

### 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  $\text{Ce}_2\text{O}_4(\text{CO}_3)_2 \cdot 4\text{K}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$ .

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.

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

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

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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.

This principle is employed by Stieglitz,<sup>1</sup> also by A. A. Noyes.<sup>2</sup> In the present instance the writer proposes its application to the group analysis.

The first method is as follows: the solution, containing salts of the alkaline-earth metals, is treated with excess of solutions of ammonium carbonate and ammonium sulfate together. Barium precipitates as sulfate, and calcium and strontium as carbonates. This mixture is brought to boiling and allowed to stand 20–30 minutes, with occasional stirring, as it has been found that the action is not immediately complete. Especially is this true in the presence of magnesium salts. Some magnesium may also be precipitated as magnesium ammonium carbonate. The mixture is then filtered, and the precipitate washed until free from precipitating agents. The precipitate is washed into a beaker, using as small an amount of water as possible, and 1.5 volumes of 1% acetic acid added, and the mixture brought to boiling, dissolving the carbonates and driving off carbon dioxide. Enough acid should, of course, be present to complete this action. The undissolved precipitate is barium sulfate. This is filtered off, using paper pulp; the precipitate is washed, and barium confirmed by the flame. The filtrate contains the acetates of calcium and strontium, possibly also some magnesium acetate. This filtrate is made slightly alkaline with ammonium hydroxide, is then treated with excess of ammonium carbonate and ammonium oxalate together, and the mixture is brought to the boiling point with stirring. It is then allowed to stand 20–30 minutes with stirring, is filtered, and the precipitate washed until free from precipitating agents. This precipitate consists of calcium oxalate and strontium carbonate. It is washed from the paper with a small amount of water, and 1.5 volumes of 1% acetic acid added, and the mixture stirred or shaken vigorously for a few minutes to dissolve the strontium carbonate and expel the carbon dioxide. As before, enough acid should be present to complete this action. It is then filtered, and the residue, consisting of calcium oxalate, washed. The filtrate is made slightly alkaline with ammonium hydroxide, and the strontium then precipitated with ammonium sulfate or ammonium carbonate, evaporating the solution if the volume is large, and confirmed with the flame, as is also the calcium in the calcium oxalate.

In the presence of both the carbonate and oxalate ion, the strontium is apparently nearly completely precipitated as carbonate, and the calcium as oxalate, provided a little time is allowed for the action to complete itself. In the absence of calcium, the entire precipitate formed upon the addition of ammonium carbonate and ammonium oxalate consists of the

<sup>1</sup> "Qualitative Chemical Analysis," 11, p. 21. "Separation and Determination of Strontium."

<sup>2</sup> "Qualitative Chemical Analysis," p. 85.

*carbonate* of strontium, and dissolves easily in acetic acid. In the absence of strontium, the entire precipitate consists of the *oxalate* of calcium. This is only very slightly soluble in cold 1% acetic acid, so that in the absence of strontium, a very faint cloudiness results when the acetic acid solution is treated with ammonium carbonate. This solubility seems to decrease if the precipitate is allowed to stand the 20-30 minutes before filtering. A small amount of magnesium may appear here as magnesium oxalate, distinguishable from calcium by the flame.

The two most important points for a clear-cut separation are, first, the sufficient washing of the precipitates, and second, allowing the precipitates to stand before filtering. In this respect the method does not differ from others. If the washing is not thorough, and the sulfate ion remains in soluble form with the residue of insoluble sulfate and carbonate, it will, of course, combine with the strontium ion, when the strontium carbonate is dissolved by acetic acid, thus causing strontium sulfate to remain in the residue with barium sulfate. In regard to the second point, the time is probably necessary because the solubilities of certain of the salts are so nearly the same, as, for instance, that of barium sulfate and barium carbonate, and that of strontium sulfate and strontium carbonate, that time must be allowed for complete reversion to the less soluble of the two, although the action is nearly complete after simply heating the mixture. This seems to be indicated by the fact that when the precipitate of carbonates and sulfates was *not* so allowed to stand, before filtering, some barium appeared in the solution of acetates of strontium and calcium, even when the mixture was subsequently only warmed and not boiled with 1% acetic acid; also, that when the mixture *had* been allowed to stand, even bringing to a boil with 1% acetic acid showed no barium in the filtrate. This seems to be also true in the case of the strontium carbonate and calcium oxalate. If filtered at once, after the addition of the precipitating agents, or after a few minutes of warming, neither the calcium flame, when a small amount of calcium is used, nor the strontium, when a small amount of strontium is used, is pure. As the following experiments will show, this is not the case when the mixture of precipitates stands after being heated.

In the following experiments the mixture analyzed contained in every case 5 cc. of a normal solution of barium chloride, 5 cc. of a normal solution of calcium chloride, and 5 cc. of a normal solution of magnesium chloride, together with the amount of strontium salt specified. This was precipitated with 15 cc. ammonium sulfate solution (M), and 15 cc. ammonium carbonate solution (250 g. to the liter) and analyzed according to the foregoing outline. In every case enough water was first added to the solution to make the total volume 100 cc. No ammonium chloride was used. In the first five experiments following, the mixture was filtered

immediately after being heated with the precipitating agents. In the last two (6 and 7), the mixture stood 30 minutes before being filtered, and no barium appeared in the filtrate. Boiling with 1% acetic acid, after being thus allowed to stand, did not affect barium. Apparently a small amount of barium is present as barium carbonate, when precipitation is first effected. This is probably completely changed to barium sulfate on standing a short time.

- (1) 0.5 cc. 0.1 *N* SrCl<sub>2</sub> Mixed ppt. of carbonate and sulfate boiled with 5% HAc. Distinct ppt. when tested for Sr with ammonium carbonate. Indeterminate flame.
- (2) 0.7 cc. 0.1 *N* SrCl<sub>2</sub> Mixed ppt. of carbonate and sulfate boiled with 5% HAc. Distinct ppt. when tested for Sr with ammonium carbonate. Mixed flame.
- (3) 1 cc. 0.1 *N* SrCl<sub>2</sub> Mixed ppt. of carbonate and sulfate boiled with 1% HAc. Distinct ppt. when tested for Sr with ammonium carbonate. Ca and some Ba in flame.

The main barium sulfate residue, after being thoroughly washed, showed no calcium or strontium flame.

- (4) 1 cc. 0.1 *N* SrCl<sub>2</sub> Mixed ppt. of carbonate and sulfate boiled with 1% HAc. Ammonium sulfate used to precipitate Sr. Slight ppt. Barium flame with trace of strontium.
- (5) 1.5 cc. 0.1 *N* SrCl<sub>2</sub> Mixed ppt. of carbonate and sulfate warmed, not boiled with HAc. Ammonium sulfate used to test for Sr. Slight ppt. Sr and Ba flame.
- (6) 1.5 cc. 0.1 *N* SrCl<sub>2</sub> Stood 30 minutes after the addition of precipitating agents. Mixed ppt. warmed, not boiled with 1% HAc. Ammonium sulfate used to test for Sr. No ppt., even on heating.

From Experiments 5 and 6 it would appear that if the mixed precipitate is allowed to stand before filtering, barium does not go into solution.

- (7) 2 cc. 0.1 *N* SrCl<sub>2</sub> Stood 30 minutes after the addition of precipitating agents. Mixed ppt. boiled with 1% HAc. Stood 20 minutes with ammonium carbonate and ammonium oxalate. Ammonium sulfate used to test for Sr. Slight ppt. Solution evaporated and precipitated with ammonium carbonate. Considerable precipitate; fine, pure strontium flame. No barium.
- 2 cc. 0.1 *N* SrCl<sub>2</sub> = 8.7 mg. of strontium.

In the following experiments the mixture analyzed contained in every case, 5 cc. *N* barium chloride solution, 5 cc. *N* strontium chloride solution, 5 cc. *N* magnesium chloride solution, together with the amount of calcium salt specified. Total volume of solution made up to 100 cc. No ammonium chloride used. Procedure the same as in preceding experiments. In Expts. 1 and 2 the mixture of precipitated oxalate and carbonate was filtered immediately after being brought to boiling with the precipitating agents. In Expt. 3 this mixture was allowed to stand 20 minutes before filtering.

- (1) 1.5 cc. 0.1 *N* CaCl<sub>2</sub> 5% HAc used for both separations.  
Cloudy residue for calcium. Red flame, not free from strontium.
- (2) 2 cc. 0.1 *N* CaCl<sub>2</sub> 1% HAc used for both separations.  
Distinct residue for calcium. Mixed flame.
- (3) 2 cc. 0.1 *N* CaCl<sub>2</sub> 1% HAc used for both separations. Stood 20 minutes with ammonium carbonate and ammonium oxalate before filtering.  
Slight residue; fine calcium flame.
- 2 cc. 0.1 *N* CaCl<sub>2</sub> = 4 mg. of calcium.

In the following experiments the mixture analyzed contained, in every case, 5 cc. *N* calcium chloride solution, 5 cc. *N* strontium chloride solution, 5 cc. *N* magnesium chloride solution, together with the specified amount of barium chloride. Total volume 100 cc. Procedure the same as in the preceding experiments. In Expts. 1 and 2 the precipitate of sulfate and carbonate was filtered immediately after being heated with the precipitating agents. In Expt. 3 this precipitate was allowed to stand 30 minutes after heating, before it was filtered.

- (1) 0.5 cc. 0.1 *N* BaCl<sub>2</sub> Mixed ppt. of sulfate and carbonate boiled with 1% HAc.  
Very slight residue. No flame test obtainable.
- (2) 1 cc. 0.1 *N* BaCl<sub>2</sub> Mixed ppt. of sulfate and carbonate boiled with 1% HAc.  
Very slight residue. Barium flame.
- (3) 1 cc. 0.1 *N* BaCl<sub>2</sub> Mixed ppt. of sulfate and carbonate stood 30 minutes.  
Boiled with 1% HAc. Considerable residue; strong barium flame.

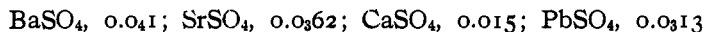
1 cc. 0.1 *N* BaCl<sub>2</sub> = 6.8 mg. of barium.

Experiments 2 and 3 are the same, except for the difference of time. In 2 probably some of the barium remains as barium carbonate, dissolving in the acetic acid.

These amounts could be easily detected, giving decided residue and good flame tests.

The second method makes use of the same principle, with somewhat different application. In this method strontium sulfate is dissolved by the use of lead acetate, the less soluble lead sulfate being formed.

The solubilities (Stieglitz) of the sulfates of the alkaline-earth metals and of lead sulfate are as follows, given in mols per liter:



It will be seen that lead sulfate lies between barium sulfate and strontium sulfate. If lead acetate is added to a suspension of calcium sulfate, strontium sulfate and barium sulfate in water, calcium and strontium go into solution as acetates, lead sulfate being precipitated. Barium sulfate is not affected.

The method is as follows: A part of the solution is first tested for barium with potassium chromate and the flame. The remainder of the solution, without removing barium, is then treated with ammonium chloride,

and precipitation effected with ammonium sulfate, the mixture being brought to boiling. Most of the calcium remains in solution. Barium and strontium, with perhaps a small amount of calcium, are precipitated as sulfates. These are filtered off through paper pulp, washed twice, and then transferred by washing to a beaker and treated with an excess of lead acetate solution (*N*). This mixture is warmed, not boiled, for a few minutes and filtered. The filtrate contains strontium acetate, the excess of lead acetate, and probably a small amount of calcium acetate. The residue contains lead sulfate and barium sulfate. The filtrate is freed from excess of lead by hydrogen sulfide, and is then tested for strontium with ammonium sulfate, or with carbonate and oxalate according to Method 1.

It appears from the following experiments that if the mixture is boiled with lead acetate, some barium goes into solution. (Expts. 1 and 2.) If, however, the mixture of sulfates is warmed, but not boiled with lead acetate, barium does not dissolve, while strontium does. (Expts. 3 and 4.)

In every case the solution analyzed contained 5 cc. *N* barium chloride solution, 5 cc. *N* Ca solution, and 5 cc. *N* magnesium chloride solution together with the specified amount of strontium. Total volume 100 cc.

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| (1) 0.3 cc. 0.1 <i>N</i> SrCl <sub>2</sub> | Precipitated sulfates boiled with lead acetate solution. Distinct cloudiness when testing for strontium with ammonium sulfate. Barium flame.  |
| (2) No SrCl <sub>2</sub>                   | Same as preceding experiment. Barium flame.   |
| (3) No SrCl <sub>2</sub>                   | Precipitated sulfates warmed but not boiled with lead acetate solution. No precipitate when tested with ammonium sulfate. Barium not dissolved.   |
| (4) 1 cc. 0.1 <i>N</i> SrCl <sub>2</sub>   | Precipitated sulfates warmed but not boiled with lead acetate. Distinct cloudiness when tested for strontium with ammonium sulfate. Strontium separated by carbonate oxalate method. Gave fine, pure strontium flame. |
- 1 cc. 0.1 *N* SrCl<sub>2</sub> = 4.3 mg. of strontium.

The principle may have a wider application in general analytical work, and perhaps even possesses some value for quantitative separations. It may be seen that there are possibilities for very clear-cut and complete separations. The two methods as given work out rapidly and very satisfactorily. The writer has made use of the first method in the laboratory with students in the first semester of qualitative analysis, with very good results.

There arises the possibility of precipitating several metals by the use of two or more precipitating agents, and then by the addition of a soluble salt of a metal not under examination, dissolving one or more of those precipitated. Or, several salts having been precipitated by one reagent, a similar displacement being carried out. For instance, possibly the carbonate, oxalate, and sulfate could all be used together, to precipitate

barium, calcium, and strontium, these then being separated, first by the use of acetic acid, then dilute hydrochloric acid. Also, in precipitating calcium oxalate and strontium carbonate together, lead acetate might be used to dissolve calcium oxalate, leaving strontium carbonate, since the solubility of lead oxalate is less than that of calcium oxalate, but the solubility of lead carbonate is somewhat greater than that of strontium carbonate. The writer has not, however, carried out these separations. A large difference in solubility does not seem to be necessary; is not in fact desirable for the carrying out of such schemes.

A separation of copper and cadmium may be made by warming a suspension of the sulfides in water with lead nitrate solution. Cadmium sulfide dissolves; copper sulfide is not affected. The excess of lead is removed with ammonium sulfate, and cadmium precipitated as a sulfide. The objection to this method is that neither ammonium sulfate nor dilute sulfuric acid completely remove the lead, so that in testing for cadmium the solution is slightly discolored by lead sulfide. This, however, is the case in the usual scheme of analysis, whenever lead is present.

The writer expects to continue work on this subject.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF GRINNELL COLLEGE.]

### ACID POTASSIUM AND ACID SODIUM PHTHALATES AS STANDARDS IN ACIDIMETRY AND ALKALIMETRY.

BY W. S. HENDRIXSON.

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Quite recently Francis E. Dodge<sup>1</sup> suggested acid potassium phthalate as a satisfactory standard in acidimetry and alkalimetry, and also suggested acid sodium phthalate as a possible standard, though having no advantages over the potassium salt. His paper contains no analytical data, but is largely theoretical, and, so far as the writer has been able to learn, these substances have not been rigidly investigated with reference to their reliability for the purpose suggested. The two substances have certain properties, as pointed out by Dodge, that are very desirable in a standard, such as ease of preparation in the pure state, comparatively ready solubility, and high molecular weights. It seemed to me a matter of interest to subject them to a careful experimental study in comparison with other standards of undoubted accuracy, to determine whether they can be relied on to give accurate results in standardization. To this end a solution of hydrochloric acid was made up by the method of Hulett and Bonner,<sup>2</sup> which should contain 0.003647 g. of hydrochloric acid per cc., and it was then further standardized by means of silver chloride, by two samples of benzoic acid, by acid potassium and acid sodium phthalates.

<sup>1</sup> *J. Eng. Ind. Chem.*, **7**, 29 (1915).

<sup>2</sup> *THIS JOURNAL*, **31**, 390 (1909).