cepted to carry out the final series of measurements in the laboratories of the Bureau. The authors wish to thank Professor Washburn of the University of Illinois, who first planned the above investigation, for suggestions which have contributed in a large measure toward the success of the work. We also thank the Director of the Bureau and Dr. Rosa for assisting in making the arrangements for completing this investigation and for making available for this determination the excellent facilities of the Bureau.

URBANA, ILL.
WASHINGTON, D. C.

THE ELECTROLYTIC REDUCTION OF IRON FOR PERMANGANATE TITRATION.[1]

BY H. C. ALLEN.

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The following work was undertaken to determine the possibility of utilizing the oxidation-reduction effect of the electric current in certain analytical operations where it is desired to quantitatively oxidize or reduce a substance before its titration with a standard solution. Numerous studies have been made of the proper conditions for the deposition of the various metals by the electric current and the oxidizing effect has been utilized in a number of cases, especially with sulfides, where, after oxidation, the substance is precipitated and determined gravimetrically. The oxidizing and reducing effect of the electric current has also claimed much attention in both the organic and inorganic fields and in many of these latter studies it has been common practice to follow the reactions and determine the quantities of substances formed by titrating with some suitable standard solution. However, these titrations have been made for the purpose of obtaining the current or energy efficiency of the processes and very little work has been done along the line of producing a quantitative yield of the substance, in a strict analytical sense, regardless of the electrical efficiency of the process.

The rotating electrode, when employed in oxidations or reductions, should make the electrolytic method, in some cases at least, a successful competitor of the chemical methods of producing the same results, since it is possible to reduce small quantities of iron, for example, in from five to fifteen minutes by means of a rotating cathode under proper conditions. Further, the method has many advantages over the usual chemical methods of reduction. Some advantages that are at once apparent are that there is no danger of getting an excess of the reducing agent into the solution which must later be removed, and no foreign material is necessarily introduced into the solution before the titration.

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[1] Presented at the Rochester meeting of the American Chemical Society, September, 1913.

It should also be possible to regulate the oxidation or reduction to a nicety, through variations in the overvoltage, by choosing suitable anodes or cathodes, as is frequently the case in commercial processes when the current efficiency and maximum yield are the main points to be considered.

Apparatus.—The apparatus used in the electrolytic reduction consisted of six rotating electrodes belted to a single countershaft which was driven by a small motor. Being only a slight modification of the machines used in a number of places it needs no special description.

The cathodes of the various metals were made by bending a piece of wire sharply back upon itself at a point about 3 cm. from one end, the other end of the wire being left long enough to attach to the rotator. A rectangular metal gauze was then placed between the two wires thus formed and the gauze was twisted around in the form of a spiral. By rotating this spiral in the proper direction a maximum stirring is obtained, and the "vortex" effect in the liquid, which would tend to draw air into the solution, is largely eliminated by rotating the electrode near one side of the vessel rather than in the center. The wire stem used was of the same metal as the gauze in each case.

The anode, when of the non-soluble type, was of platinum wire, made as small as possible to carry the current without interrupting. A short piece of platinum wire was fastened to a larger copper wire and a glass tube slipped over this and sealed off around the platinum, leaving about two centimeters of the wire exposed, which served as anode while the copper wire was fastened to the electrode holder. When soluble anodes were used the metal and size are indicated in the data.

The current was regulated by the number of lamps in series with the cell and in addition a sliding resistance was used for fine adjustment, which enabled any desired current to be obtained.

An automatic pipet was used for measuring out the solutions and the constancy of the amount withdrawn was checked at frequent intervals by weighing the quantity delivered. The extreme variations in these weights showed that the pipet could be relied upon to within about 0.1%, which was as close as the work in hand demanded.

Government standardized burets of 50 cc. capacity were used, graduated to tenths, while the quantity of permanganate used in most cases, where the reduction was complete, was approximately 20 cc. For the smaller quantities of permanganate, 10 cc. standardized burets, graduated to 0.05 cc., were used for greater accuracy.

The vessel used in most of the work was a beaker without lip of about 250 cc. capacity. During the run it was covered with a close-fitting watch glass to prevent loss by splashing and evolution of gases. The cover glass contained three holes: one for each of the electrodes and one for a thermometer.

Chemicals.—Baker's special analyzed or C. P. chemicals were used throughout the work.

Method of Procedure.—The general method of procedure was simple and consisted in delivering the solution to be reduced from the pipet into a 250 cc. plain beaker, making it up to the given amount with distilled water, placing it on the electrolytic apparatus and making the run under the conditions noted. About 0.12 g. of iron was usually taken. Two or three times during the run the cover glass and electrodes were washed down into the beaker and finally at the completion of the run they were again washed down, after lowering the beaker. The titrations were usually made with 0.1 N potassium permanganate at the temperature of the solution at the completion of the run, except at the higher temperatures, when the solution was cooled somewhat before the titration.

Experimental Part.

The surface, form and rate of rotation of the cathode, the dilution of the solution and the current strength were studied, but need not be considered, since the results obtained are not especially significant. The general effect of altering any one of these variables is easy to predict, being due largely to the same factor: getting fresh material into the sphere of action.

Cathode Material.—The subject of cathode material was not extensively studied since the object of the work was the practical reduction of the iron, and a copper gauze serves the purpose well and is easy to obtain in gauze form and quite pure.

A few runs were made with the cathodes indicated below, all other conditions being kept constant. A platinum gauze cathode was first used and then the different metals were plated on this cathode and the runs repeated.

Anode: platinum wire. Acid: 0.6 cc. conc. H_2SO_4. Solution: 175 cc. Current: 1.9 amperes. Temp.: 26°. Time: 3 minutes.

Cathode	Pt	Cu	Ag	Zn
$KMnO_4$ used, cc.	17.66	20.73	21.21	21.40

The last three metals given will reduce the iron even in the absence of a current, and this may account for their greater reducing power. The difference in potential at which the hydrogen will be liberated in the different cases may also be a considerable factor.

Solution—Acidity.—The following runs were made to determine the rate at which the iron would be reduced under the conditions given.

The first three series were made with the concentrations of acid indicated in the data. The concentrated acid (sp. gr. 1.84) is given throughout the paper.

Acidity: 0.6 cc. H_2SO_4 per 175 cc. solution. Cathode: Pt gauze, 5 × 6 cm. Anode: Pt wire. Temp.: 25°. Current: 1.6 amperes.

Time, minutes	1/2	1	2	3	4	5	8	9	10
% Fe reduced	16.1	32.6	57.4	78.2	88.7	93.8	99.4	99.6	100*

Acidity: 10 cc. H_2SO_4. All other conditions same as above.

Time, minutes	1	5	10	15	20	10
Temperature	25°	25°	25°	25°	25°	87°
% Fe reduced	23.0	76.8	94.1	99.4	100*	100*

Acidity: 35 cc. H_2SO_4 per 175 cc. solution. All other conditions same as the above.

Time, minutes	3	10	20	6	11
Temperature	28°	29°	28°	87°	81°
Current, amperes	1.9	1.9	1.9	4.0	1.9
% Fe reduced	45.3	54.8	63.5	99.2	100*

*In each of these cases a trace of ferric iron was shown by thiocyanate. The permanganate used indicated 100% reduction, to within the limit of experimental error. No blanks were subtracted from the permanganate used in titrating.

The time for complete reduction is shown to be 10 minutes with 0.6 cc. acid present while with 10 cc. acid at room temperature, 20 minutes are required. This time is cut down to 10 minutes at 87°. When as much as 35 cc. acid are present at room temperature the reduction is so slow that at the end of 20 minutes only 63% of the iron is reduced. In this case also the iron was completely reduced in 11 minutes at a temperature of 81°.

Two runs were made at room temperature with this latter acidity: one with a copper gauze and the other with a platinum gauze cathode, and complete reduction was not obtained in 75 minutes although the current was increased to 3.9 amperes during the last 15 minutes. Estimating from the intensity of the color with thiocyanate, equilibrium seemed to have been reached and it is very probable that the iron cannot be completely reduced at the lower temperature with this concentration of acid present.

The probable cause is that the greater concentration of sulfate favors the formation of persulfate which oxidizes the iron as fast as it is reduced. The higher temperatures are known to be unfavorable to the formation of persulfate, which would account for the complete reduction at the higher temperatures noted above.

In the two runs above with the copper and platinum gauze cathodes a zinc rod was substituted for the platinum wire anode after 75 minutes. With the copper cathode the iron was completely reduced, as indicated by thiocyanate, in 7 minutes while with the platinum gauze this was accomplished in 18 minutes. From this it would seem that complete reduction with the greater acidity is not possible except at the higher temperatures or by the use of a soluble anode.

If the formation of persulfate is the chief factor in preventing complete reduction of the iron, it is evident that neutralizing the excess of acid will not entirely correct the difficulty, and this was found to be the case. The same quantity of acid as used above was neutralized with sodium hydroxide until the excess of acid was less than 1 cc. sulfuric acid per 175 cc. solution and complete reduction was not obtained in 45 minutes, though a current of 3.7 amperes was employed. In this case, also, the iron was completely reduced in a few minutes by substituting a zinc rod anode for the platinum wire.

The effect of chlorides in the solution is similar and it is impossible to get complete reduction with a platinum wire anode because of the liberated chlorine, while with a soluble anode the chlorides do not interfere unless the current density becomes so great that chlorine is liberated.

Temperature—Acidity.—A number of runs were made to compare the rate of reduction at different acidities by determining the amount of iron that would be reduced in a given time. A series of these runs was made at 26° and another series at 76°.

Temperature: 26°. Cathode: Pt gauze, 5 × 6 cm. Anode: Pt wire. Solution: 175 cc. Current: 1.9 amperes. Time: 3 minutes. Average r. p. m.: 1300.

Acid, cc.	0.6	5	10	25	30	35	40	45	50
% Fe reduced	77.0	71.0	69.4	67.0	64.5	45.3	21.6	11.4	00.0

Temperature: 76°. All other conditions as above.

Acid, cc.	0.6	10	20	30	40	50	60	75	100
% Fe reduced	96.5	90.9	88.6	85.0	77.5	65.3	37.5	31.7	00.1

The general effect of acidity on complete reduction has been discussed and the above data are in accord with what has been said.

The percentage of iron reduced falls off very rapidly at room temperature with a concentration of acid from 25 to 40 cc. per 175 cc. of solution, which may be partially accounted for by the fact that this is about the acidity of maximum conductivity for sulfuric acid, and with the greater concentration of hydrogen ion present the hydrogen may be liberated in preference to the iron being reduced. However, this is not the principal factor in the rapid drop in the amount of iron reduced, as the following data with soluble anode show:

Anode: Amalgamated zinc rod 4 mm. in diameter, immersed 6.5 cm. into the solution. Cathode: Pt gauze, 5 × 6 cm. Temp.: 22°. Current: 1.9 amperes. Solution: 175 cc. Time: 3 minutes.

Acid, cc.	0.6	1	2	5	10	20	35	50	75
% Fe reduced	62.3	62.2	66.9	64.3	60.5	56.6	50.2	43.2	38.0

In this case the hydrogen at the cathode may be supposed to be liberated under much the same circumstances as with the platinum anode, but the rapid falling off in the amount of iron reduced is almost entirely absent. The difference in results obtained in the two series over this range of acidity must be largely due to the formation of persulfate at the anode, with the platinum wire, which is eliminated by the use of the soluble anode.

This view is strengthened by the fact that about this acidity is given by Richarz[1] as being best suited for a production of persulfate.

Temperature.—The effect of an increase of temperature in addition to what has already been given, is quite well shown in the two series of runs following:

Acidity: 0.6 cc. H_2SO_4 per 175 cc. solution. Cathode: Pt gauze. Anode: Pt wire. Current: 1.9 amp. Time: 3 min. Av. r. p. m.: 1400.

Temperature	1.5°	8.0°	24.0°	26.6°	49.0°	63.0°	87.0°
% Fe reduced	53.0	63.0	76.4	78.4	88.0	94.0	99.6

Acidity: 40 cc. H_2SO_4 per 175 cc. solution. All other conditions same as the above.

Temperature	13°	25°	58°	90°	100°
% Fe reduced	00.0	21.6	61.2	85.6	89.2

In all cases an increase in temperature gives an increase in reduction and the effect of too great acidity can be very largely overcome by increasing the temperature. The above data show that with 40 cc. acid present no reduction takes place at 13°, while some of the previous tests indicated that at room temperature no reduction takes place with 50 cc. acid present, and at 76° the acidity may be increased to 100 cc. before the reduction becomes zero.

Anodes.—The general use of soluble or insoluble anodes has already been discussed in connection with other variables, and here as in the case of cathodes there is no very wide latitude for choice from a practical standpoint. The platinum wire serves the purpose very well when an insoluble anode is desired, while the amalgamated zinc leaves little to be desired in the line of a soluble anode. Magnesium was tried, but, since the acid reacts so readily with it, the acidity must be controlled within much narrower limits than with zinc.

The platinum wire used in the regular runs was modified by using a larger glass tube and sealing it off at the upper end, thus leaving a bell-shaped covering around the anode. A hole was blown in the side of the glass tube above the surface of the liquid to allow the escape of the liberated oxygen without mixing with the solution. This arrangement, when used on the blanks under the same conditions as the regular platinum anode, gave a solution that required only about one-half the quantity of permanganate needed when the oxygen was liberated in the solution without any special precautions to remove it.

If a selective reduction were to be made, the choice of suitable anodes or cathodes would be an important factor, but this is not the case in the present work, and since zinc is easily obtained in a fairly pure state and the effect of impurities may be largely overcome by amalgamation, it would seem to be the most practical metal to use.

Blanks with Current.—The question of a blank determination in the

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[1] *Ann. d. Phys.*, **24**, 183 (1885); **31**, 912 (1887).

runs with platinum anode is not so easily settled, since the nature of the process taking place makes it very certain that the conditions that obtain without the iron present would give no indication of what to expect when iron is present. The sulfuric acid solution and the platinum electrodes would produce persulfate at the anode and this would react with the water for the formation of hydrogen peroxide.[1] The oxygen liberated at the anode, or from the air might also react directly with the hydrogen liberated at the cathode for the formation of hydrogen peroxide. This hydrogen peroxide would reduce the permanganate. However, in the presence of ferrous iron under the conditions of study, it would not be expected that these substances could possibly be formed to anything like the extent that they might be in the absence of the iron, since the ferrous iron would be oxidized and again reduced until equilibrium was reached.

A number of runs were made on blanks and it was found that they could be made to reduce enough permanganate to indicate 6–8% of iron in the solutions as ordinarily used. This quantity was obtained by allowing the cathode to rotate near the surface of the solution and thus create a vortex which drew down considerable quantities of air into the solution. When the cathode was rotated beneath the solution, in such a manner that no air was drawn into the solution, the reduction of permanganate, for a run of the same duration, was only about one-half the above amount.

It is quite certain that with the iron in the solution no such uncertainty exists in the electrolytic reduction as the above blanks might indicate, since a great many runs were made for complete reduction under quite different conditions, as indicated throughout the paper, and the checks obtained were very satisfactory.

The following comparisons were made between the zinc and electrolytic reductions in this connection: Two zinc reductions required 17.55 and 17.56 cc. permanganate solution for titration after deducting 0.12 cc. for a blank run at the same time. Four electrolytic reductions made from the same solution at the same time required 17.56, 17.57, 17.57 and 17.59 cc., respectively, with no deduction for a blank. From this it would seem that no great error will be made if a correction for a blank is omitted in the electrolytic reduction with platinum electrodes. While the electrolytic seem to be slightly higher than the zinc reductions, a very faint coloration was produced in a thiocyanate solution in each case after the electrolytic reduction.

When a zinc anode is used the conditions are somewhat different so far as a blank is concerned. The first two runs tabulated below were obtained by reduction with metallic zinc and the others by electrolytic reduction with zinc anode under the conditions noted:

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[1] Richarz, *Loc. cit.*

	Zinc reduction.		Electrolytic reduction.		
Time.	2 hrs.	2 hrs.	22 min.	22 min.	16 min.
Acid, cc.	7.5	7.5	5	3	1
Solution, cc.	175	175	175	175	175
Wt. Fe sol., taken	25.556	25.545	25.533	25.522	25.543
$KMnO_4$, cc. used	22.81	22.81	22.78	22.75	22.76
$KMnO_4$ less blank	22.70	22.70	22.72	22.69	22.70

A blank run with the zinc at the same time and under the same conditions as the above required 0.11 cc. permanganate.

The electrolytic blank which was run with a careful exclusion of air and on the whole was rather lower than a number of other blanks that were run, required 0.06 cc. This may account for the electrolytic runs averaging slightly higher than the zinc reductions. In these electrolytic runs the reduction was carried to a point where no color was obtained by the thiocyanate test.

Reduction with Metallic Zinc.—A number of reductions were made with metallic zinc to compare the effect of acidity with similar runs made electrolytically, and the results were interesting.

Double the quantities of material used in the electrolytic reductions were placed in a 500 cc. Erlenmeyer flask, 14 g. of zinc distributed evenly over the bottom, and at the times indicated in the table below, 50 cc. of this solution were removed with a pipet, filtered to remove the particles of zinc, and titrated. The solutions were diluted to 350 cc. and the portions removed should have required 6.75 cc. of permanganate if totally reduced.

350 cc. sol.	8.	20.	50.	70.	90.	120.	150.
Time. Min.				$KMnO_4$. Cc.			
4	0.58	0.95	1.46	1.79	1.75	1.52	0.96
11	1.46	2.36	3.69	3.71	3.61	3.08	1.96
21	2.64	4.20	5.31	5.20	5.07	4.44	2.93
31	3.92	5.48	6.07	6.07	5.88	5.29	3.59
45	5.38	6.46	6.65	6.65	6.57	6.05	4.26
60	6.24	6.66	6.76	6.74	6.77	6.49	4.30

Of the zinc used not any passed through a 60-mesh per inch sieve, 0.3% through a 40-mesh, 85.5% through a 20-mesh, and all would pass a 10-mesh sieve.

It is interesting to note that the zinc reduces fastest when the concentration of acid is from 50 to 90 cc. per 350 cc. of the solution, and this is the concentration of acid at which the electrolytic reduction with non-soluble anode is falling off the most rapidly. This is also about the concentration of greatest conductivity for the acid. It is possible that the large concentration of hydrogen ions in the solution is instrumental in keeping the surface of the zinc clean and in the best condition for reducing the iron. This particular range of concentration in connection with the electrolytic reduction has already been discussed.

The results obtained in the zinc reduction do not seem to be in entire accord with the statement of Carnegie[1] that the more nearly neutral the solution the more rapid the reduction, though the conditions are not quite the same, since he used zinc dust.

The zinc dissolves much faster in a solution containing iron than in one that does not, other conditions being the same. Hence the practice of running a blank experiment, so often recommended, is of doubtful value unless a pure zinc is used or all the zinc is finally brought into solution. This may also cause an uncertainty in methods similar to the Jones reductor method, though there is no doubt that the use of amalgamated zinc under these conditions prevents most other substances that would interfere with the titration from going into solution. The claim is made by Müller and Wegelin[2] that, when amalgamated zinc is used, there is no danger of iron precipitating on the zinc, but this phase of the subject was not studied.

Reduction without Auxiliary Current.

The method finally chosen as most practical for the reduction of ferric to ferrous iron dispenses with an outside source of current. In the course of the experimental work done in studying this method some observations of interest were made. The idea of using a substance that it is wished to reduce as a depolarizer in a short-circuited cell was first suggested by Löb[3] in connection with certain organic compounds. At this time the full value of rotating one of the electrodes was not realized and consequently the reactions proposed required several hours for completion. Since these same reactions could be obtained much quicker by purely chemical means the method has been very little studied.

The principle involved is perhaps to be found in the Gladstone-Tribe couple, and also is suggested in the numerous recommendations found in the literature to bring the zinc used in the reduction in contact with platinum. That bringing the zinc in contact with platinum has any advantage is contradicted by Müller and Wegelin[4] and data are given to show that this does not hasten the reduction of the iron. In the same paper it is recommended that the zinc be brought in contact with metallic copper or that a little copper sulfate be added to the solution to hasten reduction. The end in both cases is the same, since the copper from the copper sulfate solution would be deposited on the zinc and assist in the reduction.

In the present work the same apparatus was used as in the previous work, but no outside source of current was used. One of the electrodes was rotated and the electrolytic cell produced by the two different metals

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[1] *J. Chem. Soc.*, **53**, 468 (1888).

[2] *Z. anal. Chem.*, **50**, 615 (1911).

[3] *Ber.*, **29**, 1390 (1896).

[4] *Loc. cit.*

in the acid solution was short-circuited by closing the switch on top of the apparatus. The contact was lubricated with oil and graphite to insure the least possible external resistance.

The following are some preliminary runs that have considerable bearing on the course of the work and so are given at this place:

1. Open-circuited cell with rotating platinum gauze cathode and stationary zinc rod anode. Acid: 10 cc. sulfuric acid per 175 cc. solution. Time: 3 minutes. Temp.: 37°. Average r. p. m.: 800.

   Permanganate required for titration: 2.27 cc.

2. All conditions same as above, but cell short-circuited.

   Permanganate required for titration: 17.47 cc.

While the conditions, so far as bringing the zinc into contact with platinum, are not the same as in the paper cited above, the values show an enormous increase in the iron reduced when the zinc is in contact with platinum in this manner. In the first case, above, the only office of the platinum is to stir the solution while the zinc does the reducing, and with its already limited surface partially covered with the liberated hydrogen offers very poor conditions for the reduction of the iron.

When the platinum is brought into contact with the zinc the hydrogen is liberated from the platinum gauze with the large surface, and the greater part of the reduction takes place on this surface, either from the action of the liberated hydrogen or the electrolytic action. Whether the use of the platinum increases the rate of reduction or not is very likely a matter of relative surface and if the platinum has much less surface than the zinc it may be that the reduction will be less than without the platinum, since the reduction that takes place on the surface of the zinc itself is possibly diminished when this is brought into contact with platinum. In the case above the platinum serves to increase the active surface of the system as a whole, hence the increase in the amount of iron reduced.

3. With amalgamated copper gauze cathode, $4^1/_2 \times 20$ cm., and amalgamated zinc rod anode, closed-circuited cell and all other conditions the same as No. 1 above:

   Time for complete reduction: 27 minutes.

4. With silver plated on copper gauze, all conditions same as No. 3.

   Time for complete reduction: 11 minutes.

5. With pure copper gauze cathode, all conditions same as No. 3.

   Time for complete reduction: 8 minutes.

It is not feasible to use an open circuit when a copper cathode is used, since the copper goes into solution and deposits on the zinc in a loosely adhering mass which washes off and interferes with the titration. It is possible to get considerably more than 100% reduction as indicated by the permanganate consumed, under these circumstances.

Since copper itself is a very good reducing agent for the iron it makes very little difference in the amount of iron reduced whether the circuit is open or closed, providing proper precautions are taken to prevent the presence of metallic copper during the titration.

In a dilute acid solution, with the circuit closed, the copper also goes into solution, much the same as with the open circuit, and offers the same disadvantages. When the concentration of acid becomes as much as 10 cc. conc. sulfuric acid per 175 cc. solution none of the copper goes into solution when the cell is short-circuited, and the zinc remains clean and bright.

Amalgamated and Unamalgamated Zinc Anodes.—The following runs were made to determine the effect of amalgamating the anode in the short-circuited cell without external current: The average speed of rotation was about 600 r. p. m. and the other conditions were as given in the table.

Time, minutes	8	8	26	13*	11
Temperature	36°	36°	38°	38°	58°
Acid, cc.	10	10	10	10	10
Anode Zn rod	unamalg.	amalg.	amalg.	amalg.	amalg.
$KMnO_4$ soln. used	23.82	23.83	23.78	0.09	23.85
Loss in wt., anode	0.3062	0.1048	0.1480	0.0404	..

*Blank run with careful exclusion of air.

From these data it will be seen that by the use of amalgamated anodes only about one-third as much zinc goes into solution as when the anodes are not amalgamated, which is a point to be considered when working with impure zinc. The efficiency of the amalgamated zinc is also remarkably high, approaching 70% for complete reduction of the iron, which is another important factor in the practical reduction of the iron when the quality of the zinc is uncertain. In an ordinary reduction with metallic zinc from 3 to 5 g. of the metal would be used, whereas in the present reduction only a little more than 0.10 g. of zinc went into solution. The efficiency of the zinc for a 95% reduction of the iron was made to reach as high as 96% in a number of runs.

In the above runs the solutions withdrawn by the pipet were not weighed, which may account for the rather wide variation in the results. Complete reduction was indicated in each case by sulfocyanate.

The 26-minute run was made to test the effect of running after all the iron was reduced, which was at the end of eight minutes.

The cathode in the above trials changed in weight only a few tenths of a milligram during the run.

Rate of Reduction.—The following runs were made to determine the rate of reduction in the short-circuited cell without external current:

Cathode: Cu gauze, $4^1/_2 \times 20$ cm. Anode: Amalg. Zn rod. Acid: 10 cc. H_2SO_4. Solution: 175 cc. Temp.: 37°.

Time, minutes	$^1/_2$	1	2	3	5	8
% Fe reduced	43.2	64.1	87.0	91.7	97.9	100

This series of results shows the same general characteristics as that obtained with current and needs no comment, except perhaps to note that the iron is completely reduced in less time in this case than when a current of 1.6 amperes is employed, but this may be wholly or in part due to the fact that a larger cathode was used or the temperature of the solution was a little higher.

Blanks without Current.—Blanks run without current could be made to consume from 0.06 cc. to 6 or 7 cc. of permanganate and are no doubt worthless, probably due to the formation of hydrogen peroxide in the solution from the oxygen dissolved in the solution or from the oxygen of the air. This hydrogen peroxide could not exist in the ferrous solution and since so little zinc goes into solution during the reduction it would seem that the blank should be only that quantity of permanganate that is necessary to give the end color in a solution of the same volume, containing a like quantity of acid and iron in the ferric condition, as the iron solution to be determined. In a blank, run with the careful exclusion of air, about the same quantity of permanganate will be consumed as the excess used when ferric iron is present but this is not due to impurities in the zinc and is only an accidental agreement. These same conditions may also apply to a certain extent to any of the methods of reduction where metallic zinc is used.

Blackening of Cathode.—When using a copper cathode it was noticed that in some cases the copper would become quite black while in others it would remain bright. A few qualitative runs were made to determine the conditions that favored the blackening. This blackening did not seem to interfere with the accuracy of the determination except in a few cases with low acidity and large current, when it was evidently partly due to iron being deposited on the cathode.

Among the conditions that were found to favor the blackening were the following: (1) low acidity; (2) small zinc surface in the short-circuited cell; (or 3) comparatively large copper surface; (4) large iron concentration; (5) presence of chlorides; (6) low current density when current was employed.

Finally, as a general check on the reductions, double the quantity of solution used in the previous trials was weighed out and reduced under the conditions given below: It is believed that the results indicate about the accuracy to be obtained by the method when considerable care is used.

Time, minutes	*	30	30	30
Acid, cc	.....	2	5	15
Anode	.....	Pt wire	Amalg. Zn	Amalg. Zn
Cathode	.....	Pt gauze	Pt gauze	Cu gauze
Current amp	.....	1.9	1.6	0.0
Blank, cc.	0.17	0.00	0.13	0.13
Fe per g. of solution	0.005447	0.005448	0.005448	0.005445

*Jones reductor.

The Crescent iron ore, put out by the Bureau of Standards, gave the following results:

Time, minutes	30	30	30	45	30
Acid, cc. H_2SO_4	5	10	10	20	15
Anode	Pt wire	Amalg. Zn	Amalg. Zn	Amalg. Zn	Amalg. Zn
Cathode	Pt gauze	Pt gauze	Cu gauze	Cu gauze	Cu gauze
Current, amp	2.2	1.9	1.6	0.0	0.0
Blank, cc	0.0	0.13	0.13	0.13	0.13
% Fe	58.70	58.66	58.70	58.77	58.70

In the preliminary treatment of the ore, the recommendations of the Bureau were followed and the permanganate used in the titrations was standardized by sodium oxalate obtained from the Bureau of Standards. No correction has been applied for the small amount of titanium (0.07% TiO_2) present in the ore which may account for the values being higher than the value of 58.62% given by the Bureau of Standards.

Conclusions.

1. It is possible to get practically complete reduction of ferric iron, as indicated by permanganate consumed, by using a large platinum cathode and small platinum wire anode if the concentration of sulfate is small. No blank should be subtracted.

2. By using a soluble anode and platinum cathode, complete reduction is possible with wide range of acidity, but with low acidity some of the iron may be deposited on the cathode with high current density.

3. Chlorides must be absent with platinum anode, but with soluble anode may be present unless too great current density is employed.

4. By using a short-circuited cell with platinum gauze cathode and zinc anode, complete reduction may be obtained with wide range of acidity.

5. The most practical method of reduction in most cases is a short-circuited cell with copper gauze cathode and amalgamated zinc rod anode. The concentration of acid must be at least 10 cc. conc. H_2SO_4 per 175 cc. solution. Under these conditions 0.12 g. of iron may be reduced at room temperature in eight minutes with a zinc efficiency of 70%.

6. With short-circuited cell, chlorides do not interfere with the reduction.

7. Increase in temperature in every case increases the rate of reduction.

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NOTE.

A Thermo-Regulator for Electrically Regulated Constant Temperature Chambers.[1]—The need for an adjustable thermo-regulator for electrically controlled constant temperature chambers of any description has led the writers to devise the form represented in the accompanying illustration, Fig. 1. Regulators of this type which have been in use for some time

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[1] Published by permission of the Secretary of Agriculture.