CXV.—*The Hydrolytic Action of Low-pressure Superheated Steam on Salts of the Alkaline-earth Metals.*

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Although it is generally realised that many salts are attacked by steam at high temperatures, and it is well known, as an extreme case, that salts like magnesium chloride are largely hydrolysed at temperatures little above the boiling point of water, there is little definite information in the literature as to the general incidence and extent of the hydrolytic action of steam. The recognition that many chlorides and bromides could thus be decomposed, even by the relatively low concentration of steam formed during their dehydration, led to the general use of the well-known Harvard bottling apparatus in atomic weight determinations, but it is in relation to technical processes of thermal decomposition that most references to such phenomena are found, and the following notes indicate their general nature.

The thermal decomposition of witherite is facilitated by the presence of steam (Priestley, *Phil. Trans.*, 1788, **78**, 852; Lenoir, *Jahresber.*, 1867, **13**, 256; Heinz, *Chem. News*, 1902, **85**, 206) and a similar result is observed, apparently, when mixtures of barium carbonate with calcium carbonate and carbon (Jacquelain, *Compt. rend.*, 1851, **32**, 877), and with sodium carbonate (*Dingler's Jour.*, 1884, **254**, 436), are employed.

A patented process describes the hydrolytic decomposition of barium sulphide by steam (Leroy and Segay, D.R.-P. 100969, 1897). Fremy stated that fluorspar is decomposed by steam at a red heat, yielding calcium oxide and hydrogen fluoride (*Ann. Chim. Phys.*, 1856, **47**, 17), but Poulenc later found that strontium fluoride is not decomposed by steam at a red heat (*ibid.*, 1894, **2**, 5). It has been reported (Kunheim, "Über Einwirkung des

Wasserdampfes auf Chlormetalle bei hoher Temperatur," Gottingen, 1861) that when calcined in steam calcium chloride is decomposed less readily than magnesium chloride, but more readily than barium chloride, that this hydrolysis of calcium chloride is incomplete (Pelouze, *Compt. rend.*, 1861, **32**, 1267), and that it is accelerated when silica, alumina, or china clay are present (Solvay, *Dingler's Jour.*, 1885, **255**, 307).

When steam is passed over a red hot mixture of calcium sulphate and sodium chloride, sodium sulphate, lime and hydrogen chloride are produced (Tilghmann, *Dingler's Jour.*, 1847, **106**, 196).

Siemens (*ibid.*, 1863, **169**, 207) reported that if water vapour is passed over a molten mixture of sodium chloride with twice its weight of calcium sulphate, hydrochloric acid, sulphur dioxide, and hydrogen sulphide are evolved, while a mixture of steam and carbon dioxide under the same conditions yields only sulphur dioxide and hydrochloric acid; the residue contained undecomposed sodium chloride, sodium hydroxide, calcium sulphide, calcium oxide, and small traces of sodium thiosulphate and sodium sulphide. It has been pointed out (Buff, *ibid.*, 1864, **172**, 282; Knapp, *ibid.*, 1872, **202**, 513) that in such reactions the materials of the containing vessel, *e.g.*, iron and silica, may play an important part, and the obvious incompatibility of some of the foregoing statements may well be due to such causes.

A recent investigation (Thompson and Tilling, *J. Soc. Chem. Ind.*, 1924, **43**, 39T) has shown that the ferrous sulphide formed, together with free sulphur, on heating pyrites in an inert atmosphere is decomposed (to form ferric oxide and hydrogen sulphide) at a lower temperature in steam than in carbon dioxide or air.

Thus it is evident that the previous investigations of the hydrolytic action of steam are few in number, and with the exception of the last cited, purely qualitative in kind. It has been the object of the present investigation to secure some numerical data in a few typical cases. A weighed quantity of the salt under investigation was heated to a known temperature for a definite time in a current of steam, and the issuing steam was condensed. Titration of this condensate with standard alkali gave a measure of the extent of hydrolytic decomposition which had occurred.

EXPERIMENTAL.

Steam was passed at a constant rate over a weighed quantity of material in a porcelain boat placed in a silica tube heated electrically to the desired temperature. In the hot zone, the silica was protected by a liner-tube of stout sheet nickel. Temperatures were measured by means of a platinum–platinum-rhodium thermocouple and a Paul millivoltmeter, the hot junction of the couple being held immediately above the boat containing the salt under investigation. The couple and millivoltmeter were standardised before and after use at 100° and at the melting points of tin, lead, zinc and sodium chloride, and found to give consistent readings trustworthy to about ± 5°.

Temperature readings were taken every ten minutes (or oftener) throughout the run, and at the end the condensed steam was titrated with *N*/10-sodium carbonate solution and methyl-orange, or, in the case of carbonates, by adding *N*/10-caustic soda solution and back-titrating with *N*/10-sulphuric acid, with phenolphthalein as indicator.

Chlorides, Bromides, and Carbonates.—The table gives the data relative to these salts.

Salt.	Weight (g.).	Temp.	Time (mins.).	Acid produced as c.c. of *N*/10-acid.	Wt. of salt decomposed in 30 mins. (calculated).
Calcium chloride	1·0	970°	30	99·53	0·553
,, ,,	1·0	970	60	154·53	0·428
,, ,,	0·5	812	60	65·5	0·182
,, ,,	0·5	425	60	4·5	0·014
Strontium chloride ...	1·0	970	60	90·9	0·361
,, ,,	0·5	812	60	6·5	0·026
,, ,,	0·5	641	60	4·0	0·016
,, ,,	0·5	638	60	0·5	0·002
Barium chloride	1·0	970	30	7·0	0·073
,, ,,	1·0	970	60	19·1	0·099
,, ,,	1·0	825	30	0·3	0·003
,, ,,	0·5	809	60	Nil.	Nil.
Calcium bromide ...	0·5	690	30	31·6	0·316
,, ,,	0·5	516	30	6·0	0·060
,, ,,	0·5	463	30	4·8	0·048
,, ,,	0·5	348	30	1·2	0·012
Strontium bromide ...	0·5	780	30	20·0	0·248
,, ,,	0·5	575	30	6·2	0·076
,, ,,	0·5	443	30	1·0	0·013
Barium bromide	0·5	770	30	5·0	0·075
,, ,,	0·5	640	30	3·1	0·046
Calcium carbonate ...	1·0	558	45	13·7	0·046
,, ,,	1·0	437	60	5·3	0·013
,, ,,	1·0	390	60	Nil.	Nil.
Strontium carbonate.	1·0	679	60	9·5	0·035
,, ,,	1·0	598	60	5·8	0·022
,, ,,	1·0	455	60	0·3	0·001
Barium carbonate ...	1·0	980	60	38·6	0·190
,, ,,	1·0	684	60	17·1	0·084

Sulphates.—At 970° the sulphates of calcium, strontium, and barium were not appreciably decomposed. From the first sample of barium sulphate used, a trace of sulphuric acid, equivalent to 1·2 c.c. of *N*/10-acid, was produced in the first 5 minutes. This was proved to be due to ferric sulphate present as an impurity.

The production of acid did not continue, there was no evidence of true hydrolytic action, and the residue was not alkaline.

Phosphates.—Calcium phosphate only was examined. This gave no evidence of hydrolytic decomposition even at 970°.

Discussion.

The data recorded above make no claim to great precision, but the authors believe that they may properly be held to justify the following general conclusions.

The chlorides and bromides of calcium, strontium, and barium are all hydrolysed by steam under atmospheric pressure at high temperatures, the ease of decomposition decreasing with increasing atomic weight, the lowest temperature at which it is appreciable being as follows :

Calcium chloride . . .	425°	Calcium bromide . . .	348°
Strontium chloride . . .	640°	Strontium bromide . . .	443°
Barium chloride . . .	970°	*Barium bromide . . .	640°

* Barium bromide appears to be appreciably volatile at 770°.

These figures afford some evidence that the bromides in general are more easily hydrolysed than the chlorides, and, in conjunction with the well-known difficulty of iodide preparation and the work of Fremy and Poulenc (*loc. cit.*) on the fluorides, show that the ease of decomposition for any alkaline-earth metal increases in the order fluoride, chloride, bromide, iodide, whilst for any particular halide it increases in the order barium, strontium, calcium.

In the case of the carbonates of strontium and barium the boat was obviously attacked and this renders the interpretation of the results doubtful. Calcium carbonate evidently decomposes appreciably at 440° in steam and it is interesting to compare this result with the previous observation (Pott, "Studien uber die Dissoziation von Calcium-Strontium- und Barium Karbonat," 1905) that measurable dissociation is observed at 525°.

Qualitative experiments with sodium and potassium nitrates showed that these were largely decomposed at temperatures just under 600°, leaving a strongly alkaline residue in the boat. The gaseous products comprised both nitric acid and oxides of nitrogen, but further investigation of this decomposition was abandoned, as it was likely to require an elaboration of experimental procedure disproportionate to the results anticipated.

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