A POLAROGRAPHIC ANALYSIS OF THE TETRACYANOAURATE (III) AND THE DICYANOAURATE (I) COMPLEXES

by

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To

ABSTRACT

A method for the determination of the dicyanoaurate and tetracyanoaurate complexes using polarography has been investigated. Whereas distinct wave forms (current-voltage plots) are obtainable, many interference problems exist. Previous work has been confirmed and new data added. Dicyanoaurate I (Au $(CN)_2$) has been satisfactorily investigated and may be classified as a stable complex. Tetracyanoaurate III (Au $(CN)_4$) has been investigated and must be classified as unstable. Thus a polarographic method of quantitative analysis for a simultaneous determination of these complexes seems remote.

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CHAPTER I

INTRODUCTION

This present report completes the third year of research of the feasibility of a polarographic method for the simultaneous determination of the dicyanoaurate I and tetracyanoaurate III complexes in solution. This research was undertaken to provide a quick and reliable method of making such measurements as are necessary in an electron transfer experiment between these two complexes (1).

The polarographic method is basically a very simple investigation. A potential is applied between an anode and a cathode immersed in a solution to be tested and a plot of the current flowing through the cell as a function of the applied potential is made. A dropping mercury electrode is often used as the cathode. Such an electrode provides an essentially clean uniform surface throughout the analysis, thus aiding in the reproducibility of the results.

More importantly, however, the polarographic method has several other advantages over other methods of analysis. The sample can be very small: approximately 5 ml. samples were employed during this research project. The concentration range of the species under investigation can be quite low: 10^{-2} M - 10^{-5} M. Finally, polarographic methods generally are quite simple, as far as routine measurements are concerned, once the criteria are established. Thus polarographic analysis would seem to be an advantageous method to use.

The wave forms obtained in a polarographic analysis are of a general "step" nature, i.e. there is a distinct change in the current as a function of the voltage. The potential at which this change occurs is known as the half-wave potential and is indicative of the electroreducible species present. The current change is known as the diffusion current and is usually proportional to the concentration of the species under investigation.

These half-wave potentials are generally unique, i.e. a given ion always produces the diffusion current at the same potential under identical conditions. Thus, it is possible to simultaneously investigate two or more ions in the same solution if their half-wave potentials are reasonably separated. In such a current-voltage plot, a series of steps will result and by means of simple manipulation these steps may be resolved into separate diffusion currents and associated with specific ions.

The dicyanoaurate (I) and tetracyanoaurate (III) complexes had originally been investigated by John Herman at the University of Prague in Czechoslovakia (2). At the time, he reported that these complexes had distinct half-wave potentials and thus could be simultaneously determined. Unfortunately, the experimental conditions under which such research was conducted are not available. In the past three years, time has been spent in establishing suitable experimental conditions, as well as gathering data.

This recent work has been compiled in two separate papers (3, 4) and provides a substantial basis for the work performed this year. Neddermeyer and McClemens established the half-wave potentials of the two complexes and gathered much data supporting the proportionality between the diffusion current and the concentration of the species under investigation.

During the past year, much of this work was duplicated. The dicyanoaurate complex yielded essentially similar data. The tetracyanoaurate complex, however, has proved to be quite unstable. Also, this most recent experimentation has been aided by an IBM 1620 computer in the final analysis of some of the data. An original Union College FORTRAN program was designed to compute the best slopes and intercepts of the calibration curves and thus minimize error. It was based on a least-squares analysis of every point included in a given graph.

CHAPTER II

EXPERIMENTAL PROCEDURE

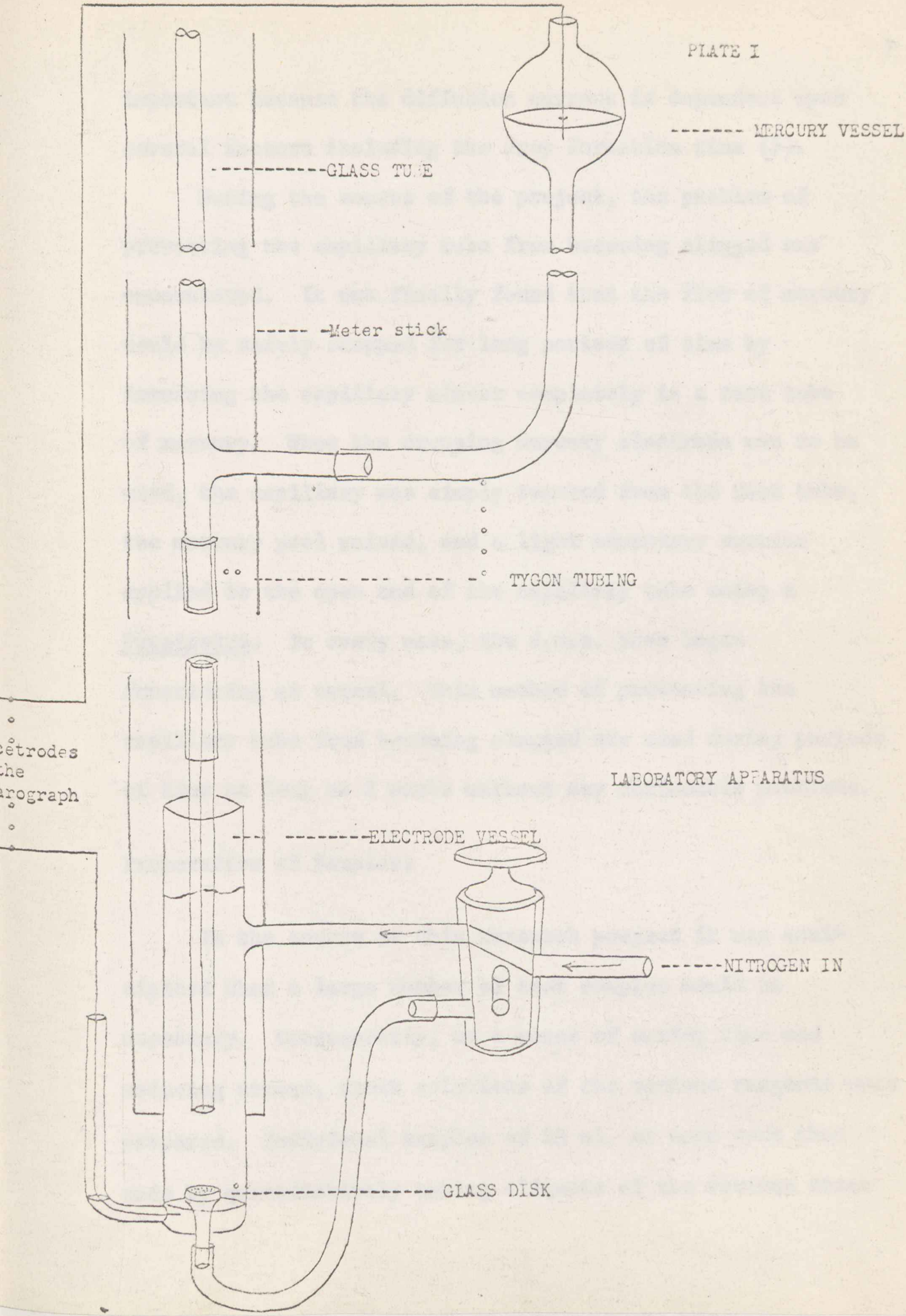
Apparatus: Sargent Model XII automatic recording polarograph, electrode vessel, and dropping mercury electrode.

The apparatus was assembled as shown in Plate I. The solution to be tested was placed in the electrode vessel. The dropping mercury electrode was then inserted into the solution and the necessary electrical connections were made. The polarograph then automatically produced the desired current-voltage curve.

The electrode vessel was so constructed that nitrogen could be either bubbled through the solution or alternately passed over the top of it. This system thus provided an easy method of de-aerating the solution and keeping the solution from absorbing oxygen once it was de-aerated.

The dropping mercury electrode, d.m.e., consisted of a fine bore glass capillary with a pool and column arrangement of mercury above it. This arrangement provided a suitable means of adjusting the drop formation time of the d.m.e. so that it remained essentially constant throughout the entire research project (3.85 sec.-4.02 sec.). This is

PLATE I



LABORATORY APPARATUS

important because the diffusion current is dependent upon several factors including the drop formation time (5).

During the course of the project, the problem of preventing the capillary tube from becoming clogged was encountered. It was finally found that the flow of mercury could be safely stopped for long periods of time by immersing the capillary almost completely in a test tube of mercury. When the dropping mercury electrode was to be used, the capillary was simply removed from the test tube, the mercury pool raised, and a light momentary suction applied to the open end of the capillary tube using a Propipette. In every case, the d.m.e. then began functioning as normal. This method of preventing the capillary tube from becoming clogged was used during periods of time as long as 2 weeks without any noticeable problems.

Preparation of Samples:

In the course of this research project it was anticipated that a large number of test samples would be necessary. Consequently, as a means of saving time and reducing errors, stock solutions of the various reagents were prepared. Individual samples of 25 ml. or more were then made by quantitatively taking aliquots of the various stock solutions and diluting them in a suitable volumetric flask.

The potassium tetracyanoaurate was prepared as follows: 1.58 g. of KCN (Fisher), was dissolved in 5.6 ml. of water in a 50 ml. Erlenmeyer flask. This solution was then added dropwise to a solution of 1.930 g. of chlorauric acid ($HAuCl_4 \cdot 3H_2O$) (B & A - Allied Chemical Corp.), dissolved in water in a 50 ml. round bottomed flask. The mixture was stirred vigorously to remove the HCN formed.

During the initial reaction, the color of the solution changes from orange to a colorless solution. Twenty minutes after this color change, the flask was placed in a 15°C thermostat and left there for 24 hours. This process precipitates the $KAu(CN)_4$ and leaves the KCl in solution thus separating the salts. The $KAu(CN)_4$ crystals were then purified and dried.

Preparation of Stock Solutions:

Stock Solution #1: 0.01 M Potassium Dicyanoaurate

1000 ml. of 0.01 M Potassium Dicyanoaurate was prepared by diluting 3.241 g. of the salt to 1000 ml. ($KAu(CN)_2 \cdot H_2O$, mol. wt. = 324.1 g. - Fisher Chemical Co.).

Stock Solution #2: 0.1 M Potassium Cyanide

100 ml. of 0.1 M Potassium Cyanide was prepared by diluting to 100 ml. 0.651 g. of the salt. (KCN mol. wt. = 65.1 g. - Fisher Chemical Co.).

Stock Solution #3: 0.01 M Potassium Tetracyanoaurate

100 ml. of 0.1 M Potassium Tetracyanoaurate was prepared by diluting 0.367 g. of the salt to 100 ml. ($KAu(CN)_4 \cdot H_2O$, mol. wt. = 367.1 g. - self-prepared, see above).

Preparation of individual samples:

Dicyanoaurate samples were prepared as follows: (Note: "D" after number of sample indicates the sample in question is a dicyanoaurate complex sample, as opposed to a tetracyanoaurate complex sample which is indicated by a "T" after the number of the sample. (See Tables I and II).

TABLE I

Sample	ml. $KAu(CN)_2$	Conc. $KAu(CN)_2$	ml. KCN	Conc. KCN	Total Vol.
1D	75	7.5×10^{-3}M.	10	10^{-2}M.	100 ml.
2D	50	5.0 "	"	"	"
3D	37	3.7 "	"	"	"
4D	25	2.5 "	"	"	"
5D	12	1.2 "	"	"	"
6D	6	0.6 "	"	"	"
7D	1	0.1 "	"	"	"

Tetracyanoaurate samples were prepared as follows:

TABLE II

Sample	ml. $KAu(CN)_4$	Conc. $KAu(CN)_4$	ml. KCN	Conc. KCN	Total Vol.
1T	18.75	7.5×10^{-3}M.	2.5	10^{-2}M.	25 ml.
2T	12.5	5.0 "	"	"	"
3T	9.3	3.7 "	"	"	"
4T	6.3	2.5 "	"	"	"
5T	3.0	1.2 "	"	"	"
6T	1.5	.6 "	"	"	"

CHAPTER III

THE DICYANOAURATE COMPLEX

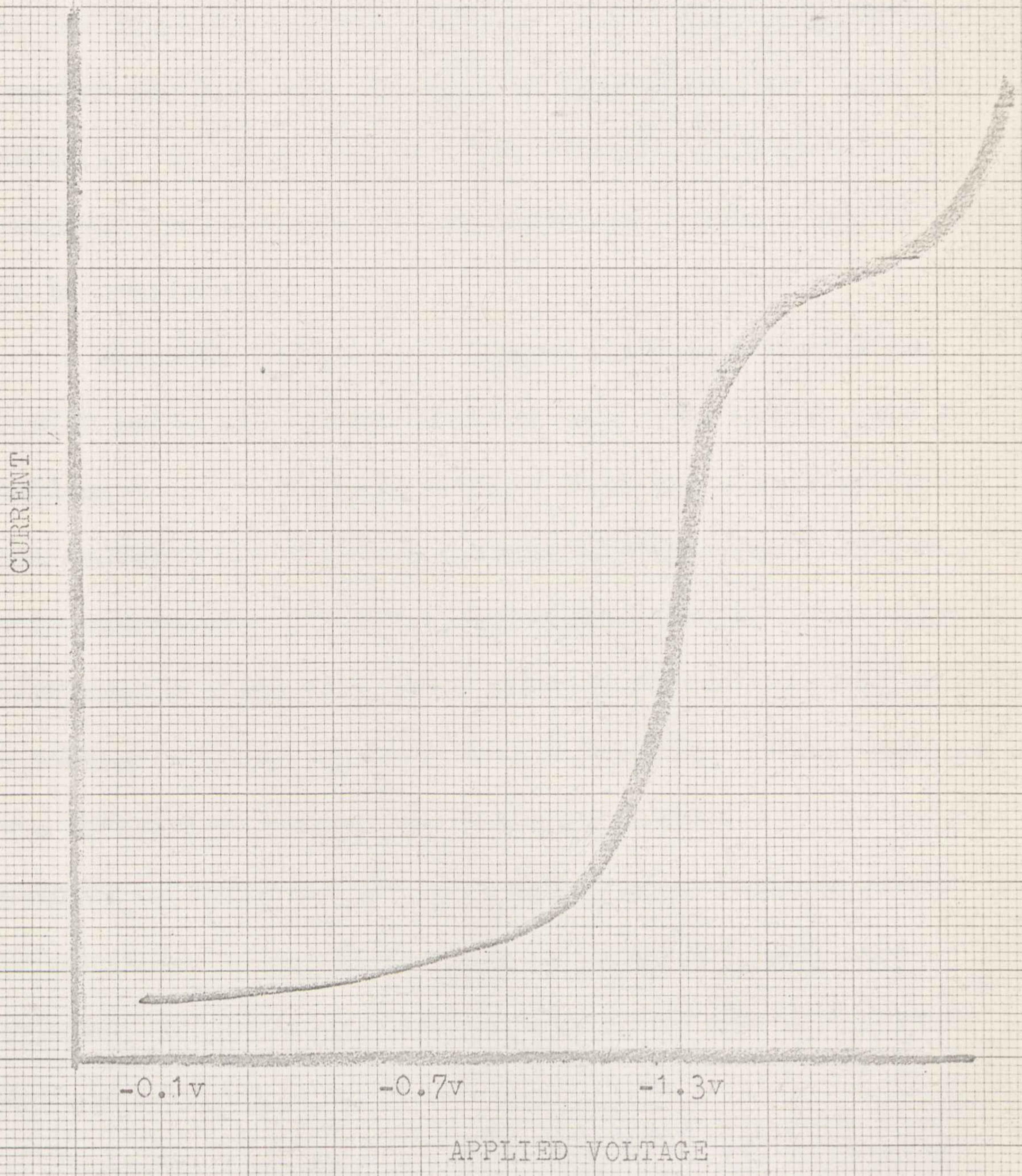
The dicyanoaurate complex was first investigated for several reasons: (1) it is commercially available as the potassium salt, (2) it is generally assumed to be the more stable of the two complexes, and (3) the greater portion of available data dealt with the dicyanoaurate complex. For these reasons, it seemed that the necessary introduction to the techniques involved in securing polarographic data should be performed with the dicyanoaurate complex.

As is the case in the majority of work in this field, a supporting electrolyte was used to carry the bulk of the current through the cell. The salt chosen for this purpose was potassium cyanide. This salt has been used successfully for the past two years and there was no reason to make a change.

Each of the dicyanoaurate complex solutions (Chapter II) was run many times. For each of the runs made, a current-voltage plot similar to Plate II was obtained. The diffusion current (the difference between the residual and limiting current plateaus) was then computed. Originally, the method

PLATE II

Typical Current-Volatage Curve
for $\mathrm{Au(CN)}_2^{-}$



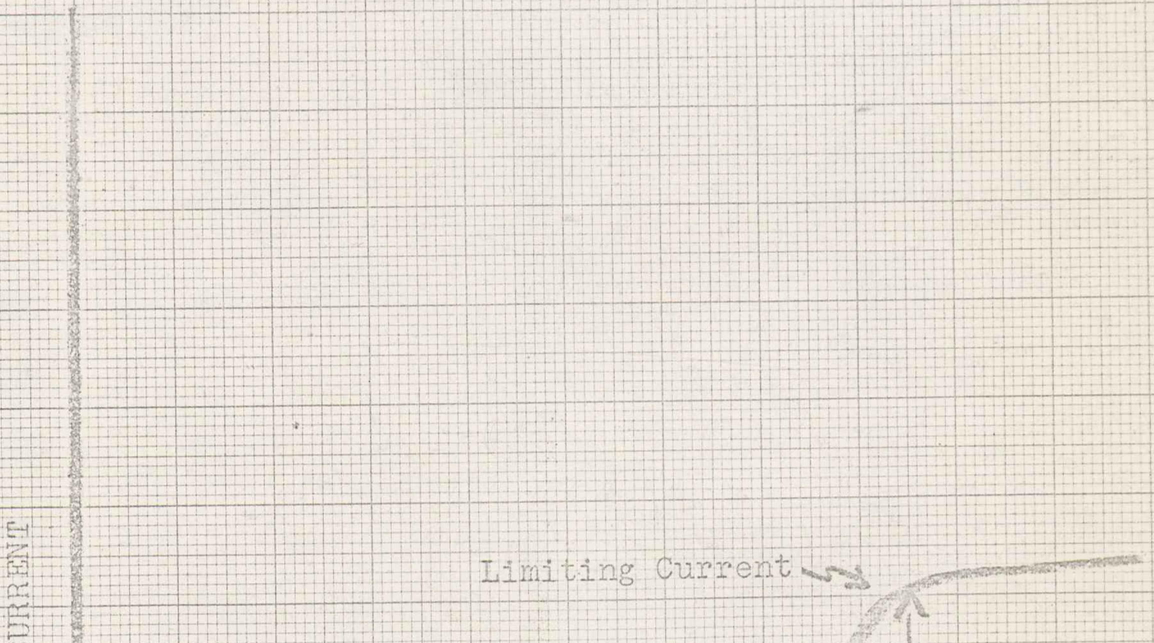
used by McClemens was employed to find the diffusion current. According to this approach, two voltages are arbitrarily chosen, one being on the residual plateau; the other being on the limiting current plateau. The difference between the current at these two voltages is then called the diffusion current. By using the same two voltages throughout the project, measurements of the diffusion currents are assumed to be consistent.

Kolthoff and Lingane suggest another method which yields supposedly better results (6). The method used by McClemens and Neddemeyer assumes that the slopes of both the residual and limiting current plateaus are identical. This assumption is very questionable. Kolthoff and Lingane alternately suggest an extrapolation of the residual current. A voltage is then selected on the limiting current plateau and the difference between the limiting current and the extrapolated residual current is the diffusion current (Plate III). This method, though ordinarily not yielding very different results, is the more theoretically sound and consequently was used throughout the experiment.

An analysis of the dicyanoaurate complex current-voltage curves revealed that the half-wave potential of this complex

PLATE III

Extrapolation Method of Determining Diffusion Current



was -1.3 volts. This is in agreement with the half-wave potentials obtained by Neddemeyer and McClemens.

Typical data associated with the dicyanoaurate complex are:

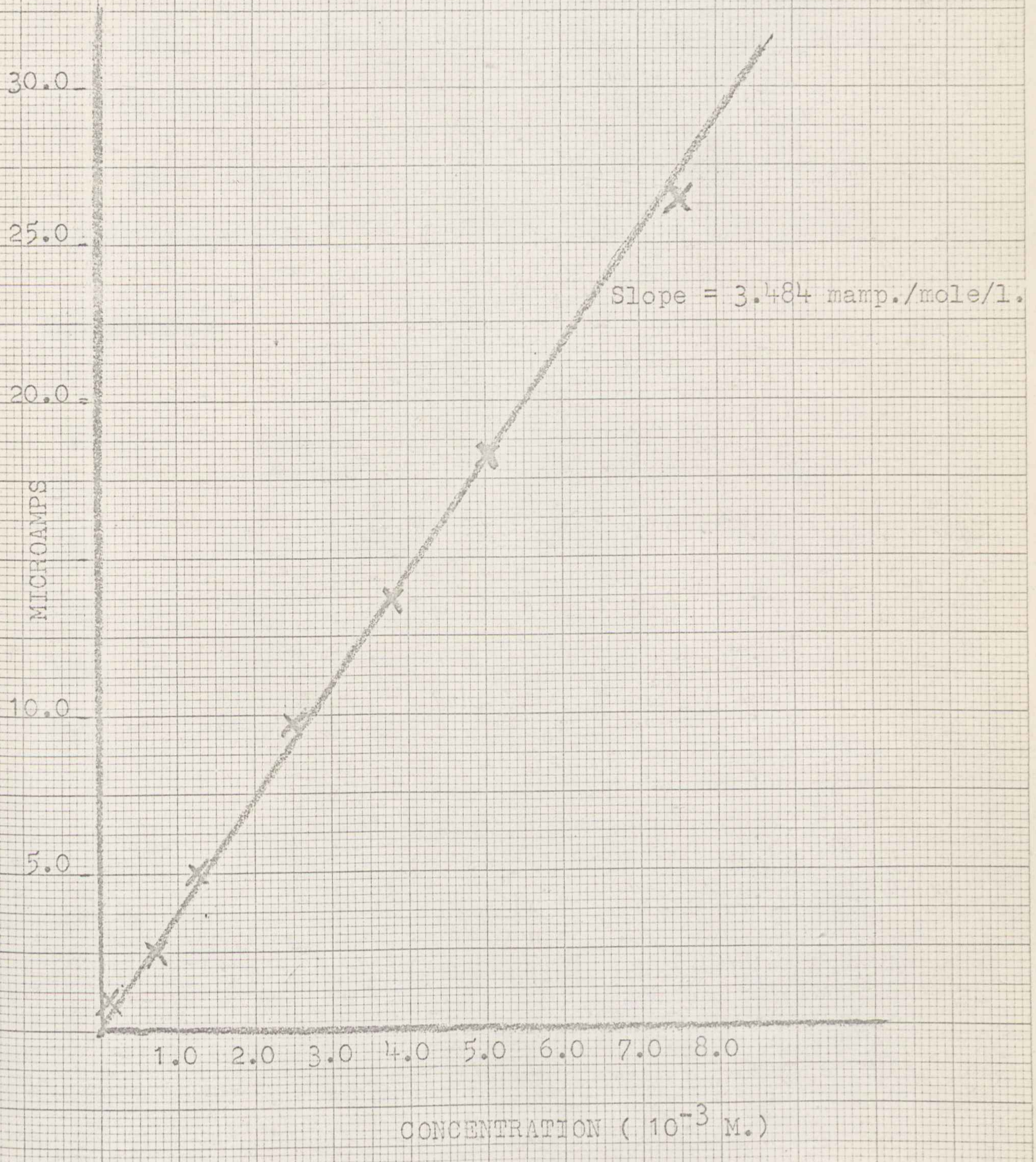
TABLE III

	Conc. $KAu(CN)_2$	Conc. KCN	i_d (Diffusion Current)
1D	7.5×10^{-3} M.	10^{-2} M.	26.6 μ amp.
1D	"	"	26.8
2D	5.0 "	"	18.4
2D	"	"	18.2
3D	3.7 "	"	13.7
3D	"	"	13.8
4D	2.5 "	"	10.1
4D	"	"	9.2
5D	1.2 "	"	4.9
5D	"	"	5.2
6D	0.6 "	"	2.7
6D	"	"	2.5
7D	0.1 "	"	1.1
7D	"	"	1.0

A calibration curve was then constructed from these data (Plate IV). The concentrations and diffusion currents

PLATE IV

Calibration Curve for $Au(CN)_2^-$



were then analyzed by an IBM computer. (See Appendix for Program). The results of this least-squares analysis of the above data are:

slope of calibration curve: 3.484 milliamp/mole/l.

y intercept - .217

As a comparison, the following data from Neddemeyer and McClemens were also analyzed using the same technique:

Neddermeyer:

TABLE IV

	Conc. $KAu(CN)_2$	Conc. KCN	i_d
8D	2.5 x 10^{-3}M.	10^{-2}M.	5.7 μ amps.
9D	5.0 "	"	11.4
10D	7.5 "	"	17.1
11D	10.0 "	"	22.9

McClemens:

TABLE V

	Conc. $KAu(CN)_2$	Conc. KCN	i_d
12D	7.5×10^{-3}M.	$1. \times 10^{-2}$M.	44.1 μ amp.
13D	5.0 "	"	30.9
14D	5.0 "	$5. \times 10^{-3}$M.	28.0
15D	3.7 "	$1. \times 10^{-2}$M.	20.2
16D	2.5 "	$1. \times 10^{-2}$M.	15.1
17D	2.5 "	$5. \times 10^{-2}$M.	10.3
18D	1.3 "	"	6.2
19D	6.3×10^{-4}M.	"	3.1
20D	1.3 "	"	0.8

All of the above data were plotted on Plate V.

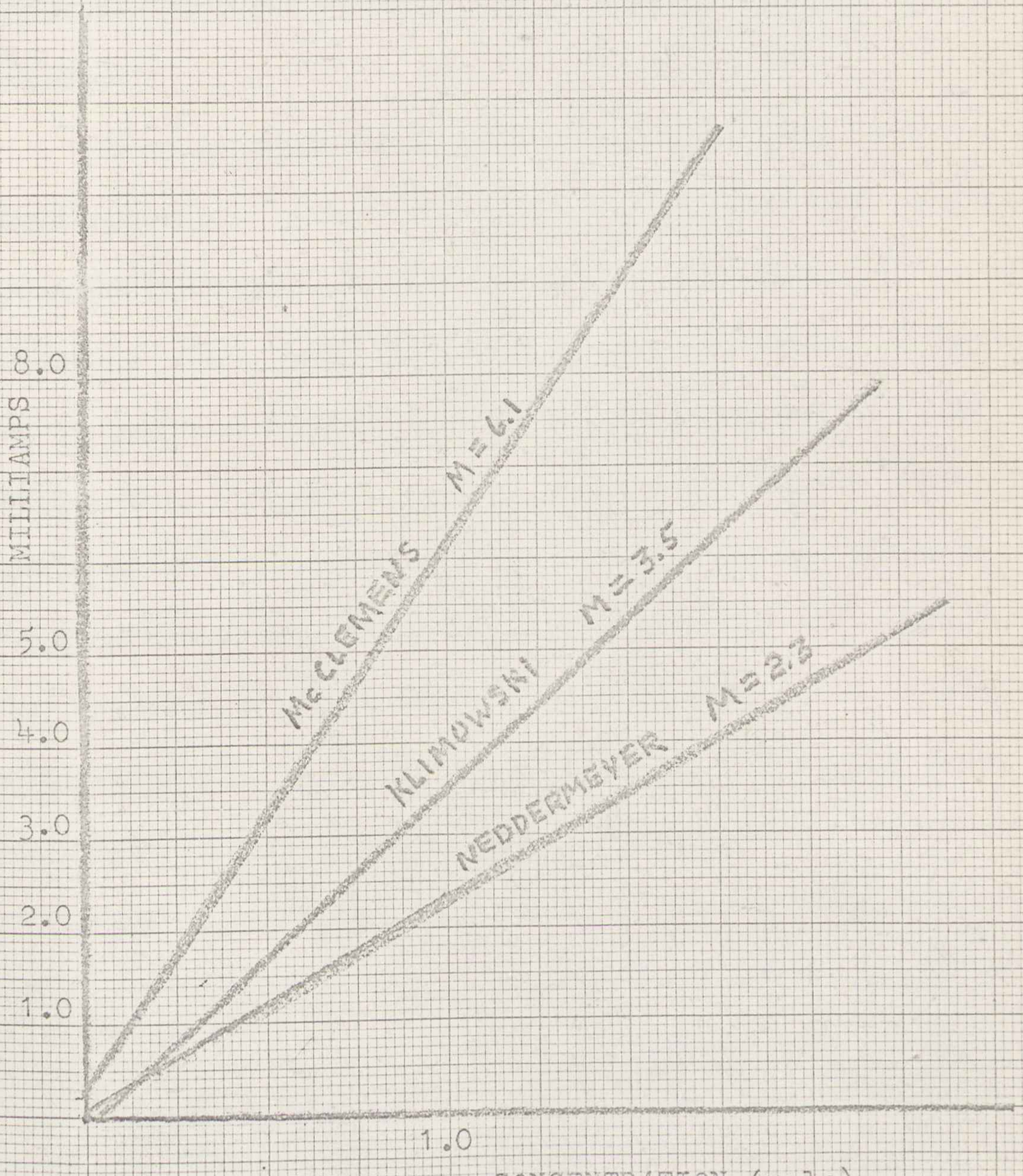
The results of this study were:

Neddermeyer:	slope:	2.295 milliamp/mole/l.
	y intercept	0.022
McClemens:	slope:	6.060 milliamp/mole/l.
	y intercept	0.204

As can be seen, there exists a considerable amount of variation between the various sets of data. Two explanations may account for some of the variation. First, the

PLATE V

Comparison of Various $Au(CN)_2^-$ Data



concentration of the supporting electrolyte in McClemens' work was not constant. This caused an appreciable change in the diffusion current for a given sample as can be seen above. Secondly, the extrapolated method of measuring the diffusion current was not used in either of the previous studies.

In McClemens' thesis, the proposition was made that some variation in the results of the project were attributable to the variation of the supporting electrolyte concentration. This lends some support to the similar statement on my part. McClemens also attributed some of the discrepancy to the fact "that in neither case was a good mathematical approach, such as a least-squares analysis, used to determine the line" (7). This last statement has been refuted by the computer study of this year. A much more intricate analysis has only further impressed the variation between his work and Neddermeyer's.

The reversibility of the reaction was reinvestigated using the same approach used by Neddermeyer and McClemens. The irreversibility of the reaction was again confirmed.

Several interesting notes on this year's work deal with deviations from the observations of the preceding years. Last year McClemens found that in the lower concentration ranges, only three polarograms could be obtained from a given sample. I did not find this to be the case this year, having obtained as many as six polarograms from a given sample. It is true that I did not venture as far as he did, nevertheless he reported this tendency at 1.3 x 10^{-3}M. I did not observe it at this concentration.

The second note deals with an observation made by Neddermeyer. He reported a reduction wave at -.3 volts which he attributed to the reduction of a gold (III) complex. A search of McClemens' work last year does not indicate that he observed a similar occurrence, nor have I during the course of this year's work.

CHAPTER IV

TETRACYANOAURATE (III) COMPLEX

The tetracyanoaurate complex, as implied before, is not readily available commercially. The method used for its preparation was developed by George Hartwell (8). It is as follows:

$$HAuCl_4 + KCN \longrightarrow KAu(CN)_4 + 4\ KCl + HCN$$

This synthesis is supposedly very temperature-sensitive, and considerable care must be exercised in performing it. The preparation of tetracyanoaurate complex, adapted from the thesis by George Hartwell, is found under "Preparation of Solutions." Test solutions of the tetracyanoaurate complex were prepared as described in Chapter II.

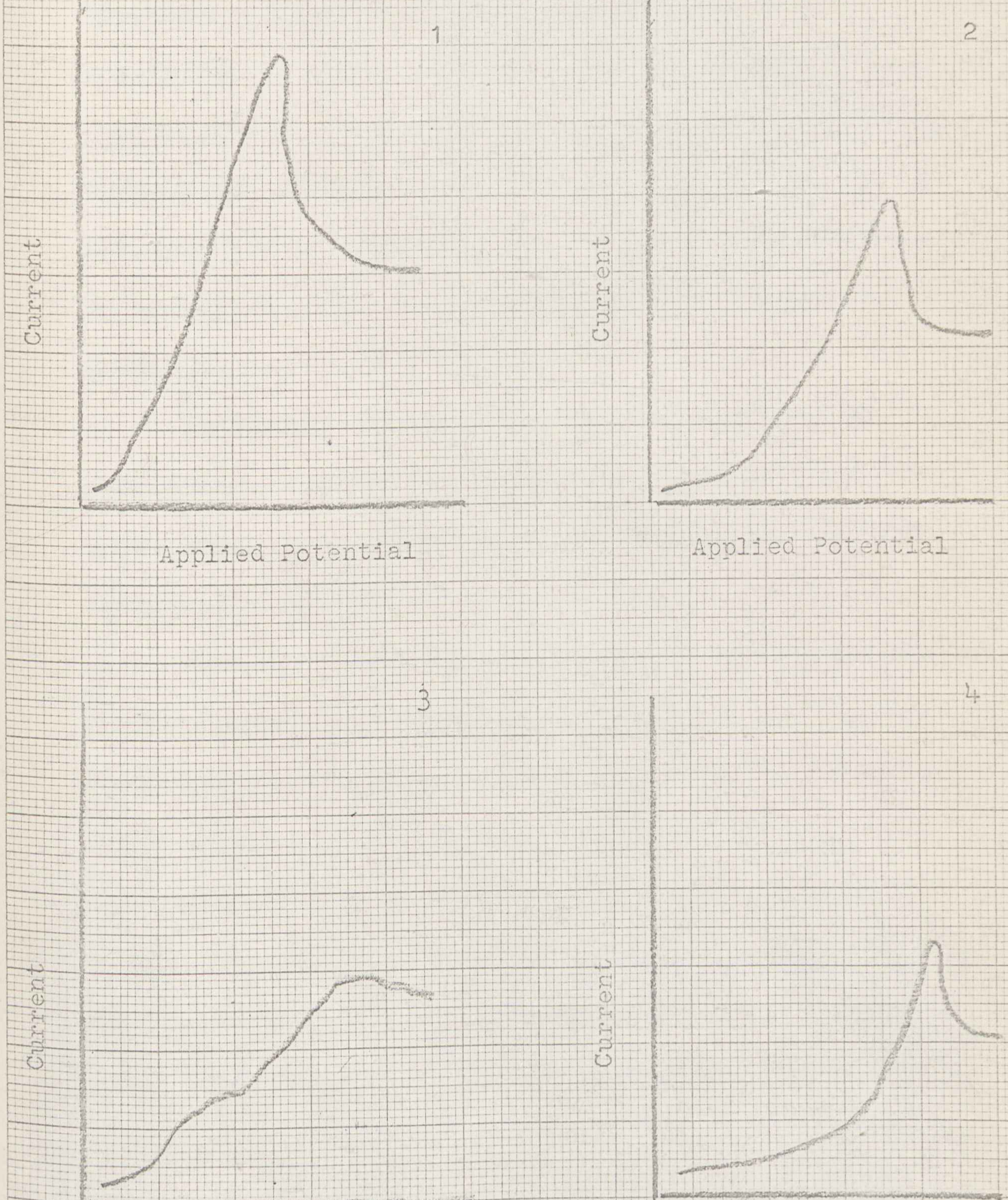
Plate VI shows typical successive tetracyanoaurate polarograms of a given sample. The variation between successive runs, all controls being constant, is self-evident.

Because of this instability, no calibration curve for the tetracyanoaurate complex was obtained, and consequently no simultaneous determinations of the two complexes were attempted.

After a few samples were run it was noted that the

PLATE VI

Successive Tetracyanoaurate Polarograms



change between various polarograms did not necessarily represent a gradual shift in the wave forms but often showed completely new forms. After a sample had been run three or four times, it was assumed that the phenomenon mentioned by Neddermeyer occurred, i.e., the gold became exhausted and the wave form disappeared. The larger problem,however, seemed to reside with the change noted among the first two or three polarograms of a given sample.

The actual investigation of the instability of the tetracyanoaurate complex, and an examination of the polarograms seems to indicate that a reaction of some sort was occurring, proceeded as follows:

From the difference between two successive polarograms, it was noticed that the change, whatever it may be, was occurring rather rapidly under some conditions and not so under others. It was therefore decided to try a constant potential plot, i.e. make a plot of current as a function of time. The cell was assembled as usual, the d.m.e. immersed in the solution, and the necessary electrical connections made. The automatic potentiometer was then disconnected and manually adjusted to -0.2 volt with respect to the d.m.e. A plot of current versus time was then automatically recorded by the polarograph.

The results were quite a surprise to say the least. The first of these constant potential curves is reproduced in Plate VII. As can be seen, after a given time, there is considerable increase in the current flow through the cell. What is even more remarkable is the <u>speed</u> with which this increase takes place. It appears to be an almost instantaneous reaction of one sort or another.

The problem now became even more complicated by this quite unusual phenomenon. This instantaneous change would seem to account for the rather unusual change between successive polarograms.

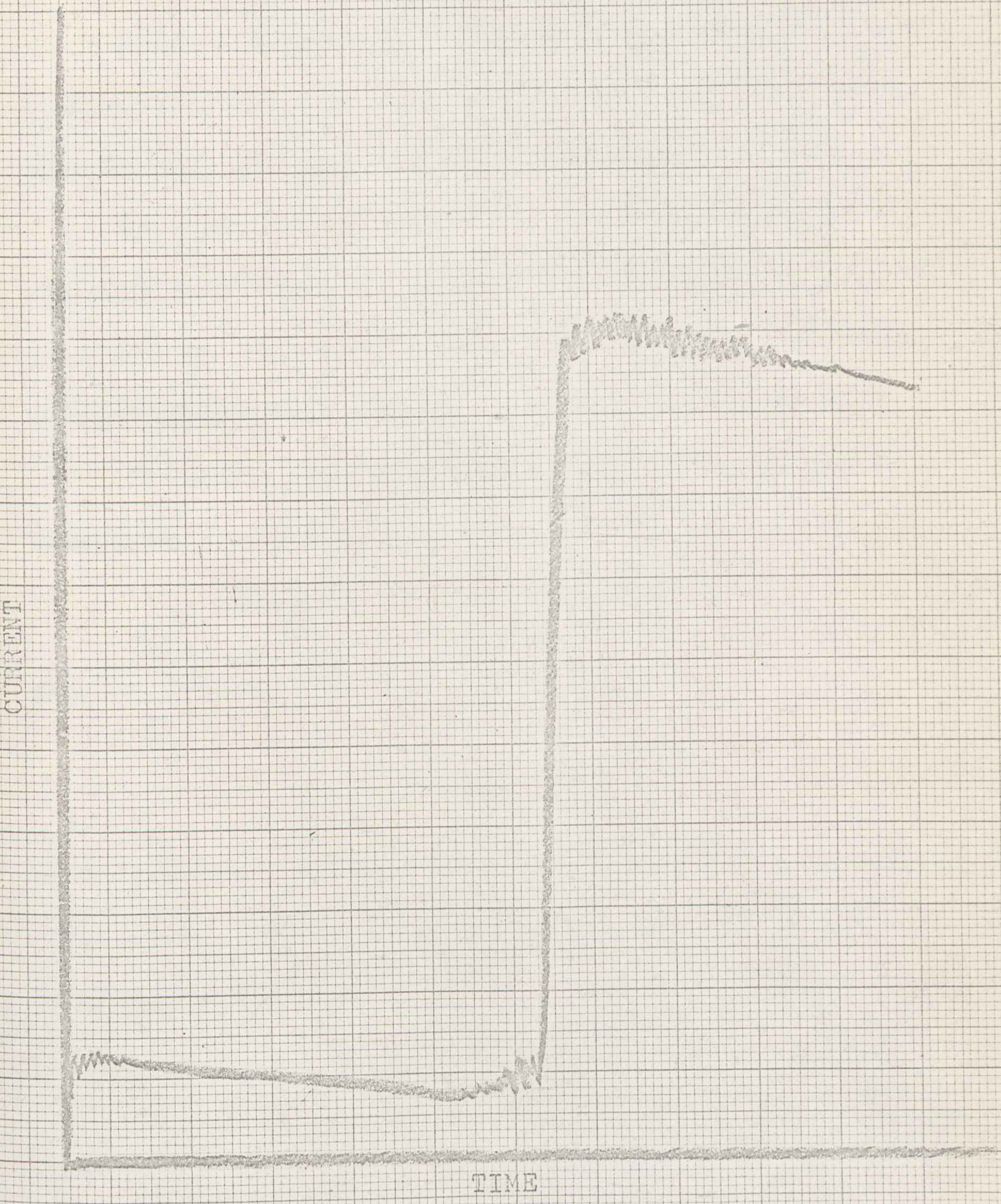
A simple exchange reaction, in the usual sense, is ruled out:

$$AX + C \longrightarrow AC + X \qquad (1)$$

This is evident because of the instantaneousness of the observed reaction. If either AC or X were the species responsible for the increase in the current flow through the cell, a gradual increase in the current should be observed as the reaction proceeds from left to right. Originally, there is no AC or X and so one observed a given current flow through the cell. After Δt time, ΔAC and ΔX has been formed. If these species were responsible for the extra current flow, an extra current flow of Δi should presently

PLATE VII

Current vs. Time Plot of $Au(CN)_4^-$



be noted. Successive intervals of Δt would result in a gradual increase in current. This does not happen.

This is not to say that an exchange reaction does not take place; this is to say only that if such a reaction is occurring it is triggered by some unusual conditions.

An attempt has been made to explain the occurrence of the step in Plate VII. In a given solution, the only ions present are: $K+$, $Au+3$, CN^-, $Hg+$, and H_2O . The other species of $H+$, $Au+$, and OH^- must also be kept in mind.

The basic reduction half reaction for the dicyanoaurate is proposed to be:

$$Au(CN)_2^- + e \longrightarrow Au + 2\ CN^- \qquad (2)$$

and the oxidation half reaction:

$$Hg \longrightarrow Hg^+ + e \qquad (3)$$

There is no proof whatsoever that the gold truly remains in this form in solution. Neddermeyer proposed that the gold might again be oxidized by the following reaction:

$$2\ Au + 4\ CN^- + \tfrac{1}{2}\ O_2 + H_2O \longrightarrow 2\ Au(CN)_2^- + 2\ OH^- \qquad (4)$$

Although he proposed this reaction to account for a different problem, there is no reason why such a situation could not be the case here.

For the tetracyanoaurate complex, the reduction half reaction may be:

$$Au(CN)_4^- + 3e \longrightarrow Au + 4\ CN^- \qquad (5)$$

Again the oxidation half reaction may be (3) above.

From general observations of many polarograms, the presence of the dicyanoaurate complex has always been found with the tetracyanoaurate complex. The dicyanoaurate complex could result from an equilibrium reaction between the two complexes as indicated above, a combination of equations (4) + (5), or could result fromthe partial reduction of gold III. If the former is the case, then the problem of simultaneous determinations of the two complexes might even seem impossible.

If Neddermeyer's equilibrium reaction were to be true, (4) + (5), it might be expected that two successive polarograms of a given sample should be identical. This might be expected from the fact that the two species are in equilibrium. As has been observed, this is not the case. If this equilibrium were to exist, the trivalent gold which was depleted appreciably during an analysis should be replenished during the time between runs and thus the second run should show a very similar tetracyanoaurate reduction peak. Once again, this has not been the case.

This presents two new possibilities. Either the Neddermeyer equilibrium reaction does not exist, or is so slow as not to effect the concentrations of the two species. In either case, we may then eliminate this reaction from practical considerations, and assume that it does not appreciably alter the general form of successive polarograms.

An attempt was now made to find consistency of one sort or another among the various constant potential polarograms. From the onset, it was noticed that the "step" portion of the wave seemed to occur at different times from the beginning of the analysis. It was felt that this might provide a clue to what was taking place.

As seen in Plate VIII, a noticeable shift in the step occurred between the various aliquots of the same sample. In each case, however, the only intended variation was the time that nitrogen was bubbled through the solution. A series of tetracyanoaurate samples were de-aerated for varying lengths of time. Polarograms were then obtained of each of these samples. As can be seen from the following table, no correlation seems to exist between the length of time nitrogen was bubbled through the solution, and the length of time before the step of the polarogram appeared.

PLATE VIII

Successive Current-Time Plots of $Au(CN)_4^-$

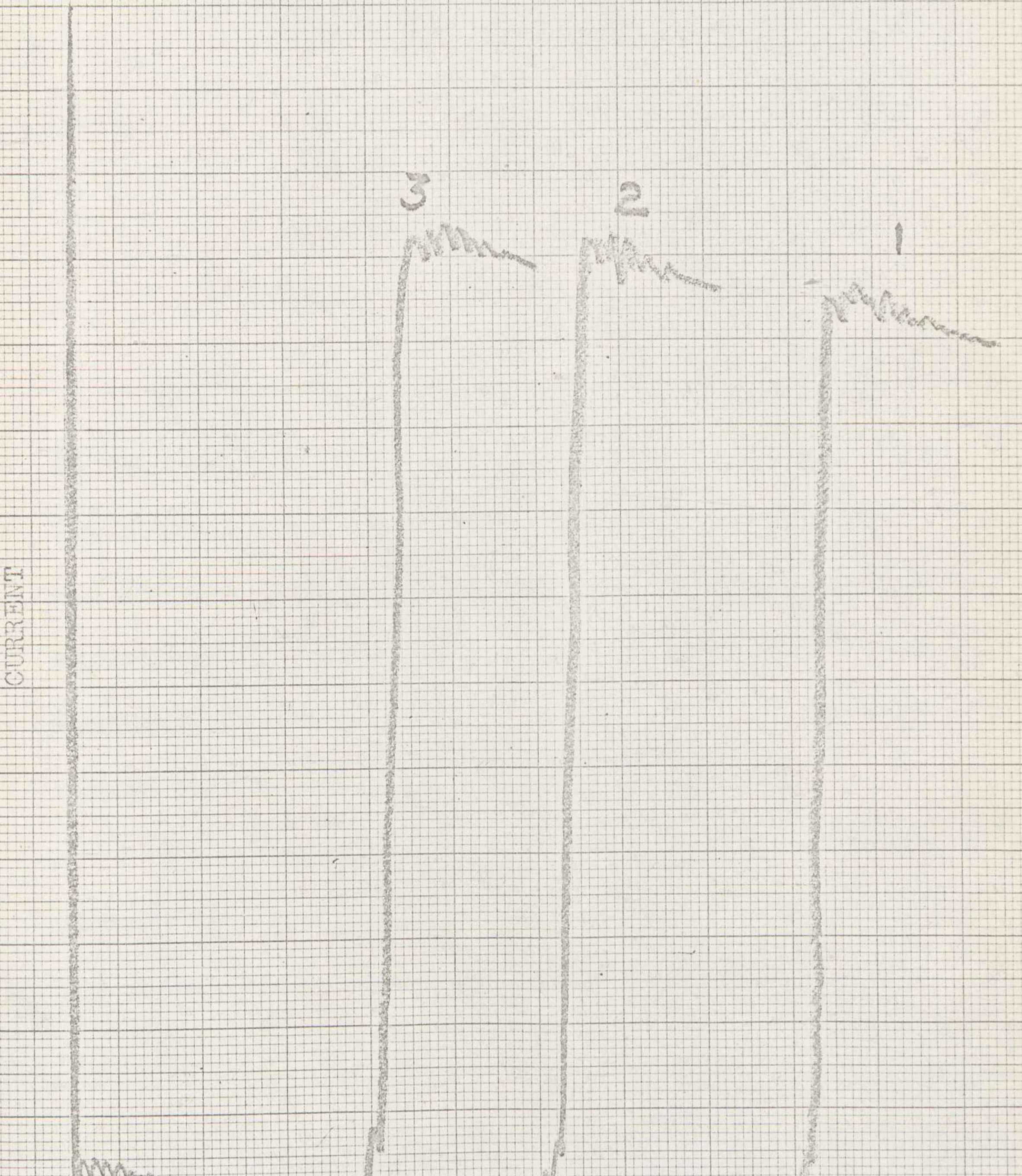


TABLE VI

Length of time N_2 bubbled	Length of time before step appears
500 s.	26.3 units
700 s.	11.1 "
1200 s.	17.8 "
1500 s.	33.0 "

It was then remembered that mercury had been present in the original samples, because of the physical setup of the polarograph. Up to this point all samples, both tetra and dicyanoaurate, were placed in the cell, the dropping mercury electrode installed, and then de-aerated for the necessary length of time. In each of these cases mercury was in contact with the gold complexes.

The relationship between the length of contact of mercury with the complex solutions was then investigated. The results seem apparent from the following table:

TABLE VII

Length of time Hg in contact with solution	Length of time before step appears
0 min.	33 units
8 "	9 "
0 "	19 "
60 "	0 "

Apparently, the step is the manifestation of mercury undergoing some sort of reaction. One possible reaction might be:

$$Au(CN)_4^- + Hg \longrightarrow Hg(CN)_2 + Au^+ + (CN)_2^{-2} \qquad (6)$$

Various attempts were made at determining if any other conditions were responsible for the step in the current-time plot. The study investigated the possibility of the step time being contingent on the time the two solutions, the tetracyanoaurate solution and the supporting electrolyte, were mixed together. The data in the following table reveals the results of this study:

TABLE VIII

Length of time sol. mixed	Length of time before step appears
1 hr.	3.0
18 "	11.5
1 "	3.3
18 "	7.0
3 "	15.5
22 "	14.5
24 "	12.3
30 "	1.0

As can be seen, there appears to be no relationship between the time of mixing and the time of formation of the step. It should be noted that at this point, it was decided not to de-aerate the solution. Several test solutions surprisingly revealed no interference from oxygen as had previously been reported.

It was also proposed that the actual increase in current might be due to the following reaction:

$$Au(CN)_4^- \longrightarrow (CN)_2^\circ + Au(CN)_2^- \qquad (7)$$

If this were the case, the step should be related to the concentration of $Au(CN)_4^-$. The following table contains the results of this part of the experiment:

TABLE IX

Conc. ($Au(CN)_4^-$)		Length of time before step appears
1T	7.5×10^{-3}M.	192 μ amp.
	"	143
	"	218
	"	202
2T	5.0×10^{-3}M.	292
	"	291
	"	330
3T	3.7×10^{-3}M.	257
	"	186
	"	282
	"	325
5T	1.2×10^{-3}M.	180
	"	16
	"	245
	"	210

As can be seen, the step does not appear to be dependent on the concentration of the tetracyanoaurate complex.

A typical phenomenon that occurred sporadically was a half-wave potential of -.45 volts. This voltage is generally assigned to the $Au(OH)_4^-$ complex. Since a reduction wave has been observed at this potential, it seemed safest to assume that some amount of $Au(OH)_4^-$ is present in solution. As Neddermeyer observed, the half-wave potential is very dependent on the concentration of the CN^-. However, extrapolation of his data indicates that the concentration of the CN^- ion would have to be in the order of 10 M for a shift to -.45 volts to take place. This possibility is therefore ruled out. This again only leaves the possibility of the $Au(OH)_4^-$ complex being present. A proposed reaction for its formation in aqueous or basic solutions is the following:

$$Au(CN)_4^- \rightleftharpoons Au(CN)_3(OH)^- \rightleftharpoons Au(CN)_2(OH)_2^- \rightleftharpoons Au(CN)(OH)_3^- \rightleftharpoons Au(OH)_4^- \qquad (8)$$

Another point to consider is the occasional shifting of the half-wave potential to more positive potentials. Such a shift is generally attributable to a loss of a complex. This similarly might indicate the destruction of the tetracyanoaurate complex.

Thus far, the various possibilities of what is happening have been discussed. Observations seem to support the propositions that the mercury is affecting the stability of tetra-complex either by reacting with it or by catalyzing another reaction, and, that a displacement reaction of the type (8) may be occurring.

It must be remembered at this point that the concentration of the supporting electrolyte was maintained at 10^{-2}M. throughout the project. This, in effect, cancels all the propositions of Neddermeyer and McClemens that in effect attribute the existence of various reductions steps and the shifting of various half-wave potentials to the variation of the supporting electrolyte concentration and the accompanying variation of the ionic strength.

As seen in the discussion above, the presence of mercury has an immense effect on the formation of the step of the constant potential polarogram. It must be noted, however, that the shift in the step also occurs, although much more slowly, even if mercury is excluded from the solution initially. This, therefore, seems to support the fact that mercury is acting as a catalyst in the reaction which is responsible for the step.

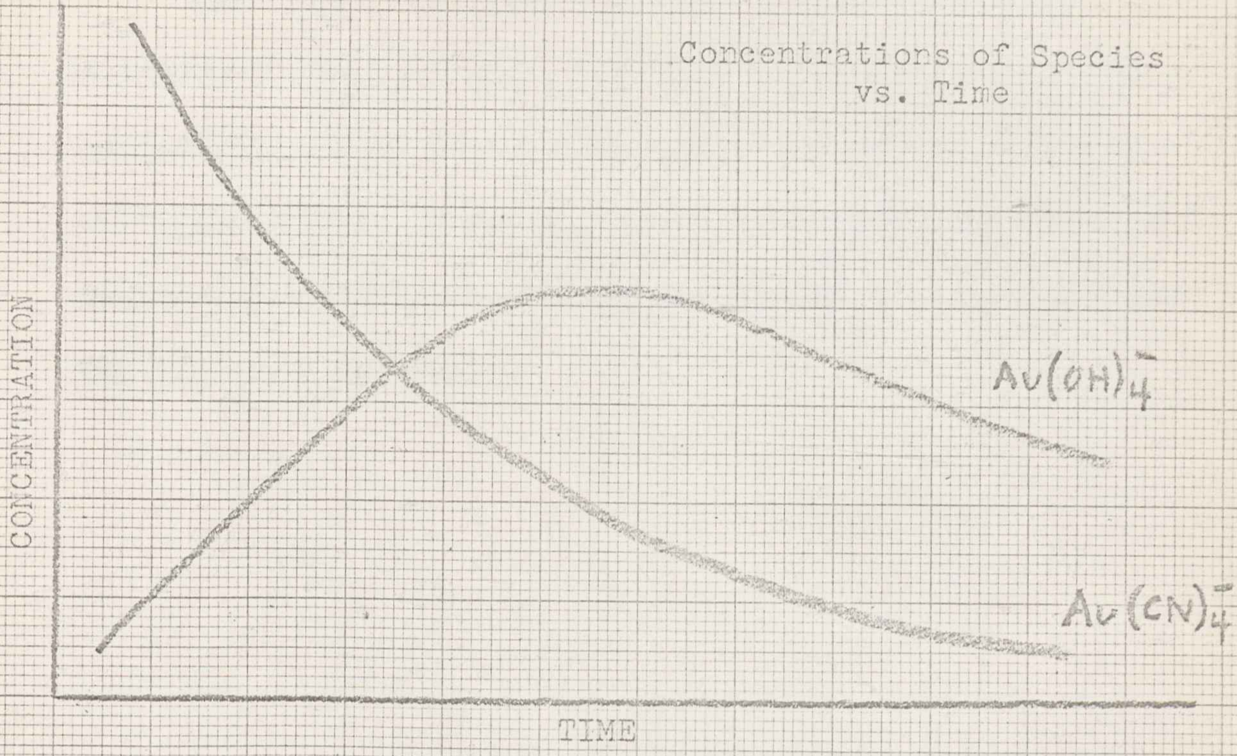
The following is a proposed reaction mechanism for the shifting of the half-wave potential and its modification as observed in an ordinary polarogram and for the increase in current through the cell as observed in a constant potential polarogram:

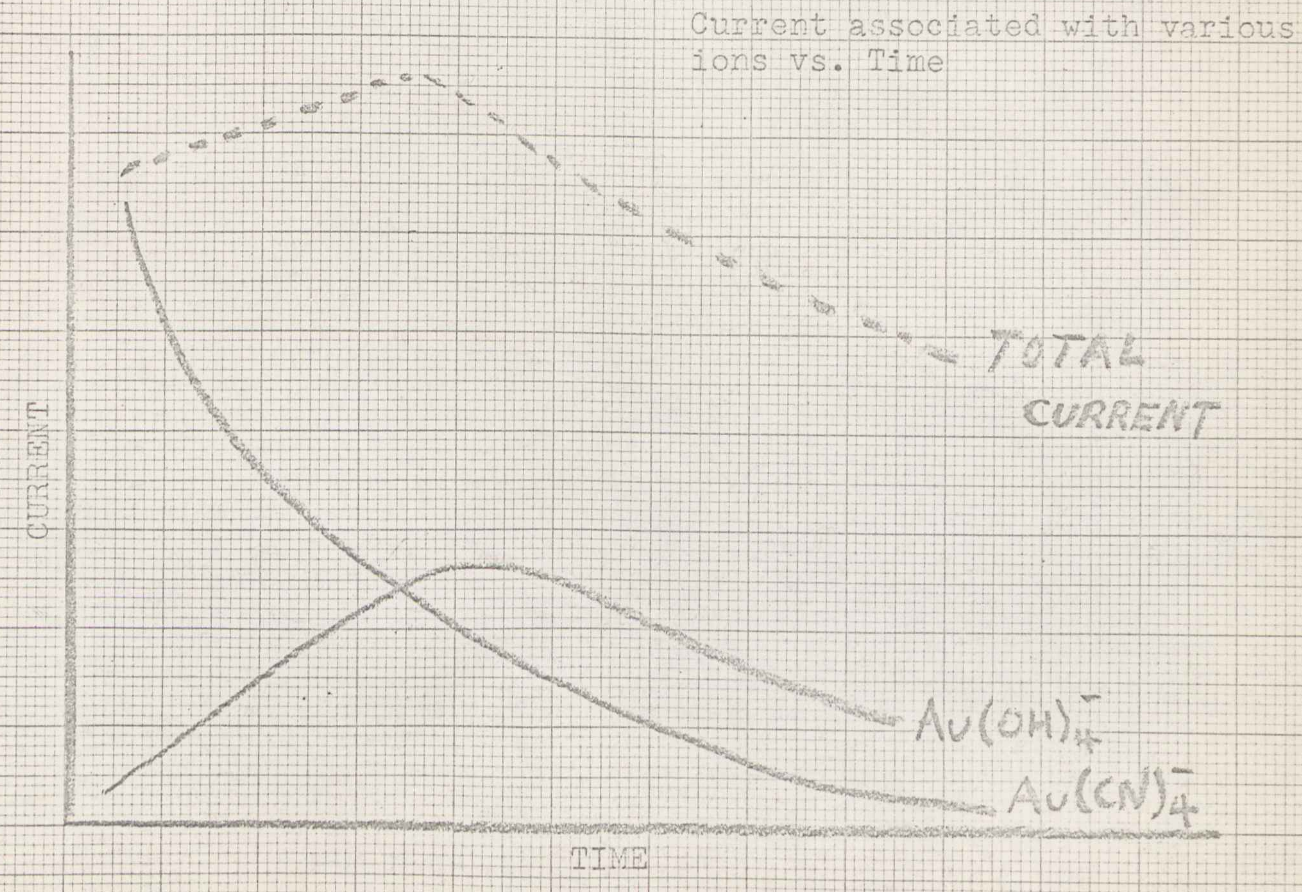
$$\mathrm{Au(OH)_4^-} \rightleftharpoons \text{various intermediates} \rightleftharpoons \mathrm{Au(CN)_4^-} \rightleftharpoons \mathrm{Au^+} + 4\ \mathrm{CN^-} \tag{9}$$

Plate IX shows a possible theoretical relationship between the species in the proposed reaction above. It is proposed that this equilibrium reaction takes place forming the two species $\mathrm{Au(OH)_4^-}$ and $\mathrm{Au(CN)_4^-}$ and their intermediates. Various polarograms have revealed the presence of different reducible species. It is also thought that the mercury, considering this newest information, acts solely as a catalyst in the above reaction (9).

If it is assumed that initially only $\mathrm{Au(CN)_4^-}$ is present, then the concentration curve for $\mathrm{Au(OH)_4^-}$ shown in Plate IX is appropriate. This conversion takes place slowly. However, once an appreciable amount of $\mathrm{Au(OH)_4^-}$ is created, its reduction produces a longer and larger diffusion current. The rapidity of the current increase in the constant potential polarogram may now be explained by saying that the mercury catalyzes the $\mathrm{OH^-}$ exchange reaction. This point may further be elaborated by stating that a certain minimum amount of mercury must be present before this catalysis becomes effective.

PLATE IX


Concentrations of Species vs. Time


Current associated with various ions vs. Time

The effect of combining the diffusion currents associated with the reduction of both $Au(OH)_4^-$ and $Au(CN)_4^-$ ions would result in a larger current flowing through the cell (Plate IX). This then is a proposition for the observed current increase through the cell as revealed by the current-time plots.

CHAPTER V

CONCLUSIONS

This experiment has not led to its initial goal: securing simultaneous determinations of the dicyanoaurate and tetracyanoaurate complexes in the same solution. The dicyanoaurate complex has been found to have essentially the characteristics assigned to it by Neddermeyer and McClemens. Some of the points noted by Neddermeyer and McClemens were not found to be true in this year's project.

The tetracyanoaurate complex was found to be much more unstable than had been previously thought. Much of the previous data could not be clearly reproduced. A more thorough investigation of many of the characteristics of the tetracyanoaurate complex than had previously been done was undertaken. From this investigation, two conclusions have been drawn. First, the tetracyanoaurate complex is quite unstable and perhaps in equilibrium with various hydroxo hybrid forms. Only more research will clearly decide this question. Secondly, the feasibility of presently running simultaneous determinations of both complexes seems more remote than had previously been thought.

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APPENDIX

This program provides a rapid means of calculating the slope and y intercept of the linear equation: $y = mx + B$. This program is intended for use in a chemistry research project dealing with a polarographic analysis of gold cyanides. In this project it is necessary to create several accurate linear calibration curves from experimental data. One of the most accurate methods available for fitting a linear equation to empirical data is based on the least-squares method of analysis. This U C Fortran program is based on this method.

The principle of least squares asserts that the best representative curve is that for which the sum of the squares of residuals is a minimum. When this condition is algebraically applied to the general equation, the following results (9):

$$M \text{ (slope)} = \frac{(n)\ \Sigma_{YiXi} - \Sigma_{Xi}\ \Sigma_{Yi}}{(n)\ \Sigma_{Xi}{}^{2} - (\Sigma_{Xi})^{2}}$$

$$b \quad = \frac{\Sigma_{Xi}{}^{2}\ \Sigma_{Yi} - \Sigma_{Xi}\ \Sigma_{XiYi}}{(n)\ \Sigma_{Xi}{}^{2} - (\Sigma_{Xi})^{2}}$$

In order to compute the constants, M and b, several summations must be carried out. These make evaluation of the constants very laborious.

A flow chart for this purpose follows. DO loops are the basis of the summation calculations and the input of the original data (steps 2 through 10). N can readily be altered from 0 to 15 to accommodate data from various experiments. The liberal input specifications of the U C Fortran system are ideal for the wide range of data that are used.

FLOW CHART

write out (1)

read N (2)

read x(i) (3)

read y(i) (4)

calc.(n)$\Sigma x_i y_i$ (5)

calc.Σx_i (6)

calc.Σy_i (7)

calc.$\Sigma x_i \Sigma y_i$ (8)

calc.(n)Σx_i^2 (9)

calc.$(\Sigma x_i)^2$ (10)

calc.M,b (11)

PRINT M,b (12)

PAUSE (13)

```
LOAD SOURCE DECK
THEN PUSH START
      PRINT
      WRITE,U@C@FORTRAN@PROGRAM@FOR@THE
      WRITE,@CALCULATION@OF@M@AND@B@IN@
      WRITE,THE@LINEAR@EQUATION@Y@=@MX@
      WRITE,+@B@
      PRINT
      WRITE,USING@THE@LEAST@SQUARES@MET
      WRITE,HOD@OF@ANALYSIS
      PRINT
      DIMENSION X(15)
      DIMENSION Y(15)
    9 READ,N
      QN=N
      DO 7 I=1,N
      READ,X(I)
    7 CONTINUE
      DO 8 I=1,N
      READ,Y(I)
    8 CONTINUE
      SUMB=0.0
      DO 1 I=1,N
      SUMA=X(I)
      SUMA=X(I)*Y(I)
      SUMB=SUMB+SUMA
    1 CONTINUE
      SUMC=SUMB*QN
      SUME=0.0
      DO 2 I=1,N
      SUMD=X(I)
      SUME=SUME+SUMD
    2 CONTINUE
      SUMG=0.0
      DO 3 I=1,N
      SUMF=Y(I)
      SUMG=SUMG+SUMF
    3 CONTINUE
      SUMH=SUME*SUMG
      SUMI=SUMC-SUMH
      SUMQ=0.0
      DO 4 I=1,N
      SUMP=X(I)
      SUMP=X(I)*X(I)
      SUMQ=SUMQ+SUMP
```

```
4 CONTINUE
  SUMR=SUMQ
  SUMR=SUMQ*QN
  SUMT=0.0
  DO 5 I=1,N
  SUMS=X(I)
  SUMT=SUMT+SUMS
5 CONTINUE
  SUMU=SUMT**2.
  SUMV=SUMR-SUMU
  SLOP=SUMI/SUMV
  ADDB=0.0
  DO 6 I=1,N
  ADDA=Y(I)
  ADDB=ADDB+ADDA
6 CONTINUE
  TOPA=SUMQ*ADDB
  TOPB=SUMT*SUMB
  TOPT=TOPA-TOPB
  B=TOPT/SUMV
  PRINT,SLOP,B
  PAUSE
  GO TO 9
  END
```

DATA INPUT SPECIFICATIONS (U C FORTRAN PROCESSING SYSTEMS)

N input: a fixed point variable of the form:

XX where X = a digit

Concentrations and diffusion currents: a floating point number of the form:

XX.X X = a digit

Data is entered one value per card, starting in the left most column. Not necessary to sign these values.