

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 Berthelot 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 $\text{K}_2\text{S}_2\text{O}_8$. Dr. James Walker has kindly made a series of conductivity determinations with dilute solutions and obtained results as follows:—

<i>v.</i>	μ .	
64	125.0	
128	130.0	
256	135.6	Δ
512	139.0	$(\mu_{1024} - \mu_{64})$
1024	140.7	15.7

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.

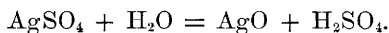
Therefore, 100 parts of water at 0° dissolve (1) 1.77, (2) 1.77, (3) 1.75 parts of potassium persulphate.

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:



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.

The reactions of this salt resemble those of the potassium compound, but are often more marked, owing to the greater solubility.

Considerable quantities have been prepared, as it forms the starting point in the preparation of the other persulphates.

Barium Persulphate.

This salt is prepared by treating a saturated solution of ammonium persulphate with barium hydrate. For this purpose it is unnecessary to use recrystallised salt, the only impurities being sulphate and free acid, which cause no extra trouble. The pure crystallised hydrate is added in some excess, as the impurities require more than the same weight of persulphate does, and also because decomposition, which would liberate acid, takes place during the subsequent operations.

The mixture of solid and solution is well rubbed up in a mortar, and then a rapid stream of air is driven through. The hydrate displaces the ammonia, forming persulphate, which dissolves, and the sulphuric acid forms insoluble barium sulphate. When the greater part of the liberated ammonia has been driven off, the remainder is removed by placing the liquid over sulphuric acid in a vacuum. Here it may be left over night, and it will probably be found, next morning, that no more ammonia remains, provided enough barium hydrate has been employed. The excess of the latter is next removed by passing in a stream of carbonic anhydride, the bicarbonate formed being subsequently decomposed by again placing it in a vacuum for a short time. The solution, which now contains pure barium persulphate, is filtered off from the sulphate and carbonate and evaporated in a vacuum, but during this operation decomposition takes place, sulphate separating out and persulphuric acid becoming liberated; so that if the concentration takes a considerable time, it is advisable to occasionally neutralise with barium hydrate solution. As soon as crystallisation commences, the evaporation is discontinued, and the salt which has separated is redissolved in the minimum quantity of water. The neutral solution, after filtering, is then cooled by means of ice until no more crystals are obtained. The salt is thus obtained in beautiful, small prisms, which are collected and dried on porous plates or between filtering paper. The mother liquor is again concentrated in a vacuum. The salt prepared in this way is quite pure, and keeps better than when the crystals are obtained directly by evaporation of the solution. In the latter case, large, interlocking prisms are, as a rule, produced. These are transparent and hard, and generally deeply striated, so that it is difficult to make out their form, but those which are at all distinct have a monosymmetric appearance. The minute crystals obtained by cooling the solution

also appear monoclinic when examined under the microscope, but between crossed Nicols show extinctions always parallel, or nearly so, to the prism axis. Sometimes, on evaporating in a vacuum, rosettes, in which the prisms radiate from a common centre, are obtained, as if crystallisation had taken place in a supersaturated solution.

The formula of the salt is $\text{Ba}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. In two different specimens the sulphate left on ignition was determined. In another, the percentage of barium was got from the amount of sulphate deposited on boiling the solution; the total SO_4 was then obtained by precipitating the filtrate with barium nitrate and adding the sulphate thus formed to the previous portion.

	Found.		Calculated.
	I.	II.	
BaSO_4 (on ignition)....	58.0	58.2	58.10
	Found.		Calculated.
Ba	33.7		34.16
SO_4 (total)	48.3		47.88
H_2O (by diff.).....	18.0		17.96

The last specimen has apparently been contaminated with some undecomposed ammonium salt.

In the course of a few days, the crystals gradually become milky from separation of sulphate; this change commences externally, and quickly spreads throughout the entire crystal, which crumbles to pieces, forming a moist, powdery mass. When once decomposition has fairly set in, it proceeds rapidly until all the barium exists as sulphate, but after this, the persulphuric acid which remains produces free sulphuric acid by its decomposition, and in presence of the latter the persulphuric acid is much more slowly decomposed, so that traces of it may still be present even after some weeks. Decomposition soon begins if the salt is kept in a dry atmosphere, so that attempts to prepare a less hydrated salt by placing it over sulphuric acid in a vacuum were fruitless. To preserve the crystals as long as possible, it was found best to keep them in an atmosphere which was always moist, wet filter paper being placed in the same vessel, but not in contact with the crystals. The salt itself is apparently not at all deliquescent.

Barium persulphate is very soluble in cold water. A single determination of the solubility at 0° was made, with the following result:—

5.598 grams of solution gave, on evaporation and ignition, 1.115 grams of barium sulphate, corresponding to 1.574 grams of anhydrous persulphate or 1.919 grams of crystallised salt. Therefore, 100 parts of water at 0° dissolve 39.1 parts of the former or 52.2 parts of the latter.

A control experiment was not performed, owing to the small quantity of material available at the time. The numbers will, however, give at least a fair approximation to the value. From the quantity of salt which crystallised out on cooling the solution, which was saturated at about 15° , it is evident that the solubility is very much higher at the latter temperature.

The salt evidently forms supersaturated solutions somewhat readily on evaporation in a vacuum. If a few drops of solution, placed on a slip of glass, be so treated, a gummy mass is obtained, which, when touched, slowly crystallises. Minute needles grow out radially from a common centre, forming fine rosettes, each of which shows a dark cross when viewed in polarised light. Pure solutions decompose gradually, somewhat slowly at first, when allowed to stand at the ordinary temperature. If a fairly dilute solution is heated, it generally remains clear till near the boiling point, when sulphate rapidly precipitates. It requires rather prolonged boiling, however, to destroy the last traces of persulphuric acid.

The behaviour of alcohol towards the salt is somewhat peculiar. If a few drops be added to an aqueous solution, it seems to accelerate the decomposition. It therefore seemed probable that the solid also would be decomposed when treated with alcohol. It was found, however, that the finely-powdered crystals dissolved in absolute alcohol, yielding a clear solution. This, when allowed to stand, slowly deposited a white solid; the action taking place rapidly when the solution was boiled. The solid was presumably barium sulphate, but, on adding water, it redissolved entirely, and this solution then slowly deposited sulphate. The persulphate was, therefore, not decomposed, but probably only dehydrated by the alcohol. This was found to be the case, as some of the dried deposit, when ignited, gave 65.39 per cent. of sulphate. The behaviour of a saturated aqueous solution, when treated with a large excess of alcohol, was then examined, when it was found that a similar product could be obtained. The liquid remained clear at first, but, on warming, a bulky precipitate separated. It was necessary to take several times as much absolute alcohol as solution, otherwise decomposition rapidly took place, free oxygen escaping, though aldehyde was also formed. In this case the product gave less sulphate on ignition—only 64.66 per cent.—and, on examining some under the microscope, crystals of the fully hydrated salt were noticed. These had, however, a “weathered” appearance, having apparently been externally dehydrated by the alcohol. The percentage of sulphate calculated for the formula $\text{Ba}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ is 67.15, and for $\text{Ba}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ is 63.84, so that, in the case of each product, the quantity of sulphate found showed that 1 mol. H_2O , at most, was present in the compound. It was found that during the

evaporation of the alcohol wetting it, the dehydrated salt again took up any water that might be present, and this fact might explain the percentage of water in the first case being higher than that required for a monohydrate. As it was possible, however, that the pure compound was really anhydrous, it was necessary to obtain a product which had no opportunity of re-forming the original salt. For this purpose some finely-powdered crystals were digested during several days with successive portions of cold absolute alcohol. The last portion of alcohol was then removed by pure ether dried over sodium; the greater part of the ether was then removed by decantation and the remainder by means of a current of dry air. A weighed portion of the residue gave, on ignition, 67.4 per cent. of sulphate. A monohydrate, as noted above, should yield only 67.15 per cent., but it was found that there was a small quantity of sulphate in the persulphate, as a portion, when dissolved in water, left a minute trace of insoluble matter. On endeavouring to further dehydrate a portion, by leaving it over sulphuric acid in a vacuum, decomposition rapidly ensued. There seems little doubt, therefore, that the compound obtained in this way has the formula $\text{Ba}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. It is interesting to note that barium perchlorate crystallises with 4 mols. H_2O . Of these, three can be easily removed, but the last cannot be abstracted without complete decomposition of the salt. The crystalline perchlorate is likewise soluble in alcohol.

The alcohol with which the persulphate was digested was tested, and found to contain no barium, so that the monohydrated salt is quite insoluble in absolute alcohol. On the addition of potassium iodide to the alcoholic liquid, iodine was liberated, so that the persulphuric acid, formed by the decomposition of the small quantity of the persulphate which also yielded the barium sulphate found in the solid product, had apparently dissolved without being decomposed by the alcohol.

Solid barium persulphate is very readily decomposed by heat, gentle warming being sufficient. In the case of the monohydrated salt, a slight cloud is formed at the moment of decomposition, but only at a much higher temperature are acid vapours freely evolved. The quantity of water is just sufficient to form pure sulphuric acid,



and this, of course, even at the comparatively low temperature of decomposition, gives up a part of its sulphuric anhydride.

Lead Persulphate.

The comparative ease with which pure barium persulphate can be obtained is due to the insolubility of the sulphate, and as lead sulphate

is also insoluble, the preparation of lead persulphate was next attempted. Owing, however, to the insolubility of the oxide and hydrate, as well as to other causes, this is a much more difficult matter. If oxide of lead is rubbed up in a mortar with a saturated solution of ammonium persulphate, considerable quantities of ammonia are liberated, but in a short time the mixture darkens from formation of peroxide of lead, and on treating with water and filtering, no soluble salt of lead is found in solution. It seemed, therefore, that the only practical method of obtaining the salt was to decompose a strong solution of barium persulphate with a slight excess of sulphuric acid in the cold, and then to neutralise the liquid with lead carbonate; this was tried and found to answer. The acid solution was not filtered off from the barium sulphate, the lead carbonate being simply added directly to the cold mixture. Brisk effervescence took place, but after this was over the liquid still had a marked acid reaction. This did not disappear if the mixture was left for a considerable time, and before very long darkening commenced from formation of the peroxide. The solution, which was found to contain a large quantity of the persulphate, was therefore filtered off and placed over sulphuric acid in a vacuum. The evaporation took a considerable time, and during the process lead sulphate separated out continuously; this was removed frequently by filtration. Owing to the decomposition, the liquid became more and more acid. Some barium hydrate solution was therefore added on one occasion, but not sufficient for complete neutralisation. It was expected that the barium would all be removed as sulphate by subsequent decomposition. Next morning the bottom of the dish was covered with a firm, coherent deposit, consisting of a mixture of barium sulphate and lead peroxide. Lead persulphate in strong solution would therefore appear to resemble the silver salt, requiring the presence of free acid to prevent deposition of peroxide. Ultimately a solid mass was obtained. This had a pearly lustre, but, though crystalline, no distinct form was observable. It was removed, quickly powdered, and then pressed between filter paper to remove as far as possible the small quantity of adhering liquid. The salt began to deliquesce, however, and was again placed in a desiccator over sulphuric acid. Here it was kept under diminished pressure for some hours, when it was found to have formed a firm, dry cake. It contained a small quantity of admixed sulphate, as shown by treating some with water, when a small residue remained. Free persulphuric acid was also present. A portion of the product was weighed out for the determination of the total lead sulphate and sulphuric acid obtained on decomposing the salt by evaporation of its solution. It was intended to estimate, subsequently, the ready-formed sulphate on a larger portion, and to make a direct determina-

tion of the water. Unfortunately, however, the remainder of the salt suddenly began to decompose with great rapidity, evolving pungent fumes which browned potassium iodide paper. The proportion of impurity could, therefore, not be determined. The analysis stated below can, consequently, give only an approximation to the composition of the salt, which at present remains doubtful.

	Found.	Calculated for	
		Pb(SO ₄) ₂ ·2H ₂ O.	Pb(SO ₄) ₂ ·3H ₂ O.
Pb	46·3	47·6	45·7
SO ₄	43·5	44·1	42·4
H ₂ O (by diff.)	10·2	8·3	11·9

Allowing for the presence of other substances, the second formula appears the more probable. If correct, this would make the persulphate agree with the perchlorate, which crystallises with 3 mols. H₂O.

As already mentioned, the salt is very soluble in water, and deliquesces in a moist atmosphere. A solution gives, with alkalis, a white precipitate of hydrate which is rapidly oxidised to peroxide. Owing to the decomposition of the material, no other properties could be examined.

Other Persulphates.

The zinc salt was prepared in solution by double decomposition between zinc sulphate and barium persulphate in the proper proportions. On evaporating the filtered liquid over sulphuric acid in a vacuum, a mass of minute needles was obtained. This deliquesced on exposure to air, but contained a large proportion of sulphate mixed with the persulphate, and the two could not be separated with the comparatively small quantity of material to hand, on account of the great solubility of the sulphate and the continual decomposition.

A similar attempt to prepare the copper salt was made, but with no more satisfactory results. In this case, also, there was decomposition with formation of a considerable quantity of sulphate and free acid. Some barium carbonate was added in the hope that, by neutralising the acid (forming ultimately barium sulphate) it would decrease the rate of decomposition. The experiment was not successful, as double decomposition gradually took place, and, next morning, the barium was in solution as persulphate, and copper carbonate was deposited. A small quantity of solution of the copper salt was evaporated to dryness, and gave a blue, crystalline solid containing sulphate and persulphate; it deliquesced on removal from the desiccator.

Attempts to prepare sodium, lithium, and magnesium persulphates directly by electrolysis proved unsuccessful. In the case of the first two this seems to be due to the great solubility of the persulphates, as, in each case, the liquid was very highly oxidised; but the only salts which separated were normal and acid sulphates, which are, evidently, less soluble in the strongly acid liquid.

In the case of magnesium, a white, muddy deposit, which consisted of dehydrated sulphate, was obtained, but no trace of persulphate was observable. The mother liquor, also, did not seem to be very much oxidised; so that it is possible that magnesium persulphate cannot be prepared, even in solution, in this way.

The preparation in a pure state of such exceedingly soluble salts, where the sulphates also dissolve so readily in water, will, apparently, be a matter attended with some difficulty, and require working on a comparatively large scale. As the barium salt cannot be kept for more than a few days, it is necessary to prepare it as wanted.

Apart from the interest attaching to the salts themselves, the preparation of pure persulphates in a solid, crystalline form is of considerable theoretical interest and importance. It conclusively proves the correctness of Berthelot's views as to the composition and nature of the "persulphuric anhydride" and "persulphuric acid" prepared by him; that they are, in fact, entitled to the names which he gave them, and cannot be considered as peroxides, as held by Mendeléeff. The fact of the occurrence of a salt-forming oxide of sulphur having the formula S_2O_7 shows that we cannot adopt the rule as to the highest salt-forming oxide of an element which was previously supposed to exist as a deduction from the periodic law. Persulphuric acid can no more be classed as a peroxide than perchloric acid can. In fact, although the persulphates would seem not to be isomorphous with the perchlorates, they exhibit many close resemblances with them, in the matter of solubility, for instance.

Berthelot, in his last paper (*loc. cit.*), has already disposed of Moritz Traube's theory as to the formation of neutral "sulphur holoxide," SO_4 , during the electrolysis of strong sulphuric acid solution. The only result given by the latter which points to the possibility of such a substance being present in the oxidised liquid, is that showing the ratio of oxidising power to sulphuric acid formed on decomposition, the sulphuric acid previously present having been removed by means of barium phosphate. As Berthelot points out, the amount of extra oxygen found might partially be due to the presence of peroxide of hydrogen. It is also possible that the solution was not completely decomposed on boiling, a result which seems not so highly improbable after the experiences with persulphate solutions already noted in this

paper. All the other results stated by Traube agree perfectly on the assumption that persulphuric acid, HSO_4 , is formed.

I hope, before long, to make a further communication to the Society on the subject of persulphates. Meanwhile, other salts—selenates, tellurates, nitrates, &c.—are being examined with a view to determining whether they, also, may not give more highly oxidised products when their solutions are electrolysed in a divided cell.

*University of Edinburgh,
August, 1891.*
