

It has been shown that copper anodes undergo electrolytic corrosion to an extent indicating the formation of some cuprous trinitride, CuN_3 , with the cupric trinitride CuN_6 formed as the main product. No gas was liberated at the anode.

With silver, cadmium, lead, and antimony anodes, the corrosion resulted in the formation of the normal trinitrides AgN_3 , CdN_6 , PbN_6 , and SbN_9 , without liberation of gas at the anode. The corrosion efficiency as calculated on the basis of the quantitative formation of these compounds was found to be slightly in excess of 100%. This is probably not attributable to ordinary experimental error, but either to a slight mechanical or chemical corrosion, or else to a tendency toward the formation of unstable compounds containing the metals in a lower state of valence.

The aluminum, iron, and nickel anodes were found to undergo corrosion accompanied by liberation of nitrogen gas, as the result of which the efficiency fell far below 100%. The aluminum anode became coated with a bulky, pyrophoric scale of varying color and texture. Deep red ferric trinitride, FeN_9 , was obtained in solution when the iron anode was employed, but this product was ammonolyzed, yielding an ammono-basic ferric trinitride. Upon the nickel anode a pink deposit, presumably an amono-basic nickel trinitride, was formed.

ITHACA, N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE MIDVALE STEEL AND
ORDNANCE COMPANY.]

AN ELECTROMETRIC METHOD FOR THE DETERMINATION OF FERROCYANIDES DEPENDING ON A CHANGE IN OXIDATION POTENTIAL.

BY G. L. KELLEY AND R. T. BOHN.

Received August 16, 1919.

In connection with some work in this laboratory, it became necessary to analyze potassium ferrocyanide solutions accurately. The oxidation of hydroferrocyanic acid by excess of iodine followed by titration with thiosulfate in the presence of alkali bicarbonate as proposed by Rupp and Scheidt¹ has been shown to be inaccurate.² Knublauch³ titrates a sulfuric acid solution of the salt with copper or zinc sulfate, using a ferric salt as indicator. Smith's electrolytic method⁴ would not distinguish between ferro- and ferricyanide ion if such were necessary. DeHaen⁵ titrated a sulfuric acid solution with permanganate, but the difficulty of determining the end-point in a yellow solution of ferricyanide is mani-

¹ *J. Soc. Chem. Ind.*, 21, 1099 (1902).

² Sutton, *Volumetric Anal.*, 10th Ed., p. 217.

³ *Ibid.*, p. 219.

⁴ *Electro-Analysis*, 5th Ed., 1912, p. 302.

⁵ *Ann. Chem. Pharm.*, 90, 160 (1854).

fest. DeHaën recommends standardizing permanganate against pure potassium ferrocyanide. We could not use the hydrated salt for this purpose because of efflorescence, and when dried at 120° , even in a stream of dry carbon dioxide, decomposition amounting to 8 to 15 parts in 10,000 occurred. Having observed that a sharp change in potential occurred during the titration of ferrocyanide with permanganate immediately before the color of the permanganate appeared, we undertook the study of the end-point.

The change in oxidation potential has been used by Crotogino¹ in titrating halogens with permanganate, by Hildebrand² in the titration of chromates, by Forbes and Bartlett in the titration of ferrous³ and chromous⁴ salts, and by Kelley and others in the titration of vanadates,⁵ chromates,⁶ and permanganates.⁷ Crotogino,⁸ using a platinum black electrode, observed that the potential of the cell $\text{Pt} - \text{K}_4\text{Fe}(\text{CN})_6 - \text{N Hg}_2\text{Cl}_2$ is 0.155 volt, while we observed the same cell to show a potential ranging from 0.20 to 0.41 volt, using a bright platinum electrode. The difference in the potential of the cell depends upon the nature of the solutions with which the electrode has been in contact, the amount of acid present, and the temperature. We believe the electrometric titration of ferrocyanides to be new.

Our apparatus consisted in part of a bright platinum wire which served as a platinum electrode, a normal calomel electrode connected with a reservoir solution to permit flushing the tip of the electrode, and a glass stirrer operated by a motor. These two electrodes dipped into the solution which was to be titrated. The e. m. f. of this cell was balanced against a variable fraction of the e. m. f. of a pair of dry cells. This was compared with a standard cell so that actual potentials for this cell could be read. A potentiometer manufactured by Leeds and Northrup was used for this purpose. It was possible to read 0.1 millivolt and to estimate to 0.01 millivolt. The weights, burets, and flasks were carefully standardized.

To study the character of the end-point, we at first employed a 0.005 *N* solution of permanganate and a solution of ferrocyanide of corresponding strength. As would be expected a gradual increase in potential occurs during the oxidation of ferrocyanide, due to the increase in concentration of ferricyanide ion, but this does not interfere with the detec-

¹ *Z. anorg. Chem.*, **24**, 225 (1900).

² *THIS JOURNAL*, **35**, 869 (1913).

³ *Ibid.*, **35**, 1527 (1913).

⁴ *Ibid.*, **39**, 1145 (1917).

⁵ *Ibid.*, **38**, 341 (1916).

⁶ *J. Ind. Eng. Chem.*, **8**, 719 (1916).

⁷ *Ibid.*, **10**, 19 (1918).

⁸ *Loc. cit.*

tion of the end-point, the appearance of which is attended by a large change in potential. This last change is due to the presence of permanganate ion. Table I shows such titration. In the example given, per-

TABLE I.
Titration of Potassium Ferrocyanide and Permanganate Solutions Approximately
0.005 *N*. Volume 250 cc. 40 cc. of Sulfuric Acid (Sp. Gr. 1.58).
Temperature, 25°.

K ₄ Fe(CN) ₆ Cc.	KMnO ₄ Cc.	Change. Cc.	E. M. F. Millivolts.	Change in Mv.	Time. Min.	Total change in Mv.	
52.07	0	0	412	0	
	49.18	49.18	522	110	
	49.38	0.20	524	2	
	49.68	0.30	525	1	
	51.95	2.27	570	45	
	52.15	0.20	583	13	
	52.25	0.10	590	7	
	52.45	0.20	619	29	
	52.55	0.10	648	29	1	..	
	662	14	2	..	
	671	9	3	..	
	680	9	4	..	
	687	7	5	68	
	52.60	0.05	705	18	1	..	
	710	5	2	..	
	720	10	3	..	
	730	10	4	..	
	739	9	5	52	end-point
	748	9	6	..	
	770	22	10	..	
	52.64	0.04	780	10	1	..	
	788	8	2	..	
	796	8	3	..	
	800	4	4	..	
	54.11	1.47	926	126	
52.77	0.70	928	2	
53.41	0.64	912	16	
53.46	0.05	904	8	1	..	
53.51	0.05	896	8	1	..	
53.56	0.05	882	14	1	..	
	872	10	2	..	
	863	9	3	..	
	855	8	4	..	
	845	10	5	51	
	836	9	6	..	
53.61	0.05	818	18	1	..	
	806	12	2	..	
	780	26	4	..	
	769	11	5	67	end-point
	758	11	6	..	
	702	56	12	..	
53.66	0.05	690	12	1	..	
	670	20	3	32	

manganate was added to the end-point, then in excess. The end-point was then found by adding ferrocyanide, followed by an excess of this solution. The end-point was taken as the point of greatest potential change in 5 minutes for each like volume of titrating solution added. The two titrations gave identical results, although differences of the order of 3 to 5 parts in 1,000 were sometimes noted, especially with the amount of sulfuric acid used in this experiment.

Having determined the nature and delicacy of the end-point, we proceeded to work with stronger solutions, using for this purpose solutions of permanganate and ferrocyanide, which were approximately 0.05 *N*. One cc. of the permanganate solution by standardization against Bureau of Standards sodium oxalate was found to be equivalent to 0.003373 g. of oxalate or 0.02127 g. of hydrated potassium ferrocyanide.

The next step in our study of this method was the effect of the concentration of sulfuric acid. From the work of Crotono,¹ one would expect a high concentration of acid to produce a high potential. This seems to be supported by other work which we have done. Obviously the lower limit of sulfuric acid concentration is that necessary to keep the products of reaction in solution. The upper limit is regulated by the fact that high concentrations of sulfuric acid cause interfering side reactions. The side reactions referred to are the decomposition of ferricyanide by sulfuric acid, giving rise to hydrocyanic acid as one of the products followed by reaction with permanganate. The occurrence of such side reactions was indicated in a variety of ways which are summarized below:

1. The increased consumption of permanganate when the titration was carried out by adding ferrocyanide to a permanganate solution. In this case a high concentration of permanganate was available for reaction with the decomposition products of the ferricyanide, as it was formed.

2. The amount of permanganate consumed in excess of the theoretical quantity increased with the concentration of permanganate, sulfuric acid and ferricyanide, and with an increase in temperature. When ferrocyanide was titrated with permanganate, this effect was not noticeable, even when the concentration of sulfuric acid was high, probably because the speed of the reaction between ferrocyanide and permanganate was so much greater than that between permanganate and the decomposition products of the ferricyanide. When the concentration of sulfuric acid was low, the consumption of permanganate on titrating this with ferrocyanide was normal. 2.5 cc. of sulfuric acid (sp. gr. 1.58) in a volume of 250 cc. of solution required two parts in one thousand more of permanganate when the ferrocyanide was added to the permanganate, than when the reverse operation was performed. With 5 cc. of acid, the difference was 3 parts in 1,000, but with 40 cc. of acid, it rose to 7 parts.

¹ *Loc. cit.*

The presence of ferricyanide in addition to that produced in the reaction had a marked effect when the ferrocyanide solution was added to a solution containing ferricyanide, together with permanganate and 40 cc. of sulfuric acid. It had almost no effect when the sulfuric acid present was 2.5 cc.

3. The presence of ferricyanide in ferrocyanide solution had almost no effect upon the titration of the ferrocyanide with permanganate in all moderate concentrations of sulfuric acid.

4. On warming a solution of ferricyanide containing sulfuric acid, the odor of hydrocyanic acid could be detected.

5. On titrating a warm solution of permanganate and sulfuric acid with ferrocyanide, the consumption of permanganate was too large.

The foregoing statements indicate that error will follow the use of concentrations of sulfuric acid greater than 5 cc. in 250 cc. volume when permanganate is titrated with ferrocyanide, and indicates likewise that some danger attends the use of the higher concentrations of sulfuric acid in the reverse titrations. These statements are illustrated, in part, in Table II.

TABLE II.

Effect of Temperature, Sulfuric Acid and Potassium Ferricyanide on the Titration of Ferrocyanide with Permanganate and on the Reverse Titration.

Volume 250 cc. Solutions Approximately 0.05 *N*.

Temperature 25°.

H ₂ SO ₄ sp. gr. 1.58. Cc.	Solution titrated.	Potassium ferro- cyanide added. G.	Permanganate ferro- cyanide ratio.
2.5	KMnO ₄	none	1.011
2.5	K ₄ Fe(CN) ₆	none	1.009
5.0	KMnO ₄	none	1.011
5.0	K ₄ Fe(CN) ₆	none	1.008
40.0	KMnO ₄	none	1.016
40.0	K ₄ Fe(CN) ₆	none	1.009
2.5	KMnO ₄	1.5	1.008
2.5	K ₄ Fe(CN) ₆	1.5	1.009
40.0	KMnO ₄	none	1.035 ¹
40.0	KMnO ₄	1.0	1.102
40.0	K ₄ Fe(CN) ₆	1.0	1.010

Table II shows titration of 0.05 *N* solutions with 2.5 cc. and 40 cc. of sulfuric acid present. On comparing these titrations with those obtained on titrating 0.005 *N* solutions with 40 cc. of sulfuric acid present, as shown in Table I, it will be noted that the change of potential is much greater near the end-point when the stronger solutions are used. With 0.05 *N* solutions it is not necessary to wait more than two minutes to determine the end-point. Table III also exhibits the favorable influence of a low concentration of sulfuric acid on this titration.

¹ Temp. 50°.

TABLE III.

Titration of Potassium Permanganate and Ferrocyanide Solutions, Approximately 0.05 *N*. Volume 250 cc. Temperature 25°.

$K_4Fe(CN)_6$ Cc.	$KMnO_4$ Cc.	Change in cc.	E. M. F. millivolts.	Change in mv.	Time. Min.	Total change.
49.25	0	0	250	(2.5 cc. H_2SO_4 Sp. gr. 1.58)		
	49.18	49.18	505	255
	49.40	0.22	506	1
	49.56	0.16	515	9
	49.64	0.08	532	17
	49.67	0.03	598	66	1	...
	650	52	2	...
	704	54	3	...
	753	49	4	221
	49.87	0.20	850	97
49.25	0	0	365	(40 cc. H_2SO_4 Sp. gr. 1.58)		
	49.18	49.18	583	218
	49.28	0.10	590	7
	49.38	0.10	600	10
	49.48	0.10	607	7	1	...
	49.57	0.09	618	11	1	...
	49.62	0.05	629	11	1	...
	49.66	0.04	652	23	1	...
	49.70	0.04	718	66	1	...
	732	14	2	...
	745	13	3	...
	761	16	4	109

One of the products of the reaction is manganous sulfate. We investigated the effect of increasing the concentration of this salt. As a result we learned that a moderate increase in concentration over that resulting from the reaction caused a precipitate of manganous ferricyanide, which coated the electrode and seriously interfered with the titration even when the concentration of sulfuric acid was high. This suggests a limit to the amount of ferrocyanide which can be titrated in this volume. This limit corresponds to about 50 cc. of a 0.05 *N* solution, and may not be greatly exceeded.

Large concentrations of hydrochloric acid reacted with the permanganate. With less than one cc. of conc. hydrochloric acid in a volume of 250 cc., no difficulty was experienced when ferrocyanide was titrated with permanganate. It is thus shown that chlorides in moderate amount do not interfere.

The substitution of potassium dichromate as the oxidizing agent for potassium permanganate was unsuccessful. This reaction requires time and high temperature for its completion. It was therefore abandoned.

The titration shown in the tables given in this paper involved about 50 cc. each of the solutions. We have also titrated smaller volumes, including some as small as 2 cc., and have found the relation between the

solutions to be the same within the same limit of error in measuring, whether dilute or strong solutions were used. The method is, therefore available for the determination of very small amounts of ferrocyanide, and in this respect it corresponds with the determination of small amounts of chromate by electrometric titration with ferrous sulfate as described by one of us elsewhere.¹ The question as to the correctness of the end-point which we have taken is only partly answered by the approximate coincidence of the electrometric end-point and the appearance of the color of the permanganic acid because of the difficulty in noting the point at which the change of color occurs. We believe, however, that the close agreement between end-points reached by titrating ferrocyanide with permanganate and permanganate with ferrocyanide is further and confirming evidence of the correctness of the end-point and that it shows that there is no need for a blank correction in this titration in work corresponding to an accuracy of one part in 500.

Method for Determining Ferrocyanide.

About one g. of potassium ferrocyanide in 250 cc. of water and 2.5 to 5.0 cc. of sulfuric acid of sp. gr. 1.58, may be titrated with 0.05 *N* permanganate. The permanganate should be standardized against Bureau of Standards sodium oxalate. Ferricyanide does not interfere. The titration should be performed by adding the permanganate slowly with constant mechanical stirring to the solution of ferrocyanide. A small precipitate may form, but this redissolves. The electrometric apparatus must be one which will indicate changes in potential of the order of one millivolt. This condition is fulfilled by the apparatus described by Hildebrand,² and, with the addition of a voltmeter, by the apparatus described by one of us.³ As the end-point is approached, the permanganate should be added dropwise, and time allowed for the completion of the reaction. This is illustrated in Table I. The end-point is taken as the point of greatest change in potential, corresponding to the addition of equal amounts of the permanganate solution. Should too much permanganate be added, the end-point may be approached from the opposite direction by adding a standard solution of ferrocyanide. The concentration of permanganate in this case is so low that the cautions given elsewhere in this paper concerning the danger of titrating permanganate with ferrocyanide are not applicable. There is even some advantage in titrating in this way in that in this titration, as in most others, depending upon a change in oxidation potential, the sharper end-points are obtained when the electrode is in contact with the oxidizing solution. Chloride in amounts equivalent to one g. of sodium chloride do not interfere. Any

¹ *J. Ind. Eng. Chem.*, **9**, 780 (1917).

² *Loc. cit.*

³ *J. Ind. Eng. Chem.*, **9**, 780 (1917).

salts which under the conditions produce a precipitate with either ferro- or ferricyanide interfere.

NICTOWN, PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY.]

THE VAPOR PRESSURES OF MERCURY IN THE RANGE 120° TO 250°.

BY ALAN W. C. MENZIES.

Received August 20, 1919.

In a former paper¹ it was pointed out that the values found by various observers for the vapor pressures of mercury are astonishingly discordant. For this and for other reasons there mentioned, the vapor pressures were redetermined at that time over the temperature range 250–435°, using the static isoteniscope.² In the present paper a report is made of measurements covering the range 120–250°, using two McLeod gages.

The Existing Data.—The more important observations within the range stated are collected in Table I, in which the observers' names are

TABLE I.
Data of Other Investigators.

Observer.	Temp.	Press. obs. mm. mercury.	Press. calc. from equation R mm. mercury.	Press. diff. Calc. — Obs. mm. mercury.	$\frac{P \text{ calc.}}{P \text{ obs.}} \times 100.$
G	248	71.39	70.29	—1.10	101.6
G	245	68.42	64.89	—3.53	103.0
Y	236.9	51.85	52.03	+0.18	99.6
G	236	51.58	50.72	—0.86	101.7
G	230.5	46.49	43.21	—3.28	107.5
G	224.5	38.82	36.56	—2.26	106.2
G	207	21.07	21.53	+0.46	97.9
H	206.9	22.58	21.47	—1.11	105.2
H	203.0	20.35	18.97	—1.38	107.3
H	190.4	12.89	12.54	—0.35	103.0
G	188	12.51	11.56	—0.95	108.2
H	184.7	11.04	10.32	—0.72	107.0
Y	183.8	9.94	10.00	+0.06	99.4
Y	183.7	9.85	9.97	+0.12	98.8
RY	183.4	9.87	9.87	—0.00	100.0
H	177.4	8.20	7.98	—0.22	102.7
G	176.5	8.22	7.73	—0.49	106.4
H	165.8	5.52	5.22	—0.30	104.3
G	157.5	3.93	3.72	—0.21	105.7
H	154.2	3.49	3.33	—0.16	104.9
G	129	1.00	1.14	+0.14	87.4

¹ Smith and Menzies, *THIS JOURNAL*, 32, 1434 (1910).

² *THIS JOURNAL*, 32, 1412 (1910).