I. CHARACTERIZATION OF THE ANODICALLY FORMED OXIDE FILM ON PLATINUM ELECTRODES

II. DEVELOPMENT OF ELECTROCHEMICAL INSTRUMENTATION

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This thesis is dedicated to my wife, Evi,
without whose support and encouragement
nothing would have been possible.

Preface

A number of persons have contributed materially to the contents of this dissertation. The guidance and direction of Professor Fred C. Anson and Dr. Robert A. Osteryoung were invaluable and vital. The help and advice of my colleagues, Joseph H. Christie, Arthur T. Hubbard, Janet G. Jones, and Peter J. Lingane contributed to any success that can be claimed.

I am indebted to the management of the Science Center of North American Aviation, Inc. for the financial support they so generously gave during my graduate tenure, in addition to making their facilities available for a portion of the research. Thanks are also due to the U.S. Army Research Office (Durham), the Alfred P. Sloan Foundation, and the National Science Foundation, who provided the funds necessary to build the instrumentation.

ABSTRACT

The oxygen containing film formed at anodically polarized platinum electrodes in oxyacid solutions has been characterized. By making use of a thin layer electrode it is shown that the film is composed of Pt(II) and Pt(IV) oxides. This was proven by oxidizing the electrodes, and then stripping the oxides with acidic chloride solution and then analyzing, coulometrically, the platinum chlorides in solution. It is shown that the discrepancy between anodic charge passed during oxidation and the cathodic charge passed during reduction is due to Pt(IV) oxide which is not reducible at potentials anodic of the hydrogen evolution reaction.

The oxides decompose slowly in formal sulfuric acid to form hydrogen peroxide and platinum; elevated temperatures accelerate the decomposition. A correlation is drawn between the presence of Pt(IV) on the surface of the electrode and "activation" of the electrode. It is concluded that the cause of activation is irreducible oxide.

A standard electrode free of oxides can be obtained by immersion in

1 F H_2SO_4 at 100° C. It is proposed that such pretreatment is an excellent point of departure for further investigations with platinum electrodes.

It is shown that ozone is evolved in sulfuric and perchloric acids at potentials more positive than 1.3 volts with respect to the saturated calomel electrode. The evolved ozone is reduced at 1.1 volts.

In the second portion the use of operational amplifiers in electrochemical control and measurement instrumentation is discussed, and the simplified theory is presented. The design and construction of a multi-purpose electrochemical control instrument is discussed and a complete set of construction instructions is given. The last section considers the use of a small general purpose digital computer as an on-line digital data acquisition instrument. The interfacing and the logical circuitry required to perform electrochemical experiments with such a computer are described.

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CHAPTER 1

Introduction

Platinum has been used as an "inert" electrode material for electrochemical and analytical studies for many years. That platinum is not truly inert and, in fact, is relatively easily oxidized, has also been long recognized by at least a few workers (1,2,3). The nature of the surface of an oxidized platinum electrode has been an issue of controversy since Bowden, in 1929, concluded from his initial use of impulse methods in electrochemistry that PtO is formed on the surface (4). Armstrong, Himsworth, and Butler (5), disputed this conclusion, maintaining that the film was adsorbed oxygen on the surface of the platinum. Both hypotheses have since been vigorously defended. Although there is general agreement that oxidation of platinum in aqueous solution forms an oxygen containing film on the surface of the electrode, its nature, stoichiometry, and general behaviour are still the source of much disagreement.

The problem is not trivial, and understanding of the nature of the electrode processes at solid electrodes requires a knowledge of the reactions which the electrode itself can undergo. In addition the mounting interest in fuel cells, especially oxygen fuel cells, has stimulated interest since platinum is the most likely material for a reversible oxygen electrode.

A complete historical review of the problem will not be attempted here. The primary points of contention are:

a) Whether the oxygen containing film is a stoichoimetric compound or an adsorbed layer of oxygen, and,

b) if a true oxide is formed, whether one, two, or three oxidation states of platinum are formed.

There has also been disagreement about the experimental observations on which these various hypothesis rest. The major points of disagreement include:

1) Some workers have found that the amount of charge required to form the film is invariably greater than the amount required to reduce the film; others deny this assertion. No clear evidence of the cause

of this discrepancy has been brought forth.

2) The platinum electrode in dilute oxyacid solutions is depolarized at potentials which are not sufficiently anodic to cause visible oxygen evolution. The nature of the depolarization, and its reality, is in doubt.

3) The platinum electrode is well poised in a number of redox systems only if it is first "activated" The activation procedure consists of first oxidizing the electrode and then reducing it. The electrode loses its "activity" upon standing in the solution at a rate that appears to depend on a number of parameters. The nature of the activation has been speculated upon by many, however, there appears to be little direct evidence concerning the mechanism of activation.

4) Although elaborate attempts have been made to achieve some "standard" platinum electrode state, none seems to have had even partial success.

Stoichiometry - The question of whether the film is adsorbed oxygen is of prime importance in fuel cell technology. An adsorbed oxygen intermediate would be capable of interacting with "fuels" and any oxidation mechanism would have to take this into account. On the other hand if the film is an electronically conductive oxide of platinum one could consider the surface only as being somewhat different from the pure metal, but not sufficiently different as to affect materially the charge transfer reaction. Another possibility is that the oxide facilitates electron transfer with certain species by making available oxygen charge-transfer "bridges" such as have been postulated for halides on mercury electrodes.

The evidence for adsorbed oxygen depends most strongly on double layer capacitance measurements (6) and rate data for the oxygen evolution reaction(7). The oxide theory rests primarily on a report of direct chemical evidence for oxidized platinum by Anson and Lingane (8). However, this work has been attacked as a basis for the claim of direct evidence (9). Additional evidence for oxide formation stems from oscillopolarography with platinum electrodes in formal sulfuric acid. The oscillopolarograms show various "bumps" on the anodic cycle; these "bumps" occur at potentials which some investigators have correlated with the thermodynamic potentials for various platinum oxides. However, such correlations are tenuous; the thermodynamic data are uncertain at best, (14), and probably wrong in at least a few cases. It is also very foolhardy to attempt a correlation of data obtained under non-equilibrium conditions with thermodynamic data unless supported by very convincing additional evidence; (rate data, analysis of compounds formed, etc.); such evidence is lacking in the present case.

Charge Balance - The discrepancy between anodic and cathodic charge is disturbing, since it appears to violate conservation laws. Of the various rationalizations for the phenomenon which have been offered since Vetter and Berndt (13) first brought attention to it, the following are still in vogue among some workers in the field.

a) Oxygen evolution has low overpotential on a freshly reduced surface; when the electrode is brought to the oxidizing potential by an externally applied voltage, the initial current is divided between oxygen evolution and oxide film formation. As the film covers the surface, the oxygen evolution reaction becomes more and more irreversible, and its rate diminishes towards zero. Most of the evolved oxygen diffuses away from the electrode so that on the subsequent reduction only the oxide film is reduced. Thus the recorded charges differ.

b) More than one layer of oxide is formed. The layer closest to the bulk metal becomes "dermasorbed" (11), and is not capable of being reduced on the subsequent reduction. The dermasorption is considered to be a diffusion phenomenon wherein the oxide diffuses "under" a few monolayers of platinum metal and thus cannot be reduced on the subsequent reduction cycle.

c) At least two oxidation states of platinum are formed when the electrode potential is made sufficiently anodic; of the two only one is reducible at potentials anodic of hydrogen evolution. The other remains on the electrode surface for long periods of time.

d) Two reduction paths are operative when the film is reduced.

$$\mathrm{PtO} + 2\mathrm{H}^+ + 2e^- \longrightarrow \mathrm{Pt} + \mathrm{H_2O} \qquad (1\text{-}1)$$

$$2\mathrm{PtO} + 2\mathrm{H}^+ + 2e^- \longrightarrow \mathrm{Pt} + \mathrm{H_2O_2} \qquad (1\text{-}2)$$

Path 1-1 would give $Q_a = Q_c$ (Q_a being the charge passed during oxidation and Q_c being the corresponding charge passed on the reduction cycle); path 1-2 would give $Q_a = 2Q_c$. A combination of these reactions would give a value of Q_a/Q_c between one and two, as has been found by most investigators.

e) Organic impurities adsorb on the electrode when it is in a reduced state. When the potential is made more anodic, these adsorbed impurities are irreversibly oxidized before the film is formed. The difference between Q_a and Q_c is simply the charge consumed in the oxidation of the adsorbed organic impurities.

<u>Depolarization</u> - A number of workers (11,5) have observed that a very small, but finite, depolarization current flows when the electrode is oxidized and held at a suitable potential (e.g. 1.2 volts) quite cathodic of the potential where massive, (observable) oxygen evolution occurs which is at about 1.5 volts. This current has been rationalized

as an oxygen evolution current which, thermodynamically, would have finite value at 1.2 volts. Another hypothesis suggests that the depolarization is due to oxide from the surface diffusing into the bulk metal along the grain boundaries. This diffusion into the bulk vacates sites on the surface where further oxidation can then take place. Oxidation of solution impurities at the anodic potentials has also been proposed (12), as an explanation of this depolarization. This explanation cannot be accepted as a reasonable hypothesis. It is very unlikely that all workers who have observed this effect would have had impure solutions.

Activation - Although there is no consensus, activation of platinum electrodes normally means that the electrode is oxidized and then reduced in formal sulfuric or perchloric adic. Activation appears to be essential to obtain reversible behaviour of the electrode in systems such as Fe(II)/Fe(III) in sulfate media. After a relatively short time (on the order of 15 minutes) in the test solution the electrode usually requires reactivation.

Two hypotheses concerning the nature of the "activated" state are in vogue. The first considers the activation as due only to surface roughening of the platinum by the oxidation and subsequent reduction. The primary evidence for this theory is the fact that the surface of a shiny electrode can be "platinized" by repeated cycling between the anodic and cathodic potential limits. One series of investigations showed that the apparent adsorption of electroactive species per unit area increased with the number of anodic and cathodic cycles to which the electrode had been subjected.

The other hypothesis argues that freshly reduced sites on the platinum surface have catalytic activity which is slowly lost by adsorption of impurities onto the surface sites. These impurities are oxidized and/or desorbed when the electrode potential is made sufficiently anodic to oxidize the surface.

Standard Electrode - Some arbitrary "standard" state of the platinum electrode is necessary if workers in different laboratories are to compare and correlate results. One obtains the impression that much work has been dismissed as "worthless" because the original worker did not treat his electrodes in some ritualistic fashion which a later author has deemed necessary (15). All the electrode treatments appear to have been chosen either arbitrarily or because the data obtained after such treatment agreed with a pet theory or conviction.

Research Goal - The primary goal of the work described in Part I of this dissertation was to obtain some concept of the nature of the surface oxide and to attempt to reconcile some of the major argument and controversies in the field. Unfortunately in most cases a qualitative picture of the mechanisms involved was the best that could be obtained.

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CHAPTER 2

Experimental

Reagent grade chemicals were used without further purification. Solutions were made with triply distilled water. Purified argon or nitrogen was used to deaerate the solutions.

Except for the experiments done with thin layer electrodes, standard platinum button electrodes (Beckman Instruments, Inc., Fullerton, California) were used. At various stages of the work the qualitative behaviour of these electrodes was compared to a platinum electrode prepared by spot welding a Pt wire to a 0.005 in. thick Pt sheet of approximately 0.5 cm^2 area. No difference in behaviour was ever observed. The button electrode was favored as the exposed area is constant within 10% from electrode to electrode; these electrodes are also very convenient to use with the electrolysis cells available.

Saturated calomel reference electrodes were used and all voltages are referred to this electrode. Initially a Beckman reference electrode with asbestos fiber salt bridge was utilized; however, during the latter portions of the work the Sargent reference electrode with ceramic frit salt bridge became available and this was then used. The latter electrode is superior owing to its lower and reproducible leak rate (3 microliters per hour) and its reproducible and low resistance (1000 ohms).

Various electrolysis cells were used throughout the work. In all cases the reference and counter electrodes were isolated by medium porosity frits in separate compartments from the indicator electrode. In much of the work no temperature regulation was used. In the work at elevated temperatures a water bath was used to circulate the hot water to a jacketed electrolysis cell; regulation in the cell for these experiments was ± 1^{o}C.

The thin layer electrode is shown in Figure 2-1 and is similar to that described by Hubbard and Anson (1). The primary difference was that a micrometer with a removable stationary anvil was used. This anvil was ground down 1/8" in diameter and a nylon tube was slipped over the region where it is attached to the micrometer. Further the

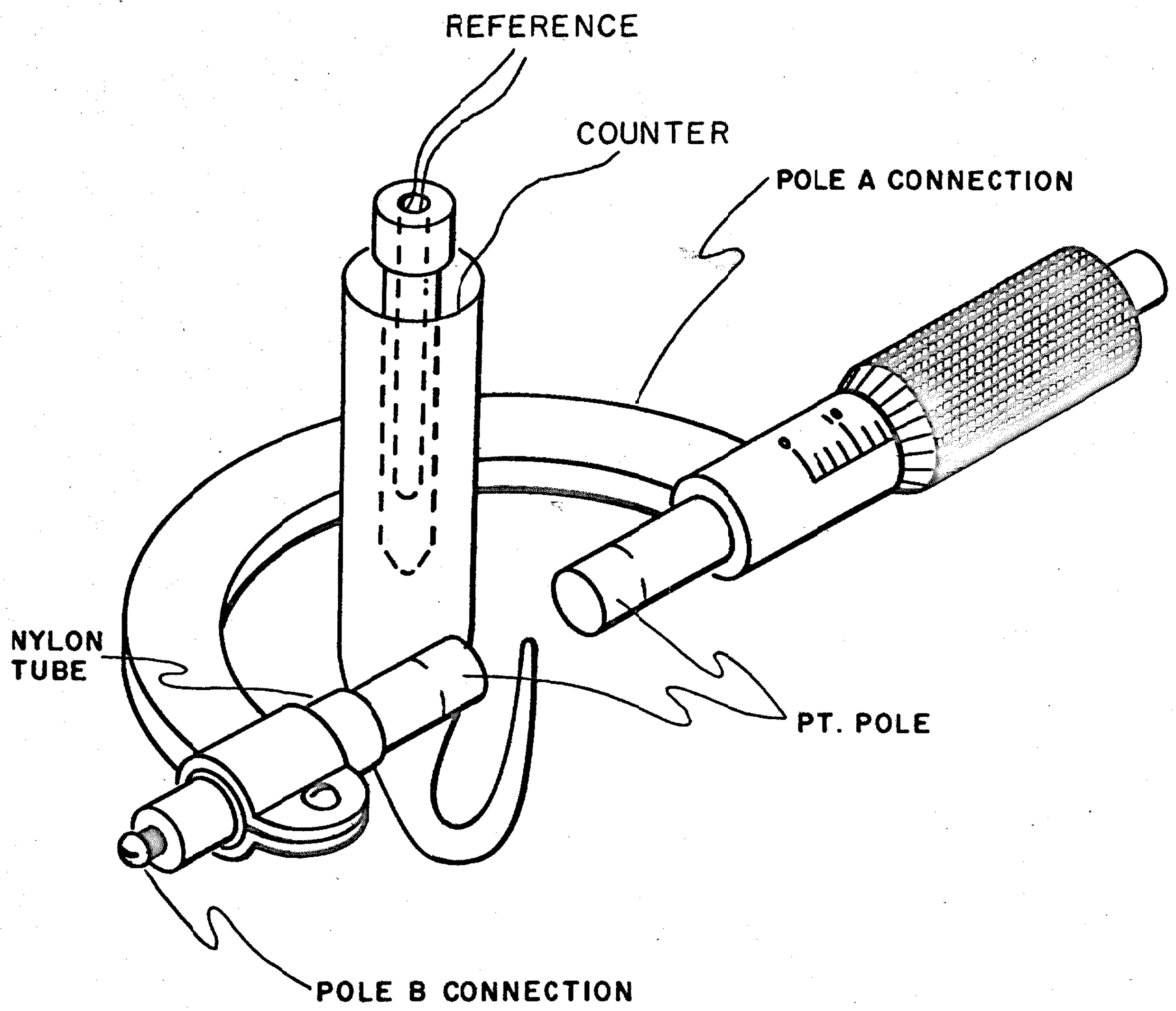

Fig 2-1. Thin layer electrode

platinum pole pieces were press-fit onto the anvils rather than using the Teflon bushings previously described. In this way contact to the poles was made much more convenient and the two poles were electrically isolated. The effective resistance between the micrometer body and the movable anvil was less than one ohm and between the two poles it was greater than one hundred megohms. After mounting, the two anvils were lapped with wet rosin to a mirror finish. The coplanarity of the two platinum poles was within one micron from one side to the other; the absolute flatness was not as critical as it was for Hubbard and Anson in proving the usefulness of thin layer electrochemistry.

Connection to the reference and counter electrodes was made by a thin capillary attached to a half inch tube in which the electrodes were placed (see Figure 2-1). The capillary, effectively a salt bridge, was positioned under the poles. The electrolyte was poured into the tube, squirting out the capillary into a vessel below. The platinum faces were washed by allowing the squirting electrolyte to impinge on them. The reference electrode and counter electrode (normally a 20 gauge platinum wire) were then inserted. After the electrolyte level in the capillary and the tube become equal, a drop of fluid always remains on the tip. The pole pieces were closed to form the gap which was then touched to the drop, causing the gap to fill by capillary action. Connection to the poles was made by clamping large alligator clips onto the body and onto the exposed screw at the end of the stationary anvil. This arrangement allows the electrode assembly to be used in a glove box or bag with comparative ease.

A useful furnace was developed for high temperature experiments with the thin layer electrode. This furnace is shown in Figure 2-2. The inner winding consisted of 1/8" copper tubing wound around a 1/2" mandrel. After winding, the tubing was varnished and baked. One layer of wet asbestos paper was laid over the copper. Eighteen gauge chromel wire was then wound as uniformly as possible over the asbestos, and the whole assembly was swathed with wet asbestos sheet and dried at 475°C. Swagelock fittings were attached at the ends of the copper tubing and these were connected to cooling water. Current which passed through

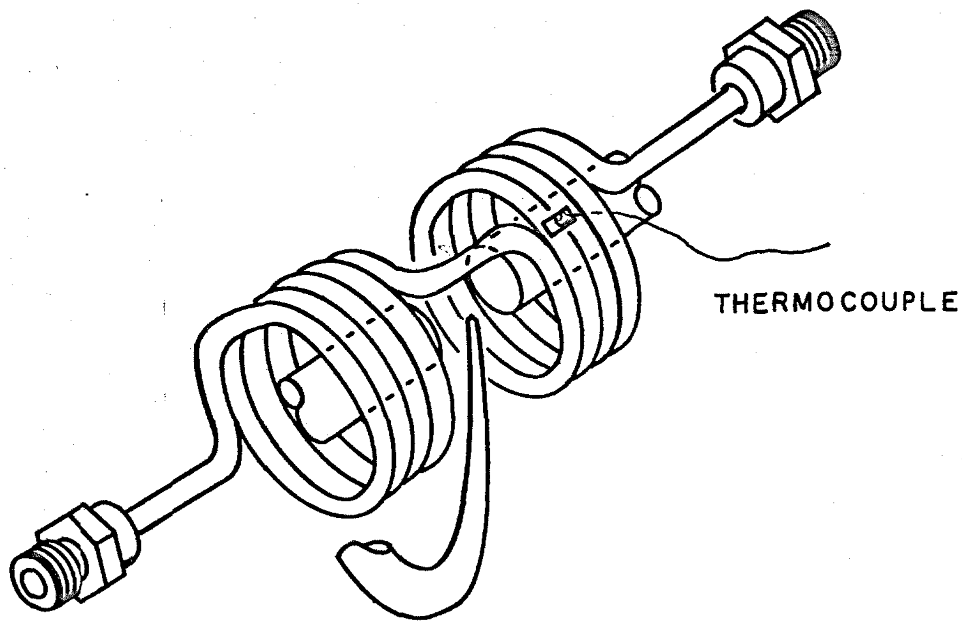

Fig. 2-2 Furnace arrangement

the chromel wire was controlled with a variable transformer. The temperature of the platinum anvil was measured using a chromel-alumel thermocouple (32 gauge wire) taped to the side of the anvil 1 cm. from the gap; an ice bath reference junction was used. The actual temperature at the working end of the anvil was probably 3-4°C lower than the measured temperature; any greater differential is unlikely because of the high thermal conductivity of platinum. The thin layer experimental work was done in a polyethylene glove bag filled with nitrogen.

The instrumentation used in the experimental work varied with time and experience gained. The basic configuration of the control and measurement circuitry is described in Chapters 5 and 6. Voltage levels were read with a Digitec digital voltmeter which has a resolution of 1 millivolt or a Moseley X-Y recorder with variable resolution. Potentials were read as measured, not as controlled. Based on the reproducibilities of potentials measured when comparing various reference electrodes, potentials are accurate to ± 8mV, plus the iR drop due to uncompensated resistance (see Chapter 6). Times up to one second were measured using a calibrated oscilloscope with an accuracy of 3%. Times longer than one second were measured with a Standard Electric timer with electric clutch. These times could be read to 1% accuracy. The current measuring resistors, the integrating resistors and the integrating capacitors were all of 0.1% accuracy.

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CHAPTER 3

Results and Discussion

General Characteristics - The gross electrochemical behaviour of a platinum electrode in 1 F H_2SO_4 can be observed using the technique of multiple cycle oscillopolarography. A typical oscillopolarogram (i-E curve at constant sweep rate) is shown in Figure 3-1.

With reference to Figure 3-1, we consider first the sweep in the positive (anodic) direction. The current between 0.2 volts and approximately 0.7 volts is essentially a capacitance current, required to charge the electrical double layer at the electrode-solution interface. Positive of 0.7 volts the anodic current increases sharply and then flattens out to a plateau extending to about 1.2 volts. Anodic of 1.2 volts there is again an increase in current; however, the region of primary interest for the characterization of the oxide film is between 0.2 and 1.2 volts.

If the sweep is halted at any potential between 0.7 and 1.2 volts, the current rapidly decays towards zero. When the sweep direction is

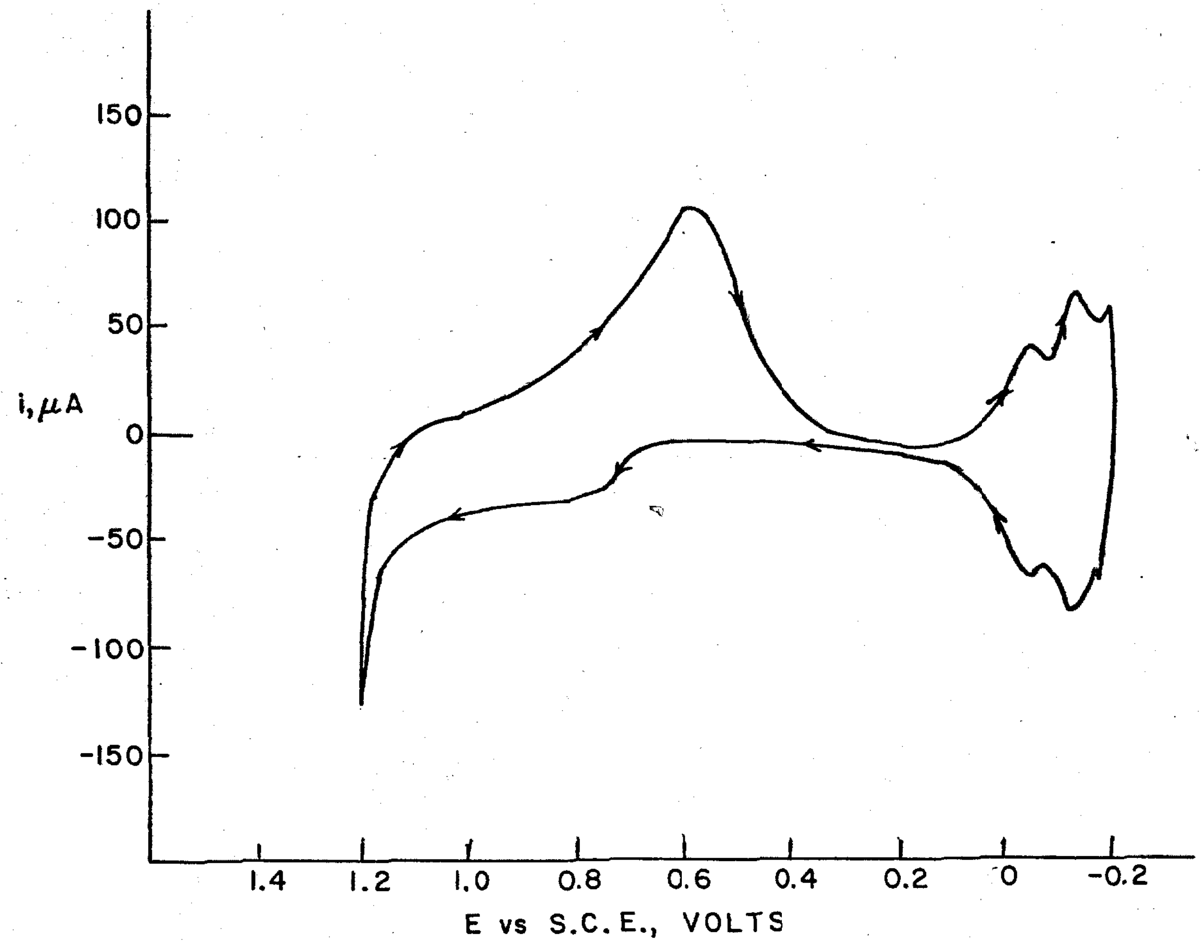

Figure 3-1. Cyclic potential sweep on a platinum button electrode in 1 F H_2SO_4. Sweep rate approximately 1 V/sec.

reversed at 1.2 volts, little cathodic current is observed until the potential is more cathodic than about 0.7 volts. The cathodic peak occurs at about 0.48 volts; the peak potential as well as the shape of the peak are dependent on the sweep rate, indicative of an irreversible electrode reaction. The morphology of the curve is unchanged if the solution is stirred, indicating that the complete reaction is not mass-transfer controlled, and that some of the product of the oxidation remains on the surface of the electrode.

If the solution contains oxygen the gross morphology is not altered, but the cathodic current peak is higher and the cathodic current between 0.4 and 0.2 volts does not go to zero. If, in the absence of oxygen, the potential is held at 1.2 volts before the return cathodic sweep is initiated, the shape of the i-E curve and the total charge passed during the cathodic sweep are not particularly sensitive to the time spent at 1.2 volts. Nevertheless, a small but significant anodic current flows at all times while the potential is held at 1.2 volts.

Hysteresis behaviour - There is a hysteresis in the net charge passed as a function of potential during a single anodic-cathodic cycle, as was first pointed out by Laitinen and Enke (1,2). Figure 3-2 shows a "hysteresis diagram" obtained in the following manner. A platinum button electrode was "cleaned" by potentiostating at 0.4 volts in a deaerated 1 F H_2SO_4. The potential was then stepped anodic to E_o for 15 seconds, then cathodic to E_W for 15 seconds; the integrator was then unshorted and the potential was stepped back to 0.4 volts and the cathodic charge passed was measured. In Figure 3-2 the most anodic point on each line is E_o, and the points on the lines represent E_W. On this time scale the surface concentration of oxide film is not a single valued function of the electrode potential, E_W; it is a function of the most anodic potential attained, E_o.

Surface Oxidation by Oxygen - If the electrode is oxidized at 1.2 volts for 15 seconds, removed from the solution into the air for 15 seconds, and then reduced at 0.4 volts, the net cathodic charge is the same as the charge measured without the exposure to air, provided

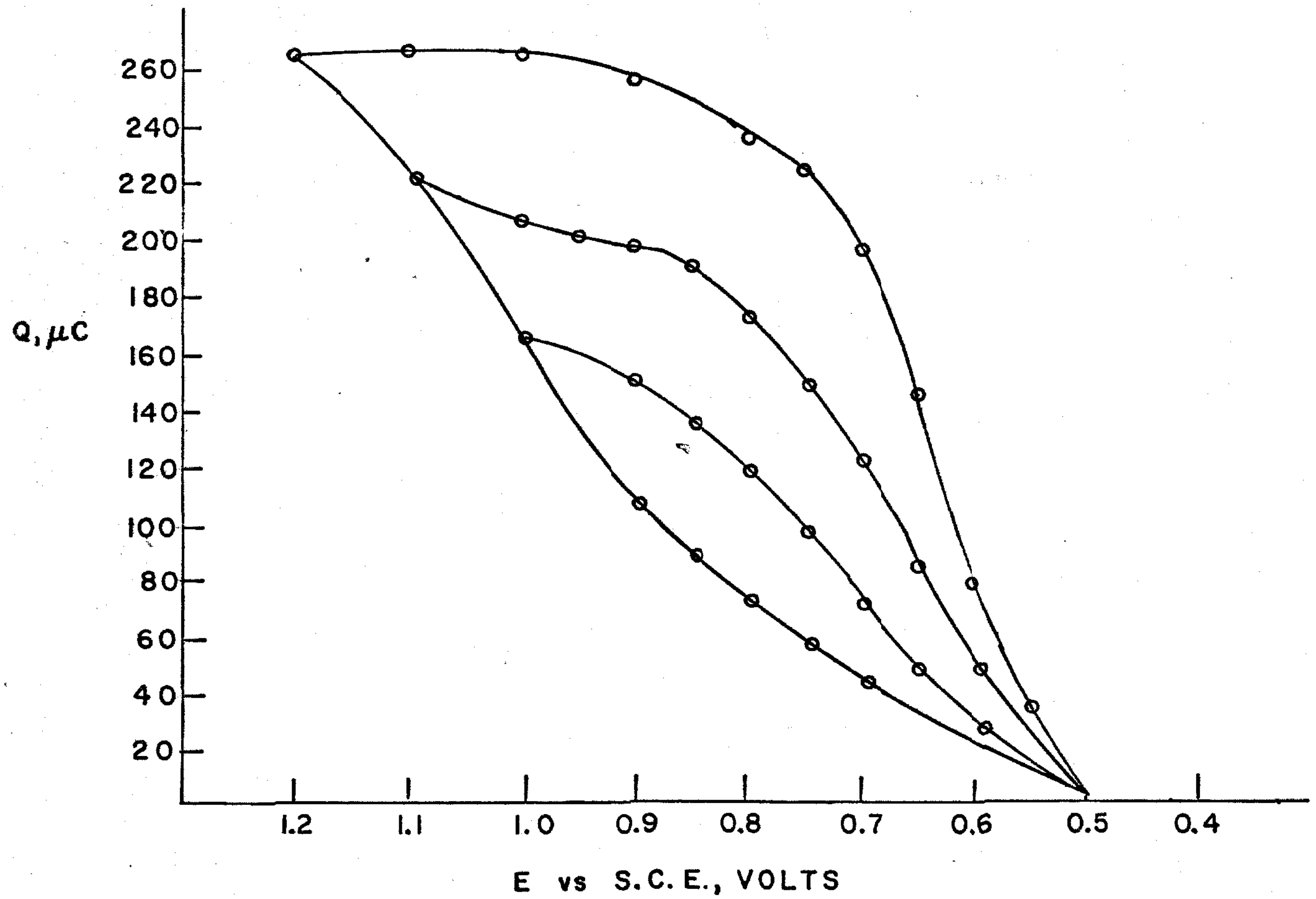

Figure 3-2. Reducible oxide as a function of oxidation potential, in 1 F H_2SO_4. Most anodic point on each line is oxidation potential, circles indicate potential at which the electrode is held for 15 sec. after oxidation.

suitable precautions are taken to insure that any oxygen carried along is removed before the reduction step.

Likewise a reduced platinum electrode exposed to the air does not appear to adsorb oxygen irreversibly on its surface. This was shown by removing a reduced electrode from the solution and then reimmersing it. No oxygen (oxide) wave was observed in a cathodic chronopotentiogram taken after one minute of deaeration. To determine whether O_2 is irreversibly adsorbed, a reduced electrode was placed into a deaerated solution at open circuit; the solution was then saturated with pure oxygen, whereupon the potential of the electrode drifted from 0.5 volts to about 0.65 volts. The solution was again deaerated with argon, and the potential drifted back to about 0.52 volts. A cathodic chronopotentiogram was then run; no wave corresponding to O_2 (oxide) was observed.

Chemical Oxidation - Strong oxidizing agents oxidize platinum in acid solution. This was shown by Giner (3), among others. Giner concluded that the film formed is adsorbed oxygen; however, no data were given to support the conclusion. An experiment to determine whether chemical and electrochemical oxidation are equivalent was performed. A platinum electrode was immersed into a 0.087 F solution of Ce(IV) in 1 F H_2SO_4. The electrode potential shifted anodic and stabilized quite rapidly at 1.27 volts. After 30 seconds the electrode was removed from the ceric solution, washed with distilled water and immersed into a deaerated 1 F H_2SO_4 solution. A cathodic chronopotentiogram was taken; 1250 microcoulombs of oxide film were found. The platinum electrode was then potentiostated at 1.27 volts for 30 seconds in the H_2SO_4 solution, removed from solution, washed, reimmersed and another chronopotentiogram was taken; again 1250 microcoulombs of oxide were found. This agreement indicated that the chemical and electrochemical oxidations produce equivalent amounts of reducible oxide on the electrode surface.

Analysis for Side Reaction Products

The explanation for the disparity between the anodic charge passed during oxidation of the platinum electrode in 1 F H_2SO_4 and the cathodic charge passed during the subsequent reduction has been the subject of a number of papers. The disparity was first noted by Vetter and Berndt (4), who postulated that the oxide is reduced to platinum and H_2O_2. Dietz and Gohr (5) also came to the same conclusion. This conclusion is in agreement with their experimental results that the ratio of anodic to cathodic coulombs, Q_a/Q_c was 2. Feldberg (6), later found that the 2:1 ratio could be obtained only after careful pretreatment and concluded that a mixture of two different oxides is formed; he concluded that the 2:1 ratio is the maximum value attainable. Other investigators have strongly disagreed. Gilman (7) has even claimed that the disparity is an artifact. Another possible explanation of the disparity is that oxygen which is evolved at the unoxidized sites diffuses away and thus charge is "lost".

Experiments to analyze for the products of the oxidation and reduction of the surface were carried out in the hope of resolving the disagreement. Oxygen evolved at the electrode during oxidation or hydrogen peroxide formed during reduction of the oxygen-containing films should be observable at the thin layer electrode since both species are electroactive at potentials amenable to analysis on platinum. Since any products formed in the thin layer cavity are trapped, diffusion away from the electrode is not possible, and the absence of these species in the cavity is necessary and sufficient evidence that they are not formed in appreciable quantity.

The following experimental procedure was followed. The thin layer electrode and the capillary salt bridge were mounted inside a glove bag which was then filled with nitrogen. The bag was kept at a positive nitrogen pressure at all times to avoid significant oxygen contamination from inevitable leaks in the polyethylene.

A 1 F H_2SO_4 solution in the glove bag was thoroughly deoxygenated. The salt bridge was filled with the H_2SO_4, and the thin layer electrode was thoroughly washed with this solution. Both poles were potentiostatically oxidized at 1.2 volts for 15 seconds, reduced for one minute at 0.4 volts and then rewashed. The cavity was adjusted to approximately fifteen microns gap thickness. Pole B was disconnected from the potentiostat circuit and Pole A was oxidized at 1.2 volts for 15 seconds. After this oxidation Pole A was disconnected; Pole B was reconnected, and was reduced galvanostically. Pole A was then galvanostatically reduced. The E-t traces (chronopotentiograms) obtained are shown in Figure 3-3.

The cleaning procedure was repeated, Pole A was oxidized for 15 seconds at 1.2 volts, and then immediately reduced, galvanostatically, after which Pole B was reduced. The E-t traces obtained are shown in Figure 3-4. In both cases the charge passed during oxidation, Q_a, was greater than the charge passed during reduction, Q_c. The experimental values of Q_a and Q_c are shown in the figures.

Figure 3-3 shows that no oxygen was evolved into the solution during the oxidation of Pole A. Had any oxygen been liberated, a potential inflection at about 0.5 volts would have been observed in the chronopotentiogram for the reduction of Pole B. Figure 3-4 shows that no hydrogen peroxide is formed during reduction of the oxide film since no potential inflection is observed at about 0.4 volts in either of the traces shown. Again Q_a was greater than Q_c. As few as ten

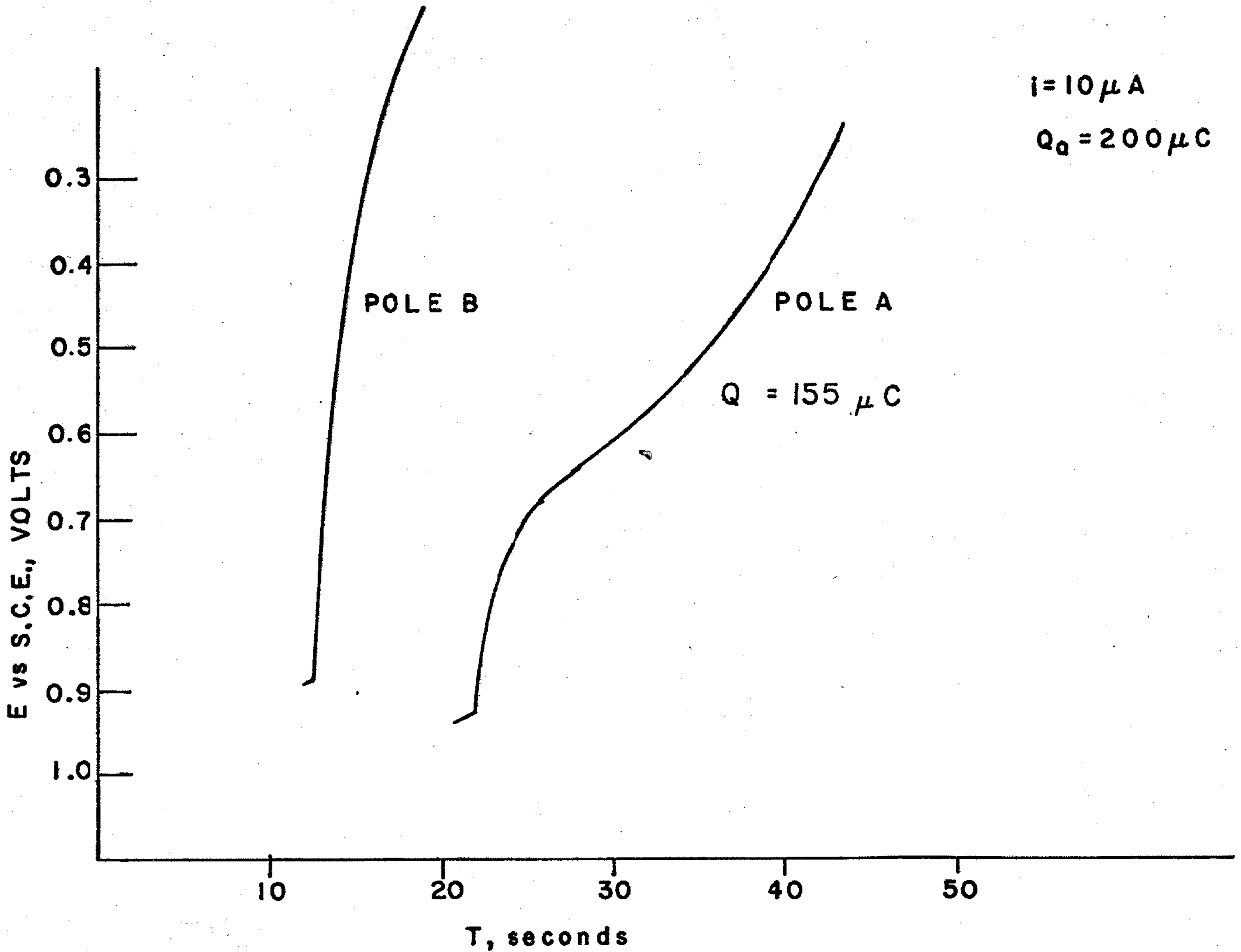

Figure 3-3. Chronopotentiogram on thin layer electrode in 1 F E_2SO_4. Pole A oxidized 15 seconds at 1.2 volts. Trace on Pole B run first.

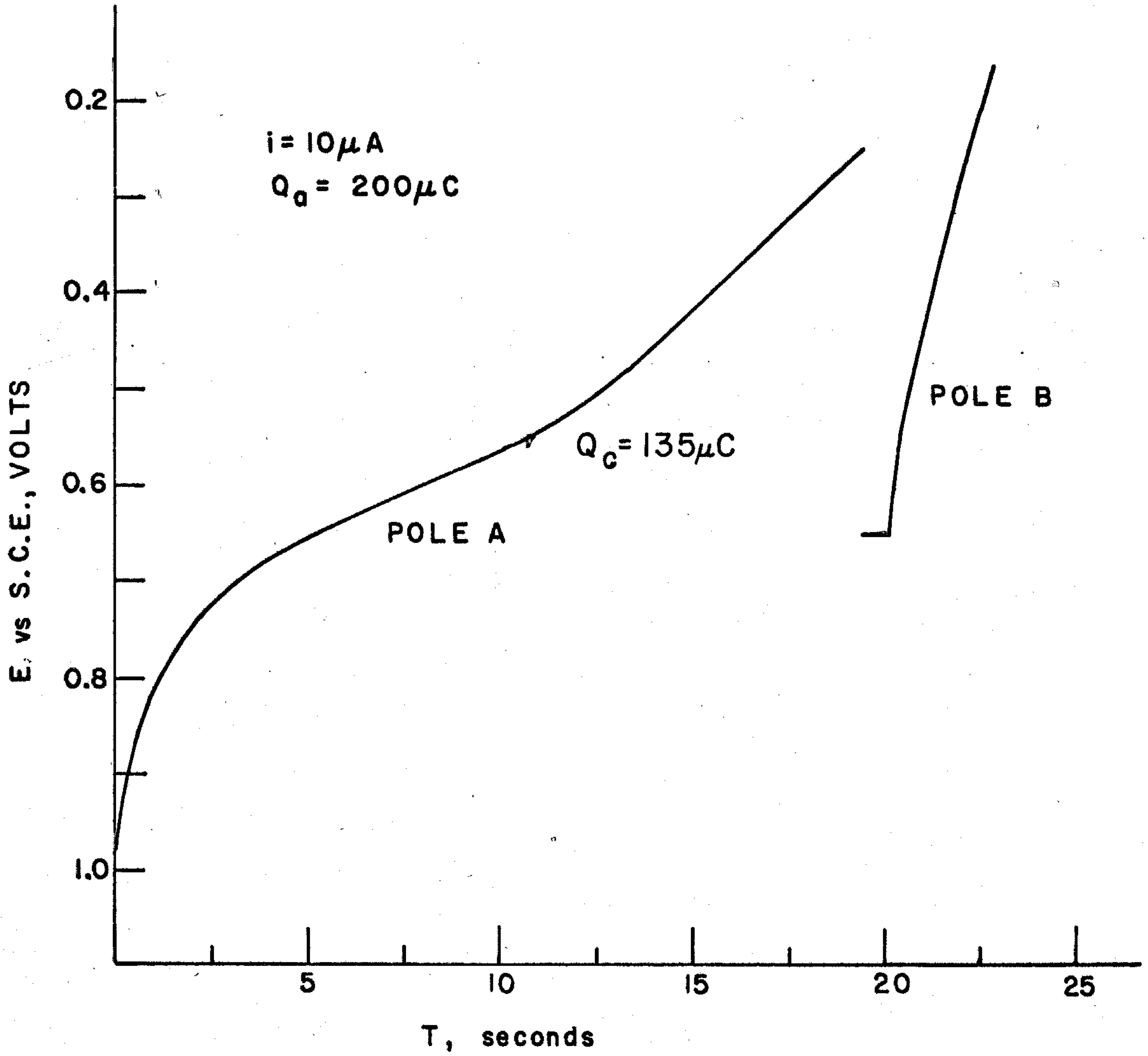

Figure 3-4. Chronopotentiograms on thin layer electrode in 1 F H_2SO_4. Pole A oxidized at 1.2 V for 15 sec. Trace on Pole A run first.

microcoulombs of either products would give an inflection, albeit a poorly resolved one.

The hypothesis that Q_a/Q_c is greater than unity because O_2 or H_2O_2 are products and diffuse away from the electrode is thus invalid. The statement must be modified to include only electroactive species in the potential region scanned; however, it is improbable that any species, e.g. platinum oxides, which would be formed would reduce at more negative potentials.

These experimental results neither indicate nor completely rule out initial oxygen formation on the electrode being oxidized since it is possible that any oxygen so formed could be adsorbed on the platinum surface; this adsorbed oxygen would probably reduce in the same potential region as the oxide film.

Time Dependent Reactions of the Oxide Film

The rate of formation of the oxide film has been considered in only two investigations (6,8). These measurements were made at rather long times (t greater than one second), primarily because of instrumental limitations.

The stability of the film in oxyacid solutions has also been passed over, except for the statement of Laitinen and Enke (2) that slow decomposition of the film was observed. This was measured by the amount of cathodic charge remaining on the electrode after a period of time, compared to the cathodic charge on the electrode determined immediately after oxidation. Unfortunately, this decomposition was sufficiently slow that it did not interfere with their experiment, and they did not investigate it any further It was of interest to verify the decomposition, identify the resulting products and measure the dependence of the ratio, Q_a/Q_c, on the extent of oxidation and time.

The first task was to measure the rate of disappearance, if any, of the reducible species formed upon oxidation of the electrode.

The rate of disappearance of reducible oxide was therefore investigated by performing the following experiment. The platinum button electrode was oxidized at 1.2 volts for 15 seconds in deaerated 1 F H_2SO_4 and reduced immediately at 0.4 volts. The cathodic charge passed during the reduction step was measured and was reproducible to about 5%. The electrode was then oxidized at 1.2 volts for 15 seconds and then left at open circuit for a period t_w. After t_w seconds had elapsed the electrode was potentiostated at the potential to which it had drifted and then the electrode was immediately stepped back potentiostatically to 0.4 volts where the remaining oxide was reduced and the net cathodic charge required for the reduction was measured. The data obtained, shown in Table 3-1, indicate that there is a disappearance of the reducible species in 1 F H_2SO_4 at room temperature. The data also suggests that there is an induction period for the disappearance of this species. The potential attained for any specific waiting time was not particularly reproducible (± 20MV) but in no instance was the drift to a potential sufficiently cathodic so that reduction of the oxide would be expected (cf. Figure 3-2).

The following experiment was then performed to investigate the effect of temperature on the rate of disappearance of the reducible oxide. A platinum button electrode was reduced at 0.4 volts and then oxidized

Table 3-1

Coulombs of reducible oxide remaining on electrode after oxidation at 1.2 volts for 60 m sec. in 1F H_2SO_4 and waiting at open circuit immersed in the solution for time t_w. Electrode area = 0.22 cm^2. Room temperature.

t_w(seconds)	E after t_w (volts)	Q_c (microcoulombs)
15	0.855 0.020	175 2
60	0.800	159
120	0.790	159
300	0.770	159
600	0.750	137.5
4960	0.690 (one value)	87.5 (one value)

at 1.2 volts in 1 F H_2SO_4 for 30 seconds at elevated temperature. The applied potential was then moved but electrode was left in the acid for various times, t_w. After t_w the electrode was potentiostated at the potential to which it had drifted and immediately potentiostatically stepped to 0.4 volts, the charge passed during the reduction being measured. The data obtained are shown in Table 3-2.

The reducible oxide disappears (decomposes) quite rapidly, and the ratio Q_a/Q_c become increasingly large. The anodic charge passed is highly irreproducible, yet the amount of reducible oxide is quite reproducible.

Stoichoimetry of the Film - Part 1

Anson and Lingane (9) have reported that the oxide film formed on platinum in sulfuric acid can be removed by reaction with acidic chloride solution at elevated temperatures. In their experiments a massive platinum electrode was galvanostatically oxidized in sulfuric acid and then immersed in a gently boiling acidic chloride solution for 30 minutes to one hour. The chloride solution was analyzed

TABLE 3-2

Coulombs of reducible oxide remaining on the electrode after oxidation in heated 1 F H_2SO_4 for 30 seconds, then waiting at open circuit for times t_w. Electrode area = 0.22 cm^2. (E after t_w was not recorded).

	t_w(seconds)	Q_a(microcoulombs	Q_c(microcoulombs)
T = 82°C	0	848	198 ± 5
	0	906	200
	30	922	117
	30	976	125
	60	815	40
	120	815	0
T = 69°C	0	632	218
	0	651	220
	30	573	211
	30	611	210
	60	674	205
	60	642	200
	120	547	190
	120	516	190
	300	523	160
	300	555	160

spectrophotometrically. They found absorption bands corresponding to $PtCl_4$ and $PtCl_6$ and concluded that both Pt(II) and Pt(IV) are present on the surface, the chloride "stripping" being due to the reactions

$$PtO + 4Cl^- + 2H^+ \longrightarrow PtCl_4^{2-} + H_2O \qquad (3\text{-}1)$$

$$PtO_2 + 6Cl^- + 4H^+ \longrightarrow PtCl_6^{2-} + 2H_2O \qquad (3\text{-}2)$$

They also recognized, however, that a possible side reaction

$$2Pt(II) \longrightarrow Pt + Pt(IV) \qquad (3\text{-}3)$$

could also conceivably explain the presence of the two species in the solution, and that therefore their results could not be taken as complete proof of the existence of two distinct oxidation states of platinum on the surface of the oxidized electrode.

Breiter and Weininger (9) disputed the conclusions reached by Anson and Lingane and suggested the following very unconvincing reaction scheme to explain the chloride stripping.

$$Pt\,O_n + 2nH^+ + 2ne^- \longrightarrow Pt^* + nH_2O \qquad (3\text{-}4)$$

$$Pt^* + 4Cl^- \xrightarrow{k_1} PtCl_4^{=} + 2e^- \qquad (3\text{-}5)$$

$$Pt^* + 6Cl^- \xrightarrow{k_2} PtCl_6^{=} + 4e^- \qquad (3\text{-}6)$$

The primary philosophic difference in these two views is that Breiter's reaction scheme does not require the existence of <u>oxidized platinum</u> on the surface of the electrode since the species PtO_n refers to "adsorbed" oxygen on the surface and not to a specific stoichoimetric compound. According to Breiter's scheme, reaction (3-4) forms an "active" platinum site Pt^*, on the surface; this site reacts with chloride according to reactions (3-5) and (3-6) and the relative rates k_1 and k_2 of the two competing reactions determine the ratio of the products found in the solution. Further, Breiter states that reaction (3-4) cannot proceed until the potential is sufficiently cathodic (on the hysteresis curve), but that once started, the overall process will increase in rate, since reactions (3-5) and (3-6) will drive the potential further cathodic, increasing the rate of (3-4). Breiter does not indicate how the potential drifts sufficiently cathodic to initiate the whole process. By the hypothesis, reactions (3-5) and (3-6) cannot account for the initial decay as the reactant, Pt*, is not present until the surface reduction begins.

A good test of Breiter's hypothesis would be the following experiment. An electrode oxidized in sulfuric acid is immersed into the chloride stripping solution and potentiostatically maintained at a potential on the hysteresis curve where the oxide is neither formed nor removed electrochemically (about 0.75 volts) (cf. Figure 3-2). If Breiter's hypothesis is correct, no stripping should take place since reaction (3-4) is inhibited and the amount of reducible oxide on the electrode should remain constant, or decrease at the same rate as it does in the sulfuric acid solution at the same temperature. If, however, the oxide is stripped in the chloride solution at this potential, the hypothesis would be invalid.

Both Breiter's argument <u>and</u> the experiment proposed above assume implicitly that the hysteresis behaviour of the platinum electrode is the same in acidic chloride and sulfate solutions. An attempt was made to determine the hysteresis curve, if any, in 0.2 F HCl - 2.8 F NaCl solution. It was found that significant, steady state anodic currents are passed at all potentials positive of 0.65 volts. This finding is in agreement with the data of Hubbard and Anson (10). Thus the hypothesis of Breiter and Weininger is probably incorrect as the electrode is depolarized at the potential quoted by these workers in the absence of oxide and there is no hysteresis in acidic chloride.

Decomposition Products of the Film

In the previous sections it was shown that the amount of reducible oxide remaining on the surface of an electrode oxidized in sulfuric acid decreases both at open circuit and when the electrode is held at potentials in the hysteresis region at room and at elevated temperatures. This disappearance can be attributed either to a transformation of the oxide to a non-reducible form (in the potential region available) or to its decomposition. If the disappearance is due to decomposition, the products formed could conceivably be detected electrochemically, *in situ*, using the thin layer electrode. The following experiments were performed with this objective. The contacts of the thin layer electrode were arranged so that either or both of the electrodes could be switched into the circuit rapidly. The electrodes were pretreated by oxidizing both poles at 1.2 volts for 15 seconds, then reducing at 0.4 volts for 2 minutes with 1 F H_2SO_4 dripping continuously through the cavity. After this pretreatment, the cavity was closed to about 15 microns (the thickness was not critical since only the total amount of species was of interest); pole B was disconnected from the circuit and pole A was oxidized at 1.2 volts for 5.1 seconds. Pole A was then disconnected and both poles were left at open circuit for a time t_w after which a cathodic chronopotentiogram was taken first on pole B (unoxidized pole) and then on pole A. The cathodic chronopotentiograms obtained after a waiting time of 3 minutes are shown in Figure 3-5. These may be compared to those shown in Figure 3-3. A distinct wave is observed at about 0.4 volts in the chronopotentiogram taken on pole B. The chronopotentiogram taken on pole A appears to have the normal morphology. (see Figure 3-3). The charge passed during the oxidation was 205 microcoulombs; from Figure 3-5 it is clear that the net anodic charge passed is again greater than

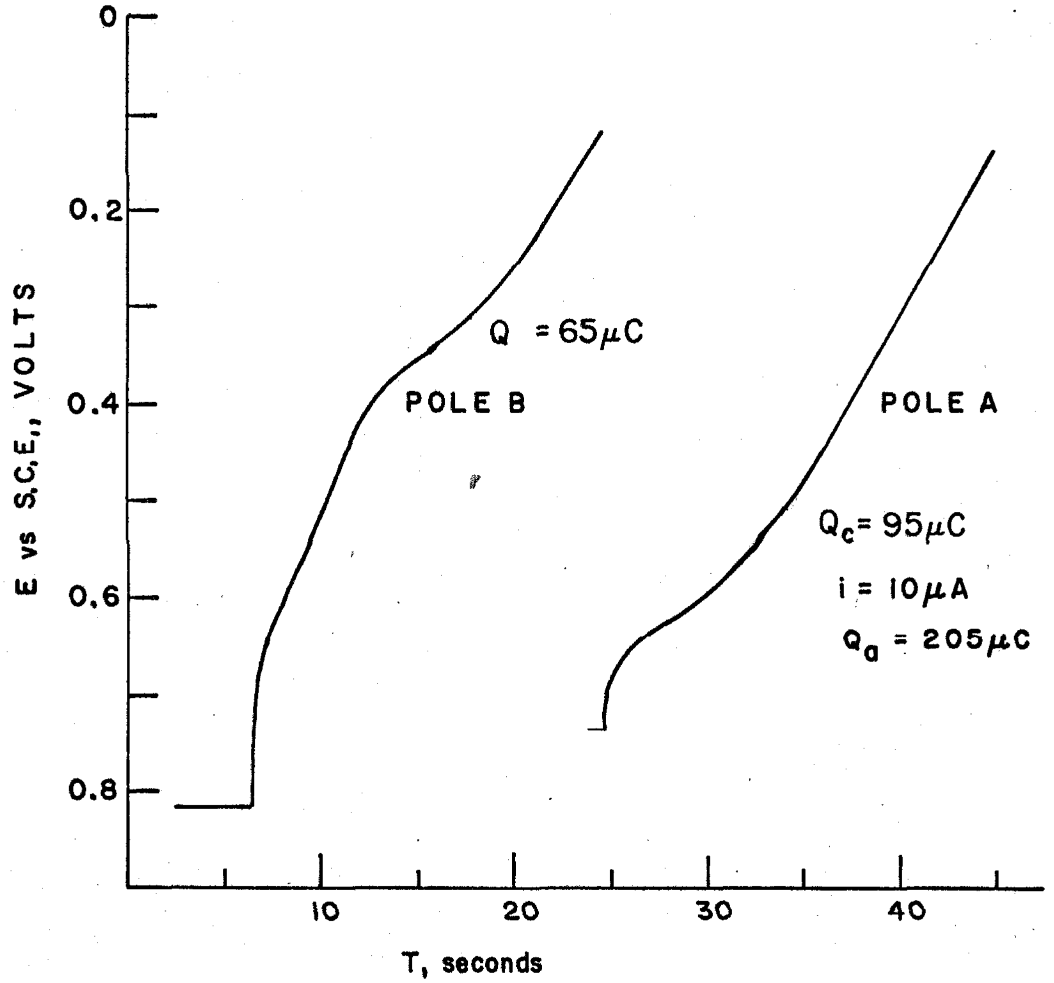

Figure 3-5. Chronopotentiograms on thin layer electrode in 1 F H_2SO_4. Pole A oxidized at 1.2 V for 5.1 sec. and then held at open circuit for 3 minutes. Trace on Pole B taken first.

the sum of the cathodic charges passed on both electrodes (including the wave at 0.4 volts).

The cathodic chronopotentiograms obtained after an oxidation time of 5 minutes are shown in Figure 3-6. Q_a was 852 microcoulombs. Two cathodic waves are apparent in the chronopotentiogram for pole B. The more cathodic of the two waves is at the same potential as the wave observed at shorter anodization times, the more anodic is at a potential attributable to oxygen.

To prove that the cathodic wave at 0.4 volts is due to hydrogen peroxide reduction, a 1 mF solution of H_2O_2 was put into the cavity and a cathodic chronopotentiogram was run. The reduction wave appeared at about 0.4 volts but was much more spread over the potential range, the transition time occuring at about 0.1 volts. A linear potential sweep experiment showed that the peroxide is very irreversibly reduced. An anodic linear potential sweep was then run on a 8 mF H_2O_2 - 1 F H_2SO_4 solution and this was compared to a sweep done on pole B after oxidation of pole A after a 4 minute wait. The i-E

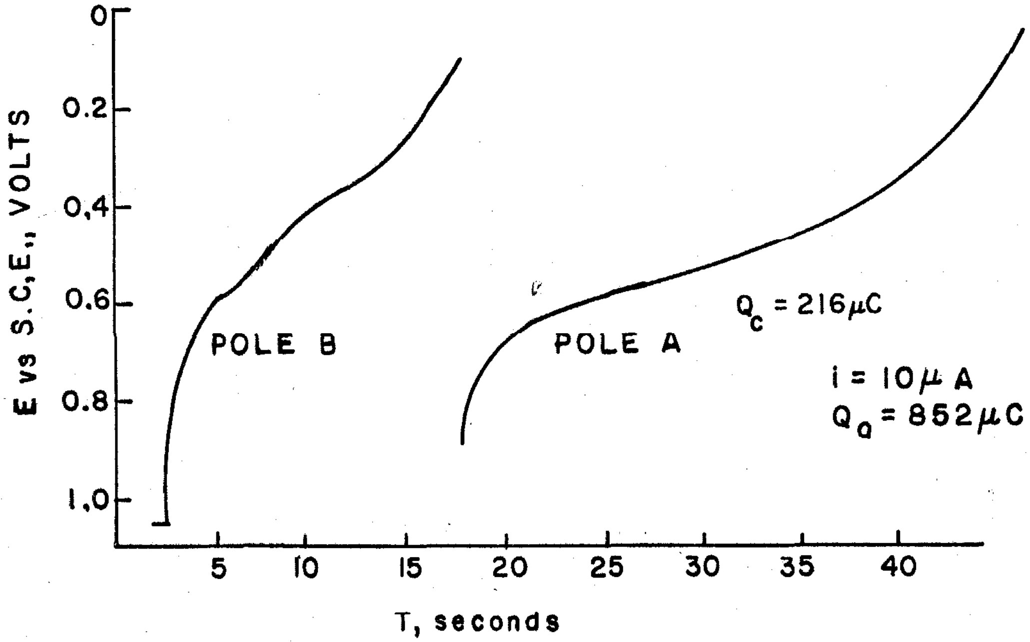

Figure 3-6. Chronopotentiograms on thin layer electrode in 1 F H_2SO_4. Pole A oxidized at 1.2 V for 5 minutes. Trace on Pole B taken first.

curves for the anodic linear potential sweeps are shown in Figure 3-7 along with the blank taken on pole B when pole A had not been oxidized. The wave for the prepared peroxide solution and the wave for the decomposition product are at the same potential. This evidence indicates that the oxidation peak at 0.9 volts is due to hydrogen peroxide, presumably formed by decomposition of the platinum oxide. It is assumed that the cathodic wave observed at about 0.4 volts in Figures 3-5 and 3-6 is due to reduction of H_2O_2.

The experiments were then repeated varying the open circuit time t_w and the anodization time t_a. Table 3-3 shows the data obtained. The data indicate that initial appearance of hydrogen peroxide takes place without a corresponding loss of reducible coulombs.

Stoichoimetry of the Film - Part 2

The appearance of hydrogen peroxide without a corresponding loss of reducible oxide during the initial stages of the decomposition suggests that there may be two forms of oxide on the surface of a platinum electrode which has been oxidized at 1.2 volts in formal sulfuric acid.

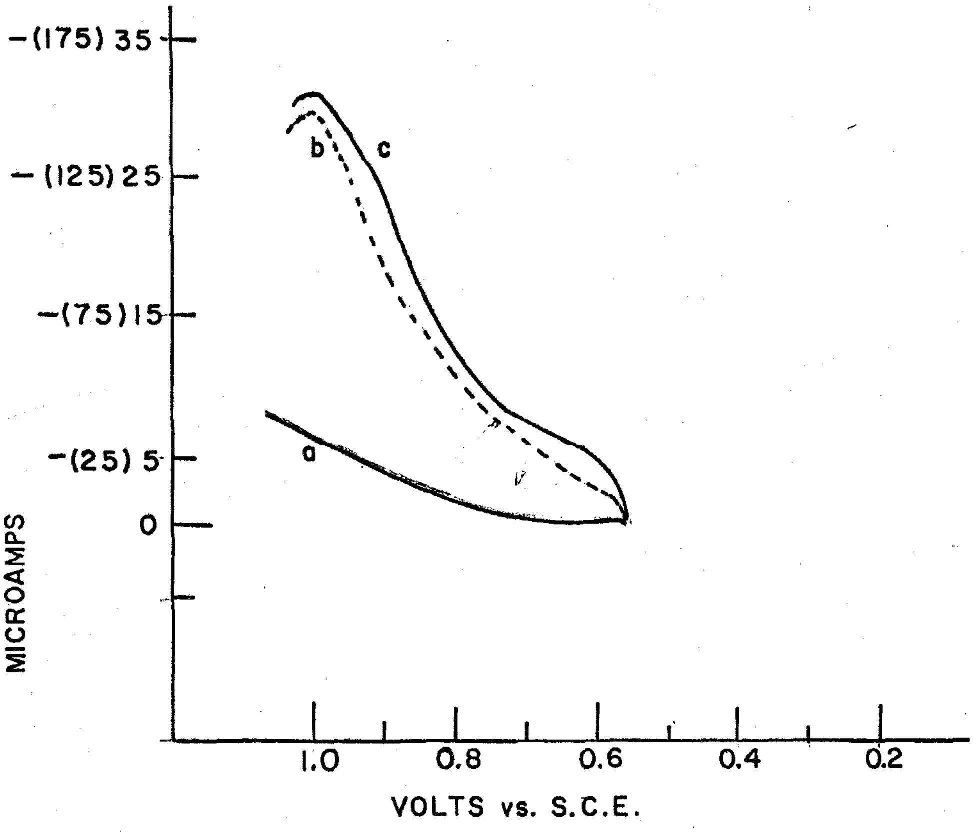

Figure 3-7. Anodic linear potential sweeps in thin layer electrode. Sweep rate 1 mV/sec. b) Pole A oxidized at 1.2 V for 15 sec; sweep run on Pole B after 4 min. wait. c) Sweep on Pole B on 8mM H_2O_2-1 F H_2SO_4 solution. a) Sweep on Pole B, Pole A not oxidized. 50 uA/div scale refers to the sweep on the peroxide solution.

TABLE 3-3

Analysis of Reaction Products in Thin Layer Electrode After Oxidation at 1.2 volts for t_a and Waiting Time t_w.

t_a seconds	t_w seconds	Q_a (1) μC	Q_c (2) μC	Q_{O_2}	$Q_{H_2O_2}$
15	0	259	112.5	0	0
15	15	284	115	0	?
15	60	248	115	0	?
15	300	315	100	0	32.5
15	600	276	95	0	36
60	0	374	111	0	0
60	60	367	107	0	0
60	300	375	107	0	?
60	600	379	108	0	22.6
120	0	560	150	0	42.5
120	120	516	151	0	488
120	300	450	153	0	48.8
120	600	466	143	0	48.7

(1) Measured on pole A during anodization

(2) Reducible oxide left on pole A after t_a and after chronopotentiogram of pole B.

(?) Indicates inflection observed but not reliably measurable (less then 5 μC).

We therefore attempted to determine the oxidation states of the species on the surface by chloride stripping (9). The thin layer electrode was pretreated in 1 F H_2SO_4 at room temperature as before. Both poles were oxidized at 1.2 volts for 15 seconds. After the oxidation, the electrodes were open circuited and thoroughly rinsed with a solution of 0.2 F HCl - 2.8 F NaCl. This rinsing effectively displaced the sulfuric acid in the salt bridge with the chloride solution. The cavity size was readjusted to 25 microns, the greater gap being required to allow for thermal expansion, and the furnace was turned on. The temperature in the cavity was kept at about 80°C for the duration of the time desired; the furnace was then turned off, the cooling water was turned on and room temperature was attained in about four minutes. The potentiostat was then turned on at the open circuit potential which the electrodes had assumed, and a very slow linear potential sweep was applied. A typical i-E curve is shown in Figure 3-8.

The positions and shapes of the peaks allowed identification of

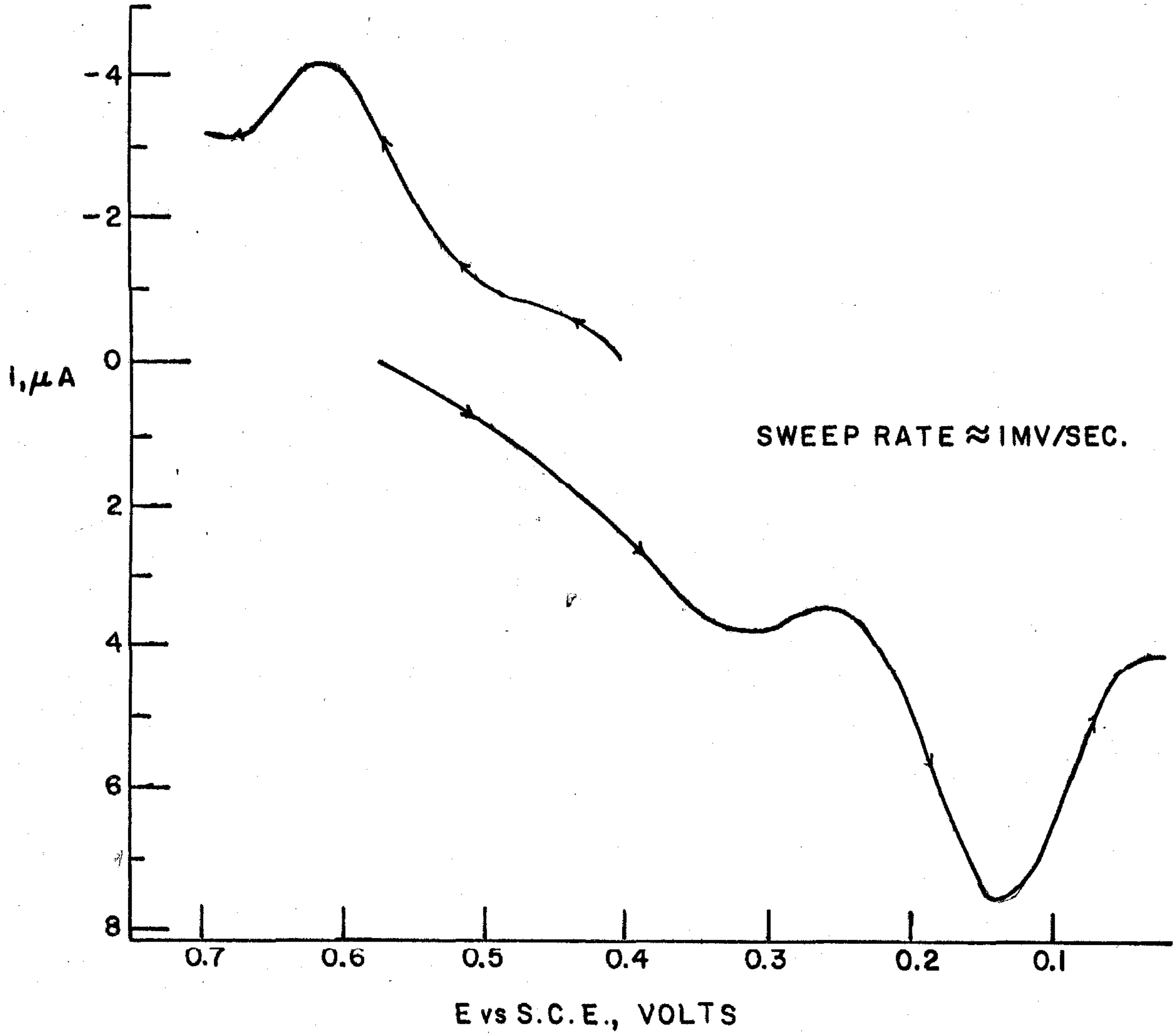

Figure 3-8. Linear potential sweep in thin layer electrode. Both poles oxidized at 1.2 V for 15 sec. Then chloride solution added and electrode heated to 80°C for 5 minutes, then cooled. Anodic sweep run first.

the species in the solution by comparison with the data of Hubbard and Anson (11) who ran slow linear potential sweeps in a thin layer electrode on various solutions of platinum chlorides. The cathodic peaks are attributed to reduction of Pt(IV) chlorides and oxychlorides. The anodic peak is due to oxidation of $PtCl_4^=$.

A number of additional similar runs were made in which the cavity was thoroughly rinsed and filled with 1 F H_2SO_4, the temperature was raised to 85°C for five minutes and then lowered to room temperature. This procedure assured that no oxide, electro-active or electro-inactive remained on the surface (see Table 3-2). The cavity was then rinsed and filled with fresh 1 F H_2SO_4 and both poles were oxidized at 1.20 volts for 30 seconds. The cavity was then filled with chloride solution, heated to 85°C for 5 minutes, and cooled to room temperature. Linear potential sweeps were applied which started from the potential attained during the open circuit drift, and the resulting current was integrated. The data are given in Table 3-4. In all cases the cathodic sweep (determination of $PtCl_6^=$) was run first. Potential sweeps, rather than potential step, was used as the potentials of the peaks are not reproducible (cf. ref. 11).

These data show that within experimental error, the sum of the coulombs of stripped platinum ion equals the total anodic coulombs passed during oxidation of the electrode. Further the ratio of anodic coulombs passed during the oxidation in the sulfuric acid to the amount of Pt(II) in the chloride solution is about the same as the values of Q_a/Q_c obtained in the sulfuric acid alone.

The experimental error during the anodic sweep is systematically high; however, it is not reproducible and therefore the "blank" was not subtracted from the measured charge. Integrator drift and small amounts of oxygen can contribute; however, the greatest error probably arises from the fact that the $PtCl_4^=$ oxidation is very irreversible and its peak tends to merge with the onset of massive platinum dissolution, thus the charges measured for total $PtCl_4^=$ tend to be high. From the apparent correspondence between the ratios Q_a/Q_c as measured in 1 F H_2SO_4 and determined from the chloride stripping experiments

TABLE 3-4

Amounts of Pt(II) and Pt(IV) in Chloride Stripping Solution After Oxidation at 1.2 volts for 30 Seconds in 1 F H_2SO_4. (See page 54 for experimental detail).

Q_a, μC(1)	Q_c(in Cl^-)μC	Q_a(in Cl^-)μC	Equivalent (2) Q_a/Q_c (in Cl^-)
830	258	700	1.56
770	150	700	1.28
880	250	788	1.44

The ratio Q_a/Q_c in 1 F H_2SO_4 was 1.41. The anodic blank is 80 ± 15uC. This was not subtracted from the data.

(1) Measured during oxidation in 1 F H_2SO_4

(2) Assuming that Pt(II) is reducible oxide.

(assuming that Pt(IV) corresponds to non reducible oxide) it is concluded that the Pt(II) on the surface represents "reducible" or "active" oxide, whereas Pt(IV) is "irreducible" on inactive oxide.

To test this conclusion pretreatment of heating at 85°C for 5 minutes in 1 F H_2SO_4 was carried out on both poles and the electrodes were oxidized at 1.2 volts for 30 seconds, and then reduced at 0.4 volts for 15 seconds in 1 F H_2SO_4 at room temperature; therefore no reducible oxide was on the surface. The cavity was then filled with the acidic chloride solution, heated to 85°C for 5 minutes, cooled to room temperature, and a linear potential sweep was applied from the equilibrium potential assumed. (0.395 to 0.410 volts in all cases). On the cathodic sweep 200 microcoulombs of Pt(IV) were found and 220 microcoulombs of Pt(II) were found on the subsequent anodic sweep. The same pretreatment was then performed on the electrodes, but the electrodes were not oxidized and reduced before chloride addition and heating. No peak corresponding to any of the platinum species was found.

These data show that the oxygen-containing film is composed of platinum species in two oxidation states. They also indicate that the electro-inactive species contain Pt(IV). The cause of the discrepancy between Q_a and Q_c in sulfuric acid is therefore due to the formation of the inactive species. Further, the decomposition studies show that it is this inactive species which decomposes more rapidly (see Table 3-3).

The last experiment, where no platinum chloride species was found if the electrodes were pretreated but not oxidized, shows that the pretreatment gives a useful "standard" reference state as a point of departure for experimental work with platinum electrodes.

Surface Saturation - A test of the conclusions presented above is given by the following experiments. If the potential of a platinum electrode in 1 F sulfuric acid is cycled repeatedly between 1.2 and 0.4 volts, the surface would become saturated with the Pt(IV) oxide and the ratio of anodic to cathodic coulombs passed during each cycle should tend towards unity. A number of such experiments were run, varying the time of the cycling (the time at each of the potentials). A typical plot of the ratio Q_a/Q_c, versus the cycle number is shown in Figure 3-9. It is clear that the ratio tends toward unity. The slight deviation from unity is attributed to the decomposition of some of the electro-inactive species during each cycle. If this explanation is correct, the ratio should be much larger in hot sulfuric acid, where it has been shown that the decomposition is very much more rapid than at room temperature.

The corresponding Q_a/Q_c versus cycle number plot for $T = 69^\circ C$ is shown in Figure 3-10, The limiting ratio is greater than that at room temperature. The first point on each plot is much higher than the subsequent points as would be expected from the previous data which indicated that on the time scale involved an appreciable amount of irreducible oxide is formed on the first cycle.

Relative Rates of Formation - As has been shown, immersing a platinum electrode in 1 F H_2SO_4 at $85^\circ C$ for 5 minutes effectively removes all the oxides. In the following experiments the ratio, Q_a/Q_c, on a "standard" electrode was determined as a function of anodization time.

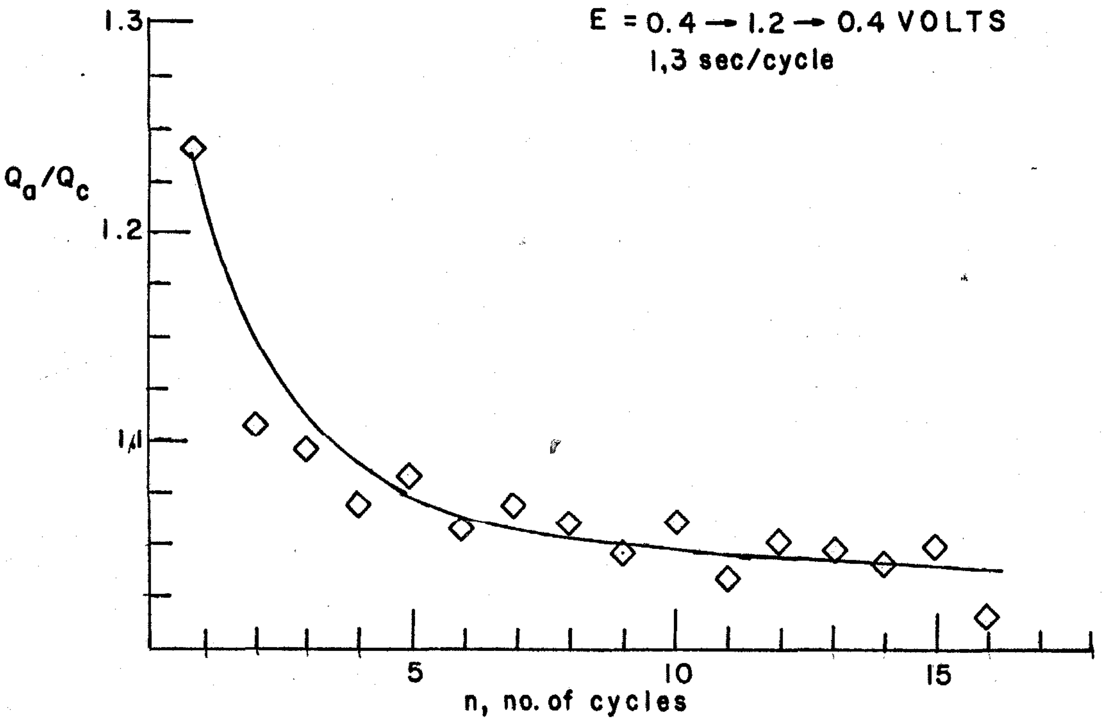

Figure 3-9. Ratio of anodic to cathodic charge passed as a function of the number of cycles between 0.4 and 1.2 V in 1 F H_2SO_4 at 27°C.

Before each run the electrode was immersed in formal sulfuric acid at 85°C for 10 minutes. It was then removed, washed with cold H_2SO_4 and potentiostated at 0.40 volts in a deaerated formal sulfuric acid solution. The potential was then stepped to 1.2 volts for a time t_a, and then back 0.4 volts, measuring the charge passed in each direction. The data are given in Table 4-5. These data show that the inactive oxide, Pt(IV), is formed more slowly at this potential than is Pt(II). A possible explanation for the slow formation of Pt(IV) is that it is not formed directly (electrochemically), but by a chemical dismutation of the Pt(II) formed electrochemically. Based on the thermodynamic data available (13) the dismutation reaction

$$2PtO \longrightarrow Pt + PtO_2 \qquad (3\text{-}8)$$

is energetically allowed.

Evolution of Ozone

In all the experimental work described in the previous sections of this chapter the potential of the platinum electrode was kept between 1.2 volts and 0 volts versus the saturated calomel electrode.

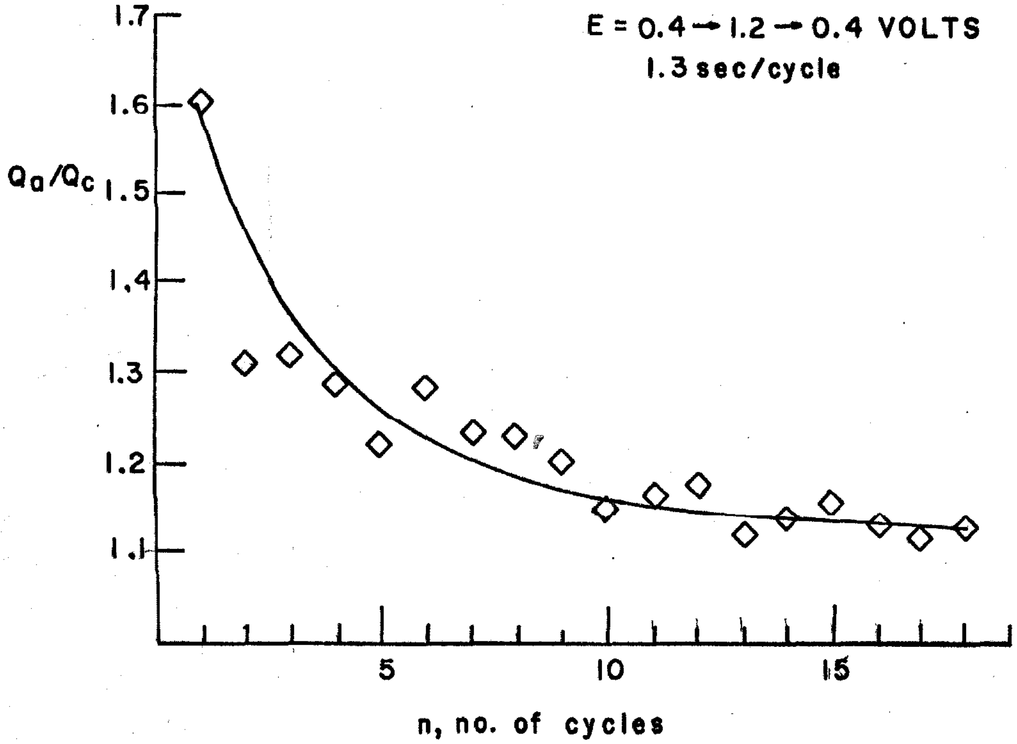

Figure 3-10. Ratio of anodic to cathodic charge passed as a function of number of cycles between 0.4 and 1.2 V in 1 F H_2SO_4 at 69°C.

TABLE 3-5

Charges Passed Upon Oxidation for Varying Amounts of Time, t_a, and Reduction in 1 F H_2SO_4 of a Platinum Button Electrode (0.22 cm^2) Which Has Been Pretreated by Soaking in 1 F H_2SO_4 at 85°C for 10 Minutes.

t_a(seconds)	Q_a(uC)	Q_c(uC)	Q_a/Q_c
0.054	68	68	1.00
0.086	114	98	1.07
0.184	116	108	1.075
0.360	122	109	1.12
0.580	158	143	1.11
0.800	170	145	1.10
1.14	173	153	1.13
5.0	240	198	1.21
10.0	250	201	1.225

The anodic limit of 1.2 volts was set because previous experimental work, using ordinary (as opposed to thin layer) electrodes, had indicated that a significant faradaic current flowed at more anodic potentials (12). At the time this current was ascribed to oxygen evolution.

Hubbard, however, (14) observed a cathodic peak at about 1.1 volts of irreproducible height in voltammetric experiments in 1 F H_2SO_4 or $HClO_4$ in which his thin layer electrode was polarized beyond about 1.25 volts. Since any species (originally thought to be an impurity in the acid) which reduces in this potential region could serious affect the results of the oxide investigation, a study of the effect was initiated.

The thin layer electrode was again used; the electrolyte was formal sulfuric acid. A slow (approximately 10 mV/sec) potential sweep was run first anodically and then cathodically with the thin layer electrode poles connected together. The current-voltage curve obtained is shown in Figure 3-10. The peaks at potentials more anodic

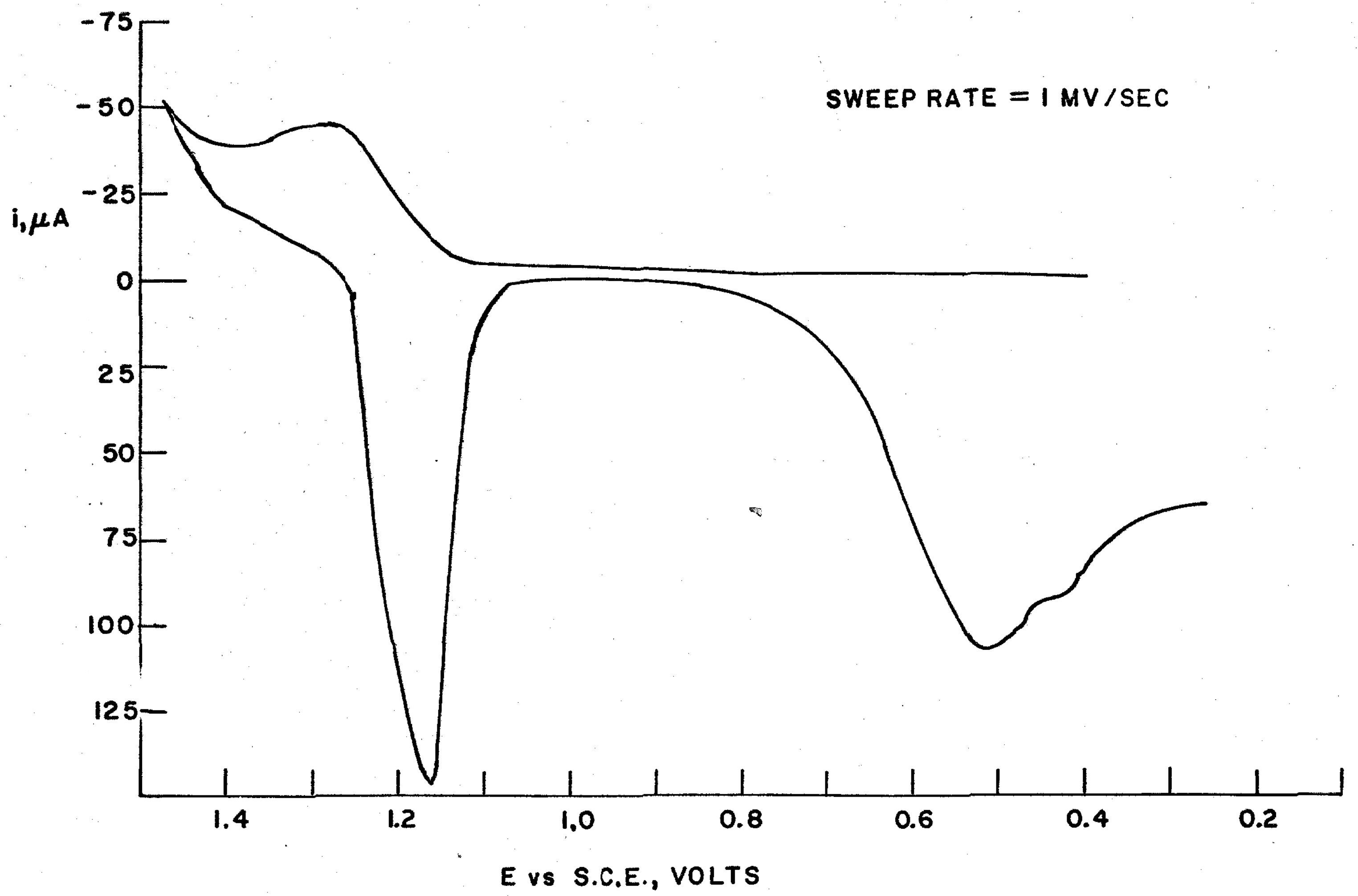

Figure 3-11. Linear potential sweep on thin layer electrode in 1 F H_2SO_4. Sweep rate approximately 10 mV/sec.

than 1.0 volts are interesting; neither the broad anodic peak at 1.3 volts nor the sharp cathodic peak at 1.1 volts has been reported in the literature.

The anodic peak could be attributed to the formation of a surface oxide, ozone, or $S_2O_8^=$; however, the appearance of a peak would be difficult to explain since the formation of none of these products would expected to be diffusion controlled, and there would be no significant depletion of reactants. The cathodic peak at 1.1 volts is surely due to the reduction of the material formed during the anodic peak.

Several experiments were carried out to identify the product of the oxidation at 1.3 volts. The thin layer electrode was filled with formal sulfuric acid; pole B was disconnected and pole A was oxidized at 1.3 volts for 30 seconds. The instrument was then switched to the galvanostatic mode, pole A was disconnected and pole B was connected. After pole B had been switched its potential was approximately 1.1 volts. A chronopotentiogram was then run on pole B; the E-t curve is shown in Figure 3-12. A clear wave is observed at 1.15 volts in addition to the oxygen and peroxide waves at 0.6 and 0.4 volts respectively. A cathodic chronopotentiogram was then run on pole A; which showed 175 microcoulombs of oxide on it. It should be noted that the wave identified as "oxygen" on pole B might well be a combination of oxide and oxygen. To determine if pole B is oxidized in this experiment it was rerun, however, this time pole A was reduced before pole B. The subsequent chronopotentiogram of pole B showed no trace of oxygen or oxide. Thus the species formed at 1.3 volts does not appear to oxidize platinum. This experimental fact is most disturbing as the potential of pole B is at 1.2 volts after the oxidation of pole A (see Figure 3-12) and therefore the electrode <u>must</u> have been oxidized. A reasonable rationalization is that one of the products formed, either by decomposition or by reduction at pole A, reduced pole B. The experiment proves, however, that the species formed on the anodic cycle is soluble as it does diffuse across the gap from pole A to pole B, as the unoxidized pole B is poised after

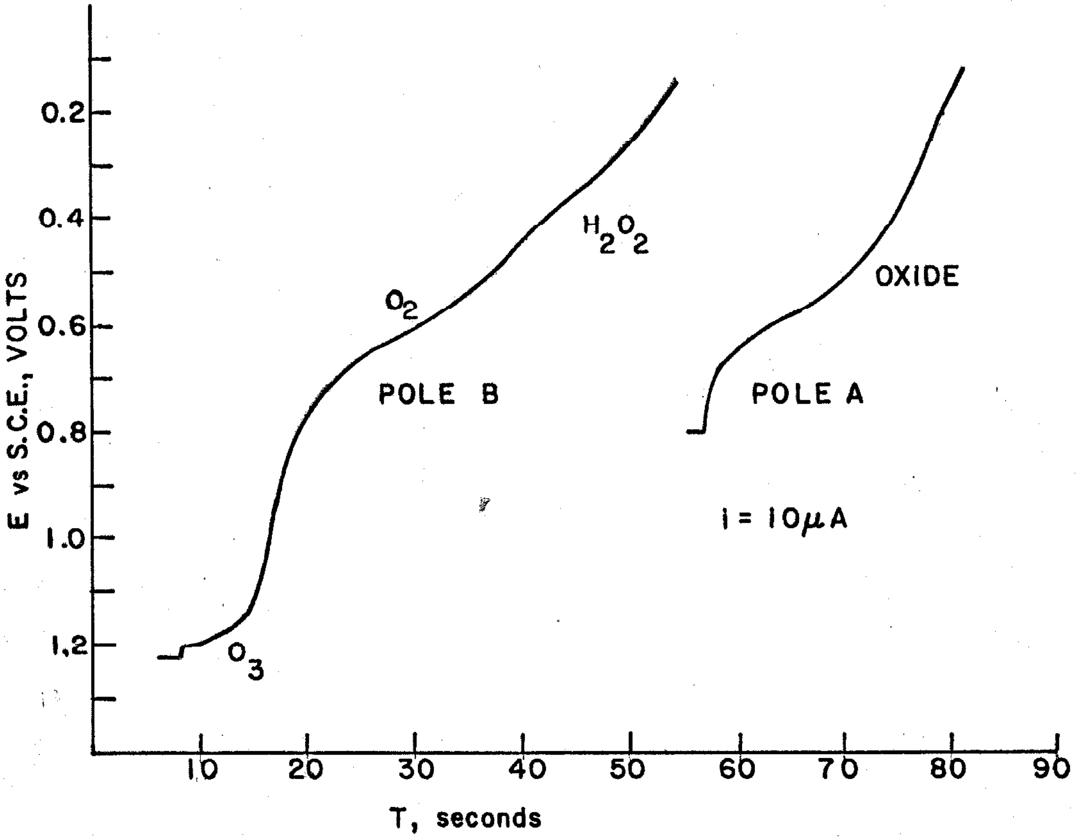

Figure 3-12. Chronopotentiograms on thin layer electrode in 1 F H_2SO_4. Pole A oxidized at 1.3 V for 30 seconds. Trace on Pole B taken first.

the oxidation of pole A.

This experiment was then repeated with a delay introduced between the time the anodic potential was turned off at pole A and the time that the cathodic chronopotentiogram at pole B was initiated. The wave at 1.1 volts disappeared quite rapidly; after a 1 minute wait no wave is observed, but very large concentrations of oxygen and hydrogen peroxide were evident.

To show that the product of the oxidation is not $S_2O_8^=$ similar experiments were run in 1 F $HClO_4$. The $HClO_4$ results were identical to those obtained in the sulfuric acid.

It was tentatively concluded that the oxidation product is ozone. Thermodynamically this is quite possible since the EMF for the reaction

$$3H_2O \longrightarrow O_3 + 6H^+ + 6e^- \qquad (3\text{-}9)$$

is 1.259 volts referred to the saturated calomel electrode. Thus the formation of O_3 at the electrode by the direct oxidation of water, whatever the mechanism, is thermodynamically possible.

To test this hypothesis ozone was generated electrochemically <u>in</u>

situ, in the following manner. An electrolysis cell was filled with 1 F H_2SO_4. The solution was not deaerated since it would be saturated with oxygen shortly after the start of the experiment. The indicator electrode was potentiostated at 1.4 volts. Two auxiliary electrodes were attached to a floating power supply (guaranteed isolation from ground of 100 megohms) with the anode in the same chamber as the indicator electrode and the cathode separated with a medium porosity frit. A current of about 1.5 amperes (effectively about 7 amperes/cm^2 with respect to the anode) was passed between the two auxiliary electrodes and the pungent odor of ozone (above the normal Pasadena O_3 level) was detected. A piece of wet starch iodide paper gave a positive test for ozone in the gas above the solution. A relatively small <u>anodic</u> current passed through the indicator electrode being potentiostated at 1.4 volts; however, this current increased slowly during the experiment. With the current still flowing through the auxiliary electrodes, the potential of the indicator electrode was moved slowly cathodically. At about 1.15 volts a cathodic current was observed and at 1.05 volts the cathodic current exceeded 300 mA and massive gas evolution was observed. When the current through the auxiliary electrodes was turned off the cathodic current through the indicator electrode, at 1.1 volts, diminished rapidly and within one minute a net anodic current was observed. The anodic current was considerably greater than that observed at this potential before the ozone generation.

From this experimental evidence it is concluded that ozone is formed at a platinum electrode in formal oxyacid solutions at potentials more positive than 1.3 volts, and that the ozone is reduced at about 1.1 volts. This conclusion is in accord with the findings of Fleskii (16) who studied the reduction of ozone in 1 F sulfuric acid at platinum, using prepared ozone solutions. The anodic "peak" observed in the thin layer electrode at about 1.3 volts is assumed to be due to the oxidation of hydrogen peroxide rapidly formed by the reaction

$$O_3 + H_2O \longrightarrow H_2O_2 + O_2 \qquad (3\text{-}10)$$

The appearance of a "peak" is due to the fact that the electrode becomes passivated toward peroxide oxidation. Figure 3-13 shows a rotating electrode polarogram taken in an 8 mF H_2O_2 - 1 F H_2SO_4 solution; the shape of the i-E curve is similar to the anodic peak observed with the thin layer electrode except that the peroxide in the thin layer experiment is not formed until the electrode potential has become sufficiently anodic that ozone can be generated.

As a further proof that the phenomenon observed is "real", as opposed to being an electronic artifact, the following experiment was run. The thin layer electrode was filled with 1 F H_2SO_4 at 69°C. Pole A was connected to the potentiostat and pole B was connected to a high impedance potential follower, so that its potential, relative to pole A and the potentials of both electrodes were monitored. Figure 3-14 shows the potential of pole B as a function of the potential of pole A; the values of both potentials are shown with respect to the S.C.E. The potential of pole A was fixed by the potentiostat and the potential of pole B varied as determined by the species at its surface. The slope in region "a" is due to iR drop in the cell.

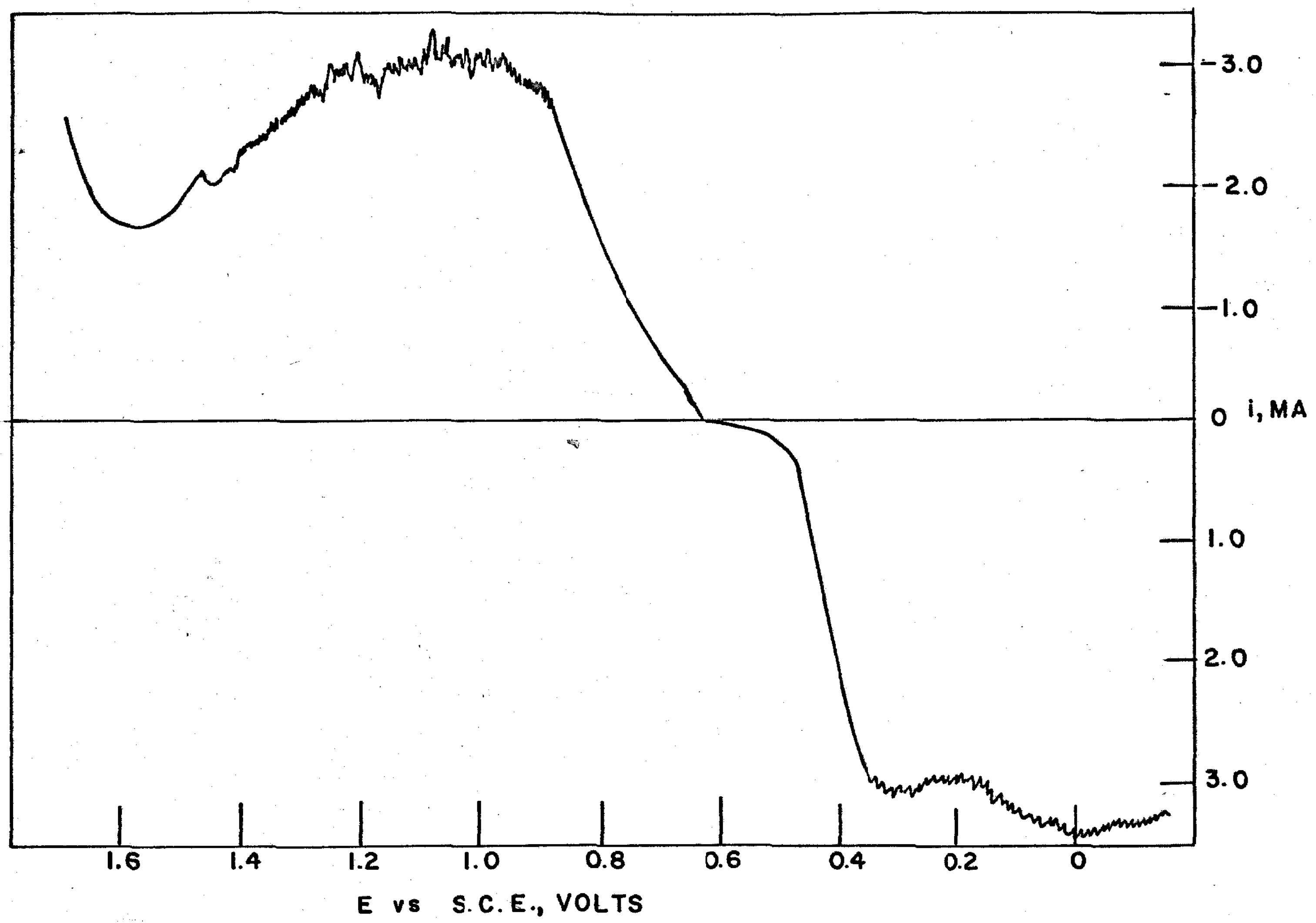

Figure 3-13. Rotating platinum electrode polarogram taken on 8 mM H_2O_2 - 1 F H_2SO_4 solution.

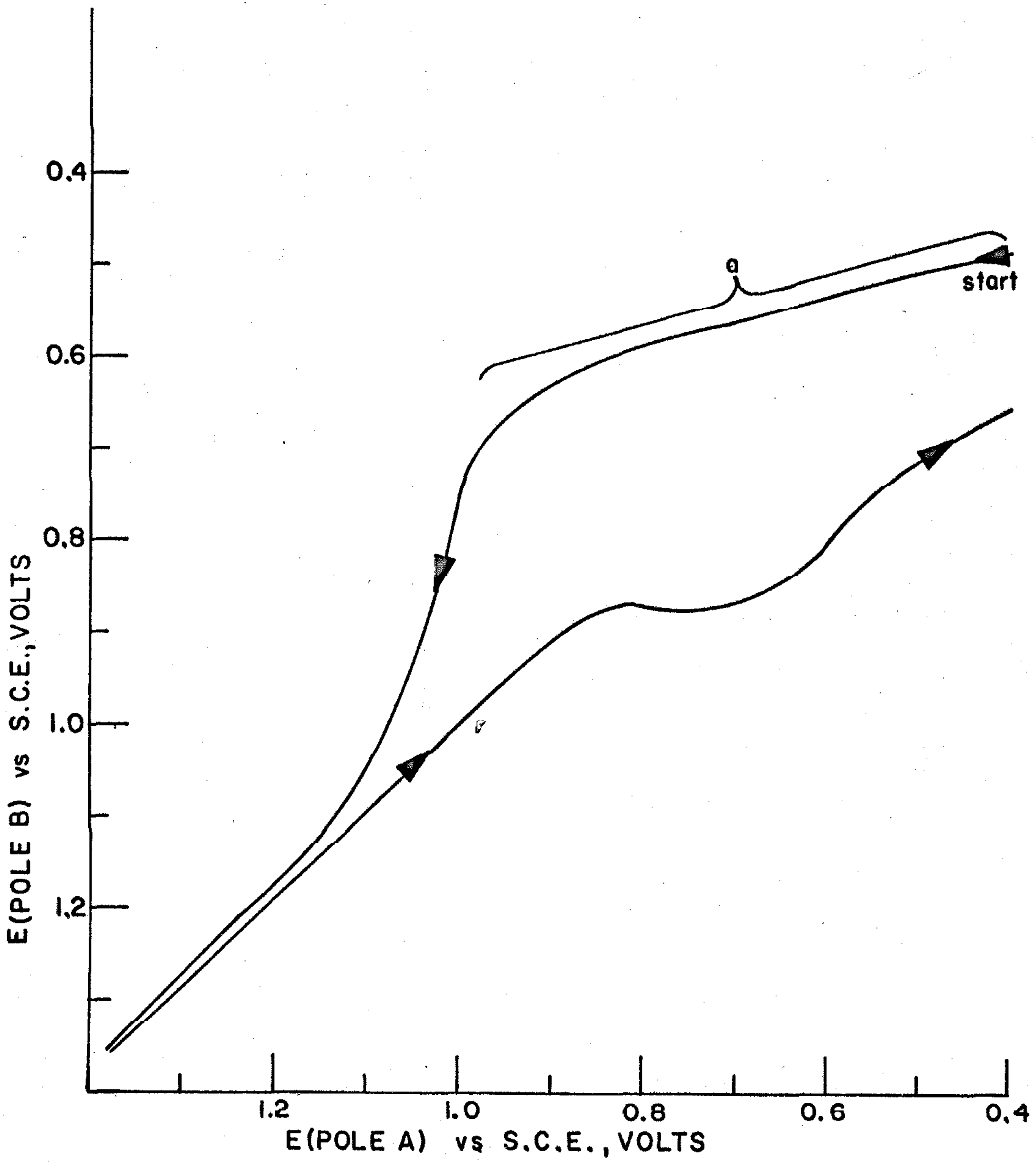

Figure 3-14. Potentials of poles A and B relative to S.C.E. during linear potential sweep on Pole A. Sweep rate 3.5 mV/sec. Temperature: 69°C.

When pole A reaches 1.0 volts the potential of pole B becomes rapidly more anodic until the potential of both A (potentiostated) and B (not potentiostated) are identical. On the return (cathodic) sweep the potential of pole B follows the potential of pole A until about 0.850 volts, at which time pole A has consumed all of the ozone formed during the anodic sweep and pole B maintains a potential corresponding to the oxygen rest potential. Thus at 69°C ozone diffuses across the gap and poises the potential of pole B. An identical experiment at room temperature gave similar results with the various regions shifted towards more positive potentials.

Discussion

The data support the conclusions stated in Chapter 4. They demonstrate the existence of two oxidized species of platinum on the surface, although the exact stoichoimetry is not yet known. Laitinen and Enke (2), as well as Feldberg (6), have postulated the existence of two oxides, but their conclusions were based on rate data and a number of assumptions, and are therefore open to question. It is difficult to rationalize the data presented here in any other terms, especially since the objections of Breiter (10) have been adequately dealt with.

The proof that a platinum electrode has on its surface a layer of oxide subsequent to an oxidation-reduction cycle necessarily leads to a reevaluation of the current theories of the nature of activation of platinum electrodes. Lingane (16) and Sawyer and Interanti (17) concluded that activation consists of covering the surface with oxide at least partially. The oxide acts as an "electron bridge" and effectively catalyzes the charge transfer reaction. Bockris and Huq (18) in their study of the oxygen evolution reaction found that a preanodization of their platinum electrodes was necessary to obtain "normal" Tafel slopes, yet Rosenthal and Veselovsky (19) found the oxygen contained in the oxide is not evolved. Hoare (21) concludes from a series of steady state polarization measurements that the enhanced reversibility is ascribable to oxygen dissolved in the Pt metal.

Anson (22) and King (23) concluded that activation is due to "platinization" of the surface by the oxidation and reduction process, and that the slow decay of the activated state is due to recrystallization of the surface. It is asserted by these workers that the "platinization" hypothesis is proven by the fact that a shiny platinum electrode resembles a platinized electrode after repeated cycling between the anodic and cathodic potential limits in 1F H_2SO_4. However, a shiny electrode is not visibly affected by a single oxidation and reduction cycle, yet the effect of a single cycle on the apparent reversibility of many electrode reactions is striking. The data of Anson and King (23), who studied V(V) reduction in formal sulfuric acid at platinum electrodes is a good example. They state that the "reversibility" of the reduction was approximately the same whether they used an "activated" electrode or a heavily platinized, aged electrode of the same apparent area. They concluded that the activation is due to surface roughening by the oxidation. This conclusion, however, is very difficult to reconcile with their data.

They show cathodic chronopotentiograms for V(V) reduction (curves 2 and 4, ref. 22b), one of which is taken on an "activated" electrode, the other on an electrode platinized in chloroplatinate solution. It is alleged that these show "small morphological differences". This is not borne out by the traces shown. The reduction on the platinized electrode commences fully 150 mV more positive and the transition time is $1\frac{1}{2}$ times as long as on the "activated" electrode. It is not clear that these two waves are in any way similar. They both show more reversible behavior; however, this is not identical behavior. Further, they show that an "activated" electrode loses its activity by sitting in a solution of supporting electrolyte for an extended period of time, or if it is immersed in hot hydrochloric acid.

It is suggested that the primary cause of "activation" is the inactive Pt(IV) on the electrode. Roughening of the surface undoubtedly occurs; however, all the data available indicates that loss of activity and decomposition or removal of the inactive oxide correlate. Further, it is difficult to rationalize similar behavior for a heavily platinized, black, electrode and a shiny electrode based upon fine particles of "catalytic" behavior without visible alteration of the surface.

In a recent communication, Breiter (24) claims to have "proven" that activation consists of oxidatively removing adsorbed organic impurities from the surface of the electrode. However, his data is based only on a study of the ratio Q_a/Q_c as a function of the number of potentiostatic sweep cycles, the general shape of the curves and the double layer capacity. He further concludes that it is these impurities that cause the discrepancy between Q_a/Q_c. None of the data he reports contradicts the conclusions we have reached, however, our data does not fit the theory that adsorbed impurities are the cause of the slow passivation of the electrode. The data of King (23) is also incompatible with such a theory as the heavily platinized electrode would surely have adsorbed organic impurities as readily as a shiny electrode and would thus have been affected and deactivated.

The conclusions reached do make consistent the data of Bockris and Wroblowa (25), who report data for the oxygen electrode potential which can be made consistent only if they assume a mixed potential, one of the reactions involving hydrogen peroxide. They note:

> "Quantitative consideration is successful in bringing consistence into the data except the vital one of the origin of the necessary H_2O_2. Thus, this must arise from some unsuspected reaction ..."

The decomposition of the Pt(IV) oxide which must be on the electrode at the reversible oxygen potential, as they find it necessary to "activate", is a good source of the peroxide these workers sought; especially as they note that the concentration of the peroxide would be micromolar to account for the potentials measured.

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CHAPTER 4

CONCLUSIONS CONCERNING THE NATURE OF THE OXIDE FORMED ON PLATINUM ELECTRODES IN OXYACID SOLUTION

The general conclusions of the work performed on the platinum oxide problems are given below. These conclusions refer to a platinum electrode in a 1 F sulfuric acid electrolyte, except where noted. All potentials are referred to a saturated calomel electrode as measured and are not corrected for the very small junction potentials.

1) Two distinct oxides of platinum are formed on the surface when the electrode is brought to a potential of 1.2 volts. One oxide is easily reducible between 0.55 and 0.4 volts, the other is totally electro-inactive at all potentials positive of the hydrogen evolution reaction.

2. The electro-inactive species decomposes to give hydrogen peroxide and a free platinum site. This site is capable of being re-oxidized at 1.2 volts. It is this decomposition and subsequent oxidation that accounts for the small depolarization current that flows

at 1.2 volts. It is not established conclusively whether the decomposition product, H_2O_2, is also oxidized at this potential on an oxide covered surface at 1.2 volts.

3) The electro-active (reducible) species is an oxide of Pt(II). The electro-inactive species (irreducible) is an oxide of Pt(IV). The exact nature of these oxides is not known, but they are probably hydrated extensively. The electro-active species decomposes at a rate considerably slower than the electro-inactive species. The final product of the decomposition of the reducible is oxygen, but because of inevitable time lapses in the experiment, it was not possible to determine whether the oxide decomposes directly to oxygen

$$2PtO \longrightarrow 2Pt + O_2 \tag{4-1}$$

or whether it first dismutates

$$2PtO \longrightarrow Pt + PtO_2 \tag{4-2}$$

and then decomposes

$$PtO_2 + 2H_2O \longrightarrow Pt + 2H_2O_2 \tag{4-3}$$

4) No oxygen is evolved directly at potentials more cathodic than 1.2 volts. The product of the electrochemical reduction of the electro-active oxide species is H_2O, not hydrogen peroxide.

5) The disparity between Q_a and Q_c is due to the simultaneous formation of oxides of Pt(II) and Pt(IV) when the electrode is oxidized, and the subsequent reduction of only the Pt(II) oxide. The rate of formation of the Pt(IV) oxide appears to be slower than that of the Pt(II) oxide.

6) Elevated temperatures accelerate the decomposition reactions. A "standard" platinum electrode surface which is free of oxides can be obtained by immersing the electrode in 1 F H_2SO_4 at approximately 100°C for about five minutes.

7) "Activation" of the platinum electrode consists of covering the surface, at least, partially, with electro-inactive Pt(IV). The slow deactivation is due to decomposition of this oxide. This conclusion is based on the correlation of the pretreatment used by other workers to obtain reversible behaviour and the presence of oxide after such

treatment as shown in this work. It is recognized that roughening of the surface takes place simultaneously.

8) Ozone is evolved at potentials more anodic than 1.3 volts. The ozone is reduced at about 1.1 volts to form oxygen.

CHAPTER 5

ELECTROCHEMICAL INSTRUMENTATION - BASIC ANALOG CIRCUITS

Although the primary goal of this research has been to elucidate the nature and characteristics of the platinum oxide film, a considerable amount of time and effort has been expended in developing suitable instrumentation necessary to control potential and current and to measure the various parameters both for the work described in the previous chapters and for a variety of other problems. This chapter presents innovations and theory necessary to deal suitably with the various instrumental problems encountered in electrochemical procedures.

The material presented is not novel and can be obtained from a number of articles and texts. The following chapter is presented in the interest of completeness and to present in one place that portion required for electrochemical instrumentation. References to the literature covering the material covered are given at the end of Chapter 6 (page 165).

An ideal potentiostat is a device which can control the potential between two electrodes regardless of the current flowing through the cell; it being assumed that one of the two is at thermodynamic equilibrium at all times, and that the other is polarizable to a greater or lesser extent. Such a definition implies the use of three electrodes; one the polarizable or "indicator" electrode, the second the reference electrode, and the third the "counter" electrode. This requirement is due to the fact that there is in reality no unpolarizable reference electrode and therefore such an electrode is used as the basis for potential measurements, but little or no net current is allowed to flow through it.

A suitable model or analog equivalent circuit representation for the indicator electrode is shown in Figure 5-1. The capacitor represents the double layer at the solution-metal interface and the resistor represents the effective resistance presented by the faradaic charge transfer reaction. The potential measured is effectively the potential difference across the capacitor. A more realistic model

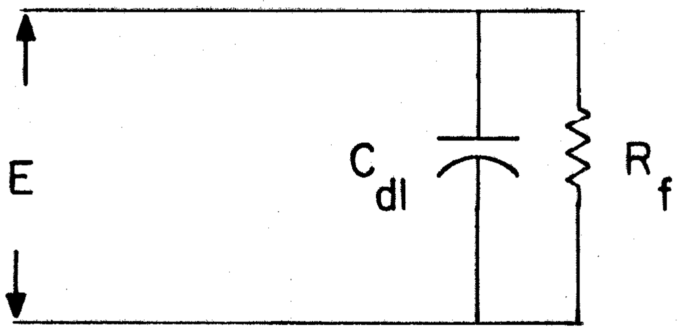


Figure 5-1. Idealized electrical analog representation of a polarizeable electrode. The faradaic impedance shown as R_f, the double layer capacitance as C_{dl}.

would include the fact that there is a finite solution resistance which is included in any measured potential when a net current flows through the indicator electrode. The analog representation of such a system is shown in Figure 5-2. A suitable operational analog for a three electrode system is given in Figure 5-3. $R_c + R_u$ is the effective electrolyte resistance between the counter and the indicator electrodes R_u is the effective resistance between reference and indicator electrodes, R_r is the resistance of the reference electrode assembly, R_f is the faradaic impedance, and C_{dl} is the double layer capacitance.

For the purpose of this discussion the faradaic impedance is shown as a pure resistive element. This is a matter of convenience as it is well known that a complete model of the impedance would have capacitative components. The analogs described, however, are quite adequate for the purpose of the discussion.

Referring to Figure 5-4, the ideal potentiostat holds E_t, the "true" potential across the indicator electrode at a predetermined value independent of counter electrode potential. In addition to

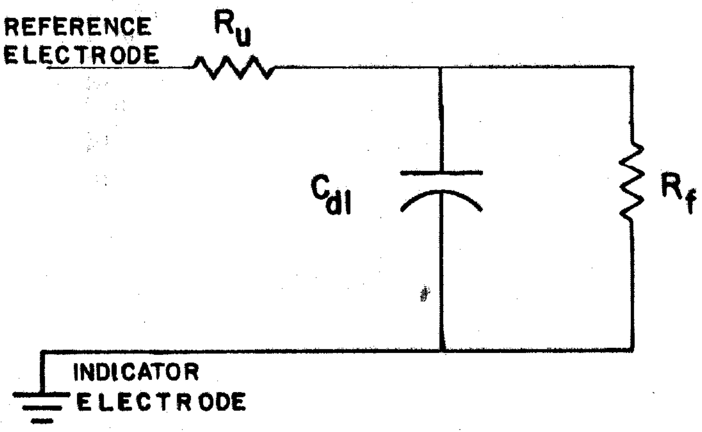


Figure 5-2. Working electrical analog representation of a polarizeable electrode.

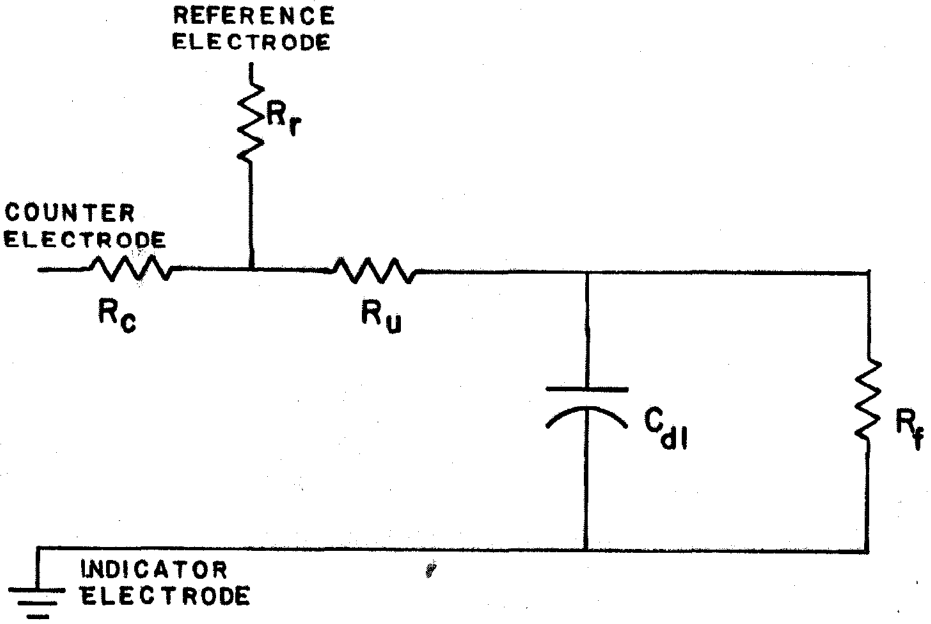


Figure 5-3. Electrical analog representation of a three electrode system.

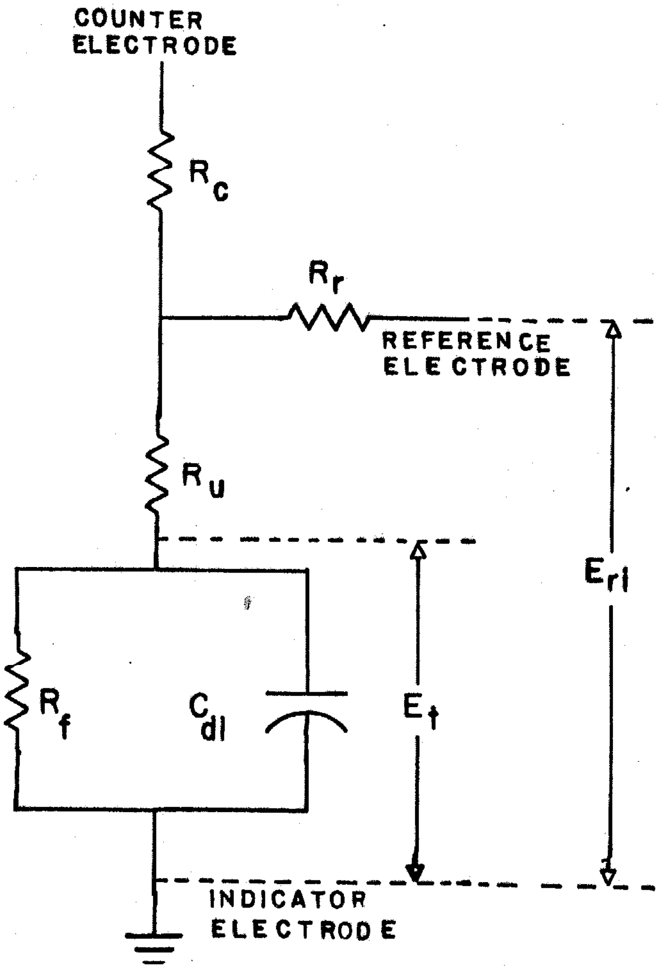


Figure 5-4. Potentials as measured and as desired in a real system. E_{ri} is the measured potential, E_t is the "true" potential of the indicator electrode with respect to the reference electrode.

this "ideal" potentiostat one must also have the capability of measuring the net current passing through the indicator electrode without disturbing the potential.

In developing a working, efficient potentiostat extensive use has been made of operational amplifiers. These devices, shown symbolized in Figure 5-5, can be considered as black boxes whose transfer function is given by

$$e_0 = G(e_1 - e_2) \tag{5-1}$$

The primary distinguishing feature of the operational amplifier is that G, the open loop gain, is a very large number, usually 10^7 and not lower than 10^5 for the systems being discussed. Such devices have been commercially available since the middle of the 1940's and have been used in electrochemical instrumentation since 1957. However, a thorough <u>operational</u> analysis of a total electrochemical instrumentation system has not been made, nor is there in the literature a complete description of a working system. In the discussion and description given, a majority of the detail is not new. However,

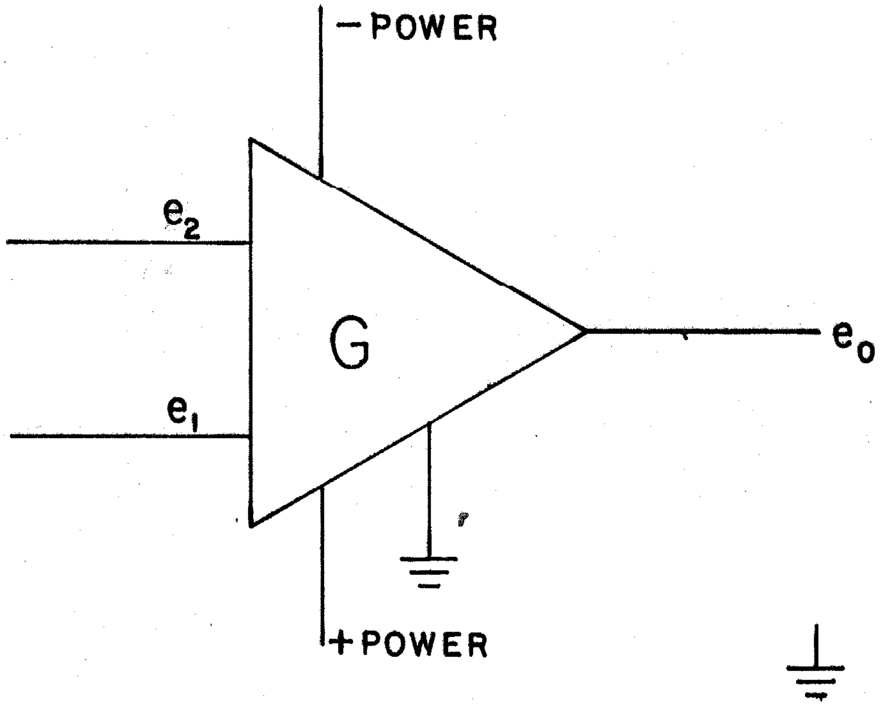


Figure 5-5. Operational amplifier "black box" representation.

the total integrated system and the instrument that has evolved is considered a novel contribution.

Referring to Figure 5-6, since $e_1 = 0$, we have

$$e_o = -G\, e_2 \tag{5-2}$$

We assume that the input impedance at the amplifier terminal is very high. Also we make the assumption that R_u is zero and that $R_r << R_{fb}$. The first assumption is realistic in terms of modern equipment that is presently available where the input impedance is greater than 10^8 ohms; the second and third assumptions will be considered in detail below. Considering e_2 a nodal point we have the relation

$$i_{in} + i_{fb} = 0 \tag{5-3}$$

or

$$\frac{E_c - e_2}{R_{in}} = \frac{e_2 - E_{ri}}{R_{fb}} \tag{5-4}$$

If

$$R_{in} = R_{fb} \tag{5-5}$$

From (5-2) $e_2 \doteq \frac{-e_o}{G}$ and by substitution

$$\frac{-2e_o}{G} = E_{ri} + E_c \tag{5-6}$$

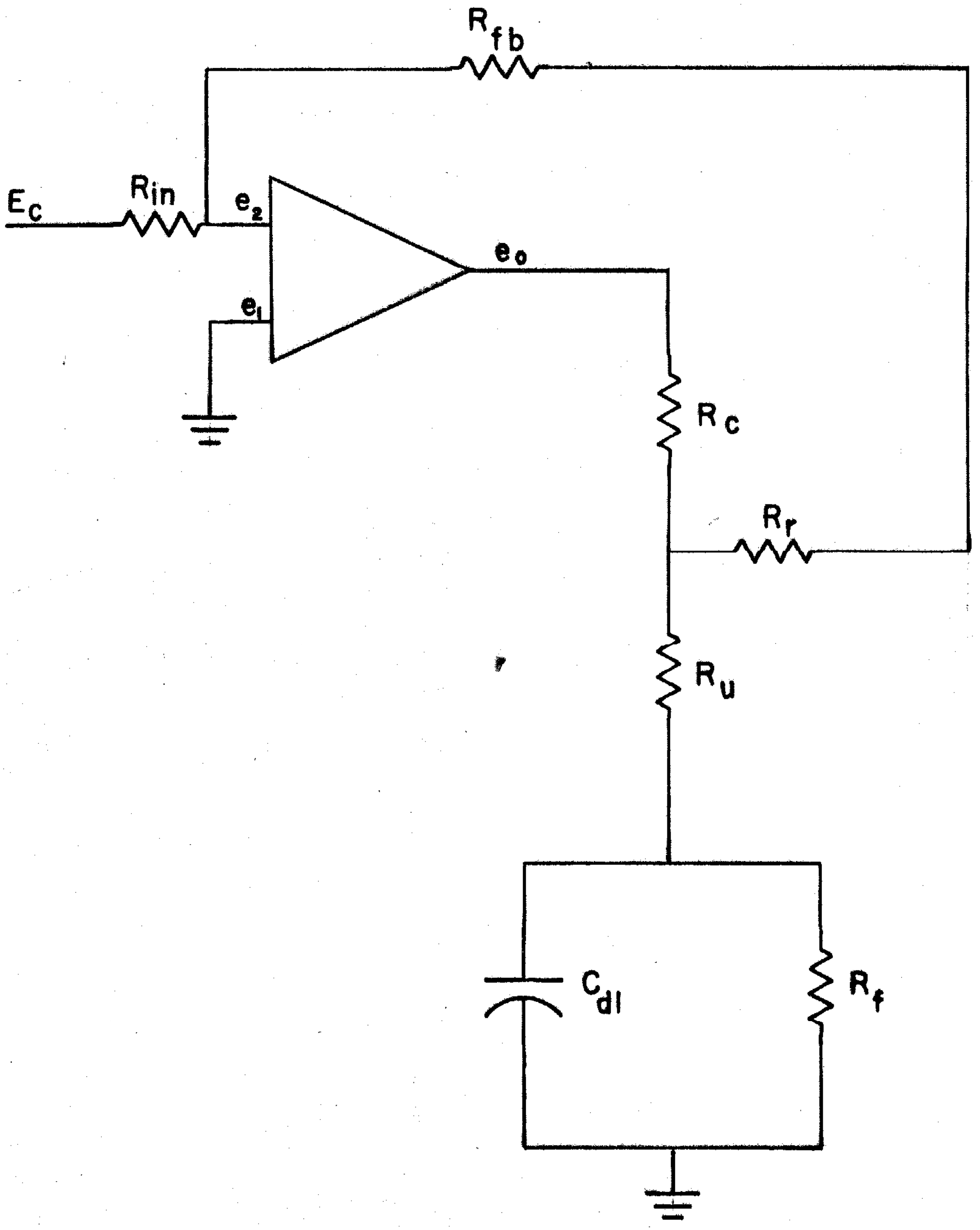


Figure 5-6. Simple potentiostat with an analog electrode as load.

but

$$E_{ri} = e_o - i_o R_c \qquad (5\text{-}7)$$

where i_o is the net current through the counter electrode and therefore

$$\frac{-2e_o}{G} = e_o - i_o R_c + E_c \qquad (5\text{-}8)$$

or

$$-e_o\left\{1 + \frac{2}{G}\right\} + i_o R_c = E_c \qquad (5\text{-}9)$$

Since $G \gg 2$ the approximation $\frac{2}{G} \approx 0$ is valid, and

$$-e_o + i_o R_c = -E_{ri} = E_c \qquad (5\text{-}10)$$

Equation (5-10) indicates that within the approximations and assumptions made, the circuit will hold E_{ri} at the value $-E_c$ independent of the current flowing through the circuit.

The assumption that $R_r \ll R_{fb}$ is not always valid. To overcome this problem we consider the circuit shown in Figure 5-7. Noting that $e_2 = e_o$ we rewrite equation (5-2)

$$e_o = G(e_1 - e_o) \qquad (5\text{-}11)$$

and again assuming that $1/G \approx 0$ we have

$$e_o = e_1 \qquad (5\text{-}12)$$

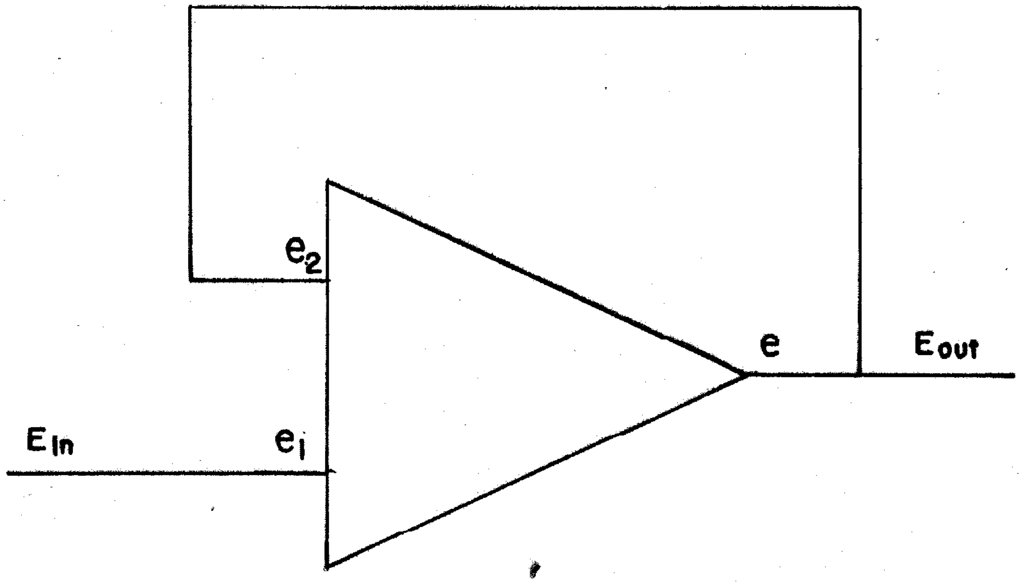
Since the input impedance at e_1 is very high and the output impedance is very low, the circuit acts as a unity gain impedance converter which can be inserted in series between the reference electrode and the feedback resistor which then "sees" a very low impedance unless, of course, the current output capability of the amplifier is exceeded. If this circuit is added to the potentiostat system in Figure 5-6, the assumption that the impedance of the reference electrode is very much less than the impedance of the feedback element is not necessary.

To measure the current use is made of the circuit shown in Figure 5-8. To analyze the circuit we apply Kirckhoff's law at the input

$$i_{in} = \frac{e_2 - e_o}{R_m} \qquad (5\text{-}13)$$

or

$$i_{in} R_m + e_o = e_2 \qquad (5\text{-}13a)$$



NOTE – HIGH Z INPUT
AMPLIFIER REQUIRED

Figure 5-7. High input, low output impedance converter with unity gain.

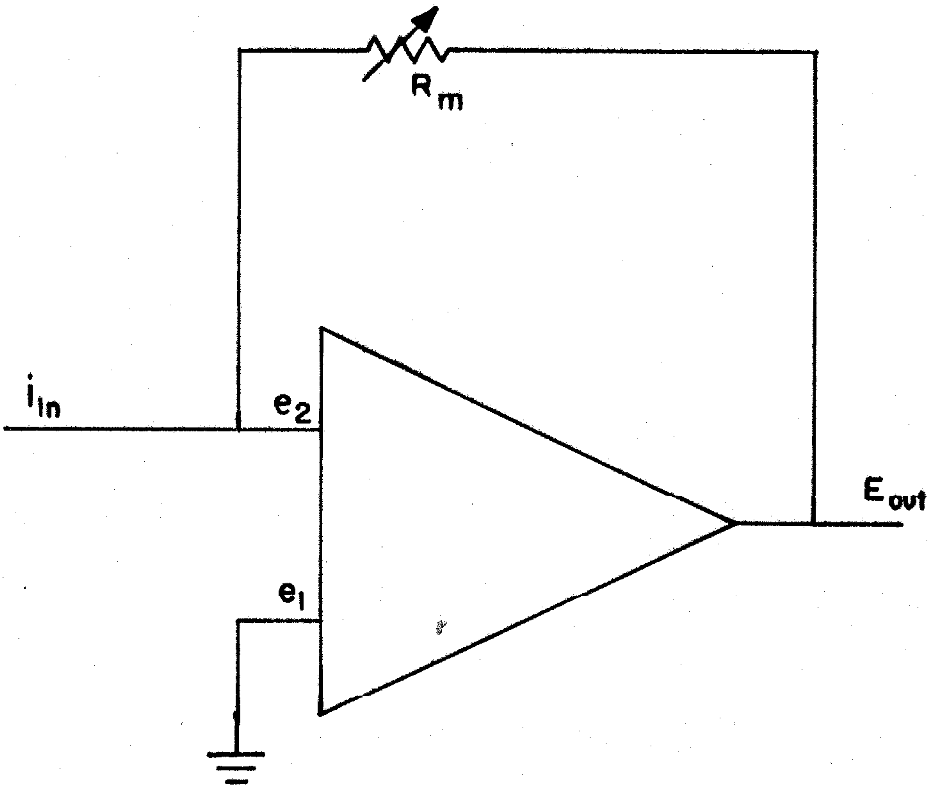


Figure 5-8. Current "follower" circuit.

Substituting this value of e_2 into the basic equation describing the operation of the operational amplifier (5-1) we obtain

$$e_o = G(e_1 - i_{in}R_m - e_o) \qquad (5\text{-}14)$$

or

$$e_o\left\{1 + \frac{1}{G}\right\} = e_1 - i_{in}R_m \qquad (5\text{-}15)$$

Since $e_1 = 0$ and $\frac{1}{G} \approx 0$, we obtain

$$e_o = -i_{in}R_m \qquad (5\text{-}16)$$

Further from equation (5-2)

$$e_1 - e_2 = \frac{e_o}{G} \qquad (5\text{-}17)$$

If the gain is greater than 10^7 volts/volt and the output is no greater than 10 volts, the largest value that $e_2 - e_1$ can achieve is one microvolt. Therefore, the terminal e_2 is a "virtual" ground and its effective input impedance to the current is a very good approximation to zero. This circuit is, therefore, a good current to voltage conversion device. In use, the input of this circuit is attached to the indicator electrode which is thus still tied to "ground" and the potential difference between reference and indicator electrodes can be measured without resorting to the use of differential amplifiers. It should be noted that this circuit requires that the amplifier be capable of delivering a current equal to the input current plus the current drawn by the voltage measuring device since the current drawn to the virtual ground through feedback resistor is precisely equal to the negative of the current coming to the input (from the indicator electrode). Figure 5-9 shows the addition of these two circuits to the circuit shown in Figure 5-6.

In all of the previous derivations it has been assumed that $R_u = 0$. That is, however, unrealistic. When current flows through the circuit the potential fed back is composed of two terms, E_{ir_u} and E_t and the relation obeyed by the potentiostatic circuit is

$$E_c = -E_{ri} = -E_t - i_0 R_u \tag{5-18}$$

Thus the true potential, which is the parameter that is supposed to be controlled is a function of the current. To correct this, a signal proportional to $i_0 R_u$ must be added to the control signal. In effect a positive (regenerative) feedback system is required. Two schemes have

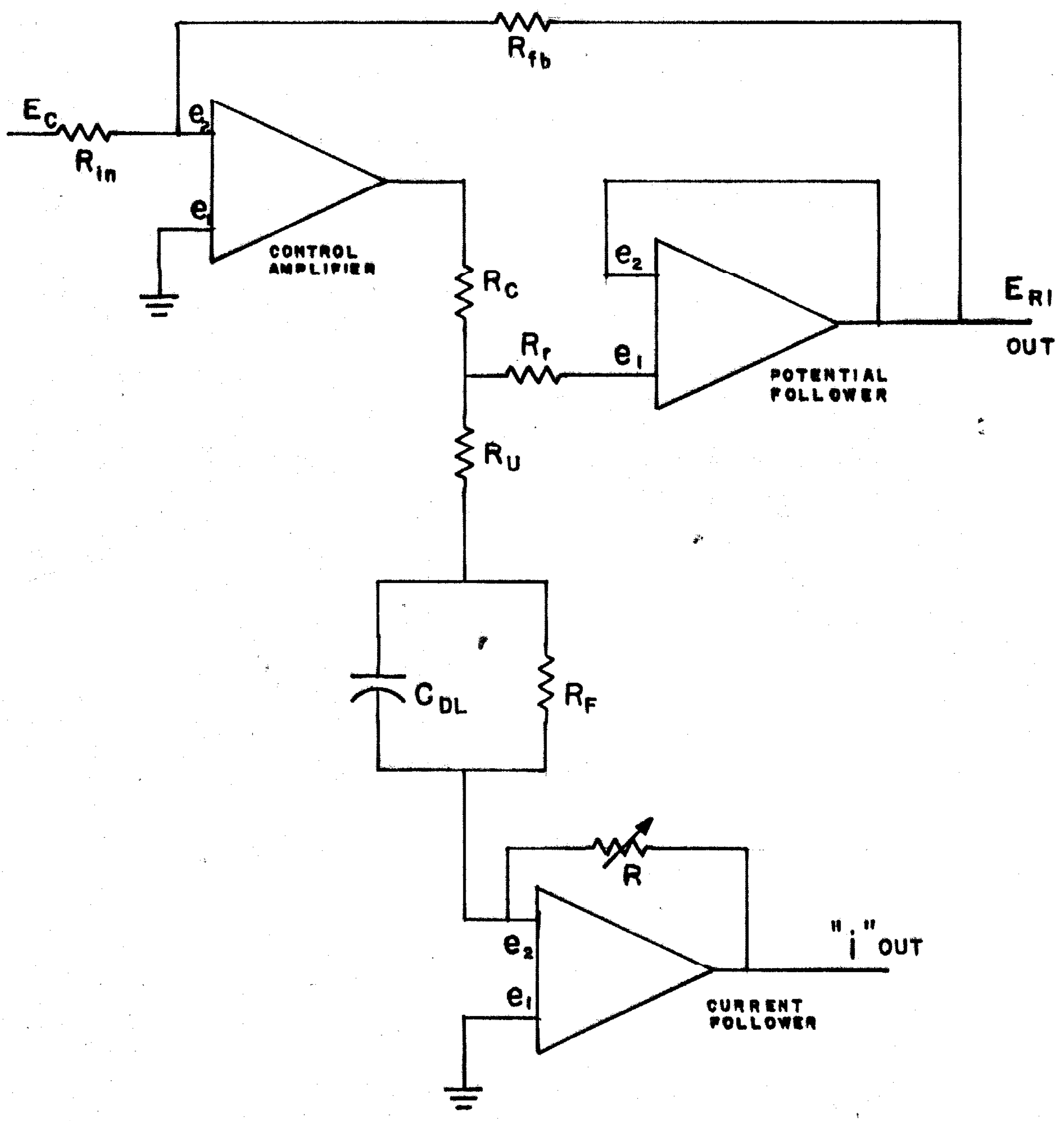


Figure 5-9. Uncompensated working potentiostat circuit with analog electrode system as load.

been devised, their relative merits will be discussed later.

Figure 5-10 shows the circuit of the scheme which has been most thoroughly tested. If we consider amplifier A4 in the figure, a simple analysis shows that if the input and feedback resistors, R_1 and R_2, are of equal value than $e_{out} = -E_{in}$. Analysis for the transfer characteristics of amplifiers A2 and A3 have been given above. Considering then, the control amplifier A1 output, e_o is given as before by

$$e_{01} = G(e_{11} - e_{21}) \tag{5-19}$$

The potential, e_{21} is obtained by summing the currents at the nodal point to zero

$$E_c - e_{21} = e_{21} - (e_{01} - i_o R_c) = e_{21} - E_{ri} \tag{5-20}$$

and

$$e_{01} = \frac{E_c + e_{01} + i_o R_c}{2} \tag{5-21}$$

We define β as $R_a/(R_a + R_b)$, that is the fraction of the potentiometer setting. The output at amplifier A3 is $-iR_m$ and the output at amplifier A4 is iR_m, therefore

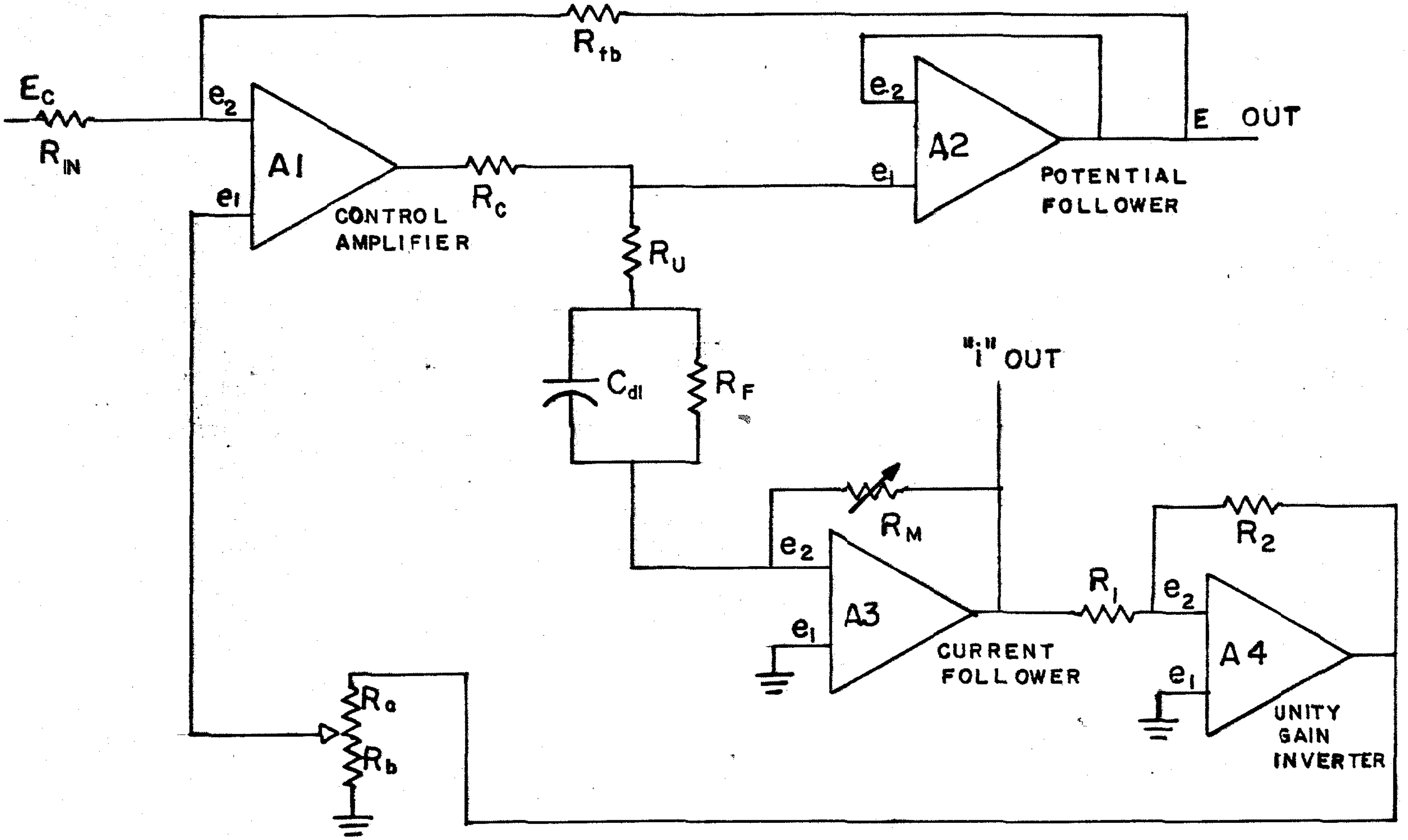


Figure 5-10. A compensated potentiostat using a differential input control amplifier.

$$e_{11} = \beta i_o R_m \tag{5-22}$$

Substituting equations (5-20) and (5-22) into (5-19) we obtain

$$e_{01} = G_1 \left\{ \beta i_o R_m - \frac{(E_c + e_{01} - i_o R_c)}{2} \right\} \tag{5-23}$$

which can be rearranged to give

$$e_{01} \left\{ 1 + \frac{2}{G} \right\} = 2 i_o R_c + \beta i_o R_m - E_c \tag{5-24}$$

and since $\frac{2}{G} \approx 0$ equation (5-24) reduces to

$$-E_c = e_{01} - i_o R_c - 2\beta i_o R_m \tag{5-25}$$

Since

$$e_{01} - i_o R_c = E_{ri} = E_t + i_o R_u \tag{5-26}$$

we can substitute

$$-E_c = E_t + i_o(R_u - 2\beta R_m) \tag{5-27}$$

and if β is chosen such that

$$\beta = \frac{R_u}{2R_m} \tag{5-28}$$

then

$$-E_c = E_t \tag{5-29}$$

That is the "true" potential of the electrode is held at E_c (the negative of this value) independent of the net current flowing through the cell. In theory we thus have an ideal potentiostat.

In a number of the techniques used in electrochemistry the parameter of interest is the net charge passed through the indicator electrode rather than the current. It is always possible, although not necessarily desirable, to determine the current as a function of time and then integrate it graphically or numerically. A more convenient and practical way is by use of operational amplifiers. The circuit for an operational integrator is shown in Figure 5-11. Using Kirckhoff's law

$$\frac{E_{in} - e_2}{R} = i_c \qquad (5\text{-}30)$$

where i_c is the current through the capacitor, given by

$$i_c = C\,\frac{d(e_2 - e_0)}{dt} \qquad (5\text{-}31)$$

Equation (5-30) can be rewritten as

$$\frac{E_{in} - e_2}{R} = C\,\frac{d(e_2 - e_0)}{dt} \qquad (5\text{-}32)$$

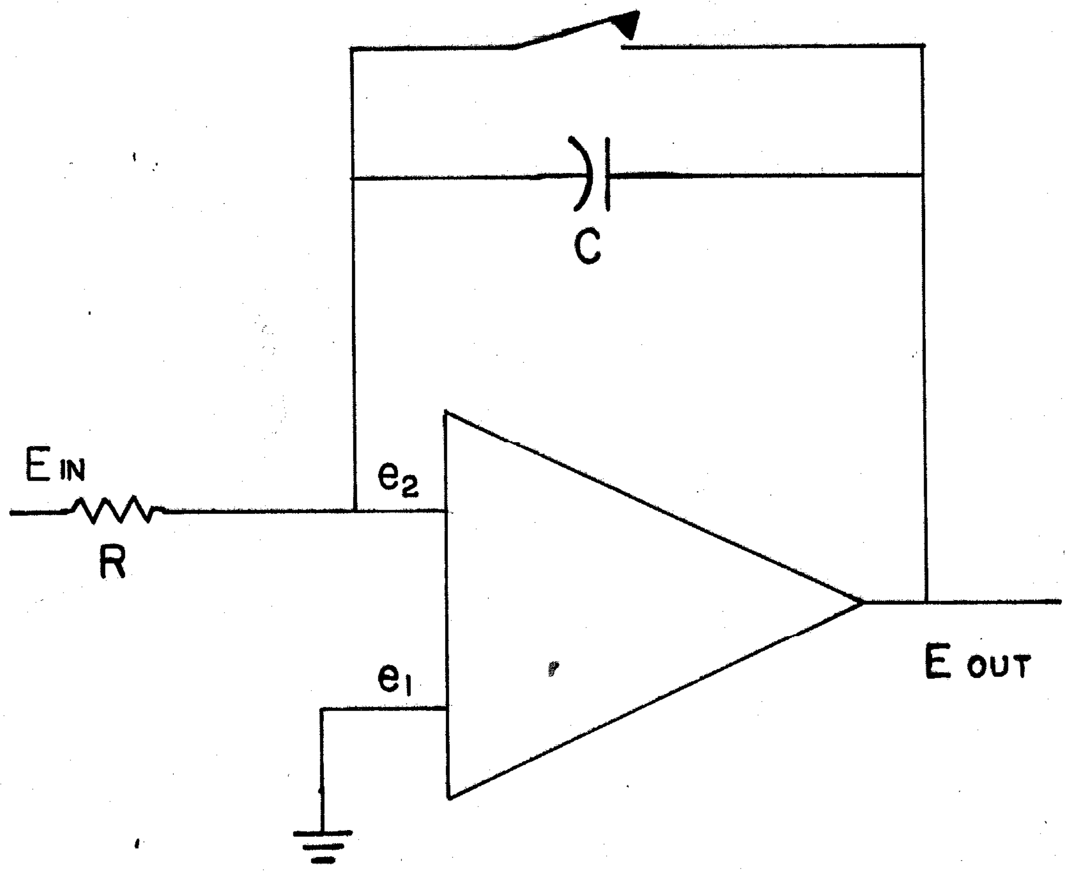


Figure 5-11. Operational Amplifier integrator circuit.

and equation (5-30) can be rewritten

$$\frac{E_{in} + \frac{e_o}{G}}{R} = C \frac{d\left\{\frac{-e_o}{G} + e_o\right\}}{dt} \tag{5-33}$$

or

$$\frac{E_{in} + \frac{e_o}{G}}{RC} = -\left\{1 + \frac{1}{G}\right\} \frac{de_o}{dt} \tag{5-33a}$$

Since $\frac{1}{G} \approx 0$ this reduces to

$$\frac{E_{in}}{R} = -C\frac{de_o}{dt} \tag{5-34}$$

Seperating the variables and integrating from 0 to t and from

$e_o = 0$ to $e_o = e_o(t)$ we form

$$e_o(t) = -\frac{1}{RC}\int E_{in}dt \tag{5-35}$$

Therefore, the output voltage is the integral over t of the input voltage times an arbitrary scale factor. If the input is a signal proportional to the current, the output is a signal proportional to the net charge passed over the time period betwen 0 and t. The t = 0 point is operationally defined as the time when a short across the capacitor is opened. If E_{in} is a constant

$$e = -\frac{E_{in}}{RC}\ \text{V/second} \qquad (5\text{-}36)$$

then the operational integrator is a good linear voltage ramp generator.

In a number of electrochemical procedures it is desirable to control the current passed through the cell, rather than the potential between the electrodes. Operational amplifiers lend themselves quite well to this task. The basic circuit is shown in Figure 5-12, where the electrical analog to the three electrode systems is again used.

Referring to Figure 5-12, amplifiers A2 and A3 are wired as amplifiers A3 and A4 respectively, in Figure 5-10. The output of amplifier A3 is given by $e_{o3} = i_{net}R_m$.

Considering amplifier A1, the Kirckhoff's law equation for the sum of the currents is

$$\frac{E_c - e_2}{R_{in}} = \frac{e_2 - i_o R_m}{R_{fb}} \qquad (5\text{-}37)$$

and assuming that $R_{fb} = R_{in}$

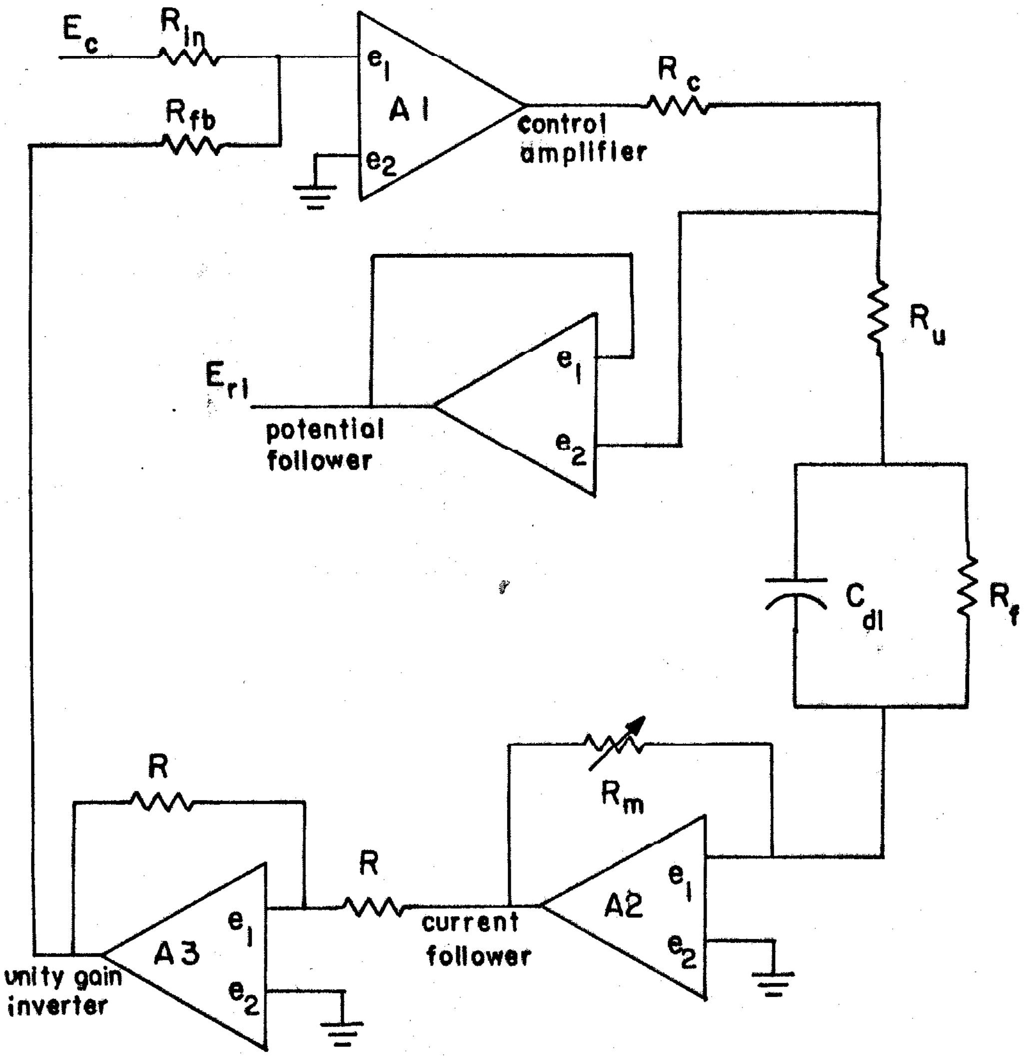
$$e_2 = \frac{E_c + iR_m}{2} \tag{5-38}$$

and since $\frac{1}{G} \doteq 0$, we have

$$i\,R_m = -E_c \tag{5-39}$$

Therefore the current through the indicator electrode is a function only of the control voltage; in effect the output of the control amplifiers, A_1, appears as a very high impedance source. This is true even if the reference electrode draws a finite amount of current.

It should be noted that the primary difference between potentiostatics, (potential control) and galvanostatics (current control) is the signal being fed back to the control amplifier. In principle it is possible to feed back any signal as long as that signal is a (single valued) positive function of the output voltage, e_o. However, if the feedback elements become complex, the stability of the system becomes tenuous and the mathematics becomes intractable.



, Figure 5-12. Galvanostatic or "constant current" circuit using operational amplifiers as active elements.

CHAPTER 6

A MULTIPURPOSE ELECTROCHEMICAL INSTRUMENT*

The principles and the theory of the use of operational amplifiers as electrochemical control elements were discussed in Chapter 5. The applications and limitations of their use as well as the construction of a complete system will be discussed in this chapter.

Deviation From Ideality - In practical use the operational amplifier is, naturally, not an ideal device. The principal deviation from ideality is that the gain, G, is a function of the frequency of the signal. A typical plot of the open loop gain versus the frequency of the signal is given in Figure 6-1. The gain is fairly constant over a region of low frequencies and begins to decrease uniformly at some fixed frequency, the value of which is a function of the particular amplifier being considered. The slope is usually set at about 20 db per decade as it has been found that this figure leads to greatest stability in

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*A portion of the material covered in this chapter was presented at the Symposium on Electroanalytical Instrumentation at the Winter Meeting of the American Chemical Society, Phoenix, Arizona, January, 1966, and was published with Dr. R.A. Osteryoung in Analytical Chemistry, 38, 1106, (1966).

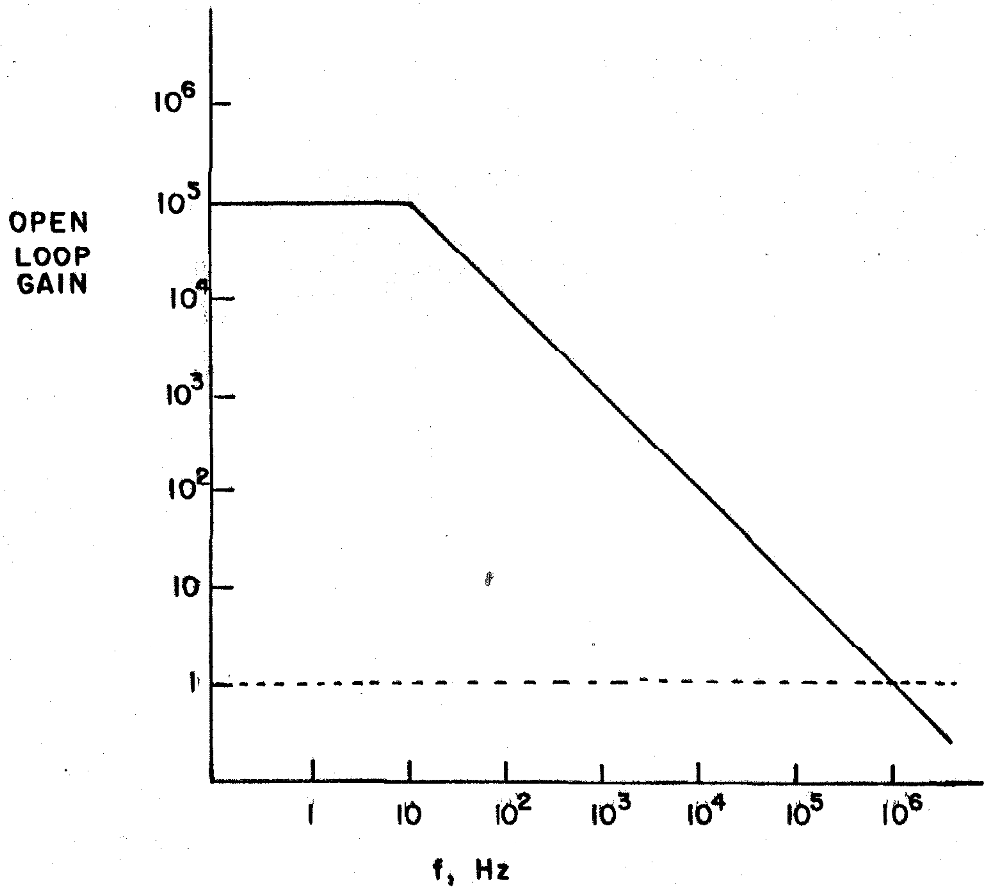


Figure 6-1. Typical operational amplifier open loop gain plotted as a function of the signal frequency.

most systems. The point where the gain crosses the zero db line is called the unity gain crossover point. If we consider a signal of frequency, f, at the unity gain crossover point passing through an inverter (A3 in Figure 5-10) the Kirchoff law equation would be

$$E_{in} - e_2 = e_2 - e_o \tag{6-1}$$

and equation (5-2) would be transformed to

$$e_o = -e_2 \tag{6-2}$$

and making the appropriate substitution we obtain

$$e_o = -1/3\,E_{in} \tag{6-3}$$

It is thus clear that the amplifier is not useful at such a frequency. Further, if a gain greater than unity is desired the maximum frequency that can be passed is considerably less than that at unity gain. It is not implied that even for a unity gain inverter can one approach the crossover frequency, as the basic assumption made in all the derivations is; that the open loop gain is much greater than one and its reciprocal can be neglected. This may not be the case at even relatively low frequencies with some amplifiers.

Noise - Noise generated throughout the system is also a major problem. The noise is generated by three sources; a) Johnson or thermal noise, b) ground loop currents, and c) electromagnetic pickup from the environment. In practice the latter two sources are usually sufficiently large to swamp the thermal noise. This is, however, not true if the feedback or input-impedances are very large, if very high gain is desired from a single stage of amplification, or if the output is sampled in such a manner as to be in synchronization with the other noise components.

Ground loop currents can become very serious if great care is not taken to assure that all ground lines are brought in parallel to a single point. This can become critical when the positive input of an amplifier is grounded, as the output of all operational amplifiers is always proportional to the difference between inputs. As all the lines have a distributed capacitance and inductance and a very low resistance, large amplitude oscillations can develop at resonant frequencies of the lines of the ground circuits. These ground loops are then amplified by the operational amplifiers and the whole system will appear to be out of control.

Electromagnetic pickup can usually be minimized by careful construction of the critical circuits. All the summing points of the amplifiers should be well shielded. The impedance between the summing point and any line connected directly to it is very low; any currents induced in such a line, however, will be amplified and appear as voltages at the output, therefore the input and feedback resistors should be connected as close to the summing point as possible, and then be shielded.

After due regard to careful construction, the inevitable high frequency noise can be removed to a greater or lesser degree by insertion of capacitance in parallel to the feedback resistors. Referring to the generalized inverter circuit shown in Figure 6-2, it can be readily shown, using the same approach as in Chapter 5, that

$$e = -\left\{Z_f / Z_i\right\} E_{in} \tag{6-4}$$

within a factor of the reciprocal of the gain. If Z_f consists of a

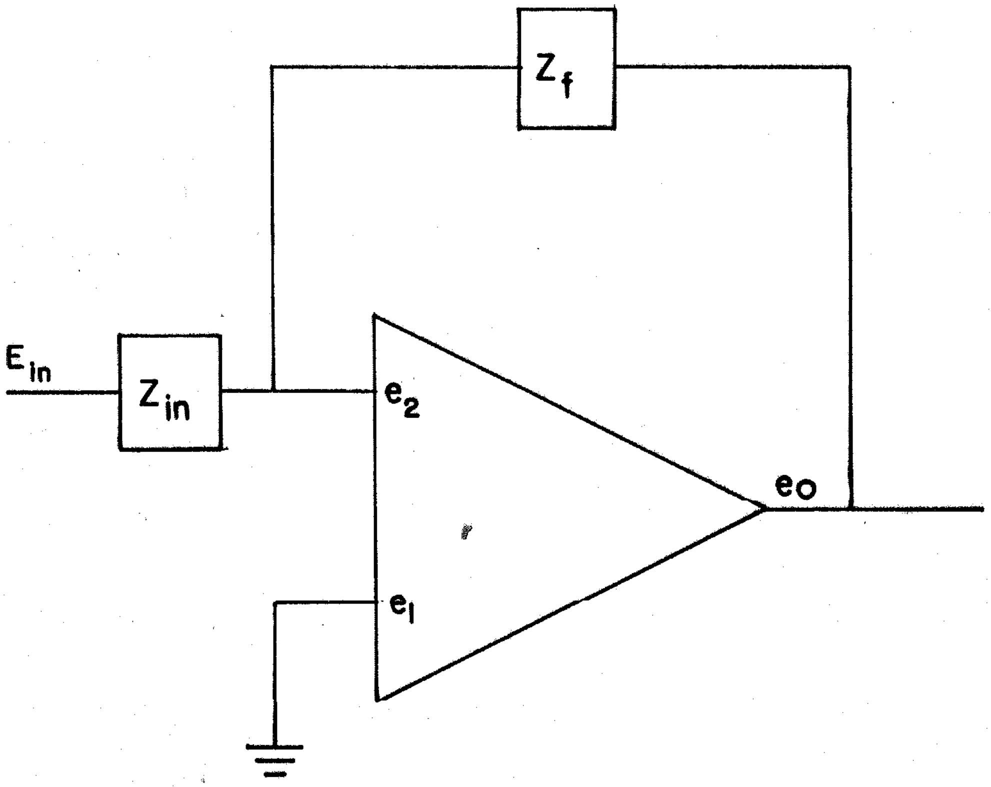


Figure 6-2. Generalized operational amplifier inverter.

resistor and capacitor in parallel, then the capacitor acts as a shunt for short duration spikes, or high frequency noise, and as an averaging circuit for low frequency noise. The capacitor, however, limits the gain at high frequencies; thus a trade-off between noise and high frequency performance is usually required.

Concepts of Instrumentation - A large number of techniques are presently in vogue for the study of electrode processess. It is not rare, but usually foolhardy, to rely completely on a single technique to obtain the experimental data; therefore it is necessary to design and construct the required instrumentation so as to afford a maximum of versatility. Three approaches to the problem are possible. The first is to use operational amplifiers built into boxes in such a manner that one can connect the various configurations together with patch cords. This method is straightforward and has the advantage that errors in conception are easily remedied. It has the drawback that for any sophisticated arrangement the patch cords resemble a rats nest, with noise problems becoming a major nuisance.

The second method is to house the amplifiers in one box to which a standard "function" module, in which the circuits for the particular technique are built, is connected.

The third method is to build into one cabinet all the primary circuits and provide some means to switch the various control elements into the standard configurations. The latter approach is more economical of parts and labor, in that many circuits can be utilized for all the techniques. Also the entire electronic assembly can be well shielded within a single enclosure. This approach was used in designing a general purpose instrument.

Design Criteria - The newer electrochemical techniques are usually short duration pulse or relaxation methods where timing and amplitude of the control signals is the major instrumental concern. However, any attempt to make provisions for all combinations of pulse amplitude and duration is not practical; also this leaves no provision for future requirements.

The general requirements for the instrument therefore called for ease of manipulation and variation of control. The design followed, to a greater or lesser extent, the following required capabilities and criteria:

1) Fast rise potentiostat.

2) Stable galvanostat.

3) Voltage sweep capability.

4) Current measurement and integration of current capability.

5) Remote operation.

6) Low noise level.

7) Ease of maintenance.

A block diagram of the instrument is shown in Figure 6-3. The control amplifier serves either as the potentiostat or the galvanostat. The function circuits serve to feed the output either to a dummy load or to the cel.. The feedback circuits switch the signal being controlled back to the summing point of the control amplifier. The control voltage circuits allow three bias potentials and a sweep circuit to be algebraically added to form the control voltage (this is the negative of the output).

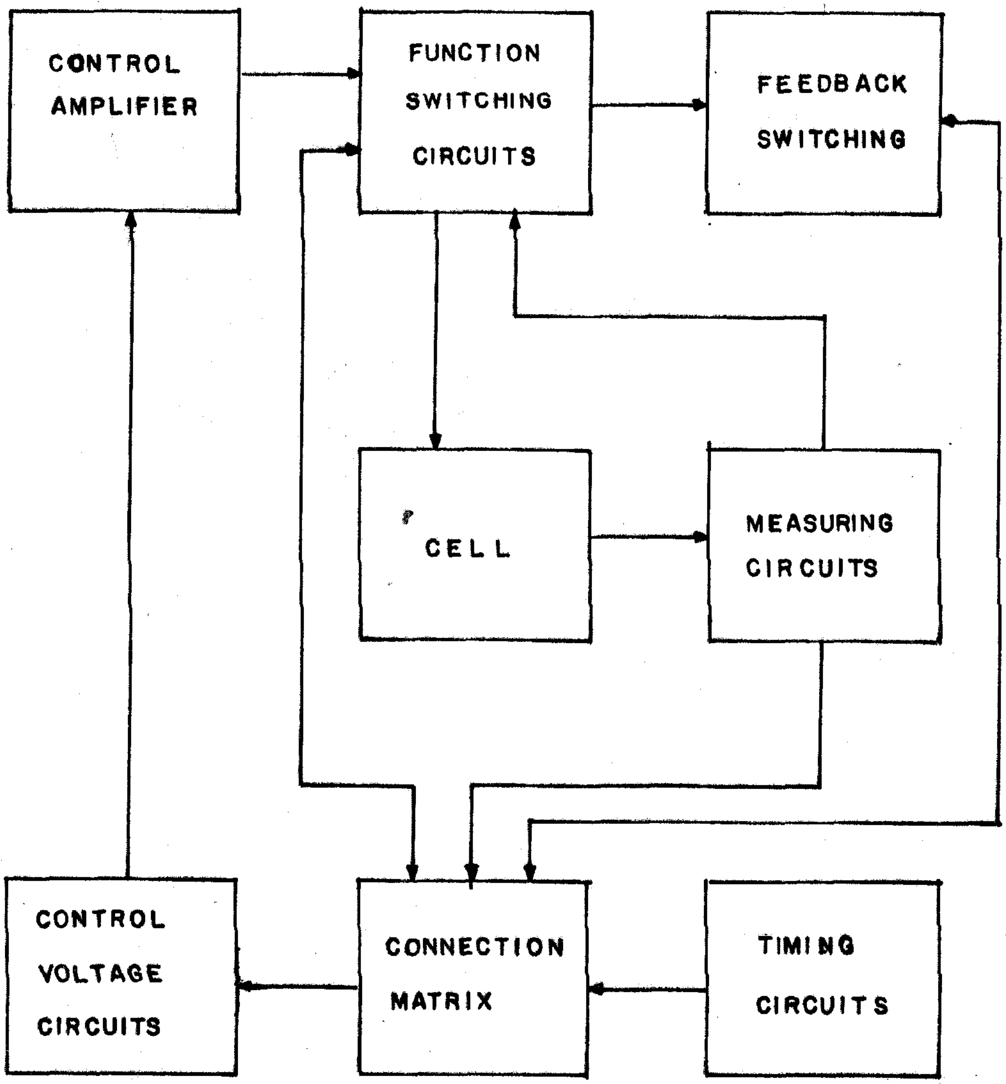


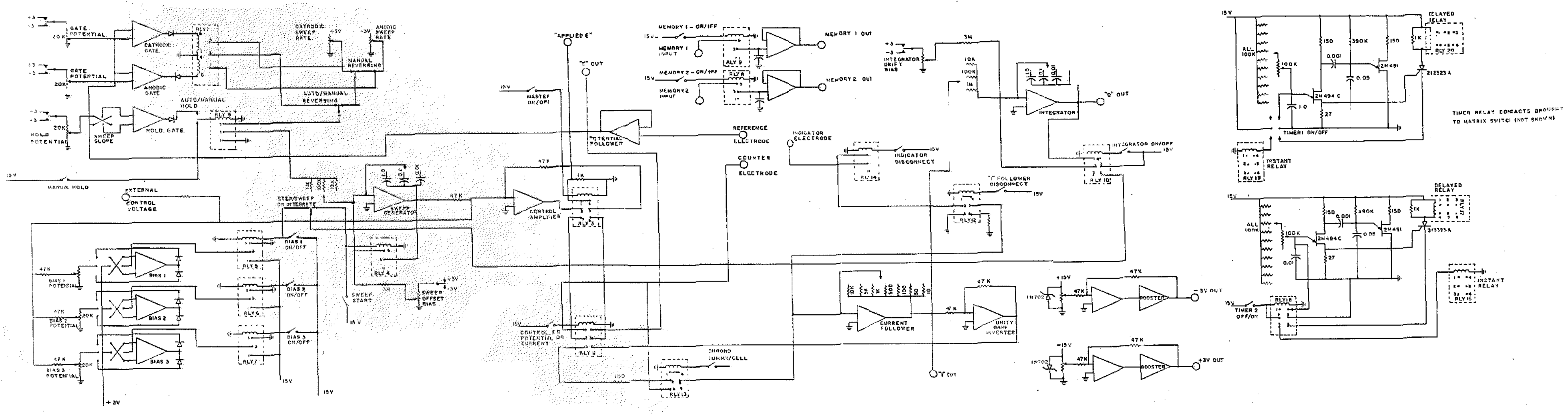
Figure 6-3. Functional block diagram of multipurpose electrochemical control instrument.

All the switching in the instrument is performed by mercury wetted relays. The inter-connection matrix allows the coils of the various relays to be connected in any desired pattern.

The philosophy of design throughout was on the basis that the actual potentials would be measured, rather than trusting the calibrated dial settings which are provided to give an indication of the setting. A complete circuit diagram is shown in Figure 6-4.

Primary Signal Circuits

The control amplifier is a high gain chopper stabilized type. (See Appendix for actual types used). The capacitor across the feedback resistor serves to limit the noise and is easily changed to suit the particular experimental conditions and requirements. The output goes to the "master" relay (RLY 3). This relay serves to shunt the output to a dummy resistor when the master is off. The drop across this dummy is also connected to the feedback so that the amplifier is always in a stable configuration. This voltage is also available as an output so that the potential to be applied can be set before power is actually ap-



TIMER RELAY CONTACTS BROUGHT TO MATRIX SWITCH (NOT SHOWN) plied to the system. Also any series of programmed potential changes can be observed without actually performing the experiment and fouling the electrode inadvertently. The normally open contacts of the master relay route the output of the control amplifier to the chrono/potstat (RLY 11). This relay serves two functions; 1) it switches the feedback from the output of the potential follower to the output of the unity gain inverter amplifier connected to the current follower amplifier, and 2) it switches the output from the control amplifier from the counter electrode (potentiostatic mode) to a chronopotentiometric switching circuit. The latter circuit switches (RLY 13) the current from a dummy load which bypasses the cell, to the cell itself.

Potential Output - The apparent potential between reference and indicator electrodes (E_{ri} in Chapter 5) is monitored by the potential follower. The input impedance at the e_1 input is very high (minimum of 10^8 ohms) and therefore reference electrodes with fairly high resistance salt bridges may be used without degradation of the potential signal or polarization of the reference electrode. However, it must be noted, that the signal sees an input to the base of a transistor, and therefore the input capacitance of the potential follower must be considered. This capacitance is on the order of 20 to 100 picofarads and must be charged through the reference electrode resistance. If this resistance is, for instance one megohm, there is an effective lag in the signal of about 3 time constants or at least 300 microseconds. Therefore, at best, a 3 KHz signal can be passed through the system with maintenance of control. Control being defined as when the input signal (control signal) is 180° out of phase with the potential of the electrode. When the phase between input and output become significantly greater or less than 180°, the equations developed in Chapter 5 do not apply any more. Thus a high impedance reference electrode can seriously impair the performance of the potentiostat in terms of its response characteristics.

<u>Indicator Disconnect</u> - In the potentiostatic mode it is the potential of the reference electrode that is being controlled with respect to ground, which is used as the signal reference potential. If the indicator

electrode is disconnected from ground no current will flow, however, the potentiostat is still operational as the reference electrode feeds back the potential. Relay 14 has been provided to disconnect the indicator electrode while in the potentiostatic mode; this feature is very convenient as it gives a means of zeroing any offsets in the current measuring and integrating amplifiers with the whole system on. In addition, the indicator electrode disconnect is useful as when doing potential step chronocoulometry and chronoamperometry in a poised system, where any currents due to slight potentiostatic offsets prior to the initiation of the experiment can seriously bias the results.

<u>Current Follower Disconnect</u> - The indicator electrode is connected to the current measuring amplifier through relay 12. This relay allows the electrode to be connected directly to ground if the current amplifier is not being used, this feature is also useful if the current measuring amplifier has been inadvertantly saturated as the summing point will not be at ground in such a condition, and this offset can seriously affect the electrode.

A choice of 7 precision film resistors for the current measuring amplifier feedback, Rm, is available on a rotary switch mounted on the control panel. It is of utmost importance that these resistors be non inductive, as an inductor in the feedback circuit acts as a differentiator with respect to the input signal. Any noise signals, fast rising spikes, etc. are amplified and the differentiated signal will tend to make the whole system oscillate.

The output of the current measuring amplifier is fed to the input of the integrator amplifier, and to the input of the unity gain inverter. The output of the inverter is used as the feedback signal when the instrument is in the galvanostatic mode.

In addition the output of the current measuring amplifier is fed to the "compensation" potentiometer. The slider of this potentiometer is then fed to a summing point resistor. This signal compensates for the resistance "seen" by the reference electrode. The circuit is analogous to that described in Chapter 5. However, in this case the signal has the same sign as the control voltage, and it can be demonstrated that if β is the fraction of the current signal feedback, the condition of compensation of R_u is

$$R_u = \beta R_m \tag{6-5}$$

rather than equation (5-28). In practice it has not been possible to totally "compensate" R_u without seriously affecting the response characteristics of the whole system. However, rise times as short as 20 Sec have been achieved using the circuit shown in Figure 5-10. The method used in the instrument described here, while in principle as good as the other, has not performed as well. The system shown in Figure 5-10 requires the use of a differential input control amplifier, these are invariably less stable with respect to drift, and have lower open loop gain than the single input (inverting) chopper stabilized types. It was felt that sacrifice of compensation characteristics was worth the vastly superior drift and gain.

The chopper stabilized amplifier is actually a combination of two amplifier stages. A modulator or chopper is inserted between the input and the first stage. The chopper applies, alternately, the signal and the reference potential (ground) to the first a.c. coupled stage. This effective a.c. signal is amplified further by the second stage, and is then demodulated, (with respect to ground) filtered and output. The output demodulation requires a rather large output capacitance. If the amplifier is driven out of control, the demodulating capacitor becomes excessively charged, and this excessive charge must "leak" off through the chopper. This causes the amplifier to "saturate" at full output, even though the control signal causing the excessive voltage excursion has long been removed. The saturated condition duration is a function of the length of the driving excursion, and times as long as ten minutes can be required before the amplifier becomes "operational" again.

The amplifier will also go into saturation for a long time if both positive and negative power are not simultaneously applied.

A number of methods have been developed to keep the amplifiers from saturating. However, these circuits all involve the use of breakdown or Zener diodes in parallel with the feedback impedance and invariably cause non linearities in the output. It was decided that non linearities would be a greater problem than saturation and therefore no fast recovery network was used for the chopper stabilized amplifiers.

Control Voltages

The instrument is required to perform a number of functions. These include polarography, chronopotentometry, potential sweep chronocoulometry, single and double potential step chronocoulometry, and oscillopolarography. A variety of control voltages at the input of the control amplifier are therefore required. These signals are added, algebraically, at the summing point of the control amplifier. The signals provided are three independent "bias" voltages and a linear voltage ramp. In addition a spare summing point resistor is brought to the front panel so that an external waveform generator may be used, if necessary.

One of the primary requirements on the design of the instrument was that no batteries be used, another was that all bias voltages be capable of being turned on in such a manner that no overshoot occur, and that the rise time be on the order of a few microseconds.

The basic switching circuitry of the bias circuits is shown in Figure 6-5. If e_1 is less than e_2, e_o is at the maximum negative value; anywhere from -10 to -12.5 volts depending on the individual amplifier. The diode at the output is backbiased and the effective output at the top of the potentiometer is zero.

When the switch is closed, e_1 becomes greater than e_2 and e_o goes from maximum negative output to maximum positive output, the value of which ranges from 10 to 12.5 volts. The rate dV/dt is a function of the quality of the amplifier. For practical purposes 10^6 volts per second is a reasonable slew rate. However, since the amplifier goes from a saturated condition into a saturated condition, the initial and final slopes are much less than this value. It should be noted that in the case of a differential non-chopper stabilized operational amplifier, the saturated condition refers only to the state of the output transistors, and not to the output capacity problem mentioned above. When the differential amplifier output transistor comes out of

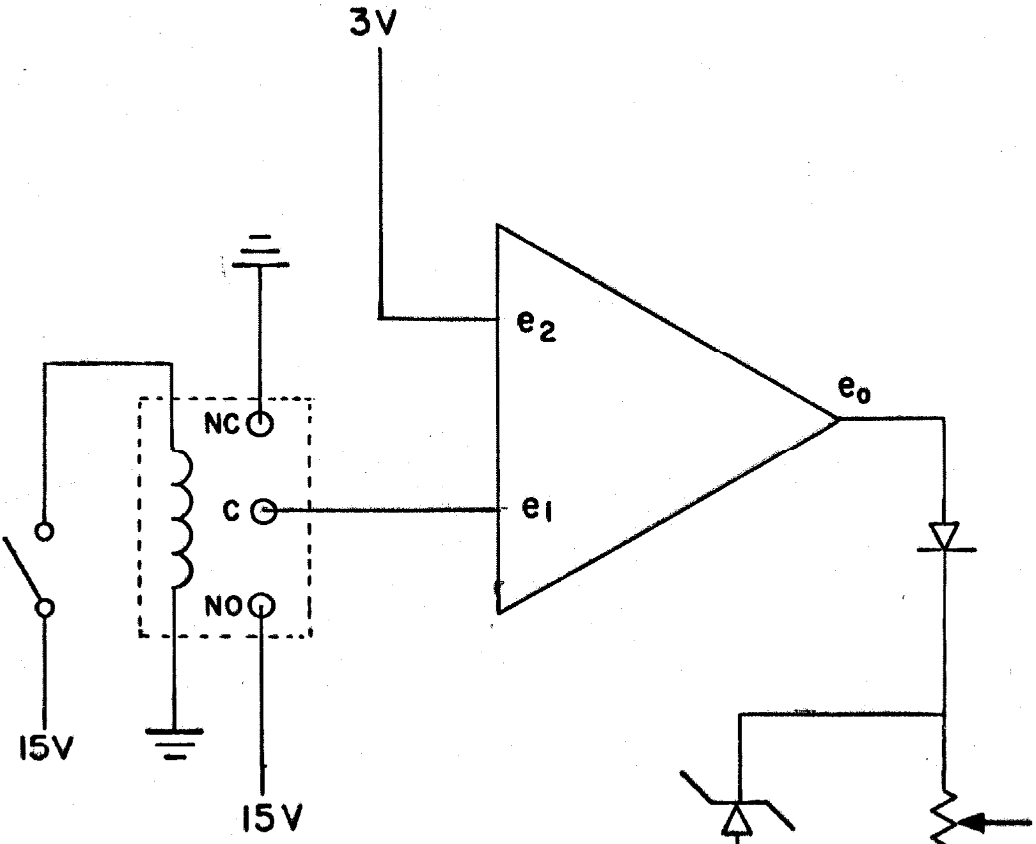


Figure 6-5. Basic switching circuit for bias potentials.

saturation a portion of the initial current must go to discharge the space charge capacitance of this transistor. Once this is accomplished the slew rate reaches its maximum value. Output stages could be designed which would overcome this problem, however, this is invariably at the expense of open loop high frequency response. A typical output is shown with the solid line of Figure 6-6. To overcome the problem of slow initial rise and indeterminacy of the final voltage, a zener diode is inserted between the output and ground, in effect cutting off the output signal very sharply at the zener breakdown voltage. The actual potential step applied at the summing point is shown by the broken line in Figure 6-6. The zener diode, in addition to providing a reproducible step potential, masks any overshoots which sometimes occur when the amplifier reaches its upper limiting voltage.

A totally different method could be envisioned for the application of the potential step. This would use relays only, as shown in Figure 6-7. The primary problem with such an arrangement is that ordinary relays bounce upon contact closure, giving an output as shown in

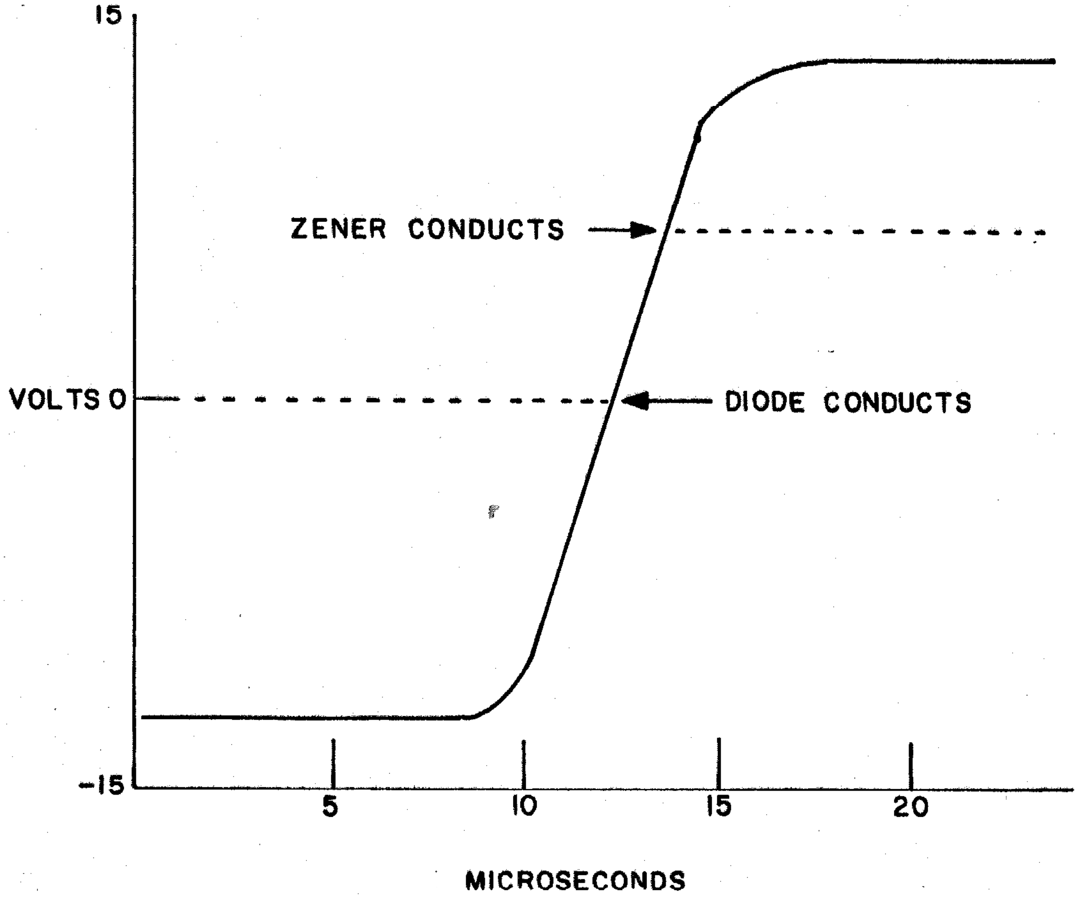


Figure 6-6. Bias amplifier output during switching.

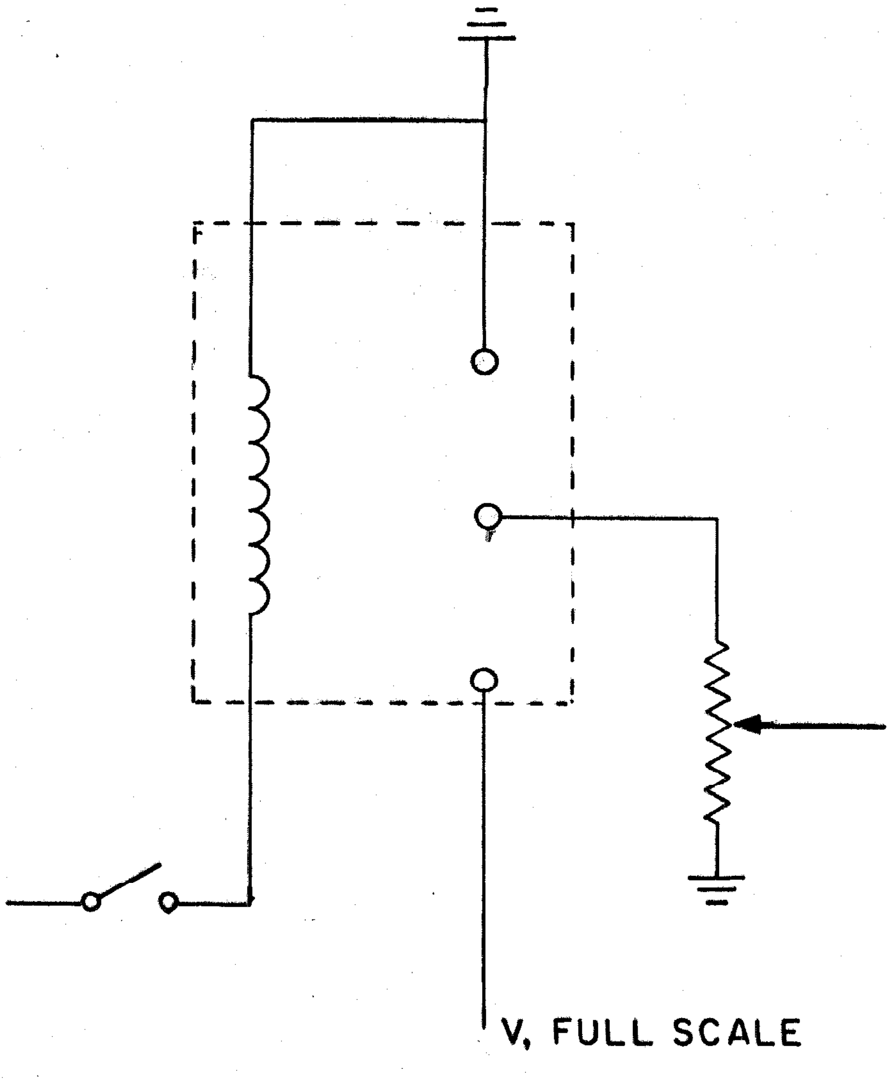


Figure 6-7. Relay method of switching bias potential into control circuit.

Figure 6-8. Mercury wetted reed relays have been extensively used to overcome this problem. However, these relays are constructed in such a manner that there is severe inductive coupling between the coil circuit and the controlled circuit. Such coupling is normally of no consequence, since the short duration voltage spikes generated have such low energy that most circuitry is not influenced. However, any voltage spike entering the control voltage circuit of the instrument under discussion can, and usually does, seriously affect the electrode.

Both positive and negative voltages are required in the bias circuits. To provide bipolar operation, a number of components were added to the basic circuit shown in Figure 6-5. The complete circuit is shown in Figure 6-9 as well as in Figure 6-4. The effect of the triple pole, double throw switch is to reverse the sense of all the voltages and devices, and therefore of the output of the circuit. A typical output at the control amplifier is shown in Figure 6-10.

The requirements on the linear voltage ramp voltages included a very wide degree of controllability of dV/dt, the capability of halting

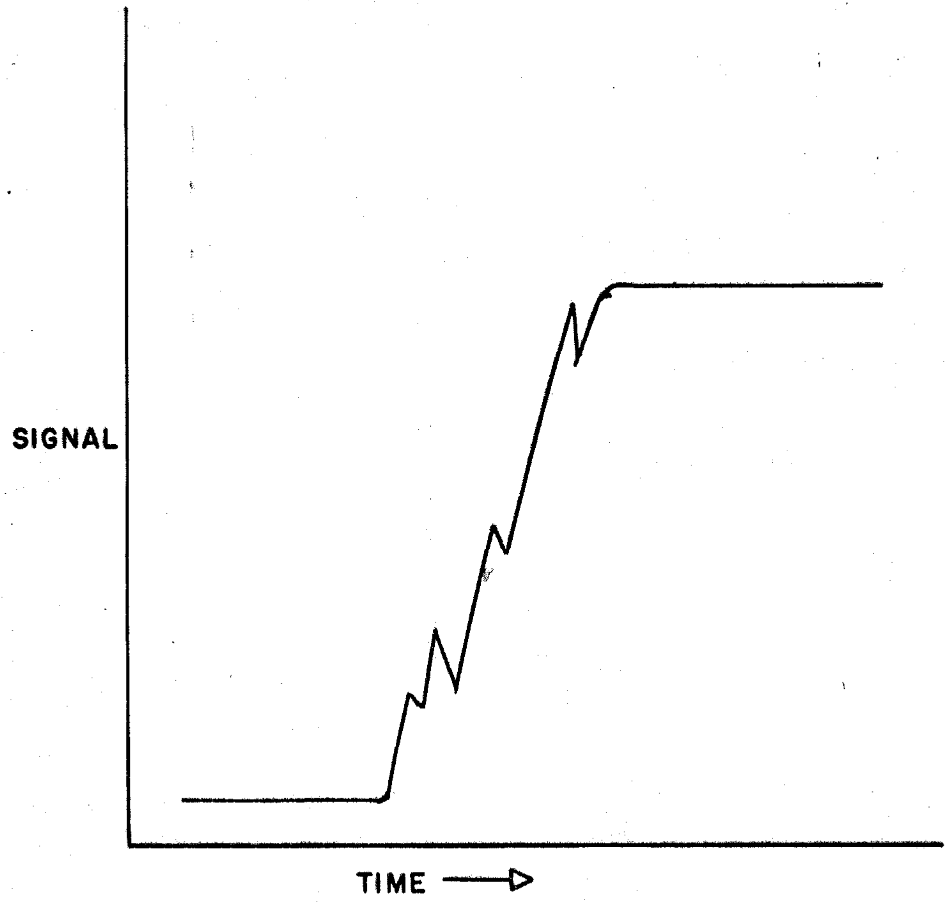


Figure 6-8. Typical transient observed during relay closure.

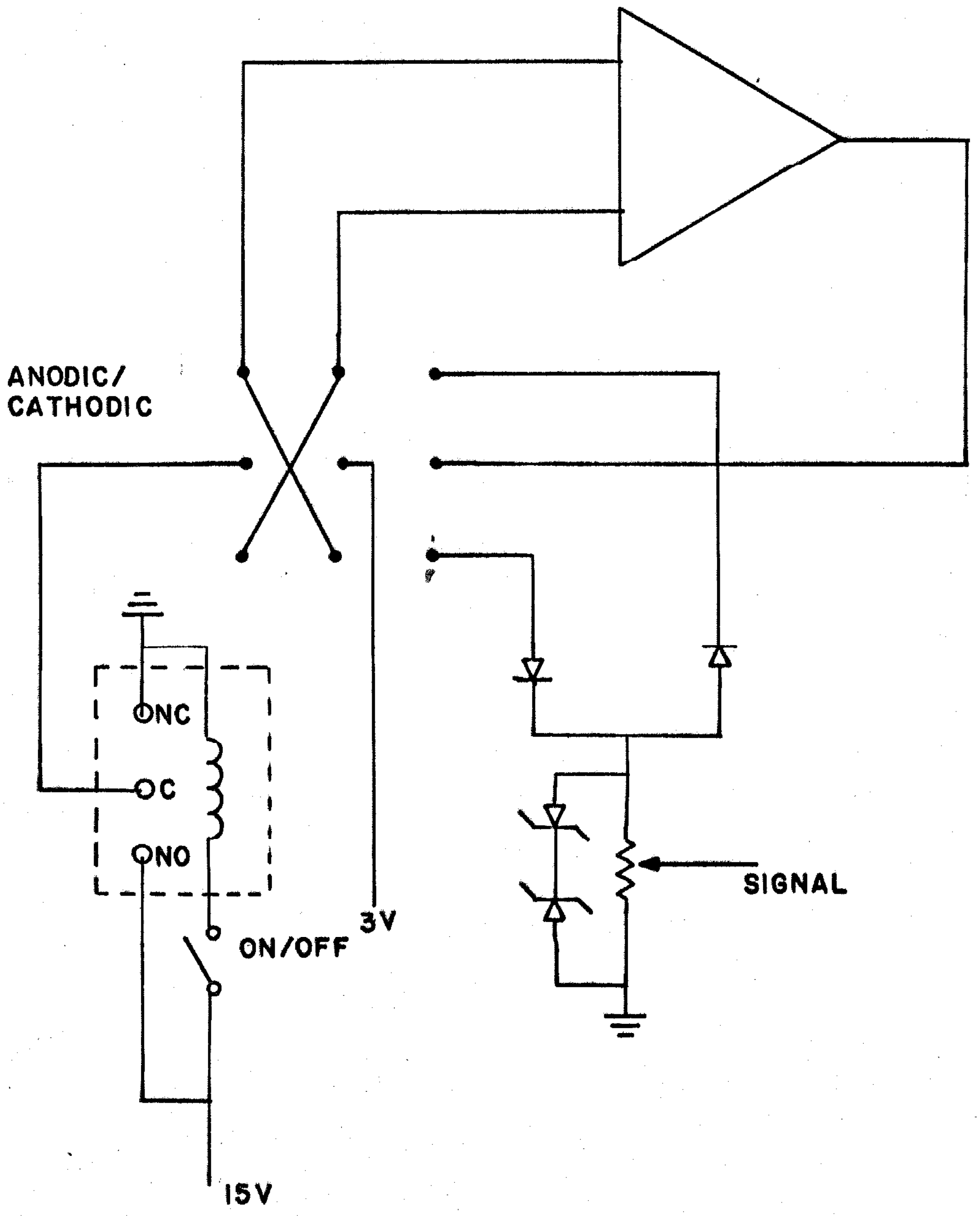


Figure 6-9. Complete bias circuit as used in chronocoulometer.

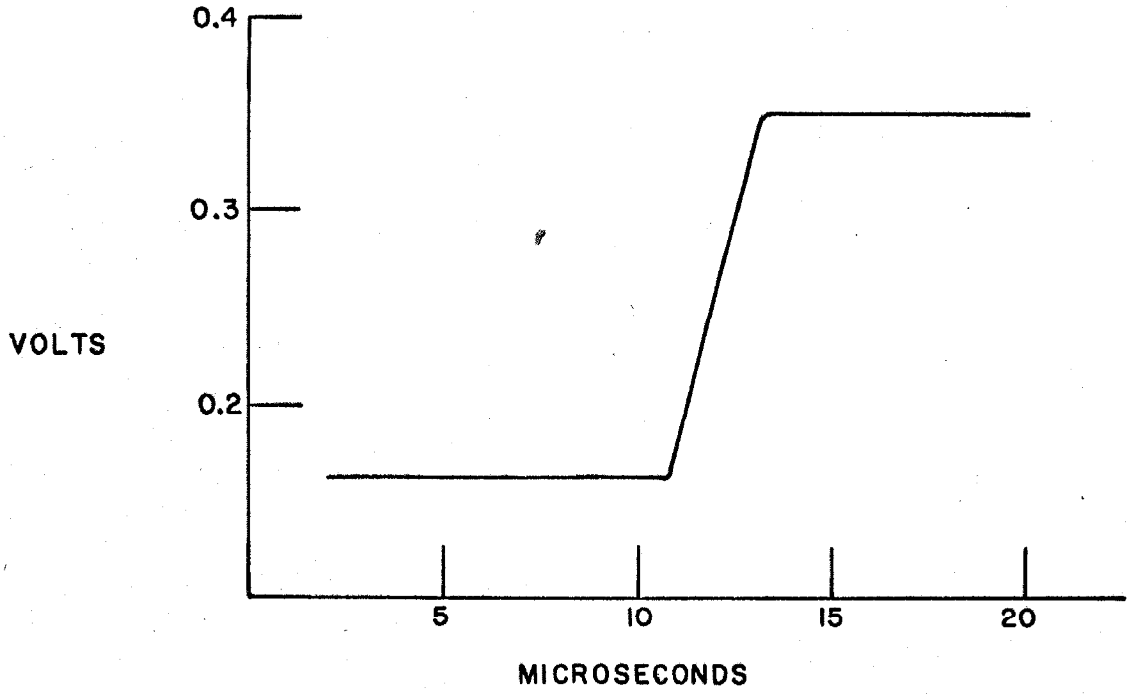


Figure 6-10. Typical potential step output of control amplifier upon switching bias circuit on.

at a given potential and restarting from that potential, and the capability to change the polarity of the sweep direction, manually, or automatically when the electrode potential has reached a given preset value. In addition it was considered desirable to have the rate controlled independently for each direction.

The ramp is generated by applying a constant voltage to the input of an operational amplifier (Sweep generator in Figure 6-4) wired as an integrator. The constant potential is derived from the cathodic or anodic sweep rate potentiometers, which have plus and minus 3.0 volts across them respectively. By varying the potential supplied to the input resistor, the sweep rate can be adjusted over a wide range, since

$$\frac{dV_{out}}{dt} = -E_{in}/RC \text{ volts/second} \qquad (6\text{-}6)$$

A set of resistors and capacitors is provided to allow order of magnitude changes in dV/dt.

The sweep will halt if the input resistor is switched to ground.

This can be done manually using the sweep hold switch and relay 2 or it can be done automatically when the electrode potential has achieved a predetermined value. This latter function is accomplished by using an operational amplifier as shown in Figure 6-11. As long as the reference potential set on the potentiometer is less than the electrode potential, the output of the amplifier is negative and the potential across the relay coil is blocked by the reverse biased diode. When the electrode potential becomes less than the reference potential the output goes to full positive saturation, and the relay is activated; in this case grounding the input to the sweep generator resistor and stopping the sweep. Since the sweep can have two slopes and go through zero, the complete switching circuit to halt the ramp requires more components; the whole circuit is shown in Figure 6-12. The "slope" switch must be set to the direction, positive or negative, of the sweep when the switch is to fire. The 'A' or 'C' switch determines the polarity of the potential at the halting point. (See the end of this chapter for a discussion of sign conventions).

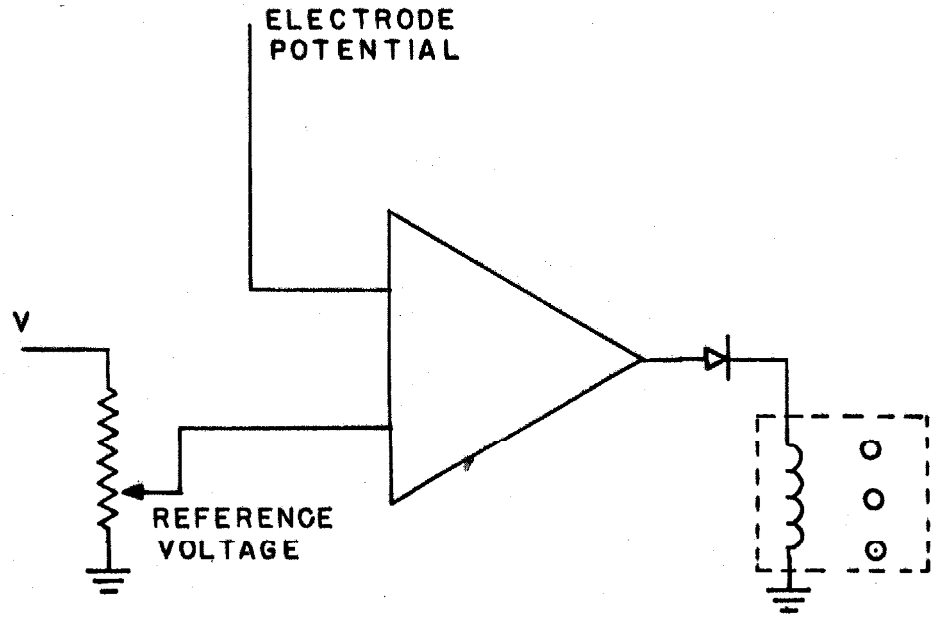


Figure 6-11. Basic potential sensitive relay control.

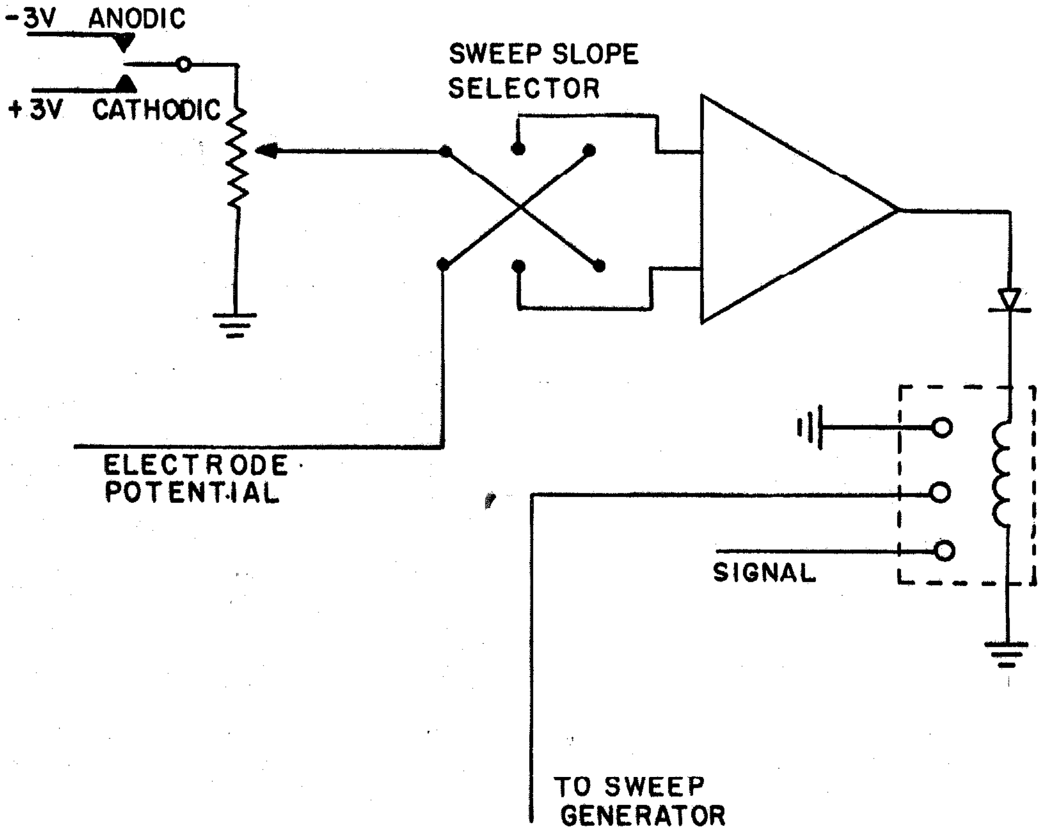


Figure 6-12. Sweep "hold" circuit of chronocoulometer.

The direction of sweep is determined manually using the manual reversing switch in Figure 6-4. The direction can be switched electronically at preset limits. This is accomplished by use of the circuit shown in Figure 6-13. The two amplifiers are used as sense switches, and are set by the two potentiometers which allows setting of the upper and lower limits. The relay (RLY 1) is a bistable double wound type. When amplifier 1 switches one coil the relay remains in that state until amplifier 2 switches through the other coil causing the relay to change contacts. The circuit is relatively foolproof since voltage levels, and not pulses, are used in the operation. The circuit becomes inoperative if the algebraic values of the setting of potentiometer 1 is less than that of potentiometer 2. In this case the sweep direction will be indeterminate.

In operation the electrode potential is set at any point, using the bias potentiometers. If the initial potential is between the limits set by the potentiometers the initial sweep direction will be indeterminate. To overcome this flaw two momentary contact switches are

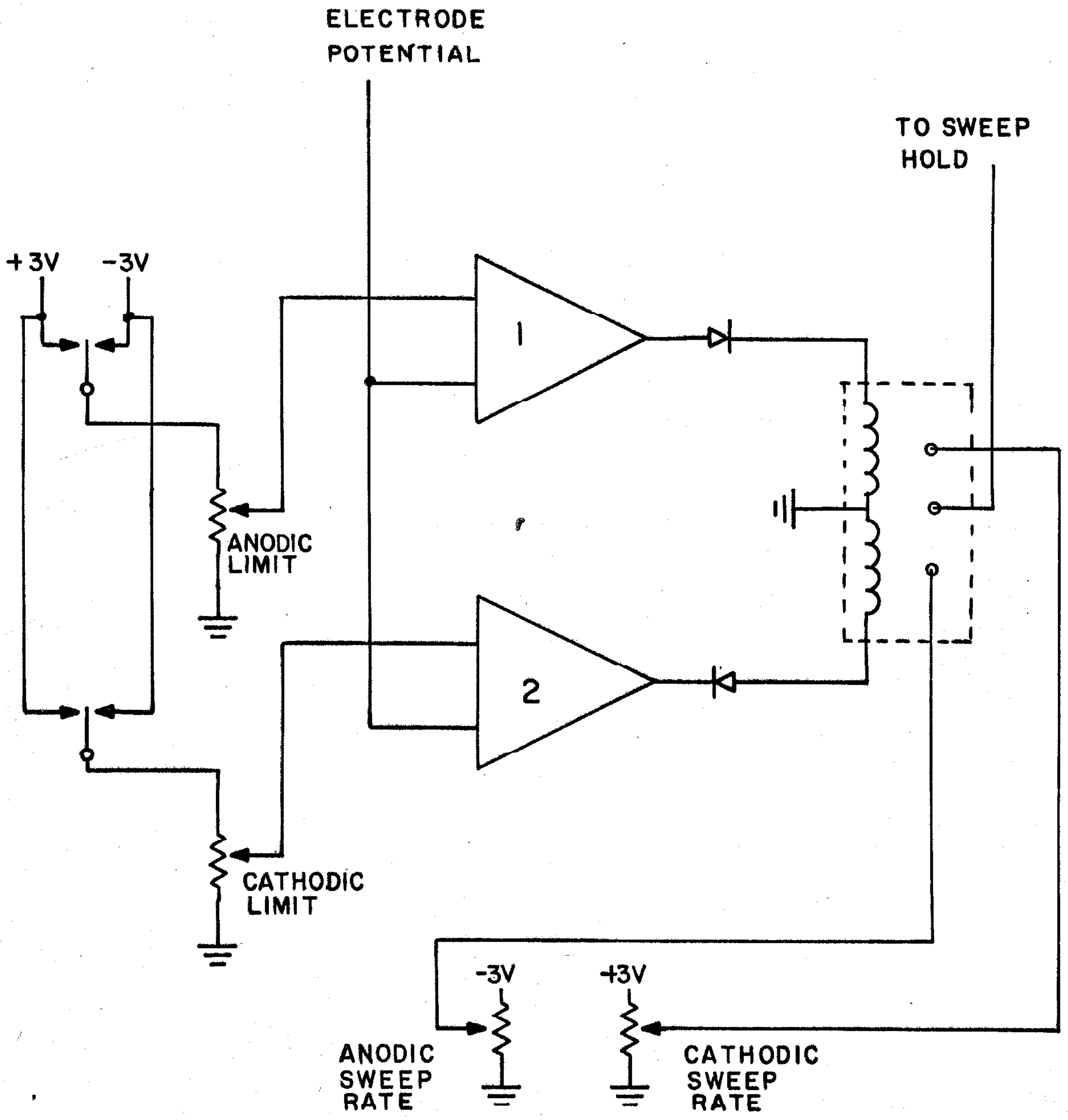


Figure 6-13. Automatic sweep reversal circuitry of chronocoulometer.

provided to choose the initial direction of the sweep. Assuming that the initial direction chosen is positive when the sweep is initiated by opening the switch across the capacitor, the electrode potential will increase until it equals the setting of the cathodic limit potentiometer. At that instant the output of the cathodic gate amplifier goes full positive, causing the relay to switch contacts which changes the direction of the sweep. The output of the cathodic limit gate amplifier goes back to full negative (zero volts across the relay coil); however, the relay remains in its switched state until the negative limit is reached, at which time the opposite action is performed by the anodic gate amplifier. The net effect is a triangular wave shape at the output of the sweep generator amplifier; the slopes of which can be individually varied. The feature of the circuit is that the parameter of interest in electrochemical studies, dV/dt, is controllable, rather than the frequency of the triangular wave.

Ancillary Circuits

In addition to the circuitry shown in Figure 6-4 and described above a number of other useful circuits have been provided to enhance the versatility of the instrument. These include two timers and two analog memory circuits. The timer circuit is shown in Figure 6-14. The circuit operates in the following manner. When the timer switch is closed, the "instant" relay is energized and the short across the capacitor is opened; this then charges through the resistor. The unijunction transistor (2N494C) blocks the capacitor from discharging until the voltage ratio between base 2 and the emitter is about 0.7. When this ratio is exceeded, the capacitor is discharged through Base 1, causing a pulse to appear at the top of the 27 ohm resistor connected to the gate of the silicon controlled rectifier. The latter blocks the current through the coil of the "delayed" relay in series with it until a pulse is received at the gate, at which time the SCR (2N2323) goes into the conduction state until the current path is blocked by an open circuit to either the anode or the cathode. The 2N491 unijunction transistor is used in the circuit to "pump" base 2 of the 2N494C. This pumping action is required if very long time delays (20 seconds or

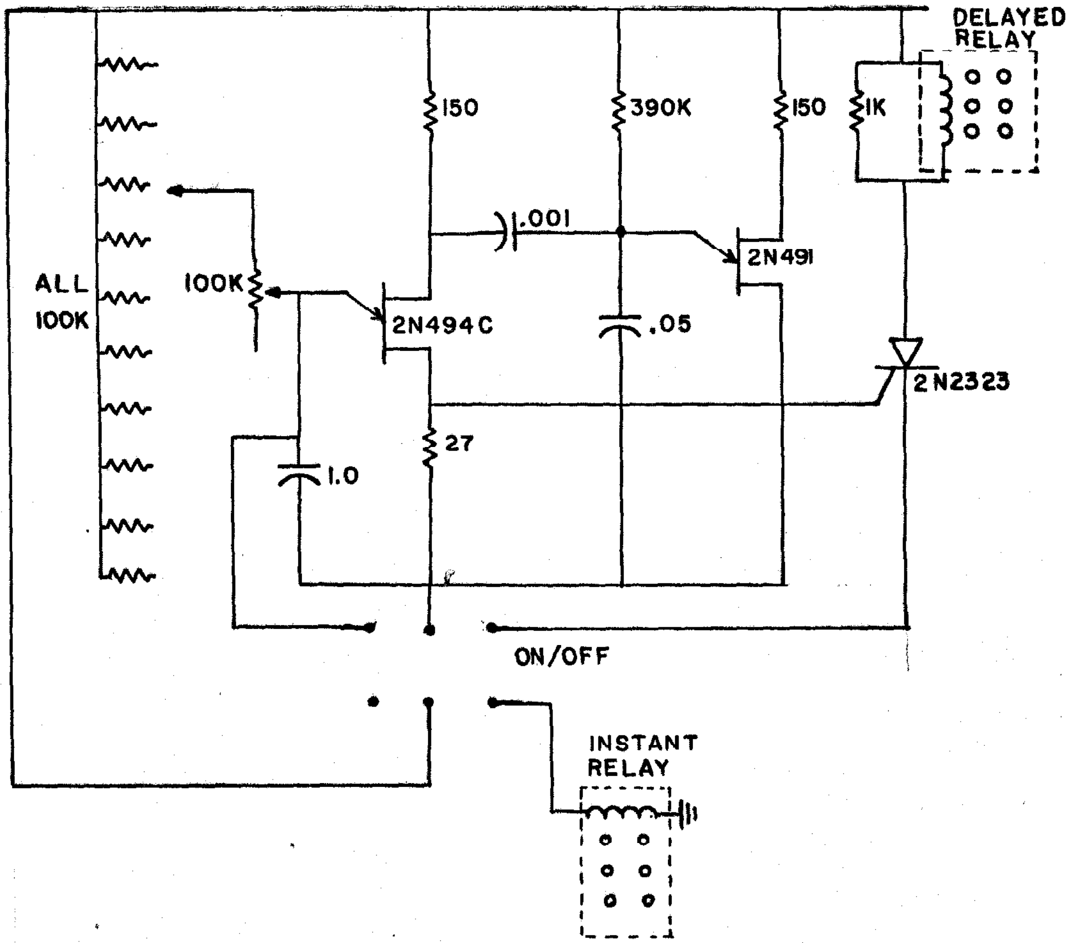


Figure 6-14. Chronocoulometer timer circuit.

longer) are desired. The net effect is that one has available a relay closure at the time of the switch closure, and another relay closure delayed by a time dependent on the values of R and C. These relay contacts are brought to connectors on the control panel of the instrument and to the switching matrix. (See following section).

The analog memory circuit is shown in Figure 6-15. A special operation amplifier is used which has a very high input impedance (10^{13} ohms typical). Any signal that comes in charges the capacitor continuously until the relay is opened. At the instant of relay opening the output of the amplifier continues to be identical to the potential across the capacitor. If the leakage across the capacitor is very small, the output will act as a memory of the last signal to appear at the input before the relay was opened. When the relay is again closed the output will immediately return to the signal then present. Two such devices have been provided.

Matrix Switching

Although a number of specialized functions have been prewired in and

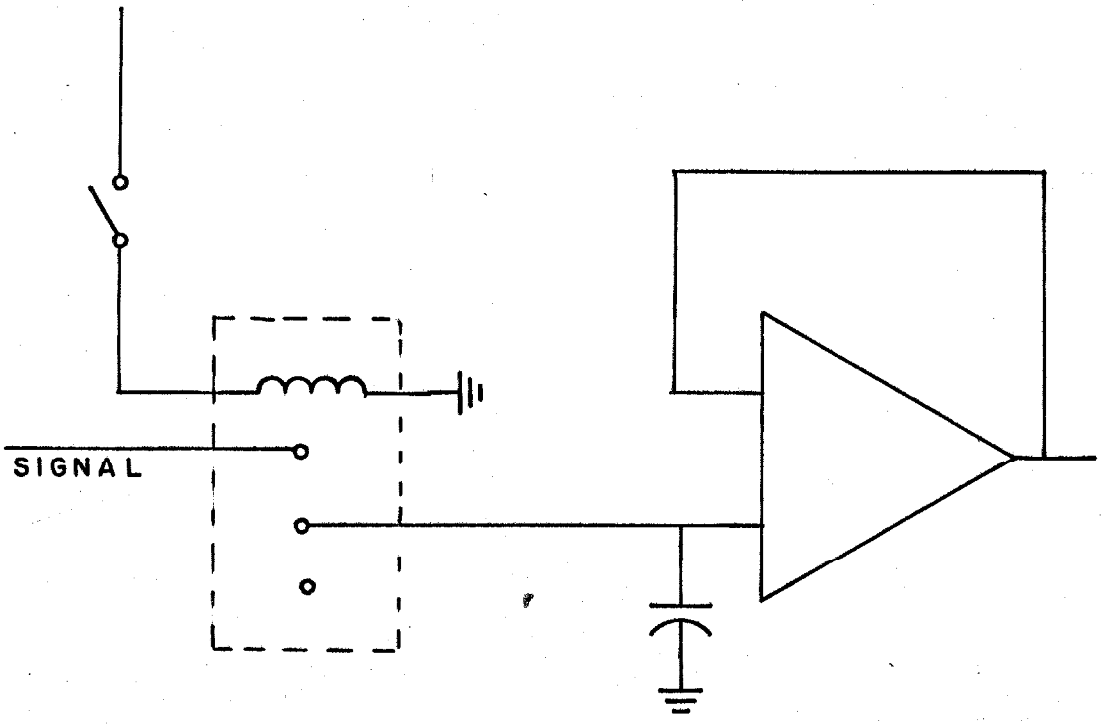


Figure 6-15. "Analog memory" or track and hold circuit.

can be switched in and out directly, it has been the experience of at least this writer that a variation of the wired-in technique is desired approximately 3 to 4 hours after an instrument is fully debugged and operational. Although it would be impossible to foretell every variant of instrumental capability desired, a special switching circuit was incorporated which should extend the time before additional wiring does become necessary.

The method used incorporates a forty by forty position manual matrix switch. This switch is constructed so that forty slides, each on a separate vertical common bus, can be connected to any one of forty horizontal metal strips on a circuit directly below the slide. Each horizontal strip has been externally connected to its corresponding numbered vertical bus bar. The top of each relay coil in the instrument plus the contacts on the instant and delayed relays of the timer relays are connected to a vertical bus bar. All the relays are energized by positive 15 volts. The net effect of the arrangement is that any switch closure on the control panel of the instrument can simultaneously energize any relay besides the primary one it was originally designed to energize by moving the slides of the matrix to the appropriate position. In addition position 38 of the matrix is wired to positive 15 volts. This allows any of the relays to be energized, or be disconnected, using contact closures of the timer relays. Thus any reasonable sequence of potential steps, sweeps, etc. can be programmed by merely moving the slides on the matrix switch to the correct settings. Any errors in switch settings may be disastrous insofar as the experiment is concerned, however, no damage can be done to the instrument itself (saturation of stabilized amplifiers, though annoying, is not considered damaging). Position 40 is wired to a connector on the control panel. This allows the choice of any relay closure for a trigger on an oscilloscope or other device.

To avoid the use of batteries and yet still have available a stable source of low voltages, two secondary power supplies were constructed using operational amplifiers. The circuit is shown in Figure 6-16. Referring to this figure, A_1 is an ordinary differential operational

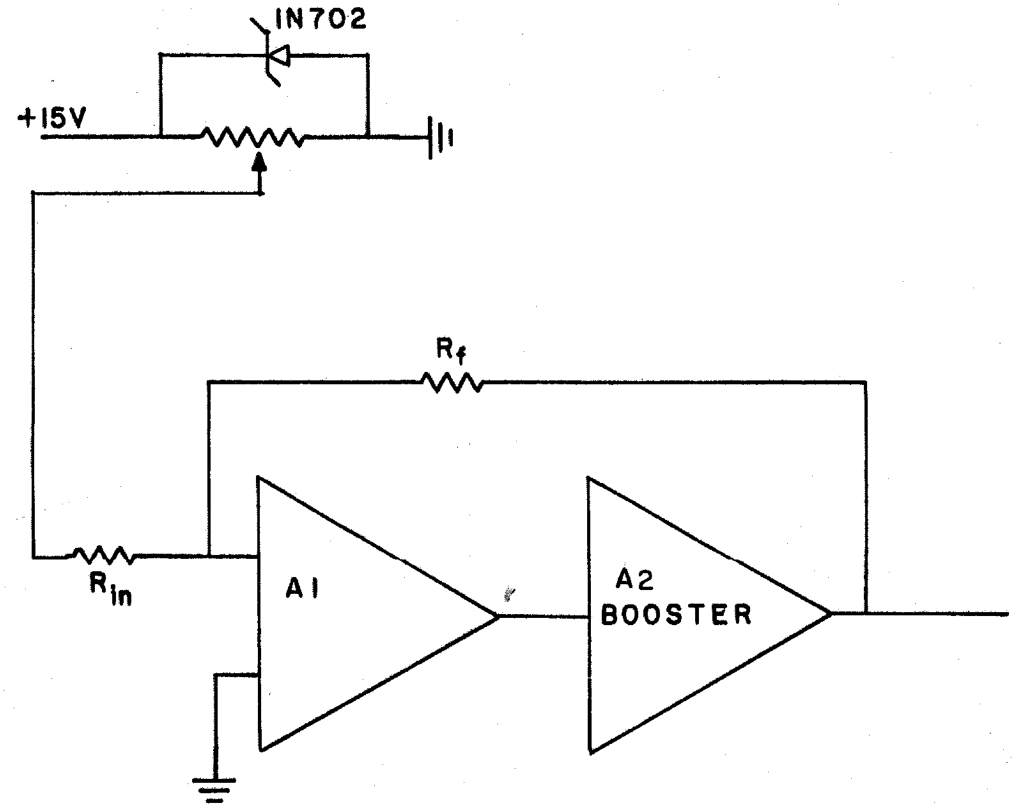


Figure 6-16. Auxiliary low voltage power supply.

amplifier, A_2 is a "booster" amplifier which has a very high current output capacity, but which has a unity voltage gain. Since this booster amplifier is within the feedback loop of the operational amplifier, its voltage output is determined by the input and feedback impedances at the summing point of the operational amplifier. The input to the operational amplifier is a potential derived from a thermally stable zener reference diode and a trimming potentiometer. This potential is set at precisely 3.0 volts; the output at the booster amplifier is therefore -30 volts. Using this arrangement 100 milliamperes of current can be drawn to power potentiometers, etc. without causing any loading effects and no batteries need be used. Total variation of the potential is less than 0.01 millivolts over an 8 hour period, well outside measurements possible with the presently available instrumentation in the laboratory.

As mentioned before, inductive coupling can be a major problem when using mercury wetted reed relays. When the coil is deenergized the magnetic field must collapse, some of the energy being transferred to the controlled circuit. To partially overcome this problem diodes were placed across each coil, cathode to the positive potential. When the switch leading power to the coil is opened, the diode acts as a shunt through which the current induced by the collapse of the magnetic field can flow. In practice this technique was 75% effective in decoupling the coil from the controlled circuit.

Sign Conventions

As has been noted previously, using the scheme outlined, it is the reference electrode potential (assumed thermodynamically constant) that is controlled with respect to the grounded indicator electrode. Therefore a positive voltage reading corresponds to the reference electrode being at an anodic potential with respect to the indicator electrode. However, the parameter of immediate interest is the potential of the indicator with respect to the reference electrode. Therefore in the instrument, a positive voltage at the output of the follower amplifier is considered a "cathodic" potential, and a negative voltage at the output as an "anodic" potential. The display one sees on a typical recording instrument, however, follows the convention normally found in the literature, that is cathodic potential increasing to the right. This convention of referring to the potential of the indicator (ground) with respect to the reference electrode being used (controlled electrode) is used throughout the instrument in labelling and in the construction notes in the appendix.

In construction of the instrument the complete circuit diagram was prepared before actual construction began. Afterwards, each of the individual circuits were tested to insure operation as intended, rather than as designed. A complete set of construction instructions were then prepared off the completed drawing. These instructions were written so that prior knowledge of electronic circuitry is not necessary to do an adequate job in physical construction. In essence, the high-fidelity instrumentation kit idea was adopted in building the instrument. The complete set of construction instructions is given in the appendix to this chapter.

The chronocoulometer described here has performed adequately in a rather large number of applications. However, a number of basic problems inherent in the design have manifested themselves.

The primary problem is the matter of timing. The relays, though free of bounce, take from 0.75 to 3.0 milliseconds to operate. This variability was considered, and care was taken that time order of critical functions is independent of relay operating time; as in the integrator circuit. As originally envisioned the instrument would be used with an oscilloscope, which could be triggered off of the critical relay energization via position 40 of the matrix switch.

However, major improvements in data acquisition methods require that potential step application, potential reversal etc. be synchronized with an external signal to within at worst 5 microseconds. This is a physical impossibility with relays. The field effect transistor (FET) can be used as an adequate substitute for relays in a large number of cases. This solid state device is different from the ordinary (bipolar) transistor in that it is essentially voltage rather than current operated. Its characteristics resemble in many ways those of the familiar vacuum tube triode. The device consists of a bar of n(p) type semiconductor at the center of which is inserted a channel of p(n) semiconductor. The parenthesized letters refer to n channel FETS as opposed to the p channel type. Leads connected to the bar are named source and drain, and for most applications are interchangable. The channel lead is termed the gate.

Considering the p channel device, if a potential is applied between source and drain with the gate left unconnected, or at zero potential, a current flows through the device. This current, sustained by the majority carriers in the material (electrons in the n type semiconductor), is determined only by the intrinsic resistivity. This can be as low as 30 ohms, although 100 ohms is a more practical figure. However, if a potential more positive by 3 or 4 volts than that at source or drain is applied to the gate, the field will effectively block the current and the FET will be turned "off". Effective off resistances on the order of 10^{12} ohms are practical.

The current between the gate and drain or source is very small, a practical value being 10^{-12} to 10^{-13} amperes for "standard" devices and 10^{-14} to 10^{-15} amperes for "MOS" types. Thus if an "on" resistance of 600 ohms and a "leakage" resistance of 10^{11} ohms can be tolerated, the device makes an excellent switch. Turn on and turn off times, with proper circuit design are on the order of 100 to 300 nanoseconds. Shown in Figure 6-17 is a complete circuit which has been tested to replace the relay across the capacitor of an integrator. The 2N3606 transistor acts as a simple switch whose collector is tied via the 1N645 diode to the gate of the FET. The emitter of the 2N3606 is brought to -15 volts to ensure that the saturation resistance of the transistor will not leave the collector at a positive voltage. The diode blocks the negative voltage from the FET gate. The 10K resistor affords a discharge path for the space charge capacitance of the FET so that it may be rapidly turned "on".

Due to their "on" resistance such devices can not be used to replace relays for those portions of the circuit carrying the current from the control amplifier. However, these controls are usually not used during critically timed and synchronized experiments.

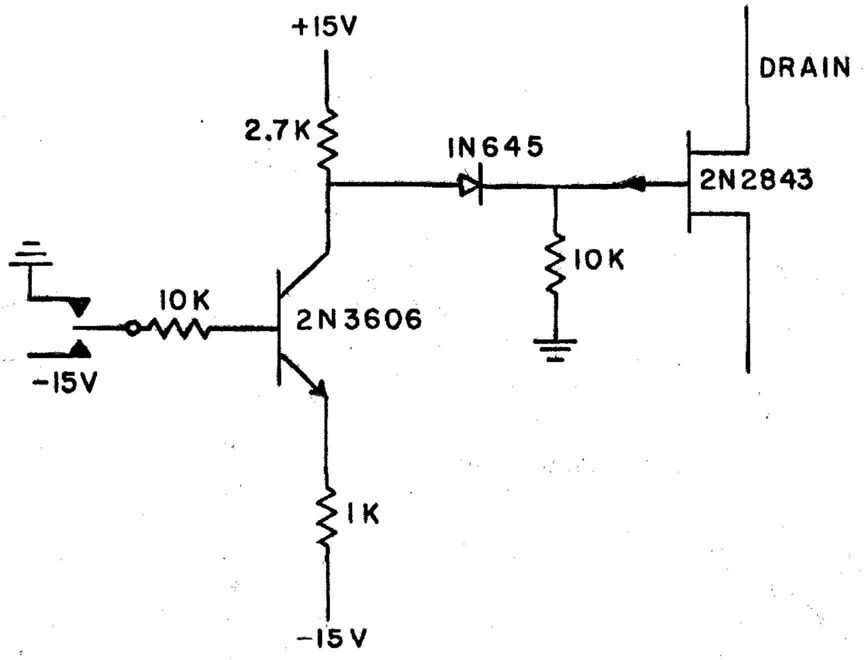


Figure 6-17. Field effect transistor relay replacement circuit.

There appears to be presently two schools of thought concerning the design and construction of electrochemical instrumentation. In one the design is such that one must "believe" that the instrument is performing as designed. Thus one cannot measure the actual electrode potentials, but must rely on measuring the inputs and assume that the actual potentials follow these signals. Although not intrinsically bad, this philosophy suffers if a person not completely familiar with all nuances of the design attempts to operate the instrument. Invariably a complete faith is developed and the worker does not attempt to search for possible electronic "gliches" which turn a Nobel Prize winning piece of research into a likely candidate for The Journal of Irreproducible Results.

I therefore feel that in the design of any instrument the output signals should be connected as directly as possible to the actual signals being controlled or measured. Further it appears imperative that the worker have at least a working knowledge of the limitations of the electronics of the particular instrument as it applies to <u>his</u>

experimental system. It is felt that blind faith should be left to theology.

Literature References

The literature abounds with descriptions of various electrochemical control and measurement circuits. The individual circuits used in building the chronocoulometer are each in themselves not novel, however, the assemblage of all the circuits in this particular manner is. No references were given in the text as the actual developer of the individual circuits is not really clear (the vendors of operational amplifiers themselves have suggested many of the concepts). However, a short bibliography of pertinent literature is given at the end of this chapter.

Acknowledgements

The basic concept of building a multipurpose instrument was developed at the North American Aviation Science Center in Thousand Oaks under the direction of Dr. Robert A. Osteryoung. The first three versions were designed and built there and invaluable

experience was gained, the lack of which would have seriously affected the final performance of the chronocoulometer. In addition, many of the circuits used were tested at the Science Center before implementation. The author would like to thank the management of the laboratory and Dr. Osteryoung for the use of their equipment and facilities. In addition thanks are due to Mr. Helmar Schlein of the Science Center for many helpful discussions and suggestions on circuit design.

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Involving the Use of Operational Amplifiers

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APPENDIX

Directions for the Construction of the Chronocoulometer

The following detailed construction directions were written explicitly for the chronocoulometer described in Chapter 6. They are complete and can be used to duplicate the instrument.

The control panel layout is usually a matter of personal choice and prejudice. The layout shown in Figure A-1 has been found convenient in this laboratory. The primary innovation is that all outputs are duplicated on both sides of the panel. This is based on the empirical fact that if connectors are placed on one side, it is the wrong side.

A schematic outline of the physical layout of the cabinet is shown in Figure A-2. A six ft. relay rack should be used. The shelves and control panel should be hinged at the points indicated so that they may be swung up to gain easy access to connectors during debugging, maintenance, and rewiring. A parts list of components that are usually not found in the laboratory is given at the end of the instructions.

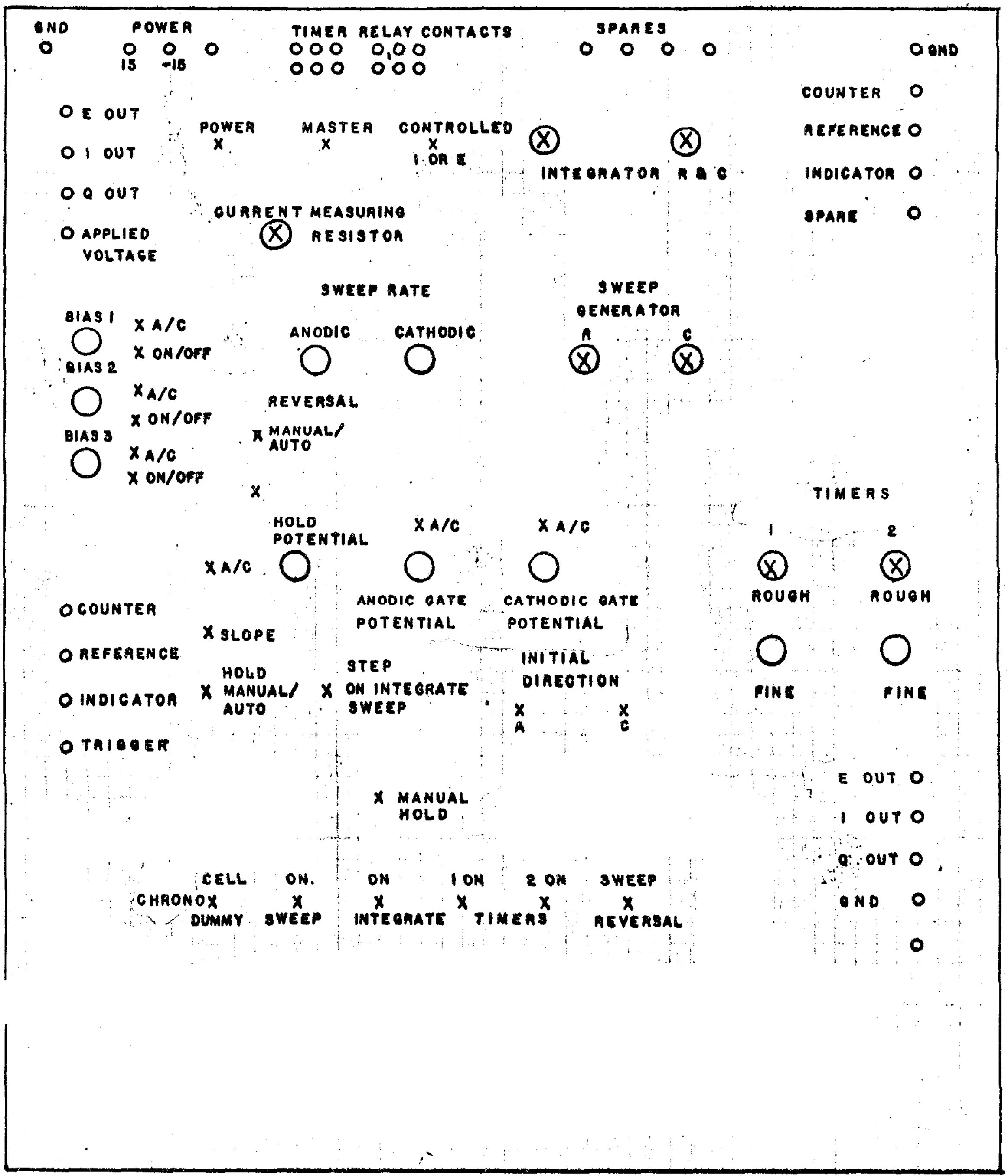
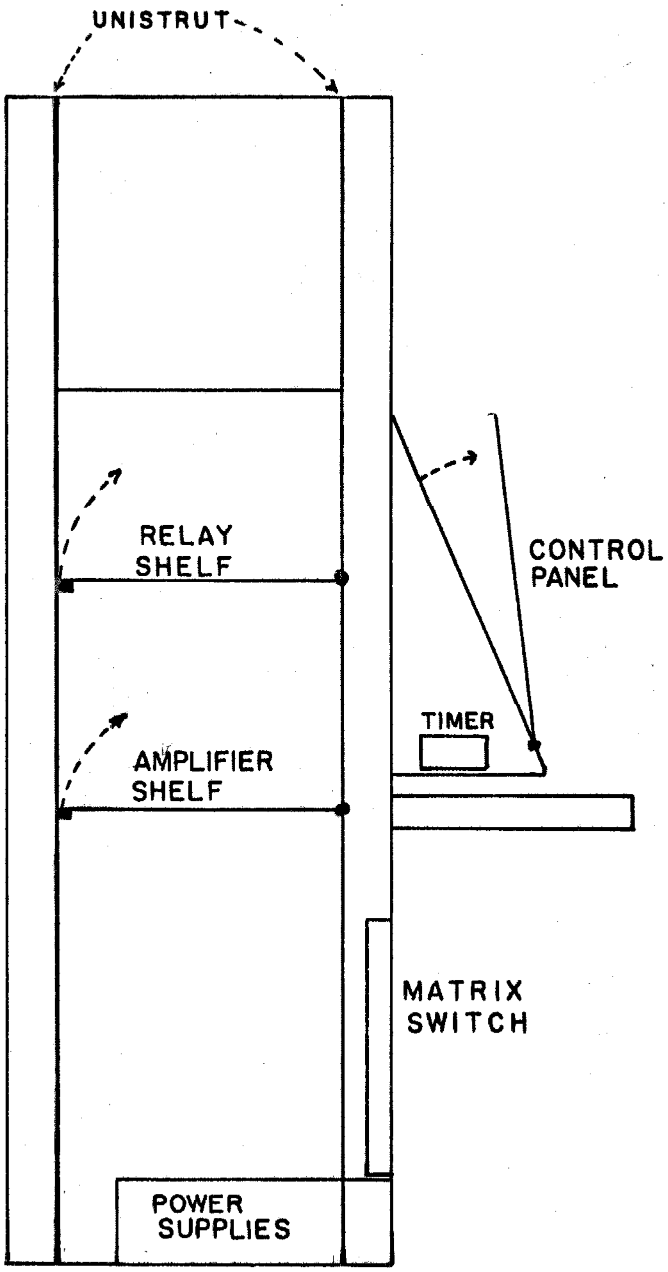


FIGURE A-1 CONTROL PANEL LAYOUT

X = SWITCH

⊗ = 10 POSITION SWITCH

○ = POTENTIOMETER



CHRONOCOULOMETER, SIDE VIEW

For construction ease, use 24AWG stranded wire and many colors. The shielded wire should be of small diameter. Type RG174/U coaxial cable is recommended.

The construction has been planned so that each shelf, the control panel, and the matrix switch may be wired separately and externally of the cabinet. After this phase is completed these sections are installed in the cabinet and interconnected.

During all phases of construction, great care should be taken to insure that all soldered joints are properly made. Use the minimum amount of solder necessary and make sure that the flux is not visible after the joint cools. In no case should ground wires be "strung". Each ground should be individually brought to one of the common bus bars. The braid of the shielded cable should always be soldered to ground at one end only.

Section I. The Amplifier Shelf.

The amplifier shelf should have mounted on it at least 11 connectors to accommodate the differential operational amplifiers and 4 connectors to accommodate the single ended chopper stabilized operational amplifiers. We shall first consider the differential amplifiers. Label these in the following way:

(1) cathodic gate
(2) anodic gate
(3) hold gate
(4) follower
(5) 3V power supply
(6) booster
(7) -3V power supply
(8) booster
(9) inverter
(10) memory 1
(11) memory 2

Label the single ended chopper stabilizer amplifiers in the following way:

(1) sweep generator

(2) integrator

(3) potentiostat

(4) current-measuring amplifier

Mount three bus wires on this shelf, label these 15 volts, -15 volts, and ground.

Mount two General Radio binding posts next to the potentiostat amplifier connector and next to the current-measuring amplifier connector respectively.

<u>NOTE</u>: In the following text, amplifier and connector will be used interchangeably.

It is assumed that the differential amplifiers used are Philbrick plug-in types such as the P65AU. If other amplifiers are used, certain modifications will have to be made to this set of instructions to conform to the pin numbers on the individual amplifiers.

Connect black wires from pins 10 of all the differential amplifiers to the -15 volt bus bar. Bring these in parallel.

Bring red wires in parallel from pins 8 of the differential amplifiers to the 15 volt bus bar.

Connect together pins 1 and 9 of each of the differential amplifiers.

Bring green leads from pins 9 of each of the differential amplifiers to the ground bus bar in parallel.

Using black wires, connect the -15 volts of each of the single ended amplifiers to the -15 volt bus bar.

Using red wires, connect the 15 volts of each of the single ended amplifiers to the 15 volt bus bar.

Connect together the signal return and the ground connection of each of the single ended amplifiers.

Using green wire, connect each of the signal return jacks of the single ended amplifiers to the ground bus bar.

<u>NOTE</u>: In the text there will be many references where one section is to be connected to another section. A typical example might be "Connect

pin 6 of relay 5 to the control panel". In such a case, solder the wire to the indicated component, leaving enough wire so that it may reach any portion of the other section mentioned, then label this wire clearly with the component name and pin number from which the wire comes.

Connect pin 6 of the follower amplifier to pin 2 of the cathodic gate.

Connect pin 6 of the follower amplifier to pin 2 of the anodic gate.

Connect pin 3 of the follower amplifier to pin 6 of the follower amplifier.

Connect a shielded wire from pin 2 of the follower amplifier to the control panel.

Bring a wire from the output of the control amplifier to one of the two binding posts situated next to it.

Bring a wire from the input of the control amplifier to the other binding post.

Connect a shielded wire from the output of the control amplifier to the relay shelf.

Connect a 47 kilohm resistor to the output of the sweep generator amplifier. From the other side of this 47 kilohm resistor go to the input of the control amplifier.

Connect the input of the sweep generator amplifier to the control panel.

Connect the input of the sweep generator amplifier to the relay shelf.

Connect the output of the sweep generator amplifier to the relay shelf, using shielded wire.

Connect a wire from pin 6 of the hold gate amplifier to the control panel.

Connect a wire from pin 2 of the anodic gate amplifier to the control panel.

Connect a wire from pin 6 of the anodic gate amplifier to the control panel.

Connect a wire from pin 6 of the cathodic gate amplifier to the control panel.

Connect a wire from pin 2 of the hold gate amplifier to the control panel.

Connect a wire from pin 3 of the hold gate amplifier to the control panel.

Connect a wire from pin 3 of the cathodic gate to the control panel.

Connect a wire from pin 3 of the anodic gate to the control panel.

Connect a shielded wire from pin 6 of the follower amplifier to the control panel.

Connect a shielded wire from pin 6 of the follower amplifier to the relay shelf.

Mount a 10 kilohm carbon potentiometer next to the 3 volt power supply amplifier.

Mount a 10 kilohm carbon potentiometer next to the -3 volt power supply amplifier.

Connect a 2.2 kilohm resistor from the -15 volt bus bar to the top of the 10 kilohm potentiometer next to the -3 volt power supply amplifier.

Connect the bottom of this potentiometer to ground.

Mount a 1 N 702 A Zener diode across the top and bottom of the potentiometer such that the anode is at the top of the potentiometer.

Connect the wiper of the potentiometer to pin 2 of the -3 volt power supply amplifier.

Connect pin 6 of the -3 volt power supply amplifier to pin 2 of the booster situated directly next to it.

Connect pin 6 of the -3 volt booster to pin 3 of the -3 volt power supply amplifier.

Connect a 2.2 kilohm resistor to the top of the 10 kilohm potentiometer, mounted next to the 3 volt power supply amplifier.

Connect the other end of this resistor to the 15 volt bus bar.

Connect the bottom of this potentiometer to the ground bus bar.

Mount a 1 N 702 A Zener diode across this potentiometer such that the cathode is at the top of the potentiometer.

Connect the wiper of this potentiometer to pin 2 of the 3 volt power supply amplifier.

Connect pin 3 of the 3 volt power supply amplifier to pin 6 of the booster situated directly next to it.

Connect pin 6 of the 3 volt power supply amplifier to pin 2 of the booster situated directly next to it.

Connect pin 6 of the 3 volt power supply booster to the control panel.

Connect pin 6 of the -3 volt power supply booster to the control panel.

Connect the input of the current measuring amplifier to one of the binding posts situated directly next to it.

Connect the output of the current measuring amplifier to the other binding post situated directly next to it.

Connect a shielded wire from the input of the current measuring amplifier to the relay shelf.

Connect a shielded wire from the input of the current measuring amplifier to the control panel.

Connect a 47 kilohm resistor to the output of the current measuring amplifier.

From the other end of this resistor go to pin 3 of the inverting amplifier.

Connect a 47 kilohm resistor to pin 3 of the inverting amplifier.

Connect the other end of this resistor to pin 6 of the inverting amplifier.

Connect pin 6 of the inverting amplifier to the relay shelf with shielded wire.

Connect pin 2 of the inverting amplifier to pin 1 of this amplifier.

Connect the output of the integrator to the relay shelf.

Connect the output of the integrator to the control panel.

Connect the input of the integrator to the contol panel.

Connect the input of the integrator to the relay shelf.

Connect pin 3 of memory 1 amplifier to pin 6 of this amplifier.

Connect pin 6 of memory 1 amplifier to the control panel.

Connect pin 2 of memory 1 amplifier to the relay shelf.

Mount a 0.1 microfarad capacitor to pin 2 of memory 1 amplifier. Connect the other end of this capacitor to ground.

Connect pin 3 of memory 2 amplifier to pin 6 of this amplifier.

Connect pin 6 of memory 2 amplifier to the control panel.

Connect pin 2 of memory 2 amplifier to the relay shelf.

Mount a 0.1 microfarad capacitor to pin 2 of memory 2 amplifier. Connect the other end of this capacitor to ground.

Connect a wire from pin 2 of bias 1 amplifier to the control panel.

Connect a wire from pin 3 of bias 1 amplifier to the control panel.

Connect a wire from pin 6 of bias 1 amplifier to the control panel.

Connect a wire from pin 2 of bias 2 amplifier to the control panel.

Connect a wire from pin 3 of bias 2 amplifier to the control panel.

Connect a wire from pin 6 of bias 2 amplifier to the control panel.

Connect a wire from pin 2 of bias 3 amplifier to the control panel.

Connect a wire from pin 3 of bias 3 amplifier to the control panel.

Connect a wire from pin 6 of bias 3 amplifier to the control panel.

Mount 3-47 kilohm resistors to the binding post which is connected to the input of the control amplifier.

Connect wires which will go to the control panel to the other end of these resistors using shielded wires.

Connect the shields of these wires to the ground connection on the potentiostat amplifier.

This completes the initial assembly of the amplifier shelf. At this stage, securely wrap all the wires into neat bundles using cable clamps and lay aside this shelf.

<u>Section II. The Relay Shelf</u>.

We will now begin wiring of the relay shelf. Mount 24 octal sockets on the shelf and label them from 1 to 24.

Mount three bus wires on the shelf - all of these bus wires will be at ground potential.

Connect pin 7 of all of the relays to the ground bus.

Connect a 1N 536 diode across pin 7 and pin 8 of each of the relays except relay 1 such that the cathode is at pin 8 of all of the relays. Make absolutely certain that you know the difference between the anode and the cathode of these diodes.

Mount a 47 kilohm resistor to pin 5 of relay 3.

Connect a wire from pin 5 of relay 2 to the control panel.

Connect a wire from pin 3 of relay 2 to the control panel.

Connect a wire from pin 1 of relay 2 to the ground bus.

Wire together pin 1 and 4 of relay 3.

Connect a 1 kilohm resistor to pin 1 of relay 3.

Connect the other end of this resistor to the ground bus.

Connect pin 3 of relay 3 to pin 2 of relay 11 using shielded wire.

Connect pin 6 of relay 3 to pin 5 of relay 11 using shielded wire.

Connect pin 1 of relay 11 to pin 5 of relay 13 using shielded wire.

Connect a 100 ohm resistor to pin 3 of relay 11.

Connect the other end of this resistor to pin 2 of relay 13.

NOTE: Make sure that the leads of this resistor do not touch the panel.

Connect pin 3 of relay 13 to pin 6 of this relay.

Connect pin 4 of relay 13 to the control panel.

Connect pin 8 of relay 11 to the control panel.

Connect pin 3 of relay 14 to the control panel

Connect pin 5 of relay 14 to pin 2 of relay 12 using shielded wire.

Connect pin 1 of relay 12 to pin 4 of relay 12.

Connect pin 3 of relay 12 to the ground bus.

Connect pin 8 of relay 14 to the control panel.

Connect a 1 kilohm resistor to pin 6 of relay 12, and connect the other end of this resistor to ground.

Connect pin 8 of relay 12 to the control panel.

Connect pin 2 of relay 15 to the control panel.

Connect pin 8 of relay 13 to the control panel.

Connect pin 8 of relay 8 to the control panel.

Connect pin 8 of relay 9 to the control panel.

Connect pin 5 of relay 8 to the control panel.

Connect pin 5 of relay 9 to the control panel.

Connect pin 5 of relay 7 to the ground bus.

Connect pin 3 of relay 7 to the control panel.

Connect pin 1 of relay 7 to pin 8 of relay 7.

Connect pin 8 of relay 7 to the control panel.

Connect pin 8 of relay 6 to the control panel.

Connect pin 3 of relay 6 to the control panel.

Connect pin 5 of relay 6 to the ground bus.

Connect pin 1 of relay 6 to pin 8 of relay 6.

Connect pin 8 of relay 5 to the control panel.

Connect pin 1 of relay 5 to pin 8 of relay 5.

Connect pin 3 of relay 5 to the control panel.

Connect pin 5 of relay 5 to the ground bus.

Connect pin 8 of relay 4 to the control panel.

Connect pin 6 of relay 10 to the control panel.

Connect a 10 microfarad capacitor to pin 5 of relay 10, and connect the other end of this capacitor to pin 6 of relay 10.

Connect pin 8 of relay 10 to the control panel.

Connect pin 3 of relay 21 to the control panel.

Connect pin 8 of relay 21 to the control panel.

Connect pin 8 of relay 2 to the control panel.

Connect pin 8 of relay 1 to the control panel.

Connect pin 4 of relay 1 to the ground bus.

Connect pin 5 of relay 1 to the control panel.

Connect pin 6 of relay 1 to the control panel.

Connect pin 3 of relay 1 to the control panel.

Connect pin 1 of relay 1 to the control panel.

Connect pin 1 of relay 11 to the control panel.

Connect pin 4 of relay 20 to the control panel.

Connect pin 5 of relay 20 to the control panel.

Connect pin 6 of relay 20 to the control panel.

Connect pin 8 of relay 19 to the control panel.

Connect pin 4 of relay 19 to the control panel.

Connect pin 5 of relay 19 to the control panel.

Connect pin 6 of relay 19 to the control panel.

Connect pin 8 of relay 18 to the control panel.

Connect pin 3 of relay 18 to pin 8 of relay 17.

Connect pin 5 of relay 18 to the ground bus.

Connect pin 1 of relay 17 to the control panel.

Connect pin 2 of relay 17 to the control panel.

Connect pin 3 of relay 17 to the control panel.

This completes the initial assembly of the relay shelf. We will now consider the control panel.

Section III. The Control Panel.

In construction of the control panel, certain conventions will be used in the terminology. They are the following:

1) When referring to switches, "Up" or "Top" will indicate that connection such that when the bat handle of the switch when viewed from the front is up the circuit is closed with respect to the common. "Down" or "Bottom" will indicate that the bat handle on the switch when viewed from the front will be down when the circuit is closed with

respect to the common. For the double throw double pole switches, we will consider circuit A as being on the left when viewed from the rear of the control panel, circuit B being on the right.

2) Potentiometers. The convention we will use is that the top of the potentiometer is the CW terminal, the bottom is the CCW terminal.

Install four bus wires. Label these 15 volts, - 15 volts, 3 volts, and -3 volts.

Connect a bus wire around the periphery of the control panel and solder this bus wire to each of the ground terminals.

Connect a wire from the "Up" on the power switch to one side of the power light.

Connect the other side of the power light to the ground bus.

Connect the A circuit "Up" of the master switch to the master light.

Connect from the common of circuit A of the master switch to the -15 volt bus.

Connect A circuit "Up" of the power switch to the 15 volt bus.

Connect the B "Up" of the power switch to the -15 volt bus.

Connect, using number 18 awg wire, the 15 volt bus to the amplifier shelf.

Connect, using number 18 awg wire, the -15 volt bus to the amplifier shelf.

Connect the common of circuit B of the master switch to 15 volts.

Connect a 10 microfarad capacitor to the "Up" of circuit B of the master switch and connect the other end of this capacitor to the common of circuit B of the master switch.

Connect the common of the "Control I or E" switch to the 15 volt bus.

Connect the "Up" of the "Control I or E" switch to one side of the light located directly to the right of this switch.

Connect the other side of the light next to the "Controlled I or E" switch to common.

Connect the common of memory 1 switch to 15 volt bus.

Connect a 10 microfarad capacitor to the common of memory 1 switch.

Connect the other end of this capacitor to the "Up" of memory 1 switch.

Connect the common of memory 2 switch to 15 volts bus.

Connect a 10 microfarad capacitor to the common of the memory 2 switch.

Connect the other end of this capacitor to the "Up" of memory 2 switch.

Connect the common of the indicator electrode disconnect switch to 15 volts.

Connect a 10 microfarad capacitor to the common of the indicator electrode disconnect switch and connect the other end of this capacitor to the "Up" of this switch.

Connect the top of the drift A/C switch to the 3 volts bus.

Connect the down of the drift A/C switch to the -3 volt bus.

Connect the common of the drift A/C switch to the top of the indicator drift bias potentiometer.

Connect the bottom of the indicator drift bias potentiometer to the ground bus.

Connect a 3.3 megohm resistor to the slider of the integrator drift bias potentiometer.

Locate the current-measuring resistor switch. This should be a single pole 11 position rotary switch.

Connect a 50 ohm precision resistor to position 2 of this switch.

Connect a 100 ohm precision resistor to position 3 of this switch.

Connect a 500 ohm precision resistor to position 4 of this switch.

Connect a 1 kilohm precision resistor to position 5 of this switch.

Connect a 5 kilohm precision resistor to position 6 of this switch.

Connect a 10 kilohm precision resistor to position 7 of this switch.

Connect a wire from the binding post to position 8.

Connect a wire from the common of the integrator resistor switch to the common of the current-measuring resistor switch.

Connect a 10 kilohm precision resistor to position 1 of the integrator resistor switch.

Connect a 100 kilohm precision resistor to position 2 of the integrator resistor switch.

Connect a 1 megohm precision resistor to position 3 of the integrator resistor switch.

Connect a wire from position 4 of the integrator resistor switch to the terminal marked "external integrator resistor".

Connect a wire from the other terminal marked "external integrator resistor" to the common of the integrator resistor switch.

Connect the ends of the three precision resistors on the integrator resistor switch and terminal 4 of this switch in parallel to the end of the three megohm resistor connected to the slider of the integrator drift bias potentiometer.

Connect a wire from the BNC connector marked Q out to the common of the integrator capacitor switch.

Connect a wire from position 1 of the integrator capacitor switch to the terminal which you will find directly next to it marked "external integrator capacitor". The other terminal directly next to it is connected to the common of the integrator capacitor switch.

Connect a 0.01 microfarad precision capacitor to position 2 of the integrator capacitor switch.

Connect a 0.1 microfarad precision capacitor to position 3 of the integrator capacitor switch.

Connect a 1.0 microfarad precision capacitor to position 4 of the integrator capacitor switch.

Connect a wire from the end of each of the above capacitors and from position 1 of the integrator capacitor switch to the 3 megohm resistor located on the slide wire of the integrator drift bias potentiometer.

On the bias 1 A/C switch, connect the "Up" of circuit A to the "down" of circuit B.

On the bias 1 A/C switch, connect the "Up" of circuit B to the "down" of circuit A.

On the bias 1 A/C switch, connect the common of circuit B to the 3 volt bus.

Connect the cathode of a 1N 536 diode to the "Up" of circuit C of bias 1 A/C switch.

Connect the anode of a 1N 536 diode to the "Down" of circuit C of the bias 1 A/C switch.

On the bias 2 A/C switch connect the "Up" of circuit A to the "Down" of circuit B.

On the bias 2 A/C switch connect the "Up" of circuit B to the "Down" of circuit A.

Connect the common of circuit B of bias 2 A/C switch to the 3 volt bus.

Connect the cathode of 1N 536 diode to the "Up" of circuit C of the bias 2 A/C switch.

Connect the anode of a 1N 536 diode to the "Down" of circuit C of the bias 2 A/C switch.

On the bias 3 A/C switch, connect the "Up" of circuit A to the "Down" of circuit B.

On the bias 3 A/C switch, connect the up of circuit B to the "Down" of circuit A.

On the bias 3 A/C switch, connect the common of circuit B to 3 volt bus.

Connect the cathode of a 1N 536 diode to the "Up" of circuit C of the bias 3 A/C switch.

Connect the anode of a 1N 536 diode to the "down" of circuit C of the bias 3 A/C switch.

Connect a wire from the common of circuit C of the bias 1 A/C switch to the top of the bias 1 potentiometer.

Connect the bottom of the bias 1 potentiometer to ground.

Connect a wire from the common of circuit C of the bias 2 A/C switch to the top of bias 2 potentiometer.

Connect the bottom of the bias 2 potentiometer to ground.

Connect a wire from the common of circuit C of the bias 3 A/C switch to the top of the bias 3 potentiometer.

Connect a wire from the bottom of the bias 3 potentiometer to ground.

Connect a wire from the common of the bias 1 On/Off switch to the 15 volts.

Connect a 10 microfarad capacitor to the common of the bias 1 On/Off switch and connect the other end of this capacitor to the top of the bias

1 On/Off switch.

Connect a wire from the common of the bias 2 On/Off switch to the 15 volts.

Connect a 10 microfarad capacitor to the common of the bias 2 On/Off switch and connect the other end of this capacitor to the top of the bias 2 On/Off switch.

Connect a wire from the common of the bias 3 On/Off switch to the 15 volts.

Connect a 10 microfarad capacitor to the common of the bias 3 On/Off switch and connect the other end of this capacitor to the up of the bias 3 On/Off switch.

Connect a wire from the "down" of the sweep drift A/C switch to the -3 volt bus.

Connect a wire from the "Up" of the sweep drift A/C switch to the 3 volt bus.

Connect a wire from the common of the sweep drift A/C switch to the top of the sweep drift bias potentiometer.

Connect the bottom of the sweep drift bias potentiometer to the ground bus.

Connect the 30 megohm resistor to the slider of the sweep drift bias potentiometer.

Connect a wire from the end of the resistor on the slider of the sweep drift bias potentiometer to the common of the sweep capacitor switch.

Connect a wire from the top of the cathodic sweep rate potentiometer to the 3 volt bus.

Connect the bottom of the cathodic sweep rate potentiometer to the ground bus.

Connect a wire from the -3 volt bus to the top of the anodic sweep rate potentiometer.

Connect the bottom of the anodic sweep rate potentiometer to the ground bus.

Connect the slider of the cathodic sweep rate potentiometer to the "down" of the manual sweep reversing switch.

Connect a wire from the slider of the anodic sweep rate potentiometer to the "Up" of the manual sweep reversing switch.

Connect a wire from the common of the manual sweep reversing switch to the "Up" of the manual or auto reversing switch.

Connect a 1 megohm precision resistor to position 1 of the sweep resistor switch.

Connect a 100 kilohm precision resistor to position 2 of the sweep resistor switch.

Connect a wire from position 3 of the sweep resistor switch to the terminal marked "external sweep resistor" located directly next to this switch.

From the other terminal marked "external sweep resistor" switch connect a wire to the common of the sweep resistor switch.

Connect the common of the sweep resistor switch to the common of the sweep capacitor switch.

Connect the cathode of a 1 N 536 diode to the "Up" of the auto or manual hold switch.

Connect a wire from the "Up" of the manual hold switch to the "Down" of the auto or manual hold switch.

Connect the common of the manual hold switch to the 15 volts.

Connect a 10 microfarad capacitor to the common of the manual hold switch and connect the other end of this capacitor to the up of the manual hold switch.

Connect the common of the sweep switch to 15 volts.

Connect a 10 microfarad capacitor to the common of the sweep switch, and connect the other end of this capacitor to the "Up" of the sweep switch.

Connect a wire from the "Up" of the sweep switch to the "Up" of the sweep on integrate/step switch.

Connect a wire from the "Up" of the bias 1 On/Off switch to the "Down" of the sweep on integrate/step switch.

Connect a 0.01 microfarad precision capacitor to position 1 of the sweep capacitor switch.

Connect a 0.1 microfarad precision capacitor to position 2 of the sweep capacitor switch.

Connect a 1.0 microfarad precision capacitor to position 3 of the sweep capacitor switch.

Connect a wire from position 4 of the sweep capacitor switch to the terminal marked "external sweep capacitor" found directly next to the sweep capacitor switch.

Connect the other terminal marked "external sweep capacitor" to the common of the sweep capacitor switch.

Connect the "Up" of circuit A of the slope switch to the "Down" of circuit B of the slope switch.

Connect the "Up" of circuit B of the slope switch to the "Down" of circuit A of the slope switch.

Connect a wire from the slider of the hold potential potentiometer to the "Up" of circuit A on the slope switch.

Connect a wire from the top of the hold potential potentiometer to the common of the hold potential A/C switch.

Connect a wire from the 3 volt to the "Up" of the hold potential A/C switch.

Connect a wire from the -3 volt to the "down" of the hold potential

A/C switch.

Connect a shielded wire from the "Up" of circuit B of the slope switch to the nearest binding post marked "E out".

Connect a wire from the 3 volts to the "Up" of the anodic gate A/C switch.

Connect a wire from the -3 volts to the "Down" of the anodic gate A/C switch.

Connect the common of the anodic gate A/C switch to the top of the anodic gate potential potentiometer.

Connect the bottom of the anodic gate potential potentiometer to the ground bus.

Connect a wire from 3 volts to the "Up" of the cathodic gate A/C switch.

Connect a wire from the -3 volts to the "Down" of the cathodic gate A/C switch.

Connect the common of the cathodic gate A/C switch to the top of the cathodic gate potential potentiometer.

Connect the bottom of the cathodic gate potential potentiometer to the ground bus.

Connect the cathode of a 1N 536 diode to the initial direction-cathodic switch.

Connect a wire from the 15 volts to the top of the initial direction-cathodic switch.

Connect the anode of a 1N 536 diode to the common of the initial direction-anodic switch.

Connect the top of the initial direction-anodic switch to the -15 volts.

Connect the common of the timer 1 R switch to the top of the timer 1 potentiometer.

Connect the common of circuits A of the timer 1 On/Off switch to the 15 volts.

Connect a 10 microfarad capacitor to the common of circuit A of the timer 1 On/Off switch and connect the other and of this capacitor to the "Up" of the timer 1 On/Off switch.

Connect the common of circuit B of the timer 1 On/Off swith to the ground bus bar.

Connect position 1 of the timer 1 R switch to 15 volts.

Connect 100 kilohm resistors from position 1 to 2 from 2 to 3 and all the way around on the timer iR switch. There should be 11 100 kilohm resistors on this switch.

Connect position 1 of the timer 2R switch to 15 volts.

Connect 100 kilohm resistors from position 1 to 2 from 2 to 3 to 4 etc. all around timer 2R switch.

Connect the common of the timer 2 On/Off switch to 15 volts.

Connect the common of the chrono On/Off switch to 15 volts.

Connect a 10 microfarad capacitor to the common of the chrono On/Off switch and connect the other end of this capacitor to the "Up" of the chrono On/Off switch.

Connect the common of the integrate switch to 15 volts.

The input and output terminals on the left side of the control panel are duplicated on the right side of the control panel.

Using shielded wires, connect the corresponding binding posts on the right hand side of the panel to those on the left hand side of the panel.

This completes the initial assembly work on the control panel.

Section IV. Switching Matrices.

Take the matrix switches and interconnect the vertical columns to the horizontal rows so that row 1 is connected to column 1 and so on.

Connect wires to columns 1 through 40 sufficiently long that they will reach the relay shelf. Label these wires with their corresponding numbers.

On the small 10 x 10 matrix interconnect the rows and columns so that row 1 is connected to column 1 etc.

Connect shielded wires to the rows 1-10 making them long enough to reach the control panel. Label these wires.

This completes all the preliminary assembly work. At this time inspect all of the wiring. Make certain that all soldering done so far is neat and that no obvious shorts or cold soldered joints can be seen.

Mount the shelves and the control panel, but at this stage do not mount the matrix switches.

Bring the bundle of wires from the amplifier shelf up through the relay shelf, but keep the bundle separated from all the other wires.

At this point there should be three bundles of wires in the general vicinity where the relay shelf and the control panel abut.

FINAL ASSEMBLY

We will now begin final assembly. When making these final connections, find the wire called for, lead it through the cable clamps and position it exactly. Once it is well positioned, cut the wire to proper length, strip it, and install it and make the solder connection. If, at any time, there is doubt as to whether a wire comes from the correct component, check. It is much easier to debug any errors made initially at this stage of the assembly than after all the wires have been soldered into place. Be extremely careful that the shielded wires do not touch each other or touch ground. If the insulation has been scratched or torn, put tape on to guarantee good insulation. This procedure will go far in avoiding ground loop problems once the instrument is in operation.

Find the wire connected to the input of the control amplifier and connect it to the open end of the 47 kilouhm resistor found at pin 5 of relay 3.

Find the wire connected to the output of the control amplifier and connect it to pin 2 of relay 3.

Find the wire from pin 6 of the following amplifier and connect it to pin 4 of relay 10. (Pin 6 is the output of the follower amplifier).

Connect a wire from the positive input pin 2 of memory 1 amplifier and connect it to pin 3 of relay 8.

Find the wire from the positive input of memory 2 amplifier pin 2 and connect it to pin 3 of relay 9.

Find the wire from the input of the sweep generator amplifier and connect it to pin 5 of relay 4.

Find the wire from the output of the sweep generator amplifier and connect it to pin 3 of relay 4.

Find the wire from the input of the integrator amplifier and connect it to pin 2 of relay 10.

Find the wire from the output of the integrator amplifier and connect it to pin 1 of relay 10.

Connect a wire from the 15 volt bus on the control panel to pin 5 of relay 21.

Connect a wire from the 3 volt bus on the control panel to pin 1 of relay 21.

Find the wire from the output of the inverter amplifier pin 6 and connect it to pin 6 of relay 11.

Find the wire from the input of the current-measuring amplifier and connect it to pin 5 of relay 12.

Connect pin of relay 13 to pin 5 of relay 12.

Connect a wire from the 15 volt bus on the control panel to pin 2 of relay 18.

Connect a wire from the 15 volt bus on the control panel to pin 6 of relay 20.

Find a wire from pin 8 of relay 11 and connect it to the UP of the controlled I or E switch on the control panel.

Find the wire from pin 8 of relay 8 and bring it to the UP of the memory 1 switch on the control panel.

Find the wire from pin 8 of relay 9 and connect it to the UP of memory 2 switch on the control panel.

Find the wire from pin 6 (output) of the follower amplifier and connect it to the BNC connector marked "E out".

Find the wire from the output of the current measuring amplifier and connect it to the BNC connector on the control panel marked "I out".

Find the wire from the output of the integrator amplifier, and connect this to the BNC connector on the control panel marked "Q out".

Find the wire from pin 4 of relay 3 and connect it to the binding post on the control panel marked "applied voltage".

Find the wire from pin 3 of relay 14 and connect it to the BNC connector marked "indicator electrode".

Find the wire from pin 8 of relay 14 and connect it to the UP of the indicator electrode disconnect switch.

Using 18 gauge wire, connect pin 6 of the 3 volt power supply amplifier to the 3 volt bus wire on the control panel.

Using 18 gauge wire, connect pin 6 of the -3 volt power supply amplifier to the bus on the control panel marked -3 volts.

Find the wire from the output of the memory 1 amplifier (pin 6) and connect it to the memory 1 binding post on the control panel.

Find the wire from the output of the memory 2 amplifier (pin 6) and connect it to the binding post marked memory 2.

Find the wire from pin 8 of relay 12 and connect it to the UP of the I measuring amp IN/OUT switch.

Find the wire connected to the input of the integrator amplifier and connect it to the open end of the 3.3 megohm resistor connected to the integrator drift bias potentiometer.

Find the wire from the output of the current measuring amplifier and connect it to the common of the I measuring resistor switch.

Find the wire from the input of the current measuring amplifier and connect it to the open end of the precision resistors and to position 1 of the I measuring resistor switch.

Find the wire from pin 2 of the bias 1 amplifier and connect it to the

DOWN of circuit A of the bias 1 A/C switch.

Find the wire from pin 3 of relay 5 and connect it to the common of circuit A of the bias 1 A/C switch.

Find the wire from pin 3 of bias 1 amplifier and connect to the DOWN of circuit B of the bias 1 A/C switch.

Find the wire from pin 2 of bias 2 amplifier and connect it to the DOWN of circuit A of the bias 2 A/C switch.

Find the wire from pin 3 of relay 6 and connect it to the common of circuit A of the bias 2 A/C switch.

Find the wire from pin 3 of bias 2 amplifier and connect it to the DOWN of circuit B of the bias 2 A/C switch.

Find the wire from pin 2 of bias 3 amplifier and connect it to the DOWN of circuit A of the bias 3 A/C switch.

Find the wire from pin 3 of relay 7 and connect it to the common of circuit A of the bias 3 A/C switch.

Find the wire from pin 3 of bias 3 amplifier and connect it to the DOWN of circuit B of the bias 3 A/C switch.

Find the wire from pin 8 of relay 5 and connect it to the UP of the bias 1 ON/OFF switch.

Find the wire from pin 8 of relay 6 and connect it to the UP of the bias 2 ON/OFF switch.

Find the wire from pin 8 of relay 7 and connect it to the UP of the bias 3 ON/OFF switch.

Find the wire from pin 5 of relay 2 and connect it to the common of the manual or auto reversing switch.

Find the wire from pin 3 of relay 1 and connect it to the DOWN of the manual or auto reversing switch.

Find the wire from the input of the sweep generator amplifier and connect it to the common of the sweep resistor switch.

Find the wire from pin 3 of relay 2 and connect it to the other end of the precision resistors found on the sweep resistor switch.

Find the wire from pin 6 (output) of the hold gate amplifier and connect it to the anode of the diode mounted on the UP of the auto or manual hold switch.

Find the wire from pin 8 of relay 2 and connect it to the common of the auto or manual hold switch.

Find the wire from pin 8 of relay 4 and connect it to the UP of the sweep switch.

Find the wire from pin 3 of relay 4 and connect it to the open end of the capacitors found at the sweep capacitor switch.

Find the wire connected to pin 2 of the hold gate and connect it to the common of circuit A of the slope switch.

Find the wire from pin 3 of the hold gate amplifier and connect it to the common of circuit B of the slope switch.

Find the wire from pin 3 of the anodic gate amplifier and connect it to the slider of the anodic gate potential potentiometer.

Find the wire from pin 2 of the anodic gate amplifier and connect it to the B and C connector marked "E out" on the control panel.

Find the wire from pin 3 of the cathodic gate amplifier and connect it to the slider of the cathodic gate potential potentiometer.

Find the wire from pin 6 of the cathodic gate amplifier and connect it to the anode of the diode found on the initial direction cathodic switch.

Find the wire connected to pin 8 of relay 1 and connect it to the cathode of the diode found mounted on the initial direction-anodic switch.

Find the wire from pin 6 of relay 1 and connect it to the anode of the diode at the initial direction-anodic switch.

Find the wire from pin 5 of relay 1 and connect it to the slider of the cathodic sweep rate potentiometer.

Find the wire from pin 1 of relay 1 and connect it to the slider of the anodic sweep rate potentiometer.

Find the wire from pin 8 of relay 19 and connect it to circuit A UP of the timer 1 ON/OFF switch.

Find the wire from pin 8 of relay 18 and bring it to the UP of the timer 2 ON/OFF switch.

Find the wire from pin 6 of relay 10 and connect it to the common of the integrate on sweep/step switch.

Find the wire from pin 8 of relay 10 and connect it to the UP of the integrate switch.

Find the wire from pin 2 of the follower amplifier and connect it to the BNC connector marked "reference electrode" on the control panel.

Find the wire from pin 1 of relay 11 and connect it to the BNC connector marked "counter electrode" on the control panel.

Mount the matrix switches on a 19" panel so that they abut horizontally Connect each slide bar to its corresponding numbered horizontal step/

Mount the panel. Connect the following components to the slide bar number as follows:

Component	Slide Bar
RLY 3 - Pin 8	1
RLY 11 - Pin 8	2
RLY 2 - Pin 8	3
RLY 4 - Pin 8	4
RLY 5 - Pin 8	5
RLY 6 - Pin 8	6
RLY 7 - Pin 8	7
RLY 12 - Pin 8	8
RLY 14 - Pin 8	9
RLY 15 - Pin 8	10
RLY 8 - Pin 8	11

RLY 9 - Pin 8	12
RLY 18 - Pin 8	13
RLY 19 - Pin 1	14
RLY 19 - Pin 2	15
RLY 19 - Pin 3	16
RLY 19 - Pin 4	17
RLY 19 - Pin 5	18
RLY 19 - Pin 6	19
RLY 20 - Pin 1	20
RLY 20 - Pin 2	21
RLY 20 - Pin 3	22
RLY 20 - Pin 4	23
RLY 20 - Pin 5	24
RLY 20 - Pin 6	25
RLY 17 - Pin 4	26
RLY 17 - Pin 5	27
RLY 17 - Pin 6	28
RLY 16 - Pin 1	29
RLY 16 - Pin 2	30
RLY 16 - Pin 3	31
RLY 16 - Pin 4	32
RLY 16 - Pin 5	33
RLY 16 - Pin 6	34
Not used	35
RLY 10 - Pin 8	36
RLY 10 - Pin 6	37

15 volts	38
Not used	39
Binding Post (Trigger)	40

Construction of 2 Timer Circuit Boards

The 2 timers will be built in individual aluminum boxes. The actual components will be mounted circuit boards.

Mount the following components on their individual boards using the schematic supplied.

Mount the 2N 494C unijunction transistor.

From the emitter of the 2N 494C mount a 1.0 F Mylar capacitor to ground.

Connect a 27 ohm resistor between Base 1 of the 2N 494C transistor and ground.

Mount a 150 ohm resistor between 15 volts and Base 2 of the 2N 494C.

Mount a 2N 491 unijunction transistor.

Connect a 0.001 F capacitor between Base 2 of the 2N 494C and the emitter of the 2N 491.

Mount a 0.5 F Mylar capacitor between the emitter of the 2N 491 and ground.

Mount a 390 K resistor between 15 volts and the emitter of the 2N 491.

Mount a 150 ohm resistor between 15 volts and Base 2 of the 2N 491.

Ground Base 1 of the 2N 491.

Connect the gate of the 2N 683 silicon controlled rectifier to Base 2N 494C transistor.

On timer 1 bring shielded wires to the control panel from the emitter of the 2N 494C, from the cathode of the 2N 683, and from the 15 volts. Bring a wire from the anode of the 2N 683 to the relay shelf. This should also be shielded.

On timer 2 bring shielded wires to the relay shelf from the emitter of the 2N 494C and from the cathode and the anode of the 2N 683.

Bring shielded wires to the control panel from the 15 volts and from the emitter of the 2N 494C. Make sure to label carefully all of these shielded wires.

Find the wire from the emitter of the 2N 494C unijunction transistor located on the timer 1 circuit and connect this to the wiper of the timer 1 potentiometer.

Find a wire from the emitter of the 2N 494C unijunction transistor on the timer 2 board and connect this to the wiper of the timer 2 potentiometer located on the control panel.

Find the wire from the emitter of the 2N 494C unijunction transistor of the timer 1 circuit board and go to the DOWN of the circuit B of the timer 1 OFF/ONN switch.

Parts List

The following is a parts list of components used in the chronocoulometer which are normally not stocked in chemistry laboratores.

All double pole relays are Type HG2A1072. All single pole relays are Type HGS 5008 except relay 1 which is a Type HGS 5013. The latter types have form C, SPDT, break-before-make contacts. The former have form D, make-before-break contacts.

The switches are normal SPDT and DPDT types, however, the particular types were chosen for their small size and the fact that they have hermetically sealed silver contacts.

The P65AU amplifiers are used for the bias, power supply, and potential sensitive gate functions. The P75AU is used for the potential follower. All single ended chopper stabilized amplifiers are type SP656.

The power supplies used are convenient, however, many types are available which will accomplish the same purpose at somewhat lower cost.

Component	No	Supplier & Part No.
Resistor, precision, metal film. 100, 500, 1K, 5K, 20K, 100K, 1M ohms	2 ea.	International Resistance Corp.
Switch, rotary ten position,	10 ea.	Alco Switch Corp., MRA-1-10
Switch, push button, spdt,	2 ea.	Alco Switch Corp., MSP-105F
Switch, toggle, spdt,	30 ea.	Alco Switch Corp., MST-105D
Switch, toggle, dpdt,	10 ea.	Alco Switch Corp., MST-205N
Cable, coaxial	500 ft.	Alpha Wire, RG-174/U
Diode	6 ea.	Texas Instruments, 1N702
Diode	18 ea.	Transitron, Inc., 1N270
Transistor	2 ea.	General Electric, 2N494C
Transistor	2 ea.	General Electric, 2N491B
Controlled Rectifier	2 ea.	General Electric, 2N2323
Capacitor, 0.1%, 0.01, 0.10 1.0 mfd.	3 ea.	Southern Electronics, Inc. PC103A2AT
Switch, 40 poles, 20 positions.	2 ea.	Cherry Electrical Products, C10-40A
Potentiometer, 10 turn, 20K ohms, 0.5% linearity	12 ea.	Bourns, Inc., Type 3500
Potentiometer, 10 turn 100K ohms, 0.5% linearity	2 ea.	Bourns, Inc., Type 3500
Ten turn dial	14 ea.	Helipot Div., Type 2606
Relay, Hg wetted, spdt	15 ea.	C.P. Clare, HGS5008
Relay, Hg wetted, dpdt	10 ea.	C.P. Clare, HG2A1072
Relay, Hg wetted, bistable double wound coil, spdt	1 ea.	C.P. Clare, HGS5013

Component	No	Supplier & Part No.
Amplifier, operational	4 ea.	Philbrick, Inc., SP656
Amplifier, operational	2 ea.	Philbrick, Inc., SP2A
Amplifier, operational	11 ea.	Philbrick, Inc., P65AU
Amplifier, operational	1 ea.	Philbrick, Inc., P75AU
Amplifier, booster	2 ea.	Philbrick, Inc., P66
Power Supply	2 ea.	Harrison Labs., 726A

CHAPTER 7

Digital Data Acquisition

A specific approach to the instrumentation requirements necessary for many of the electrochemical perturbation methods was given in Chapter 5 and 6. In this chapter we shall discuss the problems of data acquisition and describe, in detail, a solution which appears to be emminently useful, albeit quite expensive.

Most of the perturbation techniques require that the response signal be measured as a function of time and that the raw signal be then correlated with some theoretical, not necessarily linear, function of time. The time periods involved are invariably short, 100 milliseconds total elapsed time or less. This short time span precludes the use of ordinary strip chart recorders to acquire the data, and therefore the standard practice has been to use an oscilloscope and to photograph the signal versus the time sweep. The data is then read off of the picture. Such a method is inherently inaccurate. The screen of most scopes is on the order of 8 cm. square and trace widths of 2 millimeters are not uncommon. In addition parallax error of the camera also adds systematically to errors. Under ideal conditions a 3 to 4% precision can be expected.

Another major problem is that the task of reading such photographs is particularly burdensome. Thus though the techniques date back 3 to 10 years, very little actual data of use in correlating phenomena has appeared; the major emphasis by most workers being in developing newer and faster methods, and then proving that they are valid by studying some "well known system". There is thus an obvious need to automate the data acquisition process.

We first consider the normal sequence of performing an experiment. The steps are shown in Figure 7-1. It is vital that the first three steps be performed in "real time' that is in clock time. The other functions are usually time independent (and, as mentioned, time consuming). It is obvious that each of these functions could be totally automated for a given experiment. This approach has been used extensively for process control in industry. However, in a laboratory

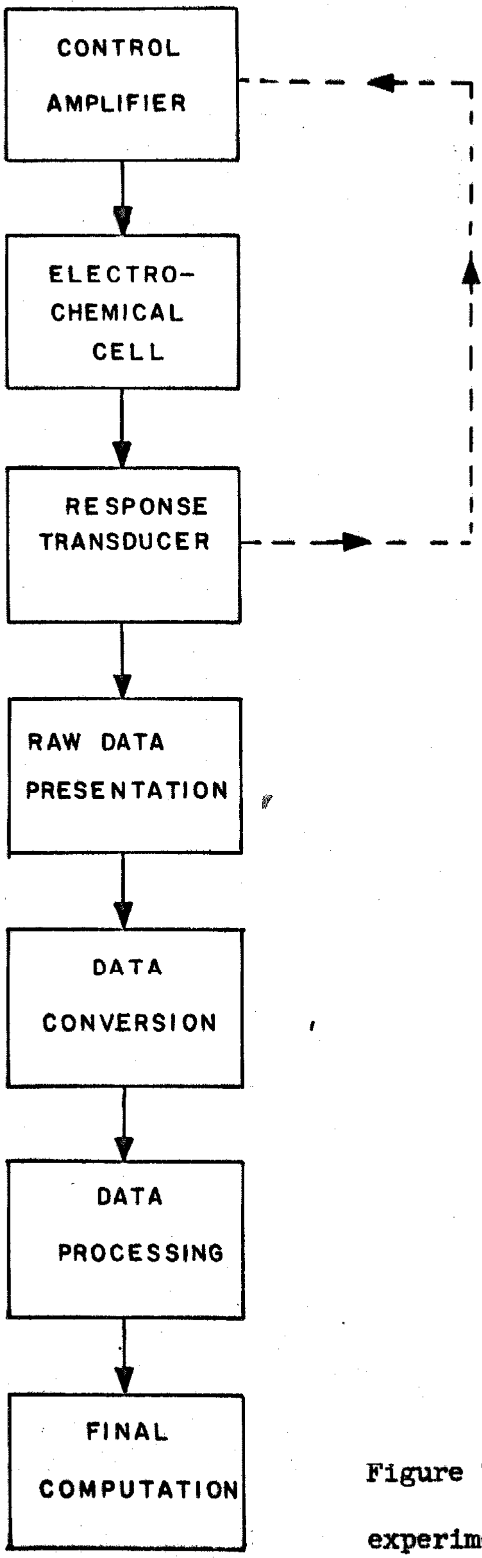


Figure 7-1. Flow chart of normal experimental sequence of operation.

such a method is worthless as the parameters necessary for total control of automation are those being sought and any given system is obsolete at the end of the debugging stage, necessitating total rewiring of the automatic controls. The investment in time and money quickly outweighs any advantages.

However, we shall consider just what generalized components are necessary for control. These are:

1) A device to switch the control voltages at the correct time.

2) A device which will record or store the data in real time which can then be read at leisure. This device should be controlled by 1) above.

3) A device which will convert the output of 2) into a form suitable for computer input.

These devices are all "hardware". That is they are all prewired to perform a specific function. To make automatic data acquisition profitable in a research laboratory one requires a machine which can be "taught" to rewire itself whenever variations in the experimental procedure are required. In essence we require a computer.

A computer is distinguished from automatic data handling equipment by the fact that the time sequence of operations to be performed is not wired, rather it is "written" into a memory at experiment time. This the sequence becomes a matter of "software". The requirements on the computer are few, but stringent. These are:

1) Capability to perform a limited number of logical operations.

2) Capability to make simple decisions.

3) Capability of easy communication with external devices.

4) High speed so that the time constant of operations is not the limiting factor in the experiment.

A computer which has these characteristics was installed and interfaced to the chronocoulometer. The following sections will describe, in some detail, the computer in relation to its use as a data acquisition system for electrochemical experimental methods.

The computer purchased is a Scientific Control Corporation Model 660-5. It has 4096 word memory, each word consisting of 24 bits. It has one index register and has indirect addressing capability.

Definitions - Before going into detailed operation we shall state a few definitions of terms to reduce ambiguities which invariably crop up in the terminology. A "bit" is one unit of binary information as it can assume values of either zero or one. A "word" is an ordered combination of 24 bits. It is the practice to number the bits of a word from left to right beginning from zero; therefore the right-most bit is bit #23.

A "register" is a combination of bistable devices arranged to form a word. Operations on data words can only be performed in registers.

The memory is composed of an array of devices, each of which can store one bit. The devices are grouped in words; these words are referred to as addresses and are assigned sequential numbers from 0 to 4095. Data can be read into the registers from the memory and from the registers into the mamory. It is thus apparent that all data must be in the form of binary numbers.

The combination of all the registers and their associated circuitry is termed the central processing unit (CPU). The CPU is composed of the following registers.

1) Accumulator (AC)

2) Extended Accumulator (EA)

3) Instruction Register (IR)

4) Location Counter (LC)

5) Index Register (XR)

6) Input/output Register (B Buffer)

An instruction is a word with the value of the bits arranged in such a manner that when decoded, the machine performs a given operation. In the SCC 660-5 the instruction is structured in the following manner. Bits 0 through 9 contain the actual operation code, i.e., add, subtract, etc. and bit 15 through 23 contain the location in the memory (the address) where the data to be operated on is stored.

It should be noted that information in the address is not destroyed when the contents of that address are transferred to a register. On the other hand old information in an address is always destroyed when new data is transferred in. This also applies, in most cases, to the registers.

Basic Operation - To illustrate the operation of the computer we assume that we have a set of instructions in the memory at addresses 0 to 200. We assume that all registers contain zero at the beginning. When the machine is started the contents of the address specified by the contents of the location counter are transferred to the instruction register. The contents of the IR are then decoded as a meaningful operation which is executed by the computer; the location counter is then incremented by one and the whole cycle begins again, this time the instruction being taken from address 1. Thus the computer, once started, takes its instructions, sequentially, from the memory. However, the computer itself has no way of determining the difference between an instruction and a piece of data. It is therefore the responsibility of the operator to insure that the sequential operation will not end up in an address containing data.

The instruction repertoire of the computer consists of the following sets:

1) Mathematical instructions; these instructions cause the computer to add, subtract, multiply or divide the contents of the AC or EA and the contents of the word addressed in the instruction, symbolized by Q.

2) Store instruction; these instructions cause the computer to store the content of the register in Q. Storage does not affect the contents of the register but does destroy the previous information in Q.

3) Logical Instructions; these instructions cause the computer to perform logical operations between Q and the AC.

4) Branch Instructions; these instructions cause Q to replace the contents of the LC and thus override the sequential execution of instructions. This "branch" can be performed based on a test of the contents of the index register.

5) Skip Instructions; these instructions cause the LC to be incremented by two rather than one based on the sign of the AC, the sign of the contents of Q or an external device condition.

6) Input/output Instructions; these instructions cause the computer to transfer the contents of Q to or from an external device such as the typewriter or to output a signal which an external device can sense.

The index register serves as an auxiliary addressing aid. If bit 1 of an instruction contains a 1, the address on which the operation will take place is determined by adding the contents of the XR to Q. There are, therefore, a set of instructions which cause the computer to load, increment, or store the data into or from the index register.

The actual programming of the computer will not be dealt with in this dissertation. Adequate programming literature has been made available by the manufacturer. In addition, many texts on programming fundamentals are available. Therefore, only those operations which directly affect data acquisition and/or control functions will be considered in detail.

Control Requirements - The requirements are that the computer control the chronocoulometer, convert the data voltage signal to a digital number, and to store this number in its memory. At that point the problem becomes a programming task to output rational numbers. To perform this task we make use of the "activate external device" instruction of the computer. This instruction has the structure 000010011xxxxxxxxxxxx in binary or 0023xxxx, or symbolically ACT3xxxx (numbers shown are in octal). Upon execution of this instruction the computer sends out, on twelve parallel lines voltage levels corresponding to the presence or absence of a 1 or zero in bits 12 to 23 respectively. In addition a 5 microsecond pulse is sent on a special line when the instruction is executed. The task of converting this set of signals into a set of operations is the essence of interfacing the computer to the chronocoulometer. Before going into the implementation of this task we must digress into the subject of logical or digital circuitry.

Digital Circuits

We consider the circuit shown in Figure 7-2. We assume that the input voltage is zero volts. Then V_B, the voltage at the base is about

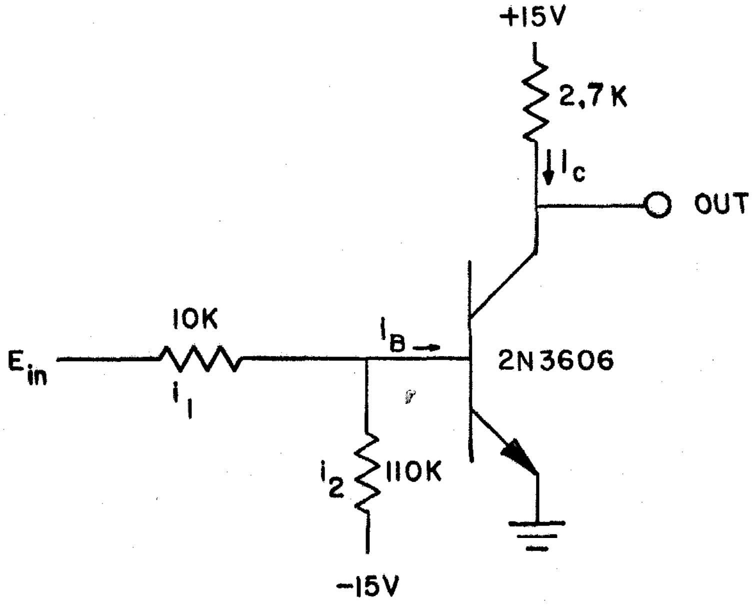


Figure 7-2. Basic digital switching circuit or inverter.

-1.5 volts as the 10K and 110K resistors act as a voltage divider. If V_B is less than the emitter voltage, the transistor is cut off and I_c, the current through the collector is zero; the output at the collector is therefore 15 volts. The dynamic current transfer ratio or current gain, h_{FE}, is defined as the ratio of collector current to base current required to turn the transistor "on" i.e., act essentially as a short. For the 2N3606 the minimum h_{FE} is about 30. If we assume that the transistor acts as a short circuit when on, the collector current is determined only by the supply voltage and the collector resistor. For the circuit under consideration this is 6.8 MA. With h_{FE} 30 the minimum base current to turn the transistor on, I_{Bmin} is given by

$$I_{Bmin} = \frac{I_c}{h_{FE}} = \frac{6.8}{30}\ \mathrm{mA} \qquad (7\text{-}1)$$

There is, however, an additional 0.136 MA from the -15 volts supply through the 110K resistor and therefore we require 0.362 MA, the base-emitter junction being considered a short circuit. The minimum voltage at the input required to turn the transistor on is therefore 3.6 volts. If the input voltage is greater than 3.6 volts, the output at the collector is essentially zero volts.

Clamping - Restricting the discussion to two signal levels, 0 and 15 volts, the circuits act as an inverter. However, if the output is loaded to any extent, the 15 V output will drop, that is the output impedance is quite high, precisely 2.7 K ohms. To overcome this we arbitrarily reduce the assumed level to 8 volts by "clamping" the output as shown in Figure 7-3. The diode is reverse biased when the transistor is saturated on. When it is turned off, the voltage rises toward 15 volts, however, the diode becomes forward biased at 8 volts and "clamps" the output at that voltage. A number of advantages accrue from this technique. First the effective output impedance is reduced to an effective zero until the maximum current, 6.8 MA is drawn. Secondly when the transistor turns off and comes out of saturation, the output rises exponentially to 15 volts as the space charge builds up.

The initial rise is rapid and then the output becomes clamped. In effect the rise time of the circuit is increased. For the rest of

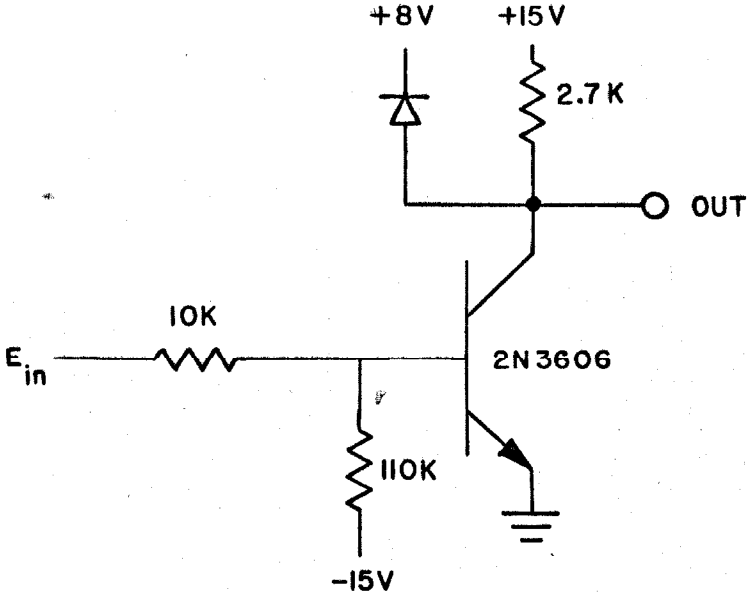


Figure 7-3. Basic digital inverter with clamped output.

the discussion in this chapter, we shall assume only these two signal levels are present, 0 and 8 volts.

Logic Circuits - We now consider the circuit shown in Figure 7-4. If E_1 and E_2 are both at zero volts, E_{out} is zero. If E_1 is at 8 volts and E_2 is at zero, D_1 is reverse biased, however, D_2 can still conduct and therefore E_{out} is zero. If both E_1 and E_2 are at 8 volts both diodes block any voltage less than 8 volts and E_{out} is 8 volts. Thus E_{out} is 8 volts if and only if both E_1 and E_2 are at 8 volts. If we consider the presence of 8 volts at the line as the assertion of a state and 0 volts as the negation, then the table in Figure 7-4 is a "truth table".

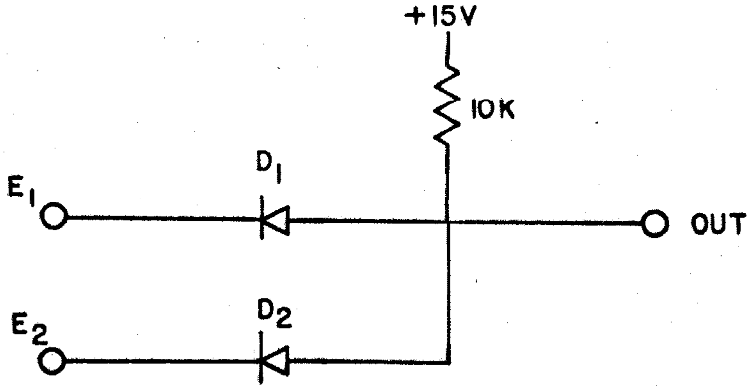
The circuit performs the logical AND function. Thus we can write

If E_1 and E_2, then E_{out}

or symbolically

$$E_{out} = E_1 \cdot E_2 \qquad (7\text{-}2)$$

We now consider the circuit shown in Figure 7-5. If E_1 and E_2 are both zero, E_{out} is zero. If either E_1 or E_2 or both are at 8 volts



TRUTH TABLE

E_1	E_2	OUT
0	0	0
0	8	0
8	0	0
8	8	8

Figure 7-4. Digital AND circuit using diode logic.

the output is 8 volts. This circuit therefore performs the inclusive or logical OR function, thus we can write

$$\text{If } E_1 \text{ or } E_2, \text{ then } E_{out}$$

or symbolically

$$E_{out} = E_1 + E_2 \tag{7-3}$$

The choice that 8 volts is the assertion of the state is totally arbitrary. If we define zero as the assertion and 8 volts as the negative and inspect the truth tables in Figures 7-4 and 7-5, it will become immediately apparent that the functions of the circuits depicted become inverted i.e., the circuit in Figure 7-4 performs the OR functions and that in Figure 7-5 performs the AND function.

In the following discussion, unless specifically noted otherwise, an 8 volt level will be considered the assertion or "1" state and the 0V level the negation or "0" state. The circuits described are commonly referred to as "gates" and this terminology will be used. If the state A is asserted or is "1" it is written A; if it is negated or "0" it is written $\bar{A}$.

These circuits, though useful, are limited as the signal output is derived from a high impedance source and is quickly degraded by only a few levels of logic. To overcome this, we combine the inverter circuit and AND gate to form the NAND gate shown in Figure 7-6. The logical function performed by this circuit may be written as

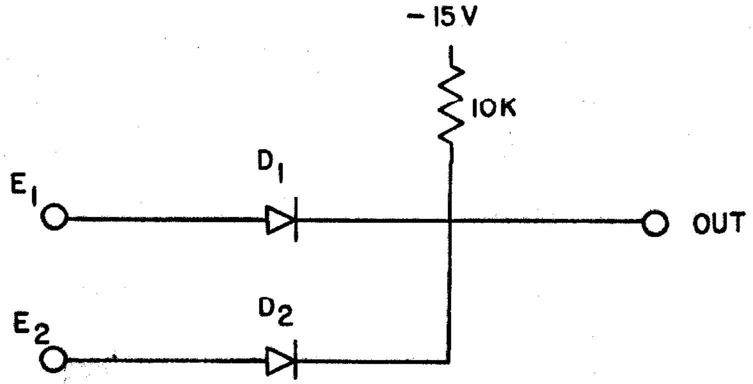
$$Y = \overline{A \cdot B}$$

Similarly the NOR circuit is shown in Figure 7-7. Its function may be written

$$Y = \overline{A + B}$$

Bistable Devices - The circuits described perform logical functions on voltage levels or pulses of sufficiently long duration (1 microsecond minimum for the devices used). For complete implementation we require a device which can act as a memory, that is a bistable circuit. Such a device, commonly called a flip-flop is shown in Figure 7-8. It is constructed by interconnecting two inverters, the output of one goes to the input of the other.

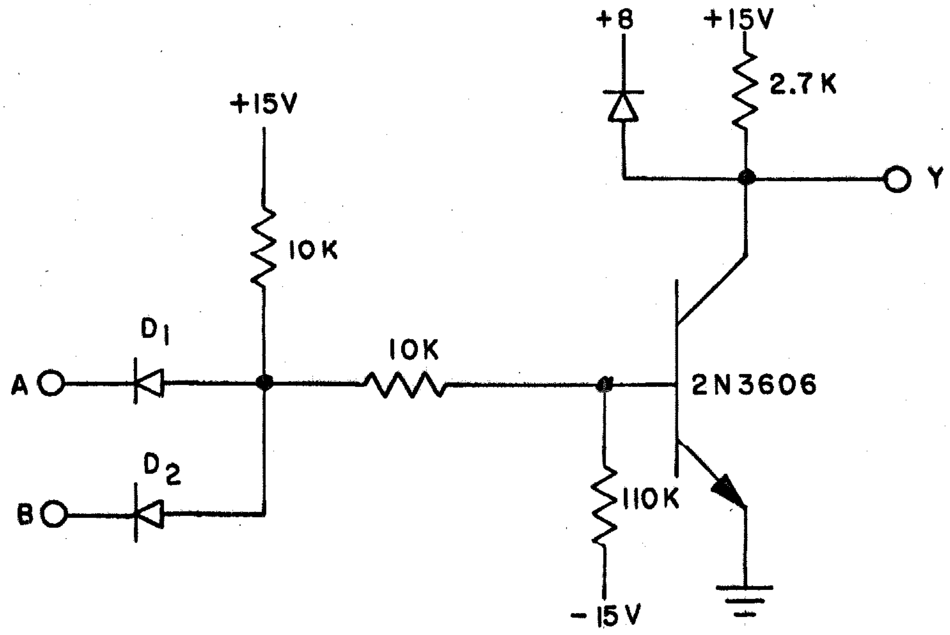
Referring to Figure 7-8, if OUT 1 is 8 volts the input to Q_2 is



TRUTH TABLE

E_1	E_2	OUT
0	0	0
0	8	8
8	0	8
8	8	8

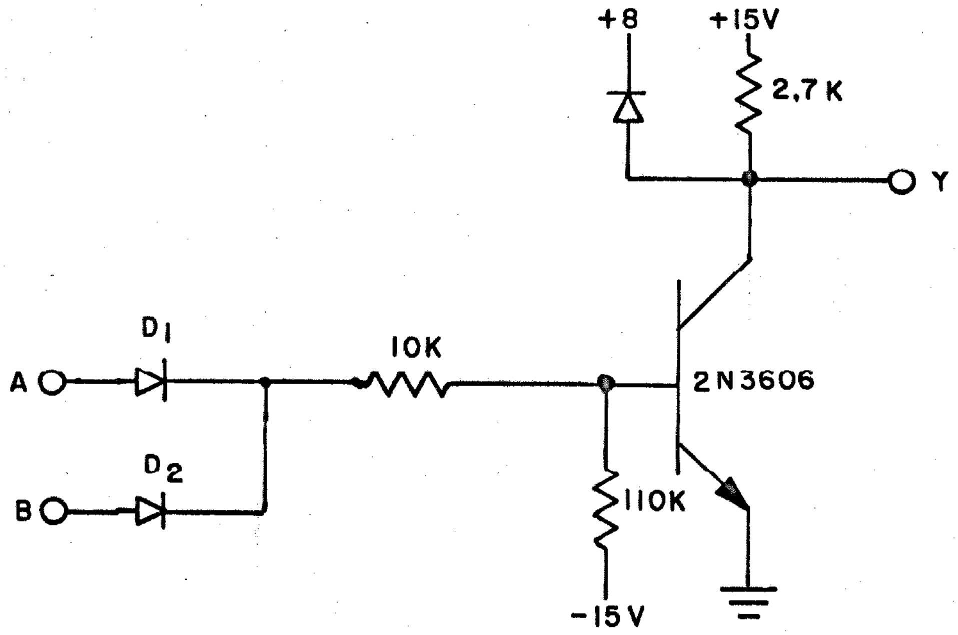
Figure 7-5, Digital OR circuit using diode logic.



TRUTH TABLE

A	B	Y
0	0	8
0	8	8
8	0	8
8	8	0

Figure 7-6. Digital NAND circuit.



TRUTH TABLE

A	B	Y
0	0	8
0	8	0
8	0	0
8	8	0

Figure 7-7. Digital NOR circuit.

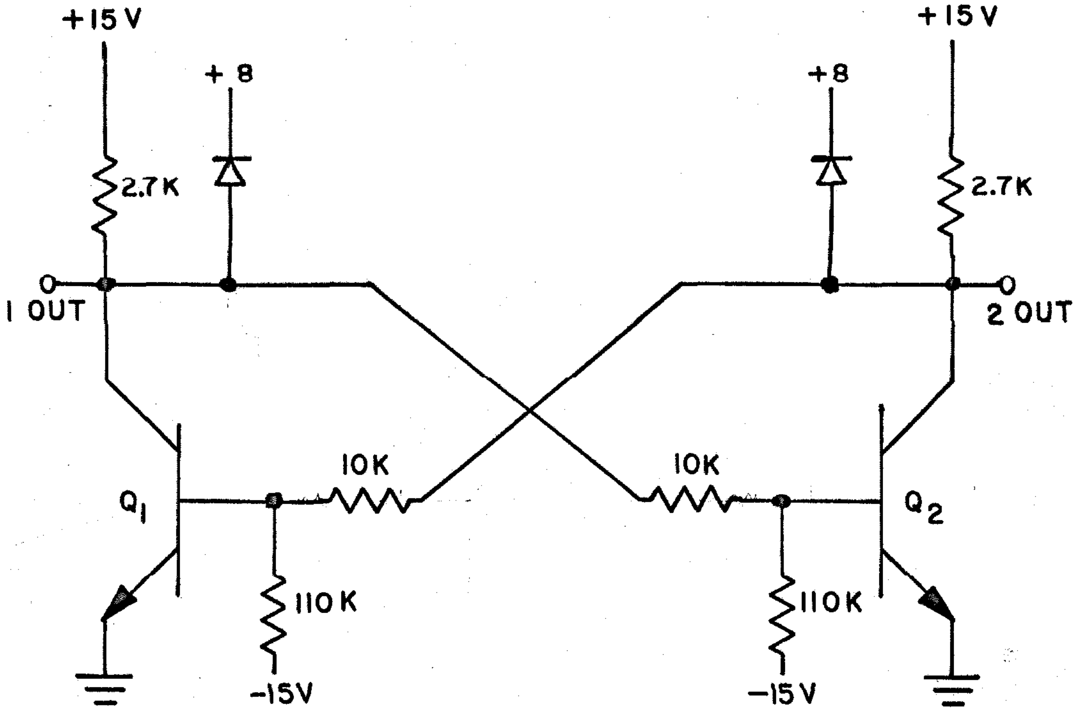


Figure 7-8. Bistable or "flip-flop" circuit.

positive and therefore the latter is "on" and OUT 2 must be zero, forcing Q_1 to remain in the off state. If OUT 1 is brought to zero, this forces Q_2 off bringing Q_1 on and this condition will remain. It can be seen that the circuit "flips" from one state to another, no intermediate levels being allowed.

There are a number of ways to force the flip-flop to change states. Direct coupling causing the device to respond to an 8 volt signal is most convenient as then the input can be "gated" with two or more signals if desired. A "direct" set and reset flip-flop is shown in Figure 7-9. The AND gates composed of diodes D3, D4, D5, and D6, are tied directly to the bases of the transistors through diodes D1 and D2. If both inputs at the direct set input are made positive, the base of Q_1 goes positive and the "1" output goes to zero. When the AND gate goes to zero, diode D2 is reverse biased and the flip-flop remains in its state until it is reset by a positive input through D1. It must be noted that at least one of the set signals at the gate must go to zero before the flip-flop can be reset. Also if only a single

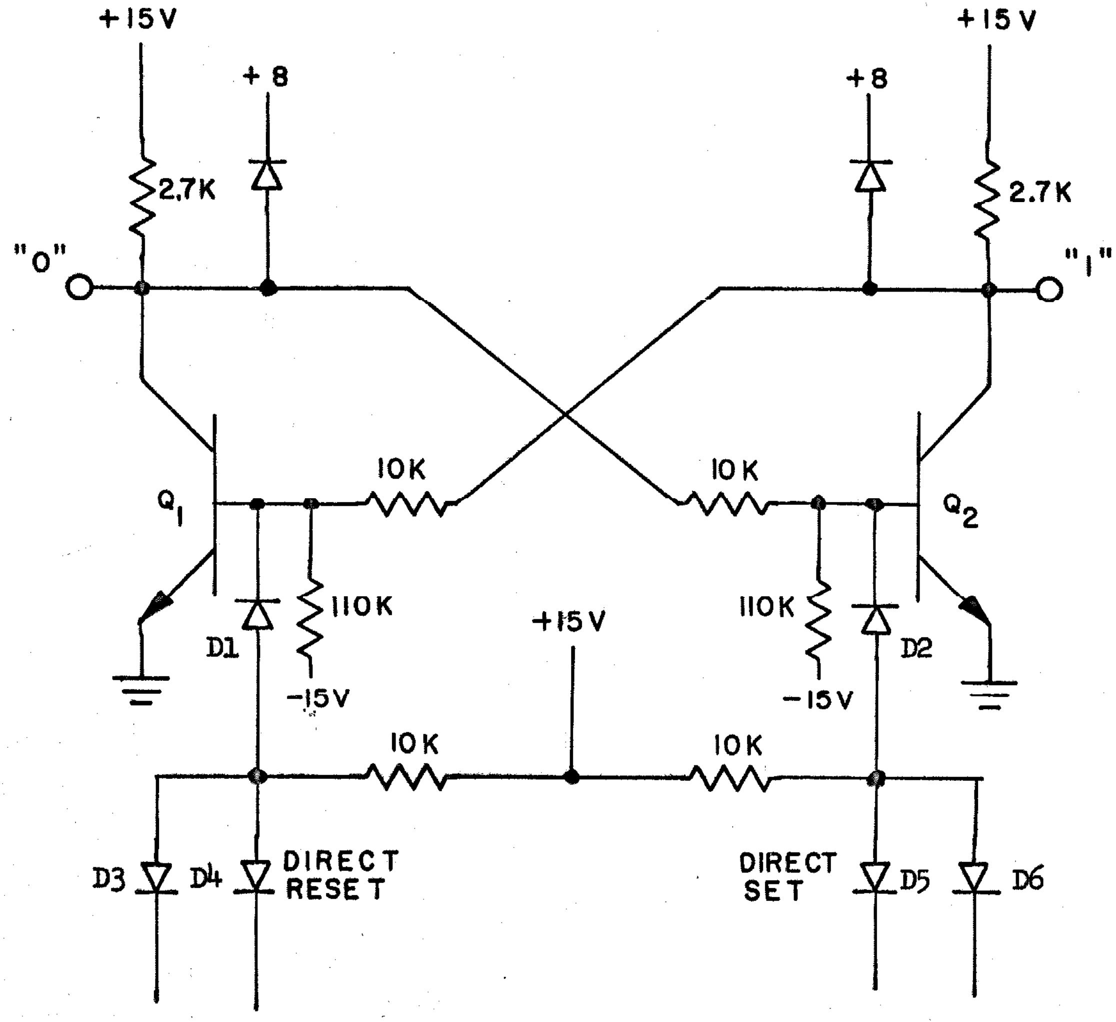


Figure 7-9. Gated direct set-reset flip-flop circuit.

line is to reset or set the device, the other diode of the AND gate may be left open or connected to 8 volts. It must not be connected to ground.

It should be noted that the output of the flip-flop "complements" the input. Thus if the device is "set" the "1" or "Y" is at 0 volts. This is never a practical problem as the other, "0" or "$\overline{Y}$", output can be used since its value is always opposite that of the "1" output.

To avoid tedious drawing it has become customary to use the symbology shown in Figure 7-10 to depict the various elements described.

Loading - When interconnecting the various circuits some consideration must be given to loading. Referring to the circuit shown in Figure 7-11, when the transistor is off effectively no current flows to the AND gates as the diodes are reverse biased. However, when the transistor is on, i.e., the output is zero, each of the AND gates contributes 1.5 MA which flows through the collector to ground. If the input of the inverter is an 8 volt signal, the excess base current,

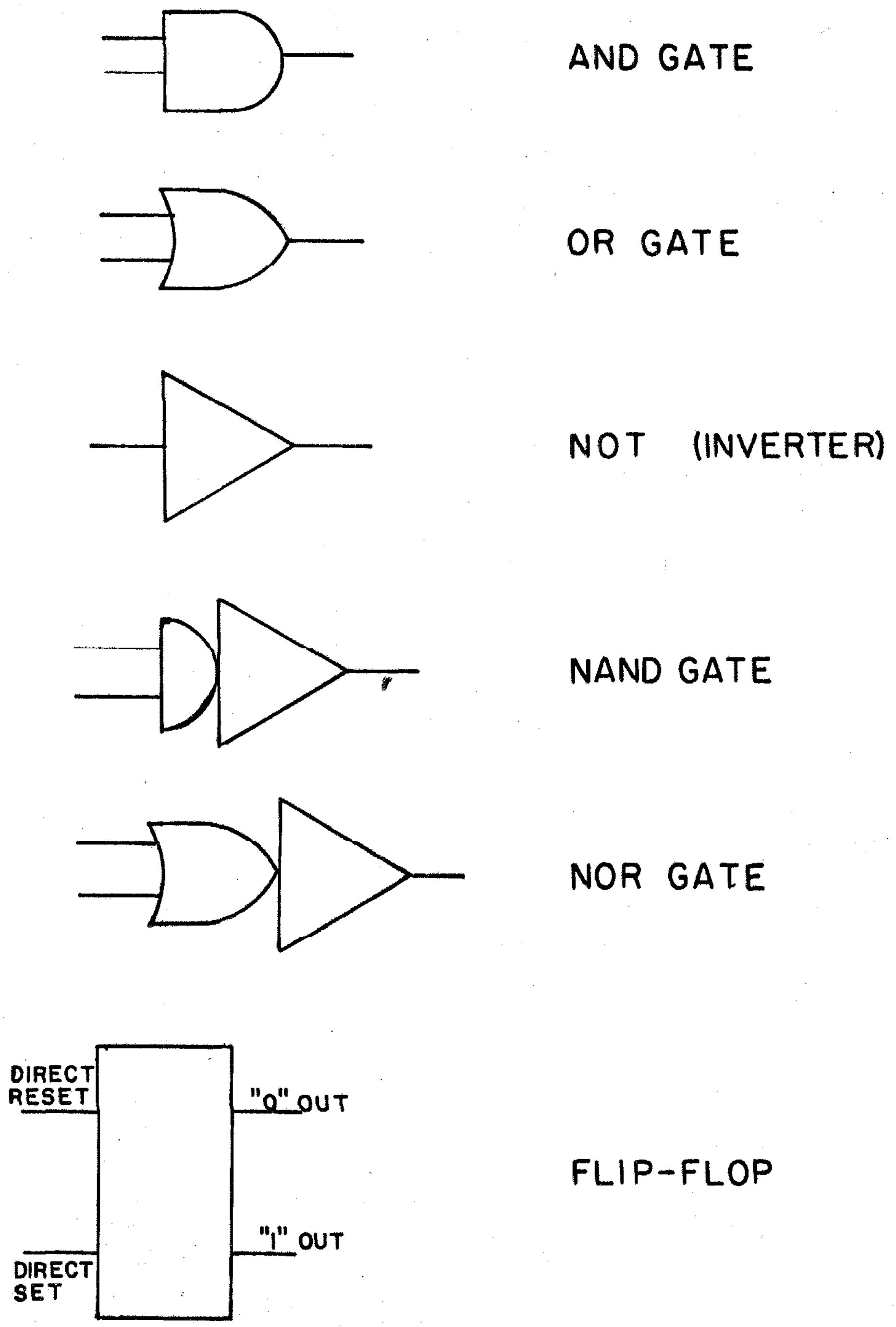


Figure 7-10. Symbolic representation of the various digital logic circuits commonly employed.

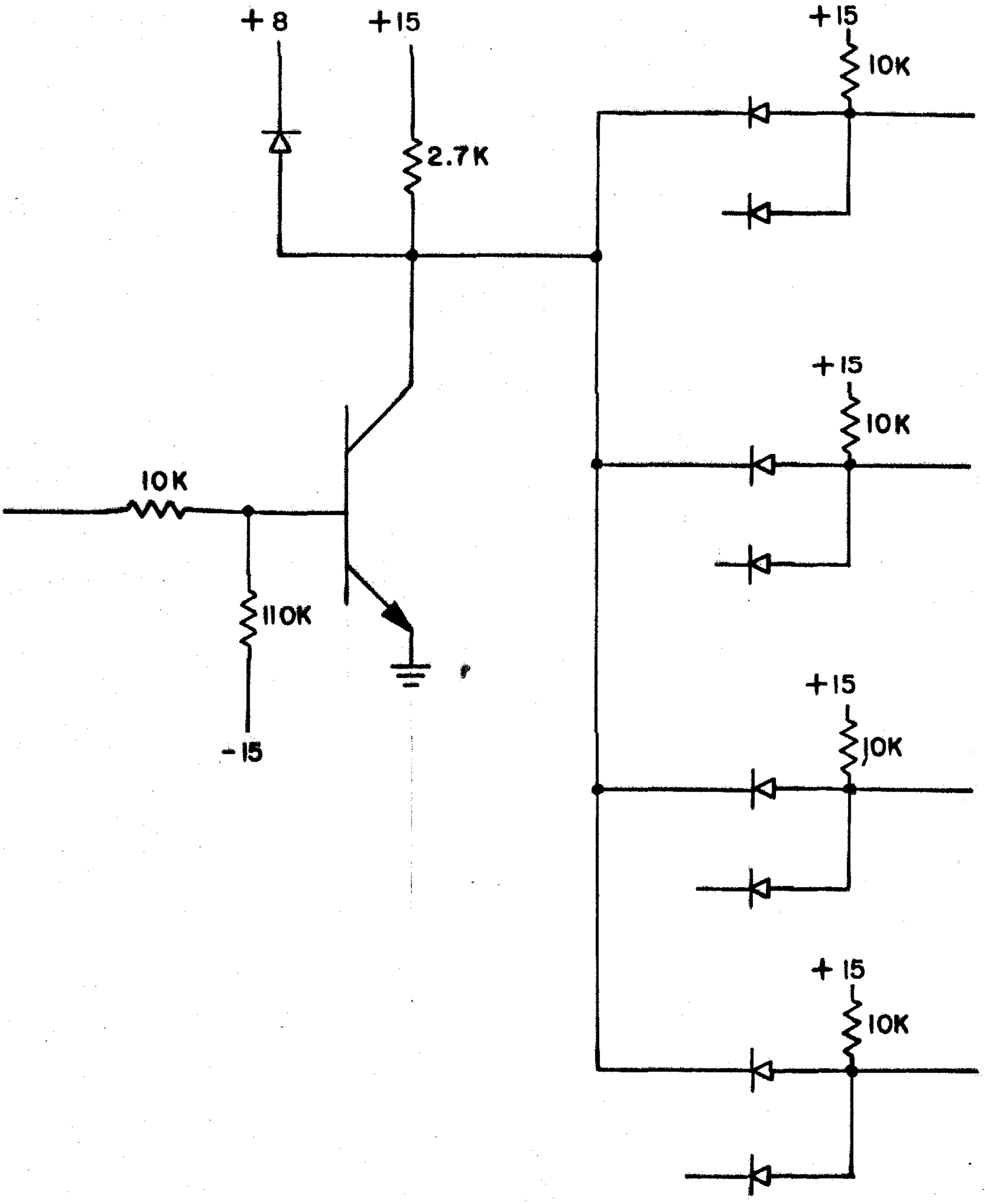


Figure 7-11. Typical loading of inverter circuit in digital circuitry.

the base current available beyond that necessary to handle the current from the collector resistor, is 0.46 MA. With an h_{FE} of 30, the device can accept a load of about 12 MA to ground, or 8 AND gates. Thus the effective "fan out" of the device is 8.

Computer Interfacing - We now can resume the discussion of interfacing the computer to the chronocoulometer. The number of possible experiments that can be done is large. To illustrate the basic method of interfacing as well as to show the feasibility of this concept of data acquisition, we shall describe in detail the arrangement used to perform double potential step chronocoulometry. In this method an electrode is potentiostated at a potential where no faradaic current due to oxidation or reduction of the species in solution occurs. The integrator is unshorted and the potential is stepped to E_f, which is assumed to be at a point where the concentration of electroactive species is driven instantaneously to zero, for a time tau. The potential is then stepped back to the initial potential and after a total time, t, the integrator is again shorted. The charge passed is measured as a function of time for both "forward" and "backward" steps and is plotted against an appropriate function of time; the data of interest being the slopes and intercepts of the plots. For a complete description of the method as well as the theory the reader is referred to the original papers (1,2,3).

The computer must perform the following operations.

1) Integrator be unshorted.

2) Forward potential step be applied.

3) Back potential step be applied.

4) Data be input at precisely known times.

An analog to digital converter (ADC) is supplied with the computer. This device will convert the voltage at its input to a digital value 4.95 microseconds after a positive pulse is received at its control input; 27 microseconds later the conversion is complete and the computer can transfer the number, held in temporary storage by the ADC, to memory. This transfer is controlled by the program and the wiring necessary has been supplied.

It is important that the potential steps by synchronized with the pulses activating the ADC or there will be a time indeterminacy of the order of the period between pulses in the t = 0 point. The pulses are derived from a Systron-Donner type 1433 counter with a crystal controlled time base guaranteed to be accurate to one part in 10^7 and stable to one part in 10^8. The 100 KHz time base signal of the counter is counted by the preset module and a pulse is output each time the number set on the dials is reached. Thus the time between pulses can be set from 10 microseconds up.

To decode the activate signal the 12 lines representing bits 12 through 23 are brought to 12 inverters so that the assertion of either a zero or a one in that bit position is available. The code chosen to initiate the experiment is 1 0 0 0 and to stop 2 0 0 0. If we represent each line by its bit position, i.e., C12, C13, etc. the condition required to turn on the experiment is ACT3·C12(0)·C13(0)·C14(1)·C15(0) ....

The decoding scheme is shown in Figure 7-12, the inverters not

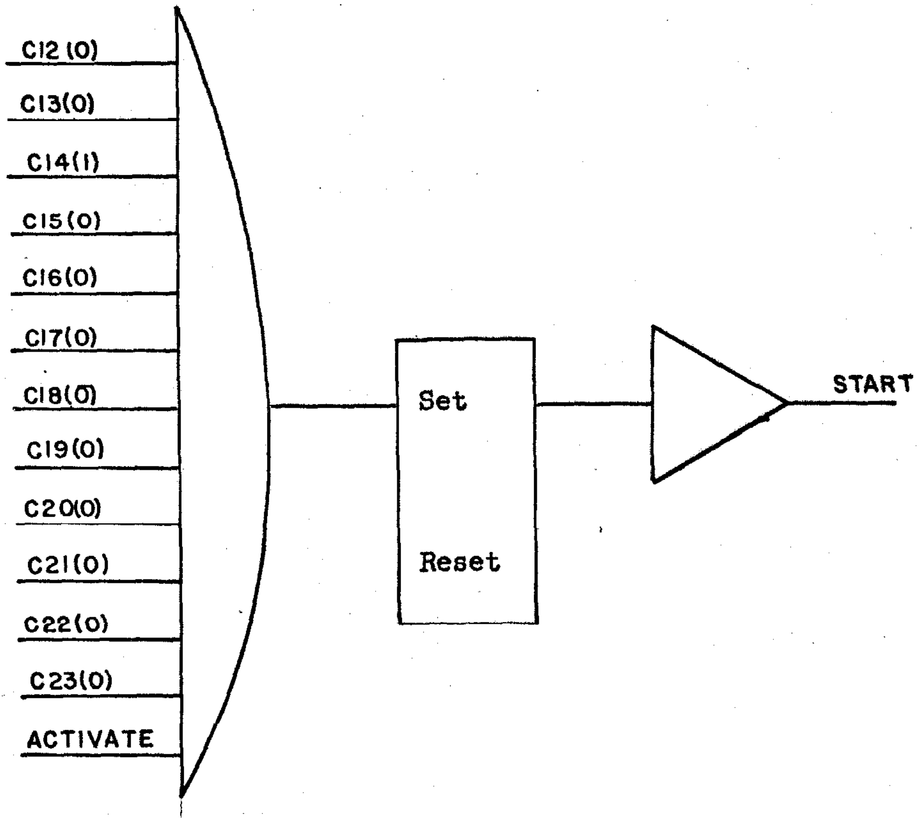
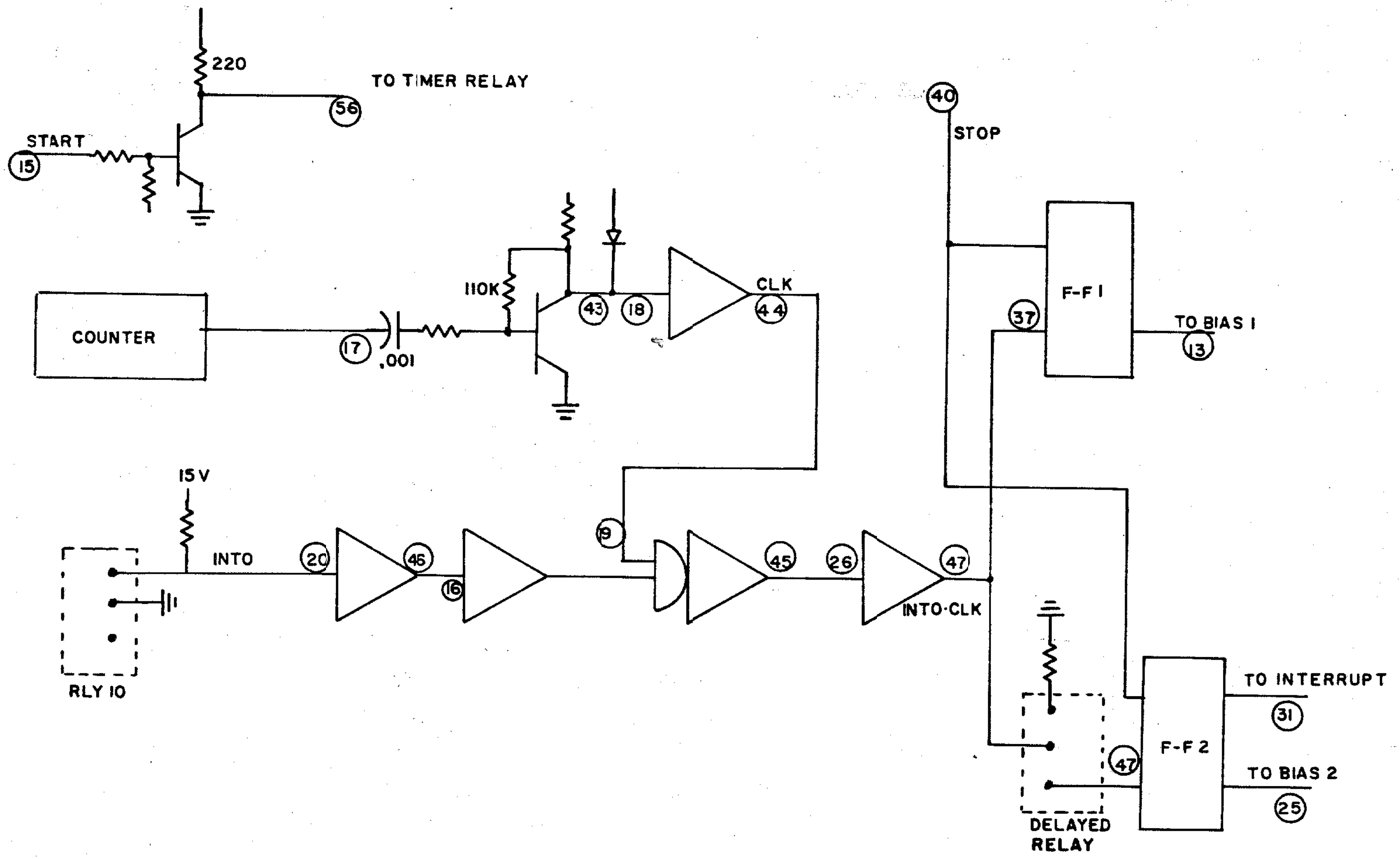


Figure 7-12. Decoding scheme used to interface chronocoulometer to SCC 660-5 computer.

being shown. Thus the flip-flop is set when the computer executes the proper activate instruction and reset by the other activate instruction, (start and stop commands). The output of the flip-flop is inverted to provide greater fan out capability and to insure that logical errors are not made by the operator by failure to remember the inversion of the signals at the flip-flop. The rest of the circuitry required to perform double potential step chronocoulometry is shown in Figure 7-13. The encircled numbers refer to the printed circuit board and pin number on the interface cage. The circuitry between 1-17 and 1-44 is required to obtain correct clock pulses. The counter puts out positive going pulses from -6V to 0V and we require pulses from 0V to 8V. The start signal derived from the flip-flop connected to the 13-input AND gate is input to relay driver whose output (1-56) drives the timer 2 start relay on the chronocoulometer (RLY 18). By means of the matrix switch the instant contacts close the integrator relay (27 to 36 and 28 to 38 on matrix switch). The integrator relay has been rewired, as shown, and when the capacitor



Fig, 7-13 Interfacing for double potential step chronocoulometry is unshorted the common contact goes from ground to 15 volts. This signal, dubbed INTO is brought to the correct level and inverted (1-20 and 1-46), reinverted (1-16) and then ANDED with the clock pulses dubbed CLK. The output, $\overline{\text{INTO}\cdot\text{CLK}}$ at 1-45 is inverted (1-26) to obtain pulses INTO·CLK at pin 1-47. The INTO·CLK signal is fed to the first flip-flop (2-37), the output of which is fed to bias 1 amplifier, replacing relay 5 which has been removed from its socket. When this flip-flop fires it causes the Bias 1 amplifier to apply the potential step to the control amplifier and thus the step to E_f is applied in synchronization with the first pulse after the integrator capacitor is unshorted. The INTO·CLK signal is also input to the analog to digital converter, which converts each time a pulse is received, and therefore the first point is read at time zero with respect to the application of the potential step. The INTO·CLK signal is also connected to the normally open contact of the delayed relay of timer 2. The normally closed contact is connected to ground via a 200 ohm resistor and the common, dubbed DLYR·CLK is connected to the second flip-flop (2-47). The output of the second flip-flop (2-25) goes to the input of bias 2 amplifier replacing relay six which has also been removed. Thus when the delayed relay closes after a time determined by the resistor setting, the flip-flop will fire upon receipt of the next pulse and cause the bias 2 amplifier to step the potential back to its original value. The second flip-flop is also connected (2-26) to the interrupt circuit of the computer. The interrupt circuit is a special input which, when enabled by the program, responds to an 8 volt signal and executes the instruction located at address 31_8 of the computer. By proper programming the computer can "sense" when the reverse step is initiated by having one instruction in this location which determines the number of points taken on the forward step. After a preselected number of points has been input, the program shuts off the chronocoulometer with the stop instruction which also resets the two flip-flops, resetting the biases. At this stage, the data is in the computer memory and the problem becomes a matter of programming.

The complete time sequence of events is shown in Figure 7-14. Note that the potential steps are synchronized with the pulses (INTO·CLK) which fire the analog to digital converter and therefore, there is, in principle at least, no time indeterminacy.

Although the system is not yet complete at the time of writing an attempt was made to carry out a double potential step experiment at a mercury electrode with a 1 mM Cd (II) solution with 1 F $NaNO_3$ supporting electrolyte. The primary shortcoming of the system is that the analog to digital converter is not yet acceptable in its operation.

However, a number of runs were made in the attempt and all the ancillary circuits described operated as designed. The problem of the ADC is only a matter of convincing the manufacturer to repair what appears to be faulty wiring, and the system will undoubtedly be functioning within a relatively short time.

The usefulness of having a small, relatively unsophisticated, computer in the laboratory cannot be overemphasized. Besides merely controlling the working of an instrument such as the chronocoulometer

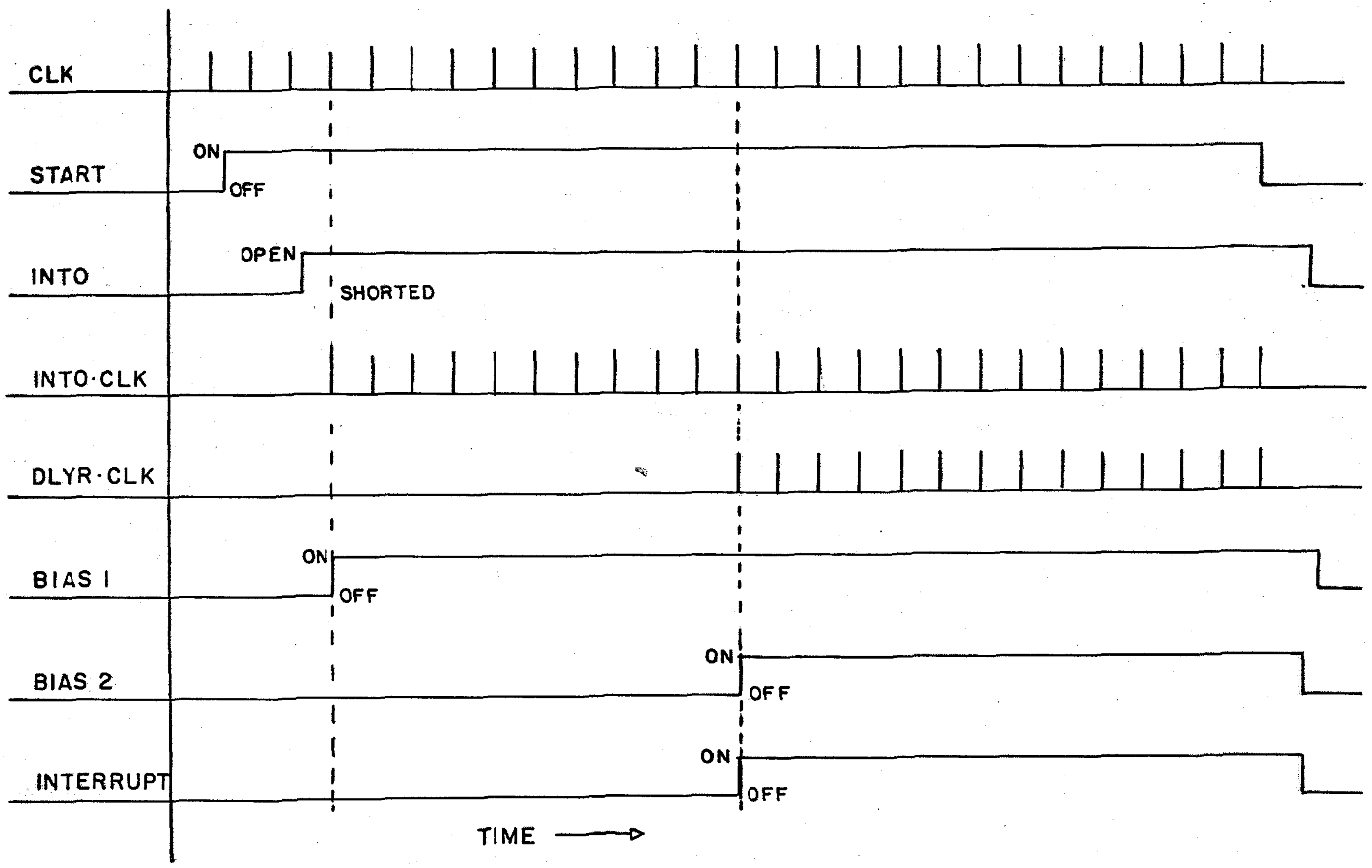


Figure 7-14. Time sequence of signals used for interfacing for double potential step chronocoulometry.

by essentially switching it on and off and then passively accepting data, the computer can be used to apply the control voltages via a digital to analog converter and it therefore becomes a part of the feedback system. It is felt that with the inherent power to perform many simple routine (and therefore uninteresting) tasks very rapidly, many experiments will be performed which hitherto had been relegated to the category of "somebody ought to".

In conclusion a major point must be brought out. The computer is a means to an end. Its power is strictly a function of the ingenuity, skill, and intelligence of the person using it. The human mind is not supplanted, rather it is complemented. With this tool available, thought on the part of the experimentalist will become perhaps even more important then in the past.

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