

LVIII.—*Estimation of Hydrogen Peroxide in the presence of Potassium Persulphate by means of Potassium Permanganate.*

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WHILE Dr. Price and I were engaged in investigating Caro's acid, we noticed that hydrogen peroxide could not be correctly estimated by titration with potassium permanganate when this acid was present. The amount of permanganate required always fell short of the theoretical amount (compare Price, Trans., 1903, 83, 546).

Since we obtained Caro's acid by the action of strong sulphuric acid on potassium persulphate, it was natural to inquire whether the potassium persulphate itself might not act in a similar manner. At the suggestion of Dr. Price, whom I take this opportunity of thanking, I have investigated the subject, and my results show that, in ordinary circumstances, a correct estimate of the hydrogen peroxide is not obtained by titration with potassium permanganate when potassium persulphate is present. This fact has an important bearing on much of the work done in connection with persulphates, as many investigators have used this method for the estimation of hydrogen peroxide, believing it to be trustworthy.

In the sequel, $N/50$ permanganate was used, except where otherwise indicated. The potassium persulphate was recrystallised and free from sulphate; the hydrogen peroxide was obtained from Merck, and guaranteed pure. All the experiments were conducted at the ordinary temperature.

1. *Time of Titration.*

It was found that the amount of permanganate varied considerably with the rate at which it was poured from the burette into the mixture of hydrogen peroxide and potassium persulphate solutions. In each of the following series, the volume titrated and the amounts of hydrogen peroxide, potassium persulphate, and sulphuric acid present were constant throughout, but the rapidity with which the titrations were effected was varied.

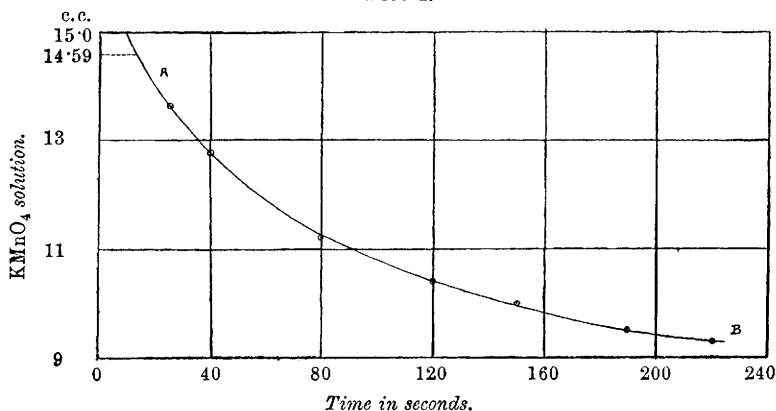
598 FRIEND: ESTIMATION OF HYDROGEN PEROXIDE IN THE

Series I. $m/85 \text{ K}_2\text{S}_2\text{O}_8$.		Series II. $m/102 \text{ K}_2\text{S}_2\text{O}_8$.	
Time of titration.	Titre in c.c. KMnO_4 .	Time of titration.	Titre in c.c. KMnO_4 .
25 secs.	13.63	5 secs.	11.00
40 „	12.78	10 „	10.87
80 „	11.22	20 „	10.78
120 „	10.42	40 „	10.49
150 „	10.02	75 „	10.31
190 „	9.52	95 „	10.30
220 „	9.28	120 „	10.15
theoretical value		theoretical value	
14.59		11.00	

Series III. $m/102 \text{ K}_2\text{S}_2\text{O}_8$.		Series IV. $m/136 \text{ K}_2\text{S}_2\text{O}_8$.	
Time of titration.	Titre in c.c. KMnO_4 .	Time of titration.	Titre in c.c. KMnO_4 .
15 secs.	12.30	0.33 mins.	10.23
20 „	12.20	1.10 „	9.89
30 „	12.09	1.83 „	9.45
60 „	11.03	2.50 „	9.33
90 „	10.65	4.00 „	9.08
150 „	10.50	7.60 „	8.71
theoretical value.		theoretical value	
12.26		10.54	

The results of Series I are shown in Fig. 1. If the curve be produced in the direction of *A*, it will not meet the vertical axis at the zero

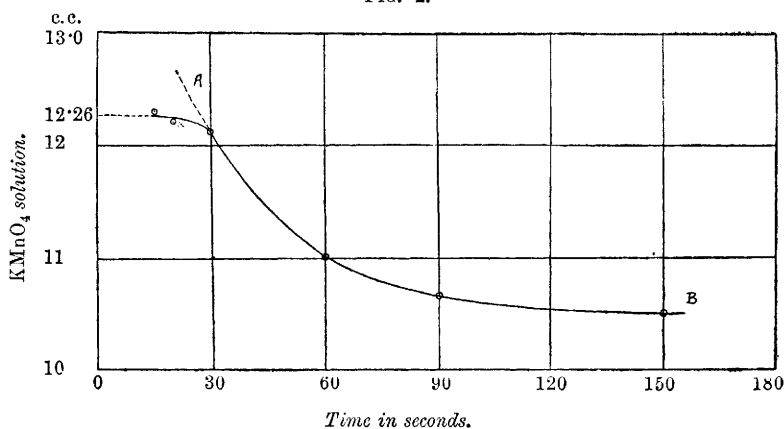
FIG. 1.



of time at a point corresponding with the theoretically correct titration (14.59 c.c.). If, however, very rapid titrations are effected, it is found that the amount of permanganate required does not exceed the theoretical amount. The curve suddenly departs from its original course, becoming nearly parallel to the horizontal axis. This is seen in Fig. 2, which represents the results of Series III. As it is almost impossible to effect a titration of any value in fewer than about 10 seconds, we cannot follow the curve right up to the zero of time.

The results of Series IV show that if the time of titration is greatly prolonged, the amount of permanganate required does not become constant, so that the curve (Figs. 1 and 2) produced in the direction

FIG. 2.



of B shows no signs of becoming parallel to the horizontal axis.

It will be clear from the above that if it is desired to compare titrations of different mixtures of hydrogen peroxide and potassium persulphate, the times of titration must be the same. The most convenient interval is perhaps 1 minute, for the curve is then not so steep as for a shorter period, and any slight error in the time of titration causes a smaller experimental error than would otherwise be the case.

In the sequel, all the titrations have been performed during this interval of time.

2. Concentration of Persulphate.

In each of the following series, the volume, time of titration, and amount of acid present were kept constant throughout, but the concentration of the potassium persulphate was varied.

In Series VIII, $N/75$ permanganate was employed.

600 FRIEND: ESTIMATION OF HYDROGEN PEROXIDE IN THE

Series VI.*		Series VII.		Series VIII.	
Concentration of $K_2S_2O_8$.	Titre in c.c. $KMnO_4$.	Concentration of $K_2S_2O_8$.	Titre in c.c. $KMnO_4$.	Concentration of $K_2S_2O_8$.	Titre in c.c. $KMnO_4$.
$m/119$	24.73	$m/119$	13.69	$m/85$	11.21
$m/159$	25.40	$m/159$	13.90	$m/122$	12.06
$m/238$	25.80	$m/238$	14.19	$m/189$	12.95
$m/476$	26.63	$m/476$	14.50	$m/283$	13.68
$m/795$	27.02	$m/795$	14.70	$m/425$	14.17
$m/1590$	27.30	$m/1590$	14.90	$m/850$	15.10
$m/3400$	27.50	$m/3400$	15.02	m/∞	16.22
m/∞	27.70	m/∞	15.36	—	—

It is clear from the foregoing tabulation that the greater the amount of potassium persulphate present, the greater is the deviation of the permanganate required from the theoretical amount. This is precisely what one might expect.

3. Dilution.

In each of the following series, the amounts of hydrogen peroxide, potassium persulphate, and sulphuric acid were kept constant, as also the time of titration, the volume alone being altered by the addition of distilled water.

Series IX.		Series X.		Series XI.	
Total volume titrated.	Titre in c.c. $KMnO_4$.	Total volume titrated.	Titre in c.c. $KMnO_4$.	Total volume titrated.	Titre in c.c. $KMnO_4$.
20	14.90	20	23.90	20	10.92
25	14.82	25	23.68	25	10.90
30	14.62	30	23.60	30	10.88
35	14.50	35	23.40	35	10.76
45	14.28	45	23.22	45	10.69
55	13.97	55	22.95	55	10.43
70	13.70	70	22.68	70	10.03
90	13.32	—	—	—	—

As the dilution increases, the effect of the potassium persulphate becomes correspondingly greater. It is quite possible that a dissociation of persulphate may account for this.

* The symbol m in the tables signifies one gram-molecule of the substance dissolved in one litre of water.

4. Concentration of Sulphuric Acid.

In each of the following series, the volume was kept constant, as also the amounts of persulphate and hydrogen peroxide, and the time of titration, but the quantity of sulphuric acid was varied.

Series XII. $m/238 \text{ K}_2\text{S}_2\text{O}_8$.

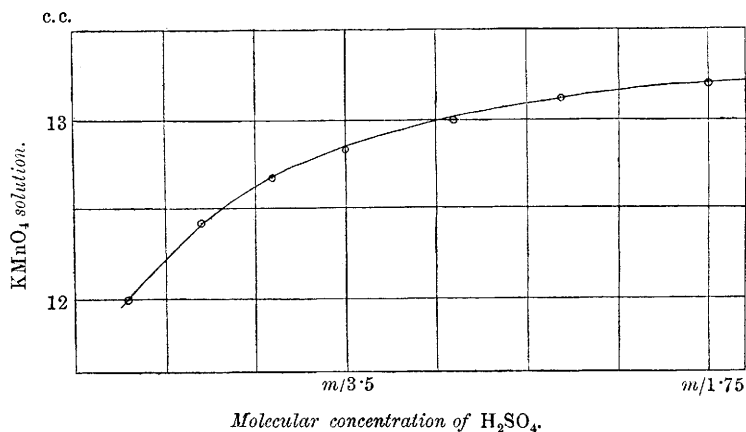
Strength of H_2SO_4 .	Titre in c.c. KMnO_4 .
$m/8.9$	12.00
$m/5.93$	12.42
$m/4.4$	12.67
$m/3.5$	12.83
$m/2.7$	12.99
$m/2.2$	13.12
$m/1.75$	13.20
Theoretical	13.62

Series XIII. $m/238 \text{ K}_2\text{S}_2\text{O}_8$.

Strength of H_2SO_4 .	Titre in c.c. KMnO_4 .
$m/12$	25.40
$m/7$	25.60
$m/5$	25.77
$m/2.3$	26.52
$m/1.8$	26.88
$m/0.9$	27.23
$m/0.6$	27.20
Theoretical	27.23

The results of Series XII are shown in Fig. 3; this diagram indicates a curve which is exactly opposite to those previously obtained.

FIG. 3.



By increasing the amount of sulphuric acid, the titration approaches more and more nearly to the true value, and indeed finally reaches it if the excess of acid is sufficiently great.

5. *Estimation of Hydrogen Peroxide.*

From the foregoing, it appears that a correct titration might be obtained if attention were paid to the following points.

1. The rapidity with which the titration is effected should be as great as possible.

2. The volume of the solution titrated should be reduced to a minimum.

3. Great excess of sulphuric acid should be employed.

That such is possible will be evident from a consideration of the following results.

Column I gives the volume of the solution titrated.

Columns II and III indicate respectively the molecular strengths of the sulphuric acid and potassium persulphate present in the solution.

Column IV gives the number of c.c. of permanganate required, and Column V the theoretical value, that is, the number which would have been required had no persulphate been present. The time of titration was about 30 seconds.

Volume.	H ₂ SO ₄ .	K ₂ S ₂ O ₈ .	KMnO ₄ required.	KMnO ₄ . Theoretical value.
25 c.c.	m/1·5	m/170	24·10 c.c.	24·16 c.c.
25	m/1·5	m/170	20·20	20·20
20	m/1·0	m/134	24·10	24·16
20	m/1·0	m/134	20·16	20·20
20	m/1·0	m/134	17·50	17·57
20	m/1·5	m/227	24·13	24·16
20	m/1·5	m/227	20·15	20·20

The above numbers show a moderate agreement, the greatest error being 0·4 per cent.

In a future paper I hope to show the cause of the varying titrations, and to give in more detail the most favourable conditions for effecting a correct titration.

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