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A POLAROGRAPHIC INVESTIGATION OF COBALT SULFATE

by

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I INTRODUCTION

Although the polarographic behavior of cobalt and its various compounds and complexes have been intensively investigated using the dropping mercury electrode, there has been virtually no published data on the voltammetry of cobalt using a mercury pool electrode. Therefore, it was felt that a voltammetric investigation of cobalt in the form of $CoSO_4 \cdot 7H_2O$ using both the dropping mercury electrode and the mercury pool electrode might prove fruitful in that the two methods could be compared and the feasability of using the mercury pool method as an analytical tool for cobalt might be evaluated.

A. Historical Background

Since the first polarographic measurements were made in 1921 by Professor Iaroslav Heyrovsky at the Charles University in Prague, the field of voltammetry has received considerable attention. Not only have innumerable techniques been developed for use at the dropping mercury electrode, but also various new types of polarizible electrodes have been developed in order to further extend the usefulness of the voltammetric method. Among these new types of electrodes is the mercury pool, and from this is derived the technique of mercury pool voltammetry.

Zlotowski (15), in connection with work on overvoltage, used a mercury pool electrode to investigate polarization phenomena. Cooke and his associates in a series of papers (13, 14, 11) studied the characteristics of the mercury pool electrode and evaluated it as an analytical tool.

Among other things, it was found that the method was 25 to 40 times more sensitive than with the dropping mercury electrode, and consequently it is possible to extend the range of useful analysis to solutions which are several fold more dilute than the limits with the dropping mercury electrode permit. It was also found that the peak heights were proportional to concentration and scan rates, and that the half wave potentials shifted slightly with concentration.

B. Purpose

The voltammetric investigation of cobalt was carried out by analysing solutions of $CoSO_4 \cdot 7H_2O$ and using K_2SO_4 as a supporting electrolyte. It was believed that the data obtained when using the dropping mercury electrode should be of the same nature as the data obtained when using the mercury pool electrode so that the two methods could be readily compared. Hence, a study of the effect of drop time and capillary characteristics upon the diffusion currents and half wave potentials was not deemed important, since there is no corressponding analog when using the mercury pool electrode. Instead, the correlation of diffusion currents with the concentration of $CoSO_4 \cdot 7H_2O$, and the reproducibility of the half wave potential with scan rate and concentration of $CoSO_4 \cdot 7H_2O$ were studied.

Once data was secured using the dropping mercury electrode, then the same solutions would be evaluated using the mercury pool electrode. If a peak could be found for cobalt, then the same factors as considered with the dropping mercury electrode would be investigated.

II THEORY

The standard polarographic technique consists of evaluating the current-voltage plots obtained when an external potential is applied to a dropping mercury electrode and ions are reduced at the mercury drop surface. A discussion of the principles and applications of polarography are given in books by Kolthoff and Lingane (3.), and Meites (4), and its principles are so widely known that they need not be discussed here further except as a reference when describing the theory of mercury pool voltammetry.

The mercury pool electrode differs notably from the dropping mercury electrode in that the electrode, formed by a mercury reservoir connected to a capillary tube from which drops of mercury are permitted to fall, is replaced by a pool of mercury in the bottom of the cell.

An advantage of such an arrangement is that the electrode now has a large surface area and hence, is more sensitive, thereby allowing one to analyse solutions more dilute than those analysed using a dropping mercury electrode. In addition to this, the problems associated with the handling of the dropping mercury electrode would be eliminated.

A serious disadvantage of this new arrangement is that, since it is more sensitive, the presence of reducible impurities is much more of a problem than with the dropping mercury electrode. In addition to this, the electrode surface is not renewable and therefore the mercury pool must be changed regularly. A final objection is that the mercury pool electrode shows an increased sensitivity to the discharge of hydrogen (13), and therefore the useful voltage range with the mercury pool electrode is less than that with the dropping mercury electrode.

Figure 2 shows the characteristic peak obtained when an ion is reduced using a mercury pool cathode. Although equations have been developed (2, 10, 12) to account for these curves, perhaps a better insight can be gained by accounting for the shape of the plot qualitatively.

As a solution is being scanned and the reduction potential of a given ion is being approached, there will be an increase in current and hence a rise in the curve. If one were using a dropping mercury electrode, this rise would continue until the diffusion current was reached, after which the current would start to level off (figure 1). In the case with the mercury pool electrode, however, the current value drops sharply instead of leveling off. This is explained by the fact that the mercury pool cathode has a much larger surface area and hence the electrode is unable to establish a steady diffusion layer. Instead, there is a subsequent thickening of this layer with time due to an appreciable depletion of the reducible species in the solution. This results in a drop in current and hence a drop in the current-voltage plot.

As the rate of scan increases, the height of the peak of a given reducible species also increases. This phenomena occurs because the diffusion layer will not be able to expand as fast with an increase in scan rate. Therefore, there will be a greater peak height due to a larger flow of reducible ions.

FIGURE 1: CONVENTIONAL POLAROGRAM FOR $CoSO_4 \cdot 7H_2O$ IN 0.01N K_2SO_4 SHOWING GRAPHICAL METHOD OF DETERMINING I_d & $E_{\frac{1}{2}}$

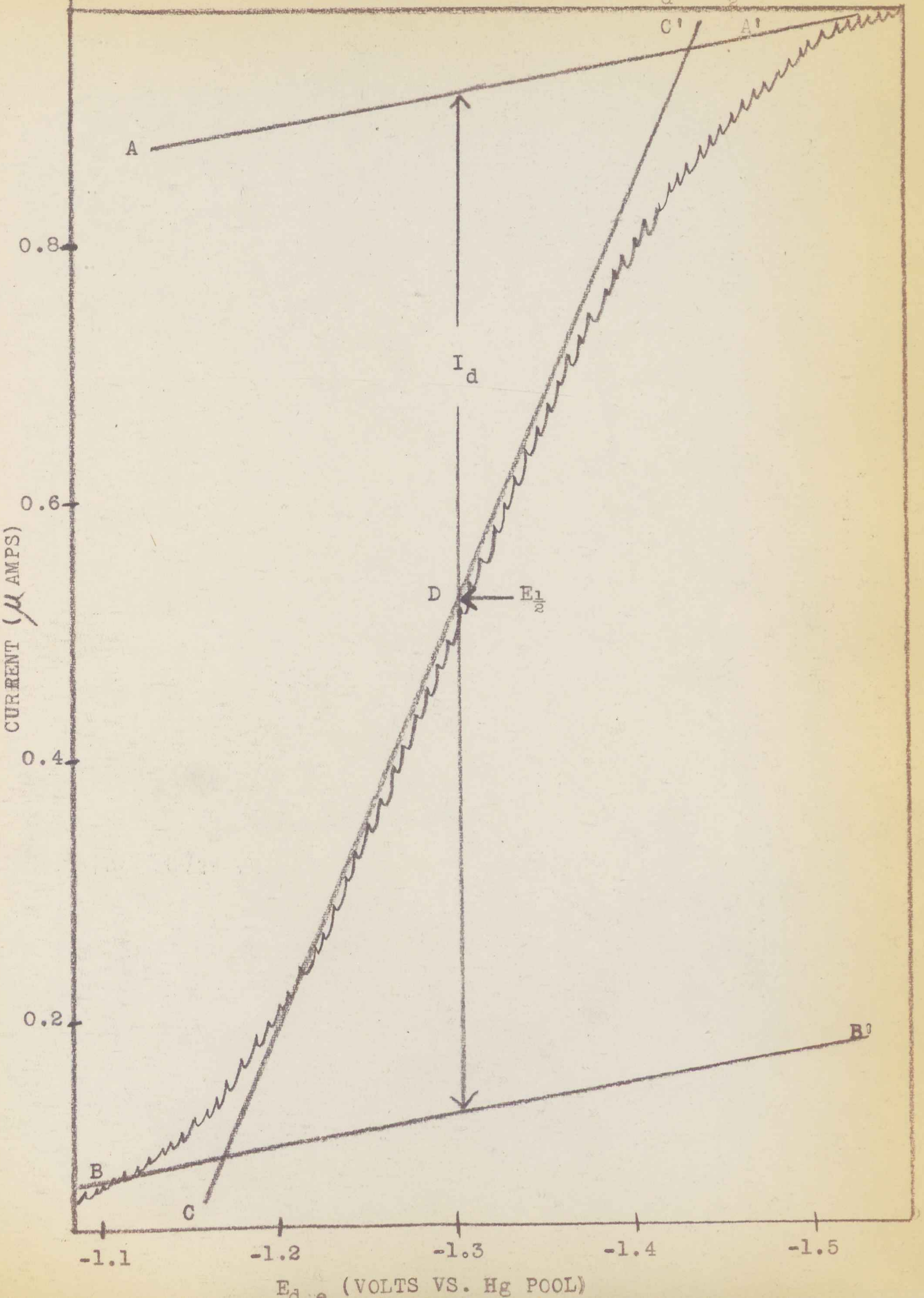
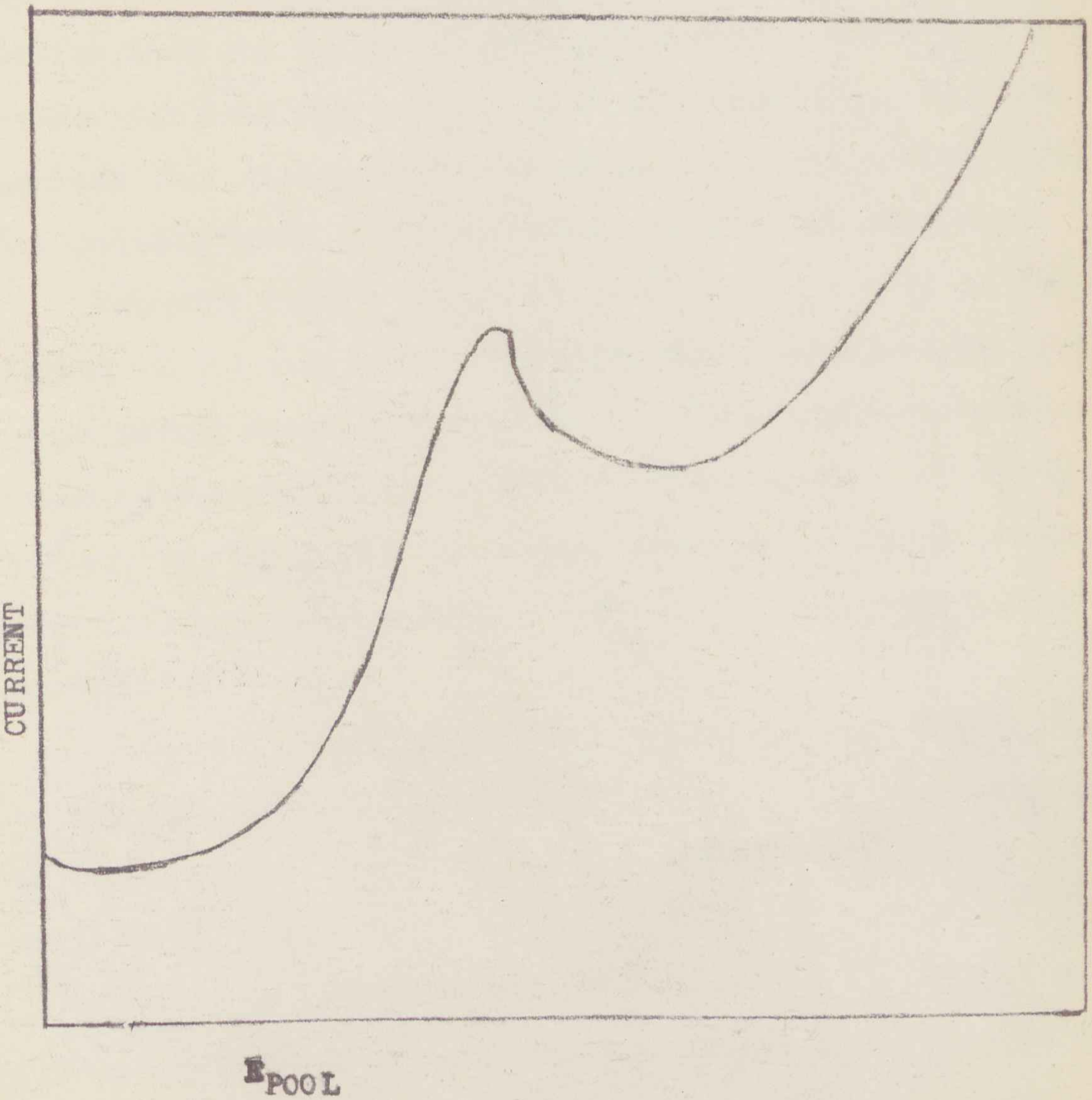


FIGURE 2

CURRENT-VOLTAGE PLOT OF A TYPICAL REDUCIBLE ION USING A MERCURY POOL ELECTRODE



III EXPERIMENTAL

A. The Dropping Mercury Electrode

The cell used in these studies is shown in figure 3. It was used both for the dropping mercury and mercury pool electrodes. When set up for dropping mercury studies, it is necessary to put the capillary through a rubber stopper which is in turn inserted through the top of the cell. The reference anode for the dropping mercury electrode is the mercury pool which is formed at the bottom of the cell. A platinum wire sealed into the bottom of the cell provided the electrical connection from the mercury pool to a side arm. The side arm was then filled with more mercury and the positive end of the polarographic leads was inserted into the side arm.

The cell itself consisted of a 12cm. pyrex glass tube. Sealed in the bottom is a sintered glass bubbler made from pyrex glass powder between 140-200 mesh. This bubbler provided a means of deaerating the solution by the passage of nitrogen through the solution. A two-way stopcock provided the means to pass nitrogen through before and over the solution during the voltammetric runs.

Attached to the pyrex tube is another side arm in addition to the one mentioned previously. This is for the reference electrode that is used in connection with the mercury pool electrode.

Since the purity of the mercury is not as crutial a factor in dropping mercury electrode work as in mercury pool studies, it was decided to work with used mercury that had been

Figure 3: THE MERCURY POOL ELECTRODE ASSEMBLY

A. Platinum Wire

B. Sintered Glass Disk

C. Nitrogen Inlet to Blanket Test Solution

D. Nitrogen Inlet to Purge Test Solution

E. Reference Electrode Compartment

F. Solution Compartment

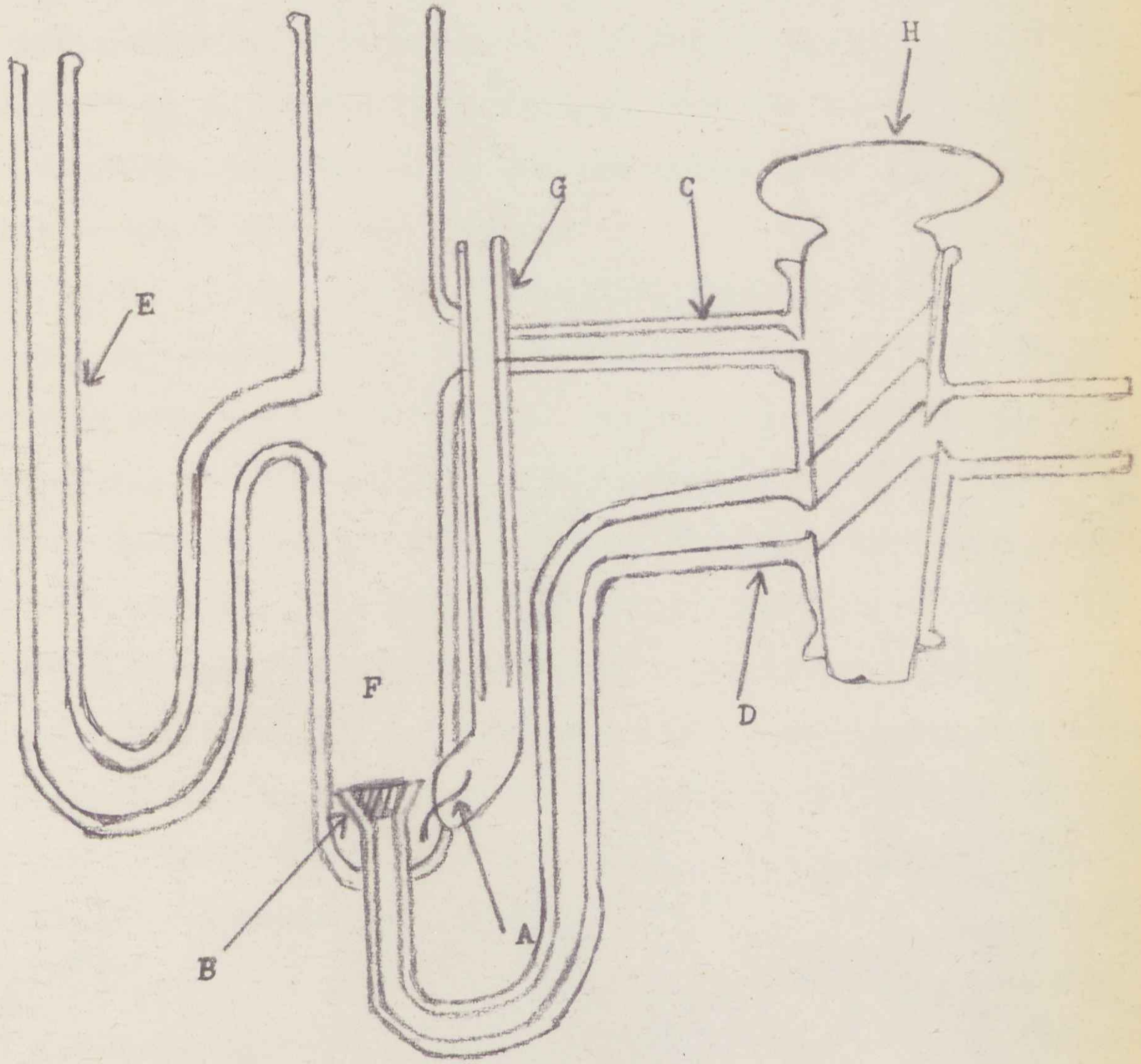
G. Lead Wire Compartment

H. Two Way Stopcock

FIGURE 3

THE MERCURY POOL ELECTRODE ASSEMBLY

(ACTUAL SIZE)



recleaned by first removing water, then subjecting it to a mercury oxifier for a few hours, and finally filtering it through a type "G" mercury filter.

It was necessary in the course of the analysis to remove oxygen that was dissolved in the solutions. This was done by passing Olin Matthinson prepurified grade nitrogen (99.996% minimum purity and an oxygen content of 8 ppm) through copper turnings, which were packed in a combustion tube and heated to 400-450°C in a Sargent model tubular electric furnace (cat. no. S-36517), from which the gas was passed into the test solution via the fritted bubbler.

It was decided that the procedure would be to pass nitrogen through the solution for fifteen minutes at a fairly vigorous bubbling rate and then over the solution at a somewhat smaller rate during the actual run. This treatment proved satisfactory for the duration of the work with the dropping mercury electrode. All connections in the nitrogen inlet system were of tygon tubing.

The Sargent model XXI polarograph was used in all of the studies, both with the dropping mercury and mercury pool electrodes. No provisions were made for damping the current fluctuations, and all the polarograms were obtained with only the natural period of the recorder limiting the pen movement.

All chemicals used were either C.P. or reagent grade and all solutions were made with distilled water. The $CoSO_4 \cdot 7H_2O$ solutions were prepared by the dilution of a 0.01N stock solution. The K_2SO_4 supporting electrolyte was 0.1N with respect to all test solutions.

The actual procedure used when working with the dropping mercury electrode consisted of adding 4 cc. of the cobalt solution and 4 cc. of 0.2N K_2SO_4 to the cell. 1.5 cc. of mercury was then added to provide an initial amount of mercury for the mercury pool reference anode. The solution was then treated with nitrogen as explained above and the polarographic data was then obtained.

In cases where maxima appeared, it was necessary to add a couple of drops of triton X-100 stock solution. The stock solution was prepared by shaking 0.2 grams of triton X-100 with 100 cc. of distilled water.

The pH of all the solutions analysed was 6.0±0.1 as measured on the model H2 Beckman glass electrode pH meter. All half wave potentials obtained by using the dropping mercury electrode are reported in this paper in reference to a mercury pool anode.

B. The Mercury Pool Electrode

As mentioned earlier, the cell used for the dropping mercury electrode was also used for the mercury pool electrode. In this procedure the mercury pool reference anode of the dropping mercury electrode analysis now becomes the polarizable mercury pool cathode of the mercury pool electrode analysis. In this case the negative end of the polarograph's leads is inserted into the side arm.

The reference electrode consists of a small helix of silver wire that has been chloridized by a brief anodic treatment in dilute HCl. The Ag, AgCl cell was made by filling up the side arm half way with saturated K_2SO_4 solution. Then saturated KCl solution was added to the outer end of the side arm until the level reached the junction of the side arm and the cell.

The silver wire was then placed in the side arm and was held in place by a small cork. As a matter of procedure, the silver wire was rechloridized at the beginning of each working day.

Triple distilled mercury was used in the mercury pool analysis. It was found that persistant irregularities in the current-voltage plots could be reduced by allowing the mercury to remain for approximately 24 hours in a grease-free buret before dispersing (13).

All chemicals were either C.P. or reagent grade. The K_2SO_4 was recrystalized once before making up the supporting electrolyte solution. All solutions were made with doubly distilled water. The pH of the solutions were all 6.0±0.1 as measured on the model H2 Beckman glass electrode pH meter.

The above techniques were basic to all the work with the mercury pool electrode. In the initial stages of this investigation, 6 cc. of 0.2N K_2SO_4 were added to 6 cc. of $CoSO_4 \cdot 7H_2O$ solution and then 2 cc. of mercury were added to form the pool. The solution was deserated for fifteen minutes after which the solution was scanned voltaically. After several different runs proved fruitless in that no peak characteristic of cobalt could be located, a new procedure was initiated.

It was decided to add 5 cc. of 0.2N K_2SO_4 and 5 cc. of doubly distilled water to the cell, add 2 cc. of mercury, and deaerate for fifteen minutes. Then, varying amounts of 0.01N $CoSO_4 \cdot 7H_2O$ stock solution were added to the cell and nitrogen was passed through the solution for a couple of minutes more in order to mix the solution and remove any traces of oxygen. Nitrogen was passed over the solution during the actual run.

In a modification of this procedure, a couple of drops of a very dilute solution of $NaHSO_3$ were added to the blank solution in order to just pick up the peak for the reduction of the bisulfite ion. The resulting solution was then deaerated again for a couple of minutes in order to mix the solution and remove any further traces of oxygen. The solution was then scanned voltaically in order to obtain a current-voltage plot of the solution without the presence of cobalt. Then a small amount of the 0.01N $CoSO_4 \cdot 7H_2O$ stock solution was added and the solution was again deaerated and run through the polarograph to see what, if any, changes occured.

The purpose of the addition of the bisulfite ion was to remove any traces of oxygen and to see if the presence of the bisulfite ion would produce a cobalt peak due to the formation of a complex of the cobalt with the bisulfite.

IV RESULTS

A. The Dropping Mercury Electrode

The half wave potentials and diffusion currents of the polarograms obtained by using the dropping mercury electrode were evaluated as shown in figure 1. In this procedure, a line AA' is drawn across the peaks of the oscillations on the plateau and another line BB' is drawn across the peaks of the oscillations on the portion of the curve just preceding the rising portion of the wave. Then a line CC' is drawn across the peaks of the oscillations on the steepest part of the wave, and a point D is found on CC' which is equidistant from AA' and BB'. This point represents the half wave potential and was found by moving a ruler across the polarogram perpendicular to the voltage axis. The diffusion current was then taken to be equal to the perpendicular distance between lines AA' and BB' at the half wave potential, measured in millimeters, times the sensitivity setting measured in microamps per millimeter.

This procedure is exactly the same as that suggested by Meites (5), except that the use of the mid-points of the oscillations is recommended instead of the peaks in drawing the lines. It was decided to use the peaks because the polarograph operating manual suggested doing so.

Table 1 presents data on the effect of the concentration of cobalt on the half wave potential and diffusion current. The table shows that the diffusion current due to the reduction of cobalt (II) ions is directly proportional to the concentration. This is also shown in figure 4 where the diffusion current is plotted versus concentration. It is also seen that the half

TABLE 1

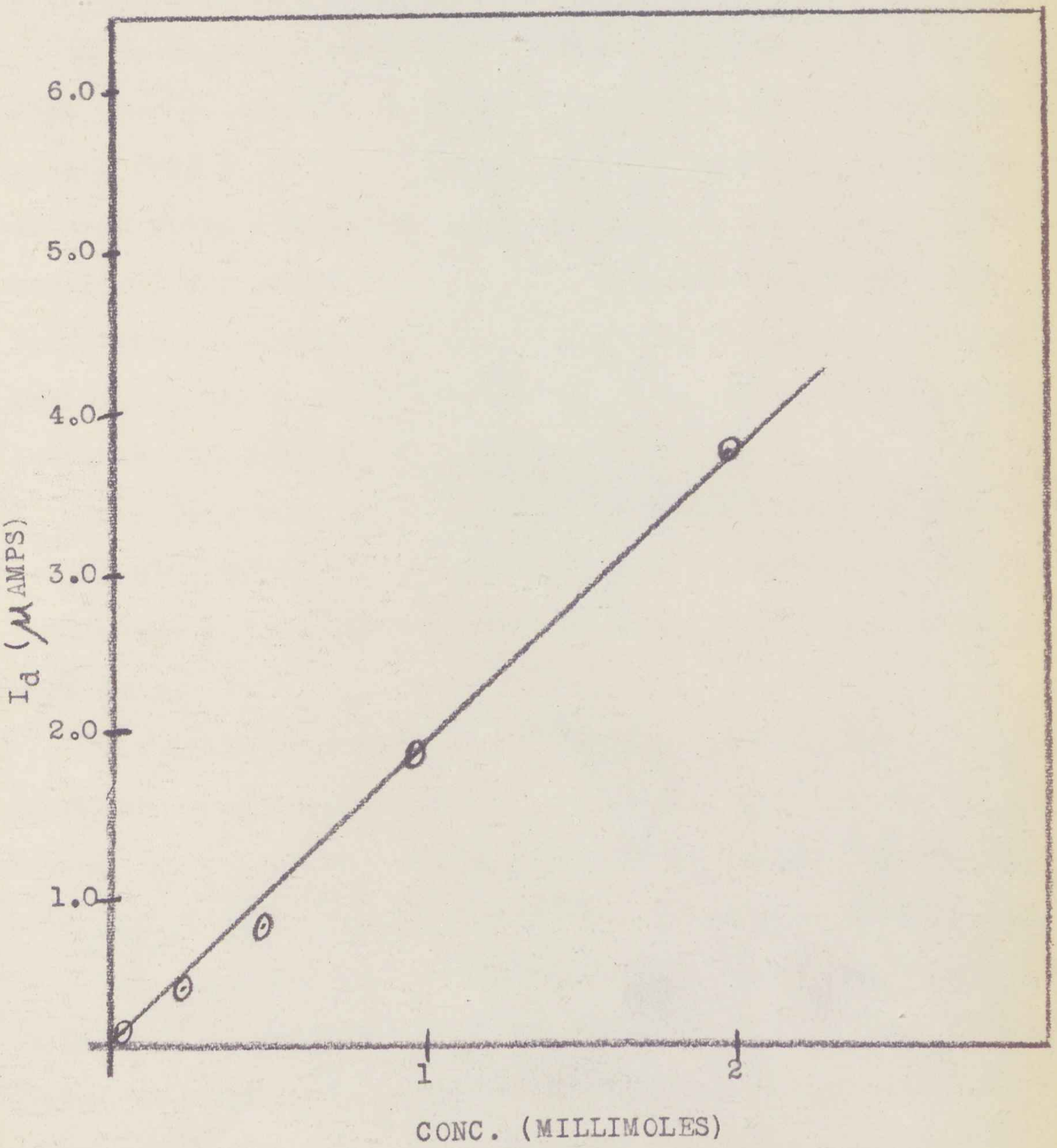
EFFECT OF CONCENTRATION ON $E_{\frac{1}{2}}$ AND I_d[1] USING THE DME

Conc. $CoSO_4 \cdot 7H_2O$, mm	Sensitivity, μa/mm	$E_{\frac{1}{2}}$	I_d, μa	I_d/C
8.00	0.080	-1.68	17.36	2.17
4.00	0.040	-1.61	8.36	2.09
2.00	0.020	-1.57	3.76	1.88
1.00	0.020	-1.56	1.82	1.82
0.50	0.010	-1.56	0.79	1.58
0.25	0.006	-1.48	0.40	1.60
0.05	0.003	-1.50	0.06	1.20

[1] Using a scan rate of 2.5 volts/13.5 min. and an initial drop time of 8±1 sec.

FIGURE 4

PLOT OF I_d VS. CONCENTRATION USING DATA FROM TABLE 1



wave potential is shifted to more positive values as the concentration is decreased.

Table 2 shows the influence of scan rate on the diffusion current and half wave potential. It shows that the half wave is shifted to more positive potentials and the diffusion current is reduced as the scan rate is increased.

It can be seen upon comparison of tables 1 and 2 that the half wave potentials in table 2 are all shifted to more positive values than those of table 1. The only change in procedure that occured while taking the data for table 2 was that a different capillary was used with a shorter initial drop time. Since the half wave potentials are independent of the capillary characteristics, m, the mass of the mercury drop, and t, the drop time, no suitable explanation can be given.

The fact that the half wave potential shifts to less negative values with decreasing concentration of reducible cobalt ion is indicative of an irreversible reaction (6) and will be investigated presently.

The increase in the I_d/C constant with increasing concentration can perhaps be explained by the fact that at higher concentrations, the period of the recorder pen is larger and therefore may tend to give slightly higher than predicted diffusion currents.

The apparent rise in the diffusion current with scan rate in table 2 is perhaps analogous with the rise of peak height with increasing scan rate using the mercury pool electrode. This suggests that the diffusion layer is not set up as fast with an increase in scan rate and hence the diffusion current will be slightly higher than predicted due to a greater flow of reducible

TABLE 2

EFFECT OF SCAN RATE ON $E_{\frac{1}{2}}$ AND I_d[2] USING THE DME

Scan Rate, Volts/13.5 min.	$E_{\frac{1}{2}}$	I_d, μa
3.0	-1.38	0.93
2.0	-1.37	0.89
1.5	-1.35	0.86
1.0	-1.30	0.80
0.5	-1.30	0.74

[2] At a concentration of 2.5×10^{-4}M $CoSO_4 \cdot 7H_2O$ with a sensitivity of 0.004 and an initial drop time of 6 sec.

The apparent shift of the half wave potential to slightly more positive values with a decrease in scan rate in table 2 can be considered practically negligible. Its occurence is perhaps due to a slower recorder response at higher scan rates.

It was mentioned earlier that the shift of the half wave potential to more positive values with decreasing concentration was indicative of an irreversible reaction. Via the method explained by Meites (7), it is possible to prove that the reduction of cobalt (II) is an irreversible process. This may be shown as follows.

Assuming that the reduction process takes place as

(1) $Co^{++} + 2e + Hg = Co(Hg)$,

then it can be shown that

(2) $E_{d.e.} = E_{\frac{1}{2}} - \frac{0.0591}{n} \log \frac{i}{i_d - i}$

where $E_{d.e.}$ = potential of the DME

i_d = diffusion current

i = current at $E_{d.e.}$

$E_{\frac{1}{2}}$ = half wave potential

Therefore, if the process is reversible, a plot of $E_{d.e.}$ versus the log $\frac{i}{i_d - i}$ should be a straight line whose slope is equal to $-\frac{0.0591}{n}$ volts at 25°C and whose zero intercept should be the half wave potential of the cobalt ion. Figure 5 is a plot of this using data obtained from the wave illustrated in figure 1.

TABLE 3

PLOT OF $E_{d.e.}$ VERSUS LOG $\frac{i}{i_d-i}$ (FIGURE 5), DATA TAKEN FROM FIG. 1

Solution = 2.5×10^{-4}N $CoSO_4\cdot7H_2O$

Scan Rate= 1 volt/13.5 min.

Initial Drop Time = 6 sec.

Sensitivity = .004μa/mm

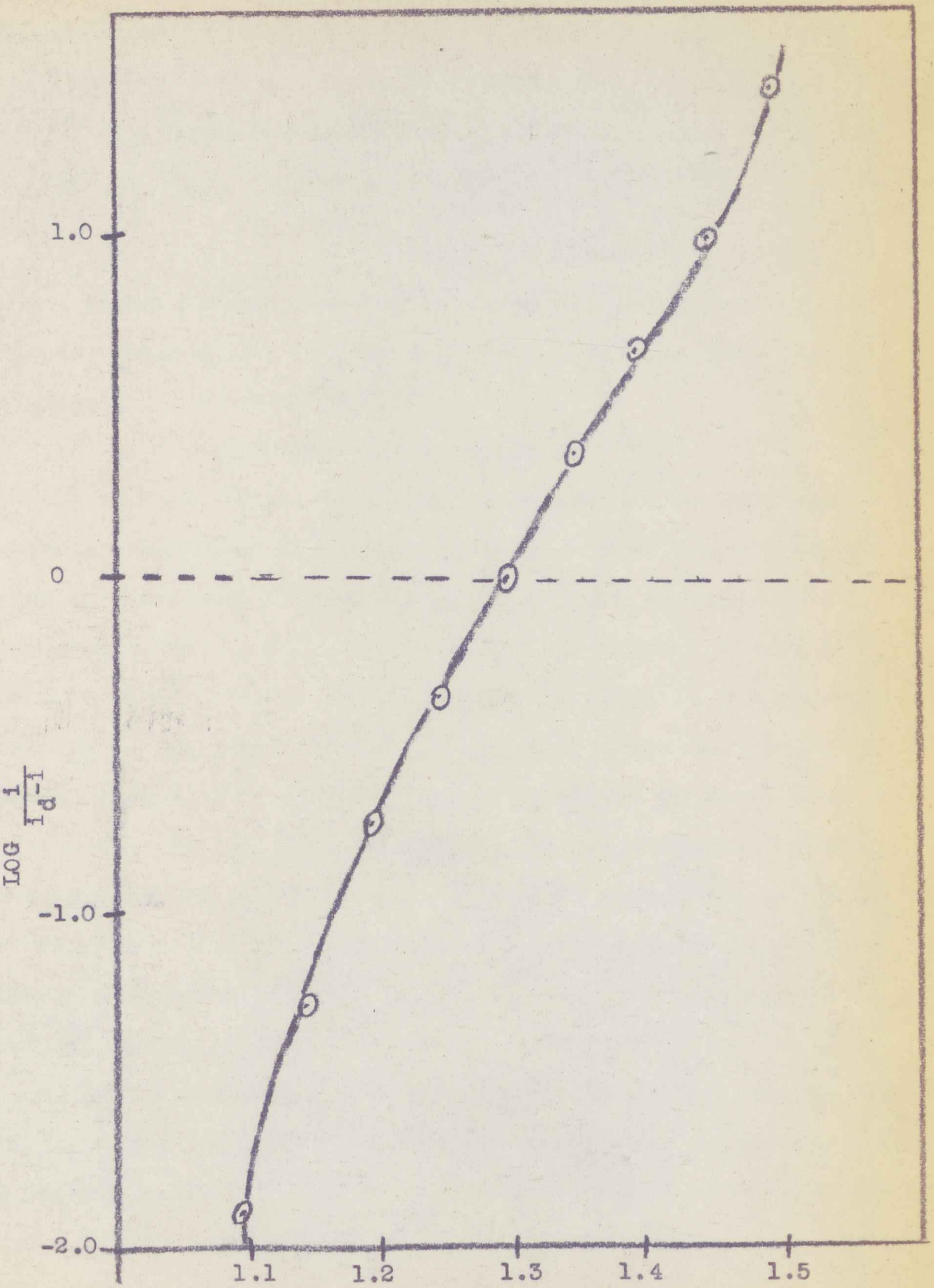
I_d = 0.80μa

$E_{\frac{1}{2}}$ = -1.30 volts

$E_{d.e.}$,volts	i, μa	$\frac{i}{i_d-i}$	$\log\frac{i}{i_d-i}$
-1.10	0.01	0.0127	-1.896
-1.15	0.04	0.0526	-1.279
-1.20	0.12	0.177	-0.752
-1.25	0.24	0.428	-0.369
-1.30	0.39	0.952	-0.021
-1.35	0.52	1.86	0.270
-1.40	0.65	4.33	0.637
-1.45	0.72	9.00	0.954
-1.50	0.77	25.67	1.409

FIGURE 5

PLOT OF $E_{d.e.}$ VS. LOG $\frac{i}{i_d - i}$ USING DATA OBTAINED FROM FIGURE 1



As can be seen, there is no linear relationship and hence one must conclude that the reduction is an irreversible process.

Another method which can be used is also derived from Meites (8). If the reaction is reversible, then it may be shown that

$$(3)\quad E_{3/4} - E_{1/4} = \frac{-0.0564}{n} = -.0282$$

where n = 2 for $Co^{\#} \rightarrow Co(Hg)$

Table 4 shows the results obtained from analysing several different polarograms in this manner confirms the fact that the process is irreversible.

B. Mercury Pool Electrode

The results of the investigation using the mercury pool electrode could best be termed "erratic". When the method of adding an increment of 0.01N $CoSO_4 \cdot 7H_2O$ stock solution to a previously prepared blank is used, any one of four events is possible. First, there can be a positive shift in the hydrogen discharge of about 0.1 to 0.2 volts. Two, there can be the appearance of a peak whose half wave potential is about -0.8 volts versus the Ag, AgCl electrode. Three, there can be the appearance of the aforementioned peak plus a positive shift in the hydrogen discharge, or four, there can be no change in the polarogram at all. Figure 6 shows the characteristic peak mentioned above.

An interesting aspect of the appearance of the peak is that the peak gets higher with successive scans until it reaches a maximum height, after which, it starts to decrease in height. In fact, it is entirely possible to miss this peak on a first scan, if it decides to show up at all.

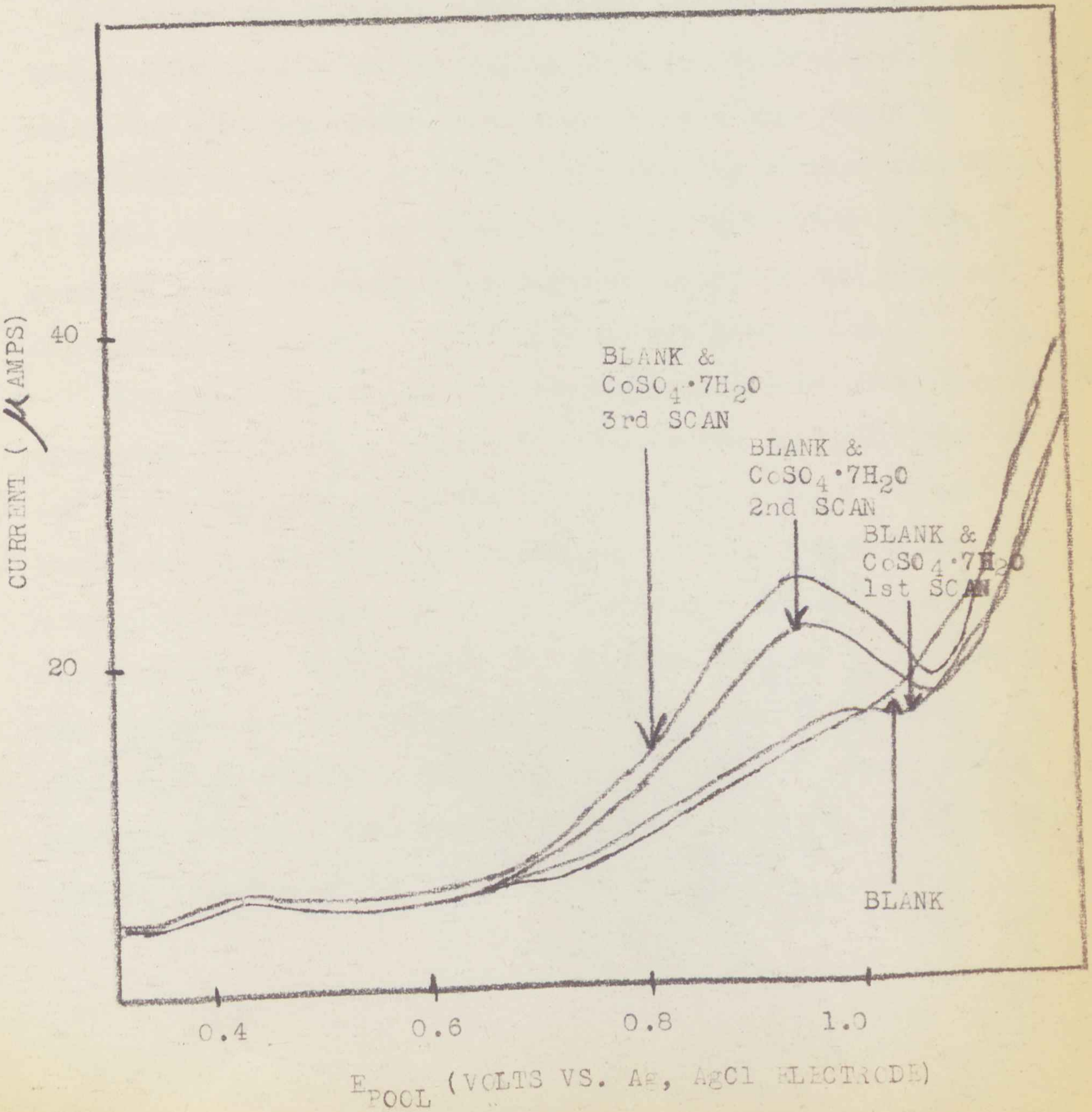
TABLE 4

TEST OF REVERSIBILITY OF Co USING THE $E_{3/4}-E_{1/4}= -0.0282$ CRITERIA

Conc. $CoSO_4 \cdot 7H_2O$, mm	Scan Rate, Volts/ 13.5 m	$E_{3/4}$	$E_{\frac{1}{4}}$	$E_{3/4}-E_{1/4}$
1.00	1	-1.600	-1.475	-0.125
1.00	2.5	-1.589	-1.513	-0.076
0.50	1	-1.615	-1.500	-0.115
0.50	2.5	-1.589	-1.513	-0.076
0.25	1	-1.515	-1.410	-0.105
0.25	1.5	-1.420	-1.280	-0.140
0.25	2.0	-1.538	-1.425	-0.113
0.10	1	-1.460	-1.360	-0.100

FIGURE 6

CURRENT-VOLTAGE PLOT SHOWING APPEARANCE OF PEAK ON SUCCESSIVE SCANS AFTER ADDITION OF 1cc 0.01N $CoSO_4 \cdot 7H_2O$ TO BLANK SOLUTION



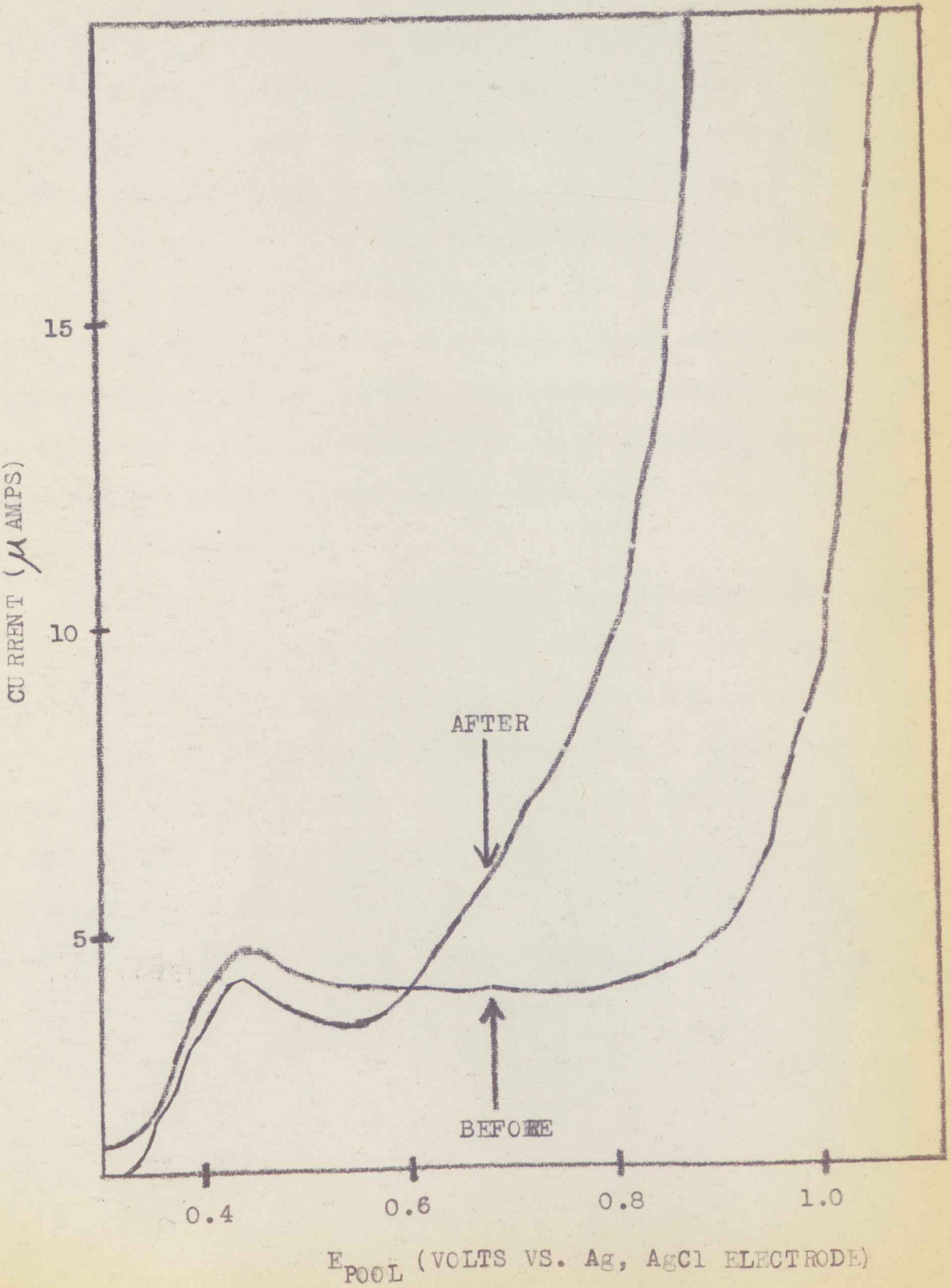
The question of whether or not this peak is due to the cobalt is as yet open to question. A reverse scan run on this peak showed no peak itself thereby indicating an irreversible process. Hence this does not eliminate cobalt. However, it does not eliminate oxygen, which also gives an irreversible wave, or any other irreversible reducible impurity in the solution. Since the size and appearance of this peak is rather erratic, the peak cannot be said to be definately due to the cobalt.

Perhaps the positive shift of the hydrogen discharge, though also erratic in nature, is of more significance. By assumming that the cobalt wave appears at a more negetive potential, as was the case with the dropping mercury electrode, it would no doubt not be seen. The only indication of its presence would therefore be a positive shift of the hydrogen discharge. This seems like a more likely conclusion.

The use of the bisulfite ion produced a peak whose half wave potential was at about -0.4 volts versus the Ag,AgCl electrode and was characteristic of the bisulfite ion alone. It was believed that the presence of the bisulfite ion might produce a complex with the cobalt and result in a complexed form which would manifest itself in a peak at a less negative potential and thereby bringing it off of the steep rise due to the discharge of hydrogen. The only result was that there was a positive shift of the hydrogen discharge as mentioned previously. This is illustrated by figure 7.

FIGURE 7

CURRENT-VOLTAGE PLOT BEFORE AND AFTER ADDITION OF $CoSO_4 \cdot 7H_2O$ TO BLANK SOLUTION AND $NaHSO_3$



V. DISCUSSION FOR FURTHER WORK

It was determined in this investigation that the quantitative and qualitative analysis of cobalt using just a $CoSO_4 \cdot 7H_2O$ solution and a K_2SO_4 supporting electrolyte is not very fesible with a mercury pool electrode. The hypothesis is that the cobalt is reduced at a too negative potential to be seen. If the hypothesis is correct, then there are two possible ways to eliminate this problem. One method is to find a complexing agent or electrolyte for the cobalt so that the half wave potential of the complex appears at a more positive potential. The other possibility which is somewhat related to the former is to change the pH to higher values. In this manner, the hydrogen reaction is retarded and hence one can extend the useful range of analysis. Perhaps a combination of these two methods will result in the desired solution to the problem.

For instance, if one assumes that the reagents which shift the cobalt wave to more positive potentials at the dropping mercury electrode will do the same at the mercury pool electrode, one can find in the literature (1,9) various electrolytes and complexing agents which will shift the half wave potentials of cobalt (II) to more positive values. An example of this is to complex the cobalt with pyridine or SCN^-. Another possibility is to try to complex cobalt with ammonia.

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