2. The general conclusion is that strong electrolytes form undissociated molecules and complex anions; they differ only in degree from such an extreme case as that of cadmium iodide. Electrolytes would all seem to fall within a triangle whose corners represent extreme dissociation, extremely weak electrolytes and complete formation of complex ions, respectively.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. VIII. USE OF METHYL RED, ERIO GLAUCINE AND ERIO GREEN INDICATORS IN THE REACTION BETWEEN CERIC AND FERROUS IONS

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Introduction

A number of applications of ceric sulfate in volumetric analysis have been described recently.[1] The use of various organic substances, for example, methyl red, methylene blue and methyl orange, as irreversible oxidation–reduction indicators in the titration of trivalent antimony with ceric sulfate was proposed by Rathsberg.[2] We have shown that methyl red may be used as an indicator in the titration of hydroquinone with ceric sulfate.[3]

We have found that methyl red is an excellent indicator in the titration of ferrous salt with ceric sulfate or *vice versa*. Upon titration of a ferrous solution with ceric sulfate, the ferrous salt is oxidized first; a slight excess of ceric sulfate oxidizes the methyl red to a substance that is brownish in concentrated solution and yellow in very dilute solution. The oxidation product is destroyed upon standing in contact with an excess of ceric sulfate.

When ceric sulfate is being titrated with ferrous sulfate solution, the latter is added rapidly until the color of the ceric ion has almost disappeared. Methyl red is added, and is oxidized to the yellowish product. Upon further addition of ferrous salt, there is a transition from yellow to violet when a slight excess of ferrous salt is present. If phosphoric acid be added, the color change agrees well with the potentiometric end-point. The color change of methyl red is much more rapid than that of diphenylamine under the same conditions. In agreement with Willard and Young[4]

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[1] A bibliography is given in the preceding paper of this series, THIS JOURNAL, **52**, 1443 (1930); reference to the older literature is given by Willard and Young, *ibid.*, **50**, 1322 (1928), and by Furman, *ibid.*, **50**, 755 (1928).

[2] Rathsberg, *Ber.*, **61**, 1664 (1928).

[3] Furman and Wallace, THIS JOURNAL, **52**, 1443 (1930).

[4] Willard and Young, THIS JOURNAL, **50**, 1336 (1928).

we find that the use of diphenylamine is unreliable in the determination of cerium with ferrous sulfate.

During the progress of our work with methyl red there appeared two publications by Knop[5] in which he suggested the use of two triphenylmethane dyes, erio glaucine and erio green, as reversible oxidation–reduction indicators in the titration of ferrocyanide with permanganate. We have found that these indicators are excellent for certain titrations with, or of, ceric sulfate.

Experimental

Ceric sulfate solutions of approximately 0.1 or 0.05 *N* oxidizing power and 1 *N* in sulfuric acid were prepared from commercial hydrated ceric oxide (45% CeO_2) and were standardized potentiometrically against pure sodium oxalate.[6]

Methyl Red as Indicator.—Two-tenths g. of a Kahlbaum preparation was treated with 100 cc. of 6 *N* sulfuric acid. Nearly all of the material dissolved, and the slight residue was filtered off; 0.05 cc. of the solution is adequate for a titration.

Titration of Ferrous Iron with Ceric Sulfate.—The data are presented in Table I.

TABLE I

TITRATION OF APPROXIMATELY 0.1 *M* MOHR'S SALT SOLUTION WITH 0.1120 *M* CERIC SULFATE

Ferrous soln., cc.	25	25	25	25	50	50	10	10
Initial vol., cc.	50	100	235	50	150	200	50	100
H_2SO_4 concn., *N*	0.3	0.2	0.75	3.6	1.2	1.0	0.6	0.3
Ceric soln. used	22.36	22.38	22.34	22.35	44.64	44.62	8.92	8.93
Ceric soln. calcd.	22.32	22.32	22.32	22.32	44.64	44.64	8.93	8.93

The calculated values are based on the average of four concordant potentiometric determinations. In each case 0.05 cc. of indicator was used. If the solution is stirred vigorously by hand, there is a sharp end-point even when the indicator is added at the start of the titration. It is desirable, however, to add the indicator when the ceric sulfate has begun to be consumed slowly. The determinations of Table I do not show clearly what correction, if any, should be applied when 0.1 *N* solutions are used. From the results with 0.05 *M* solutions it seems safe to apply a correction of 0.03 cc. to be subtracted from the buret reading in the titration of 0.1 *M* solution, this correction being approximately half of that found in Table II.

In Determinations 1–4 the ceric solution was 0.0593 *N*, and in Nos. 5–8, 0.0552 *N*. The calculated values are based on sets of four concordant

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[5] Knop, *Z. anal. Chem.*, **77**, 111 (1929); Knop and Kubelkova, *ibid.*, **77**, 125 (1929).

[6] The details of preparation, standardization and a description of the apparatus are given by Furman and Evans, THIS JOURNAL, **51**, 1129 (1929).

TABLE II

TITRATION OF APPROXIMATELY 0.05 *M* FERROUS SOLUTION WITH 0.05 *M* CERIC SULFATE

	1	2	3	4	5	6	7	8
Initial volume, cc.....	100	110	150	100	35	60	200	125
Initial acid concn., *N*.	0.5	0.7	0.3	0.6	0.2	0.2	0.3	1.2
Acid used...........	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	H_2SO_4	HCl	H_2SO_4
Ceric soln. used, cc....	41.24	41.25	16.48	16.47	8.03	20.01	20.00	39.98
Ceric soln. calcd., cc..	41.20	41.20	16.42	16.42	8.00	19.96	19.96	39.92

potentiometric determinations. On the average 0.05 cc. of ceric sulfate needs to be subtracted from the buret reading in order to make the indicator values coincide with the potentiometric ones. When hydrochloric acid is present, the color change is not as sharp as in sulfuric acid solution, but the change is very distinct.

The methyl red end-point is satisfactory in solutions which have been reduced with stannous chloride in excess, the excess being destroyed with mercuric chloride. A solution of ferric alum in dilute sulfuric acid required per 25 cc.: 21.69, 21.70, 21.68 cc. of 0.0948 *N* ceric solution after stannous chloride reduction, and 21.70, 21.73, 21.71 cc. of the ceric solution after passage of 25-cc. portions through a Jones reductor.

If Mohr's salt is used as a secondary standard, the correction of 0.03 cc. of 0.1 *N* ceric solution brings the methyl red end-point in good agreement with the potentiometric.

Ceric sulfate vs. sodium oxalate, *N*	0.1079	0.1081	0.1080
Mohr's salt used, g.	1.0502	1.3260	1.0072
Ceric solution uncorrected	24.85	31.33	23.82
Normality	0.1077	0.1079	0.1078
Applying 0.03 cc. corr., *N* =	0.1079	0.1080	0.1080

Titration of Ceric Sulfate with Ferrous Sulfate.—The ferrous sulfate is added until the solution is pale yellow (slight excess of ceric ion), 0.05 cc.

TABLE III

TITRATION OF 0.1073 *N* CERIC SULFATE WITH FERROUS SULFATE

Series I

Ceric sulfate used, cc.	25	25	25	10	10	10	Av. per 25 cc.
Ferrous sulfate, cc.							
Methyl red	29.80	29.83	29.79	11.94	11.92	11.91	29.81
Potentiometric	29.87	29.85	29.85	11.96	11.93		29.86
Diphenylamine	29.85	29.89		11.90	11.91		29.81

Series II

Ceric solution used, cc.	25	25	25	25	
Ferrous sulfate, cc.					
Methyl red	30.02	30.04	30.03	30.02	30.03
Potentiometric	30.01	30.05	30.06		30.04
Diphenylamine	30.08	30.07	30.11	30.07	30.08

of methyl red is added, and immediately afterward 25 cc. of the sulfuric–phosphoric acid mixture (150 cc. of each concentrated acid per liter) which is used in Knop's[7] diphenylamine method. The yellow color of the solution becomes much less intense, but no precipitation of cerium phosphates occurs. The ferrous sulfate is added slowly until the solution suddenly becomes pale violet. Upon standing the violet color deepens. Some results are presented in Table III.

Five one-hundredths cc. of methyl red or 0.05 cc. of 1% diphenylamine was used. The behavior of diphenylamine is erratic, and the position of the end-point depends upon the speed of titration at the end-point.

Behavior of Methyl Red on Oxidation and Reduction.—This study is still in a preliminary stage as far as the mechanism of the reaction is concerned. A brief résumé of some qualitative experiments may be of interest. Ceric sulfate appears to be the only oxidizing agent which gives the intermediate oxidation product of methyl red under the conditions used in volumetric analysis. Bromate, permanganate and chlorine carry the oxidation so far that no colored product is formed on reduction with ferrous salt. The violet-colored substance is formed when the reduction is carefully performed with stannous chloride; sulfite, on the other hand, carried the reduction to a colorless stage.

Methyl red shows the same oxidation–reduction behavior after recrystallization from glacial acetic acid, as before purification.

The violet-colored reduction product is extracted from aqueous solution by ether to give an orange-red solution, and by benzene to give a violet-red solution. In the latter solvent methyl red forms an orange or yellow extract, although largely present in the red form in the strongly acid aqueous layer. Thus far it has not been possible to obtain the violet substance in a form pure enough for analysis.

Erio Glaucine and Erio Green Indicators.—Erio Glaucine A (Schulz No. 506) and Alkali Fast (erio) Green A were obtained from the National Aniline and Chemical Company, New York; 0.1% aqueous solutions were prepared, and 0.5 cc. of either solution was used for a single titration. Knop[7] states that the compositions of the rose-colored oxidation products are not known. Either indicator forms a greenish-yellow color in acid solution; in pure water the colors are blue and green, respectively. A very slight excess of ceric sulfate colors either indicator rose or red; in the presence of a ferric salt the color is orange or pale rose. There is a short time interval necessary for the development of the full color change at the end-point; the danger of over-titration is slight. The results are summarized in Table IV.

The determinations were made as closely together as possible, in point of time, with alternation of indicator and potentiometric determinations.

[7] Knop, This Journal, **46**, 263 (1924).

TABLE IV

USE OF ERIO GLAUCINE AND ERIO GREEN IN TITRATION OF FERROUS SULFATE WITH 0.0948 *N* CERIC SULFATE

Erio Glaucine Indicator

Ferrous sulfate, cc.	25	25	25	25	50	50	Av. per 25 cc.
Initial acid concn., *N*	0.7	3.0	0.35	3 *N*	2	2	
Acid	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl	
Initial volume, cc.	25	50	50	50	75	75	
Ceric sulfate, cc.	23.05	23.04	22.99	23.00	45.99	45.98	23.01

Erio Green Indicator

Ferrous sulfate	25	25	25	25	50	50	
Initial acid concn., *N*	0.7	3.0	3.0	0.75	2.0	2.0	
Acid	H_2SO_4	H_2SO_4	HCl	HCl	H_2SO_4	HCl	
Initial volume, cc.	25	50	50	100	75	75	
Ceric solution, cc.	22.98	23.01	23.03	22.98	45.97	45.91	22.98

Potentiometric

Ferric solution, cc.	25	25	25	25	50	50	
Ceric solution used, cc.	22.99	23.03	23.00	23.03	45.98	45.89	22.99

There does not appear to be any correction to be applied in working with 0.1 *N* solutions.

The reverse titration was studied. It was found that either indicator could be added immediately before the start of a titration. The color was initially orange; when nearly all of the ceric ion had been reduced the rose tint predominated. At the end-point there was a sharp transition to yellow with a slight time interval needed for the color change.

TABLE V

TITRATION OF 0.1028 *N* CERIC SULFATE WITH FERROUS SULFATE

Erio Glaucine Indicator

Ceric solution, cc.	10	10	10	25	25	Av. per 25 cc.
Initial H_2SO_4 concn., *N*	1	0.67	0.7	1.4	1	
Initial volume, cc.	40	65	100	60	85	
$FeSO_4$ used, cc.	11.97	12.00	11.98	29.95	29.98	29.96

Erio Green Indicator

Ceric solution, cc.	10	10	10	25	25	
Initial H_2SO_4 concn., *N*	1	0.67	0.7	1.4	1	
Initial volume, cc.	40	65	100	60	85	
$FeSO_4$ used, cc.	11.99	11.96	11.98	29.95	29.95	29.95

Potentiometric

Ceric solution, cc.	10	10	25	25	25	
$FeSO_4$ used, cc.	11.99	11.98	29.99	29.99	29.95	29.98

Within the limits of error of these determinations there appears to be no indicator correction.

It seemed of interest to determine whether the presence of calomel and mercuric chloride would interfere with the functioning of the indicators. A solution of ferric alum, acidified with sulfuric acid, was prepared, and aliquot portions were reduced by the stannous chloride method with subsequent addition of excess of mercuric chloride. Portions of the solution were reduced by the Jones reductor, and an average of 23.09 cc. of 0.0945 *N* ceric sulfate was required per 25 cc. of alum solution.

TABLE VI

TITRATIONS AFTER REDUCTION WITH STANNOUS CHLORIDE

Erio Glaucine Indicator

Alum solution, cc.	25	25	25	10	10
Ceric solution found, cc.	23.05	23.13	23.09	9.23	9.22
Error, cc.	−0.04	+0.04	±0.00	±0.00	−0.01

Erio Green Indicator

Alum solution, cc.	25	25	10	10
Ceric solution found, cc.	23.11	23.08	9.22	9.24
Error, cc.	+0.02	−0.02	−0.01	+0.01

A number of other uses of erio glaucine and erio green in titrations with ceric sulfate are being studied.

Summary

Methyl red in dilute sulfuric acid solution may be used as indicator in the titration of ferrous ion with ceric, or *vice versa*. In the latter case the indicator must be added near the end-point, and phosphoric acid must be present. A correction must be applied in the former titration.

A new behavior of methyl red upon mild oxidation–reduction treatment has been described.

Erio glaucine and erio green are excellent indicators for the titration of ferrous ion with ceric, or *vice versa*. No correction need be applied in either case with a 0.1 *N* standard solution.

The three indicators are satisfactory in hydrochloric acid solution as well as in sulfuric, and in the presence of calomel and excess of mercuric chloride.

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