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J.A.B.

Potentiometric Titrations with Ceric Sulphate

A THESIS

by

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## Potentiometric Titrations

### With Ceric Sulphate

Ceric salts are theoretically ideal as oxidation agents, for they give exceedingly high normal oxidation potentials, (about 1.45 volts), and, since the cation is the primary active constituent, the valence change is simple, only one change being possible,  $- Ce^{++++} + e = Ce^{+++}$ .

Although Barbieri first proposed the use of a solution of Ceric Sulphate in volumetric analysis in 1905, no extensive investigation of its applications in the potentiometric field was made until 1928, when N. H. Furman, and Willard and Young simultaneously made a systematic study of the use of ceric sulphate as an improved standard oxidizing agent.

These investigators found that ceric solutions, .5 or 1 M in  $H_2SO_4$ , were stable for periods ranging from three to ten months. Satisfactory methods for standardization against oxalate were developed by both Furman, and Willard and Young, and it was found that the reaction is accurate, and rapid above  $70^\circ$  in  $H_2SO_4$  solution, and above  $90^\circ$  in HCl solution. If iodine monochloride is used as a catalyst, the titration may be carried out at room temperature in HCl solution.

Willard and Young also developed methods for the determination of iron, iodide, arsenic, antimony, vanadium, and some organic acids oxidizable by ceric sulphate. Furman investigated the oxidation of ferrocyanide, uranium, hydrogen peroxide, hydroquinone, and thiosulphate, and also studied the use of certain indicators in titrations with ceric sulphate.

These investigations indicate that ceric sulphate is an exceedingly versatile oxidizing agent, useful in many laboratory procedures. It has been found particularly valuable for the determination of reducing agents in the presence of high concentrations of HCl, where a similar use of potassium permanganate is impossible. In addition to the potentiometric method of determining the end-point, the Walden indicator, o-phenanthroline ferrous complex, has been used with great satisfaction. The stability of standard ceric sulphate solutions has been proven over a wide range of  $H_2SO_4$  concentrations, (10 - 40 cc. conc.  $H_2SO_4$  per liter), and at the present time they may be cheaply prepared, the cost ranging from 5 to 17 cents per liter of tenth normal solution, depending on the quality of the salt used.

Since, as the above summary shows, ceric sulphate does have definite possibilities as a standard oxidizing agent, the following investigation was attempted with two objects in view: First, to conduct a preliminary investigation of the use of ceric sulphate solutions in some potentiometric laboratory oxidation procedures. Second, to conduct a more extensive study of the oxidation by ceric sulphate of bivalent platinum.

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Preparation of Ceric  
Sulphate Solutions

The ceric sulphate solutions used were made by dissolving ceric ammonium sulphate obtained from G. F. Smith Co., in distilled water to which enough concentrated  $H_2SO_4$  had been added to make the resulting solution 0.5 molar. The first solution prepared was made according to directions found on page 52 of G. F. Smith's booklet, Ceric Sulphate. 80 grams of ceric ammonium sulphate was stirred with 500 cc. of water containing 28 ml. conc.  $H_2SO_4$ , sp. gr. 1.84, and then transferred to a liter flask and diluted to the mark. The resulting solution was not clear, however, and repeated stirring and mixing did not make it so. There appeared to be present a suspension of a very fine crystalline yellow salt, part of which settled to the bottom upon standing over night. The solution was filtered, but the filtrate was still cloudy, and upon standing a light yellow precipitate again settled in the bottom of the flask.

By standardization against  $Na_2C_2O_4$ , the normality of the solution was found to be .1087. It was thought that this might be too concentrated a solution to be stable, so it was diluted to approximately .07 N. The resulting solution was perfectly clear, and its normality remained constant over a period of several weeks. Other solutions of this approximate normality were prepared, and all were clear solutions that remained stable as long as they were used.

A dilute solution, approximately .02 N, was prepared by diluting the .07 N solution, but immediately

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after dilution it became cloudy. When this solution was made .05 M with respect to  $H_2SO_4$ , the cloudiness disappeared, and the solution became clear. The .02 N solution remained stable as long as used.

Preparation of Iodine Mono-  
Chloride Solution for Use as a Catalyst

A .5 M iodine monochloride solution was prepared as directed on page 53 of G. F. Smith's booklet. 10 g. of KI and 6.74 g. of  $KIO_3$  were dissolved in 90 ml. of water, and then 90 ml. of conc. HCl was added. The reaction is as follows:



Five cc. of chloroform was added, and the solution was adjusted by adding small portions of KI and  $KIO_3$ , until the color of the chloroform was a very faint orange. 10 ml. of this solution was then diluted to 1000 ml. to make a .0005 M solution which was used in portions of 5 - 10 ml. as a catalyst.

Preparation of Indicator Solutions

A .025 M solution of O-phenanthroline ferrous complex was purchased from G. F. Smith Co. One drop of this was used as an indicator in the titration of oxalate in HCl solution, and also in the  $H_2O_2$  titrations.

A 0.1% solution of Erio Glaucine A. was prepared by dissolving one gram of the salt in 1000 ml. of water. This was added in 0.5 ml. portions in the titration of ferrous iron.

A one per cent solution of methylene blue was prepared by dissolving one gram of the dye in 100 ml. of water. This was used experimentally in several titrations.

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The Standardization of Ceric Sulphate  
Solutions with Standard Sodium Oxalate or Oxalic  
Acid

The concentration of the Ceric Sulphate solutions was determined by titrating weighed portions of Standard Sodium Oxalate, and the Normalities obtained by this method were found to be accurate within the limits of experimental error in both hydrochloric and sulphuric acid solutions, under varying conditions of temperature and volume. It was found that sulphuric acid solution is more suitable than hydrochloric acid solution in carrying out the titration by the potentiometric method, since the change in potential is greater, and equilibrium is reached more rapidly. When the potentiometric method is not desirable, a satisfactory standardization may be made using ortho phenanthroline ferrous complex as an indicator in hydrochloric acid solution.

Standardization by the Potentiometric  
Method in Hydrochloric Acid Solution

In hydrochloric acid solution the titrations were carried out by the potentiometric method, and also by using o-phenanthroline ferrous complex as an indicator. When the potentiometric method was used, weighed amounts of sodium oxalate were placed in beakers containing various amounts of water and concentrated HCl, and the resulting solutions were titrated with ceric sulphate solution. The electrode system used is fully described in the appendix, and consisted of a bright platinum wire as one electrode, and a normal calomel electrode, connected to the titration beaker by means of a N K<sub>2</sub>SO<sub>4</sub> salt bridge, as the other. The solution being titrated was kept

at the desired temperature by means of a Bunsen burner shielded from drafts, and it was stirred continuously by a motor driven glass stirrer.

It was found that the conditions of the titration could be widely varied and accurate results still be obtained. A marked change in volume had no effect upon the end-point, and the quantity of HCl can be greatly increased without producing any marked change in rapidity of the equilibrium, but the temperature has to be kept above  $60^{\circ}$  C. in order for the equilibrium to be rapid and sensitive enough to be practical.

A temperature of  $85-90^{\circ}$ , and an initial volume of 150 cc., containing 20 cc. of concentrated HCl, were found to be the conditions best suited for titration in HCl solution. When these conditions are fulfilled, and the solution is well stirred continuously, it is necessary to wait about two or three minutes after each addition near the end-point in order to allow the e.m.f. to become constant enough for an accurate reading to be made. The break in potential in this case is about 0.200 volt for an addition of .05 cc. of .066 N Ceric Sulphate solution. (See Graph I)

Use of o-Phenanthroline Ferrous Complex  
as an Indicator in the Titration of  
Oxalate in Hydrochloric Acid Solution

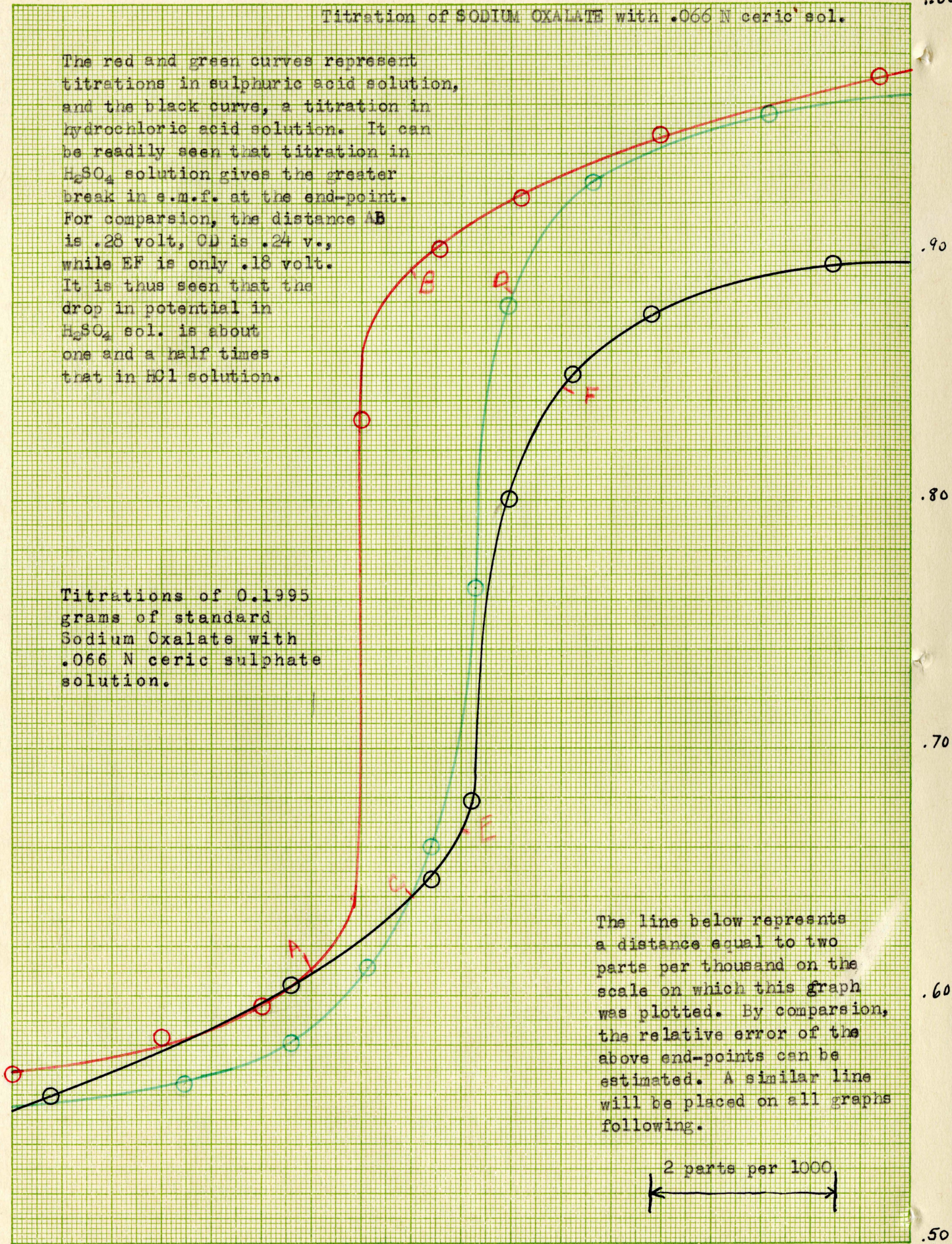
When the titration was carried out using o-phenanthroline ferrous complex as an indicator, the directions given in G. F. Smith's pamphlet, - Ceric Sulphate -, were followed. Weighed portions of the  $\text{Na}_2\text{C}_2\text{O}_4$  were placed in a 400 ml. beaker, and dissolved by addition of 20 ml. of HCl and 5 ml. of ICl diluted with water to 100 ml. The solution was then heated to



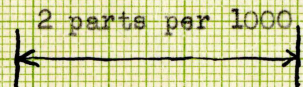
Titration of SODIUM OXALATE with .066 N ceric sol.

The red and green curves represent titrations in sulphuric acid solution, and the black curve, a titration in hydrochloric acid solution. It can be readily seen that titration in  $H_2SO_4$  solution gives the greater break in e.m.f. at the end-point. For comparison, the distance AB is .28 volt, CD is .24 v., while EF is only .18 volt. It is thus seen that the drop in potential in  $H_2SO_4$  sol. is about one and a half times that in HCl solution.

Titration of 0.1995 grams of standard Sodium Oxalate with .066 N ceric sulphate solution.



The line below represents a distance equal to two parts per thousand on the scale on which this graph was plotted. By comparison, the relative error of the above end-points can be estimated. A similar line will be placed on all graphs following.



44.0                      44.1                      44.2                      44.3                      44.4  
cc. ceric sulphate →

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Millimeters, 10th lines heavy.

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fifty degrees, using a thermometer as a stirring rod. After the addition of one drop of a .025 M solution of o-phenanthroline ferrous complex, the ceric sulphate solution was titrated in until the color of the indicator was pale blue, and there was no return of any pink color after an interval of one minute.

The temperature must be carefully regulated, if it drops below  $45^{\circ}$  the end-point does not occur with sufficient rapidity to be practical, and if it rises above  $52^{\circ}$ , the color of the indicator disappears, supposedly due to decomposition. The addition of 5-10 ml. of .005 M ICl is necessary to hasten the attainment of an equilibrium. One drop of indicator solution is sufficient to produce a color intense enough, so that the change from pink to blue can easily be detected by the eye in ordinary light. If more than one drop is added, the amount of ceric sulphate required to produce the color change is increased, so that an error of several parts per thousand is produced.

#### Titration of Oxalate in Sulphuric Acid Solution with Ceric Sulphate

In sulphuric acid solution the titrations were carried out by the potentiometric method described above in connection with the titration in HCl solution. As in the HCl solution it was found that the titration could be carried out successfully using a wide range of initial volumes, but for the sake of convenience an initial volume of 150 cc. seems to be most suitable. The quantity of  $H_2SO_4$  may be varied to some extent, but when more than 10 cc. of the concentrated acid are added equilibrium is reached too slowly to be practical. Equilibrium is attained very rapidly when the amount of acid present is between two and three cc.

If the temperature drops below  $70^{\circ}$ , equilibrium is attained very slowly, but between  $90^{\circ}$  and  $95^{\circ}$  it is attained very rapidly. The break in potential in this case varies from .275 to .300 volt for an addition of .05 cc of

.066 N ceric solution, while in HCl solution the break is only about .200 volt. (See Figure I) Moreover, in H<sub>2</sub>SO<sub>4</sub> solution it is necessary to wait but one minute after each addition of ceric sulphate near the end-point before equilibrium is attained, while in HCl solution two or three minutes are required and even then the galvanometer is not quite as sensitive as in the H<sub>2</sub>SO<sub>4</sub> solution.

It is, therefore, concluded that the standardization of ceric sulphate against sodium oxalate can be carried out more satisfactorily in H<sub>2</sub>SO<sub>4</sub> solution than in HCl solution, since the break in potential in H<sub>2</sub>SO<sub>4</sub> is nearly one and a half times that found in HCl solution, and since the equilibrium is reached more quickly and more satisfactorily in the H<sub>2</sub>SO<sub>4</sub> solution.

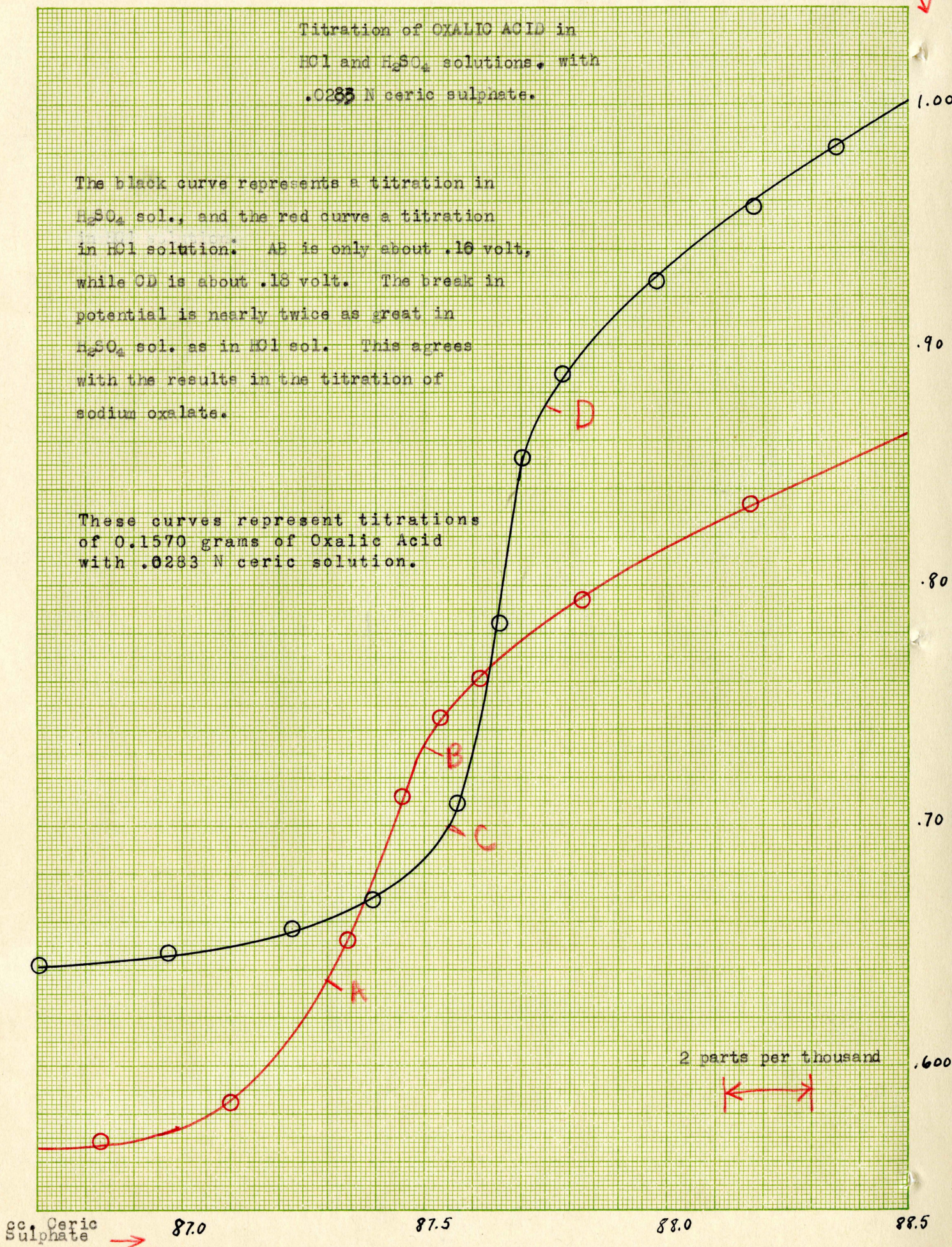
Standardization against Oxalic Acid

The standardization against oxalic acid was found to be entirely similar to that with sodium oxalate, although the sodium oxalate solution reached an equilibrium more satisfactorily near the end-point than did the oxalic acid. In this case, as in the sodium oxalate titration, H<sub>2</sub>SO<sub>4</sub> solution was found to be more satisfactory than HCl solution. The rise in potential was found to be nearly twice as great in H<sub>2</sub>SO<sub>4</sub> solution as in HCl, and the equilibrium was reached more rapidly in H<sub>2</sub>SO<sub>4</sub> solution. (See Figure II)

Titration of OXALIC ACID in  
HCl and H<sub>2</sub>SO<sub>4</sub> solutions, with  
.0283 N ceric sulphate.

The black curve represents a titration in  
H<sub>2</sub>SO<sub>4</sub> sol., and the red curve a titration  
in HCl solution. AB is only about .16 volt,  
while CD is about .18 volt. The break in  
potential is nearly twice as great in  
H<sub>2</sub>SO<sub>4</sub> sol. as in HCl sol. This agrees  
with the results in the titration of  
sodium oxalate.

These curves represent titrations  
of 0.1570 grams of Oxalic Acid  
with .0283 N ceric solution.



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Millimeters, 10th lines heavy.

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The Determination of the  
Ratio between Ceric Sulphate Solutions and  
Ferrous Ammonium Sulphate Solutions

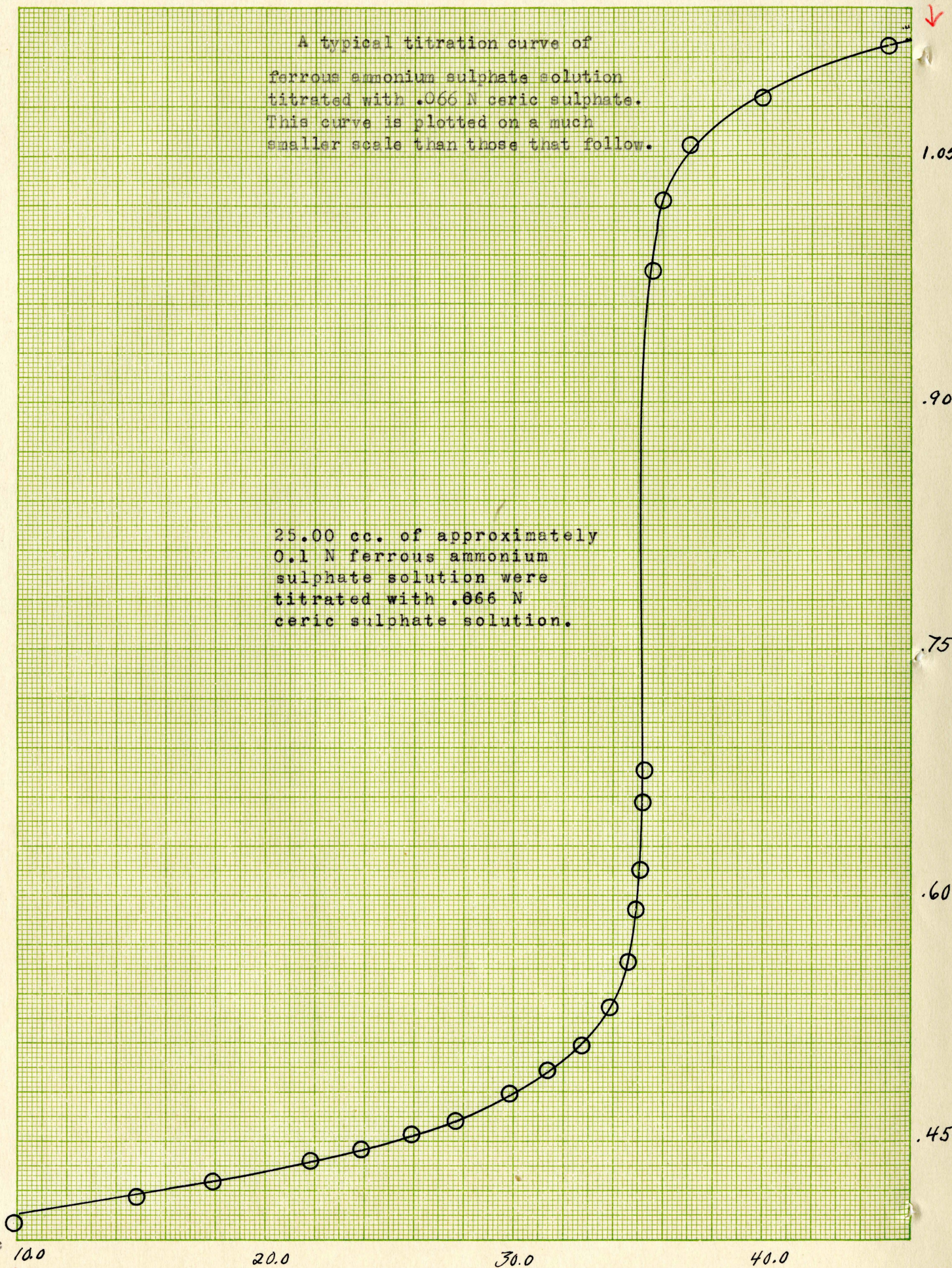
Several solutions of Ferrous Ammonium Sulphate of different concentrations were prepared, and their normalities were determined by titrating with ceric sulphate solutions which had been standardized against  $\text{Na}_2\text{C}_2\text{O}_4$ . The normalities thus found agreed excellently among themselves, and also with the value calculated from the weight of Mohr's salt used in the preparation of the solutions.

Most of the titrations were carried out with an approximately .08 N solution of ferrous ammonium sulphate about .2 M in respect to  $\text{H}_2\text{SO}_4$ , which was protected from oxidation by the air by being kept in an atmosphere of hydrogen, and titrated from an automatic burette described in the appendix.

In addition to the titrations of the ferrous ammonium sulphate solution with ceric sulphate, several of the reverse titrations were made, in which the ceric solution was titrated with ferrous solution. Titrations were made in both HCl and  $\text{H}_2\text{SO}_4$  solution, and accurate results were obtained in dilute HCl solution, and in dilute or concentrated  $\text{H}_2\text{SO}_4$  solution. It was found that Erio Glaucine A. may be used with satisfaction as an indicator in dilute  $\text{H}_2\text{SO}_4$  solution at room temperature.

A typical titration curve of ferrous ammonium sulphate solution titrated with .066 N ceric sulphate. This curve is plotted on a much smaller scale than those that follow.

25.00 cc. of approximately 0.1 N ferrous ammonium sulphate solution were titrated with .066 N ceric sulphate solution.



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Millimeters, 10th lines heavy.

cc. ceric sulphate 10.0

Potentiometric Titration of Ferrous Ammonium Sulphate in H<sub>2</sub>SO<sub>4</sub> Solution

In sulphuric acid solution the titrations were carried out by the potentiometric method, and also by using Erio Glaucine A. as an indicator. In the potentiometric titrations the same electrode system and apparatus was used that is described in connection with the standardization against Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in HCl solution. The burettes were arranged so that either the ceric sulphate or the ferrous ammonium sulphate could be titrated in, and the ratio between the two solutions could be determined by titrating either of them with the other. In most cases, however, the ferrous ammonium sulphate was put into the 250 ml. beaker containing about 150 ml. distilled water, and the necessary acid. This solution was heated until the desired temperature was reached, and then titrated with ceric sulphate.

It was found that the conditions of the titration could be widely varied, and accurate results still be obtained. The equilibrium was rapid and sensitive enough to be practical at any temperature above 30°, and at any concentration of H<sub>2</sub>SO<sub>4</sub> below 20 cc. of the concentrated acid in 150 cc. of solution.

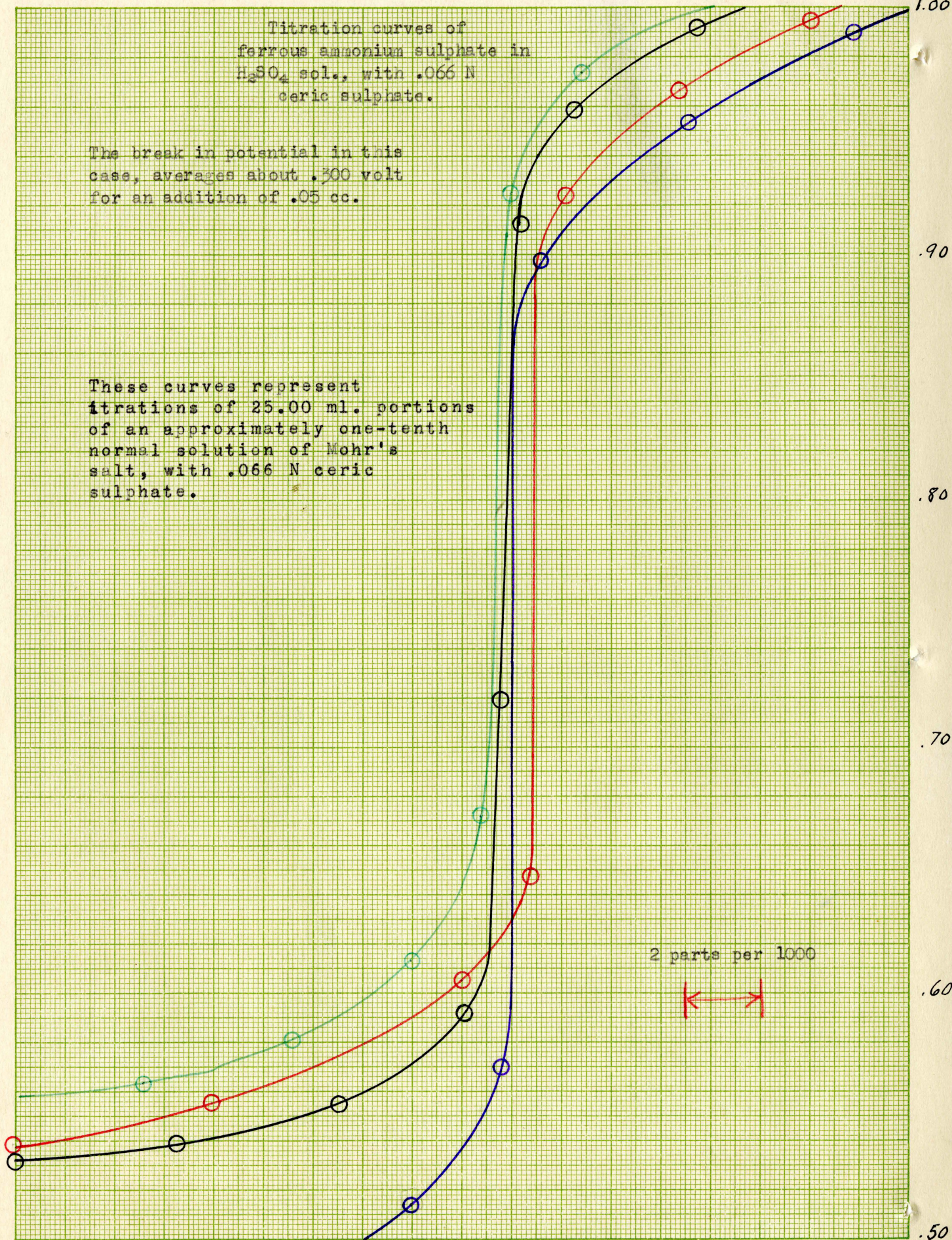
When no acid is present except that contained in the ceric solution and the ferrous solution, the titration may still be carried out with satisfaction, but it cannot be carried out in alkaline solution due to the formation

14 volts

Titration curves of ferrous ammonium sulphate in  $H_2SO_4$  sol., with .066 N ceric sulphate.

The break in potential in this case, averages about .300 volt for an addition of .05 cc.

These curves represent titrations of 25.00 ml. portions of an approximately one-tenth normal solution of Mohr's salt, with .066 N ceric sulphate.



2 parts per 1000

cc. of 34.5 ceric sulphate →

34.7

34.9

35.1

35.3

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Millimeters, 10th lines heavy.



of a white precipitate, (probably an oxide of cerium), so that more ceric sulphate solution is required than is equivalent to the ferrous solution.

A temperature of 85-90°, and an initial volume of 150 cc., containing 2 to 5 cc. of concentrated H<sub>2</sub>SO<sub>4</sub> were found to be the conditions best suited for titration in sulphuric acid solution. When these conditions are fulfilled, and the solution is kept well stirred, it is not necessary to wait at all for equilibrium to be reached near the endpoint, for by the time the burette reading can be made and recorded the potentiometer will have become constant. The break in potential in this case is about .320 volt for an addition of .05 cc. of .066 N ceric sulphate, ( see Graph 4), or about .220 volt for an addition of .05 cc. of .0283 N ceric sulphate solution. (See Graph 5 )

The reverse titration ( ceric sulphate titrated with Ferrous ammonium sulphate solution) occurs with equal rapidity and sensitiveness of equilibrium under widely varying conditions. In this case, a temperature of 85 - 95°, and an initial volume of 150 cc. containing about 10 cc. of concentrated H<sub>2</sub>SO<sub>4</sub>, seemed to be the conditions best suited for the titration. As in the titration of ferrous solution with ceric, it is not necessary to wait for equilibrium to be reached. In this case the potential drops about .400 volt for an addition of .05 cc. of .08 N ferrous ammonium sulphate solution. (See Graph 5 and 6)

cc. of ferrous solution →

28.4

28.6

28.8

29.0

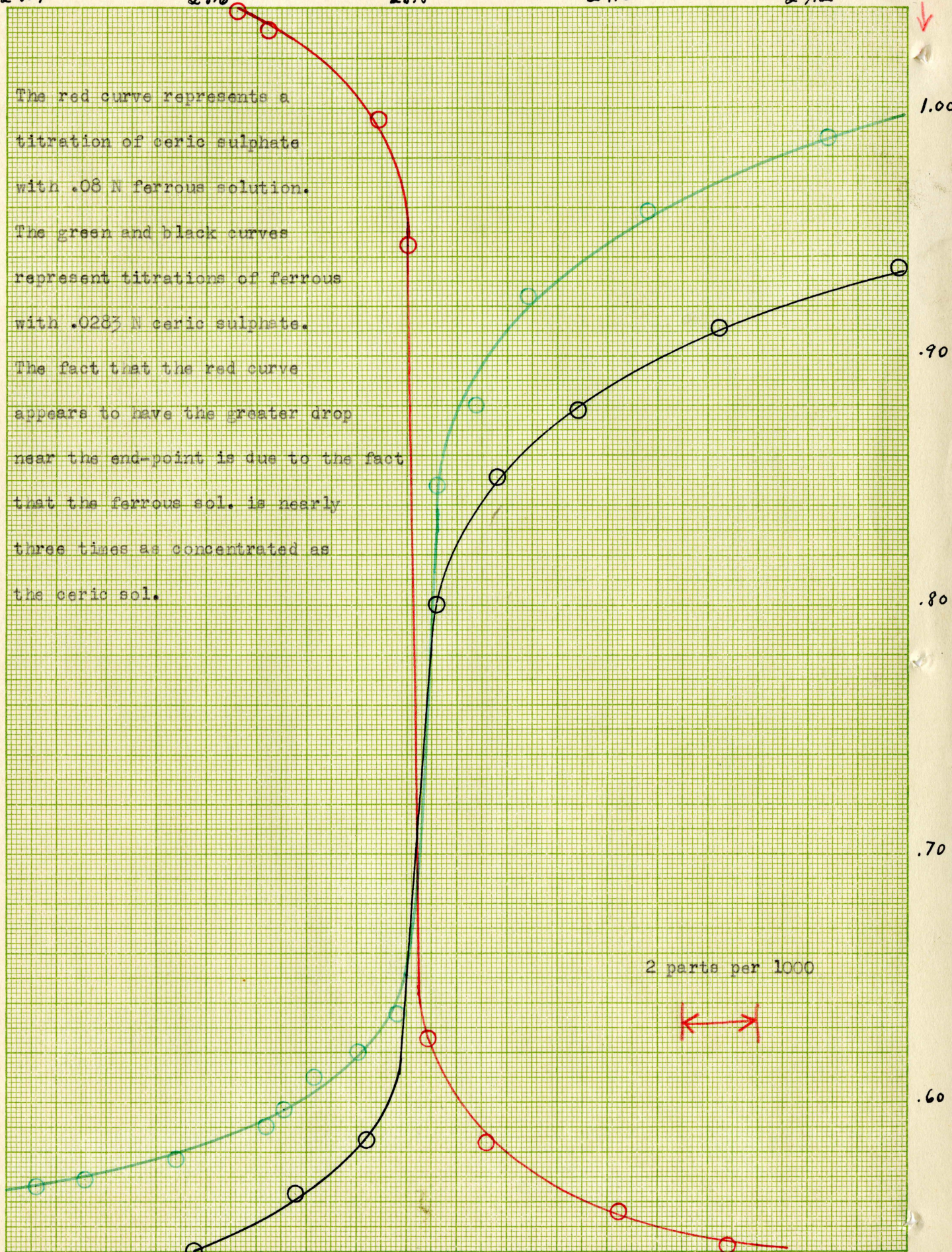
29.2

VOLTS ↓

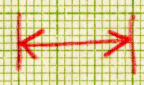
The red curve represents a titration of ceric sulphate with .08 N ferrous solution.

The green and black curves represent titrations of ferrous with .0283 N ceric sulphate.

The fact that the red curve appears to have the greater drop near the end-point is due to the fact that the ferrous sol. is nearly three times as concentrated as the ceric sol.



2 parts per 1000



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Millimeters, 10th lines heavy.

cc. of Ceric sulphate →

36.1

36.3

36.5

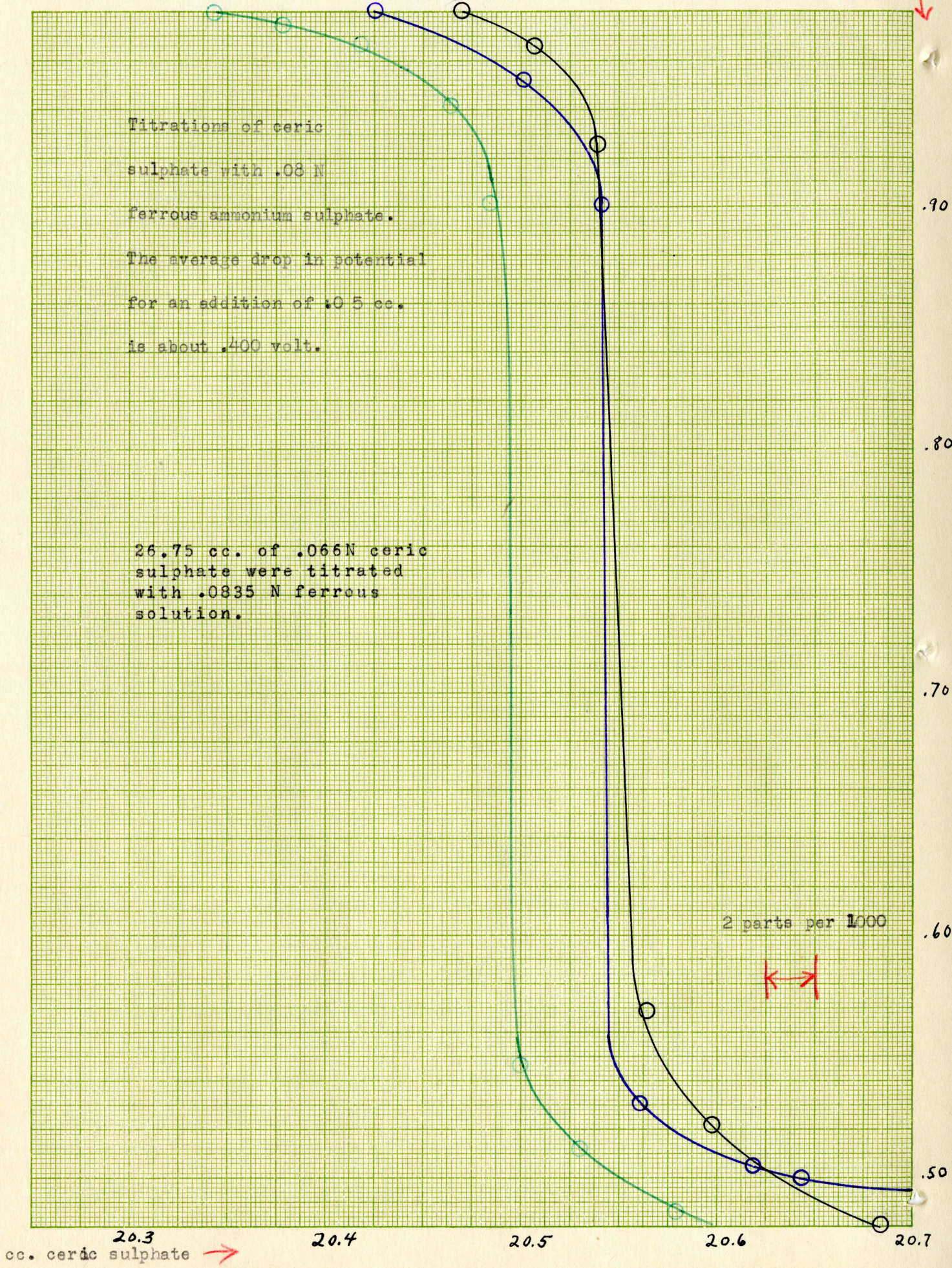
36.7

36.9

Titrations of ceric  
 sulphate with .08 N  
 ferrous ammonium sulphate.  
 The average drop in potential  
 for an addition of .05 cc.  
 is about .400 volt.

26.75 cc. of .066N ceric  
 sulphate were titrated  
 with .0835 N ferrous  
 solution.

2 parts per 1000



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cc. ceric sulphate → 20.3 20.4 20.5 20.6 20.7

Titration of Ferrous Ammonium Sulphate  
Using Erio Glaucine A. as an Indicator

When the titration was carried out using Erio Glaucine A. as an indicator, the directions given on page 56 of G. F. Smith's pamphlet were followed. A measured quantity of ceric sulphate solution was placed in a 250 ml. beaker, and diluted by the addition of 25 - 50 ml. of water, and 2 - 3 ml. of 1:1 H<sub>2</sub>SO<sub>4</sub>. This solution was titrated with the Mohr's salt solution until the yellow ceric ion color was almost bleached out. 0.5 ml of Erio Glaucine A. was added, and the color of the solution turned red. The ferrous iron solution was slowly added drop by drop, with constant stirring until the red solution turned a permanent yellow or yellowish green. ( The above directions are a modified summary of those given by G. F. Smith.)

Since the color change involved is a little difficult to recognize accurately, it was found best to have both the ferrous solution and the ceric solution in burettes. When this was done, very accurate results could be rapidly obtained by adding a few drops of ferrous solution past the end-point, and then adding just enough ceric solution to obtain the red color again. Then, the addition of one drop of ferrous solution should produce the required color change. By following this method of titration, the eye becomes more accustomed to the color

change involved, and it can be recognized more accurately. This titration occurs best at room temperature, for if the solution is heated, the indicator appears to decompose. The results obtained by this method agreed well with those obtained by the potentiometric method.

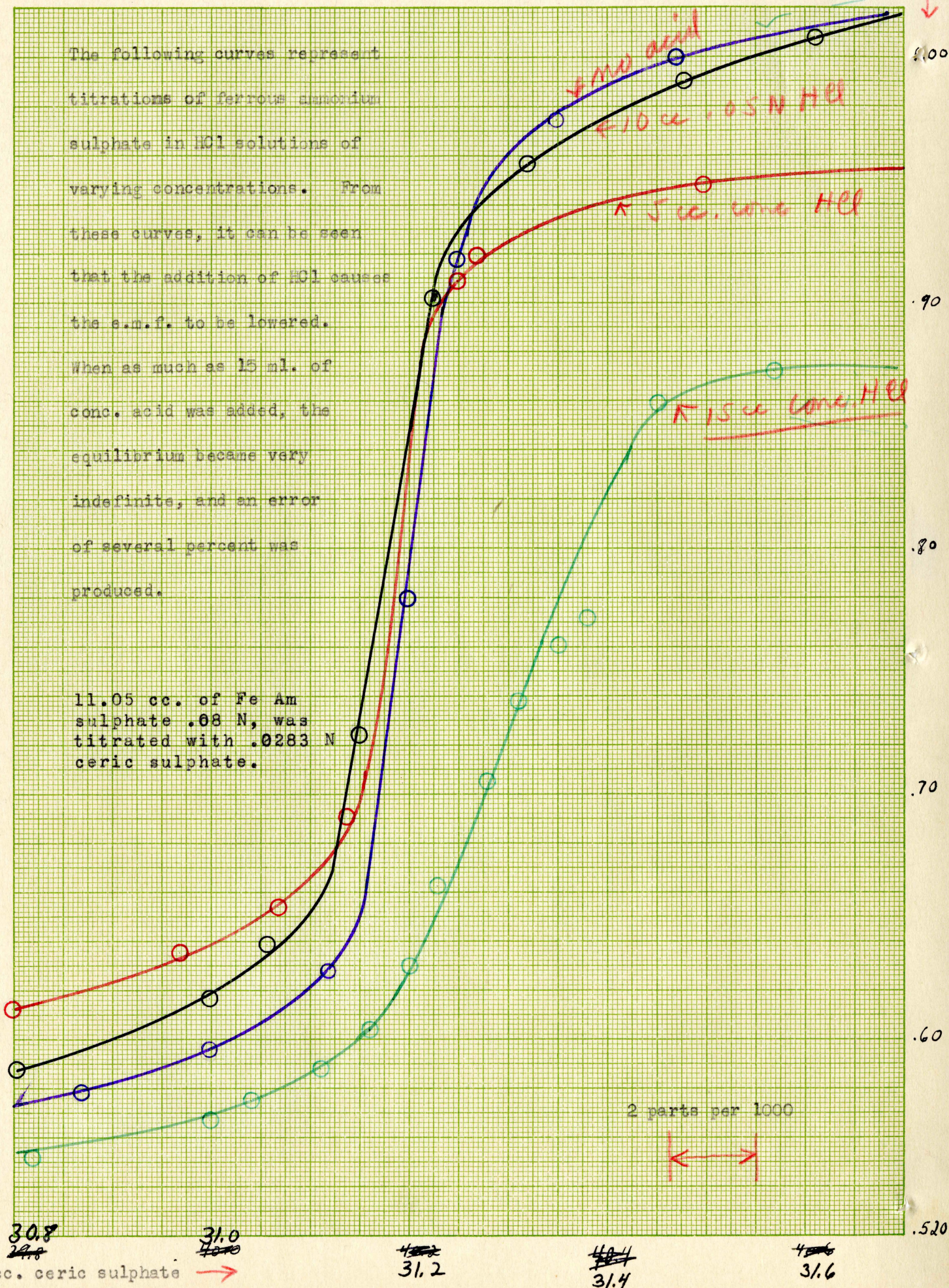
Titration of Ferrous Ammonium Sulphate in HCl Solution

In HCl solution, the titrations were carried out by the potentiometric method, as in H<sub>2</sub>SO<sub>4</sub> solution. Again it was found that the titration could be carried out ~~xxx~~ successfully over a wide range of temperature and volume. The concentration of the HCl must be kept below 10 cc. of conc. HCl in 150 ml. of solution, however, for when more HCl is present the end-point becomes indefinite, and an error of several percent is introduced, because more ceric solution is required than would ordinarily be necessary. (See Graph 7)

Although the titration may be carried out around 50°, it proceeds much more rapidly when the temperature is 85 - 95°. It was found that the addition of 20 ml. of 2 N HCl gives the proper acidity to the solution. When these conditions are fulfilled the reaction proceeds with a rapidity comparable to that in H<sub>2</sub>SO<sub>4</sub> solution, and it is not

The following curves represent titrations of ferrous ammonium sulphate in HCl solutions of varying concentrations. From these curves, it can be seen that the addition of HCl causes the e.m.f. to be lowered. When as much as 15 ml. of conc. acid was added, the equilibrium became very indefinite, and an error of several percent was produced.

11.05 cc. of Fe Am sulphate .08 N, was titrated with .0283 N ceric sulphate.



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Millimeters, 10th lines heavy.

30.8  
~~29.8~~  
cc. ceric sulphate → 31.0  
~~40.0~~  
31.2  
~~40.4~~  
31.4  
~~40.6~~  
31.6

necessary to wait for an equilibrium to be established. The break in potential in this case is similar to that in  $H_2SO_4$  solution, being about .200 volt for an addition of .05 ml. of .283 N ceric sulphate solution. (See GRAPH 7 and 8)

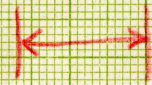
Titration of ferrous ammonium sulphate in HCl sol.

As in graph 7, the addition of much HCl causes a lowering in e.m.f.

13.00 cc. of .08 N ferrous solution was titrated with .0283 N ceric sol.

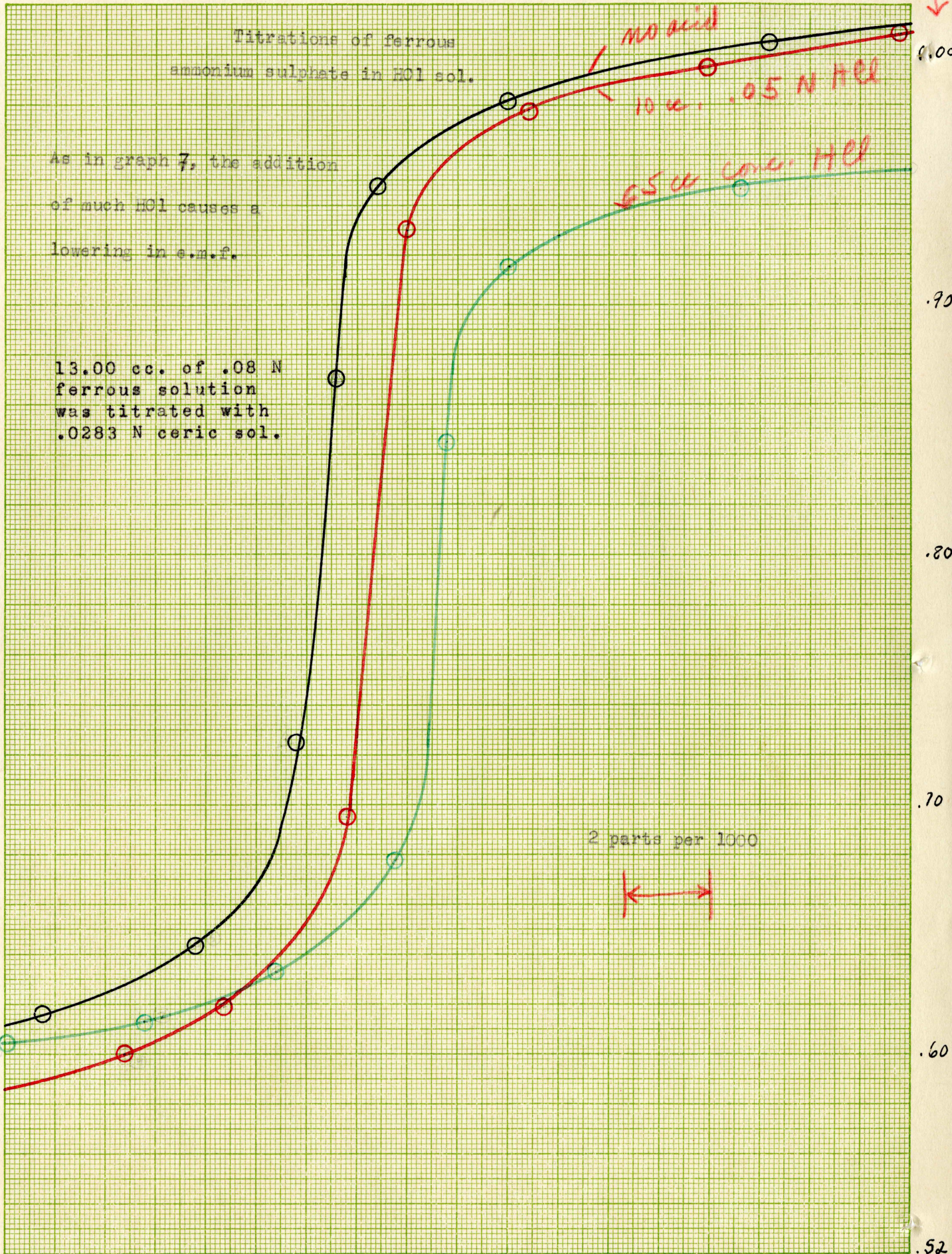
NO acid  
10 cc. .05 N HCl  
65 cc. conc. HCl

2 parts per 1000



36.4 cc. ceric sulphate → 36.6 36.8 37.0 37.2

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Millimeters, 10th lines heavy.





The Use of Ceric Sulphate  
in the Determination of the Rate of  
Decomposition of Hydrogen Peroxide under the  
Influence of Various Catalysts

The applicability of ceric sulphate as a substitute for  $\text{KMnO}_4$  in a practical laboratory procedure is shown by the following experiment, in which the effects of various catalysts on the decomposition of hydrogen peroxide was observed by following the rate of decomposition by means of titrations with ceric sulphate solution.

The following procedure is that found in Experiment 41 - Daniels, Matthews, and Williams, except that the .066 N ceric sulphate solution was used in place of the .01 N  $\text{KMnO}_4$  solution suggested.

A stock solution of  $\text{H}_2\text{O}_2$  was prepared by diluting the 3% commercial solution with about four volumes of distilled water. 25 cc. quantities were placed in small Erlenmeyer flasks, and 5 cc. of solutions of various catalysts were added, and mixed thoroughly. The solutions were kept at  $25^\circ$  in a thermostat, and the time of mixing was recorded. 5 cc. samples were withdrawn at intervals. and pipetted rapidly into

dilute HCl, and then titrated immediately with ceric sulphate.

It is best if the solution is blown out of the pipette in to the acid, since the error introduced by blowing out the pipette is less than that caused by the delay in titrating if the pipette is allowed to drain in the usual way.

The titrations were made by quickly heating the solution to 50°, adding one drop of o-phenanthroline ferrous complex as an indicator, and titrating rapidly until the color of the indicator began to fade. Readings were then taken on the potentiometer, and it was found that the indicator end-point agreed exactly with the end-point obtained by the potentiometric method.

The effects of the following catalyts were studied: (a) Platinized asbestos. (b) Platinized asbestos + trace of mercuric chloride. (c) .05 M Ferric chloride, .5 M with respect to HCl. (d) 0.5 M FeCl<sub>3</sub> solution, .5 M with respect to HCl. (e) Solution d to which enough CuCl<sub>2</sub> has been added to give .05 M CuCl<sub>2</sub>. (f) Cu Cl<sub>2</sub> solution, .5 M with respect to CuCl<sub>2</sub>, and .5 M in HCl.

In each case, four or five titrations were made during the first half of the decomposition, and from the values obtained the velocity constants for the different decompositions were calculated by the equation:

$$k = \frac{2.303}{t} \log \frac{C_0}{C}$$

The values for k, thus obtained, agreed well with each other, and also with recorded values.

Several titrations were made to determine the concentration of the  $H_2O_2$  solution in the absence of catalysts, and all the values obtained were accurate within the limits of experimental error. (See Graph 9) The concentration of the HCl into which the  $H_2O_2$  was pipetted was varied, and was found to give the best results when the HCl solution was 1.5 N. When the concentration of the HCl was above 5N, the reaction did not proceed in a quantitative manner, and the equilibrium was much too unconstant to be practical.

When 10 cc. of iodine monochloride was added the titration could be carried out satisfactorily at room temperature, but at 50 - 60° equilibrium was reached more rapidly, and it was not necessary to wait at all before the potentiometer reading became constant. The break in potential in this case is about .250 volts for an addition of .05 cc. of .066 N ceric sulphate solution. (See Graph 9)

In summary, it was found that the following procedure gives the best results in titrating  $H_2O_2$  solution where rapidity is necessary. A measured portion of the  $H_2O_2$  solution is blown from a pipette into 150 cc. of 1.5 N HCl. This solution is heated quickly to 50°, one drop of o-phenanthroline ferrous complex is added, and a dilute ceric sulphate solution is titrated in rapidly, until the color of the indicator begins to fade. Potentiometer readings are then made until the end-point is reached. In this way, a titration can be made in about five minutes, and accurate results still be obtained.

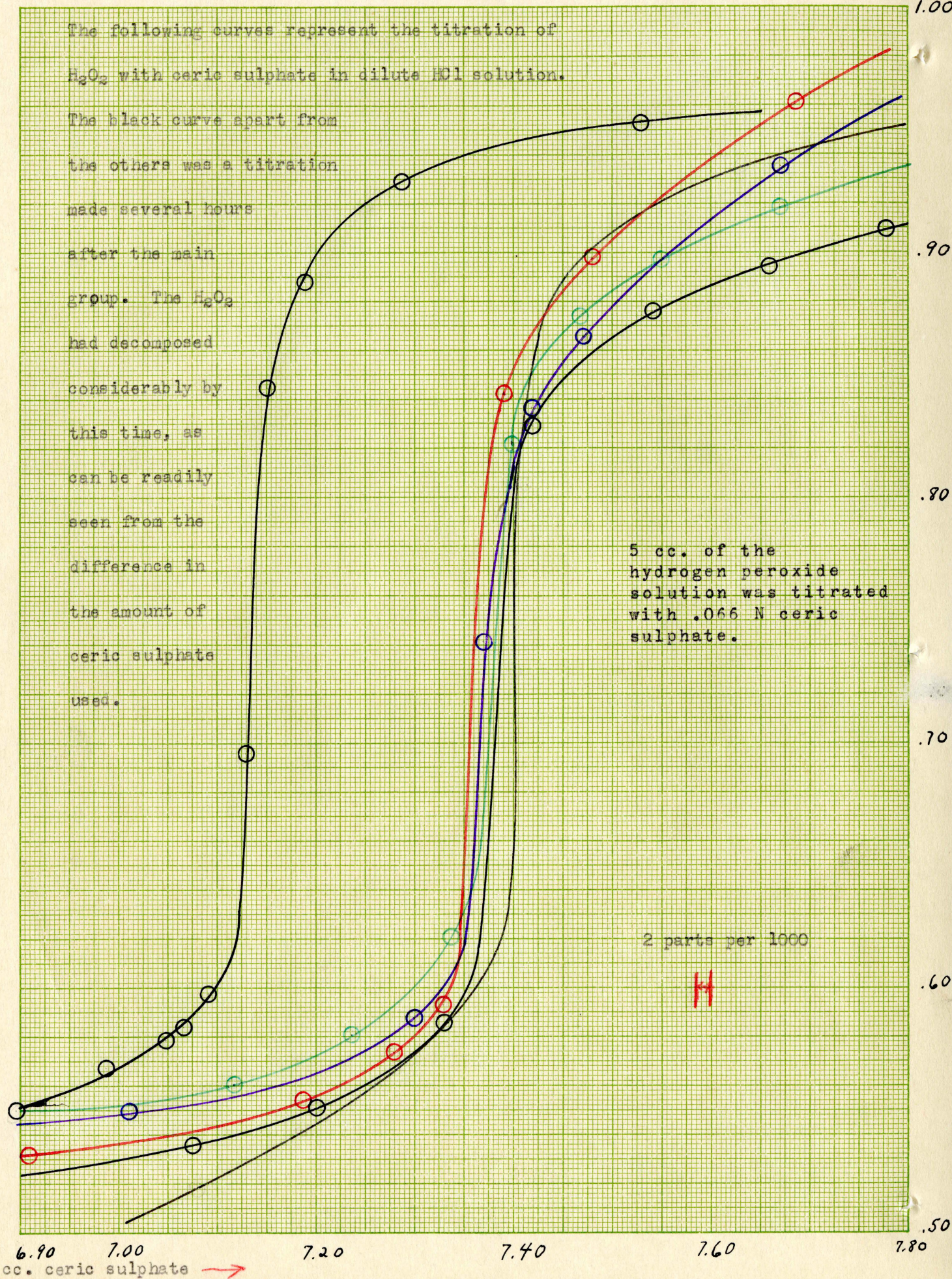
The following curves represent the titration of  $H_2O_2$  with ceric sulphate in dilute HCl solution.

The black curve apart from the others was a titration made several hours after the main group. The  $H_2O_2$  had decomposed considerably by this time, as can be readily seen from the difference in the amount of ceric sulphate used.

5 cc. of the hydrogen peroxide solution was titrated with .066 N ceric sulphate.

2 parts per 1000

H



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Millimeters, 10th lines heavy.

The Titration of  
Bivalent Platinum with Ceric  
Sulphate Solution

A solution of a bivalent platinum salt was prepared by dissolving enough  $K_2PtCl_4$ , <sup>2.5073 grams</sup> (of unknown purity, but probably very pure), in <sup>250 ml. of</sup> distilled water, so that an approximately .05 N solution was obtained. A number of preliminary experiments were made on the  $K_2PtCl_4$  solution, in which one cc. portions of the platinum solution were diluted and roughly titrated with the ceric solution, in order to determine the nature of the change in potential, and the conditions under which it best occurs.

Titration were made in hydrochloric, acetic, and sulphuric acid solutions, and it was found that the reaction between the ceric and platinum ions was quantitative in character, and that a large change in potential did occur near the end-point.

The titrations were carried out by the potentiometric method, using the apparatus described before. In some cases o-phenanthroline ferrous complex was used as an indicator in addition to the potentiometer readings. In addition to the titrations of platinum with ceric sulphate, several of the

reverse titrations were carried out in which the ceric sulphate was titrated with the  $K_2PtCl_4$  solution.

Titration of  $K_2PtCl_4$   
in Acetic Acid Solution

The results of the preliminary experiments suggested that the titrations might be carried out successfully in acetic acid solution, so several titrations were made using various concentrations of acetic acid.

In dilute acetic acid solution, the reaction was not quantitative, and no accurate results could be obtained. In concentrated solutions, accurate results could be obtained, and a definite break in potential occurred, (See Graph 10) but equilibrium was reached very slowly, and it was not sensitive enough to be practical.

Even at a temperature of  $95^\circ$ , and a concentration of 20 cc. of glacial acetic acid in 150 ml., the equilibrium was reached too slowly for practical use. If three or four minutes was waited after each addition, however, an accurate curve could be obtained. (See Graph 10)

In all acetic acid solutions, a white precipitate was present throughout the whole titration, but upon the addition of a strong acid, the precipitate dissolved, and the titration occurred with the same rapidity that it would in

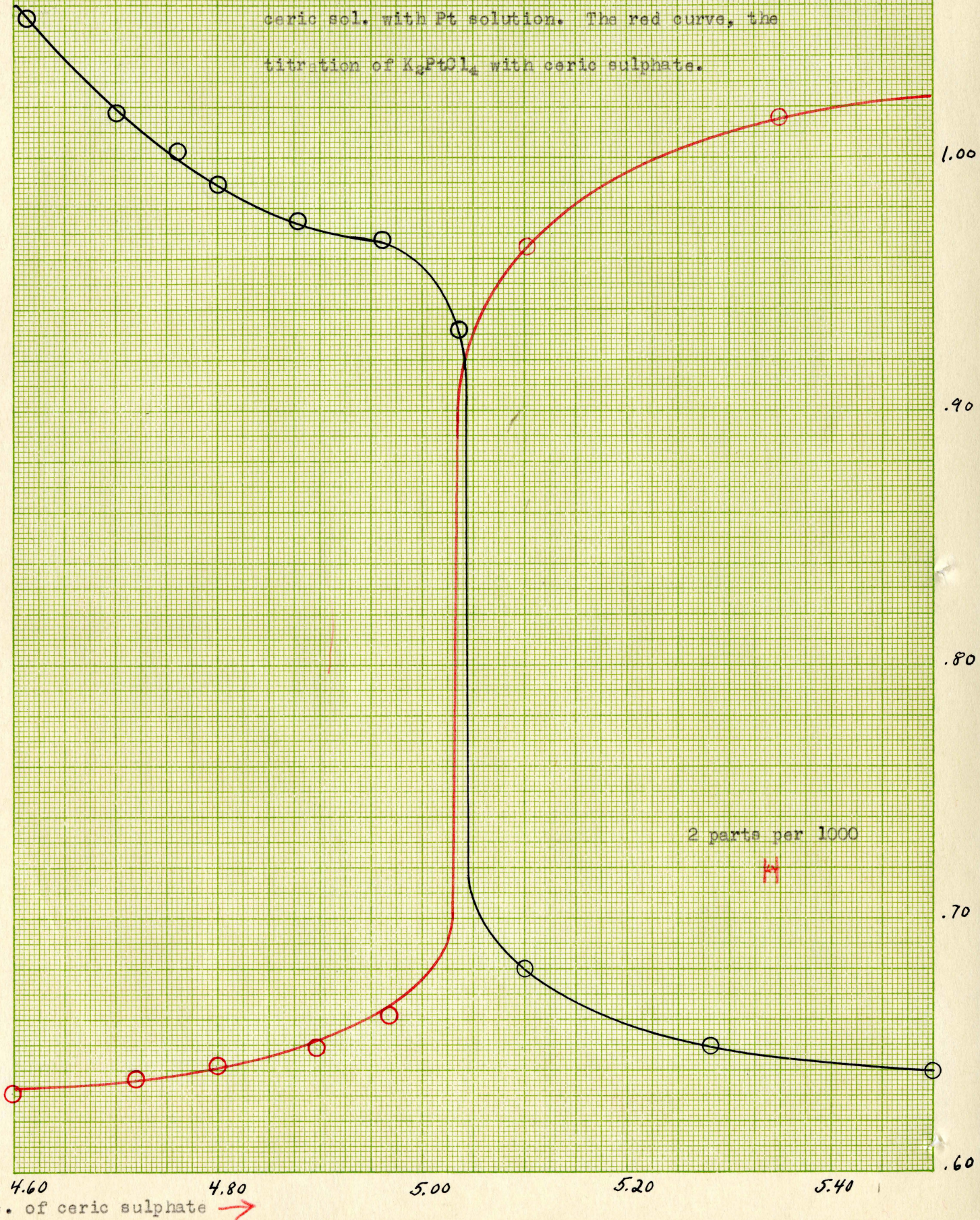
cc. of platinum sol. →  
5.60 5.75

5.90

6.10

6.30

These two curves represent titrations in acetic acid sol. The black curve is the titration ceric sol. with Pt solution. The red curve, the titration of  $K_2PtCl_6$  with ceric sulphate.



the case of the strong acid alone. It is therefore, concluded that glacial acetic acid does not furnish sufficient acidity for the titration of  $K_2PtCl_4$  with ceric sulphate, but the presence of acetic acid does not hinder the titration when a stronger acid is added to the solution.

Titration of  $K_2PtCl_4$  in  
Sulphuric Acid Solution

It was found that when the titration was carried out in sulphuric acid solution, the conditions of the titration could be widely varied, and results of reasonable accuracy still be obtained. The equilibrium was rapid and sensitive enough to be practical at any temperature above  $50^\circ$ , and at any concentration of  $H_2SO_4$  below 30 cc. of the concentrated acid in 150 ml. of solution.

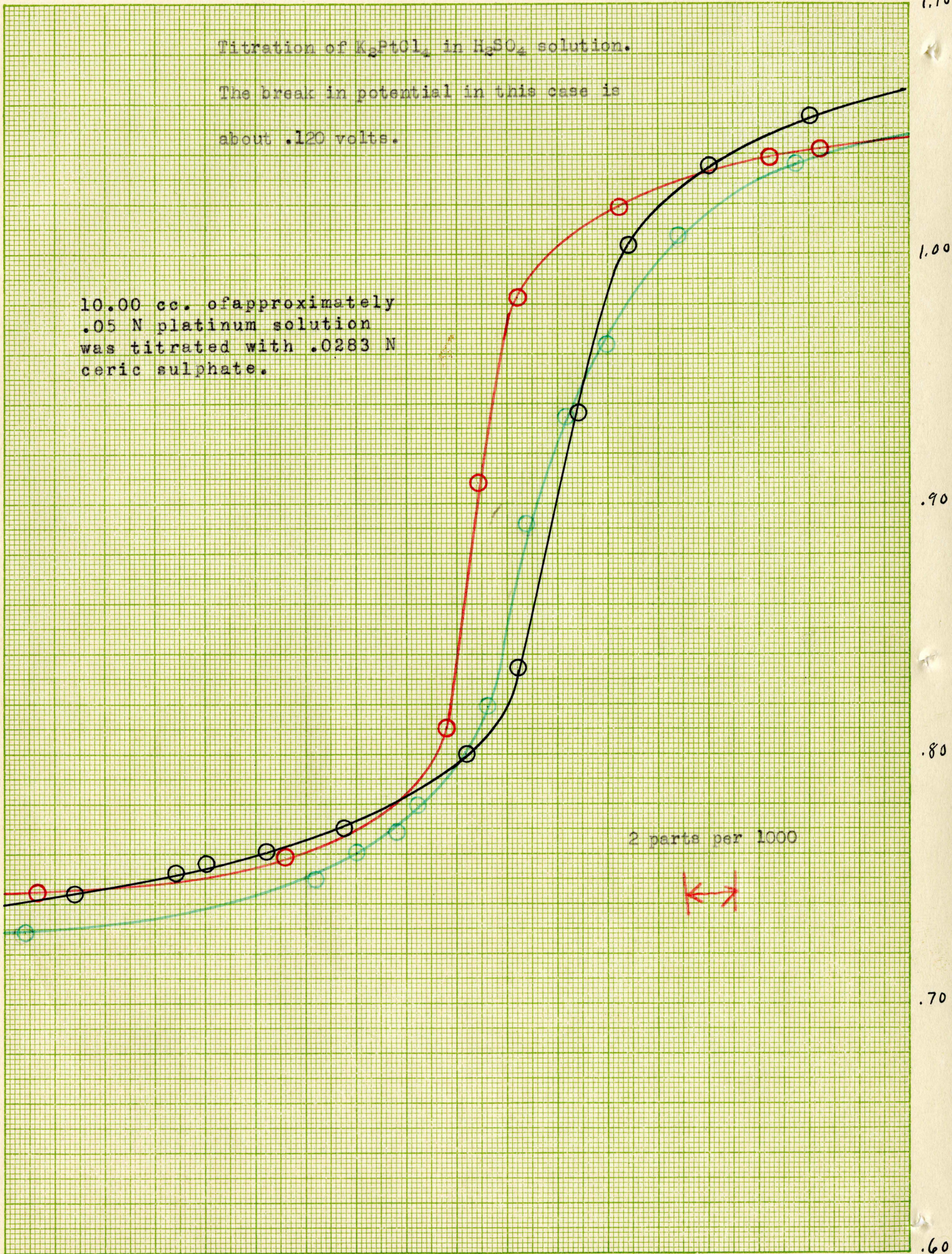
Several titrations were made at  $50^\circ$ , using o-phenanthroline ferrous complex as an indicator, and the results obtained corresponded with those obtained by the potentiometric method.

A temperature of  $85 - 90^\circ$ , and an initial volume of 150 cc. containing 5 cc. of concentrated  $H_2SO_4$  were found to be the conditions best suited for the potentiometric titration in sulphuric acid solution. When these conditions are fulfilled, and the solution is kept well stirred, it is necessary



Titration of  $K_2PtCl_6$  in  $H_2SO_4$  solution.  
 The break in potential in this case is  
 about .120 volts.

10.00 cc. of approximately  
 .05 N platinum solution  
 was titrated with .0283 N  
 ceric sulphate.



2 parts per 1000



16.4 cc. ceric sulphate → 16.6

16.8

17.0

17.2

.60

.70

.80

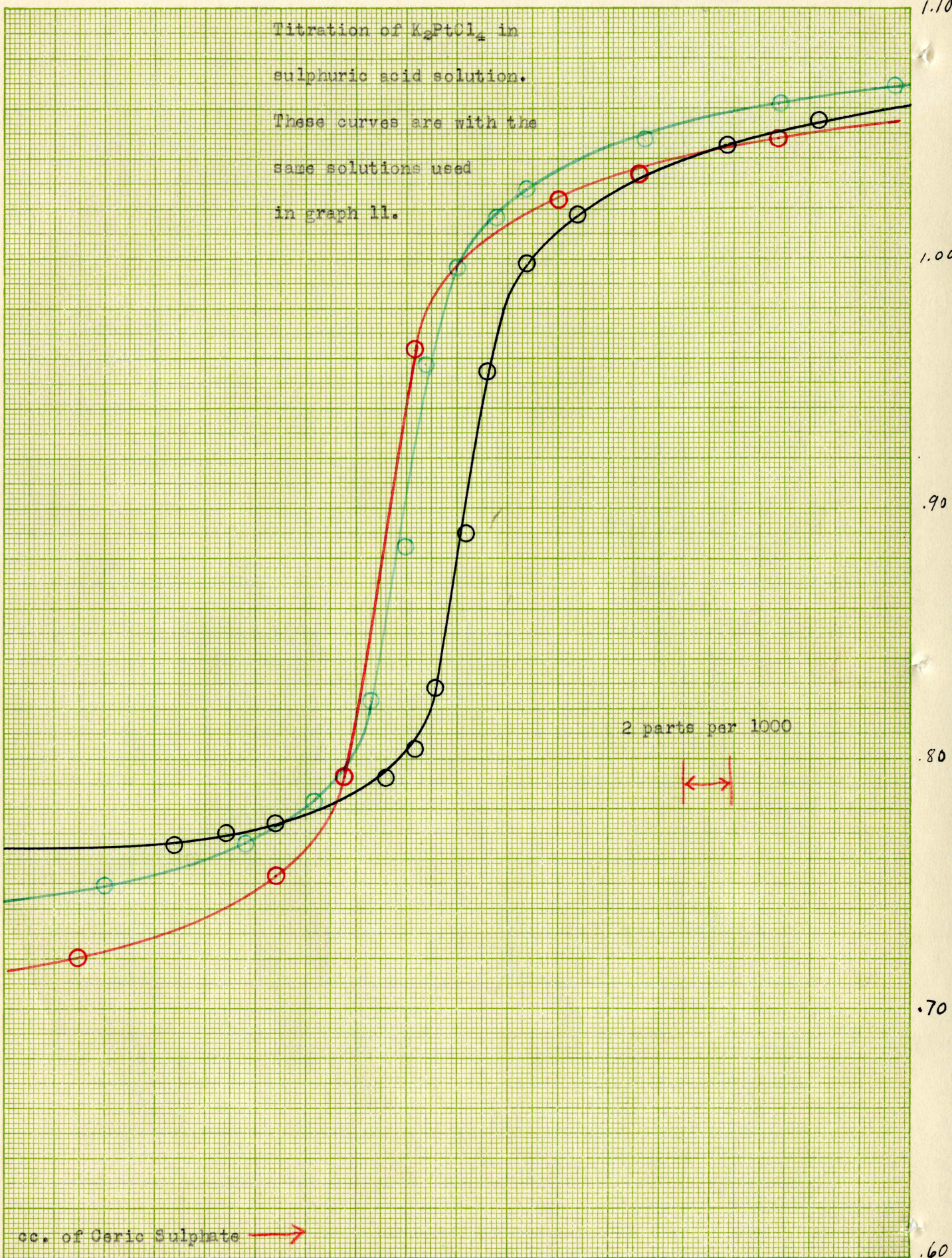
.90

1.00

1.10

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 Millimeters, 10th lines heavy.

Titration of  $K_2PtCl_4$  in sulphuric acid solution. These curves are with the same solutions used in graph 11.



cc. of Ceric Sulphate →

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Millimeters, 10th lines heavy.

to wait only about half a minute near the end-point before equilibrium is reached. The break in potential in this case is about .120 volt for an addition of .05 cc. of .066 N ceric sulphate. (see Graph 11 and 12)

Titration of  $K_2PtCl_4$  in  
Hydrochloric Acid Solution

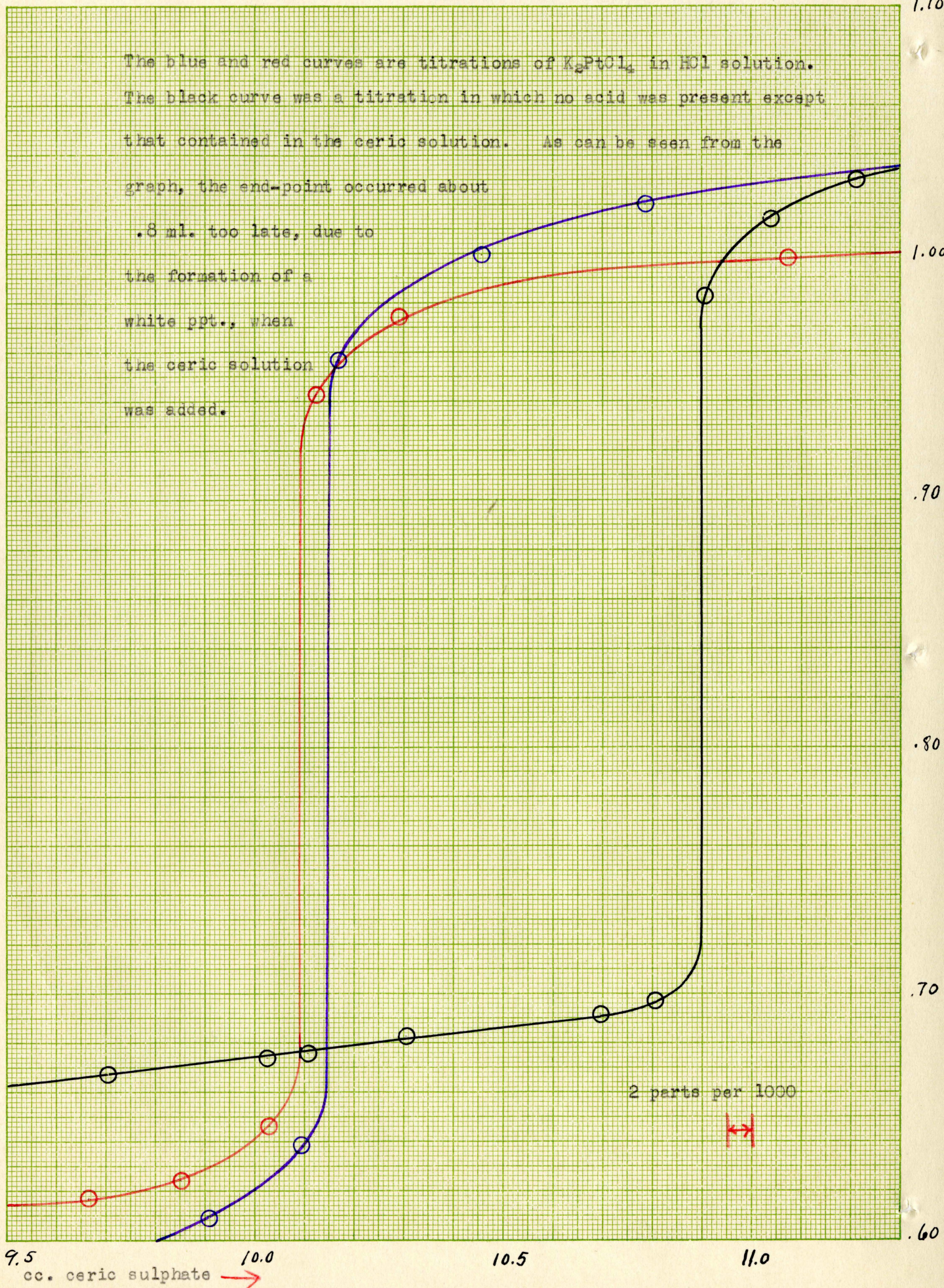
In the potentiometric titration of  $K_2PtCl_4$  in HCl solution, it was found that equilibrium was reached very quickly and sensitively when the concentration of HCl was carefully regulated. A temperature of 85 - 95°, and an initial volume of 150 cc. were found to be best suited for the titration.

A titration was made in which no acid was present except that in the ceric sulphate solution. The equilibrium was neither rapid nor constant, and a white precipitate was present in the solution throughout the titration. As seen in Graph 13, the end-point occurred about .8 ml. too late, probably due to the formation of an oxide of cerium.

When more than 15 ml. of concentrated HCl was present in 150 cc., the drop in potential was so small, and the equilibrium was so unconstant as to render the titration impractical. (See Graphs 14 and 15)

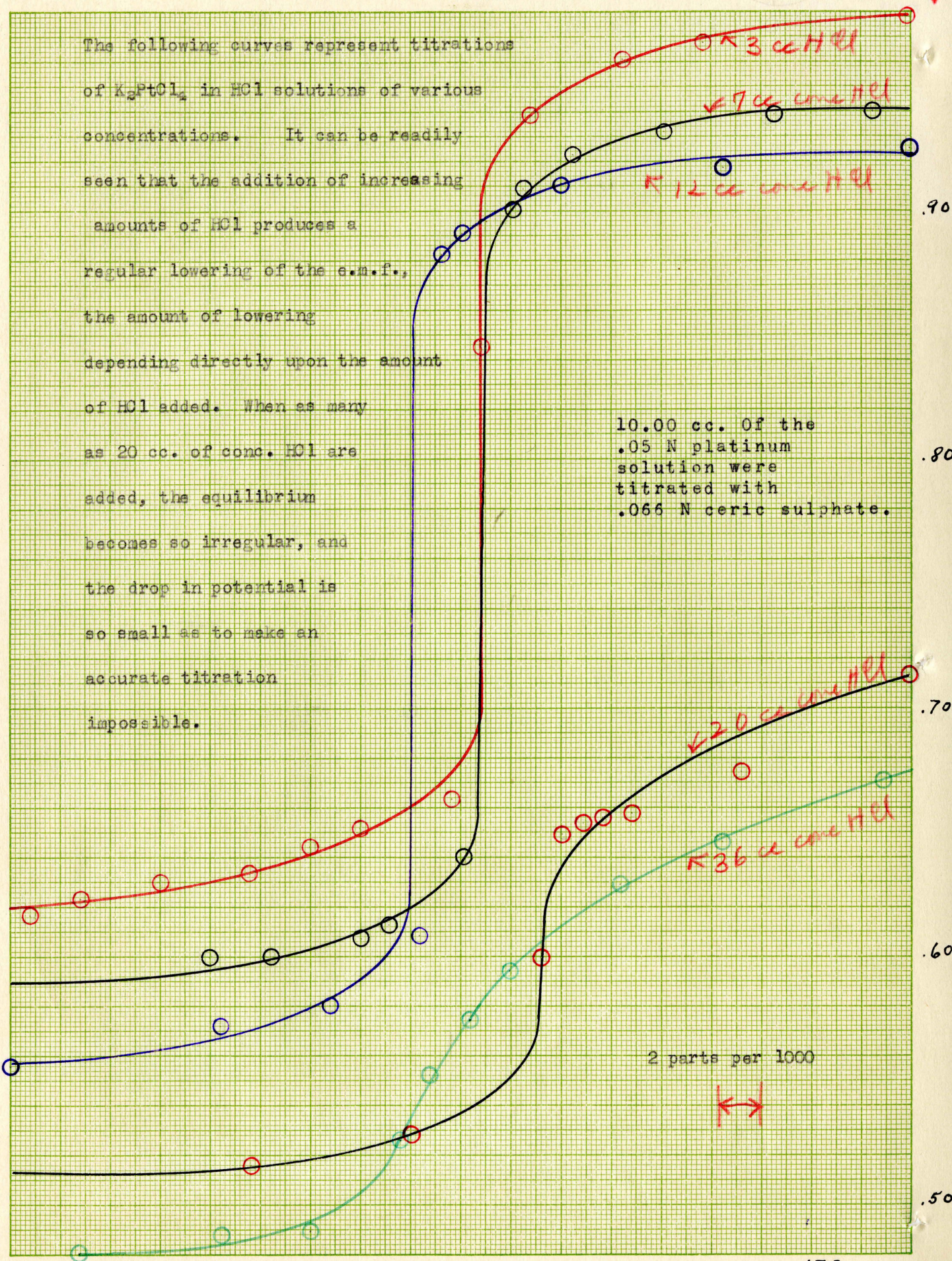
When the concentration was kept between the two limits (0 - 15 cc.) mentioned above, the equil-

The blue and red curves are titrations of  $K_2PtCl_6$  in HCl solution. The black curve was a titration in which no acid was present except that contained in the ceric solution. As can be seen from the graph, the end-point occurred about .8 ml. too late, due to the formation of a white ppt., when the ceric solution was added.



The following curves represent titrations of  $K_2PtCl_6$  in HCl solutions of various concentrations. It can be readily seen that the addition of increasing amounts of HCl produces a regular lowering of the e.m.f., the amount of lowering depending directly upon the amount of HCl added. When as many as 20 cc. of conc. HCl are added, the equilibrium becomes so irregular, and the drop in potential is so small as to make an accurate titration impossible.

10.00 cc. Of the .05 N platinum solution were titrated with .066 N ceric sulphate.



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Millimeters, 10th lines heavy.

16.4 16.6 16.8 17.0 17.2  
cc. of ceric sulphate →

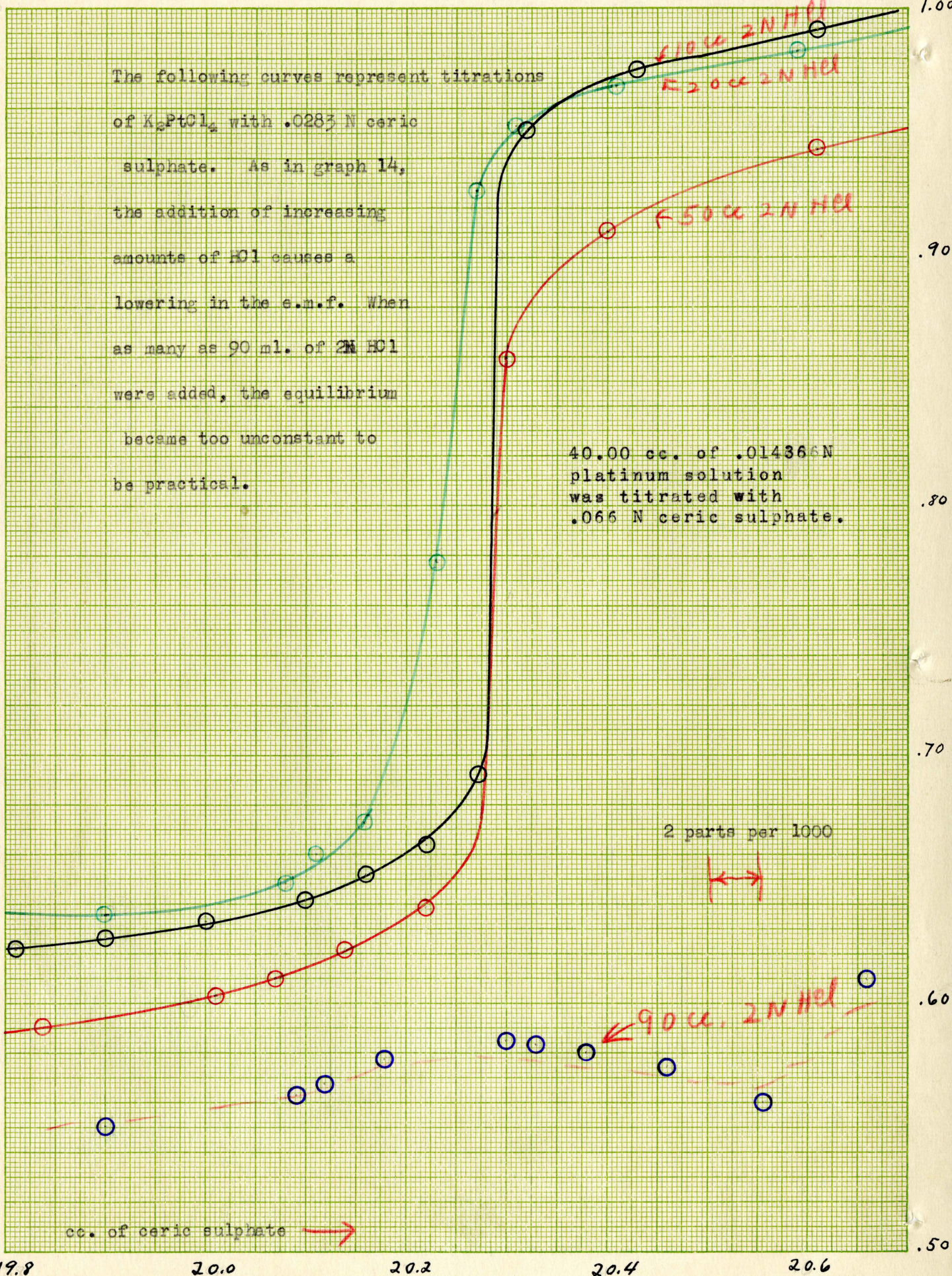
2 parts per 1000

↔

The following curves represent titrations of  $K_2PtCl_6$  with .0283 N ceric sulphate. As in graph 14, the addition of increasing amounts of HCl causes a lowering in the e.m.f. When as many as 90 ml. of 2N HCl were added, the equilibrium became too unconstant to be practical.

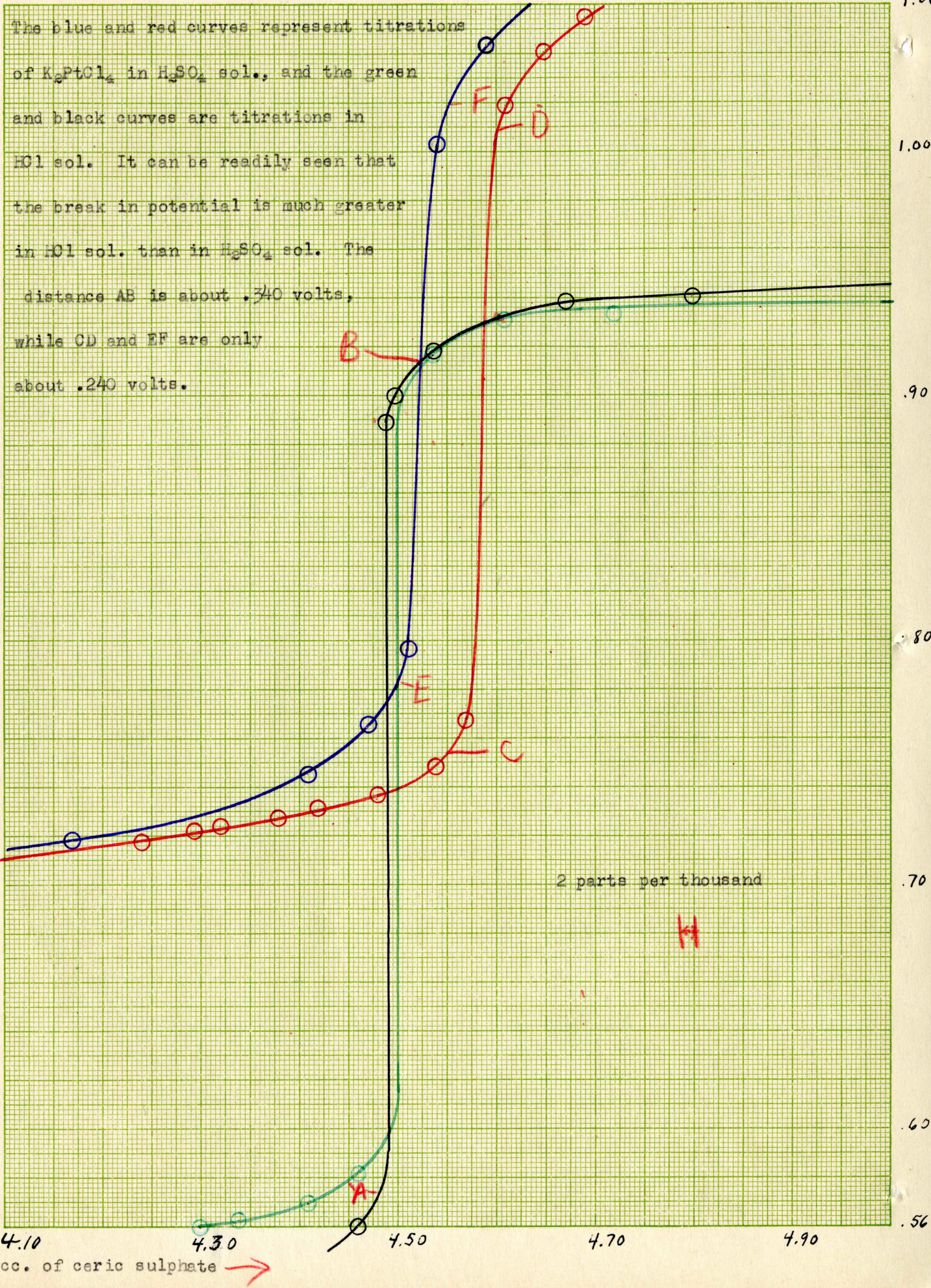
40.00 cc. of .01436 N platinum solution was titrated with .066 N ceric sulphate.

2 parts per 1000



ilibrium was found to be very rapid and constant, so that it was necessary to wait only about half a minute near the end-point, and after the end-point is reached, it becomes constant immediately. On addition of .05 ml. of .066 N ceric sulphate a break of about .280 volt was obtained, (See Graph 16), and an addition of .05 ml. of .0283 N ceric sulphate gave a break of about .200 volt. (See Graph 15) This is nearly three times the break in potential in  $H_2SO_4$  solution, (See Graph 11) so it is concluded that hydrochloric acid solution gives the better end-point, since the rate of attaining equilibrium in the two cases is about the same. (See Graph 16)

It is readily seen from Graphs 14 and 15, that the addition of varying amounts of HCl produces a regular lowering of the e.m.f., the amount of lowering depending directly upon the amount of HCl added. From a number of experiments, it was found that 25 cc. of 2N HCl was the amount which gave the best equilibrium, and the greatest drop in potential.



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Millimeters, 10th lines heavy.



Conclusion

In conclusion, the following summary is given, in which the more important experimental results and procedures are briefly outlined.

Standard ceric sulphate solutions may be made by dissolving ceric ammonium sulphate, or pure ceric sulphate in distilled water to which enough concentrated sulphuric acid has been added to make the resulting solution 0.5 molar in respect to acid. If these solutions are less than .08 N with respect to ceric sulphate they will remain perfectly clear and stable for a period of at least two or three months.

Ceric sulphate solutions may be conveniently standardized by titrating against accurately weighed portions of Standard Sodium Oxalate, and the Normalities obtained by this method were found to be accurate within the limits of experimental error in both hydrochloric and sulphuric acid solutions, under varying conditions of temperature, concentration, and volume. It was found that sulphuric acid solution is more suitable than hydrochloric acid solution in carrying out the titration by the potentiometric method, since the change in potential is greater, and

equilibrium is reached more quickly. When the potentiometric method is not desirable, a satisfactory standardization may be made using ortho phenanthroline ferrous complex as an indicator in hydrochloric acid solution. The following conditions were found to be best for titrating sodium oxalate using the potentiometric method of determining the end-point:

Temperature of solution: 85 - 95 C.

Initial Volume: 150 cc.

Acid concentration: 2 or 3 cc. of Conc. Sulphuric per 150 cc. of solution.

It was found that Ferrous Ammonium Sulphate solutions could be accurately titrated with ceric sulphate solutions in both dilute hydrochloric acid, and dilute or concentrated sulphuric acid solution. The normalities found by this method agreed excellently among themselves, and also with the value calculated from the weight of Mohr's salt used in the preparation of the solutions. It was found that Erio Glaucine A. may be used with satisfaction as an indicator in dilute sulphuric acid solution at room temperature. The titration may be carried out either by titrating ferrous with ceric, or vice versa, ceric solution with ferrous. The following conditions were found to be best for carrying out the titrations by the potentiometric method:

Temperature of solution: 90 C.

Initial Volume: 150 cc.

Acid concentration: 3 cc. of Conc. sulphuric acid or 20 cc. of 2N HCl.

Accurate results were also obtained in the titration of hydrogen peroxide solutions with ceric sulphate solution. It was found that the following procedure gave the best results in titrating catalyzed peroxide solutions where rapidity is imperative. A measured portion of the peroxide solution is blown from a pipette into 150 cc. of 1.5 N HCl. This solution is heated quickly to 50 degrees C., one drop of o-phenanthroline ferrous complex is added, and a dilute (about .02 N) ceric sulphate solution is titrated in rapidly until the color of the indicator begins to fade. Readings are then made on the potentiometer until the usual end-point is reached. In this way, a titration can be made in about five minutes, and accurate results still be obtained.

It was found that K Pt Cl could be accurately titrated with ceric sulphate solution, either in hydrochloric or sulfuric acid solution. The results obtained using o-phenanthroline ferrous complex as an indicator corresponded with those in which the potentiometric method was used. It was found that a carefully regulated concentration of HCl will give better results than when sulphuric acid solution is used. From the results of a number of experiments, it was found that 25 cc. of 2 N HCl gives the proper acid concentration, when the initial volume of the solution to be titrated is 150 cc., and a temperature of 85 - 95 C. is used. If no acid is used, the equilibrium is neither rapid, constant,

nor accurate, and if more than 15 ml. of the concentrated acid is present, the drop in potential is so small, and the equilibrium so unconstant as to render the titration impractical. The titration should, therefore, be carried out under the following conditions:

Temperature of solution: 85 - 95 C.

Initial volume: 150 cc.

Acid concentration: 25 ml. of 2 N HCl,  
per 150 ml. of solution.

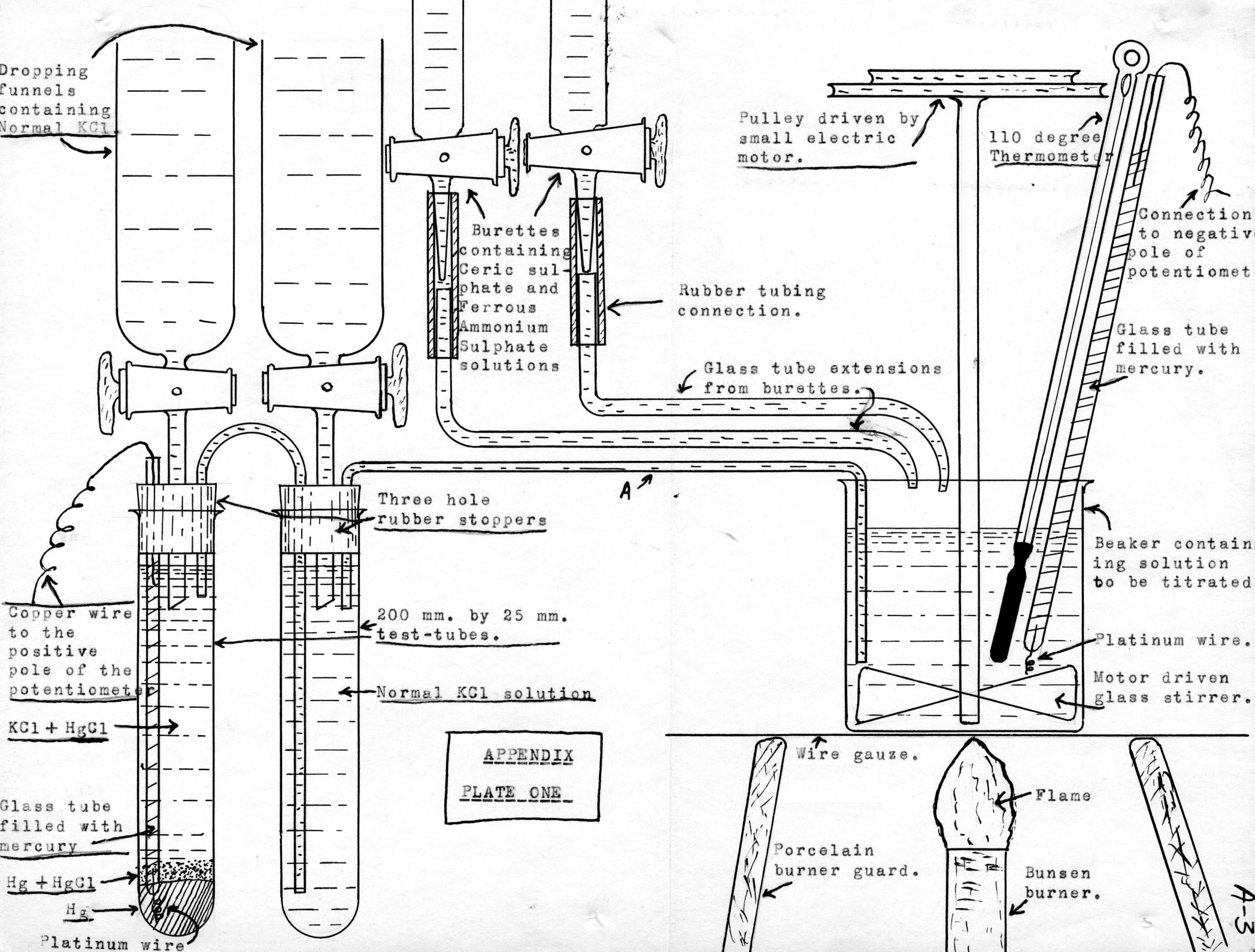
APPENDIX

Appendix -

The accompanying sketches should give a rough idea of the general nature of the apparatus used in the experimental work on this thesis. This apparatus consisted essentially of a Potentiometer, a Normal Calomel electrode, a platinum electrode, burettes for titrating in the solutions, and means for stirring and heating the solution to be titrated. The potentiometer set-up was that ordinarily used with the Queen potentiometer, but the rest of the apparatus possesses a few original touches found to be necessary when titrating solutions near 100 degrees.

It was found that an ordinary calomel electrode was unsatisfactory when used at high temperatures, because its short arm brought it too near the solution being heated, and a gelatin salt bridge would melt, and therefore could not be used. The calomel electrode shown in Plate One was devised for use when the solution being titrated was near the boiling point, and was found to be perfectly satisfactory and even more convenient than the calomel electrode of the usual type. It consists of two 200 by 25 mm. Pyrex test tubes, one of which contains a layer of mercury, and a solution of normal KCl saturated with calomel, and

the other contains normal KCl. Three hole rubber stoppers are placed in the top of each, and tightly fitted so no air can leak in. Two dropping funnels containing normal KCl, a glass tube filled with mercury, having a platinum wire sealed at the end, and hollow glass tubing bent as required are arranged as shown in the drawing. By opening the stopcocks of the dropping funnels the glass connecting tubes can be filled with solution, and if the connections are all airtight, the solution will not leak out. Tube A is about ten or twelve inches long, so that the electrode will be far enough removed from the flame not to be affected by the heat. The test-tube containing the N KCl acts as a salt bridge, and should be removed occasionally so that the calomel electrode can be flushed out. Tube A should be flushed out after each titration. The burettes each have glass tube extensions about eight or ten inches long, as shown, so that they will be far enough away from the flame not to be affected by the heat. The ends of these glass tubes are drawn out to a fine capillary, so that the size of the drops during the titration will be as small as possible. A motor driven glass stirrer was arranged as shown, and the solution being titrated was kept well stirred at all times. A 250 cc. beaker was found to be a convenient size for carrying out most of the titrations. The solution was heated by





a Bunsen burner placed in a porcelain burner guard to protect the flame from drafts, so that a small flame could be conveniently maintained. A Hoffman screw-clamp is placed on the rubber tubing connected to the burner, outside the burner guard, so that the size of the flame can be conveniently regulated. A 110 degree thermometer is placed in the solution, so that the temperature at the time of titrating may be known. A glass tube filled with mercury, and having a platinum wire sealed in the end is used as the second electrode.

Since a solution of ferrous ammonium sulphate is oxidized upon exposure to the air, the automatic burette shown in Plate Two was devised, so that the solution could be kept under an atmosphere of hydrogen at all times, thus preventing any atmospheric oxidation. The solution was placed in a five liter wide-mouthed bottle, closed by a tightly fitting three hole rubber stopper that was sealed down so it would not be blown out by the pressure of the hydrogen. A rubber tube connected the hydrogen tank with the glass tube in the stopper as shown. A three way glass stopcock was placed in the stopper, and one of the arms stops near the top of the bottle, but the other extends to the bottom. The third arm is extended to the top of the burette by means of a thick walled glass tube of small inside bore, which is drawn out to a taper at one end, so that the hole in the stopper at the top

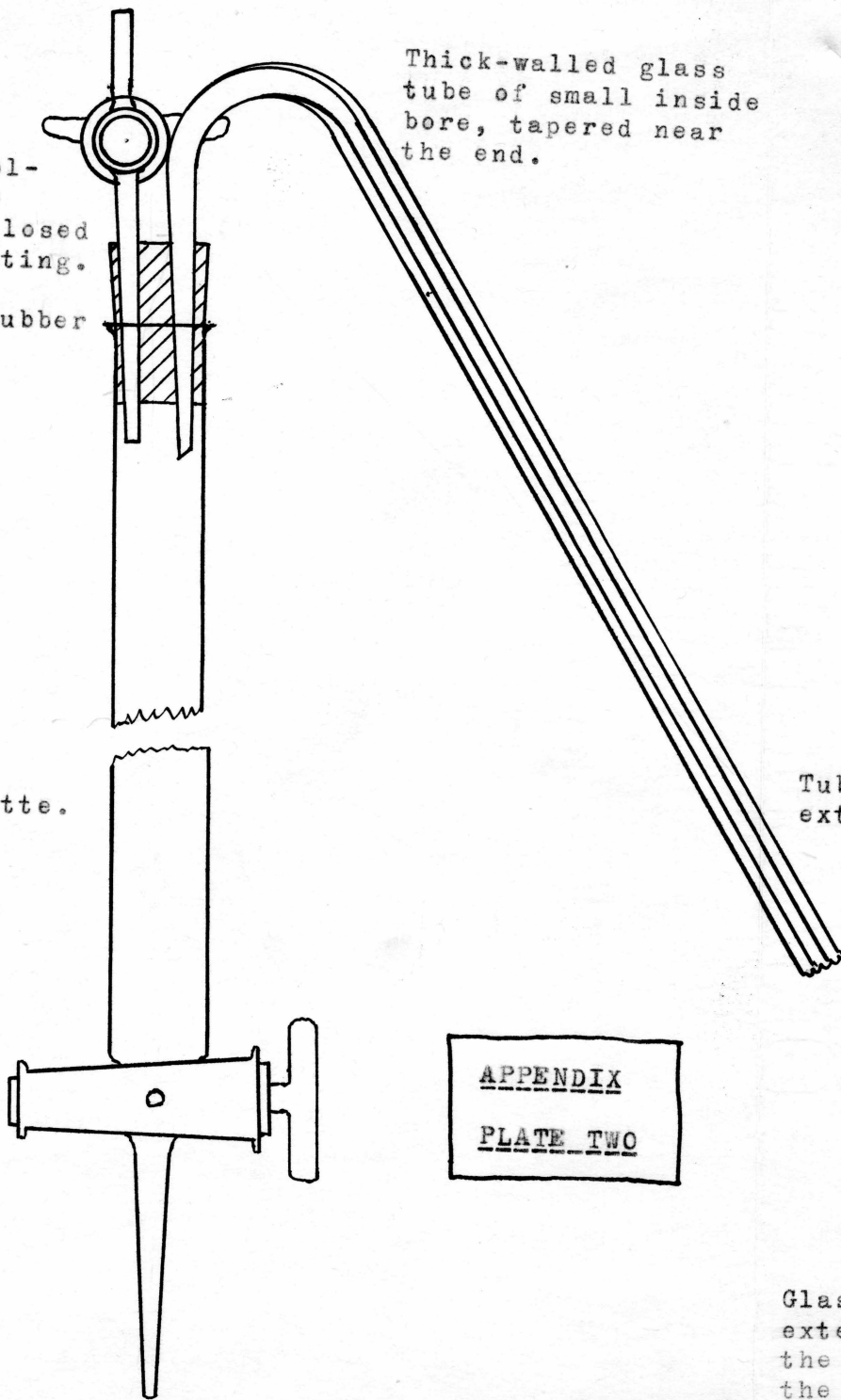
Stopcock

Open when running solution into burette; closed when titrating.

Two-hole rubber stopper.

Thick-walled glass tube of small inside bore, tapered near the end.

50 cc. burette.



APPENDIX  
PLATE TWO

(A)

Tube A.

Rubber tubing sleeve.

3-way glass stopcock.

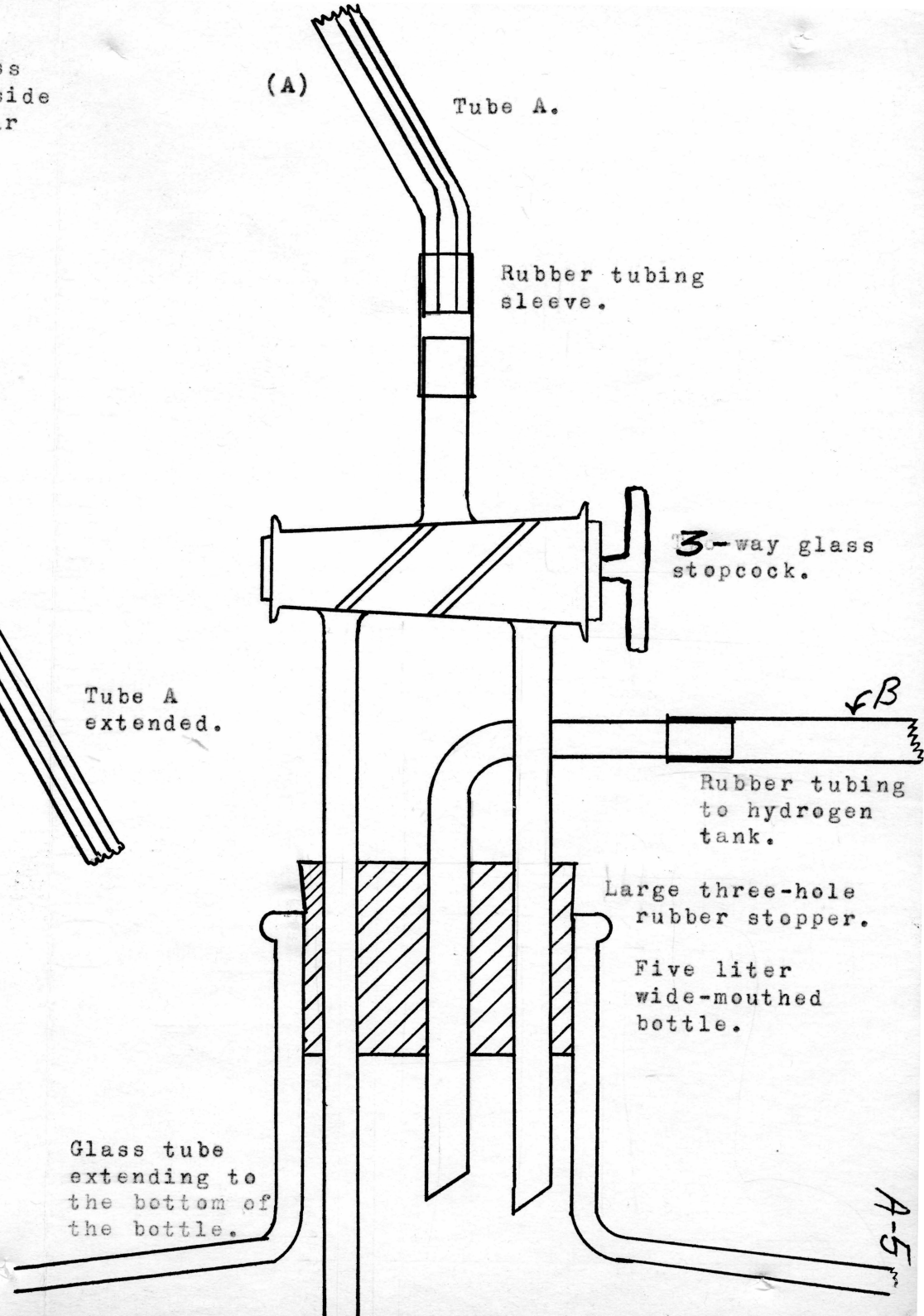
Tube A extended.

Rubber tubing to hydrogen tank.

Large three-hole rubber stopper.

Five liter wide-mouthed bottle.

Glass tube extending to the bottom of the bottle.



A-5

of the burette could be kept very small. A stopcock obtained from the end of a broken burette was used as an outlet when the solution was being run into the burette, but was closed during the titration. When the 3-way stopcock is arranged as shown, the solution will be blown up through tube A, and into the burette. When the burette is filled within four or five cc. of the top, the stopcock is turned, and hydrogen is blown through the tube, forcing the solution remaining in the tube into the burette. The stopcock at the top of the burette is then closed, and the titration may be carried out.

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