V.—*The Decomposition of Carbon Dioxide by the Silent Electric Discharge.*

By ALFRED HOLT, jun.

IN 1885 Shenstone described an experiment * to the Physical Society which illustrated the changes that occur in the nature of an electric discharge passing between parallel glass plates.

When the glass surfaces were about 1 cm. apart, the discharge consisted of a few large sparks like those produced by an induction coil. On diminishing the distance between the plates, the sparks became more numerous.

When the distance between the plates was about 1 mm., the sparks became fewer, and a glow made its appearance. If the air between the plates was moist, the glow vanished and the sparks reappeared.

A similar change was observed in the discharge when oxygen was substituted for air, but the glow was feebler.

The investigations of Lenard on the chemical effects brought about by ultra-violet light (*Ann. Physik*, 1900, **70**, 486), and the researches undertaken by many experimenters with induction sparks, point to the conclusion that the silent discharge acts by reason of ultra-violet light as well as by the heating effects produced by the sparks occurring under certain conditions.

Since the decomposition of moist and dry carbon dioxide both by sparks and ultra-violet light has been investigated, it seemed to the author that a study of the action of the silent discharge on this gas would throw additional light on the nature of the discharge itself.

Brodie has shown that carbon dioxide dried over sulphuric acid is decomposed into carbon monoxide and oxygen, and that a very large proportion of the oxygen thus produced is ozonised (*Phil. Trans.*, 1874, **164**, 83).

The action of sparks has been examined by several authors, particularly by Dixon (Trans., 1885, **47**, 571) and Collie (Trans., 1901, **79**, 1063). Their results show that the gas is decomposed whether moist or dry, and that the shorter the spark and the lower the pressure of the gas the larger is the amount decomposed.

Chapman, Chadwick, and Ramsbottom (Trans., 1907, **91**, 942), in studying the chemical action of ultra-violet light, found no action

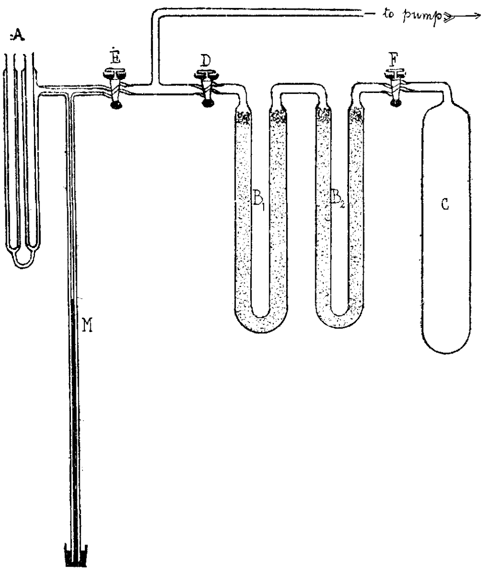
* This experiment is described at the end of a paper published in conjunction with Cundall (Trans., 1887, **51**, 610).

on moist carbon dioxide; the dry gas, however, was decomposed to an extent which varied inversely with the pressure.

In the present research, only the amounts of carbon monoxide and oxygen produced in the decomposition were determined, the apparatus employed proving unsuitable for the estimation of the ozone. The oxygen was always found to be more or less ozonised. In a future communication, the author hopes to give some details concerning the amount of ozone produced during the decomposition of carbon dioxide by the silent electric discharge under varying conditions of pressure and dryness.

The apparatus employed in the present investigation is illustrated in Fig. 1.

FIG 1.



The carbon dioxide was obtained by heating pure sodium hydrogen carbonate in the vessel *C*; B_1 and B_2 were long U-tubes filled with phosphoric oxide; *A* was the ozoniser; *M* a manometer. The tubes containing the phosphoric oxide were removed during the experiments with moist gas, but the apparatus was otherwise unaltered. In the experiments with the dry gas, a drop of sulphuric acid was placed on the top of the mercury column in the manometer in order to protect the bright surface of the mercury from the action of ozone. When experimenting with the moist gas, a drop of water replaced the sulphuric acid, as it served both to protect the surface of the mercury and to saturate the gas with water vapour.

The method of carrying out an experiment was as follows: the whole apparatus was evacuated, the tap *D* was shut, and B_1 and B_2 filled with carbon dioxide. The tap *F* was then closed, and the gas allowed to dry in contact with the phosphoric oxide for at least twelve hours.

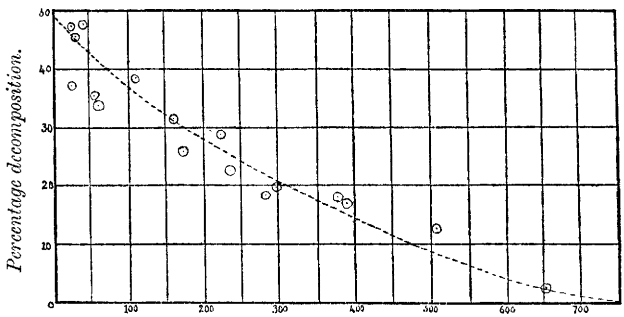
The tap *D* was now opened, and the gas passed into the ozoniser, the pressure being read on the manometer. The taps *E* and *D* were shut, and the space between them and the pump evacuated.

The silent discharge was passed through the gas in the ozoniser until the pressure, as indicated by the manometer, became constant. The tap *E* was then opened, and the gas pumped out and analysed.

The decomposition of dry carbon dioxide is shown by the curve in Fig. 2. The amount of gas decomposed varied inversely as the pressure.

The actual decomposition at any one pressure varied, alterations in

FIG. 2.



Pressure in millimetres.

the degree of dryness of the gas and intensity of the discharge producing considerable changes. As a result of a large number of experiments, the greatest percentage of carbon dioxide is decomposed when the gas has been very carefully dried and the discharge is strong.

Similar experiments were carried out with ozonisers, in which the annular space through which the discharge passed varied from 0·5 mm. to 5 mm. in breadth.

It was found, *ceteris paribus*, that the narrower the space the greater is the decomposition.

The numbers given below were obtained in one series of experiments, in which the gas was as far as possible of uniform dryness and the discharge of constant intensity.

Pressure in mm.	30	60	165	235	300	388	652
Percentage decomposition ...	48·4	35·9	31·0	21·8	19·9	16·4	2·6

Entirely different results were obtained with the moist gas, the decomposition becoming greater as the pressure increased.

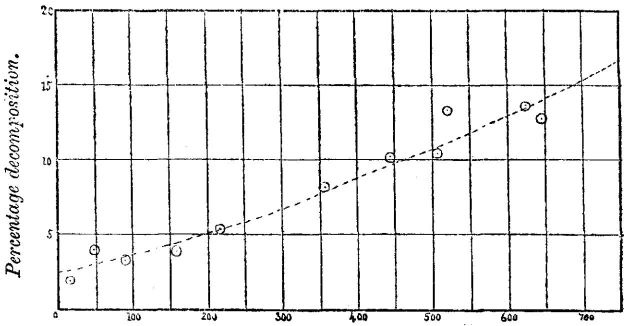
The following numbers show the actual amount of decomposition recorded in one series of experiments, the curve in Fig. 3 representing the mean of all the values obtained for different pressures.

Pressure in mm.	50	85	220	355	448	525	628
Percentage decomposition ...	3·8	4·0	5·5	8·1	10·3	13·5	14·0

As in the case of the dry gas, a weak discharge, or the use of an ozoniser with a wide annular space, diminished the amount of decomposition.

An examination of the results shows that dry carbon dioxide is decomposed by the silent discharge to about the same extent as by

FIG. 3.



Pressure in millimetres.

sparks or ultra-violet light, but that the moist gas decomposes quite differently.

Two explanations can be given of the behaviour of the moist gas, one resulting from the interaction of the decomposition products, the other from changes occurring in the nature of the discharge itself.

If the following series of reactions took place in moist carbon dioxide to an extent varying inversely with the pressure of the gas, the decomposition would be greater as the pressure increased.

$$2CO_2 = 2CO + O_2$$
$$3O_2 = 2O_3$$
$$O_3 + CO = CO_2 + O_2.$$

But Remsen and Southworth (*Ber.*, 1875, **8**, 1414) have shown that ozone and carbon monoxide do not react together under varying conditions, and the author has also carried out some experiments with these gases at diminished pressures and obtained negative results; it would seem, therefore, that this cycle of reactions does not take place to any appreciable extent. Changes taking place in the discharge itself afford the simplest explanation of the behaviour of the moist gas.

It seems probable that in the moist gas the discharge at low pressures consists almost entirely of ultra-violet light, but as the pressure increases, more and more sparks occur in the discharge, and bring about the decomposition of the gas.

The changes which Shenstone observed when the discharge passed through a moist atmosphere are exactly in accordance with this view, the sparks becoming more numerous in a wet gas and with increasing pressure.

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