oxalate. They did not use a divided cell, the operation being carried out practically as in the quantitative electrolytic deposition of cobalt.

University of Edinburgh,
August, 1891.

LXXIV.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF EDINBURGH.

No. V. *The Persulphates.*

By HUGH MARSHALL, D.Sc., F.R.S.E.

PERSULPHURIC anhydride, S_2O_7, was first described by Berthelot in 1878 (*Compt. rend.,* **86**, 20, 277). He obtained it by subjecting a well-cooled mixture of sulphurous anhydride and oxygen to the "silent discharge" in an ozone tube. By treating the anhydride with water he obtained a solution which, while containing chiefly sulphuric acid formed by decomposition of the new substance, possessed oxidising properties, and might therefore be supposed to contain persulphuric acid. Subsequently (*ibid.,* **86**, 71) he showed that a similar solution is formed at the anode during the electrolysis of fairly concentrated sulphuric acid. The oxidising properties of such a solution had been previously observed, but attributed to ozone and peroxide of hydrogen. By cautiously neutralising with barium hydrate and filtering, a solution was obtained which, on boiling, deposited barium sulphate, while free sulphuric acid, equivalent in quantity to the barium sulphate, remained dissolved. This seemed to prove that the substance was really an acid corresponding to the anhydride, although it was found impossible to obtain the salts in the solid state. Mendeléeff (*Bull. Soc. Chim.,* **38**, 168), however, adopted a different view, holding that the new compounds were peroxides corresponding to barium peroxide, hydrogen peroxide, &c., and would not form salts.

Further papers on the subject have since been published by Moritz Traube (*Ber.,* **22**, 1518) and also by Richarz, chiefly with reference to the direct formation of peroxide of hydrogen. The former endeavoured to show that the formula adopted by Berthelot and also his view as to the nature of the compound were incorrect. He proposed the formula SO_4 and the name "sulphur holoxide." Early this year, however, I discovered a method of preparing solid per-

sulphates, as mentioned in the preceding paper on cobaltic salts, and a short preliminary note on the potassium salt was read before the Royal Society of Edinburgh (*Proc. Roy. Soc. Edin.*, **18**, 63). Recently, another paper, "On Sulphur Holoxide," has been published by M. Traube (*Ber.*, **24**, 1764);* this has been promptly replied to by Berthelot (*Compt. rend.*, **112**, 1481).

In the present paper I intend to describe, so far as they have been examined, those persulphates which I have as yet succeeded in preparing, as the completion of the investigation will probably require some considerable time. The salts described have not yet been subjected to proper crystallographic examination, so the exact crystalline forms are as yet doubtful. These and many other points must be reserved for a subsequent paper.

Potassium Persulphate.

The discovery of this salt, as already stated, was purely accidental. A fairly acid solution of cobalt and potassium sulphates was being electrolysed in a "divided" cell (this vol., p. 761), when, after a day or two, a quantity of small crystals separated. These, when filtered from the blue mother liquor, proved to be colourless, and were, therefore, supposed to be simply potassium sulphate. They were, however, washed with cold water, and a solution of a small quantity tested with barium chloride solution. This gave only a faint precipitate, but, on warming, barium sulphate slowly separated and chlorine was evolved. The solution also liberated iodine from potassium iodide and showed other oxidising actions. When heated, acid fumes were evolved and pure potassium sulphate remained. This seemed all to point to the salt being a persulphate, and analysis confirmed this view.

The next thing was to prepare, if possible, further quantities of the salt. A saturated solution of potassium hydrogen sulphate was electrolysed in the apparatus described and figured on p. 765, the inner cell being filled with dilute sulphuric acid. A current of 3—3½ ampères was employed, and in the course of two days a white, crystalline deposit began to form. This proved to be potassium persulphate. After a considerable quantity had collected, it was separated from the mother liquor by filtration through perforated platinum foil and then dried on porous plates. The mother liquor

* In an abstract of Traube's paper which appeared in "Notes" of *Nature*, **44**, 163, it is stated that Bertholet obtained *crystals* of persulphuric acid on the anode in the electrolysis of sulphuric acid. It is hardly necessary to say that this is erroneous; he obtained crystals of the *anhydride* by means of the " silent discharge."

was then put back, the basin filled up with more of the original solution, and the process continued. A further deposit began to form in an hour or two, and after 24 hours the salt was again removed. This was repeated several times until a considerable quantity had been collected. Starting as above described, simply from the double sulphate, the product first obtained is finely granular, and is easily separated. As the mother liquor gets more and more acid, however, the deposit gets much finer and is apt to run through the perforated platinum along with the liquid.

The dry salt obtained in this way is somewhat impure, containing sulphate and free acid. A nearly pure product can be got with the earlier crops by washing them with cold water after filtering, but with the fine deposits this is hardly possible. In any case it is much better to recrystallise the salt. For this purpose it is treated with hot distilled water so as to obtain a nearly saturated solution, and this, after filtering as quickly as possible, is then rapidly cooled. During the treatment with hot water, slight decomposition takes place, but the amount is inconsiderable unless the solution itself be heated for some time. The solution deposits the salt in the form of minute prisms, which are collected and dried. By allowing the solution to cool slowly, large crystals, generally tabular, are deposited, though long prisms sometimes grow from the surface of the liquid. By spontaneous evaporation, large, flat tables can be obtained. The crystals appear to be asymmetric, and the minute prisms show, in polarised light, numerous examples of twinning. Large twinned crystals have also been observed, the twinning plane being the tabular face.

The composition of the salt is represented by the formula KSO_4. As already mentioned, potassium sulphate is left on ignition, oxygen and sulphuric anhydride being evolved. The percentage of the former was determined, the oxidising power estimated by standard ferrous sulphate and permanganate solutions, whilst the amount of oxygen evolved on heating was also measured. In the latter case the salt was placed in a test-tube provided with a double-bored cork. By one tube, pure carbonic anhydride was introduced, while by another the gases were passed into a nitrogen measuring tube filled with a strong solution of caustic alkali. When all the air was displaced, the salt was heated till non-absorbable gas ceased to be evolved. The volume of oxygen from a given weight of salt was thus obtained.

Results of analysis :—

	Found.	Calculated for KSO_4.
K_2SO_4	64·2	64·4
SO_4 (from extra oxygen found by titration).	35·5	35·6

1·422 gram gave, at 752 mm. and 15°, 63·1 c.c. of oxygen, weighing 0·0848 gram, equal to 5·96 per cent. Theory, 5·92 per cent.

As regards the correct molecular formula, it would appear to be KSO_4 and not $K_2S_2O_8$. Dr. James Walker has kindly made a series of conductivity determinations with dilute solutions and obtained results as follows :—

$v.$	$\mu.$	
64	125·0	
128	130·0	Δ
256	135·6	$(\mu_{1024} - \mu_{64})$
512	139·0	15·7
1024	140·7	

In the case of potassium perchlorate, the corresponding value of Δ, as given by Ostwald, is 15·0, and in the two cases the values of μ are almost identical for the various concentrations.

Potassium persulphate is sparingly soluble in cold water. Three determinations of the solubility at zero were made in the manner recommended by Victor Meyer:—

I. 9·738 grams of solution gave on evaporation and ignition 0·1093 gram of potassium sulphate, equivalent to 0·1695 gram of persulphate.

II. 14·851 grams of solution gave 0·1664 gram of sulphate, equivalent to 0·2581 of persulphate.

III. 24·219 grams gave 0·269 gram of sulphate, or 0·4172 of persulphate.

Therefore, 100 parts of water at 0° dissolve (1) 1·77, (2) 1·77, (3) 1·75 parts of potassium persulphate.

In aqueous solution the persulphate gradually decomposes at the ordinary temperature, with formation of potassium hydrogen sulphate and liberation of oxygen, but the process is a very slow one. After three months, a solution, pure to start with, was found to contain a considerable proportion of sulphate. The greater part, however, was found to be still undecomposed. The pure solution is neutral to test papers, and the progress of the decomposition can be noticed by observing the amount of acid liberated. The solution gave, with chromic acid and permanganate solutions, no indications of the presence of hydrogen peroxide. Another saturated solution was left for several weeks in contact with pure metallic zinc, and there still remained a considerable quantity of persulphate. To the same liquid a little copper sulphate solution was added, so as to form a zinc-copper couple. Three days later, traces of persulphate still existed in the solution.

The solution does not yield a precipitate with any reagent such as would give rise to ordinary double decomposition resulting in the formation of an insoluble salt. In fact, potassium persulphate, like the perchlorate, seems to be less soluble than the corresponding salt of any other metal. Any precipitates which are formed are, therefore, due to complete decomposition of the persulphate. Thus a clear solution of persulphate, when mixed with one of a barium salt, slowly deposits barium sulphate, often forming a thin layer closely adhering to the sides of the tube, and very difficult to remove. This decomposition is very much accelerated by heating the liquid. Even then, however, it takes some time, and a solution which has been briskly boiled often gives, after filtering and again boiling, a considerable further precipitate.

A solution of a lead salt also deposits sulphate on warming it with the persulphate. If alkali be added to the mixture (not previously heated) and then warmed, the hydrate first thrown down is changed to peroxide. A solution of lead hydrate in potassium hydrate also yields a precipitate of lead peroxide if boiled with the persulphate.

With silver nitrate, no immediate precipitate is obtained, but the liquid gradually acquires an inky appearance, and, after some time, a black precipitate of peroxide of silver separates. The liquid at the same time becomes strongly acid. This action is apparently due to the fact that silver persulphate is decomposed by water like some other silver salts of acids of sulphur, sulphuric anhydride being removed :

$$AgSO_4 + H_2O = AgO + H_2SO_4.$$

The accumulation of acid seems to stop the action, as the cautious addition of dilute alkali produces a further precipitation. This reaction—noticed before the nature of the salt was known—was at first supposed to be a reducing one, with separation of metallic silver, and the behaviour with Fehling's solution was next observed. Here, on gently warming, a reddish precipitate separated. This was assumed to be cuprous oxide, but was in reality peroxide. Both of these peroxides decomposed with evolution of oxygen when they were allowed to stand in contact with the liquid. In the case of silver, the brown basic hydrate (or oxide) precipitated by alkalis is gradually turned black by solution of persulphate.

With neutral solutions of manganous and cobaltous salts, partial precipitation of higher oxides takes place on heating with persulphate. In the cold, the addition of alkali precipitates the lower oxides ; but these immediately darken, forming manganese peroxide and cobaltic oxide respectively.

Solutions of nickel salts behave similarly in presence of alkali, but without the latter no precipitation takes place.

Ferrous sulphate solution is rapidly oxidised to ferric by persulphate solution. The green colour changes to brown, but this becomes much paler if acid be then added. It appears as if some basic salt were formed when the solution is neutral. With strong solutions, a considerable rise of temperature is noticeable, as is also the case when solid persulphate is added to strong ferrous sulphate solution.

Potassium iodide gives no immediate reaction with persulphate solution, but, after some seconds, the liquid becomes pale yellow, iodine being liberated. The reaction takes a considerable time before it is complete. It proceeds much more quickly, however, if the temperature is raised. The addition of dilute sulphuric acid seems to have little, if any, effect.

Organic colouring matters—litmus and turmeric, for example—are slowly bleached by a solution of persulphate. This is probably due to the action of free persulphuric acid liberated by partial decomposition.

Paper and cloth become quite rotten after being dipped in a solution of persulphate.

Potassium ferrocyanide becomes readily oxidised to ferricyanide when warmed with persulphate solution.

Alcohol, in presence of water, is oxidised to aldehyde when warmed with persulphate. A dilute solution of the latter is, however, somewhat slowly reduced by alcohol, even in presence of acid, and may be boiled with it without complete decomposition occurring immediately, as shown by its still liberating iodine from potassium iodide. Solid persulphate is not decomposed by absolute alcohol, in which it is insoluble, even on boiling. An attempt to convert benzyl alcohol into the aldehyde directly was also unsuccessful, the crystals of persulphate being practically unattacked at the boiling point of the former liquid.

Experiments performed for the purpose of determining the exact decomposition temperature gave no satisfactory result, owing to the apparent impossibility of getting absolutely pure, dry material. The method tried was as follows :—A fine glass tube, similar to those used for melting-point determinations, but much longer, was closed at one end. Into the bottom of this some finely-powdered persulphate was introduced. The tube was then exhausted, and mercury allowed to enter. The small quantity of air remaining separated the latter from the persulphate. The tube was then fastened to a thermometer, and the whole heated in a bath of sulphuric acid. The occurrence of decomposition would be shown by the rapid rise of the column of mercury, the motion due to the expansion of the small quantity of air being slight, and steady. The evolution of gas began, however, to be quite marked a little above 100° ; but, even after

heating to fully 250°, some persulphate remained undecomposed. It is easy to see that the least trace of moisture, or of acid, present in the salt would cause this behaviour, and the presence of these it seems to be impossible to avoid.

Potassium persulphate has a cooling, saline taste, but leaves a peculiar after-taste, possibly due to persulphuric acid.

Freshly-purified persulphate emits no odour, but, after being kept for some time, a peculiar smell is noticeable on opening the bottle. In the case of a not very pure product ozone is evolved slowly. Other persulphates, much more soluble in water, and not so easily freed from it, as, for instance, the ammonium salt, seem to decompose more readily; and here, also, sometimes ozone is evolved, whilst, in other cases, the above-mentioned peculiar odour is strongly marked. It would seem to be due to persulphuric acid or anhydride. On one occasion, when some lead persulphate decomposed suddenly, the vapours were very pungent, not resembling ozone in the least, and rapidly browned potassium iodide paper held near the salt. With the small quantity of substance and the rapid decomposition, it was impossible, however, to prove the presence or absence of a sulphur compound. Berthelot found that, even at 0°, persulphuric anhydride possessed considerable vapour pressure, and can be sublimed without decomposition.

When a solid persulphate is gently warmed with strong nitric or sulphuric acid, the oxygen liberated is evolved largely in the form of ozone. A similar evolution is also observed during the evaporation of strong solutions on the water-bath. With hydrochloric acid, chlorine is obtained in place of oxygen.

Ammonium Persulphate.

This salt is formed in a manner precisely similar to that of the potassium salt. The solution for electrolysis was prepared by saturating dilute sulphuric acid (about 1 to 6 by volume) with ammonium sulphate. As in the case of the potassium salt, it may be several days before persulphate begins to crystallise out, but, after that, the separation goes on steadily. Here, also, the nature of the deposit varies with each succeeding crop. When, at length, the separation of the solid from the mother liquor becomes difficult, it is better, instead of simply adding more original solution, to use only about half of the mother liquor, and, after diluting it with water, to saturate with solid ammonium sulphate. The early deposits are much more granular than with the potassium salt, and it is exceedingly easy to collect them.

Owing to its great solubility, even at low temperatures, the purifi-

cation of the salt is not so easy as that of the potassium compound. It is, in fact, rather difficult to obtain really pure specimens in quantity, and it does not keep so well as the potassium salt. If a saturated solution is evaporated in a vacuum at the ordinary temperature, long, thin prisms generally separate at first. These have a rhombic appearance, and, between crossed Nicols, show extinctions parallel to the axis. If left undisturbed, they grow more rapidly laterally than in the other directions, and assume the form of lozenge-shaped, apparently monosymmetric tables, having the plane of symmetry at right angles to the original prism axis. The crystals thus formed from solutions of the crude salt are generally large, and quite transparent. When this purer product is dissolved and recrystallised, the crystals obtained are generally large and badly formed, having a lamellar structure, which makes them non-transparent. Some of these have often the appearance of thick, rhombic prisms. Owing to their lamellar structure, they retain mother liquor, and, therefore, slowly decompose throughout their whole extent. To obtain a pure specimen, it is best to cool with ice a solution saturated at the ordinary temperature, or slightly higher. The greater part, however, remains in solution, and the mother liquor must be afterwards evaporated in a vacuum.

For the analysis of the salt, a weighed quantity was dissolved in water, evaporated to dryness, and redissolved. This solution was then titrated with standard baryta water to determine the amount of free acid. The remainder of the sulphate was then precipitated as barium salt, and the whole collected and weighed. The total SO$_4$ thus found should be double that found by titration. The ammonia was also determined.

	Found.	Calculated.
NH$_4$	15·6	15·8
SO$_4$ (total)	83·9	84·2
SO$_4$ (by titration)	42·3	43·1

As already stated, the salt is very soluble in cold water, and a very considerable fall of temperature takes place on dissolution. The following determinations of the solubility at 0° were made:—

I. 4·880 grams of solution gave, on evaporation, treating with ammonia solution, and drying, 2·085 grams of ammonium sulphate, corresponding to 1·799 grams of persulphate.

II. 2·887 grams gave, on heating as above, 1·229 grams of sulphate, corresponding to 1·06 of persulphate.

Therefore, 100 parts of water dissolve, at 0°, (1) 58·4, (2) 58·0, parts of ammonium persulphate.