LX.—*The Decomposition of Carbonic Acid Gas by the Electric Spark.*

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The decomposition of carbonic acid gas by frictional electricity was observed by Landriani and Van Marum; Dalton and Henry repeated the experiment, and examined the gas produced in the decomposition. In 1800, Henry thus describes the effect of the spark on carbonic acid:—

"When the electric shock has been repeatedly passed through a portion of this acid gas, its bulk is enlarged, and a permanent gas is produced which is evidently a mixture of oxygenous and hydrogenous gases; for, when an electric spark is passed through the gas that remains after the absorption of the carbonic acid by caustic alkali, it immediately explodes. These results take place even on electrifying carbonic acid from marble, previously calcined at a low red heat to expel its water, and then distilled in an earthen retort." (*Phil. Trans.*, 1800.)

Buff and Hofmann (*Chem. Soc. J.*, **12**, 293) found that an induction spark between platinum wires produced a partial decomposition of carbonic acid, which proceeded rapidly at first and then more slowly, until the liberated carbonic oxide and oxygen combined with an explosion to reform the original volume of carbonic acid.

Berthelot (*Bull. Soc. Chim.* [2], **13**, 99) on repeating these experiments found that the decomposition reached no definite limit. On passing the sparks, the volume increased, reached a maximum, and then diminished suddenly but without explosion. When carbonic acid was added to an explosive mixture of carbonic oxide and oxygen, a spark caused explosion and complete combination when the carbonic acid was less than 60 per cent. of the whole, but when the carbonic acid was more than 60 per cent. no explosion occurred, but a series of sparks produced a partial combination which approached no fixed limit.

The experiments of one of us (*Phil. Trans.*, 1884) having shown that no explosion is propagated by a spark in a mixture of carbonic oxide and oxygen dried by standing over anhydrous phosphoric acid, it seemed of interest to repeat the experiments on the decomposition of carbonic acid when dried in a similar manner, and to compare the results with those obtained by the prolonged action of the spark on a dried mixture of carbonic oxide and oxygen. Carbonic acid dried over

anhydrous phosphoric acid was submitted to a series of induction sparks in an eudiometer by means of a chain composed of short pieces of platinum fused into small glass beads, similar to that described by Bunsen. The eudiometer was fitted into the gas analyser described in the paper referred to above. The amount of decomposition varied from time to time, approaching no fixed limit. The maximum decomposition was about 45 per cent., under 100 mm. pressure. Similar results were obtained on introducing a Leyden jar into the circuit of the secondary coil of the Ruhmkorff, but the amount of decomposition was less.

On passing a series of induction sparks through a dried mixture of carbonic oxide and oxygen, partial combination took place gradually, but no fixed limit was reached.

To ascertain what effect a variation in the length of the spark produced on the decomposition, we had an eudiometer made having two pairs of platinum wires, $1\frac{1}{2}$ mm. and 6 mm. apart respectively. This eudiometer was partly filled over mercury with carbonic acid dried by passing through oil of vitriol. Some anhydrous phosphoric acid was introduced into the gas, which was then allowed to stand for several days. The volume when measured and reduced to 0° and 760 was 52·10 c.c. A series of sparks was then passed between the first pair of terminals, $1\frac{1}{2}$ mm. apart, from a Ruhmkorff coil with two Grove cells (1 pint size). The volume gradually increased, and when the coil ceased to act the volume was found to be 62·34 c.c. (reduced to 0° and 760), showing an increase of 10·19 c.c., due to the decomposition of 39·08 per cent. of the original carbonic acid into carbonic oxide and oxygen. The cells were renewed, and the sparks passed continuously for six hours; the volume was then 61·01, showing a decomposition of 33·97 per cent. Three fresh cells were then connected with the Ruhmkorff, and sparks passed between the second pair of terminals (6 mm. aperture) for five hours; the volume was then 60·02, equivalent to a decomposition of 30·20 per cent. Finally one cell alone was used with the smaller aperture (1·5 mm.), and the coil left all night; in the morning it had stopped, and the volume was 63·45, showing a decomposition of 43·33 per cent.

The temperature during the above experiments varied between 10° and 15°, and the pressure was about 500 mm.

These experiments showed considerable variations, but the shorter spark was accompanied by the greater decomposition.

Another set of experiments were made in an eudiometer, with terminals of an alloy of iridium and platinum, the aperture being about 1 mm.

No great variations were observed in this series.

The action of the spark, obtained by inserting a Leyden jar in the

Time from starting.	Volume corrected.	No. of cells.	Temperature. C.	Pressure. mm.	Percentage decomposition.
0 hr.	23·84	—	—	—	—
6 hrs.	27·13	2	12°·0	598	36·0
12 „	26·39	2	14°·0	589	35·8
16 „	26·21	1	12°·8	589	35·4
23 „	26·81	1	13°·2	588	35·7
28 „	26·17	1	13°·6	600	34·8
33 „	25·79	3	15°·0	601	34·4

secondary circuit of the coil, which worked with three cells, was tried between platinum terminals 1 mm. apart.

Time from starting.	Volume corrected.	Temperature. C.	Percentage decomposition.
0 hr.	35·42	—	—
3½ hrs.	41·61	10°·0	34·9
8 „	41·91	16°·5	36·6
11 „	41·92	12°·0	36·7
16 „	39·6	11°·7	23·6
23 „	40·26	13°·5	26·8
25 „	40·23	13°·0	26·7

At the conclusion of this series of experiments, there was a considerable black deposit on the tube, consisting partly, if not entirely, of volatilised platinum, the terminals being at the conclusion of the experiments 0·3 mm. further apart than at the commencement. The widening of the aperture, owing to the volatilisation of the platinum, was accompanied by a decrease in the volume of carbonic acid decomposed.

Another set of experiments was made, using an eudiometer with wires of iridium-platinum alloy 1 mm. apart. Four cells were used, and a Leyden jar inserted in the secondary circuit. Pressure about 500 mm.

Time from starting.	Volume corrected.	Temperature. C.	Percentage decomposition.
0 hr.	25·3	19°·1	—
5 hrs.	29·7	19°·0	34·78
12 „	29·1	19°·5	30·04
18 „	28·5	20°·2	25·30
23 „	28·8	19°·9	27·67

A light black deposit was found in the tube at the conclusion of experiments.

In another series with the same terminals, and with four cells and a Leyden jar, the following volumes were observed.

Time from starting.	Volume corrected.	Percentage decomposition.
0 hr.	16·68	—
7 hrs.	18·88	26·37
15 „	18·56	22·54
22 „	18·31	19·54

The pressure was about 650 mm.

The higher pressure was accompanied by less decomposition.

The variations of volume, which accompanied changes in the nature of the electric discharge, mask the effect of varying pressures in the above experiments. In order to eliminate as far as possible the effect of variations in the spark, a differential process was adopted suggested by Leslie's differential thermometer. Two similar eudiometers were prepared and fitted with wires made of an alloy of platinum and iridium, each wire ending in a sphere about 2 mm. in diameter. These spheres were brought to the same distance apart in the two tubes. On bringing an equal volume of dried carbonic acid into the two tubes, and sending a series of sparks from one Ruhmkorff coil through both tubes at the same time, the gases in the two vessels were found to be equally affected, their volumes varying exactly together so long as the pressure was kept equal in the two tubes. The more feeble the spark, the greater the decomposition of the carbonic acid was found to be. Other conditions being the same, the less the pressure the greater the decomposition of the carbonic acid was found to be.

100 volumes of carbonic acid were introduced into both tubes; in one of them the gas was kept at a pressure of 700 mm. of mercury, and in the other at 500 mm. After an hour, the volumes were measured, and afterwards at intervals of two hours:—

Time from starting.	Volume corrected. Under 500 mm. pressure.	Volume corrected. Under 700 mm. pressure.	Remarks.
—	100·0	100·0	
1 hr.	106·3	103·6	
3 hrs.	119·8	113·7	
5 „	104·3	102·6	The cells were renewed about four hours from the start.
7 „	106·0	104·0	

The gas under the less pressure suffers greater decomposition than the other.

In another experiment, a greater difference of pressure was maintained in the two tubes.

Time from starting.	Volume corrected. Under 250 mm. pressure.	Volume corrected. Under 650 mm. pressure.
0 hr.	100·0	100·0
1 ,,	105·1	100·9
3 hrs.	104·5	100·8
5 ,,	103·3	100·4
7 ,,	112·5	103·3

A greater difference of pressure is acccompanied by a greater difference in the percentage of carbonic acid decomposed in the two tubes.

When 100 volumes of dried carbonic acid were brought into one tube, and 150 volumes of a dried mixture of carbonic oxide and oxygen were brought into the other, and a series of sparks were passed through both from the same coil, the volume of carbonic acid increased, and the volume of carbonic oxide and oxygen diminished, until after some hours they became equal under the same pressure. On a further prolonged passage of the spark the two volumes altered together, sometimes increasing and sometimes diminishing, as the nature of the spark varied.

Time from starting.	Carbonic oxide and oxygen. Volume corrected.	Carbonic acid. Volume corrected.
0 hr.	150·0	100·0
1 ,,	124·6	116·4
3 hrs.	121·5	117·0
5 ,,	120·5	117·0
7 ,,	109·3	107·5
9 ,,	107·3	107·3
11 ,,	115·6	115·6
14 ,,	114·3	114·3

A coil of fine platinum wire was heated by a current to whiteness in dried carbonic acid. No permanent alteration of volume was produced. Now Deville has shown that carbonic acid suffers partial decomposition in contact with white-hot platinum. It follows that the dissociated carbonic oxide and oxygen completely reunite under the conditions of the experiment. We were therefore able to predict that a white-hot platinum wire would produce complete combination of dry carbonic oxide and oxygen, even if no explosion occurred in the

mixture. Into the carefully dried eudiometer, standing in the mercury trough, some oxygen was passed, and then two plugs of anhydrous phosphoric acid were introduced into the gas. The platinum wire was then maintained at a white heat for an hour in order that any hydrogen occluded by the metal might be oxidised and absorbed by the drying material. After cooling, the required volume of carbonic oxide, which had been standing for some days over anhydrous phosphoric acid, was introduced, and the mixture was allowed to stand for a week. On heating the platinum wire to redness in the well-dried mixture, it immediately glowed intensely, and after some minutes complete combination was found to have taken place between the two gases. No flame was visible round the glowing wire.

It seems probable that the somewhat abrupt contractions of volume observed by Berthelot in the partially decomposed carbonic acid may have been due to the heating of the platinum wires by the discharge, and the consequent combination of the carbonic oxide and oxygen in the mixture.

The equilibrium observed between the rate of decomposition of carbonic acid and the rate of combination of its products of decomposition appears to differ in one respect from the equilibrium observed in other gaseous systems, such as that studied by Lemoinne between hydrogen and iodine, and the product of their combination, hydric iodide. Whilst hydrogen and iodine probably unite directly together, as hydrogen and chlorine do, carbonic oxide and oxygen require, under the conditions of our experiments, an intermediary to effect their combination. It is uncertain whether the oxidation of the carbonic oxide is brought about in the neighbourhood of the wires by steam molecules still present in the mixture in spite of our process of drying, or by the platinum itself, or in some other way. Possibly, in the course of the spark and in contact with the white-hot metal, some molecules of carbonic oxide are dissociated, and the gaseous carbon is then completely oxidised at one step, as it appears to be in the "explosive wave" formed in the explosion of carbonic oxide and oxygen in a long tube.