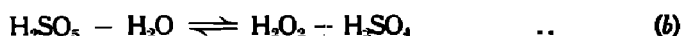
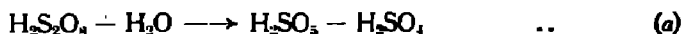


BEHAVIOUR OF PERSULPHATE IN SULPHURIC ACID SOLUTIONS

BY YUGUL KISHORE GUPTA

Behaviour of persulphate in sulphuric acid solution of different concentrations has been studied by estimating its hydrolytic products, permonosulphuric acid and hydrogen peroxide. The method of estimation of these substances in presence of each other works well and the difficulty encountered by the previous workers has been solved. It is confirmed that first permonosulphuric acid and then hydrogen peroxide are formed as the concentration of sulphuric acid is increased. The graphical results show that there are two maxima for permonosulphuric acid and one for hydrogen peroxide. The second maximum for permonosulphuric acid proves that it is reformed at higher concentrations of sulphuric acid. The reaction between hydrogen peroxide and sulphuric acid has also been studied. The possibility of estimating persulphate in suitable concentrations of sulphuric acid, iodometrically and with permanganate, has been indicated. The results are slightly different if the mixing of the reactants is reversed.

Persulphate or perdisulphuric acid is known to hydrolyse first to permonosulphuric acid and then to hydrogen peroxide in sulphuric acid solutions. Elbs and Schönherr (*Z. Elektrochem.* 1895, 1, 417, 468) found the hydrolysis to increase with the increasing concentration of sulphuric acid. Palgne (*Z. anorg. Chem.*, 1920, 112, 97) calculated the rate constants for the two reactions, which were found to be unimolecular:



Altire (*Z. angew. Chem.*, 1909, 22, 1713) studied the rate of hydrolysis of Caro's acid to hydrogen peroxide and measured the equilibrium constant for reaction (b). Based on these observations standard methods were developed for the preparation of permonosulphuric acid either by the hydrolysis of potassium persulphate (Caro, *ibid.*, 1898, 11, 845) or by the action of chlorosulphonic acid on hydrogen peroxide (d'Ans and Friederich, *Z. anorg. Chem.*, 1910, 43, 1880) at low temperatures, pointing to the reversible nature of reaction (b). Several workers investigated the decomposition of persulphate at higher temperatures (70° or above) and some, in sulphuric acid solutions of low concentration. The product of decomposition is oxygen, and the mechanism of the process is different from the reactions (a) and (b) in both neutral or acid solutions because these reactions take place in high concentrations of sulphuric acid. Recently Szabo *et al.* (*Z. anorg. allgem. Chem.*, 1956, 287, 152) have investigated the decomposition of persulphate in sulphuric acid solution, catalysed by metal ions.

In the present communication a detailed study of these reactions has been made by employing a wide range of concentration of sulphuric acid whereby not only the results of previous workers are confirmed but some additional interesting observations have also been made. The reaction (a) and probably the forward reaction (b) are slow, but a kinetic study of these in high concentrations of sulphuric acid could not be made because the mixing of sulphuric acid raises the temperature of the reaction mixture to a great extent. The results show only a qualitative behaviour of persulphate in sulphuric acid solutions of different concentrations.

There has always been a problem to estimate the persulphate and its hydrolytic products in presence of each other. The method of Palme (*loc. cit.*), though fairly suitable, is time consuming, requiring three determinations, one of which is indirect. Ceriometric determination of these compounds in presence of each other, as recommended by Csanyi and Solymosi (*Z. anal. Chem.*, 1954, 142, 423) also could not be employed in the present investigation because it requires heating and adjustment of the acidity of the solutions, factors both of which would influence reactions (a) and (b). In the present case it was possible to estimate the persulphate, hydrogen peroxide, and permonosulphuric acid by making two determinations, viz., iodometry in dilute solutions of potassium iodide, and the titration with the permanganate. The latter was found to be quite suitable for the estimation of hydrogen peroxide. The presence of perdisulphuric acid does not interfere if the concentration of sulphuric acid is low and the titration is quickly carried out.

It has been found, however, that perdisulphuric acid either does not exist or does so only in very small concentration in presence of hydrogen peroxide. The possibility of a reaction between hydrogen peroxide and perdisulphuric acid therefore does not arise. The presence of permonosulphuric acid is also without any interference, as reported by Baeyer and Villiger (*Ber.*, 1900, 33, 2488). No manganaous sulphate was added as sulphuric acid was quite sufficient for the purpose although the titration was attended with an induction period, depending on the acid concentration. In the present case the burette reading, for which the pink colour persisted for 5 to 10 seconds, was recorded. Some difficulty was encountered while titrating solutions containing a small amount of hydrogen peroxide and a large amount of permonosulphuric acid, but there was no difficulty at all in high sulphuric acid medium or when a large quantity of hydrogen peroxide was present. For iodometric determinations 10 c.c. of *N*/50 potassium iodide was mixed with the reaction mixture. A preliminary study indicated that permonosulphuric acid quantitatively liberated iodine from such solutions of potassium iodide, whereas hydrogen peroxide did so in about 10 to 15 minutes if the acid concentration was normal or above. Dilute solutions of persulphate will liberate negligible amounts of iodine from such solutions even in 15 minutes if the concentration of sulphuric acid is lower than one normal. The reaction mixture was added to potassium iodide solution and it was quickly titrated against a solution of sodium thiosulphate. This titrated solution was then kept for about 15 minutes and again titrated against thiosulphate. The method of calculation has been shown later.

EXPERIMENTAL

The potassium persulphate used was of E. Merck, 'pro analysi' quality and sulphuric acid was of A.R. quality (sp. gr. 1.84) from Orient Scientific Industries, Agra. All other chemicals used were of B.D.H.-A.R. quality. Persulphate solutions were always freshly prepared by direct weighing and their concentrations were checked by arsenite (Gupta and Ghosh, *Anal. Chim. Acta*, 1957, 17, 379) or Eckardt's method (*Chem. News*, 1900, 81, 38).

Requisite quantities of distilled water and H_2SO_4 (conc.) were taken in 500 c.c. conical flasks to obtain the desired concentrations of the acid in 50 c.c. solutions. The volume of the distilled water together with that of the acid in each flask was 40 c.c. Finally 10 c.c. of 0.1N persulphate solution was added. A 5 c.c. sample was taken out after an hour, diluted, and estimated for hydrogen peroxide with 0.01N- KMnO_4 . Another 5 c.c. sample was diluted, added to 10 c.c. of $\text{N}/50\text{-KI}$ containing a little starch solution, and quickly titrated against 0.01N sodium thiosulphate. This was then kept for about 15 minutes and again titrated for the liberated iodine. Tetrathionate made no complication. Dilution also had no effect on reaction (a) or (b). On the other hand, it helps check the reactions. 0.05N Persulphate (10 c.c.) was also used to note the effect of concentration.

The experiments were repeated by taking first distilled water and persulphate solution in the conical flask, and then adding H_2SO_4 . Experiments were also performed with H_2O_2 (10 c.c. of 0.1N and 0.05N) and different concentrations of H_2SO_4 .

Calculation of the Concentrations

At lower concentrations (below 3.6M) of H_2SO_4 , when no H_2O_2 is present, the first quick iodometric titration estimates the permonosulphuric acid. The original oxidant (persulphate) minus this estimation furnishes the concentration of perdisulphuric acid.

In slightly higher concentrations (3.6 to 4.5 M) of the acid, when a small amount of hydrogen peroxide is also present, the first quick iodometric titration gives permonosulphuric acid as above and the second iodometric titration gives both H_2O_2 and permonosulphuric acid, and hence perdisulphuric acid can again be calculated.

At higher concentrations of the acid no perdisulphuric acid is present because the second iodometric titration gives the total oxidant equivalent to original persulphate.

The concentration of permonosulphuric acid can now be calculated by subtracting the concentration of H_2O_2 (determined by the permanganate) from the total oxidant (second iodometric titration). The first iodometric titration no longer gives permonosulphuric acid alone. A part of the liberated iodine is due to H_2O_2 . In fact, the liberation of iodine from potassium iodide for the first quick titration depends on the concentrations of (1) permonosulphuric acid, (2) hydrogen peroxide, and (3) sulphuric acid. Hence as the amounts of H_2O_2 and H_2SO_4 increase in the mixture, much more iodine is liberated than what is expected from permonosulphuric acid alone.

A comparative study of these first iodometric titrations of different mixtures, however, indicates qualitatively whether the concentration of permonosulphuric acid is increasing or decreasing. At still higher concentrations of the acid, the total oxidant, as estimated by the second iodometric titration, also becomes less. This estimated total oxidant, subtracted from the initial oxidant, provides the amount of oxygen, the decomposition product of H_2O_2 .

The reaction mixtures were always qualitatively tested for the presence or otherwise of H_2O_2 by titanium sulphate (Vogel, "A Textbook of Macro and Semimicro Qualitative Analysis", 1959, p. 599) and of perdisulphuric acid by a 2% acetic acid solution of benzidine (*ibid.*, 1959, p. 380). In order to make the latter test, the sulphuric acid of the mixture was first neutralised by solid sodium carbonate before adding benzidine solution.

TABLE I

Volume of the reaction mixture = 50 c.c. Reaction mixture titrated each time = 5 c.c.
 $K_2S_2O_8$ taken = 10 c.c. of 0.1N

Overall conc. of H_2SO_4	0.01N- $KMnO_4$ required (c.c.) after				0.01 N-Thiosulphate (c.c.) required after							
	1hr.	1day.	2days.	3days.	1hr.		1day.		2days.		3days.	
					1st.	2nd.	1st.	2nd.	1st.	2nd.	1st.	2nd.
3.6M	0	0	0	0	2.65	..	8.60	..	9.35	..	9.95	..
4.5	0	0.05	0.10	1.10	5.80	..	10.15	..	10.10	..	9.40	10.50
5.4	0	1.15	2.05	3.10	9.75	10.30	9.40	10.60	8.50	10.60	7.45	10.55
6.3	2.85	4.30	5.85	7.40	8.90	10.60	6.60	10.60	5.10	10.60	4.00	10.50
7.2	7.85	9.15	9.55	9.55	3.65	10.60	2.60	10.60	2.10	10.40	1.85	10.15
8.1	9.40	9.55	9.45	9.30	2.85	10.60	3.50	10.50	2.70	10.40	3.25	10.00
9.0	8.35	8.25	8.00	7.60	5.50	10.10	4.40	9.50	4.45	9.60	4.10	9.10
9.9	6.80	6.10	5.80	5.05	5.20	9.00	5.05	8.25	3.25	7.80	3.95	6.95
10.8	4.85	4.40	4.00	3.75	3.70	7.40	3.35	7.10	3.20	6.65	2.85	6.05
12.6	1.20	0.95	0.90	0.85	2.65	3.70	2.30	3.20	2.00	2.70	1.70	2.35

N.B. 1st and 2nd refer to the iodometric titrations, immediately and after 15 minutes respectively.

Considering the observations at 4.5M of H_2SO_4 (Table I), 5.80 c.c. gives permonosulphuric acid and $10.60-5.80=4.80$ c.c. is the concentration of the remaining persulphate or perdisulphuric acid. After 3 days, 1.10 c.c. gives H_2O_2 and 9.40 c.c. gives permonosulphuric acid. The second iodometric titration value is 10.50; hence perdisulphuric acid is equal to $10.60-10.50=0.10$ c.c. of thiosulphate, and there is no oxygen.

At 5.40M acid concentration after 3 days, 3.10 c.c. is H_2O_2 and 7.45 c.c. is permonosulphuric acid. Oxygen is equivalent to $10.60-10.55=0.05$ c.c. of the thiosulphate, and there is no perdisulphuric acid. That 0.05 c.c. is oxygen and not perdisulphuric acid, easily follows from the fact that the second iodometric titration value increases and then decreases as the reaction progresses.

DISCUSSION

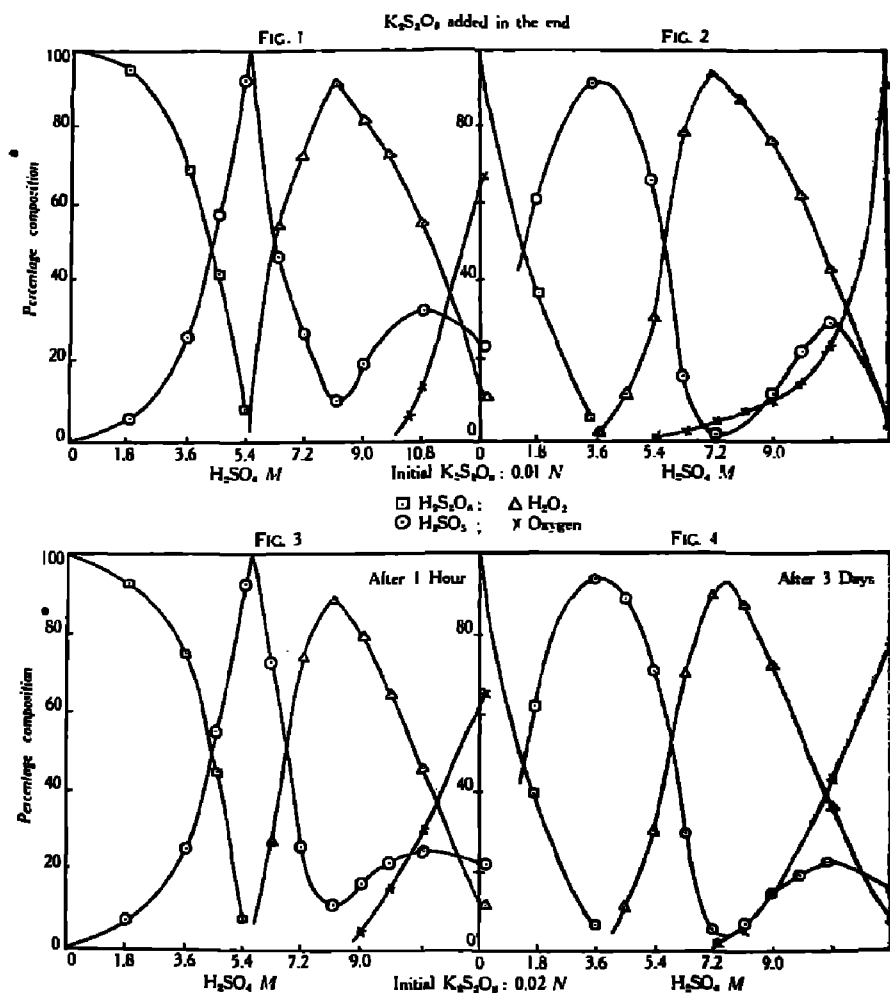
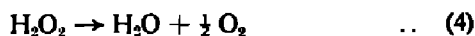
A typical set of results is shown in Table I. Figures 3 and 4 correspond to the results on the first and the fourth day of this table. Similar types of figures were obtained for the results of second and third day. Some of the results are shown in Figs. 1—8.

It may be seen from Figs. 1 to 4 that from persulphate or perdisulphuric acid, successively permonosulphuric acid and hydrogen peroxide are formed, and finally the latter decomposes, giving off oxygen. As the concentration of H_2SO_4 is increased, the amount of permonosulphuric acid increases, attains a maximum, then decreases, and increases again finally to decrease. This is easily inferred from the figures where there are two maxima for permonosulphuric acid. There is only one maximum for H_2O_2 . It appears therefore that first permonosulphuric acid is ~~formed~~ from perdisulphuric acid.

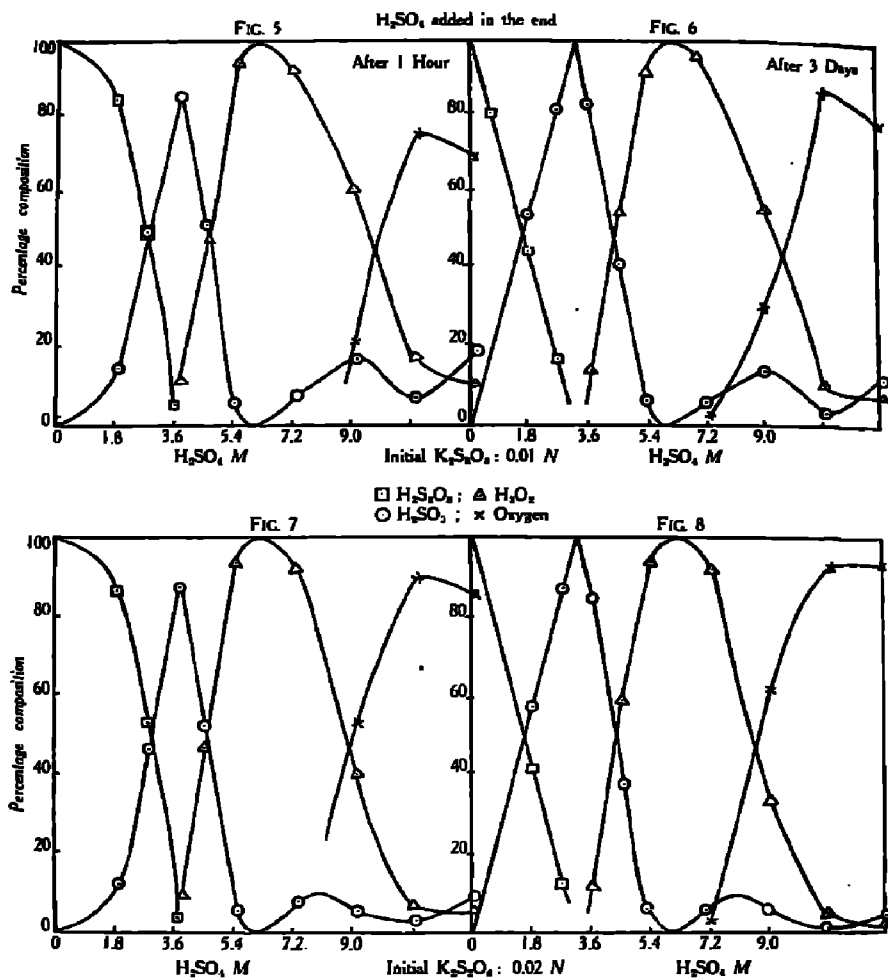
$\text{H}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_5 + \text{H}_2\text{SO}_4 \quad \dots (1)$ (approx. between 1.8 and 5.4M of H_2SO_4)
 Permonosulphuric acid gives hydrogen peroxide:

$\text{H}_2\text{SO}_5 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \quad \dots (2)$ (predominantly between 5.4 and 8.1M of H_2SO_4)
 Hydrogen peroxide is then used up in two ways. It reacts with sulphuric acid reproducing permonosulphuric acid :

$\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{SO}_5 + \text{H}_2\text{O} \quad \dots (3)$ (between 8.1 and 10.8M of H_2SO_4)
 Secondly hydrogen peroxide decomposes according as

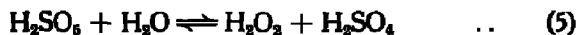


The decomposition is rapid and, in fact, very rapid in 12.6M- H_2SO_4 or above. It also takes place at lower concentrations of the acid, but only after 3 days. Thus there are two alternative reaction paths for hydrogen peroxide. At one stage reaction (3) predominates, but at higher



concentrations of sulphuric acid reaction (4) predominates. This explains the second maximum for permonosulphuric acid as also the decrease in the concentration of H_2O_2 . At high concentrations of H_2SO_4 , the lesser concentration of permonosulphuric acid is attributed not to its decomposition, but to the fact that its formation by reaction (3) is less in presence of predominating reaction (4).

The reaction of H_2O_2 with H_2SO_4 (relevant figures not shown) proves that reaction (2) is reversible, i.e.,



The formation of permonosulphuric acid begins at about 8.1M concentration of H_2SO_4 and at very high acid concentration, its formation is less due to decomposition of H_2O_2 .

The observations have been recorded also at intervals of 24, 48 and 72 hours. All the reactions are shifted to right with time. The effect of time is not well observed in case of reaction (2) because of the predominating reaction (4), which decreases the concentration of hydrogen peroxide.

The experiments were also carried out by adding H_2SO_4 in the last. The results are shown in Figs. 5 to 8. These differ from other results in so far that the reactions (1), (2), and (3) take place within lower limits of concentration of H_2SO_4 . The addition of H_2SO_4 liberates much heat, which quite obviously increases the rates of all the reactions. It may also be mentioned that a fraction of persulphate decomposes by this heat, giving probably oxygen in such cases because the total oxidant estimated iodometrically (second titration) is somewhat always less than the original concentration of persulphate. No such complications are involved when the persulphate is mixed after addition of H_2SO_4 and the solution is cooled. It is not clear why the amount of permonosulphuric acid increases for the third time in about 12.6 M - H_2SO_4 (Figs. 5 to 8).

In the reaction H_2O_2 - H_2SO_4 , when sulphuric acid, instead of the peroxide, is added in the last, permonosulphuric acid is never present in large amount; in fact it is much less than in its parallel case when the peroxide is added in the last. The decomposition of H_2O_2 by the heat produced by the mixing of H_2SO_4 seems to be the reason again (relevant figures not shown).

The second maximum for permonosulphuric acid never goes high in any case, showing thereby that not much permonosulphuric acid is produced from reaction (3). This reaction is favourable in only very strong acid solutions, when unfortunately a rapid decomposition of H_2O_2 takes place. The reaction H_2O_2 - H_2SO_4 (adding H_2O_2 in the last) was studied with higher concentrations (N and $2N$) of H_2O_2 in about 15 M - H_2SO_4 solution, when H_2O_2 decomposed, and no permonosulphuric acid was formed. The usual method for the preparation of permonosulphuric acid from chlorosulphonic acid and hydrogen peroxide is possible probably because it is carried out at low temperatures or because chlorosulphonic acid has very little decomposing action on H_2O_2 .

Two interesting observations have been made which lead to the possibility of a quantitative determination of persulphate. From Figs. 5 to 8 it may be seen that in about 5.94 M acid solution, the whole of the persulphate is present in the form of H_2O_2 , which may be titrated against the permanganate. No such possibility is seen from Figs. 1 to 4 where the persulphate is added in the last. A separate communication has been made elsewhere for such an estimation. Similarly a possibility of estimating persulphate iodometrically in about 5.4 M acid solutions is apparent from Figs. 1 to 4. Work is in progress to prepare permonosulphuric acid at ordinary temperatures by a simple method and to stabilise it.

Gupta and Ghosh (this *Journal*, 1958, 35, 483) have reported that no red trivalent manganese is formed in 5.4 M - H_2SO_4 solution because hydrogen peroxide produced in the system reacts with Mn(III) . In the present investigation very little H_2O_2 is formed in such solutions (Figs. 1-4). Qualitative test for H_2O_2 with titanium sulphate, employed by Gupta and Ghosh (*loc. cit.*), might be misleading. When titanium sulphate prepared in H_2SO_4 (conc.) is added to the reaction mixture, the high concentration of the acid of titanium sulphate solution produces H_2O_2 , which responds to the test. In order to make this test in such solutions, a drop or two of the test solution should always be added to about 2 c.c. of the reaction mixture. Hence it is believed that Mn(III) is not formed because permonosulphuric acid, which is predominantly present in 5.4 M acid solutions, probably does not oxidise Mn(II) . Gupta and Ghosh (*ibid.*, 1959, 36, 237) have also reported that Caro's acid does not oxidise Mn(II) . The anticatalytic action of Mn(II) in the oxidation of oxalate (Gupta and Ghosh, *J. Inorg. Nucl. Chem.*, 1959, 11, 320), and arsenious (Gupta, this *Journal*, 1959, 36, 643; Gupta and Misra, *Bull. Chem. Soc., Japan*, 1959, 32, 1306) and formic (Gupta and Nigam, this *Journal*, 1960, 37, 125) acids by persulphate can now be attributed to the formation of permonosulphuric acid, which probably does not oxidise the above acids. All these acids are, however, oxidised by the persulphate, a process which takes place by a free radical mechanism. The formation of permonosulphuric acid is catalysed by Mn(II) , as has been reported

by Szabo *et al.* (*loc. cit.*). The results of the present investigation further explain the observation of Gupta and Ghosh (*Naturwiss.*, 1958, 45, 184) as to why Mn(III) is formed only between the concentration limits of 3.6 to 5.4*M* of sulphuric acid. The most favourable concentration is 3.6 *M*, above which Caro's acid begins to be formed and below which there is insufficient sulphuric acid to hold Mn(III) in solution.

The results are fairly reproducible if care is taken to take exactly identical volumes of H₂SO₄ (conc.) in each case. While carrying out experiments to note the effect of concentration of persulphate, equal volumes of persulphate solutions of different concentrations should be added. It is not only the overall acid concentration that matters, but also the concentration of the acid in the solution to which persulphate is added, and which therefore should be identical in all cases for noting the effect of concentration of persulphate. In the other case, when sulphuric acid is added in the last, the reproducibility is less due evidently to the mode of mixing of sulphuric acid having some influence. If the mixing is standardised, say, by adding 0.5 c.c. at a time, the results do not deviate by more than 5 to 10%.

It may also be mentioned that if 100 c.c. or 25 c.c. solutions of reaction mixture are prepared instead of 50 c.c., no identical results are obtained. A volume contraction of 5 to 7% also took place by mixing of sulphuric acid with water or the persulphate solution, and this was taken into consideration while calculating the concentrations of different species in the reaction mixture.

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