XXXIX.—*Decomposition of Water by the joint action of Aluminium and of Aluminium Iodide, Bromide, or Chloride, including instances of reverse action.*

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In the course of our work with the copper-zinc couple, we described somewhat briefly a series of bodies which may be regarded as zinc ethylate in which chlorine, bromine, or iodine has taken the place of one C_2H_5O, and which may well be termed *zinc-halogen ethylates.* The non-crystalline character of these compounds, coupled with the difficulty of removing the alcohol with which they necessarily become associated, render their study difficult and after all unsatisfactory. We thought, however, that some knowledge of the reactions of bodies of this character might be obtained, could we succeed in replacing the zinc by some other metal. We therefore set to work in the hope of preparing an analogous aluminium compound, and in so doing observed a phenomenon which induced us to undertake the experiments detailed below. We give them much in the order in which they were made.

Experiment I.—2 grams of aluminium-foil 42 cm. long, 5 cm. wide, cut in small pieces, were placed in a flask with 20 c.c. of water and 7 grams of iodine. Evolution of gas, which proved to be hydrogen, took place at once at the ordinary temperature. The flask was kept in water at 12°, and the following measurements made :—

Collected in the first	15	minutes	......	650 c.c.
,, ,, second	15	,,	....	1050 ,,
,, ,, third	15	,,	....	300 ,,
,, ,, next	40	,,	....	110 ,,
				2110 ,,

The residue in the flask was quite thick and extremely difficult to wash. It consisted of a little aluminium and the elements of aluminic oxide and iodide.

Experiment II.—Similar to experiment I, but only 2 grams of iodine were employed. There was a very slight action noticeable at the ordinary temperature. The flask was now heated by immersion in boiling water. In 15 minutes the whole of the iodine had disappeared, and there was

Collected in the first 30 minutes.......... 300 c.c.
,, ,, second 30 ,, ... 400 ,,
,, ,, third 30 ,, ... 250 ,,

The evolution continued in a diminishing ratio for 17 hours, the total gas obtained measuring 1915 c.c. The aluminium left in the flask weighed 0·284 gram.

Experiment III.—Similar to experiments I and II, a still smaller quantity of iodine (1·44 gram) being employed. At a temperature of 100°, in 15 minutes, the free iodine had disappeared and 80 c.c. of gas were collected. The experiment was continued for 23 hours, 1341 c.c. of gas being collected. One gram of aluminium was found in the residue.

These experiments differ only in the amounts of iodine employed; still it is evident that the hydrogen obtained bears no relation to this iodine, but is practically proportional to the amount of metal used up.

This suggested that the decomposition of water which obviously takes place was probably occasioned by a series of decompositions and recompositions of the aluminic iodide produced in the first instance by the direct union of its elements. Further evidence of this appeared desirable, and the following experiments were accordingly made.

Experiment IV.—2 grams of aluminium with 20 c.c. of aqueous hydriodic acid containing 2 grams of anhydrous HI were placed in a flask fitted with a delivery-tube. At the ordinary temperature there was no action in 15 minutes, but upon immersing the flask in boiling water, evolution of hydrogen took place immediately.

In the first 15 minutes .... 200 c.c. had collected.
,, second 15 ,, ... 190 ,, ,,

And the evolution of gas proceeded in a diminishing ratio for 18 hours, when action practically ceased. There remained 0·352 gram of aluminium in the flask, showing that 1·648 grams had undergone oxidation during the experiment. This is equivalent to 2020 c.c. of hydrogen, while the amount actually obtained was 2004 c.c. The hydrogen in the 2 grams of acid employed amounted to only 175 c.c.. It is therefore evident that the greater part of the hydrogen must have come from the decomposition of water.

Experiment V.—As doubts may arise in the mind with regard to the part played by the iodine and hydriodic acid in the experiments already described, we instituted the following additional experiment:—3·8 grams of pure anhydrous aluminic iodide were mixed with 2 grams of finely cut aluminium foil and 20 c.c. of water were added, little by little, so as to prevent a rise of temperature from the combination of the iodide with water. The flask was heated to 100°. Hydrogen was at once evolved, measuring 200 c.c. in 15 minutes, and continued in a diminishing ratio for 6 hours, when ·065 of metallic aluminium was found in the flask, showing that 1·935 had been used up, a quantity equivalent to 2372 c.c. of gas. The actual amount obtained was 2187 c.c.

That water readily decomposes by the joint action of aluminium and its iodide is a fact well established by these experiments. But why this reaction?

Water forms a definite crystalline hydrate with aluminic iodide (Weber, *Pogg. Ann.*, cvii, 264), and from our own observation we know that the iodide dissolves in water without apparent decomposition. According to Deville, we also know that aluminium decomposes water at a white heat only, and we have found that the metal employed by us could be boiled in water for hours without the production of a trace of hydrogen. Yet water undergoes rapid decomposition in presence of the two substances, either of which alone does not affect it.

Two explanations have presented themselves.

First. That the aluminium undergoes direct oxidation at the expense of the water, in consequence of the disturbing influence of the iodide—

$$2Al + Al_2I_6 + 3H_2O = Al_2O_3 + Al_2I_6 + 6H,$$

that is to say, the iodide undergoes no change.

Second. That the aluminium of the iodide is oxidized and the iodide regenerated, which may thus be brought about—

$$\begin{aligned} Al_2I_6 + 3H_2O &= Al_2O_3 + 6HI \\ 6HI + 2Al &= Al_2I_6 + 6H, \end{aligned}$$

and so on, which may be supposed to take place through the intervention of oxyiodides.

It is well known that hydrated haloid aluminium salts split up by heat and give off free acid. We endeavoured to find some direct evidence of the presence of free acid in solutions such as we used in our experiments, but without conclusive result, although we found that a small quantity of hydrobromic acid was given off from a saturated solution of the hydrated aluminic bromide (containing excess of the crystalline hydrate) when heated to 100° C.

Either view accounts for the facts, but which is the truer we at present see no means of determining, although the latter seems to us more probable.

We thought it would be of considerable interest to determine whether other metals or other compounds could be substituted for aluminium and its iodide.

Neither zinc nor iron, heated with their respective iodides in water, yielded any hydrogen; but both zinc and iron, when heated with aqueous aluminic iodide, occasion the decomposition of water.

Experiment VI.—6·5 grams of zinc foil cut in small pieces were heated at 100° C. with 10·69 grams of aluminic iodide (slightly basic) and water.

In the first 15 minutes ...... 100 c.c. hydrogen were collected.
„ second 15 „ ...... 40 „ „ „
„ third 15 „ ...... 14 „ „ „

The action was continued for 49 hours when the evolution of gas had almost ceased. The total measured 681 c.c. The aluminic iodide taken is equivalent to 880 c.c. In the flask there was noticeable a white powder, which proved to consist mainly of aluminic oxide with a very little zinc oxide. The liquid consisted principally of a solution of zinc iodide with a little aluminic iodide or oxide. The zinc remaining was also found to be studded here and there with crystalline metallic plates, presumably metallic aluminium.

It is evident, from the results of this experiment, that zinc replaces aluminium from its iodide in aqueous solution, and this gives at once the elements of the original reaction.

The action may be represented thus :—

$$Al_2I_6 + 3Zn = 3ZnI_2 + Al_2$$
$$Al_2 + Al_2I_6 + 3H_2O = Al_2O_3 + Al_2I_6 + 6H.$$

Experiment VII.—The action with iron is extremely slow. 8 grams of iron in fine wire were heated to 100° with the same quantity of Al_2I_6 solution as in the last experiment. In 41 hours 493 c.c. of hydrogen had collected, when its evolution practically ceased. Ferrous and aluminic iodide were found in solution, and either aluminium, or more probably its oxide, adhering to the iron.

Experiment VI has shown that zinc replaces aluminium from its iodide when in solution. It now occurred to us to ascertain whether the reverse action was possible (*i.e.*, whether zinc could be replaced by aluminium).

Experiment VIII.—9·9 grams of iodine, equivalent to the amount of Al_2I_6 employed in experiment VI, were heated with an excess of pure zinc and 20 c.c. of water until the solution was perfectly colourless. After removing the undissolved zinc, 2 grams of aluminium were added and the whole heated by immersion in water at 100°. No signs of action were apparent for 15 minutes, when gas began to be evolved, and this continued at an increasing rate for 3 hours, after which it slowly declined, until in 15 hours 1538 c.c. had collected. The residue in the flask was of a thick pasty consistency, from which water dissolved zinc iodide and a little aluminic iodide or oxide. The portion insoluble in water consisted principally of aluminic oxide with some zinc, probably as oxyiodide. This experiment was repeated several times with different quantities of zinc iodide with practically the same result.

An experiment similar to the last was made, an equivalent amount of ferrous iodide being employed. Action commenced at once upon heating to 100°, and the aluminium-foil became quickly coated with a black substance which was found to be metallic iron. The hydrogen collected during 16 hours measured 1917 c.c. As in previous experiments, the residue in the flask was very pasty. Water dissolved from it a little ferrous iodide and some aluminic iodide, the portion insoluble being principally aluminic oxide and metallic iron.

The evolution of hydrogen in the two experiments just described is in all probability to be attributed to the replacement of zinc and iron by aluminium and the formation of aluminic iodide, which, in presence of aluminium, would give the original reaction; thus:—

$$3FeI_2 + Al_2 = 3Fe + Al_2I_6$$
$$Al_2I_6 + 3H_2O + Al_2 = Al_2O_3 + Al_2I_6 + 6H.$$

Of course some of the hydrogen in the ferrous experiment might (since iron was actually found) have been due to the action of an aluminium-iron couple upon the water present. Whether this be so or not, it is certain that iron and zinc can replace aluminium, which, in its turn, by slightly altering the conditions, can replace both zinc and iron. It is possible that this may take place through the intervention of oxy-salts in solution; thus the action of water on zinc iodide, for example, may be the production more or less of such a compound as $Zn_2OI_2.2HI.$ or $\left\{\begin{array}{l}ZnHI_2\\O\\ZnHI_2\end{array}\right.$, the hydriodic element of which would yield up its hydrogen under the action of the aluminium, and this would of course give all the elements of the original reaction.

It now appeared to us of interest to ascertain whether the bromide or chloride could take the place of the iodide in the original reaction. Experiments were accordingly made.

Experiment IX.—Similar to experiment VI, an equivalent quantity, 2·49 grams, of aluminic bromide being employed. At 100° evolution of hydrogen commenced at once.

During the first 15 minutes .... 120 c.c. were collected.
" next 45 " .... 750 " "

The action continued in a diminishing ratio for 6 hours, when it was found that 2378 c.c. of gas had been given off. Aluminic oxide and bromide, with a very little aluminium remained in the flask.

Experiment X.—Similar to experiment IX, an equivalent quantity, 1·24 grams, of aluminic chloride being employed.

In first 15 minutes...... 50 c.c. of gas were given off.
In first hour .... 1770 " " "

The action continued in a rapidly diminishing ratio for about six hours, when a total of 2345 c.c. of gas had been reached. The residue in the flask was similar to that of the previous experiment.

It is evident from this that both the bromide and chloride of aluminium act much in the same manner as the iodide.

A comparison of results, as seen in the subjoined table, is of interest:—

Time.	Equivalent quantities of		
	Al_2I_6.	Al_2Br_6.	Al_2Cl_6.
15 minutes	200 c.c of H	120 c.c.	50 c.c.
60 "	550 "	870 "	1770 "
6 hours	2187 "	2378 "	2345 "

The same quantity of aluminium, viz., 2 grams, was employed in all the experiments. This is theoretically equivalent to 2453 c.c. of hydrogen. It should be mentioned that the aluminic haloïd salts were purposely made slightly basic.

Apart from the theoretical interest attaching to the experiments detailed above, we have reason for believing that the reactions described are of value, as they may afford the means of hydrogenizing in neutral solution compounds on which the copper-zinc couple has no influence.