A POLAROGRAPHIC OXYGEN ELECRODE FOR THE MEASUREMENT AND RECORDING OF OXYGEN DENSITY IN FRESH WATER

By

BENNY L. PIERCE

Bachelor of Science

Central State College

1960

Submitted to the faculty of the Graduate School of
the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
May, 1963

A POLAROGRAPHIC OXYGEN ELECTRODE FOR
THE MEASUREMENT AND RECORDING OF
OXYGEN DENSITY IN FRESH WATER

THESIS APPROVED:

Thesis Adviser

Dean of the Graduate School

PREFACE AND ACKNOWLEDGEMENT

Knowledge of the amount of free oxygen in fresh water has many uses in the natural and physical sciences.

Accurate measurements of these concentrations have formerly been possible only in the laboratory by the tedious method of titration. Recent improvements in the polarographic oxygen electrode have allowed continuous monitoring of oxygen concentrations at remote sites.

The purpose of this study is to present a system using the oxygen electrode, whereby concentrations may be determined, and this information recorded and collected periodically.

In this paper, a brief historical background of the development of the polarographic measurement is presented, together with details of the specific system involved for this application. Various design features which include detection, amplification, recording, environment, and packaging are discussed.

The author wishes to express his sincere appreciation to Mr. Edward Allen and Mr. Joe Zinn for their valuable comments and suggestions, and to Mr. R. F. Buck for permission to use the thesis subject. Also, special thanks are due Dr. Harold Fristoe, who encouraged and aided the author as thesis advisor.

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER I

INTRODUCTION AND HISTORICAL SKETCH

In the accelerating world competition to increase scientific knowledge, scientists are confronted with increasingly complex problems of chemical analysis.

One of the newer, important methods of analysis available today is polarography. Polarography may be defined as an analytical method of chemical analysis based on the electrolysis of a small amount of the substance to be analyzed in a cell containing one indicator electrode and one reference electrode. The current obtained from the reaction is a function of the concentration of the reacting substance and the voltage necessary to produce the reaction. Of the various methods of analysis available, the polarographic method offers speed, convenience in the laboratory and lends itself to systems of instrumentation, wherein continuous data may be recorded in the field. Polarography is helping to solve problems in such diverse fields as metallurgy, medicine, physiology, explosives, plastics, mining, and rocket propellants.

The intimate involvement of oxygen in nature makes its accurate measurement a matter of great interest. The reduction of molecular oxygen at a dropping mercury electrode and at solid electrodes has been reported by many investigators. This phenomenon can either be a hindrance to the scientist who is working with substances that are reduced at potentials which also reduce oxygen, or can be turned into an advantage as the basis for the determination of dissolved oxygen.

In the acquatic sciences, a knowledge of the distribution of dissolved oxygen in space and time is the basis for quantitative and qualitative deductions regarding the behavior of systems. The variety of investigations to which it has been applied include the biological oxygen demand in domestic sewage evaluation of biological production potential of various waters, continuous flow respirometry of aquatic invertebrates and fishes, determination of respiration and photosynthesis in algae, analyzing respiratory gases for oxygen, and determination of vertical profiles of oxygen in marine and fresh water. For example, Worthington[1] evaluated oxygen data obtained in the North Atlantic during the past 25 years and concluded that there has been no mixing of deep water with surface water for the past 140 years. Information about deep ocean circulation has the obvious present day application of the possibility of dumping radioactive wastes in the oceans.

Pritchard and Carpenter[2] utilized knowledge of currents and oxygen concentrations measured in existing impoundments to predict the behavior of impoundments not yet constructed. Such considerations are important in regulating the degree to which oxygen may be depleted by dumping industrial and biological wastes in rivers and streams.

Polarographic systems for the study of dissolved oxygen concentrations are not new. Dropping mercury electrodes and bare platinum electrodes were used by Giguere and Lauzier[3] for the determination of dissolved oxygen content in natural waters.

Muller[5] detailed some of the factors governing the behavior of a stationary electrode in a flowing solution. He concluded that results were producible as long as test conditions such as rate of flow of solution, applied voltage, temperature, and the concentration of the supporting electrolyte were kept constant.

The sensitivity of a bare electrode decreases with time, apparently due to impurities plating out on the electrode. Olson, Brackett, and Crickard[6] partially overcame this limitation by applying a five to ten cycle-per-minute square wave with periodic shorting periods to the electrode. Such a method tends to remove impurities which are reversibly deposited on the electrode.

In an effort to overcome the shortcomings of a bare electrode, Davies and Brink[7] covered the metal with agar and also a membrane of collodion. Clark[8] was among the first to cover the electrode with a plastic film permeable to molecular oxygen but at the same time, impermeable to other dissolved constituents.

Reeves and Rennie[9] described the use of a membrane covered electrode to study oxygen tension in urine. This instrument was not temperature compensated and thus had to be used with careful temperature control.

Føyn[10] used a dropping mercury electrode with a zinc reference electrode to measure vertical oxygen profiles in Norwegian fjords. This system appears to have been the first successful attempt to obtain a continuous indication of dissolved oxygen in subsurface waters. However, the device as originally described was not temperature compensated.

The design and implementation of a system, based on the method of polarography, to monitor vertical oxygen profiles in fresh water is the subject of this thesis.

Feasibility studies were undertaken with the following basic requirements in mind. The over-all system was to be capable of remote operation with a minimum amount of supervision over extensive areas of river or lake. This thesis was a logical result of these preliminary studies.

REFERENCES

[1]Worthington, L. V., Deep-Sea Research. I (1954) p. 244.

[2]Pritchard and Carpenter to Kanwisher, Quoted in John Kanwisher "Polarographic Oxygen Electrode," Limnology and Oceanography. IV (April, 1959) pp. 210-217.

[3]Giguere, P. A. and Louis Lauzier, "Le Dosage Polarographique De L'Oxygéne Dissous Dans L'Eau De Mer," Can. J. Research. B 23-24 (1945) p. 76.

[4]Ibid., p. 223.

[5]Muller, O. H., "Polarographic Study with a Microelectrode Past which an Electrolyte is Flowing," J. Am. Chem. Soc. LXIX Pt. 2 (1947) p. 2992.

[6]Olson, R. A., F. S. Brackett, and R. G. Crickard, "Oxygen Tension Measurement by a Method of Time Selection Using the Static Platinum Electrode with Alternating Potential," J. Gen. Physiol. XXXII (1949) p. 681.

[7]Davies, P. W. and F. Brink, "Microelectrodes for Measuring Local Oxygen Tension in Animal Tissues," Rev. Sci. Instr. XIII (1942) p. 524.

[8]Clark, L. C. Jr. et al., "Continuous Recording of Blood Oxygen Tensions by Polarography," J. Appl. Physiol. VI (1953) p. 189.

[9]Reeves, R. B. and D. W. Rennie, Federation Proc. XVI (1957) p. 693.

[10]Føyn E., Rept. Norwegian Fish Market Invest. XI (1955) p. 3.

CHAPTER II

STATEMENT OF SYSTEM REQUIREMENTS

The system requirements mentioned in Chaper I may be outlined as follows:

1) A six-station network to cover up to 50 miles of stream or lake

2) Four electrodes at different depths at each station

3) Temperature monitored at one depth at each station

4) An electrode measuring oxygen concentrations from 0 to 15 parts per million ± 10% and temperature calibrated through a range from 32° F. to 90° F.

5) Data to be recorded at the rate of set readings per hour.

6) Each station capable of independent operation up to 48 hours.

7) Each station in a sealed enclosure with a bouy and anchor and a flashing warning light.

Since the stations must cover such an extensive area, the use of an interwired system is not feasible. With this in mind, two alternatives exist.

1) Each station could be equipped with a transmitter to send data to a central recorder at prescribed intervals. (For greater flexibility, a receiver might be included to allow interrogation whenever desired).

2) Each individual station could be equipped with a recorder.

The second of these possibilities was decided to be the most feasible for several reasons such as smaller cost, greater reliability, and smaller power consumption. Perhaps the most important single factor in making this decision is that no external power is available; therefore, recorded data may be collected at the time that battery packs are replaced.

Amplifier

From experimental results with the electrodes, it was found that the signal output current was such that several problems existed in the design of a suitable amplifier.

The smallest output from the electrodes with an applied potential of 0.6 volts and low oxygen concentration is approximately two microamperes. Thus, the amplifier must be capable of amplifying this low dc current from a high impedance source.

The stability requirements are quite stringent, since any change in amplifier parameters with time or temperature would tend to be amplified as a signal change.

The power consumption must be held to a minimum since internal battery power is specified.

Recorder

The recorder to be selected must have the following features:

1) High sensitivity
2) Acceptable response time
3) Relatively small size
4) Low power requirements
5) Acceptable chart drive speed
6) Acceptable drive motor voltage requirements.

Temperature Gage

The temperature gage must be capable of measuring temperatures from 32° F. to 90° F. with an accuracy of at least ± 1° F. throughout this range. Since rapid temperature transients will not be encountered, the gage response time is not a design factor.

Timer

The timer must provide two related functions.

1) The timer will initiate the data gathering and readout cycle once per hour. When readout is completed, all equipment must be deactivated for power conservation purposes until the next cycle is initiated.

2) The readout time length of each different datum must be controlled.

Data Switching Function

A switching system must be designed which will make the data available to the recorder in a programmed sequence.

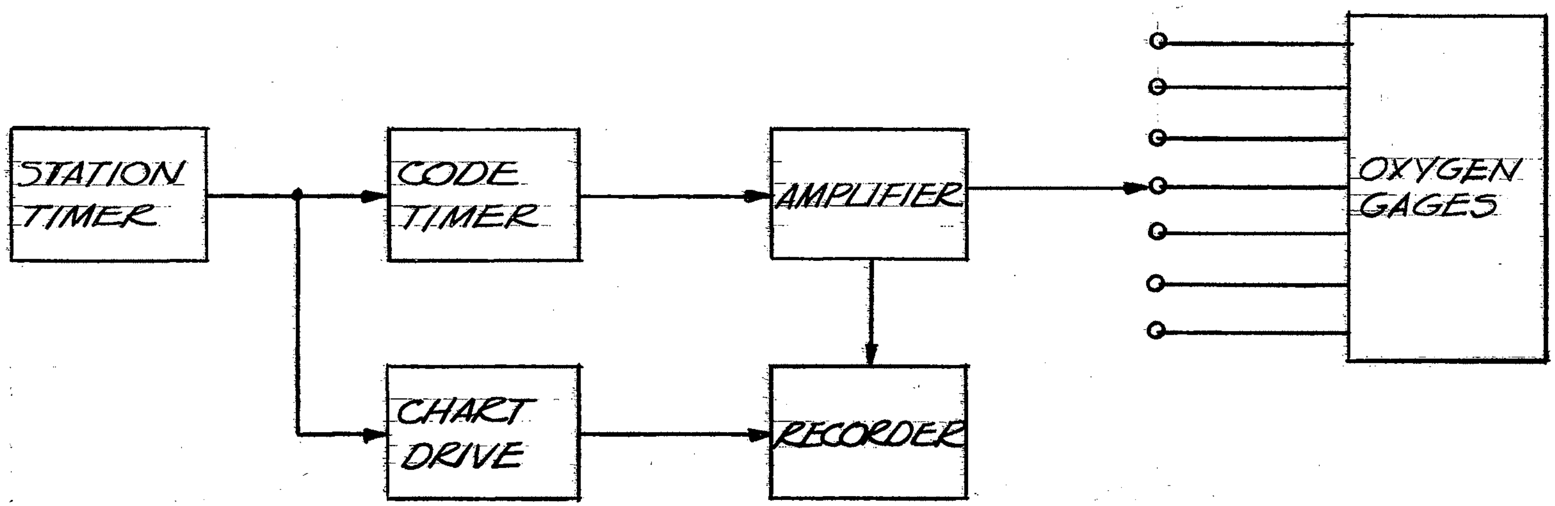
Power

Although the system requirements do not specify a particular value for the power supply, some comments governing its choice can be made. The battery pack should be small in physical size and weight. It must have the capability of supplying all necessary power for 48 hours. For reasons of economy, it should be rechargeable.

Package

The principle design objectives were to facilitate assembly, ease rework and troubleshooting problems, provide a rigid framework for mounting the system components, ease battery pack replacement, facilitate removal of the strip chart, and provide a waterproof environment for the components. In addition, weight and volume should be minimized for ease of handling and servicing.

In this chapter, the author has listed the system requirements and has attempted to describe the building blocks which will enable the system to perform the desired functions. A block diagram of the system as it has evolved is shown in Figure 2-1.



BLOCK DIAGRAM

FIGURE 2-1

CHAPTER III

LOGICAL APPROACH TO THE SYSTEM DESIGN

In the design of any system, one should first set down the basis for design in some systematic order.

1) Design objectives - This tabulation should define the function (s) the system must perform as completely as possible.

2) Intersystem compatibility - In the event the system being designed is a subsystem of a network of other systems, then the relationship between systems must be studied to insure compatibility.

3) Design limitations - All system specifications and requirements which could influence or restrict the system design should be thoroughly studied by the designer before proceeding with the design.

The author has attempted to fulfill the three objectives listed above throughout the earlier chapters. At this point, some insight should have been gained about the particular problems inherent in the design of such a system.

The next step in the design of a system is that of establishing a design philosophy. Reviewing the requirements as outlined in Chapter II, it was decided to divide the system into the following functional areas:

1) Construction and calibration of the oxygen electrodes

2) Design of a suitable amplifier

3) Design of the associated subsystems such as the timer and temperature gage.

The physical arrangement of the electrode shown in Figure 3-1 is a combination of a carbon indicator electrode and a silver, silver-oxide reference electrode which is concentric around the platinum, 0.5% N potassium hydroxide as an internal electrolyte.

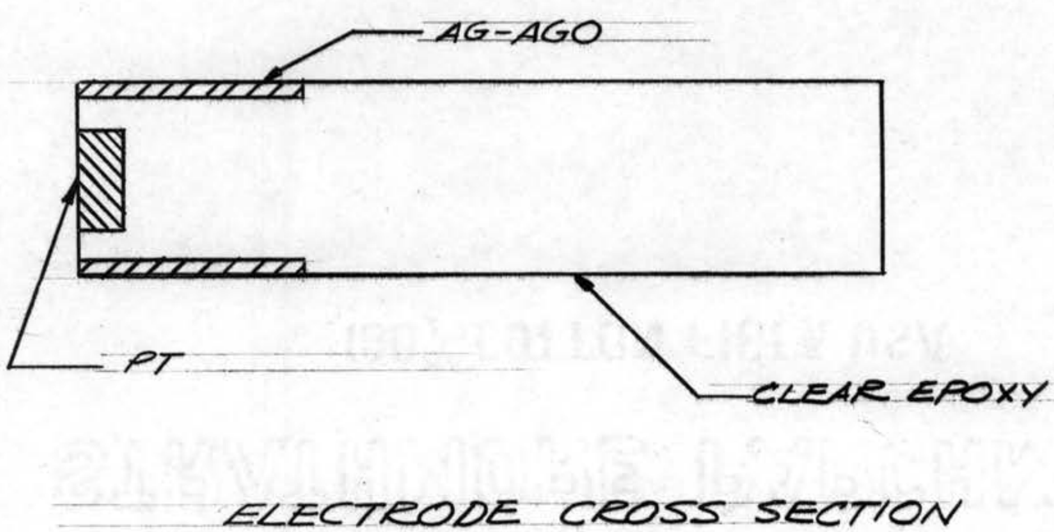


Figure 3-1

A polyethylene membrane is stretched tightly over both electrodes and held in place by a retaining ring. The film is placed over the electrode while the whole assembly is held submerged in a 0.5% N solution of potassium hydroxide. A small amount of the solution is trapped under the membrane and forms a thin layer between the plastic and the electrodes.

The principle of operation is as follows: The plastic film, being permeable to dissolved oxygen but much less so to other dissolved substances, permits the passage of oxygen to the carbon electrode where it is reduced to hydroxyl under operating conditions. The plastic prevents the passage of substances which would plate out on the carbon electrode and change its sensitivity. The end result is the formation of silver oxide on the surface of the silver. The silver oxide then becomes the reference electrode which makes contact with the solution to complete the circuit with the carbon indicator electrode. Since the silver can be made quite thick, such a device will last for many months of continuous use.

The diffusion situation is as follows: When the device is turned on, a current flows because the potassium hydroxide has previously established oxygen tension equilibrium across the film. The current decreases after a few seconds as the oxygen in solution behind the film is depleted. Oxygen from the test solution begins to diffuse across the film because of the gradient which has been produced. Equilibrium is soon reached where the oxygen consumed at the electrode is equal to the oxygen diffusing across the film.

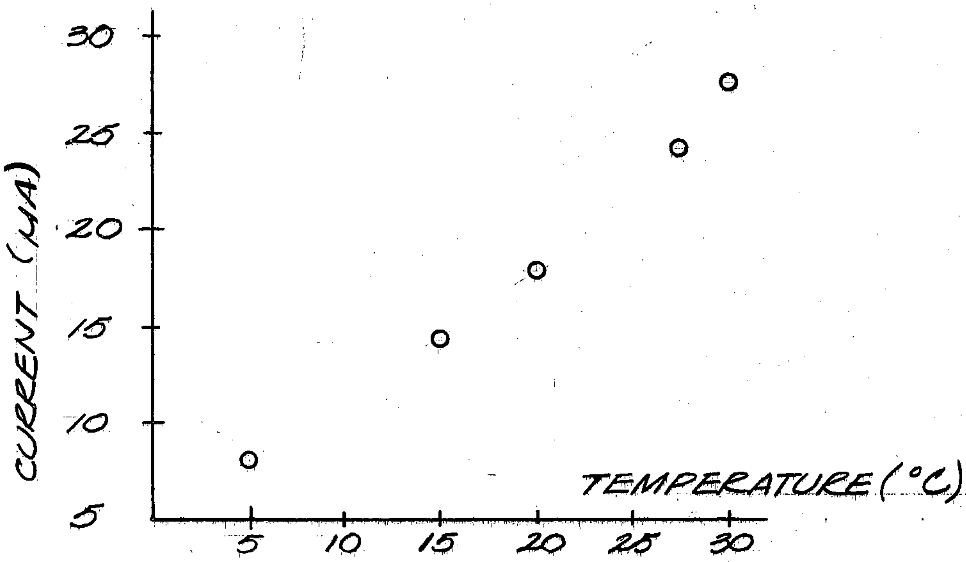
The tension increment across the film is nearly equal to the tension in the test solution since that in the KOH is very low. Since the value of current is only about 1/1000 of the current which would flow if the electrode was bare, the system is nearly independent of the flow of water past the device. A slight current of about 1 cm/sec brings the current nearly to saturation.

There are five properties of the system which have practical importance. These properties are the temperature coefficient, the time required to reach equilibrium, the flow characteristics, the current-oxygen concentration relationship, and the stability.

Temperature Compensation

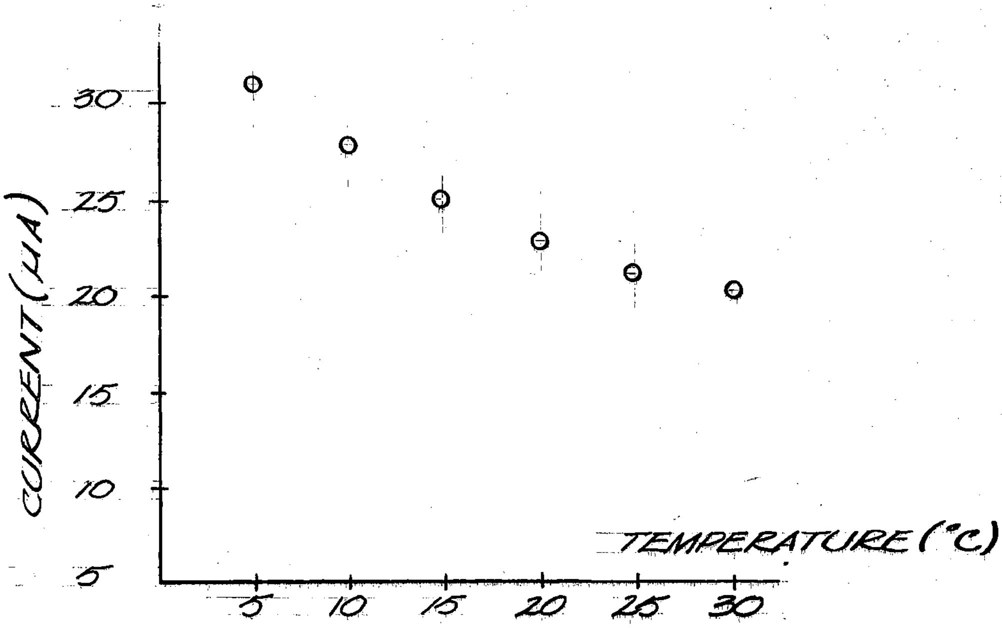
The electrode system is an amperometric device in which the oxygen concentration rather than the applied voltage determines the magnitude of the current which flows. The device exhibits a positive temperature coefficient of approximately five per cent per degree centigrade. The high temperature dependence is due to a combination of two factors; the effect of the temperature on oxygen concentration and the temperature coefficient of the device itself. Figure 3-2 shows the change in electrode current with temperature. Figure 3-3 shows the variation of oxygen concentration in air saturated solutions with temperature.

Since the temperature coefficient of the device is positive, it is possible to partially compensate for this temperature dependence by using the negative temperature coefficient of a thermistor. However, since the temperature dependence is not linear, (varying from about



ELECTRODE CURRENT VS. TEMPERATURE

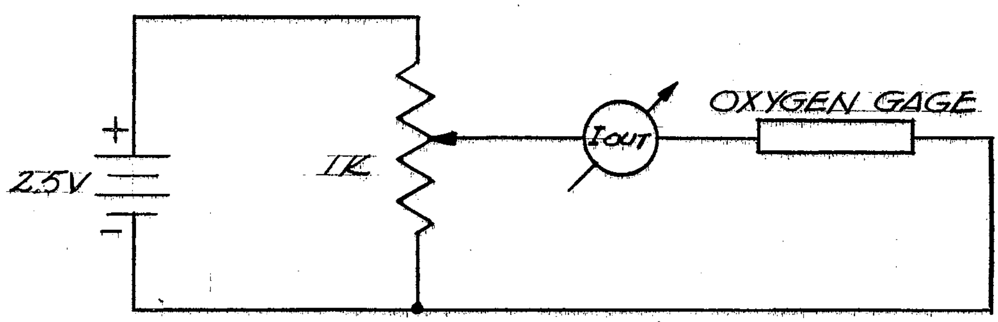
Figure 3-2



DISSOLVED OXYGEN VS. TEMPERATURE

Figure 3-3

four per cent per degree at 10° centigrade to about 8.5 per cent per degree at 25° centigrade) a preliminary decision was to temperature calibrate the electrode system rather than attempt compensation. With this in view, a temperature readout circuit was incorporated into the over-all system. The circuit used for electrode calibration purposes is shown in Figure 3-4.



OXYGEN GAGE CALIBRATION CIRCUIT

Figure 3-4

Time Constant

In the system as described, there are several barriers to diffusion; the thin layer of potassium hydroxide trapped beneath the plastic membrane, the plastic membrane itself, and possibly a thin film of liquid at the outside surface of the plastic membrane.

Effect of Flow

Previous bare electrode systems have shown a significant dependence on the veolocity of the test solution past the electrode. (Muller 1947). In the present system, so little oxygen diffuses from the solution through the film, there is much less dependence on flow velocity. A disc of filter paper placed on the platinum electrode will further decrease this dependence.

Stability

The system has shown marked sensitivity to change in applied potential. This dependence has necessitated using Zener diode voltage regulation of the power supply.

After operation has stabilized, there is little change in characteristics with time, if environmental conditions are held constant.

Small fluctuations in electrode current have been traced to the formation of small bubbles on the surface of the film.[11] This trouble is usually noted when the solution has been warmed from a lower temperature and is thus supersaturated.

The over-all performance of these polarographic oxygen electrodes has been studied with a recording potentiometer together with independent physical determinations. Operation of the electrode may be summed up as follows.

1) Current is a linear function of oxygen tension.

2) It is stable to within a few per cent over a period of several days.

3) Short period changes in sea water of 0.01 ml per liter can be detected.

4) The device reaches 90 per cent of full response within 20 seconds and 99 per cent of full response in two minutes.

The above outline represents the approach to the design of the system employed by the author. This should not imply that the above represents the only method of solution to the problem or even the optimum one because in general, any such solution will reflect the designer's background and experience.

The majority of the problems encountered in the design of a suitable amplifier circuit were a result of the temperature range over which the amplifier is required to function.

The basic consideration which had a significant bearing on the amplifier design philosophy regarded the selection of the basic amplifying device. As might be expected, the choice lay between vacuum tubes and transistors. The vacuum tube is inherently a high impedance device which in itself is a desirable characteristic insofar as powering is concerned. However, the heater power required more than offsets this savings in signal power. Also, its operating theory being based on self-destruction, the vacuum tube has an inherently short life. The transistor, on the other hand, requires no heater power, is small and rugged, and has a theoretically infinite life expectancy.

Today, there are available two similar types of transistors which differ in certain of their parameters. These two types are differentiated by the type of semiconductor used in their construction, namely, germanium and silicon. A brief operational comparison is given here.

1) Temperature - Silicon units operate satisfactorily at temperatures of 175° C. or higher; whereas, operation of germanium is restricted to maximum temperatures of about 100° C. Both types can be operated at low temperatures.

2) Cutoff currents - Silicon transistors have leakage currents 100 or more times lower than that of comparable germanium units.

3) Current amplification factor - The change in alpha with temperature is generally more noticeable with silicon transistors.

4) Collector voltage - Higher maximum collector voltage ratings are available in silicon units.

5) Saturation resistance - Silicon devices exhibit much higher collector to emitter resistance than germanium units.

6) Cost - Germanium transistors are available at considerably lower cost.

For a low level dc amplifier, there are several characteristics which indicate the use of silicon transistors. In general, these are superior temperature characteristics and the ability to operate more efficiently at low current levels.

The major difference between an ac and a dc amplifier is that in the dc case, direct coupling must be used; that is, transformers or capacitors cannot be used for coupling purposes between stages. This makes it very difficult to design a stable dc amplifier since any change in gain, due to a temperature change for example, will be amplified as an input signal by following stages.

Since this is the case, it is often desirable when amplification of a dc signal is required, to avoid the use of the straight dc amplifier and resort to modulation or mechanical chopper techniques. In this method, an ac signal is formed whose magnitude is proportional to the dc signal being amplified, and the resulting ac signal is amplified by conventional methods. After sufficient amplification, the signal is converted to direct current. This method suffers from difficulties such as questionable reliability of mechanical components. The use of transistor choppers removes the objection of using mechanical components, but there are other considerations such as: rapid recovery from overload, freedom from hash, simplicity, and small size due to the absence of transformers and capacitors.

A dc amplifier may be designed in either a balanced or an unbalanced configuration. One of the most commonly used techniques for balancing the temperature dependent drifts of resistively-coupled transistor amplifiers employs the emitter-coupled difference amplifier. Since temperature stability is the major problem encountered, the differential type amplifier was chosen.

There are two basic considerations in the design of a differential amplifier.

1) A high degree of dc stability

2) A high common mode rejection

These will be discussed separately.

D. C. Stability

An amplifier used to amplify very low frequency signals must have a high degree of dc stability. This is necessary if the circuit is to amplify input signals and at the same time reject extraneous signals introduced by temperature and gain variations and other undesirable effects. In theory, the output signal of a differential amplifier is proportional to the difference between the two input signals. Thus, extraneous signals introduced at the inputs due to environmental changes are canceled at the output.

Drift in direct-coupled dc differential amplifier originates chiefly in the differential input transistors and is primarily due to temperature and aging changes in I_{CBO}, V_{BE}, and h_{FE}. The source of drift due to reverse saturation currents can be virtually eliminated by using silicon transistors with room temperature saturation currents in the order of one millimicroamp. Variations in h_{FE} and V_{BE}, however are not so well ordered and remain as important sources of drift. By using well-matched transistors, variations in current gain can be minimized. The most difficult obstacle to overcome is the matching of the V_{BE} characteristic. The base-emitter voltage is quite temperature dependent. Even though the base-emitter voltage drops of the differential transistors are in series opposition, a drift of 20 micro volts referred to the input will result from a 0.01° C. temperature differential between these two transistors. The use of two matched transistors in one can or a transistor clip designed for this purpose alleviates this problem.

In addition, there is also a drift source due to the different temperature coefficients of the base-emitter junctions. Since the base-emitter voltage at constant current is nearly linear with temperature, compensation is possible. This may be accomplished by the use of diode having an equivalent temperature coefficient or an auxillary circuit which provides a current which is linearly dependent on temperature.

Common Mode Rejection

The common mode rejection of the amplifier is a measure of its ability to reject a signal common to its two isolated inputs. The common mode rejection factor is sensitive to unbalance in the signal source and emitter resistances. For a high common mode rejection, the impedance between the emitters and ground should be extremely high. One method to accomplish this is to supply the emitter bias current with a constant current source. This can be done through the use of a transistor in the emitter circuits which is biased in the common base configuration. Thus, the effective impedance between the differential transistor emitters and ground is the very high output impedance of the common base transistor.

In addition to the primary considerations, it is also desirable that both the input and output terminals be at ground potential with zero input signal. With this condition satisfied, several stages can be conveniently cascaded for higher gain. Also with both input and output at the same potential, heavy dc feedback may be used between output and input. Since with no signal input the base of each transistor is at ground potential, the collectors cannot be at ground potential for proper biasing. If the amplifier contains only a simple stage of amplification, a voltage dropping network must be used to return the output terminals to ground. For a single-ended output, the translation may be accomplished by a resistor network or an emitter follower circuit. When more than one stage of amplification is required, the voltage translation may be conveniently accomplished by the use of complementary-type transistors in succeeding stages. If the second stage is a differential amplifier, the double-ended output of the first stage may be used to drive the second stage directly. By using this method, imbalance in the first stage is attenuated by the common-mode rejection of the second stage. The use of a double-ended output has the added advantage that any difference in the small signal gain between the differential transistors is cancelled in the output.

For the reasons listed above, the circuit chosen is a two stage differential amplifier with a transistor in the common base configuration as a constant current source for the emitters. This configuration is seen to provide optimum dc stability and common mode rejection.

The operation of the amplifier, shown in Figure 3-5, is as follows. Since the base of Q101 is held at -0.7 volts, the difference between this voltage and the voltage on the base of Q103 is the differential signal which is amplified. As the dc signal enters Q101, the current will increase in that unit. Because of emitter coupling, then, the current in the other transistor in this stage will decrease by an equal amount. Thus, each half of the amplifier effectively amplifies equal signals which are 180° out of phase. Should, however, the two out-of-phase signals be unequal in the first stage, the difference acts differentially on the second stage, tending to rectify the unbalance which has been introduced. A balanced signal in the first stage, then, may not stay balanced, but any unbalance tends to be resolved in the final stage. The dummy gage shown in Figure 3-6 was used in testing the amplifier.

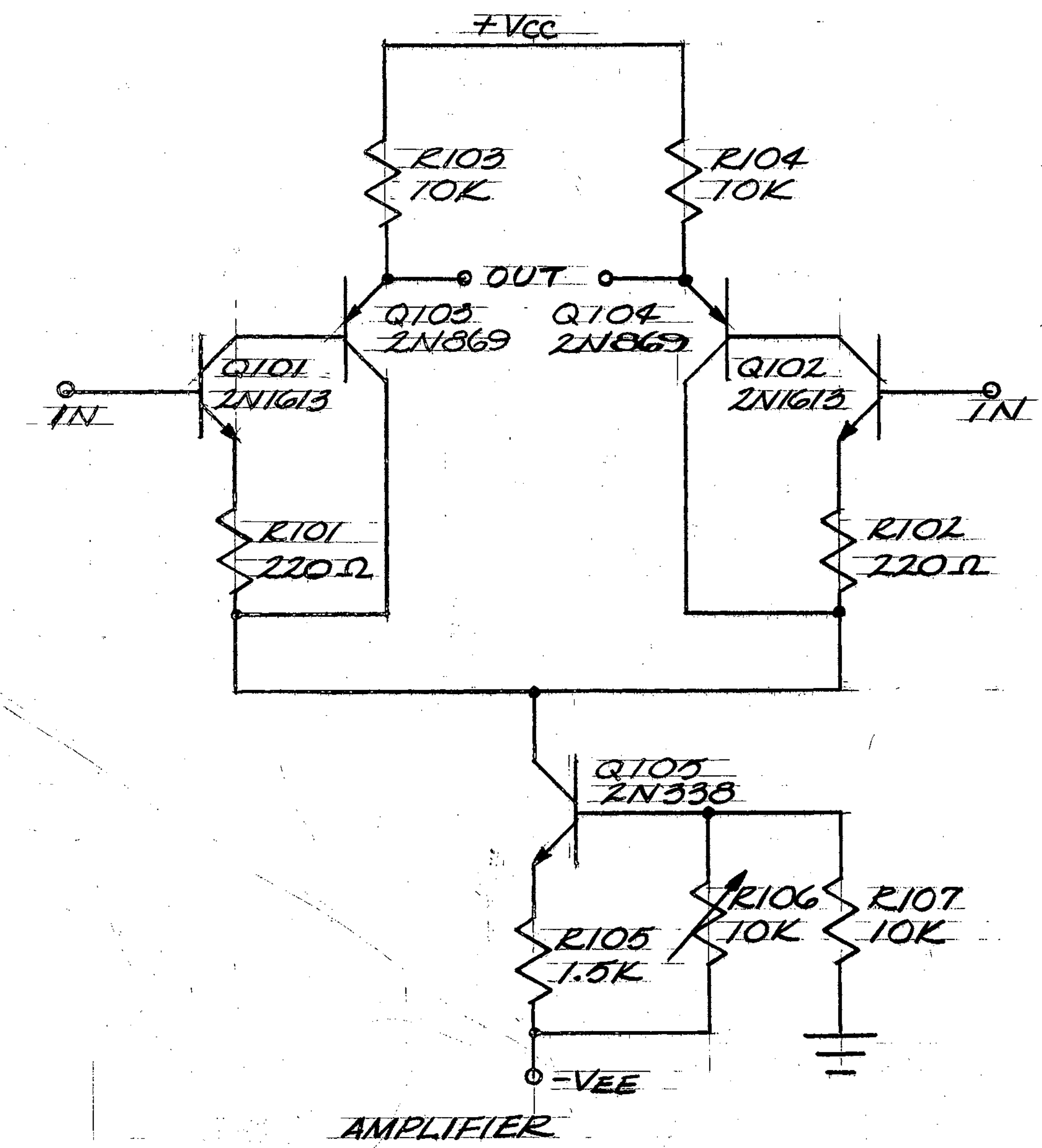


Figure 3-5

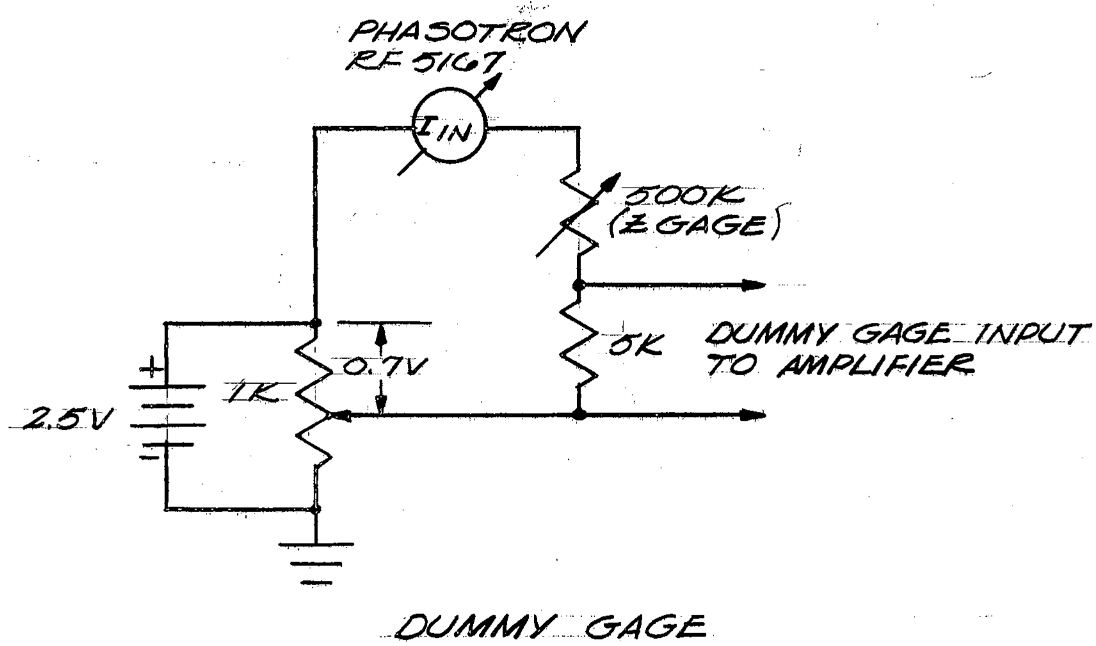


Figure 3-6

From previous experience, it was felt that the code timer and the data switching function could be combined into one functional block. These two functions are closely interrelated because the comand switching signal is the result of the code timer sequence.

For reasons of simplicity, an electronic rather than mechanical timer was chosen. There are many timing circuits available for consideration. Three such circuits come readily to mind.

1) Blocking oscillator

2) Binary counter

3) Relaxation oscillator

From a practical standpoint, only the relaxation oscillator provides a realistic answer. This circuit requires far fewer components, and the timing frequency is quite independent of temperature and fluctuations in supply voltage. Figure 3-7 shows how a unijunction transistor can be used with a relay to obtain a precise time constant.

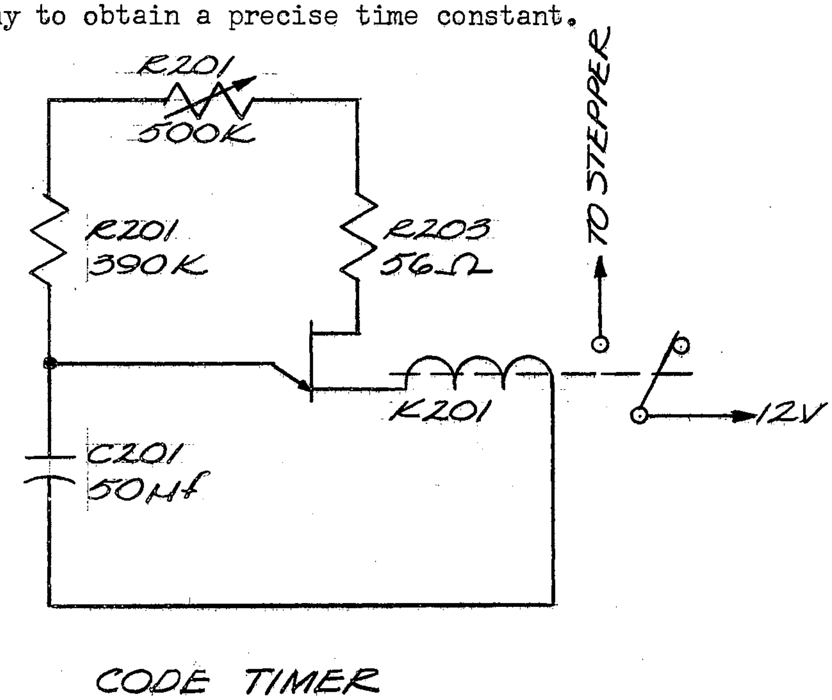


Figure 3-7

When power is applied to the circuit, (the function of the station timer) capacitor C201 is charged to the peak point voltage at which time the unijunction transistor fires and the capacitor discharges through relay K201, thus, causing it to close. This, in turn, energizes the stepper coil which controls the switching function. The time constant of the circuit is determined by the series resistors R201 and R202 and capacitor C201. The frequency of oscillation is is given by the equation

$$f = \frac{1}{R_T C201 \left(\frac{1}{1-n} \right)}$$

where R_T is the sum of R201 and R202 and n is the intrinsic stand-off ratio, a parameter of the unijunction device. Although n can be measured with some effort, it is constant over wide ranges of interbase voltage and temperature, and ranges from .56 to .68.

The practical choice for a data switch was a self-powered rotary switch with sufficient positions to handle the data requirements. As mentioned previously, the data required were:

1) Station code
2) Time code
3) Temperature code
4) Oxygen electrode, No. 1
5) Oxygen electrode, No. 2
6) Oxygen electrode, No. 3
7) Oxygen electrode, No. 4 .

In addition to these requirements, it was felt that zero, half and full scale calibration should be added. The use of a twelve position switch would allow the addition of another data source, if desired, and would be utilized for calibration during the interim. A typical readout using the above scheme is shown in Figure 3-8. In addition to the twelve position switch, it is necessary to provide the capability of switching the power on and holding it on for the total readout time.

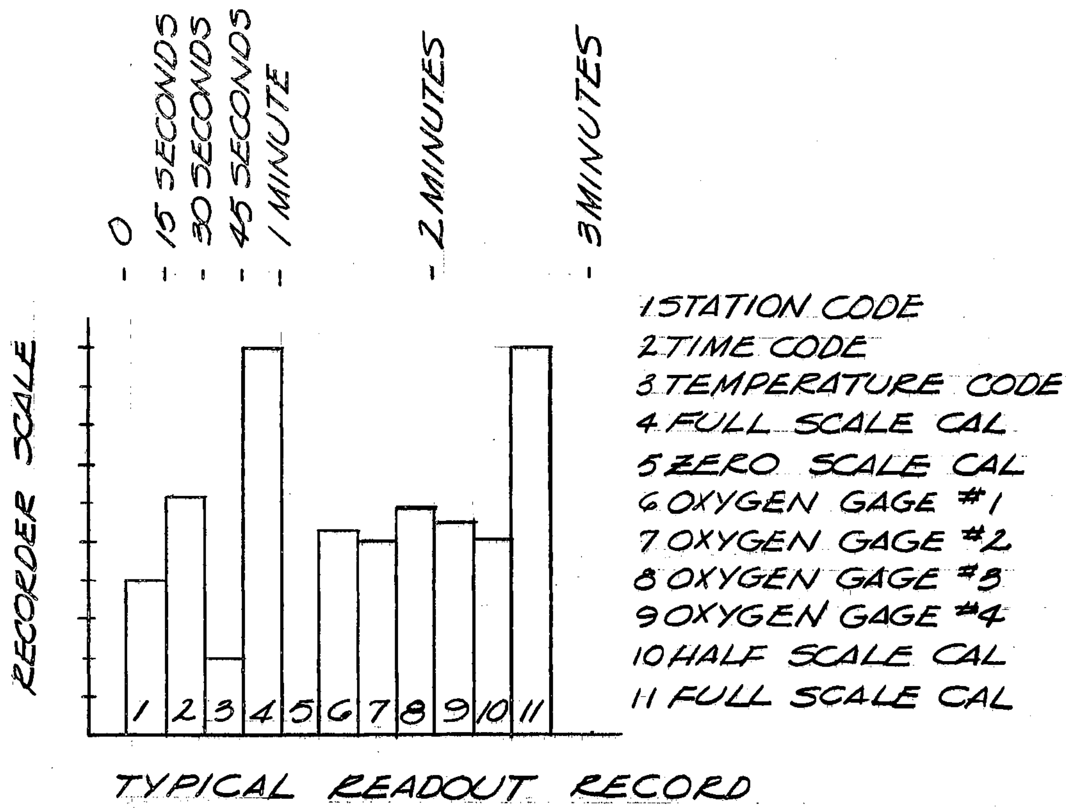


Figure 3-8

The design of the station timer was somewhat unique insofar as the rest of the system is concerned. Because the station timer must run without interruption for an extended period of time, the decision here was to use a completely mechanical timer. As has been mentioned, the principle function of the station timer is to initiate the data readout cycle, but it was felt that the station timer should also end the cycle. The station timer is a spring driven clock which closes a momentary switch once per hour to initiate the data gathering and readout cycle, holds it closed during the cycle, and opens the switch after the cycle is completed. Also, a rotary switch was incroporated into the timer to provide for a time code readout. A schematic of this timer is shown in Figure 3-9. The function of R302 is that of current limitation, while R302 allows fine adjustment of the time code amplitude.

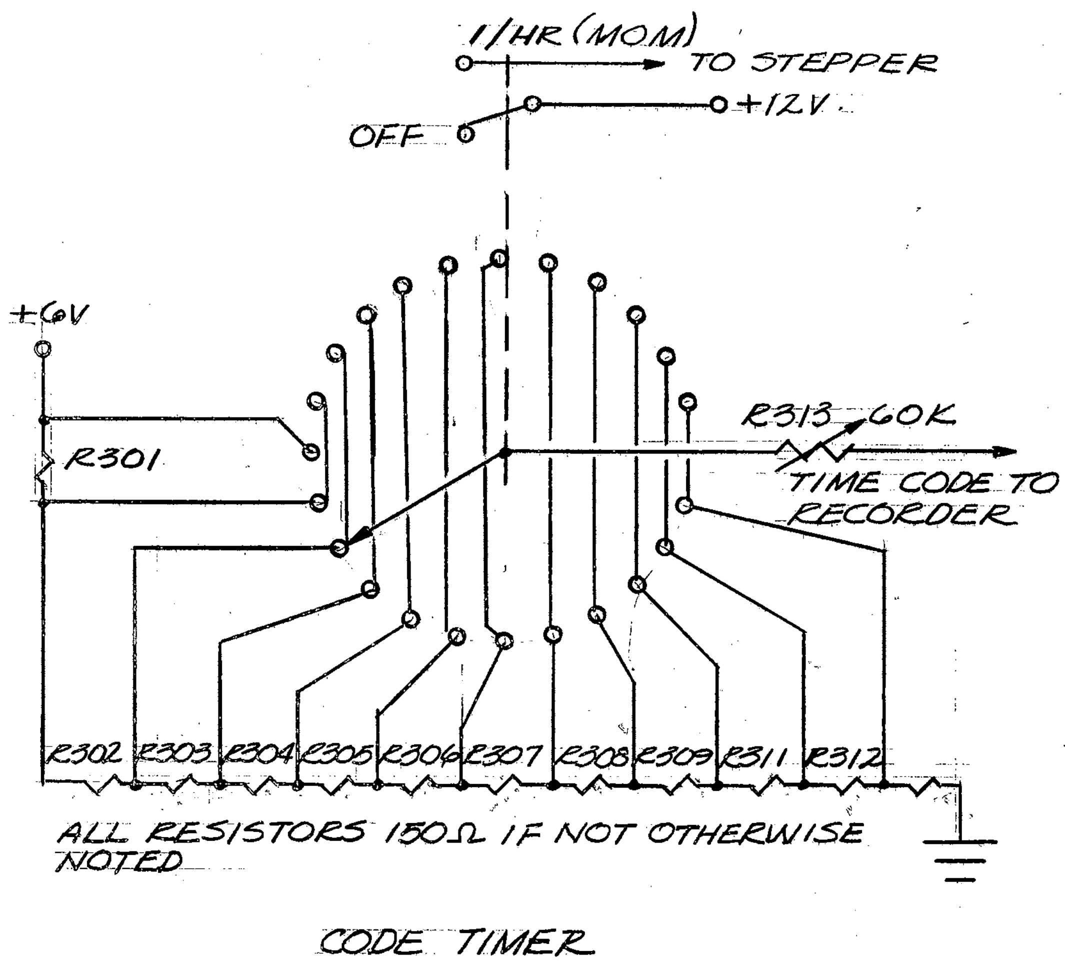


Figure 3-9

The principle considerations in the design of the temperature gage were reliability and simplicity. The circuit decided upon, as shown in Figure 3-10, was a simple voltage divider incorporating a resistive element with a high temperature coefficient.

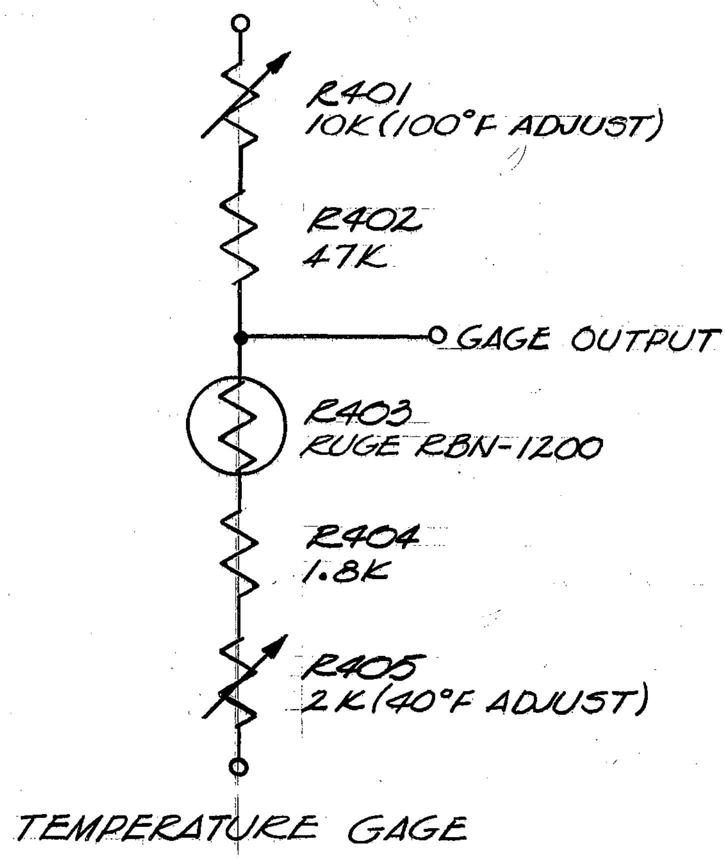


Figure 3-10

In summarizing Chapter III, the author wishes to point out that the logical design and organization of the complete system has been discussed in detail. An attempt has been made to justify in the reader's mind every phase of the design and to present a firm basis for each design decision.

REFERENCES

[11] John Kanwisher, "Polarographic Oxygen Electrode," _Limnology and Oceanography_, IV No. 2, (April 1959), pp. 210-217.

CHAPTER IV

FINAL DESIGN OF THE SYSTEM

Again, correlating the thesis subject to a generalized system design effort, one should consider that there are at least two legitimate approaches to the design of any system. One requires a standard array of functionally independent building blocks to be designed by the engineer and fitted together to form a compatible system. In the second approach, the system designer works out a specific system design using interconnected black boxes which eventually must be filled with suitable components and devices so as to satisfy the system requirements. Common characteristics of both methods are that the building blocks must be compatible to one another so that when assembled, there will not be any abrupt functional discontinuities apparent in the system, and the fact that normally the production engineer is not consulted until it is too late to make any changes in the design which will facilitate manufacture.

The approach used by the author was the latter of the two methods. With the design requirements and specifications in mind, a system was worked out using black boxes which would satisfy these requirements. In the preceding chapter, preliminary decisions were made regarding the make-up of these building blocks. These decisions must now be finalized, and particular components and devices must be chosen which will perform the required functions and insure that compatibility has been maintained.

Because of the interrelationship among the various components, a logical approach to the selection of a power supply must be used to insure intrasystem compatibility.

It was felt that the recorder was the least flexible insofar as the availability of a suitable recorder with a useable drive motor voltage requirement. The recorder selected was a miniaturized automatic chart recorder, the Rustrak Mac, manufactured by the Rustrak Instrument Company. This recorder is ideally suited for the system and has the following characteristics:

1) Response time - maximum, 1 second
2) Compact size
3) Galvanometer sensitivity - as low as 100 microampers dc
4) Chart speed - 15 inches per hour available
5) Drive motor - 6 volt dc motor available
6) Power requirement - 3.7 amperes at 6 volts.

The selection of the data switch is also an important consideration with respect to the power supply. A rotary switch manufactured by E. Shrack Company provides all functions required of this component. The stepper coil requires 12 volts to energize and draws 0.33 amperes. The rotary portion of the switch provides four wafers of twelve positions each. In addition, there are three SPDT switches which are controlled by a cam. These lend themselves to the power supply switching function, since they switch only after one complete cycle of the stepper coil.

With the two requirements mentioned above, the power supply must supply ± 12 volts and +6 volts. In addition, it must be remembered that the oxygen electrodes require a negative potential of -0.7 volts. No mention has been made of the requirements of the differential amplifier because the ± 12 volt taps of the battery pack are sufficient for transistor bias.

With the necessary voltages as listed, the current requirements of the system must be determined in order to assure that batteries of sufficient storage capacity are used. From these calculations, it is seen that the system requires approximately two-ampere hours of storage capacity for 24 hours of service. A five-ampere hour battery pack, then, will power the system for the prescribed 48 hour period with a 20% safety factor. There are several types of wet cell batteries which have the required storage capacity and conform to the size and weight restrictions which were specified previously. The nickel-cadmium sintered plate storage batteries manufactured by Gould-National Batteries Corporation are relatively inexpensive and have a reputation of good reliability. These cells have a nominal voltage of 1.25 volts per cell. The battery pack, then, is composed of 21 ACT Nicad batteries, tapped at the appropriate voltages.

The designer of a transistor amplifier must have a usable knowledge of basic semiconductor definitions, transistor operating theory, biasing techniques, parameter variations, and the methods of predicting gain and circuit impedances. In addition, he must know the specifications for the particular circuit to be designed. For most practical designs, information of the following types is necessary:

1) Desired gain
2) Input and output signal levels
3) Input impedance
4) Operating temperature range
5) Load and source characteristics
6) Available supply potentials
7) Cost weight and size requirements.

After collection of the pertinent requirements, the design may be initiated.

All of the above requirements with the exception of the first, fifth, and sixth have been specified in previous chapters. With the decisions regarding the power supply and the recorder, all information needed to design the amplifier is at hand. With the circuit as specified in the previous chapter, it remains to choose the transistor types and determine the values of the various components.

As mentioned before, the differential pair transistors must have the following characteristics:

1) Low saturation currents
2) Close to h_{FE} tracking
3) Close to V_{BE} tracking.

Recent significant advances in transistor technology by which junction surfaces are passivated (e.g. Fairchild 2N1613) have resulted in V_{BE} tracking between two transistors superior by an order of magnitude over previously available devices. Further, these transistors are available in pairs which are matched for both V_{BE} and h_{FE} tracking. Since the saturation current (I_{CBO}) of these transistors is very low, (0.001 microamphere) they are ideally suited to be used as the first stage differential transistors. As was pointed out in the proceeding chapter, the final stage differential transistors are much less critical with respect to parameter changes than are the first stage transistors. The Fairchild 2N861 transistor is also available in matched pairs, and it is PNP type device. It satisfies the complementary symmetry requirement for succeeding stages. The choice of a transistor for the emitter current source (actually a current sink, since the 2N1613 is a NPN type) is not as critical as that for the other transistors. A General Electric 2N338 was chosen for this application. This is a NPN type silicon transistor.

For best results, the corresponding resistors in each half of the amplifier should be matched as closely as possible. With this in mind, Ohimite $\frac{1}{4}$ watt resistors with a 1% tolerance were selected. The theoretical calculations necessary for the design of the amplifier are shown in Appendix A as are the calculations for all the circuits used.

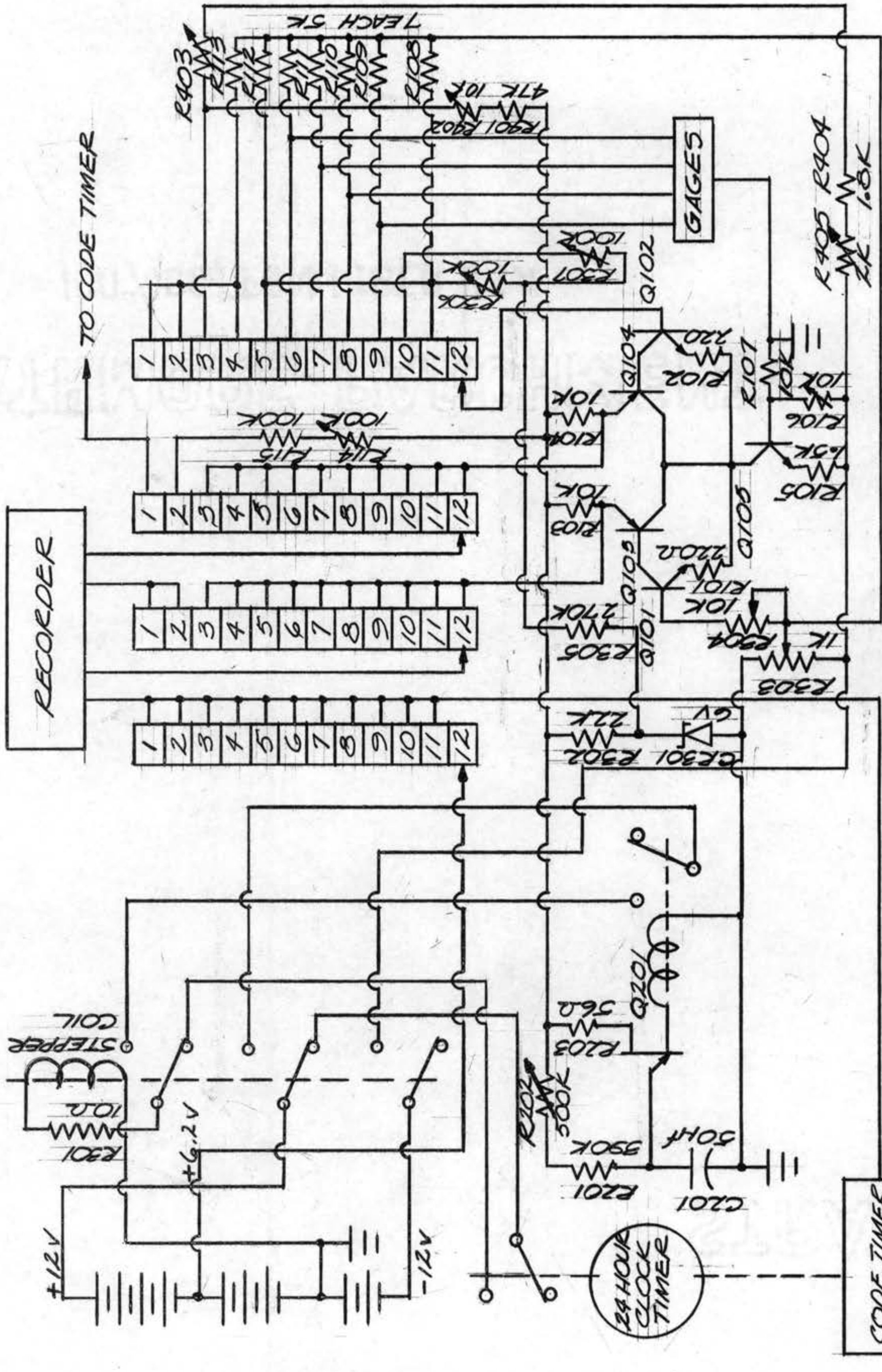
The relay used in the code timing circuit must have fast operating times, low coil resistance, and low operating power. These requirements are imposed because the unijunction transistor is a high speed, low power switching device. The relay selected was a Potter and Brumfield SC11DB. This relay is used as a DPDT switch with one set of contacts holding the relay closed and a second set for the control function. With a recorder chart drive speed of 15 inches per hour, the code timer was designed to switch three times per minute. This is to allow the electrodes to reach full output before recording their signals. With the selected value of C201 equal to 50 mf, the required resistance is approximately 400K-OHM. With R201 equal to 390K-OHM, R202 is used as a fine time constant adjustment.

The full scale and half scale calibration circuit is a simple voltage divider. A Texas Instruments 653C3 6.8 volt Zener diode was used to maintain a constant reference voltage. This procedure was followed to prevent changes in battery voltage from affecting the calibration current.

An attempt was made to standardize components as much as possible on the grounds that procuring, stocking, and testing would be greatly simplified. The fixed resistors chosen were Ohmite $\frac{1}{4}$ watt Little Red Devils in tolerances of $\pm 1\%$, $\pm 5\%$, and $\pm 10\%$, depending upon the application. These resistors are available in all RETMA values and have a good history of reliability. All variable resistors are Bourns Trimpots.

All components, with the exception of the station timer, were mounted on a $3\frac{1}{2}$" x $3\frac{1}{2}$" x 3/32" phenolic board. Although much simplification would result in the use of a printed circuit board, the use of such a board was not feasible in the prototype model. The station timer was mounted in a can approximately 3" in diameter and 4" in height. The battery pack was mounted in trays supplied by the battery manufacturer.

Briefly summarizing Chapter IV, the basis for the design of all circuitry, and the choosing of all components and devices used in the systems have been discussed with an effort to reveal the author's thinking in the area. A complete schematic of the system, as it has now evolved, is shown in Figure 4-1.



SCHEMATIC
FIGURE 4-1

CHAPTER V

SUMMARY AND CONCLUSION

The primary object of this thesis was to present the philosophy, procedures, and methods used in arriving at a logical solution to a unique problem in system design. Actually, the basic problem involved both system and design engineering in that it was necessary to design and implement a suitable amplifier and also to integrate the components into a compatible system which fulfilled all system requirements. The design was treated in a logical manner in that the development of the system was described sequentially, chapter by chapter, as it evolved from an idea to hardware.

Although a network of several stations was never implemented, laboratory experiments with the prototype indicate that this is feasible with the system as it has been developed.

The intrasystem compatibility and the success of the prototype tends to support the procedures, approaches taken, and decisions made by the author during the development of the system. This system was unique only in the particular function performed and the design limitations placed upon it. Thus, the author believes that the systematic procedures outlined and used are applicable to a wide range of system design problems.

Based on experience, both prior to and as a result of compiling the material for this thesis, the author has concluded that the classroom training of an engineer must be supplemented by common sense, unbiased thought, and experience.

A SELECTED BIBLIOGRAPHY

Armed Services Technical Information Agency. _Polarography,_ by Gerald C. Whitnack, AD No. 257562, Technical Article 11.

Carritt, Dayton E. and John W. Kanwisher. "An Electrode System for Measuring Dissolved Oxygen," Analytical Chemistry. XXXI (Jan., 1959).

Clark, L. C. Jr. et al. "Continuous Recording of Blood Oxygen Tension in Animal Tissues," _J. of Applied Physiol._ VI (1953).

Davies, P. W. and F. Brink. "Microelectrodes for Measuring Local Oxygen Tension in Animal Tissues," _Rev. Sci. Instr._ XIII (1942).

DeMatteis, W. M. and J. W. Halligan. "Designing Transistorized Differential Amplifiers," _Electronic Design._ (August 2, 1962).

Fairchild Semiconductor Corporation. _The Design of High-Stability DC Amplifiers,_ by Paul J. Beneteau, APP-23.

______. _A New Transistorized Differential Amplifier,_ by David F. Hilbiber, TP-16.

Føyn E. _Rept. Norwegian Fish Market Invest._ XI (1955).

Giguere, P. A. and Louis Lauzier. "Le Dosage Polarographique De L'Oxygéne Dissous Dans L'Eau De Mer," _Can. J. Research._ B 23-24 (1945).

Hurley, Richard B. _Junction Transistor Electronics._ New York: John Wiley and Sons, Inc. (1958).

Kanwisher, John. "Polarographic Oxygen Electrode," _Limnology and Oceanography._ IV No. 2 (April, 1959).

Matzen, W. T. and J. R. Biard. "Differential Amplifier Features DC Stability," _Electronics._ (Jan. 16, 1959).

Middlebrook and Mead. "Transistor AC and DC Amplifiers with High Input Impedance," _Semiconductor Products._ (March, 1959).

Muller, O. H. "Polarographic Study with a Microelectrode Past Which an Electrolyte is Flowing," J. Am. Chem. Soc. LXIX (1947).

Okada, R. H. "Stable Transistor Wideband DC Amplifiers," AIEE Electronics and Communications. (March, 1960).

Olson, R. A., F. S. Brackett, and R. G. Crickand. "Oxygen Tension Measurement by a Method of Time Selection Using the Static Platinum Electrode with Alternating Potential," J. Gen. Physiol. XXXII (1949).

Pritchard and Carpenter to Kanwisher. Quoted in John Kanwisher "Polarographic Oxygen Electrode," Limnology and Oceanography. IV No. 2 (April, 1959)

RCA Review. Stabilization of Wideband Direct Current Amplifiers for Zero Gain, by Goldberg. (June, 1950).

Reeves, R. B. and D. W. Rennie. Federation Proc. XVI (1957).

Slaughter. "The Emitter-Coupled Amplifier," Wescon Proc. (1954).

Williams, S., Tarpley, and Clark. "DC Amplifier Stabilized for Zero Gain," AIEE Transactions. LXVII (1948).

Worthington, L. V. Deep-Sea Research. I (1954).

APPENDIX A

COMMON BASE CURRENT SOURCE

References:

1. The Design of High Stability DC Amplifiers by Bénéteau
2. Designing Transistorized Differential Amplifiers by De Matteis and Halligan
3. Junction Transistor Electronics by Hurley

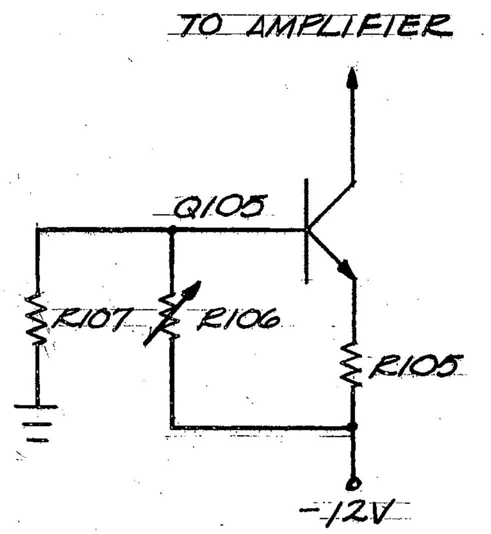


Fig. A-1. Current Source Configuration

$V_{EE} = -12$ v $\qquad I_C = 2$ ma $\qquad Q_5 = 2N338$

The emitter current may be determined from the equation:

$$I_C = \alpha I_E + I_{CBO}$$

$$\text{or} \quad I_E = \frac{I_C}{\alpha}.$$

The saturation current term is neglected because of its small magnitude. Since h_{FE} rather than h_{FB} is specified, the expression must be altered to the following form.

$$I_E = \frac{(h_{FE} + 1)}{h_{FE}} I_C$$

The value of B is found from manufacture's specifications and has a value of 65 at 25° C. with I_C equal to 2 ma and V_{CE} equal to 5 volts.

$$I_E = \frac{66}{65} (2 \text{ ma}) = 2.032 \text{ ma}$$

The base current is determined from the equation:

$$I_E = I_C + I_B$$

$$\text{or } I_B = I_E - I_C.$$

Substituting the value of I_C and I_E, we have:

$$I_B = .032 \text{ ma}.$$

To prevent cutoff of the differential transistors, the emitters must be at a negative potential of about 4 volts. The V_{CE} drop was assumed to be 5 volts as a first approximation. Thus, the $I_E R105$ drop is approximately

$$I_E R_3 \simeq -V_{EE} + V_{CE} + 4 \text{ volts}$$

$$\simeq 3 \text{ volts}$$

Then:

$$R105 = \frac{3 \text{ volts}}{2.032 \text{ ma}}$$

$$= 1.42 \text{ K}$$

Selecting the nearest RETMA size resistor

$$R105 = 1.5 \text{ K}.$$

With the operating conditions as outlined, V_{BE} is found to be approximately 0.6 volts. The base voltage may be expressed as:

$$V_B = -V_{EE} + I_E R105 + V_{BE}$$

$$= -12\,v + 3.048\,v + 0.6\,v$$

$$= -8.352\,v$$

For stabilization purposes, choose

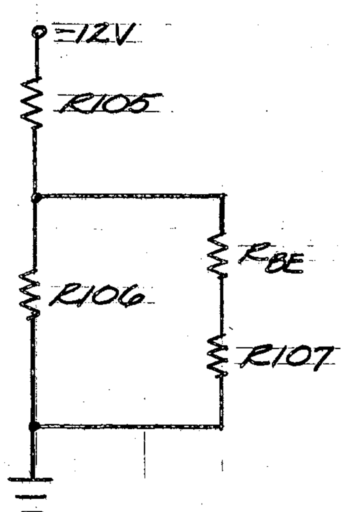
R107 = 10K

Then:

$$I_{(R107)} = \frac{V_B}{R107}$$

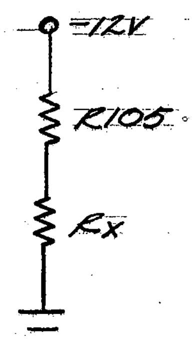
$$= 0.835\ \text{ma.}$$

The bias network with the shunt regulator may be depicted by the resistor network, as shown below.



RESISTOR NETWORK

Fig. A-2.



EQUIVALENT NETWORK

Fig. A-3.

The unknown resistance R_2 may be found as follows. The equivalent resistance R_X in Figure A-3 is equal to

$$R_X = \frac{-V_{BE} + V_B}{IR105}$$

$$= 4.36 \text{ K}$$

The equivalent resistance may be written:

$$\frac{1}{R_X} = \frac{1}{R105 + R_{BE}} + \frac{1}{R106}$$

or

$$R106 = \frac{R_X(R105 + R_{BE})}{(R105 + R_{BE}) - R_X}.$$

To determine R_2, it is first necessary to compute the value of R_{BE}.

$$R_{BE} = \frac{V_{BE}}{\underline{+}B}$$

$$R_{BE} = 15 \text{ K}$$

Whence:

$$R106 = \frac{(4.36K)\ (16.5K)}{16.5K - 4.36K}$$

$$R106 = 5.92 \text{ K}$$

Choose R_2 to be a 10K potentiometer, and thus the design of the current sink is completed.

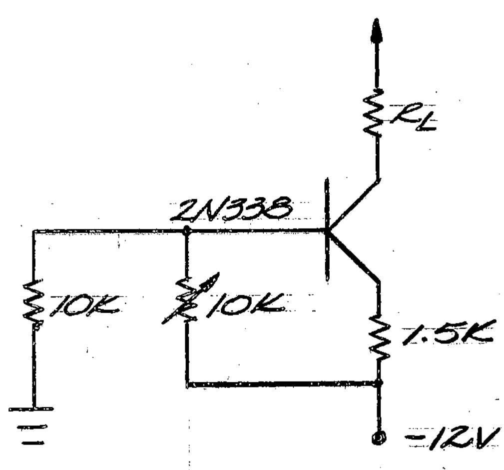


Fig. A-4. Final Current Sink Circuit With Component Values

Amplifier Circuit

References:

1. A New Transistor Differential Amplifier by Hilbiber
2. Designing Transistorized Differential Amplifiers by De Matteis and Halligan
3. The Design of High-Stability DC Amplifiers by Bénéteau
4. Transistor AC and DC Amplifiers With High Input Impedance by Middlebrook and Mead

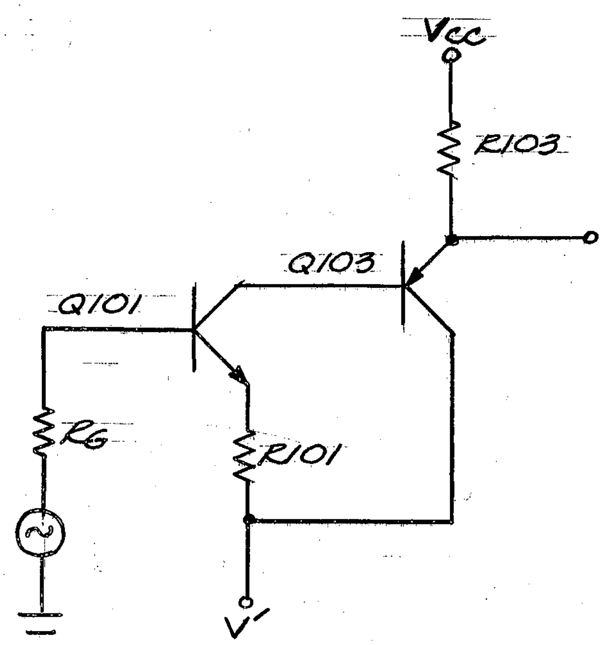


Fig. A-5. One Half of the Differential Amplifier

The simplest way to design the amplifier is to first consider one pair only. With V' approximately -3 volts, a load resistor was chosen which would allow V_{CE} to be 10 volts.

$$R103 = \frac{V_{CC} - V_{CE} - V'}{I_C}$$

$$R103 = \frac{5\ v}{500\ ua}$$

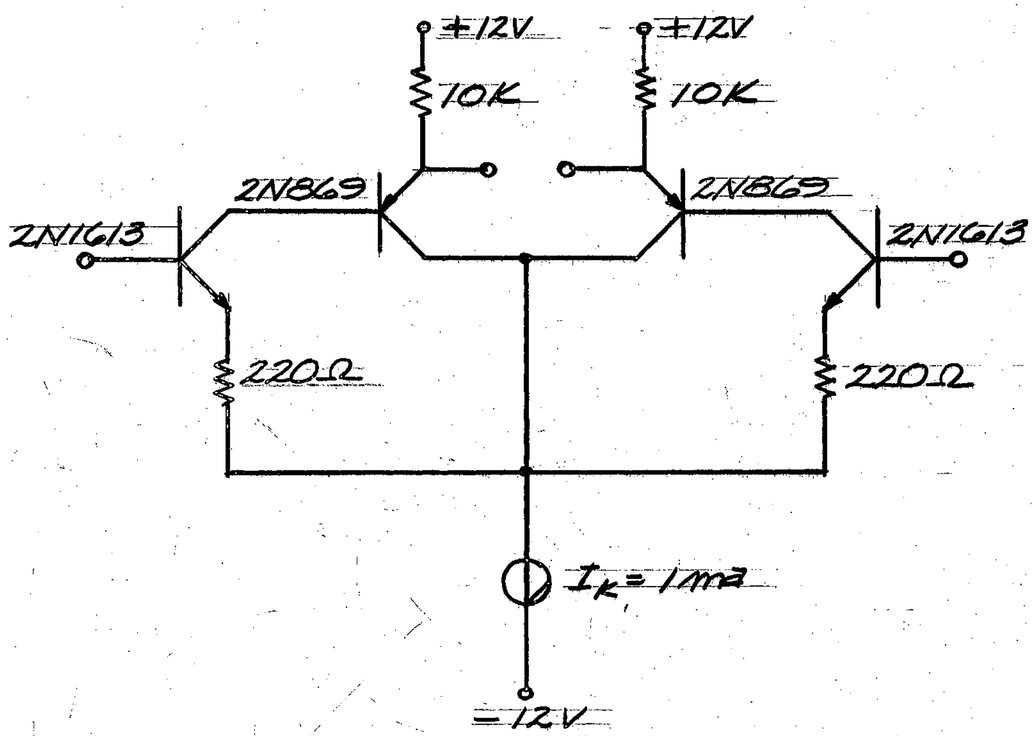
$$R103 = 10\ K$$

It may be shown that the optimum value of R_E is given by the equation[1]

Ref. (1):

$$R101 = \frac{h_{ie}}{h_{oe}\ h_{fe}\ R_L}$$

$$R101 = 220\ \Omega$$



COMPLETE AMPLIFIER

Fig. A-6

The input impedance of the amplifier is given by

$$Zin = \frac{h_{ie}\ h_{fe}\ R_E + \Delta^{he}\ R_L}{1 + h_{oe}\ R_L}$$

where the h parameters are a combination of the complementary pair transistors. These may be shown to be approximately[1]

Ref. (1):

$$h_{ie} = h_{ie_1}$$

$$h_{fe} = -h_{fe_1}\ h_{fe_2}$$

$$h_{re} = h_{re_1}\ \ h_{re_2}$$

$$h_{oe} = h_{oe_2}.$$

Substituting, the input impedance is found to be

$$Zin \simeq 500\ K$$

Referring to Figure A-5, the current gain is given by

$$A_i = \frac{I_{E2}}{I_{B1}}$$

$$= \frac{h_{FE_1}\ h_{FE_2}\ I_{B_1} + h_{FE_1}\ I_{B_1}}{I_{B_1}}$$

$$= \frac{I_{B_1}\ h_{FE_1}\ (h_{FE_2} + 1)}{I_{B_1}}$$

$$= h_{FE_1}\ (h_{FE_2} + 1)$$

$$\simeq 500$$

VITA

Benny L. Pierce

Candidate for the Degree of

Master of Science

Thesis: A POLAROGRAPHIC OXYGEN ELECTRODE FOR THE MEASUREMENT AND RECORDING OF OXYGEN DENSITY IN FRESH WATER

Major Field: General Engineering

Biographical:

Personal Data: Born in Pittsburg, Kansas, December 16, 1935, the son of Bennie G. and Ruth K. Pierce.

Education: Attended grade school and high school in Bartlesville, Oklahoma; graduated from College High School in 1953; received a Bachelor of Science degree from Central State College, with a double major in Math and Physics in May, 1960; completed course work for the Master of Science degree in May, 1963.

Professional Experience: Entered the United States Air Force in 1957 and have completed six years in the ready reserve as an electronics technician; Student Instructor, Department of Physics, Central State College; Electronics technician and draftsman for the Electronics Lab of the Oklahoma State University Research Foundation; Senior Research Engineer in Research and Development for Electra Manufacturing Company.