APPLICATION OF THE CATHODE RAY
OSCILLOGRAPH TO POLAROGRAPHIC ANALYSIS

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INTRODUCTION

The object of this work is to devise a method of reproducing on a cathode ray oscillograph the current-voltage curves that are obtained with the Fisher Electropode, and from these curves to predetermine directly the half-wave potentials of the elements present in a test solution. This test solution is composed of copper, lead, cadmium, and zinc ions in a supporting electrolyte of .1 normal K Cl.

HISTORICAL

About twenty years ago at the Charles University in Prague, the polarographic method of analysis was developed by Professor Jaroslav Heyrovsky and his colleagues. The principle of this new method of analysis was based on the fact that when an electrolyte solution is electrolyzed in a cell consisting of a dropping mercury electrode and a second non-polarizible electrode (usually a pool of mercury), it is possible to determine from the resulting current-voltage curve both the nature and the concentration of the reducible or oxidizable substances present.

TERMINOLOGY AND THEORY

Polarographic analysis depends on the principle of electroly Electrolysis can be defined as a chemical reaction taking place under the influence of an electromotive force produced by having electrodes immersed in the solution.

At the cathode the reaction is an electro-reduction, while at the anode an equal amount of electro-oxidation will occur. Th current-voltage curve results when the current is plotted against the voltage applied across the cell.

A schematic diagram for obtaining a current-voltage curve with a dropping mercury electrode is shown in Fig. 1, (1).

A typical current-voltage curve, for a single ion, obtained with a dropping mercury electrode is shown in Fig. 2, (1).

The portion of the curve between points A and B is called the residual current. This is the very small current flowing through the cell before the decomposition potential is reached. Point B shows the value of the decomposition voltage which is the electromotive force needed to start the electrolysis of the ion present. From points D to E is the limiting current which gradually reaches a constant value and becomes independent of the applied voltage. The limiting current, under optimum conditions, is found to be directly proportional to the concentration of the electro-reducible material. It is on this fact that the quantitative phase of polarographic analysis is made possible, (1).

The concentration of the electro-reducible material at the surface of the mercury drop tends to decrease as the material is reduced. However, the loss of material is compensated by the diffusion of more material from the body of the liquid to the surface of the mercury drop. The rate of diffusion depends on the concentration difference between the surface layer and the body of the solution. As the applied electromotive force is increased, the concentration at the surface of the mercury drop becomes so very small with respect to the concentration in the body of the solution that the difference in concentration approaches a constant value that is equal to the concentration of the solution. Thus the rate of diffusion must approach a constant.

A SIMPLE POLAROGRAPHIC CIRCUIT

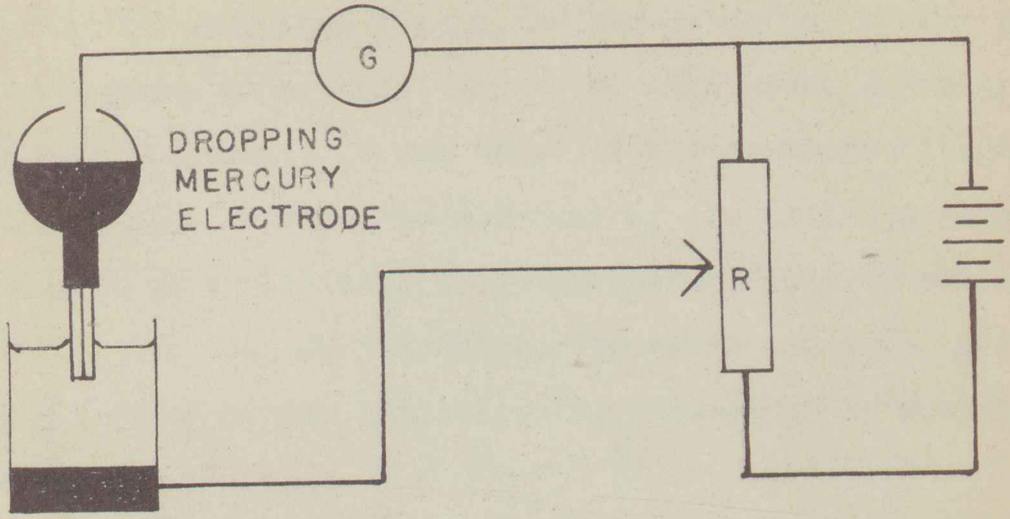


FIG. 1

CURRENT-VOLTAGE CURVE

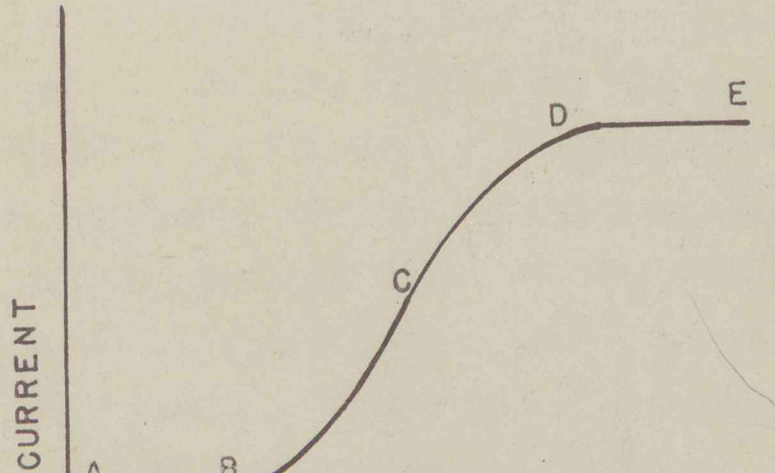


FIG. 2

With an excess of an indifferent ion in solution, the limiting current becomes dependent on the rate of diffusion and hence is called the diffusion current, (1).

Point C denotes the half-wave potential. The half-wave potential, as can be seen from Fig. 2, is the potential of the mercury electrode against an external reference electrode, (usually a saturated calomel electrode) at the point on the current-voltage curve where the current is equal to one-half of the limiting value.

The half-wave potential is independent of the concentration, and each ion has its own characteristic half-wave potential. This fact is the basis of the qualititative polarographic analysis to be studied.

The unknown is easily found by comparing the experimental value of the half-wave potential with the reference list available ("Half-Wave Potentials of Inorganic Compounds") (9).

In analysing by polarographic methods, there must be present in the solution another ion for which the analysis is not being conducted. The presence of the excess ion serves to increase the diffusion current. The concentration of this ion may range from .1 N to 1.0 N. The ion must be chosen so that it will not produce a current increase at a voltage below those ions for which the analysis is being made. This ion is the indifferent ion and the solution containing the indifferent ion is called the supporting electrolyte. The test solution is added to the supporting electrolyte in such amounts as to vary the concentration of test ions from 10^{-2} to 10^{-6} equivalents per liter, (8).

In many cases, the current-voltage curve will show a maximum or a peak at point D in Fig. 2. The cause is still not definitely known; but the peak can be eliminated for more accurate readings by the addition of a dye solution or a maximum suppressor as it is called. One such maximum suppressor is composed of three parts of 0.2% alcoholic methyl red and two parts of 0.2% alcoholic bromcresol green. Only 2.5 cc of the maximum suppressor is needed per liter of the supporting electrolyte, (8).

EXPERIMENTAL

The first step was to obtain current-voltage curves of the test solution by use of the Fisher Electropode. This gives a standard from which to work. That is, the curves to be obtained on the cathode ray oscillograph should have the same general shape; and the half-wave potentials obtained from the oscillograph curves should have the same values as obtained with the Fisher Electropode.

The Electropode is a trade name for a type of polarographic apparatus which employs a calibrated potentiometer dial for reading the voltage, and a galvanometer for the current readings. As a rule, atmospheric oxygen is removed from the solution to be tested as its presence will be indicated on the current-voltage curves. However, during all of the work done in this experiment, the oxygen was not removed as it afforded another substance for which to test.

In the first run made with the electropode, the values of current and voltage were tabulated and then plotted. Figure 3 is a rough curve which indicates the voltage range to be covered in smaller increments, namely, from .1 to 1.2 volts.

CURRENT-VOLTAGE CURVE

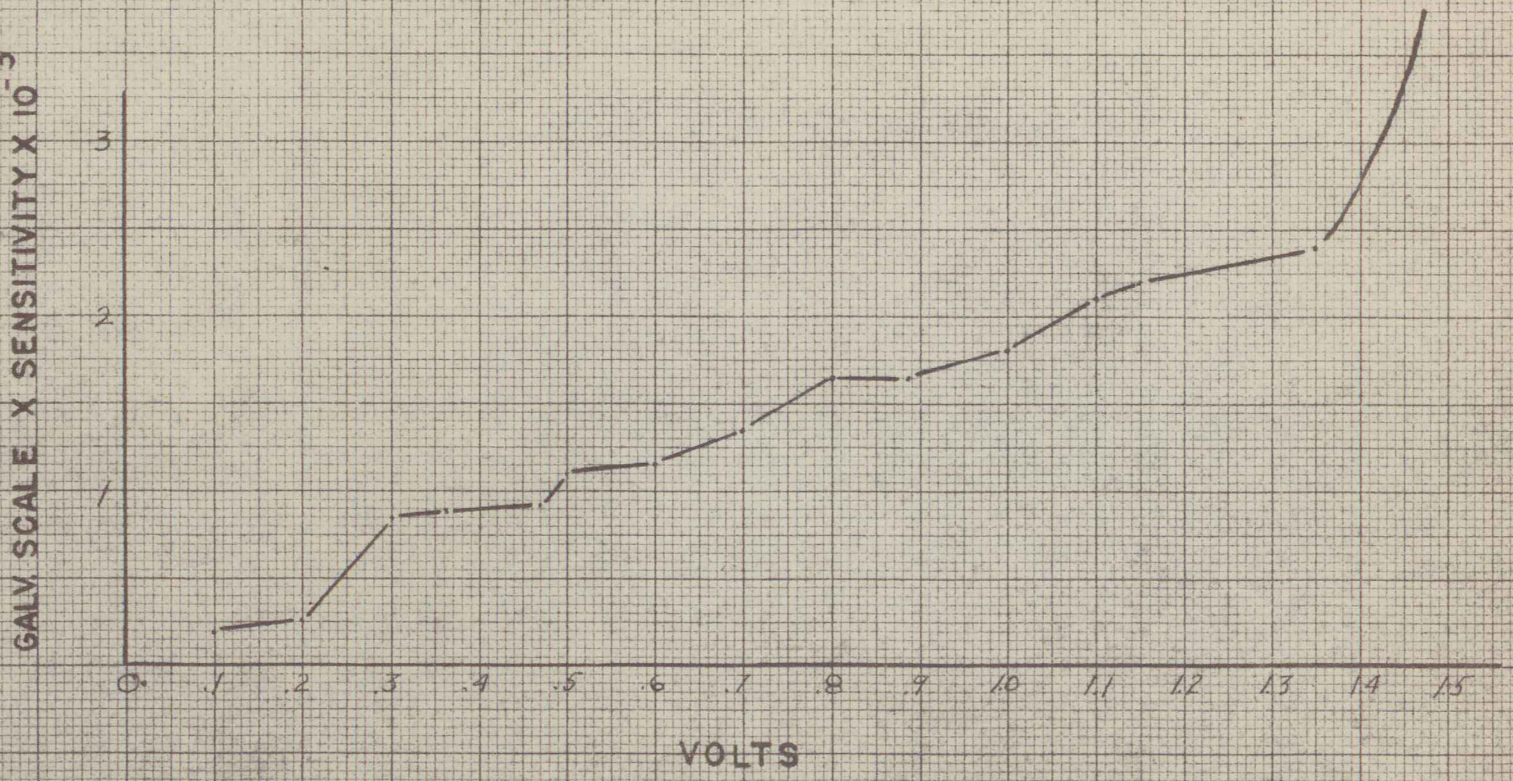


FIG. 3

DATA FOR FIG. 3

Voltage	Galvanometer Scale (mm)	Galv. Scale X Sensitivity	Sensitivity
.10	12	240	20 X
.20	27	540	
.30	44	880	
.47	43	870	
.50	55	1100	
.60	59	1180	
.70	69	1380	
.81	81	1620	
.885	82	1640	
1.00	9	1800	200 X
1.12	10.5	2100	
1.35	12	2400	
1.45	15	3000	
1.50	28	5600	

Figure 4 indicates the curve obtained by plotting directly on the graph paper the current-voltage readings of the second run, using smaller voltage increments. The half-wave potentials obtained from Fig. 4 as compared to those given in the tables ("Half-Wave Potentials of Inorganic Substances") are indicated below:

SUBSTANCE	HALF-WAVE POTENTIAL (Graph)	HALF-WAVE POTENTIAL (Tables)
Zinc ion	-1.07	-1.02
Cadmium ion	-0.68	-0.64
Lead ion	-0.46	-0.44
Oxygen	-0.10	-0.18
Copper ion	*	+0.03

* No positive voltage was used in this experiment.

CURRENT-VOLTAGE CURVE

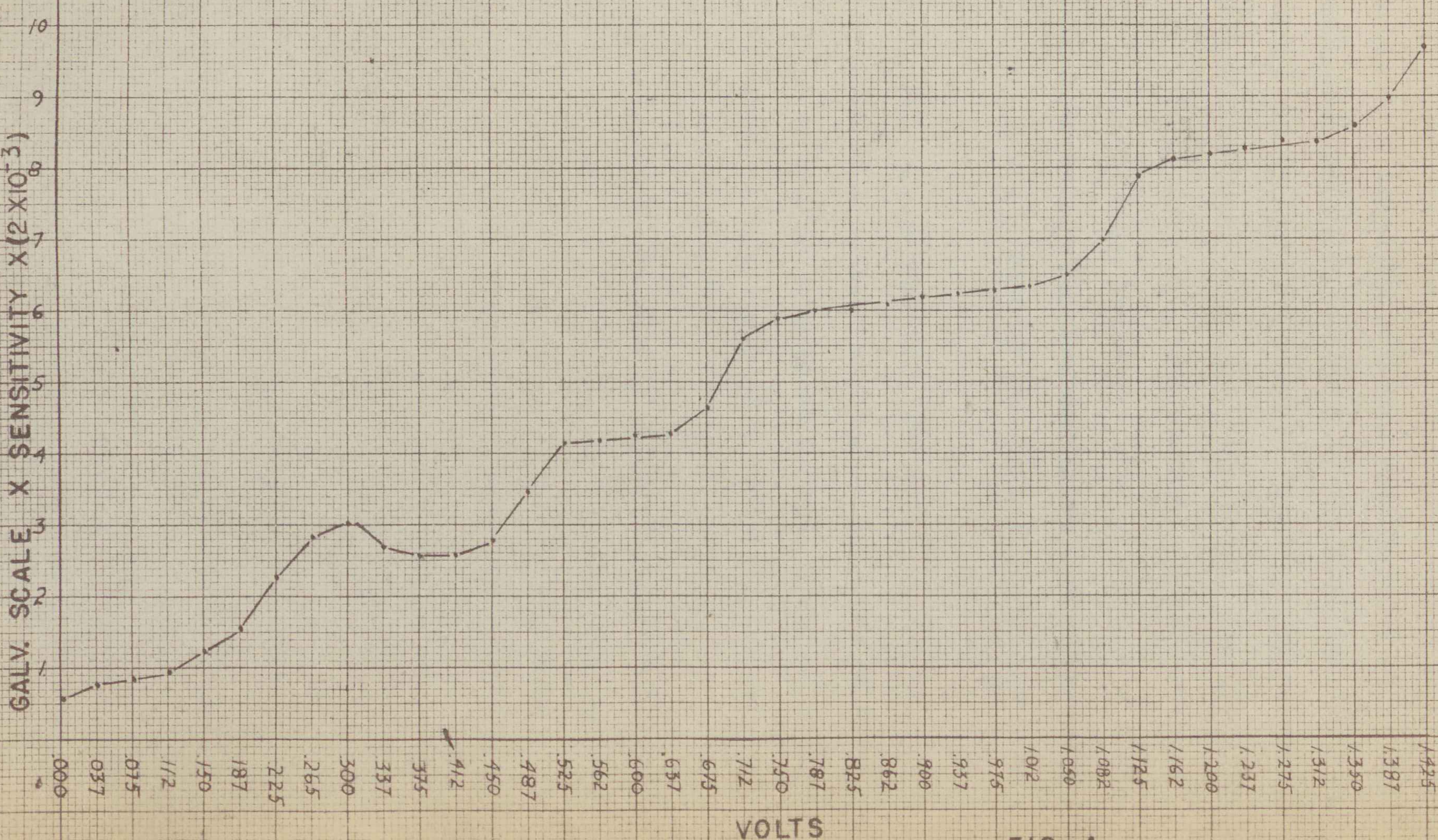


FIG. 4

The difference between the experimental values and the tables can be accounted for by the fact that the values given in the tables are with reference to a saturated calomel electrode at 25°. The saturated calomel electrode was not used in the experimental run.

The next step was to design a circuit in which the current-voltage curves would be reproduced on a cathode ray oscillograph. In a 60 cycle sine wave, (Fig. 5), the voltage starts at zero, rises to a maximum value, then decreases through zero to a minimum and rises back to zero. All voltage values above zero are considered negative, and all voltage values below zero are considered positive.

The voltage range needed for the substances in the test solution is from 0 to -1.5 volts. However, a majority of the inorganic ions will be reduced someplace between 0 and -3 volts. Thus, 0 to -3 volts was decided upon as a desirable voltage range to obtain.

By superimposing the AC voltage on a DC voltage, it is possible to eliminate all the positive voltage values. The proper value of the AC voltage may be determined from the equation:

$$\text{peak voltage} = \frac{\text{root mean square value (meter value)}}{.707}$$

Thus a peak AC voltage of 1.5 volts (1.06 volts root mean square value), superimposed on 1.5 volts DC, will give a maximum peak value of 3 volts (Fig.6).

Figure 7 shows a schematic diagram of the circuit used. The battery, B, supplies 22.5 volts DC, and the voltage drop across $R_{\frac{1}{2}}$ is equal to 15.9 volts root mean square value or to 22.5 volts peak value. The voltage divider, D, is used to pick off the required voltage to be applied across the dropping mercury electrode. An

A SINE WAVE

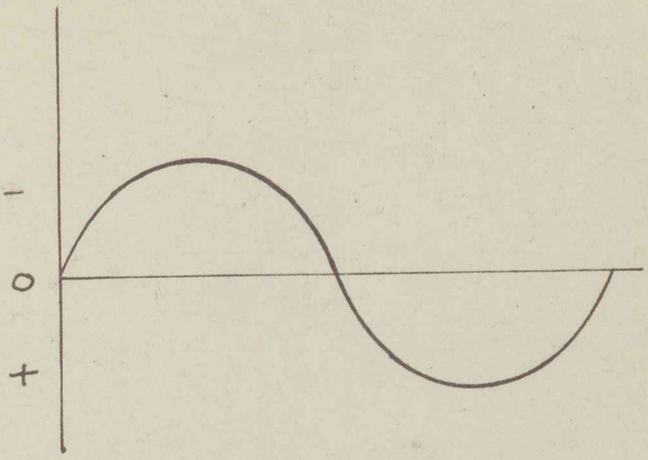


FIG. 5

SINE WAVE SUPERIMPOSED ON DC VOLTAGE

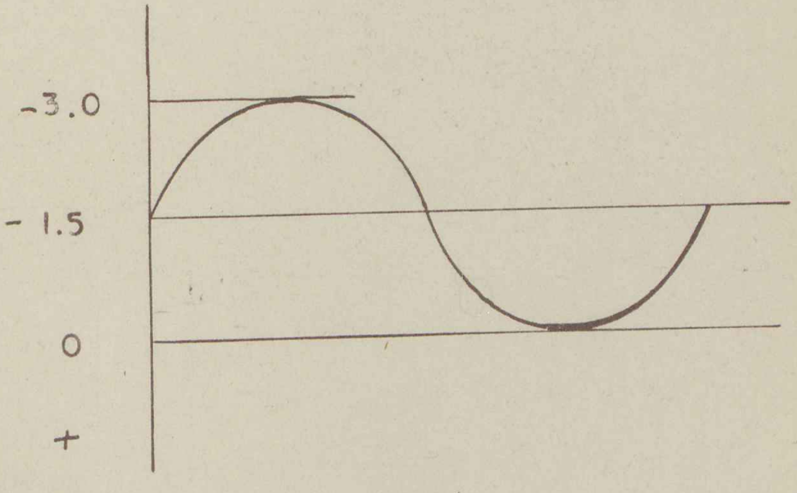


FIG. 6

SCHEMATIC CIRCUIT DIAGRAM

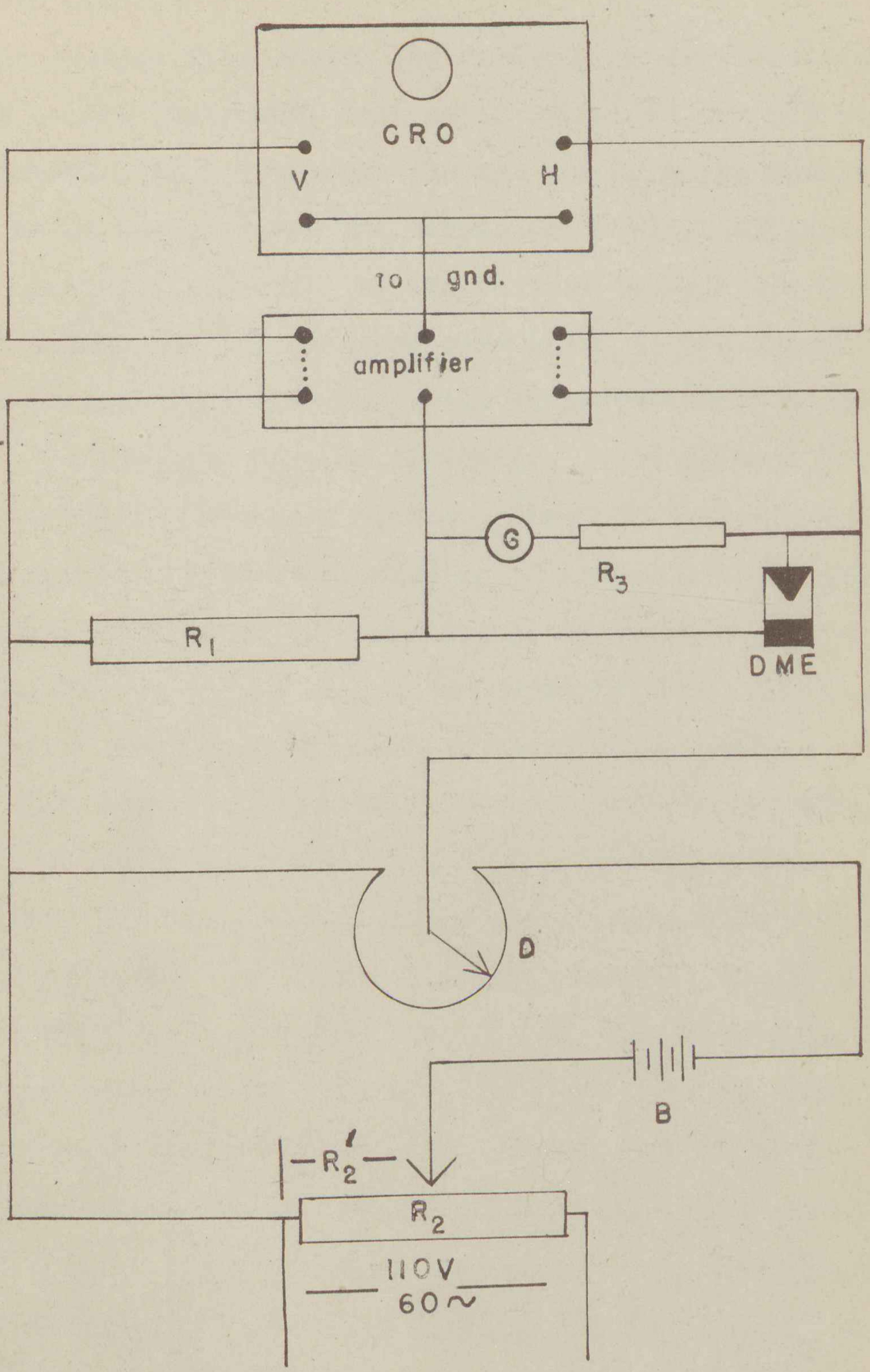


FIG. 7

amplifier stage was needed to supplement the amplification factor of the cathode ray oscillograph. Figure 8 is a diagram of the amplifier circuit.

The voltage drop across the dropping mercury electrode is impressed on the horizontal deflection plates of the cathode ray oscillograph. And the current through the dropping mercury electrode is impressed on the horizontal deflection plates of the cathode ray oscillograph. As the current through the dropping mercury electrode will have the same value as the current through R_1, the voltage drop across R_1 will be proportional to the current through the dropping mercury electrode. This voltage is applied to the vertical deflection plates. Accurate measurements of the voltage applied across the dropping mercury electrode can be made with only a high resistance voltmeter, at least 20,000 ohms per volt, as the current is only a few microamperes. A vacuum tube voltmeter is another instrument which could be used.

A high resistance voltmeter was constructed by using a sensitive galvanometer in series with a .5 megohm resistance. The sensitivity of the galvanometer was calculated to be .03 microamperes per millimeter. This will measure only the DC portion of the applied voltage. However, as the peak AC voltage is, at all times, twice the DC voltage, the value obtained need only be doubled to give the absolute value of the peak voltage.

Using a solution containing cobalt ions, the galvanometer deflection at the half-wave potential was 36 millimeters. Equating the given half-wave potential value to the deflection, times a constant, k, we have:

$$(36)\ (k) = .880$$

$$k = .033$$

SCHEMATIC AMPLIFIER DIAGRAM

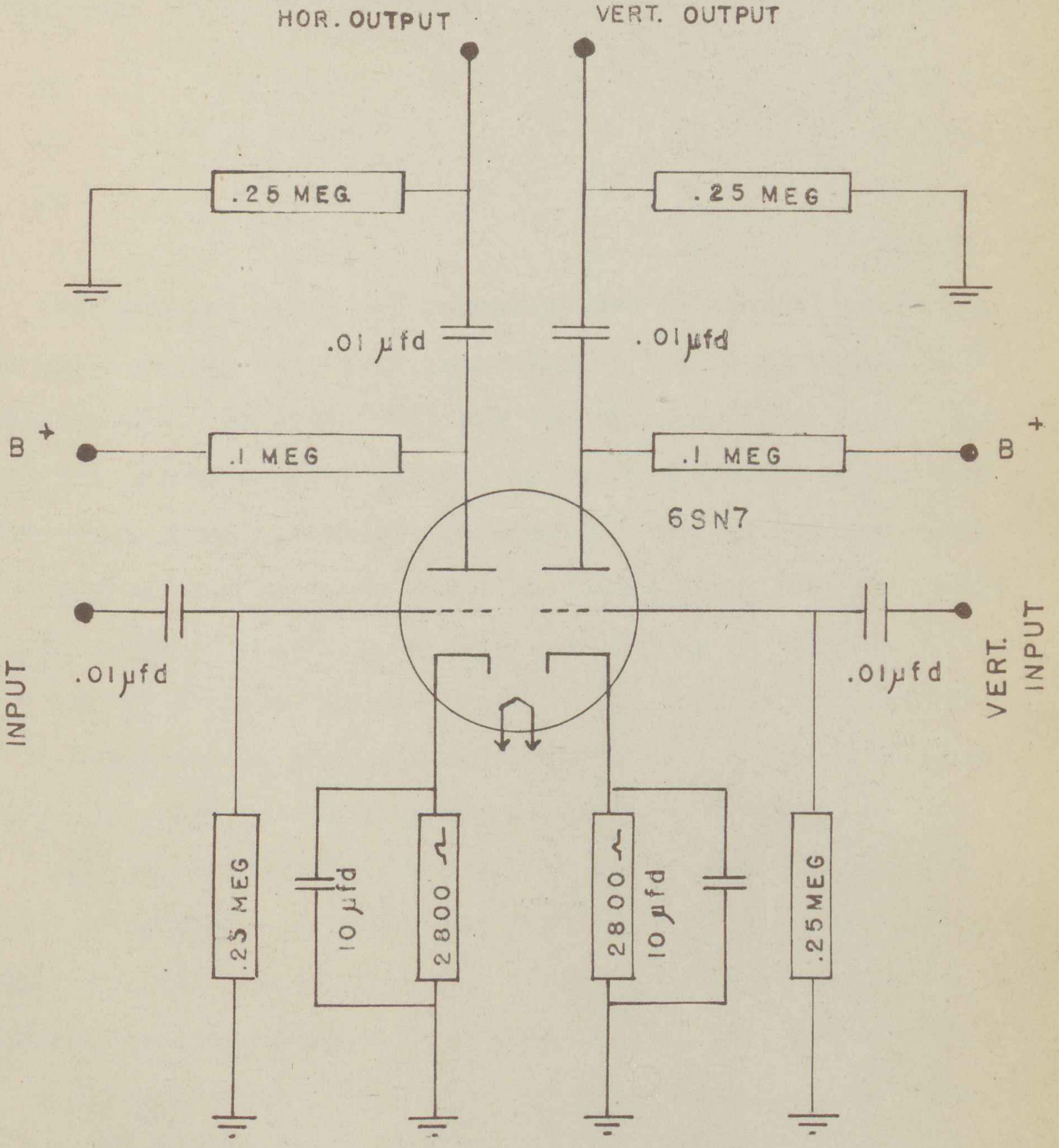


FIG. 8

The constant, k, includes the sensitivity of the galvanometer and the factor of two that compensates for the AC voltage not measured. The results obtained by this method are:

DEFLECTION (mm)	HALF-WAVE POTENTIAL (Calculated)	HALF-WAVE POTENTIAL (Tables)	SUBSTANCE
29	.95	.99	Zinc ion
18	.59	.59	Cadmium ion
14	.46	.39	Lead ion
1	.03	.18	Oxygen

The primary error was caused by the difficulty in fixing the point of the half-wave potential on the trace shown on the oscillograph. At lower voltages the trace becomes smaller, and thus the possible error would tend to be greater. The return trace also caused considerable trouble. As the voltage is decreased, the return trace tends to rotate about the top portion of the curve, from right to left, distorting the curve.

Figure 9 shows how the trace on the oscillograph appeared at a voltage above the half-wave potential for zinc. Fig. 10 shows the trace at the half-wave potential of zinc.

One way to eliminate the heavy return trace on the oscillograph is to use a 60 cycle saw tooth wave in place of the sine wave. The saw tooth wave rises linearly to a maximum valve then almost instantly drops to a minimum value. The sudden drop is of such short duration that the return trace is eliminated.

A saw tooth oscillator and a single stage resistance coupled amplifier were constructed to provide the voltage supply (fig. 11). The circuit used (fig. 12) is essentially the same as used with the sine wave. The input voltage is taken across a half megohm resistance. A one megohm potentiometer serves as a voltage divider, used to pick off the required voltage needed.

CRO TRACES

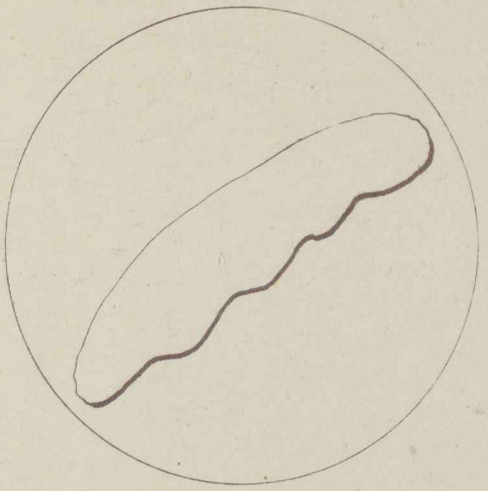


FIG. 9

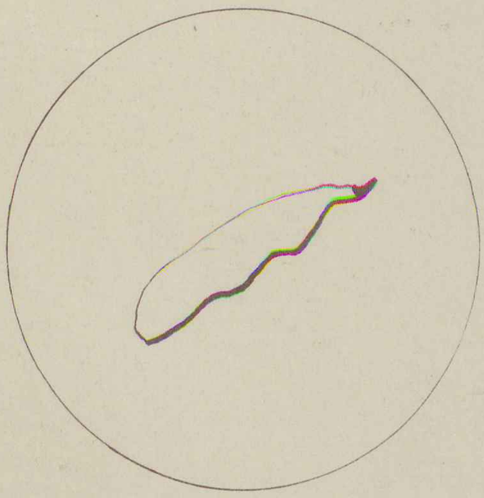


FIG. 10

SAW TOOTH GENERATOR

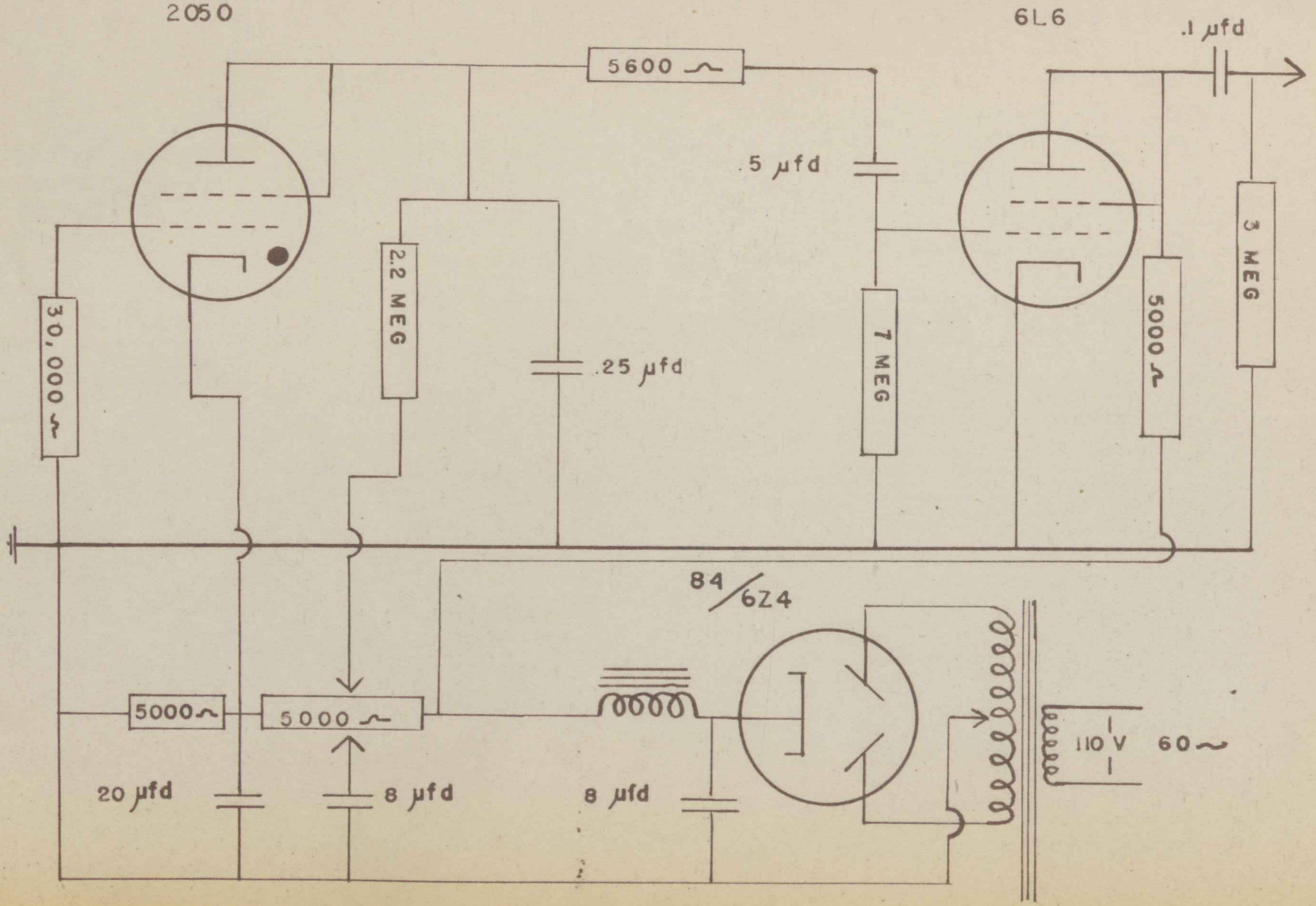


FIG. 11

SCHEMATIC CIRCUIT DIAGRAM

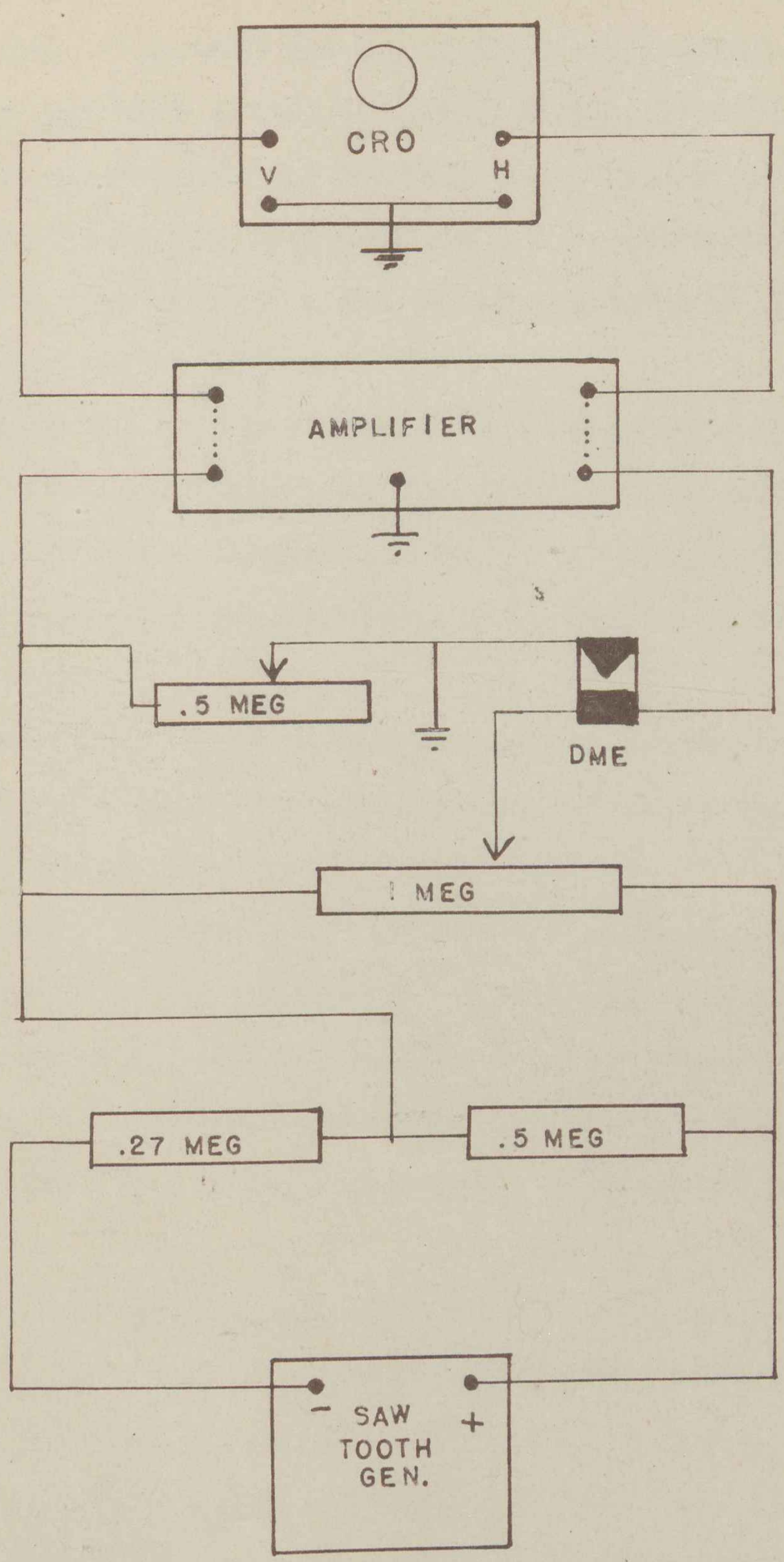


FIG. 12

The voltage drop across the dropping mercury electrode is passed through a single resistance-coupled amplifier and impressed on the horizontal deflection plates of the oscillograph.

The voltage drop across the half-megohm potentiometer is proportionial to the current through the dropping mercury electrode. This voltage is impressed on the vertical deflection plates of the oscillograph after passing through a single stage resistance-coupled amplifier.

The amplifier used was constructed from two 6L6 tubes; one for the vertical amplification, one for the horizontal. Figure 13 is a schematic diagram for one of the tubes. A 6SN7 tube was used at first but the saw tooth wave was too distorted to be of any value.

A satisfactory curve with a negligible return trace was obtained on the cathode ray oscillograph by using the circuit given in figure 12.

The maximum current drawn from the saw tooth generator is of the magnitude of milliamperes. In the 6L6 tube (fig. 11) the current flowing between ground and the cathode was only 18 milliamps. This means that any instrument used to measure a voltage drop across any part of the circuit must draw practically no current.

A slide back vacuum tube voltmeter is an ideal device to be used here. This instrument measures the peak value of the wave and draws a negligible amount of current. As no such instrument was readily available, and time did not permit its construction, it was not possible to measure the half-wave potentials of the ions in the test solution. If the vacuum tube voltmeter had

R-C AMPLIFIER

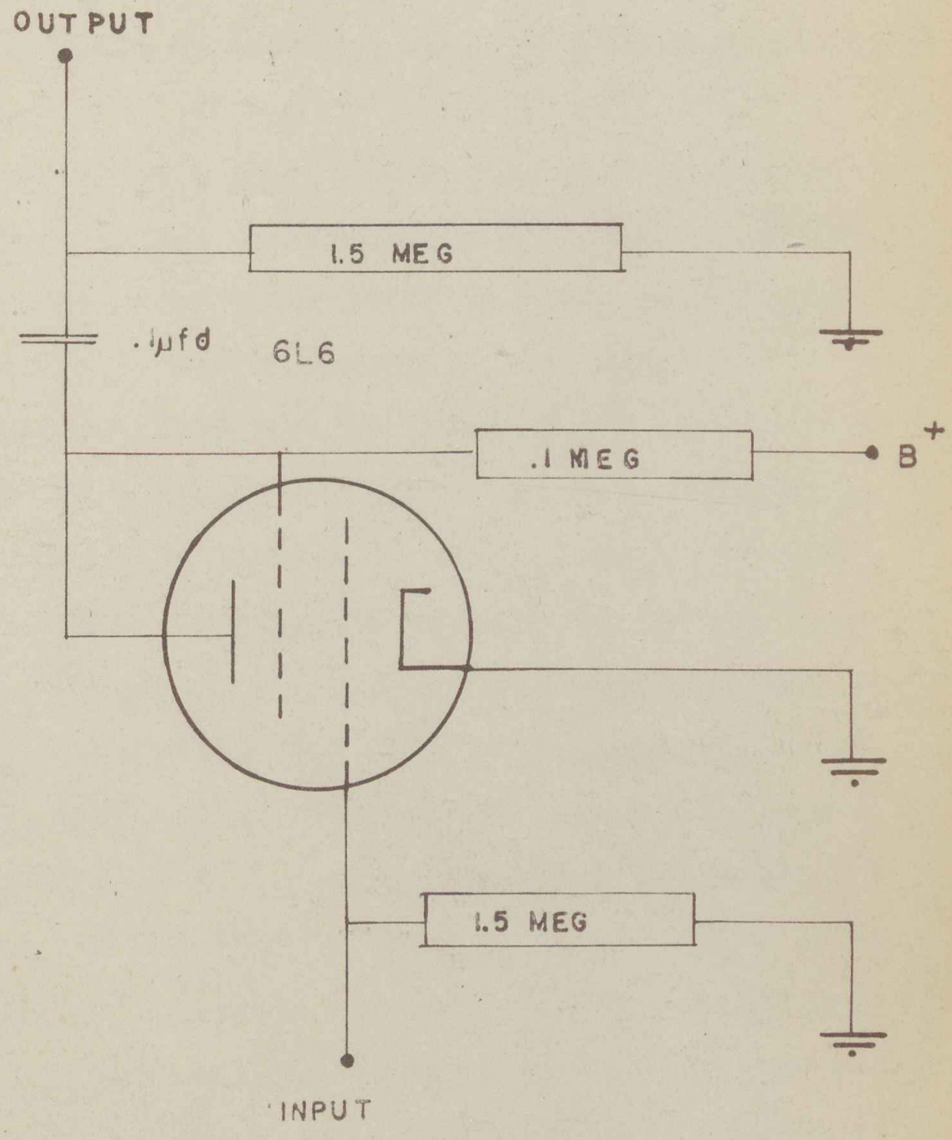


FIG. 13

been available, the half-wave potentials would be measured by reading the voltage drop across the dropping mercury electrode when the top of the trace corresponded to point c of figure two.

SUMMARY

This experiment shows that the cathode ray oscillograph can be used in polarographic analysis at least to give fair qualtitative results.

The 60 cycle sine wave proved to be the most convenient voltage to use but the heavy return trace makes a good reading difficult. The 60 cycle saw tooth wave eliminated the heavy return trace but is not as easy to obtain nor to measure as the sine wave.

A high resistance voltmeter (at least 20,000 ohms per volt) is needed to read the voltage drop across the dropping mercury electrode if the sine wave voltage is used. However, a vacuum tube voltmeter is needed to read the voltage out-put of a saw tooth generator, and from this value to compute the proper D.C. voltage to put in the circuit (fig. 12) between the half-megohm resistance and the one-megohm potentiometer. Once the proper D.C. voltage is in the circuit a high resistance voltmeter can then be used across the dropping mercury electrode. The voltmeter will measure only the D.C. component of the voltage drop but the ratio of the D.C. voltage to the peak A.C. voltage will be constant. From the reading of the voltmeter the half-wave potential of a reducible substance may be determined.

SUGGESTIONS FOR FUTURE WORK

1. Investigate the quantitative possibilities of using a differential circuit that would directly indicate the concentration of the ion at its half-wave potential.

Figure 14 is one possible circuit. When there is no change in the current, it will flow through the resistance. When the current changes due to the decomposition of an ion, the change should cause a current to pass through the capacitor. This signal could then be amplified and impressed on the vertical deflection plates of the oscillograph.

Figure 15 shows what the trace might look like for three different ions, each at a different concentration.

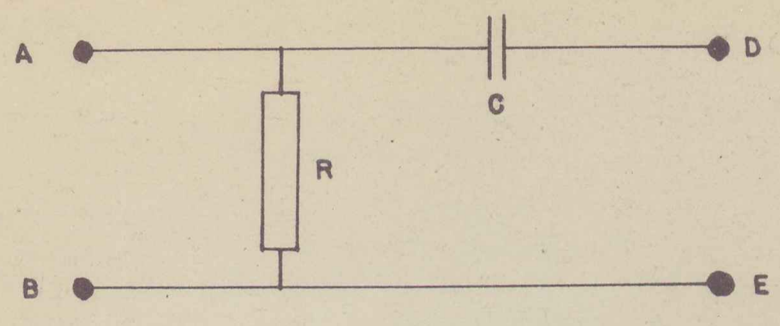
2. As each drop of mercury falls, the trace flickers momentarily. This can be eliminated by synchronizing the drop time to the frequency (1).

Another method worth investigating would be the use of a commutator or an electrical equivalent with a high frequency voltage and a long persistance oscillograph screen.

Figure 16 shows that a high frequency will cause several traces while the mercury drop forms, (A to B). When the drop breaks and falls, random traces are observed, (B to C). As the new drop forms, (C to D), the traces reappear.

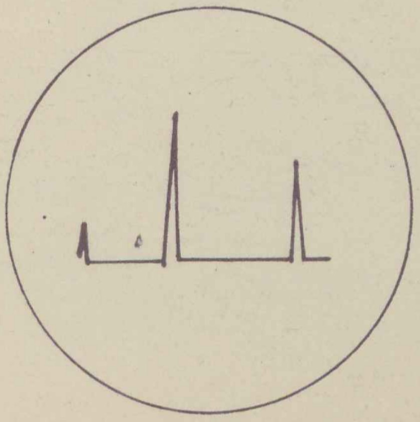
The commutator could be adjusted so as to prevent the portion of figure 16 between B and C from being reproduced on the oscillograph.

The persistancy of the screen then could keep the last trace, L, visible until the first trace, F, from a new drop is reproduced, and in this way a steady trace should be observed on the oscillograph.



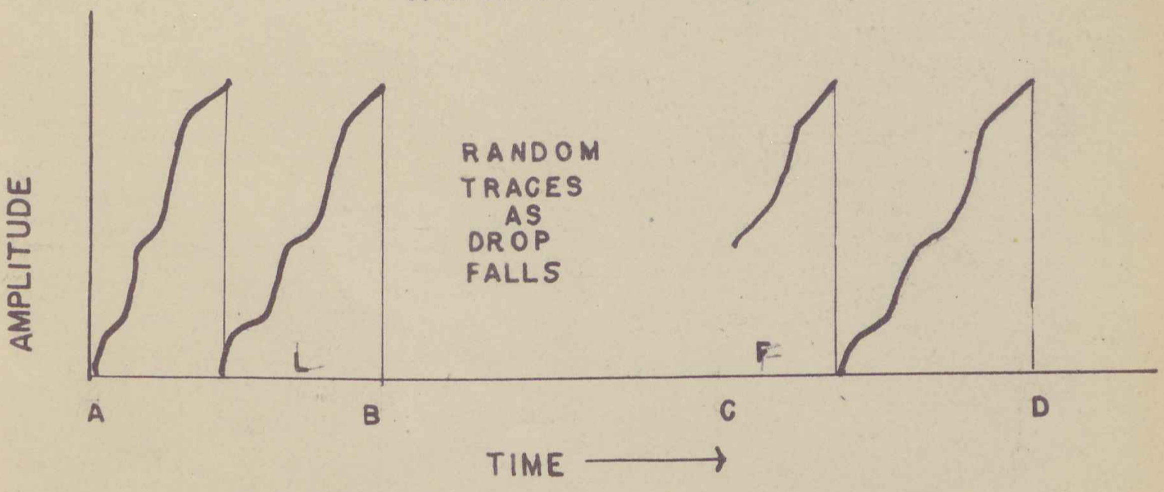
SCHEMATIC CIRCUIT DIAGRAM

FIG. 14



C.R.O. TRACE

FIG. 15



AMPLITUDE vs TIME

FIG. 16

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