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# The Precipitation of Calcium Tungstate from Sodium Tungstate Solution

Martin E. Messner

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# THE PRECIPITATION OF CALCIUM TUNGSTATE
# FROM
# SODIUM TUNGSTATE SOLUTION

by

Martin E. Messner

A Thesis

Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
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# INTRODUCTION

In view of the great need for tungsten in the present industrial world it is necessary that all known tungsten sourves be utilized to the greatest possible extent. Scheelite ores promise to be an increasingly important source of tungsten, inasmuch as the discovery of vast new deposits has been made and known deposits of high grade ores have practically been depleted.

Since the basic chemical reactions are so poorly understood, it was the opinion of the author that an endeavor to improve the quantitative precipitation of calcium tungstate ( $CaWO_4$ ) from a solution containing tungstic acid or $WO_3$ would be most rewarding. Work on this problem, therefore, was not only an interesting chemical study, but also had an important economic aspect.

The variable factors involved in any precipitation problem are many and sometimes large in their effect. Some of these factors are: (1) temperature; (2) time; (3) concentration of solutions and reagents; (4) possible precipitation reagent. The interrelationships of these variables seem practically unknown, and references to previous work with one exception are not to be found.

The exception is the investigation by K. D.

Loughridge (1) of the United States Vanadium Corporation. He recommended:

> "Add six pounds of lime per unit of tungstic oxide and allow the solution to agitate for six hours at between 80° and 85° centigrade. Complete the precipitation with alternate additions of 10 grams of calcium chloride and five grams of lime at hourly intervals."

No reason was given for the quantity of reagent added nor for the temperature used.

Any considerations of a precipitation problem should also include the purity of the chemicals used, the cost of chemicals, the purity of the product obtained and the overall recovery.

# THE PROBLEM

The purpose of this investigation was an attempt to determine the optimum conditions for maximum precipitation of $CaWO_4$ from a solution of $Na_2WO_4$.

Pure components were used so that the additional factors presented by the presence of impurities would not have to be considered. These might have appeared in the form of harmful side reactions or simple contamination of the solutions. It was not the object of this thesis to study scheelite itself but rather to determine some basic chemical information which could be later applied to a study of scheelite utilization. The basic chemistry of reactions involving scheelite are therefore the next step in the program of investigation.

The experiments herein presented were all performed with an eye to preservation of the greatest degree of purity, and care was especially taken to obtain results which would provide dependable basic information.

# POTENTIOMETRIC INVESTIGATION

## THEORY

At the onset it was decided that a system of experimentation employing potentiometric means would be the most rapid, and thereby allow the greatest possible amount of experimentation in the limited time. This belief was in error, however, and a very limited number of satisfactory results were obtained.

When one solution is added to another, as in a titration, two very important determinations can be made. These are the endpoint of the titration and activity of the hydrogen ion present during the titration. This is true for acid-base, oxidation, or precipitation reactions. The reaction that was involved here was of the latter type; the precipitation of $CaWO_4$ from a solution of $Na_2WO_4$ by the addition of the salts of calcium.

When a hydrogen-ion-indicating electrode and a reference electrode are immersed in the solution that is being titrated the electromotive force between the electrodes can be determined. This can be done by two methods; measurement of the electromotive force and measurement of the pH, which is hydrogen-ion activity stated in a more useful exponential form.

When a simple acid-base titration is made the concentration of either hydroxyl or hydrogen ions is very small at the end point, and any further addition of either of these, even drop-wise, produces a marked concentration change by comparison. A vast change in hydrogen activity is the net result.(2) This is an indication of the end point in potentiometric titrations.

If the solution is considered before and after the addition of the precipitant the end point break in the curve can be understood. When a solution is strongly acid or alkaline the addition of a few more hydrogen or hydroxyl ions has very little effect on the E.M.F. Near the end point a much smaller addition, in the milliliter range, will produce a very marked change in the E.M.F. This rapid change in E.M.F., when plotted, will indicate the end point or stoichiometric point for that chemical reaction.

## FISHER TITRIMETER

The instrument used in the potentiometric titrations was the Fisher Senior Titrimeter, improved model. Basically this instrument consists of two parts, a titrimeter stand and a titrimeter unit. The stand is a support on which the beaker containing the sample is placed, an assembly for holding the electrodes, and an eye control used during the titration. The titrimeter unit consists of a highly sensitive, vacuum tube, slide back D.C. voltmeter. Measurements can be made from two slide wire scales: one calibrated in pH units from pH 0.0 to pH 12.5 and the second in volts from -1.0 volt to $\underset{+\,?}{-}$ 1.0 volt.(3) See plate No. 1.

Any additional information regarding the Fisher Titrimeter may be obtained from " A Manual of Volumetric Analysis with the Fisher Titrimeter."(3)

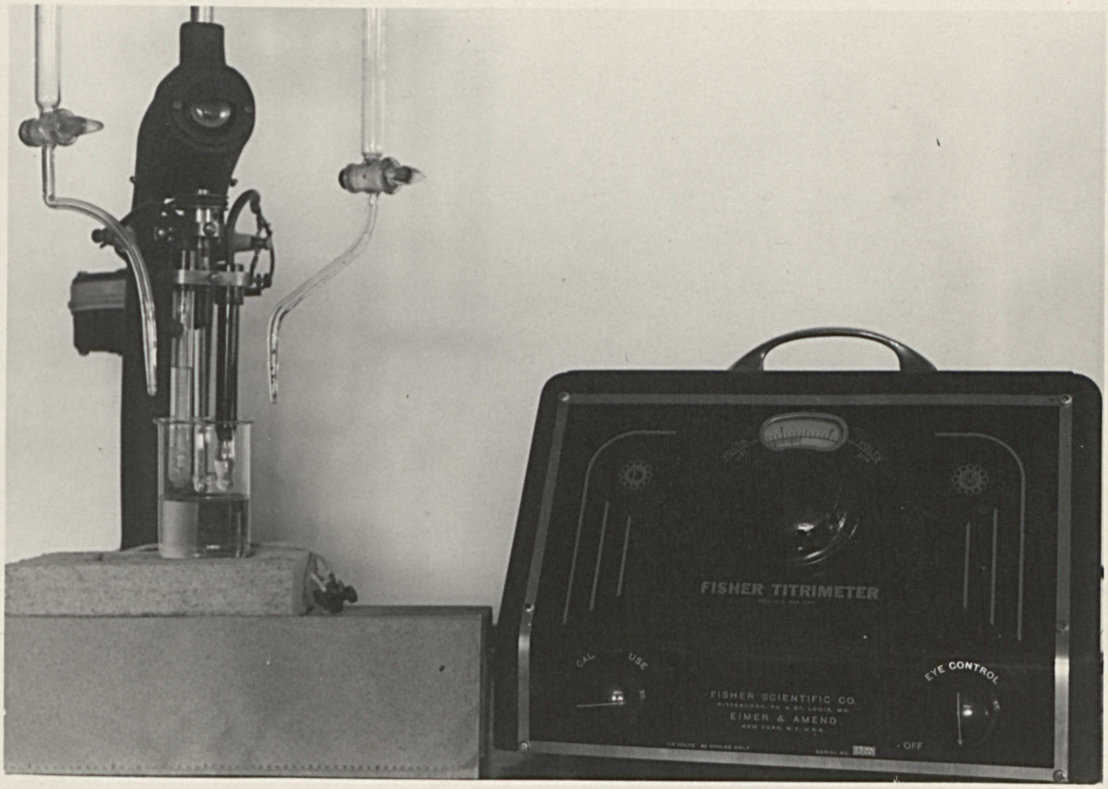


Plate No. 1. Fisher Senior Titrimeter

Left - Titrimeter Stand. Right - Titrimeter Unit.

## BASIC EQUATIONS

The basic reactions studied were:

$$Na_2WO_4 \quad + \quad Ca(OH)_2 \quad = \quad 2NaOH \quad + \quad CaWO_4$$

$$Na_2WO_4 \quad + \quad CaCl_2 \quad = \quad 2NaCl \quad + \quad CaWO_4$$

It was believed that these reactions could be followed through potentiometric means. At first the addition of lime ( hydrated ) should have produced a smooth curve when plotting E.M.F. or pH on the ordinate and ml additions of lime on the abcissa. At the end point a sharp inflection was desired.

These results were only partially forthcoming. The curve was indeed smooth and when plotted produced no point of inflection. This was therefore of little value in determining the end point.

A second precipitation procedure was tried employing calcium chloride ( $CaCl_2$ ) as the precipitant. This proved of little value also, as again no end point could be seen. A description of these tests, the data and observations follow.

## POTENTIOMETRIC TESTS

### Test No. 1.

0.10 N $Na_2WO_4$ titrated with 0.10 N $Ca(OH)_2$ at room tempeature using a calomel-glass electrode system. See Table No. 1. and Figure No. 1. , Curve No. 1.

### Test No. 2.

0.10 N $Na_2WO_4$ titrated with 0.10 N $CaCl_2$ at room temperature using a calomel-glass electrode combination. See Table No. 2. and Figure No. 1., Curve No. 2.

### Test No. 3.

0.10N $Na_2WO_4$ titrated with 0.10 N $CaCl_2$ at room temperature using a calomel-platinum electrode system. See Table No. 3. and Figure No. 2.

### Test No. 4.

0.10 N $Na_2WO_4$ titrated with 0.01 N $CaCl_2$ at 65° C using a platinum-tungsten stirrer electrode. See Table No. 4. and Figure No. 3.

Test No. 1.

The titration procedure was as follows. Fifty ml of distilled water and twenty ml of 0.10 N $Na_2WO_4$ were entered into a 150 ml beaker and placed on the Fisher Titrimeter. Through use of the attached stirrer agitation was immediately begun. To this solution a total of 30 ml of 0.10 N $Ca(OH)_2$ was added in 5 ml additions from a burette. The test was run at room temperature, approximately 20°C. The electrode system was a calomel-glass combination, reference and indicator electrode respectively.

Table No. 1.

| ml 0.1 N $Ca(OH)_2$ | Total ml $Ca(OH)_2$ | pH |
|---|---|---|
| 5 ml | 5 ml | 11.2 |
| 5 ml | 10 ml | 11.5 |
| 5 ml | 15 ml | 11.6 |
| 5 ml | 20 ml | 11.8 |
| 5 ml | 25 ml | 12.0 |
| 5 ml | 30 ml | 12.15 |

As stated previously, the curve obtained from these data was almost a straight line after the break at the first 5 ml lime addition. At the equivalence point, 20ml of lime, no inflection was noted. The test was continued past the 30 ml lime addition plotted and no appreciable pH change was noted. The time lapse from the start of the test until its conclusion was approximately 30 minutes. Of particular interest was the fact that no visible precipitate of $CaWO_4$ could be seen at any time during the test, nor at its conclusion. After the solution had remained standing for another 30 minutes a precipitate began to appear and the following day the entire inside of the beaker, covered with solution, was coated with a fine precipitate. No attempt was made to recover or weigh the precipitate.

Several important factors were to be noticed from this first test. One was the apparent lack of sensitivity of the calomel-glass electrode system to this particular reaction. This is evident from the curve in Figure No. 1. A second conclusion is the extremely slow rate of reaction at room temperature, indicating the need for an elevated temperature. A third would be the limited solubility of lime in water at room temperature.

The lime solution when added had the appearance of a suspension, and made it difficult to add a solution of uniform concentration. When it was entered into the beaker the suspended lime went into solution immediately. By no means of least importance was the affect of the precipitate that did form. It was very fine, almost colloidal, and adhered rather strongly to the glass. This was especially true at any point on the glass where a scratch was present. A quantitative removal would have been difficult.

Test No. 2.

Another test was made using $CaCl_2$ in place of lime as the precipitating agent. The procedure followed was identical to the previous test. To a solution of 50 ml of water and 20 ml of 0.10N $Na_2WO_4$ in a beaker additions of 0.10 N $CaCl_2$ were made to a total of 24 ml. The temperature and electrode system remained the same.

Table No. 2.

| ml 0.1N $CaCl_2$ | Total ml $CaCl_2$ | pH |
|---|---|---|
| 5 ml | 5 ml | 8.55 |
| 5 ml | 10 ml | 8.65 |
| 5 ml | 15 ml | 8.70 |
| 2 ml | 17 ml | 8.70 |
| 2 ml | 19 ml | 8.70 |
| 0.5 ml | 19.5 ml | 8.70 |
| 0.5 ml | 20.0 ml | 8.70 |
| 0.5 ml | 20.5 ml | 8.70 |
| 0.5 ml | 21.0 ml | 8.80 |
| 1.0 ml | 22.0 ml | 8.80 |
| 2.0 ml | 24.0 ml | 8.80 |

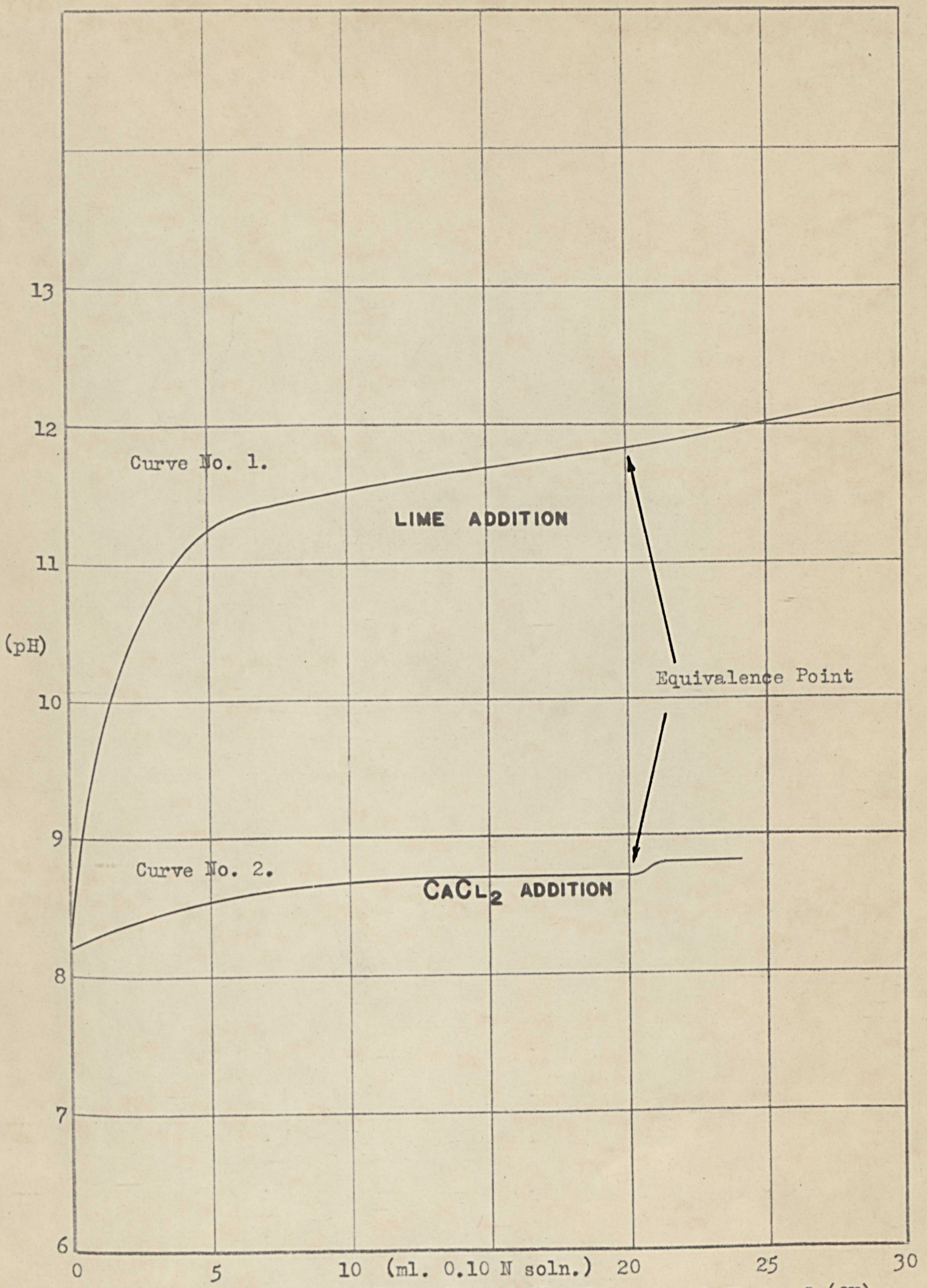


Fig. 1. Potentiometric Titration of $Na_2WO_4$ with $CaCl_2$ or $Ca(OH)_2$.

From the graph of the curve, No. 2. Figure No. 1. it is to be noted that the pH readings would indicate no end point for this reaction either. A break is seen in the curve between the 20.5 ml and 21 ml additions of $CaCl_2$, but it is very slight in size and difficult to interpret. Nothing approaching a normal end point break is evident and further investigation would indicate that the inflection was a freak. One feature was especially noticable when this test was compared with the previous one. Almost immediately upon the addition of the first 5 ml of $CaCl_2$ a precipitate appeared. This test was also continued past the stoichiometric point with no change in pH.

Although the desired results were not forthcoming the observations made are most interesting, especially when compared with those of the first test. In general, the values for the pH were considerably below ( three units on the pH scale ) those obtained in the lime test. Also, there was no sharp increase in pH at the beginning of the test and the following conclusions could be reached.

$CaCl_2$ is a far superior precipitating agent for obtaining $CaWO_4$ than is $Ca(OH)_2$ when time is considered. The excess of $CaCl_2$ as ions in solution were much more rapidly taken up by precipitation than were those of $Ca(OH)_2$, thereby giving a much smoother curve. This would be substantiated by the visible $CaWO_4$ precipitate during titration in the second test, and the general lowering of the pH. The reaction rate of the $CaCl_2$ addition was considerably greater than that of $Ca(OH)_2$ addition at room temperature.

Test No. 3.

Kolthoff(4) mentions the qualifications necessary for potentiometric determinations in the following way:

> " Any reaction which can be made the basis of an ordinary titration can be useful for potentiometric purposes, if a suitable indicator electrode is available."

The next approach to the problem was one of determining the proper electrode system. In many titrations of metallic ion concentrations special precaution must be taken to avoid oxidation and polarization. For these titrations platinum is used as an indicator electrode because of its inert nature. Therefore, a platinum-calomel electrode system was decided upon.

It was decided that the test would be made measuring the E.M.F. between the electrodes rather than the pH of the solution.

Fifty ml of water and 20 ml of 0.10 N $Na_2WO_4$ solution were entered into the titration beaker, and placed on the Fisher Titrimeter. To this solution a total of

25 ml of 0.10 N $CaCl_2$ was added in stages by means of a burette. The E.M.F. was read following each addition, providing just enough time for the E.M.F. to become constant. The instrument was set for the 0 to - 1.0 voltage range and the test was conducted at room temperature.

Table No. 3.

| ml 0.1 N $CaCl_2$ | Total ml $CaCl_2$ | E.M.F.(volts) |
|---|---|---|
| 5.0 ml | 5.0 ml | -0.220 |
| 5.0 ml | 10.0 ml | -0.210 |
| 5.0 ml | 15.0 ml | -0.200 |
| 2.5 ml | 17.0 ml | -0.192 |
| 1.0 ml | 18.5 ml | -0.188 |
| 0.5 ml | 19.0 ml | -0.181 |
| 0.5 ml | 19.5 ml | -0.181 |
| 0.5 ml | 20.0 ml | -0.195 |
| 0.5 ml | 20.5 ml | -0.195 |
| 0.5 ml | 21.0 ml | -0.197 |
| 1.0 ml | 22.0 ml | -0.200 |
| 3.0 ml | 25.0 ml | -0.200 |

Figure No. 2. was plotted from the above data and would at first glance appear to be a typical potentiometric curve. Upon closer investigation it can be seen that the

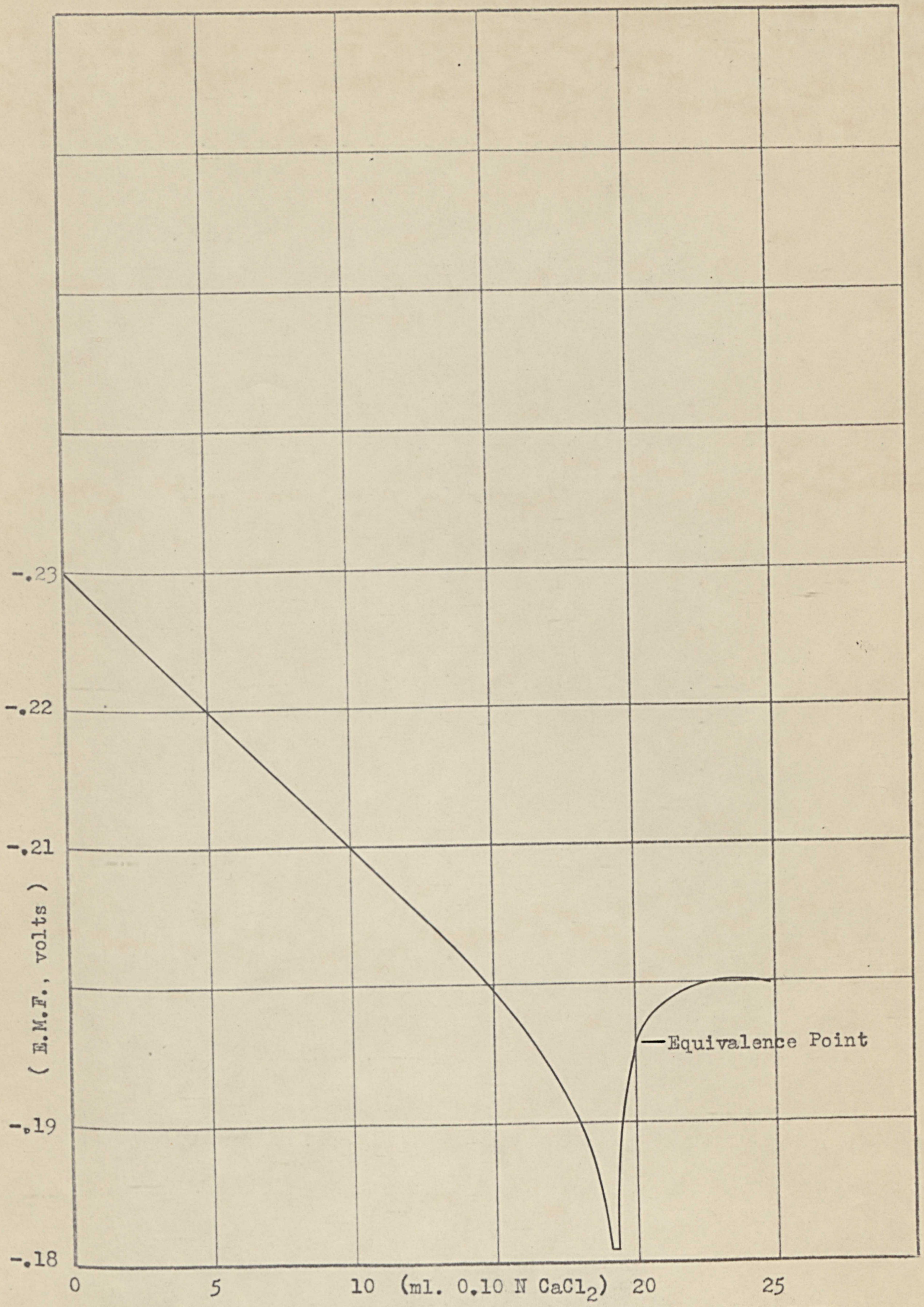


Fig. 2. Potentiometric Titration of $Na_2WO_4$ with $CaCl_2$.

break in this curve came at the point where the $CaCl_2$ addition was 18.5 ml, or 92.5 percent of the calculated equivalent amount. The formation of the precipitate closely paralleled that described in Test No. 2.

From this test and three more conducted with the platinum-calomel electrode combination it was evident that these electrodes were not the answer to the $CaWO_4$ precipitation problem. In these other tests the concentrations were varied and the end point on the various curves did not remain constant. The equivalent amount of $CaCl_2$ needed varied from 80 percent to 94 percent in these tests. Considering the difficulty arising with the lime precipitation in the first tests it was decided that no tests using lime as the addition reagent would be made.

Test No. 4.

K.D.Loughridge (1) in his work at Bishop, California, had included in his laboratory procedure the following:

> " - - - - , agitated for six hours at between 80° and 85°C."

By means of a few preliminary tests it was evident that an increase in temperature would increase the rate of precipitation of $CaWO_4$ when either $CaCl_2$ or $Ca(OH)_2$ was used as the addition agent. From this information the next series of tests were prepared.

The remaining electrode combination for use with the Fisher Titrimeter was a one piece platinum-tungsten stirrer electrode described in the literature(3) as well suited for some special titrations. The special titrations were not mentioned. Its compact physical characteristics were most advantageous when considering the limited space available in a 250 ml beaker. The platinum and tungsten wires were attached to the stirrer thus eliminating the necessity for placing three sep$\overset{a}{e}$rate objects in the beaker.

A means of controlling the temperature was necessary. A small hot plate, controlled by use of a Variac, was imbedded in a piece of asbestos brick. The coils of the hot plate were covered with several sheets of asbestos paper to insure more uniform heating, and prevent possible glass breakage.

In this test the concentration of the $CaCl_2$ solution that was added was changed to a 0.01 N one, thereby permitting a more quantitative check on the additions. Five ml of 0.10 N $Na_2WO_4$ and 50 ml of water were entered into the 250 ml beaker on the Fisher Titrimeter. Heat was applied to the solution and was maintained at 65°C. The addition of 0.01 N $CaCl_2$ totaled 150 ml, three times the equivalent amount. Again, time was allowed after each addition to permit the E.M.F. of the solution to become constant. The following data was obtained.

Table No. 4.

| ml 0.01 N $CaCl_2$ | Total ml $CaCl_2$ | E.M.F.(volts) |
|---|---|---|
| 5 ml | 5 ml | -0.271 |
| 5 ml | 10 ml | -0.276 |
| 5 ml | 15 ml | -0.260 |
| 5 ml | 20 ml | -0.251 |
| 5 ml | 25 ml | -0.241 |
| 5 ml | 30 ml | -0.241 |
| 5 ml | 35 ml | -0.240 |
| 5 ml | 40 ml | -0.230 |
| 5 ml | 45 ml | -0.222 |
| 5 ml | 50 ml | -0.211 |
| 5 ml | 55 ml | -0.220 |
| 5 ml | 60 ml | -0.210 |
| 5 ml | 65 ml | -0.187 |
| 5 ml | 70 ml | -0.183 |
| 5 ml | 75 ml | -0.185 |
| 5 ml | 80 ml | -0.185 |
| 10 ml | 90 ml | -0.184 |
| 10 ml | 100 ml | -0.186 |
| 10 ml | 110 ml | -0.188 |
| 10 ml | 120 ml | -0.186 |
| 10 ml | 130 ml | -0.191 |
| 10 ml | 140 ml | -0.191 |
| 10 ml | 150 ml | -0.192 |

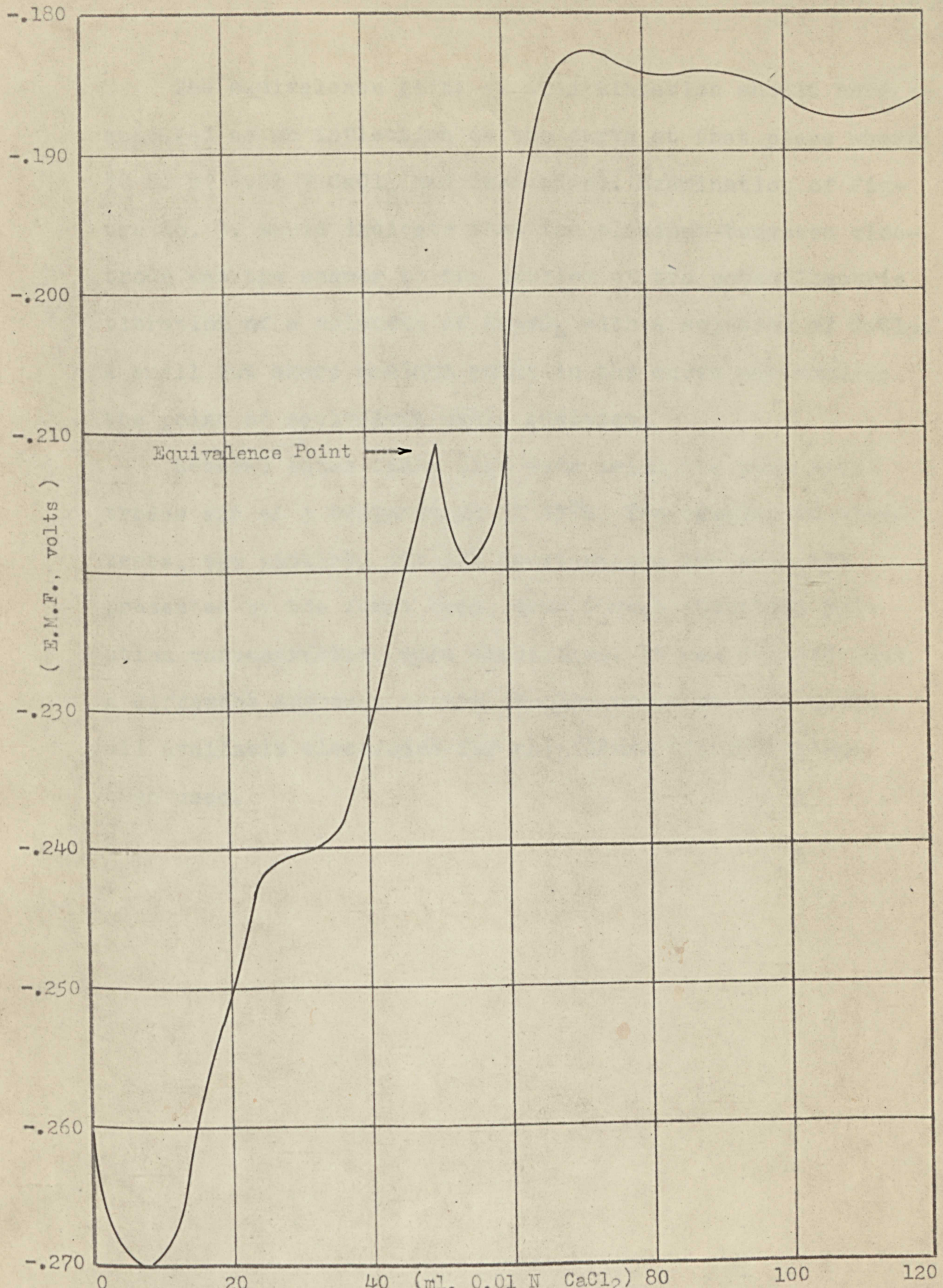


Fig. 3. Potentiometric Titration of $Na_2WO_4$ with $CaCl_2$.

The equivalence point in this titration should have appeared as an inflection on the curve at that place where 50 ml of 0.01 N $CaCl_2$ had been added. Examination of Figure No. 3. would indicate that the platinum-tungsten electrode was the answer to the problem of the potentiometric titration of a solution of $Na_2WO_4$ with a solution of $CaCl_2$. A small but sharp maximum point in the curve was seen at the point of equivalent $CaCl_2$ addition.

Several other tests were made using the same electrodes and at a temperature of 65°C. The results of these tests, not plotted, did not substantiate the evidence presented by the first test, even though identical solution concentrations were maintained. It was decided that a different approach to the problem would be made since all available electrodes for the Fisher Titrimeter had been used.

## TIME TEMPERATURE INVESTIGATION

During the previous tests the effects of time and temperature were noted: (1) a temperature increase speeds up the rate of reaction; (2) the amount of precipitate is a function of time after the addition of titrant, longer time giving more precipitate. The exact effect of time and temperature were important enough to merit meet special investigation.

A time and temperature investigation, although quite basic, can often lead to important results when precipitation reactions are studied. The equations studied in this section were:

$$Na_2WO_4 + Ca(OH)_2 = 2NaOH + CaWO_4$$
$$Na_2WO_4 + CaCl_2 = 2NaCl + CaWO_4$$

TEST NO. 9.

Twenty five ml of 0.10 N $Na_2WO_4$ was entered into each of thirty 100 ml beakers. One ml of 0.10 N $CaCl_2$ was also added to the first beaker, two ml of the same $CaCl_2$ solution was added to the second, and thence until 30 ml of $CaCl_2$ had been added to beaker No. 30. Immediately after the $CaCl_2$ was added to each beaker the solutions were stirred to insure uniform mixing.

The entire set of 30 beakers was then moved to a glass enclosed case which had been previously calked to prevent as little contamination as possible from circulating air. The solutions were not stirred again and remained in the case for 72 hours at which time the test was concluded.

The solutions were filtered through No. 42 Wat~~h~~man filter paper and the $CaWO_4$ precipitate which had formed was washed three times with distilled water. The filter paper and contained precipitate was burned in a gas-fired muffle at about 180°C,? thereby avoiding the possible conversion of $CaWO_4$ to some other form and rendering it useless in this experiment. Weighings were made of the $CaWO_4$ on an analytical balance and results were tabulated in Table No. 5.

The curves on Figure No. 4 graphically present the results of this test.

Table No. 5.

| Beaker No. | ml $Na_2WO_4$ 0.10 N. | ml $CaCl_2$ 0.10 N. | wt $CaWO_4$ ppt | Percent Maximum |
|---|---|---|---|---|
| 1 | 25 ml | 1 ml | 0.0144 gm | 100.0 |
| 2 | 25 ml | 2 ml | 0.0284 gm | 98.7 |
| 3 | 25 ml | 3 ml | 0.0434 gm | 100.1 |
| 4 | 25 ml | 4 ml | 0.0573 gm | 99.5 |
| 5 | 25 ml | 5 ml | 0.0701 gm | 97.3 |
| 6 | 25 ml | 6 ml | 0.0849 gm | 98.2 |
| 7 | 25 ml | 7 ml | 0.0996 gm | 98.8 |
| 8 | 25 ml | 8 ml | 0.1186 gm | 103.0 |
| 9 | 25 ml | 9 ml | 0.1274 gm | 98.4 |
| 10 | 25 ml | 10 ml | 0.1389 gm | 96.4 |
| 11 | 25 ml | 11 ml | 0.1560 gm | 98.4 |
| 12 | 25 ml | 12 ml | 0.1671 gm | 96.6 |
| 13 | 25 ml | 13 ml | 0.1832 gm | 97.8 |
| 14 | 25 ml | 14 ml | 0.1945 gm | 96.5 |
| 15 | 25 ml | 15 ml | 0.2126 gm | 98.4 |
| 16 | 25 ml | 16 ml | 0.2237 gm | 97.0 |
| 17 | 25 ml | 17 ml | 0.2367 gm | 96.8 |
| 18 | 25 ml | 18 ml | 0.2542 gm | 98.0 |
| 19 | 25 ml | 19 ml | 0.2612 gm | 95.5 |
| 20 | 25 ml | 20 ml | 0.2788 gm | 96.8 |
| 21 | 25 ml | 21 ml | 0.2877 gm | 95.2 |
| 22 | 25 ml | 22 ml | 0.3000 gm | 94.7 |

(continued)

Table No. 5. (continued)

| Beaker No. | ml $Na_2WO_4$ 0.10 N. | ml $Cacl_2$ 0.10 N. | wt $CaWO_4$ ppt | Percent Maximum |
|---|---|---|---|---|
| 23 | 25 ml | 23 ml | 0.3119 gm | 94.3 |
| 24 | 25 ml | 24 ml | 0.3169 gm | 91.8 |
| 25 | 25 ml | 25 ml | 0.3179 gm | 88.3 |
| 26 | 25 ml | 26 ml | 0.3185 gm | 88.5 |
| 27 | 25 ml | 27 ml | 0.3176 gm | 88.3 |
| 28 | 25 ml | 28 ml | 0.3170 gm | 88.1 |
| 29 | 25 ml | 29 ml | 0.3177 gm | 88.2 |
| 30 | 25 ml | 30 ml | 0.3186 gm | 88.5 |

Two curves were plotted in Figure No. 4 from the data in Table No. 5. The first is a graph of the maximum precipitate obtainable from the calculated amount of tungsten in solution. The second is a graph of the actual precipitate obtained in the 72 hr test. The two curves are very nearly superimposed upon each other providing that there is at least a 250 percent excess of $WO_4^=$ ions in solution. Beyond that point the actual precipitation curve falls below that of the maximum. At the equivalence point the actual precipitation curve breaks sharply yielding 88.5 percent of the maximum possible precipitate.

At the conclusion of the tests the precipitate had settled to the bottom of the beakers, and the solution remaining above the precipitate appeared to be clear.

This would indicate that additional time would have yielded no more precipitate, at room temperature.

The 20 percent excess of $CaCl_2$ that was present in the beakers had little effect on the amount of precipitate after the maximum had been reached at the equivalence point. Greater $CaCl_2$ excess would probably have had the same effect.

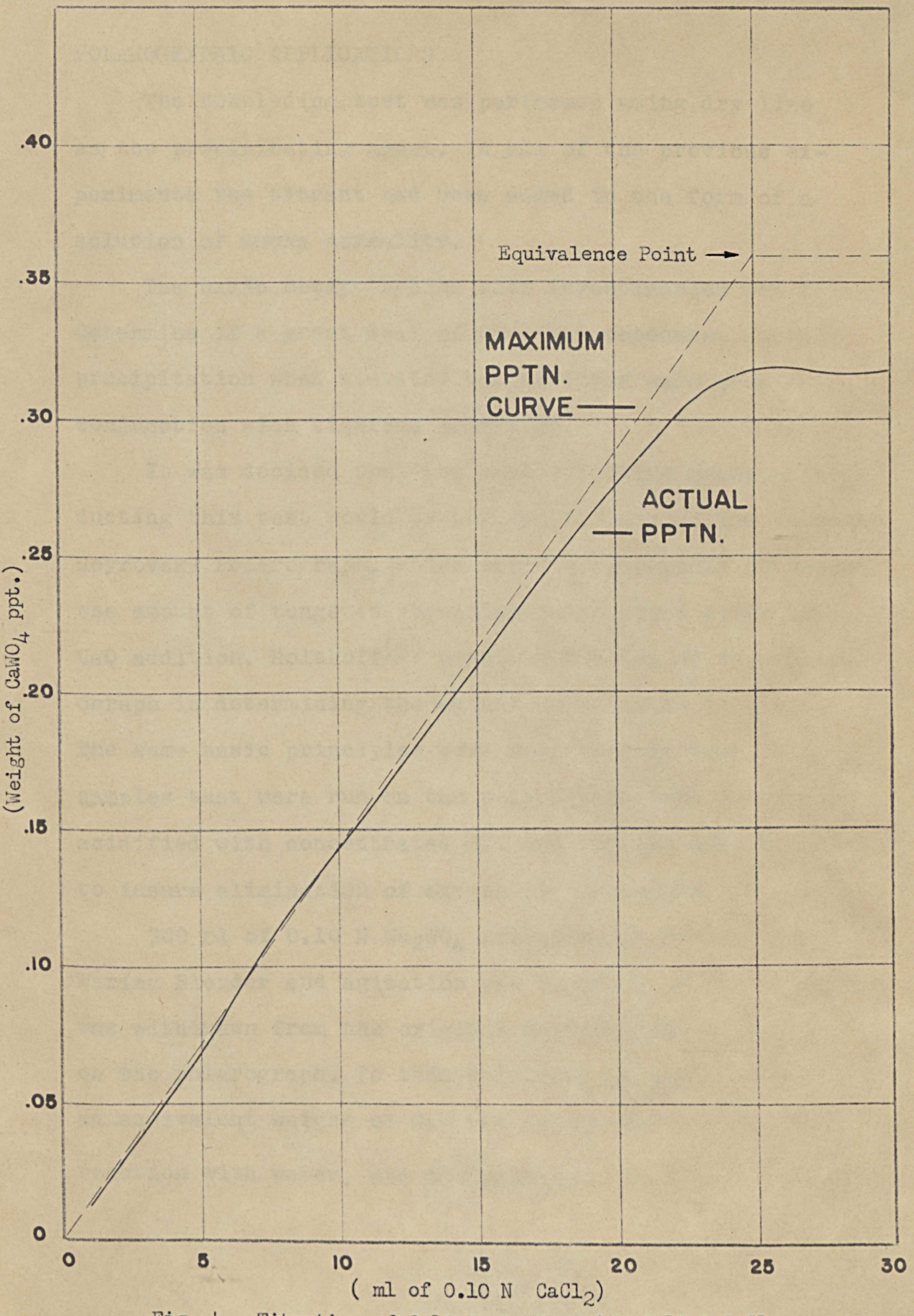


Fig. 4. Titration of 0.10 N $NaWO_4$ with 0.10 N $CaCl_2$.

## POLAROGRAPHIC APPLICATIONS

The concluding test was performed using dry lime as the precipitating agent. In all of the previous experiments the titrant had been added in the form of a solution of known normality.

The basic motive behind this investigation was to determine if a great deal of time was necessary for the precipitation when elevated temperatures were used in conjunction with vigorous agitation.

It was decided that the most effective means of conducting this test would be through the use of the Sargent-Heyrovsky Polarograph, which would very rapidly determine the amount of tungsten remaining in solution after the CaO addition. Kolthoff(5) mentions the use of the polarograph in determining the amount of tungsten in steel. The same basic principles were used in this test. All samples that were run on the polarograph were filtered, acidified with concentrated HCl and bubbled with nitrogen to insure elimination of oxygen in the sample.

500 ml of 0.10 N $Na_2WO_4$ solution was placed in a Waring Blender and agitation was begun. A 10 ml sample was withdrawn from the original solution for analysis on the polarograph. To this solution, in the blender, an equivalent weight of CaO was added. Through the lime reaction with water, and the agitation itself, the temp-

erature of the solution reached a maximum of 88° C several minutes after the start of the test. This temperature remained constant.

Test No. 2 was conducted with an equivalent CaO addition and samples for polarographic analysis were drawn out of the blender 15 min, 30 min, 45 min and 60 min after the start of the test. Test results are listed in Table No. 6, and a graph is presented in Figure No. 5.

Test No. 3 was conducted in a similar manner, with a double-equivalent CaO addition. Samples were withdrawn 30 min and 60 min after the start of the test. Results can be seen in Table No. 7 and Figure No. 5.

A set of standardization tests were run on 0.10 N, 0.01 N, and 0.001 N $Na_2WO_4$ solution. The result of these tests was the desired straight-line graph. Plate No. 2 shows the curves of all three tests, and includes vital information regarding them.

Table No. 6.

| Sample No. | Withdrawl time after start of test (min) | Percent tungsten remaining in soln. |
|---|---|---|
| 1. | 0 min | 100.00 % |
| 2. | 15 min | 17.80 % |
| 3. | 30 min | 13.30 % |
| 4. | 45 min | 13.00 % |
| 5. | 60 min | 11.50 % |

Table No. 7.

| Sample No. | Withdrawl time after start of test (min.) | Percent tungsten remaining in soln. |
|---|---|---|
| 1. | 0 min | 100.00 % |
| 2. | 30 min | 0.445 % |
| 3. | 60 min | 0.223 % |

Both of the tests employing polarographic analysis were of one hour duration. However, both of the curves of Figure No. 5 have a pronounced break 20 minutes after the CaO addition. This indicates that within 20 minutes most of the eventual precipitate had formed.

A marked difference was noticed between the two tests. The equivalent addition test produced a curve which developed into a straight-line function while 13 percent of the tungsten remained in solution. The curve of the double-equivalent test, however, did not evolve into a straight-line function until less than 0.5 percent of the original tungsten was left in solution. These tests were conducted on solutions at 88° C, and this elevated temperature would tend to speed up the rate of reaction. The vigorous agitation caused by the blender would also promote a more rapid formation of precipitate.

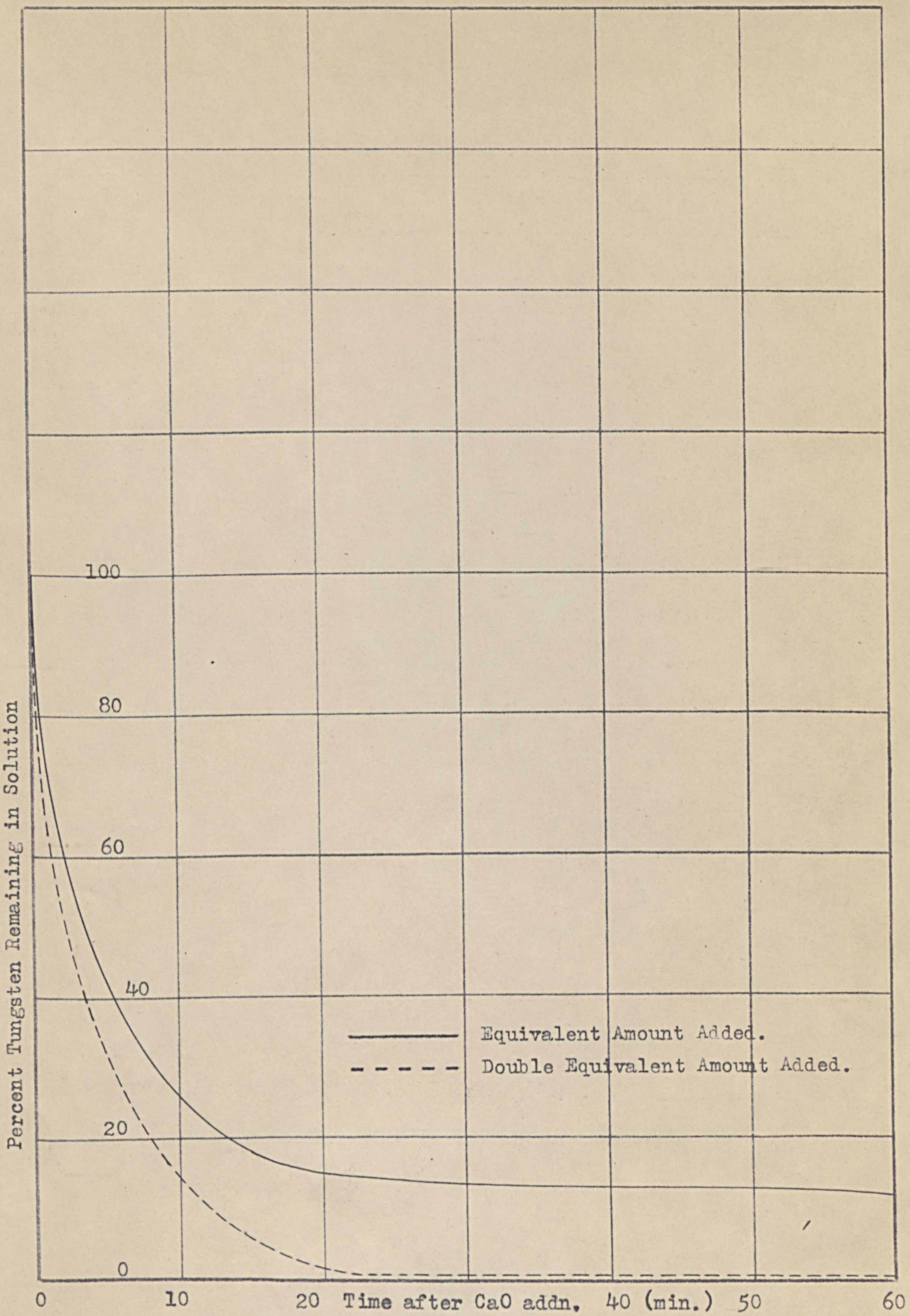


Fig. No. 5. Percent Tungsten Remaining in Soln. after CaO addn.

### TEST NO. 1

STANDARDIZATION

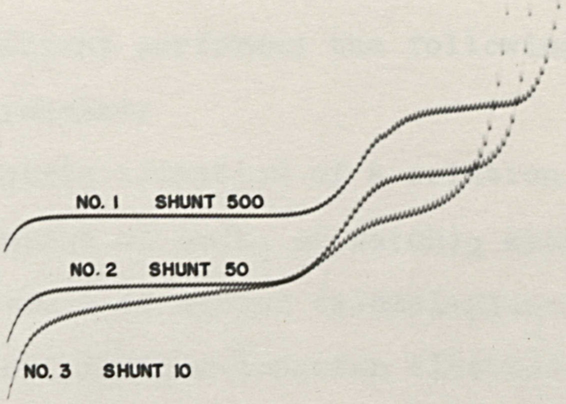
ALL SOLUTIONS
20% H O
80% CONC. HCL

SPAN, 0 TO -1 VOLT

NO. 1 - 0.1 N $Na_2WO_4$

NO. 2 - 0.01 N "

NO. 3 - 0.001 N "



### TEST NO. 2

500 ML. 0.1 N $Na_2WO_4$ (.025 MOLE)

1.401 GM. CAO (.025 MOLE)

ALL SOLUTIONS, 20 % $H_2O$
80 % CONC. HCL

SPAN, 0 TO -1. VOLT

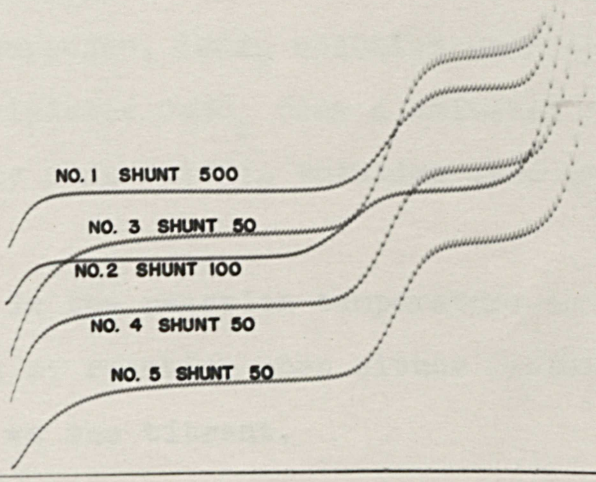
NO. 1 ORIGINAL SOLN. (NO CAO)

NO. 2 15 MIN. AFTER CAO ADDN.

NO. 3 30 " " " "

NO. 4 45 " " " "

NO. 5 1 HR. " " "



### TEST NO. 3

500 ML. 0.1 N $Na_2WO_4$ (.025 MOL)

2.802 GM. CAO (.050 MOLE)

ALL SOLUTIONS
20% $H_2O$
80 % CONC. HCL

SPAN, 0 TO -1. VOLT

NO. 1 ORIGINAL SOLN. (NO CAO)

NO. 2 15 MIN. AFTER CAO ADDN.

NO. 3 45 MIN. AFTER

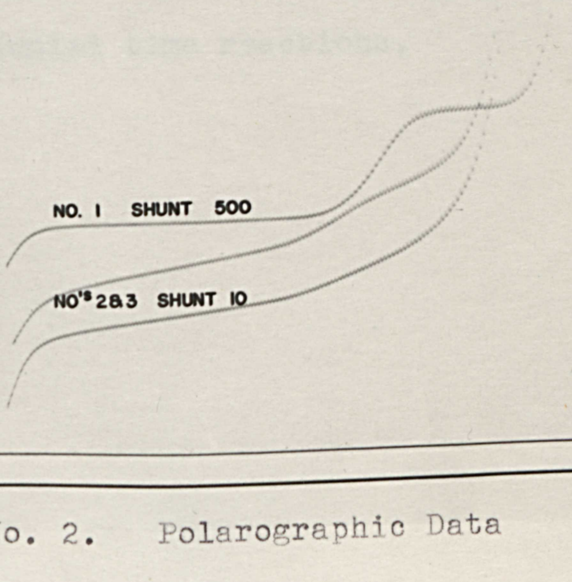


Plate No. 2. Polarographic Data

# CONCLUSIONS

From the investigations performed the following conclusions have been reached:

1. The potentiometric titration of a solution of $Na_2WO_4$ with a solution of $CaCl_2$ or $Ca(OH)_2$ appears to give a false result if either calomel-glass, calomel-platinum or platinum-tungsten electrode combinations are used.

2. At room temperature, $CaCl_2$ solution used as a titrant will precipitate $CaWO_4$ from a solution of $NaWO_4$ more quickly than $Ca(OH)_2$ solution used as a titrant.

3. An increase in the reaction temperature will speed up the rate of reaction when either $Ca(OH)_2$ or $CaCl_2$ is used as the titrant.

4. Titrant in excess of the equivalent amount does not alter the amount of precipitate formed in room temperature, extended time reactions.

## SUGGESTIONS FOR FURTHER INVESTIGATION

Future work on this problem could include:

1. A more detailed investigation of the precipitation problem with regard to time.
2. Extensive use of the polarograph in determination of reaction rates.
3. Determination of the effect of a mixture of titrants.
4. A study of the effect of excess titrant on the amount of precipitate formed.
5. Application of basic principles to a study of scheelite ore.

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