low temperature specific heat measurements, extrapolated from room temperature with aid of the best available heat data, give a constant more than 100 times this value. Christiansen's indirect equilibrium measurements give a constant about 34% smaller than our value.

3. The equation for the standard free-energy change in the methanol reaction, derived from our equilibrium measurements and the best available heat data, is $\Delta F = -20{,}857 + 41.17T \log T - 0.01423T^2 - 54.42T$.

4. The yields of methanol at high pressures, as obtained practically and as predicted by our thermodynamic data, compare favorably.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. VIII. THE DETERMINATION OF CHROMIUM IN THE PRESENCE OF MANGANESE, IRON AND VANADIUM

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Introduction

The present volumetric methods for chromium depend upon its oxidation to the hexavalent form by an excess of some suitable reagent and its subsequent reduction, after removal of the excess oxidizing agent, by standard ferrous sulfate added either (1) directly to an end-point which may be determined either electrometrically, with diphenylamine or diphenylbenzidine[1] as internal indicator, or with ferricyanide as external indicator, or (2) in excess, the excess being determined by back titration with standard dichromate or permanganate. In the absence of oxidizing agents such as ferric iron, excess iodide may be used as the reducing agent, the iodine liberated being titrated with thiosulfate. A method using arsenite[2] and another with excess arsenite, followed by back titration with bromate have been described.[3] If persulfate in the presence of silver ions[4] is employed to oxidize the chromium, the excess is destroyed by boiling, and moderate amounts of manganese, converted into permanganate, are reduced to manganous salt by the addition of chloride ions and further boiling. If permanganate is the oxidizing agent, a filtration is always required. In certain cases oxidation is effected by per-

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[1] The authors have described the use of diphenylbenzidine as an indicator in the titration of chromic plus vanadic acids with ferrous sulfate, Willard and Young, *Ind. Eng. Chem.*, **20**, 769 (1928). The results using this indicator are the same when chromic acid alone is titrated with ferrous sulfate.

[2] Zintl and Zaimis, *Z. angew. Chem.*, **40**, 1286 (1927); **41**, 543 (1928).

[3] Spitalsky, *Z. anorg. Chem.*, **69**, 179 (1910).

[4] Kelley and Conant, *J. Ind. Eng. Chem.*, **8**, 719 (1916).

oxide in alkaline solution.[5] Thus it is seen that all of the methods in use require considerable time to remove the excess of oxidizing agent, and the presence of manganese always lengthens the time for an analysis.

A more rapid volumetric method for chromium, and one in which large amounts of manganese cause no interference or delay, is, therefore, highly desirable. The present paper describes such a method in three different modifications: in one case the chromium is oxidized by a measured excess of standard ceric sulfate, the excess being titrated differentially in the presence of chromic acid with standard sodium nitrite or oxalate; in the second method the chromium is oxidized by excess ceric sulfate, nitrite added in slight excess to destroy the ceric salt, then urea to remove all nitrite, after which the chromic acid is titrated with standard ferrous sulfate; in the third method the chromium is oxidized by excess ceric sulfate, sodium azide added in excess to destroy the ceric salt and the chromic acid titrated with standard ferrous sulfate. In all three procedures iron may be present and also vanadium. With the latter element the sum of chromium and vanadium is determined, but it is possible to obtain the percentage of vanadium later with the same solution.

Experimental

In the experimental work chromium was used in the form of a potassium chrome alum solution standardized by the persulfate method, vanadium as vanadyl sulfate and manganese as manganese sulfate. The ceric sulfate solution was that prepared for earlier work[6] and was 0.5 M in sulfuric acid. It was standardized against sodium oxalate.[6] The sodium nitrite,[7] ferrous sulfate[6] and vanadyl sulfate[8] solutions were standardized against ceric sulfate of known strength.

Preliminary experiments showed that the direct titration of chromic salt in hot solution with ceric sulfate was not possible although the oxidation is more rapid than with any other oxidizing agent. With an excess of ceric salt the oxidation of chromium was very rapid in hot solution. Before this reaction could be studied, a method for removing the excess of ceric salt had to be devised.

A number of reducing agents were tested for their differential possibilities by titrating with them 200 cc. of solution containing 20 cc. of 0.1 N ceric sulfate, 100 mg. of chromium as potassium dichromate, 0–40 mg. of

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[5] The methods mentioned for which references have not been given are described in any of the standard reference texts on Analytical Chemistry or in special texts devoted to Steel Analysis.

[6] Willard and Young, This Journal, **50**, 1322 (1928); also Furman, *ibid.*, **50**, 755 (1928).

[7] Willard and Young, This Journal, **50**, 1379 (1928).

[8] Furman, This Journal, **50**, 1675 (1928); Willard and Young, *Ind. Eng. Chem.*, **20**, 972 (1928).

vanadium as ammonium vanadate and varying amounts of acid. Using sodium nitrite[7] the reduction of ceric sulfate was selective in the presence of 5–10 cc. of concd. nitric, sulfuric or perchloric acid. The temperature of the solution during titration was held between 50 and 60°. The reaction at the end-point was a little slow but satisfactory and the break in potential averaged 150–200 mv. per 0.05 cc. of 0.1 *N* sodium nitrite. Using sodium oxalate the reduction was selective with 2–5 cc. of concd. sulfuric acid or 5–20 cc. of concd. nitric or perchloric acid per 200 cc. The temperature during titration was 70–80°, the reaction at the end-point about as rapid as with nitrite and the break in potential from 100–150 mv. per 0.05 cc. of 0.1 *N* oxalate. Experiments using either hydrogen peroxide or ferrous sulfate as the reducing agent were not successful.

Oxidation of Chromium with Ceric Salt

A. Use of Standard Ceric Sulfate and Titration of the Excess with Standard Sodium Nitrite.—To measured portions of a standard solution of potassium chrome alum were added the indicated volumes of acid and standard ceric sulfate. The volume of the solution at the time of oxidation and the temperature maintained during the oxidation process are shown in Table I. After the oxidation the solution was diluted to 200 cc. and the excess ceric sulfate titrated electrometrically at 50–60° with standard sodium nitrite added from a buret with the tip beneath the surface of the liquid.

TABLE I

OXIDATION WITH EXCESS STANDARD CERIC SULFATE. TITRATION OF EXCESS WITH NITRITE

	Acid, cc.	Vol. at time of oxidation	$Ce(SO_4)_2$, 0.1 *N*, cc.	Temp. for oxidation, °C.	Cr. taken, g.	Cr found, g.
	5	100	40	65 for 5 min.	0.04557	0.04556
	5	100	30	65 for 5 min.	.04557	.04525
HNO_3	5	100	30	65 for 20 min.	.04557	.04556
sp. gr.	5	100	40	65[a]	.04557	.04554
1.42	5	200	40	65 for 5 min.	.04557	.04561
	10	200	40	65 for 5 min.	.04557	.04561
	5	150	75	65 for 5 min.	.09114	.09108
	10	75	40	65 for 5 min.	.04557	.04355
H_2SO_4,	10	75	40	100[b]	.04557	.04554
sp. gr.	10	75	30	100[b]	.04557	.04487
1.5	10	75	30	100 for 5 min.	.04557	.04562
	20	100	40	100[b]	.04557	.04552
$HClO_4$,	5	100	40	100[b]	.04557	.04562
70%	5	100	40	65[a]	.04557	.04556

[a] Solution heated to 65° and titrated at once.

[b] Solution heated to 100° and titrated at once.

Forty cc. of ceric sulfate for 45–46 mg. of chromium represents 12 cc. excess of oxidizing agent. The first four experiments show that the rate of oxidation of the chromium increases with the volume of ceric salt used. It is also seen that the oxidation proceeds more quickly in nitric or perchloric acid than in sulfuric acid solution. Variations in acid, volume of solution at time of oxidation and amount of chromium did not alter the accuracy of the method. Other experiments in which as much as 2 g. of iron or 24 mg. of vanadium or both were added were entirely satisfactory. In the presence of iron the reaction with nitrite was somewhat slower, although not more than ten to fifteen minutes was required for a titration and the break in potential was smaller, while in the presence of vanadium the ceric salt used for the oxidation gave accurately the vanadium plus chromium content of the solution. In all later experiments the procedure of oxidizing the chromium with the ceric salt in a volume of 150 cc. by heating to 100° was adopted. If there was no nitric acid present, the solution was allowed to stand for three to five minutes before diluting it to 300 cc. and titrating with nitrite (this dilution gave the correct temperature for the nitrite titration). Such a procedure for chromium is obviously much more rapid than any in use at the present time.

Stability of Nitrite Solution

The supply of 0.1 N sodium nitrite which was used over a period of five weeks remained constant in normality within less than one part in a thousand, even though the stock bottle was opened a number of times during this interval and no precautions were taken to exclude air. Thus nitrite has a decided advantage in this respect over a number of reducing agents.

B. Use of Standard Ceric Sulfate and Titration of the Excess with Standard Sodium Oxalate.—Solutions in which the oxidation of the chromium was carried out exactly as indicated in Table I were titrated electrometrically at 70–80° with standard sodium oxalate. These titrations were slightly more rapid than the nitrite reaction provided that iron was absent. Satisfactory results were obtained in the presence of as much as 1 g. of iron but with larger amounts the nitrite titration is to be preferred. Since sodium nitrite solution, however, is more stable than oxalate, it was used in the greater part of the later work.

C. Use of Ceric Sulfate, Removal of the Excess with Nitrite Followed by Urea and Titration of Chromic Acid with Standard Ferrous Sulfate.—Acid solutions of chromic salt similar to those described in Table I were prepared and the chromium oxidized in hot solution with an excess of ceric salt. After cooling to room temperature nitrite was added, from 5 to 15 cc. more than that required to destroy all ceric sulfate, followed at once by urea to remove excess nitrite. After the addition of 25 cc. of sulfuric acid, sp. gr. 1.5, the chromic acid was titrated electrometrically with standard ferrous sulfate. The results for chromium were always low, the error varying from 0.1–1.5 mg. according as 5 to 15 cc. excess of nitrite had been used. It seemed probable, therefore, that quantitative results could be obtained if the volume of nitrite was controlled more accurately. It was found that an excess of 0.25–0.50 cc. gave no trouble and the error with 1.0 cc. was very slight, provided always that any excess of nitrite was removed at once with urea. Results were identical whether the nitrite was added to the solution at room temperature or at 50–60°. In the method finally adopted the chromium was oxidized in hot solution in a volume of 150 cc., the solution diluted to 300 cc., 0.1 *N* sodium nitrite added in rapid drops until the potential indicated that an excess was present, followed at once by 0.2–0.3 g. of urea. After adding sulfuric acid the solution was titrated with standard ferrous sulfate. Results obtained from a number of experiments are given later in Table II.

Effect of the Presence of Manganese. Nitrite Method

Preliminary experiments showed that a manganous salt is oxidized to a considerable extent in acid solution by ceric sulfate with the formation of permanganate, which changes to manganese dioxide if much manganese or nitric acid is present or if the solution is heated. It was also noticed that nitrite is very effective in dissolving manganese dioxide in acid solution. Solutions similar to those used in Table I, containing also varying amounts of manganese, were oxidized in a volume of 150 cc. with ceric salt. During the heating the permanganate color disappeared but a precipitate was not formed unless nitric acid was present, the manganese content high or the chromium content low. It appeared as if some of the manganese was oxidized first by the ceric salt to permanganate, which was effective in oxidizing chromium. The hot solution was diluted to 300 cc. and treated at once with excess nitrite followed by urea, as described in the preceding paragraph. After the addition of sulfuric acid, the chromic acid was titrated electrometrically with 0.1 *N* ferrous sulfate. Forty cc. of 0.1 *N* ceric sulfate, an approximately 10 cc. excess, was used for the oxidation. Results are given in Table II.

In experiments in which a precipitate of manganese dioxide was formed, the nitrite had to be added slowly, drop by drop, especially if a nitric acid solution was used or much iron was present, to avoid an excess of nitrite at any time. The end-point was reached directly after the solution had cleared. If no MnO_2 was present the nitrite could be added in much more rapid drops. The total time required for the determination of chromium by either method was seldom more than twenty minutes. Results were most satisfactory in perchloric and in sulfuric acid solutions, and only slightly less satisfactory in the sulfuric acid solutions containing nitric acid. With nitric acid alone quantitative results were obtained but the reduction of the MnO_2 was quite slow. The experiments also show that

Table II

Oxidation with Ceric Sulfate in the Presence of Manganese and Iron. Removal of Excess Oxidizing Agent with Nitrite Followed by Urea. Titration of Chromic Acid with Standard Ferrous Sulfate

Acid, cc. (H_2SO_4, sp. gr. 1.5)	Fe, g.	Mn, mg.	V, mg.	$NaNO_3$ excess, 0.1 *N*, cc.	Cr taken, g.	Cr found, g.	Remarks
5	0	25	0	1.0	0.05342	0.05333	Slight MnO_2 ppt.
5	0	25	0	2.0	.05342	.05312	Slight MnO_2 ppt.
5	0	25	0	3.0	.05342	.05303	Slight MnO_2 ppt.
2.5	0	25	0	3.0	.05342	.05304	Heavier MnO_2 ppt.
10	0	10	0	1.0	.05342	.05308	No MnO_2 ppt.
10	0	10	0	0.25	.05342	.05335	No MnO_2 ppt.
10	0	100	0	.25	.05342	.05335	Heavy MnO_2 ppt.
10[a]	0	100	0	.25	.10684	.10670	Heavy MnO_2 ppt.
10[b]	0	100	0	.25	.02137	.02132	Heavy MnO_2 ppt.
10	2	25	0	1.0	.05342	.05340	No MnO_2 ppt.
5	2	25	0	1.0	.05342	.05338	No MnO_2 ppt.
5[c,d]	2	25	24	1.0	.05342	.05333	No MnO_2 ppt.
HNO_3, (sp. gr. 1.42)							
5	0	20	0	1.0	.05342	.05332	Heavy MnO_2 ppt.
15	0	10	0	1.0	.05342	.05330	Heavy MnO_2 ppt.
5	0	50	0	1.0	.05342	.05338	Heavy MnO_2 ppt.
5	2	25	0	1.0	.05342	.05349	Slight MnO_2 ppt.
5[c,d]	2	25	24	1.0	.05342	.05368	Slight MnO_2 ppt.
$HClO_4$, 70%							
2.5	0	25	0	1.0	.05342	.05341	Slight MnO_2 ppt.
10	0	25	0	0.25	.05342	.05343	Slight MnO_2 ppt.
10	2	25	0	.25	.05342	.05340	No MnO_2 ppt.
H_2SO_4 (sp. gr., 1.5) + HNO_3 (sp. gr., 1.42); 5 cc. of each acid in the following experiments							
..	0	25	0	0.25	.05342	.05344	Considerable MnO_2 ppt.
..	0	100	0	.25	.05342	.05123	Heavy MnO_2 ppt.
..	0	75	0	1.0	.05342	.05335	Heavy MnO_2 ppt.
..	2	25	0	1.0	.05342	.05335	No MnO_2 ppt.
[a]	2	25	0	1.0	.10684	.10653	No MnO_2 ppt.
[b]	2	25	0	1.0	.02137	.02168	Considerable MnO_2 ppt.
[c,d]	2	25	24	1.0	.05342	.05322	No MnO_2 ppt.

[a] 70 cc. of 0.1 *N* $Ce(SO_4)_2$ used.

[b] 20 cc. of 0.1 *N* $Ce(SO_4)_2$ used.

[c] 50 cc. of 0.1 $Ce(SO_4)_2$ used.

[d] Solution cooled to 5–10° before titration with ferrous sulfate.

the reducing action of the nitrite on the chromic acid becomes evident with a large excess of nitrite or with high acid concentration. It is seen that ferric salts are effective in preventing the formation of MnO_2. One extremely important point is that this procedure for chromium is accurate and simple, even in the presence of as much as 100 mg. of manganese.

Since the action between nitrite and MnO_2 is quite rapid in many instances, the possibility of a direct titration with standard nitrite was investigated. Solutions prepared and oxidized as in Table II were used. Representative results are shown in Table III.

TABLE III

OXIDATION WITH STANDARD CERIC SULFATE IN THE PRESENCE OF MANGANESE AND IRON. DIRECT TITRATION WITH STANDARD NITRITE

Acid cc. (H_2SO_4, sp. gr., 1.5)	Fe, g.	Mn, mg.	V, mg.	Cr taken, g.	Cr found, g.	Remarks
5	0	10	0	0.05342	0.05347	No MnO_2 ppt.
10	0	75	0	.05342	.05364	Considerable MnO_2 ppt.
10	0	100	0	.05342	.05282	Considerable MnO_2 ppt.
10	2	20	0	.05342	.05364	No MnO_2 ppt.
10	1	75	0	.05342	.05367	Heavy MnO_2 ppt.
10[a]	2	20	24	.05342	.05362	No MnO_2 ppt.
(HNO_3, sp. gr., 1.42)						
5	0	20	0	.05342	.05358	Considerable MnO_2 ppt.
5	0	50	0	.05342	.05347	Heavy MnO_2 ppt.
5	0	75	0	.05342	.05081	Heavy MnO_2 ppt.
5	1	50	0	.05342	?	Too slow
5	1	20	0	.05342	.05359	Considerable MnO_2 ppt.
5[a]	1	20	24	.05342	?	Very slow reaction
($HClO_4$, 70%)						
2.5	0	10	0	.05342	.05359	No MnO_2 ppt.
10	0	25	0	.05342	.05367	Heavy MnO_2 ppt.
10	1	20	0	.05342	.05364	Slight MnO_2 ppt.
H_2SO_4 (sp. gr., 1.5) + HNO_3 (sp. gr., 1.42), 5 cc. of each acid in the following experiments						
[b]	0	20	0	.10684	.10699	No MnO_2 ppt.
[c]	0	20	0	.02137	.02147	Considerable MnO_2 ppt.
..	2	20	0	.05342	.05367	No MnO_2 ppt.
..	1	50	0	.05342	.05366	Heavy MnO_2 ppt.
[a]	2	20	24	.05342	.05367	No MnO_2 ppt.

[a] 50 cc. of 0.1 *N* $Ce(SO_4)_2$ used.

[b] 70 cc. of 0.1 *N* $Ce(SO_4)_2$ used.

[c] 20 cc. of 0.1 *N* $Ce(SO_4)_2$ used.

Sulfuric or sulfuric and nitric acid solutions were most satisfactory, nitric acid solutions least so. Perchloric acid solutions were satisfactory in the absence of iron. With no MnO_2 precipitate the reaction between ceric salt and nitrite was rapid; otherwise, the precaution of adding the nitrite quite slowly to avoid any excess during the titration had to be taken. Even then a titration always required less than ten minutes if a sulfuric or sulfuric and nitric acid solution was used.

Effect of the Presence of Manganese. Oxalate Method

It was found that the direct titration of excess ceric sulfate with oxalate in the presence of MnO_2 precipitate after a chromium oxidation was slightly more rapid than the nitrite titration. In the oxalate method results accurate to a few hundredths of a milligram of chromium were always obtained in solutions containing 5–20 cc. of concd. nitric acid, 5–15 cc. of perchloric acid or 2 cc. of concd. sulfuric plus 5 cc. of concd. nitric acid per 200 cc., the titrations being made at 70–80°. In a sulfuric acid solution the reaction was quantitative but much slower, as was to be expected from earlier work.[6] The results were quantitative with as much as 40 mg. of manganese in the nitric acid solutions, or with 50 mg. of manganese in the perchloric or nitric plus sulfuric acid solutions. When the manganese precipitated out during the oxidation process, the oxalate was added in rather slow drops. The results were satisfactory in the presence of 1 g. of iron, but with more iron the titration became very slow.

Sodium Azide Method

Since hydrazoic acid may be determined by oxidation to nitrogen with excess ceric salt,[9] it seemed important to test the differential possibilities of this reagent for reducing ceric sulfate in the presence of chromic acid. In preliminary experiments 25 cc. of 0.1 *N* potassium dichromate was diluted with 10 cc. of sulfuric acid (sp. gr., 1.5) and water to a volume of 300 cc. Five to twenty cc. of 0.1 *M* sodium azide was added and the solution allowed to stand for thirty minutes before titration of the chromic acid with ferrous sulfate. A blank varying from −0.44 to −0.55 cc. was obtained, indicating slight reduction of the chromic acid by the hydrazoic acid. It was thought that some stronger reducing agent in the commercial sodium azide might be causing the trouble, though the blank varied only slightly when the azide content was changed from 5 to 20 cc. One portion of azide solution was purified by acidifying and distilling the hydrazoic acid into sodium hydroxide solution; another portion by acidifying, adding enough dichromate to destroy any stronger reducing agent present and to react with about 10% of the hydrazoic acid and distilling into sodium hydroxide. After adjustment to 0.1 *M*, 20 cc. portions of these two solutions were tested for their action on dichromate, using the procedure described above. The blank in each case was −0.56 cc. Therefore nothing was accomplished by purifying the azide.

Experiments were then made involving the oxidation of a standard chromic salt solution with excess ceric sulfate, addition of excess azide and titration of the chromic acid electrometrically with standard ferrous sulfate. The oxidation procedure already described was used. After oxidation the solution was diluted to 300 cc., cooled to 35–40°, the amount of azide indicated in Table IV added (a solution of the commercial salt was used) and the solution allowed to stand for the given time. Twenty to 25 cc. of sulfuric acid (sp. gr., 1.5) was added and the chromic acid titrated. In the results given under the column "Cr found" in Table IV,

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[9] Martin, This Journal, 49, 2133 (1927).

a correction of +0.2 mg. of chromium has been added in every experiment, as an absolute error of this magnitude was always evident.

TABLE IV

OXIDATION WITH CERIC SULFATE IN THE PRESENCE OF MANGANESE AND IRON. REMOVAL OF EXCESS OXIDIZING AGENT WITH SODIUM AZIDE. TITRATION OF CHROMIC ACID WITH STANDARD FERROUS SULFATE

Acid cc. (H_2SO_4, sp. gr., 1.5)	Fe, g.	Mn, mg.	V, mg.	NaN_3, 0.1 M, cc.	Time azide acted, min.	Cr taken, g.	Cr found, g.	Remarks
5	0	20	0	20	10	0.05369	0.05367	Considerable MnO_2 ppt.
10	0	25	0	20	10	.05369	.05367	No MnO_2 ppt.
20	0	25	0	20	10	.05369	.05364	No MnO_2 ppt.
10	0	25	0	20	5	.05369	.05373	No MnO_2 ppt.
10	0	25	0	30	10	.05369	.05364	No MnO_2 ppt.
10	0	25	0	50	10	.05369	.05345	No MnO_2 ppt.
10	0	25	0	20	60	.05369	.05364	No MnO_2 ppt.
10	0	25	0	20	12 hrs.	.05369	.05292	No MnO_2 ppt.
10	0	25	0	30	60	.05369	.05354	No MnO_2 ppt.
10^a	0	25	0	20	5	.05369	.05364	No MnO_2 ppt.
10^a	0	25	0	20	10	.05369	.05368	No MnO_2 ppt.
10	0	75	0	20	10	.05369	.05370	Considerable MnO_2 ppt.
10	0	100	0	20	10	.05369	.05348	Heavy MnO_2 ppt.
10	2	25	0	20	10	.05369	.05363	No MnO_2 ppt.
$10^{b,e}$	2	25	24	20	30	.05369	.05360	No MnO_2 ppt.
10^c	0	25	0	20	10	.10738	.10712	No MnO_2 ppt.
10^d	0	25	0	20	10	.02147	.02152	Considerable MnO_2 ppt.
(HNO_3, sp. gr., 1.42)								
5	0	25	0	20	10	.05369	.05373	Considerable MnO_2 ppt.
15	0	25	0	20	10	.05369	.05365	Heavy MnO_2 ppt.
5	0	50	0	20	10	.05369	.05365	Heavy MnO_2 ppt.
5	2	25	0	20	10	.05369	.05382	Slight MnO_2 ppt.
$10^{b,e}$	2	25	24	20	30	.05369	.05373	Very slight MnO_2 ppt.
($HClO_4$, 70%)								
5	0	25	0	20	10	.05369	.05365	Considerable MnO_2 ppt.
10	0	25	0	20	10	.05369	.05364	Slight MnO_2 ppt.
10	2	25	0	20	10	.05369	.05369	No MnO_3 ppt.
H_2SO_4 (sp. gr., 1.5) + HNO_3 (sp. gr., 1.42), 5 cc. of each acid in the following experiments								
..	0	50	0	20	10	.05369	.05364	Heavy MnO_2 ppt.
..	0	75	0	20	15	.05369	.05343	Heavy MnO_2 ppt.
..	2	25	0	20	10	.05369	.05365	No MnO_2 ppt.
..	$2^{b,e}$	25	24	20	30	.05369	.05372	No MnO_2 ppt.

[a] NaN_3 added to the solution at 60–65°.

[b] 45 cc. of 0.1 N $Ce(SO_4)_2$ used.

[c] 70 cc. of 0.1 N $Ce(SO_4)_2$ used.

[d] 20 cc. of 0.1 N $Ce(SO_4)_2$ used.

[e] Solution cooled to 5–10° before titration with $FeSO_4$.

The hydrazoic acid acts more slowly on the manganese dioxide than either nitrite or oxalate. Six to eight minutes was always sufficient, however, to dissolve a heavy precipitate. Expts. 10 and 11 indicate that the azide may be added at a higher temperature without causing reduction of the chromic acid. In this warmer solution the effect of the hydrazoic acid may be unpleasant to some persons. If such experiments are conducted in a hood or the solution cooled to 35–40° before the azide is added, the odor of the acid is hardly noticeable. The tendency for the results to be uniformly low by 0.2 mg. of chromium might indicate slight reduction of chromic acid, but the constancy of this error with variation in the amounts of chromium and azide used and in the time the azide acts is difficult to explain. The fact that an error of less than 1 mg. of chromium is caused by leaving the hydrazoic acid in contact with the chromic acid for twelve hours shows that commercial sodium azide is an ideal substance for removing excess of ceric salt after a chromium oxidation. The method is rapid in the presence of large amounts of manganese.

A thermionic voltmeter, Type DP-2, purchased from the General Electric Company was used for the titrations described in this paper The instrument has infinite resistance and can therefore be connected directly to the platinum and silver chloride electrodes throughout a titration without danger of polarization. This makes unnecessary the use of a galvanometer or potentiometer and a continuous reading of the potential is obtained.

Use of Indicator

After the excess of ceric sulfate has been reduced by a very slight excess of nitrite, and the latter destroyed by urea, the chromic acid may be titrated with ferrous sulfate, using about 0.3 cc. of 0.1% diphenylbenzidine or diphenylamine as indicator. Five to 10 cc. of phosphoric acid (85%) must be added and if the solution contains 2 cc. of concd. sulfuric acid in 200 cc. the end-point is sharp and cerous phosphate precipitates so slowly that the solution is hardly opalescent when the titration is finished. If 4 cc. of sulfuric acid is present, the end-point is less distinct but still fairly good. Cerous phosphate does not precipitate at all under these conditions. With more acid the end-point becomes very poor. If too much sulfuric acid is present, a suitable amount of sodium phosphate may be added.

The indicator method has no advantage over the electrometric, because in any case the latter is required to determine the amount of nitrite to be added.

When sodium azide is used to reduce the excess of ceric salt, the color of the indicator is so weakened that a satisfactory titration is impossible.

The application of the methods described above to the rapid determination of chromium in steel will be made the subject of a subsequent paper.

Summary

1. A volumetric method for chromium, more rapid than any in use, has been developed. The chromium is oxidized with excess ceric salt, three possibilities in procedure being described: (*a*) oxidation with a measured excess of standard ceric sulfate, the excess being titrated differentially in the presence of chromic acid with standard sodium nitrite or oxalate; (*b*) oxidation with excess ceric sulfate, addition of nitrite in slight excess to destroy the ceric sulfate, followed by urea to remove all nitrate, after which the chromic acid is titrated with standard ferrous sulfate; (*c*) oxidation with excess ceric sulfate, the excess being removed with sodium azide, and the chromic acid titrated with standard ferrous sulfate. The excess of nitrite must be small and the time of action short, while with azide a large excess acting for a considerable time has no reducing action on the chromium.

2. Iron does not interfere. If vanadium is present, the sum of the chromium and vanadium is determined.

3. The method is equally applicable and rapid in the presence of large amounts of manganese. Even though some of the latter may precipitate as manganese dioxide during the oxidation, it is readily dissolved by the reducing agent.

4. Diphenylbenzidine or diphenylamine may be used as indicator in method (*b*) but not in (*c*).

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. IX. PREPARATION AND STABILITY OF SOLUTIONS

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Introduction

The method used by the authors to purify U. S. P. cerous oxalate and to prepare a large supply of ceric sulfate has been described in the first paper in this series.[1] From subsequent work,[2] especially from that dealing with the determination of vanadium and of chromium, it seemed important to investigate more thoroughly the grades of ceric oxide available in order to find the most convenient and inexpensive materials for use. Information concerning the stability of ceric sulfate solutions has also been obtained.

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[1] Willard and Young, THIS JOURNAL, 50, 1322 (1928).

[2] Willard and Young, *ibid.*, 50, 1334, 1368, 1372, 1379 (1928); 51, 139 (1929); *Ind. Eng. Chem.*, 20, 972 (1928).