

XXXIII.—*The Dioxides of Calcium and Strontium.*

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ALTHOUGH the existence of peroxides of calcium and strontium has been known for a considerable time, the fact having been announced by Thénard in 1817, I am not aware of any account of the properties or composition of these substances ever having been published, and therefore beg to lay before the Society an account of some experiments I have lately made.

It is usually stated that lime and strontia, unlike baryta, do not absorb oxygen at a high temperature; but in order to establish the fact that no absorption took place at any temperature, I placed fragments of lime and strontia in the sealed ends of pieces of bent combustion-tube,

which were filled with oxygen and placed over mercury in such a manner that if any absorption took place it could be observed; the ends of the tubes containing the lime and strontia were heated in a sand-bath placed over a large bunsen burner, and subsequently directly by the flame of the burner, till a temperature was reached at which the glass began to fuse; but no absorption took place in either tube, although in a similar tube in which some baryta had been placed, and which was heated in the same sand-bath, the oxygen was readily and completely absorbed at a moderate temperature. These three tubes were placed side by side in the same sand, and dipping into the same trough, and were many times heated and allowed to cool, the temperature being carried a little higher on each occasion.

Sir Benjamin Brodie (*Phil. Trans.*, 1863, p. 409) states that he has ignited lime and strontia with potassium chlorate, but did not succeed in obtaining any higher oxide of either metal, although in the case of baryta this process is an easy method of obtaining a crude peroxide of barium.

As has been mentioned before, the existence of peroxides of calcium and strontium was first announced by Thénard, who obtained the hydrates of these oxides in the form of shining scales, when he added a solution of hydrogen peroxide to lime or strontia water (*Annales de Chimie*, viii, 1817, p. 312).

“Quoiqu’il en soit, lorsque l’on verse un excès d’eau de baryte dans l’acide nitrique ou l’acide hydrochlorique oxygéné, et à plus forte raison sur-oxygéné, il se forme un précipité cristallin d’hydrate de deutoxide de barium. Ce précipité est très-abondant en paillettes nacrées et peu solubles dans l’eau. Celle-ci à 10 degrés le décompose et le transforme en gaz oxygène et en baryte ou protoxide de barium. La strontiane et la chaux sont susceptibles d’être sur-oxidées toutes deux de même que la baryte, par les acides sur-oxygénés. L’hydrate de deutoxide de strontium ressemble beaucoup à celui de barium; celui de chaux est en paillettes plus fines.”

In order to repeat his experiments I caused some sodium peroxide to be prepared by heating metallic sodium in a flask through which air carefully freed from carbon dioxide and moisture, and then pure and dry oxygen were passed, until the sodium was completely converted into peroxide. (Compare Mr. A. Vernon Harcourt’s paper, *Chem. Soc. J.*, xv, 267.)

This substance affords a ready means of preparing these dioxides, as on the addition of an aqueous solution of sodium peroxide to the solution of a salt of strontium, the hydrated dioxide of that metal forms in shining scales having a pearly lustre. With calcium the case is somewhat different, as when a neutral or alkaline solution of sodium peroxide is added to the solution of calcium salt, the hydrated dioxide

of this metal is thrown down in the form of an extremely finely divided white precipitate. It appears almost impossible to obtain the substance pure in this form, as, in addition to its being exceedingly difficult to filter from its finely divided condition, it decomposes very readily. When, however, a considerable excess of lime water is added to a solution of sodium peroxide rendered acid by hydrogen nitrate, the dioxide forms slowly in scales somewhat similar in appearance to the corresponding strontium compound.

Calcium Dioxide.

The calcium peroxide obtained in this manner was well washed and dried on blotting-paper, a sheet of gutta-percha being folded round the paper to preserve the peroxide from the air.

Sir Benjamin Brodie has shown that hydrogen peroxide and potassium permanganate decompose each other, an equal amount of oxygen being given up by either substance. This reaction afforded an easy means of estimating the amount of oxygen contained in the peroxide of calcium and strontium when dissolved in a dilute acid.

Three preparations of calcium peroxide obtained in the before-mentioned manner gave the following results on analysis:—

No. 1. ·0993 gram of the peroxide gave ·0625 gram of calcium sulphate.

·1257 gram of the peroxide gave ·0784 gram of calcium sulphate.

·0674 gram of the peroxide reduced 12·65 c.c. of a solution of potassium permanganate, of which 1 c.c. = ·0003622 gram of oxygen.

·0859 gram of the peroxide reduced 16·45 c.c. of the same permanganate solution.

No. 2. ·1123 gram of the peroxide gave ·0688 gram of calcium sulphate.

·1053 gram of the peroxide gave ·0646 gram of calcium sulphate.

·1214 gram of the peroxide reduced 23·95 c.c. of the same permanganate solution.

·0891 gram of the peroxide reduced 17·2 c.c. of the same permanganate solution.

·0545 gram of the peroxide reduced 10·7 c.c. of the same permanganate solution.

No. 3. ·1340 gram of the peroxide gave ·0858 gram of calcium sulphate.

·0637 gram of the peroxide reduced 12·7 c.c. of the same permanganate solution.

When the hydrated calcium peroxide is heated in a current of dry carbon dioxide, the whole of the water is driven off, together with half the oxygen contained in the substance, and calcium carbonate is formed.

·4588 gram of the peroxide was placed in a weighed silver boat and heated in a combustion-tube by a small bunsen burner, whilst a current of dry carbon dioxide was passed over the substance, and the water collected in a weighed calcium chloride tube; ·2106 gram of carbonate and ·3017 gram of water were obtained. These numbers agree best with a substance, having for its composition $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$.

	Theoretical.		Prep. 1.		Prep. 2.		Prep 3.	
CaO ..	56	25·92	25·91	25·68	25·22	25·28	26·36	25·70
O	16	7·40	6·79	6·93	7·14	6·99	7·11	7·22 —
8H ₂ O..	144	66·66	—	—	—	—	—	65·76

The hydrated calcium peroxide decomposes slowly when it is allowed to remain in the solution from which it has been precipitated, but when dry, provided it is kept from the air, or rather from the carbon dioxide contained in it, it is a stable substance.

When the hydrate of calcium peroxide is heated to about 100° in a current of dry air free from carbon dioxide, the substance loses its crystalline appearance, the water it contains is driven off, and anhydrous calcium peroxide is left in the form of an extremely light and very pale buff-coloured powder. It is scarcely, if at all, soluble in water, but dissolves readily, without any evolution of oxygen in dilute acids, even in hydrogen acetate. It is also soluble in ammonium chloride, but not in ammonium hydrate.

(1.) ·1869 gram of the hydrate was heated in a weighed silver boat which was placed in a piece of combustion-tube heated in a water-bath, and air carefully dried and free from carbon dioxide was passed over it for half an hour, the temperature of the bath being 100° ; the hydrate lost ·1213 gram, and ·0639 gram of the resultant substance reduced 32·75 c.c. of a solution of permanganate, of which 1 c.c. contained ·0003622 gram of oxygen.

(2.) ·0940 gram of the hydrate heated to 100° for an hour lost ·0612 gram, and ·0313 gram of the residue reduced 16·2 c.c. of the permanganate solution.

(3.) ·0914 gram of the hydrate heated to 100° for an hour, lost ·0590 gram, and ·0306 gram of the residue reduced 15·4 c.c. of permanganate.

(4.) ·1116 gram of the hydrate heated to 128° for an hour, lost ·0722 gram, and ·0380 gram of the residue reduced 19·8 c.c. of permanganate.

These numbers give the percentage loss of weight in the four cases

as (1), 64.90; (2), 65.10; (3), 64.55; (4), 64.69, and the amount of oxygen in the residue as (1), 18.57; (2), 18.74; (3), 18.23; and (4), 18.87.

The theoretical loss of weight is 66.66 per cent. and 22.22 per cent. of oxygen ought to have been found in the residue, supposing it to have consisted of pure anhydrous calcium dioxide. The difference in all probability was caused by the original hydrated calcium dioxide having contained some calcium hydrate, which would still retain its water at a temperature sufficiently high for the dehydration of the dioxide.

Strontium Dioxide.

As has been before mentioned, when the solution of a salt of strontium is added to an aqueous solution of sodium peroxide, the hydrated peroxide of strontium forms in crystalline scales.

At the ordinary temperature, this substance begins to decompose almost as soon as it has formed, but when the solutions are cooled down to about 5°, it no longer decomposes so readily.

After this dioxide has been washed and dried on blotting-paper, it is a stable substance very similar in appearance and behaviour to the corresponding calcium compound. A specimen of this substance gave on analysis the following results:—

- 5460 gram heated whilst carbon dioxide was passed over it, gave
- 2940 gram of water, and ·3096 gram of strontium carbonate.
- 1672 gram yielded ·1154 gram of strontium sulphate.
- 1706 " " ·1192 " " "
- 1562 gram reduced 25.05 c.c. of a solution of potassium permanganate, of which 1 c.c. = ·0003622 gram of oxygen.
- 2042 gram reduced 32.3 c.c. of the same permanganate solution.

These numbers correspond best with the theoretical composition of a hydrate containing 8 molecules of water.

	Theoretical.				
SrO.....	103.5	39.28	39.79	38.93	39.41
O.....	16.0	6.07	5.80	5.73	—
8H ₂ O	144.0	54.65	53.846	—	—

Under slightly different conditions, strontium dioxide appears to form two other fairly stable compounds with water—in one twelve molecules, and in the other ten molecules of water are present.

The analysis of the 12-molecule substance gave the following results:—

·3206 gram of the substance reduced 38.35 c.c. of a solution of potassium permanganate, of which 1 c.c. = ·00036025 gram of oxygen.

·0639 gram reduced 8·25 c.c. of the same solution.
 ·6671 gram yielded ·3671 gram of strontium sulphate.
 ·4968 " " ·2769 " " "
 ·8807 " " ·3870 " " carbonate, and
 ·5696 " water.

These numbers give the percentage composition as—

	Theoretical.						
SrO.....	103·5	30·85	—	—	31·03	31·43	30·83
O.....	16·0	4·77	4·59	4·65	—	—	—
12H ₂ O....	216·0	64·38	—	—	—	—	64·67

The analysis of the 10-molecule substance gave the following results :—

·1325 gram of the substance gave ·0819 gram of strontium sulphate.

·1384 gram of the substance reduced 19·95 c.c. of a potassium permanganate solution, which contained ·0003622 gram of oxygen in 1 c.c.

·1852 gram of the substance reduced 26·35 c.c. of the same permanganate solution.

·7164 gram of the substance gave ·3539 gram of strontium carbonate.

·7056 gram of the substance gave ·3444 gram of strontium carbonate and
 ·4188 gram of water.

The percentage composition of the hydrate of strontium dioxide, as deduced from these figures is as follows :—

	Theoretical.					
SrO	103·5	34·55	34·86	—	34·66	34·25
O	16·0	5·34	5·221	5·153	—	—
10H ₂ O	180·0	60·10	—	—	—	59·35

When these different hydrates of strontium dioxide are heated to 100° in a current of dry air free from carbon dioxide, they lose all the combined water, and the anhydrous dioxide is left in the form of a white powder. It is little if at all soluble in water, but alters slightly in appearance when mixed with it.

It is entirely soluble in dilute acids, even in hydrogen acetate, without any evolution of oxygen; and also in ammonium chloride, but not in ammonium hydrate.

·2189 gram of the hydrate containing 8 molecules of water lost in 3 minutes at 100°, ·1180 gram, and ·0997 gram of the residue reduced 34 c.c. of a solution of potassium permanganate, of which 1 c.c. = ·0003622 gram of oxygen.

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·1410 gram of the same hydrate lost under similar circumstances ·0753 gram, and ·0651 gram of the residue reduced 21·85 c.c. of the same permanganate solution.

The percentage loss of weight in the two cases is 53·9, and 53·4, and the amount of oxygen in the residue 12·35 and 12·16 per cent. Theoretically, the loss of weight should have been 54·65, and 13·39 per cent. of oxygen ought to have been found.

·2633 gram of the hydrate containing 10 molecules of water lost ·1568 gram at 100° in 60 minutes, and ·1034 gram of the residue reduced 39·95 c.c. of the same permanganate solution.

·1364 gram. of the same hydrate lost ·0816 gram at 100° in 40 minutes, and ·0540 gram of the residue reduced 18·9 c.c. of the same permanganate solution.

The percentage loss of weight, as deduced from these numbers, is 59·55 and 59·82, and the amount of oxygen found 12·59 and 12·68. Theoretically, the loss of weight should have been 60·1.

·3934 gram of the substance containing 12 molecules of water lost ·2454 gram on being heated to 100° for 30 minutes, and ·1461 gram of the residue reduced 48·4 c.c. the same permanganate solution.

·2128 gram of the same hydrate lost under similar conditions ·1328 gram, and ·0794 gram of the residue reduced 26·15 c.c. of the same permanganate solution.

The loss of weight was 62·38 and 62·41 per cent., and 12·0 and 11·93 was the percentage of oxygen in the residue. Theoretically, the substance should have lost 64·38 per cent.

I have not as yet been able to devote any time to the investigation of the conditions under which these different hydrates of strontium dioxide are formed; and as just at present I have not sufficient leisure to go on with the enquiry, I think it best to lay before the Society some account of the experiments I have already made; and I hope at no distant date to have the honour of bringing under the notice of the Society some further account of these substances, and of their properties.

In conclusion, I must add that my best thanks are due to Mr. Harcourt, not only for the use of the Christ Church laboratory, where these experiments were made, but also for the many valuable suggestions and the assistance he has given me during their progress.
