[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MAINE]

THE ELECTROMETRIC TITRATION OF MANGANESE BY THE VOLHARD METHOD[1]

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The Volhard method is generally recognized as one of the best of the volumetric methods for the determination of considerable amounts of manganese, the chief objection to its use being the difficulty in recognizing the end-point in the presence of the heavy brown precipitate which forms during the titration. An electrometric method of determining the end-point would seem, therefore, to be particularly desirable in this case.

Several attempts have been made in this Laboratory[2] to apply the electrometric method to this titration, using the ordinary potentiometer system with calomel–platinum electrodes and also using the polarized electrode system described by Willard and Fenwick.[3] Neither of these methods gave satisfactory results. A break was obtained near the end-point but it was uncertain and irregular. Müller and Wähle,[4] using the ordinary potentiometer system, state that about seven minutes is required to attain constant potential when near the end-point. The method of differential titration described by Cox[5] and modified by MacInnes and Jones[6] was also tried but without satisfactory results, due probably to the slowness with which constant potential is attained. Finally, the method described by Foulk and Bawden,[7] and called by them the "dead stop end-point" was tried and, after some modification, was found to give satisfactory results.

Discussion

In the dead stop end-point as described by Foulk and Bawden, two platinum electrodes were used in the solution to be titrated and a very small potential was applied to the electrodes, a potential so small that the back electromotive force of polarization balanced it and no current flowed, as shown by the zero deflection of a galvanometer in the circuit. At the end-point of the titration both electrodes were depolarized and a permanent galvanometer deflection was obtained. Assuming the polarization to be due to oxygen at the anode and hydrogen at the cathode, it is evident that in order to obtain a permanent galvanometer deflection the

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[1] A considerable part of the preliminary work on this method was done by M. H. Clapp as a part of his Senior Thesis, 1927.

[2] Senior Theses by A. M. Varney, 1921, and E. E. Lineken, 1923.

[3] Willard and Fenwick, THIS JOURNAL, **44**, 2504 (1922).

[4] Müller and Wähle, *Z. anorg. allgem. Chem.*, **129**, 33 (1923).

[5] Cox, THIS JOURNAL, **47**, 2138 (1925).

[6] MacInnes and Jones, *ibid.*, **48**, 2831 (1926).

[7] Foulk and Bawden, *ibid.*, **48**, 2045 (1926).

anode must be depolarized by some suitable reducing agent and the cathode by some suitable oxidizing agent.

Now in the Volhard titration of manganese, a practically neutral solution of a manganous salt is being titrated with permanganate and accordingly the cathode will become depolarized as soon as a slight excess of permanganate has been added to the solution. No satisfactory means of depolarizing a platinum anode in this solution could be devised, but if the platinum is replaced by silver and a trace of chloride ion is added to the solution, a permanently depolarized anode is obtained and the flow of current through the solution and consequent galvanometer deflection is controlled wholly by the polarization or depolarization of the cathode. Furthermore, when a silver anode is substituted for platinum, a potential is developed between the two electrodes and no outside source of current is required.

Experimental Method

The apparatus required is very simple; the titrations may be made in a 400-cc. beaker, a short piece of platinum wire being used as the cathode and a piece of silver wire as the anode. The electrodes are connected directly to a galvanometer. A good mechanical stirring device is also essential and it is desirable to have the apparatus so arranged that the beaker may be heated during titration either by a small hot-plate or directly by a burner.

The solutions are prepared for titration in the usual way with the addition of 2 or 3 drops of 6 N hydrochloric acid to furnish the necessary chloride ion. As the permanganate is added the galvanometer needle fluctuates violently but no permanent deflection is obtained and if the addition of permanganate is stopped for a short time the needle returns slowly to zero. As the end-point is approached, the needle returns more and more slowly toward zero, and at the end-point a full scale deflection is obtained which remains unchanged for a considerable time.

The temporary depolarization of the cathode before the end-point is reached may be due in part to deposition on the cathode of finely divided zinc manganite, which acts as a depolarizer and produces a galvanometer deflection which may be mistaken for the true end-point unless the titration is conducted with due care. The last few drops of permanganate should be added one at a time, waiting after each drop until the galvanometer needle begins to return toward the zero point. The final drop produces a full scale deflection which persists for a considerable time, the exact time depending on the sensitiveness of the galvanometer and the surface area of the cathode. In case of doubt, the end-point may be checked by filtering a little of the solution and noting the color. With the proper combination of galvanometer and electrodes, a definite electrometric end-point may be obtained with a very slight excess of permanganate, giving an almost imperceptible pink color to the solution.

The following table shows the results actually obtained in two series of nine consecutive titrations. The test solutions were made by reducing approximately 0.1 N permanganate with hydrogen peroxide in sulfuric acid solution. Three drops of 6 N hydrochloric acid were then added and the solution was made just neutral to methyl orange with ammonia. Five grams of zinc sulfate was added, the solution was diluted to about 300 cc., heated to 90° and titrated as previously described with the approximately 0.1 N permanganate. The first column of the table shows the volume of permanganate reduced; the second column gives the theoretical volume of permanganate required for titration, which is two-thirds of the volume reduced plus a 0.05 cc. blank for the zinc sulfate used; the third and fourth columns give the volume of permanganate actually used and the titration error.

Table I

Results of Titrations

$KMnO_4$ reduced, cc.	$KMnO_4$ required, cc.		Error	$KMnO_4$ reduced, cc.	$KMnO_4$ required, cc.		Error
	Theoretical	Actual			Theoretical	Actual	
16.37	10.97	11.03	+0.06	18.10	12.11	12.11	0.00
16.97	11.37	11.39	+ .02	18.24	12.21	12.25	+ .04
16.05	10.75	10.83	+ .08	18.20	12.19	12.19	.00
25.48	17.03	17.03	.00	28.42	18.99	18.98	− .01
26.29	17.57	17.57	.00	28.02	18.73	18.68	− .05
28.03	18.68	18.71	+ .03	28.52	19.07	19.03	− .04
32.07	21.43	21.40	− .03	47.77	31.89	31.86	− .03
32.48	21.71	21.71	.00	42.59	28.45	28.40	− .03
34.78	23.18	23.22	+ .04	36.08	24.11	24.08	− .03

The galvanometer used in most of this work was a pointer type instrument with a rated sensitivity of one scale division per microampere and a resistance of 250 ohms. With this galvanometer connected directly to the electrodes, and using 3 cm. of platinum wire (about 0.05 cm. in diameter) as a cathode, the end-point was shown by a full-scale deflection which remained unchanged for a full minute. With a galvanometer of twice this sensitivity and 1000 ohms' resistance, about a minute and a half had to be allowed at the end-point when the same electrodes were used. With a given galvanometer, the time required for the end-point probably can be regulated to a considerable extent by varying the area of the cathode.

The size and nature of the silver anode seem to be immaterial. Ordinary silver wire was used most of the time, but both platinum wire and platinum foil plated with silver were used also with no apparent difference in result. The silver plate, however, is gradually converted into silver chloride and requires occasional renewal.

It seems to be necessary to clean the electrodes frequently, possibly after each titration. The adhering zinc manganite may be removed easily by dipping the electrodes in acidified hydrogen peroxide solution and the film of silver chloride can be dissolved from the anode with ammonia.

Summary

A modification of the "dead stop end-point" method of electrometric titration has been described, and it has been shown that this method may be applied satisfactorily in the Volhard titration of manganese.

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