This indicates that the double sulfate has the ratio 1 : 1 : 2 and the formula $Gd_2(SO_4)_3.Na_2SO_4.2H_2O$. This is similar to the compound with potassium sulfate according to Benedict.

DURHAM, N. H.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

THE EXTRACTION OF BERYLLIUM FROM GADOLINITE.

BY C. JAMES AND G. A. PERLEY.

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The most important elements contained in gadolinite comprise beryllium and those of the rare-earth family. Usually the first named is either neglected or else separated by the use of sodium bicarbonate or ammonium carbonate. Since the iron group precipitate contains no aluminium, or at the most mere traces, the beryllium and iron may be separated by the use of an excess of sodium hydroxide. The writers discovered a much simpler method which consists of the fractional precipitation of the hydroxides by means of sodium hydroxide. When a concentrated solution of the chlorides or sulfates of beryllium and ferric iron is precipitated with sodium hydroxide at the boiling point, ferric hydroxide, or a basic salt, is thrown down before the beryllium. If dilute solutions be used, glucinum hydroxide accompanies the ferric hydroxide and the separation is very poor. From the large number of experiments carried out, the following seems to be the simplest manner for working up the mineral:

The gadolinite was first crushed, and then finely powdered in a ball mill. Both sulfuric and hydrochloric acids were used in the attack. Although hydrochloric acid at first seems preferable, it is much inferior, since heating with concentrated sulfuric acid rapidly renders the silica insoluble. The decomposition was finally carried out in a large cast iron vessel capable of taking seventy-five kilos at a charge. The vessel was fixed in brickwork, and the mixture heated until dense white fumes of sulfuric acid were copiously evolved. The sulfated mineral was then stirred with water in a large copper tank. By adding the material slowly, the temperature was not allowed to rise, and a strong solution of the sulfates was obtained. The whole was then left until the silica had settled and the supernatant liquid had clarified. The clear liquid was siphoned off and precipitated with a hot solution of oxalic acid and allowed to stand for about twelve hours. The crystalline rare earth oxalates were filtered off and well washed with boiling water. The filtrate from the above, containing the beryllium and iron, may be treated several different ways, the best all-round method being as follows: The solution is heated and treated with some oxidizing agent, such as potassium bromate, in order to remove the oxalic acid, after which about a liter of ammonium hydroxide is added, followed by a concentrated solution of sodium hydroxide until the odor of ammonia makes its appearance. The whole is then well boiled and the hydroxides separated by filtration. It is advisable to always test the filtrate for beryllium for fear that an excess of sodium hydroxide has been added. However, the end point as shown by the appearance of ammonia is usually very sharp. This operation may be carried out in a large copper tank fitted with a propeller. The next step consists in separating the iron and beryllium. The hydroxides are stirred with enough hydrochloric or sulfuric acid to dissolve about two-thirds of the whole. This should bring about the solution of all the beryllium together with some iron. The mass is filtered and the residue tested for beryllium. If the latter is found to be present, another extraction must be made. The acid extract is heated to boiling and carefully precipitated with sodium hydroxide until a small amount of the filtered liquid gives a light colored precipitate with ammonium hydroxide—showing that nearly all the iron has been removed. The liquid is separated by filtration, again heated to boiling, treated with a small amount of sodium hypobromite and precipitated with sodium hydroxide until a small amount of the liquid gives a white precipitate of hydroxide when treated with ammonium hydroxide. The mass is filtered and the filtrate separated from the last traces of iron by adding sodium hydrogen sulfide. The two last residues which contain beryllium are worked up with the next lot. The addition of ammonium acetate and hydrogen sulfide before the sodium hydrogen sulfide helps in the separation of traces of copper and iron, but causes trouble in the final precipitation of the basic beryllium carbonate. The addition of too much hypobromite prevents the rapid separation of the last traces of iron, owing to oxidation of the sulfide produced. After the removal of all the iron, the beryllium is thrown down as the basic carbonate by adding a concentrated solution of sodium carbonate to the boiling liquid. After thoroughly boiling, the precipitated basic carbonate is filtered off and well washed with boiling water. It is necessary to test all the final filtrates, and to boil off all hydrogen sulfide before precipitating the beryllium as basic carbonate, otherwise a product giving a greenish oxide is obtained.

Another method for preparing beryllium basic carbonate from the filtrate after the separation of the rare-earth oxalates is applicable only when the liquid is very rich in beryllium. The liquid containing the iron and beryllium is oxidized to remove the oxalic acid and to convert the iron to the ferric condition, and then precipitated while boiling with sodium hydroxide until nearly all the iron is removed. The last portions of iron are removed by more sodium hydroxide and sodium hydrogen sulfide as described above.

These methods for the separation of iron and beryllium, although of no use quantitatively, are by far the best on the large scale, since the various stages can be carried out with great rapidity. The resulting beryllium product is entirely soluble in sodium bicarbonate, a test which Parsons has shown to be very delicate. The separation of aluminium from beryllium will be described in a later paper.

DURHAM, N. H.

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

A STUDY OF INDICATORS FOR THE DETERMINATION OF TEMPORARY HARDNESS IN WATER.

BY JOHN F. NORTON AND H. I. KNOWLES.

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Temporary hardness in water is due largely to the presence of calcium and magnesium bicarbonates. On heating, these decompose according to the equation

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O.$$

The bicarbonates, being salts of a weak acid and a relatively strong base, are hydrolyzed in solution, imparting alkaline properties to the water.

$$Ca(HCO_3)_2 + 2H_2O \rightleftarrows Ca(OH)_2 + 2H_2CO_3.$$

The most rapid and satisfactory method for determining temporary hardness is by titration of the alkali with standard acid in the presence of a suitable indicator. For this latter purpose, methyl orange is in quite general use, although the committee on Standard Methods[1] of Water Analysis recommends lacmoid, erythrosine or phenacetolin.[2] Peters[3] suggests alizarine, while Blacker[4] claims that dimethylamidoazobenzene gives good results. Howard[5] and Pope recommend methyl red and certain of its derivatives. Reichard[6] offers an inorganic indicator—bismuth oxyiodide.

Indicators are weak tautomeric acids or bases. According to Noyes[7] the fundamental equations upon which the theory of indicators is based are:

$$(H^+) = \frac{1-\alpha}{\alpha}\,\frac{K_{IA}}{\gamma}$$

for acid indicators and

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[1] "Standard Methods of Water Analysis," *Am. Pub. Health Assn.*, 1912, p. 37.

[2] We are informed that the next report on Standard Methods will give preference to methyl orange.

[3] *Apoth. Ztg.*, 18, 25 (1903).

[4] *Chem. Ztg.*, 37, 56 (1912).

[5] *J. Chem. Soc.*, 99, 1333 (1911).

[6] *Pharm. Zentr.*, 53, 1033 (1912).

[7] THIS JOURNAL, 32, 815 (1910).