XIV.—*On the Volatility of Barium, Strontium, and Calcium.*

By Prof. J. W. MALLET, University of Virginia.

IN some experiments on the action of metallic aluminum upon sodium carbonate at very high temperatures, I used a lime crucible inside one of hard carbon, and, finding the lime partially sintered together (from the formation of calcium aluminate) and easily removable with scarcely any mechanical loss, I weighed it as well as the residue it enclosed. The result of the weighing, after considering the oxidation of aluminum, separation of carbon, &c., at once suggested the idea that an appreciable quantity of calcium must have been reduced and volatilised. This idea has been confirmed by further and more careful examination, and the same fact observed in reference to barium and strontium.

The two following forms of experiment were used:—

(*a*.) A solid piece of ingot aluminum weighing 10—20 grams was placed in the middle of 20—25 grams of dry sodium carbonate enclosed in a little cornet of tissue paper (weighing but about 0·3 gram) and embedded in 30—40 grams of lime freshly prepared from fine white marble. This was contained in a crucible of Bunsen's hard carbon, with well fitted cover of the same, which was placed in an outer plumbago crucible, the intervening space being packed with well rammed lamp-black, and a plumbago ware cover placed over all.

(*b*.) The same arrangement was repeated, except that the sodium carbonate and paper cornet were omitted, and the aluminum—either in three or four embedded pieces or in admixed filings—was in direct contact with the lime.

Baryta and strontia were similarly treated; only one experiment being made with strontia, and that in form (*a*).

The extremely high temperature of the wind furnace used was derived from the combustion of the hard carbon deposit from coal-gas retorts, and was maintained for several—usually five or six—hours.

The evidence of the reduction and volatilisation of the metals in question falls under three heads—

1. The absolute disappearance of a portion of the calcium, barium, or strontium placed in the crucible as oxide when the residue after heating was carefully examined. The examination extended to four separate portions of the crucible contents, namely, the more or less metallic nucleus of the aluminum left in the centre, the remains of the surrounding alkaline earth,* the whole of the hard carbon crucible and cover crushed and pulverised, and the whole of the lamp-black from between this and the plumbago crucible.† The first generally afforded a very little of the calcium, &c., partly as aluminate and partly as oxide mechanically entangled on the surface; the second reproduced the greater part of that used; the third yielded no inconsiderable amount, absorbed as aluminate into the pores of the hard carbon; and in the fourth the barest traces were discoverable.

These materials were first exhausted by heating with strong hydrochloric acid; the crucible and lamp-black were burned to ash, and what remained of each was then thoroughly broken up by fusion with sodium hydrate, &c., taking care to remove a little silica completely by hydrofluoric acid. Although the lime, baryta, and strontia used were very nearly pure, anhydrous, and free from carbonate, the real amount of metal in each was determined as oxalate and sulphate respectively in a separate sample.

In every experiment there was loss to a weighable extent of the metal of the alkaline earth. The precise numerical results are, of course, not very important, as the intensity of furnace temperature, and the time it lasted, were not accurately measurable, but the following figures are quoted :—

32·171	grm. of	(real)	CaO	taken	lost	(*a*)	—	·803	grm.	= 2·49	p. c.
36·246	,,	,,	,,	,,	,,	(*a*)	—	1·139	,,	= 3·15	,,
34·710	,,	,,	,,	,,	,,	(*b*)	—	·765	,,	= 2·24	,,
33·847	,,	,,	,,	,,	,,	(*b*)	—	·782	,,	= 2·31	,,
42·321	,,	,,	BaO	,,	,,	(*a*)	—	·834	,,	= 1·97	,,
45·444	,,	,,	,,	,,	,,	(*b*)	—	·799	,,	= 1·76	,,
39·087	,,	,,	SrO	,,	,,	(*a*)	—	·891	,,	= 2·28	,,

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* These two portions were merged into one when aluminum *filings mixed* with the oxide were used.

† A trifling quantity of lime occurring in the ash of the carbon crucible and lamp-black, was by separate experiments determined and allowed for.

2. In these experiments the aluminum could take up oxygen only from the sodium carbonate, from the lime, &c., and from carbon monoxide penetrating the crucible and lamp-black. When no alkaline carbonate was used, the quantity of metallic aluminum left in the residue, as determined by the amount of hydrogen evolved on solution,* seemed to show that oxidation took place to a decidedly greater extent when lime or baryta was present than when the metal was heated *by itself* in the hard carbon crucible (obtaining oxygen only from CO); and when sodium carbonate was also employed, the oxidation exceeded that referable to the whole of the oxygen in this salt, plus the amount which I had been led by the last named experiment to attribute to carbon monoxide.† This goes to show that the lime, baryta, &c., are not volatilised as oxides, but after reduction to the metallic state, which conclusion is, independently, much more likely than the reverse.

3. By observing at short intervals with the spectroscope the light carbon monoxide flame of the furnace during the heating of the crucibles, the characteristic lines of the metals volatilised were, in the later stages of the heating, distinctly seen, though with some difficulty, on account of the glare of light from the fuel and the furnace walls. I should not lay much stress upon this in reference to calcium, although it did not appear in an examination made of the ash of the retort carbon fuel by one of my laboratory students, but the barium and strontium spectra are far less likely to have been derived from any extraneous source. The lines were seen only when the furnace was at a very high temperature. They seemed to be more distinct when sodium carbonate was used than in its absence, and the losses of weight experienced seem to confirm the supposition that under the former condition volatilisation occurred to greater extent, but of this I do not feel quite sure.

If it be so, it is in accord with the view lately expressed in another paper, that reduction of sodium carbonate by aluminum takes place by two stages;—1st, separation of carbon and formation of sodium aluminate; and, 2nd, reduction of the latter by more aluminum,—this second change occurring at a much higher temperature than the former. The bearing of this question, as to *sodium vapour* reducing lime and baryta at a very high temperature, upon Davy's‡ supposed

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* Checked as to impurities in the metal used by a similar comparative experiment with a piece of the same ingot which had not been heated.

† The extent to which carbon monoxide penetrated the crucible must have varied much during the heating, as the porosity of the crucible was altered by incipient fusion. It is remarkable, the experiments being carried on under no materially increased pressure, that in each case, but especially when baryta was used, the residue of alkaline earth contained a very appreciable amount of carbonate, as also of cyanide.

‡ Sir H. Davy "*Elements of Chemical Philosophy*," and Bakerian Lecture for 1809.

reduction vapour of the same by potassium (at probably a much lower temperature), is not without interest. The accuracy of his results has been doubted, though they have never, I believe, been directly refuted by more recent experiment. Matthiessen's remarks* as to the incapability of potassium and sodium to decompose calcium chloride are not inconsistent with the idea of reduction at temperatures high enough to volatilise both the alkaline chloride or oxide formed and the metal reduced. In my experiments, however, I have no doubt that the aluminum was at any rate the chief reducing agent.

The above results are not altogether surprising, in view of the well known wasting away of lime points in the oxyhydrogen flame, the production of spectra of barium, strontium, and calcium from the oxides in a good ordinary blowpipe flame, &c. They connect themselves in an interesting way with the occurrence of the lines of the metals in question in the solar, and in part in stellar spectra.

The extent to which volatilisation can be carried in close vessels is, however, remarkable, and must modify the views generally entertained of a radical difference in this respect between the metals of the alkalies and those of the alkaline earths. As between the members of the latter group, calcium would seem from these results to be the most volatile, and barium the least, the reverse of what I should from analogy have expected, though inability to measure, or even closely estimate, such high temperatures as have been used in the above experiments makes this largely matter of conjecture.