

COMPOUNDS OF METALLIC HYDROXIDES WITH IODINE.

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SCHLAGDENHAUFFEN¹ describes a method for the quantitative determination of magnesium in a solution containing barium, strontium and calcium without previously removing these metals. He employed a reagent prepared by adding iodine to a two per cent. solution of potassium hydroxide, in sufficient quantity to produce a golden yellow solution. This reagent gives, even with very dilute solutions of magnesium salts, a dark, reddish-brown precipitate. An apparently similar precipitate was obtained by the same author by adding iodine, dissolved in potassium iodide solution, to a solution of a magnesium salt and then cautiously adding potassium hydroxide solution. Excess of the latter reagent entirely decolorizes the precipitate, leaving magnesium hydroxide. The nature of the brown precipitate does not seem to have been determined by Schlagdenhauffen, and therefore it appeared of interest to examine it with a view to ascertaining if it is of constant composition.

In order to prepare quantities of the precipitate, solution of magnesium sulphate was mixed with enough solution of iodine in potassium iodide to impart to it a dark brown color. Potassium hydroxide solution was then added in sufficient quantity to produce a bulky precipitate, leaving the solution still dark-brown. The brown precipitate, when filtered off and sucked as dry as possible, if washed with hot water, loses all its color and decreases considerably in bulk, leaving a white residue of magnesium hydroxide. The washings are colorless, neutral to test papers, and give the reactions of magnesium and of iodides. Cold water acts on the precipitate in a similar manner, but only very slowly. If washed with water saturated with iodine, no iodide is dissolved out, as was determined by titrating the aqueous solution of iodine before and after the washing. When exposed to the air the dry precipitate loses iodine very slowly; dried in a vacuum no iodine is lost. This was proved quantitatively by determining the ratio of iodine to magnesium in some of the freshly precipitated substance, and then in the same precipitate when dried in a vacuum; in both cases the ratio was the same.

¹ *J. Pharm. Chem.* (4), 27, 375.

A portion of the moist precipitate gave on analysis :

0.0330 gram silver iodide, or 0.0178 gram iodine, and 0.0771 gram magnesium pyrophosphate, or 0.0168 gram magnesium.

Therefore I : Mg :: 1 : 4.9.

Dried in a vacuum, same precipitate gave 0.0289 gram iodine by titration, and 0.0452 gram magnesium oxide or 0.0272 gram magnesium.

Therefore I : Mg :: 1 : 4.9.

Chloroform, ether, alcohol, and potassium iodide all extract a little iodine from the dried precipitate, but none of them extract the whole of it. Sulphurous acid and sodium thiosulphate both decolorize the precipitate completely. The precipitate dissolves completely in acids, giving a solution colored brown by free iodine. On heating the dry substance to 100° C. water is given off, but no iodine; this fact was proved by a determination of the ratio of iodine to magnesium before and after heating. On ignition in a sublimate tube, the substance, previously heated to 100° C., gives off water and then iodine, and if ignited strongly enough leaves pure magnesia. Advantage was taken of this latter reaction to obtain a quick method for determining the iodine and magnesium.

The substance was weighed in a platinum boat, ignited in a piece of combustion tubing, having one end drawn out and passed through an India rubber stopper so as to dip into a solution of sulphurous acid contained in a small flask. A current of air being sucked through the apparatus, the iodine is absorbed in the flask and can be determined either by adding dilute nitric acid to the sulphurous acid solution and precipitating with silver nitrate, or by employing instead of sulphurous acid a known quantity of standard thiosulphate solution and titrating back with standard iodine. The residue from the ignition in the tube contains a small quantity of iodine, which is given off on stronger ignition, leaving pure magnesia. The results of analyses of five different preparations are given below.

A. The ratio of iodine to magnesium was determined in some freshly precipitated substance. In a given weight there was found 0.0902 gram silver iodide, or 0.0487 gram iodine, and 0.1650 gram magnesium pyrophosphate, or 0.0361 gram magnesium.

I : Mg :: 1 : 3.8.

B. Freshly precipitated gave ratio I : Mg :: 1 : 4.9 (as above).
Dried in a vacuum,

	Per cent.
0.1008 gram substance gave 0.0452 gram MgO	= 44.84
0.0289 gram I	= 28.67
H ₂ O by difference	= 26.49
	100.00

I : Mg :: 1 : 4.9.

MgO : H₂O :: 1 : 1.06.

C. The precipitate dried in a vacuum over sulphuric acid was heated to 100° C. in a steam cupboard till constant in weight. The iodine and magnesium were determined by the ignition method described above. The water was determined directly by ignition in a combustion tube, the iodine being absorbed by a red hot silver spiral and the water collected in a sulphuric acid tube.

Substance taken = 0.1185 gram.

	Per cent.
MgO = 0.0616 gram	= 51.98
I = 0.0307 gram	= 25.90

Water. Substance taken, 0.1990 gram.

H ₂ O = 0.0430 gram	= 21.93
	99.81

I : Mg :: 1 : 6.3.

H₂O : MgO :: 1 : 1.05.

D. Dried *in vacuo* over sulphuric acid.

Substance taken = 0.0610 gram.

	Per cent.
MgO = 0.0300 gram	= 49.18
I = 0.0166 gram	= 27.21
H ₂ O by difference	= 23.61
	100.00

I : Mg :: 1 : 5.6.

MgO : H₂O :: 1 : 1.07.

As it seemed probable that the low percentage of iodine in "C" might be due to loss of iodine on heating to 100° C., the ratio of iodine to magnesium was determined in the next preparation (E) both before and after heating to 100°.

E. This precipitate was produced under slightly different conditions from the former ones. A very large excess of iodine was employed and the precipitate was left standing for twenty-four hours in contact with an excess of iodine. The precipitate when filtered off and dried in a vacuum had a dark greenish-black appearance and yielded, on pounding up, a very dark purplish brown powder.

Precipitate dried in a vacuum.

Substance taken = 0.3584 gram.

	Per cent.
MgO = 0.1185 gram	= 33.06
I = 0.1759 gram	= 49.07
H ₂ O by difference	= 17.87
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	100.00

I : Mg :: 1 : 2.1.

MgO : H₂O :: 1 : 1.2.

Precipitate heated to 100° C. for three hours.

Substance taken = 0.3303 gram.

	Per cent.
MgO = 0.1130 gram	= 34.21
I = 0.1686 gram	= 51.04
H ₂ O by difference	= 14.75
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	100.00

I : Mg :: 1 : 2.1.

H₂O : MgO :: 1 : 1.03.

Collecting the above results we get the following ratios :

A. I : Mg :: 1 : 3.8.

B. I : Mg :: 1 : 4.9, MgO : H₂O :: 1 : 1.06.

C. I : Mg :: 1 : 6.3, H₂O : MgO :: 1 : 1.05.

D. I : Mg :: 1 : 5.6, MgO : H₂O :: 1 : 1.07.

E. I : Mg :: 1 : 2.1, H₂O : MgO :: 1 : 1.03.

These results show that the precipitate is simply magnesium hydroxide with a variable quantity of iodine carried down with it, giving a body resembling the lakes. Aluminum acetate gives a similar precipitate, but not so stable as the magnesium one. Aluminum sulphate, however, will not react thus. Moist magnesium hydroxide (freshly precipitated and washed), on shaking up with iodine solution, takes up iodine, although more slowly than that precipitated in presence of the iodine, while it does not seem capable of taking up so much.

On trying the action of potassium hydroxide in presence of iodine on the salts of the other metals of the magnesium group, colored precipitates were formed with zinc and cadmium salts. Glucinum sulphate gave a dark-brown precipitate which dissolved upon standing; when more potassium hydroxide was added a precipitate of hydroxide formed. With strong solutions of calcium and strontium salts, a very peculiar reaction took place, a dark, greenish-brown precipitate being produced, which changed to reddish-brown, and on standing for a short time dissolved completely. Excess of potassium hydroxide gradually took the color out of the precipitate, but much more slowly than with magnesium. Barium salts do not react in this way at all. Lithium chloride behaves in a somewhat similar manner to calcium salts; a dark-brown precipitate is formed, which soon dissolves. On adding a little more potassium hydroxide, the same precipitate again forms and again dissolves up.

The cadmium and zinc precipitates are much more stable than the above. The cadmium precipitate (from cadmium nitrate), when filtered off and washed with water saturated with iodine, is very gelatinous and of a dark purple brown color; on drying in a vacuum it gradually loses its color till it becomes a pale buff, when no further change takes place. On heating this buff-colored powder in a platinum boat in a combustion tube, water and iodine were given off, leaving a brown residue of cadmium oxide; the oxide was dissolved in nitric acid and tested for iodine; none present.

The formation of the zinc precipitate depends on the salt used and also on the strength of the solution; neither the sulphate nor chloride gives the precipitate while the acetate does. When a solution containing forty grams zinc acetate per liter is employed, a brown flocculent precipitate is formed, which does not change on standing. If the brown precipitate be filtered off and dried in a vacuum, it gives off all its iodine, leaving a white powder. In a solution containing fifteen grams zinc acetate per liter, the brown flocculent precipitate at first formed takes up more iodine on standing with a large excess of iodine and becomes crystalline and of an olive green color. This green precipitate when filtered off and washed with water is not decomposed, but if left exposed to the air in a moist state rapidly turns

brown, losing iodine. Dried in a vacuum the precipitate is not decomposed. The dirty green powder thus obtained is not so stable as the magnesium compound; it smells of iodine, and when left exposed to the air gradually becomes white. When heated to 100° in a steam cupboard iodine vapor is given off. On ignition in a platinum boat in a combustion tube, water and iodine are given off first, then a small white sublimate of zinc iodide. As this prevented any speedy method of determining the zinc in the substance, the ordinary method of precipitation with sodium carbonate was employed. The difficulty of washing and drying large precipitates without decomposing them necessitated the employment of small quantities for analysis.

A. Substance taken = 0.0949 gram.

	Per cent.
ZnO = 0.0500 gram	= 52.68
AgI = 0.0485, or I = 0.0250 gram	= 27.61

Water determined directly (as in magnesium compounds.)

Substance taken = 0.1724 gram.

H ₂ O = 0.0294 gram	= 17.05
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97.34

I : Zn :: 1 : 2.9.

ZnO : H₂O :: 1 : 1.4.

B. Substance taken = 0.0616 gram.

	Per cent.
ZnO = 0.0982 gram	= 48.80
AgI = 0.1150 gram, or I = 0.0621 gram	= 30.88
H ₂ O by difference	= 20.32

100.00

I : Zn :: 1 : 2.5.

ZnO : H₂O :: 1 : 1.9.

C. Substance taken = 0.3409 gram.

	Per cent.
ZnO = 0.1731 gram	= 50.77
AgI = 0.2035 gram, or I = 0.1094 gram	= 32.09
H ₂ O by difference	= 17.14

100.00

I : Zn :: 1 : 2.4.

ZnO : H₂O :: 1 : 1.8.

The excess of water above what would correspond to zinc oxide is evidently due to incomplete drying, as the substance cannot be heated to 100° without decomposition.

I would take this opportunity of expressing my cordial thanks to Professor Crum Brown and Dr. Leonard Dobbin for many important suggestions received during the investigation.

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VARIATIONS IN THE COMPOSITION OF RED LEAD.¹

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IN the manufacture of red lead and orange mineral, the color is ordinarily the property of first importance, since its chief use is as a pigment; and except so far as the color is dependent on the degree of oxidation, the latter is not the subject of special consideration.

For certain purposes, however, the degree of oxidation is important, and having occasion to examine a large number of samples of red lead from various sources, I adopted the method of digesting in saturated solution of normal lead acetate, by which the litharge in excess of that in combination as Pb_3O_4 (or $2PbO.PbO_2$) is dissolved out and separated. The samples were all examined qualitatively for anything which might be considered as adulteration, but otherwise neglecting the small amounts of silica, lime, oxide of iron, and carbon dioxide normal to the commercial article, for the preliminary and approximate tests. In this way a series of results was obtained showing a variation in the amount of actual red lead from 41 to 92 per cent., as given in the tabular statement.

No. or mark.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Red lead, Pb_3O_4	51.0	56.0	72.0	75.0	41.0	90.0	89.5	70.0	87.0	89.5
Litharge, PbO	49.0	44.0	28.0	25.0	59.0	10.0	10.5	30.0	13.0	10.5

No. or mark.	517.	140.	C.	BWL.	C.	BWL.	C.	L. B.	BWL.	L. B.
Red lead, Pb_3O_4	60.0	84.0	50.0	60.0	58.0	77.0	66.0	90.0	73.5	87.5
Litharge, PbO	40.0	16.0	50.0	40.0	42.0	23.0	34.0	10.0	26.6	12.5

The figures for red oxide are in most instances a little high because of the insoluble impurities which have not been determined and deducted, but the point which it is desired to bring out, is the large amount of monoxide in some samples,

¹Read before the January meeting of the New York Section of the American Chemical Society.