A/D FLAG ERROR
S /
S FALT6,J000
S      CLA CLL
      WRITE(1,743)
743    FORMAT('ERROR 6')
S      CLA CLL
S      JMP I FALT6
S /
S /SUBROUTINE FALT8
S /THIS SUBROUTINE INDICATES T ZERO CONVERSION ERROR
S /
S FALT8,J000
S      CLA CLL
      WRITE(1,744)
744    FORMAT('ERROR 8')
S      CLA CLL
S      JMP I FALT8
S /
S /SUBROUTINE FALT9
S /THIS SUBROUTINE INDICATES T FULL SCALE CONVERSION ERROR
S /
S FALT9,J000
S      CLA CLL
      WRITE(1,745)
745    FORMAT('ERROR 9')
S      CLA CLL
S      JMP I FALT9
S /
S /SUBROUTINE TYPG
S /THIS SUBROUTINE READS THE TTY AND CHECKS FOR A "G"
S /
S TYPG, J000
S AA,   CLA CLL
S AS,   4SF          /KEYBOARD STRUCK YET,
S      JMP AS        /NO, CHECK AGAIN
S      4RB          /YES, READ CHARACTER
S      TLR          /ACKNOWLEDGE IT ON PRINTER
S      TAD V7471    /SUBTRACT 307
S      SZA          /IS IT A "G".
S      JMP AA       /NO, GO CHECK AGAIN
S      CLA CLL
S      JMP I TYPG    /YES, RETURN TO MAIN PROGRAM
S V7471,7471        /-307

```

```

S /
S /SUBROUTINE DCODE
S /THIS SUBROUTINE DECODES PARAMETER WORDS
S /COMPUTES PM,RV,XUNI,ES,RCELL,CCELL
S /IT MUST BE ENTERED WITH PARA WORD IN AC
S /PARA WORD FORMAT:
S /
S / FIRST 4 BITS (MSB) ARE FOR REMAINDER OF AVERAGE
S / NEXT 4 BITS FOR UNITS VALUE (BINARY 1-10)
S / NEXT 2 BITS FOR GAIN INFO (BINARY VALUE 0-3)
S / NEXT 2 BITS FOR PM INFO (BINARY 1-3)
S /
S DCODE, J000
S      DCA SPPJ      /STORE PARA WORD
      XUNI=0.
      PM=.005
      RV=10000.
S      TAD SPPJ
S      AND MSK1      /MASK ALL BUT PM BITS
S DC1,   DCA SPPJ
S      TAD SPPJ
S      SNA
S      JMP DC2      /ALL SET.
S      CLA CLL      /YES, CONTINUE
S      B4=PM*10.    /NO, ADJUST
S      CMA
S      TAD SPPJ      /ADD -1
S      JMP DC1      /SET UP NEXT ITERATION
S MSK1, J003
S DC2,   TAD SPPJ
S      AND MSK2      /MASK ALL BUT GAIN BITS
S DC3,   DCA SPPJ
S      TAD SPPJ
S      SNA
S      JMP DC4      /ALL SET.
S      CLA CLL      /YES, CONTINUE
S      RV=RV*10.    /NO, ADJUST
S      TAD DC7774
S      TAD SPPJ      /SET UP NEXT ITERATION
S      JMP DC3
S MSK2, J014
S DC4,   TAD SPPJ
S      AND MSK3      /MASK FOR ALL BUT GAIN BITS
S DC5,   DCA SPPJ
S      TAD SPPJ      /GAIN DEINCREMENTER
S      SNA
S      JMP DC6      /ALL SET.
S      CLA CLL      /YES, CONTINUE
S      XUNI=XUNI+1.  /NO, ADJUST
S      TAD DC7760
S      TAD SPPJ      /SET UP FOR NEXT ITERATION
S      JMP DC5
S MSK3, J360
S DC6,   DCA SPPJ
S      CLA CLL      /MASK FOR ALL BUT UNITS BITS
S      ES=(2*(12.5/4096.))+6.25
S      RCELL=PM/((ES/RV)+((10.*XUNI)/RV))
S      CCELL=.1./RCELL
S      TAD SPPJ      /RETURN WITH REMAINDER IN AC
S      TAD DC7400
S      JMP I DCODE   /MASK ALL BUT REMAINDER BITS
S DC7400,7400
S      END
S      /MASK FOR ALL BUT REMAINDER BITS

```

CBTALR

PROGRAM LISTING

```

S /PROGRAM NAME: C3TALR.FT
S /FORTRAN-SAGE: KEITH J. CASERTA 1/31/74
S /THIS IS THE ARRAY ARRANGER FOR COMPUTERIZED CONDUCTANCE SYSTEM DATA
S /WHICH TAKES A TEMP-COND ARRAY (OF UP TO 500 POINTS FOR
S /DOUBLE PRECISION INCLUDED DATA) AND ARRANGES IT IN ORDER
S /OF INCREASING THERMISTOR RESPONSE. IT THEN SELECTS 1 T
S /INTERVAL WHICH CORRESPONDS TO THE LARGEST T INTERVAL AND MOVES
S /THROUGH THE ARRAY, AVERAGING ALL T AND G POINTS IN THAT INTERVAL.
S /THE NEW ARRAY CONSISTS OF THE REAL FORTRAN G INFO, AND THE INTEGER
S /TIME INFO
S /*****PROGRAM WILL RUN ONLY IF DOUBLE PRECISION DATA IS TAKEN****
S /THE NEW DATA IS WRITTEN 16 BLOCKS BEYOND THE ORIGINAL DATA
S /STARTING ADDRESS.
S /
COMMON TCDATA,VARA
DIMENSION TCDATA(500),VARA(6)
S JODEF QUY 7405 /MULTIPLY
S JODEF DIV 7407 /DIVIDE
S JODEF VMI 7411 /NORMALIZE
S JODEF SHL 7413 /SHIFT LEFT
S JODEF ASR 7415 /ARITHMETIC SHIFT RIGHT
S JODEF LSR 7417 /LOGICAL SHIFT RIGHT
S JODEF MQL 7421 /LOAD MULTIPLIER QUOTIENT
S JODEF SCL 7403 /STEP COUNTER LOAD FROM MEMORY
S JODEF SCA 7441 /STEP COUNTER LOAD INTO AC
S JODEF MQA 7501 /MQ LOAD INTO AC
S JODEF ERASE 6054 /ERASE DISPLAY SCOPE
S JODEF STORE 6057 /SET SCOPE IN STORE MODE
S ABSY4 PHP 0074 /PH POINTER
S ABSY4 PWP 0075 /PW POINTER
S ABSY4 IVP 0076 /I/V POINTER
S ABSY4 JNITS 0077 /OFFSET UNITS POINTER
S ABSY4 ASET 0100 /GENERAL POINTER
S ABSY4 SPARA 0101 /PARAMETER POINTER
S ABSY4 SPPU 0102 /INDIRECT ADDRESS IN FIELD 1 POINTER
S ABSY4 SPPW 0103 /INDIRECT ADDRESS IN FIELD 1 POINTER
S ABSY4 PSET 0104 /FORTRAN LOWER MANTISSA POINTER
S /
S /
S /THE INITIALIZATION SECTION BEGINS HERE
S /
S /
100 READ(1,100)IBLK
FORMAT('FIRST BLOCK TO READ ',I5)
CALL RTAPE(1,IBLK,2046,TCDATA)
IF(NARA(5))310,310,312
310 WRITE(1,311)
311 FORMAT(' ',NO.1)
CALL EXIT
312 ITRV=NARA(4)
IPTS=NARA(6)
IA=0
I9=0
IP1=0
IP2=0
ITIME=0
IK=0
IT=-2
S ISZ PTOT
S ISZ PTOT
S SKP
S PTOT, =TOT

```

```

S /
S /
S /BEGIN TO ORDER THE ARRAY IN DECREASING T
S /
S /
S      CLA CLL
      DO 707 I=1,ITRVL
      IA=IA+4
      IB=IA
S      CLA CLL
S      TAD =IA          /SET ADDRESS OF FIRST T POINT
S      TAD (0177
S      DCA ASET
S      6211          /CDF 1
S      1500          /BRING IN FIRST T POINT
S      6201
S      DCA SPPJ
      IP1=I+1
      DO 201 J=IP1,ITRVL
      IB=IB+4
S      CLA CLL
S      TAD =IB          /SET ADDRESS OF T POINT TO COMPARE
S      TAD (0177
S      DCA SPARA
S      6211
S      1501
S      6201
S      DCA SPPJ
S      JMS ORDER      /30 CHECK FOR NECESSARY ORDER REVERSAL
S      CLA CLL
201  CONTINUE
707  CONTINUE
S /
S /
S /BEGIN TO SCAN FOR THE MAXIMUM T INTERVAL
S /
S /
      IA=0
      IB=0
      IP2=ITRVL-1
S      CLA CLL
      DO 204 I=1,IP2
      IA=IA+4
S      CLA CLL
S      TAD =IA          /SET ADDRESS OF T POINT TO CONSIDER
S      TAD (0177
S      DCA ASET
S      TAD ASET
S      TAD (0004
S      DCA SPARA
S      6211
S      1501
S      CIA
S      1500          /SUBTRACT T(N+1) FROM T(N)
S      6201
S      DCA =J
S      CLA CLL
      IF (IB-J) 203,204,204
203  IB=J
204  CONTINUE

```

```

S /
S /
S /BEGIN ROUTINE TO AVERAGE ALL T AND Q POINTS WITHIN AN INTERVAL
S /
S /
S      CLA CLL
S      DCA IVP          /WILL CONTAIN NUMBER OF POINTS SELECTED
S      DCA #DIV
S      DCA #HP
S      DCA #WP
S      WP=0
S      TOT=0.
S      JSTIK=0
S      ISTIK=0
S      IE=0
S      CLA CLL
S      TAD (0203
S      DCA SPARA          /SET ADDRESS OF FIRST T POINT
S      TAD (0200
S      DCA ASET
S      TAD (0200
S      DCA JNITS
S      JMS TCALC          /30 CALCULATE FIRST T VALUE (REAL)
S      TB=(FLOAT(IB)+10.)/4096.
S      CLA CLL
S      TAD (0177
S      DCA SPARA
S      EXTENT=T-T9
S      DO 207 I=1,ITRVL
S      CLA CLL
S      TAD (0034
S      TAD SPARA
S      DCA SPARA
S      JMS TCALC          /30 CALC NEW T
S      IF(T-EXTENT)205,206,203
S #205, CLA CLL CML RAR /AC=4000
S      6211
S      1500          /BRING IN CURRENT REMAINDER
S      6201
S      DCA #JSTIK
S      ZL=FLOAT(JSTIK)
S      CLA CLL CML RAR /AC=4000
S      15Z ASET
S      6211
S      1500          /BRING IN CURRENT Q DATA
S      6201
S      DCA #ISTIK
S      Z=FLOAT(ISTIK)
S      CLA CLL
S      15Z ASET
S      6211
S      1500          /BRING IN CURRENT PARA WORD
S      6201
S      JMS DCODE          /30 DECODE
S      TOT=TOT+CCELL
S      WP=WP+1
S      CLA CLL
S      15Z ASET
S      6211
S      1500          /BRING IN T INFO
S      6201
S      TAD #WP
S      DCA #WP          /ADD IN LSB

```

```

S      RAL
S      TAD @HP      /ADD IN MSB
S      DCA @HP
S      ISZ ASET      /SET UP FOR NEXT POINT
S      ISZ @DIV      /INCREMENT DIVISOR
S      JMP #207
S #206, CLA CLL
      KMP=F_OAT(MP)
      TOT=TOT/KMP
S      CLA CLL
S      TAD #TOT
S      6211
S      3477      /STORE FIRST WORD OF CALCULATED G
S      6201
S      ISZ JNITS
S      TAD #TOT#
S      6211
S      3477      /STORE SECOND G WORD
S      6201
S      ISZ JNITS
S      TAD I PYOT
S      6211
S      3477      /STORE THIRD G WORD
S      6201
S      ISZ JNITS
S      TAD @HP      /ADD IN LSB T INFO
S      MCL
S      TAD @HP      /ADD IN MSB
S      DVI      /DIVIDE
S #DIV, 0000      /DIVISOR, SET UP DURING RUN
S      CLA CLL
S      MCA      /LOAD AVERAGE INTO AC
S      6211
S      3477      /STORE T INFO
S      6201
S      ISZ JNITS
S      DCA @HP
S      DCA @HP
S      DCA @DIV
S      ISZ IVP      /ADD ONE TO NUMBER OF WORDS POINTER
      MP=0
      TOT=0.
      EXTENT=EXTENT-TB
      IF(IE)205,205,205
207    CONTINUE
      IE=1
      GO TO 215

S /
S /OUTPUT THE NUMBER OF DATA POINTS SELECTED, THE CHOSEN T INTERVAL,
S /AND WRITE THE ARRANGED ARRAY ONTO TAPE,
S /
S #208, CLA CLL
S      TAD IVP
S      DCA #I
      VARA(4)=I
      WRITE(1,101)I,15
101    FORMAT(/,'TOTAL: ',POINTS.SELECTED,' ',15,/, 'INTERVAL CHOSEN: ',15)
      IBLK=15.<16
      CALL WTape(1,IBLK,2045,TCDATA)
      CALL EXIT

```

```

S /SUBROUTINE ORDER
S /THIS SUBROUTINE COMPARES THE MAGNITUDE OF TWO T POINTS,
S /IF THE LARGER IS SECOND TO THE SMALLER IN ARRAY ORDER,
S /IT WILL MOVE THE LARGER T POINT SET INTO THE SMALLER'S
S /POSITION AND VICE VERSA
S /
S ORDER, 0000
S     CLA CLL
S     TAD SPPJ
S     DCA TPPJ
S     TAD SPPH
S     DCA TPPH
S     TAD (7764           /-12
S     DCA TWELV
S ST,     CLA CLL
S     DCA P           /ZERO BIT TEST POINTER
S     TAD TPPJ
S     RAL           /SET BIT OF FIRST T TESTED INTO LINK
S     SZL
S     ISZ P           /BIT IS ONE, SET P
S     DCA TPPJ       /STORE ROTATED WORD
S     CLA CLL
S     TAD TPPH
S     RAL           /SET BIT OF SECOND T TESTED INTO LINK
S     DCA TPPH       /STORE ROTATED WORD
S     SZL
S     CLA CLL CMA     /-1
S     TAD P           /DESET P
S     SPA           /COMPARE
S     JMP FIXER       /NEW T GREATER, REARRANGE
S     SZA           /ARE BITS THE SAME,
S     JMP I ORDER     /NO, FIRST T LARGER, RETURN
S     ISZ TWELV       /ALL BITS COMPARED
S     JMP ST          /NO, CHECK NEXT BIT
S     JMP I ORDER     /YES, RETURN
S TPPU, 0000
S TPPH, 0000
S /
S /FIXER ROUTINE
S /THIS ROUTINE INTERCHANGES THE CURRENT TWO T DATA SETS BEING CONSIDERED
S /
S     PAGE
S FIXER, CLA CLL
S     TAD (7775
S     TAD ASET
S     DCA P4P
S     TAD P4P
S     DCA P4P
S     5211
S     1474
S     DCA 4R           /STORE REMAINDER IN TEMPORARY LOC
S     ISZ P4P
S SP, 5211
S     1474
S     DCA 40           /STORE G DATA IN TEMPORARY LOC
S     ISZ P4P
S     1474
S     DCA 4P           /STORE PARA WORD IN TEMPORARY LOC
S     ISZ P4P
S     1474
S     DCA 4T           /STORE T DATA IN TEMPORARY LOC

```



```

S      6201
S      TAD (7775
S      TAD SPARA
S      DCA IVP
S      TAD IVP
S      DCA JNITS
S      CLA CLL
S      6211
S      1476
S      3475      /STORE SECOND R IN FIRST R LOC
S      ISZ PWP
S      ISZ IVP
S SQ,  6211
S      1476
S      3475      /STORE SECOND G DATA IN FIRST G DATA LOC
S      ISZ PWP
S      ISZ IVP
S      1476
S      3475      /STORE SECOND PARA IN FIRST PARA LOC
S      ISZ PWP
S      ISZ IVP
S      1476
S      DCA SPPJ      /SET NEW UPPER T
S      TAD SPPJ
S      3475      /STORE SECOND T DATA IN FIRST T DATA LOC
S      6201
S      TAD 4R
S      6211
S      3477      /STORE FIRST R IN SECOND R LOC
S      ISZ JNITS
S SR,  6211
S      TAD 4D
S      3477      /STORE FIRST G DATA IN SECOND G DATA LOC
S      ISZ JNITS
S      TAD 4P
S      3477      /STORE FIRST PARA IN SECOND PARA LOC
S      ISZ JNITS
S      TAD 4T
S      3477      /STORE FIRST T DATA IN SECOND T DATA LOC
S      6201
S      JMP I ORDER
S THLV, 0000
S P,    0000
S HR,   0000
S HD,   0000
S HP,   0000
S HT,   0000
S /
S /SUBROUTINE TCALC
S /THIS SUBROUTINE CALCULATES A REAL VALUE FOR THE T VOLTAGE
S /
S TCALC, 0000
S      CLA CLL CHL RAR /AC=4000
S      6211
S      1501      /ADD IN T WORD
S      6201
S      DCA =ITIME
S      CLL
S      T=FLCAT(ITIME)
S      T=T*(10./4096.)*5.
S      CLA CLL
S      JMP I TCALC

```

```

S /
S /SUBROUTINE DCODE
S /THIS SUBROUTINE DECODES PARAMETER WORDS
S /AND COMPUTES PH, RV, XJN, ES, AND CCELL
S /IT MUST BE ENTERED WITH THE PARA WORD IN THE AC
S /PARA WORD FORMAT:
S /
S /      FIRST 4 BITS (MSB) ARE UNUSED
S /      NEXT 4 BITS FOR UNITS VALUE (BINARY 1-10)
S /      NEXT 2 BITS FOR GAIN INFO (BINARY 0-3)
S /      NEXT 2 BITS FOR PH INFO (BINARY 1-3)
S /
S DCODE, 0000
S      DCA SPPJ      /STORE PARA WORD
S      TN=TN
S      TN=TN
S      TL=TL
S      XJN=0.
S      PH=.005
S      RV=10000.
S      TAD SPPJ
S      AND (0003      /MASK ALL BUT PH BITS
S DC1,   DCA SPPJ
S      TAD SPPJ
S      SNA            /ALL SET.
S      JMP DC2        /YES, CONTINUE
S      CLA CLL
S      PH=PH*10.
S      CLA CLL CHA    /-1
S      TAD SPPJ        /SET UP NEXT ITERATION
S      JMP DC1
S DC2,   TAD SPPJ
S      AND (0014      /MASK ALL BUT GAIN BITS
S DC3,   DCA SPPJ
S      TAD SPPJ
S      SNA            /ALL SET.
S      JMP DC4        /YES, CONTINUE
S      CLA CLL        /NO, ADJUST
S      RV=RV*10.
S      CLA CLL
S      TAD (7774
S      TAD SPPJ
S      JMP DC3
S DC4,   TAD SPPJ
S      AND (0360      /MASK ALL BUT OFFSET UNITS BITS
S DC5,   DCA SPPJ
S      TAD SPPJ
S      SNA            /ALL SET.
S      JMP DC6        /YES, CONTINUE
S      CLA CLL        /NO, ADJUST
S      XJN=XJN*1.
S      CLA CLL
S      TAD (7763
S      TAD SPPJ      /SET UP FOR NEXT ITERATION
S      JMP DC5
S DC6,   CLA CLL
S      ES=(Z*(12.5/4096.)*6.25)
S      ES=(ZL*(12.5/4096.)*6.25)/FLOAT(IPTS)
S      ES=ES+ES
S      CCELL=((ES/RV)+((10.*XJN)/RV))/PH
S      IF(I<772,257,772

```

```

S #772, CLA CLL
S      TAD SPPJ
S      CIA
S      TAD #IK
S      SVA          /PARA WORDS THE SAME.
S      JNP #257      /YES CONTINUE
S      CLA CLL      /NO, THREE POINTS IN A ROW.
S      IF(IT)774,774,773
S #773, CLA CLL IAC RT. /AC=4
S      TAD SPARA      /SET ADDRESS OF NEXT PARA WORD TO CHECK
S      DCA PSET
S      6211
S      1504
S      6201
S      CIA          /MAKE NEGATIVE
S      TAD SPPJ
S      SZA          /COMPARE CURRENT AND NEXT PARA WORDS
S      JNP #774
S      CLA CLL
S      Z1=TV-TM
S      Z2=TM-TL
S      ZV=TL-(Z1+Z2)/2.
S      ZT=ZT+ZV-CCELL
774    IT=-3
257    TK=CCELL
       CCELL=CCELL+ZT
       IT=IT+1
S      CLA CLL
S      TAD SPPJ
S      DCA #IK
S      CLA CLL
S      JNP I DCODE
      END

```

CCLALF

PROGRAM LISTING

```

S /PROGRAM NAME: CCLALF.FT
S /FORTRAN-S49R: KEITH J. CASERTA REVISED 2/10/74
S /THIS IS THE DATA OUTPUT ROUTINE
S /FOR THE TEMP-COND CURVE
S /IT IS DESIGNED TO FOLLOW THE ARRAY ARRANGER, CSTALR.FT
S /AND WILL FUNCTION ONLY IN THE ARRAY ARRANGED SEQUENCE
S /XYSYS.SB AND AXIS.S3 MUST BE LOADED WHEN THIS PROGRAM IS COMPILED.
S /
COMMON TCDATA,VARA
DIMENSION TCDATA(580),VARA(6)
S
S DPDEF MUY 7405 /MULTIPLY
S DPDEF DVI 7407 /DIVIDE
S
S DPDEF NMI 7411 /NORMALIZE
S
S DPDEF SHL 7413 /SHIFT LEFT
S
S DPDEF ASR 7415 /ARITHMETIC SHIFT RIGHT
S
S DPDEF LSR 7417 /LOGICAL SHIFT RIGHT
S
S DPDEF MOL 7421 /LOAD MULTIPLIER QUOTIENT
S
S DPDEF SCL 7403 /STEP COUNTER LOAD FROM MEMORY
S
S DPDEF SCA 7441 /STEP COUNTER LOAD INTO AC
S
S DPDEF MOA 7501 /MO LOAD INTO AC
S
S DPDEF SKPDS 0351 /SKIP ON SCOPE DISPLAY FLAG
S
S DPDEF ERASE 0354 /ERASE DISPLAY SCOPE
S
S DPDEF VSTORE 0355 /SET SCOPE IN NON-STORE MODE
S
S DPDEF WTSR 0356 /SET SCOPE IN WRITE-THROUGH MODE
S
S DPDEF STOR 0337 /SET SCOPE IN STORE MODE
S
S DPDEF XLOAD 0361 /LOAD HORIZONTAL D/A
S
S DPDEF YLOAD 0362 /LOAD VERTICAL D/A
S
S DPDEF INTENS 0364 /INTENSIFY BEAM
S
S DPDEF XLP 0365 /XLOAD + INTENS
S
S DPDEF YLP 0366 /YLOAD + INTENS
S
S ABSY4 PHP 0074 /PH POINTER
S
S ABSY4 PWP 0075 /PW POINTER
S
S ABSY4 IVP 0076 /I/V POINTER
S
S ABSY4 JNITS 0077 /OFFSET UNITS POINTER
S
S ABSY4 ASET 0100 /GENERAL POINTER
S
S ABSY4 SPARA 0101 /PARAMETER POINTER
S
S ABSY4 SPPU 0102 /INDIRECT ADDRESS IN FIELD 1 POINTER
S
S ABSY4 SPPW 0103 /INDIRECT ADDRESS IN FIELD 1 POINTER
S /
S /
S /THIS IS THE INITIALIZATION AND PRINT-OUT SECTION
S /
S /
S DTOUT,CIA CLL
READ(1,942)IB-CLPT,TIM
942 FORMAT('FIRST BLOCK TO READ: ',I3,/, 'OUTPUT ON LPT. (1=YES, 0=NO
+)',I3,/, 'TIME BETWEEN POINTS (SECS): ',E14.6)
CCEL=0.
S
S CIA CLL
S ISZ CCEL
S ISZ CCEL
S TAD CLPT
S SZL
S JMP NXT
S JMP EROS
S CCEL, CCEL
S NXT, CIA CLL
WRITE(3,404)
404 FORMAT(/, 'TEMP-COND',/, ' POINT',5X, 'TIME',13X, 'R(M)',12X, 'G(M)',
+12X, 'G(C)',12X, 'TEMP',/,11X, '(SEC)',11X, '(CHMS)',10X, '(MHOS)',10X,
+'(44OS)',10X, '(VOLTS)',/)
S EROS, STORE

```

```

S      ERASE          /ERASE DISPLAY SCOPE
S      CLA CLL
S      ISTI=0
S      CALL RTAPE(1,13LK,2045,TCDATA)
S      ITRVL=NARA(4)
S      IPTS=NARA(6)
S      IT=-2
S      IK=0
S      APTS=FLOAT(IPTS)
S      CLA CLL
S      TAD HLPT        /CHECK TO SEE IF PRINTOUT IS DESIRED
S      SZA
S      JMP NXU
S      JMP #415
S NXU,  CLA CLL
S      TAD (0200
S      DCA SPARA      /SET ADDRESS OF FIRST DATA POINT
S      DO 411 LA=1,ITRVL
S      JMS CALC      /30 CALCULATE CONDUCTANCE
S      JMS Talc      /30 CALCULATE TEMP
S      RCELL=1./CCELL
S TH,  CLA CLL
S      $666
403    WRITE(3,405)LA,XTIM,RCELL,CCELL,CORG,Y
405    FORMAT(14,5(4X,E12.6))
406    XTIM=XTIM+TIM
411    CONTINUE
S /
S /
S /BEGIN OPTION ROUTINE TO PLOT THE COMPLETE DATA SET
S /
S /
415    WRITE(1,416)
416    FORMAT('OPTIONS: 1)PLOT AXES',/,9X,'2)PLOT CORRECTED DATA',/,9X,
+ '3)FIT',/,9X,'4)CALL EXIT',/)
S      CLA CLL
S RPL1, <SF          /KEYBOARD STRUCK YET,
S      JMP RPL1
S      <RB          /YES, READ CHARACTER
S      TLS          /ECHO
S      TAD (7517      /CHECK
S      SVA          /IS IT A "1".
S      JMP RPL2      /YES, 30
S      TAD (7777      /NO, CHECK
S      SVA          /IS IT A "2".
S      JMP RPL3      /YES, CONTINUE
S      TAD (7777      /NO, CHECK
S      SVA          /IS IT A "3".
S      JMP RPL4      /YES, 30
S      CALL EXIT
S RPL2, ERASE        /ERASE SCOPE
S      CLA CLL
S      NDIVX=10
S      NDIVY=10
S      CLA CLL
S      CALL AXIS(NDIVX,NDIVY)
S      JMP #415
S RPL4, CLA CLL
S      MA=1
S      JMP #417

```

```

S /
S /REQUEST RANGE AND PLOT POINTS
S /
S RPL3, CLA CLL
368 MA=0
417 READ(1,418)LA, LB
418 FORMAT('FROM POINT ',15,/, 'TO POINT ',15)
S TY, CLA CLL
      READ(1,829)NOPE:
829  FORMAT('USING X-Y PLOTTER, (1=YES, 0=NO): ',15)
      4A=4*LA
S      CLA CLL
S      TAD (0174          /SET UP ADDRESS OF FIRST REMAINDER
S      TAD #KA
S      DCA SPARA
S      CLA CLL CMA      /AC=7777
S      DCA ASET
      DO 605 I=LA, LB
S      JMS CALC          /30 CALCULATE CONDUCTANCE
S      ISZ ASET          /FIRST PASS,
S      JMP #372          /NO, CONTINUE
370 XAVE=CCELL
      XBVE=CCELL
      V=CCELL
372 Z=CCELL
S      JMS SCALE          /30 SCALE
S      CLA CLL
S      ISZ SPARA
606 CONTINUE
      YVOLT=2047./(XAVE-XBVE)
      YAVE=XAVE
      YBVE=XBVE
S      CLA CLL
S      TAD (0174          /SET ADDRESS FOR TEMP
S      TAD #KA
S      DCA SPARA
S      CLA CLL CMA      /AC=7777
S      DCA ASET
      DO 607 I=LA, LB
S      TAD (0003          /SET PROPER TEMP ADDRESS
S      TAD SPARA
S      DCA SPARA
S      JMS Talc          /30 CALCULATE TEMP
S      ISZ ASET          /FIRST PASS,
S      JMP #802          /NO, CONTINUE
      XAVE=Y
      XBVE=Y
      V=Y
802 Z=Y
S      JMS SCALE          /30 SCALE
S      CLA CLL
607 CONTINUE
      XVOLT=2047./(XAVE-XBVE)
S      STORE          /SET SCOPE IN STORE MODE
S      CLA CLL
S      TAD (0174          /SET JP DATA ADDRESS
S      TAD #KA
S      DCA SPARA
      DO 470 I=LA, LB
S      JMS CALC          /30 CALCULATE CONDUCTANCE
374 Y=(CCELL-YBVE)*YVOLT
      -Y=IFIX(Y)

```

```

S      JMS TALC      /30 CALCULATE TEMP
      X=(Y-XBVE)*XVJLT
      LX=IFIX(X)
      IF(NJPE)830,830,831
S 830, JMS FPLT
      30 TO 470
S 831 CALL XYST(LX,LY)
      CALL XYEND
S 470 CONTINUE
      CLA CLL
      CALL XYEND
      IF(MA-1)415,475,415
S /
S /TRANSFER THE SCALING PARAMETERS ONTO TAPE WITH THE DATA SET
S /
S 475 TCDATA(671)=XAVE
      TCDATA(672)=XBVE
      TCDATA(673)=YAVE
      TCDATA(674)=YVJLT
      VARA(1)=LA
      VARA(2)=LB
S      CLA CLL
      CALL WTAPE(1,13L4,2046,TCDATA)
      CALL EXIT
S /
S /SUBROUTINE CALC
S /
S /THIS SUBROUTINE CALCULATES THE CONDUCTANCE
S CALC, J000
S      CLA CLL
S      6211
S      1501      /BRING IN UPPER 3 WORD
S      6201
S      DCA =CCELL
S      ISZ SPARA
S      6211
S      1501      /BRING IN SECOND 6 WORD
S      6201
S      DCA =CCELL#
S      ISZ SPARA
S      6211
S      1501      /BRING IN LOWER 3 MANTISSA
S      6201
S      DCA I PCEL
S      ISZ SPARA
S      JMP I CALC
S /
S /SUBROUTINE TALC
S /THIS SUBROUTINE CALCULATES THE TEMPERATURE VOLTAGE
S /
S TALC, J000
S      CLA CLL CML RAR /AC=4000
S      6211      /CDF 1
S      1501      /ADD IN TEMP DATA
S      6201      /CDF 0
S      DCA =ISTIK
      Z=FLJAT(ISTIK)
      Y=(Z*10./4096.)*5.
S      CLA CLL
S      ISZ SPARA
S      JMP I TALC      /RETURN

```



```

S /
S /SUBROUTINE SCALE
S /
S /THIS SUBROUTINE SETS UP SCALED SCOPE PARAMETERS
S SCALE, 1000
S      CLA CLL
609     XVOLT=V-Z
        IF(XVOLT)407,450,409
407     IF(XAVE-Z)408,450,450
408     XAVE=Z
        GO TO 450
409     IF(XBVE-Z)450,450,410
410     XBVE=Z
450     CONTINUE
S      CLA CLL
S      JMP I SCALE      /RETURN
S /
S /SUBROUTINE FPLT
S /THIS SUBROUTINE PLOTS DATA QUICKLY ON THE SCOPE
S /
S FPLT, 1000
S      CLA CLL CML RTR /AC=2000
S      TAD BLX          /BRING UP X VALUE
S      RAL              /SCALE
S      CMA
S      XLOAD            /LOAD X D/A
S      CLA CLL CML RTR /AC=2000
S      TAD BLY          /BRING UP Y VALUE
S      RAL              /SCALE
S      CMA
S      YLP              /LOAD Y D/A AND PLOT
S      CLA CLL
S      JMP I FPLT      /RETURN TO MAIN PROG
S      END

```

CDTALC
PROGRAM LISTING

```

S /PROGRAM NAME:          CDTALC.FT
S /FORTRAN-SABR: KEITH J. CASERTA          2/17/74
S /THIS IS THE FITTING ROUTINE FOR THE TEMP-COND CURVES
S /WHICH WILL RUN IN BK 3 OF CORE AND PRODUCE A CUBIC FIT
S /IT CAN ONLY BE RUN IN THE SEQUENCE IN WHICH CDTALC.FT IS USED
S /IT IS CALLED AFTER CGLALF.FT
S /
      COMMON TCDATA,VARA
      DIMENSION TCDATA(580),VARA(6)
      DIMENSION AR(4,5),BR(4)
S      ABSY4  PHP      0074      /PH POINTER
S      ABSY4  PHP      0075      /PW POINTER
S      ABSY4  IVP      0076      /I/V POINTER
S      ABSY4  JNITS     0077      /OFFSET UNITS POINTER
S      ABSY4  ASET      0100      /GENERAL POINTER
S      ABSY4  SPARA     0101      /PARAMETER POINTER
S      ABSY4  SPPU      0102      /INDIRECT ADDRESS IN FIELD 1 POINTER
S      ABSY4  SPPW      0103      /INDIRECT ADDRESS IN FIELD 1 POINTER
S /
S /
S /INITIALIZE THE ROUTINE TO FIT TEMP-COND DATA
S /
S /
      READ(1,942)IBLK
942      FORMAT('FIRST BLOCK TO READ: ',I5)
      CALL RTAPE(1,IBLK,2046,TCDATA)
      KL=VARA(1)
      KM=VARA(2)
      ITRV=KM-KL+1
      IT=4*KL
      COR0=0.
      ISTI=0
S      CLA CLL
S      ISZ PCOL
S      ISZ PCOL
S      SKP
S      PCOL, COR0
S      CLA CLL
S      TAD MKT
S      TAD (C174
S      DZA SPARA
S /
S /
S /CALCULATE SUMMATIONS FOR A LEAST-SQUARES CUBIC FIT
S /
S /
      DO 490 MA=KL,KM
S      JMS CALC          /30 CALCULATE CONDUCTANCE
S      JMS TALC          /30 CALCULATE TEMP
S      CLA CLL
      XS=Y*Y
      XC=XS*Y
      XI=XI+Y
      XIS=XIS+XS
      XIC=XIC+XC
      XIO=XIO+XS*XS
      XIF=XIF+XS*XC
      XIX=XIX+XC*XC
      YI=YI+CJRG
      XIY=XIYI+Y*CJRG
      XISY=XISY+XS*CJRG
      XICY=XICY+XC*CJRG
490      CONTINUE

```

```

S /
S /
S /SET UP THE DETERMINANTS
S /
S /
      AR(1,1)=FLOAT(ITQVL)
      AR(1,2)=XI
      AR(1,3)=XIS
      AR(1,4)=XIC
      BR(1)=VI
      AR(2,1)=XI
      AR(2,2)=XIS
      AR(2,3)=XIC
      AR(2,4)=XIO
      BR(2)=XIV
      AR(3,1)=XIS
      AR(3,2)=XIC
      AR(3,3)=XIQ
      AR(3,4)=XIF
      BR(3)=XISY
      AR(4,1)=XIC
      AR(4,2)=XIO
      AR(4,3)=XIF
      AR(4,4)=XIX
      BR(4)=XICY
S /
S /
S /BEGIN THE PIVOTAL CONDENSATION
S /
S /
      DO 20 K=1,3
      CP1=CP1+1
      L=K
      DO 21 I=CP1,4
      IF(A3S(AR(I,K))-A3S(AR(L,K)))21,21,20
20      _=1
21      CONTINUE
      IF(L<)25,25,23
C      INTERCHANGE ROWS
23      DO 24 J=K,4
      DJMHY=AR(K,J)
      AR(K,J)=AR(L,J)
24      AR(L,J)=DJMHY
      DJMHY=BR(K)
      BR(K)=BR(L)
      BR(L)=DJMHY
C      ELIMINATION
25      DO 29 I=CP1,4
      DJMHY=AR(I,K)/AR(L,K)
      AR(I,K)=0.
      DO 29 J=CP1,5
      AR(I,J)=AR(I,J)-DJMHY*AR(L,J)
29      BR(I)=BR(I)-DJMHY*BR(L)
C      BACK SUBSTITUTION
      AR(4,5)=BR(4)/AR(4,4)
      CP3
30      CP1=CP1+1
      DJMHY=0.
      DO 31 J=CP1,4
      DJMHY=DJMHY+AR(K,J)*AR(J,5)
31

```

```

      AR(K,5)=(BR(K)-DU44Y)/AR(K,K)
      K=K-1
      IF(K)32,32,30
S /
S /OUTPUT THE EQUATION
S /
32      WRITE(1,580)AR(4,5),AR(3,5),AR(2,5),AR(1,5)
580      FORMAT(/,' G = ',E16.8,' T(3) * ',E16.8,' T(2)',/,9X,' + ',E16.8
      ,', T * ',E16.8/)
S /
S /WRITE THE COEFFICIENTS OF THE FITTED EQUATION INTO THE DATA SET
S /
      TCDATA(675)=AR(1,5)
      TCDATA(676)=AR(2,5)
      TCDATA(677)=AR(3,5)
      TCDATA(678)=AR(4,5)
      TCDATA(679)=0.
      TCDATA(690)=0.
      CALL WTape(1,13L4,2046,TCDATA)
      CALL EXIT
S /
S /SUBROUTINE CALC
S /THIS SUBROUTINE CALCULATES THE CONDUCTANCE
S /
S CALC, 0000
S      CLA CLL
S      9211
S      1501          /BRING IN UPPER 3 WORD
S      6201
S      OCA =COR3
S      ISZ SPARA
S      9211
S      1501          /BRING IN SECOND 6 WORD
S      6201
S      OCA =COR3#
S      ISZ SPARA
S      9211
S      1501          /BRING IN LOWER MANTISSA
S      6201
S      OCA I PCEL
S      ISZ SPARA
S      CLA CLL
S      JMP I CALC      /RETURN
S /
S /SUBROUTINE Talc
S /THIS SUBROUTINE CALCULATES THE TEMPERATURE VOLTAGE
S /
S Talc, 0000
S      CLA CLL CML RAR /AC=4000
S      9211          /CDF 1
S      1501          /ADD IN TEMP DATA
S      6201          /CDF 0
S      OCA =ISTIK
S      Z=FLDAT(ISTIK)
S      Y=(Z*10./4096.)*5.
S      ISZ SPARA
S      CLA CLL
S      JMP I Talc      /RETURN
S      END

```

CFPTLI
PROGRAM LISTING

```

S /PROGRAM NAME: CPTLI.FT
S /FORTRAN-SAS9: KEITH J. CASERTA REVISOR 11/27/73
S /THIS IS THE PLOTTING ROUTINE FOR THE FITTED TEMP-COND DATA
S /WHICH PLOTS MEASURED TEMP AS X, AND CALCULATED COND AS Y
S /FROM ANY INTEGER FIT UP TO A FIFTH ORDER EQUATION
S /IT FOLLOWS CPTLF.FT OR MAY DIRECTLY FOLLOW!
S /CDTTL.FT, CDTTLO.FT, CDTTL3.FT,
S /CDTAL.FT, CDTALO.FT, CDTAL3.FT, OR CDTALF.FT.
S /XSYS.SB MUST BE LOADED WHEN THIS PROGRAM IS COMPILED.
S /
      COMMON TCDATA,VARA,EXTRA
      DIMENSION TCDATA(500),VARA(6)
S /
S /
S /READ THE DATA AND SET UP THE COEFFICIENTS AND SCALING PARAMETERS
S /
S /
      READ(1,942)IBLK
942  FORMAT('FIRST BLOCK TO READ: ',I5)
      CALL RTAPE(1,IBLK,2046,TCDATA)
      IBLK=IBLK+16
      CALL RTAPE(1,IBLK,6,EXTRA)
      XAVE=TCDATA(671)
      XBVE=TCDATA(672)
      YAVE=TCDATA(673)
      YVOLT=TCDATA(674)
      A1=TCDATA(675)
      A2=TCDATA(676)
      A3=TCDATA(677)
      A4=TCDATA(678)
      A5=TCDATA(679)
      A6=TCDATA(680)
      TADD=(XBVE-XAVE)/500.
      XADD=2047./500.
S /
S /
S /CALCULATE THE CURVE AND PLOT
S /
S /
      Y=A6*(XBVE**5)+A5*(XBVE**4)+A4*(XBVE**3)+A3*(XBVE*XBVE)+A2*XBVE+
      +A1
      Y=(Y-YAVE)+YVOLT
      LX=0
      LY=171X(Y)
      CALL XYST(LX,LY)
      T=XBVE
      X=0.
      DO 1 I=2,500
      T=T-TADD
      X=X+XADD
      Y=A6*(T**5)+A5*(T**4)+A4*(T**3)+A3*T**2+A2*T+A1
      Y=(Y-YAVE)+YVOLT
      LX=171X(X)
      LY=171X(Y)
      CALL XYPLT(LX,LY)
1  CONTINUE
      CALL XVEVD
      CALL EXIT
      END

```

CCLMLT
PROGRAM LISTING


```

S /PROGRAM NAME: COLMLT,FT
S /FORTRAN-SASRI KEITH J. CASERTA 9/4/73
S /THIS IS THE OUTPUT SET FOR THE TDA ROUTINE
S /WHICH CONTAINS THE PROVISIONS FOR TITRATION ANALYSIS
S /IT READS THE DATA FROM TAPE AND OUTPUTS ON THE LPT
S /
S / 1)POINT NUMBER
S / 2)VOLUME OF TITRANT ADDED
S / 3)SAMPLED VOLTAGE
S / 4)RAW CONDUCTANCE
S / 5)CONDUCTANCE CORRECTED FOR SCALE CHANGES
S / 6)CONDUCTANCE CORRECTED FOR DILUTION
S / 7)CONDUCTANCE CORRECTED FOR TEMP IF TEMP RUNS WERE MADE
S / 8)CONDUCTANCE CORRECTED FOR DILUTION AND TEMP
S / 9)THERMISTOR RESPONSE
S /IF THE OPERATOR DESIRES PRINT-OUT. WHEN THE DATA SET HAS BEEN
S /SCANNED, IT OUTPUTS, ON THE TTY, THE MAXIMUM AND MINIMUM FOR
S /ALL CONDUCTANCES CALCULATED. IT IS RUN FOLLOWING COLMLT,FT.
S /
COMMON VARA
DIMENSION VARA(2046)
S JPODEF MUY 7405 /MULTIPLY
S JPODEF DIV 7407 /DIVIDE
S JPODEF NMI 7411 /NORMALIZE
S JPODEF SHL 7413 /SHIFT LEFT
S JPODEF ASR 7415 /ARITHMETIC SHIFT RIGHT
S JPODEF LSR 7417 /LOGICAL SHIFT RIGHT
S JPODEF MOL 7421 /LOAD MULTIPLIER QUOTIENT
S JPODEF SCL 7403 /STEP COUNTER LOAD FROM MEMORY
S JPODEF SCA 7441 /STEP COUNTER LOAD INTO AC
S JPODEF MOA 7501 /MO LOAD INTO AC
S JPODEF ERASE 6034 /ERASE DISPLAY SCOPE
S JPODEF STORE 6037 /SET SCOPE IN STORE MODE
S ABSYM PMP 0074 /PM POINTER
S ABSYM PWP 0075 /PW POINTER
S ABSYM IPV 0076 /I/V POINTER
S ABSYM JNITS 0077 /OFFSET UNITS POINTER
S ABSYM ASET 0100 /GENERAL POINTER
S ABSYM SPARA 0101 /PARAMETER POINTER
S ABSYM SPPU 0102 /INDIRECT ADDRESS IN FIELD 1 POINTER
S ABSYM SPPW 0103 /INDIRECT ADDRESS IN FIELD 1 POINTER
S /
S /
S /THIS IS THE INITIALIZATION SECTION
S /
S /
S DTOUT,CLA CLL
READ(1,900)I8L4,LPT
900 FORMAT('FIRST BLOCK TO READ: ',I5,/, 'OUTPUT ON LPT. (1=Y,0=N)')
*,I5)
CALL RTAPE(1,I8L4,2046,VARA)
LP=VARA(2043)
ITRV=VARA(2044)
LD=VARA(2045)
IPTS=VARA(2046)
APTS=FLOAT(IPTS)
S CLA CLL
S TAD RLP
S SVA
S JMP #903
S CLA CLL
901 READ(1,902)A2,A3,A4,A5,A6
902 FORMAT('T(1): A2 = ',E16.8,/, 'T(2): A3 = ',E16.8,/, 'T(3): A4 = ',
*,E16.8,/, 'T(4): A5 = ',E16.8,/, 'T(5): A6 = ',E16.8)

```

```

903 READ(1,904)VZERO
904 FORMAT('INITIAL VOLUME (MLS): ',E14.6)
      TIM=.2
      NDIVX=10
      NDIVY=10
      IT=-2
      I4=0
S     CLA CLL
S     TAD R-PT
S     SZA
S     JMP VXU
S     JMP VXT
S NXU, CLA CLL
S     6666
      WRITE(3,404)
404   FORMAT(/,' TITRATION',/, ' POINT',2X,' TITRANT',9X,' ES',8X,' GCELL
      * (M)',5X,' GCELL(C)',5X,' GCELL(D)',5X,' GCELL(T)',4X,' GCELL(D-T)',6X,
      * 'TEMP')
      WRITE(3,905)
905   FORMAT(9X,' (MLS)',8X,' (VOLTS)',6X,' (MHOS)',7X,' (MHOS)',7X,' (MHOS
      *)',7X,' (MHOS)',7X,' (MHOS)',6X,' (VOLTS)',/)
S /
S /
S /BEGIN TO CALCULATE DATA AND MAXIMA AND MINIMA
S /
S /
S NXT, STORE
S     ERASE           /ERASE DISPLAY SCOPE
S     CLA CLL
S     TAD (0200       /SET UP FIRST DATA WORD ADDRESS
S     DCA ASET
      DO 411 LA=1,ITRYL
S     JMS 3JMS       /30 CALCULATE RAW CONDUCTANCE
S     JMS 3CD        /30 CALCULATE DILUTION CORRECTED CONDUCTANCE
S     CLA CLL CMA    /-1
S     TAD RLA
S     SZA
S     JMP PAM
S     CLA CLL
979   43=CCELL
      3Q=CCELL
      4C=CORG
      3C=CORG
      43D=3D
      3GD=3D
      3D TO 999
S PAM, CLA CLL
980   IF(M3-CCELL)981,519,982
981   4G=CCELL
      3D TO 519
982   IF(CCELL-8Q)983,519,519
983   33=CCELL
519   IF(M3-CORG)520,994,521
520   4C=CORG
      3D TO 994
521   IF(CORG-3C)522,984,984
522   3C=CORG
984   IF(M3D-3D)985,988,986
985   43D=3D
      3D TO 999
986   IF(QD-83D)987,989,988
987   3GD=3D

```

```

S /
S /DETERMINE IF T POINTS WERE TAKEN AND CALCULATE IF THEY WERE
S /
S #988, CLA CLL
S      TAD #LPT
S      SVA
S      JMP #403
S #988, CLA CLL CMA      /-1
S      TAD #LA
S      SZA
S      JMP KULIA
S      TAD #LD      /SET UP PROPER ADDRESS FOR FIRST TEMP POINT
S      TAD (0202)    /SET UP STANDARD TEMP
S      DCA SPARA
S      6211
S      1501      /ADD IN TEMP INFO
S      6201
S      TAD (4000)    /CHANGE TO 2'S COMPLIMENT
S      CLL
S      DCA #ISTIK
S      Z=FLD(ISTIK)
S      TS=Z*(10./4096.)*5.
S KULIA, CLA CLL
S      JMS 3CT      /30 CALC TEMP CORRECTED 3
S      JMS 3CTD     /30 CALC T-D CORRECTED 6
S      CLA CLL CMA      /-1
S      TAD #LA
S      SZA
S      JMP PAT
989      43T=3T
          33T=3T
          48TD=8TD
          33TD=8TD
          30 TO 403
S PAT,   CLA CLL
990      IF(43T-3T)991,994,992
991      43T=3T
          30 TO 994
992      IF(8TD-33T)993,994,994
993      33T=3T
994      IF(43TD-3TD)995,403,996
995      43TD=3TD
          30 TO 403
996      IF(8TD-33TD)997,403,403
997      33TD=8TD
S /
S /OUTPUT DATA ON THE LINEPRINTER IF REQUESTED TO
S /
S #403, CLA CLL
S      TAD #LPT
S      SZA
S      JMP NXV
S      JMP #406
S NXV,   CLA CLL
S      6666
          WRITE(3,405)LA,XTIM,ES,CCELL,COR3,GD,GT,3TD,T
405      FORMAT(1X,I4,9(1X,E12.6))
406      XTIM=XTIM+TIM
411      CONTINUE

```

```

S /
S /OUTPUT MAXIMA AND MINIMA
S /
      WRITE(1,998)H3,B3,HC,BC,HGD,BGD
998  FORMAT(/,5X,'MAX 3(M) = ',E14.6,5X,'MIN 3(M) = ',E14.6,/,5X,'MAX
      * G(C) = ',E14.6,5X,'MIN 3(C) = ',E14.6,/,5X,'MAX G(D) = ',E14.6,5X
      *, 'MIN 3(D) = ',E14.6)
S      CLA CLL
S      TAD BLP
S      SVA
S      JMP B124
S      CLA CLL
999  WRITE(1,978)H3T,B3T,H3TD,B3TD
978  FORMAT(/,5X,'MAX 3(T) = ',E14.6,5X,'MIN 3(T) = ',E14.6,/,5X,'MAX
      * G(T-D) = ',E14.6,5X,'MIN G(T-D) = ',E14.6)
124  CALL EXIT
S /
S /SUBROUTINE GJNC
S /THIS SUBROUTINE CALCULATES RAW CONDUCTANCE
S /
S GUNC, J000
S      CLA CLL
S      TAD BLD
S      SZA
S      JMP CEL
S      JMP CEM
S CEL, CLA CLL
S      9211
S      1500          /ADD IN REMAINDER
S      9201
S      TAD (4000
S      CLL
S      DCA =JSTIK
S      Z=FLOAT(JSTIK)
S      CLA CLL
S      ISZ ASET
S CEM, 9211
S      1500          /ADD IN DATA
S      9201
S      TAD (4000          /CHANGE TO 2'S COMPLIMENT
S      CLL
S      DCA =ISTIK
S      Z=FLOAT(ISTIK)
S      CLA CLL
S      ISZ ASET          /SET UP FOR PARA WORD
S      9211
S      1500          /ADD IN PARA WORD
S      9201
S      JMS DCODE          /30 DECODE
S      ISZ ASET          /SET UP FOR NEXT POINT
S      CLA CLL
S      JMP I GJNC          /RETURN
S /
S /SUBROUTINE GCD
S /THIS SUBROUTINE CALCULATES DILUTION CORRECTED 3
S /
S GCD, J000
S      CLA CLL
S      30=((VZERO*XTI1)*COR3)/VZERO
S      CLA CLL
S      JMP I GCD          /RETURN

```

```

S /
S /SUBROUTINE OCT
S /THIS SUBROUTINE CALCULATES TEMPERATURE CORRECTED Q
S /
S OCT, J000
S   CLA CLL
S   6211
S   1500           /ADD IN TEMP POINT
S   6201
S   TAD (4000      /CHANGE TO 2'S COMPLEMENT
S   CLL
S   DCA =ISTIX
S   Z=FLJAT(ISTIX)
S   T=Z*(10./4096.)*5.
S   3T=A5*((TS=5)-(T=5))+A5*((TS=4)-(T=4))+A4*((TS=3)-(T=3))+A
S   +3*((TS=2)-(T=2))+A2*(TS-T)+CORQ
S   CLA CLL
S   ISZ ASET       /SET UP FOR NEXT POINT
S   JMP I OCT      /RETURN
S /
S /SUBROUTINE OCTD
S /
S OCTD, J000
S   CLA CLL
S   3TD=((VZERO*XTIM)+3T)/VZERO
S   CLA CLL
S   JMP I OCTD     /RETURN
S /
S /SUBROUTINE DCODE
S /THIS SUBROUTINE DECODES PARAMETER WORDS
S /COMPUTES PH,RV,XUNI,ES,RCCELL,CCELL
S /IT MUST BE ENTERED WITH PARA WORD IN AC
S /PARA WORD FORMAT:
S /
S /          FIRST 4 BITS ARE UNUSED
S /          NEXT 4 BITS FOR UNITS VALUE (BINARY 1-10)
S /          NEXT 2 BITS FOR GAIN INFO (BINARY VALUE 0-3)
S /          NEXT 2 BITS FOR PH INFO (BINARY 1-3)
S /
S DCODE, J000
S   DCA SPPJ       /STORE PARA WORD
S   TN=TN
S   TM=TM
S   TL=TL
S   XUNI=0.
S   PH=.005
S   RV=10000.
S   TAD SPPJ
S   AND MSK1       /MASK ALL BUT PH BITS
S   DCA SPPJ
S   TAD SPPJ
S   SVA
S   JMP DC2        /ALLSET.
S   CLA CLL       /YES, CONTINUE
S   PH=PH*10.     /NO, ADJUST
S   CMA
S   TAD SPPJ
S   JMP DC1        /ADD -1
S   MSK1, J003     /SET UP NEXT ITERATION
S   DC2, TAD SPPJ  /MASK ALL BUT PH BITS
S   AND MSK2
S   DCA SPPJ
S   TAD SPPJ
S   SVA           /ALL SET.

```

```

S      JMP DC4          /YES, CONTINUE
S      CLA CLL          /NO, ADJUST
S      RV=RV+10,
S      TAD DC7774
S      TAD SPP4          /SET UP NEXT ITERATION
S      JMP DC3
S      MSK2, 0014        /MASK FOR ALL BUT GAIN BITS
SDC7774, 7774          /GAIN DEINCREMENTER
S      DC4, TAD SPPJ
S      AND MSK3          /MASK ALL BUT OFFSET UNITS BITS
S      DC5, DCA SPP4
S      TAD SPP4
S      SNA
S      JMP DC6          /ALL SET.
S      CLA CLL          /YES, CONTINUE
S      XJN1=XUN1+1.      /NO, ADJUST
S      TAD DC7760
S      TAD SPP4          /SET UP FOR NEXT ITERATION
S      JMP DC5
S      MSK3, 0340        /MASK FOR ALL BUT UNITS BITS
SDC7760, 7760          /UNITS DEINCREMENTER
S      DC6, CLA CLL
80      ES=(Z*(12.5/4096.))+6.25)
S      IF(L)312,312,311
S11     ESL=(ZL*(12.5/4096.))+6.25)/APTS
S      ES=ES+ESL
S12     CCELL=((ES/RV)*(10.*XUN1/RV))/PH
S      IF(L)772,775,772
S      =772, CLA CLL
S      TAD SPPJ          /BRING UP CURRENT PARA WORD
S      CIA
S      TAD =IK
S      SNA
S      JMP =775          /PARA WORDS THE SAME.
S      CLA CLL          /YES CONTINUE
S      IF(IT)774,774,773 /NO, 3 POINTS IN A ROW.
S      =773, CLA CLL IAC RA. /AC=0002
S      TAD =LD
S      TAD =LP
S      TAD ASET
S      DCA SPARA
S      5211
S      1501
S      5201
S      CIA
S      TAD SPPJ          /COMPARE CURRENT AND NEXT PARA WORDS
S      92A
S      JMP =774
S      CLA CLL
S      Z1=TV-T4
S      Z2=TV-TL
S      ZV=T.- (Z1+Z2)/2.
S      ZT=ZT+ZV-CCELL
774     IT=-3
775     TK=CCELL
S      CORG=CCELL+ZT
S      IT=IT+1
S      CLA CLL
S      TAD SPPJ          /BRING UP CURRENT PARA WORD
S      DCA =IK
S      JMP I DCODE
S      END

```

CDPMLT
PROGRAM LISTING

```

S /PROGRAM NAME:      CDMULT.FT
S /FORTRAN-543R: KEITH J. CASERTA      9/4/73
S /THIS IS THE OUTPUT SET FOR THE TDA ROUTINE
S /WHICH CONTAINS THE PROVISIONS FOR TITRATION ANALYSIS
S /IT READS THE DATA FROM TAPE AND OUTPUTS ON THE SCOPE AND PLOTTER
S /UNDER COMMAND OF THE OPERATOR:
S /
S / 1)AXES
S / 2)RA4 COND
S / 3)CONDUCTANCE CORRECTED FOR SCALE CHANGES
S / 4)CONDUCTANCE CORRECTED FOR DILUTION
S / 5)CONDUCTANCE CORRECTED FOR TEMP IF TEMP RUNS WERE MADE
S / 6)CONDUCTANCE CORRECTED FOR DILUTION AND TEMP
S /IT IS RUN FOLLOWING CDMULT.FT
S /XSYS.SR AND AXIS.S3 MUST BE LOADED WHEN THE PROGRAM IS COMPILED
S /

```

```

COMMON VARA
DIMENSION VARA(2046)
S      JPDF  MUY      7405      /MULTIPLY
S      JPDF  DIV      7407      /DIVIDE
S      JPDF  VMI      7411      /NORMALIZE
S      JPDF  SWL      7413      /SHIFT LEFT
S      JPDF  ASR      7415      /ARITHMETIC SHIFT RIGHT
S      JPDF  LSR      7417      /LOGICAL SHIFT RIGHT
S      JPDF  MOL      7421      /LOAD MULTIPLIER QUOTIENT
S      JPDF  SCL      7403      /STEP COUNTER LOAD FROM MEMORY
S      JPDF  SCA      7441      /STEP COUNTER LOAD INTO AC
S      JPDF  MOA      7501      /MO LOAD INTO AC
S      JPDF  ERASE    6034      /ERASE DISPLAY SCOPE
S      JPDF  STORE    6037      /SET SCOPE IN STORE MODE
S      ABSYM  PMP      0074      /PH POINTER
S      ABSYM  PWP      0075      /PW POINTER
S      ABSYM  IVP      0076      /I/V POINTER
S      ABSYM  JNITS    0077      /OFFSET UNITS POINTER
S      ABSYM  ASET     0100      /GENERAL POINTER
S      ABSYM  SPARA    0101      /PARAMETER POINTER
S      ABSYM  SPPU     0102      /INDIRECT ADDRESS IN FIELD 1 POINTER
S      ABSYM  SPPW     0103      /INDIRECT ADDRESS IN FIELD 1 POINTER
S /
S /

```

```

S /THIS IS THE INITIALIZATION SECTION
S /
S /

```

```

S DTOUT,CLA CLL
      READ(1,900)IBLK
      FORMAT('FIRST BLOCK TO READ ',15)
      CALL RTAPE(1,IBLK,2046,NARA)
      LP=NARA(2043)
      ITRV=NARA(2044)
      LO=NARA(2045)
      IPTS=VARA(2046)
      APTS=FLOAT(IPTS)
      CLA CLL
      TAD RLP
      SVA
      JMP #903
      CLA CLL      /BEGIN TO CALC STANDARD TEMP
      TAD #.0
      TAD (0202
      DCA SPARA
      CLA CLL CHL RAR /AC=4000
      S211
      1501

```


!

903
903

90
90

1

**S
S
S
S
S
S
S**

```

S      5201
S      C=LL
S      DCA =ISTIX
        Z=FLJAT(ISTIX)
        TS=Z*(10./4096.)*3.
901     READ(1,902)A2,A3,A4,A5,A6
902     FORMAT('T(1): A2 = ',E16.8,/, 'T(2): A3 = ',E16.8,/, 'T(3): A4 = ',
+ ,E16.8,/, 'T(4): A5 = ',E16.8,/, 'T(5): A6 = ',E16.8)
903     READ(1,904)VZE=0
904     FORMAT('INITIAL VOLUME (MLS): ',E14.6)
        TIM=.2
        NDIYK=10
        NDIYV=10
        IT=-2
        IX=0

S /
S /
S /BEGIN OPTION ROUTINE TO PLOT
S /
S /
S LINDA,CLA CLL
S      JMP #415
700     CALL XYEND
415     WRITE(1,416)
416     FORMAT('PLOT OPTIONS: 1)AXES',/,14X,'2)RAW DATA',/,14X,'3)C CORR
+ ECTED DATA',/,14X,'4) CORRECTED DATA',/,14X,'5)T CORRECTED DATA',
+ /,14X,'6)D-T CORRECTED DATA',/,14X,'7)CALL EXIT',/)

S      CLA CLL
S RPL1, <SF                      /KEYBOARD STRUCK YET.
S      JMP RPL1
S      <RB                      /YES, READ CHARACTER
S      T=LS                      /ECHO
S      TAD (7517)                /CHECK
S      SVA                      /IS IT A "1".
S      JMP RPL2                  /YES, 30
S      TAD (7777)                /NO, CHECK
S      SVA                      /IS IT A "2".
S      JMP RPL3                  /YES, CONTINUE
S      TAD (7777)
S      SVA                      /IS IT A "3".
S      JMP RPL4                  /YES CONTINUE
S      TAD (7777)
S      SVA                      /IS IT A "4".
S      JMP RPL5                  /YES, CONTINUE
S      TAD (7777)
S      SVA                      /IS IT A "5".
S      JMP RPL6                  /YES, CONTINUE
S      TAD (7777)
S      SVA                      /IS IT A "6".
S      JMP RPL7                  /YES, CONTINUE
S      CALL EXIT
S RPL2, CLA CLL
        CALL AXIS(NDIYK,NDIYV)
S      JMP #415
S /
S /BEGIN ROUTINE TO PLOT RAW 3 DATA
S /
S RPL3, CLA CLL
S      JMS AYDR                  /30 READ AND SET UP
S      JMS 3JNC                  /30 CALC. RAW G
S      Y=CCELL
S      JMS 3LF                    /30 PLOT FIRST POINT

```

```

      48=L3+1
      DO 908 I=M8,LC
S      CLA CLL
S      TAD MLP
S      SVA
S      J4P =701
S      CLA CLL
S      ISZ ASET
S =701, J4S 3JNC      /30 CALC RAW G
      Y=CC3LL
S      J4S PLOT      /30 PLOT
908     CONTINUE
      GO TO 700

S /
S /BEGIN ROUTINE TO CALCULATE SCALE CHANGE CORRECTED G
S /
S RPL4, CLA CLL
S      J4S ANDR      /30 READ AND SET UP
S      J4S 3JNC      /30 CALC RAW G
      Y=CC33
S      J4S PLF      /30 PLOT FIRST POINT
      48=L3+1
      DO 775 I=M8,LC
S      CLA CLL
S      TAD MLP
S      SVA
S      J4P =776
S      CLA CLL
S      ISZ ASET
S =776, J4S 3JNC      /30 CALC RAW G
      Y=CC33
S      J4S PLOT      /30 PLOT
775     CONTINUE
      GO TO 700

S /
S /BEGIN ROUTINE TO PLOT DILUTION CORRECTED DATA
S /
S RPL5, CLA CLL
S      J4S ANDR
      XB=FLOAT(L9)
      XTIM=TIM*(XB-1.)
S      CLA CLL
S      J4S 3JNC      /30 CALC RAW G
S      J4S 3CD      /30 CALC D CORRECTED G
      Y=GD
S      J4S PLF      /30 PLOT FIRST POINT
      48=L3+1
      DO 910 I=M8,LC
S      CLA CLL
S      TAD MLP
S      SVA
S      J4P =703
S      CLA CLL
S      ISZ ASET
703     XTIM=XTIM+TIM
S      J4S 3JNC      /30 CALC RAW G
S      J4S 3CD      /30 CALC D CORRECTED G
      Y=GD
S      J4S PLOT      /30 PLOT
910     CONTINUE
      GO TO 700

```

```

S /
S /BEGIN ROUTINE TO PLOT T CORRECTED G
S /
S RPL6, CLA CLL
S     JMS ANDR
S     JMS SJNC      /30 CALC RAW G
S     JMS SCT       /30 CALC T CORRECTED G
S     Y=GT
S     JMS PLF       /30 PLOT FIRST POINT
S     YB=LB+1
S     DO 912 I=MB,LC
S     JMS SJNC      /30 CALC RAW G
S     JMS SCT       /30 CALC T CORRECTED G
S     Y=GT
S     JMS PLOT      /30 PLOT
912   CONTINUE
      GO TO 700

S /
S /BEGIN ROUTINE TO PLOT D-T CORRECTED DATA
S /
S RPL7, CLA CLL
S     JMS ANDR
S     XB=FLOAT(LB)
S     XTIM=TIM*(XB-1.)
S     CLA CLL
S     JMS SJNC      /30 CALC RAW G
S     JMS SCT       /30 CALC T CORRECTED G
S     JMS SCTD      /30 CALC D-T CORRECTED G
S     Y=GT0
S     JMS PLF       /30 PLOT FIRST POINT
S     YB=LB+1
S     DO 914 I=MB,LC
S     XTIM=XTIM+TIM
S     JMS SJNC      /30 CALC RAW G
S     JMS SCT       /30 CALC T CORRECTED G
S     JMS SCTD      /30 CALC D-T CORRECTED G
S     Y=GT0
S     JMS PLOT      /30 PLOT
914   CONTINUE
      GO TO 700

S /
S /SUBROUTINE GJNC
S /THIS SUBROUTINE CALCULATES RAW CONDUCTANCE
S /
S GUNC, 0000
S     CLA CLL
S     TAD WLD
S     SZA
S     JMP CEL
S     JMP CEM
S CEL,  CLA CLL
S     6211
S     1500          /ADD IN REMAINDER
S     6201
S     TAD (4000
S     CLL
S     DCA WJSTIK
S     ZL=FLOAT(JSTIK)
S     CLA CLL
S     ISZ ASET
S CEM,  6211
S     1500          /ADD IN DATA

```

```

S      9201
S      TAD (4000      /CHANGE TO 2'S COMPLEMENT
S      CLL
S      DCA =ISTIK
S      Z=FLJAT(ISTIK)
S      CLA CLL
S      ISZ ASET      /SET UP FOR PARA WORD
S      9211
S      1500      /ADD IN PARA WORD
S      9201
S      JMS DCODE      /30 DECODE
S      ISZ ASET      /SET UP FOR NEXT POINT
S      CLA CLL
S      JMP I GJNC      /RETURN
S /
S /SUBROUTINE GCD
S /THIS SUBROUTINE CALCULATES DILUTION CORRECTED Q
S /
S GCD, 0000
S      CLA CLL
S      3D=((VZERO*XTI4)*COR3)/VZERO
S      CLA CLL
S      JMP I GCD      /RETURN
S /
S /SUBROUTINE GCT
S /THIS SUBROUTINE CALCULATES TEMPERATURE CORRECTED Q
S /
S GCT, 0000
S      CLA CLL
S      9211
S      1500      /ADD IN TEMP POINT
S      9201
S      TAD (4000      /CHANGE TO 2'S COMPLEMENT
S      CLL
S      DCA =ISTIK
S      Z=FLJAT(ISTIK)
S      T=2*(10./4096.)*3.
S      3T=A5*((TS**5)-(T**5))+A5*((TS**4)-(T**4))+A4*((TS**3)-(T**3))+A
S      *3*((TS**2)-(T**2))+A2*(TS-T)+CORQ
S      CLA CLL
S      ISZ ASET      /SET UP FOR NEXT POINT
S      JMP I GCT      /RETURN
S /
S /SUBROUTINE GCTD
S /THIS SUBROUTINE CALCULATES DILUTION AND TEMPERATURE CORRECTED Q
S /
S GCTD, 0000
S      CLA CLL
S      3TD=((VZERO*XTIM)*3T)/VZERO
S      CLA CLL
S      JMP I GCTD      /RETURN
S /
S /SUBROUTINE ANDR
S /THIS SUBROUTINE DETERMINES THE NUMBER AND RANGE OF POINTS TO PLOT
S /
S ANDR, 0000
S      READ(1,416)LB,,CYHI,YLO
416      FORMAT('FROM POINT ',I5,/, 'TO POINT ',I5,/, 'UPPER Q ',E14.6,/,
S      *, 'LOWER Q ',E14.6)
S      CLA CLL
S      CLA CLL
S      TAD (0200      /SET UP ADDRESS OF FIRST POINT

```

```

S      DCA ASET
      ZT=0.
      IT=-2
      LA=1
929    IF(L3-L4)531,531,530
S #530, JMS 3JNC      /30 CALC RAW Q
S      CLA CLL
S      TAD RLP
S      SZA
S      ISZ ASET
S      CLA CLL
      LA=LA+1
      30 TO 529
S #531, JMP I AYOR
S /
S /SUBROUTINE PLP
S /THIS SUBROUTINE SETS SCALING PARAMETERS AND PLOTS FIRST POINT
S /
S PLP, 0000
S      CLA CLL
      YSCA.=2047./(Y4I-YLO)
      ISCA.=2047./(LC-L3)
      Y=(Y-YLO)*YSCA.
      LY=FIX(Y)
      LX=0
      CALL XYST(LX,LY)
S      CLA CLL
S      JMP I PLP      /RETURN
S /
S /SUBROUTINE PLOT
S /THIS SUBROUTINE PLOTS ALL REMAINING INDICATED POINTS
S /
S PLOT, 0000
S      CLA CLL
      Y=(Y-YLO)*YSCA.
      LY=FIX(Y)
      LX=LX+ISCA
      CALL XYP.T(LX,LY)
S      CLA CLL
S      JMP I PLOT      /RETURN
S /
S /SUBROUTINE DCODE
S /THIS SUBROUTINE DECODES PARAMETER WORDS
S /COMPUTES PH,RV,XUNI,ES,RCCELL,CCELL
S /IT MUST BE ENTERED WITH PARA WORD IN AC
S /PARA WORD FORMAT:
S /
S /      FIRST 4 BITS ARE UNUSED
S /      NEXT 4 BITS FOR UNITS VALUE (BINARY 1-10)
S /      NEXT 2 BITS FOR GAIN INFO (BINARY VALUE 0-3)
S /      NEXT 2 BITS FOR PH INFO (BINARY 1-3)
S /
S DCODE, 0000
S      DCA SPPJ      /STORE PARA WORD
      TM=TM
      TM=TL
      TL=TL
      XUNI=0.
      PH=.005
      RV=10000.
S      TAD SPPJ

```

```

S      AND MSK1          /MASK ALL BUT PH BITS
S DC1, DCA SPP4
S      TAD SPP4
S      SNA              /ALL SET.
S      JMP DC2          /YES, CONTINUE
S      CLA CLL          /NO, ADJUST
S      PH=PH+10.
S      CMA              /ADD -1
S      TAD SPP4          /SET UP NEXT ITERATION
S      JMP DC1
S MSK1, J003            /MASK ALL BUT PH BITS
S DC2, TAD SPPJ
S      AND MSK2          /MASK ALL BUT GAIN BITS
S DC3, DCA SPP4
S      TAD SPP4
S      SNA              /ALL SET.
S      JMP DC4          /YES, CONTINUE
S      CLA CLL          /NO, ADJUST
S      RV=RV+10.
S      TAD DC7774
S      TAD SPP4          /SET UP NEXT ITERATION
S      JMP DC3
S MSK2, J014            /MASK FOR ALL BUT GAIN BITS
SDC7774, 7774          /GAIN DEINCREMENTER
S DC4, TAD SPPJ
S      AND MSK3          /MASK ALL BUT OFFSET UNITS BITS
S DC5, DCA SPP4
S      TAD SPP4
S      SNA              /ALL SET.
S      JMP DC6          /YES, CONTINUE
S      CLA CLL          /NO, ADJUST
S      XJN1=XJN1+1.
S      TAD DC7760
S      TAD SPP4          /SET UP FOR NEXT ITERATION
S      JMP DC5
S MSK3, 0360            /MASK FOR ALL BUT UNITS BITS
SDC7760, 7760          /UNITS DEINCREMENTER
S DC6, CLA CLL
80      ES=(ZL*(12.5/4096.)*6.25)
          IF(L3)312,312,311
311      ESL=(ZL*(12.5/4096.)*6.25)/APTS
          ES=ES+ESL
312      CCEL=((ES/RV)*(10.*XJN1/RV))/PH
          IF(I4)772,257,772
S #772, CLA CLL
S      TAD SPPJ          /BRING UP CURRENT PARA WORD
S      CIA
S      TAD #1K
S      SNA              /PARA WORDS THE SAME,
S      JMP #257          /YES CONTINUE
S      CLA CLL          /NO, 3 POINTS IN A ROW.
          IF(I1)774,774,773
S #773, CLA CLL IAC RA. /AC=0002
S      TAD #LD          /SET ADDRESS OF NEXT PARA WORD TO CHECK
S      TAD #P           /FOR ANOTHER IMPENDING SCALE CHANGE
S      TAD ASET
S      DCA SPARA
S      #211
S      1501            /BRING IN NEXT PARA WORD
S      #201

```

9
9
9
9
9

774
257

9
9
9
9


```

S      CIA
S      TAD SPPJ          /COMPARE CURRENT AND NEXT PARA WORDS
S      SZA
S      JMP #774
S      CLA CLL
S      Z1=TY-TY
S      Z2=TY-TL
S      ZY=T.- (Z1+Z2)/2.
S      ZT=ZT+ZY+CELL
774     IT=-3
257     T<=CELL
S      CORG=CELL+ZT
S      IT=IT+1
S      CLA CLL
S      TAD SPPJ          /BRING UP CURRENT PARA WORD
S      DCA #IK
S      JMP I DCODE
S      END

```

FILE II
PROGRAM LISTING

```

S /PROGRAM NAME: FILE11.PT
S /KEITH J. CASERTA      5/4/74
S /THIS PROGRAM EXECUTES ANY OF THREE OPTIONS:
S /    1)IT WILL READ AN EDITOR GENERATED FILE FROM DTA1
S /        AND WRITE IT ON THE SYSTEM TAPE AS AN OPEN FILE FOR
S /        USE WITH COMHELP. IN ORDER TO DO THIS, THE OPERATOR
S /        MUST KNOW THE ABSOLUTE BLOCK NUMBER (DECIMAL) ON THE
S /        DTA1 WHERE THE PROGRAM IS STORED AND THE NUMBER
S /        OF OS/8 BLOCKS IT OCCUPIES. THIS INFORMATION MAY
S /        BE OBTAINED BY CALLING PIP AND GETTING A LISTING OF
S /        DTA1 (/E OPTION). IF DTA1 POSSESSES AN OS/8 SYSTEM
S /        AREA, THE FIRST PROGRAM BEGINS AT BLOCK 112 (DECIMAL),
S /        EACH OS/8 BLOCK WHICH THE PIP LISTING INDICATES THAT
S /        IT OCCUPIES IS EQUAL TO TWO ABSOLUTE TAPE BLOCKS.
S /        IF THE TAPE DOES NOT INCLUDE AN OS/8 SYSTEM AREA,
S /        THE FIRST PROGRAM BEGINS AT ABSOLUTE TAPE BLOCK
S /        14 (DECIMAL).
S /
S /    2)IT WILL CREATE A PLOTTING FILE BY ALLOWING THE OPERATOR
S /        TO INPUT THE X AND Y COORDINATES OF ALL POINTS WHICH
S /        ARE CONNECTED IN PLOTTING AS STRAIGHT LINES. SCALING
S /        FACTORS FOR BOTH THE X AND Y VALUES MAY BE INPUT.
S /        ALL POSITIVE INTEGERS FROM 0 TO 2047 ARE VALID
S /        COORDINATE VALUES. A "-1" IS USED AS A LINE DELIMITER
S /        AND A "-2" INDICATES AN END-OF-FILE. THE FILE IS
S /        WRITTEN AS AN OPEN FILE ON THE SYSTEM TAPE.
S /        THE FILE MAY BE EDITED WITH THIS SAME OPTION. THE
S /        NAME IS INPUT TO CALL IT FROM TAPE. THE EDITING
S /        FUNCTIONS INCLUDE CHANGING POINTS, DELETING POINTS,
S /        INSERTING POINTS, CHANGING SCALING FACTORS, AND
S /        SEARCHING THE ARRAY FOR A PARTICULAR X OR Y VALUE.
S /
S /    3)IT WILL PLOT A FILE PREVIOUSLY GENERATED. THE FILE
S /        NAME MUST BE INPUT.
S /
COMMON IP,IFILE,ITOT,IBLK,M
DIMENSION IFILE(128),IP(2,300)

S /
S /SELECT MAJOR OPTION
S /
1000  WRITE(1,2)
2      FORMAT('OPTIONS: 1)CREATE A TEXT FILE',/,9X,'2)CREATE OR EDIT A
+PLOTTING FILE',/,9X,'3)PLOT A FILE')
1      READ(1,5)IMM
5      FORMAT(' ',15)
GO TO (6,50,150),IMM

S /
S /BEGIN TO GENERATE TEXT FILE
S /
6      READ(1,10)FNAME,IBLK,ITOT
10     FORMAT('DESIRED NAME OF OUTPUT FILE',A6,/, 'FIRST BLOCK TO READ'
+ ',15,/, 'TOTAL OS/8 BLOCKS',15)
      ITOT=ITOT+2
      CALL OPEN('DTA0',FNAME)
      DO 4) I=1,ITOT
      CALL RTAPE(1,IBLK,128,IFILE)
      WRITE(4,20)(IFILE(I),I=1,128)
20     FORMAT(128A2)
      IBLK=IBLK+1
40     CONTINUE
      CALL CLOSE
160    GO TO 1000

```

```

S /
S /BEGIN GRAPHICS FILE OPTIONS
S /
90      READ(1,170)KTY
170     FORMAT('EDIT PREVIOUS FILE=1,CREATE NEW FILE=0: ',15)
      <TR=0
      IF(KTY)51,51,190
S /
S /ROUTINE TO GENERATE GRAPHIC DISPLAY
S /
51      READ(1,110)FNAME,XSCALE,YSCALE
110     FORMAT('DESIRE NAME OF PLOTTING FILE: ',A6,/, 'X SCALING FACTOR
      * (REAL): ',E16.8,/, 'Y SCALING FACTOR (REAL): ',E16.8)
      DO 130 I=1,300
111     READ(1,120)IP(1,I),IP(2,I)
120     FORMAT('X = ',15,/, 'Y = ',15)
      IF(IP(1,I).EQ.1)140,130,125
125     IP(1,I)=FLOAT(IP(1,I))*XSCALE
      IP(2,I)=FLOAT(IP(2,I))*YSCALE
130     CONTINUE
140     CALL OPEN('DT40',FNAME)
      WRITE(4,150)(IP(1,I),I=1,300)
      WRITE(4,150)(IP(2,I),I=1,300)
150     FORMAT(300A2)
      CALL CLOSE
      GO TO 1000
S /
S /ROUTINE TO EDIT GRAPHICS FILE
S /
180     READ(1,1181)KTS
1181    FORMAT('FILE IN BUFFER=1,FILE ON TAPE=2: ',15)
      GO TO (209,1180),<TS
1180    READ(1,191)FNAME
191     FORMAT('NAME OF FILE TO FIX: ',A6)
      CALL OPEN('DT40',FNAME)
      READ(4,150)(IP(1,I),I=1,300)
      READ(4,150)(IP(2,I),I=1,300)
209     WRITE(1,909)
909     FORMAT('INSERT A POINT=1,/, 'DELETE A POINT=2,/, 'CHANGE A POINT
      * =3,/, 'CHANGE SCALING FACTORS=4,/, 'SEARCH=5,/, 'ALL DONE=6')
      READ(1,5)KTS
      GO TO (211,217,182,500,600,140),<TS
S /
S /ROUTINE TO INSERT POINTS INTO GRAPHICS FILE
S /
211     READ(1,212)INFO,XSCALE,YSCALE
212     FORMAT('IN FRONT OF POINT: ',15,/, 'X SCALING FACTOR: ',E16.8,/, '
      * Y SCALING FACTOR: ',E16.8)
      IF(IP(1,INFO))1629,628,628
628     IX=FLOAT(IP(1,INFO))/XSCALE
      IY=FLOAT(IP(2,INFO))/YSCALE
      GO TO 629
1629     IX=IP(1,INFO)
      IY=IP(2,INFO)
629     WRITE(1,444)INFO,IX,IY
444     FORMAT('POINT ',15, ' ',15,/, 'X = ',15,/, 'Y = ',15,/)
      READ(1,213)IPT
213     FORMAT('NUMBER OF POINTS TO INSERT: ',15)
      IF(IPT)209,209,214
214     <TW=301-INFO-IPT
      <TU=300
      <TS=300+IPT

```

```

      DO 215 I=1,KTH
      IP(1,KTJ)=IP(1,KTS)
      IP(2,KTJ)=IP(2,KTS)
      KTH=KTH+1
      KTS=KTS+1
215  CONTINUE
      DO 216 I=1,IPT
      READ(1,120)IP(1,INFO),IP(2,INFO)
      IF(IP(1,INFO))531,530,530
630  IP(1,INFO)=FLOAT(IP(1,INFO))*XSCLF
      IP(2,INFO)=FLOAT(IP(2,INFO))*YSCLF
631  INFO=INFO+1
216  CONTINUE
      READ(1,917)KTS
817  FORMAT('ALL DONE=1,INSERT MORE POINTS=0,EDIT OPTIONS=-1 ',15)
      IF(KTS)209,211,140

S /ROUTINE TO DELETE POINTS FROM A GRAPHICS FILE
S /
217  READ(1,918)IPT,INFO,XSCLF,YSCLF
818  FORMAT('DELETE FROM POINT: ',15,/, 'TO POINT: ',15,/, 'X SCALING
+FACTOR: ',E16.8,/, 'Y SCALING FACTOR: ',E16.8)
      IF(IPT)1533,632,532
632  MX=FLOAT(IP(1,IPT))/XSCLF
      MY=FLOAT(IP(2,IPT))/YSCLF
      DO TO 633
1633 MX=IP(1,IPT)
      MY=IP(2,IPT)
633  WRITE(1,444)IPT,MX,MY
      IF(IP(1,INFO))1633,634,634
634  MX=FLOAT(IP(1,INFO))/XSCLF
      MY=FLOAT(IP(2,INFO))/YSCLF
      DO TO 635
1635 MX=IP(1,INFO)
      MY=IP(2,INFO)
635  WRITE(1,444)INFO,MX,MY
      READ(1,445)KTS
445  FORMAT('CONTINUE=1,SKIP DELETION=2 ',15)
      DO TO (446,209),KTS
446  KTS=300+INFO
      INFO=INFO+1
      DO 219 I=1,KTS
      IP(1,IPT)=IP(1,INFO)
      IP(2,IPT)=IP(2,INFO)
      IPT=IPT+1
      INFO=INFO+1
218  CONTINUE
      READ(1,219)KTS
219  FORMAT('ALL DONE=1,DELETE MORE POINTS=0,EDIT OPTIONS=-1 ',15)
      IF(KTS)209,217,140

S /ROUTINE TO CHANGE POINTS IN A GRAPHICS FILE
S /
182  READ(1,193)KTS,XSCLF,YSCLF
183  FORMAT('POINT TO CHANGE: ',15,/, 'X SCALING FACTOR: ',E16.8,/, 'Y S
+CALING FACTOR: ',E16.8)
      IF(IP(1,KTS))943,942,942
842  IP(1,KTS)=FLOAT(IP(1,KTS))/XSCLF
      IP(2,KTS)=FLOAT(IP(2,KTS))/YSCLF
843  WRITE(1,120)IP(1,KTS),IP(2,KTS)
      READ(1,120)IP(1,KTS),IP(2,KTS)
      IF(IP(1,KTS))844,945,845

```

```

845      IP(1,KTS)=FLOAT(IP(1,KTS))*XSCLF
      IP(2,KTS)=FLOAT(IP(2,KTS))*YSCLF
844      READ(1,195)KTS
185      FORMAT('ALL DONE=1,CHANGE ANOTHER POINT=0,EDIT OPTIONS=-1: ',15)
      IF(KTS)209,182,140

S /
S /ROUTINE TO CHANGE THE SCALING FACTORS OF A GRAPHICS FILE
S /
900      READ(1,501)XSCLE,YSCLE,XSCLF,YSCLF
901      FORMAT('OLD X SCALING FACTOR: ',E16.8,/, 'OLD Y SCALING FACTOR: ',
+ ,E16.8,/, 'NEW X SCALING FACTOR: ',E16.8,/, 'NEW Y SCALING FACTOR: ',
+ ,E16.8)
      DO 502 I=1,300
      IF(IP(1,I))502,635,636
636      IP(1,I)=(FLOAT(IP(1,I))/XSCLE)*XSCLF
      IP(2,I)=(FLOAT(IP(2,I))/YSCLE)*YSCLF
902      CONTINUE
      READ(1,503)KTS
903      FORMAT('ALL DONE=1,EDIT OPTIONS=0: ',15)
      IF(KTS)209,209,140

S /
S /ROUTINE TO SEARCH THE GRAPHICS BUFFER FOR A VALUE
S /
600      READ(1,601)IC,ID,YSCLF
601      FORMAT('SEARCH FOR X VALUE=1, Y VALUE=2: ',15,/, 'VALUE TO BE FOUND: ',15,/,
+ 'SCALING FACTOR: ',E16.8)
      IF(I)639,637,637
637      ID=FLOAT(ID)*YSCLF
638      IC=0
      DO 604 I=1,300
      IF(IP(IC,I)-ID)604,602,604
602      WRITE(1,603)I
603      FORMAT('POINT ',15)
      IC=1
604      CONTINUE
      IF(IC)605,605,607
605      WRITE(1,606)
606      FORMAT(/, 'VALUE DOES NOT APPEAR',/)
607      READ(1,508)KTS
608      FORMAT('ALL DONE=1,SEARCH AGAIN=0,EDIT OPTIONS=-1: ',15)
      IF(KTS)209,600,140

S /
S /BEGIN ROUTINE TO PLOT A FILE
S /
189      READ(1,1181)KTS
      DO TO (1190,1922),KTS
1522      READ(1,190)FNAME
190      FORMAT('NAME OF FILE TO PLOT: ',A6)
      CALL IOFEN('DTA0',FNAME)
      READ(4,150)(IP(1,I),I=1,300)
      READ(4,150)(IP(2,I),I=1,300)
1190      MX=IP(1,1)
      MY=IP(2,1)
      MX1=0
      CALL SCOST(MX,MY)
      DO 290 I=2,300
      MX=IP(1,I)
      MY=IP(2,I)
      IF(MX-1)1000,193,194
193      MX1=1

```

```
30 T3 200
194 IF(MX1)195,196,195
195 CALL SCOST(MX,MY)
      MX1=0
      30 T3 200
196 CALL SC3PL(MX,MY)
200 CONTINUE
      30 T3 1000
      END
```

CBHELP
PROGRAM LISTING


```

S /PROGRAM NAME: C9HELP.FT
S /KEITH J CASERTA 5/2/74
S /THIS IS THE COMPUTERIZED CONDUCTANCE SYSTEM INSTRUCTIONAL PACKAGE.
S /IT IS DESIGNED TO TEACH THE NOVICE USER THE NECESSARY FUNDAMENTALS
S /TO PERMIT HIM TO OPERATE THE COMPUTERIZED CONDUCTANCE SYSTEM,
S /IN ADDITION, IT SERVES AS A CONTINUAL REFERENCE TO THE EXPERIENCED
S /USER
S /IT MUST BE COMPILED WITH THE XSYS.SB AND SCOPE.SB PLOTTING ROUTINES,
S /
      DIMENSION IP(2,300)
      IY=1405
      LPT=0
      FNAME=0.
      LA=0
      LB=0
      LM=1
S /
S /BEGIN INITIAL DIALOG
S /
      READ (1,61)IX
61      FORMAT('DO YOU LIKE INSTRUCTIONS FOR USING THIS PROGRAM. (TYPE
      *E YES OR NO)')*,A2)
      IF(IX-IY)63,62,63
62      FNAME='CORELM'
S      JMS RFILE
S      CLA CLL
63      READ(1,101)LPT
101      FORMAT('OUTPUT ON LPT=1, ON TTY=0, SKIP INITIAL DIALOG=-1',I5)
      IF(LPT)215,214,297
S =287, JMS JLP /30 SET UP LPT
S      CLA CLL
214      FNAME='ASTART'
S      JMS RFILE
S =215, CLA CLL
      FNAME='BSTART'
      LPT=0
S      JMS RFILE
S      CLA CLL
      -4=0
S /
S /
S /BEGIN SELECTION OF MAJOR OPTION
S /
S /
      READ(1,299)N
289      FORMAT(' ',I5)
288      DO TO (311,313,315,317,319,321,323,325,327,347,346),N
S /
S /OPTION TO TERMINATE
S /
346      WRITE(1,328)
328      FORMAT(/,'I AM TERMINATING',/, 'I HOPE I HAVE BEEN OF ASSISTANCE'
      *,/)
      CALL EXIT
286      READ(1,330)N
330      FORMAT('TYPE NUMBER OF NEXT OPTION',I5)
      DO TO 299
S /
S /GENERAL SYSTEM DESCRIPTION OPTION
S /

```

```

311  FNAME='3CCBD'
      ISK=1
S    JMS PLOT
S    CLA CLL
      FNAME='3CCB2'
      ISK=0
S    JMS PLOT
S    CLA CLL
      FNAME='3GSDC'
S    JMS PFILE
S    CLA CLL
      30 TO 295
S /
S /DESCRIPTION OF THE INSTRUMENT OPTION
S /
313  FNAME='CINSOP'
      LM=1
      LOT=0
S    JMS PFILE
S    CLA CLL
      LM=0
      READ(1,197)N
700  30 TO (701,702,703,704,705)N
701  FNAME='ANALG'
      ISK=1
S    JMS PLOT
S    CLA CLL
      FNAME='ANAL2'
      ISK=0
S    JMS PLOT
S    CLA CLL
      FNAME='ANAL3'
S    JMS PLOT
S    CLA CLL
      FNAME='ANALG'
      30 TO 705
702  FNAME='SSC9D'
      ISK=1
S    JMS PLOT
S    CLA CLL
      FNAME='SSC92'
      ISK=0
S    JMS PLOT
S    CLA CLL
      FNAME='SCONDM'
      30 TO 705
703  FNAME='MEASS'
      ISK=1
S    JMS PLOT
S    CLA CLL
      FNAME='MEAS2'
      ISK=0
S    JMS PLOT
S    CLA CLL
      FNAME='MEASS'
      30 TO 705
704  FNAME='TE4D4'
      ISK=1
S    JMS PLOT
S    CLA CLL

```

```

      FNAME='STE402'
      ISK=0
S      JMS PLOT
S      CLA CLL
      FNAME='STE40H'
      GO TO 706
705      FNAME='CORDER'
S 706, JMS RFILE
S      CLA CLL
      READ(1,707)IX
707      FORMAT('WOULD YOU LIKE A DISCUSSION OF ANY OTHER MODULE, ',A2)
      IF(IX-IY)296,708,296
708      READ(1,709)N
709      FORMAT('PLEASE TYPE THE MODULE'S OPTION NUMBER: ',I5)
      GO TO 700
S /
S /DISCUSSION OF CONDUCTANCE MEASUREMENT OPTION
S /
315      FNAME='ACCGRP'
      ISK=1
S      JMS PLOT
S      CLA CLL
      FNAME='CDOCMC'
S      JMS RFILE
S      CLA CLL
      GO TO 296
S /
S /DISCUSSION OF THE BIPOLAR PULSE TECHNIQUE OPTION
S /
317      FNAME='BPCIP'
      ISK=1
S      JMS PLOT
S      CLA CLL
      FNAME='DCTBPT'
S      JMS RFILE
S      CLA CLL
      READ(1,350)IX
350      FORMAT('WOULD YOU BE INTERESTED IN A DISCUSSION OF THEORETICAL E
      +RRQ, ',A2)
      IF(IX-IY)296,331,296
331      FNAME='CDOTEC'
S      JMS RFILE
S      CLA CLL
      GO TO 296
S /
S /INSTRUCTIONS FOR ROUTINE OPERATION OPTION
S /
319      FNAME='CIFROC'
S      JMS RFILE
S      CLA CLL
      GO TO 296
S /
S /INSTRUCTIONS FOR PULSE WIDTH SELECTION OPTION
S /
321      FNAME='PREVLR'
      ISK=1
S      JMS PLOT
S      CLA CLL
      FNAME='CIFPWS'
S      JMS RFILE
S      CLA CLL
      GO TO 296

```

```

S /
S /INSTRUCTIONS FOR ROUTINE ADJUSTMENT OPTION
S /
323     FNAME='CIFRAC'
S       JMS RFILE
S       CLA CLL
S       30 TO 286

S /
S /ERROR MESSAGE SUMMARY AND TROUBLESHOOTING OPTION
S /
329     READ(1,190)IX
180     FORMAT('WOULD YOU LIKE AN ERROR SUMMARY,','A2)
        IF(IX-IY)192,191,192
181     FNAME='CCE4SC'
S       JMS RFILE
S       CLA CLL
182     WRITE(1,183)
183     FORMAT('I COMPUTE THAT YOU MUST BE EXPERIENCING SOME DIFFICULTY,
        .')
        READ(1,194)IX
184     FORMAT('WOULD YOU LIKE SOME HELP,','A2)
        IF(IX-IY)296,195,286
185     FNAME='TROJBL'
        LM=1
        LPT=0
S       JMS RFILE
S       CLA CLL
        LM=0
        WRITE(1,186)
186     FORMAT('PLEASE INDICATE THE NUMBER OF THE PROBLEM,/, WHICH BEST
        • DESCRIBES YOUR DIFFICULTY',/,)
        READ(1,197)N
187     FORMAT(13)
623     IF(N-14)499,493,499
498     30 TO (301,502,503,504,505,506,507,508,509,510,511,512,513),N
499     N=N-13
        30 TO (514,515,516,517),N
501     FNAME='CPR081'
        30 TO 519
502     FNAME='TRBFLG'
        30 TO 519
503     FNAME='CPR083'
        30 TO 519
504     FNAME='CPR084'
        30 TO 519
505     FNAME='CPR085'
        30 TO 519
506     FNAME='CPR086'
        30 TO 519
507     FNAME='CPR087'
        30 TO 519
508     FNAME='CPR088'
        30 TO 519
509     FNAME='CPR089'
        30 TO 519
510     FNAME='CPR010'
        30 TO 519
511     FNAME='CPR011'
        30 TO 519
512     FNAME='CPR012'
        30 TO 519

```

```

513     FNAME='CPRD13'
      30 TO 518
514     FNAME='CPRD14'
      30 TO 519
515     FNAME='CPRD15'
      30 TO 519
516     FNAME='CPRD16'
      30 TO 519
517     FNAME='CPRD17'
S 518, JMS RFILE
S     CLA CLL
      READ(1,520)IX
620     FORMAT('WOULD YOU LIKE A DISCUSSION OF ANY OTHER PROBLEM. ',A2)
      IF(IX-IY)296,621,296
621     READ(1,522)Y
622     FORMAT('PLEASE TYPE THE NUMBER OF THE PROBLEM: ',I5)
      30 TO 623
S /
S /SELECTION OF A PROGRAM SET FOR SPECIFIC EXPERIMENTS OPTION
S /
327     WRITE(1,630)
630     FORMAT('THE NAMES OF THE PROGRAMS IN THE COMPUTERIZED',/, 'CONDUCT
+TANCE SYSTEM ARE CODED FOR',/, 'EASY RECOGNITION. WOULD YOU LIKE')
      READ(1,531)IX
631     FORMAT('AN EXPLANATION OF THIS CODE, ',A2)
      IF(IX-IY)633,632,633
632     FNAME='CPRGEX'
S     JMS RFILE
S     CLA CLL
633     FNAME='CSDAPS'
      LM=1
      LPT=0
S     JMS RFILE
S     CLA CLL
      LM=0
      WRITE(1,519)
519     FORMAT('PLEASE TYPE THE NUMBER WHICH CORRESPONDS TO THE',/, 'TYPE
+ OF EXPERIMENT YOU WISH TO PERFORM')
      READ(1,197)N
6     30 TO (501,602,603,604,605,606,607,608,609,610,650),N
601     FNAME='CFLCW2'
S     JMS RFILE
S     CLA CLL
      READ(1,511)IX
611     FORMAT('WOULD YOU LIKE AN EXPLANATION OF THE PROGRAM SET. ',A2)
      IF(IX-IY)679,612,679
612     FNAME='CEXPL2'
S     JMS RFILE
S     CLA CLL
679     READ(1,690)IX
680     FORMAT('WOULD YOU CARE TO VIEW SAMPLE DATA. ',A2)
      IF(IX-IY)296,691,296
681     FNAME='PTITPL'
      ISK=1
S     JMS PLOT
S     CLA CLL
      FNAME='CTITPL'
      30 TO 520
602     FNAME='CFLCW3'
S     JMS RFILE
S     CLA CLL
      READ(1,511)IX
      IF(IX-IY)692,613,682

```

```

613  FNAME='CEXP13'
S    JMS RFILE
S    CLA CLL
602  READ(1,590)IX
      IF(IX=1Y)296,693,296
603  FNAME='CHEXEL'
      ISK=1
S    JMS PLOT
S    CLA CLL
      FNAME='CHEXEL'
      30 TO 520
603  FNAME='CFLOW1'
S    JMS RFILE
S    CLA CLL
      READ(1,611)IX
      IF(IX=1Y)296,614,296
614  FNAME='CEXP11'
      30 TO 520
604  FNAME='CFLOW6'
S    JMS RFILE
S    CLA CLL
      READ(1,611)IX
      IF(IX=1Y)296,615,296
615  FNAME='CEXP16'
      30 TO 520
605  FNAME='CFLOW4'
S    JMS RFILE
S    CLA CLL
      READ(1,611)IX
      IF(IX=1Y)296,616,296
616  FNAME='CEXP14'
      30 TO 520
606  FNAME='CFLOW5'
S    JMS RFILE
S    CLA CLL
      READ(1,611)IX
      IF(IX=1Y)296,617,296
617  FNAME='CEXP15'
      30 TO 520
607  FNAME='CFLOW7'
S    JMS RFILE
S    CLA CLL
      READ(1,611)IX
      IF(IX=1Y)296,618,296
418  FNAME='CEXP17'
      30 TO 520
608  FNAME='CFLOW8'
S    JMS RFILE
S    CLA CLL
      READ(1,611)IX
      IF(IX=1Y)296,619,296
619  FNAME='CEXP18'
      30 TO 520
609  FNAME='CFLOW9'
      30 TO 520
610  FNAME='CFLD10'
      30 TO 520
650  FNAME='CFLD11'
S  =520, JMS RFILE
S    CLA CLL

```

```

      READ(1,3)IX
3      FORMAT('WOULD YOU LIKE A DISCUSSION OF ANY OTHER EXPERIMENT, ',A
      *2)
      IF(IX-IY)296,4,285
4      READ(1,3)N
5      FORMAT('PLEASE TYPE THE NUMBER OF THE EXPERIMENT: ',I5)
      30 TO 6

S /
S /CREATING OR CHANGING A CBHELP FILE OPTION
S /
347      FNAME='COCACF'
S      JMS RFILE
S      CLA CLL
      30 TO 296

S /
S /SUBROUTINE RFILE
S /THIS SUBROUTINE READS A FILE GENERATED WITH FILEST AND
S /OUTPUTS IT TO THE TTY OR LPT
S /
S RFILE,0000
S      CLA CLL
      IF(L4)213,213,212
213      READ(1,100)LPT
100      FORMAT('OUTPUT ON LPT=1, ON TTY=0',I5)
      IF(LPT)212,212,205
S #206, JMS OLP /30 SET UP LPT
S      CLA CLL
212      CALL IOOPEN('DT40',FNAME)
211      READ(4,203)(I=(1,I),I=1,128)
203      FORMAT(128A2)
S      JMS SCRAM /30 UNSCRAMBLE
S      CLA CLL
      DO 204 I=1,192
      LA=I*(2,I)
S      CLA CLL
S      TAD #LA
S      TAD (7546
S      SNA /IS IF A CNTRL "Z",
S      JMP I RFILE /YES, RETURN
S      CLA CLL
      IF(LPT)275,275,276
S #275, CLA CLL
S      TAD #LA
S PLP, TSF /TEST TTY FLAG
S      JMP OLP
S      TLS /ECHO CHARACTER
S      CLA CLL
      30 TO 204
S #276, CLA CLL
S      TAD #LA
S PLL, 5661 /TEST LPT FLAG
S      JMP PLL
S      5666 /OUTPUT CHARACTER
S      CLA CLL
204      CONTINUE
      30 TO 211

S /
S /SUBROUTINE OLP
S /THIS SUBROUTINE SETS UP THE LPT FOR OUTPUT
S /

```

```

S OLP, 0000
S CLA CLL
S 9662 /CLEAR LPT FLAG
S 9661 /TEST FLAG (SEE IF LPT IS OFF)
S JMP XFI
S JMP OLPT /33 TELL TO TURN ON LPT
S WFI, 9662
S 9661
S JMP XFI
S JMP WFI
S XFI, CLA CLL
S TAD (7700
S DCA SET2 /DELAY LOOP
S FP, ISZ SET1
S JMP FP
S ISZ SET2
S JMP FP
S TAD (0213 /CARRIAGE RETURN
S 9664
S YFI, 9661
S JMP YFI
S CLA CLL
S TAD (0214 /FORM FEED
S 9666
S ZFI, 9661
S JMP ZFI
S CLA CLL
S JMP EXP
S SET1, 0000
S SET2, 0000
S OLPT, CLA CLL
220 WRITE(1,220)
S FORMAT(1,TURN ON LPT,1/)
S JMP WFI
S EXP, CLA CLL
S JMP I OLP
S /
S /SUBROUTINE SCRAM
S /THIS SUBROUTINE UNSCRAMBLES OS/8 DEC TAPE PACKED ASCII INTO
S /DISCRETE 9 BIT VALUES
S /
S SCRAM,0000
S CLA CLL
S <T=1
S <A=0
S <B=0
S <C=0
S <D=0
S DO 400 <=1,127,2
S <A=I*(1,<)
S <B=I*(1,<+1)
S CLA CLL
S TAD #4A /BEGIN TO REARRANGE DATA
S AND (0377
S DCA #4C
S TAD #4B
S AND (0377
S DCA #4D
S TAD #4A /BEGIN TO COMBINE THIRD CHARACTER CODE
S AND (7400
S RTR
S RTR

```



```

S      DCA =KA
S      TAD =KB
S      AND (7400
S      RTL
S      RTL
S      RAL
S      TAD =KA
S      DCA =KA
S      CLA CLL
          IP(2,KT)=KC
          KT=KT+1
          IP(2,KT)=KD
          KT=KT+1
          IP(2,KT)=KA
          KT=KT+1
400    CONTINUE
S      JMP I SCRAM
S /
S /SUBROUTINE PLOT
S /THIS SUBROUTINE GENERATES GRAPHICS DISPLAYS FOR C3HELP ROUTINES
S /
S PLOT, 0000
S      CLA CLL
          CALL IOPEN('DTA0',FNAME)
          READ(4,920)(IP(1,I),I=1,300)
          READ(4,920)(IP(2,I),I=1,300)
920    FORMAT(300A2)
          IF(IX-1Y)923,923,921
921    READ(1,930)IX
930    FORMAT('WOULD YOU LIKE A HARD COPY OF THE DIAGRAM, ',A2)
923    MX=IP(1,1)
          MY=IP(2,1)
          MX1=0
          IF(IX-1Y)935,936,935
935    CALL SCOST(MX,MY)
          GO TO 937
936    CALL XYST(MX,MY)
937    DO 950 I=2,300
          MX=IP(1,I)
          MY=IP(2,I)
          IF(MX+1)960,943,945
          IF(IX-1Y)942,941,942
941    CALL XYEND
942    MX1=1
          GO TO 950
945    IF(IX-1Y)946,947,946
946    IF(MX1)948,949,949
948    CALL SCOST(MX,MY)
          MX1=0
          GO TO 950
949    CALL SCOST(MX,MY)
          GO TO 950
947    IF(MX1)951,952,951
951    CALL XYST(MX,MY)
          MX1=0
          GO TO 950
952    CALL XYST(MX,MY)
950    CONTINUE
960    IF(IX-1Y)952,951,952
961    CALL XYEND
S #962, CLA CLL
S      JMP I PLOT
          END

```