A modified form of the static isoteniscope method was used, with the precautions and corrections previously described.[1] The thermometry was in agreement to 0.1° with the 1914 scale of the Reichsanstalt. Chattaway and Berger both report slight decomposition at the boiling point. The behavior of the sample studied in the isoteniscope made it clear that such decomposition is appreciable even below 100°.

The values in the table below are given for every 5°, and were obtained graphically from the observed values.

TABLE I.

Vapor Pressure of Tetranitro-methane.

Temperature. Degrees.	Pressure in mm. Hg at 0°.	Temperature. Degrees.	Pressure in mm. Hg at 0°.
40	26.6	90	239
45	34.4	95	286
50	44.2	100	339
55	56.1	105	400
60	70.6	110	470
65	88.1	115	550
70	109	120	640
75	134	125	743
80	164	125.7	760
85	199		

Using the vapor-pressure curve thus defined to test the character of the liquid according to the criterion suggested by Hildebrand,[2] one obtains, using his units, a value of 13.9 for the entropy of vaporization divided by *R* at the temperature (near 70°) at which the concentration of the vapor is 0.00507 mole per liter. Assuming the vapor is normal, this would indicate slight, if any, association or abnormality in the liquid at this temperature.

PRINCETON, N. J.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

ELECTROMETRIC TITRATIONS, WITH SPECIAL REFERENCE TO THE DETERMINATION OF FERROUS AND FERRIC IRON.[3]

BY J. C. HOSTETTER AND H. S. ROBERTS.

Received July 12, 1919.

Introductory.

In the study of the oxides of iron now in progress at the Geophysical Laboratory, it has become increasingly evident that the ordinary methods for determining small amounts of ferrous oxide in the presence of much ferric oxide are not susceptible of the precision attained in some of the

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[1] See THIS JOURNAL, 32, 1412 (1910).

[2] THIS JOURNAL, 37, 970 (1915).

[3] Read at the Buffalo Meeting of the American Chemical Society, April 9, 1919.

other measurements on the oxides, as, for instance, that of magnetic susceptibility.[1] Especially was it necessary to be able to distinguish accurately between the ferrous iron contents of ferric oxides when the latter contained less than 0.1% FeO,[2] since easily measureable differences in the magnetic susceptibilities of such oxides have been found. The method which is described herein permits of the determination of a few tenths of a milligram of ferrous iron in the presence of any quantity—up to 100 g.—of ferric iron. The essential details of this method were developed before the entry of the United States into the war and, extended to include the determination of total iron, the method found many applications in the determination of iron in raw materials for optical glass, in optical glasses themselves, in glass pots, and, to quote an example in quite a different field, in the determination of iron in sulfur chloride.[3]

This method is, in brief, the direct electrometric titration of the ferrous iron with standard dichromate. The various factors affecting this determination have been studied in some detail and as sharp end-points can now be obtained with 0.01 N or even with 0.0005 N dichromate solutions as with the more concentrated solutions usually employed. Furthermore, the technic of the method for larger quantities of ferrous iron has now been developed to such an extent that oxidation and reduction titrations carried out electrometrically must hereafter be considered precision analytical methods capable of giving results to one part in a thousand or better.

Electrometric titrations for the determination of various elements have been proposed from time to time and some excellent work of direct and indirect application to analytical procedure has been recorded in the foreign literature,[4] but not until the work of Hildebrand,[5] describing simplified apparatus, appeared in this country did the method receive much recognition. Shortly after the appearance of Hildebrand's paper came the work of Forbes and Bartlett,[6] who described an anomalous increase of potential produced by certain reducing agents and took advantage of this effect for conveniently locating end-points electrometrically. In

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[1] R. B. Sosman and J. C. Hostetter, *Trans. Am. Inst. Mining Eng.*, **58**, 409–433, 434–444 (1917).

[2] In previous publications it has been shown that Fe_2O_3 and Fe_3O_4 probably form a continuous series of solid solutions (Sosman and Hostetter, THIS JOURNAL, **38**, 807–833 (1916)), and that all ordinary ferric oxides, both artificial and natural, carry determinable amounts of ferrous oxide.

[3] At Edgewood Arsenal.

[4] R. Behrend, *Z. phys. Chem.*, **11**, 466–491 (1893); R. Peters, *Ibid.*, **26**, 193 (1898); C. Fredenhagen, *Z. anorg. Chem.*, **29**, 396–458 (1892); W. Böttger, *Z. phys. Chem.*, **24**, 253–301 (1897); F. Crotognio, *Z. anorg. Chem.*, **24**, 225–262 (1900); Ostwald, Luther and Drucker, "Physico-Chemische Messungen," p. 454.

[5] THIS JOURNAL, **35**, 847–871 (1913).

[6] *Ibid.*, **35**, 1527 (1913).

1916 Kelley and Conant applied the latter method to the determination of vanadium,[1] and chromium,[2] in steels, making the method applicable to routine testing, and later Kelley and others developed compact apparatus[3] and extended the method to the determination of manganese.[4] Bichowsky[5] has titrated zinc with ferrocyanide and in the course of his investigations[6] was able to produce curves (volume of ferrocyanide against electromotive force) showing all variations from the "normal" curve to that described by Forbes and Bartlett.

In Hildebrand's work the end-point of the titration was taken as the point of inflection in the curve showing the relation between the voltage developed and the volume of oxidizer (dichromate) added. Forbes and Bartlett, on the other hand, and later Kelley and Conant, simply made use of the greatly increased deflection of the galvanometer as an indication of the end-point, taking advantage of the increased sensitivity given by the anomalous rise. The latter method has been applied by these authors to routine work and with remarkable success. Our problem, however, was quite different and it seemed preferable to use the graphical method, as being of more general applicability. The time consumed in plotting is merely a matter of a few minutes and the shape of the curve is frequently of great value in indicating the presence of impurities—such as organic matter in hydrofluoric acid—in the solution being titrated.

Apparatus and Method.

The first set-up used was essentially that described by Hildebrand and the effects of certain variables were studied with it. After preliminary studies had demonstrated the successful application to our problems, apparatus was designed which permitted the thorough study of variables under controlled conditions. Later also a simplified potentiometer was devised by Roberts,[7] the use of which eliminates the millivoltmeter from the set-up and makes the entire outfit very compact. This potentiometer is essentially a slide-wire and its successful use assumes that the voltage of the cell (dry cell or storage) remains steady or only shifts gradually during a titration; readings are taken as numbers proportional to the voltage.

Titrating Head.—A few words may be inserted here to describe the "titrating head" used to cover the flask which contains the solution to be titrated, in order that the atmosphere above the solution may be controlled, and also to support the calomel half-cell and the platinum elec-

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[1] THIS JOURNAL, 38, 341 (1916).

[2] *J. Ind. Eng. Chem.*, 8, 718 (1916).

[3] *Ibid.*, 9, 780 (1917).

[4] *Ibid.*, 10, 19 (1918).

[5] *Ibid.*, 9, 668 (1917).

[6] *J Wash. Acad. Sci.*, 7, 141 (1917).

[7] THIS JOURNAL, 41, 1359 (1919).

trode. Carbon dioxide or nitrogen (freed from oxygen) is passed through the flask before and during a titration; the entrance tube for carbon dioxide extends about half way into the flask. The calomel half-cell is made as shown in Fig. 1; the tube making connection with the solution has an internal diameter of about 1 mm. and is turned upwards at the bottom in order to prevent the heavy potassium or sodium chloride solution from running into the flask with a corresponding amount of lighter solution traveling up into the small tube and hence escaping the reaction. This connecting tube is not sealed to the titrating head but passes loosely through a tube which supports it, thus permitting adjustment for different sized flasks. The calomel cell is made up with strong sodium or potassium chloride solution, such high concentration being desirable in order to reduce the resistance of the titrating system with consequent increase in electrical sensitivity and to raise its boiling point so that bubbles of steam may not form in the capillary. A small extension tube is sealed to the tip of the buret.

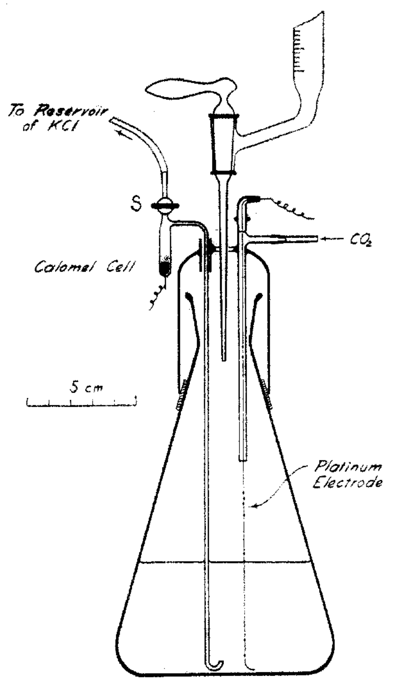

Fig. 1.—Flask covered by "Titrating Head" which supports the calomel half-cell and platinum electrode and also permits the maintenance of a neutral atmosphere within the flask.

The electrode consists of a single platinum wire (0.4 mm. diam.) sealed into a tube ground into the carbon dioxide tube as shown in the sketch; this joint enables one to wash down the tube and electrode upon which solution may have spattered during the titration.

Method of Investigation.—The method of study followed here was, in its essentials, simply the electrometric titration of a few milligrams of ferrous iron under a variety of conditions, followed by comparison of the curves so obtained. The success of any titration in the preliminary experiments was judged by the character of the graph near the change of curvature and the precision with which the point of inflection could be determined. Later the quantitative side of the problem was studied. The results of the experiments defining conditions, recorded in this paper, are therefore expressed mainly in the form of curves.

Methods of Plotting.—The usual method of directly plotting the relations between volume of oxidizer V, and electromotive force E, is satisfactory for most cases. A convenient scale of coördinates which enables one to read the end-point with the precision ordinarily required as 1 cm. for 1 cc. against 1 cm. for 100 millivolts. In cases where the point of inflection is not readily determined on the graph plotted to this scale—as when too little acid is present during the titration—other ratios in which the voltage scale is increased may be used with advantage. A little practice enables one, however, to locate by inspection the point of inflection with the desired accuracy.

In some cases the plotting of $\Delta E/\Delta V$ against V is a distinct advantage; this derivative passes through a maximum at the point of inflection and consequently its relation to V may serve for the location of the end-point. Even such a curve as that of No. 4 in Hildebrand's paper,[1] which was caused by too low a concentration of acid in the solution being titrated and which he pronounced "unsatisfactory" can be made to yield a fairly satisfactory maximum corresponding to the point of inflection if $\Delta E/\Delta V$ instead of E is plotted against V. Reference to Fig. 2, which gives typical curves for the titration of ferrous iron by dichromate, shows the sharp maximum obtainable by plotting the derivative against volume.

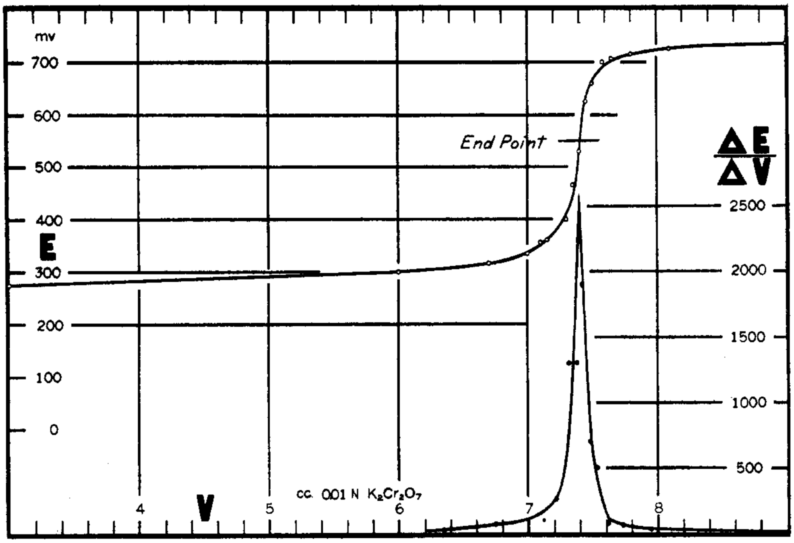

Fig. 2.—Titration of 4.1 mg. of ferrous iron in 70% conc. hydrochloric acid with dichromate solution yielding typical curve of potential E, against volume of dichromate, V. Plotting ΔE over ΔV gives a sharp maximum corresponding to the point of inflection which is the "end-point" of the titration.

The End-Point.

"Electrometric methods, unlike most of the other methods of volumetric analysis, are not merely special methods applicable to but one reac-

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[1] *Loc. cit.*, Fig. 15, p. 870.

tion under a rigorously limited set of experimental conditions as are our indicator methods, but they are perfectly general methods based not on the accident of the discovery of a new indicator but on a perfectly general principle. If we consider the reaction A + B ⟶ C + D and introduce into the reaction mixture an electrode whose E. M. F. depends on the concentration of any of the reacting substances, say B the change of the E. M. F. as you add or subtract more or less of that substance is proportional not to the amount added but to the percentage change of concentration of that substance, and accordingly, the maximum percentage change of concentration and hence of E. M. F. occurs at the point where the concentration of B equals that of C, *i. e.*, occurs at the end-point (equilibrium point) of the reaction."[1]

The shape of the curve relating electromotive force and concentration as the iron is oxidized follows from the logarithmic ratio of the concentrations in the well-known equation for the electromotive force of such cells. The voltage changes very slightly with the first additions of oxidizing agent, but as the one ion disappears the amount of oxidizing agent necessary to depress its concentration to, say 1% of its former value, rapidly becomes smaller. Just as soon as the concentration of one ion becomes negligibly small the reverse process takes place with respect to the oxidizing ion from the added reagent. Up to this point the oxidizing agent has been reduced as rapidly as it was added and consequently no concentration of the oxidizing ion can develop until the reducing material is completely oxidized. When this point is reached the same reasoning will account for the increase of potential which is rapid at first as the concentration of the new ion increases slightly and then increases less rapidly as the concentration of the oxidizing ion increases. The point at which this change of direction occurs is obviously therefore the "end-point" of the particular reaction.

Experimental evidence that such a point of inflection actually corresponds to the end-point was obtained in two ways. In the first series definite amounts of ferrous iron were titrated electrometrically, and the quantities so determined, taking the point of inflection as the end-point, were checked against those known to be present. In the second series the titration of a ferrous solution with permanganate showed that the pink color indicating the end-point appeared exactly at the point of inflection when small quantities of ferrous iron were titrated in sulfuric acid solution. This subject will be referred to later.

Electrodes.—Experiments were made on electrodes of different materials and some of the curves obtained during this study are shown in Fig. 3. The "normal" curve is shown for purposes of comparison. These

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[1] Quoted from an unpublished address by Dr. F. R. Bichowsky of this laboratory, before the Chemical Society of Washington, April 12, 1917.

curves were obtained by carrying out a titration with several different wires immersed in the iron solution making readings on the different electrodes *seriatim.* Palladium is not suitable as an electrode for these titrations as evidenced by the curve of its electromotive force against dichromate; the voltage rises slightly at first and then remains constant, or nearly so, throughout the course of the titration.[1] The influence of palladium is also seen in the curve for the palladium-gold alloy which is intermediate between the palladium curve and that for gold, the latter electrode giving a comparatively small rise near the end-point. The curve shown here for platinum "B" which had been originally covered with platinum black was obtained only after repeated treatment of the electrode with acid. The improvement in the shape of the curve, which was initially, in other titrations, not much above that for palladium, was probably due to reduction of surface by solution[2] of the finely divided platinum black. In experiments with platinum electrodes of different area it was found that the best results, as evidenced by steadiness of potential and extent of rise near the end-points, were obtained with an electrode presenting the least possible surface to the solution. A small platinum wire (0.4 mm. diameter, for instance), was found to be satisfactory; it is used in the bright condition and between titrations is kept in 1 : 1 hydrochloric acid.

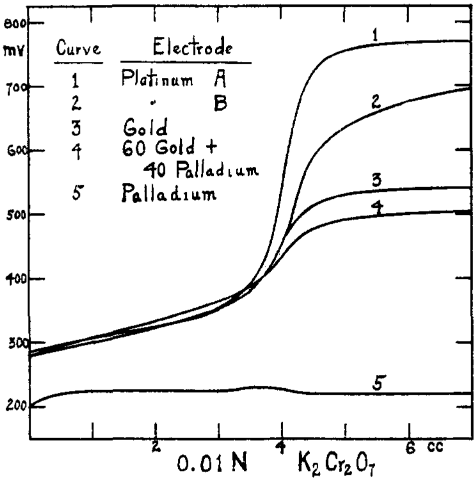

Fig. 3.—Titration curves obtained with electrodes of different metals. The most satisfactory curve is given by platinum of small area (Curve 1).

Electrodes were found to be very sensitive to contamination—as a result of which very irregular curves are obtained, which are quite unsuitable

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[1] It is not unlikely that the curve for a palladium electrode will depend to some degree upon the amount of hydrogen, or other reducing gases, condensed within it. This, in turn, would depend upon whether the electrode had been previously ignited in a gas flame, or by heating in air (as electrically). If curves of the type shown in No. 5 of Fig. 3 can be consistently reproduced (and there is much evidence that they can) the possibility is at once suggested that an electrode of palladium can be substituted for the calomel electrode with a considerable simplification of apparatus.

[2] It is interesting to note in this connection that a bright platinum foil electrode presenting approximately 5 sq. cm. area to the solution, lost 0.17 mg. during a titration carried out in strong HCl. In this case, however, the solution was exposed to the air.

for good work. An electrode must be thoroughly cleaned before use—by acid treatment followed by an ignition—and should be kept under hydrochloric acid between titrations. The irregular results frequently obtained before the electrodes are satisfactorily clean are probably polarization effects, and may lead to an appreciable error in the end-point. Curve 2, in Fig. 3, is typical of the action of a dirty platinum electrode. The lowering of E. M. F. increases greatly after the end-point is passed and thereby shifts the point of inflection to the right. This, of course, introduces an error into the determination which can be avoided by keeping the electrode clean. The condition of the electrode can readily be ascertained from the shape of the curve obtained from a test titration of ferrous solution in 1 : 1 hydrochloric acid.

Irregular results were also obtained when the stream of carbon dioxide, or nitrogen, was passed through the solution in order to assist stirring. This appears to be a logical method of stirring, but it was found that these gases bubbling over the platinum electrode in contact with the solution gave irregular deflections of the galvanometer corresponding somewhat to the bubbles of gas. The carbon dioxide tube was, therefore, shortened as shown in Fig. 1, and satisfactory results have since been secured.

Effect of Temperature.—Sudden changes of temperature are to be avoided but gradual drifting may be tolerated inasmuch as this merely shifts the slope of the curves to a slight extent and this cannot be mistaken for a point of inflection involving a large potential difference. Certain reactions are best carried out at higher temperatures—as the reduction of ferric iron with stannous chloride to be described later—and we have found no difficulty whatever in carrying out the titration at temperatures which gradually fell from the boiling point of water to 60 or 70° at the end of the titration.

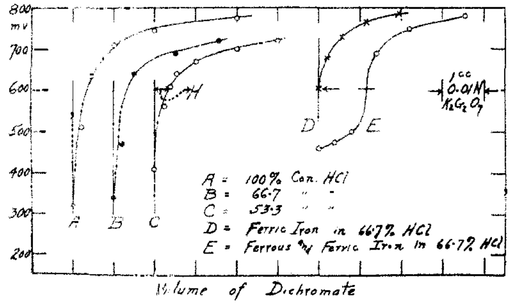

Fig. 4.—Curves A, B, and C resulted from the "titration" of hydrochloric acid with dichromate solution. D is the titration of ferric iron in hydrochloric acid solution. E is the titration of ferrous iron in the presence of ferric iron. The distance H disappears when ferric iron is present.

Blanks.

Plotting the voltage obtained by adding potassium dichromate (0.01 *N*) to hydrochloric acid gives curves like A, B, and C, shown in Fig. 4. These curves rise sharply from an initial voltage that is increased as the acid is made less concentrated; the acidities are 100%, 66.7%, and 53.3% of the concentrated acid, respectively. The first thought is to consider that the horizontal distance H from the vertical axis to the curve, at the voltage corresponding to the point of inflection as given in Curve E, represents the blank for these conditions. However, if one "titrates" a carefully made ferric solution with dichromate the curve rises very sharply as before, but the initial voltage is now near the usual inflection voltage and the more completely ferric the solution the nearer the initial voltage approaches that at the point of inflection (Curve D). Consequently the "blank" as found in the first test does not apply to the actual working conditions in which ferric iron is present. The curve resulting from the titration of ferric iron with dichromate may also be considered as evidence that the end-point is actually the point of inflection.

Blanks caused by ferrous iron or other reducing material present as impurities must obviously be considered. The shape of the curve is, under these conditions, quite different.

Effect of Acidity.

Hydrochloric Acid.—Hildebrand showed that the "end-point" was very satisfactory if ferrous iron were titrated in 33% conc. hydrochloric acid (by volume) and an even greater change in potential was obtained near the end-point where 67% acid was used. From this it is evident that considerable variation in acidity is permissible. Too low an acid concentration, however, gives curves such as that of Hildebrand's, previously mentioned.

Sulfuric Acid.—The titration of ferrous sulfate was also carried out in sulfuric acid solutions and the results are shown in Fig. 5, which gives all the essential data. The effect of high acidity in increasing the voltage change is again evident from the curves, and the fact demonstrated that satisfactory points of inflection may be secured over a wide range of acidity, from 17 to 67% of the concentrated acid, and very likely this range can be extended in either direction.

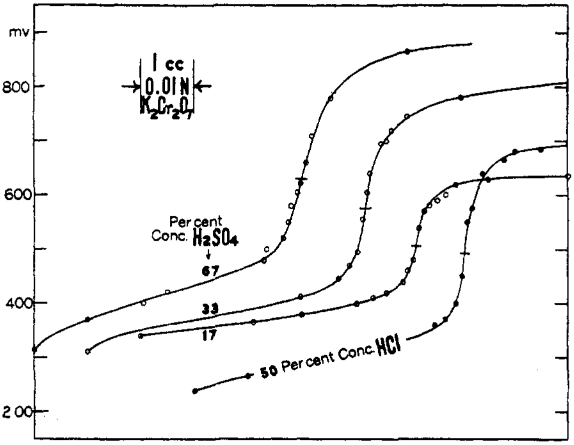

Fig. 5.—Showing change in the titration curve with varying concentration of sulfuric acid. High acidity favors large rise of potential near the end-point. The curve in 50% conc. hydrochloric acid is given for comparison. Ferrous iron = 4.24 mg.; total volume of solution, 150 cc.

Nitric Acid.—Because of its oxidizing action nitric acid must be absent from solutions to be titrated in this manner. The voltage of a ferric nitrate solution was found to be about the same as that given with excess dichromate, under our conditions of acidity.

Hydrofluoric Acid.—Two series of titrations of ferrous iron in the presence of hydrofluoric acid accompanied by hydrochloric acid and also by sulfuric acid showed that hydrofluoric acid was without detrimental effect. Its inertness indicated that the method could be applied to the direct determination of ferrous oxide in silicates and subsequently many glasses and glass pots were analyzed for ferrous iron in this manner. In the course of his work on the analysis of optical glasses, our colleague, J. B. Ferguson, obtained some irregular results when hydrofluoric acid was present in the iron solution during titration and later this was traced to the presence of impurities (probably organic matter), in the hydrofluoric acid; the organic matter was oxidized slowly by dichromate and gave a sloping curve which somewhat obscured the point of inflection. Some lots of acid showed this irregular action while others gave smooth, normal curves. This subject will be considered more in detail elsewhere.

Effect of Acidity when Using Dilute Dichromate.—From the data just presented it is evident that the electrometric titration of ferrous iron may be successfully carried out in solutions of widely varying acidity for concentrations of dichromate in the range of 0.1 N to 0.005 N.

When using 0.001 N dichromate, however, the acidity and volume of the iron solution become highly important. The curves obtained on titrating with 0.001 N dichromate, iron solutions containing 0.56 mg. ferrous iron in 10 and also in 35 cc. of 25% sulfuric acid, showed very little rise of potential and, at best, gave an obscure end-point. On the other hand, good curves may be obtained with 0.001 N and even 0.0005 N dichromate if this has been made up with acid, and if the volume of solution to be titrated is small. The solid curves of Fig. 6 represent the titration of about 0.56 mg. metallic iron in various amounts of 25% conc. sulfuric acid; the oxidizer in each case was 0.001 N dichromate in 25% conc. sulfuric acid, about 10 cc. being required to reach the end-point. This series illustrates the advantage of working with a small volume. The dotted curve is taken from the titration of half this quantity of iron in 10 cc. of 25% conc. sulfuric acid, the oxidizer in this case being 0.0005 N dichromate in 25% sulfuric acid.

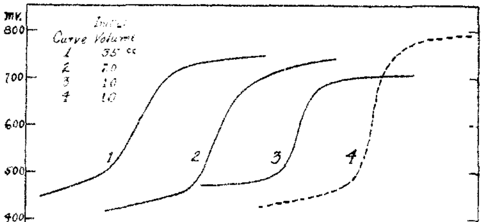

Fig. 6.—Titrations with 0.001 N and 0.0005 N potassium dichromate.

Effect of Ferric Iron on the Titration of Ferrous Iron.

After the preliminary work on the effects of acidity had been completed, titrations of small amounts of ferrous iron were carried out with the addition of successively larger portions of ferric iron. The result, as was to be expected, was a shortening of the difference in potential at the end-point, mainly because of the increased initial potential. The potential at the point of inflection was also increased under these conditions. However, the points of inflection were still perfectly sharp even at the higher concentrations of ferric iron as is evident from the curves given in Fig. 7. The ferrous iron titrated in the last curve was only 1 part to 2600 ferric. In the work on the determination of ferrous iron in ferric salts the ferrous iron content titrated directly was at times only 0.0002% (of the salt) and even under these extreme conditions the end-point obtained was perfectly definite.

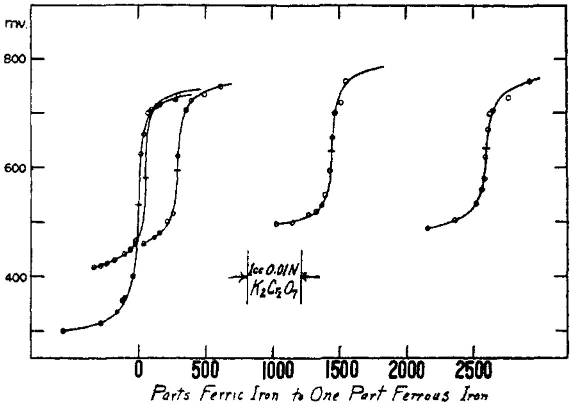

Fig. 7.—Change in titration curve of ferrous iron caused by additions of ferric iron. The change of potential near the end-point is reduced as the ratio of ferric iron to ferrous increases but the end-point is still easily located.

Determination of Ferrous Iron In Ferric Compounds.

Conditions having been established for the determination of ferrous iron in the presence of large quantities of ferric iron the former was determined in a number of ferric salts. In order to dissolve the ferric compound in the absence of air the solution was effected in an atmosphere of carbon dioxide in the dissolving flask shown in Fig. 8. This is a modification of the one formerly used[1] and possesses the additional advantage that spatterings on the combination stopper and funnel can be more readily washed off.

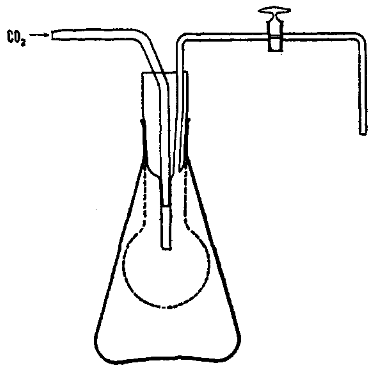

Fig. 8.—Flask for dissolving salts or oxides in an inert atmosphere.

Method.—Ten g. of the salt (sulfate or chloride) is dissolved in water in an

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[1] R. B. Sosman and J. C. Hostetter, THIS JOURNAL, 38, 822 (1916).

atmosphere of carbon dioxide and the solution treated with an equal volume of conc. hydrochloric acid. The funnel-stopper of the flask is now removed and the titrating head put in place, the stream of carbon dioxide through the flask continuing to flow. Electrical connection is made by allowing the capillary connecting with the calomel cell to fill by manipulating the small stopcock shown at S in Fig. 1. The solution is now titrated with 0.01 *N* potassium dichromate and the results plotted.

TABLE I.—FERROUS IRON IN FERRIC SALTS.
By Electrometric Titration.

Ferric salt.	Maker.	Grade.	Lot No.	% ferrous iron.
Ammonium sulfate...	J. T. Baker	C. P. analyzed	102711	0.0005
Ammonium sulfate...	Baker & Adamson	C. P. analyzed	..	0.0035
Ammonium sulfate...	Baker & Adamson	C. P. analyzed	..	<0.0005
Ammonium sulfate...	Baker & Adamson	C. P. analyzed	..	<0.0005
Ammonium sulfate...	Baker & Adamson	C. P. analyzed	..	0.010
Ammonium sulfate...	Kahlbaum	White label	P 2112	0.00025
Ammonium sulfate...	Squibb	Reagent	12098	<0.0002
Bromide............	Kahlbaum	White label	Z 3012	5.41
Chloride:				
Hydrated crystals..	J. T. Baker	C. P. analyzed	12611	0.0005
Hydrated crystals..	J. T. Baker	C. P. analyzed	32913	0.0005
Hydrated crystals..	Baker & Adamson	C. P. analyzed	..	0.0022
Hydrated crystals..	Baker & Adamson	C. P. analyzed	..	0.004
Hydrated crystals..	Eimer & Amend	Pure	..	0.004
Hydrated crystals..	Kahlbaum	"Zur analyse"	..[1]	0.0014
Hydrated crystals..	Kahlbaum	White label	D 0708	0.0005
Hydrated crystals..	Squibb	Reagent	17453	0.004
Sublimed..........	Baker & Adamson	C. P. analyzed	..	..[2]
Sublimed..........	Kahlbaum	White label	C 070?	0.404
Sublimed..........	Merck	Reagent	S 3597 12716	0.020
Sulfate.............	J. T. Baker	C. P. analyzed	12315	<0.0003

The change of voltage with the first drop of dichromate is, in itself, an excellent criterion as to the presence of ferrous iron. The curves of Fig. 9 show the change in the form of the curve in the titration of successively increasing small amounts of ferrous oxide. Ferric iron was present to the extent of 1660 mg. in each titration. The scale of volumes in Fig. 9 is much larger than in the other figures.

Results on the percentage of ferrous iron in a number of ferric salts have been collected in Table I, which shows a considerable variation in ferrous iron content. The salts analyzed were taken from our stock shelves; the ferrous iron varies from 0.0003 to 0.020%, although there are several exceptions.

It should be pointed out here that the percentages of ferrous iron reported in these ferric salts were of necessity determined in solution and

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[1] Not distinguishable.

[2] Contains metallic iron

some proportion of the ferrous iron found may have arisen from action of the solvent on a solid salt—in which the iron was all in the "ferric" condition—by attainment of equilibrium between ferrous and ferric iron. This would arise as a consequence of the relation developed by Peters:[1] these two ions are in equilibrium and the concentration of one does not normally reach zero. Ferrous iron might form by hydrolysis also, since the hydrolysis of ferric salts, especially the chloride, probably involves the formation of intermediate ions containing ferrous iron.[2] The amounts of ferrous ion developed by these reactions are small under our conditions, but it should be constant, under identical conditions, for each type of salt. Since, however, variations in ferrous iron content of these salts were actually found, differences must have existed in the salts themselves. The lowest values found may have been formed as indicated above, but it is unlikely that the larger percentages can be accounted for in this manner.

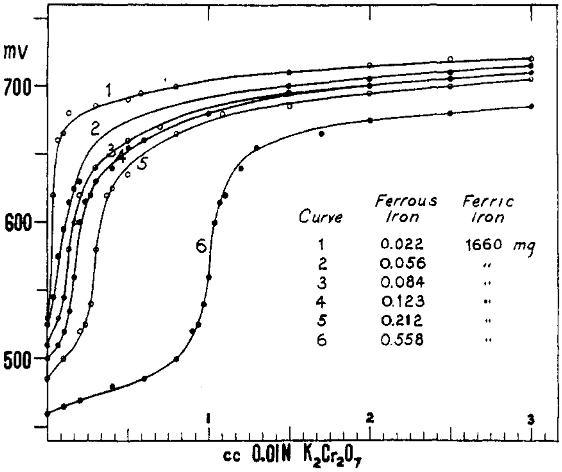

Fig. 9.—Small amounts of ferrous iron titrated in the presence of 1660 mg. ferric iron.

A number of old samples of ferric chloride which had stood loosely stoppered on the stock room shelves for possibly 10 years were examined and some observations on these may be of interest. The salt in one of these bottles was covered with a layer of saturated solution; 10 g. of the moist salt was found to contain 0.11 mg. of ferrous oxide, whereas 3 cc. of the solution over the salt gave 0.16 mg. Expressed on the basis of total iron the salt contained approximately one part ferrous iron in 30,000 while the solution in contact with it showed double this amount. Hydrolysis involving the formation of an intermediate ferrous ion would account for the higher percentage in the solution.

Reduction of Ferric Chloride by Boiling.—The following experiment is interesting in showing that the small amount of ferrous iron formed by reduction on boiling aqueous ferric chloride in ordinary air may be readily determined electrometrically. While no special precautions were taken

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[1] *Loc. cit.*

[2] H. M. Goodwin, *Z. phys. Chem.*, **21**, 1–15 (1896); W. Spring, *Rec. trav. chim.*, **16**, 237–249 (1897).

to insure the absence of traces of reducing material from the water or the air, the results indicate that the solution was reduced notwithstanding the ease with which the air oxidizes ferrous solutions containing chloride. A solution of ferric chloride (10 g. crystals in 50 cc. water) was boiled in a flask for 5 minutes, after which the solution was allowed to stand on the hot plate for 30 minutes. Some precipitation of ferric hydrate took place during this treatment. This precipitate was dissolved when the solution was treated with 100 cc. of conc. hydrochloric acid previous to the titration. The solution now showed 0.76 mg. ferrous iron. Ten g. of the salt dissolved and titrated without having been boiled showed 0.22 mg., the difference of 0.54 mg. having developed during the treatment at the higher temperature, notwithstanding the fact that the solution was freely exposed to the air during this time. Other similar experiments confirmed this.

The similar reaction in the case of ferric bromide has been known for many years.[1]

Ferric Oxides.—Several determinations of ferrous oxide in ferric oxides from different sources are given in Table II; the ferrous iron was determined in a solution of 10 g. of the oxide dissolved in 1:1 hydrochloric acid. The last 3 oxides were produced by ignition of certain salts over the blast lamp. This ignition was carried out in platinum using an asbestos board screen to carry away reducing gases. The small amounts of ferrous oxide (0.024 to 0.055%) found in the ignited product are formed by reduction in one or all of the following ways: namely, (1) reduction by platinum,[2] (2) by reducing gases from the flame, (3) by dissociation of ferric oxide even in air.[3] The magnetic susceptibilities of these oxides were previously determined and confirm the presence of ferrous oxide.[4]

The Determination of Large Amounts of Ferrous Iron.—The method previously discussed may be applied equally well to the determination of large quantities of ferrous iron if the accuracy given by volume buret is sufficient. For higher precision,

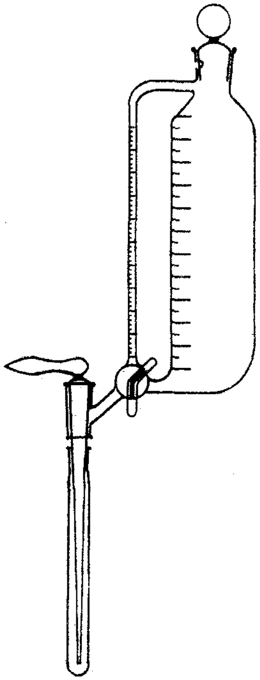

Fig. 10.—Modified weight buret for electrometric titrations. The small volume buret sealed to the weight buret is used for titrating near the end-points.

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[1] L. L. DeKoninck, *Z. angew. Chem.*, **3**, 149 (1889).

[2] Robert B. Sosman and J. C. Hostetter, *J. Wash. Acad. Sci.*, **5**, 293–303 (1915).

[3] J. C. Hostetter and R. B. Sosman, THIS JOURNAL, **38**, 1188–1198 (1916).

[4] R. B. Sosman and J. C. Hostetter, *Trans. Am. Inst. Mining Eng.*, **58**, 418 (1917).

the only necessary modification in the method is the use of a weighing buret[1] for the dichromate solution.

The inconvenience of weighing the buret and solution after the addition of each drop near the end-point may be avoided in two ways. The first method uses strong oxidizing solution (as 0.1 *N*) for the entire titration; the solution is delivered, however, from the modified weighing buret shown in Fig. 10. This buret permits the use of a small volume buret (1 cc. capacity reading to 0.01 cc.) for the end-point while the larger reservoir is drawn upon for most of the titration. The manipulation of the buret is obvious from the figure. The weight of solution corresponding to the unit graduation must, of course, be previously determined.

TABLE II.—FERROUS OXIDE IN FERRIC OXIDES FROM DIFFERENT SOURCES.

Source of ferric oxide.	% FeO.
Merck, Iron Oxide Reagent (Lot 1041) (from Nitrate)	0.015
Kahlbaum, Eisenoxyd "Zur Analyse mit Garantieschein" (Lot 4478)	0.033[2]
Ignition over blast lamp of:	
Ferric Nitrate (J. T. Baker)	0.055
Ferric Hydrate, C. P., Moist (J. T. Baker)	0.024
Ferrous Sulfate (J. T. Baker)	0.050

The second method for titrating with strong dichromate is the use of the weighing buret until the voltage indicates the proximity of the region of inflection, after which the titration is completed with a dilute solution

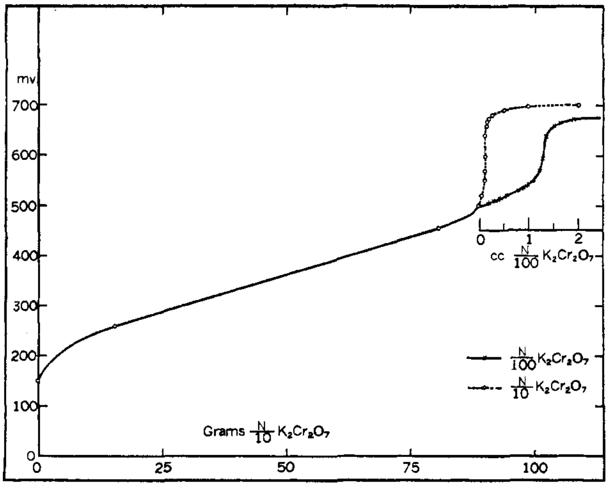

Fig. 11.—Method of plotting results when 0.01 *N* dichromate solution, delivered from a volume buret, is used for the end-point region, while 0.1 *N* dichromate solution, from a weight buret, is used for most of the curve.

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[1] This buret should have an extended tip sealed to it and the protecting cap should be lengthened correspondingly.

[2] Not homogeneous; some portions contain as much as 0.043% FeO.

delivered from a volume buret. For convenience and also in order to minimize errors in the graduations of the buret, the dilute solution is made up so that 1 cc. corresponds to 0.1 g. of the stronger solution. The plot of the dilute solution against voltage is made on a scale such that the point of inflection can be located to within 0.02 to 0.04 cc., corresponding to 0.002 to 0.004 g. of the more concentrated solution (see Fig. 11). It is thus seen that the end-point error is reduced to a minimum by this procedure, giving the possibility of a precision in titrations of this kind greater than that attained by the use of other methods.

TABLE III.—ELECTROMETRIC TITRATION OF LARGE AMOUNTS OF FERROUS IRON.
Metallic Iron (Electrolytic, Langbein-Pfanhauser).

Weight. G.	Acid	Weight 0.1 N $K_2Cr_2O_7$. G.	"Iron value." Fe per g. $K_2Cr_2O_7$ soln. G.
0.5107	HCl	91.555	0.005578_0
0.5163	HCl	92.560	0.005578_0
0.4693	HCl	84.201	0.005573_5
0.4479	HCl	80.267	0.005580_1
0.3858	H_2SO_4	69.165	0.005577_9
0.5235	H_2SO_4	93.875	0.005576_1
0.5449	H_2SO_4	97.750	0.005574_4
		Av.,	0.005576_9

The results given in Table III were obtained by the second method described above. Electrolytic iron (rolled sheet from Langbein-Pfanhauser) was dissolved in acid in an atmosphere of carbon dioxide and hydrogen without any other special precautions and the solution so obtained titrated directly. The figures shown in the table as "iron-value" of the dichromate merely indicate the ratio of dichromate to this iron for comparative purposes. The maximum error in this series is 1 part in 800. The deviations in this series could have been reduced by first reducing electrometrically, with stannous chloride as described below, the small amount of ferric iron formed in the solution, probably from dissolved oxygen in the acid and water used to effect solution of the iron. Inasmuch as our primary interest was the determination of small amounts of iron the work on large quantities was not continued further.

Electrometric Titration of Ferric Iron with Stannous Chloride.

The direct determination of ferric iron by titration with stannous chloride has previously been carried out by utilizing the disappearance of the yellow color[1] or the action on methylene blue[2] as the end-point. Electrometrically this titration may be carried out very successfully. Fig. 12 shows a curve relating voltage and volume of stannous chloride (0.005 N) used in a typical titration of ferric iron. The voltage change at the end-

[1] W. W. Scott, "Standard Methods of Chemical Analysis," 1917, p. 221.

[2] C. Russo, *Gazz. chim. ital.*, **44**, 1–8 (1914).

point is from about +250 millivolts to —100. This change in sign necessitates a reversing switch in the circuit or, more conveniently, the location of the "zero" point on the potentiometer at some distance from one end as has been done in the instrument described by Roberts.

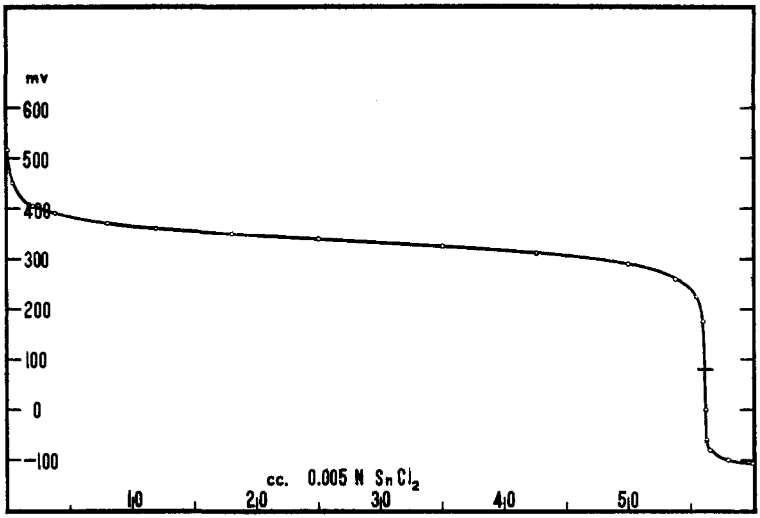

Fig. 12.—Electrometric titration of ferric iron with 0.005 *N* stannous chloride solution.

Determination of Ferric Iron in Ferrous Salts.—The titration just described enables us to determine directly small amounts of ferric iron in the presence of ferrous iron, and, as an application of this method, determinations were carried out on ferrous salts. These salts are frequently used as convenient standards in oxidimetry and a knowledge of the ferric iron content is necessary if a correct standardization is to be made. Table IV summarizes a few results showing the percentages of ferric iron in freshly opened ferrous salts and also in bottles which have stood loosely stoppered for some years. The error introduced, when using such a salt as a standard, by assuming that all of the iron is ferrous, is indicated in the last column of the table, in which the ferric iron is calculated to the percentage of total iron.

TABLE IV.—FERRIC IRON IN FERROUS SALTS OF REAGENT QUALITY.

Salt.	Bottle.[1]	Maker.	Lot No.	% ferric iron in salt.	% ferric iron of total iron.
Ferrous ammonium sulfate.	Sealed	J. T. Baker	61013	0.028	0.20
Ferrous ammonium sulfate.	Opened	J. T. Baker	61013	0.047	0.33
Ferrous ammonium sulfate.	Opened	J. T. Baker	6211	0.043	0.30
Ferrous sulfate............	Sealed	Squibb	7624	0.08	0.41
Ferrous sulfate............	Opened	Baker & Adamson	...	0.22	1.10

[1] *Sealed* (by maker); *Opened* (loosely stoppered for at least 2 years).

The stannous chloride solution is conveniently standardized by electrometric titration against dichromate as described below.

Electrometric Titration of Potassium Dichromate with Stannous Chloride.

The electrometric titration of dichromate with stannous chloride, or the reverse titration, may be readily carried out with the same apparatus. The titration is made in acid solution at an elevated temperature since the reaction proceeds rather slowly at room temperature. Inasmuch as the reaction is between a very strong oxidizer and a powerful reducing agent, the voltage change is very large, namely, from about +600 mv. to —100 mv. Fig. 13 shows a typical curve for this titration.

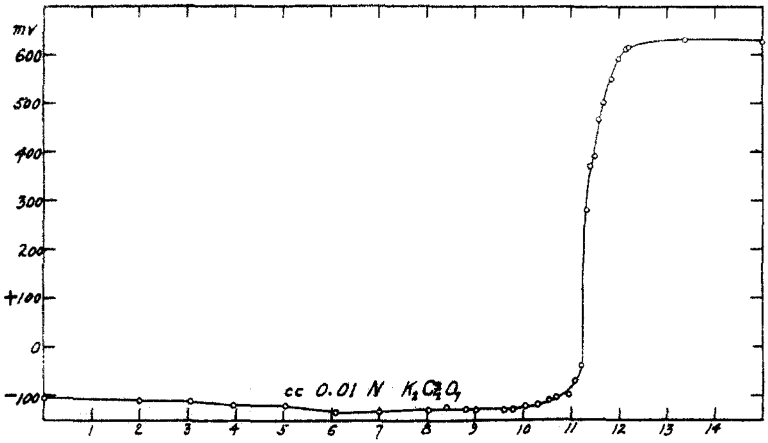

Fig. 13.—Electrometric titration of stannous chloride with potassium dichromate solution.

Combination Method for the Determination of Total Iron.

The two reactions just described may be readily combined in one operation to give total iron. In this determination the iron solution is completely reduced, as shown by the color change as well as by voltage, with concentrated stannous chloride solution which is added in slight excess. The solution (at 70° or 80°) is now oxidized with standardized dichromate solution plotting E. M. F. against volume as usual. The resulting curve shows two points of inflection. The first point indicates when the excess of stannous chloride is used up and the second corresponds to the complete oxidation of ferrous iron. The volume of dichromate between these two end-points obviously represents that required by the iron.

The shape of the curve and the effect of varying concentrations of hydrochloric acid are shown in Fig. 14.

Applications of Method for Total Iron.

The method just described has been successfully used in the determination of iron in raw materials for optical glass—such as sand,[1] sodium

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[1] John B. Ferguson, *J. Ind. Eng. Chem.*, 9, 941 (1917).

and potassium salts, barium carbonate, zinc oxide, borax and boric acid, and the oxides of lead. None of these substances interferes with the method, although when iron is determined in a nitrate it must be precipitated first as hydroxide[1] in order to separate it from the interfering nitric acid.

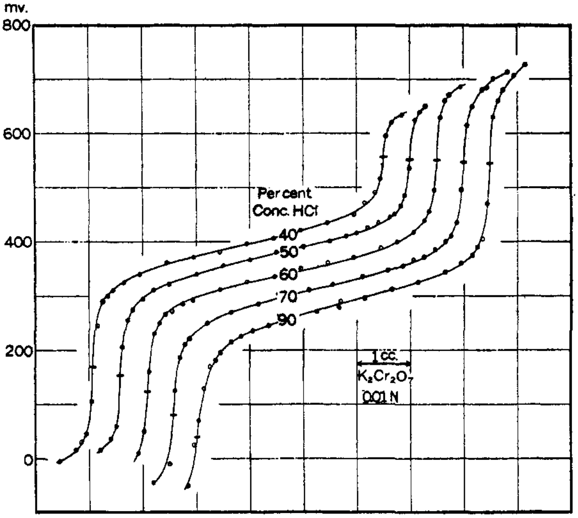

Fig. 14.—Electrometric titration of iron which has been reduced with slight excess of stannous chloride. The amount of dichromate solution corresponding to the iron is the volume between the two end-points.

It is obvious that such metallic oxides as are not reduced by stannous chloride need not interfere with this method of determining total iron. Actual tests made in the presence of manganous manganese and titanium (as TiO_2) show definitely that these exert no deleterious effect on the titration; vanadic oxide, on the other hand, is reduced by stannous chloride and consequently must be determined separately and deducted from the total of iron and vandium.

Application of Electrometric Method to the Determination of "Blanks."

In their paper Bartlett and Forbes[2] show the magnitude of the errors inherent in the use of an outside indicator when titrating with dichromate. They were enabled to do this by simultaneously studying the titration electrometrically and also with the outside indicator. In similar manner much information may be gained by electrometrically studying such reactions as permanganate titrations. Fig. 15 shows curves obtained when titrating ferrous iron with permanganate under different conditions

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[1] A small amount (1 cc.) of saturated alum solution is added before precipitation in order to ensure complete separation of the ferric hydroxide.

[2] This Journal, **35**, 1527 (1913).

of acidity, and different concentrations of ferric iron, which are somewhat representative of conditions frequently met in actual practice. Curve 1, where 2.87 mg. of ferrous iron was titrated with 0.01 *N* potassium permanganate in 17% conc. sulfuric acid shows the development of the pink end-point at the exact point of inflection. The presence of 28.7 mg. of ferric iron (as sulfate) in a similar solution containing 8% conc. sulfuric acid masked the pink color of the end-point to such an extent that the color change did not take place until after the point of inflection was passed by 0.35 cc.; which, therefore, represents the "blank" for these conditions (Curve 2). The titration of the same amount of ferrous iron in the presence of 57.3 mg. ferric iron in phosphoric acid (2.5% by volume of the 85% acid) was free from blank (Curve 3) even though the amount of ferric iron was double that present in the previous titration represented in Curve 2. Adding 5% conc. sulfuric acid to the phosphoric acid solution gave a blank of 0.07 cc. potassium permanganate (Curve 4) with other conditions, such as ferric iron content, identical. Curve 5 represents the titration of 2.87 mg. ferrous iron in the presence of 250 mg. ferric iron, added as chloride, and 6% of titrating mixture.[1] The blank was greatly increased here—amounting to about 0.50 cc., which was changed but slightly by the addition of 0.5% conc. hydrochloric acid. Other data on these titrations are presented in Table V.

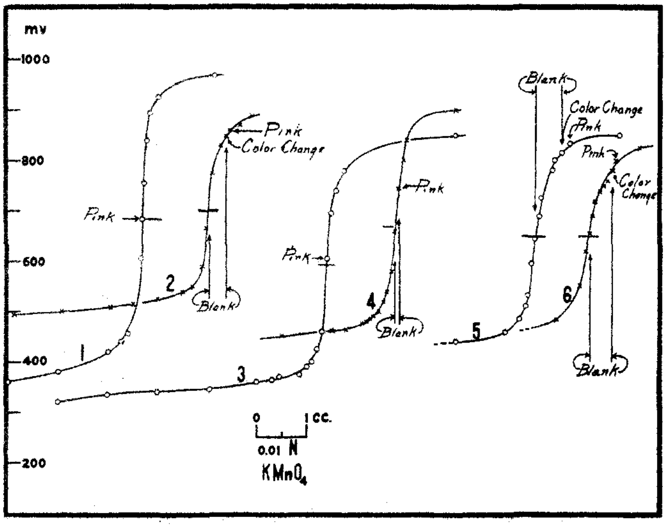

Fig. 15.—Electrometric titrations of ferrous iron with 0.01 *N* permanganate solution. The volume of permanganate solution required to give a color end-point after the point of inflection has been passed represents the "blank" for those particular conditions.

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[1] Bur. Standards, *Circ.* 26 (2nd Ed.), 11 (1911).

TABLE V.—ELECTROMETRIC TITRATIONS WITH 0.01 N PERMANGANATE.
(Ferrous Iron = 2.87 Mg.)

Curve No. (Fig. 14.)	Total volume. Cc.	Ferric iron added. Mg.	Acidity conditions.	"Blank" 0.1 N $KMnO_4$. Cc.
1	150	0.0	17% sulfuric (conc.)	0.0
2	200	28.7	10% sulfuric (conc.)	0.35
3	200	57.3	2.5% phosphoric (85%)	0.0
4	200	57.3	2.5% phosphoric (85%) and 5.0% sulfuric (conc.)	0.07
5	215	250	6% titrating mixture. Ferric iron added as chloride	0.50
6	220	250	6% titrating mixture. 0.5% hydrochloric (conc.). Ferric iron added as chloride.	0.45

Summary.

The advantages of the electrometric method for oxidizing and reducing reactions may be summarized as follows:

1. This method permits the use of potassium dichromate with its numerous advantages.

2. The reduction of the solution with electrometric control eliminates the removal of excess reducing agent which must be done with the usual methods of reduction.

3. Conditions, such as acidity, need not be controlled except within very wide limits, and hydrochloric, sulfuric or hydrofluoric acid, or mixtures of these, may all be used. In contrast to these wide limits, note the narrow acid limits (1.5 to 2.5% by volume of sulfuric acid) within which the reduction with sulfur dioxide or hydrogen sulfide must be carried out[1] and the precautions which must be taken in a permanganate titration in the presence of either chlorides or fluorides.

4. The sensitivity and accuracy of the method make possible (*a*) the determination of a few tenths of a milligram of tin, chromium, ferrous or ferric iron, and probably many other elements, in the presence of large quantities of some other element, and (*b*) the determination of blanks involved in some of the ordinary determinations by reducing or oxidizing agents.

5. The time within which a determination can be carried out is greatly shortened. The content of ferrous and ferric iron in a silicate, for instance, can be determined in from 15 to 30 minutes.

6. The precision attainable is comparable to the best of the ordinary volumetric determinations.

WASHINGTON, D. C.

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[1] W. F. Hillebrand, "Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* 422. See page 107 for reference to H_2S; work of R. S. McBride on SO_2 quoted in footnote on page 108.