LXXXIV.—The Persulphuric Acids.*

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MUCH attention has been paid during the past two years in the Chemical Department of the Central Technical College to the study of the behaviour of solutions of sulphuric acid on electrolysis, as well as to the manner in which solutions of 'persulphuric' acid undergo hydrolysis. This work has been undertaken in order to elucidate the part which 'persulphuric' acid plays in the accumulator (compare Armstrong and Robertson, *Proc. R. S.*, 1891, **50**, 105), and to ascertain to what extent the production of this acid must be taken into account in discussing the electric conductivity of solutions of sulphuric acid, as well as in determining the origin of the products such solutions yield when electrolysed under various conditions (compare Armstrong, Presidential Address, Trans., 1895, **6**, 1156).

In the course of the inquiry, it became necessary to repeat and extend Berthelot's observations on the interaction of hydrogen peroxide and sulphuric acid (Ann. Chim. Phys., 1878, [v], 14, 345).

The experiments have led to results which appear to have an important bearing on the interpretation of the nature of the product formed by the interaction of sulphuric acid and potassium persulphate, which Caro (*Zeit. angew. Chem.*, 1898, 845) has shown to be possessed of special properties, and which Bamberger and von Baeyer and Villiger have recently made use of as an oxidising agent under the name of 'Caro's reagent.'

Von Baeyer and Villiger have suggested that the acid characterised by Caro is a persulphuric acid composed of hydrogen peroxide and sulphuric anhydride in the ratio $H_2O_2: SO_3$. The experiments described in the following pages appear to favour the conclusion that

* Electrochemical Studies. No. I, from the Chemical Dept., C.T.C.

its composition may be $H_2O_2: 4SO_3$, whilst the acid, of which salts were first prepared by Marshall, is of intermediate composition, $H_2O_2: 2SO_3$. The members of such a series of persulphuric acids may be provisionally distinguished as 'persulphuric,' 'perdisulphuric,' and 'pertetrasulphuric' acids.

The substance analysed by Berthelot in 1878 was the anhydride, S₂O₇, which he obtained by combining oxygen with either of the lower oxides of sulphur by means of the electric discharge. He assumed that the corresponding acid was formed on dissolving this anhydride in water, and as he found that when moderately concentrated solutions of sulphuric acid were electrolysed they acquired properties similar to those possessed by solutions of the anhydride S₂O₇, he came to the conclusion that the same acid is formed during electrolysis. The correctness of this assumption was apparently placed beyond doubt by the discovery made by Marshall in 1891 of a series of well-defined salts derived from the anhydride S₂O₇; at all events, it has not been called in question up to the present time.

It was expressly pointed out by Berthelot in his original paper (*loc. cit.*) that persulphuric acid "se forme également, toujours à l'état dissous, lorsqu'on mélange avec précaution et en évitant toute élévation de température une solution d'eau oxygénée avec l'acide sulfurique soit concentré, soit étendu d'une quantité d'eau inférieure à l équivalent. Mais la combinaison n'a point lieu quand l'acide sulfurique est étendu à l'avance de 2 équivalents d'eau, ou davantage. Dans tous les cas, elle demeure partielle, c'est-à-dire qu'il subsiste une portion de l'eau oxygénée."

It will be noticed that in this passage he states that the peroxidation is confined to acids containing but a very small proportion of In a later paper, he discusses the formation of persulphuric water. acid on electrolysing solutions of sulphuric acid of various degrees of concentration, and also makes frequent reference to the production of hydrogen peroxide both during electrolysis and as a product of the decomposition of persulphuric acid; but he nowhere recognises that the proportions in which the two compounds are formed are in any way interdependent. In fact, in concluding his paper (Ann. Chim. Phys., 1880, [v], 21, 193), he remarks, "Cette formation d'eau oxygénée ne paraît pas due à une réaction lente de l'eau contenue dans les liqueurs et à un équilibre résultant entre les deux composés suroxygénés, comme on aurait pu le penser d'abord. En effet, la liqueur diluée avec 20 volumes d'eau, et qui s'est conservée presque sans variation pendant neuf jours (98 mgr. reduits à 90 mgr.), n'a donné lieu à aucune formation appréciable d'eau oxygénée.

"La formation de l'eau oxygénée est donc simultanée avec la décomposition lente de l'acide persulfurique. Elle en est probablement corrélative, comme nous l'avons déja admis plus haut pour rendre compte de sa formation par electrolyse."

Our experiments, however, lead us to conclude that in a system comprising 'persulphuric acid' and hydrogen peroxide together with sulphuric acid and water, there is a definite state of equilibrium between the two peroxidised products, and that under constant conditions the ratio of hydrogen peroxide to 'persulphuric acid' is entirely determined by the ratio of water to sulphuric acid; the ratio of hydrogen peroxide to 'persulphuric acid' is therefore ultimately the same in a mixture prepared from hydrogen peroxide and sulphuric acid as in a solution of equal strength prepared by electrolysis.

Experimental Method.---The method used in determining the ratio of hydrogen peroxide to 'persulphuric' acid was that used by Berthelot, and depends on the fact that whilst potassium permanganate is reduced by hydrogen peroxide, it is not affected by 'persulphuric acid,' and that the latter readily oxidises ferrous sulphate to ferric sulphate. In dilute solution at low temperatures, 'persulphuric' acid is very stable, and is not decomposed to any appreciable extent, either into sulphuric acid and oxygen, or into sulphuric acid and hydrogen peroxide; a mixture containing about 10 volumes of water to 1 volume of sulphuric acid was found to be stable at 0°, no change being perceptible in the amount of hydrogen peroxide or of 'persulphuric acid' after a week. In analysing the solutions, it is necessary that the acid should be rapidly diluted, and that no heating should take place during the dilution; if this condition is not fulfilled, the equilibrium is disturbed, and the proportion of 'persulphuric' acid is lowered accordingly. For this reason, the acid mixture was slowly delivered from a pipette on to an excess of ice, so that the temperature fell below 0° during the dilution. Special care was necessary in the case of acids containing less than one equivalent of water; these were poured directly on to a large quantity of ice without any attempt at measuring the volume of the mixture, and portions of the diluted mixture were then titrated. After diluting, the hydrogen peroxide was first estimated by running in potassium permanganate from a burette until a permanent coloration was produced. When only a small amount of hydrogen peroxide was present, it was found to be advisable to add a few drops of a solution of manganese sulphate, as otherwise the first drop of potassium permanganate produces a pink coloration, which persists for some time in the ice-cold solution, and there is a danger of overlooking the presence of hydrogen peroxide. The interaction of hydrogen peroxide and potassium permanganate, in fact, appears to belong to the class of actions which only take place in presence of a catalytic agent. After destroying the hydrogen peroxide, the 'persulphuric' acid was estimated by adding an excess of ferrous sulphate solution, and titrating back in the usual way.

It was soon found that the ratio of 'persulphuric' acid to hydrogen peroxide was very largely influenced by minute differences in the proportions of sulphuric acid and water, and that any error in the estimation of the sulphuric acid would be reproduced five-fold in the persulphuric ratio. It was therefore necessary to take special precautions in standardising the sulphuric acid and in preparing the acid mixtures. It was, in fact, desirable that the value of the acid should be known, if possible, within 0.02 per cent., and this high degree of accuracy could only be obtained by determining the density (compare Pickering, Trans., 1890, 57, 64; Marshall, J. Soc. Chem. Ind., 1899, 18, 6). In all the later experiments, the acid used was drawn off by a siphon from a bottle containing about seven litres, and measured out from a repeating burette into flasks fitted with a rubber stopper and drying tube, the acid in the bottle and burette being also protected by drying apparatus. To determine the density, 10 c.c. of water were run into a dry flask and carefully mixed with about 80 grams of the acid from the repeating burette; the flask, water, and acid were weighed to 0 001 gram, and the density of the mixture was then determined at 18°, relatively to water at 18°, with the aid of a The concentration of the density tube about 5 c.c. in capacity. diluted acid could be deduced to within 0.01 per cent. from the table given by Marshall, and it was easy to calculate the concentration of the original acid from the value so found. As showing the accuracy of the method, the six values determined in the case of the acid used in the last series of experiments may be quoted, namely, 93.70, 93.81, 93 66, 93 78, 93 76, 93 76, mean value 93 75, mean error 0.04.

The mixtures to be titrated were prepared in a similar way, but 20 c.c. of hydrogen peroxide (20 vols.) were taken in place of the water, and the weighings were made to 0.01 gram only; the flasks containing the mixtures were closed by rubber stoppers each fitted with a tube drawn out to a minute capillary, in order to allow of the escape of oxygen, whilst preventing the entrance of moisture. In making the weaker mixtures, 40 c.c. of a dilute hydrogen peroxide solution was used, whilst in the case of those of higher concentration 5 c.c. of a "50 volume" hydrogen peroxide * was taken, in order to diminish the quantity of acid required, and so as to lessen the danger due to heating during the dilution, which has already been referred to. Commercial hydrogen peroxide always contains a considerable quantity of chlorine, which is given off on mixing it with sulphuric acid; the greater part of this may be removed by adding silver

* We were indebted for this to Mr. Tyrer, who had kindly prepared it at Dr. Armstrong's request.

sulphate, but it has been found to be necessary to leave a trace of chlorine in the solution, as the merest trace of silver suffices to render the acid mixtures so unstable that they lose the whole of their oxidising power in the course of a few hours.

Temperature does not appear to have any very marked influence on the equilibrium; a mixture which was examined to test this point gave 61.2 per cent. of persulphuric oxygen at 35° and 62.4 per cent. at 18° .

The rate at which the equilibrium is reached is very largely influenced by the concentration of the acid; in fact, it would seem that a state of equilibrium is only established when it is present in large excess; this case appears to be analogous to that of the two iso-dibutylenes described by Butlerow (Annalen, 1877, 189, 44), which undergo isomeric change, and come to a state of equilibrium only in presence of strong sulphuric acid. In the case of the more concentrated mixtures, the equilibrium is very rapidly reached, and there is little difficulty in obtaining trustworthy measurements, but in the less concentrated solutions the change takes place only slowly, and it becomes increasingly difficult to obtain concordant results.

To ascertain whether the same equilibrium could be arrived at by starting from persulphuric acid in place of hydrogen peroxide, a mixture of sulphuric acid and water was electrolysed in a divided cell, and a number of acid mixtures were prepared, using the anode acid in place of the hydrogen peroxide of the preceding experiments. A portion of the anode acid was decomposed by warming with platinum foil, and standardised by determining its density in the usual way. Owing to the additional sources of error thus introduced, these determinations are less trustworthy than those depending on the use of hydrogen peroxide, but the values obtained show a satisfactory agreement with the calculated values, as will be seen on referring to Table I, in which the mixtures prepared from electrolytic acid are marked with an asterisk.

A single experiment was also made, in which a solution of commercial 'ammonium persulphate' was used in place of hydrogen peroxide. The percentage of 'persulphuric oxygen' was found to be 90.9 when ammonium persulphate solution was used, and 90.7in a comparison experiment with an equal volume of hydrogen peroxide.

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Sulphuric acid	Sulphuric acid	Formula of acid	Persul I	Persulphuric oxygen per cent.			ka.
per cent. mols. per cent.	$\mathrm{H_2SO_4}, n\mathrm{H_2O}.$	Obs.	Calc.	Diff.		2	
per cent. 88.65 87.0 *86.36 85.59 *84.66 84.5 84.5 82.9 *82.81 82.31 81.7 80.48 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.75 80.48 80.46 80.75 80.48 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.08 80.46 80.06 79.9 79.69 79.69 78.52 78.51 78.01 77.57 77.20 76.91 76.63 75.48 75.18 75.48 75.18 74.91 74.51 *4.51 *4.51 *4.53 75.18 74.95 75.84	$\begin{array}{c} 1 \\ 1 \\ 1 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 1$	$H_2SO_4, nH_2O.$ 0.6968 0.8136 0.8598 0.9169 0.9858 1.0000 1.028 1.122 1.129 1.219 1.321 1.355 1.357 1.357 1.357 1.357 1.357 1.357 1.357 1.357 1.357 1.357 1.409 1.4488 1.504 1.537 1.537 1.539 1.574 1.607 1.635 1.635 1.657 1.677 1.677 1.677 1.714 1.753 1.770 1.798 1.820 1.841 1.863 1.876 1.929	Obs. 96.5 95.6 93.1 92.7 92.2 92.2 92.2 92.2 92.2 88.9 87.6 86.8 80.3 80.3 80.2 79.2 78.4 77.6 76.6 76.6 75.6 75.6 75.6 75.6 75.6	Calc. 98.2 96.2 95.4 94.2 92.4 91.7 91.2 88.1 88.0 86.3 84.3 84.3 80.9 79.9 79.8 78.2 77.5 76.6 76.3 75.6 73.5 71.6 70.0 68.9 67.1 65.4 63.9 62.7 63.9 62.7 55.4 55.4 54.3 53.2 52.2 51.6 49.0	Diff. -1.7 -0.6 -1.0 -1.1 +0.3 +0.5 +1.0 +0.8 -0.4 +0.5 +0.6 +0.3 -0.6 +0.3 -0.6 +0.3 -0.6 +0.3 -0.6 +0.3 -0.3 -0.3 -0.3 -0.3 -0.3 -0.3 -0.1 +0.5 +0.5 +0.5 +0.5 +0.5 +0.5 +0.5 +0.5 +0.5 +0.5 +0.5 -0.6 +0.3 -0.6 +0.3 -0.3 -0.3 -0.3 -0.1 +0.5 -0.1 -0.3 -0.1 +0.5 -0.1 -0.3 -0.1 +0.5 -0.1 -0.3 -0.1 +0.5 -0.1 -0.3 -0.1 +0.5 -0.1 -0.5 -0.1 +0.5 -0.1 -0.5	$\begin{array}{c} 11 \cdot 48 \\ 12 \cdot 37 \\ 12 \cdot 37 \\ 12 \cdot 76 \\ 11 \cdot 5 \\ 12 \cdot 55 \\ 12 \cdot 0 \\ 12 \cdot 25 \\ 11 \cdot 89 \\ 12 \cdot 22 \\ 12 \cdot 17 \\ 12 \cdot 01 \\ 12 \cdot 19 \\ 12 \cdot 23 \\ 12 \cdot 19 \\ 12 \cdot 32 \\ 12 \cdot 32 \\ 12 \cdot 32 \\ 12 \cdot 32 \\ 12 \cdot 33 \\ 12 \cdot 63 \\ 12 \cdot 56 \\ 13 \cdot 01 \\ 12 \cdot 56 \\ 13 \cdot 01 \\ 12 \cdot 56 \\ 13 \cdot 01 \\ 12 \cdot 56 \\ 13 \cdot 03 \\ 13 \cdot 18 \\ 12 \cdot 56 \\ 13 \cdot 33 \\ 12 \cdot 78 \\ 13 \cdot 58 \\ 1$	$\begin{array}{c} 10\ 68\\ 11\ 51\\ 11\ 83\\ 10\ 48\\ 11\ 13\\ 10\ 89\\ 11\ 07\\ 10\ 74\\ 11\ 04\\ 10\ 95\\ 10\ 77\\ 10\ 79\\ 10\ 95\\ 10\ 77\\ 10\ 79\\ 10\ 95\\ 11\ 20\\ 10\ 78\\ 10\ 78\\ 10\ 78\\ 10\ 78\\ 10\ 78\\ 10\ 78\\ 10\ 78\\ 11\ 20\\ 10\ 94\\ 10\ 62\\ 11\ 08\\ 10\ 73\\ 11\ 14\\ 10\ 57\\ 11\ 24\\ \end{array}$
73.83 73.18 71.19 71.15 71.12 70.48 70.31 69.06	34 13 33 41 31 21 31 18 31 15 30 50 30 31 29 07	1.9311.9932.2042.2072.2102.2792.2992.440	48.0 45.6 38.0 37.4 36.7 35.1 33.7 28.4	$\begin{array}{c} 43.9\\ 48.9\\ 46.1\\ 37.3\\ 37.2\\ 37.0\\ 34.5\\ 33.8\\ 29.3\end{array}$	$ \begin{array}{r} -0.9 \\ -0.5 \\ +0.7 \\ +0.2 \\ -0.3 \\ +0.6 \\ -0.1 \\ -0.9 \end{array} $	12.85 13.22 14.50 14.17 13.87 14.61 14.15 14.07	10.50 10.71 11.43 11.09 10.80 11.60 10.81 10.32

 TABLE I.—Equilibrium between Hydrogen Peroxide and 'Persulphuric'

 Acid in presence of Sulphuric Acid and Water at 18°.

Sulphuric acid per cent.	Sulphuric acid mols. per cent.	Formula of acid H ₂ SO ₄ ,nH ₂ O.	Persulphuric oxygen per cent.			k.	ka.
			Obs.	Calc.	Diff.		-
$\begin{array}{c} 67 \cdot 45 \\ 66 \cdot 56 \\ 65 \cdot 64 \\ 60 \cdot 95 \\ 54 \cdot 93 \\ 45 \cdot 72 \end{array}$	28.0326.7726.0022.2820.5213.40	2.567 2.736 2.847 3.487 4.466 6.463	25.721.819.49.9 $4.20.8$	$ \begin{array}{r} 25 \cdot 8 \\ 21 \cdot 8 \\ 19 \cdot 6 \\ 11 \cdot 2 \\ 5 \cdot 6 \\ 2 \cdot 0 \end{array} $	$ \begin{array}{r} -0.1 \\ 0 \\ -0.2 \\ -1.3 \\ -1.4 \\ -1.2 \end{array} $	15.00 15.82 15.81	10·84 10·96 10·71

TABLE I.—Equilibrium between Hydrogen Peroxide and 'Persulphuric' Acid in presence of Sulphuric Acid and Water at 18° (continued).

In Table I, the percentage composition of the acid is given in column 1, and the molecular percentage composition in column 2. In calculating these values, the hydrogen peroxide solution has been reckoned as water, and no attempt has been made to make any correction for the small weight of active oxygen which it contains. In column 3, the number of molecules of water per molecule of the acid is tabulated as the formula of the acid H_2SO_4,nH_2O . Column 4 gives the percentage of the total active oxygen present in the form of 'persulphuric oxygen' (that is, indifferent to potassium permanganate).

In the figure, the percentages given in column 4 are plotted as abscissæ, whilst the percentages in columns 1 and 2 are the ordinates in the curves (p. 957) marked III and IV respectively.

It will be noticed that the conversion of hydrogen peroxide into 'persulphuric' acid, and vice versa, takes place for the most part within very narrow limits of concentration; thus, on increasing the strength of the acid from 70 to 80 per cent., the proportion of 'persulphuric oxygen' increases from 31 to 78 per cent., an increase of 47 per cent. in the proportion of 'persulphuric' acid for an increase of only 10 per cent in the strength of the sulphuric acid. The same fact is illustrated by the proportions of 'persulphuric oxygen' corresponding to the hydrates of sulphuric acid, namely :

H ₂ SO ₄ ,H ₂ O	••••••	92 p	er cent.
$H_2SO_4, 2H_2O$		46	"
$H_2SO_4, 3H_2O$	•••	17	"
$H_2SO_4, 4H_2O$	•••••	7	,,

From this table, it appears that 85 per cent. of the change takes place between the limits H_2SO_4 , H_2O and H_2SO_4 , $4H_2O$; above H_2SO_4 , $\frac{1}{3}H_2O$ and below H_2SO_4 , $10H_2O$, the change is virtually complete.

Curves showing the equilibrium between hydrogen peroxide and 'persulphuric acid' in presence of sulphuric acid and water.



Form of the Equilibrium Curve.—The equilibrium curve for the system—sulphuric acid, water, 'persulphuric' acid, hydrogen peroxide—is extremely similar to that corresponding with the simple quartic equation

$$\frac{c_1}{c_2} = k \left(\frac{c_3}{c_4}\right)^4,$$

where c_1, c_2 represent the relative molecular proportions of the 'persulphuric' acid and hydrogen peroxide, whilst c_3, c_4 represent the molecular proportions of sulphuric acid and water respectively. The two curves are so similar that on the small scale of the figure it would not be possible to represent them clearly by separate lines. If, however, the values of k be calculated for each point, it is found that they steadily increase as the concentration decreases; this is clearly shown

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in the table, in which the values of k, calculated on this basis, are given in column 7.

The curve can, however, be represented with a very considerable degree of accuracy by the equation

$$\frac{c_1}{c_2} = k_1 \left(\frac{c_3}{c_4}\right)^2 + k_2 \left(\frac{c_3}{c_4}\right)^4$$

where $k_1 = 0.63$ and $k_2 = 10.96$.

The percentages, $\frac{100 c_1}{c_1 + c_2}$, calculated from this formula, are tabulated in column 5, and the differences between the observed and calculated values are given in column 6. It could hardly be expected that a simple algebraical expression should be found which would cover the wide range of chemical change involved in diluting the sulphuric acid from 100 per cent. to 0 per cent., but fortunately in this case the greater part of the change takes place within very narrow limits of concentration, namely, between 85 and 55 per cent., and the disturbances due to the changing nature of the acid are therefore largely avoided. Between the limits of 65 per cent. and 81 per cent., within which the percentage of 'persulphuric' oxygen increases from 19 per cent. to 81 per cent., the maximum error in the 40 observations is less than 1 per cent., and the average error is 0.33 per cent.

In order to test the accuracy of the formula used, the value of k_1 has been assumed to be 0.63 throughout, and the value of k_2 has then been calculated for each point on the curve; the values of k_2 thus obtained are given in the last column of the table, and are extremely steady throughout the series.

Nature of the Products.-In discussing our results, no attention has thus far been paid to the possible nature of the substances concerned in the equilibrium, and the algebraical formula arrived at is independent of any theoretical interpretation that may be given of the chemical change. It is now necessary to consider what this may be. The existence of a series of crystalline compounds containing sulphuric anhydride and water in different proportions serves to suggest that there may be a series of 'persulphuric' acids containing different proportions of sulphuric anhydride and hydrogen peroxide. The interaction of sulphuric acid and hydrogen peroxide may then be represented by equations such as

According to the law of mass-action, the equilibrium between hydrogen peroxide and the different 'persulphuric' acids would be represented by the equations

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$$\begin{aligned} kc_2c_3 &= c_1c_4 \quad \text{or} \quad \frac{c_1}{c_2} &= k\frac{c_3}{c_4} \\ kc_2c_3^2 &= c_1c_4^2 \quad \text{or} \quad \frac{c_1}{c_2} &= k\left(\frac{c_3}{c_4}\right)^2 \\ kc_2c_3^4 &= c_1c_4^4 \quad \text{or} \quad \frac{c_1}{c_2} &= k\left(\frac{c_3}{c_4}\right)^4, \quad & & & & & & & \\ \end{aligned}$$

where c_1, c_2, c_3, c_4 are the concentration of the four components of the system.

If, as Berthelot supposed, the sole product of the action were a 'perdisulphuric acid' of the formula $H_2S_2O_8$, the equilibrium must correspond with an equation of the second order, and would be represented by an equilibrium curve similar to II in the figure, which was plotted from the formula

$$\frac{c_1}{c_2} = 3\left(\frac{c_3}{c_4}\right)^2;$$

although this curve is similar in type to the experimental curve, it will be seen that the reversal of curvature is much less pronounced. The effect of lowering the order of the equation is seen in curve I in the figure, which was plotted from the equation

$$\frac{c_1}{c_2} = \frac{3}{2} \frac{c_3}{c_4};$$

in this curve, the reversal of curvature has entirely disappeared and the curve does not bear the slightest resemblance to the experimental curve. It is therefore evident that the experimental curve must be represented by an equation of a higher, rather than of a lower, order than the second. The formula H_2SO_5 (von Baeyer and Villiger, *Ber.*, 1900, 33, 124), which actually gives curve I in the figure, must therefore be rejected.

The experimental curve, however, approximates very closely to the curve deduced from an equation of the fourth order, such as

$$\frac{c_1}{c_2} = 12.6 \left(\frac{c_3}{c_4}\right)^4,$$

and assuming that the chief product of the interaction is a 'persulphuric' acid of the series H_2O_2,nSO_3 , it is evident that it must be the *fourth* member, that is, its formula must be $H_2O_2,4SO_3$ or $H_2S_4O_{14}$.

The small, but steady, deviations of the experimental curve from that deduced from the simple equation of the fourth order are in the direction of the curves of lower order, and serve to indicate that along with the acid $H_2S_4O_{14}$ there is produced a much smaller amount of some simpler acid of the series, and it appears only fair to suppose that this is the acid $H_2S_2O_8$, which Berthelot assumed was alone

formed. The equation for an equilibrium between H_2O_2 , $H_2S_2O_3$, and $H_2S_4O_{14}$ would be of the form

$$\frac{c_1}{c_2} = k_1 \left(\frac{c_3}{c_4}\right)^2 + k_2 \left(\frac{c_3}{c_4}\right)^4,$$

where k_1 is the equilibrium constant for the 'perdisulphuric' and k_2 that for the 'pertetrasulphuric' acid. Taking $k_1 = 0.63$ and $k_2 = 10.96$, this equation gives results which agree very closely with the observed values for the equilibrium, and there can be little doubt that it represents the experimental data as closely as they can be represented by a simple algebraical equation. There is at present no method known by which the persulphuric acids may be separately estimated, but it will be of interest to record the calculated proportions of H_2O_2 , $H_2S_2O_8$, and $H_2S_4O_{14}$ in some of the mixtures.

TABLE II.

Composition of the acid.	H ₂ O ₂ .	H ₂ S ₂ O ₈ .	H ₂ S ₄ O ₁₄ .
$H_{2}SO_{4} + H_{2}O_{4}$	7 ·9	5.0	87·1
$H_{2}SO_{4} + 1.50H_{2}O_{4}O_{4}$	29 ·2	8.1	62·7
$H_2SO_4 + 1.99H_2O$ $H_2SO_4 + 2.57H_2O$ $H_2SO_4 + 3.49H_2O$	53 9 74 2 88 8	7·1 4·6	18·7 6·6
$\begin{array}{c} H_{2}^{2}SO_{4}^{2} + 4.47H_{2}^{2}O \\ H_{2}SO_{4}^{2} + 6.46H_{2}O \end{array}$	94·4	3·0	2.6
	98·0	1·4	0.6

A qualitative test is, however, available for distinguishing the 'perdisulphates' and 'pertetrasulphates,' Caro (Zeit. angew. Chem., 1898, 845) having shown that the 'perdisulphates' produce a brown precipitate in a neutral solution of aniline, but that the neutral salts of the acid formed by the interaction of 'perdisulphates' and sulphuric acid have the property of oxidising aniline to nitrosobenzene. On applying this test, it was found that a mixture of hydrogen peroxide with a large excess of sulphuric acid gave a considerable quantity of nitrosobenzene, but only a trace of the brown precipitate characteristic of the 'perdisulphates'; a mixture of hydrogen peroxide with an equal bulk only of sulphuric acid gave, however, a much more pronounced brown precipitate and only a small amount of nitroso-There can therefore be little doubt as to the presence of benzene. both 'perdisulphuric' and 'pertetrasulphuric' acids in the product, the relative proportion of 'perdisulphuric acid' being greatest in the more dilute solutions.

It is scarcely necessary to say that the conclusions we have arrived at must be verified by the analytical examination of the product; but

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as Caro has stated that he is engaged in completing his discovery, we have not thought it right to extend our experiments in this direction. We may mention, however, that solutions containing a very large proportion of the peroxidised acids may be obtained, not only by electrolysing solutions of sulphuric acid, but also by mixing sulphuric acid with hydrogen peroxide, and then concentrating by freezing out the hydrate H_2SO_4, H_2O .

If our conclusion be accepted, it will follow that the account given by Berthelot, and, in fact, by all who have studied the acid, applies to 'pertetrasulphuric acid' rather than to 'perdisulphuric acid,' which appears under all conditions to be by far the minor product and the less stable, although its salts are more stable than those of 'pertetrasulphuric acid.' The production of 'perdisulphates' on electrolysing solutions of acid sulphates, whilst solutions of sulphuric acid yield chiefly 'pertetrasulphates,' is of interest as an indication that the electrolysis proceeds on very different lines in the two cases.

Attention may also be directed to the fact that, inasmuch as the persulphuric acids are formed by the interaction of sulphuric acid and hydrogen peroxide, it is clear that the affinity of hydrogen peroxide must be greater than that of water for sulphuric anhydride.

In conclusion, the authors desire to express their thanks to Dr. Armstrong, at whose suggestion the research was carried out, and to whom they are indebted for much valuable help during the whole course of the work.

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[It is proposed to extend the method here described to the study of the peroxides of other acids. H. E. A.]