

A ZINC - COPPER COUPLE FOR THE REDUCTION OF IRON
FOR PERMANGANATE TITRATION.

by

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The following work was undertaken to determine the practical value of electrolysis for the reduction of iron for its quantitative determination by titration with potassium permanganate, and the best type of apparatus and most suitable conditions for this reduction. Hence, accuracy of results and time required were the chief points considered and no attention was paid to either current or energy efficiency. It is a continuation of the work of Dr. H. C. Allen, described in a paper published in 1914, under the title, "The Electrolytic Reduction of Iron for Permanganate Titration".

Electrolysis has been much studied as a reducing agent, both in organic and inorganic fields, in the quantitative determination of substances by titration with suitable standard oxidizing solutions. Where conditions make its use possible, it has usually been found far more satisfactory than ordinary chemical methods.

While the rotating cathode or anode has been much used to hasten the reduction, or the electrolytic action, by keeping the solution thoroughly stirred, the attempt has been made in this work to accomplish the same result with the escaping gases, thereby allowing the apparatus to be much simplified. The advantages of electrolysis over ordinary chemical methods are obvious. There is no danger of

introducing an excess of reducing agent, which would have to be removed before titration. Very little foreign material which might contain impurities that would make the determination inaccurate or which might in itself impair the accuracy of the titration, goes into the solution.

The first type of apparatus tried, in attempting to utilize the escaping gases to stir the solution, was made by cutting circular pieces of copper gauze which would just fit inside the beaker to be used and then inserting a number of small zinc rods through them to hold them in place and make good connections between the zinc and copper. It was found that this apparatus was not satisfactory because the gases, escaping about evenly all over the surface of the copper, did not give sufficient stirring to cause the reduction to proceed rapidly enough. It was seen that the gases escaped more freely near the zinc rods, so a single zinc rod was used instead of several. It was necessary to use a larger zinc rod in this case in order to give a large enough area of zinc exposed to the solution. This formed a series of plates of copper gauze connected through the center with a zinc rod. This did the work satisfactory but as the zinc dissolved the rod became smaller and the copper plates became loose and would not stay in the proper position.

The copper discs were then wired in position with heavy copper wire and the zinc rod inserted in the center as before but in this case, when some of the zinc had dissolved the connection between the zinc and the copper became poor and the electrolytic action did not proceed as rapidly as it should.

The apparatus finally decided upon as the most suitable was made as follows:- A strip of gauze of the cathode metal was cut the width of the beaker used to contain the solution and about eight inches in length. This was bent back upon itself at intervals of the width of the beaker and the corners trimmed off so it would just go inside the beaker. This formed a series of circular plates of gauze each connected with the one next it at one side. A hole was then cut in the center of each plate large enough to allow the anode metal in the form of a rod to be inserted. The rods used in this work were about two centimeters in diameter and ten centimeters long. The holes for the anode were not cut exactly in line so that it was necessary to spring the gauze a little to allow the anode to be inserted. The gauze was elastic enough to form a sort of spring which held the anode firmly in place and at the same time insured good connections between the electrodes where the anode passed through each plate of the cathode, at all times. This apparatus was dropped into the ferric solution made acid with sulfuric acid and the beaker covered with a watch glass and allowed to remain until the reduction was complete.

This formed a short circuited voltaic cell in which the iron solution made acid with sulfuric acid was the electrolyte and acted as a depolarizer. It was found that the reduction could be made almost as quickly by this means without the use of an auxiliary current as it could with the use of such a current. This allows a much wider application of the method as an outside source of current is not necessary.

The object of using a single large rod of metal for the anode instead of a number of smaller ones was to get most of the escaping gases to be released at the center of the beaker instead of at all parts of it. This caused the solution to form a current upward in the center of the beaker and downward at the sides which stirred the solution so thoroughly that the reduction proceeded as rapidly as it would if a rotating cathode or anode were used. This allowed a motor, which would be necessary if a rotating electrode were used, to be dispensed with in the use of this apparatus.

If it were possible to use zinc, amalgamated with mercury in this apparatus, less of the metal and practically none of the impurities contained in it would go into solution. However its use was found impossible. The first difficulty encountered in its use was that when the copper was placed in the acid solution in contact with the amalgamated zinc, it also became amalgamated and the electrolytic action stopped. This difficulty was overcome by surrounding the zinc anode with a glass tube in which a large number of holes were blown to allow free contact between the stirred solution and the anode. The connection between the cathode and anode was made by a heavy copper wire passing from the anode over the top of the tube and connecting with the copper cathode. This eliminated the amalgamation of the copper but the gases released, were insufficient to stir the solution. This apparatus was allowed to stay in a solution containing five cubic centimeters of acid per two hundred cc., for one hour and it was found that only 53% of the iron had been reduced.

The unamalgamated zinc offers no such objections and the zinc going into solution is too small in amount

to affect the accuracy of the determination. When five cubic centimeters of concentrated sulfuric acid per two hundred cc. of solution, were used only .8 grams of zinc was dissolved. The zinc is very readily obtained in a very pure state so not enough impurities go into solution to affect the determination in any way.

A tall beaker without a lip, and of about three hundred cubic centimeters capacity is the best for containing the solution for this reduction. This is covered with a watch glass during the reduction to prevent spattering, or the solution being carried out of the beaker by the escaping gases.

The iron solution was delivered into the beaker by means of a twenty five cc. automatic pipette. The amount of solution delivered by the pipette was weighed a number of times and it was found to be constant to one tenth of one per cent, which was close enough for this work.

The titrations were made from a fifty cubic centimeter burette graduated to tenths of a cubic centimeter and calibrated by the Government Bureau of Standards.

Chemicals:-

The metals used in this work were nearly pure and had been prepared for the purpose of quantitative work. The sulfuric acid used was 98% pure. C. P. chemicals were used throughout.

Solutions:-

The iron solution was prepared by dissolving ferric sulfate in water and adding forty cubic centimeters of sulfuric acid per liter. This solution was found to be .1082 normal and contained .1512 grams of iron per twenty five cubic centimeters.

The permanganate solution used was standardized by titrating it against C. P. sodium oxalate and it was found to be .1426 normal. Several determinations were made in which twenty five cubic centimeters of the iron solution were placed in an Erlenmeyer flask, five cubic centimeters of concentrated sulfuric acid and four or five grams of granulated zinc were added. The air was excluded from the flask by inserting a cork containing a glass tube drawn out to a capillary at one end. All the zinc was allowed to dissolve and the solution tested for complete reduction with thiocyanate solution. It was found to require, 19.00 cc., 19.06 cc., 18.99 cc., and 19.03 cc. of the permanganate to titrate the solution. 19.03 cc. was taken as the correct value for twenty five cubic centimeters of the iron solution and it was found that titration after electrolytic reduction gave this value with very little variation due to experimental error. This variation was found to be much less than was possible when the reduction was made with metallic zinc.

Manipulation:-

For these runs, twenty five cubic centimeters of the ferric solution were run into a beaker of about three hundred cubic centimeters capacity from a pipette, the desired quantity of concentrated sulfuric acid added and the solution made up to two hundred cubic centimeters with distilled water. The apparatus described above was then dropped into the solution and the beaker covered with a watch glass and allowed to stand until a drop of the solution removed from the beaker with a stirring rod gave no coloration or only a very slight one with potassium thiocyanate solution. The watch

glass and the sides of the beaker were washed down from time to time during the run to prevent loss by the ferric solution clinging there and not being reduced. This precaution is necessary for the liquid from the watch glass was tested a number of times for ferric with potassium thiocyanate after the solution in the beaker was entirely reduced. It was found that this liquid gave a strong coloration. The beaker was left uncovered for a number of runs and it was found that enough ferric solution could be lost in this way^{so} that the solution would require a cubic centimeter less of permanganate for titration after the solution in the beaker showed complete reduction. This caused an error of about six percent and spoiled the determination.

After complete reduction, the electrodes were removed from the solution and washed thoroughly with distilled water, the wash water being allowed to run back into the beaker. The solution was then titrated in the same beaker with potassium permanganate solution described above.

Effect of acidity upon completeness of reduction:-

It was found that the iron could not be completely reduced with this apparatus if the concentration of the acid exceed six cubic centimeters of concentrated sulfuric acid per two hundred cc. of solution, however long the run was allowed to continue. This was true of all the metals used as electrodes and the concentration of acid which just prevented complete reduction was about the same in each case. The lack of complete reduction was indicated by a faint color with thiocyanate solution and the color shown, became stronger as the concentration of the acid was increased. The amount of iron left unreduced was estimated by adding the ferric sulfate solution^a drop at a time to two hundred cubic centimeters of

water and sulfuric acid of the same concentration as that used in the run until a drop of the mixture gave the same intensity of color with the thiocyanate solution as that produced by a drop of the solution from the beaker after the run. Each of these runs was allowed to continue one hour, after which it was considered that no more iron would be reduced. The results of this estimation showed that when a concentration of acid of from five to ten cubic centimeters was used, one drop of the original ferric solution was required to produce a like color. Each additional four cubic centimeters of acid used per two hundred cc. solution left a quantity of iron unreduced, equivalent to one additional drop of the original ferric solution. Thus, when thirty five cubic centimeters of acid were used the iron left unreduced was equivalent to eight drops of the original ferric solution. Each drop was .05 cc. as measured by counting a number of drops from the burette and dividing the cubic centimeters run out by the number of drops. When thirty five cubic centimeters of acid were used for the run, .40 cc. of the ferric solution was left unreduced. This is 1.6% of the total iron used in the solution and is much above the error which is allowable. A number of runs were made using granulated zinc as the reducing agent under the same conditions as above. About the same results were obtained as with the electrolytic reduction. This probably accounts for the lack of a high degree of accuracy in the determination of iron by reduction with zinc since the usual conditions of the determination make the quantity of acid present, indefinite.

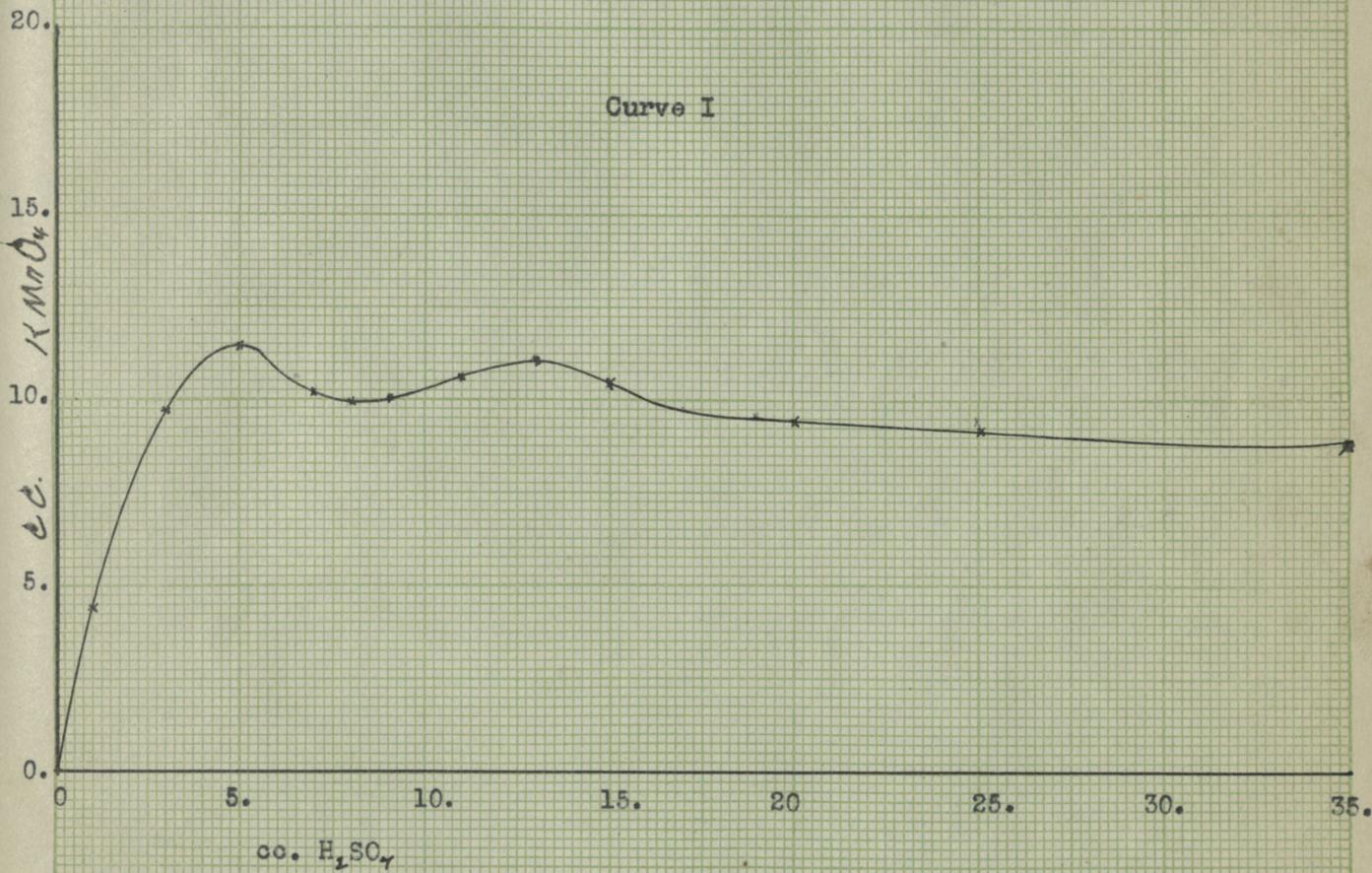
Effect of acidity upon rate of reduction:-

The following series of runs shows the effect of acidity upon the rate of reduction at different stages of the run. A zinc anode and copper cathode as described above were used. The temperature was kept constant at thirty degrees by bringing the solution to that temperature and then setting the beaker in a pan of water kept at ^N this temperature, during the run. Each run was allowed to continue just five minutes. The acid is given in cubic centimeters per two hundred cc. of solution and the permanganate is given in the number of cubic centimeters required to titrate the amount of iron reduced.

cc. Acid	1	3	5	7	8	9	11	15	25	35
cc. $KMnO_4$	6.54	9.95	11.54	10.78	9.98	10.06	11.10	10.39	10.20	9.00

As the concentration of the acid is raised, the rate of reduction increases rapidly at first, then falls off slightly, then raises and finally gradually falls again. This gives a curve with two maximum points (Curve E).

This strange behavior is caused by both the copper and the zinc going into solution and reducing the iron when a concentration of acid less than ten cubic centimeters per two hundred cc. of solution, is used. The copper evidently goes into solution until the concentration of sulfuric acid raises the conductivity of the solution enough to overcome the tendency of the copper to dissolve. Of course, in this case one additional equivalent of zinc must go into solution for each equivalent of copper prevented from dissolving and this will also reduce part of the iron. However, an equivalent of zinc does not reduce nearly as much iron as an equivalent of copper and this will explain the behavior noted above.



Cathode - Copper

Anode - Zinc

Temperature 30' C.

Time 5 minutes.

When ten cubic centimeters of acid per two hundred cc. of solution are used, about 1.6 grams of zinc goes into solution before the iron is reduced until only a faint coloration is produced with thiocyanate solution. This shows that, in this case, the efficiency of the zinc in reducing the iron is only about 12%. Copper does not dissolve in acid with the evolution of hydrogen and must, therefore, be 100% efficient in reducing the iron. This is shown to be the case in a method for the determination of copper, given in Schimpf's Volumetric Analysis and a number of other texts. By this method, the copper to be analyzed, is dissolved in acid and the lead and other metals, which would interfere, are precipitated and filtered off. The copper is then precipitated as metallic copper by the addition of zinc and the copper separated by filtration. The precipitated copper is then added to an acidified ferric solution and the air excluded. After the copper has all dissolved, the amount of iron reduced is determined by titration with standard permanganate solution and since the efficiency of the copper in reducing iron is 100% the amount of copper in the sample taken is easily calculated.

In order to prove that this is the true explanation of the curve described above, a few series of runs were made using different metals for the cathode and anode. The same type of curve was obtained in every case where copper was used as the cathode but was not noted in any case where some other metal, either soluble or insoluble, was used in its place. The metal used as the anode had no effect on the type of curve obtained.

This copper going into solution, however, in no way affects the accuracy of the determination of iron for all of it will be redeposited before the iron is all reduced and none will be in the solution when the titration is made.

The results of a similar run with a platinum cathode and zinc anode are given below. As before, the solution was kept at a temperature of thirty degrees and each run was allowed to continue five minutes.

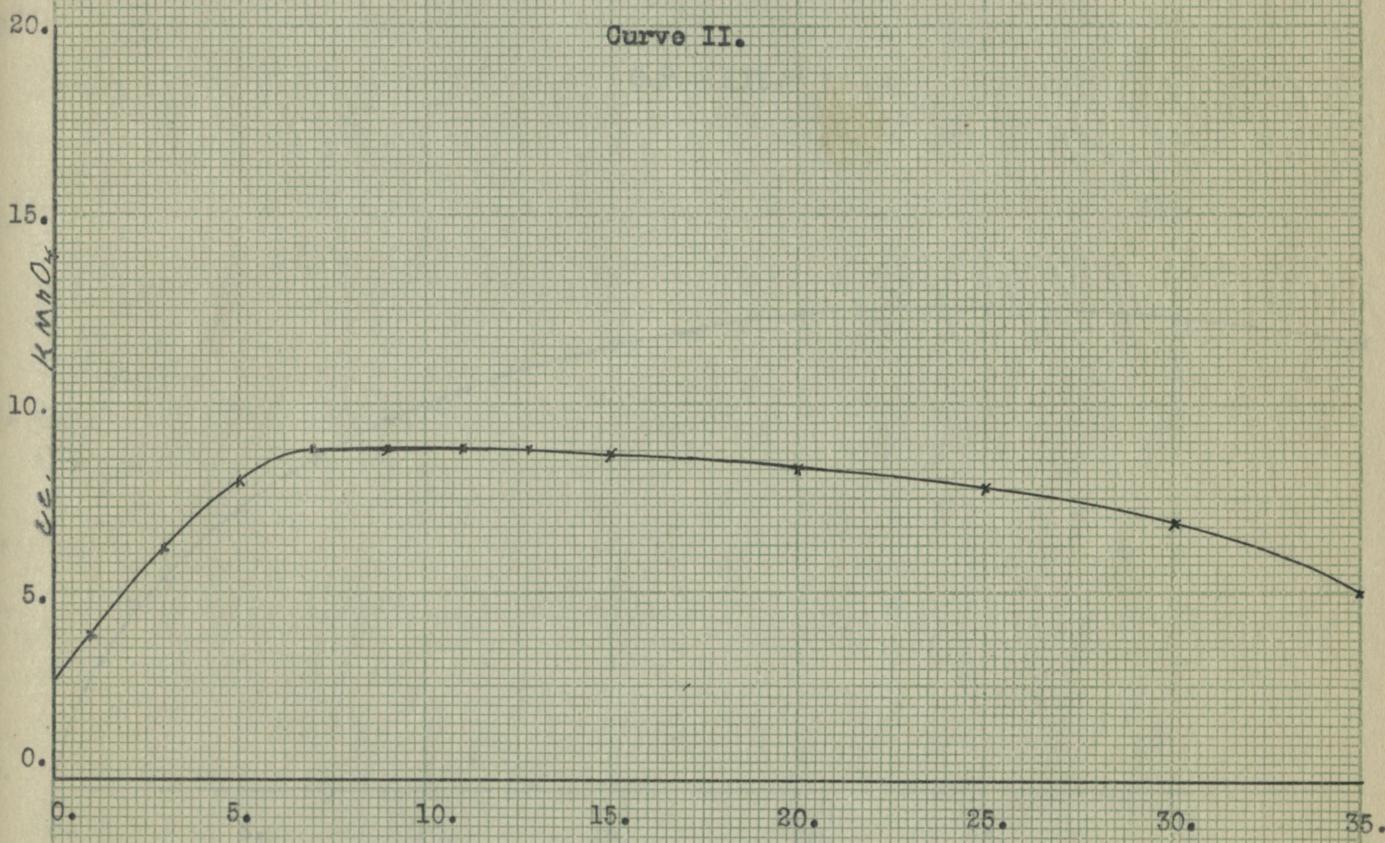
cc. Acid	1	3	5	7	9	11	13	15	20	25	30	35.
cc. $KMnO_4$	3.20	5.81	7.16	9.10	8.93	8.83	8.61	8.27	8.18	7.25	6.39	5.42

In this case the curve (Curve II) raises rapidly as the increased concentration of the acid causes the zinc to go into solution faster until the acid reaches a concentration where the oxidizing effect of the sulfuric acid causes the reduction to gradually fall off. No two maximum points are observed in this curve as was seen in the former curve where copper was used instead of platinum.

At first, it was thought possible that the difference in the above curves might be due to the use of a soluble cathode in one case and an insoluble one in the other, so a series of runs was made using nickel as the cathode and zinc as the anode. As before the temperature was allowed to remain at thirty degrees and each run was allowed to continue for five minutes. The following results were obtained.

cc. Acid	1	3	5	7	9	11	15	25	35
cc. $KMnO_4$	3.37	5.76	7.32	8.51	9.62	10.45	11.77	12.52	11.61

These results, plotted in curve III, show but one maximum point. This curve is of the same type as that given when platinum was used but the rate of reduction seems to be



Cathode - Platinum Cubic centimeters sulfuric acid

Anode - Zinc.

Temperature 30' C.

Time 5 Minutes



Cubic centimeters sulfuric acid.

Cathode - Nickel

Anode - Zinc

Temperature 30°C.

Time 5 Minutes

greater. This, however, means little as it may be due to the difference in surface of the electrodes or better contact between the anode and cathode in one case than in the other.

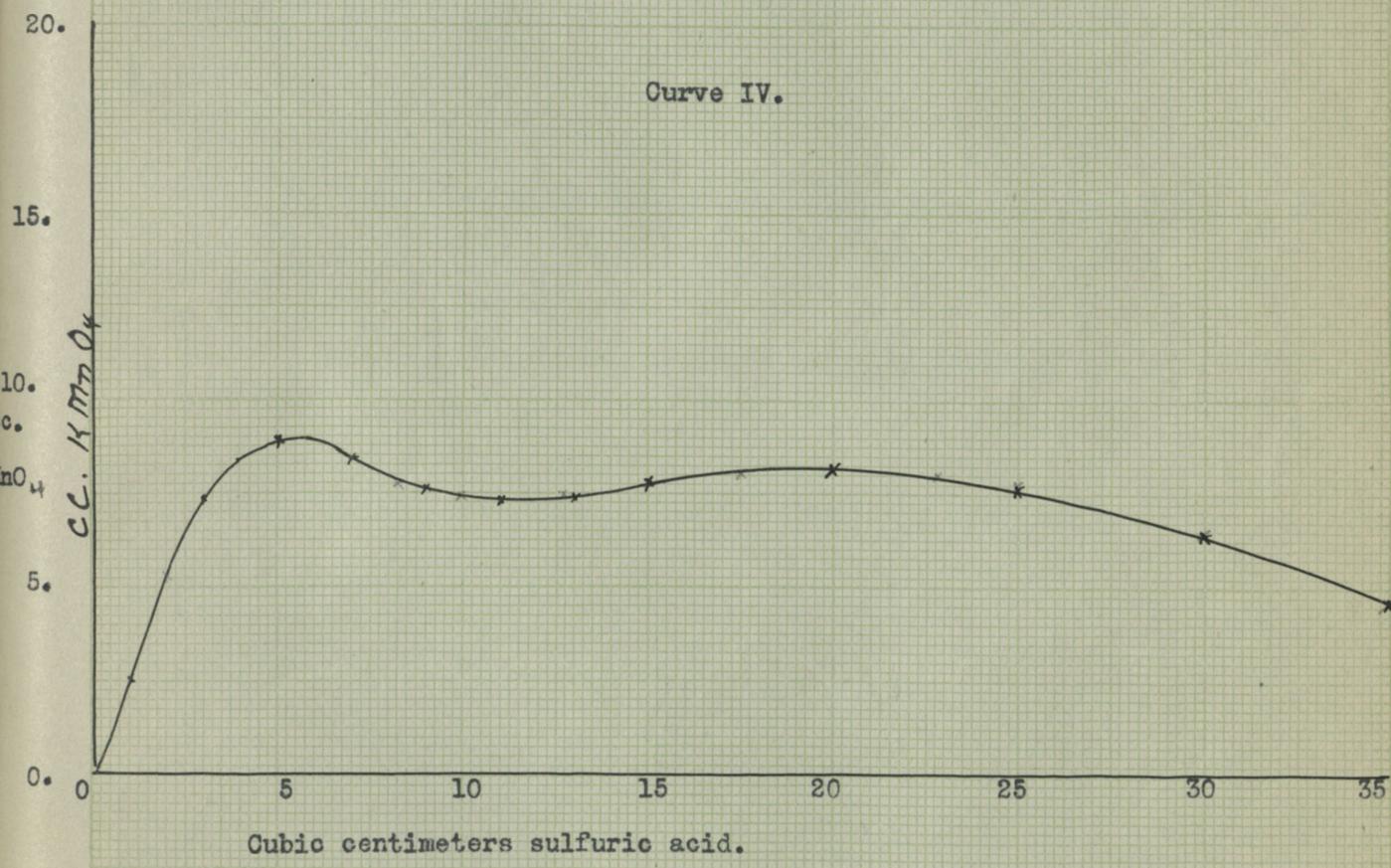
In order to find out if the anode used had any effect upon the type of curve given, a series of runs ~~was~~ made in which copper was used as the cathode and cadmium as the anode. All other conditions were kept the same as in the preceding runs and the results are given below.

cc. Acid	1	3	5	7	9	11	13	15	25	30	35
cc. K_2MnO_4	2.99	7.08	9.11	8.36	7.68	7.50	7.62	7.85	7.84	6.78	2.75

The curve (Curve IV) plotted from this data shows that two maximum points are again present. This points to the fact that the anode metal has no effect whatever upon the type of curve produced and that since copper is the only metal tried as cathode, which produced a curve with two maximum points, that the copper must be the cause of the peculiar behavior. Tests were made for the presence of copper in the solutions after the runs listed above in a number of cases and it was found that the copper ceased going into solution when the acid had reached a concentration of ten cubic centimeters per two hundred cc. of solution. The acid was, in every case, measured in terms of concentrated sulfuric acid.

Rate of reduction at various stages of the reduction:-

The rate of reduction at different stages of the run was studied at thirty and ninety degrees temperature.



Cathode - Copper
 Anode - Zadmium
 Temperature - 30° C.
 Time - 5 minutes

The following series of runs was made with the temperature kept constant at thirty degrees and with three cubic centimeters of acid per two hundred cc. solution. This concentration of acid seems the best for the reduction as the rate is rapid and the iron is completely reduced, as is shown by the absence of color with thiocyanate solution. A copper cathode and zinc anode were used in these runs with the following results.

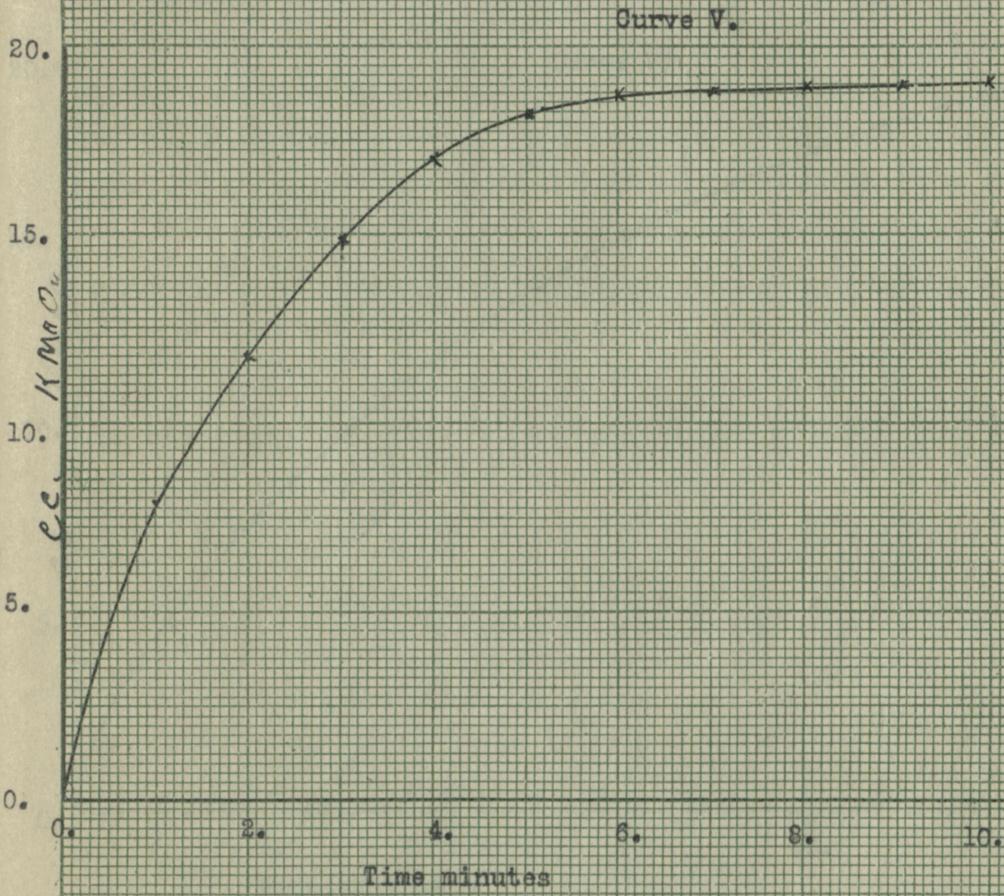
Min. time	2	4	6	8	10	12	14	16	18	20
Cc. $KMnO_4$	5.01	7.33	10.11	12.15	13.92	15.25	16.48	17.50	18.45	19.02

These results, plotted in curve VI, show that the rate of reduction becomes smaller as the concentration of the ferric ion decreases.

The conditions for the following runs were the same as those for the above except that the temperature was kept at ninety degrees instead of thirty. The results were as follows.

Min. time	1	2	3	4	5	6	7	8	9	10
Cc. $KMnO_4$	7.65	11.75	14.85	17.01	18.23	18.62	18.84	18.87	18.94	19.01

But half the time is required for complete reduction at this temperature as is required at thirty degrees. The curve (Curve V) plotted from these results, shows that the rate of reduction is much higher at first in this case than in the preceding one but that the decrease in the concentration of the ferric ion causes a much more rapid decrease in the rate of reduction than was the case before.

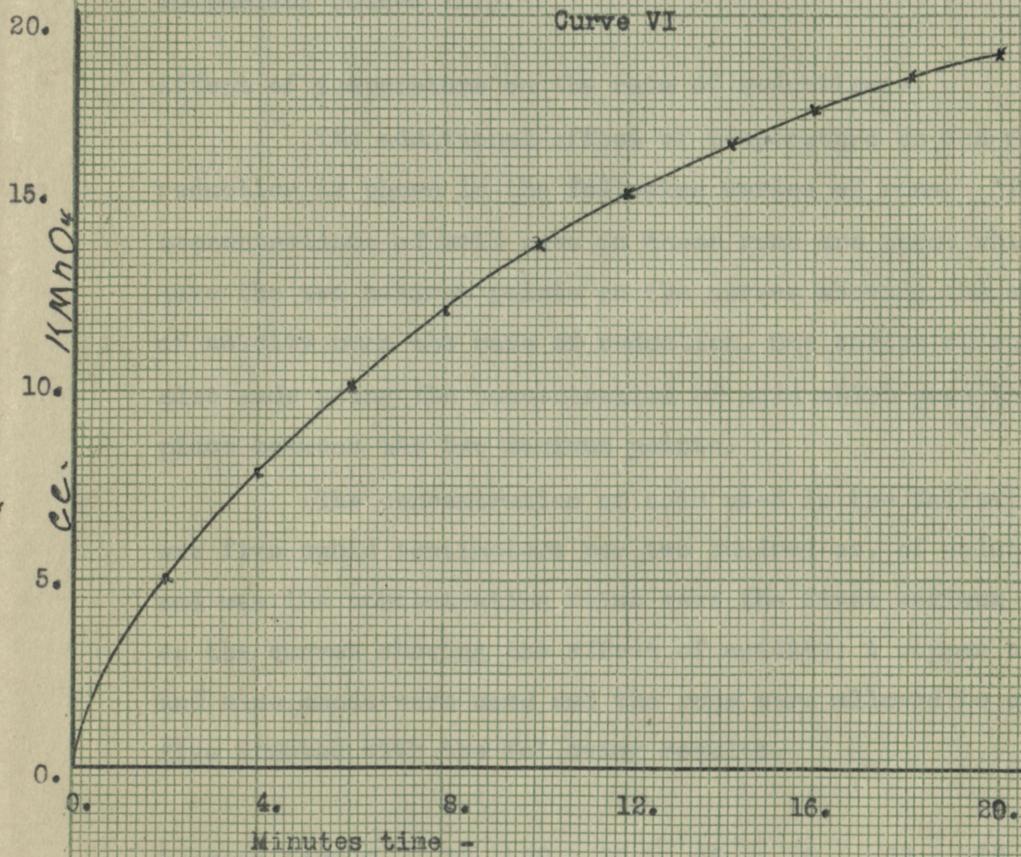


Cathode - Copper.

Anode - Zinc.

Temperature - 20° C.

H₂SO₄ - 3 cc.



Cathode - Copper.

Anode - Zinc.

Temperature 30° C.

H₂SO₄ - 3 cc.

This causes the curve to vary more from a straight line. The iron is completely reduced at the higher temperature and shows no color with thiocyanate solution. Where speed is desired, it seems that it would be better to perform the reduction in a hot solution than in a cold one since no undesirable conditions arise. These two curves are plotted for purposes of comparison (Curve VII).

Effect of temperature on the rate of reduction:-

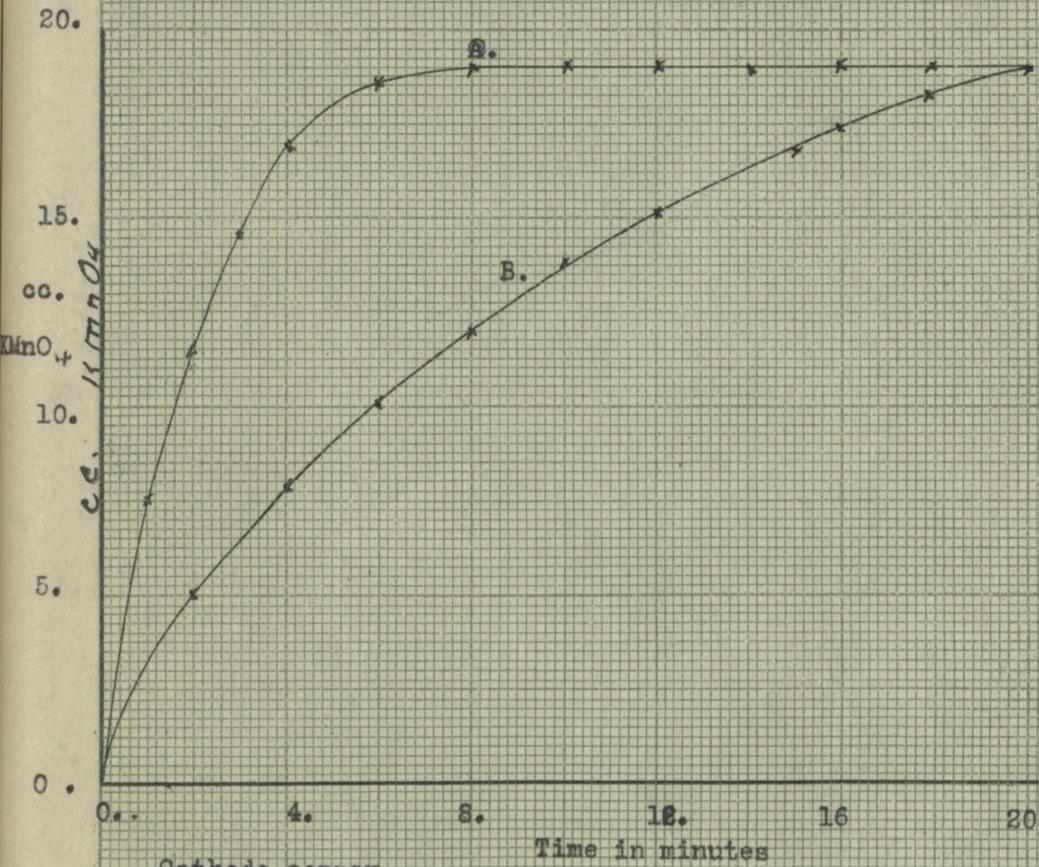
The additional effect of temperature on the rate of reduction is shown in the following series of runs. The concentrations of acid used in these runs are those which gave the two maximum points on the curves showing the effect of acidity upon the rate of reduction. One series of runs was also made using the concentration of acid which gave the low place between the two maximum points.

The concentration of acid used in the following runs was five cubic centimeters per two hundred cc. of solution and was the concentration which gave the first maximum point on the curves showing the effect of acidity. A copper cathode and zinc anode were used and the runs were allowed to continue five minutes with the following results.

Degrees temp.	0	10	20	30	40	50	60	70	80	90
Cc. KMnO_4	5.00	6.03	7.71	10.44	12.40	13.22	14.21	16.11	17.25	17.51

These results, plotted (Curve VIII), show that the rate of reduction increases as the temperature is raised but not uniformly.

Curve VII.



Cathode copper

Anode - Zinc

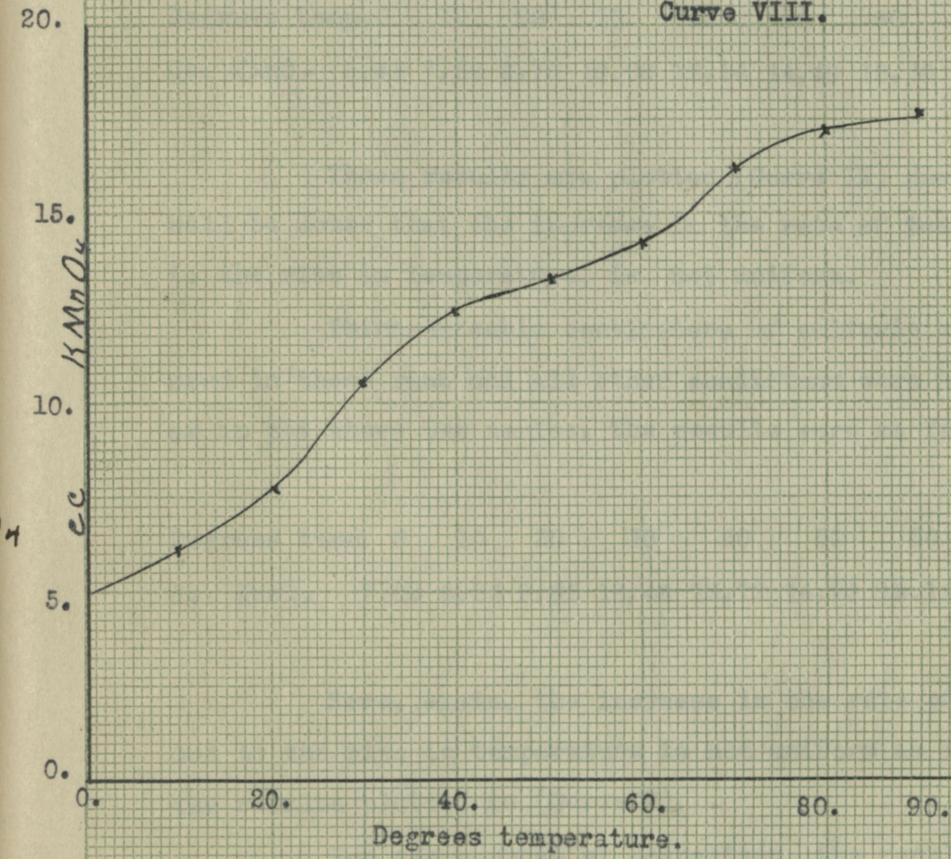
Sulfuric acid 3 cc.

Temperature 90° & 30° C.

A. temperature 90°

B. temperature 30°

Curve VIII.



Cathode - Copper.

Anode - Zinc.

Time - 5 Minutes.

H₂SO₄ - 5 cc.

The following runs were made under the same conditions as those in the preceding series except that eight cubic centimeters of acid were used instead of five. This concentration of acid gave the low place between the two maximum points on the acidity curves. The following results were obtained.

Degrees temp.	0	10	20	30	40	50	60	70	80	90
Cc. $KMnO_4$	5.42	7.32	8.76	10.02	12.54	14.49	15.38	15.92	16.38	17.24

These results are plotted (Curve IX) Here also it will be noted that the increase in the rate of reduction, due to the rise in temperature, is not uniform.

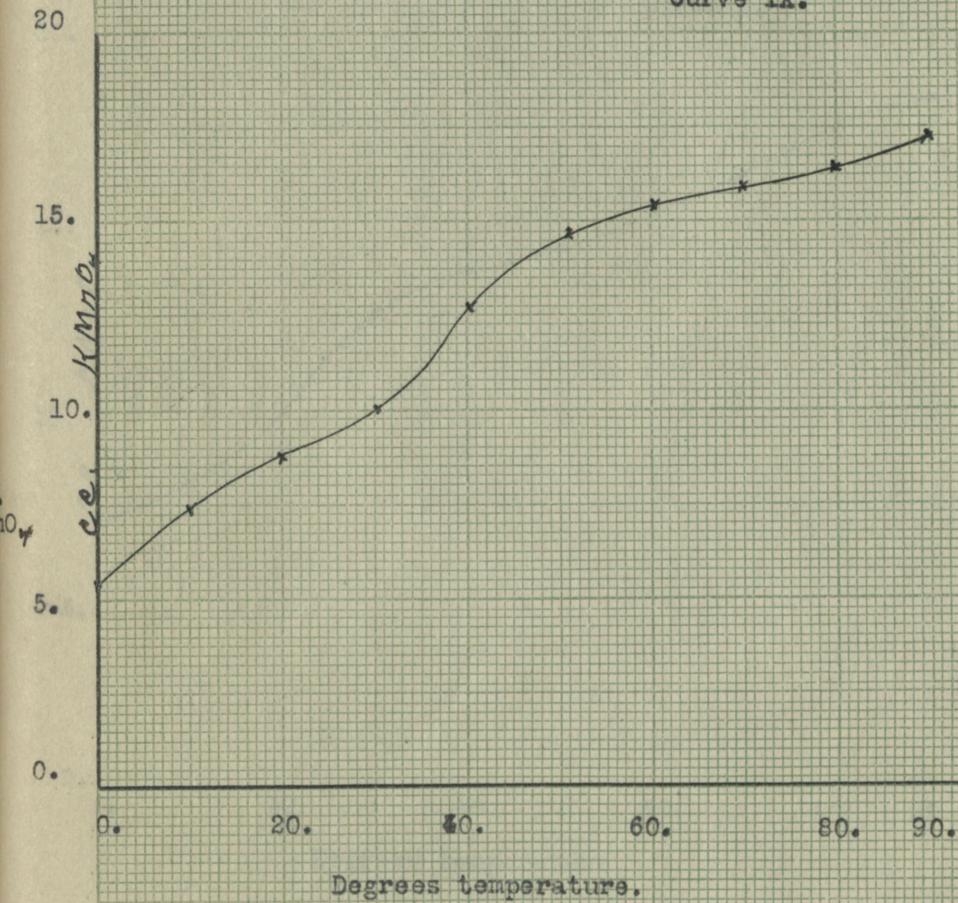
Thirteen cubic centimeters of sulfuric acid were used in these runs and all other conditions were kept the same as in the above two series. The results were as follows.

Degrees temp.	0	10	20	30	40	50	60	70	80	90
Cc. $KMnO_4$	7.24	8.23	9.82	12.48	13.72	14.25	15.12	16.18	17.55	18.22

Here, again, the increase in the rate of reduction due to the rise in temperature is not uniform as is shown by the results plotted in (Curve X).

For the purpose of comparison, the results of the three series of runs given above are plotted on (Curve XI), Where the concentrations of the acid, which gave the two maximum points in the acidity curves, were used, the curves obtained are almost parallel but in the case where the acid used was the same as that which gave the low point between the two maximum points, the irregularities in the curve were the reverse of the other two.

Curve IX.



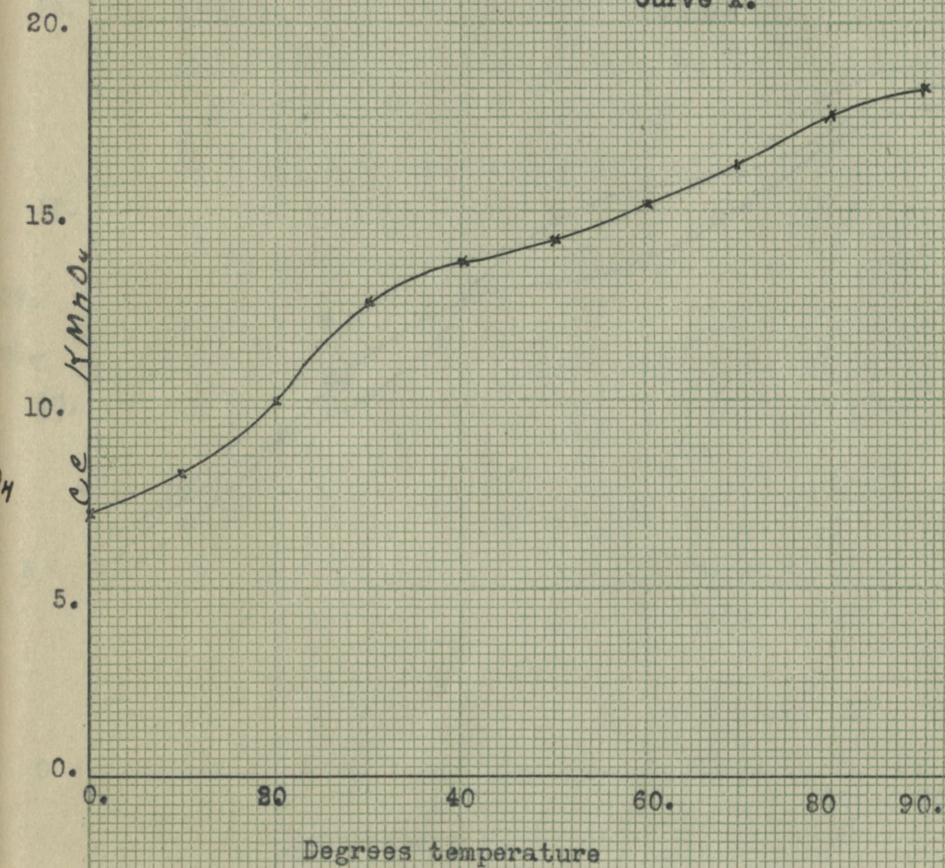
Cathode - Copper.

Anode - Zinc.

Time - 5 M. nutes.

H_2SO_4 - 8 cc.

Curve X.

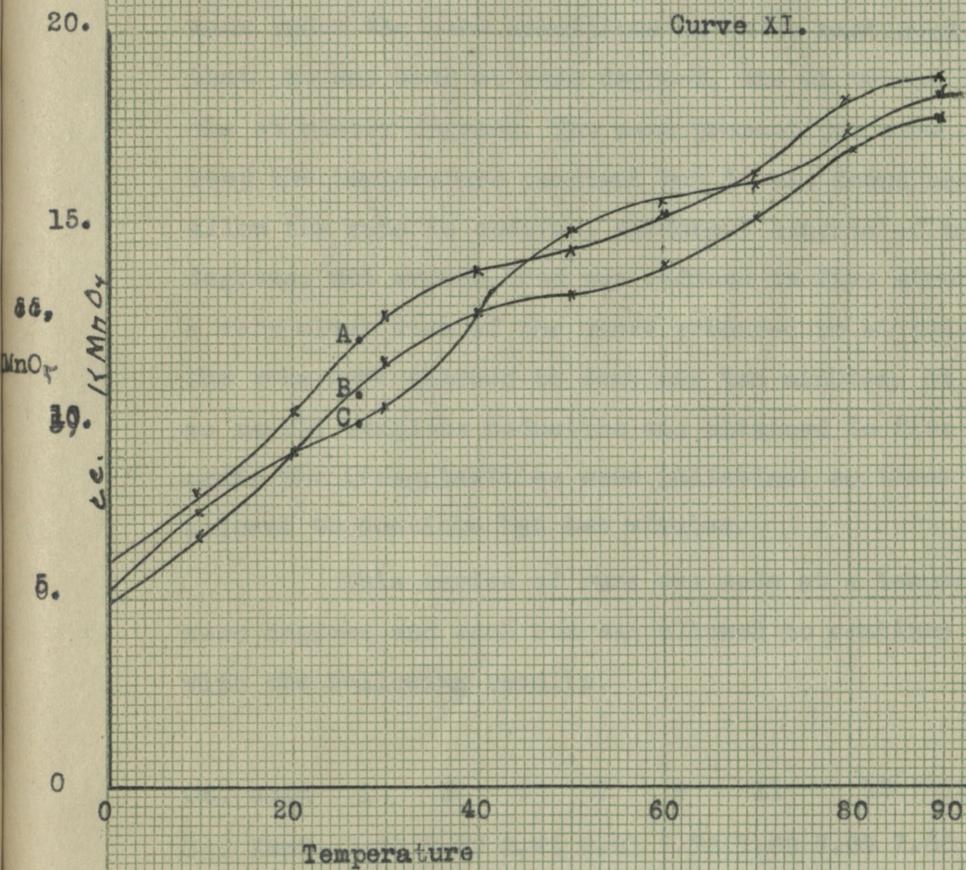


Cathode - Copper

Anode - Zinc.

Time - 5 Minutes.

H₂SO₄ - 13 cc.



Cathode - Copper

Anode - Zinc

Time - 5 Minutes

Acid - 5 , 8 , & 13 cc.

A. acid 5 cc.

B. acid 13 cc.

C. acid 8 cc.

The effect of temperature on the cuves showing the rate of reduction as the acidity is increased:-

A few series of runs were also made to determine the effect of temperature on the two high places in the curves showing the rate of reduction as the acidity was increased, as was noted in the first part of this paper. These runs were made under the same conditions as those mentioned before except that one was made at zero degrees, one at thirty degrees, and one at ninety degrees. The same precautions were observed to keep the temperature constant but it was found necessary to allow the runs to continue different lengths of time. At zero degrees, not enough iron was reduced in five minutes to give a very clear idea of the curve produced so at this temperature the runs were allowed to continue ten minutes. At ninety degrees so nearly complete reduction was obtained in five minutes that again the irregularities were indistinct so these runs were allowed to continue byt two minutes.

This series of runs was made at a temperature of zero degrees and each run was allowed to continue ten minutes with the following results.

Cc. acid	1	3	5	7	9	11	13	15	20	25	35
Cc. $KMnO_4$	3.25	7.32	8.91	8.21	7.76	7.62	7.69	7.86	8.26	7.78	7.57

These results, plotted (Curve XII) show that the two maximum points are still present but that the second high place is rather flat and not so high as the first.

The conditions for these runs were the same as for the above except that they were made at a temperature of thirty degrees instead of zero.



Cathode - Copper

Anode - Zinc

Temperature 0° C.

Time 10 Minutes

Cc. acid	1	3	5	7	9	11	13	15	20	25	35
Cc. KMnO	3.51	7.86	9.46	8.73	8.49	8.83	10.11	10.72	9.82	7.01	6.55

In this case, the height of the two high places on the curve (Curve XIII) plotted from these results, are more nearly equal than on the preceding curve.

In this series of runs, the conditions were the same as in the two former series except that the temperature was ninety degrees, in this case, and the runs allowed to continue but two minutes. The following results were obtained.

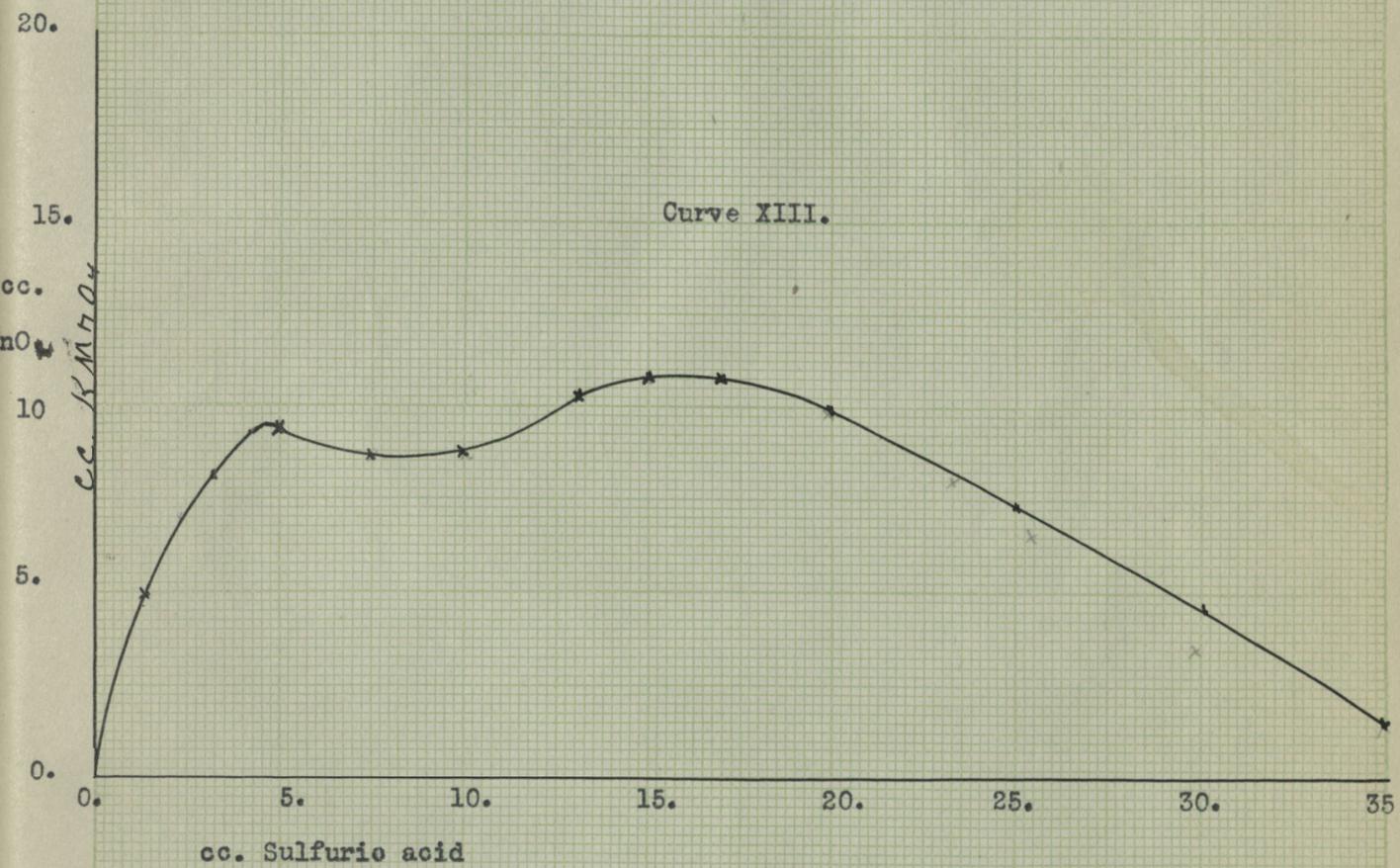
Cc. acid	1	3	5	7	9	11	13	15	20	35
Cc. KMnO	6.37	12.87	15.03	14.92	15.13	15.81	16.91	17.26	15.53	9.56

(Curve XIV) plotted from these results, shows that the first high place, which is caused by the copper going into solution, has almost disappeared. This points to the conclusion that the copper has less effect upon the rate of reduction at the higher temperatures than it does at the lower.

To aid in the comparison of the results of the three series of runs given above, the results are plotted on (Curve XV). The points of agreement and disagreement between them have already been pointed out.

Summary:-

From the foregoing work, it has been concluded: That electrolysis furnishes an easy and extremely accurate method for the reduction of iron for its quantitative determination by titration with permanganate. It was found that good checks could easily be obtained by this method and that they agreed with other methods of determination.



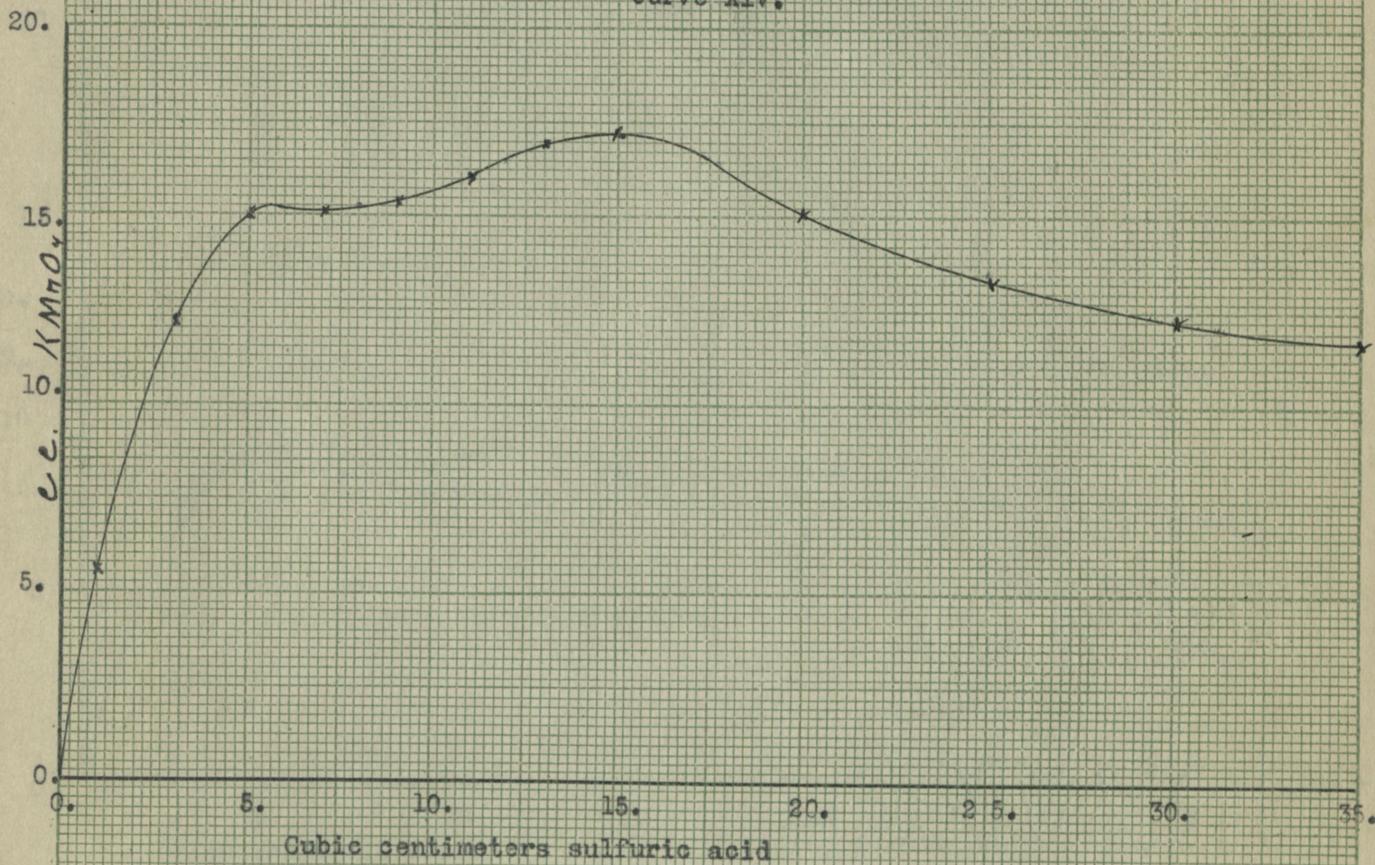
Cathode - Copper

Anode - Zinc.

Temperature 30' C.

Time - 5 minutes

Curve XIV.

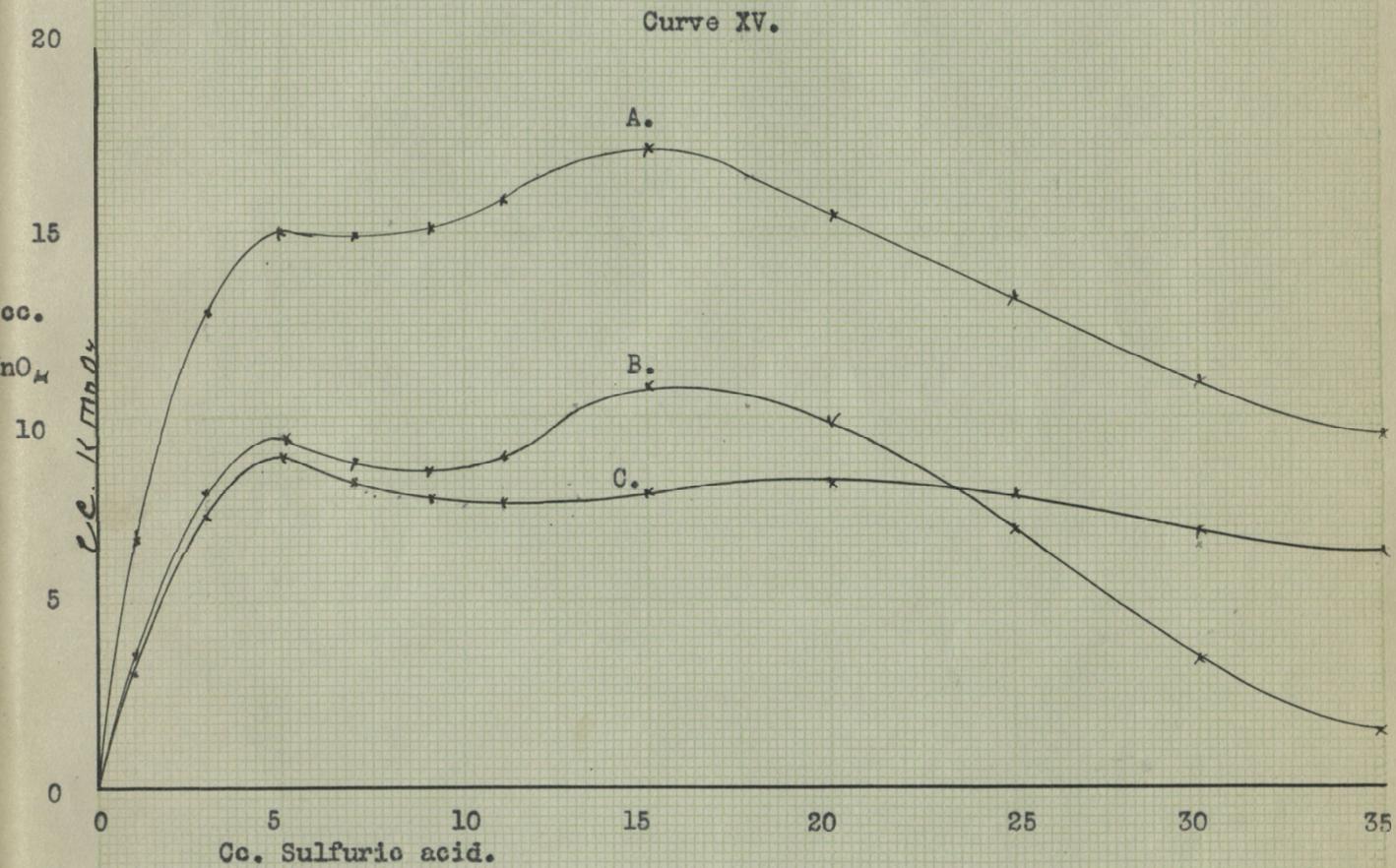


Cathode - Copper

Anode - Zinc.

Temperature - 90° C.

Time 2 Minutes.



Cathode - Copper

Anode - Zinc

Temperature - 90', 30', & 0'. C.

Time - 2, 5, & 10 Minutes

A. temperature 90', time 2 minutes

B. temperature 30', time 5 minutes

C. temperature 0', time 10 minutes.

That the use of an auxillary current is unnecessary for this reduction.

That the use of rotating cathodes or anodes is also unnecessary.

That a zinc anode and copper cathode, of the form described, forms the best means of carrying out this reduction, because of the ease of obtaining these metals in a pure state in the form desired, and because of their efficiency for this purpose.

That temperature affects the rate of reduction, the rate being increased when the temperature is raised and decreased when the temperature is lowered.

That the copper goes into solution at first and hastens the reduction of the iron but that it produces no error in the determination since it is all again deposited before titration.

That the best concentration of acid, for this work, is about three cubic centimeters concentrated sulfuric acid per two hundred cc. of solution. A concentration of more than five cc. will not allow complete reduction of the iron, either by electrolysis or with metallic zinc.

That the time required for complete reduction with this apparatus, and at a temperature of ninety degrees, is about ten minutes.

Finis.

University of Kansas,
Department of Chemistry,
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