

of 6 metals against silver have been obtained, and all these values have been summarized in a thermo-electric diagram.

6. The entropy of the metal electrons at low temperatures has been discussed.

7. The possibility of using thermo-electric data as a means of determining  $C_v$  for metals at higher temperatures has been pointed out, and the  $C_v$  curves for 15 metals have been drawn in agreement with existing thermo-electric data.

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[CONTRIBUTION FROM THE EPPLEY LABORATORY]

## THE ELECTROMETRIC TITRATION OF DICHROMATE WITH FERROUS SULFATE

BY MARION EPPLEY AND WARREN C. VOSBURGH

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It has been shown by Forbes and Bartlett<sup>1</sup> that, due to the peculiar relationship between electromotive force and amount of ferrous salt added in the electrometric titration of dichromic acid, end-points could be determined without plotting curves. This method of titration has been applied by Kelley and collaborators<sup>2</sup> in several analytical methods. It has been assumed that the point at which the great change in electromotive force occurs represents the point at which an amount of ferrous salt equivalent to the dichromate present has been added. The accuracy of this assumption apparently has not been determined. In the present investigation the conditions affecting the electrometric titration of dichromate with ferrous sulfate were investigated and the relation determined between the quantities of each reacting.

It was found that, although it was possible to determine accurately the point at which the great change in electromotive force occurs by the method of Forbes and Bartlett and to duplicate results very well under constant conditions, the ratio of ferrous ion to dichromate ion varied with the concentration of the dichromate. Under certain conditions dichromic acid appeared to oxidize more than an equivalent amount of ferrous ion, the error being about 0.4%. Therefore, the method is to some extent empirical and its accuracy is dependent on the care taken to standardize the experimental conditions.

### Experimental

**Effect of Acidity on the End-point.**—The effect of acidity of the solution on the shape of the titration curve and on the end-point was deter-

<sup>1</sup> Forbes and Bartlett, *THIS JOURNAL*, **35**, 1535 (1913).

<sup>2</sup> Kelley and Conant, *J. Ind. Eng. Chem.*, **8**, 719 (1916). Kelley, Adams and Wiley, *ibid.*, **9**, 781 (1917). Kelley and Wiley, *ibid.*, **13**, 1053 (1921).

mined. A constant amount of dichromate in solutions of varying acidity was titrated with ferrous sulfate. The curves were plotted and the end-points taken as the middle points of the nearly vertical straight portions. Some representative curves are shown in Fig. 1 and the results are given in Table I. The apparatus used is described below.

TABLE I  
EFFECT OF ACIDITY ON THE END-POINT

Twenty-five-cc. portions of a 0.1 *N* potassium dichromate solution were diluted to 250 cc. with water and various amounts of hydrochloric or sulfuric acid, and the dichromate titrated with 0.1 *N* ferrous sulfate solution. The results in Section C are not comparable with those in A and B, as different solutions were used.

A. Hydrochloric acid		B. Sulfuric acid		C. Hydrochloric acid	
Acid <i>M</i>	FeSO <sub>4</sub> Cc.	Acid <i>M</i>	FeSO <sub>4</sub> Cc.	Acid <i>M</i>	FeSO <sub>4</sub> Cc.
0.4	25.18	0.4	25.18	0.1	24.93
0.6	25.18	0.6	25.17	0.2	24.95
1.0	25.15	1.0	25.18	0.3	24.94
2.0	25.18	1.5	25.20	0.4	24.96
2.5	25.16	2.0	25.20	0.5	24.96
3.0	25.14	2.5	25.18	0.6	24.99
4.0	25.13	3.0	25.18	0.8	24.99
6	25.05	4.0	25.17	1.0	24.99
...	...	5.4	25.18	2.0	24.99

Table I shows that when the end-points are determined by plotting the curves, constant results are obtained in solutions with acid concentrations between 0.4 *M* and 2.5 *M* hydrochloric acid or over 0.4 *M* sulfuric acid. Titration in the more dilute acid solutions was troublesome due

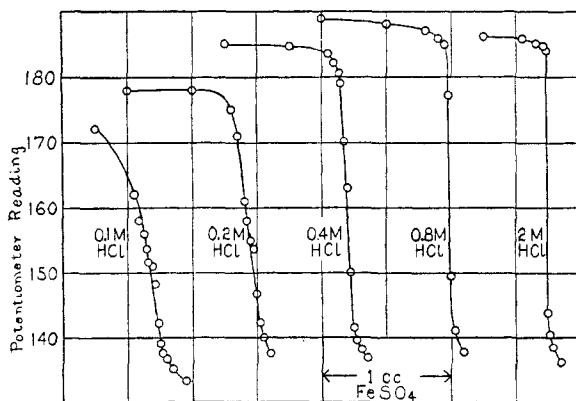


Fig. 1.—Titration curves for solutions of different acid concentrations.

to the time required for the electromotive force to become constant. If the end-point is to be determined without plotting, the lower limit of acidity must be raised somewhat. In this case the end-point is taken as

the point where the first large permanent galvanometer deflection results from a small addition of ferrous sulfate. Fig. 1 shows that in the more dilute acid solutions there is an appreciable difference between the middle point of the nearly vertical straight portion of the curve and a point near the top, which might be taken as the end-point if the curve was not plotted. In the more concentrated acid solutions the difference is negligible. For example in a 2 *M* hydrochloric acid solution practically all the drop in electromotive force was caused by the addition of about 0.02 cc. of ferrous sulfate solution. End-points determined without plotting should be accurate within 0.02 cc. when the hydrochloric acid or sulfuric acid concentration is at least 0.6 *M*.

A comparison of Sections A and B of Table I shows that titrations made in sulfuric acid solutions give slightly higher results than those made in hydrochloric acid solutions.

**Effect of Fluoride and Phosphate Ions.**—To determine what effect reduction of the concentration of ferric ion would have on the end-point, titrations were made in solutions containing phosphate ion and fluoride ion, respectively.

A solution of a volume of 250 cc. containing 75.00 cc. of a 0.03 *N* potassium dichromate solution, 75 cc. of 6 *M* hydrochloric acid solution and portions of a strong hydrofluoric acid solution, as noted, was prepared and the dichromate titrated with a 0.1 *N* ferrous sulfate solution.

TABLE II  
EFFECT OF FLUORIDE ION  
Ferrous sulfate solution, cc.

H <sub>2</sub> F <sub>2</sub> Cc.						Av.
None	26.22	26.25	26.24	26.25	26.24	26.24
3	26.23	26.25	...	...	...	26.24
5	26.21	26.21	26.20	...	...	26.21
10	26.22	26.21	...	...	...	26.215

The larger amounts of fluoride ion had the effect of reducing the amount of ferrous sulfate required by a little over 0.1%. The shape of the curves was slightly affected also, the slope at the end-point being a little less than that of the curve for 0.8 *M* acid in Fig. 1.

The presence of 100 cc. of a 0.1 *M* sodium phosphate solution in titrations under similar conditions made no noticeable difference in the amount of ferrous sulfate required. An excess of ferric ion likewise had no effect.

**Concentration of Dichromate.**—The following experiments show that the amount of ferrous sulfate required to titrate electrometrically a given amount of dichromate varies with the concentration of the dichromate.

Solutions were prepared of varying volume but in each case 2 *M* with respect to hydrochloric acid and containing 25 cc. of a potassium dichromate solution. In the experiments of Section A of Table III the potas-

sium dichromate solution was 0.1 *N* and the titration was made with a 0.1 *N* ferrous sulfate solution. In the experiments of Section B, 0.03 *N* solutions were used. The end-point was taken as the point at which the first large permanent galvanometer deflection occurred. It was considered reached when a permanent deflection of over 5 divisions was caused by about 0.02 cc. of reagent. No trouble was experienced in stopping at the exact end-point, even when titrating with a weight buret.

It was shown by plotting curves for titrations with 0.03 *N* solutions that for volumes up to 300 cc. the end-points as determined in this manner should be accurate within 0.01 to 0.02 cc. For the two cases in which the volume is greater than this the straight portion of the curve has a smaller slope, but the error in determining the end-point could not be greater than 0.02 to 0.03 cc.

TABLE III  
EFFECT OF CONCENTRATION OF DICHROMATE

A. Solutions 2 *M* with respect to hydrochloric acid and containing 25.00 cc. of 0.1 *N* dichromate solution were titrated with 0.1 *N* ferrous sulfate solution.

Volume, cc.	37	75	150	250	300	450	750	900
FeSO <sub>4</sub> , cc.	{ 24.81	24.79	24.78	24.74	24.75	24.70	24.69	24.66
	{ 24.79	...	...	24.76	...	24.69	24.69	24.67

B. Similar solutions containing 25.00 cc. of 0.03 *N* dichromate solution were titrated with a 0.03 *N* ferrous sulfate solution.

Volume, cc.	75	150	300	450	600
FeSO <sub>4</sub> , cc.	{ 24.85	24.81	24.75	24.72	24.66
	{ 24.85	24.83	24.75	24.70	24.67

It is evident from Table III that the results of the titration of dichromate with ferrous sulfate can vary more than 0.5% when the dichromate concentration varies. If the results of the titration are to be reproducible to any high degree, therefore, the procedure must be standardized as to concentration of the dichromate. It follows, also, that the conditions under which the observed end-point denotes the addition of an amount of ferrous sulfate stoichiometrically equivalent to the dichromate present must be rather limited.

The results obtained by Brandt<sup>3</sup> in the titration of ferrous ion with dichromate, using diphenylcarbazide as the indicator, show a similar change in the ratio of ferrous salt to dichromate with change in the amount of dichromate titrated. In this case, however, the change in the ratio can be explained in view of the work of Barneby and Wilson<sup>4</sup> as due to Brandt's neglecting to correct for the amount of dichromate required to oxidize the indicator.

**Effect of Exclusion of Air.**—McCrosky<sup>5</sup> showed that under some condi-

<sup>3</sup> Brandt, *Z. anal. Chem.*, **53**, 9 (1914).

<sup>4</sup> Barneby and Wilson, *THIS JOURNAL*, **35**, 159 (1913).

<sup>5</sup> McCrosky, *ibid.*, **40**, 1662 (1918).

tions the determination of dichromate by the iodide method was quite appreciably affected by the presence of air. Hostetter and Roberts<sup>6</sup> maintained an atmosphere of carbon dioxide in the electrometric titration of ferrous iron with dichromate. It is improbable, however, that air would affect the titration of dichromate with ferrous sulfate, since the concentration of ferrous ion is always slight and its rate of oxidation by oxygen in acid solution is small compared with its rate of reaction with dichromate ion. Some experiments showed that the presence of air in this titration had an effect of less than 0.1%.

Air was expelled from 225 cc. of 2.7 *M* hydrochloric acid solution by boiling and cooling in an atmosphere of carbon dioxide. When this solution was cool, 25.00 cc. of 0.1 *N* dichromate solution was added and the dichromate titrated with 0.1 *N* ferrous sulfate solution, the atmosphere of carbon dioxide being maintained throughout. Control experiments were made without boiling or excluding air during the titration. The results are given in Table IV. Similar experiments with a different set of solutions showed no difference between the results in air-free and air-containing solutions, respectively.

TABLE IV  
EFFECT OF EXCLUSION OF AIR

FeSO <sub>4</sub> , cc., CO <sub>2</sub> atmosphere	25.32	25.32	25.34	...
FeSO <sub>4</sub> , cc., air atmosphere	25.35	25.31	25.36	25.36

**Titration of Dichromate with Standard Ferrous Sulfate.**—The decrease in ferrous sulfate required with increasing dilution of the dichromate indicates one of two things: either more than one equivalent of ferrous sulfate has been added for each equivalent of dichromate in the more concentrated solutions at least; or in most cases the reaction is incomplete and some dichromate is present when the apparent end-point is reached. To investigate this problem titrations were made under the conditions of the solution of 250cc. volume in Table III A, but with a known amount of dichromate and a ferrous sulfate solution which had been standardized by means of a standard permanganate solution.

Portions of the potassium dichromate samples described below were weighed and dissolved in about 150 cc. of water. The solutions were acidified with 100 cc. of a 5 *M* hydrochloric acid solution and the dichromate titrated with a standard ferrous sulfate solution, details of the standardization of which, by means of a standard permanganate solution, are given below. The results are shown in Table V.

As a check on the determinations of Table V, solutions were prepared containing 2.4508 g. in 500 cc., or 0.09996 equivalents in a liter, of some of the dichromate samples. Solutions were prepared of 250cc. volume

<sup>6</sup> Hostetter and Roberts, *THIS JOURNAL*, **41**, 1337 (1919).

containing 25.00 cc. of the dichromate solution and 1.5 *M* with respect to hydrochloric acid, and the dichromate was titrated with 0.09701 *N* ferrous sulfate solution using a weight buret. Using samples of dichromates 7, 16, 22 and 25, the results for the normality of the solutions were, respectively, 0.44, 0.43, 0.34 and 0.31% too high.

TABLE V

## TITRATION OF DICHROMATE WITH STANDARD FERROUS SULFATE

The solutions at the start were 2 *M* with respect to hydrochloric acid and 0.01 *N* with respect to dichromate.

No.	Potassium dichromate		Equiv. per liter	Ferrous sulfate		Dichromate		Difference	
	Weight					Calc. wt.			
	1	2		1	2	1	2	1	2
	G.	G.		Cc.	Cc.	G.	G.	%	%
1	0.12255	0.1226	0.09987	25.14	25.17	0.1231	0.12325	0.4	0.5
4	0.1226	0.1227	0.09987	25.13	25.19	0.12305	0.12335	0.4	0.5
6	0.12265	0.1227	0.09987	25.17	25.18	0.12325	0.1233	0.5	0.5
6	0.12257 <sup>a</sup>	0.12257 <sup>a</sup>	0.09732	25.81	25.81	0.1232	0.1232	0.5	0.5
7	0.1224	0.1226	0.09987	25.10	25.13	0.1229	0.12305	0.4	0.4
11	0.1226	0.1226	0.09967	25.19	25.20	0.1231	0.12315	0.4	0.4

<sup>a</sup> 25.00 cc. of 0.1000 *N* solution.

It is thus shown that under some conditions when the dichromate is titrated with ferrous sulfate electrometrically an excess of ferrous ion above the theoretical of 0.3 to 0.5% is required. This difference cannot be ascribed to experimental errors.

TABLE VI

TITRATION OF A KNOWN AMOUNT OF DICHROMATE IN 0.003 *N* SOLUTION WITH A STANDARD FERROUS SULFATE SOLUTION

Dichromate No.	Ferrous sulfate solution			Dichromate <i>N</i>	
	Equiv. per liter	Cc.	Cc.		
6	0.02917	25.71	25.73	0.03001	
16	0.02917	25.72	25.73	0.03001	
16	0.09732	7.70	7.71	0.03001	
24	0.03026	{ 24.79 24.84	{ 24.85 24.80	{ 24.84 24.82	0.03005

In order to determine whether or not an excess of ferrous ion was required to produce the decrease in electromotive force at the observed end-point, 0.01 *N* permanganate solution was added to solutions in which dichromate had been titrated with 0.1 *N* ferrous sulfate solution. An average of about 0.1 cc., equivalent to 0.01 cc. of the ferrous sulfate solution, was required to bring the electromotive force back to a value equal to or higher than that before the end-point.

According to Table III if dichromic acid in a 0.01 *N* solution required for titration 0.4% more ferrous sulfate than the theoretical, a solution 3 or 4 times as dilute should give nearly theoretical results. Therefore, titration of dichromate in a 0.003 *N* solution was tried. Table VI shows

that under these conditions a quantity of ferrous sulfate less than 0.1% too high was required.

Solutions were prepared of dichromates 6 and 16 containing 0.7355 g. in 500 cc., or 0.03 equivalents in a liter. Twenty-five-cc. portions were titrated with standard ferrous sulfate solution in a solution of 250cc. volume and 2 *M* with respect to hydrochloric acid.

**The Titration of Ferrous Ion with Dichromate.**—Since it has been shown that when dichromate is titrated with ferrous sulfate it shows an apparent excess of oxidizing capacity, the reverse titration was tried to determine whether it appears to oxidize more than the theoretically equivalent amount of ferrous sulfate in this case also. The curve for this titration has been shown by Hildebrand<sup>7</sup> and Hostetter and Roberts<sup>8</sup> to be a normal one.

A little sodium hydrogen carbonate was dissolved in 140 cc. of boiled water and 85 cc. of a 6 *M* hydrochloric acid solution added, the carbon dioxide generated serving to sweep out dissolved oxygen.<sup>8</sup> Then 25.00 cc. of ferrous sulfate solution was added and the solution was titrated with 0.1000 *N* solution of dichromate No. 6. The titration was carried out in an atmosphere of carbon dioxide and the electrode was not put into the solution until near the end-point. After it was introduced electromotive-force measurements were made after each addition and the curve plotted. For 25.00 cc. of 0.09732 *N* ferrous sulfate solution, equivalent to 24.33 cc. of 0.1 *N* solution, 24.22, 24.25, 24.23 and 24.25 cc. of the dichromate solution were required. The latter was thus apparently 0.10037 *N*. When the same solutions were compared by means of the method of Forbes and Bartlett<sup>1</sup> the dichromate was found to be 0.10043 *N* as shown in Table V.

The former titration was attempted with 0.03 *N* solutions under the same conditions of volume and acidity as in the experiments of Table III B but the slope of the curve at the end-point was so small that it could only be determined that the results were in approximate agreement with those of Table III B.

### Apparatus and Materials

**Apparatus.**—The potentiometer used was in principle similar to that described by Roberts.<sup>9</sup> The slide wire was 38 cm. long and was provided with a scale of 200 arbitrary units, so arranged that the zero point was at the 60th scale division. Two dry cells in parallel were used as the potentiometer battery. The total resistance of the potentiometer circuit was 86 ohms. The ordinate 192 in the curves of Fig. 1 corresponded to about 1 volt.

The galvanometer had a sensitivity of about 50 megohms; while this was more than necessary for many titrations, it was not too sensitive for the titration of dichromate with

<sup>7</sup> Hildebrand, *THIS JOURNAL*, **35**, 870 (1913).

<sup>8</sup> Kolthoff, *Pharm. Weekblad*, **58**, 1510 (1921).

<sup>9</sup> Roberts, *THIS JOURNAL*, **41**, 1359 (1919).

ferrous sulfate. In this case the system has an extra low sensitivity until the end-point is passed.

The calomel electrode was of the saturated potassium chloride type.

The platinum electrodes were made by fusing pieces of B. and S. No. 28 platinum wire, 2 to 3 cm. long, in the ends of soft glass tubes. It was found that when Pyrex glass was used the resulting electrodes behaved as if "poisoned," and would not give a sharp end-point. No further treatment succeeded in making them work satisfactorily.

Hostetter and Roberts<sup>10</sup> emphasize the danger of errors due to contamination of the platinum electrodes and recommend acid treatment followed by ignition for cleaning before use. During the course of this investigation it was found that electrolysis for a few minutes of dil. sulfuric or hydrochloric acid with the contaminated electrode as the anode was a more effective and simpler means of removing the contamination. Electrodes did not become contaminated so quickly in the titration of dichromate with ferrous sulfate as in the reverse titration. This would indicate that the contamination may be connected with the presence of reducing substances, such as ferrous ion, in the solution, and may consist of hydrogen dissolved in the platinum. An electrode which had been made the cathode in the electrolysis of a dil. acid solution gave a much lower potential difference in contact with a dichromic acid solution than one which had been made the anode in the electrolysis. The change in electromotive force at the end-point when the dichromic acid was titrated was correspondingly smaller in the case of the first electrode.

**Potassium Dichromate.**—The potassium dichromate was purified by recrystallizing from redistilled water and drying to constant weight at 160°. No. 22 was a dried sample of commercial c. p. material. No. 1 was recrystallized once, No. 4 twice, Nos. 6 and 24 thrice and Nos. 7, 11, 16 and 25 four times.

The oxidizing action of some of these preparations toward hydriodic acid has been shown in another communication.<sup>11</sup> The results indicated that less than 0.1% of impurities was present. However, since the amount of ferrous sulfate required to titrate samples of the potassium dichromate preparations was in excess of the theoretical it was thought well to make tests for the presence of chromium trioxide.<sup>12</sup> Samples of Nos. 4, 7, 16, 22 and 25 were titrated with 0.03 *N* alkali solution by the conductivity method recommended by Kolthoff<sup>12</sup> but no indication of chromium trioxide was obtained.

As an additional check the chromium content of No. 16 was determined gravimetrically by the barium chromate method<sup>13</sup> and also by precipitating as mercurous chromate and weighing as chromic oxide.<sup>13</sup> The results obtained by the first method averaged 0.1% higher than the calculated and those by the second method 0.2% lower than the calculated.

**Ferrous Sulfate Solutions.**—The ferrous sulfate solutions were prepared from c. p. ferrous ammonium sulfate. They were made about 0.6 *M* with respect to sulfuric acid, except in the case of the 0.03 *N* solution which was 0.2 *M*. Ferrous sulfate solutions are oxidized appreciably in contact with air. The results of titrations were, therefore, considered comparable only when obtained within 8 hours of each other or when standardized ferrous sulfate solutions were used.

The standard ferrous sulfate solutions were standardized shortly before use by means of standard permanganate solutions. The permanganate solutions were generally standardized or checked just before use. Bureau of Standards sodium oxalate, dried

<sup>10</sup> Ref. 6, p. 1343.

<sup>11</sup> Vosburgh, *THIS JOURNAL*, **44**, 2120 (1922).

<sup>12</sup> Kolthoff, *Z. anal. Chem.*, **59**, 403 (1920).

<sup>13</sup> Treadwell, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1913, 3rd Ed., vol. 2, p. 104.



at 105° and kept in a desiccator, was used and the procedure of McBride<sup>14</sup> followed. Portions of the ferrous sulfate solution to be standardized were diluted with 150 to 200 cc. of recently boiled water and 10 cc. of 6 *M* sulfuric acid and the ferrous ion titrated with a standard permanganate solution. All volumetric apparatus used was standardized. Approximately the same rate of flow of the permanganate was used when titrating the ferrous sulfate with a volume buret as in the standardization of the permanganate. The volume of permanganate solution required was corrected in both titrations by subtracting the amount necessary to produce a visible color in blank determinations.

### Summary

The practical limits of acidity for the electrometric titration of dichromic acid with ferrous sulfate have been determined.

The amount of ferrous sulfate required to titrate a given amount of dichromic acid varies with the concentration of the latter.

Dissolved air has a negligible effect on the titration.

Hydrofluoric acid in sufficient concentration reduces the amount of ferrous sulfate required by about 0.1%.

When the ferrous sulfate solution was standardized by means of a standard permanganate solution the amount required to titrate a known amount of dichromate in 0.01 *N* solution of the latter was about 4 parts in a thousand higher than the calculated.

When the dichromate concentration was 0.003 *N* the amount of ferrous sulfate required was about 0.1% higher than the calculated.

The titration of ferrous ion with a potassium dichromate solution gives results which agree with those obtained with the reverse titration.

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[CONTRIBUTION FROM THE LABORATORY OF THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

## THE USE OF THE NEWER INDICATORS IN TITRATIONS OF ALKALOIDS

BY WILLIAM J. MCGILL

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Not since Kippenberger's study<sup>1</sup> of the adaptability of certain indicators for alkaloidal titrations has there been any extended or systematic work on this subject.<sup>2</sup> The indicators recommended in the United States, British, French, and German pharmacopeias have been selected, it seems, principally with a view to the sharpness of the end-points they afford in the titration rather than because they give a marked color change at or near the correct end-point of the titration.

<sup>14</sup> McBride, *THIS JOURNAL*, **34**, 415 (1912).

<sup>1</sup> Kippenberger, *Z. anal. Chem.*, **39**, 201 (1900).

<sup>2</sup> An article discussing the use of the newer indicators in alkaloidal titrations, based on data obtained by colorimetric methods has been published by Evers, *Pharm. J.*, **1921**, 470 and is reprinted in the *J. Am. Pharm. Assoc.*, **10**, 676 (1921).