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CONDUCTIVITY MEASUREMENTS UPON OXIDATION-REDUCTION REACTIONS.[1]

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Measurements of electrical conductivity have been made use of in the study of a wide variety of chemical reactions. In some cases the study has been for purely theoretical purposes, in others the measurements have been used to determine the end point of a reaction for analytical purposes. In general the conductivity of a solution changes with the addition of a reacting substance, and if the conductivity and the amount of substance added are plotted on rectangular coördinates we obtain two "conductivity-reaction" curves whose point of intersection approximates the end point of the reaction. The conditions which determine the accuracy with which the point of intersection can be plotted are, first, the degree of curvature of the two curves, and secondly, the nature of the angle of intersection. Ideal conditions are present when the two curves are straight lines, and when they intersect at an acute angle. It has been shown in a number of special cases that the intersecting curves are sufficiently linear, and the angle of intersection sufficiently acute, to permit the ready plotting of the end point of the reaction with an accuracy equal to, and in some cases greater than, that obtainable by ordinary analytical procedure. The most extensive work in this field has been done by Dutoit[2] and his co-workers, who have made a rather exhaustive study of the conditions which must be fulfilled in order that the conductivity measurements may lead to accurate analytical results. Two types of reaction made use of in ordinary volumetric analysis have been studied—neutralization reactions and precipitation reactions. The former type has been used frequently where the usual "indicators" are unsatisfactory, as in the determination of the acidity of highly colored liquids, in the analysis of mixed acids, in the study of biological solutions, and in other cases. The latter type has been used in a variety of reactions, sometimes replacing a common volumetric process, sometimes used in cases where no volumetric process is available. Dutoit's work upon the best conditions for work of this kind, the sources of error, and the probable minimum of error which may be readily attained, in the case of neutralization and precipitation reactions, represents the most thorough study which has been made in this field, and it is to be regretted that some later investigators have apparently failed to familiarize themselves with his experimental

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[2] *J. chim. phys.*. 8 (1910); *Compt. rend.*, 154, 349 (1912); *Bull. soc. chim.*, [4] 7, Appendix (1910).

results and his conclusions. This failure is especially apparent in a recent paper by F. H. van Suchtelen and A. Itano[1] which, owing to neglect of numerous precautions advised by Dutoit, and owing to unjustifiable assumptions as to the linearity of the conductivity-reaction curves, leads to entirely unwarranted conclusions as to the accuracy of the method for the determination of the end point of reactions. A number of typical conductivity-reaction curves are given in this paper (incidentally including many cases previously studied by Dutoit) in which the end points of the reaction are in almost every case given as in "exact" agreement with the theoretical value. Recalculation of the results, however, and re-plotting the curves on a larger scale shows that in practically every case the actual point of inflection of the curves differs from the true end point by from 1 to 6%!

Although, as indicated above, many neutralization and precipitation reactions have been studied with the aid of conductivity measurements, a third type of reaction extensively used in volumetric analysis—the oxidation-reduction reaction—has been entirely neglected. The writer has been unable to find in the literature any experimental data bearing upon this subject, and it was not until the present investigation was well under way that he discovered that Dutoit, in an address before the Société chimique de France,[2] suggested the possibility that conductivity measurements could be successfully applied to the determination of the end point of oxidimetric and iodometric reactions.

The present paper deals with the experimental investigation of certain typical oxidimetric reactions. The general nature of the conductivity-reaction curves, the experimental technique, the probable error of the determination, and the influence of various factors, are discussed.

Apparatus and Technique.

The standard method of Kohlrausch for the determination of conductivity[3] was used throughout.

The electrolytic cell used throughout this investigation was one which had been previously used in some as yet unpublished work carried out in this laboratory on conductivity measurements in solutions of highly dissociated electrolytes. It consists essentially of a large glass vessel, rectangular in shape, and of dimensions 14.5 × 8 × 10 cm., fitted with a wooden cover which serves to support the electrodes. These electrodes are circular, about 2 cm. in diameter, of heavy platinum connected to glass tubes by stout platinum wires sealed into the glass. The glass tubes are in turn fixed rigidly into the wooden cover in such a way that the electrodes are located in opposite corners of the cell. The com-

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[1] THIS JOURNAL, 36, 1793 (1914).

[2] *Bull. soc. chim.*, 7, Appendix (1910).

[3] Findlay, "Practical Physical Chemistry."

plete cell is shown in Fig. 1. A circular opening in the cover serves to admit a rotating stirrer, and to facilitate the addition of reagents to the cell.

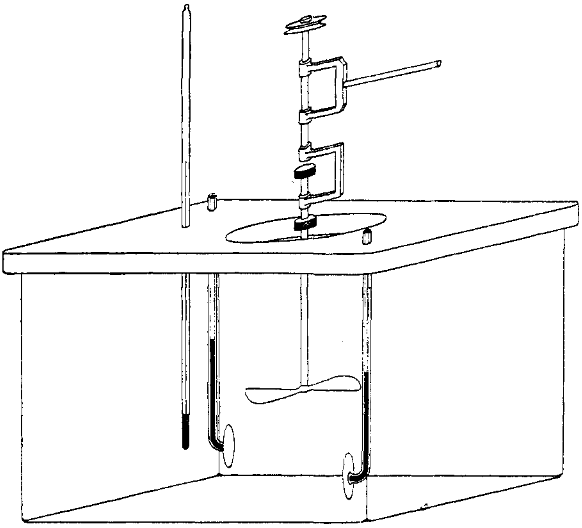
Fig. 1.

The advantages of using a large cell of this type, capable of containing conveniently 500–600 cc. of solution are as follows: It has been shown by Dutoit that in general the conductivity curves are more nearly linear in any given reaction when the volume of the solution is very large in comparison with the volume of the added reagent. This result may be obtained, as was done by Dutoit, by using a rather small cell (capacity 40 cc.) and very small additions of reagent (usually fractions of a cubic centimeter), but the experimental error in the measurement of volumes of liquid considerably less than 1 cc. is at best considerable, and it seemed best in this investigation to use a volume of solution sufficiently large to permit the addition of reagent in 2 cc. or 5 cc. portions, which with a good pipet can be measured with a high degree of accuracy.

The Wheatstone bridge was of the slide wire type, and was carefully calibrated. In a part of the experimental work ratio coils[1] 4.5 × the resistance of the bridge wire were installed, and the effective length of the bridge increased tenfold by this device.

In the earlier work no attempt was made to achieve a degree of accuracy greater than that readily obtainable with the simplest conductivity outfit. In later work (Tables III–V, Figs. 4–7) where a greater degree of accuracy was sought, and where the ratio coils were employed with the bridge wire, certain precautions were observed in order to increase the sensitiveness of the apparatus. The entire apparatus was insulated from induced currents by mounting it upon a table covered with a sheet iron top, and the bridge was shielded from the cell and from the balancing resistance by sheet iron partitions.

The experiments were carried out at 25°, the temperature being kept

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[1] Ostwald-Luther, "Physiko-Chemische Messungen."

constant within about 0.02° by an electrically heated thermostat. In order to avoid long waits in allowing the temperature of the cell to arrive at that of the bath a sensitive thermometer was fitted permanently into the cell through a hole in the cell cover, and the temperature of the solution was brought to that of the bath by the judicious addition of small amounts of hot water.

The general technique of an experiment was as follows: The solution, approximately 500 cc. in volume, was placed in the cell, brought to the temperature of the bath, and stirred vigorously for a minute or so. The stirrer was then stopped, and the point of balance on the bridge determined and recorded. The desired amount of reacting substance, usually 2 or 5 cc., was then added from a pipet, the solution stirred vigorously, and the point of balance again taken. This process was repeated until a fair excess of the reagent had been added. It was found that the position in which the stirrer (in some cases a bladed glass stirrer, in others one of the Witt type) came to rest affected the conductivity of the cell to an extent sufficient to cause irregular readings. To obviate this a mark was made upon the pulley of the stirrer, and a corresponding mark upon the cover of the cell. When the stirrer was stopped the pulley was turned by hand until the mark on the pulley was directly above that on the cell cover. In this way it was assured that the position of the stirrer was the same in all cases.

In calculating the results the following methods were employed: The amount of reagent added was always plotted as abscissa; as ordinate was plotted in some cases the conductivity, calculated from the equation $C = x/(100 - x)R$, where x is the bridge reading in centimeters and R the balancing resistance. In other cases simply the ratio of the two arms of the bridge was plotted as ordinate, as the absolute value of the conductivity is of no importance in this work. Where ratio coils were used the ratio of the two arms of the bridge is given by the expression $r = 450 + x/550 - x$, and in these experiments this function was plotted as ordinate. It has been the habit of some investigators in this field merely to plot the bridge readings directly. This practice will usually lead to less satisfactory results than those obtained by plotting the ratio of the bridge arms, as, if the conductivity curve is linear, of necessity the bridge reading curve will not be, and there will be a corresponding uncertainty in the determination of the end point. Of course if the conductivity curve is not approximately linear, plotting the bridge readings may serve.

In this investigation the oxidation of ferrous sulfate by potassium bichromate was studied in varying concentrations of hydrochloric and sulfuric acid, and likewise the reduction of potassium bichromate by ferrous sulfate in acid solution. Some experiments were also carried out upon the oxidation of ferrous sulfate by potassium permanganate. In all of these experiments solutions of ferrous ammonium sulfate, containing varying amounts of acid, were employed, and the concentration of ferrous iron was carefully checked by ordinary volumetric methods immediately after the determination by the conductivity method.

The results obtained in the different cases will be discussed separately.

Oxidation of Ferrous Sulfate in Hydrochloric Acid Solution.

Tables I, II, III and IV contain the results of typical experiments carried out upon the oxidation of ferrous sulfate in the presence of varying amounts of hydrochloric acid. The measurements are given in detail in a

TABLE I.—OXIDATION OF FERROUS SULFATE IN ACID SOLUTION BY 0.1 *N* POTASSIUM BICHROMATE.

	Expt. 1. (Curve 5, Fig. 2.) 0.025 *N* HCl.		Expt. 2. (Curve 8, Fig. 2.) 0.04 *N* HCl.		Expt. 3. (Curve 4, Fig. 2.) 0.045 *N* HCl.	
0.1 *N* $K_2Cr_2O_7$ added. Cc.	Bridge reading. Cm.	Cond. (mhos × 10^4).	Bridge reading. Cm.	Cond. (mhos × 10^4).	Bridge reading. Cm.	Cond. (mhos × 10^4).
0	50.15	251.50	53.55	384.20	50.49	339.87
5	48.20	232.62	52.20	364.00	49.16	322.33
10	46.10	213.82	50.78	344.00	47.74	304.57
15	43.87	195.38	49.29	324.00	46.26	286.93
20	41.48	177.20	47.75	304.60	44.73	269.77
25	40.82	172.45	47.68	303.60	44.63	268.70
30	40.90	173.02	47.65	303.40	44.63	268.70
35	40.98	173.57	47.62	303.03	44.64	268.83
40	41.06	174.10	47.59	303.67	44.65	268.97
End point from direct titration	21.38 cc.		19.90 cc.		20.20 cc.	
End point from conductivity	21.40 cc.		19.95 cc.		20.10 cc.	

TABLE II.—SUMMARY OF EXPERIMENTS SIMILAR TO THOSE IN TABLE I.

				End point	
No.	Curve.	Titrating solution.	Acidity, *N*.	by direct titration. Cc.	from conductivity. Cc.
4	1, Fig. 2	0.1 *N* $K_2Cr_2O_7$	0.018 H_2SO_4	19.90	18.90
5	2, Fig. 2	0.1 *N* $K_2Cr_2O_7$	0.02 HCl	19.93	19.80
6	3, Fig. 2	0.1 *N* $K_2Cr_2O_7$	0.025 H_2SO_4	20.05	20.00
7	6, Fig. 2	0.1 *N* $K_2Cr_2O_7$	0.03 HCl	19.93	19.15
8	7, Fig. 2	0.1 *N* $K_2Cr_2O_7$	0.035 HCl	21.38	21.30
9	9, Fig. 2	0.1 *N* $K_2Cr_2O_7$	0.05 HCl	20.05	20.00
10	1, Fig. 3	0.2 *N* $K_2Cr_2O_7$	0.03 H_2SO_4	4.49	4.50
11	2, Fig. 3	0.2 *N* $K_2Cr_2O_7$	0.035 H_2SO_4	4.45	4.40
12	3, Fig. 3	0.2 *N* $K_2Cr_2O_7$	0.05 H_2SO_4	22.00	22.00
13	4, Fig. 3	0.2 *N* $K_2Cr_2O_7$	0.06 H_2SO_4	22.00	21.95
14	5, Fig. 3	0.2 *N* $K_2Cr_2O_7$	0.02 HCl	10.38	10.40
15	6, Fig. 3	0.2 *N* $K_2Cr_2O_7$	0.03 HCl	11.04	11.00
16	7, Fig. 3	0.2 *N* $K_2Cr_2O_7$	0.035 HCl	10.38	10.40
17	8, Fig. 3	0.2 *N* $K_2Cr_2O_7$	0.05 HCl	11.04	10.98

few cases, and in others in order to save space, merely the calculated and observed end points are given, showing the amount of experimental error. Several of these measurements are represented by the curves of Figs. 2, 3 and 4. (In the actual determination of the end point of the reaction the curves were plotted on a much larger scale than that represented here.) In Figs. 2 and 3 the conductivity is plotted as ordinate;

FIG. 2

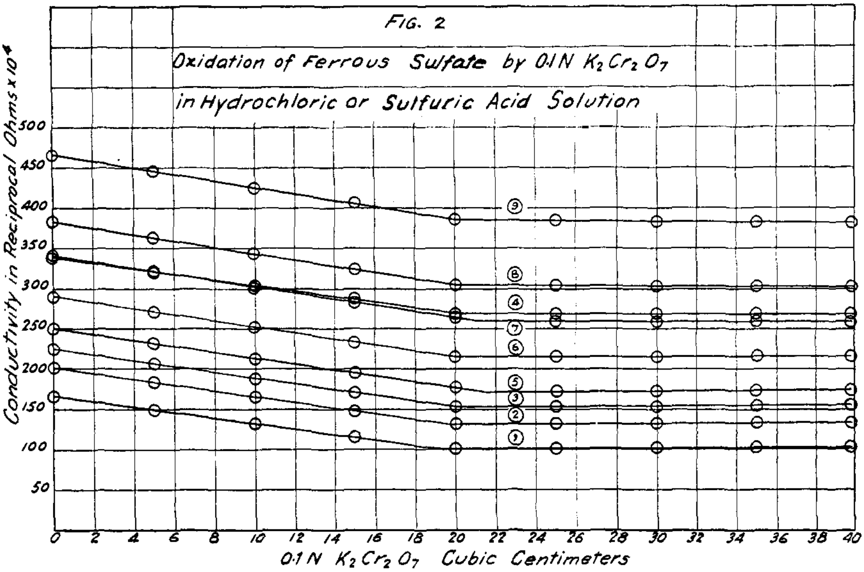
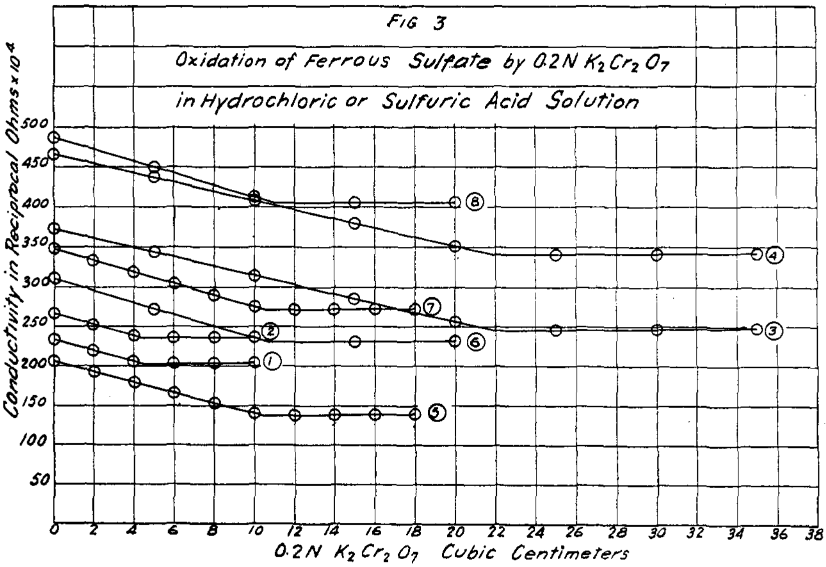


FIG 3



in Fig. 4 the ratio of the bridge arms is plotted as ordinate. As pointed out above, the measurements given in Tables I and II were carried out with no especial precautions to ensure high accuracy, and serve to indicate the general nature of the "conductivity-reaction" curves, and the degree of accuracy with which the end point of the reaction may be determined under these conditions. The amounts of ferrous sulfate vary from about 10 to 50 cc. 0.1 N $FeSO_4$. The concentrations of hydrochloric acid vary from about 0.02 N to 0.07 N. The total volume of the solution was invariably 500 cc. The titrating solution was either 0.1 N or 0.2 N $K_2Cr_2O_7$.

These preliminary experiments brought out the following points:

(*a*) The general type of the curves is that of the neutralization of an acid by a weak base, or of a base by a weak acid. The conductivity drops during the progress of the reaction, and then changes very little with the excess of bichromate. The conductivity may rise slightly, fall slightly, or remain constant after the end point has been passed, this depending upon the acidity of the solution. The reason for the drop in the conductivity during the progress of the reaction is given by the reaction, which may be represented as

$$(1)\quad 6Fe^{++} + Cr_2O_7^{=} + 14H^{+} = 6Fe^{+++} + 2Cr^{+++} + 7H_2O.$$

The concentration of hydrogen ion falls during the reaction, and since the hydrogen ion in these strongly acid solutions carries most of the current, the conductivity of the solution must fall with it. After the end point is reached further addition of bichromate causes little change in the conductivity.

(*b*) The curves are very nearly linear, both before and after the end point has been reached. This is especially true when the concentration of hydrochloric acid is between the limits of 0.037 N and 0.045 N. Within these limits the curve is linear within the limit of error of the experiment. At lower concentrations of acid the curve is very slightly concave toward the abscissa; at higher concentrations of acid it is slightly convex toward the abscissa. In no case is the deviation from a straight line much more than the experimental error. This fact is of considerable importance from a practical standpoint, for it diminishes greatly the number of observations necessary to determine the end point with accuracy, and lessens the time of an experiment.

(*c*) The slope of the conductivity curves before the end point has been reached is nearly independent of the concentration of acid.

(*d*) The time necessary for the conductivity to become constant after the addition of a given portion of bichromate is inappreciable except when the concentration of acid is very low, or when the measurement happens to be made in the *immediate vicinity of the end point.* Experience showed that if the amount of bichromate added in any given case was almost exactly that necessary for complete oxidation of the ferrous salt the conductivity fell slowly over a period of several minutes (or less at the higher concentrations of acid) before becoming constant. Even after waiting for several minutes before taking the bridge reading the value for the conductivity obtained was usually not in line with the other measurements, and caused an error in plotting the end point. It was found better, then, to neglect any point measured in the immediate vicinity of the end point, and plot the curves entirely from the other points. Incidentally it may be noted that Dutoit found that in the measurement of precipitation reactions it is often necessary to neglect any measurements made very near the point of inflection of the curve.

(*e*) The end point determined from the curves in cases where the concentration of hydrochloric acid was below 0.025 *N* was almost always somewhat lower than that determined by direct titration by the usual volumetric methods. Apparently this is due to atmospheric oxidation of the ferrous salt, which occurs at much higher velocity at low acid concentration than at high. Except with very small amounts of iron it was found advisable to use a concentration about 0.04 *N* both to prevent oxidation, and to obtain a linear curve. When as much as 50 cc. of 0.1 *N* iron is present it is best to increase the concentration to 0.06 *N*.

(*f*) No particular difference could be seen in the curves obtained with 0.1 *N* and 0.2 *N* bichromate. Perhaps the latter solution gave more concordant results, and in the more accurate experiments (Tables III and IV) this alone was used.

(*g*) As may be seen from the results given in Tables I and II the end points obtained by plotting the conductivity curves agree very well with those determined by direct analysis. The difference between observed and calculated results is seldom as great as 0.1 cc. of 0.1 *N* $K_2Cr_2O_7$ or 0.05 cc. of 0.2 *N* $K_2Cr_2O_7$, except in the solutions containing very little acid, and this corresponds to just about the degree of accuracy which the usual process of titration of ferrous salts with potassium bichromate is capable of yielding, when potassium ferricyanide is used as indicator. The conductivity measurements, then, give a degree of accuracy about equal to that obtainable by direct titration, even when no special precautions are taken to ensure accuracy. As will be shown below, these results may be much improved upon by increasing the accuracy of the conductivity measurement.

Table III and Fig. 4 give the results of experiments upon solutions of ferrous sulfate in hydrochloric acid solution, in which the effective length of the bridge was increased tenfold by the use of ratio coils, and the accuracy of the experiment increased by shielding the apparatus from

TABLE III.—OXIDATION OF FERROUS SULFATE IN ACID SOLUTION BY 0.2 *N* POTASSIUM BICHROMATE.

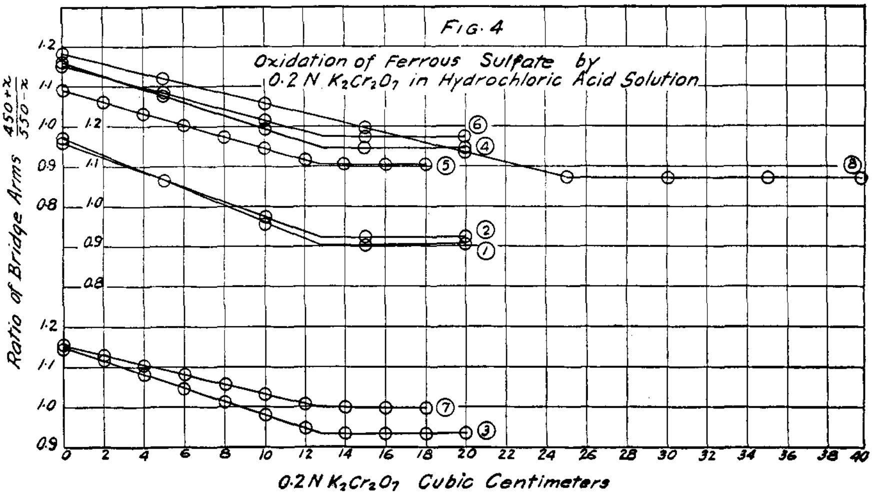
	Expt. 1. (Curve 3, Fig. 4.) 0.045 *N* HCl.		Expt. 2. (Curve 8, Fig. 5.) 0.045 *N* H_2SO_4.		Expt. 3. (Curve 11, Fig. 5.) 0.06 *N* H_2SO_4.	
0.2 *N* $K_2Cr_2O_7$ added. Cc.	Bridge reading. Cm.	Ratio of bridge arms.	Bridge reading. Cm.	Ratio of bridge arms.	Bridge reading. Cm.	Ratio of bridge arms.
0	84.59	1.1486	91.24	1.1798	92.23	1.1845
2	77.34	1.1157	82.65	1.1398	...	....
4	69.74	1.0822	73.76	1.0998	...	....
5	...	....	...	....	74.80	1.1043
6	61.87	1.0486	64.45	1.0597	...	....
8	53.70	1.0249	54.89	1.0197	...	....
10	45.25	0.9811	44.92	0.9798	55.98	1.0241
12	36.48	0.9473	37.58	0.9515	...	....
14	33.00	0.9342	37.84	0.9526	...	....
15	...	....	...	....	50.17	1.0007
16	32.96	0.9341	38.11	0.9536	...	....
18	32.96	0.9341	38.37	0.9547	...	....
20	32.96	0.9341	38.72	0.9557	50.43	1.0017
End point from direct titration...........	12.78 cc.		11.45 cc.		11.50 cc.	
End point from conductivity..........	12.77 cc.		11.44 cc.		11.50 cc.	

TABLE IV.—SUMMARY OF EXPERIMENTS SIMILAR TO THOSE IN TABLE III.

				End point	
No.	Curve.	Titrating solution.	Acidity. *N*.	by direct titration. Cc.	from conductivity. Cc.
4.....	1, Fig. 4	0.2 *N* $K_2Cr_2O_7$	0.035 HCl	12.75	12.74
5.....	2, Fig. 4	0.2 *N* $K_2Cr_2O_7$	0.04 HCl	12.77	12.77
6.....	4, Fig. 4	0.2 *N* $K_2Cr_2O_7$	0.045 HCl	12.75	12.74
7.....	5, Fig. 4	0.2 *N* $K_2Cr_2O_7$	0.05 HCl	12.70	12.68
8.....	6, Fig. 4	0.2 *N* $K_2Cr_2O_7$	0.055 HCl	12.77	12.75
9.....	8, Fig. 4	0.2 *N* $K_2Cr_2O_7$	0.06 HCl	25.10	25.11
10.....	1, Fig. 5	0.2 *N* $K_2Cr_2O_7$	0.03 H_2SO_4	11.37	11.42
11.....	2, Fig. 5	0.2 *N* $K_2Cr_2O_7$	0.035 H_2SO_4	11.37	11.41
12.....	3, Fig. 5	0.2 *N* $K_2Cr_2O_7$	0.035 H_2SO_4	11.46	11.46
13.....	4, Fig. 5	0.2 *N* $K_2Cr_2O_7$	0.04 H_2SO_4	11.46	11.47
14.....	5, Fig. 5	0.2 *N* $K_2Cr_2O_7$	0.045 H_2SO_4	11.46	11.45
15.....	6, Fig. 5	0.2 *N* $K_2Cr_2O_7$	0.045 H_2SO_4	11.50	11.51
16.....	7, Fig. 5	0.2 *N* $K_2Cr_2O_7$	0.045 H_2SO_4	11.50	11.49
17.....	9, Fig. 5	0.2 *N* $K_2Cr_2O_7$	0.05 H_2SO_4	11.50	11.52
18.....	10, Fig. 5	0.2 *N* $K_2Cr_2O_7$	0.05 H_2SO_4	11.50	11.50
19.....	....	0.2 *N* $K_2Cr_2O_7$	0.06 H_2SO_4	22.74	22.73
20.....	12, Fig. 5	0.2 *N* $K_2Cr_2O_7$	0.07 H_2SO_4	11.45	11.46

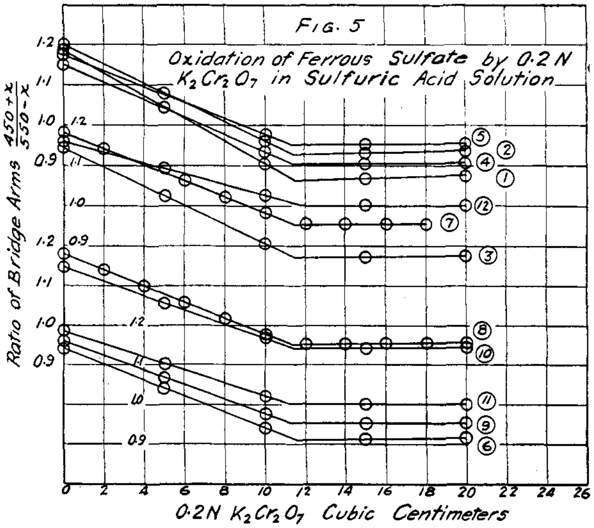
induced currents (see above). These results bring out the following additional facts:

(*a*) In the case of solutions approximately 0.035 *N* to 0.045 *N* to HCl and containing 25 cc. 0.1 *N* ferrous sulfate the change in conductivity on the addition of successive portions of 2 or 5 cc. of 0.2 *N* potassium bichromate is constant within a few tenths of a per cent. (until the end point has been passed) which is hardly more than the error of measurement of the pipet. The curve is therefore almost exactly linear.



(In this figure and in Figs. 5, 6 and 7 the origin of the ordinates has been shifted somewhat, as indicated on the margin, in order to permit plotting several curves in the same figure.)

(*b*) The end point of the reaction can be determined from the curves with an error of usually not more than 0.01 to 0.02 cc. of 0.2 *N* bichromate, which is *distinctly better* than the results which can be obtained by direct titration. Even when larger or smaller amounts of hydrochloric acid are used than those mentioned above, and the curves in consequence not so nearly linear, it is easily possible to determine the end point with an error of not more than about 0.02 cc. of 0.2 *N* bichromate.



The Oxidation of Ferrous Sulfate in Sulfuric Acid Solution.

Tables I, II, III and IV, and Figs. 2, 3 and 5 give the results of experiments on the oxidation of ferrous sulfate in the presence of varying amounts of sulfuric acid. Tables I and II and Figs. 2 and 3 contain the results of the preliminary experiments made without especial precautions, and Tables III and IV and Fig. 5 those in which a more accurate technique was employed.

The preliminary experiments lead to results almost identical with those obtained under similar conditions with hydrochloric acid. The general type of the curve is the same, the slope is nearly the same, and the experimental error in the determination of the end point is of the same order of magnitude. The curves are if anything more nearly linear than is the case with hydrochloric acid, for with all amounts of sulfuric acid greater than 150 cc. of 0.1 *N* acid, the curves are linear within the error of the experiment.

Tables III and IV and Fig. 5 contain the results of more accurate measurements on the sulfuric acid solutions, using ratio coils as described above. These results show that for solutions containing between 175 and 350 cc. of 0.1 *N* sulfuric acid the curves are almost perfectly linear. In most cases the deviation from the linear is quite within the limit of error of the experiment. Expt. No. 2, Table III, plotted in Curve 8, Fig. 5, shows very strikingly how small the deviation from the linear may be. The end point in such cases can be easily determined within 0.01 cc. either by a large scale plot, or by solving algebraically the equations for the two curves.

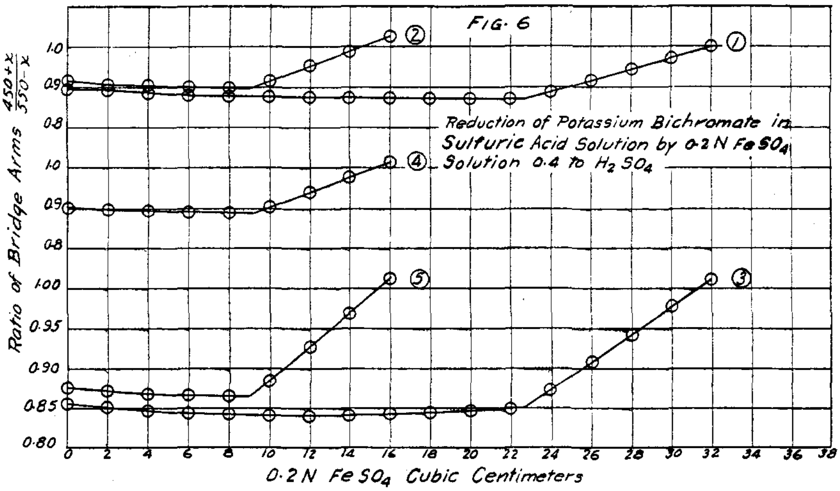
Reduction of Potassium Bichromate by Ferrous Sulfate.

In addition to the experiments done upon the oxidation of ferrous salts by potassium bichromate, a number of experiments were carried out in which the ferrous salt was added to a solution of potassium bichromate acidified with varying amounts of sulfuric or of hydrochloric acid. Table V contains the results of two of these experiments, and certain typical curves are plotted in Figs. 6 and 7. In all of these determinations the solution in the electrolytic cell consisted of a solution of potassium bichromate, acidified with sulfuric or hydrochloric acid, and diluted to a volume of 500 cc. The experimental technique was exactly like that in the experiments hitherto described. The titrating solution consisted of a solution of ferrous ammonium sulfate either 0.1 or 0.2 *N* as regards iron, and containing in addition in some cases no acid, and in other cases sufficient sulfuric or hydrochloric acid to make the solution 0.1, 0.2, or 0.4 *N* as regards acid. The type of curve obtained in this reaction will naturally vary with the acidity of the ferrous solution. In titrating with a ferrous solution to which no acid has been added (Curve 3, Fig. 7) the curve is similar to those obtained for the oxidation of ferrous salts by potas-

TABLE V.—REDUCTION OF POTASSIUM BICHROMATE IN ACID SOLUTION BY FERROUS SULFATE.

0.2 *N* $FeSO_4$ added. Cc.	Expt. 1 (Curve 4, Fig. 6). 0.04 *N* H_2SO_4. Titrated with 0.2 *N* $FeSO_4$, 0.4 *N* H_2SO_4.		Expt. 2 (Curve 3, Fig. 7). 0.05 *N* H_2SO_4. Titrated with 0.2 *N* $FeSO_4$, 0.0 H_2SO_4.	
	Bridge reading. Cm.	Ratio of bridge arms.	Bridge reading. Cm.	Ratio of bridge arms.
0	24.19	0.9018	70.11	1.0838
2	22.72	0.8967	62.09	1.0495
4	21.73	0.8929	54.04	1.0164
6	20.65	0.8891	46.06	0.9844
8	20.14	0.8873	38.17	0.9538
10	24.31	0.9023	31.30	0.9279
12	34.39	0.9394	33.16	0.9348
14	44.05	0.9764	35.00	0.9417
16	53.34	1.0135	36.84	0.9487
End point from direct titration..	9.19 cc.		9.84 cc.	
End point from conductivity....	9.20 cc.		9.82 cc.	

sium bichromate, that is, the conductivity drops with the progress of the reaction, due to diminishing acidity, and then changes very little after the end point has been passed. In titrating with a ferrous solution in which the normality as regards acid is equal to the normality as regards iron (Curves 1 and 2, Fig. 7) the curve drops somewhat during the reduction and then rises fairly steeply after the end point has been passed. In cases where the normality of the solution as regards acid is twice that of its normality as regards iron (Curves 1–5, Fig. 6) the conductivity



changes very little during the reaction and then rises quite sharply after the reaction is complete. As shown in Equation 1 seven hydrogen ions are used up in the oxidation of three ferrous ions, so that the hydrogen-ion content of the bichromate solution is reduced very little by the addition of a ferrous solution containing six hydrogen ions for every three ions of ferrous iron. In all cases the acidity of the bichromate solution also influenced somewhat the nature of the curve, as is evident from a comparison of Curves 1 and 3, Fig. 6. An inspection of the curves in this table shows that in no case is there the same approach to straight lines as is shown by the curves in the previous tables. The curve of reduction is invariably somewhat convex as regards the X axis; the second branch of the curve is nearly linear. The solution which permitted the most accurate measurement of the point of inflection is probably that which

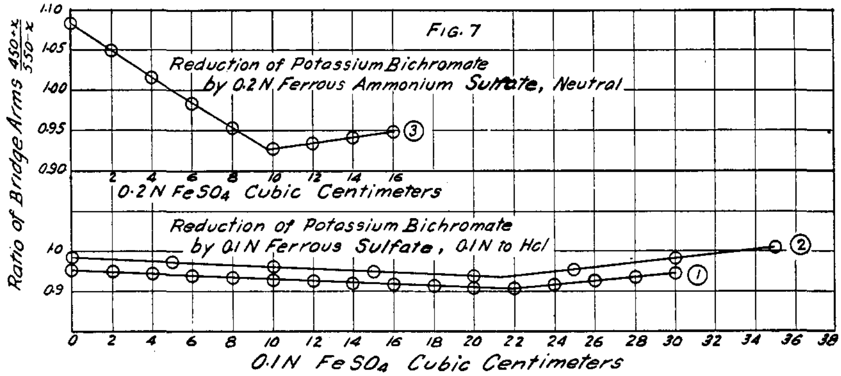


Fig. 7

is 0.2 N as regards iron, and 0.4 N as regards acid. If this solution is used for titrating a solution of bichromate not less than 0.04 N as regards sulfuric acid the end point can be calculated readily with a very fair degree of accuracy. On account of the distinct curvature of the branches of the curves it is necessary to take a greater number of points on the curves than is necessary in the case of the oxidation curves. Not more than 2 cc. of 0.2 N ferrous solution should be added at a time, and in some cases it is better to add the solution 1 cc. at a time, taking measurements after each addition.

Altogether it is obvious that by making various combinations of concentrations of ferrous salt and acid, and by varying the acidity of the bichromate solution, it would be possible to obtain numerous types of curves. There seemed to be nothing to be gained from this study, however, as the principal types of curve are represented in Figs. 6 and 7.

Oxidation of Ferrous Sulfate by Potassium Permanganate.

A number of experiments were carried out in which potassium permanganate replaced potassium bichromate as oxidizing agent in the reaction with ferrous sulfate in sulfuric acid solution. No experimental data on this reaction will be included in the present paper, and no typical curves shown, partly because the results are so far not quite so satisfactory as in the case with potassium bichromate, and partly because the investigation of oxidation reactions involving this reagent is being continued. However, certain general conclusions which could be drawn from the experimental work so far completed will be summarized briefly herewith.

(*a*) The conductivity-reaction curves for potassium permanganate are similar in general type to those obtained with potassium bichromate. The slope of the curve during the oxidation is not quite so great as in the reaction with bichromate.

(*b*) The curves are perfectly linear within the limit of error of the experiment, for almost any concentration of sulfuric acid above 125 cc. in the total volume of 500 cc.

(*c*) The end point of the reaction tends to come lower than that determined by direct titration, apparently due to two causes. One of these consists in atmospheric oxidation, which proceeds at a higher rate than in the case of oxidations with bichromate. It seems probable that the presence of the manganese ion acts catalytically in accelerating the atmospheric oxidation of the ferrous salt, though this is not altogether certain.

(*d*) A second source of error is the influence of the rate at which the portion of permanganate solution necessary for complete oxidation took place. If this last portion was added at the usual rate of delivery of the pipet a precipitate of manganese dioxide usually appeared, and when this was the case the calculation of the end point invariably led to erroneous results. It is necessary therefore to add the last portion of permanganate very slowly, and unless the total amount of iron present is approximately known, all of the permanganate must be added very slowly in order to avoid overrunning the end point. This constitutes on obvious limitation of the usefulness of the method for the determination of iron, especially considering the simplicity and accuracy of the direct titration of ferrous iron by permanganate, a simplicity and accuracy which is hardly shared by the titration with bichromate.

General Discussion of Results.

The experiments recorded in this paper constitute, so far as the writer has been able to ascertain, the first applications of the measurement of electrolytic conductivity to the typical oxidation-reduction reactions of analytical chemistry. They show that in this type of reaction, as in the cases involving a neutralization or a precipitation, the measurement of conductivity may serve to determine the end point of the reaction, replacing the usual "indicator." With the practical applications of the method to the problems of analytical chemistry the present paper is not concerned, although it may be noted that the results in Tables III and IV show that in the case of the oxidation of ferrous salts by potassium bichromate a higher degree of accuracy is attainable with proper precautions than is ordinarily possible by the direct titration by the customary process.

This work seems to open up a rather promising field for further investigation. The use of other oxidizing agents than potassium bichromate and potassium permanganate; the reaction of these substances with a variety of reducing agents; the possible determination of two or more oxidizable substances in the same solution (as can be readily accomplished in the case of two acids in the same solution), and the practical application of the method to cases in which the procedure of ordinary volumetric analysis in unavailable or uncertain, are problems which present themselves at once. Work will be continued along these lines in this laboratory.

Summary.

(1) Measurements have been made of the change of conductivity of solutions of ferrous salts during their oxidation by potassium bichromate and potassium permanganate.

(2) It has been shown that the conductivity measurements may serve to determine the end point of the reaction with a degree of accuracy equal to or greater than that obtainable by the usual volumetric procedure.

(3) The experimental technique, the general nature of the "conductivity-reaction" curves, and the influence of various factors upon these curves, have been discussed.

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS.]

REDUCING MATTER EXTRACTABLE FROM FILTER PAPER.

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In the determination of iron with potassium permanganate, it is sometimes necessary to precede the titration by a filtration, *e. g.*, to remove free sulfur formed during reduction with H_2S. Recently there were described by Boller[2] some experiments which were designed to show that such filtration through filter paper previous to titration with potassium permanganate was without effect. Since the results appear to be at variance with earlier conclusions of Hillebrand,[3] it was desired to conduct some additional experiments which might throw light on the subject, which is of importance in connection with an extensive investigation of methods for the determination of iron now in progress at the Bureau of Standards.

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[1] Published with permission of the Director, Bureau of Standards.

[2] "Beiträge zur titrimetrischen Bestimmung des Antimons. Zinns, Titans, Eisens, und Urans." Dissertation, Zürich (1915).

[3] "Analysis of Silicate and Carbonate Rocks." U. S. Geol. Survey, *Bull.* 422, 15 (1910).