LXI.—*The Decomposition of Methane. Part I.*

By Cyril William Hart Jones.

The object of the present work is to investigate (*a*) the thermal decomposition of methane under various conditions of temperature, pressure, and times of heating and (*b*) the behaviour of the gas when subjected to the action of the electric spark.

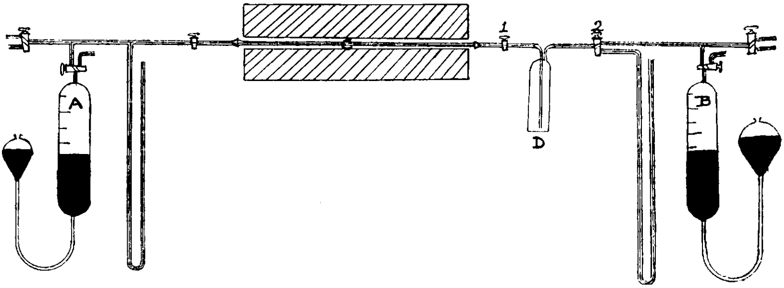
The methane used was natural gas from a South Wales colliery. It contained 92·5% of methane, 3·5% of hydrogen, and 3·9% of nitrogen. Analyses were carried out in a Bone and Wheeler apparatus, following the scheme of Williams-Gardner (*Fuel*, 1925, 4, 430).

A. Thermal Decomposition of Methane.

The apparatus is shown diagrammatically in Fig. 1. The dried methane from the cylinder was introduced to the graduated gas holder, A. The apparatus was exhausted and the gas passed at the desired pressure and rate of flow to the gas holder, B, through the heated quartz capillary tube, C. This tube, of 1 mm. internal diameter and 2 mm. wall thickness, was 120 cm. long, and a length of

80 cm. was heated to a constant temperature by means of an electric tube furnace. D is a condenser cooled in a mixture of acetone and solid carbon dioxide. After passage of the gas, the apparatus was exhausted, tap 1 closed, and tap 2 opened to the manometer. The condenser was allowed to attain room temperature, and thus the presence of easily condensable hydrocarbons was indicated, whilst oil or solid matter could be seen on the walls of the condenser. After each experiment a stream of oxygen was passed through the heated quartz tube to burn out any carbon formed, so that the internal surface of the tube was the same at the beginning of each experiment.

FIG. 1.



Results.—In the first series of experiments the gas was passed at constant pressure between the gas holders ten or twelve times, the percentage increase in pressure at constant volume being noted after each passage. Samples of the gas taken after such treatment showed the only decomposition products to be carbon and hydrogen, the former forming a hard, lustrous, coherent coating on the walls of the quartz tube. The temperature range investigated was 700—1080°, and the rates of flow were 100, 200, or 300 cm. per sec. The pressures were between 10 and 70 cm. of mercury. At 700° the increase in pressure was very small, at 800° and a rate of flow of 200 cm. per sec. the increase after ten passages through the tube was 2·5%, whilst at 1080° and a rate of 100 cm. per sec. it was 32·0% for the same number of passages. For intermediate temperatures the increase lay between these values, being lower at greater rates of flow. The increase in pressure was greater during the earlier passages through the tube than during the later ones.

In the second series of experiments the gas was passed only once through the tube under similar conditions of temperature and pressure to the above. In no case did more than 5% of the methane decompose, and, as judged from the amount of hydrogen present in the heated gas, this decomposition was almost entirely into carbon and hydrogen. At 800° and 900° traces of olefinic hydrocarbons were formed, but the amounts were too small to admit of accurate determination. At 1000° appreciable amounts were formed, as shown in Table I, which shows the relation between the pressure of gas during the heating and the proportion of olefins for two different rates of flow. At 300 cm./sec. the proportions were smaller and the results less trustworthy.

TABLE I.

Gas pressure, cm.	10	20	30	40	50	60	70
Olefins, %, at 100 cm./sec.	0·13	0·78	1·25	1·55	1·75	1·61	0·84
,, ,, 200 ,,	Trace	0·27	0·49	0·38	0·16	0·15	Trace

Small amounts of acetylene were formed at all temperatures and pressures, the maximum yield occurring at a pressure of 30—40 cm. Easily condensable hydrocarbons were not formed under the experimental conditions.

The work is being continued at the same and higher temperatures and at the same and lower flow speeds, and a much improved apparatus is being constructed.

B. The Sparking of Methane.

The apparatus consisted of an explosion pipette of about 200 c.c. capacity, fitted with platinum wire electrodes and connected to a constant-volume manometer. After having its pressure measured in the manometer, a quantity of methane was passed into the pipette and brought to the desired pressure. The spark was passed intermittently in order to avoid overheating the electrodes, the pressure of the gas being kept constant. The pressure of the gas at constant volume was measured at frequent intervals and samples were drawn off and analysed; the pressure was found to rise in accordance with the values shown in Table II. The influence of pressure on the course of the reaction is noteworthy, decomposition being much faster at higher concentrations.

TABLE II.

Time of sparking (mins.).	Percentage increase in pressure at given pressures (cm.) during sparking.						
	10.	20.	30.	40.	50.	60.	70.
1	5·5	13·0	17·25	22·5	21·0	28·0	28·5
2	10·5	22·5	30·0	37·0	35·0	46·0	47·0
3	15·5	30·0	39·0	47·0	46·0	60·0	62·0
4	20·0	35·5	46·0	56·0	58·0	71·0	74·0
5	23·5	41·5	52·5	63·0	63·5	79·5	81·5
6	27·0	47·0	57·5	70·0	72·0	85·0	87·5
7	30·0	51·5	61·5	73·5	77·0	88·5	90·5
8	33·0	58·0	61·5	77·0	—	92·0	93·5
9	36·0	58·0	69·5	80·0	—	—	—
10	37·5	61·8	71·0	81·5	—	—	—

From these figures it may be calculated that the reaction is mainly bimolecular, but tends to become more complex as the decomposition proceeds. Analysis of the sparked gas showed the main reaction to be direct decomposition to carbon and hydrogen, but high percentages of olefinic and acetylenic hydrocarbons are formed, as shown in Table III.

TABLE III.

Time of sparking (mins.).	Olefins, %, at stated pressures.			Acetylenes, %, at stated pressures.		
	40 cm.	60 cm.	70 cm.	40 cm.	60 cm.	70 cm.
1	1·10	2·05	3·90	7·50	4·85	5·20
2	1·55	3·15	5·35	8·45	7·40	7·75
3	1·90	3·70	5·90	8·90	7·55	7·80
4	2·20	4·05	6·00	9·00	7·00	7·85

The formation of both olefins and acetylenes is very rapid at first, but there is a tendency for the percentage of these components to reach a steady level. The yield of olefins appears to be roughly proportional to the pressure of the gas during sparking, but the highest yield of acetylenes is obtained at about ½ atmosphere.

Small amounts of complex solid and liquid hydrocarbons were formed on the walls of the pipette. The carbon produced by direct decomposition of the gas to its elements tended to form a bridge across the spark gap.

Summary.

1. The decomposition of methane when passed through a heated quartz tube is chiefly into its elements. Small amounts of olefinic and acetylenic hydrocarbons are also formed.

2. When methane is subjected to the electric spark discharge, carbon, hydrogen, olefins, and acetylenes are formed, together with small quantities of higher unsaturated hydrocarbons.

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THE SIR WILLIAM RAMSAY LABORATORIES OF PHYSICAL
AND INORGANIC CHEMISTRY, UNIVERSITY COLLEGE,
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