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# Polarographic Studies of the Dicyanoaurate and Tetracyanoaurate Complexes

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# POLAROGRAPHIC STUDIES OF THE DICYANOAURATE AND TETRACYANOAURATE COMPLEXES



by

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# POLAROGRAPHIC STUDIES OF THE DICYANOAURATE AND TETRACYANOAURATE COMPLEXES

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science with a Major in Chemistry.

By Peter Neddermeyer

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# TABLE OF CONTENTS

# LIST OF PLATES

# LIST OF TABLES

ABSTRACT

A polarographic study of the dicyanoaurate and the tetracyanoaurate complexes has been made . Distinct current-voltage curves were obtained for both complexes with and without supporting electrolyte . The half-wave potentials were found to be -.2 and -1.3 volts for the $Au(CN)_4^-$ and the $Au(CN)_2^-$ waves ,respectively . The dicyanoaurate wave was studied as a function of cyanide and hydroxide concentrations and the shape and position of the wave was found to vary therewith. The easily and accurately determinable diffusion currents were found to be directly proportional to the complex ion concentrations . Thus , polarography has been shown to be a good quantitative method of analysis for the two gold-cyanide complexes.

# CHAPTER I

## INTRODUCTION

Until recently, no fairly rapid, relatively simple but accurate quantitative method of analysis for the two gold cyanide complex ions had been perfected. A method meeting these requirements has been urgently sought in order that an electron transfer experiment[1] between the dicyanoaurate and tetracyanoaurate ions may be conducted. One such analytical method which has been investigated is polarography.

Generally, a polarographic analysis requires only a small volume of solution, yields good results and is easily and rapidly conducted. The data obtained is in the form of a current-voltage curve for which the current is plotted as a function of the applied potential. The potential at which a distinct current change occurs is known as half-wave potential and is indicative of the electroreducible specie present. The accompanying current change, known as the diffusion current, is usually proportional to the concentration of the specie. Also, more than one electroreducible specie may be analyzed in the presence of the other at the same time. Because of these reasons, polarography was chosen as the analytical method to be investigated.

The dicyanoaurate and tetracyanoaurate complexes had previously been studied polarographically by John Herman[2] at the University of Prague in Czechoslovakia. He reported that distinct current-voltage curves are obtainable for each of the two gold-cyanide complexes and that the diffusion currents are apparently proportional to the complex concentrations. Unfortunately he does not report the conditions or the concentration ranges for which this analytical method is valid. It was therefore decided to try to reproduce the current-voltage curves and to also investigate the effects upon these curves of changing such parameters as cyanide ion concentration and pH.

# CHAPTER II

## GENERAL EXPERIMENTAL PROCEDURES

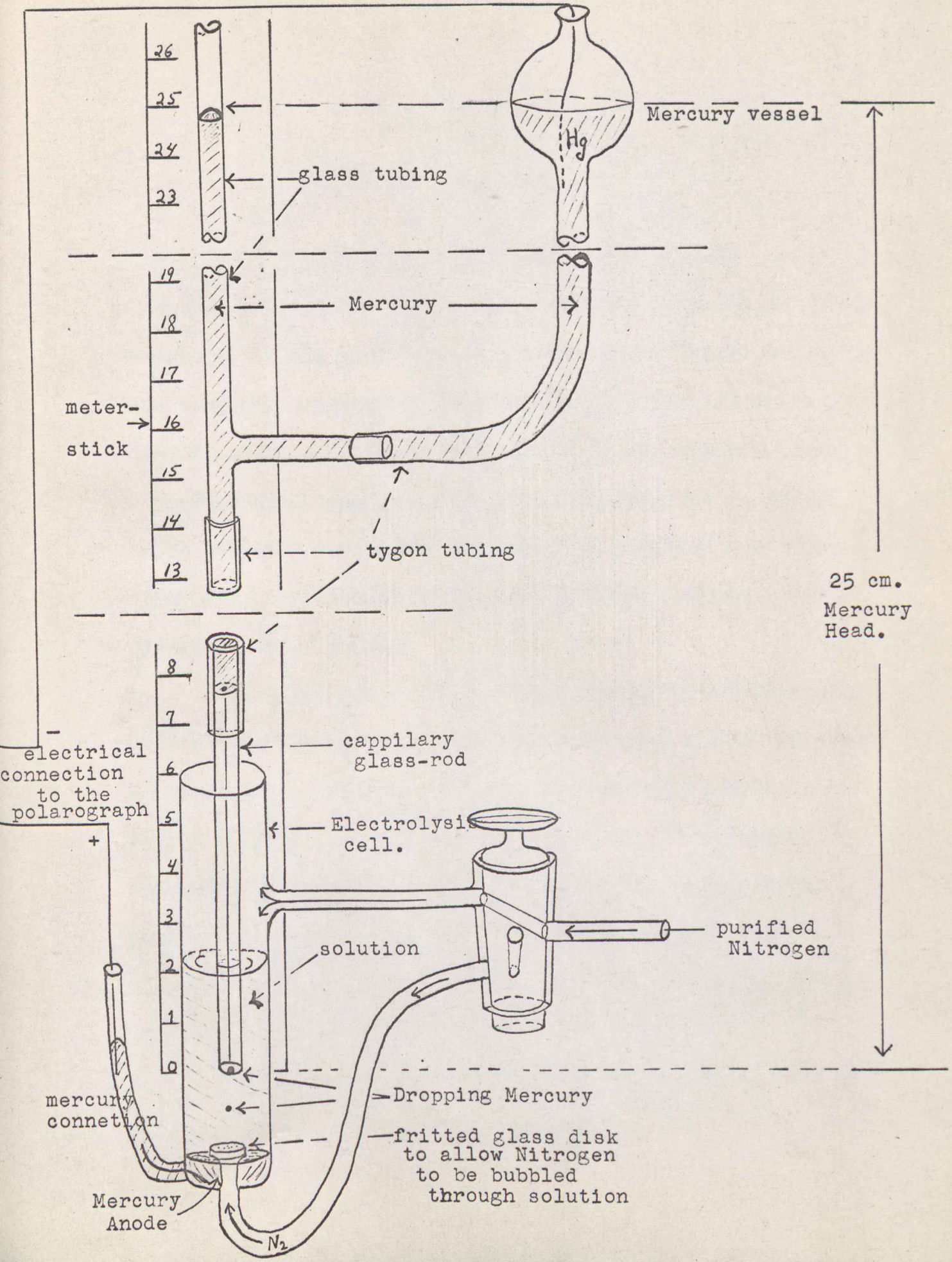
The experimental apparatus (Plate #1) consisted of a Seargent automatic recording polarograph, an electrode vessel and a dropping mercury electrode. The solution to be tested, along with clean mercury were placed into the electrode vessel, the dropping mercury electrode was placed just into the top of the solution and then all electrical connections were completed after which the polarograph automatically produced the desired current-voltage curve.

The electrode vessel had been especially constructed so that pure nitrogen which swept all oxygen out of the solution, could first be bubbled through the solution and then made to pass over the solution while the polarogram was being taken. The dropping mercury electrode consisted of a fine bore capillary glass rod from which a small mercury sphere drops every few seconds. The mercury head was kept at 25. cm. at all times and for all polarograms.

The polarograph performed almost so perfectly throughout the year that polarograms of the same solutions taken at various time intervals were almost completely superimposable.

Plate - 1

Apparatus



# CHAPTER III

## THE DICYANOAURATE COMPLEX

The dicyanoaurate complex was first studied rather than the tetracyanoaurate complex because it is commercially available as the potassium salt whereas the latter has to be prepared from chlorauric acid ($H\ AuCl_4$). The potassium dicyanoaurate salt ($K\ Au\ (CN)_2 \cdot 2\ H_2O$) was quantitatively dissolved to produce one hundred milliliters of a .100 M stock solution. Aliquots of this gold solution were then quantitatively diluted to produce solutions suitable for polarographic analysis.

At first, great emphasis was placed on obtaining the current-voltage curve for the dicyanoaurate complex described by Herman. In order to keep the gold cyanide solutions as simple as possible, potassium cyanide was chosen as the supporting electrolyte since the gold salt contained both potassium and cyanide ions. The current-voltage curve obtained is shown on Plate #2a. The half-wave potential is -1.3 volts vs. the mercury pool.

Next of interest was, of course, whether the diffusion current is directly proportional to the gold cyanide

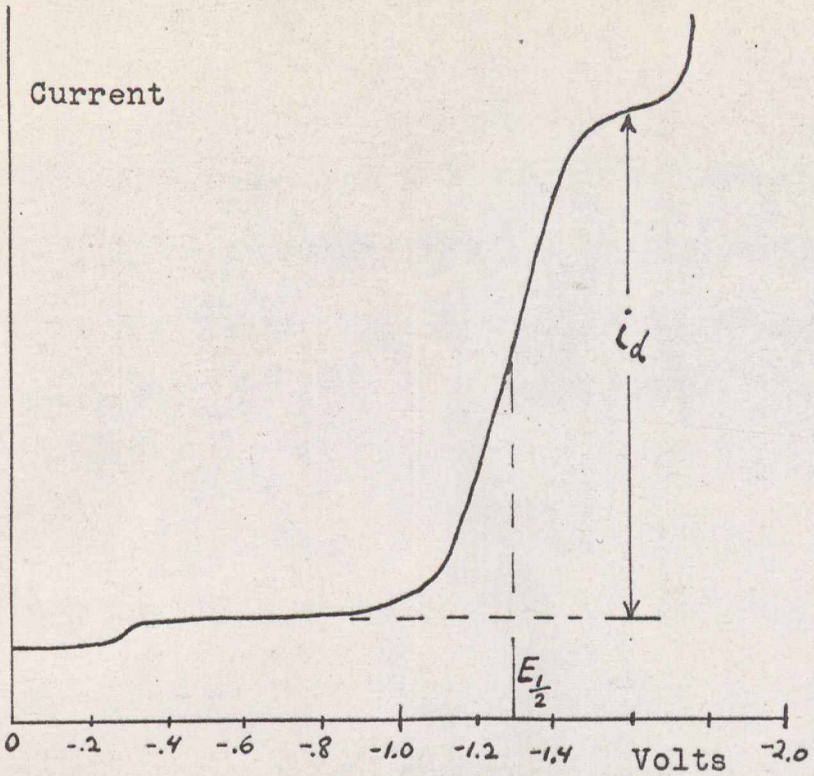



Plate 2-a

A typical $Au(CN)_2^-$

Current-Voltage Curve

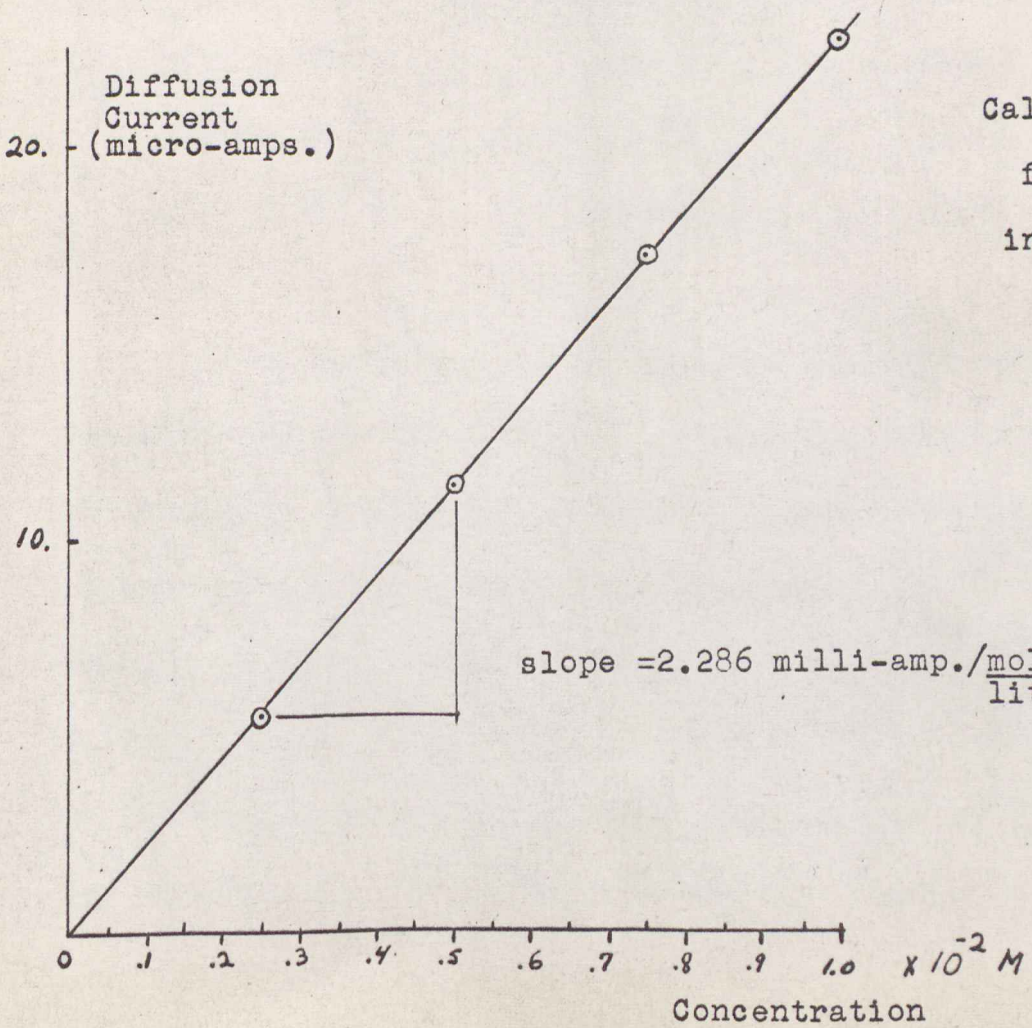



Plate 2-b

Calibration Line

for $Au(CN)_2^-$

in .010M KCN

concentration. The data for a set of solutions in which the gold cyanide concentration is varied while all other factors are being kept constant is given below and plotted on Plate 2b.

TABLE I

Data

| $[Au(CN)_2^-]$ | $[\overline{KCN}]$ | Diffusion Current |
|---|---|---|
| $.250 \times 10^{-2}$ M | .010 M | 5.71 microamp. |
| $.500 \times 10^{-2}$ M | .010 M | 11.43 " |
| $.750 \times 10^{-2}$ M | .010 M | 17.14 " |
| $1.00 \times 10^{-2}$ M | .010 M | 22.86 " |

It is necessary to explain how the diffusion currents are obtained and the possible difficulties one may encounter. The residual current and limiting current never become exactly parallel to the horizontal (voltage) axis and thus one can obtain different diffusion currents for the same current-voltage curve by simply taking the current difference at two different voltage values. If the only variable in a set of solutions is the dicyanoaurate concentration, then

very good diffusion current values are obtained by taking the current differences at two specific voltage values for all sets of solution. It matters not which two voltage values are chosen as long as these two values are used throughout.

As the data and accompanying graph indicate, it is quite possible to use the polarograph as a quantitative tool for the analysis of the dicyanoaurate ion to a concentration of at least $1.0 \times 10^{-2}$ molar. This statement is true when the supporting electrolyte is a .010 M KCN solution. Next, the effects of changing the $K\ AU(CN)_2^-$ concentration is investigated. In order to make sure that all possible extremes of variation of the cyanide concentration be investigated, all one need do is obtain polarograms of gold cyanide solutions which contain no supporting electrolyte, as concentrated a cyanide solution as desirable and several others with intermediate concentrations. To say the least, the final result is startling.

Anyone familiar with polarography knows that a supporting electrolyte is needed in order that reproducible results be obtained; in fact, most times without supporting electrolyte, significant polarograms cannot be obtained. It was, however, considered worthwhile to attempt to obtain a

polarogram without any supporting electrolyte. The startling result was a current-voltage curve almost exactly like that obtained with a .01 M KCN supporting electrolyte solution, and which also gives a very good calibration line of diffusion current vs. concentration. Below is given the data obtained for the dicyanoaurate without any supporting electrolyte.

TABLE II

| $[Au(CN)_2^-]$ | Diffusion Current | $E_{1/2}$ | Ionic Strength |
|---|---|---|---|
| .100 M | 52.11 μ.a. | -1.18 | .100 |
| .050 M | 25.95 μ.a. | -1.27 | .050 |
| .025 M | 12.08 μ.a. | -1.35 | .025 |

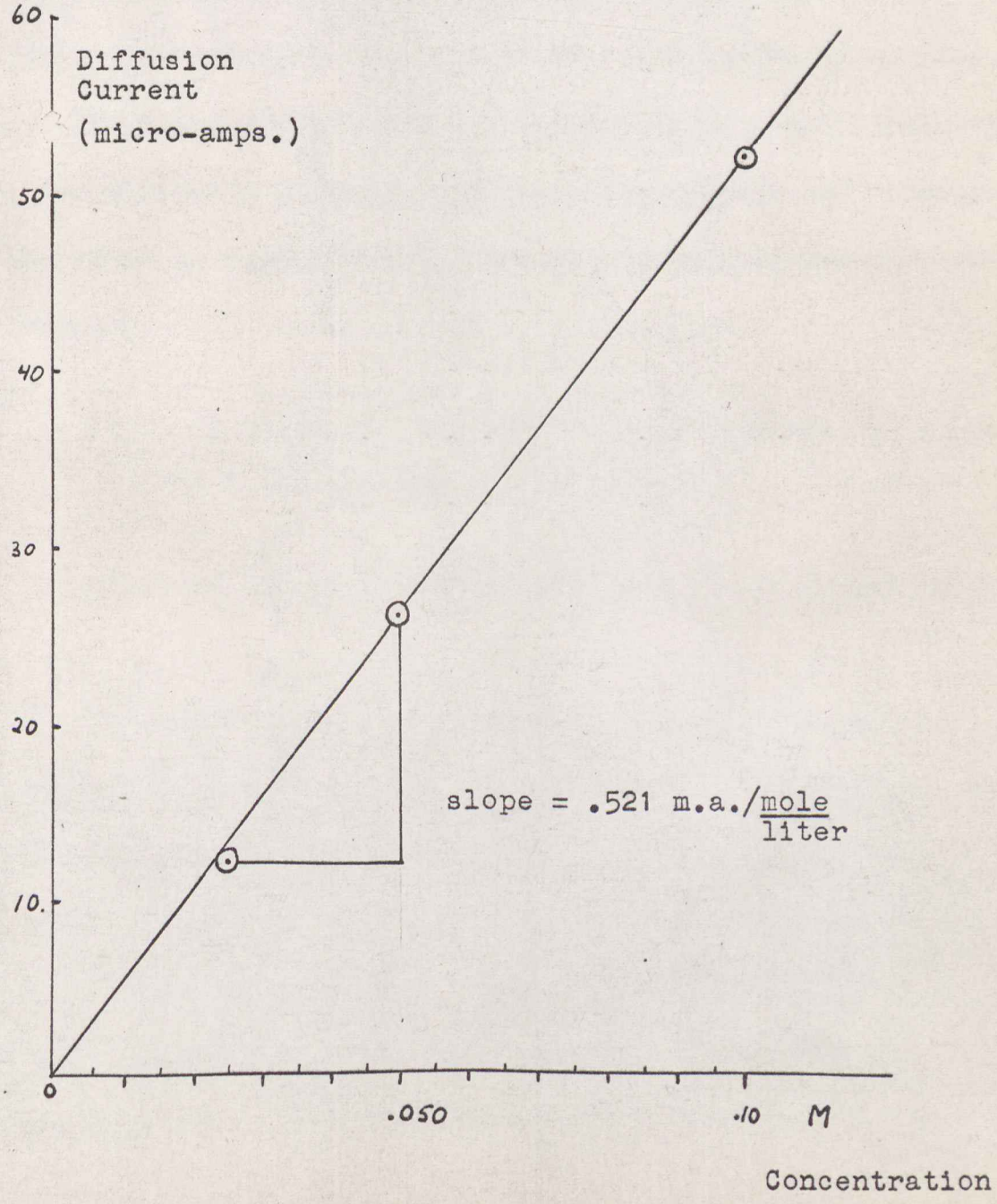
See Plate 3.

Thus, here is illustrated that a very good calibration line is obtained which makes it possible to analyze quantitatively a dicyanoaurate solution which is less concentrated than .10 molar. It does not seem unlikely that even more concentrated solutions will fit the calibration line. A more concentrated solution was not available and thus no current-voltage curve could be obtained.

It is of interest to notice that as the dicyanoaurate

Plate 3

Calibration Line for $Au(CN)_2^-$
without supporting electrolyte.



concentration increased, the half-wave potential moved to more positive values. This phenomena is not unexpected since the half-wave potential is a function of the ionic strength of a solution. It will later be noted that with increasing cyanide concentration even more pronounced shifts will be produced for the half-wave potential. A look at the slopes of the calibration curves from Plate #2b and #3 reveals that smaller diffusion currents will result per mole. of dicyanoaurate when no supporting electrolyte is present as when it is present.

Slope of Plate #2b calibration line = 2.286 $\frac{\text{milliamp.}}{\text{mole.}}$
.010 M KCN supporting electrolyte:

Slope of Plate #3 calibration line = .521 $\frac{\text{milliamp.}}{\text{mole.}}$

This shows that the supporting electrolyte carries approximately 76% of the current, while the rest is that due to the reduction of the gold salt.

The question may arise as to whether greater accuracy is obtained with or without the supporting electrolyte in the quantitative analysis for dicyanoaurate. At first glance it would appear that with supporting electrolyte one obtains

greater accuracy since the slope in this case is about five times greater than that for no supporting electrolyte. Thus a given uncertainty in the diffusion current would produce a smaller uncertainty in the concentration for the graph with the greater slope (the calibration curve obtained with supporting electrolyte). If the process by which one obtains the diffusion current is kept in mind, it soon becomes evident that both calibration lines produce the same uncertainty in the concentrations. The diffusion current is found by taking the difference in the limiting current and residual current. This difference is expressed in millimeters (a distance measurement) and then multiplied by a given factor which converts millimeters to microamps. Since the width of the graph paper is constant and the sensitivity is adjusted such that the increase in current, S, covers much of that width, it is apparent that if the uncertainty in the distance measurement for two different graphs is a particular value, $\pm \Delta S$, then the percent error will be $\frac{100 \Delta S}{S}$ which is relatively constant for all graphs since they are expanded to cover much of the paper width. Thus, it is seen that the same relative per cent of error is apparently present in all concentration determinations.

So far it has been determined that although the presence of excess cyanide ion as supporting electrolyte does not affect the shape of the current-voltage curve of dicyanoaurate ion, its presence does affect the slope of the calibration curve of diffusion current vs. concentration when compared to solutions containing no supporting electrolyte. Also, it was seen that in the case of no excess cyanide the half-wave potential of the dicyanoaurate wave was moved to more positive potentials with increasing $Au(CN)_2^-$ concentration. Next, the effect upon the current-voltage curves of changing the cyanide concentration was investigated. The resultant data is given below and the current-voltage curves are shown on Plate #4. For all these curves, the $Au(CN)_2^-$ concentration was kept $5.0 \times 10^{-3}$ M.

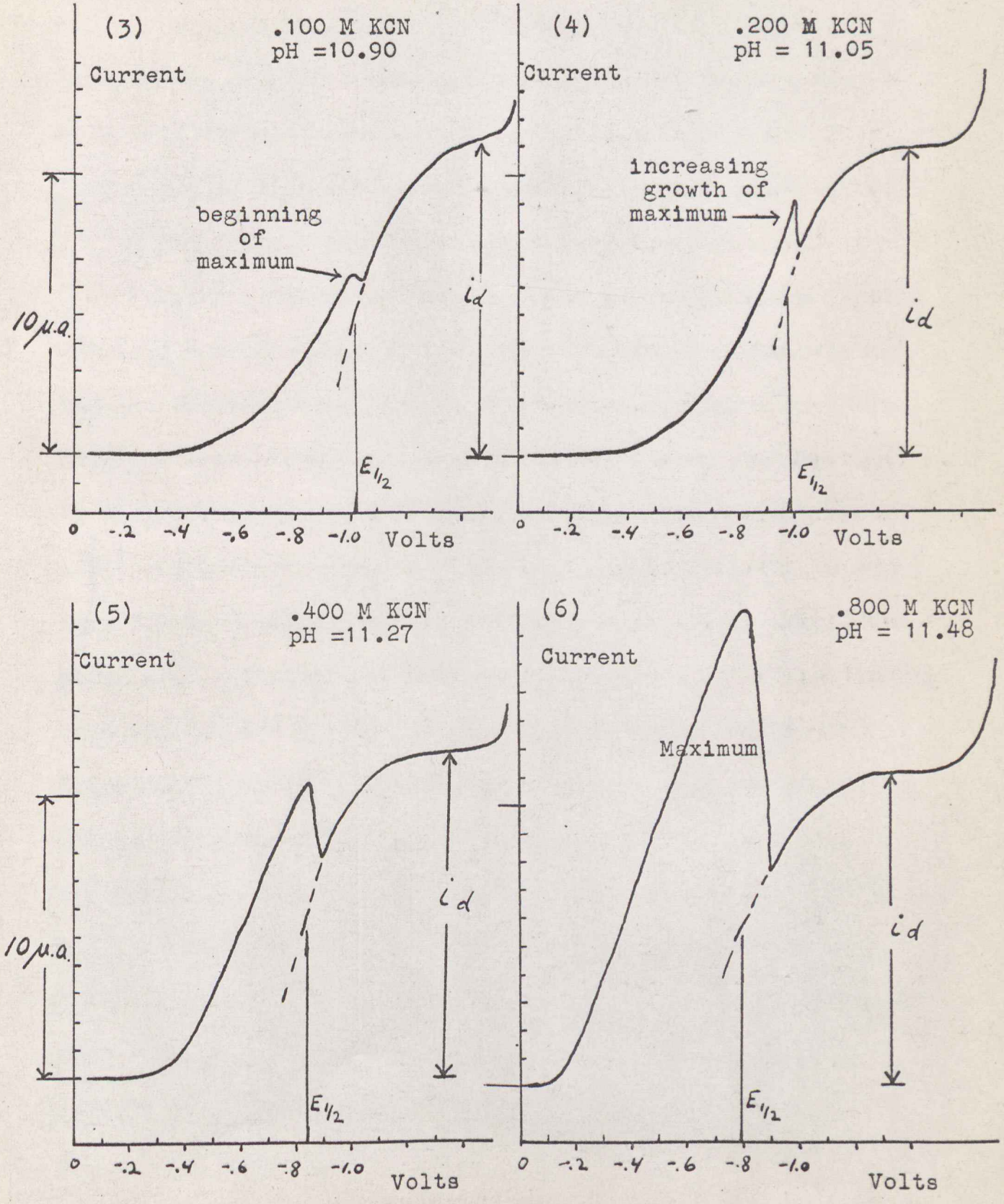
TABLE III

$[Au(CN)_2^-] = 5.00 \times 10^{-3}$ M

| Solution # | $[CN^-]$ | pH | id | $E_{1/2}$ | Ionic Strength |
|---|---|---|---|---|---|
| 1 | .010 M | 10.41 | 11.7 ± .2μ.a. | -1.28 | .0150 |
| 2 | .050 M | 10.76 | 11.1 | -1.08 | .0550 |
| 3 | .100 M | 10.90 | 11.2 | -1.02 | .1050 |
| 4 | .200 M | 11.05 | 11.0 | - .98 | .2050 |
| 5 | .400 M | 11.27 | 11.5 | - .85 | .4050 |
| 6 | .800 M | 11.48 | 11.0 | - .80 | .8050 |
| | | | avg. = 11.3 ± .3 | | |

Plate 4

Current-Voltage Curves of $Au(CN)_2^-$ with variable KCN and constant $Au(CN)_2^-$ concentrations.



Before discussing the data, it would be of interest to look at the current-voltage curves (Plate #4) obtained for each cyanide concentration. These current-voltage curves are reproduced as faithfully as is possible in order that the reader may plainly see the various effects.

For all of these cases, the dicyanoaurate concentration was kept constant at $5.0 \times 10^{-3}$ M, and only the potassium cyanide concentration was varied. The numbers on each of the graphs correspond to the solution number listed in Table III. It is observed that when the cyanide concentration reaches .10 M instead of obtaining the usual smooth half wave, a small kink starts to appear about half way up the curve. This kink grows with increasing cyanide concentration until a real strong maximum is obtained for the .80 M KCN solution. There is no apparent correlation between the height of this maxima and the KCN concentration, and at first the reason for this maximum was unknown. It is to be noted that once the maximum had been reached, the automatic recording pen went back to tracing out the dicyanoaurate curve as if the maximum had not been present. This latter segment of the dicyanoaurate curve has been extrapolated in order that the half-wave potentials of the waves can be ascertained.

These maxima may be the result of the complete destruction of a loose gold cyanide complex formed at higher cyanide concentrations or it may be the result of the reduction of a hybrid gold-hydroxy-cyanide complex which might conceivably be formed at these higher pH values. After all, the pH increases substantially with increasing cyanide concentration through hydrolysis. Because there was no evident explanation for these maxima, other than these hypothetical reasons, it was decided to determine whether the maxima were a function of the increased cyanide concentration or the increased hydroxide concentration. If it is doubted that an increase in cyanide concentration produces any substantial increase in hydroxide ion concentration, then it should be noted from solutions 1 and 2 in Table III that a tenfold increase in the cyanide concentration produces a .49 pH unit increase; i.e., a $10^{.49}$ or a 3.1 fold increase in hydroxide concentration. Thus, the hydroxide concentration increase cannot be neglected.

It seems logical that if one takes a dicyanoaurate solution which is .01 M with respect to KCN and which formerly gave no indication of a maximum and now makes it alkaline, its polarogram should reveal whether the increased hydroxide

concentration causes the maxima. A solution of the following constitution: $5.0 \times 10^{-3}$ M $Au(CN)_2^-$, .01 M KCN, pH = 10.41 was brought up to a pH of 11.55 (a 14-fold increase in hydroxide concentration) and its polarogram taken over a period of weeks. No apparent change in the curves was noticed. Since this increase in pH may not have been drastic enough, the pH was raised to 12.50; i.e., (a 123-fold increase in $[OH^-]$) and still no maximum was observed. Thus, the maxima must be the result of the increased KCN concentration.

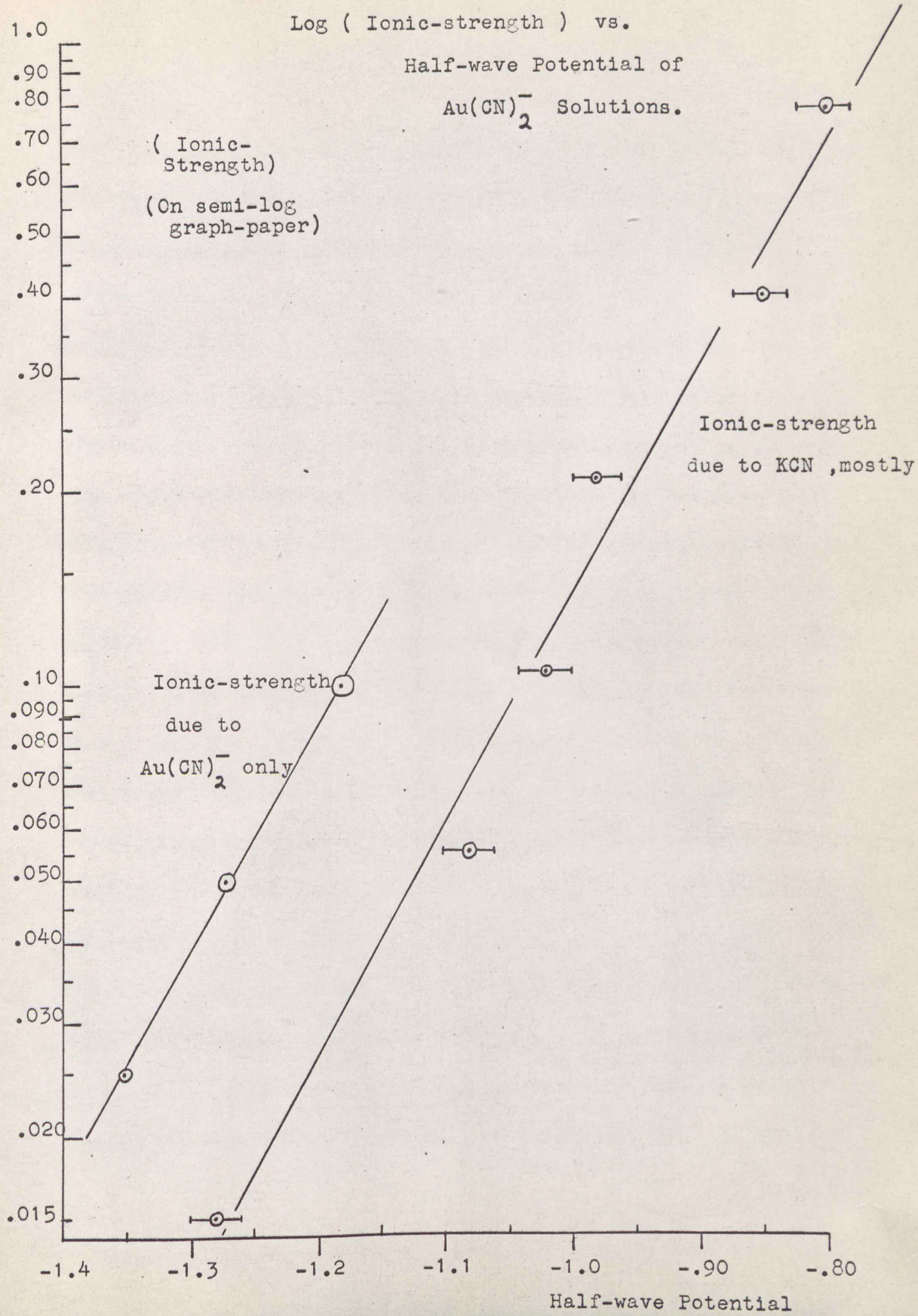
The maxima are, however, not due to a loose gold-cyanide complex which might be formed when the cyanide concentration is increased. The maxima are due to the increasing ionic strength which accompanies the increase in KCN concentration. A study of the literature[3] reveals that at higher ionic strengths, the dropping mercury electrode momentarily depolarizes. "The potential of the dropping electrode remains constant from the beginning of the discharge until the maximum is reached, and that no concentration polarization occurs. Immediately after the maximum is passed, and the current decreases suddenly, the dropping electrode becomes almost completely concentration polarized." Thus, the KCN

does not act specifically upon the dicyanoaurate wave, but it produces an ionic strength which is a determining factor for the maxima formation.

Data from Table III, which is plotted on Plate #5, reveals that the ionic strength also has an effect upon the half-wave potentials; i.e., an increase in ionic strength shifts the half-wave potentials to more positive values. Plate #5 has on it two lines. The long line is obtained from current voltage curves where the ionic strength was varied by changing the KCN concentration (the $Au(CN)_2^-$ was kept $5.0 \times 10^{-3}$ M) whereas for the short line, the only contribution to the ionic strength is due to the $Au(CN)_2^-$. Although the two lines are not superimposed, it is quite significant that the two slopes are the same. From these two slopes it can be inferred that a tenfold increase in ionic strength will shift the half-wave potential by .29 volts toward more positive potentials.

In this discussion of variations in the whole half-wave structure and ionic strength, etc., one important factor has not been mentioned, and that is the diffusion current which determines the applicability of polarography to the analysis of

Plate 5


Log ( Ionic-strength ) vs.
Half-wave Potential of
$Au(CN)_2^-$ Solutions.
( Ionic-
Strength)
(On semi-log
graph-paper)
1.0
.90
.80
.70
.60
.50
.40
.30
.20
.10
.090
.080
.070
.060
.050
.040
.030
.020
.015
Ionic-strength
due to KCN , mostly
Ionic-strength
due to
$Au(CN)_2^-$ only
-1.4
-1.3
-1.2
-1.1
-1.0
-.90
-.80
Half-wave Potential

dicyanoaurate. While the ionic strength and the whole wave structure changes so erratically, is the diffusion current changing and thus negating polarography as an analytical tool?

The data from Table III will readily show that the diffusion current is not changed excessively. For solution #1, several polarograms were obtained over a period of two weeks and their corresponding diffusion currents were averaged to obtain a value of 11.7 $\pm$ .2 μ.a. The $\pm$ .2 μ.a. represents the average deviation of all the diffusion currents from the average. Thus it is evident that for any solution, the uncertainty in the diffusion current is approximately 2 per cent; i.e., (.2 out of 11.7 is a $\frac{.2}{11.7}$ x 100% deviation or 1.7%). The values for the diffusion currents in which the conditions other than the gold cyanide concentration were drastically changed when averaged, yielded a value of 11.3 $\pm$ .3 microamp. This represents an average deviation of about 3 per cent ( $\frac{.3}{11.3}$ x 100 = 2.7%). This amply reveals that when the other conditions in the solution are changed, the diffusion current does not change appreciably, proving that the polarographic method of analysis for dicyanoaurate is valid over a whole

range of ionic strengths. This fact is quite important since it reveals that if the supporting electrolyte produces an ionic strength equal to or greater than .0150, one need not worry about adjusting the ionic strength in order that valid quantitative data be obtained. Thus, in the ultimate application of polarography for the analysis of gold (I) cyanide, greater simplicity and saving of time can be realized.

When no maxima appear in a polarographic wave, the wave can be analyzed to reveal certain thermodynamic information. Theoretical treatment[4] of the reduction half wave reveals that the following relationship should hold for a <u>reversible</u> reduction.

$$E_{d.e.} = E_{1/2} - \frac{.0591}{n} \log \left( \frac{i}{id-i} \right)$$

n = # of electrons

i = current height

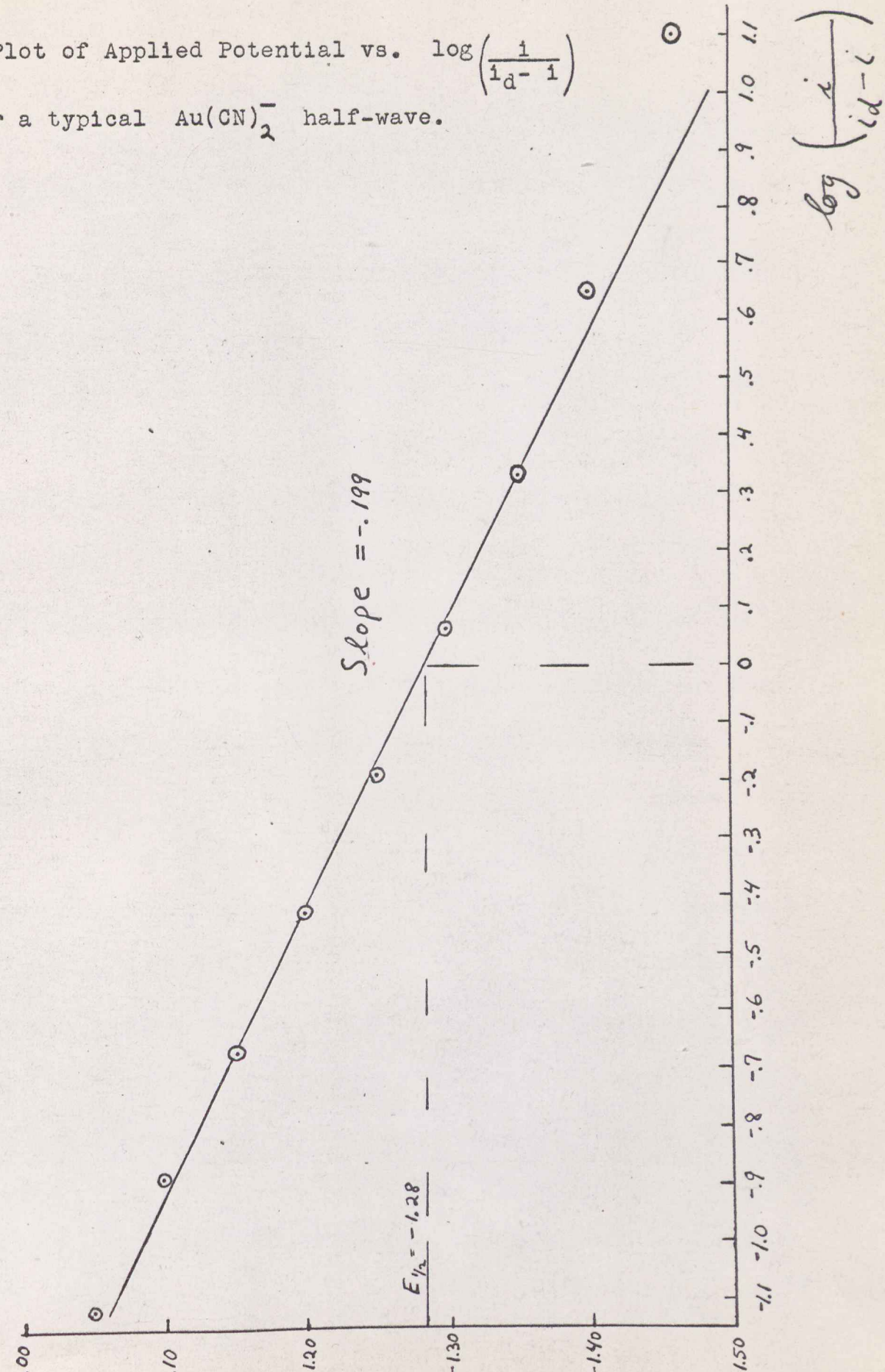
A plot of $E_{d.e.}$ vs. $\log \left( \frac{i}{id-i} \right)$ should yield a straight line with a slope of $- \left( \frac{.0591}{n} \right)$.

On Plate #6, is given the plot of $E_{d.e.}$ vs. $\log \left( \frac{i}{id-i} \right)$ for a $5.0 \times 10^{-3}$ M $Au(CN)_2^-$ in .01 M KCN solution. The slope

Plate 6

Plot of Applied Potential vs. $\log\left(\frac{i}{i_d - i}\right)$

for a typical $Au(CN)_2^-$ half-wave.



of the experimental line is - .199 as compared to the theoretical value of $\frac{.0591}{n}$ = .0591 since n = 1.

This difference in the slope shows that the reduction of the dicyanoaurate complex is not reversible. If the reduction were reversible, then the value for the slope would yield a value for "n" of .297 which could not be correct. This plot also reveals a more accurate value for $E_{1/2}$ since $E_{d.e.} = E_{1/2}$ when the log term equals zero. This value for $E_{1/2}$ (- 1.285) agrees closely with -1.28 which was obtained directly from the half wave. It is quite apparent that the polarograph's usefulness is not limited to quantitative analysis only.

The study of the dicyanoaurate half-wave cannot be considered complete without mentioning the sporadic appearance of a half-wave at about -.3 volts. Another look at Plate #2a will show the very small half-wave which has sometimes appeared in some of my dicyanoaurate solutions. Since only a reduction produces a half-wave, something other than the dicyanoaurate is being reduced at this low potential. Apparently, this reduction is also irreversible since a plot of

$E_{d.e.}$ vs. log $\left(\frac{i}{id-i}\right)$ yields a slope of -.240 and a half-wave potential of -.450 for a $2.5 \times 10^{-3}$ M $Au(CN)_2^-$ with $[CN^-] = 7.5 \times 10^{-3}$ M. This half-wave does not make a regular appearance but puts in an appearance occasionally. It has never been considered important to study this half-wave, since the dicyanoaurate wave has been of primary importance. Some of this wave's characteristics have, however, been determined. The wave, when present, appears only in solutions of low cyanide concentrations. An explanation for this phenomena may be that at higher cyanide concentrations (increasing ionic strength) the wave may be moved to more positive potentials or so close to the zero potential that its presence may not be detected. At first it was suspected that the wave may be due to an impurity in the KCN which is 92% pure, but the wave also appears when no excess KCN is present. Next, it was suspected that dissolved oxygen might conceivably be causing this wave but upon flushing with nitrogen, the wave is still present. Next was investigated whether the wave may be due to some tetracyanoaurate ions which might have been formed by the oxidation of the dicyanoaurate ions:

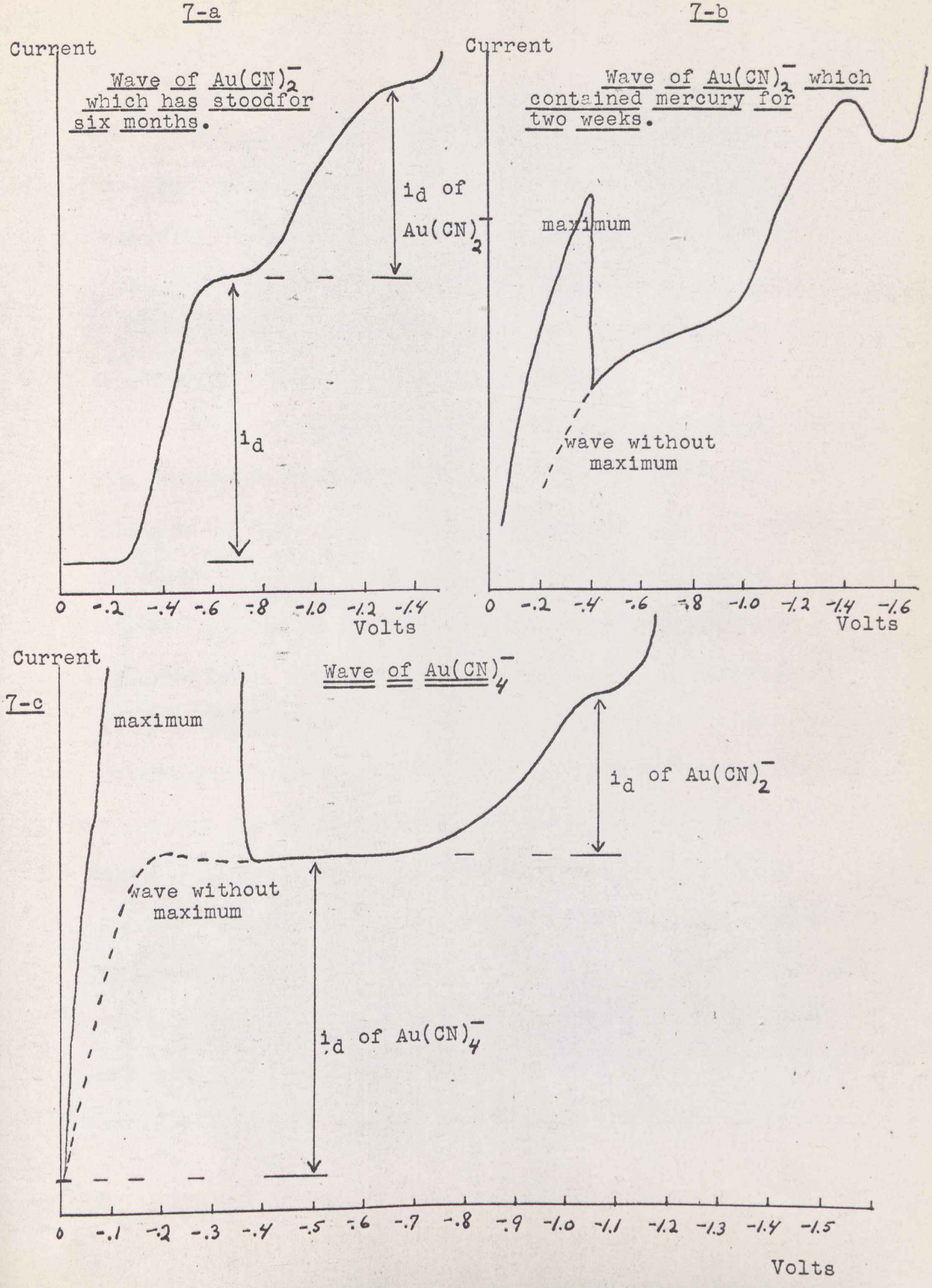
A solution which was swept through with oxygen for

sixteen hours showed absolutely no half-wave although half of this same solution which had not been swept with oxygen revealed a half-wave at -.4 volts. Thus, oxygen makes the wave disappear instead of enhancing it.

The wave height seems to be proportional to the dicyanoaurate concentration and it seems to grow with the passage of time. In a freshly prepared dicyanoaurate solution, this wave at -.4 volt is approximately one-seventh the height of the dicyanoaurate wave. In a solution which was about six months old, the wave at -.4 volts had grown so that it was 1.4 times as large as the dicyanoaurate wave. The current voltage curve of this solution is shown on Plate #7a. Originally, the curve was similar to the one shown on Plate #2a. After such a long time, the dicyanoaurate wave has diminished and become indistinct while the wave at -.4 volts has become quite distinct and greatly amplified. Thus, with time, something must happen to the dicyanoaurate which diminishes its wave height and some other reducible species must be produced.

Another clue in this puzzle is presented by the polarograph of a dicyanoaurate solution which had been standing for two weeks with mercury in the bottom of the vial containing

# Plate 7


7-a
Current
Wave of $Au(CN)_2^-$ which has stoodfor six months.
$i_d$ of $Au(CN)_2^-$
$i_d$
0 -.2 -.4 -.6 -.8 -1.0 -1.2 -1.4
Volts
7-b
Current
Wave of $Au(CN)_2^-$ which contained mercury for two weeks.
maximum
wave without maximum
0 -.2 -.4 -.6 -.8 -1.0 -1.2 -1.4 -1.6
Volts
7-c
Current
Wave of $Au(CN)_4^-$
maximum
$i_d$ of $Au(CN)_2^-$
wave without maximum
$i_d$ of $Au(CN)_4^-$
0 -.1 -.2 -.3 -.4 -.5 -.6 -.7 -.8 -.9 -1.0 -1.1 -1.2 -1.3 -1.4 -1.5
Volts

this solution. The c-v curve is shown on Plate #7b; formerly, a curve like that shown on Plate #4 -(4) was obtained. There is quite obviously a large difference between the two polarographs. Now, a maxima is present at -.4 volts which is covering the half-wave present and the dicyanoaurate wave has completely changed.

All of this data suggests only one possibility: that the monovalent gold is oxidized to the trivalent gold which can then be reduced at the applied potential of -.4 volts. In support of this hypothesis is given (Plate #7c) the current-voltage curve for the tetracyanoaurate complex. Unfortunately, a maximum reared itself for most tetracyanoaurate solutions between 0 and -.4 volts applied emf. One polarogram, however, did not do so and the wave was like that described by the dotted line between 0 and -.4 volts. The great similarity between the three polarograms on Plate #7 is quite evident, especially between #7a and #7c. If this is the explanation for the puzzling wave at -.4 volts, how may the presence of tetracyanoaurate be explained (a) for the solution which contained <u>only</u> dicyanoaurate but which stood undisturbed for six months and (b) for the dicyanoaurate

solution with excess cyanide ion which was exposed to the mercury for two weeks? It has already been shown that oxygen does not oxidize the dicyanoaurate complex to tetracyanoaurate and since only potassium dicyanoaurate was present for case (a) a reaction which might proceed as follows could cause $Au(CN)_4^-$ to be produced.

$$3\ Au\ (CN)_2^- \rightleftharpoons Au\ (CN)_4^- + 2\ Au + 2\ (CN)^-$$

No gold precipitate was observed, but that may have been due to the low concentration of the dicyanoaurate complex so that all the gold produced may actually have been suspended in the solution without being observed. Also the cyanide process; i.e., the following reaction

$$2\ Au + 4\ CN^- + 1/2\ O_2 + H_2O \longrightarrow 2\ Au\ (CN)_2^- + 2\ OH^-$$

may have removed any gold precipitated. In the case where mercury was exposed to the dicyanoaurate complex, the same type of process as described just now may have occurred only at a faster rate with the mercury acting as a catalyst. It must be remembered that this explanation of the half-wave at -.3 volts

is only a supposition suggested by the data without actually proving the hypothesis.

# CHAPTER IV

## THE TETRACYANOAURATE COMPLEX

The current-voltage curve obtained for the tetracyanoaurate complex has already been shown in Plate #7c. The diffusion current for the tetracyanoaurate complex is the difference in current indicated on the graph of Plate #7c; i.e., between zero volts and minus .5 volts. Here, as for the dicyanoaurate complex, the formation of a maxima does not interfere with the diffusion current determination. In addition to the current increase due to the trivalent gold cyanide, at -.4 volts, a current increase is attributable to the dicyanoaurate complex at -1. volts. The data listed below and Plate #8

TABLE IV

Data

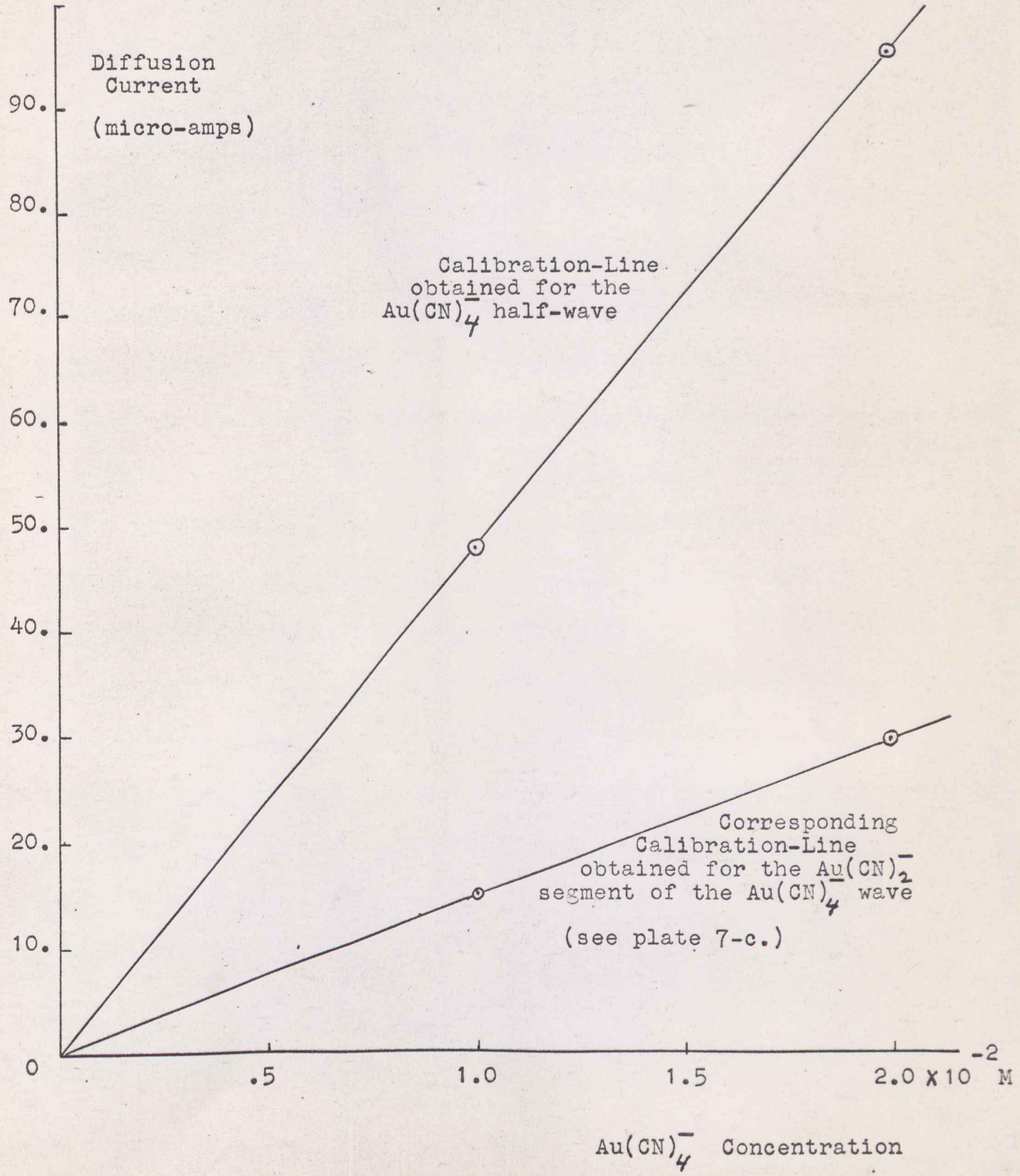
| $[\bar{K}\ Au(CN)_4^-]$ | $[\bar{KCN}]$ | id $[\bar{Au}\ (CN)_4^-]$ | id $[\bar{Au}(CN)_2^-]$ |
|---|---|---|---|
| $1.0 \times 10^{-2}$ M | .01 | 48.4 μ.a. | 15.3 μ.a. |
| $2.0 \times 10^{-2}$ M | .01 | 95.2 μ.a. | 29.8 μ.a. |

suggests that polarography is also a valid method for the quantitative analysis of the tetracyanoaurate complex.

Plate - 8

Calibration Line for $Au(CN)_4^-$.

(Diffusion Current vs. Concentration )



The per cent of Au in K Au $(CN)_4 \cdot \frac{3}{2} H_2O$ is 53.7%; this analysis leaves very little doubt that the original salt was nothing but the tetracyanoaurate.

The potassium tetracyanoaurate salt apparently contained no potassium dicyanoaurate and thus the polarogram was that for the tri-valent gold only. The only explanation left for the appearance of the dicyanoaurate wave is that the tetracyanoaurate complex is first reduced to the dicyanoaurate complex and then at the greater potential, the dicyanoaurate complex is reduced to gold. This fact immediately suggests that a method of quantitative analysis for both of the gold cyanide complexes in the presence of each other is possible. For the analysis of the two complexes in the presence of each other, the diffusion current for the tetracyanoaurate complex is readily determined and the concentration of this complex may then be found from the calibration line such as that on Plate #8. The concentration of the dicyanoaurate complex may then be found by subtracting the dicyanoaurate current height which corresponds to the tetracyanoaurate complex concentration (see Plate #8) from the experimental diffusion current of the dicyanoaurate complex and using this value on the

monovalent gold cyanide complex calibration line on Plate #2b.

No polarograms of a mixture of the two complexes has yet been taken and thus only experimental work yet to be performed will reveal if the above mentioned method is valid. At least it has been shown that polarography is a good method of quantitative analysis for the two gold cyanide complexes independently of each other. The effects of changing some of the parameters for the dicyanoaurate complex solution upon the wave of this complex have been thoroughly investigated and reported. It was also suggested that there might exist an auto-oxidation-reduction reaction in the dicyanoaurate complex solution which eventually produces the tetracyanoaurate complex. In addition to all this, the polarograms have revealed that the reduction of the dicyanoaurate complex is not reversible.

# CHAPTER V

## SUGGESTED ADDITIONAL EXPERIMENTAL WORK

Since very little work was done on the tetracyanoaurate complex, it is suggested that the half-wave of this complex be investigated more thoroughly. Once work on this complex has been done, a solution containing both of the gold-cyanide complexes should be studied in order to check the hypothesis that they can be quantitatively analyzed in the presence of each other. The possibility exists that the reduction of the tetracyanoaurate complex to the dicyanoaurate is a reversible process; this can be checked by making an $E_{d.e.}$ vs. log $(\frac{i}{id-i})$ plot of the tetracyanoaurate wave. If the slope of the resultant line is $-\frac{.0591}{2}$ then the process at the electrode is a reversible one; if the slope should be $-\frac{.0591}{3}$ then the tetracyanoaurate complex is directly reduced to Au, disproving the given hypothesis of step-wise reduction. Any other slope would only show that the electrode process is irreversible. Should the first-mentioned case be true, then it is suggested that an equilibrium between the two complexes, however slowly attainable, may exist. The work on the polarographic analysis

of the gold cyanide complexes done so far is only a small segment of the work that needs yet to be done in order that the chemistry of the gold cyanide complexes be more easily understood.

# BIBLIOGRAPHY

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