TITRATION OF IRON BY POTASSIUM PERMANGANATE

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THE TITRATION OF IRON BY POTASSIUM PERMANGANATE.

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INTRODUCTION.

It is well known that ferrous salts cannot be oxidized quantitatively by potassium permanganate in the presence of hydrochloric acid without using one of the several "guard solutions" recommended for that purpose. The reaction with hydrochloric acid and the mechanism of the protecting influence of the "guard solution" are in general not understood. Ostwald (Foundations of Analytical Chemistry) says: "the solution must be acid with sulphuric acid but not with hydrochloric acid, since permanganate oxidizes the latter in the presence of iron salts. It is a catalytic reaction which goes on here, but very little is known yet of the laws which regulate it". On account of the desirability of titrating an iron solution in the presence of hydrochloric acid from the viewpoint of the technical analyst, Asso. Professor B. B. Freud is engaged in studying the whole problem. As a part of this larger problem, I have titrated

ferrous salts with permanganate in the presence of sulphuric acid and hydrochloric acid, with wide variations in hydrogen ion and chlorine ion concentration. This work is necessary because of serious discrepancies in the literature. Qualitatively the disturbing influence of chlorine ions has long been known, but its exact quantitative influence has not been determined.

The object of this work was to get definite and reliable data, and the plan followed was:-

(1) To titrate ferrous ions of a definite concentration in the presence of hydrogen and sulphate ions of definite but varying concentrations. The maximum concentration of sulphuric acid used was determined by the solubility of ferrous sulphate in aqueous sulphuric acid.

(2) To titrate the same ferrous ion concentration in the presence of hydrogen and chlorine ions of the same ion concentrations as were employed before. The maximum hydrochloric acid concentration used was determined by the ability to get a definite end point.

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THEORETICAL.

If hydrochloric acid is present in the solution when ferrous iron is titrated with potassium permanganate it is known that the results obtained are inaccurate. The reason for this discrepancy is usually attributed to the reaction between hydrochloric acid and potassium permanganate according to the following equation:

$$10\ HCl + Mn_2O_7 \rightarrow 2MnO + 5H_2O + 5Cl_2$$

If this reaction is regular and if discrepancies are due merely to liberation of chlorine, then the amount of chlorine evolved should be equivalent in oxidizing power to the excess of permanganate. W. C. Birch (Chemical News, Vol.99) measured this excess and found that the amount of permanganate was less than that calculated from the above equation. This points to another relation beside that which liberates chlorine.

Birch advances the theory that the reaction between hydrochloric acid and potassium permanganate is as follows:

$$Mn_2O_7 + 14\ HCl \rightarrow 2\ Mn\ Cl_3 + 7H_2O + 4Cl_2$$

This would explain the suppression of chlorine when manganous salts are added, as Rice (Journal Chemical Society 1899) has shown that $MnCl_2$ and free chlorine when sealed up in a tube, react slowly to give $MnCl_3$. Pickering (Journal Chemical Society 1879) also has shown that the amount of manganic salt produced when MnO_2 dissolves in hydrochloric acid was increased by the presence of $MnCl_2$.

The use of manganous salts for this purpose was first proposed by C. Zimmerman (Ber. d. Chem. Ges. 1884, 15).

EXPERIMENTAL.

The ferrous salt used was ferrous sulphate ($FeSO_4 \cdot 7H_2O$), Baker's Analyzed Chemicals. Its analysis by the manufacturer showed a trace of ferric sulphate. Although ferrous ammonium sulphate is much more stable than ferrous sulphate, it was thought desirable to use ferrous sulphate, as the solution of ammonium sulphate would introduce NH_4 ions and complicate the work.

The potassium permanganate solution used was approximately tenth normal. It was standardized against sodium oxalate obtained from the Bureau of Standards. The method was as follows: (N.S.McBride, Journal American Society Vol.34.)

In a 400cc. beaker, 0.25 gram of sodium oxalate was dissolved in 200cc. hot water (80-90°C.) and 10cc. (1:1) sulphuric acid added. The solution was titrated at once. The permanganate was added slowly, not more rapidly than 10 to 15 cc. per minute, and the last 0.5 to 1.0cc. were added dropwise, allowing each drop to be discolorized before the next was introduced. The excess of permanganate used to cause an end point color was estimated by matching the color in another beaker containing the same amount of acid and hot water.

The sulphuric acid used was chemically pure sulphuric acid, sp.gr. 1.83, manufactured by the Grasselli Chemical Co. The hydrochloric acid was chemically pure hydrochloric acid, sp.gr. 1.20 manufactured by the same firm.

I. Solubility of Ferrous Sulphate in Sulphuric Acid.

It was necessary to determine the solubility of ferrous sulphate in aqueous sulphuric acid solution in order to titrate as concentrated sulphuric acid solution as possible. One gram of ferrous sulphate was dissolved in increasing amounts of water and concentrated sulphuric acid run in from a burette until precipitation of anhydrous ferrous sulphate occured.

TABLE I.

Water.	Sulphuric acid to precipitate.
5.0	3.50
10.0	9.15
15.0	15.05
20.0	24.15
25.0	50.00
30.0	63.50
40.0	200. (no precipitation)

These values were plotted and from the curve it was decided to start titrating with a maximum concentration of 160cc. sulphuric acid and 40cc. water.

II. Titration with Sulphuric Acid.

One gram of ferrous sulphate was used for

each titration. The procedure was as follows: The ferrous sulphate was weighed into a 400cc. beaker and the water added from pipettes. When the salt was dissolved, sulphuric acid, sp.gr. 1.83, was added from pipettes. In every case the total bulk of solution was 200cc. The solution was cooled in a bath of running water to 20°C. It was then titrated with Xtenth normal permanganate.

TABLE II.

No.	cc H_2O	cc H_2SO_4	Normality.	cc XN $KMnO_4$
1	40	160	27.0	37.50
2	40	160	27.0	37.80
3	40	160	27.0	37.55
4	40	160	27.0	37.50
5	45	155	26.2	37.65
6	45	155	26.2	37.30
7	45	155	26.2	37.27
8	45	155	26.2	37.30
9	50	150	25.3	37.32
10	50	150	25.3	37.46
11	50	150	25.3	37.45
12	50	150	25.3	37.43
13	55	145	24.5	37.05
14	55	145	24.5	37.08
15	55	145	24.5	37.05
16	60	140	23.6	37.35
17	60	140	23.6	37.30
18	60	140	23.6	37.30
19	65	135	22.8	37.30
20	65	135	22.8	37.30
21	65	135	22.8	37.30
22	70	130	21.9	37.18

TABLE II CONT'D

No.	ccH_2O	cc H_2SO_4	Normality	cc XN $KMnO_4$
23	70	130	21.9	37.35
24	70	130	21.9	37.36
25	70	130	21.9	37.38
26	75	125	21.1	37.30(?)
27	75	125	21.1	36.80
28	75	125	21.1	36.75
29	75	125	21.1	36.73
30	75	125	21.1	36.72
31	80	120	20.3	36.80
32	80	120	20.3	36.65
33	80	120	20.3	36.80
34	80	120	20.3	36.81
35	85	115	19.4	36.40
36	85	115	19.4	36.43
37	85	115	19.4	36.42
38	90	110	18.6	36.50
39	90	110	18.6	36.50
40	90	110	18.6	36.50
41	95	105	17.75	36.64
42	95	105	17.75	36.70
43	95	105	17.75	36.70
44	100	100	16.9	36.82
45	100	100	16.9	36.85
46	100	100	16.9	36.85
47	100	100	16.9	36.88
48	105	95	16.5	37.10
49	105	95	16.5	36.93
50	105	95	16.5	36.94
51	105	95	16.5	36.92
52	110	90	15.2	37.00
53	110	90	15.2	36.98
54	110	90	15.2	36.97
55	115	85	14.36	37.00
56	115	85	14.36	36.95
57	115	85	14.36	36.95
58	120	80	13.5	36.96
59	120	80	13.5	36.94
60	120	80	13.5	36.98
61	125	75	13.7	36.95

TABLE II CONT'D.

No.	cc H_2O	cc H_2SO_4	Normality	cc XN $KMnO_4$
62	125	75	12.7	36.95
63	125	75	12.7	36.90
64	130	70	11.8	37.00
65	130	70	11.8	37.00
66	130	70	11.8	37.00
67	135	65	11.0	36.98
68	135	65	11.0	36.97
69	135	65	11.0	36.98
70	140	60	10.13	36.95
71	140	60	10.13	36.95
72	140	60	10.13	36.95
73	145	55	9.2	36.90
74	145	55	9.2	36.92
75	145	55	9.2	36.93
76	150	50	8.45	36.90
77	150	50	8.45	36.90
78	150	50	8.45	36.90
79	160	40	6.75	36.95
80	160	40	6.75	36.95
81	160	40	6.75	36.95
82	170	30	5.07	36.92
83	170	30	5.07	36.94
84	170	30	5.07	36.92
85	180	20	3.38	36.83
86	180	20	3.38	36.80
87	180	20	3.38	36.85
88	185	15	2.53	37.05
89	185	15	2.53	36.95
90	185	15	2.53	36.95
91	185	15	2.53	36.90
92	190	10	1.69	36.80
93	190	10	1.69	36.82
94	190	10	1.69	36.70
95	190	10	1.69	36.80
96	195	5	0.845	36.80
97	195	5	0.845	36.80
98	195	5	0.845	36.80

The strength of permanganate used was as follows;-

Titration No.	1 to 5	incl.	.0981 normal.
" "	6 " 30	"	.0979 " .
" "	31 " 98	"	.0980 " .

In titrating the higher acid concentrations it was found that if the titration was carried on slowly the solutions turned brown thus obscuring the end points. If titrated rapidly the end point is fairly sharp.

III. Titration with Hydrochloric Acid.

One gram of ferrous sulphate was used for each titration. The water and acid were added in the same manner as in the titration with sulphuric acid. The solutions were cooled to 20°C. before titrating.

TABLE III.

No.	cc H_2O	cc HCl	Normality	cc XN $KMnO_4$
99	199	1	0.164	37.50
100	199	1	0.164	37.53
101	198	2	0.328	37.60
102	198	2	0.328	37.63
103	197	3	0.492	37.69
104	197	3	0.492	37.60
105	197	3	0.492	37.67
106	195	5	0.820	37.65
107	195	5	0.820	37.63

TABLE III CONT'D.

No.	cc H_2O	cc HCl	Normality	cc XN $KMnO_4$
108	190	10	1.64	37.58
109	190	10	1.64	37.56
110	180	20	3.28	37.60
111	180	20	3.28	37.40
112	175	25	4.10	37.60
113	175	25	4.10	37.55
114	170	30	4.92	37.40
115	170	30	4.92	37.50
116	160	40	6.56	no definite end point.

When the concentration of the acid increased beyond half normal the yellow color of the solution obscured the end point to such an extent that the results could not be taken very accurately. No odor of chlorine was given off during the titrations.

CONCLUSION.

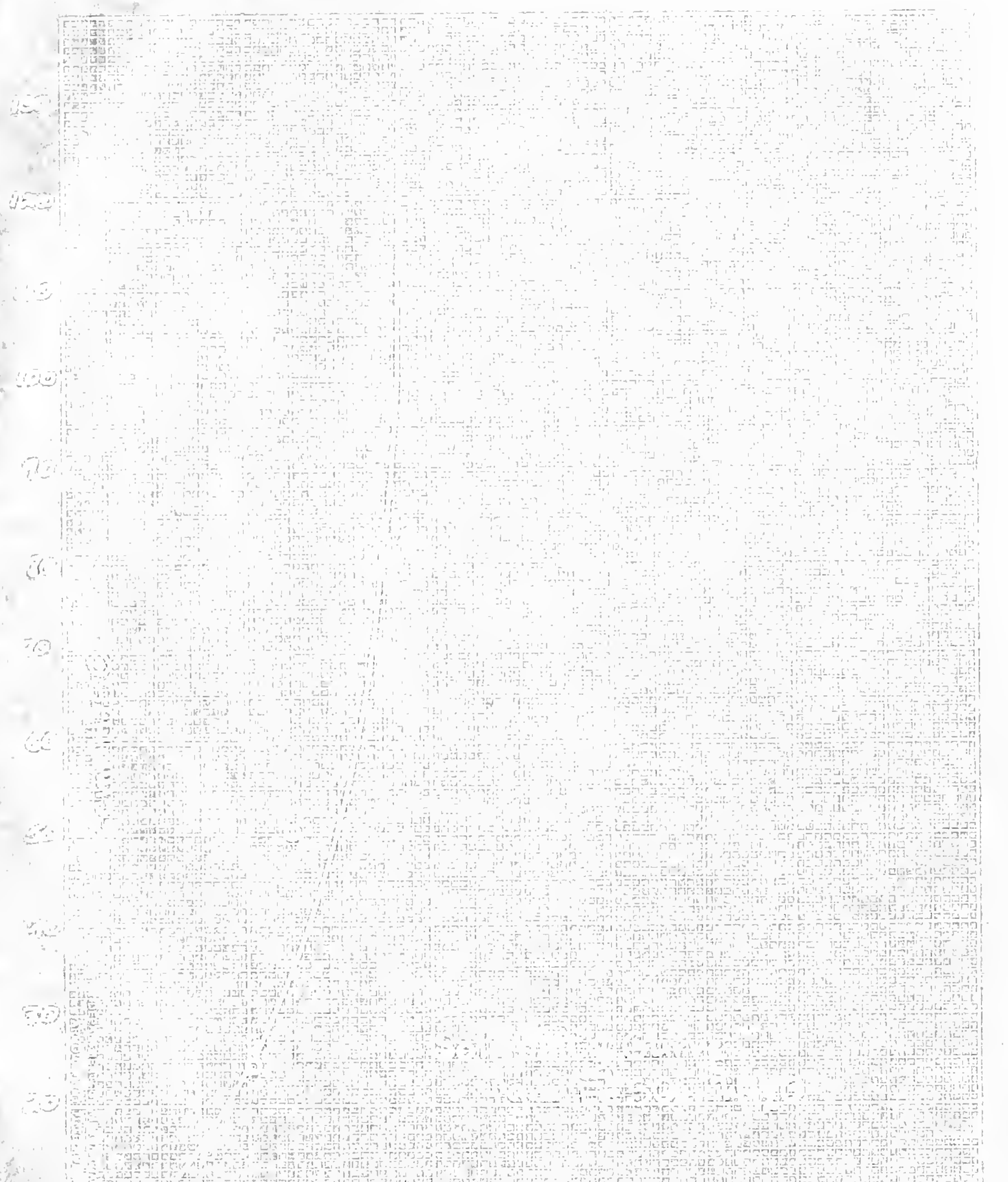
1. It is definitely determined that variations in the concentrations of hydrogen ions from 0.0N to 15.N in the presence of SO_4 ions of the same concentration does not influence the amount of permanganate required.

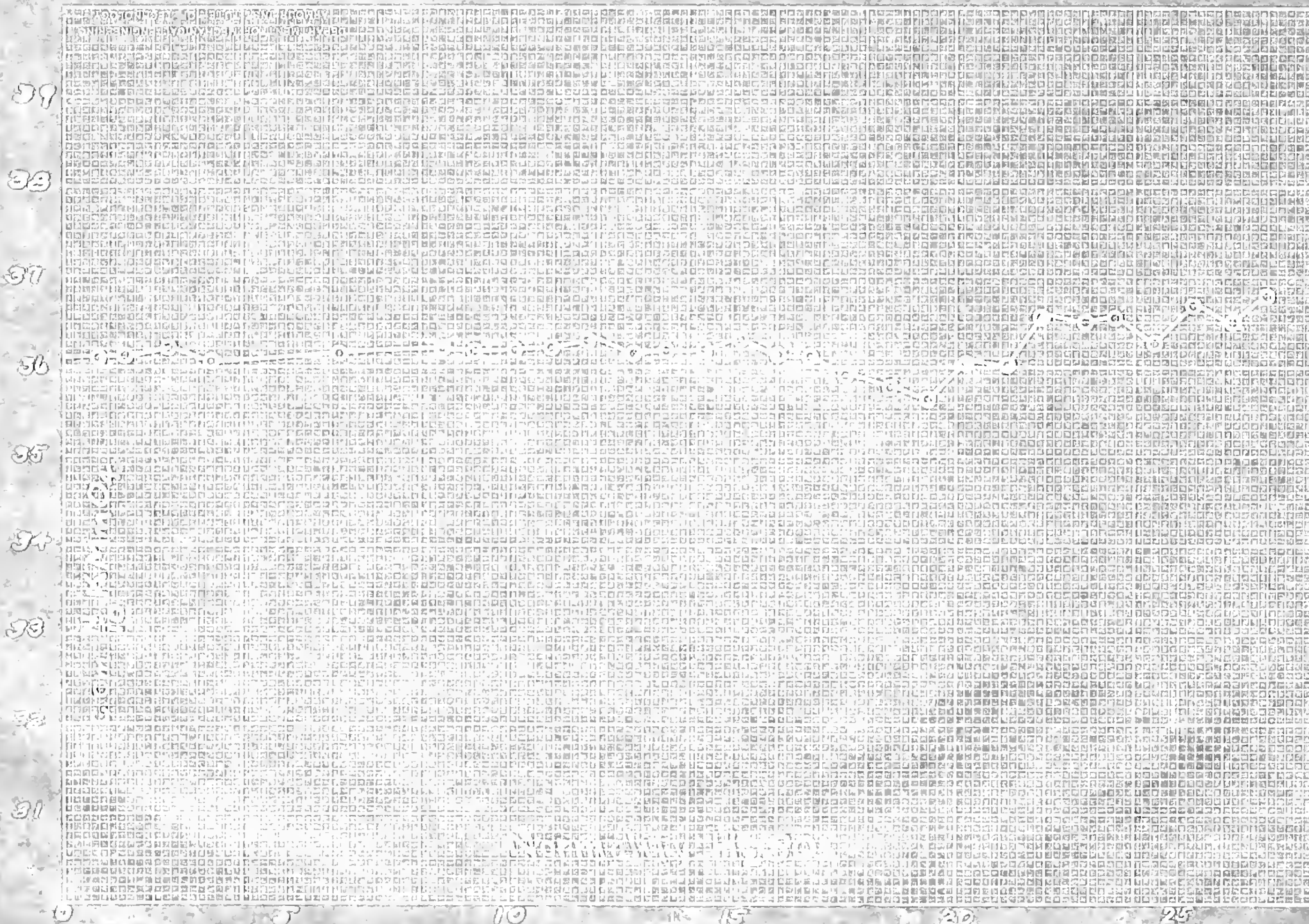
2. A concentration of hydrogen ions great-

er than 15.N in the presence of SO_4 ions of the same concentration influences the amount of permanganate required by as much as 3%.

3. In case of a concentration of hydrogen and chlorine ions greater than 0.5N the end point cannot be accurately determined.

4. For hydrogen ion concentrations below 0.5N in the presence of chlorine ions of the same concentration, ferrous salts can be titrated with an error of not more than one half of one percent.

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