Applying a correction of 0.3 calorie per gram, the final value for the isothermal heat of solution of calcium oxide in $HCl·200H_2O$ at 20° becomes 828.9 calories per gram (mean calorie 16 to 20°). This is equivalent to 194.4 kj. or 46.50 $cal.^{20°}$ per mole.

The samples of calcium oxide used in Expts. 9 and 10 were heated at 1200° for three hours after being brought to constant weight in the usual way at 800 to 900°. In another case a sample was heated at 1200° for twenty-four hours without giving an appreciable change in the heat of solution. The results indicate that the heat of solution is not materially affected by the temperature of ignition between the limits 800 and 1200°.

Summary

The heat of solution of calcium oxide in $HCl·200H_2O$ at 20° was found to be 194.4 kilojoules or 46.50 $cal.^{20°}$ per mole. The heat of solution was found not to be materially affected by the temperature of ignition between 800 and 1200°.

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THE IODOMETRIC DETERMINATION OF IRON

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Introduction

In the course of an investigation the demand arose for a rapid, fairly accurate method of determining iron in a precipitate of ferric hydroxide. A review of the various volumetric processes for determining iron was therefore made. Oxidation methods, using standard permanganate or dichromate solutions, involve the preliminary reduction of the ferric solution. In the reduction methods solutions of stannous chloride or of a titanous salt are commonly used, but both of these solutions are so unstable as to require frequent standardization or elaborate precautions in storage. The use of sodium thiosulfate for the direct titration of a ferric salt has been investigated,[1] but the conditions under which accurate results can be obtained are apparently very strictly limited.[2] An iodometric method, in which iodide is added to a ferric salt solution and the liberated iodine titrated with thiosulfate, was originally proposed by Mohr.[3]

The iodometric method appeared to offer great advantages, provided a simple process giving exact results could be found. However, experiments

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[1] Kremer, *J. prakt. Chem.*, **84**, 339 (1861).

[2] Norton, *Am. J. Sci.*, **18**, 25 (1899).

[3] Mohr, *Ann. Chem. Pharm.*, **105**, 53 (1858).

by procedures found in standard texts were unsatisfactory, and statements at variance with these procedures were found in the literature. Thus Treadwell-Hall[4] directs that "the greater part of the acid" be neutralized, that five grams of potassium iodide be used, that the air in the flask be removed by carbon dioxide and finally that the reaction be allowed to proceed for twenty minutes. Sutton[5] "nearly neutralizes" the acid, adds "an excess of strong solution of potassium iodide" and heats in a closed flask at 50–60° for about twenty minutes before cooling and titrating. Joseph[6] states that "fair accuracy" can be obtained without taking "any special precautions" if to the ferric solution acidified with hydrochloric acid, "whose amount does not seem to be of any great importance" is added a few grams of potassium iodide and the iodine liberated is titrated "at once." His duplicate analyses show variations as great as 2%. Kolthoff[7] found that accurate results were obtained upon adding 1.5 g. of potassium iodide to 10 ml. of ferric chloride solution which contained 2.5 millimoles of iron and which was 0.1 molal in hydrochloric acid, and then allowing this to stand for five minutes and titrating. The same author also states that more concentrated hydrochloric acid seemed to retard the reaction as well as to cause considerable air oxidation. Kurt Böttger and Wilhelm Böttger[8] carried out a series of experiments in which to 20 ml. of a solution 0.1 molal in sulfuric acid and containing 1.6 millimoles of ferric sulfate they added 10 ml. of a 15% hydrochloric acid solution and allowed this solution to react with 3–4 g. of potassium iodide in a total volume of about 60 ml. for various lengths of time up to one hour. These experiments gave results from 1–2% high. A corresponding series of experiments in which oxygen of the air was eliminated gave correct results. They did not mention the work of Kolthoff. Very recently Grey[9] has studied this method and states: "Numerous experiments have shown that 5.5 moles of potassium iodide are required per atom of iron, and the concentration in the titrated liquid should be adjusted to about $M/7.5$, and the acid concentration should be $N/3$–$3N$. In such a case the liberation of iodine will be strictly proportional to the iron present, within the limits 0.056–56 mg. of iron in 10–50 cc. of liquid." The experimental results are not shown. It is further stated that "the solution after titration by thiosulfate may be shaken violently with air for two hours without any return of the blue color, even when the acidity is that of N hydrochloric acid." This is surprising in view of the observed air

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[4] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, **1928**, Vol. II, 7th ed., p. 577.

[5] Sutton, "Volumetric Analysis," 11th ed., **1924**, p. 743.

[6] Joseph, *J. Soc. Chem. Ind.*, **29**, 187 (1910).

[7] Kolthoff, *Pharm. Weekblad.*, **58**, 1510 (1921).

[8] Böttger and Böttger, *Z. anal. Chem.*, **70**, 214 (1927).

[9] Grey, *J. Chem. Soc.*, 35–39 (1929).

oxidation of iodide in acid solutions which have been reported by others;[10] likewise the possibility that such oxidation may occur previous to the thiosulfate titration is apparently not considered.

Approximate calculations of the equilibrium which should be attained when a ferric salt and iodide react have been made by Böttger and Böttger[8] and by Fales.[11] These calculations indicate that with an excess of iodide, and especially upon reduction of the liberated iodine with thiosulfate, the reaction should be complete within the usual limits of error of volumetric work. Studies of the rate of the reaction between ferric salts and iodide have been made by Schukarew,[12] by Brönsted and Pedersen,[13] by Sasaki,[14] and by Wagner;[15] while the reverse reaction, the oxidation of a ferrous salt by iodine, has been investigated by Banerji and Dhar.[16] Although these investigations were principally concerned with the mechanism of the reactions involved, the results of the rate measurements would seem to indicate difficulty in forcing the reaction to completion within a short time.

In view of this situation, a study of the method was undertaken, especially as to the effect of the acid concentration upon the reaction between the iodide and the ferric salt, as to the amount of "oxygen error" occurring when the titration is carried out in air under various conditions and as to the amount of potassium iodide necessary.[17]

Preparation of the Solutions.—An approximately 0.1 molal solution of ferric chloride was prepared by dissolving an "Analyzed" brand of $FeCl_3 \cdot 6H_2O$ in approximately 0.1 molal hydrochloric acid. Tests for ferrous salt with potassium ferricyanide solution gave negative results. This solution was standardized as to iron content by two different methods. The first three values given below were obtained using the Zimmermann-Reinhardt method; the other values by displacing the chloride in the solution with sulfuric acid, reducing the ferric sulfate with aluminum and titrating the reduced solution with permanganate. An atmosphere of carbon dioxide was maintained during

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[10] (a) Bray and Miller, THIS JOURNAL, **46**, 2204 (1924); (b) Popoff and Whitmore, *ibid.*, **47**, 2259 (1925); (c) Böttger and Böttger, *Z. anal. Chem.*, **70**, 209 (1927).

[11] Fales, "Inorganic Qualitative Analysis," The Century Co., New York, **1925**, p. 291.

[12] Schukarew, *Z. physik. Chem.*, **38**, 353 (1901).

[13] Brönsted and Pedersen, *ibid.*, **103**, 307 (1922).

[14] Sasaki, *Z. anorg. Chem.*, **137**, 181–203, 291–327 (1924).

[15] Wagner, *Z. physik. Chem.*, **113**, 261 (1924).

[16] Banerji and Dhar, *Z. anorg. allgem. Chem.*, **134**, 178 (1924).

[17] A preliminary investigation of this method was made by Mr. Willard A. Findlay. The detailed experimental study was carried out as a group problem by the honor students of a class in quantitative analysis. Experiments numbered 1, 2, 3, 4 and 5 of Table I were performed by S. C. Dorman, R. P. Coleman, R. E. Morris, W. A. Findlay, and J. B. Hatcher, respectively. Experiments 1, 2, 3, 4 and 5 of Table II were carried out by L. E. Kinsler, T. R. White, W. F. Eberz, C. H. Gregory, and G. M. Webb, respectively. The results shown are representative of a larger number of experiments than those actually recorded.

the reduction and titration. The permanganate solution had been standardized against sodium oxalate obtained from the Bureau of Standards. The results of the standardizations of the ferric chloride solution in millimoles per liter were as follows: 99.15, 99.18, 99.15, 98.91, 98.99, 98.91, 99.24, 99.14, 98.95; mean, 99.07.

The sodium thiosulfate solution used was standardized against the same permanganate solution under the conditions recommended by Bray and Miller.[18] Referring the thiosulfate and ferric chloride solutions to the same permanganate solution eliminated the need of knowing the exact absolute value of the permanganate.

Effect of Hydrochloric Acid and of Air.—In order to test the effect of the hydrochloric acid concentration and also the effect of the presence of the oxygen of the air, experiments were carried out as follows: 25-ml. portions of the ferric chloride solution were pipetted into a 250-ml. glass-stoppered conical flask; the amount of hydrochloric acid present was then adjusted to the value shown in the second column of Table I, 3.0 g. of solid potassium iodide was introduced, the solution mixed and the reaction mixture allowed to stand for five minutes in the stoppered flask. The volume of the solution was approximately 30 ml. This solution was then diluted to approximately 100 ml. and immediately titrated with the standard sodium thiosulfate solution, the usual starch indicator being used.

The results are given in Table I. The third column shows the volume of thiosulfate used when this first end-point was obtained. The time

TABLE I

EFFECT OF HYDROCHLORIC ACID IN THE PRESENCE OF AIR

Expt.	Milli-equiv. of HCl present	1st end-point	Ml. of thiosulfate[b] after five minutes	After ten minutes	Expt.	Milli-equiv. of HCl present	1st end-point	Ml. of thiosulfate[b] after five minutes	After ten minutes
4	[a]	25.01	25.15		1	24	25.37		
2	0.25	25.33			2	24	25.39		
3	0.25	25.30			3	24	25.37		
5	0.25	25.35			4	24	25.36		
	Av.	25.33			5	24	25.40		
1	2.5	25.31	25.32			Av.	25.38		
1	6.0	25.38			1	48	25.38	25.39	25.40
2	6.0	25.31			2	48	25.36	25.37	
3	6.0	25.34			3	48	25.37		
4	6.0	25.31	25.32		4	48	25.40		25.42
5	6.0	25.36			5	48	25.32		25.46
	Av.	25.34	25.34			Av.	25.37	25.37	25.40
1	12	25.34	25.35	25.36	1	96	25.52	25.56	
2	12	25.31			2	96	25.46		
3	12	25.35			3	96	25.40	25.45	
4	12	25.35			4	96	25.43		25.45
5	12	25.38			5	96	25.32	25.44	25.45
	Av.	25.35	25.35	25.36		Av.	25.43	25.47	25.47

[a] Neutralized almost to precipitation.

[b] Where volumes and averages are omitted they are the same as in the preceding column.

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[18] Bray and Miller, THIS JOURNAL, **46,** 2204 (1924).

required for this titration varied from five to ten minutes. To test the stability of this end-point, the solutions were in all cases allowed to stand for two five-minute intervals in the stoppered flask, and if any further iodine color developed it was titrated. The fourth and fifth columns show the total volume of thiosulfate used when more was required. Weight burets or calibrated volume burets were used in making the titrations. The calculated volume of thiosulfate was 25.33 ml.

In the experiments in which the air was excluded the ferric chloride solution was brought just to boiling for three minutes and then cooled while a rapid stream of carbon dioxide gas was passed above the solution. The potassium iodide was then introduced and the solution allowed to stand for five minutes under a slight pressure, but no appreciable flow, of the carbon dioxide. The solution was then diluted to 100 ml. with water that had been saturated by passing a vigorous stream of carbon dioxide through it and then was titrated. The results of these experiments are shown in Table II. Although the solutions were allowed to stand for two five-minute intervals after obtaining the first end-point, in no case did further iodine color develop after the first five-minute interval. The calculated volume of thiosulfate was 25.33.

TABLE II

EFFECT OF HYDROCHLORIC ACID IN THE PRESENCE OF CARBON DIOXIDE

Expt.	Milli-equiv. of HCl present	1st end-point	Ml. of thiosulfate[b] after five minutes	Expt.	Milli-equiv. of HCl present	1st end-point	Ml. of thiosulfate[b] after five minutes
1	[a]	25.03		1	24	25.33	
2		25.18	25.21	2	24	25.10	25.29
3		25.29		3	24	25.37	
4		24.55	24.74	4	24	25.29	25.34
5		25.25		5	24	25.26	25.33
	Av.	25.06	25.10		Av.	25.27	25.33
1	6	25.39		1	48	25.32	
2	6	25.21	25.22	2	48	25.19	25.30
3	6	25.26		3	48	25.34	
4	6	25.34		4	48	25.31	25.35
5	6	25.31		5	48	25.27	25.34
	Av.	25.30	25.30		Av.	25.28	25.33
1	12	25.39		1	96	25.30	25.32
2	12	25.25	25.38	2	96	25.15	25.29
3	12	25.37		3	96	25.30	25.34
4	12	25.35		4	96	25.28	25.34
5	12	25.33		5	96	25.27	25.33
	Av.	25.34	25.36		Av.	25.26	25.32

[a] Neutralized almost to precipitation.

[b] Where volumes and averages are omitted they are the same as in the preceding column.

Effect of the Iodide Concentration.—To determine the effect of varying the potassium iodide used, experiments were carried out by Mr. Willard A. Findlay in air and with conditions similar to those in Table I, using 12 milli-equivalents of hydrochloric acid and the amount of potassium iodide indicated in the first column of Table III. The calculated volume of thiosulfate was 34.68 ml.

TABLE III

EFFECT OF EXCESS OF IODIDE WHEN USING HYDROCHLORIC ACID

KI used, g.	1st end-point	Ml. of thiosulfate after five minutes	After ten minutes
1.0	33.95	34.22	34.40
2.0	34.5	34.58	34.58
3.0	34.67	34.67	34.67
5.0	34.67	34.67	34.67

Effect of the Presence of Sulfuric Acid and of the Iodide Concentration.—A brief study was made by Mr. W. A. Findlay of the reaction between iodide and ferric sulfate in sulfuric acid solution. An approximately 0.1 molal ferric sulfate solution which was 0.25 molal in sulfuric acid was used. The procedure was the same as with the hydrochloric acid solutions in the presence of air with the exception that 4 g. of potassium iodide was added. The effect of the amount of sulfuric acid present is shown in Table IV. The calculated volume of thiosulfate was 29.31 ml.

TABLE IV

EFFECT OF SULFURIC ACID IN THE PRESENCE OF AIR

H_2SO_4 present, milli-equivalents	1st end-point	Ml. of thiosulfate after five minutes	After ten minutes
Neutralized	27.35	27.72	27.77
6	29.12	29.19	29.25
12	29.29	29.34	29.37
18	29.28	29.29	29.29
18	29.32	29.34	29.34
18	29.27	29.30	29.32
24	29.37	29.37	29.39
30	29.39	29.39	29.42
72	29.49	29.49	29.51

The experiments shown in Table V were made to show the effect of the excess of iodide present when using sulfuric acid. The procedure was the

TABLE V

EFFECT OF EXCESS OF IODIDE WHEN USING SULFURIC ACID

KI used, g.	1st end-point	Ml. of thiosulfate after five minutes	After ten minutes
0.5	13	14	15
1.0	22.6	23.5	24.0
2.0	28.80	28.92	29.30
3.0	29.18	29.26	29.26
4.0	29.28	29.29	29.29
8.0	29.36	29.36	29.37

same as that above, 18 milli-equivalents of sulfuric acid being present. The calculated volume of thiosulfate was 29.31 ml.

Discussion of the Results

The experiments given in Table I, which were carried out in the presence of air, show that under the conditions of the procedure used permanent end-points and results consistent to 0.2% can be obtained when there are present 0.25 to 12 milli-equivalents of hydrochloric acid in 30 ml. of solution. If the solution is nearly neutralized unstable end-points and low results are obtained. This is to be expected because of the hydrolysis of the ferric chloride under these conditions. With more than 24 milli-equivalents of hydrochloric acid the "oxygen error" becomes pronounced, as shown by the unstable end-points and high results. The experiments given in Table II, carried out under carbon dioxide, show that the accuracy obtained in the presence of air when less than 12 milli-equivalents of acid was present is at least partly due to compensating errors, namely, to a negative error, probably caused by insufficient acid to prevent hydrolysis of the ferric chloride, and a positive "oxygen error." When 12 milli-equivalents of hydrochloric acid are present during this reaction between iodide and ferric chloride, or the acid is approximately 0.5 molal, the values obtained in carbon dioxide reach a maximum. The decrease observed in the values for the first end-point as the acid is increased above 12 milli-equivalents, while possibly a rate effect, is in accord with the decrease in the potential of the ferric-ferrous electrode which has been observed by Carter and Clews[19] and by Popoff and Kunz,[20] as the hydrochloric acid in the solution is increased. This effect is attributed by these authors to complex formation between the hydrochloric acid and the ferric chloride. When air is present this effect is overcome by a greater oxygen error. It is indicated that the oxygen error is at a minimum when the hydrochloric acid concentration is most favorable for the reaction between the ferric chloride and iodide. The experiments given in Table III show that 3 g. of potassium iodide is the minimum amount permissible under the conditions of these experiments. The experiments of Tables IV and V indicate that the effect of sulfuric acid is to increase the amount of acid and of iodide necessary and to make the end-point less stable. The above results are confirmatory of the experiments and conclusions of Kolthoff.[7]

Test Analyses

In order to test this method the following analyses were carried out by Mr. C. H. Gregory. A sample containing 2.3667 g. of "Sibley" Iron Ore, Standard Sample No. 27 of the Bureau of Standards and containing ac-

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[19] Carter and Clews, *J. Chem. Soc.*, **125**, 1880 (1924).

[20] Popoff and Kunz, This Journal, **51**, 382 (1929).

cording to the average of the Bureau of Standards determinations 69.26% iron, was weighed out. This was treated with hydrochloric acid and the insoluble residue was filtered out and treated with hydrofluoric acid in a platinum crucible; the hydrofluoric acid was expelled by adding sulfuric acid and evaporating this just to dryness. The residue remaining was dissolved in hydrochloric acid and added to the first solution. Dilute permanganate solution was added to this cold solution until the first perceptible pink color was noted and the solution then evaporated until the volume was about 5 ml. Five ml. of 6 molal hydrochloric acid was then added, the solution diluted to 250 ml. in a weighed flask and the flask and solution weighed. Two approximately 25-ml. portions of this solution were then weighed into conical flasks and treated by the same procedure as was used in obtaining the results shown in Table I. Two other samples were then treated by the same procedure, except that the air was displaced by carbon dioxide in the manner previously described. Weight burets were used in the titrations. The results of these analyses are shown in Table VI.

TABLE VI

ANALYSIS OF IRON ORE NO. 27 OF THE BUREAU OF STANDARDS

Method	Air not removed	Air not removed	Under CO_2	Under CO_2
Fe found, %	69.23	69.19	69.16	69.16
Fe present, %	69.26	69.26	69.26	69.26

Summary

The conditions determining the reliability of the simple iodometric determination of ferric iron originally suggested by Mohr have been studied. Experiments have been described which show that an accuracy of 0.2% is obtained when the reaction between the ferric chloride and iodide is allowed to take place in a closed flask for five minutes in about 30 ml. of a solution which contains 3 g. of potassium iodide and from 0.25 to 25 milli-equivalents of hydrochloric acid, and this solution is then diluted to approximately 100 ml. and titrated with thiosulfate. Permanent end-points are obtained under these conditions. The accuracy of this procedure has also been confirmed by test analyses.

Experiments carried out under carbon dioxide show that this accuracy is in most cases partly the result of compensating errors—an incomplete reaction and an "oxygen error."

When sulfuric acid is used more acid is required, a higher concentration of iodide is necessary and the end-points are not as permanent.

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