

and most remarkable feature brought out by this mode of classifying the elements is the existence in various parts of the system of groups or series of related elements from the highest term of which alone "progression" takes place. The existence of such groups in the case of the iron and platinum metals and some of the rare earths, has long been recognised—but not their significance. It is not unlikely that some of the columns will be "cleared" of such groups when atomic weights generally are known with a closer approach to certainty. Of their existence in column 4, there can be no doubt; but if in column 7 rubidium were put at 84, 85 could be transferred to column 8; and if lower down in the same column, caesium were put at 131, 132 and 133 could be transferred to column 8, or the necessary "correction" might be made perhaps with greater advantage by including in column 4 two terms (81 and 82) in the fifth, and three (128, 129, 130) in the seventh period: column 7 would then be free from "grouped" elements. Such groups, however, are undoubtedly as characteristic of column 8 as of column 4; whether they are of column 9 is open to question—the cerium group might well follow barium in column 8; but wherever they may come, it is clear that the elements of this group are a very numerous body, and that a remarkable expansion may be looked forward to in this part of the table. Column 11 might also, by a similar process, be cleared of grouped elements. If such a clearance turn out to be possible, grouped elements will be characteristic of only three of the families—those in columns 4, 8 and 12.

Making allowances in the manner suggested, the "smoothed" scheme is arrived at which is embodied in Table II.

The possibilities disclosed by a system of classification such as that here suggested are remarkable, but they are on the surface and need not be dwelt upon. Speculation on such a subject will be justified if it but lead to further appreciation of the rhythm which undoubtedly underlies the relationships subsisting among the elements. That work in plenty is left for the chemist to do is certain.

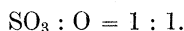
"Persulphuric Acids." By HENRY E. ARMSTRONG, V.P.R.S., and T. MARTIN LOWRY, D.Sc. Received March 13,—Read March 20, 1902.

Although it was observed by Faraday in 1834 that "if the acid were very strong, a remarkable disappearance of oxygen took place" on electrolysing aqueous solutions of sulphuric acid,* it was not until 1878 that its disappearance was at all satisfactorily accounted for by the discovery of *persulphuric acid* by Berthelot.

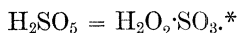
* 'Recherches in Electricity,' series vii, § 728.

Only the anhydride, S_2O_7 , was isolated by Berthelot, but he concluded that the corresponding acid was formed (1) on dissolving the anhydride in water, (2) on electrolysing strong solutions of sulphuric acid, and (3) by the interaction of hydrogen peroxide and ordinary sulphuric acid. The correctness of these conclusions appears to have been regarded as beyond question after Marshall had discovered in 1891 that well-defined salts of "Berthelot's acid" could be prepared by electrolysing solutions of potassium or ammonium hydrogen sulphate. Doubt arose, however, when Caro, in 1898, discovered that if Marshall's salts were acted on by sulphuric acid, a new acid was obtained having properties markedly different from those associated with Berthelot's acid. "Caro's acid" soon acquired importance as an oxidising agent, owing to the good use that was made of it by Bamberger and by von Baeyer and Villiger.

Having found that Caro's acid liberated iodine very rapidly whereas Berthelot's acid acted but slowly on iodides, these latter chemists were able to devise a process by which the one acid could be estimated in presence of the other. By removing sulphuric acid by means of barium phosphate, they obtained a solution containing Caro's acid and Berthelot's acid, in which they determined the amount of each of these substances as well as the amount of sulphate to which the persulphuric acids gave rise when decomposed. Their results led them to conclude that the ratio of sulphur to active oxygen in Caro's acid was



Placing the simplest possible interpretation upon this result, they assigned to the acid the formula—



Meanwhile, the problem had been studied from a somewhat different point of view by Lowry and West,† who had determined the equilibrium subsisting between hydrogen peroxide and "persulphuric acid" in presence of sulphuric acid and water, and had found that the ratio which the hydrogen peroxide bore to total "persulphuric acid" was entirely dependent on the ratio which the water bore to the sulphuric acid—the ratio of hydrogen peroxide to "persulphuric acid" being ultimately the same in a mixture prepared from hydrogen peroxide and sulphuric acid as in a solution of equal strength prepared by electrolysis. The experimental curve approximated very closely to a curve deduced from an equation of the fourth order, and assuming that the chief product of interaction was a persulphuric acid of the series $\text{H}_2\text{O}_2 \cdot n\text{SO}_3$, it was to be supposed that it was the fourth term of the

* 'Ber. Deut. Chem. Ges.,' 1901, 853.

† 'Chem. Soc. Trans.,' 1900, 950.

series, viz., $\text{H}_2\text{O}_2 \cdot 4\text{SO}_3$. But there were indications that some simpler acid was also present in small quantity.

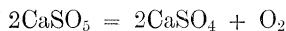
These results applied mainly to concentrated solutions, 85 per cent. of the change taking place between the limits expressed by the formula $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$; and virtually no peroxidation of the sulphuric acid took place below the limit expressed by the formula $\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. Von Baeyer and Villiger, on the other hand, had dealt with a product existing in dilute solution. The different conclusions deduced from the two sets of results were, therefore, not necessarily discordant; it was possible that the product examined by Baeyer and Villiger had been formed by hydrolysis from the "higher" acid which Lowry and West's observations had indicated was present in concentrated solutions. It is also to be noted that the determination of the ratio of active oxygen to sulphur is sufficient to determine the composition of the acid only in the case of the acid being one of the $\text{H}_2\text{O}_2 \cdot n\text{SO}_3$ series; obviously, other types of "persulphuric acid" are possible.

If we consider what must be the properties of the persulphuric acids generally, it is clear that whereas the salt of a dibasic acid of the formula H_2SO_5 would remain neutral on withdrawal of the peroxide oxygen, salts of higher acids would yield more or less sulphuric acid when decomposed. As a carefully neutralised solution of Caro's acid becomes acid when heated, the salt originally present in it cannot be one derived directly from the acid H_2SO_5 —assuming that this is dibasic.

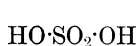
We are much indebted to Mr. A. J. Cook for having made a long series of determinations which show that the ratio of the increase in acidity to active oxygen lost is

$$\text{SO}_3 : \text{O} = 1 : 2,$$

a result which finds expression in the formula $\text{H}_2\text{S}_2\text{O}_9$ but is in direct opposition to the formula H_2SO_5 ; thus, supposing the calcium salt to be used:



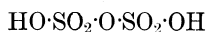
The probability that the acids in question have the composition suggested is considerable, if the manner in which sulphuric acid may be expected to undergo electrolysis be taken into account. Strong solutions of the acid may be supposed to contain both sulphuric and disulphuric acids, and it may be expected that both would "peroxidise"; on electrolysis the former would give perdi- and the latter pertetra-sulphuric acid, thus—



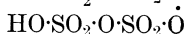
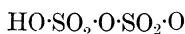
Sulphuric acid.



Perdisulphuric acid.



Disulphuric acid.

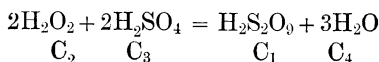


Pertetrasulphuric acid.

An acid of the formula $\text{H}_2\text{S}_2\text{O}_9$ may be regarded as the anhydro-acid derived from permonosulphuric acid, *i.e.*, as $\left. \begin{array}{l} \text{HO}\cdot\text{O}\cdot\text{SO}_2 \\ \text{HO}\cdot\text{O}\cdot\text{SO}_2 \end{array} \right\} \text{O}$. It is scarcely necessary to say that the interpretation now put upon the data afforded by solutions of Caro's acid will need to be verified, and cannot be accepted as final until salts of the acid have been isolated. This we are engaged in doing.

Further consideration, in the light of the facts brought forward by Baeyer and Villiger and in the present communication, of the results arrived at by Lowry and West, has served only to confirm the conclusion that the chief product of oxidation of sulphuric acid by hydrogen peroxide in presence of less than 50 per cent. of water is an acid richer in sulphur trioxide than perdisulphuric acid, and to justify the assumption on which they based the formula $\text{H}_2\text{S}_4\text{O}_{14}$ —namely, that the acid is a member of the series $\text{H}_2\text{O}_2 \cdot n\text{SO}_3$. Lowry and West determined only the ratio of peroxide oxygen to persulphuric oxygen, and paid no attention to the total oxidising power of the solution. That they were justified in this course is apparent from the fact that no change in the ratio of the two forms of oxygen was observed on varying the strength of the peroxide solution from 10 to 40 "volumes," nor was any change observed as the oxidising power gradually decreased when the acid decomposed.

If the main product of the interaction had been an acid of the formula $\text{H}_2\text{S}_2\text{O}_9$, this would not have been the case, as the equilibrium represented by the equation



would depend on the total oxidising power of the solution as well as on the proportion of sulphuric acid and water; this is seen most clearly when the equation of mass action,

$$\text{KC}_2^2\text{C}_3^2 = \text{C}_1\text{C}_4^3,$$

is transposed into the form

$$\frac{\text{C}_1}{\text{C}_2} = \text{K} \left(\frac{\text{C}_3}{\text{C}_4} \right)^2 \cdot \frac{\text{C}_2}{\text{C}_4},$$

which indicates that the ratio C_1/C_2 of persulphuric oxygen to peroxide oxygen depends not only on the ratio C_3/C_4 of sulphuric acid to water and on the concentration C_4 of the water in the solution, but also on the actual concentration C_2 of the hydrogen peroxide. The fact that the equilibrium is independent of total oxidising power can only be explained if the chief products of interaction are members of the series $H_2O_2 \cdot nSO_3$, or hydrates thereof.

As there was no sufficient evidence to justify the assumption that a third persulphuric acid was present in the solutions they examined, Lowry and West had no alternative but to regard Caro's acid as pertetrasulphuric acid, and their simpler member of the series as the acid corresponding to Marshall's salts. The determination of the ratio of sulphur to active oxygen by Baeyer and Villiger has rendered such a limitation impracticable, and we now feel not only that it is justifiable but that we are compelled to postulate the existence of *at least three persulphuric acids, viz. :—*

Pertetrasulphuric acid	$SO_3 : O = 4 : 1$
Perdisulphuric acid	$SO_3 : O = 2 : 1$
Peranhydrosulphuric acid (Caro's acid)	$SO_3 : O = 1 : 1$

In carrying out his experiments, Mr. Cook nearly neutralised solutions of Caro's acid by means of a carbonate and then neutralised the liquid by means of either sulphuric acid or caustic soda, portions being taken out and tested with methyl orange. Measured portions of the neutral solution were run as quickly as possible into flasks containing a little dilute sulphuric acid to arrest decomposition; the persulphuric acids were then estimated by Baeyer and Villiger's method. Portions of the same solution were heated at 100° until all oxidising power was lost, and the acidity developed was estimated by caustic soda, using methyl orange as indicator.

Solution I.—This was prepared by digesting potassium persulphate at $60\text{--}70^\circ$ with a solution containing only 10 per cent. of sulphuric acid. At the end of about 2 hours the cooled solution was diluted and neutralised with chalk. The amount of iodine liberated at once by the Caro's acid present, expressed in terms of decinormal thio-sulphate solution, was equivalent to 41.54 c.c.; the amount of iodine liberated slowly by the perdisulphuric acid present was equivalent to 1.05 c.c. The acid liberated on warming the solution was equivalent to 22.06 c.c. The calculated amount, assuming the ratio $2O : SO_3$, would be $1.05 + \frac{1}{2}41.54 = 21.82$ c.c.

In the subsequent experiments 15 grammes of potassium persulphate was digested with from 35 to 25 c.c. of concentrated sulphuric acid at the ordinary temperature during 1—2 hours. The solution was then diluted with ice and neutralised: in Experiments 2, 3, 4 and 6 with chalk, in 5 with sodium bicarbonate, and in 7 with sodium carbonate,

using phenol phthalein as indicator. In Experiment 7 the solution was mixed with excess of caustic soda before warming it to decompose the per-salts, and the excess was subsequently determined. No hydrogen peroxide was present except in solution 5, in which case the amount was determined by permanganate and allowed for.

The following are the results obtained in terms of decinormal solutions :—

	Caro's acid.	Perdisulphuric acid.	Acid liberated.	
			Found.	Calculated.
I	41·54	1·05	22·1	21·8
II	38·8	5·91	26·6	25·3
III	35·0	2·77	20·2	20·3
IV	39·24	2·24	21·3	21·8
V.....	37·3	1·56	21·5	20·2
VI	49·8	3·43	28·7	28·3
VIII	23·3	0·71	12·2	12·4

“The Conditions determinative of Chemical Change and of Electrical Conduction in Gases, and on the Phenomena of Luminosity.” By HENRY E. ARMSTRONG, V.P.R.S. Received March 13,—Read May 1, 1902.

In his communication to the Chemical Society on the union of oxygen and hydrogen, read at the meeting on February 19,* Mr. H. Brereton Baker has added another to his brilliant series of proofs that interactions supposed to take place between two substances are in reality of a more complex character; and having successfully demonstrated, in the case of the gases referred to, that water alone does not determine the interaction, he has, I believe, carried the investigation to the final stage which it was essential it should reach to make it a complete discovery of the nature of the process.

Mr. Baker has shown that when a mixture of hydrogen and oxygen [most carefully prepared by electrolysing a solution of barium hydrate] is enclosed in a chamber of hard Jena glass [cleansed in the most careful manner possible], and the mixture is dried as thoroughly as may be [by means of phosphoric anhydride which has been carefully purified by distilling it in a current of air], no appreciable interaction takes place between the gases, even on heating the tube to redness. If the drying be not carried too far, however, water is gradually but very slowly formed—finally in sufficient quantity to be visible: and yet, even when water is visibly present, no explosion takes place.

The interpretation I would give of these observations is as follows :—

* ‘Chem. Soc. Proc.,’ 1902, p. 40.