[CONTRIBUTION FROM THE INSTITUTE OF ANALYTICAL CHEMISTRY OF CHARLES UNIVERSITY]

Volumetric Determinations in Strongly Alkaline Solutions. II. The Titration of Manganese with Ferricyanide

BY O. TOMÍČEK AND J. KALNÝ

The direct oxidimetric titration of cobaltous salts by potassium ferricyanide has been described and the former determination of other metals in this way was mentioned in a previous communication.[1] In the present paper we wish to present the results of experiments on the determination of manganous salts by ferricyanide. Only G. Grube and W. Brause[2] have mentioned the possibility of this oxidation in cyanide medium, without, however, having made further investigations of the problem.

Materials and Apparatus

Potassium ferricyanide solutions were prepared, stored and their normality determined exactly as in the previous communication.[1]

Manganese Salts and Solutions.—A solution of manganous sulfate pentahydrate (Kahlbaum–Schering) was used. An 0.05 *m* solution was prepared and its titer determined by weight, partly after dehydrating in an electric oven at a temperature not over 500° and partly after precipitation as manganese ammonium phosphate ($MnNH_4PO_4 \cdot H_2O$) and ignition to manganese pyrophosphate ($Mn_2P_2O_7$).[3]

Sodium Hydroxide.—For this determination it was necessary to prepare a sodium hydroxide solution free from oxygen. Pure 30 to 50% solution of sodium hydroxide in bottles was covered with a 2-cm. layer of pure benzene. Through it was led for twelve to twenty-four hours a weak stream of hydrogen, which was prepared from zinc and pure hydrochloric acid and purified by washing first with concentrated titanous chloride, saturated with sodium citrate, and then with water. The solution was kept in well-stoppered vessels, and before each titration again hydrogen was bubbled through it. To transfer the solution, a pipet was used into which first some benzene had been sucked.

Other salts and reagents used, as well as the organic solvents (glycerol of sp. gr. 1.23, ethylene glycol) were of usual purity and free from traces of manganese.

The sample of dialogite was kindly given to us by Prof. Dr. F. Slavík, director of the Mineralogical Institute of Charles University in Prague. The samples of steel and manganese alloys came to us from the Vítkovice Means, Steel Iron Corporation, Čs.R. through the kindness of Ing. F. Wald, Chief of their Analytical and Research Laboratory.

The apparatus used as well as the calibrated vessels were the same as described in the previous communication.[1] The titration vessels were of hard glass throughout.

Manganese Titration

In the beginning, potentiometric titrations of 0.05 molar solutions of manganous sulfate with ferricyanide were tried at various temperatures and with varying concentrations of ammonia, sodium carbonate or sodium hydroxide, and also potassium cyanide, however without marked success. Only when a few substances were added which form complexes with three- and four-valent manganese, better results are obtained. Especially additions of glycerol, ethylene glycol or tartaric acid proved to be very suitable. After many experiments the conditions were found for a quantitative oxidation of manganous salts in a medium of sodium hydroxide by potassium ferricyanide.

(1) The Oxidation of Mn^{II} to Mn^{IV} in the Presence of Glycerol or Glycol.—The titration vessel, containing from 30 to 50 cc. of not more than 0.02 *m* manganous salt to which about 5 cc. of glycerol had been added and which was covered by a 2-cm. layer of pure benzene, was closed with a rubber stopper. It was then placed in a larger vessel, filled with cold water or ice, and cooled to about 10–12°, then a gentle stream of carbon dioxide free from oxygen was passed through for ten minutes. Furthermore, about 10 cc. of sodium hydroxide (free from oxygen) was added in such a way that the solution could not come in contact with air. The solution, which then should at least be 1.5 to 2 *n* sodium hydroxide, was titrated with 0.1 *m* potassium ferricyanide; the color was at first weakly, later intensely, red. The potential quickly attains stable values and a distinct jump in potential appears only after enough ferricyanide corresponding to the oxidation of Mn^{II} to Mn^{IV} has been added. The inflection potential under these conditions is about 0.00 volt compared to the saturated calomel electrode. At the transition of Mn^{II} to Mn^{III} no definite maximum is reached. The course of the oxidation is demonstrated in Fig. 1, Curve 1. Instead of the glycerol mannite may be used; however, here the potential in the neighborhood of the equivalence point is still less steady than in the case of glycerol.

Much more stable potentials and therefore also sharper jumps at the point of equivalence (Mn^{II}–Mn^{IV}) may be obtained if instead of glycerol under the same conditions ethylene glycol is added. The course of a titration is demonstrated in Fig. 1, Curve 2. The inflection potential is here about −0.05 volt against the saturated calomel electrode. Yet even glycol which was purified by distillation used up a certain amount of the 0.1 *m* potassium ferricyanide—in our experiments 0.18 cc. After making this correction, the results were accurate.

(2) Oxidation of Mn^{II} to Mn^{III} in the Presence of Tartaric Acid.—If in the above-mentioned experimental procedure instead of glycerol or glycol, tartaric acid (10 cc. of a 10% solution, or even more) was added, in a solution of 2 *n* sodium hydroxide the oxidation proceeded to trivalent manganese. After addition of the theoretical quantity of

---

[1] O. Tomíček and F. Freiberger, THIS JOURNAL, **57**, 801 (1935).

[2] G. Grube and W. Brause, *Ber.*, **60**, 2273 (1927).

[3] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 349.

potassium ferricyanide, a sharp, well-reproducible potential jump was observed, which thus very clearly indicated the end of the titration. The reaction liquid is colored deep red. A further jump of potential, corresponding to the transition of Mn^{III} to Mn^{IV} could, however, not be observed, due to oxidation of the tartaric acid itself. The course of a titration is shown in Curve 3, Fig. 1. The inflection potential is -0.30 volt against the saturated calomel electrode. A concentration of about 1.5 *n* alkali at the end of the titration is most advantageous, but a larger alkalinity does not interfere.

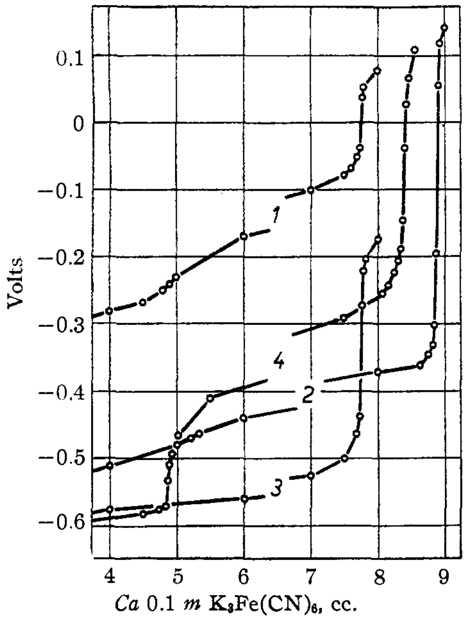

Fig. 1.—Curve 1. 10 cc. of 0.05 *m* $MnSO_4$ with 3 cc. of glycerol, 30 cc. of water and 10 cc. 50% NaOH. Inflection 9.76 cc. (calcd. 9.78). Curve 2. 10 cc. of 0.05 *m* $MnSO_4$ with 5 cc. of ethylene glycol, 30 cc. of water and 10 cc. of 50% NaOH. Inflection 10.89 cc. (calcd. 10.70). Curve 3. 20 cc. of 0.05 *m* $MnSO_4$ with 10 cc. of 10% tartaric acid, 20 cc. of water and 10 cc. of 50% NaOH. Inflection 9.76 cc. (calcd. 9.78). Curve 4. 10 cc. of 0.05 *m* $MnSO_4$ with 10 cc. of 10% tartaric acid, 5 cc. of ethylene glycol, 35 cc. of water 10 cc. of 50% NaOH. Inflection 5.35 and 10.89 cc. (calcd. 5.35 and 10.70 cc.). The curve No. 4 is shifted to the left by 0.5 cc.

By this most satisfactory method some determinations were carried out, the results of which are shown in Table I.

TABLE I

0.05 *m* $MnSO_4$, cc.	*Ca.* 0.1 *m* $K_3Fe(CN)_6$ Calcd., cc.	Used, cc.	Manganese Calcd., mg.	Found Mg.	%
5.00	2.445	2.44	13.64	13.61	99.78
10.00	4.890	4.88	27.28	27.22	99.78
15.00	7.335	7.34	40.92	40.94	100.04
20.00	9.780	9.76	54.56	54.44	99.77
25.00	12.225	12.25	68.20	68.32	100.19
30.00	14.670	14.67	81.84	81.80	99.95

It may be seen that if the correct working conditions are maintained, the method is accurate to ±0.2%.

(3) **Oxidation of Mn^{II} to Mn^{III} and Mn^{III} to Mn^{IV}.**—Combining the determinations described under (2) and (1), it is possible to carry out the oxidation of manganous salts with ferricyanide in steps. To 10 cc. of 0.05 *m* manganous sulfate were added 10 cc. of a 10% solution of tartaric acid and 5 cc. of ethylene glycol; this mixture was diluted with 25 cc. of water and, after having passed carbon dioxide through it, 10 cc. of a 50% solution of sodium hydroxide was added and the titration carried out with about 0.1 *m* potassium ferricyanide. The course of the titration, marked by two distinct maxima, is demonstrated in Curve 4, of Fig. 1. The quantity of ferricyanide used for the first maximum corresponds with the theoretical amount, while that for the second maximum is higher by 0.18 cc.

(4) **Analytical Procedure.**—From the experiments carried out so far, the following working method has been selected as most advantageous. In the described titration vessel the manganous salts—which may contain also salts of other metals, as will be shown later—are diluted with water, so that the manganese content is at the most 0.02 *m*. Then 10 cc. of a 10% solution of tartaric acid (if necessary, more) is added and a 2-cm. layer of pure benzene is poured on top. The vessel is then closed with a rubber stopper and its contents cooled to 10–12°. Next a stream of carbon dioxide is led through the solution for ten minutes, finally the sodium hydroxide solution is added until the solution is at least 1.5 to 2 normal, and at once titrated with 0.1 or 0.05 *m* potassium ferricyanide until maximum inflection. The number of cc. of 0.1 *m* potassium ferricyanide spent indicates the amount of manganese in mgmoles.

Titration of Manganese in the Presence of Other Metals.—For the determination of manganese, especially if other metals are present, the described method of oxidation in the presence of tartaric acid is preferable. The results of experiments carried out in this way are compiled in Table II. From these it may be seen that compounds of the following elements do not interfere: copper, nickel, cobalt, antimony, zinc, iron, aluminum, three- and five-valent arsenic and also phosphates and molybdates. If iron is present, it is always necessary to oxidize it first to the ferric condition; it is well to remove a large excess of iron by the Rothe method.[1] Cobaltous salts, if they are not present in predominant quantities besides small amounts of manganese do not interfere, because their inflection potential under these conditions lie about 0.3 volt higher. Chloride and nitrate ions also do not interfere.

Practical Analytical Applications.—In order to prove the applicability of the method, the manganese content was determined in (1) dialogite from Litošice, (2) in technical manganese, prepared

TABLE II

0.05 *m* $MnSO_4$ cc.	added g.	*Ca.* 0.1 *m* $K_3Fe(CN)_6$ calcd., cc.	used, cc.[a]
5.00	0.6 $FeCl_3$	2.675	2.67
5.00	1.2		2.67
10.00	0.3	5.35	5.35
20.00	.3	10.70	10.68
20.00	.9		10.72
5.00	.06 $CuSO_4$ cryst.	2.675	2.68
5.00	.12		2.67
10.00	.06	5.35	5.34
5.00	.15 $NiSO_4$ cryst.	2.675	2.67
5.00	.3		2.67
10.00	.15	5.35	5.36
5.00	.05 $CoSO_4$ cryst.	2.675	2.68
5.00	.1		2.67
10.00	.05	5.35	5.37
5.00	.1 $(NH_4)_2MO_4$ cryst.	2.675	2.67
5.00	.2		2.67
10.00	.1	5.35	5.34
5.00	.2 $ZnSO_4$ cryst.	2.675	2.67
5.00	.1		2.67
10.00	.1	5.35	5.35
5.00	.4 $Na_2NH_4PO_4$ cryst.	2.675	2.67
5.00	.8		2.67
10.00	.4	5.35	5.35
5.00	.2 $NaAsO_2$ cryst.	2.675	2.68
5.00	.1		2.67
10.00	.1	5.35	5.35
5.00	.4 $Na_2NH_4AsO_4$ cryst.	2.675	2.67
5.00	.2		2.69
10.00	.2	5.35	5.34
5.00	.4 SbOK tartrate cryst.	2.675	2.67
5.00	.2		2.67
10.00	.2	5.35	5.36

[a] Mean of three determinations.

aluminothermically, (3) in a Mn–Al alloy, (4) in a sample of specular pig iron and (5) in a sample of steel.

The general procedure throughout was to bring a suitable amount of the sample into solution by nitric acid (d. 1.4). In the mineral analysis, the insoluble remainder was removed by filtration. In the analysis of technical manganese, the silicic acid, separated during the dissolution, was in one case filtered off; in another case the manganese was titrated in the unfiltered liquid; in both instances the results were the same; the presence of silicic acid does not interfere. In the steel sample No. 34, the iron was first removed according to Rothe,[1] because the manganese content in the alloy was less than 1%. If, however, it contained more than 5% of manganese, the removal of iron was not necessary, and it was sufficient to increase the amount of tartaric acid added.

The course of the determination is in all cases quick and reliable; the results are in very good agreement with manganese contents determined by the usual methods.

The sample of dialogite from Litošice (Čs.R. consisted of larger and smaller fragments and had been analyzed by V. Veselý.[4] An average sample was pulverized, 1.2726 g. of the powder weighed out and after bringing it into solution made up with water to 200 cc. For a single determination 20 cc. was taken. The mean of three determinations gave 43.97% Mn, which agrees well with the figure given (56.75% MnO = 43.95% Mn).

The results of the other analyses are compiled in Table III.

TABLE III

	Technical Manganese Calcd.	Found	Mn-Al Alloy Calcd.	Found
Al	...	...	56.80	...
Mn	*ca.* 97	95.25	39.25	39.26
	Rest Fe + SiO_2		Rest Fe + Si	
	Specular Pig Iron No. 31		Steel No. 34	
C	4.83	...	0.12	...
Cu	0.19	...	.19	...
Mn	14.10	14.08	.48	0.479
P	0.22	...	.18	...
S	.015	...	.025	...
Si	.27	...	.08	...
Ti	.05	...	...	...

The simultaneous titration by ferricyanide of cobalt, manganese and other metals mentioned[1] above will be described in the next paper.

Summary

1. The course of oxidation of manganous salts by potassium ferricyanide was investigated in strongly basic (hydroxide) medium with additions of glycerol, mannite, ethylene glycol and tartaric acid.

2. A new, simple and quick potentiometric titration of manganese with ferricyanide is described.

3. No influence upon the determination is shown by compounds of Cu^{II}, Zn^{II}, Ni^{II}, Co^{II}, As^{III}, As^{V}, Sb^{V}, Fe^{III}, Al^{III}, phosphates and molybdates.

4. The applicability of this method was tested by the analysis of various alloys and of the mineral dialogite.

PRAGUE, CZECHOSLOVAKIA RECEIVED APRIL 26, 1935

---

[4] Veselý. *Rozp. České Akademie*, tř. II. XXXI. No. 9 (1922). Its composition was given as follows: MnO, 56.75%; FeO, 3.60%; CaO, 2.13%; CO_2, 34.83%; and insoluble remainder, 2.91%.