EQUILIBRIUM IN ELECTRODELESS DISCHARGE.

PART IV. ELECTRODELESS DISCHARGE THROUGH CARBON DIOXIDE.

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Carbon dioxide was prepared by treating potassium bicarbonate with phosphoric acid and fractionating the product several times. It was transferred to the apparatus through the siphon and the discharge is started in the usual way.

The pressure increases immediately when the discharge is passed. If after switching off the discharge, liquid air bath is under the trap T_2 the gauge shows the presence of non-condensible gases. When the discharge is passed through these non-condensible gases keeping liquid air under T_2 during the experiment the pressure falls to zero within a minute. When the liquid air is removed the pressure rises to the original value. This gas is nothing else but carbon dioxide formed back in presence of a liquid air-bath. Table I gives the results of the experiments:—

TABLE I.

Starting pressure of CO_2	Final pressure of CO_2	Amount of CO_2 decomposed	Pressure of non-condensed product	Ratio 4 : 3
1	2	3	4	5
0·1850	0·1425	0·0425	0·0625	1·47
0·1700	0·1320	0·038	0·0580	1·52
0·1050	0·0750	0·0300	0·0450	1·50

The first column gives the pressure of the gas before the discharge is started; the second column gives the pressure of carbon dioxide which remains undecomposed and condenses in liquid air. Column 3 represents the amount of carbon dioxide decomposed and column 4 the corresponding pressure of the non-condensible product which is a mixture of two volumes of carbon monoxide and one volume of oxygen. The last column gives the ratio of the amount of

non-condensible constituents obtained to the amount of carbon dioxide decomposed. The results show that the reaction taking place in the tube is $2CO_2 \rightleftharpoons 2CO + O_2$ and that dissociation occurs to the extent of about 25 per cent.

In every case, if another discharge is passed in the non-condensible gases obtained by the action of first discharge, in presence of liquid air, the pressure at once falls to zero and the discharge ceases automatically; the original pressure of carbon dioxide is restored on removing liquid air. The whole cycle of operations can be repeated a number of times. In presence of a liquid air trap during the discharge, carbon dioxide is frozen out from the discharge vessels and the equilibrium is shifted from left to right.

The colour of the discharge was greenish blue. The space under the two coils had more greenish tinge than the space between them. The spectrum showed enormous number of bands throughout the visible region when observed by a direct vision spectrascope. Fig. 2, No. 7 in Part II (This *Journal*, 1937, **20A**, page 39) shows the spectrum of the discharge taken with a quartz spectrograph. The spectrum resembles that obtained by Knauss and Cotton (*Phys. Rev.*, 1931, **38**, 1190) by passing an electrodeless discharge in carbon monoxide. Bands belonging to the Ångstrom system and the fourth positive band system of carbon monoxide have been observed in this kind of the discharge.

Experiments were done to study the effect of adsorbed water vapour on the dissociation of carbon dioxide in the quartz tube which had initially taken up 0.0725 mm. of hydrogen as described in Part II. The results are given in Table II.

TABLE II.

Expt. No.	Pressure of CO_2 mm.	Pressure after 1st discharge, mm.	Same as 2, but with liquid air, mm.	Pressure of condensed gas obtained by a discharge in 3 mm.
	1	2	3	4
1	0·23	0·35	0·27	0·20
2	0·20	0·42	0·34	0·16
3	0·16	0·43	0·35	0·20

Starting with a pressure of 0.23 mm. in the tube (Experiment 1, Table II) the equilibrium pressure after the discharge was passed was 0.35 mm. which fell only to 0.27 mm. after putting in the liquid air trap. This means that carbon dioxide was dissociated to the extent of 70% as compared to 25% when no hydrogen was present in the tube. If, now the discharge was switched on, the pressure of the condensible product obtained was 0.20 mm.

The non-condensible gas was pumped off and the discharge started in the condensible product (Experiment 2). The pressure now rose to 0.42 mm. of which 0.08 mm. was condensible. After starting the discharge again the pressure of condensible product obtained was 0.16 mm. which, on subsequent decomposition, gave a pressure of 0.43 mm. Of this again, 0.08 mm. was condensible.

The results of these experiments show that in presence of hydrogen, carbon dioxide dissociates to the extent of about 70% in the electrodeless discharge.

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