tion is considerably higher than the value calculated from conductivity data. Using $\alpha_0 + 0.90$, the solubility product of silver nitrite at 25° is $L = 5.86 \times 10^{-4}$.

Summary.

1. Measurements have been made of the conductivity of aqueous solutions of silver nitrite at 25°. The results obtained indicate that hydrolysis of the salt takes place.

2. The solubility of silver nitrite has been determined at a number of temperatures between 1 and 60°.

3. The decrease produced in the solubility of silver nitrite by the addition of silver or nitrite ions has been measured at 25°. It has been found that equimolar quantities of these ions bring about approximately the same decrease in the solubility.

4. Calculations of the solubility of silver nitrite, in the presence of different quantities of silver nitrate, indicate that the degree of dissociation of silver nitrite in a saturated solution is considerably greater than is indicated by conductivity measurements.

5. From the data obtained in the solubility measurements, a mean value of 0.90 has been calculated for the degree of dissociation of silver nitrite in a saturated solution at 25°. Using this value, the solubility product of silver nitrite is 5.86×10^{-4} at 25°.

SWARTHMORE, PA.

THE DERIVATIVES OF PERCERIC OXIDE.

[FIRST PAPER.[1]]

BY C. C. MELOCHE.

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The preparation and analysis of a derivative of perceric oxide was first described by Cleve,[2] who found that perceric hydroxide corresponded to the oxide CeO_3. In the same year Lecoq de Boisbaudran[3] published a note confirming the conclusions of the former investigator. However, the work of von Knorre[4] does not entirely substantiate the conclusions of Cleve, and Mengel[5] agrees with von Knorre in his position. Pissarjewski[6] has also contributed to the study of perceric hydroxide.

Methods for the preparation of a perceric potassium carbonate solution were first described by Job.[7] He showed that the oxidation could be

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[1] This paper is the abstract of part of a thesis submitted to the Graduate Faculty of the University of Wisconsin for the Degree of Doctor of Philosophy.

[2] *Bull. soc. chim.*, [2] **43**, 53 (1885); *Jahrb. Fortsch. Chem.*, **1885**, 491.

[3] *Compt. rend.*, **100**, 605 (1885); *Chem. News*, **51**, 148 (1885); *Jahrb. Fortsch. Chem.*, **1885**, 493.

[4] *Z. angew. Chem.*, **1897**, 723.

[5] *Z. anorg. Chem.*, **19**, 71 (1899).

[6] *J. Russ. Phys. Chem. Ges.*, **32**, 609 (1900); *Centr.*, [1] **1901**, 86.

[7] *Compt. rend.*, **128**, 178, 1098 (1899); *Ann. chim. phys.*, [7] **20**, 246, 253, 261 (1900).

effected by air as well as by hydrogen peroxide, and isolated the double compound. Baur[1] prepared crystals of perceric potassium carbonate by the third method described by Job, and concluded that the crystals obtained by this method had not been analyzed by Job. Baur on the basis of his analysis assigned the formula $Ce_2O(CO_3)_2O_3.4K_2CO_3.10H_2O$ to the compound. Job gave to the crystals which he had prepared the formula $Ce_2O_3(CO_3)_3.4K_2CO_3.12H_2O$.

The use of alkaline cerous carbonate as a carrier for oxygen has been investigated to some extent by Job[2] and Baur.[3] The absorption of oxygen by alkaline cerous solutions has been studied by Baur.[4] An investigation of the autoxidation of cerous salts has also been conducted by Engler[5] in connection with his work on the activity of oxygen.

Perceric Potassium Carbonate.

Reference was made above to Job's[6] discovery of a double potassium perceric carbonate having the formula $Ce_2O_3(CO_3)_3.4K_2CO_3.12H_2O$. He prepared this compound by the interaction of ceric ammonium nitrate and hydrogen peroxide in a strong solution of potassium carbonate. Cerous nitrate was also found to be suitable for this preparation.

Instead of working in strong potassium carbonate solution, as was done by Job, it has been found advantageous to pass a stream of carbon dioxide through the potassium carbonate solution until a large part of the potassium is removed as the bicarbonate. The filtered liquid, when kept at 5° for twenty-four hours, deposits ruby red crystals. The details of the method are as follows:

To 175 cc. of a saturated potassium carbonate solution 5 cc. of 30% hydrogen peroxide are added and then 13 g. of cerous ammonium nitrate dissolved in about 15 cc. of water are slowly added with stirring. The mixture is heated rapidly to 60° and kept at that temperature as long as the color of the solution deepens. As soon as the reaction is complete, carbon dioxide is passed through, and, after the temperature has decreased somewhat, the vessel is placed in cold water to which a piece of ice is added occasionally. The stream of carbon dioxide is continued until no further precipitation of potassium bicarbonate takes place. The mixture is then cooled to 0°, or slightly above, until as much as

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[1] *Z. anorg. Chem.*, 30, 256 (1902); *Centr.*, [1] 1902, 1046.

[2] *Compt. rend.*, 134, 1052 (1902).

[3] *Loc. cit.*, p. 253.

[4] *Ber.*, 36, 3038 (1903); *Centr.*, [2] 1903, 931: *Ber.*, 37, 795 (1904); *Centr.*, [1] 1904, 991.

[5] *Ber.*, 36, 2642 (1903); *Centr.*, [2] 1903, 547; *Ber.*, 37, 49 (1904); *Centr.*, [1] 1904, 566; *Ber.*, 37, 3268 (1904); *Centr.*, [2] 1904, 1280; C. Engler and J. Weissburg, "Kritische Studien über die Vorgänge der Autoxidation" (Braunschweig, 1904, Friedrich Vieweg und Sohn), p. 112.

[6] *Loc. cit.*

possible of the potassium bicarbonate has crystallized out. Meanwhile, the passage of carbon dioxide is continued. Rapid filtration through glass wool is the best method for the separation of the potassium bicarbonate. Although part of the perceric compound seems to separate out in a finely divided form it is not retained by the glass wool. The filtrate is warmed to 40° and stirred, whereupon this finely divided material passes into solution. This solution is now passed through an asbestos filter to remove that portion of the original perceric precipitate which remains undissolved. The deeply colored liquid is covered and kept at about 5° for 24 to 48 hours. The separated crystals are thrown upon a Büchner funnel provided with a hardened filter and washed with a little ice water. The water is rapidly sucked off and the crystals are air dried by continuing the suction.

The analysis of the compound gave the following results:

	I.	II.	Av.	Ratio. Det.	Ratio. Probable.	Theoret. comp.
Ce	22.37	22.51	22.44	1.98	2	22.74
K_2O	30.98	31.21	31.10	4.09	4	30.56
CO_2	21.42	21.37	21.40	6.03	6	21.39
O[1]	3.93	3.86	3.90	3.02	3	3.89
O[2]	3.56	3.35	3.46	2.68	3	3.89
H_2O	17.74	17.70	17.72	12.20	12	17.52

The preceding results correspond to the formula $Ce_2O_4(CO_3)_2.4K_2CO_3.12H_2O$. The compound prepared by Job was $Ce_2O_3(CO_3)_3.4K_2CO_3.12H_2O$. The one prepared by Baur was $Ce_2O_4(CO_3)_2.4K_2CO_3.10H_2O$.

The method of analysis was as follows: The cerium was precipitated as oxalate and weighed as CeO_2 according to the usual gravimetric method. The potassium in the filtrate was converted to the sulfate and weighed as such with the customary precautions. The carbon dioxide was determined gravimetrically by evolution and absorption in potassium hydroxide solution, sp. gr. 1.27. Sulfuric acid (1 : 5) was found to be best adapted for the decomposition. The method used for the determination of available oxygen was a modification of the one employed by Job. The procedure was as follows:

A small suction flask was fitted with a three-hole, tightly fitting, rubber stopper about one-quarter of an inch thick. A dropping funnel, a buret and a carbon dioxide delivery tube were attached. The side neck of the flask was made the outlet for carbon dioxide. About 1.2 g.[3] of ferrous ammonium sulfate were weighed out and placed in the dry flask. Carbon dioxide which had been washed with water and dried by means of concentrated sulfuric acid was passed through the flask until all the air had been expelled. A small amount of cold boiled water just sufficient to dissolve the ferrous ammonium sulfate was added through the dropping funnel. After solution was complete 50 cc.

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[1] Available oxygen.

[2] Unavailable oxygen, determined by difference.

[3] On account of temperature conditions, etc., it will sometimes be necessary to use as little as 0.7 g. of ferrous ammonium sulfate and a correspondingly smaller amount of sample. In any case no more ferrous iron should be present than can be precipitated and redissolved by about 50 cc. of the sodium pyrophosphate solution.

of saturated sodium pyrophosphate solution was introduced. A precipitate was formed which, on shaking, redissolved in the excess of reagent. If this was not the case a little more sodium pyrophosphate was added. The 0.5 g. sample of potassium perceric carbonate, dissolved in 20 cc. of saturated potassium bicarbonate solution, was now added through the dropping funnel and followed by 10 cc. of the same potassium bicarbonate solution. The minimum amount of cold boiled water was used to wash the solution of cerium into the flask completely. Titration could then be effected by means of standard potassium permanganate solution from the buret. The end point was the first appearance of a faint yellow color, which is due to the oxidation of a small amount of cerium to the ceric condition. The standardization was conducted in exactly the same manner, except that no cerium was dissolved in the potassium bicarbonate solution. In this case, since no cerium was present, the end point was indicated by the first appearance of a faint pink color due to a slight excess of permanganate. Alkaline ferrous pyrophosphate solution is readily oxidized by gaseous oxygen, so tha tair must be rigidly excluded. The results obtained by this method were checked by an entirely different method to be described later.

The total water was determined by the direct method, that is, by heating in a current of dry air, absorbing the water in concentrated sulfuric acid and weighing. The unavailable oxygen was obtained by difference.

Perceric potassium carbonate parts with its water of crystallization readily. If left in a good desiccator over sulfuric acid or calcium chloride for only a few minutes the compound changes from a transparent ruby red to an opaque orange color. Exposure to air for any considerable length of time produces a similar effect.

The study of the mode of combination of the oxygen in the compound $Ce_2O_4(CO_3)_2.4K_2CO_3.12H_2O$ presents many interesting features. For convenience we may classify the oxygen as follows:

(I) Three cerous oxygen atoms; (II) One ceric oxygen atom; (III) Two perceric oxygen atoms.

The three cerous oxygen atoms are unavailable. One of the remaining three atoms that are available[1] differs from the other two. All three are available in alkaline solution, but in acid solution a result is obtained which corresponds to one atom of available oxygen for every two atoms of cerium.

Job's method of determining total available oxygen presents the advantage that in the presence of considerable potassium bicarbonate no insoluble compounds are formed. No hydrated manganese dioxide is precipitated and the manganese of the permanganate is reduced to the divalent condition. However, on account of the peculiar nature of the perceric compound, it was thought desirable to study the total available oxygen by an altogether different method. The ordinary methods used for the determination of available oxygen are not applicable in this instance. As a matter of fact, the compound can not be dissolved in a mineral

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[1] In the following discussion the word available will be applied to oxygen present in such form that it can be used efficiently for the wet oxidation of common reducing agents such as ferrous ammonium sulfate.

acid without complete decomposition and the liberation of two-thirds of its available oxygen in the gaseous state. The behavior of perceric potassium carbonate toward acid ferrous sulfate and potassium iodide solutions will be discussed quantitatively later in this paper. The alternative method for the determination of the total available oxygen will be described first. The principle utilized is that the perceric compound on treatment with sulfuric acid in excess yields free oxygen. The remaining available oxygen can be determined by one of the usual methods, for example, by means of ferrous ammonium sulfate and potassium permanganate.

The determination of the free oxygen liberated on treatment with sulfuric acid was made in an apparatus (see Fig. 1) constructed especially for the purpose. The details of the method are as follows:

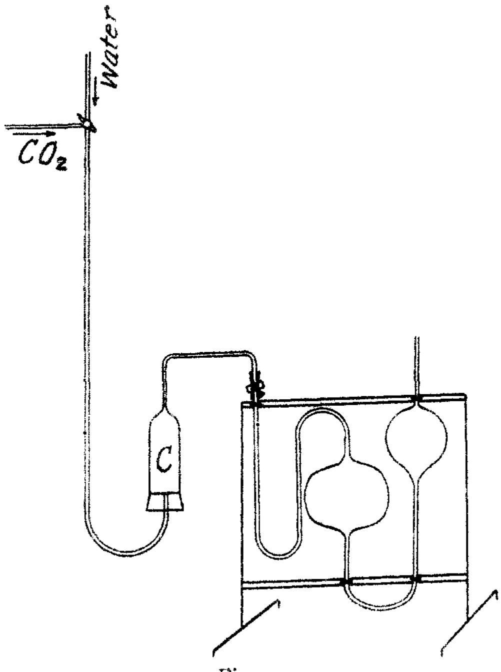

Fig. 1.

About 0.5 g. of the potassium perceric carbonate was weighed out and placed in the decomposition cell C. The air was then displaced by a stream of carbon dioxide which had been washed with water and moist phosphorus. The decomposition cell was connected to a pipet containing $33^1/_3\%$ potassium hydroxide solution. Decomposition of the sample was accomplished by treating with an excess of sulfuric acid (1 : 3). The acid was admitted through the bottom of the cell under sufficient pressure to prevent the loss of gas through the inlet. The apparatus was so constructed that water could be admitted instead of the acid to force the gas into the absorption pipet. The carbon dioxide was first absorbed and the residue of oxygen returned to the gas buret and measured. Later, the oxygen was absorbed by means of alkaline pyrogallate solution in the regular manner. The small residue, presumably nitrogen, was returned to the buret, measured and subtracted.

The values obtained for the gaseous oxygen liberated when the compound $Ce_2O_4(CO_3)_2.4K_2CO_3.12H_2O$ was treated with sulfuric acid in excess were:

% oxygen	2.554	2.505	2.557
Ratio of Ce : O in atoms	2 : 1.995	2 : 1.958	2 : 1.998

It is thus seen that when the above compound is treated as stated two atoms of oxygen are immediately and quantitatively evolved.

For the determination of the available oxygen which remains after treatment with dilute sulfuric acid, a separate sample was employed. The decomposition was first effected with a small amount (about 5 cc.) of dilute sulfuric acid (1:3). A weighed excess of ferrous ammonium sulfate was then dissolved in cold boiled water, acidified with sulfuric acid and added to the solution of the sample. The volume was then brought to about 200 cc. and the excess of ferrous ammonium sulfate titrated with potassium permanganate. The available oxygen remaining in solution was found to be as follows:

% oxygen	1.26	1.24
Ratio of Ce : O in atoms	2 : 0.98	2 : 0.97

These results, and those obtained above, show that when the potassium perceric carbonate is treated with dilute sulfuric acid two atoms of oxygen are evolved, while one atom remains in solution and is available for the oxidation of ferrous ammonium sulfate. The results obtained by this alternative method are in good agreement with those obtained by the ferrous pyrophosphate method. The ratio of the number of atoms of cerium to the number of atoms of total available oxygen is therefore 2:3 according to both methods.

It is of interest to note that the available oxygen remaining after treatment with dilute sulfuric acid is present in the form of hydrogen peroxide, as is shown by the addition of titanium sulfate solution. That the solution contains no ceric sulfate is indicated by the fact that it does not possess the bright yellow color characteristic of a ceric sulfate solution. The sulfuric acid solution of the compound under discussion not only oxidizes ferrous ammonium sulfate, but also reduces potassium permanganate solution, a further indication that the remaining available oxygen is present as hydrogen peroxide.

In this connection it is well to examine the results obtained by the ordinary methods for the determination of available oxygen. On the basis that part at least of the available oxygen was present in the form of combined hydrogen peroxide, a determination of the available oxygen was made by the iodimetric method modeled after the method of Kingzett for hydrogen peroxide. The concentrations were preserved as nearly as possible the same as in the Kingzett method, considering the fact that the perceric compound was dissolved in potassium bicarbonate solution.

The following was the method adopted: Two grams of potassium iodide were dissolved in 150 cc. of cold boiled water and 35 cc. of sulfuric acid (1 : 2) added, then, with constant stirring, 20 cc. of saturated potassium bicarbonate solution containing 0.5 g. of perceric potassium carbonate were added. About 30 cc. of wash water were required. After allowing to stand for 5 minutes the titration was made with sodium thiosulfate, using freshly prepared starch paste as indicator. One cc. of the sodium thiosulfate solution was equivalent to 0.0005055 g. oxygen. The results obtained were

% oxygen	1.34	1.34
Ratio of Ce : O in atoms	2 : 1.048	2 : 1.048

It will be observed that two-thirds of the available oxygen is not available by this method.

An attempt was also made to determine the total available oxygen by dissolving the sample in dilute (1:10) sulfuric acid containing a weighed excess of Mohr's salt and titrating the excess of the latter with potassium permanganate solution. The results obtained were discordant, but corresponded to somewhat over one atom of available oxygen for every two atoms of cerium.

Since the three available oxygen atoms in perceric hydrate can be determined by treating in the cold with a dilute sulfuric acid solution of ferrous ammonium sulfate and titration of the excess with potassium permanganate, it was thought that the double perceric potassium carbonate, after hydrolysis in the cold, might yield similar results by the same method, but the results obtained were very similar to those obtained above without previous hydrolysis.

The loss of about two-thirds of the oxygen may be regarded as a physical one. The above work indicates that it is impossible for perceric compounds to exist in a solution acid with a mineral acid such as sulfuric acid; also, the compound in contact with water alone undergoes rapid hydrolysis. It is therefore evident that, in the presence of acid, contact is necessary to make this oxygen available in the nascent form. The reason for the fact that a large portion of the oxygen is not available for wet oxidation is similar to the one which must also be assigned for the fact that large portions of the hydrogen are not available when certain of the metals are treated with dilute hydrochloric acid.

This loss of oxygen is, however, easily explained on a purely chemical basis. Ratios already given, the fact that after treatment with acid one oxygen remains in solution as hydrogen peroxide, and the other facts cited in the following, indicate that the equation representing the reaction under discussion may be written as follows:

$$2CeO_3 + 3H_2SO_4 = Ce_2(SO_4)_3 + O_2 + H_2O_2 + 2H_2O$$

The autoreduction, by which the oxygen is produced, is probably intramolecular, so that the oxygen is evolved in the molecular rather than in the atomic state.

That there are only two atoms of peroxide oxygen in the perceric complex seems reasonable from the following considerations: If three atoms were present more than one molecule of hydrogen peroxide would probably remain in solution after treatment with cold dilute sulfuric acid. If only one atom of peroxide oxygen were present, it is improbable that any hydrogen peroxide would remain after treatment with acid, since the following reaction takes place quantitatively:

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + O_2 + H_2SO_4$$

The presence of peroxide oxygen is indicated qualitatively by the following reactions: When a 10% solution of the perceric potassium carbonate in 23% potassium carbonate solution was treated with a strong potassium-carbonate solution of potassium ferricyanide, potassium permanganate, potassium manganate, potassium hypochlorite, or potassium hypobromite, a lively evolution of oxygen was observed. Likewise, when a 10% solution of the same compound in saturated potassium bicarbonate solution was treated with lead dioxide, oxygen was evolved. In this connection the structural formula which Engler[1] has suggested for Job's compound is of interest.

A very interesting property of perceric solutions which has not been mentioned above is their behavior toward hydrogen peroxide. The dark red-brown precipitate produced by the addition of this reagent corresponds possibly[2] to CeO_4, but no detailed study of it has yet been made.

The remarkable stability of the double potassium perceric carbonates is one of their most interesting characteristics. This is illustrated by the comparative permanency of the potassium carbonate solution. The solution will keep for months with only slight decomposition. Such behavior is in marked contrast with that of a similar solution of hydrogen peroxide. As previously stated, the compounds part with their water easily. The remaining complex, however, can be heated for long periods above 110° without decomposition. Job[3] states that by heating the compound $Ce_2O_3(CO_3)_3.4K_2CO_3.12H_2O$ to 110° the compound $Ce_2O_3(CO_3)_3.4K_2CO_3$ was obtained free from water. It was still soluble in potassium carbonate solution and produced the characteristic blood-red coloration, and, furthermore, the available oxygen remained intact. This work would indicate that the peroxide oxygen is not combined as hydrogen peroxide. The compound $Ce_2O_4(CO_3)_2.4K_2CO_3.12H_2O$ was desiccated and later heated for several hours to 110–120°. A test showed that after this treatment a little water still remained. The heating was then continued at 133–138° for two hours. A trace of water still remained, however. The dried material was for the most part soluble in potassium carbonate and yielded the characteristic blood-red solution. Two analyses gave for the content of available oxygen the following results:

(I) 4.35%   (II) 4.42%

The percentage required by theory for the anhydrous compound is 4.72%. It seems then that the process of drying at 133–138° is accompanied by the loss of small amounts of the available oxygen. In this case the loss was about 0.3%.

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[1] *Ber.*, **36**, 2642 (1903); Engler and Weissburg, *Loc. cit.*

[2] Job. *Ann. chim. phys.*, [7] **20**, 261 (1900).

[3] Job, *Ibid.*, [7] 20, 251 (1900).

Summary.

A different procedure for the preparation of perceric potassium carbonate has been described. The compound prepared by this method is somewhat different from other similar compounds prepared by Job and Baur. Analysis shows that the formula is $Ce_2O_4(CO_3)_2.4K_2CO_3.12H_2O$.

The manner in which the oxygen is combined has been studied in considerable detail. It has been shown that two-thirds of the available oxygen is to be regarded as peroxide oxygen.

Two different methods for the determination of total available oxygen have led to the same conclusions. This work has confirmed Job's observation that the ordinary methods for the determination of total available oxygen are not applicable in such instances.

The preparation and properties of various other perceric derivatives will be given in another paper.

In conclusion, the author wishes to acknowledge his indebtedness to Professor Victor Lenher for helpful suggestions and for the interest which he has at all times manifested in the above work.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE COLLEGE OF WASHINGTON.]

TWO METHODS OF SEPARATION OF THE METALS OF THE ALKALINE-EARTH GROUP.

BY ALICE G. PATERSON.

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Both methods are based on the slight differences in solubility of the relatively insoluble salts of the group, both being applications of the principle involved in fractional precipitation.

According to this principle, as is well known, if a precipitating agent, such as ammonium carbonate, is added to a solution containing a mixture of salts of metals whose carbonates are relatively insoluble, such as those of the alkaline earths, the least soluble carbonate is the one to be first precipitated. The carbonates continue to be precipitated in order of their solubility, with exceptional action only in the case of very high concentration. However, if barium, for instance, is precipitated as a carbonate, and then a solution of a sulfate is added, it is converted into the less soluble sulfate. Also, if barium is precipitated as a carbonate and a solution of a strontium salt is then added, barium carbonate dissolves, strontium carbonate being formed.

If, then, two or more precipitating agents are added to a solution containing a mixture of salts, any given metallic ion will unite with that acid ion which forms the least soluble salt.