ART. III.—*On the Chromites of Magnesium*; by W. R. NICHOLS, student at the Massachusetts Institute of Technology.

THE extent of the power possessed by some of the hydrated sesquioxys, notably by the hydrate of chromium, to hold magnesia and several other of the metallic protoxyds in insoluble combination, appears never to have been distinctly recognized by chemists. Fresenius, it is true, remarks* that sesquioxys of chromium cannot be separated (quantitatively)[†] by ammonia from the alkaline earths, since, even though carbonic acid be completely excluded, portions of the alkaline earths are thrown down in combination with the sesquioxys of chromium. But his statement is far less forcible than the facts in the case demand.

Other chemists have fallen into the grave error of supposing that magnesium can be separated from chromium, with sufficient accuracy for the ordinary purposes of qualitative analysis, by mere addition of ammonia-water to throw down hydrate of chromium, after the solution to be analyzed has been mixed with chlorid of ammonium. Galloway[†] has developed a plan for separating the hydrates of iron, aluminum and chromium as a distinct group or class, by adding chlorid of ammonium and ammonia to the boiled filtrate from the precipitate produced by sulphuretted hydrogen in the ordinary course of an analysis. According to Galloway, this ammonia precipitate is collected by itself and examined for iron, aluminum and chromium; sulphid of ammonium is then added to the filtrate to throw down cobalt, nickel, zinc and manganese; carbonate of ammonium is next employed to precipitate barium, strontium and calcium, while the magnesium, if any be present, is finally detected by means of phosphate of sodium in the usual way.

As will appear, however, from the following experiments, it would be quite impossible in many cases to detect magnesium in this way in presence of chromium. From a solution con-

* Quantitative Chemical Analysis, 4th ed. London, 1865, p. 372.

† Manual of Qualitative Analysis, 4th ed. London, 1864, p. 84 et seq.

taining any considerable proportion of sesquioxyd of chromium as well as magnesium, the greater part or the whole of the latter will be thrown down, together with the chromium, on the addition of ammonia, even when the solution is highly charged with chlorid of ammonium.

Sulphid of ammonium, also, like ammonia, throws down from mixed solutions of chromium and magnesium a compound precipitate well-nigh insoluble in water and saline solutions. If no serious difficulty has been met with hitherto in detecting magnesium in presence of chromium by the ordinary method of qualitative analysis, it is doubtless owing to the fact that, in pursuing this method, some of the magnesium thrown down in combination with chromium will be encountered when the precipitate produced by sulphid of ammonium comes to be examined in regular course for (barium, strontium, calcium and) magnesium, which may have fallen down in combination with phosphoric, boracic, oxalic, or silicic acid, or in the form of fluorids; and this, even if nothing but chromium and magnesium are present.

As thrown down either by ammonia or by sulphid of ammonium, the compound precipitate of chromium and magnesium is nearly or quite insoluble in solutions of the fixed caustic alkalies, and even when the precipitate is dissolved in chlorhydric acid and the solution mixed with cold soda lye, all the magnesium and most of the chromium is re-precipitated. Since this behavior of the precipitate toward soda lye points clearly to the existence of chemical attraction or affinity between the magnesia and the chromic oxyd, I have devoted particular attention to the study of the precipitates thus produced by soda.

Equivalent quantities of chrome alum and Epsom salt were weighed out and dissolved in water with addition of chlorid of ammonium and the mixture was treated with ammonia-water in slight excess. It was found to make no difference with regard to the completeness of the precipitation whether the salts were dissolved together with addition of chlorid of ammonium, or separately, the chlorid of ammonium being added to the solution of sulphate of magnesium before mixing the two solutions.

After the addition of ammonia to the mixed solution of chrome alum and sulphate of magnesium, an attempt was made in each case to determine the amount of magnesium in the filtrate by precipitation with phosphate of sodium. Negative results were obtained for the most part in these trials, as will be seen below.

The precipitate thrown down by ammonia was dissolved in

boiling dilute chlorhydric acid, the solution thoroughly cooled, and then mixed with an excess of a cold aqueous solution of caustic soda. The precipitate produced by the soda was filtered as rapidly as possible, washed somewhat with water, dried, ignited and weighed, while the filtrate was boiled to precipitate any chromium which had dissolved. The hydrate of chromium thrown down by boiling was collected on a filter, was washed, dried, ignited and weighed by itself.

I. 2.5098 grm. of chrome alum and 0.5240 grm. of Epsom salt were taken, so that the mixture contained 1.19 equivalent of Cr_2O_3 and 1 equivalent of MgO . No magnesium could be detected in the filtrate from the precipitate produced by ammonia in this mixture. The ammonia precipitate dissolved in chlorhydric acid, and treated with caustic soda in excess, gave up only 0.0103 grm. of Cr_2O_3 to the soda, while 0.3753 grm. of Cr_2O_3 went down again with the magnesium.

An analysis of the ignited soda precipitate gave the following results:—

	Taken.	Found.		Theory (MgO , Cr_2O_3).
(I.) MgO	0.0847	0.0831	18.13	20.73
Cr_2O_3	0.3843	0.3753	81.87	79.27
	<hr/> 0.4690	<hr/> 0.4584	<hr/> 100.00	<hr/> 100.00

II. 2.4979 grm. of chrome alum and 0.6150 grm. of Epsom salt were taken, so that the mixture contained 1 equivalent of Cr_2O_3 and 1 equivalent of MgO . Sulphid of ammonium was used as the precipitant in this instance, and 0.0105 grm. of MgO was found in the filtrate from it. When the precipitate was dissolved in chlorhydric acid and treated with soda lye, 0.0181 grm. of Cr_2O_3 went into solution in the soda.

III. 2.469 grm. of chrome alum and 0.302 grm. of Epsom salt were taken, so that the mixture contained 2.02 equivalents of chromic oxyd for 1 equivalent of magnesia. No magnesium could be detected in the filtrate from the ammonia precipitate. 0.0400 grm. of Cr_2O_3 was held dissolved by the soda, and 0.3393 grm. of Cr_2O_3 was thrown down again with the magnesia when the precipitate, after solution in chlorhydric acid, was treated with soda in excess.

An analysis of the ignited soda precipitate gave the following results:—

	Taken.	Found.		Theory (MgO , $2\text{Cr}_2\text{O}_3$).
(III.) MgO	0.0488	0.0492	12.66	11.56
$2\text{Cr}_2\text{O}_3$	0.3780	0.3393	87.34	88.44
	<hr/> 0.4268	<hr/> 0.3885	<hr/> 100.00	<hr/> 100.00

IV. 2.0244 grm. of chrome alum and 0.2500 grm. of Epsom salt were taken, so that the mixture contained 2 equivalents of chromic oxyd for 1 equivalent of magnesia. A trace of magnesium was detected in the filtrate from the ammonia precipitate, and 0.0337 grm. of MgO was obtained from the soda precipitate. 0.1167 grm. of Cr_2O_3 was thrown down on boiling the filtrate from the soda precipitate.

V. 2.3967 grm. of chrome alum and 0.3005 grm. of Epsom salt were taken, so that the mixture contained 1.97 equivalent of Cr_2O_3 for 1 equivalent of MgO . No magnesium was detected in the filtrate from the ammonia precipitate. 0.0250 grm. of Cr_2O_3 was thrown down on boiling the filtrate from the soda precipitate.

VI. 1.0120 grm. of chrome alum and 0.5000 grm. of Epsom salt were taken, so that the magnesia should be in large excess, the proportion of magnesia to chromic oxyd in this case being as 2 to 1. 0.0077 grm. of MgO was obtained in the filtrate from the ammonia precipitate, and 0.0765 grm. of MgO in the soda precipitate. No chromium was found in the filtrate from the ammonia precipitate, while 0.1508 grm. was obtained from the soda precipitate. The results may be tabulated as follows:

	Taken.	Found		Theory
		in the soda precipitate.		($2MgO, Cr_2O_3$).
(VI.) $2MgO$	0.0809	0.0765	33.66	34.34
	0.1549	0.1508	66.34	65.66
	<hr/> 0.2358	<hr/> 0.2273	<hr/> 100.00	<hr/> 100.00

The soda precipitates, after having been ignited and weighed, were decomposed by fusion with carbonate of sodium and nitrate of potassium in the usual way.* The chromium was then determined as chromate of lead, and the magnesium in the form of pyrophosphate.

It was found to be impossible, in this way, to convert all the chromium into a soluble compound in one operation. On treating the fused mass with water, there remained undissolved, on every occasion, a certain quantity of a fine, whitish-yellow substance, which was so finely divided as to pass at first quite readily through the filter; it could be collected only by returning the filtrate to the filter several times. A second fusion with carbonate of sodium and nitrate of potassium was consequently resorted to in each case, in order to complete the decomposition. The yellow color of the fused mass and of the solutions obtained after these second fusions, showed clearly enough that, whatever the real composition of the unresolved powder may be, a certain proportion of chromium is always

* Fresenius. Quantitative Analysis, p. 372.

contained in it. It should be stated that considerable difficulty was encountered in filtering the chromite of magnesium precipitated by caustic soda, especially in those cases where a comparatively large proportion of chromium remained dissolved in the excess of soda, for hydrate of chromium is gradually deposited from such solutions even in the cold. Toward the close of the filtration a certain portion of the chromium, which was dissolved at first, is in this way precipitated upon the filter and added to the mass of chromite of magnesium.

The foregoing experiments were undertaken at the suggestion of Prof. F. H. Storer, by whom my attention was called to the subject in the autumn of 1867.

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