[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

# THE TITRATION OF SOLUTIONS OF PERMANGANATE AND SODIUM ARSENITE

By William T. Hall and Carl E. Carlson

Received March 19, 1923

The manganese content of iron, steel and other alloys is frequently determined by oxidation to permanganate followed by titration with sodium arsenite solution.[1] It has often been assumed[2] that the titration reaction may be expressed as follows: $2MnO_4^- + 5HAsO_3^{--} + 6H^+ \longrightarrow 2Mn^{++} + 5HAsO_4^{--} + 3H_2O$. This equation assumes oxidation of the tervalent arsenic to the quinquivalent condition and reduction of the permanganate to manganous salt; each atom of maganese furnishes 5 oxidation equivalents and each atom of arsenic requires 2.

In fact, Bussy[3] and Moser and Perjatel[4] have titrated arsenite with permanganate in hydrochloric acid solution and found the above reaction correct. Vanino,[5] Kuhling,[6] and Klemenc[7] have pointed out, however, that the oxidation of the arsenite toward the end of the titration is very slow. The first two have established the fact that the rate of reaction is accelerated by heating the solution nearly to boiling. Lang[8] has recommended the addition of a little chloride or bromide to hasten the reaction.

Pean de St. Gilles[9] carrying out the same titration under different conditions obtained a brown precipitate containing manganese probably in the quadrivalent state. Lenssen,[10] Kessler,[11] and Brauner[12] titrated an arsenite solution with permanganate and found the oxidation of the arsenite complete but the permanganate only reduced to the tervalent manganic condition. This corresponds to a loss by each atom of manganese of 4 oxidation equivalents. On the other hand, Waitz[13] found that in a sulfuric acid solution the permanganate appeared to lose 4.5 oxidation equivalents.

In the reverse titration of permanganate with arsenite solution Kessler obtained an olive-green solution and each molecule of permanganate appeared to lose 3.5 oxidation equivalents. In the analysis of steel by the Volhard method Deiss[14] found permanganate is reduced to a state intermediate between $Mn_2O_3$ and $MnO_2$. Recently Bose[15] in his

---

[1] Compare *Proc. Am. Soc. Test. Materials*, **1915**, 210.

[2] Hall and Williams, "The Examination of Iron, Steel and Brass," McGraw-Hill Book Co., **1921**.

[3] Bussy, *Compt. rend.*, **24**, 774 (1847).

[4] Moser and Perjatel, *Monatsh.*, **33**, 751 (1912).

[5] Vanino, *Z. anal. Chem.*, **34**, 426 (1895).

[6] Kuhling, *Ber.*, **34**, 404 (1901).

[7] Klemenc, *Z. anal. Chem.*, **61**, 448 (1922).

[8] Lang, *Chem.-Ztg. Rep.*, **48** (1905).

[9] de St. Gilles, *Ann. chim. phys.*, **55**, 385 (1859).

[10] Lenssen, *J. prakt. Chem.*, **78**, 197 (1859).

[11] Kessler, *Pogg. Ann.*, **118**, 17 (1863).

[12] Brauner, *Z. anal. Chem.*, **55**, 242 (1916).

[13] Waitz, *ibid.*, **10**, 174 (1871).

[14] Deiss, *Chem.-Ztg.*, **34**, 237 (1910).

[15] Bose, *Chem. News*, **117**, 379 (1918).

study of the reaction found the manganese reduced only to an average valence of 3.3, and Geloso[16] titrated permanganate in a sulfuric acid solution with arsenite and obtained the same result. He also worked to an emerald-green end-point and determined the acidity limits within which this end-point could be obtained. He found that sulfates of zinc, nickel, aluminum, magnesium and potassium had no effect upon this end-point, but those of manganese and silver did.

In order to overcome the slow rate of reaction between permanganate and arsenite, to eliminate a colored precipitate or solution which obscures the end-point and to complete the reduction of the manganese to the manganous state, several indirect titrations have been proposed. These depend on adding an excess of permanganate and titrating the excess with some reducing agent. For a reducing agent Pean de St. Gilles used a ferrous salt, Vanino and Kano[17] hydrogen peroxide, and Brauner and Klemenc oxalic acid.

This review of the literature on the titration of sodium arsenite and permanganate solutions shows that it is possible under certain conditions to make the reaction take place according to the above equation, but the conditions are certainly different from those that prevail in an ordinary steel analysis. The accelerating effect of an excess of acid might be predicted from the above equation on the basis of the mass-action principle. On the other hand, experience with the iodimetric titration of arsenic indicates that in neutral or alkaline solutions the arsenate anion is more stable than the arsenite anion, but in strongly acid solutions the tervalent arsenic cation appears to be formed easily by reduction of the arsenate anion. Apparently an excess of acid favors the reduction of the manganese to the manganous condition more than it hampers the oxidation of the arsenic, and hydrochloric acid favors the reduction of tervalent and quadrivalent manganese more than sulfuric acid does. The retardation of the reaction in the presence of considerable acid must be due to the difficulty of oxidizing the arsenite in the presence of much acid.

## Experimental Part

Inasmuch as most of the previous work has been with solutions containing sulfuric or hydrochloric acid and since in steel analysis nitric acid is most commonly used, it was of interest to study the reaction under conditions more nearly approximating those of procedures in which the sodium arsenite titration has been recommended for titrating the permanganate formed from the manganese in a sample of steel. The problem was first attacked by two students in quantitative analysis who had not had previous experience with the titration and who had practically no knowledge of the literature on this titration.

Mr. A. Cohen prepared a 0.0222 *N* solution of sodium arsenite. Several portions of this solution were titrated under conditions similar to those obtained in the analysis of steel by the bismuthate method except that all the titrations were made in the permanganate. Upon the addition of

[16] Geloso, *Compt. rend.*, **171**, 1145 (1920).

[17] Kano, *J. Chem. Soc. Japan*, **42**, 699 (1921).

permanganate the colorless solutions became yellowish-green, turning to a clear green just before a distinct pink color was obtained by an excess of permanganate. After standing for an hour or more the titrated solutions became a muddy brown and some manganese dioxide was precipitated. The analyses indicated a reduction corresponding to the formation of the compound $Mn_2O_3.2MnO$, thus agreeing with the work of Waitz. The results varied within about 3% of the total volume of permanganate used and were not sufficiently close to justify the adoption of this titration as a standard method of procedure. Attempts to carry out the titration under the conditions which prevail in the persulfate method for determining manganese, namely, in a solution containing 1.5 *N* sulfuric acid and 0.03 *N* nitric acid, resulted in a reduction of permanganate to approximately the dioxide. Experiments were also tried to determine the effect of adding manganous sulfate solution used in the Zimmermann-Reinhardt method for titrating iron. The results were very erratic although in one case a normal reduction of the permanganate was obtained.

Mr. C. F. Schell carried out a series of experiments which are summarized in Table I. No attempt was made to duplicate the conditions prevailing

Table I

Titration of 0.1100 *N* Potassium Permanganate with 0.0673 *N* Disodium Arsenite

| | Soln. contained 100 cc. of water and | | | | |
|---|---|---|---|---|---|
| | Concd. $H_2SO_4$ Cc. | $KMnO_4$ Cc. | Temperature | Valence of Mn in reduced state | Remarks |
| 1 | 5 | 20 | cold | 3.35 | A clear green obtained with 24 cc. of $Na_2HAsO_3$ and no further change on adding 50 cc. |
| 2 | 5 | 20 | hot | 4.02 | $KMnO_4$ reduced to $MnO_2$ |
| 3 | 10 | 20 | hot | 3.6 | Acid served to retard the oxidation of the arsenic |
| 4 | 7 | 20 | hot | 3.8 | |
| 5 | 25 | 20 | cold | .. | No reduction |
| | Concd. HCl | | | | |
| 6 | 5 | 20 | hot | .. | Decomposed before adding any arsenite |
| 7 | 5 | 20 | cold | 2.94 | Upon adding an excess of arsenite the green color disappeared |
| 8 | 5 | 20 | cold | 3.15 | ...... |
| | 6 *N* acetic | | | | |
| 9 | 10 | .. | cold | .. | Soln. turned brown with 7 cc. of arsenite; no further change with 50 cc. Soln. too faintly acid |
| | Concd. $H_2SO_4$ | | | | |
| 10 | 5 | 24.62 | cold | 3.7 | Excess of arsenite titrated with $KMnO_4$ |

in steel analysis but the results show the need for carefully specifying the conditions of titration if the sodium arsenite reaction is to continue in favor as a means of determining the amount of permanganate in solution.

## Electrometric Titrations

After these preliminary experiments by Cohen and Schell the titration was studied electrometrically. Kelley and his co-workers[18] found that permanganate formed in the analysis of steel can be titrated electrometrically with mercurous nitrate solution and the reduction corresponds to the formation of $Mn_4O_7$ ($Mn_2O_3.2MnO_2$) in which the average valence of the reduced manganese is 3.5.

An arsenite solution was prepared of the concentration recommended by the American Society of Testing Materials for the routine analysis of steel. It was titrated against an iodine solution which had been standardized against potassium bromate. A permanganate solution was prepared in the usual way and standardized against sodium oxalate. The ratio between the permanganate and the arsenite solution was also checked by indirect titration with hydrogen peroxide. Table II shows the results obtained in the electrometric titration[19] when a solution of 25 cc. of permanganate and 100 cc. of nitric acid, d. 1.13, was titrated with arsenite. A tungsten electrode was substituted for the calomel, after the first few determinations, in order to eliminate any effect on the end-point due to the presence of potassium chloride.

TABLE II

ELECTROMETRIC TITRATION IN NITRIC ACID SOLUTION

| $KMnO_4$, 0.1133 *N* Arsenite, 0.09641 *N* | | | $KMnO_4$, 0.1133 *N* Arsenite, 0.09641 *N* | | |
|---|---|---|---|---|---|
| $KMnO_4$ Cc. | Arsenite Cc. | Valence of Mn in the reduced state | $KMnO_4$ Cc. | Arsenite Cc. | Valence of Mn in the reduced state |
| Calomel electrode | | | Tungsten electrode | | |
| 24.92 | 22.29 | 3.197 | 24.92 | 21.80 | 3.278 |
| 24.92 | 22.18 | 3.216 | 24.92 | 21.79 | 3.280 |
| 24.92 | 22.11 | 3.223 | 24.95 | 21.87 | 3.270 |
| 24.92 | 22.11 | 3.223 | 24.94 | 21.76 | 3.287 |
| 24.92 | 22.22 | 3.204 | 24.95 | 21.75 | 3.290 |
| | Av. | 3.213 | | Av. | 3.281 |

The next set of determinations was made with 100 cc. of sulfuric acid of various concentrations, substituted for the nitric acid.

To determine whether potassium chloride had any marked effect on the end-point a series of determinations was made by adding various amounts of potassium chloride to 100 cc. of 2.5 *N* sulfuric acid and 25 cc. of 0.1133 *N* permanganate solution and titrating with 0.09641 *N* arsenite solution. The theoretical volume of arsenite required was calculated

---

[18] Kelley, *J. Ind. Eng. Chem.*, **10**, 19 (1918).

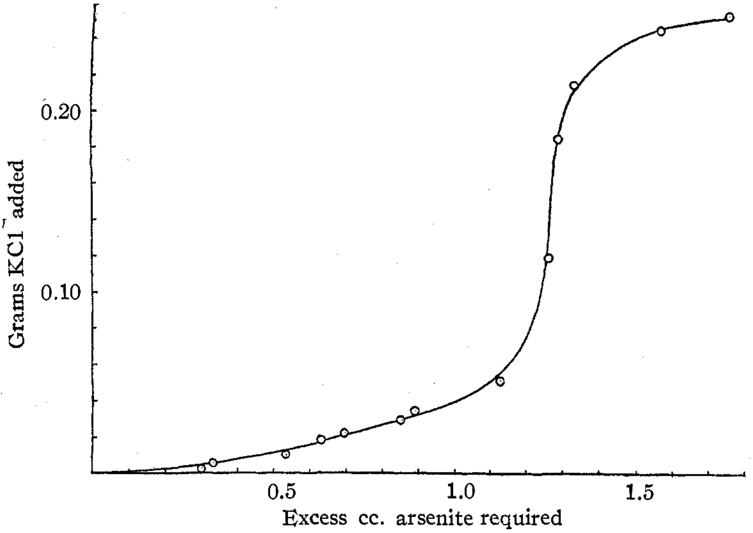
[19] A Wendt titration apparatus was used for these titrations.

TABLE III

ELECTROMETRIC TITRATION IN SULFURIC ACID SOLUTION

| KMnO$_4$, 0.1133 *N* | Arsenite, 0.09641 *N* | | | KMnO$_4$, 0.1133 *N* | Arsenite, 0.09641 *N* | | |
|---|---|---|---|---|---|---|---|
| Conc. of H$_2$SO$_4$ *N* | KMnO$_4$ Cc. | Arsenite Cc. | Valence of Mn in the reduced state | Concn. of H$_2$SO$_4$ *N* | KMnO$_4$ Cc. | Arsenite Cc. | Valence of Mn in the reduced state |
| 1 | 24.98 | 21.56 | 3.326 | 3 | 25.03 | 21.59 | 3.330 |
| 1 | 24.93 | 21.46 | 3.337 | 4 | 24.96 | 21.59 | 3.320 |
| 3 | 24.95 | 21.63 | 3.311 | 2.5 | 24.96 | 21.55 | 3.327 |
| 6 | 24.99 | 21.74 | 3.299 | 2.5 | 24.92 | 21.37 | 3.349 |
| 3 | 25.10 | 21.67 | 3.326 | 3 | 24.96 | 21.43 | 3.347 |
| 3 | 24.92 | 21.41 | 3.344 | 2.5 | 24.98 | 21.42 | 3.351 |
| | | | | | | | Av. 3.331 |

from the volume of permanganate, assuming a reduction to 3.333 as established in the above series of determinations. In the accompanying plot, the excess of arsenite in cubic centimeters is shown plotted against the weight in grams of potassium chloride added.



Finally a few titrations were made with the arsenite in 100 cc. of 2.5 *N* sulfuric acid and the permanganate as the titrating solution.

TABLE IV

REVERSE TITRATION IN SULFURIC ACID SOLUTION

| KMnO$_4$, 0.1133 *N* | Arsenite, 0.09641 *N* | | KMnO$_4$, 0.1133 *N* | Arsenite, 0.09641 *N* | |
|---|---|---|---|---|---|
| KMnO$_4$ Cc. | Arsenite Cc. | Valence of Mn in the reduced state | KMnO$_4$ Cc. | Arsenite Cc. | Valence Mn in the reduced state |
| 23.63 | 24.90 | 2.517 | 23.55 | 24.90 | 2.501 |
| 23.55 | 24.90 | 2.501 | 23.60 | 24.90 | 2.511 |
| | | | | | Av. 2.507 |

All of these electrometric titrations were made at room temperature.

## Summary

Under the conditions that usually prevail in the analysis of steel, the electrometric titration of permanganate with sodium arsenite solution causes the manganese to be reduced from a valence of 7 to an average valence of 3.3 when the bismuthate method is used. This agrees with the results obtained by Bose and by Geloso. The reaction between the permanganate may be expressed as follows: $6\ MnO_4^- + 11\ H_2AsO_3^- + 15\ H^+ \longrightarrow 2\ Mn^{++++} + 4\ Mn^{+++} + 11\ HAsO_4^{--} + 13\ H_2O$. The reduced condition corresponds to the oxide $Mn_3O_5$ but it is improbable that such an oxide actually exists. The color of the solution indicates the presence of tervalent manganese and the fact that manganese dioxide often separates on standing shows that the quadrivalent manganese readily assumes the condition of colloidal dioxide and finally forms the gel. Probably this reaction takes place: $2\ Mn^{++++} + 4\ Mn^{+++} + 8\ H_2O \longrightarrow 2\ Mn^{++} + 4\ MnO_2 + 16\ H^+$. The fact that halide causes a more complete reduction of the manganese is in accord with the usual behavior of halogen hydride in permanganate titrations. It prevents the formation of colloidal dioxide and keeps the manganese in a more reactive condition.

The electrometric titrations show that when arsenite is titrated with permanganate in 2.5 *N* sulfuric acid solution the manganese is reduced to an average valence of 2.5 just as Waitz found more than 50 years ago. $4\ MnO_4^- + 9\ HAsO_3^{--} + 14\ H^+ \longrightarrow 2\ Mn^{++} + 2\ Mn^{+++} + 9\ HAsO_4^{--} + 7\ H_2O$. Whenever the reaction between permanganate and arsenite is used in practice to determine either manganese or arsenic it is important to pay attention to such details as temperature, acid concentration and presence of halide or manganous salt and to standardize the solutions under exactly the same conditions that prevail in the analysis.

CAMBRIDGE 39, MASSACHUSETTS