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CAMBRIDGE, MASS.

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

GADOLINIUM SODIUM SULFATE.

BY D. W. BISSELL AND C. JAMES.

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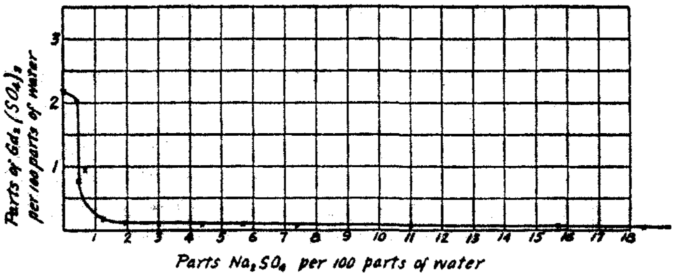
This investigation seemed to be of peculiar interest, since, according to some observers, gadolinium sodium sulfate was insoluble in sodium sulfate solution, while at least one other has suggested that its solubility might be used for a means of separation. Of course, the solubility of gadolinium sulfate in sodium sulfate solution might first increase and later decrease. This is true in the case of yttrium, and would explain the different observations that have been published. However, the following work shows that, when sufficient sodium sulfate was added so as to leave a slight excess, only about 0.6 g. of gadolinium sulfate was contained in a liter.

Pure hydrated gadolinium sulfate was prepared as follows: Gadolinium material was first separated from europium and less soluble earths by crystallizing the double magnesium nitrates in the presence of bismuth magnesium nitrate. The more soluble portions were then converted to the bromates and fractionated until the least soluble portions gave a pure white oxide. This bromate was converted into the oxalate and the latter treated with concentrated sulfuric acid and heated until all fumes ceased to be evolved. The anhydrous sulfate was next dissolved in water, and carefully crystallized over the steam bath. The crystals were removed, dried and finely powdered.

Bottles containing various amounts of gadolinium sulfate and sodium sulfate were made up, and about 50 cc. of water added to each. They were then rotated in a thermostat at 25° for several months. After they had settled, the liquid phase was analyzed in the following manner: Two samples were drawn from each bottle and transferred to tared weighing bottles. The first was diluted, heated to boiling, and treated with a warm solution of ammonium sebacate. The precipitate was washed free from sodium, ignited and weighed as the oxide Gd_2O_3. The results were calculated as $Gd_2(SO_4)_3$ and as the equivalent of sulfur trioxide. The second sample was diluted, heated to boiling, acidified with hydrochloric acid and the total SO_3 precipitated as barium sulfate with barium chloride. This gave the total SO_3, and by subtracting from this the SO_3 in combination with the gadolinium, the amount in the sodium sulfate was obtained. The results of the analysis as parts per 100 parts of water were as follows:

Bottle.	Parts of $Gd_2(SO_4)_3$ per 100 parts of water.	Parts of Na_2SO_4 per 100 parts of water.	Bottle.	Parts of $Gd_2(SO_4)_3$ per 100 parts of water.	Parts of Na_2SO_4 per 100 parts of water
1	2.15	0.00	10	0.06	5.71
	2.08	0.42	11	0.05	7.46
3	2.04	0.44	12	0.05	11.02
4	0.76	0.47	13	0.06	15.74
5	0.88	0.66	14	0.05	18.54
6	0.17	1.26	15	0.05	22.02
7	0.10	1.94	16	0.05	27.05
8	0.07	3.01	17	0.05	27.40
9	0.07	4.39			

The resulting curve is shown in the figure, and is similar to that obtained for samarium sodium sulfate.[1] The solubility of the pure gadolinium sulfate at 25° was slightly lower than that given by Benedict.[2]



The procedure for the analysis of the solid phase was as follows: A sample was removed by means of a platinum spoon and pressed dry with filter paper. It was then well mixed and divided into two portions which were weighed. The samples were then transferred to beakers, dissolved in water acidified with hydrochloric acid, and the gadolinium and sodium sulfates determined by the methods used above. A study of the curve shows that there is probably only one compound formed between the two sulfates. The lines joining the points of the liquid and solid phases upon the triangular diagram, were so nearly parallel that the point of intersection could not be settled with accuracy. It appeared, however, that the probable ratio was one to one. In order to prove this the solid phase was taken from bottles widely separated, washed on filter paper and dried. The analyses were carried out as before described, while water was determined by difference.

	$Gd_2(SO_4)_3$.	Na_2SO_4.	H_2O.	Ratio.
1	76.37	19.32	4.31	1:1:2
2	76.30	19.25	4.45	1:1:2

[1] THIS JOURNAL, 36, 634 (1914).

[2] *Z. anorg. Chem.*, **22**, 409 (1899).

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.

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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