

A METHOD FOR DETERMINING THE
CONCENTRATION OF OXYGEN IN AQUEOUS SOLUTIONS

by

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Thesis Supervisor

Accepted by _____
Chairman, Departmental Committee
on Graduate Students

"A Method for Determining the
Concentration of Dissolved Oxygen in Aqueous Solutions"

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Thomas C. Wolford

Submitted to the Department of Meteorology on May 19, 1962 in
partial fulfillment of the requirements for the degree of
Master of Science.

Abstract

The purpose of the investigation described in this thesis was to develop a device which could determine the concentration of dissolved oxygen in sea water. The instrument developed, measures the amount of dissolved oxygen by constant potential coulometry. A reproducibility of one part per thousand was an important design consideration of this device.

Up to the present time the only recommended method for dissolved oxygen determination has been the Winkler method. The need for a new approach to this problem is evident when the uncertainties of the Winkler method are considered.

Dr. Dayton E. Carritt, a chemical oceanographer of Woods Hole Oceanographic Institution, states that the uncertainties inherent in current dissolved oxygen determinations under some conditions are on the order of 1 ml in 5 ml. These uncertainties, furthermore, are tied to an entire series of reactions and very difficult if not impossible to eliminate.

The instrument which was built demonstrated the feasibility of determining the concentration of dissolved oxygen in sea water by constant potential coulometry, but it did not achieve the desired degree of precision.

Suggestions have been made for modifications on the basis of the experience gained with this instrument which may allow the desired degree of precision to be achieved.

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I. INTRODUCTION

It is first necessary to discuss electrolysis before a description of the chemical transducer which is found in the dissolved oxygen determining device. A previous discussion of electrolysis will also be useful when discussing the reasons for choosing the constant potential coulometric method of determining dissolved oxygen.

There are two main types of designations which may be applied to electrochemical cells. The term galvanic cell is used when an electrode reaction occurs spontaneously when the electrodes are externally connected. In an electrolysis cell the reactions at the electrodes are forced to occur by applying an external electromotive force to them.

To obtain a representation of the actual chemical process or processes which occur in a cell, half reactions are employed. The half reactions are the actual chemical reactions occurring at each electrode of the cell. The sum of the half reactions is the net cell reaction. These reactions will include the electrons transferred.

In accordance with the convention of J. J. Lingane the cathode and the anode of a cell are defined in the following manner. The cathode is the electrode at which reduction takes place where reduction is taken to mean the consumption of electrons. By similar reasoning the anode is the electrode where oxidation occurs and oxidation is defined as supplying the

electrode with electrons. There is one underlying principle which applies to the sign convention of the electrodes and it is this: The cathode is always negative with respect to the anode.

Since it would be impractical to list the emf of all possible combinations of electrodes and it is desirable to have some means of tabulating the relative electron donating ability of the individual electrodes some type of standard electrode is necessary. It is impossible to measure the emf of a single electrode, therefore, one can arbitrarily be selected as having zero emf. The hydrogen electrode was selected as the reference. It consists of a platinum or palladium or gold electrode immersed in a solution which is saturated with hydrogen gas at a known partial pressure. The standard electrode potential of an electrode represents the tendency of an electrode to deliver electrons through an external circuit relative to the hydrogen electrode to do so.

It is generally assumed that the same "current" flows in the electrochemical cell that flows through the external circuit. This idea should be examined in more detail. There is electron flow in the external circuit of a cell and positive and negative ion migration in the cell. The electrons which are transferred at each electrode upset the electroneutrality of the solution at the surface of the electrodes. This causes a potential gradient to arise between the solution in the immediate vicinity of the electrodes and the remaining volume of the electrolyte. There is also a concentration gradient

established in the electrolyte due to the electron transfer at the electrodes. Therefore the movement of ions in an electrolyte result from the action of the potential gradient and concentration gradient. Two new terms can now be defined, electrical migration and diffusion. Electrical migration is the movement of ions due to the influence of the potential gradient and diffusion is the movement of ions due to the influence of the concentration gradient. Flow of current through an electrochemical cell is then accomplished by the migration of positive and negative ions under the influence of the potential and concentration gradient.

Some interesting information can be gained by discussing the current vs. voltage curves of an electrochemical cell with various combinations of electrolytes and electrodes.

The first case to be considered is two silver electrodes in a solution of dilute silver nitrate, (AgNO_3). If a slight external voltage is applied to the cell and a graph of the resulting current as a function of the applied voltage is plotted, the result is very nearly linear as illustrated by curve 1 in figure [1]. This result is very similar to the linear relationship that exists for electron flow through a metallic conductor.

To obtain a linear relationship such as illustrated by curve 1, the solution must be well stirred in order that the silver ion concentration throughout the solution be as uniform as possible. Regardless of the efficiency of the stirring process there will always be a concentration gradient in the solution due to the half cell reaction which occurs at one of

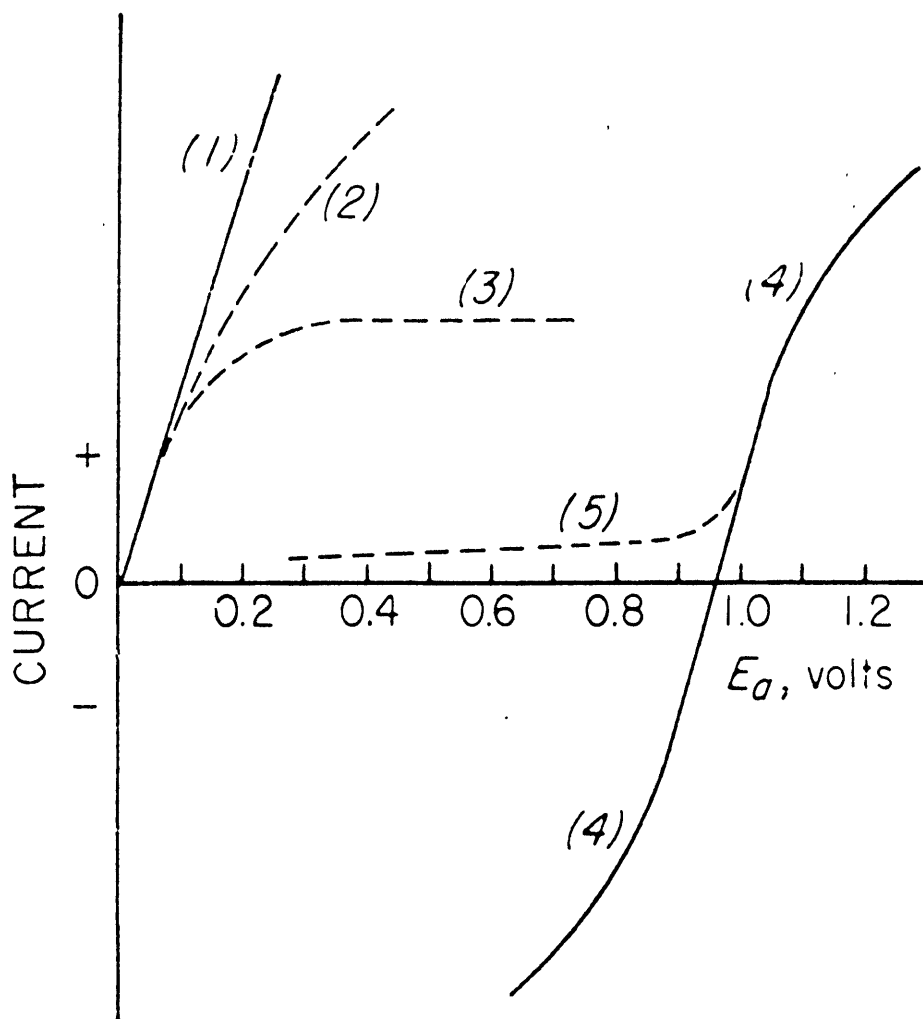


Fig. 1. Schematic current-voltage curves.

E_a - Applied external voltage.

- 1). Two Ag electrodes in dilute $AgNO_3$, well stirred.
- 2). Deviation of above cell from linearity due to "back emf."
- 3). Two Ag electrodes in dilute $AgNO_3$, no stirring.
- 4). Zn and Ag electrodes in a one molar solution of $ZnCl_2$ saturated with $AgCl$.
- 5). Pt and Ag electrodes in above solution.

the electrodes, i.e., $\text{Ag}^+ + \text{e}^- = \text{Ag}^0$. This causes the development of an opposing or "back emf", which increases as the applied voltage increases and causes the current to increase at a less than linear rate. The current-voltage curve will then become concave with respect to the applied voltage axis. This is illustrated by curve 2 in figure 1. The difference in voltages of curves 1 and 2 at equal currents is a measure of the back emf.

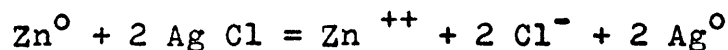
Curve 3 of figure 1 is obtained under the following set of rather special circumstances

1. The solution should be fairly dilute.
2. One of the electrodes is quite small.
3. The solution isn't stirred.

The limiting current now results from the fact that above a certain applied voltage, the rate of reduction of silver ions at the cathode becomes so great that the current is limited by the rate of supply of ions from the body of the solution and is practically proportional to the bulk concentration of the solution. This statement will be verified by a mathematical discussion that follows later.

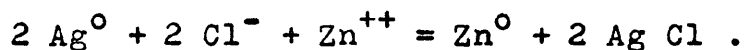
A voltage-current curve is obtained that is different from the preceding three if two different electrode reactions occur in the same electrolytic solution. If a zinc electrode and a silver electrode are placed in a solution of zinc chloride (Zn Cl_2) saturated with silver chloride (Ag Cl) a curve with different characteristics is obtained.

If an external emf is applied in opposition to the spontaneous emf of the cell a current flows in the external circuit. [In this example the emf of the cell is +0.96V] When the applied voltage is less than +0.96V the cell causes the current flow in the external circuit. The cell reaction is as follows:



When the applied emf is exactly equal to the emf of the cell, no current flows in the external circuit. (This is the basis of the potentiometric method for measuring the emf of a cell.)

If the applied voltage is greater than +0.96V, current will flow in the opposite direction in the external circuit. The cell reaction now is:



the reverse of the above equation. The above, logically enough, constitutes the definition of a reversible cell. This type of cell produces a current-voltage plot represented by curve 4 in figure 1.

The most common case encountered with electrochemical cells is the condition where one or both of the electrodes are not in equilibrium with the solution. This case will now be discussed.

Consider the preceding cell with the zinc electrode replaced by a platinum electrode. There is no definite spontaneous emf since the platinum electrode isn't in equilibrium with the solution.

In this solution the platinum electrode acts as a noble electrode, i.e., one that serves only to transfer electrons from the solution to the external circuit without being oxidized itself. Any metal behaves nobly when the solution lacks ions of the metal and when the oxidation potential of the solution is smaller (more reducing) than that of the metal so oxidation of it can not occur. If an applied emf is connected to the cell with its negative side connected to the platinum electrode and its potential gradually increased, the current will rise slowly until approximately +0.96V and then rise more rapidly until it merges with the curve previously obtained for the zinc electrode. The two curves merge because the platinum electrode is gradually plated with zinc, effectively making it thermodynamically equivalent to a zinc electrode. This is shown graphically in curve 5 of figure 1.

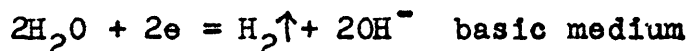
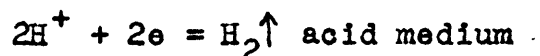
An important fact has been demonstrated by the above examples. It is very evident that the cells are non-linear circuit elements which do not obey Ohm's Law. This means that current flow through a circuit containing an electrochemical cell can not be calculated in advance since the cell presents a varying resistance which depends upon the applied voltage.

There is another type of current potential curve, which can be plotted to yield useful information. If the potential of the working electrode vs. an external reference electrode is plotted as a function of the current through the cell, a curve is obtained which doesn't reflect the iR drop through the cell or the current dependent back emf. This type of curve

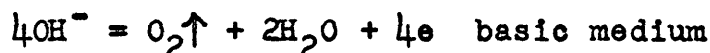
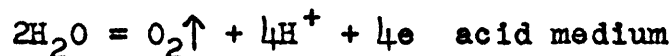
depends entirely upon the characteristics of the reaction at the working electrode. This property makes this type of representation a very useful one. For an example of such a curve see figure 2.

In general the curve will have one or more diffusion limited "plateaus" between the potential where a noticeable current is observed and the potential where either the reduction or oxidation of water occurs.

The cathode reactions for the reduction of water are:



the anode reactions for the oxidation of water are:



Thus the working electrode is limited as to what potentials it may assume.

If the cation or anion has a oxidation or reduction potential less than that of water it may be determined in an aqueous solution.

There are three main methods by which all electrolysis may be carried out. They are the following:

1. Maintain a constant current through the cell.
2. Maintain a constant applied voltage across the cell.
3. Maintain the working electrode at a fixed potential with respect to some reference electrode.

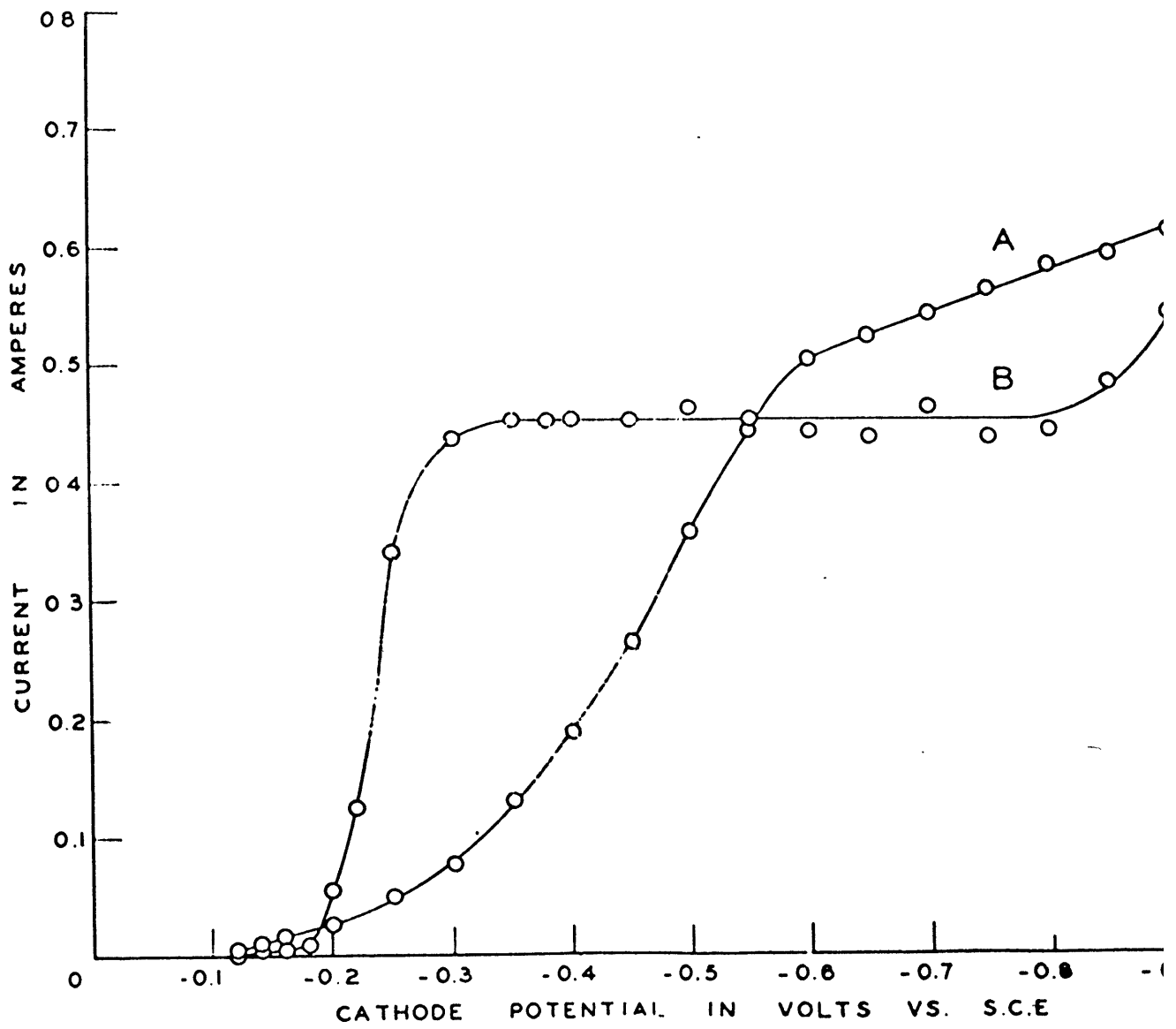


Fig. 2. Curves representing current electrode potential curves.

In constant current electrolysis there is very little control of the working electrode potential and consequently very little selectivity as to what reaction is to occur at the electrodes.

In the constant applied voltage method there is a little more selectivity over the potential of the working electrode but the control is relatively coarse and electrolysis with this method requires a very long time.

Therefore it appears if any degree of appreciable selectivity is going to be achieved it will have to be with the method where the potential of the working electrode is maintained constant with respect to some external reference electrode.

The theory behind constant potential coulometry will now be considered in a little more detail. Consider an electrolyte containing two substances A and B whose current-cathode potential curves are given in figure 3. To obtain appreciable reduction of substance A the cathode potential must be greater than a but to keep the reduction of B negligible less than b. The voltage "a" is called the decomposition voltage of A and the voltage "b" is called the decomposition voltage of B. For reduction of A to occur at 100% efficiency the cathode potential must be kept between a and b. If the voltage is greater than b reduction of both A and B will occur and the efficiency of B's reduction will be less than 100%, unless all of A has been previously removed.

If the current flow through the cell is large the potential of the working voltage may change enough (in the negative

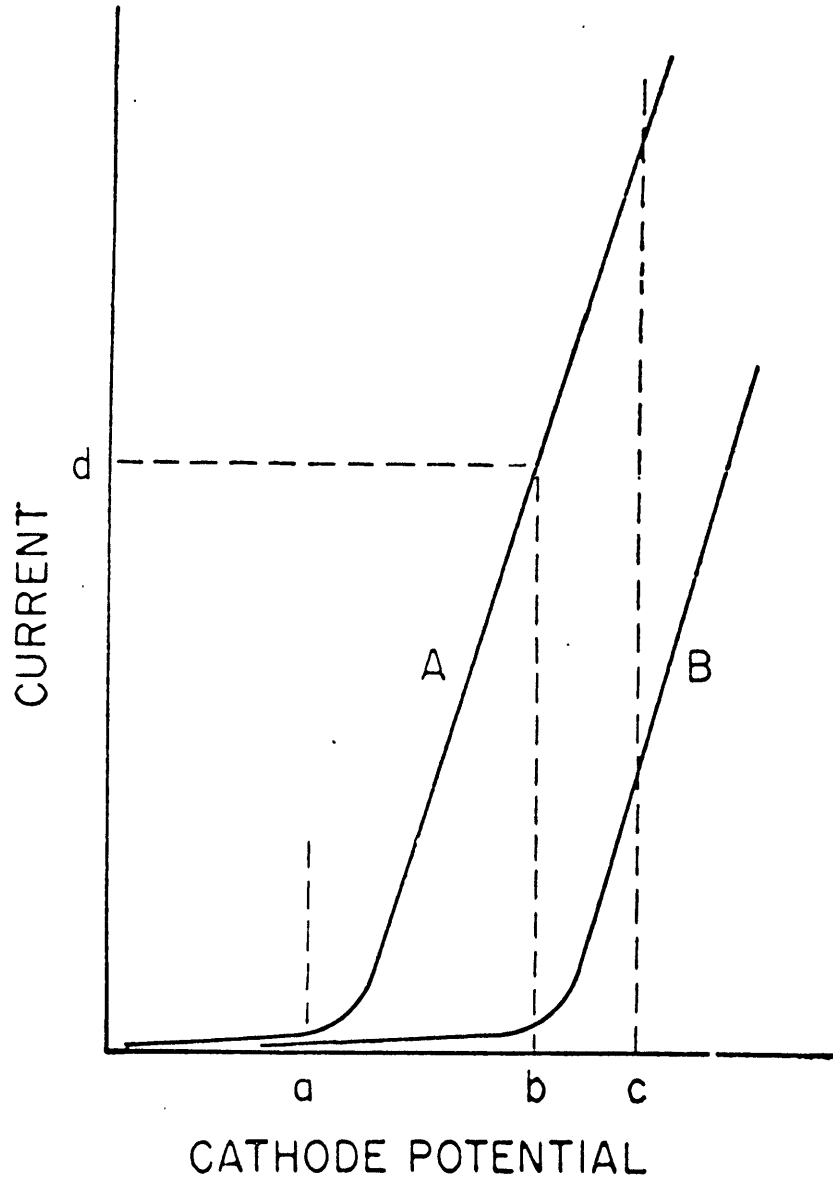


Fig. 3. Schematic current-cathode potential curves for two substances whose separation is desired.

direction if the working electrode is the cathode) to make some type of potential controlling device necessary. If the total current flow through the cell is small enough a potential regulating device isn't necessary, since the variation in voltage isn't enough to cause the working electrode to shift from a to b if the potential is initially set at value slightly greater than a. This allows the elimination of a potentiostat in the circuit with the resulting simplification in circuit design.

In the following section a quantitative approach to constant potential coulometry will be considered.

The current at any time t is given by:

$$i_t = nF \frac{dN}{dt}$$

where:

n = # of electron equivalents per molar unit of the reaction.

F = the faraday constant

$\frac{dN}{dt}$ = # of moles that react at the electrode in unit time.

If diffusion through the layer of solution in immediate contact with the electrode is the current-controlling factor.

Fick's Law¹ can be utilized giving:

$$\frac{dN}{dt} = DA \left(\frac{dC}{dx} \right)$$

where:

D = The diffusion coefficient of the reacting substance

A = Electrode area

¹ For a complete development see Moore, W. J., Physical Chemistry, 2nd edition, Prentice-Hall, Inc. 1955, pp. 448.

$\frac{dC}{dX}$ = concentration gradient at the electrode surface,
a function of the actual concentration in the
electrolyte.

This equation only gives the steady state condition for diffusion.

The instantaneous current is equal to:

$$i_t = NF DA \left(\frac{dC}{dX} \right)$$

If the solution is well stirred, theoretically there is a thin diffusion layer and the concentration is approximated by a linear function.

$$\frac{dC}{dX} = \frac{C - C_o}{d}$$

where:

C = concentration in the body of the solution

C_o = concentration at the electrode surface.

d = thickness of diffusion layer.

Another expression can be written for the instantaneous current.

$$i_t = NFDA \frac{C - C_o}{d}$$

When the electrode potential increases much beyond the decomposition potential $C_o \ll C$

Therefore, $i_t \approx \frac{NFD}{d} C$

The above equation presents a theoretical basis for the often observed relationship of the limiting current being directly proportional to the bulk concentration of the substance which is undergoing oxidation or reduction. This equation holds

only if the effective diffusion layer thickness is a constant, independent of concentration of the diffusion material.

since $N = CV$ the equation:

$$i_t = NF \frac{dN}{dt}$$

can be written

$$i_t = NFV \frac{dC}{dt}$$

equating this to:

$$i_t = \frac{NFDAC}{d}$$

we obtain if $\frac{dC}{dt}$ is negative.

$$\frac{dC}{dt} = -\frac{DAC}{vd}$$

integrating from 0 to t gives $C_t = C_0 e^{-\frac{DAT}{vd}}$

or if i is proportional to concentration: $i_t = i_0 e^{-\frac{DAT}{vd}}$

The value of this equation is that it permits a logical basis for the choice of components in an electrochemical cell which gives the best possible results.

To balance the equation dimensionally the following units must be assigned to the various quantities.

$$A = \text{cm}^2$$

$$V = \text{cm}^3$$

$$d = \text{cm}$$

$D = \text{cm}^2/\text{minute}$ or by introducing the factor 60 then is equal to cm^2/sec .

The time necessary for electrolysis will be shorter the

larger the ratio of A to V. The time will also be shorter the smaller d, and d is kept small by efficient stirring. D is also a function of temperature and its temperature coefficient is approximately equal to 2^o/o per degree.

There are two assumptions in the above derivations.

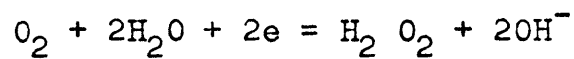
1. One or both of the electrodes are not in equilibrium with the solution before electrolysis.
2. The instantaneous current is entirely diffusion controlled.

II. Briefly Describing Theory Behind Oxygen Measuring Device.

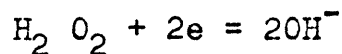
It was found in making polarographic determinations with dropping mercury electrode of various substances that their characteristic waves were masked by the wave of oxygen unless the dissolved oxygen was first removed from the solution by flushing with nitrogen gas.

The characteristic current-potential curve of oxygen as determined with a dropping mercury electrode is shown in figure 4.

The reaction responsible for the first "plateau" on the wave is:



The second plateau results from:



If the electrode used is a small platinum wire a different shaped current-potential curve results. This current-

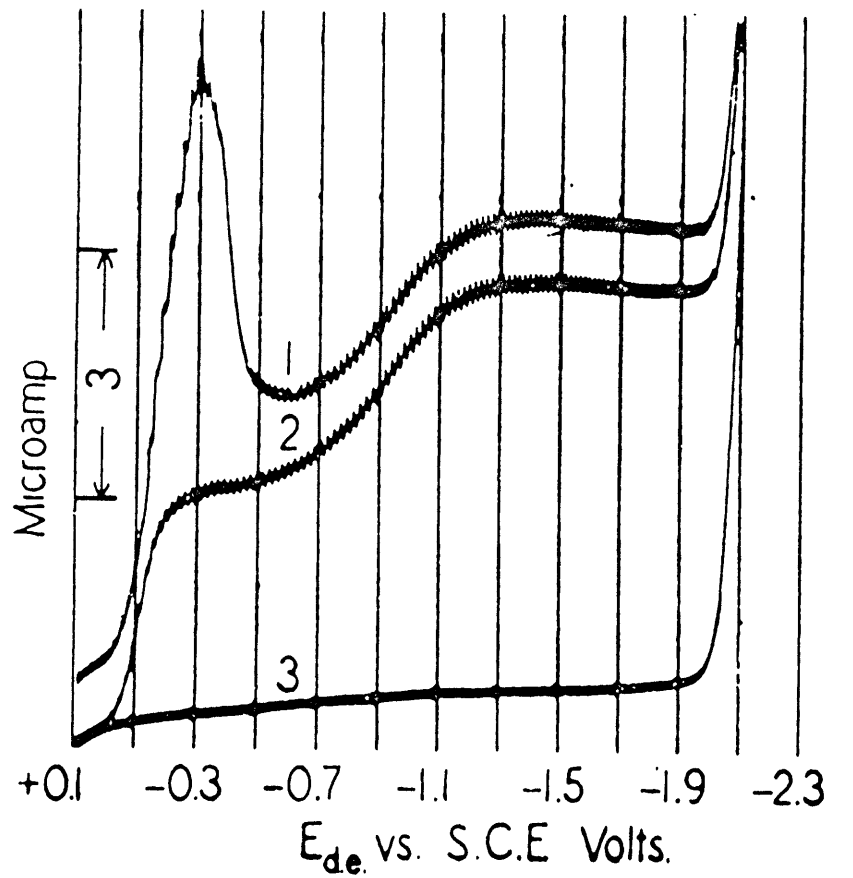
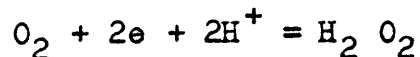


Fig. 4. Polarograms of Oxygen

- 1). 0.05N, KCl solution saturated with air.
- 2). After a trace of methyl was added.
- 3). Residual current after O_2 removed by N_2 flushing.

potential curve is shown in figure 5.

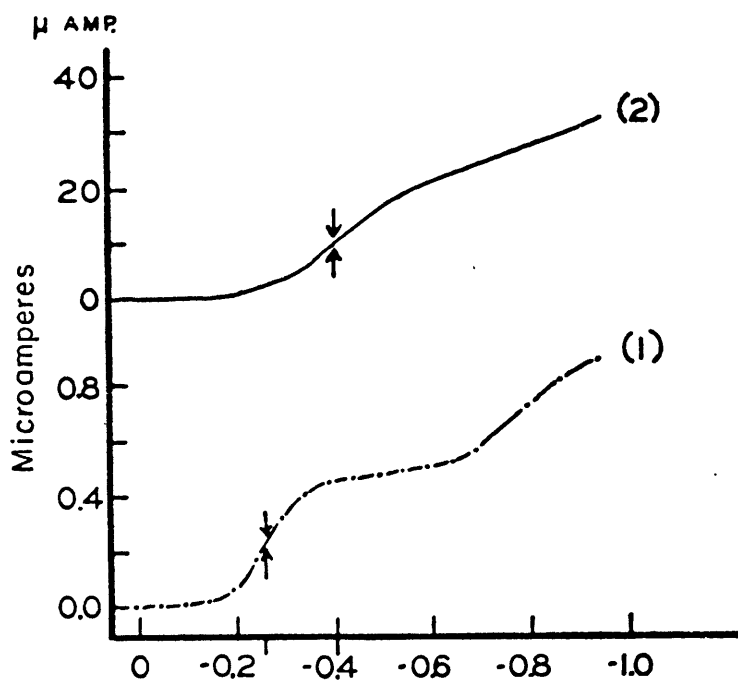
As can be seen from the curve this oxygen wave has only one plateau. It first begins at approximately $-0.4V$ with respect to a saturated calomel electrode and results from the following reaction:



The basic mechanism for the operation of the dissolved oxygen determining device is now clearly evident. If the potential of a platinum electrode with respect to a saturated calomel cell is maintained at a voltage of approximately $-0.5V$, the above reaction is caused to occur until all available dissolved oxygen is reduced. To measure the total number of oxygen molecules reduced it is only necessary to integrate the total amount of current which has flowed during the reduction. The current is integrated from the time that the reaction is first initiated until the time that the current decays to its residual value.

When the concentration of oxygen is determined in the above manner it is assumed that the electrode reaction is 100% efficient. Any other reducing reaction which may be occurring at the same time introduces an error into the value determined for the dissolved O_2 determination.

If the concentration of dissolved oxygen in sea water is assumed to be 9 ml/liter the concentration in molar form is 4×10^{-4} moles/liter. Since the concentration of dissolved oxygen is so low, the initial current flow can be expected to



Cathode potential in volts vs saturated calomel electrode.

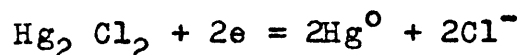
Fig. 5. Curves representing the reduction of dissolved oxygen on a platinum cathode.

- 1). The reduction of dissolved oxygen on a rotating platinum wire.
- 2). The reduction of oxygen on a stationary platinum wire.

be small. [It turns out to be in the tenth of milliamp range]. Therefore, the iR drop across the cell will be small and if so a potentiostat need not be used. If it is decided that the potentiostat as such can be eliminated from the circuit, a new concept may be introduced. The anode as a separate electrode may be eliminated and the reference electrode made to perform a dual function. The reference electrode must function as both the reference electrode and as the anode. If an appreciable current (1 ma) is to flow a reference electrode must have several special characteristics. These characteristics will now be discussed.

The primary characteristic that the reference electrode must possess is an unaltered potential as current flows through it. Low resistance is the second characteristic that the cell should have. The electrode should be easy to assemble and its components should be stable in contact with the atmosphere.

These above requirements are fulfilled by the saturated calomel electrode. This electrode consists of a mercury electrode in contact with a solution saturated with mercurous chloride ($Hg_2 Cl_2$) and potassium chloride ($K Cl$). The cell reaction is:



The potential of the electrode is given by the following formula:

$$E = + 0.242 - 7.6 \times 10^{-4} (T - 25)$$

where $T =$ Temperature $^{\circ}C.$, or $E = + 0.242V$ at $25^{\circ}C$ with respect to a standard hydrogen electrode. It can easily be verified by

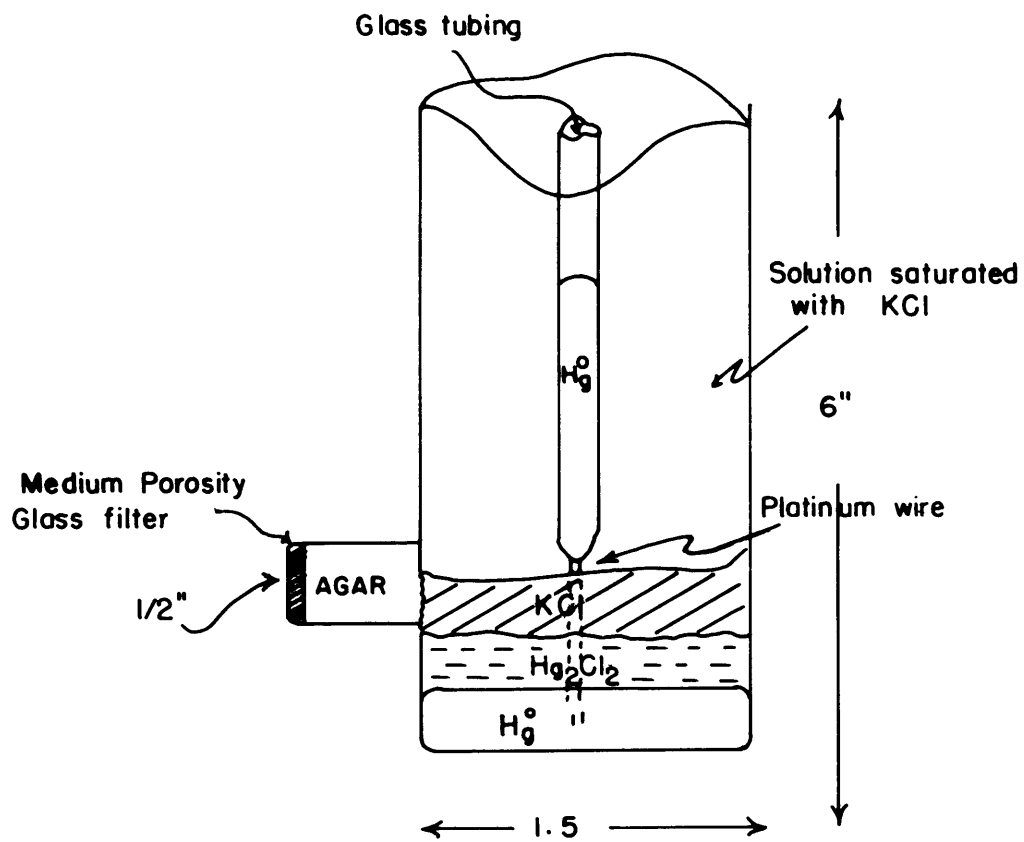


Fig. 6. Saturated calomel electrode.

substitution that a temperature variation of $\pm 7^{\circ}\text{C}$ results in a variation of potential of ± 5 millivolts. Hence the electrode is adequate for use at room temperatures without serious error. A saturated calomel electrode is shown in figure 6.

III. Definition of the Terms Used

The terminology used in describing the performance of the dissolved oxygen determining instrument is drawn from three main sources.

1. From the course "Instrumentation and Research methods" (7.911) and notes given by Dr. Kurt S. Lion in the Dept. of Biology.
2. From selected notes and lectures of a course "Meteorological Instruments" (19.22) offered by Dr. Delbar P. Kelly in the Department of Meteorology.
3. From the three volumes of Instrument Engineering by C. S. Draper, W. McKay and S. Lees, the first edition published by the McGraw-Hill Book Company, Inc. in 1952.

Since there is ambiguity associated with the usage of common words when describing an instrument and coupled with a lack of standard instrument terminology it is necessary to define any terms used in describing an instrument.

An element may be considered as a unit which performs one task. It is usually represented by a block in a block diagram.

In electrical instrumentation, all elements may be classified under three main types. The three types are defined as follows.

The first type of element is the input transducer which converts a non-electric magnitude into a corresponding electric

one. There are seven recognized types of input transducers, mechanical, thermal, magnetic, electrical, optical, nuclear radiation and chemical.

An element with an electrical input and an electrical output is known as a modifier. This element changes or modifies an electrical quantity in some fixed manner.

The last classification of types of elements is the output transducer. Output transducers are elements which have an electrical input but a non-electrical output. All types of meters, recorders and display elements belong in this category.

Any instrumentation element may also be characterized by the following general properties:

The first of these properties is the input characteristics. Input characteristics are defined by the type of input, the useful range of the input quantity for which the element can be used, and the effect of the element upon the preceding stage or upon the object under investigation.

The second of these properties is the transfer characteristics. The transfer characteristics are defined by the transfer function, the instrument error, and the response to environmental influences.

The last of the general properties possessed by any element in an electric instrument is output characteristics. The output characteristics of an element are defined by the type of output, the useful output level or range, and the output impedance.

Unfortunately there were some terms in the above definitions which themselves need defining. These terms are defined below.

Transfer function--relationship between the magnitude of the input quantity, Q_i , and the output quantity or result Q_o .

$$Q_o = f(Q_i)$$

Sensitivity--derivative of the transfer function $\frac{dQ_o}{dQ_i} = S$

Instrument error--when an instrument doesn't follow $Q_o = f(Q_i)$ exactly but has the output $Q_o = f(Q_i) + F$ where F = the absolute error of the result or output quantity.

The error function is usually complex and therefore requires standardized terms to define it. The error function can be decomposed into three parts, the scale error, dynamic error, and noise and drift.

Each of the terms used in the above definition also need defining.

The scale error can be composed of four parts. The observed output may deviate from the correct output by an amount which is constant throughout the entire range of the instrument. The observed output may deviate from the correct value by a constant factor throughout the range of the instrument. The experimentally observed transfer function may deviate from the one derived theoretically. The output of the instrument may depend on the applied input quantity and also upon the past history of the element (this will be defined as hysteresis).

Dynamic error has a rather straightforward definition. The output of the instrument doesn't follow the variation with time of the input precisely or it depends upon a time function.

Noise and drift are signals or a signal, originating in the

element, that appears at the output terminals or is superimposed upon the output signal. If enough information of a statistical nature of the noise is available it is possible to distinguish between the output signal and the noise.

This completes the list of special definitions needed to describe both the oxygen determining instrument and its performance.

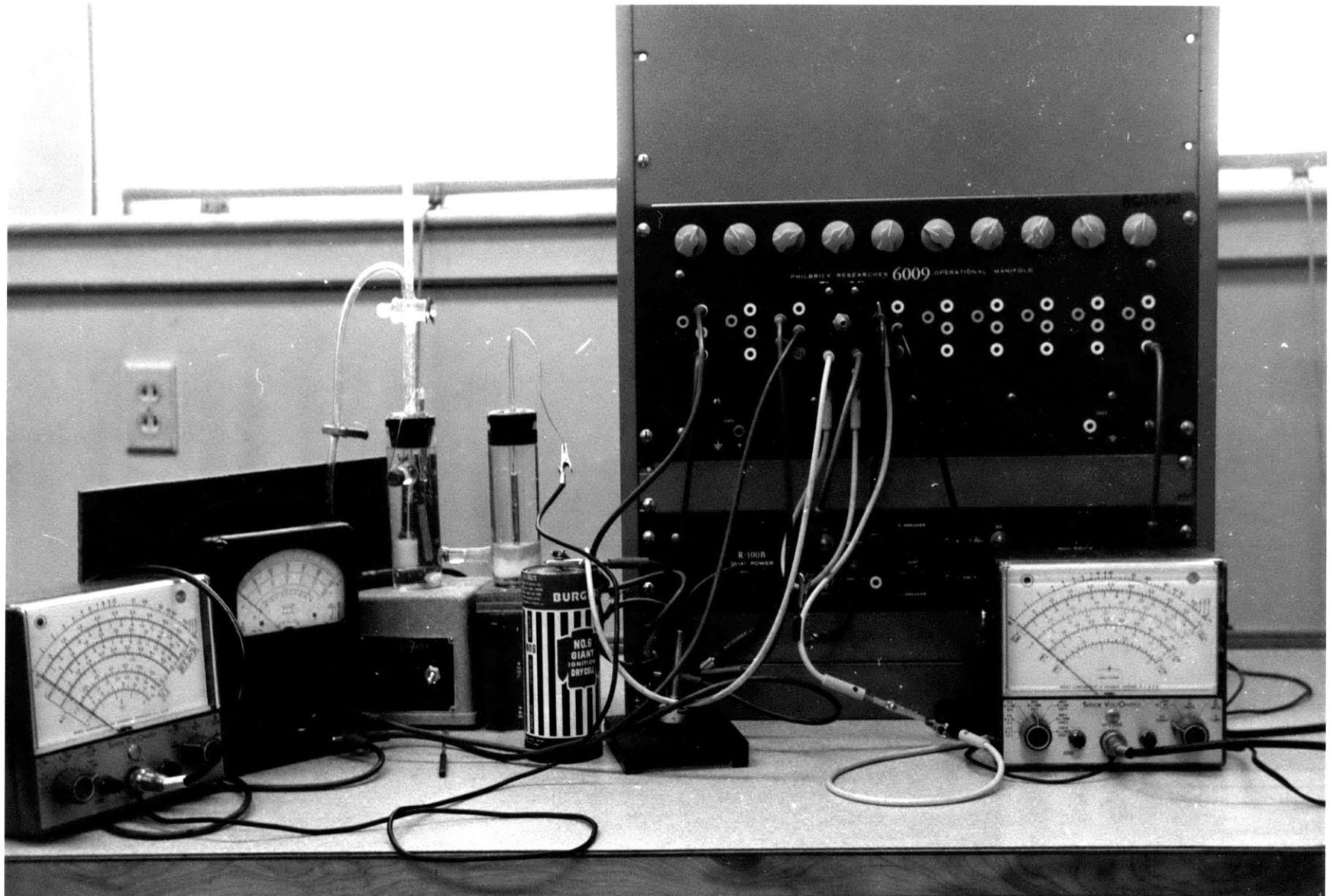
IV. Describing the Instrument

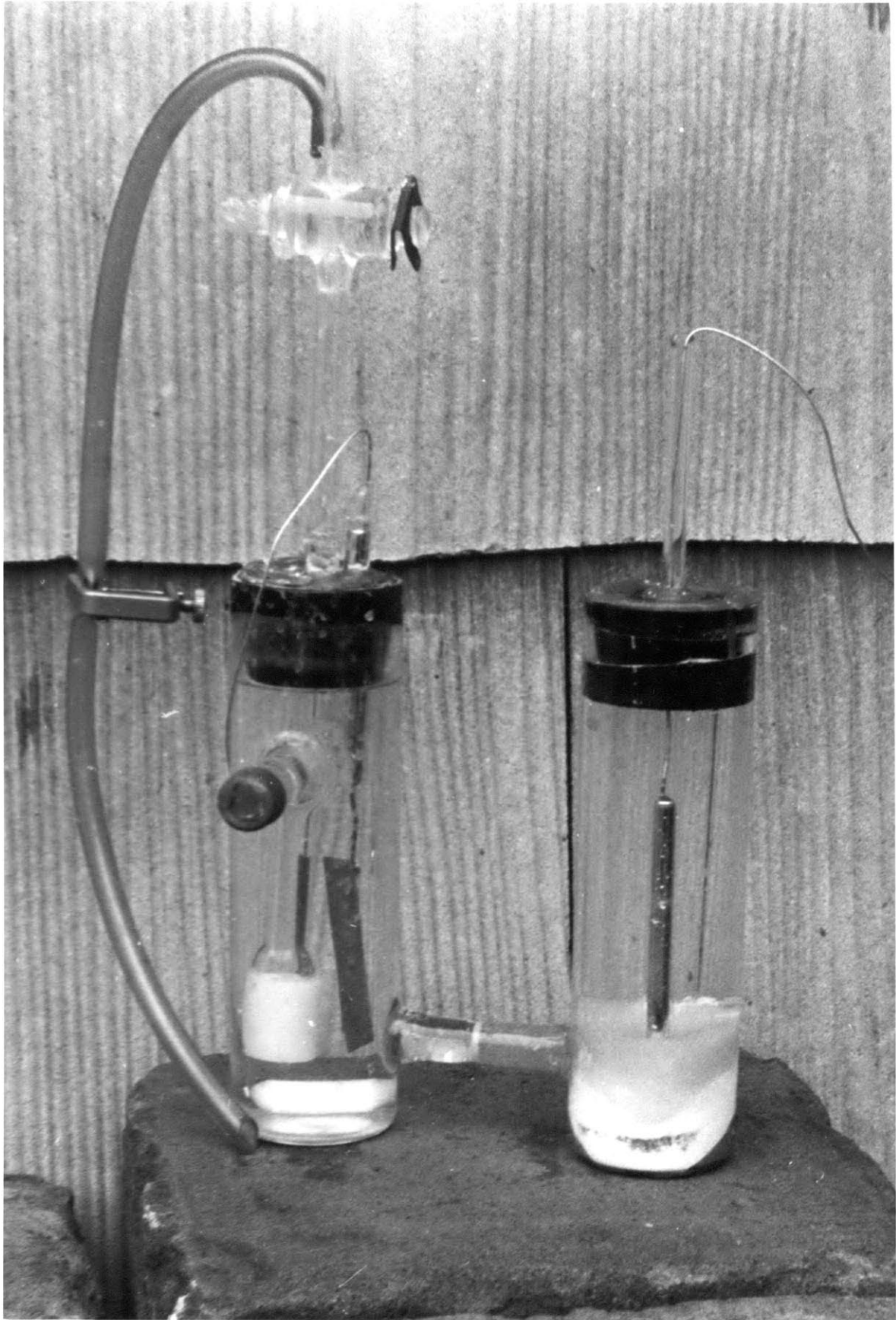
An actual idea of the physical size of the oxygen determining device and the electrochemical cell may be obtained from the following photographs.

The instrument is composed of a polarographic H-cell which was made to function as an electrochemical cell. The electrical part of the device is mounted in a desk top rack manufactured by the Bud Radio Corporation. The rack contains a Philbrick 6009 operational manifold and a \pm 300VDC regulated power supply, R-100B.

Mounted in the rear are three Philbrick operational amplifiers. Two meters were used as monitors. A R.C.A. senior voltohmyst Type WV-98A was used to check the voltage applied to the working electrode. A Tripolet model 630 was used to determine the amount of current passing through the cell. The integrated value of the voltage was read on another R.C.A. voltohmyst.

The physical configuration of the electrochemical cell may be seen from the photographs. This electrochemical cell wasn't





designed specifically for constant potential coulometry and hence the ratio of the area of the working electrode to the volume of the cell is poor. This means that the reduction of the dissolved oxygen will take longer.

Choosing a proper cell for use in this instrument proved to be a difficult problem. There are just 2 manufacturers which produce cells suitable for constant potential coulometry. They are E. H. Sargent and Company of Chicago, Illinois and Leeds and Northrup Company of Philadelphia, Pennsylvania.

None of the commercially manufactured cells were designed to operate with the sample isolated from the atmosphere. The cell finally selected for use was one which had been previously fabricated for use as a polarographic cell. This particular cell was selected because it was immediately available and because it was constructed with a flat bottom, which allowed the use of a magnetic stirrer. This cell also required very little modification to permit the sample to be electrolyzed isolated from the atmosphere.

The problem of selecting a correct integrator was considered in more detail than the difficulties surrounding the design of the electrochemical cell. A careful literature search was conducted in pertinent journals and abstracts contained in the Massachusetts Institute of Technology libraries.

Each integrator or coulometer as it is called in the chemical literature, was examined with two criteria in mind. These criteria were, did it have the required degree of precision and could it be assembled or easily obtained.

After this search was completed, and a suitable integrator selected, and built, a much more practical integrator which completely filled the specifications was accidentally uncovered.

It is possible to construct an integrator using an operational amplifier produced by the G. A. Philbrick Company of Boston, Massachusetts. When the proper type and value of resistor and capacitor are appropriately connected, an integrator with a reproducibility of $\pm 0.1\%$ can be built. This integrator will be described in more detail in a following section.

V. Technical Description of the Instrument

The oxygen determining device may be represented by the block diagram given in figure 8.

The terms shown in the generalized functional diagram in figure 8 will now be defined.

C_{O_2} - concentration of dissolved oxygen injected into the electrochemical cell.

I_{CT} - chemical transducer output current.

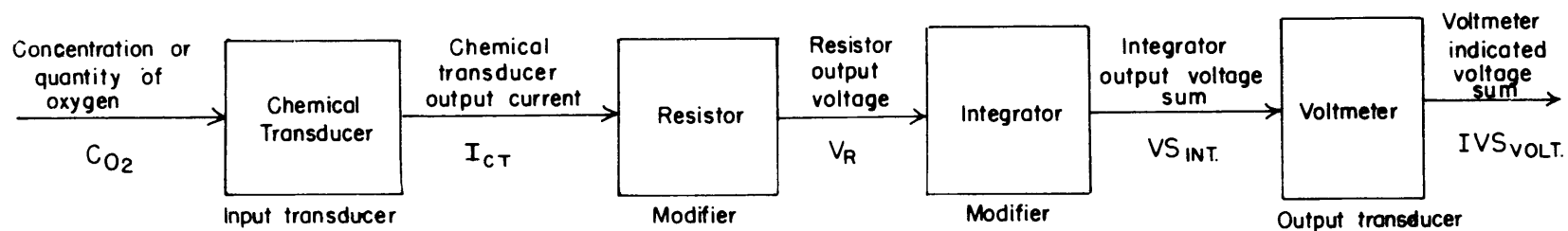
V_R - resistor output voltage.

$VS_{INT.}$ - integrator output voltage sum.

$IVS_{VOLT.}$ - voltmeter indicated voltage sum.

To operate this instrument as it now appears, it is only necessary to inject a sample containing dissolved oxygen gas and read the voltage as indicated on the voltmeter. The sequence of events is the following.

The chemical transducer transduces or changes the concentration of dissolved oxygen to a current by means of the



$$V_{S INT.} = \frac{1}{RC} \int_0^{\tau} V_R dt$$

Fig. 8. Generalized functional diagram of dissolved oxygen indicating instrument.

following reaction $O_2 + 2e + 2H^+ \rightarrow H_2O_2$. The chemical transducer output current is modified by the resistor into the resistor output voltage. This was done because the integrator is a voltage integrator not a current integrator. The integrated output voltage sum is transduced by the voltmeter into an indicated value for the output of the integrator.

The complete schematic of the circuit is shown in figure 9.

The design of the instrument will now be discussed in more detail. At this point the reader might refer to the discussion of feedback in the appendix. Further information concerning feedback can be obtained from the book by T. S. Gray¹ or the advertising literature published by the G. A. Philbrick Company of Boston, Massachusetts. The advertising literature of the G. A. Philbrick Company also contains a technical description of the components utilized.

The K2-XA operational amplifier connected as shown in the schematic will operate as a constant potential source effectively keeping the potential of the working electrode at any desired value. The value of potentiometer R_2 is chosen to keep the current drain of battery B_1 low. R_1 is chosen to have a value that will limit the amount of the current that the amplifier must supply to a value it is designed to supply when the potentiometer wiper is at one extreme of the potentiometer. The drift of the K2-XA is stated to be ± 8 millivolts per day referred to input.

The value of R_3 is chosen to be considerably smaller than the estimated resistance of the electrochemical cell. R_3 here

¹ Gray, T. S., Applied Electronics 2nd edition (1954)
John Wiley and Sons, Inc., New York.

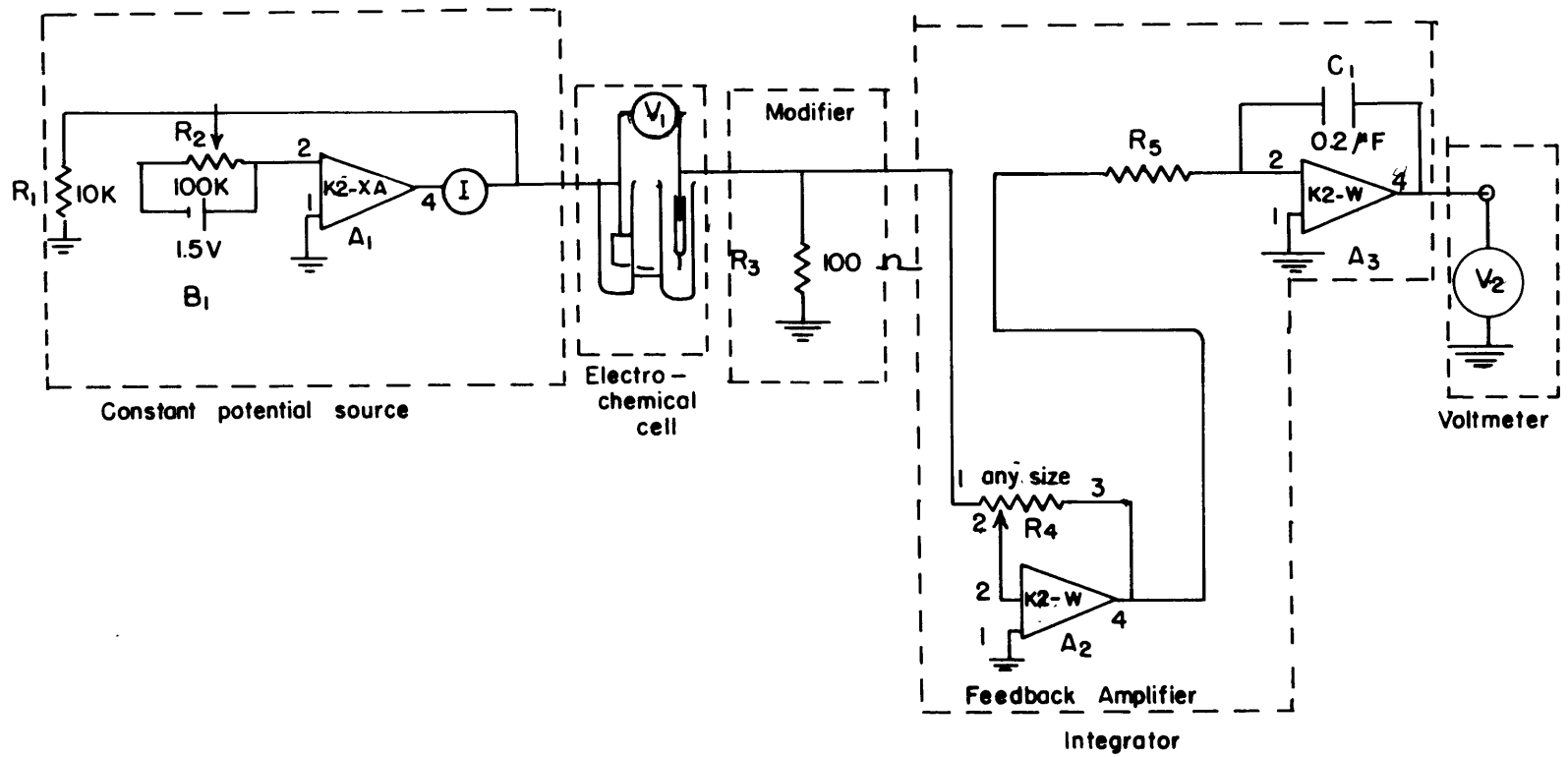


Fig. 9. Schematic of dissolved oxygen determining instrument.

is a modifier changing a ΔI which is some function of time to a ΔE which is a function of time.

The K2-W operational amplifier is connected to function as a feedback amplifier. Its gain will be determined by the position of the wiper of potentiometer R_4 . The function of A_2 must be discussed in conjunction with the method of selection of R_5 and C_1 .

The only restriction on the capacitor C_1 is that it must not charge during the course of integration to a voltage greater than the rated output voltage of the amplifier. The R-C constant is adjusted until the voltage, over the course of integration, is less than the output swing of the amplifier. To facilitate finding this value the gain of A_2 is adjusted until the final voltage on C_1 is less than the output swing of A_3 . Then the resistance from 2 to 1 and 2 to 3 of R_4 is measured and the gain of A_2 determined. If the gain is less unity, then the voltage drop A_2 can be calculated and this effect incorporated in the value of R_5 . R_5 is constrained as to the value it can assume. It must be small with respect to 100 megohms.

If high quality components are utilized in the feedback circuit of the integrator, integrations with a reproducibility of $\pm .1\%$ are possible. The requirement for the capacitor is on the order of $.10^7$ megohm-microfarads.

The important point in the above discussion that should be emphasized is the ease that circuits can be designed and built to give the desired results. An entirely new circuit

with radically different characteristics could be designed and built in approximately 10-15 minutes when plug-in type operational amplifiers are utilized.

VI. Experimental Procedure

The actual experimental procedure followed with this device was a relatively simple one. Preparation of the platinum working electrode was the first operation undertaken. The working electrode consisted of a 0.032" diameter platinum wire attached 1" X 2" X 0.006" platinum plate. The platinum wire was first welded to the plate using an 80 microfarad 450WVDC capacitor as a source and discharging it through the wire and plate. However, the resulting weld lacked the mechanical strength required.

It finally became necessary to drill a small hole through the plate and crimp the wire to the plate. An electrical connection was made to the working electrode by sealing the platinum wire into a soft glass tube and filling the tube with mercury and inserting a wire into the mercury.

The electrode was washed in 0.1 normal nitric acid, (HNO_3) and then heated to a red heat over a bunsen flame to remove all traces of grease and impurities. At this time the platinum electrode had a bright shiny look and at no time during the experiments could any change in appearance be detected after cleaning.

A supporting electrolyte of one normal sodium sulphate (Na_2SO_4) was then placed into the working electrode compartment.

A #8,3 hole stopper was then inserted into the working electrode chamber and all connections were sealed with Apiezon wax.

When the stopper was inserted into the cell the platinum cathode was positioned as close as possible to the tip of the salt bridge. The electrode was placed in this position to minimize the iR drop through the cell.

After the supporting electrolyte has been placed in the cell it was necessary to deaerate it. The dissolved oxygen in the supporting electrolyte may be removed by two different methods. Dissolved O_2 may be removed by constant potential coulometry or by flushing with nitrogen gas. Of the two methods flushing with nitrogen gas and then removal by constant potential coulometry is the best and the quickest method. Figure 10 is a current vs. time curve for the removal of dissolved oxygen by constant potential coulometry from the supporting electrolyte. As a check to determine if all the dissolved oxygen has been removed and to see if there are no oxygen leaks in the system, set the potential of the working electrode to approximately $-0.5VDC$ and read the value of the residual current. The value should be approximately 10 microamps.

Introduce the sample whose oxygen content it is desired to measure into the cell through a serum cap using a hypodermic needle. For a method of obtaining a sample with a known oxygen content see the appendix.

It was noticed as the hypodermic needle was being filled with the test sample fine bubbles of air were forming on the inside of the syringe and when the sample was injected not all the gas returned to the solution. The hypodermic was filled

by withdrawing the plunger and pouring the sample into the syringe and then replacing the plunger and decreasing the volume to the desired value.

To determine the optimum control potential at which to operate this cell it is first necessary to plot a current-electrode potential curve of the reaction under the same conditions that will prevail during electrolysis.

The current electrode potential curve is determined very simply. The potential of the working electrode was increased in steps of 0.1 volts or 0.05 volts and current readings are taken for each step. These values were plotted on graph paper and the cell is operated at the potential just about midway on the plateau. Such a curve for a the current-electrode potential cell is given in figure 11.

When selecting the operating point the following consideration should be kept in mind. The apparent observed potential of the working electrode is related to the actual voltage by the following relationship

$$E_{obs} = E_{true} + iR$$

where

E_{obs} = voltage observed at the working electrode

E_{true} = actual voltage at the working electrode

iR = ohmic drop in potential between the working electrode and the tip of the salt bridge.

The polarity of the iR drop is such that the observed potential is more negative than the true potential.

After the optimum control point is chosen electrolysis is

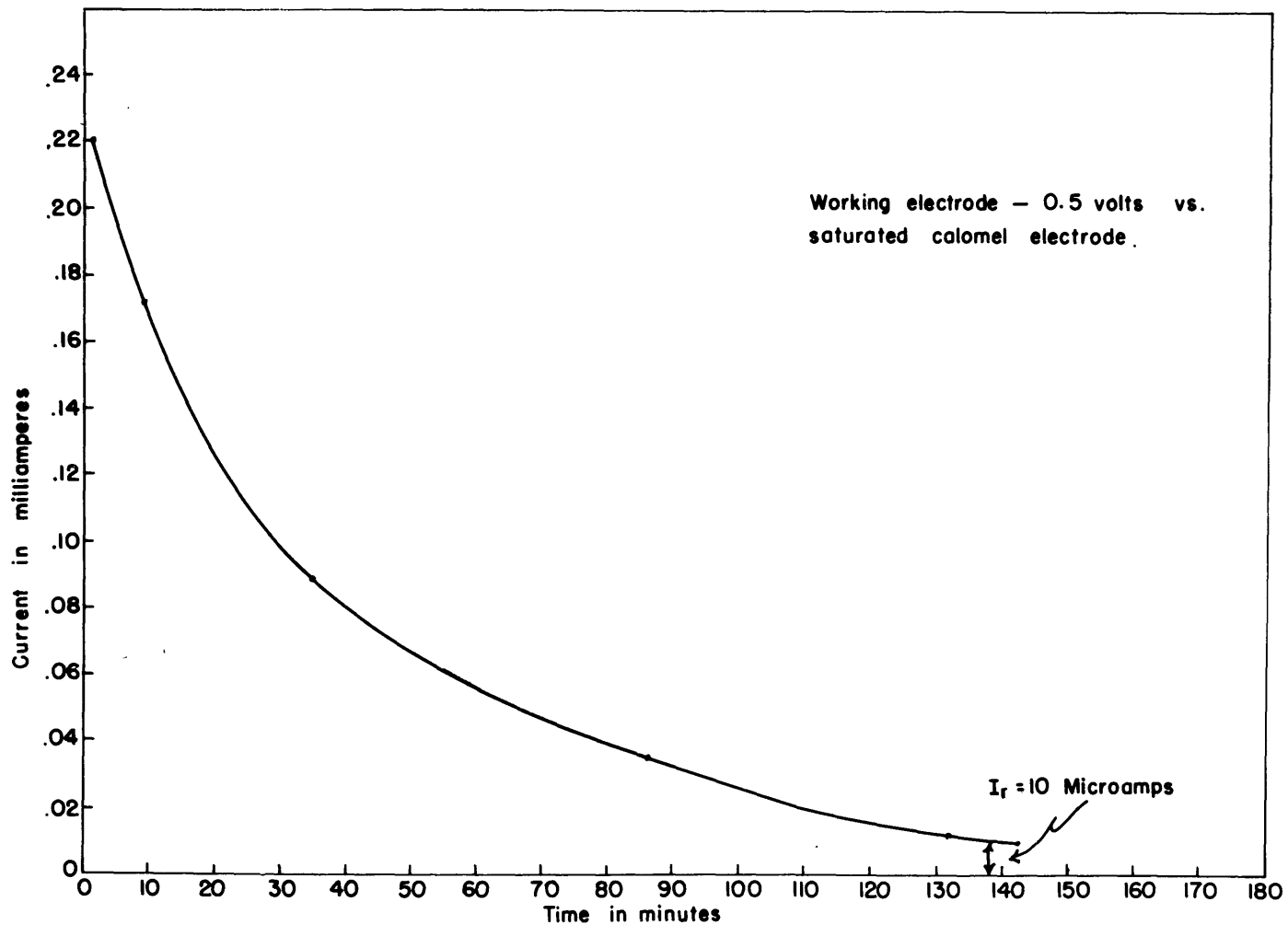


Fig. 10. Removal of dissolved oxygen from a one normal Na_2SO_4 solution by constant potential coulometry.

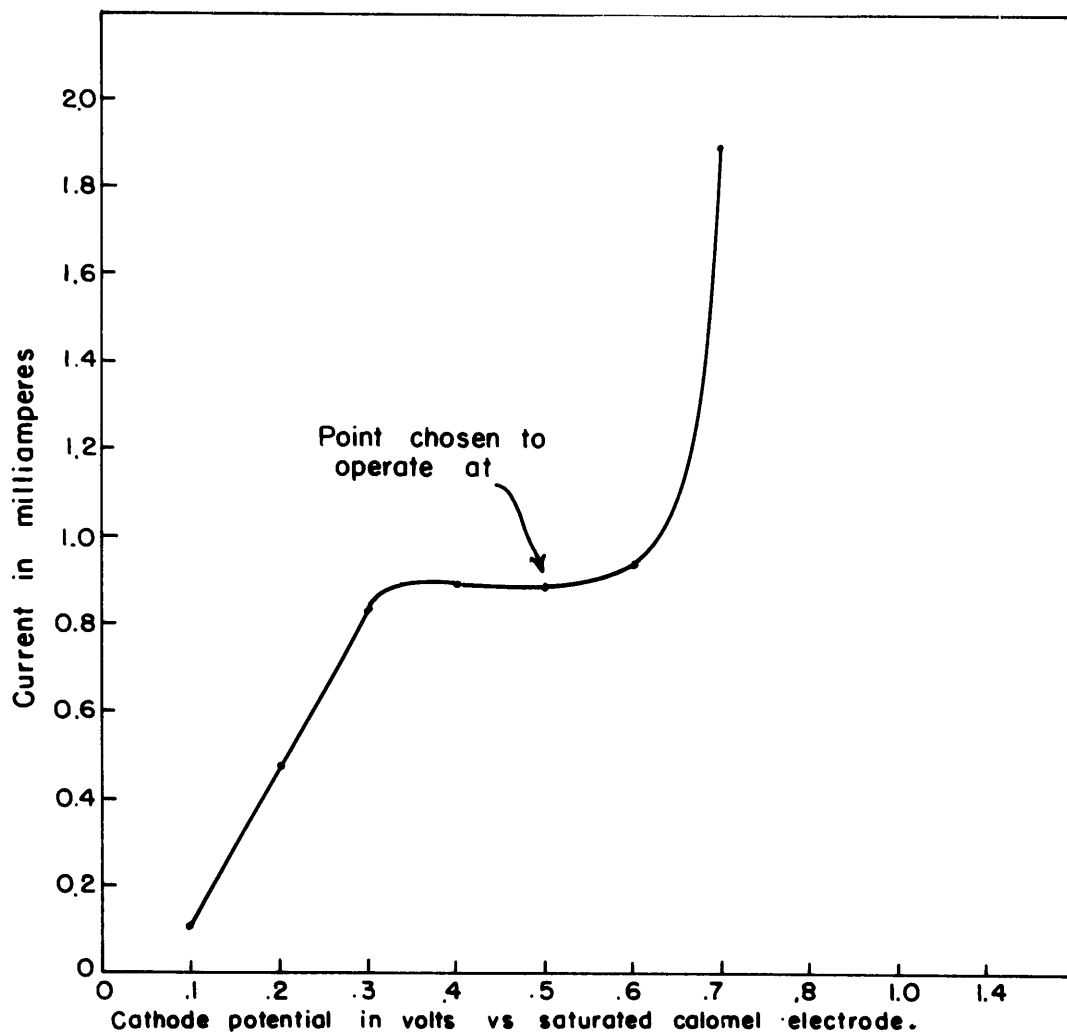


Fig. 11. Current-cathode potential curve for the reduction of Dissolved oxygen on a platinum electrode in a one normal solution of Na_2SO_4 supporting electrolyte.

is started and the current is integrated until the current flowing through the cell had decayed to the value of the residual current.

Samples were injected into the working electrode until it began to show signs of contamination. The electrolyte was adjudged to be contaminated when the level of the residual current varied unreasonably.

The temperature of the sample was taken just prior to injection into the working electrode compartment. The temperature was taken with a centigrade thermometer whose bulb was kept continually immersed in the unused portion of the sample.

VII. Presentation of the Data

The first series of tests run with this instrument were for the purpose of determining the transfer function of the instrument and the transfer function of the electrochemical cell. After a transfer function for the instrument was obtained, it was desired to inject a known predetermined concentration of oxygen into the instrument several times to obtain a quantitative idea of the reproducibility of the instrument. The transfer function of the instrument is shown in figure 12. Figure 13 is the transfer function of the input transducer.

As is readily evident from the two figures there is a paucity of data. There is a legitimate reason for this scarcity and it is evident from figure 10. The time required to electrolyze a sample down a residual current is on the order of 150 minutes. This is due to a poor electrolytic cell design.

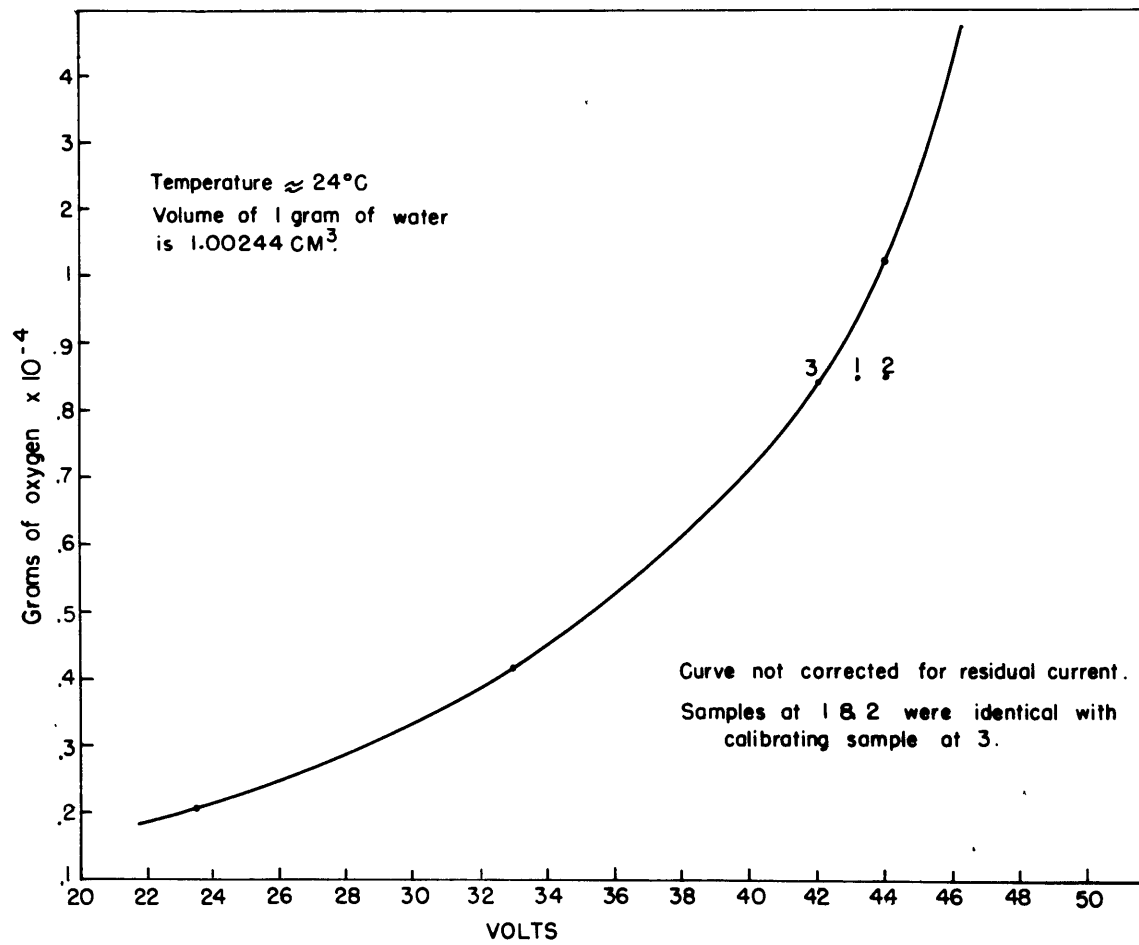


Fig. 12. Transfer function of the dissolved oxygen determining device.

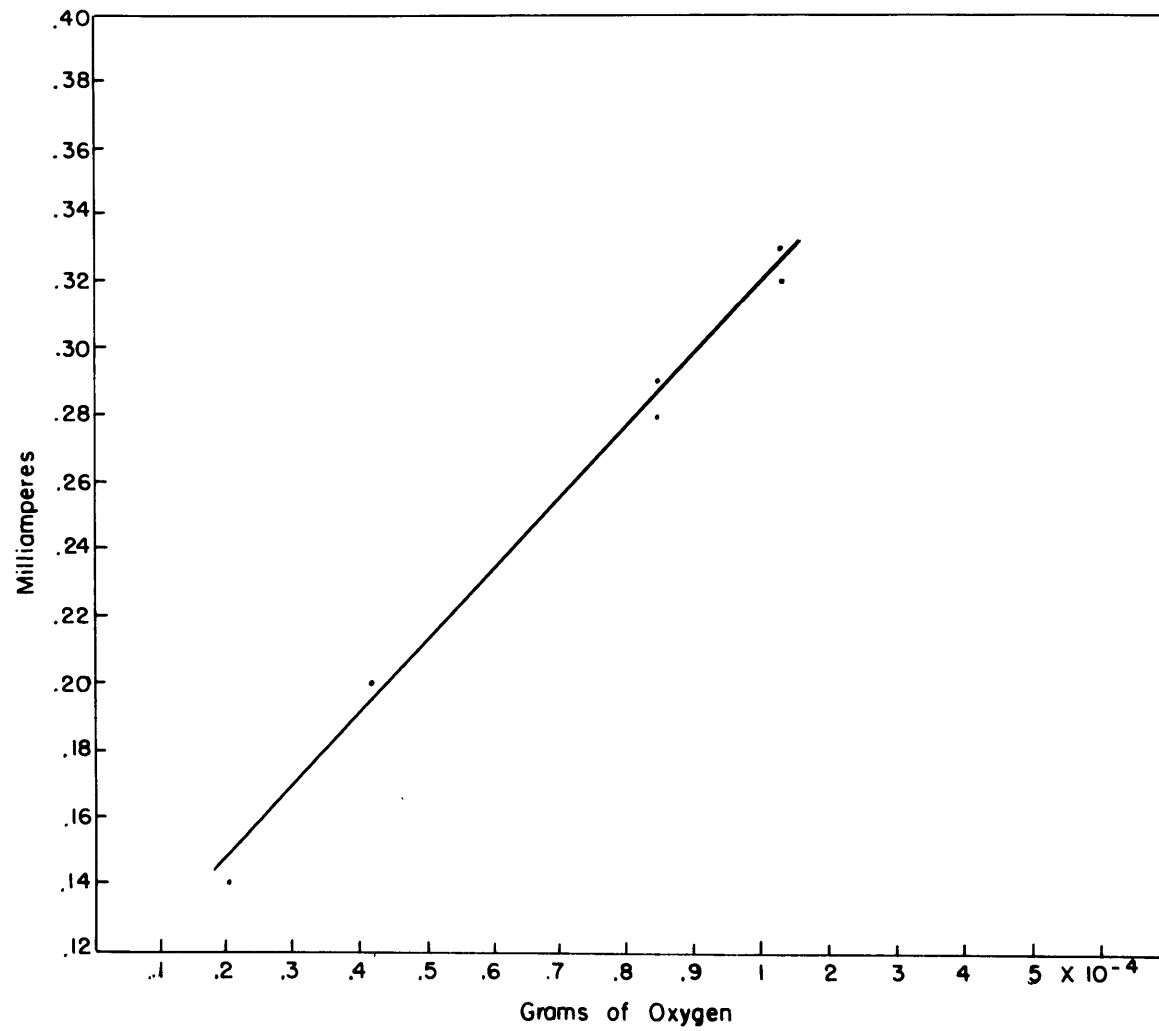


Fig. 13. Transfer function of chemical transducer

VIII. Analysis of All Errors

After seeing the data plotted in graphical form it is a logical step to consider in some detail the errors affecting this instrument. Each element will be discussed separately and any input which could cause a deviation of the observed output quantity will be examined in detail.

Since it is necessary to measure in some manner the volume of the sample which is injected into the input transducer, this is a good place to begin. There is a volume error in measuring the sample, it is estimated to be ± 1 of a cubic centimeter. Since the sample sizes ranged in size from 2.5cc. to 15cc. the error varied from 0.66% to 4%. It would be logical to find some non-linearity in the transfer function of this transducer at the small sample size end and we do.

A second error arises from the reliability of the table from which is determined the oxygen content of the calibration sample. The table is reliable to the first decimal place, i.e., if the oxygen content of the sample is given as 8.35ppm for a given temperature 5 is uncertain. An error is introduced due to the variation of dissolved oxygen in the sample with temperature. Since the observed temperature variation was $\pm 1.5^{\circ}\text{C}$ this error was adjudged to be slight.

Another type of error was due to the diffusion of O_2 from the atmosphere into the cell and hence into the supporting electrolyte. It can be shown that this is negligible. It is done by electrolyzing the supporting electrolyte until the residual current reaches a small value. The cell is then allowed to stand for a period of time and then the residual current is

read and compared with the first value. If the stopper is well sealed with wax the leakage is negligible

Due to the construction of the electrochemical cell when the supporting electrolyte was flushed with nitrogen gas, some of the gas remained in a small airspace immediately under the rubber stopper. The error due to any oxygen trapped in this space would be small.

There could also be an error due to other reductions taking place at the cathode. This would cause a working electrode efficiency of less than 100^o%. After consulting a table of standard oxidation potentials ² there doesn't appear to be any reductions which would occur to an appreciable extent. This is further verified by visual examination of the platinum cathode. It never lost its bright shiny appearance in over 30 hours of electrolysis. It is also for this reason that hysteresis of the cathode is ruled out as a source of error.

There could be an error induced by the working electrode drifting far enough in the negative direction until hydrogen evolution occurred. This was never observed to occur and the potential control circuit appeared to be very stable.

The resistor which acted as a modifier also had a temperature input. There were two methods by which the temperature of the resistor could vary. The first is by variation of the ambient temperature of the environment and the second is a heating effect due to the current flow. Since the temperature

² See Latimer in bibliography.

coefficient of resistivity of carbon is listed as $-.0005$ a temperature variation of $\pm 1.5^{\circ}\text{C}$ was adjudged insignificant. It appears that the resistor isn't a source of appreciable system errors.

The integrator also has inputs which may contribute to the overall system error. Temperature compensation has been built into the operational amplifier used in the circuit so errors due to ambient room temperature variations are assumed to be small. It is designed to give results reproducible to $\pm 0.1\%$ up to 65°C . The drift of this amplifier is stated to be ± 5 millivolts/day referred to the input. If better results are desired the K2-W amplifier can be stabilized with a K2-P stabilizing amplifier and the drift reduced to a submillivolt level. There is one source of error which might be quite appreciable in this instrument due to the long electrolysis time required. This is an error due to the leakage of the capacitor. This can be considered as a resistor in parallel with the capacitor. See the appendix for the calculation. The value of this resistor for an error of $\pm .17\%$ in 150 minutes or 9000 seconds is 4.5×10^{13} ohms. This is not an unreasonable value for mylar or polystyrene computer type capacitors. Thus it appears even though the integrator extends over a long period of time the integrator maintains its reproducibility.

The factors influencing the errors of the output transducer are more difficult to ascertain since it is a commercially produced instrument. The output transducer is a R.C.A. Senior

voltohmyst, vacuum tube voltmeter model [WV-98A]. Specifications of this instrument may be obtained from the Radio Corporation of America in Camden, New Jersey.

There is an error introduced due to the zeroing adjustment. The zero of the instrument either drifted or was accidentally moved during the course of several integrations. There is a very definite scale error associated with this instrument. It is estimated that the error in voltage readings is ± 1 volt on the 50 volt scale. The largest value this error reached was 4.29% for the lowest reading of the integrator output voltage sum. It could logically be expected to see this deviation on the transfer function of the instrument.

There is an error associated with the output transducer which results from deciding the exact time to stop the integration. If the integration is to be stopped when the current decays to a value of 10 μ A. there is a difficulty in ascertaining when this point is reached.

IX. Suggested Improvements of the Oxygen Determining Device

If the instrument just described can be considered as a prototype model, and a device to verify the principle of operation, which allowed the builder to gain designing and operating experience, many valuable suggestions can be made to improve it.

There are four main improvements necessary to make this device a precise measuring instrument.

An electrochemical cell must be designed which will shorten the electrolysis time to approximately 10 minutes.

Some type of adjustable meter relay is necessary to stop the integration when the residual current through the cell drops to a preselected value.

A more precise method of determining either the weight or the volume of the sample which is injected into the cell.

It is necessary to select a method which will permit the voltage of the integrating capacitor to be measured more precisely.

As an aid in design of an electrochemical cell a previously developed equation will be utilized

$$i_t = i_o e^{-kt}$$

where $k = \frac{DA}{Vd}$

It is recalled that

D = diffusion coefficient

A = area of working electrode

V = volume of the cell

d = thickness of the diffusion layer.

The cell should have the as large a ratio of electrode area to cell volume as possible. To obtain maximum electrode area a platinum gauze electrode in the form of a right circular cylinder appears to be the best in this respect. Such an electrode may be obtained from the E. H. Sargent Company of Chicago, Illinois. To keep the cell resistance as low as possible the

cross sectional area of the salt bridge which connects the reference electrode and the working electrode should be as large as possible.

Efficient stirring of the solution will permit d to be made as small as possible thus decreasing electrolysis time. This will also aid in determining the initial cell current when a sample is injected.

A suitable type of adjustable meter relay should be a Simpson 29XA adjustable meter relay. This meter has non-locking contacts which may be positioned anywhere along the instrument scale arc by means of an external front-adjusted gear drive mechanism. This will allow the selection of the value of residual current at which the integration will be stopped.

The volume of the sample to be injected could be measured in a pipette prior to transfer to a hypodermic needle for injection.

There is one feature of this instrument which has so far been unmentioned. The voltage remains upon the capacitor until the capacitor is externally discharged. This allows any method for measuring this voltage which might require some time. This allows the integrator output voltage sum to be measured by potentiometric methods.

A large reduction in the physical size of the components necessary for the electrical circuitry of this instrument can be obtained by using a Philbrick model MK operational manifold.

This is manufactured by the George A. Philbrick Company of Boston, Massachusetts. Use of the model MK operational manifold permits a reduction in size to the overall dimensions of $17\frac{5}{16}$ " X $6\frac{7}{8}$ " X 8". The power requirements of this is 115VAC, 60 cycle with a power rating of 175 watts. Its weight is approximately 30 pounds. Everything could be included in this unit except the input and output transducer.

Appendix

Feedback is defined as a voltage or current proportional to the amplifier output voltage or current which is fed back and superimposed on the input signal. If the amplification increases, the feedback is positive or regenerative, and if the amplification decreases, the feedback is negative or degenerative.

The advantages of a negative feedback are as follows:

1. It tends to flatten the frequency response characteristics
2. It extends the range of uniform response
3. It reduces nonlinearity and phase distortion
4. It improves the stability of the amplifier making the gain less dependent on the operating voltages or on variations in tube characteristics.
5. It tends to make the gain less dependent on the load.

Positive feedback has exactly the opposite effects of those listed above. In practice negative feedback is much more common.

It is very easy to determine if the feedback is current or voltage feedback. With voltage feedback the voltage feedback is equal to zero when the load is short circuited. With current feedback the feedback voltage is equal to zero when the

load is open circuited.

There are several assumptions usually made when analyzing a feedback circuit.

1. The circuit parameters including the tube coefficients over the operating range are constant.
2. The circuit is operating in a steady state condition with sinusoidal excitation.
3. The feedback voltage is connected in a series with the grid.
4. The input impedance of the amplifier is large, compared to the other associated impedances.
5. The amplifier is unilateral, i.e., it transmits the signal only in one direction.
6. Any reaction the amplifier and source might have on the feedback network can be neglected.

See figure 14 for a diagram of the circuit.

Series injection is used in the above circuit for purposes of analysis.

The indicated voltages are as follows:

- E_g = input voltage applied to amplifier terminals
 E_{pk} = resultant voltage at the output terminals
 βE_{pk} = portion of E_{pk} feedback in series with the input voltage.

The voltage between the grid and cathode terminals has the following form.

$$E_{gK} = E_g + E_{pk}$$

The gain of the amplifier = K or $\frac{E_{pk}}{E_{gK}}$

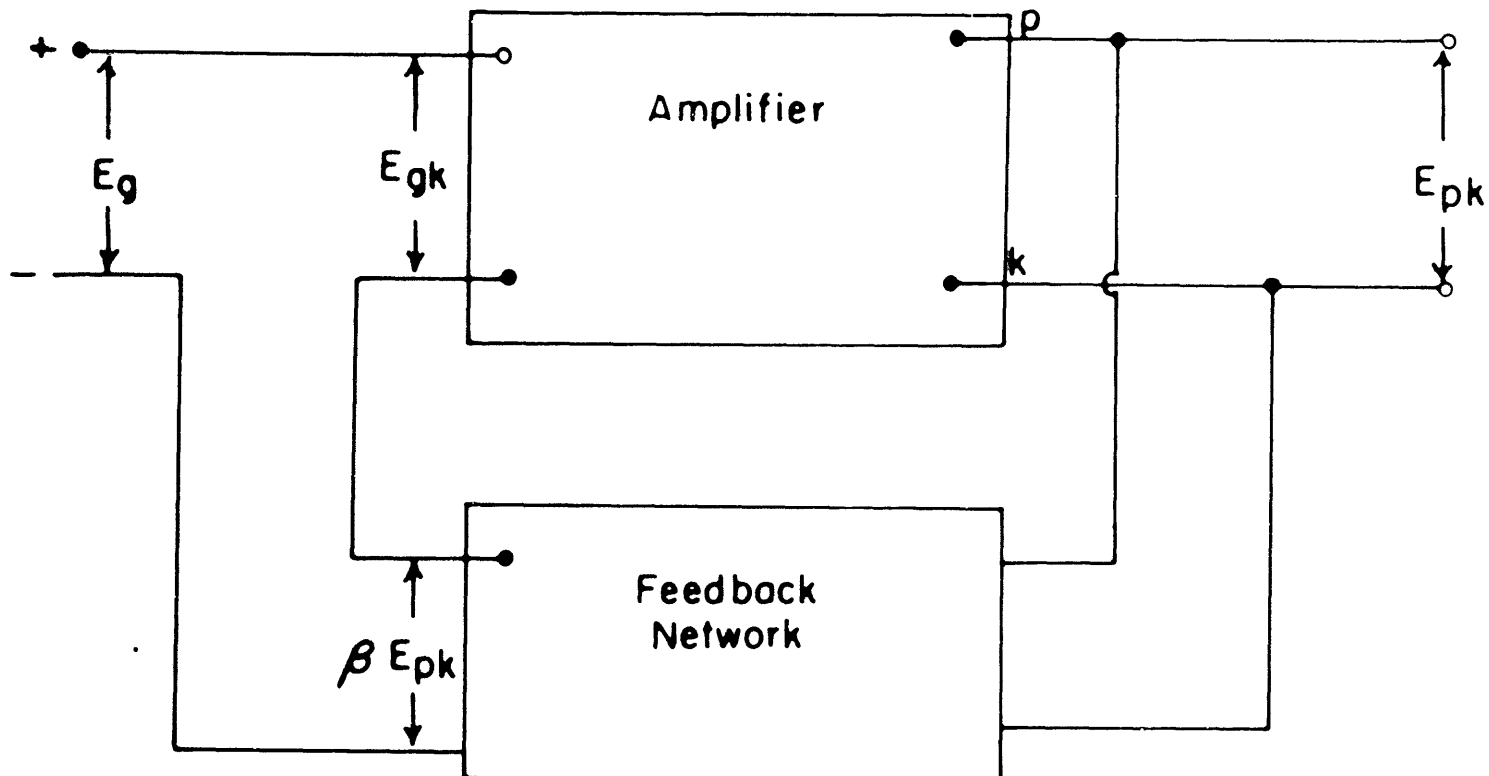


Fig. 14. Amplifier with series injection feedback

so $E_{pk} = KE_{gk}$

substituting into the first equation results in

$$E_{pk} = KEg + K\beta E_{pk}$$

or

$$E_{pk} = \frac{KEg}{1-K\beta}$$

Now consider the overall gain of the amplifier including the effect of feedback.

$$K_r = \frac{\text{output potential}}{\text{input signal potential}} = \frac{E_{pk}}{E_g}$$

by substitution the following relationship is obtained:

$$K = \frac{K}{1-K\beta}$$

where K , K and β may be complex quantities.

Consider a negative feedback and the voltage fed back ($K\beta$) that is very large compared to one, the following equation is obtained:

$$K = \frac{1}{\beta}$$

This equation leads to a very important conclusion. The actual gain of a properly designed amplifier when used with feedback is a function only of the components in the feedback circuit.

A Method for Preparing a Sample with a Known Oxygen Concentration

Dissolve 5.0 gms. of powdered gelatin in 75 milliliters

of hot water. Cool the solution and add 2.0 grams of phenol (carbolic acid) and 0.3 grams of sodium chloride (NA Cl). Adjust the volume of the mixture to 100 milliliters with distilled water.

To obtain an air saturated calibration solution add the gelatin-phenol-sodium chloride solution at the rate of 2 milliliters of solution per 100 milliliters of distilled water. Saturate with air by bubbling for one hour at a constant temperature and allow it to stand for one-half hour. This solution will contain an amount of dissolved oxygen given by table (1). Table (1) is obtained from table (2) as shown from the following sample calculation.

This calculation will verify the value of oxygen concentration at 26°C found in table (1).

In the gelatin-phenol-sodium chloride solution there is 7.3 grams of solute per 100 milliliters of solution. The assumption is made that all of the solute acts the same as an equal weight of sodium chloride in lowering the solubility of oxygen. If 2 milliliters of the gelatin-phenol-sodium chloride solution is added for each 100 milliliters of distilled water there will be 1.465×10^{-1} grams of solute per 100 milliliters of distilled water, or 1465 PPM of chloride in the water. Interpolating the value at 26°C and 760 centimeters of mercury from table 8.10 PPM of dissolved oxygen is obtained. The results of the above calculation are believed to be accurate to the first decimal place.

**Table I. Dissolved Oxygen in Water
at Various Temperatures**

(Solution contains 10 ml. of gelatin-phenol-
salt solution per pint)

Temperature		Dissolved Oxygen, P.P.M. by Wt.
° C.	° F.	
10	50	11.2
11	51.8	10.9
12	53.6	10.7
13	55.4	10.4
14	57.2	10.2
15	59.0	10.0
16	60.8	9.8
17	62.8	9.6
18	64.4	9.4
19	66.2	9.2
20	68.0	9.0
21	69.8	8.9
22	71.6	8.7
23	73.4	8.6
24	75.2	8.4
25	77.0	8.3
26	78.8	8.1
27	80.6	8.0
28	82.4	7.8
29	84.2	7.7
30	86.0	7.5

SOLUBILITY OF OXYGEN IN FRESH WATER AND IN SEA WATER OF
STATED DEGREES OF SALINITY AT VARIOUS TEMPERATURES WHEN EXPOSED TO WATER
SATURATED AIR AT A TOTAL PRESSURE OF 760 MM Hg. DRY AIR IS ASSUMED TO
CONTAIN 20.90 PER CENT OXYGEN.*

(Calculated by G. C. Whipple and M. C. Whipple from measurements of C. J. J. Fox.)

C°	Chlorides in Sea Water (parts per million)					Difference per 100 ppm Cl	Dissolved Oxygen in Chloride-free Water	
	0	5000	10000	15000	20000		C°	ppm
°C	Dissolved oxygen in parts per million by weight					ppm	C°	ppm
0	14.62	13.79	12.97	12.14	11.32	0.0165	30	7.6
1	14.23	13.41	12.61	11.82	11.03	.0160	31	7.5
2	13.84	13.05	12.28	11.52	10.76	.0154	32	7.4
3	13.48	12.72	11.98	11.24	10.50	.0149	33	7.3
4	13.13	12.41	11.69	10.97	10.25	.0144	34	7.2
5	12.80	12.09	11.39	10.70	10.01	.0140	35	7.1
6	12.48	11.79	11.12	10.45	9.78	.0135	36	7.0
7	12.17	11.51	10.85	10.21	9.57	.0130	37	6.9
8	11.87	11.24	10.61	9.98	9.36	.0125	38	6.8
9	11.59	10.97	10.36	9.76	9.17	.0121	39	6.7
10	11.33	10.73	10.13	9.55	8.98	.0118	40	6.6
11	11.08	10.49	9.92	9.35	8.80	.0114	41	6.5
12	10.83	10.28	9.72	9.17	8.62	.0110	42	6.4
13	10.60	10.05	9.52	8.98	8.46	.0107	43	6.3
14	10.37	9.85	9.32	8.80	8.30	.0104	44	6.2
15	10.15	9.65	9.14	8.63	8.14	.0100	45	6.1
16	9.95	9.46	8.96	8.47	7.99	.0098	46	6.0
17	9.74	9.26	8.78	8.30	7.84	.0095	47	5.9
18	9.54	9.07	8.62	8.15	7.70	.0092	48	5.8
19	9.35	8.89	8.45	8.00	7.56	.0089	49	5.7
20	9.17	8.73	8.30	7.86	7.42	.0088	50	5.6
21	8.99	8.57	8.14	7.71	7.28	.0086		
22	8.83	8.42	7.99	7.57	7.14	.0084		
23	8.68	8.27	7.85	7.43	7.00	.0083		
24	8.53	8.12	7.71	7.30	6.87	.0083		
25	8.38	7.96	7.56	7.15	6.74	.0082		
26	8.22	7.81	7.42	7.02	6.61	.0080		
27	8.07	7.67	7.28	6.88	6.49	.0079		
28	7.92	7.53	7.14	6.75	6.37	.0078		
29	7.77	7.39	7.00	6.62	6.25	.0076		
30	7.63	7.25	6.86	6.49	6.13	.0075		

* Under any other barometric pressure, P, the solubility may be obtained from the corresponding value in the table by the formula:

$$S' = S \frac{P}{760} = S \frac{P'}{29.92}$$

in which S' = Solubility at P or P'.

S = Solubility at 760 mm or 29.92 in.

P = Barometric pressure in mm and

P' = Barometric pressure in in.

The second decimal place in the above table is not accurately known. The average difference from the mean of five different investigators represents 0.07 ppm. Until further data are obtained, however, the second decimal place has been retained in the table.

Sample Calculation for Determining
Size of Leakage Resistance of the Integrating Capacitor

For an error of $\pm 1\%$ in 9000 seconds the capacitor must
have a self time constant of

$$T = R_L C = 9 \times 10^6 \text{ seconds.}$$

$$\text{if } C = 0.2 \mu\text{f then } R_L = \frac{9 \times 10^6}{0.2 \times 10^{-6}}$$

or 4.5×10^{13} ohms or 4.5×10^7 megohms.

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