CXXXVII.—*Estimation of Iron by Permanganate in the Presence of Hydrogen Chloride.*

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OWING to the ease with which ferrous iron undergoes quantitative oxidation in contact with potassium permanganate, it is unfortunate that the reaction should yield inaccurate results in the presence of hydrogen chloride.

T. W. Harrison and F. M. Perkin (*Analyst*, 1908, **33**, 43) have shown that, even when the concentration of the hydrogen chloride is as low as $N/25$, the titrations are not accurate to within 2 per cent. W. Colet Birch (*Chem. News*, 1909, **99**, 61) has recently studied the modification detailed by Loewenthal and Lenssen (*Zeitsch. anal. Chem.*, 1861, **1**, 329) and Fresenius (*ibid.*, p. 361), but finds that it only gives approximate results.

It appeared to the present author, however, that the results obtained by different investigators did not agree sufficiently well amongst themselves, indicating that some constant source of error had been overlooked, and it was with the object of discovering this that the present research was undertaken.

Experiments were performed with $N/10$ -solutions of both specially pure and commercial potassium permanganate, but the results were

always the same. As the commercial salt is generally used in analytical practice, the results recorded in this paper are such as were obtained by using the latter solution, except where the contrary is stated. The ferrous iron solution was obtained by dissolving ferrous sulphate in water with the addition of just sufficient sulphuric acid to prevent the precipitation of basic salt. T. Warynski (*Ann. Chim. anal.*, 1909, **14**, 45) has shown that such solutions are very stable in contact with air. It was therefore unnecessary to use ferrous ammonium sulphate, as did Harrison and Perkin, and this is a decided advantage, since the presence of ammonium sulphate renders the titrations less accurate, as Birch has recently shown.

1. Velocity of Titration.

It was important to discover if the rate at which the permanganate is added to the ferrous solution affects the value of the titration. In each of the following three series the volumes titrated and the amounts of ferrous sulphate and hydrogen chloride were constant throughout, but the rapidity with which the titrations were effected was varied. A drop of manganese sulphate solution was added in each case before the titration was commenced.

Series I.		Series II.		Series III.	
50 c.c. 2 <i>m</i> *HCl.		50 c.c. <i>m</i> HCl.		50 c.c. <i>m</i> /2HCl.	
5 c.c. FeSO ₄ .		5 c.c. FeSO ₄ .		5 c.c. FeSO ₄ .	
Time of titration.	KMnO ₄ .	Time of titration.	KMnO ₄ .	Time of titration.	KMnO ₄ .
secs.	c.c.	secs.	c.c.	secs.	c.c.
15	25·35	10	24·90	10	24·33
25	24·50	17	24·72	25	23·85
45	24·00	35	24·16	50	23·80
110	23·85	70	23·80	160	23·75
190	23·84	220	23·67	—	—
Theoretical value 23·52		Theoretical value 23·52		Theoretical value 23·52	

* *m* signifies the molecular weight in grams per litre of solution.

The permanganate was run out of the burette at a uniform rate throughout each individual titration, and the flask was gently shaken all the time. The times of titration given above are therefore a direct measure of the shaking to which the ferrous sulphate solution was subjected.

Reference to the curve in which these results are given shows that :

(1) The error decreases as the time of titration increases, until the latter reaches about 100 seconds, after which the effect is negligible.*

* Since the above was written, Mr. G. Cecil Jones, F.I.C., has kindly drawn my attention to the fact that Skrabal was, in 1903, aware of the fact that greater accuracy could be obtained by adding the permanganate slowly (*Zeitsch. anal. Chem.*, 1903, **42**, 373).

(2) The error increases with the concentration of the hydrogen chloride, but the difference is less marked when the time of titration exceeds 100 seconds.

It is clear, therefore, that if comparable results are to be obtained with different mixtures, the times of titration should not be less than about 100 seconds. The titrations recorded in the sequel have therefore been carried out with this velocity unless otherwise stated.

It was now necessary to determine if variation in the rate of

addition of the first and last few c.c. of permanganate would appreciably affect the value of the titration. The results obtained are given in series IV.

Series IV.

A. 25 c.c. 2mHCl. 5 c.c. FeSO₄.

	Commercial KMnO ₄ , c.c.	Error, c.c.
(1) The whole titration completed in 15 seconds	24.40	1.17
(2) 22 c.c. KMnO ₄ added in 7 seconds and the titration completed slowly.....	23.50	0.27
(3) Ditto, after an interval of 60 seconds	23.48	0.25
(4) Ditto, " " 300 "	23.48	0.25
(5) The whole titration effected slowly (100 seconds)	23.40	0.17
(6) Theoretical value	23.23	—

B. 50 c.c. $m\text{HCl}$. 25 c.c. FeSO_4 .

	Pure KMnO_4 , c.c.	Error, c.c.
(1) The whole titration completed in 15 seconds	24.40	1.60
(2) 21 c.c. KMnO_4 added in 7 seconds and the titration completed slowly.....	23.10	0.30
(3) Ditto, after an interval of 60 seconds	23.02	0.22
(4) Ditto, ,, ,, 300 seconds	23.05	0.25
(5) The whole titration effected slowly (100 seconds)	22.92	0.12
(6) Theoretical value	22.80	—

From the above it is clear that it is the rate at which the last few drops of permanganate are added to the ferrous solution which affects the value of the titration most. This is readily explained on the assumption that the reduction of the permanganate takes place in two stages. First, a partial reduction, resulting in the oxidation of some of the iron and the formation of an unstable perchloride of manganese. The latter substance now oxidises the ferrous iron according to the equation :

until equilibrium is established. If this latter reaction proceeds comparatively slowly, it is clear that when the last few drops of permanganate are added rapidly, excess must be taken before all the ferrous iron becomes oxidised and the usual pink colour indicative of the end-point can appear. On the other hand, prolongation of the time of titration beyond that required for equilibrium to be attained cannot affect the final result, as is well shown by titrations 2, 3, and 4 in series IV (A and B), and by the curve embodying the results of series I, II, and III. We may therefore hope to obtain accurate titrations in the presence of any substance which can cause equilibrium to be attained when the mass of the manganese perchloride is negligibly small, always provided that the rate of titration is sufficiently slow. As will be seen later, such a substance is manganous sulphate.

2. The Effect of Dilution.

As is evident from the results given in series V and VI, dilution slightly increases the error of titration. The end-point, however, becomes clearer, which is a decided advantage when working by gaslight.

Series V.

25 c.c. $m\text{HCl}$. 5 c.c. FeSO_4 .

Total volume titrated, c.c.	Water, c.c.	KMnO_4 , c.c.
30	0	23.73
80	50	23.78
130	100	23.90
180	150	23.98
Theoretical value		23.52

Series VI.

10 c.c. $2m\text{HCl}$. 5 c.c. FeSO_4 .

Total volume titrated, c.c.	Water, c.c.	KMnO_4 , c.c.
15	0	23.70
65	50	23.75
115	100	23.78
165	150	23.82
Theoretical value		23.48

These results are in agreement with those obtained by Birch (*loc. cit.*) under different conditions.

3. Action of Sulphuric Acid.

The results given in series VII show that the presence of small quantities of sulphuric acid tends to decrease the error of titration. This is in harmony with the results obtained by Skrabal, Kessler, and others. When present in large excess, however, the action of the acid appears to be less favourable.

Series VII.

A. With Commercial KMnO_4 .

Total volume titrated, c.c.	Conc. of HCl.	Conc. of H_2SO_4 .	Titre in c.c. KMnO_4 .	Correct titre, c.c.	Error, c.c.
65	m/3	—	23·80	23·48	0·32
65	m/3	3m	23·75	23·48	0·27
115	m/6	—	23·80	23·48	0·32
115	m/6	4m	23·90	23·48	0·42
80	m/3	—	23·25	23·00	0·25
80	m/3	2·5m	23·25	23·00	0·25
130	m/5	—	23·33	23·00	0·33
130	m/5	3m	23·52	23·00	0·52

B. With Pure KMnO_4 .

125	m/2·5	—	23·16	22·45	0·71
125	m/2·5	1·6m	23·12	22·45	0·67
225	m/4·5	—	23·23	22·45	0·78
225	m/4·5	1·8m	23·16	22·45	0·71
325	m/6·5	—	23·30	22·45	0·85
325	m/6·5	2·5m	23·38	22·45	0·93

4. Effect of Age of Permanganate Solution.

The permanganate solution was prepared by dissolving the requisite amount of ordinary potassium permanganate in cold water, as is usual in works. The solution was kept in a glass-stoppered bottle exposed to the diffused light of the laboratory. If it had been pure it would have remained unaltered for many months, as has been shown by Gardner and North (*J. Soc. Chem. Ind.*, 1904, **23**, 599), and more recently by Collitt (*Pharm. J.*, 1908, **27**, 724). The present author observed some years ago, however, that permanganate which had not been specially purified gave uncertain results in certain cases after keeping for two or three days (*Trans.*, 1905, **87**, 1369). It was important, therefore, to discover if the reaction under consideration is affected by the age of the permanganate solution, as it is inconvenient to make up a fresh one every time a titration is to be made.

In series VIII and IX are given the results of titrating 5 c.c. of ferrous sulphate solution with fresh and old permanganate solutions respectively in the presence of varying quantities of hydrogen-chloride.

Series VIII.

HCl, c.c.	KMnO ₄ (fresh), c.c.	Error c.c.
0	23.48	0.00
10 (2 <i>m</i>)	23.70	0.22
25 (2 <i>m</i>)	23.90	0.42
50 (<i>m</i>)	23.90	0.42
50 (2 <i>m</i>)	23.93	0.45

Series IX.

HCl, c.c.	KMnO ₄ (7 days old), c.c.	Error, c.c.
0	23.23	0.00
10 (2 <i>m</i>)	23.48	0.25
25 (2 <i>m</i>)	23.54	0.31
50 (<i>m</i>)	23.50	0.27
50 (2 <i>m</i>)	23.70	0.47

From the above results it is clear that if the permanganate is kept free from organic matter there is little to choose between a fresh solution and one several days old.

5. Action of Manganous Sulphate.

Attention has been repeatedly called to the fact that addition of manganous sulphate to the ferrous salt to be titrated in the presence of hydrogen chloride decreases the error considerably (see Kessler, *Zeitsch. anal. Chem.*, 1863, **1**, 329; Zimmerman, *Ber.*, 1881, **14**, 779; Hauffe, *Chem. Zeit.*, 1897, **21**, 894; Willenz, *Chem. Zentr.*, 1899, **i**, 638; Baxter and Frevert, *Amer. Chem. J.*, 1905, **34**, 109; Harrison and Perkin, *loc. cit.*; Birch, *loc. cit.*). Opinion, however, seems to be divided as to the amount of the salt which should be taken. Treadwell (*Anal. Chem.*, 1st Ed., **ii**, 483) suggests that the amount should not exceed that of the iron salt in solution. On the other hand, A. Müller (*Stahl u. Eisen*, 1906, **26**, 1477) employs larger quantities. Harrison and Perkin state that variation in the amount of manganous sulphate does not affect the titration materially when not less than one gram is taken. Their own results, however, do not seem to justify this statement (*loc. cit.*, p. 44), and by a curious oversight, neither the concentration of the iron solution nor that of the permanganate is given.*

The great difficulty experienced in titrating solutions containing considerable quantities of manganous sulphate is that of determining the end-point, for in concentrated solution, in the presence of hydrogen chloride, the usual pink tint caused by the permanganate is apt to be fugitive, producing a brown coloration. This may be avoided by diluting largely, but, as is shown above, dilution tends to increase the error.

* In a private communication Dr. Perkin has kindly informed me that he used *N*/10-permanganate solution.

In series X are given the results of experiments performed in order to determine the effect of increasing the concentration of the manganous sulphate. The salt used was analysed, found to be free from iron, and to be correctly represented by the formula $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$.

Series X.

Total volume titrated, 65 c.c. Conc. of HCl, $m/3$.

Weight of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. grams.	KMnO_4 . c.c.	Error, c.c.	Remarks.
0.0	23.75	0.27	End point clear
0.1	23.60	0.12	" "
0.25	23.60	0.12	" "
0.5	23.52	0.04	" "
1.0	23.50	0.02	" "
2.0	23.48	0.00	Fugitive end point
3.0	23.48	0.00	End point momentary
5.0	—	—	No clear end point

Theoretical value = 23.48 c.c.

These results show that when not less than one gram of manganese sulphate is present the titrations under the special conditions of the above experiments are accurate.

6. *Correct Titrations.*

It is clear from the above that we may expect to obtain accurate estimations of ferrous iron by titration with potassium permanganate in the presence of hydrogen chloride provided that :

1. The titration is effected slowly and with constant shaking.
2. A sufficient quantity of manganous sulphate is present.
3. The volume of the ferrous solution is sufficiently large to ensure a good end-point, but not so great as to reduce the accuracy of the titration.

That our expectations may be realised is shown by the results detailed in series XI.

Series XI.

Total volume titrated, 200 c.c.

Weight of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. grams.	Conc. of HCl.	KMnO_4 required, c.c.	Theoretical value, c.c.	Error, c.c.
3.0	$m/4$	27.50	27.47	0.03
2.0	$m/4$	25.38	25.34	0.04
2.0	$m/4$	25.36	25.32	0.04
3.0	$m/5$	27.50	27.47	0.03
2.0	$m/5$	25.38	25.34	0.04
3.0	$m/8$	27.48	27.47	0.01
2.0	$m/8$	25.40	25.34	0.06

In order to ensure thorough mixing of the permanganate with the ferrous solution, the orifice of the burette was made smaller, so that thirty seconds were required to deliver 30 c.c. of liquid when the tap was full on. The permanganate was added at such a rate that the individual drops could be distinguished as they fell, and the ferrous solution was well shaken all the time. As the end point was approached, the permanganate was added very slowly, the colour of each drop disappearing before the next drop was added. There was no odour of chlorine perceptible at the end of the titrations.

It will be evident that, when the above precautions are rigidly observed, fairly accurate estimations of ferrous iron may be made in the presence of any concentration of hydrogen chloride not exceeding $m/4$ by titration with $N/10$ potassium permanganate, provided the volume titrated does not exceed 200 c.c. and the weight of manganous sulphate is not less than 2 grams. The results were found to be slightly less accurate if the concentration of the hydrogen chloride exceeded $m/4$ and the weight of manganous sulphate was appreciably less than 2 grams. The results given above agree well within the usual range of experimental error. The end-points were just as well defined as when the pure permanganate solution was employed.

The research is being continued with the object of determining the most suitable concentrations of permanganate and manganous sulphate for the estimation of varying quantities of ferrous salts under different conditions of acidity.

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