ON THE DECOMPOSITION OF METHANE, ETHANE AND ETHYLENE BY ELECTRIC SPARK.

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Berthelot(1) has already reported that methane decomposition by heat tends to form acetylene, ethane and hydrogen, in accordance with the following equations:

(1) $2CH_4=C_2H_2+3H_2$, (2) $2CH_4=C_2H_6+H_2$.

Ethane by heating yields ethylene, acetylene, methane, and hydrogen

(3) $C_2H_6=C_2H_4+H_2$, (4) $2C_2H_6=C_2H_2+2CH_4+H_2$

whilst ethylene tends to form ethane, acetylene and hydrogen,

(5) $C_2H_4=C_2H_2+H_2$, (6) $2C_2H_4=C_2H_6+C_2H_2$.

Acetylene was thus regarded by him as the ultimate decomposition product of hydrocarbons by heat.

The experiment for the decomposition of methane by the electric arc was carried out by W.A. Bone and D.S. Jerdan(2) and the gaseous products were noticed to be composed in the following proportion:

$$C_2H_2 : H_2 : CH_4=9.8 : 85.6 : 2.5.$$

and this ratio is maintained when acetylene is treated under the same conditions.

W.A. Bone and H.F. Coward(3) studied the decomposition of methane in the presence of porcelain at temperatures between 500° and 1200°, paying attention specially to the time factor for heating, and came to the following conclusions:—

(1) The rate of decomposition of methane in the presence of porcelain is appreciably below 700°, and for the most part it decomposed directly into carbon and hydrogen as postulated by M. Meyer and V. Altmeyer(4), and the process is probably reversible at all temperatures.

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(1) *Compt. rend.*, **62** (1866), 905; **63**, 788.

(2) *J. Chem. Soc.*, **71** (1897), 41.

(3) *J. Chem. Soc.*, **93** (1908), 1197.

(4) *Ber.*, **40** (1907), 2134.

(2) The formation of acetylene and olefines could be detected only so long as the methane concentration exceeded 60%.

Lately R.C. Cantelo⁽¹⁾ has conjectured the possibility of the production of the higher hydrocarbons thermodynamically, such as ethylene and acetylene from methane by heating, and this assumption was supported by the experimental results arrived at by H.V. Wartenberg.⁽²⁾

Recently R.V. Wheeler⁽³⁾ and F. Fischer⁽⁴⁾ have independently studied the acquisition of benzene from methane.

According to the investigation of S.C. Lind on the exposure of methane to α-radiation, ethane and ethylene are formed and ethane and propane behave similarly to methane in forming saturated and unsaturated hydrocarbons resulting from the elimination of hydrogen or lower hydrocarbons which subsequently build up the higher members by addition or condensa. tion as a result of valencies freed in the process.

On turning our attention to the molecular structure of methane, the infra-red absorption spectrum of methane have arrived at a tetrahedral structure of the methane molecule accepted already by chemists, but the experiments on the scattering of light, the absorption spectrum of the ultra-violet rays, and X-ray analyses are interpreted by numerous investigators in favor of the pyramidal structure which has been discussed by Weissenberg,⁽⁵⁾ and the four valencies of carbon are not equivalent but consist of two different types, so that the six electrons of the carbon atom are distributed in three shells, two electrons in 1_1, 2_1, and 2_2 orbits, and accordingly the elimination of the hydrogen atom from the methane molecule should take place in succession, to form radicals of different reactivity.

$$CH_4 \longrightarrow -CH_3,\ =CH_2,\ \equiv CH,\ \equiv C.$$

Free radicals and hydrogen liberated from methane by heating or by radiating an α-particle, give a mixture of hydrocarbons still interacting since the reactions continue under further heating or radiation unless the products should be shifted from the sphere of the reaction system. As a matter of fact, the products so far studied in the thermal decomposition of methane, are so complicated by simultaneous and successive reactions to such a degree that only their broader aspects have been worked out.

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(1) *J. Phys. Chem.*, **28** (1924), 1036.

(2) *Z. physik. Chem.*, **61** (1908), 366.

(3) *Fuel*, **7** (1928), 535.

(4) *Brennstoff-Chem.*, **9** (1928), 309.

(5) *Naturwiss.*, **15** (1927), 662; v. Henri, *Chem. Rev.*, **3** (1927), 189; J.K. Morse, *Proc. Nat. Acad. Sci.*, **14** (1928), 166.

Owing to the difficulty of interpreting the mechanism of reactions from these data, even with the accurate analysis of the products separated from the reaction product from time to time, the writer has undertaken the present investigation to study the chemical mechanism of the decomposition of methane by the electric spark, in which comparatively unstable products would be produced retarding the complex side reactions.

The apparatus employed in the experiment is shown in the accompanying figure (Fig. 1).

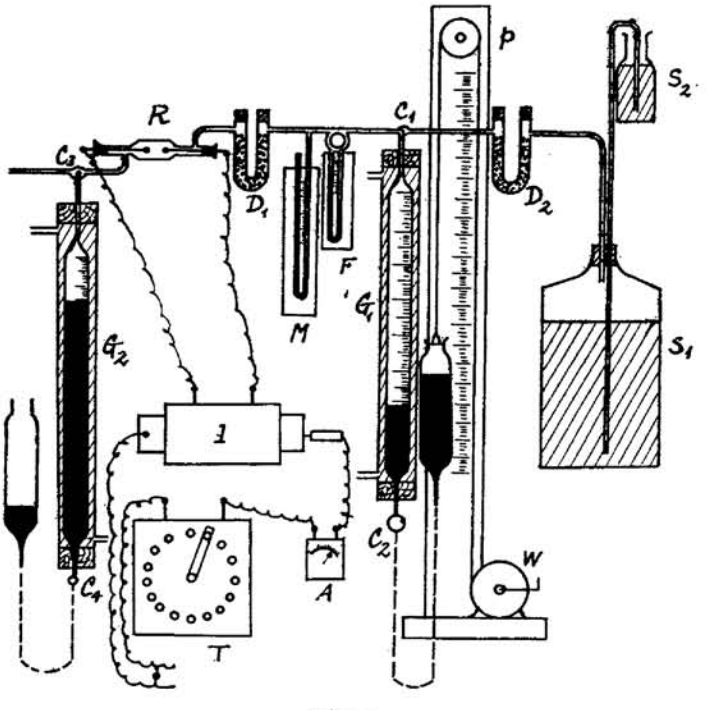

Fig. 1.

In the experiment, 100 c.c. of methane dried by passing into the dryers D_1 and D_2 containing calcium chloride, were passed into a reaction tube R the velocity being regulated with a flowmeter F and a manometer M; each reaction tube consists of a bulb of 1.5–3.5 cm. diameter and 2.0–7.0 cm. length, provided with spherical brass electrodes of 0.5–0.2 cm. diameter, and the sparks were produced between these electrodes by applying 110 volts D.C. with the aid of the induction coil I, to which the rheostat T and the ammeter A are connected. A receiver G of 150 c.c. capacity for the gaseous products is also connected to the reaction tube, which contained mercury and was cooled with a water jacket to maintain a constant temperature.

As the gaseous products contain acetylene, ethylene, and hydrogen, as well as small quantities of heavy unsaturated hydrocarbons, special methods were adopted for their analysis. Acetylene was estimated with an absorbent in which 20 gr. of mercuric cyanide were dissolved in 100 c.c. of 2-N sodium hydroxide solution and saturated with ethylene and benzene, and for the estimation of ethylene another absorbent was used, composed of 20 gr. mercuric nitrate, 100 c.c. 2-N nitric acid saturated with sodium nitrate and benzene. The heavy hydrocarbons were estimated by fuming sulphuric acid. Ethane, if present, the sample being completely freed from acetylene, ethylene and the heavy hydrocarbons were subjected to oxidation with a palladium sponge at 100° to eliminate any hydrogen, the residual gas was subsequently exploded completely with an excess of oxygen, and the amount of ethane calculated by the ratio C/A(1) determined in the usual manner. The carbon deposited on the wall of the reaction tube was composed of carbon and some unsaturated hydrocarbon which can easily be dissolved by fuming sulphuric acid.

The percentage of the reaction products were calculated on nitrogen free bases.

Table 1.

Electrode dia. 1.0 cm. Spark gap 2.0 cm. Spark voltage 33,000 volts.

Gas velocity c.c./hour.	Percentage of decomposed CH_4	Percentage of gaseous products calculated for decomposed CH_4					Ratio of products
		Volume	H_2	C_2H_2	C_2H_4	C_2H_6	H_2/C_2H_2
510	74.7	187.6	150.3	32.7	2.7	1.2	4.60
513	79.0	203.2	163.3	34.9	3.0	1.3	4.68
926	65.5	193.2	157.9	33.2	2.0	—	4.79
963	57.4	195.4	160.7	31.7	2.3	—	5.07
1005	74.7	204.2	163.6	35.3	3.0	2.2	4.64
1360	57.7	196.9	163.7	34.9	2.9	—	4.69
1360	44.0	209.4	171.2	35.9	2.5	—	4.77
1578	58.6	194.9	160.1	32.9	2.3	—	4.87
1989	57.7	192.6	157.0	31.5	3.6	—	5.01
2070	48.6	192.7	157.2	30.7	1.8	—	5.12
	Mean	196.5	160.2	33.4	2.6	—	4.81

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(1) C : contraction after explosion; A : absorbed volume.

The spark voltages in the experiments were calculated referring to those measured by Heydweiller(1) for various lengths of sparks between electrodes of various diameters at normal atmospheric pressure and temperature.

Table 2.

Electrode dia. 2.0 cm. Spark gap 2.0 cm. Spark voltage 47,000 volts.

Gas velocity c.c./hour.	Percentage of decomposed CH_4	Percentage of gaseous products calculated for decomposed CH_4					Ratio of products
		Volume	H_2	C_2H_2	C_2H_4	C_2H_6	H_2/C_2H_2
552	75.0	203.2	164.6	32.6	2.6	1.5	5.00
616	76.3	195.3	160.6	29.5	1.8	2.1	5.44
806	71.7	206.3	167.1	33.6	2.3	1.9	5.01
902	74.1	202.3	162.8	33.1	2.4	1.5	4.92
1181	77.4	204.2	168.4	33.0	2.0	—	5.10
1233	66.2	187.2	163.3	32.9	2.4	—	5.07
1396	63.8	201.7	166.1	33.5	2.4	—	4.97
1787	60.1	195.6	159.4	32.9	2.3	—	4.99
1916	62.1	200.4	164.7	33.0	2.0	—	4.99
	Mean	199.6	164.1	32.7	2.3	—	5.04

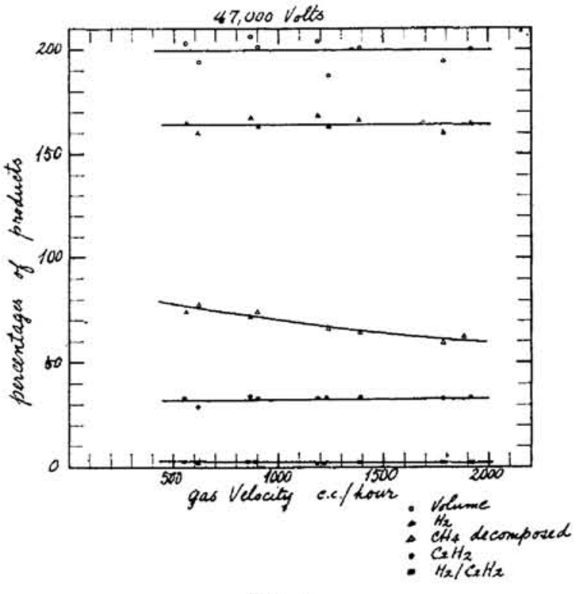

Fig. 2.

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(1) J.A. Fleming, " The Wireless Telegraphist's Pocket Book," p. 109.

In Fig. 2, yields of acetylene and hydrogen, volume of the products, and ratio H_2/C_2H_2 are plotted against gas velocity. From these experimental results shown in Fig. 2, the decomposition of methane seems to occur at an uniform rate.

The following series of experiments were carried out at various spark voltages and results as mean value for each product are shown in Table 3.

Table 3.

Spark voltage (volts)	Spark gap (cm.)	Volume change of reaction gas calculated for decomposed CH_4	Percentage of gaseous products calculated for decomposed CH_4				Ratio of products
			H_2	C_2H_2	C_2H_4	C_2H_6	H_2/C_2H_2
8,000	—	178.3	138.2	30.0	0.9–5.8	0–6.7	4.78
20,000	1	185.0	150.0	33.5	7.0–8.0	—	4.80
23,000	2	183.0	145.0	30.0	3.2–9.8	0–17.1	5.03
23,700	3	188.2	150.0	33.8	3.0–5.6	0–2.5	4.46
24,000	4	192.1	155.4	31.8	2.7–4.4	0–1.3	4.73
33,000	2	196.5	160.2	33.4	1.8–3.6	0–2.2	4.81
47,000	2	199.6	164.1	32.7	1.8–2.8	0–2.1	5.04

The decomposition rate of methane was decreased inversely to gas velocity, while the production of acetylene remained constant, and the production of ethylene and ethane was decreased at high voltages. The yield of acetylene, consisting of about 30 % of the product, is immensely great in our case when compared with the result of the thermal decomposition of methane.

As regards the mechanism of the formation of acetylene from methane, the theory which seems to fit the fact, is to assume a temporary formation of the radical $-CH_3$ from methane by a collision of electrons in the process of the ionisation of the molecule, which will then be converted by destroying the electrical tension among the electrons of the radical, into radicals $\equiv CH$ and $\equiv C$ which will polymerise with one another to produce an electrical neutral molecule of acetylene and carbon, and also form methane by hydrogenation. The radicals $-CH_3$, $=CH_2$, in the same manner, would form, on the one hand, ethane and ethylene, and on the other, methane by hydrogenation.

Formation of radicals	Polymerisation	Hydrogenation
$CH_4 \rightarrow -CH_3+H$	$\rightarrow C_2H_6$	$\rightarrow CH_4$
$\rightarrow =CH_2+2H$	$\rightarrow C_2H_4$	$\rightarrow CH_4$
$\rightarrow \equiv CH+3H$	$\rightarrow C_2H_2$	$\rightarrow CH_4$
$\rightarrow \equiv C+4H$	$\rightarrow C_x$	$\rightarrow CH_4$

The decomposition of methane under a spark with considerably high voltage, will be shown by the equation,

$$3CH_4=C_2H_2+5H_2+C$$

in which two reactions were supposed to occur simultaneously.

$$CH_4 \rightleftarrows C+2H_2 \text{ .... (a)}$$

$$2CH_4 \rightleftarrows C_2H_2+3H_2 \text{ .... (b)}$$

When the electric spark voltage is very high or the gas velocity is very small, the reaction (a) is increased at the expense of ethane and ethylene.

The Decomposition of Ethylene and Ethane.

As will be understand in the foregoing theory for the formation of acetylene from methane, the radicals such as $-CH_3$ and $=CH_2$ were assumed to occur in the course of the transformation, which will result from the collision of electrons to produce $\equiv CH$, and for verification of this hypothesis which evidently demands production of the radical $\equiv CH$ by the action of an electric spark from $=CH_2$ and $-CH_3$ generated from a molecule of ethylene and of ethane, these gases were subjected to the action of an electric spark.

The ethylene used in the experiment was prepared by decomposition of ethylene-bromide (b. p. 130°–131.5°) with zinc powder, and washed by an alkali solution of pyrogallol to remove the oxygen in the gas. Ethane was also prepared by Grignard's method, that is, by the decomposition of ethyl magnesium iodide with water, and the generated gas was washed with fuming sulphuric acid, and the oxygen removed by contact with yellow phosphorus.

The results of the decomposition of ethylene are summarized in the following table.

Table 4.

Electrode dia. 1.0 cm. Spark gap 2.0 cm. Spark voltage 33,000 volts.

Gas velocity c.c./hour	Percentage of decomposed ethylene	Percentage of products calculated for decomposed ethylene				Ratios of products		
		Volume	C_2H_2	H_2	CH_4	C_2H_2/H_2	CH_4/H_2	CH_4/C_2H_2
754	85.2	196.7	56.2	132.4	6.7	0.43	0.05	0.12
798	81.0	200.0	58.4	133.4	6.6	0.44	0.05	0.11
1262	75.4	197.0	64.8	124.5	6.4	0.52	0.05	0.10
1609	74.3	198.9	64.4	127.2	5.5	0.51	0.04	0.09
1823	74.0	198.6	64.1	127.4	5.6	0.50	0.04	0.11
2170	71.0	196.5	61.0	124.6	4.3	0.49	0.04	0.08
2198	70.0	190.7	62.7	128.4	4.5	0.49	0.04	0.07
2651	60.4	190.0	67.8	124.1	5.3	0.55	0.04	0.08
2823	58.0	199.8	68.4	125.1	4.8	0.54	0.04	0.07
3115	58.0	188.8	63.1	122.4	3.4	0.52	0.03	0.05

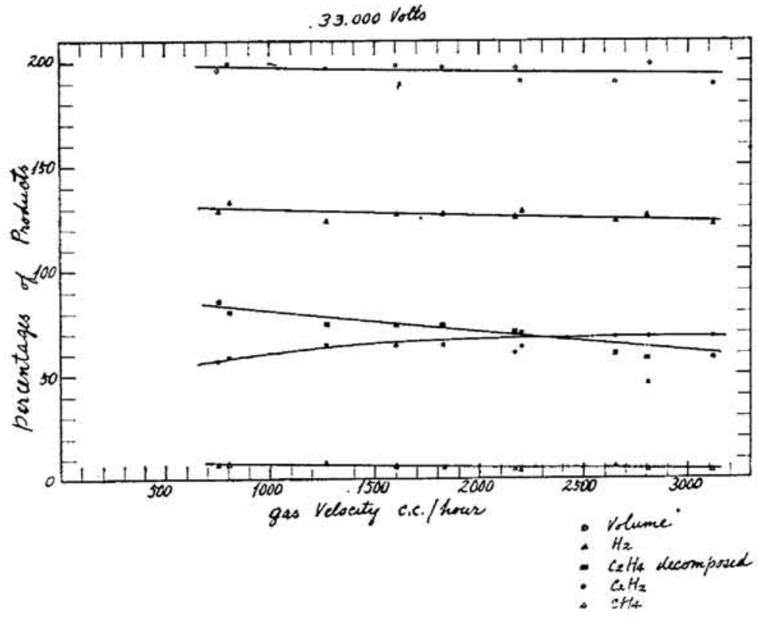

Fig. 3.

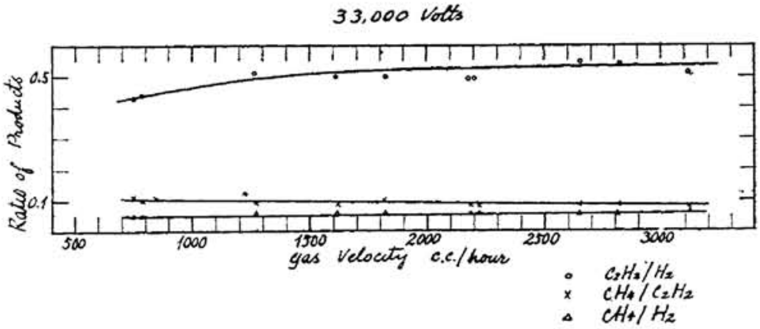

Fig. 4.

The production of hydrogen and methane is increased at a lower gas velocity, the ratio of acetylene to hydrogen in a reaction product increases almost proportionally to the gas velocity but the production of methane to acetylene, and of methane to hydrogen decreases, as indicated in Fig. 4.

The formation of acetylene and methane from ethylene can be explained by assuming that the ethylene molecule produced a radical $=CH_2$ temporarily by the collision of an electron, which was successively converted into radicals $\equiv CH$, $\equiv C$, and they tend to produce acetylene and carbon by polymerisation or methane by hydrogenation.

The fact that the production of acetylene increases with the gas velocity and the absence of ethane in the product certified the theory for the formation of $\equiv CH$ from $=CH_2$, but its hydrogenation is in a minimum degree.

Experimental results for the decomposition of ethane by an electric spark are shown in Table 5 and Fig. 5.

Acetylene, ethylene and hydrogen are the main reaction products and the deposited carbon is similar in nature to that produced by methane.

The production of acetylene and ethylene is almost constant with a gas velocity greater than 1000 c.c. per hour, but that of methane and hydrogen decreases slightly, that is, the ratio of acetylene to hydrogen is constant, but that of methane to ethylene, of methane to acetylene, and of methane to hydrogen, decrease and that of ethylene to acetylene and of ethylene to hydrogen, increase pari passu with the gas velocity, as shown in Fig. 6.

These experimental results indorse the opinion that the radicals $=CH_2$ and $\equiv CH$ are formed from $-CH_3$ dissociated from the ethane molecule, which then proceeds to produce the electric neutral molecules C_2H_4 and C_2H_2.

Table 5.*

Electrode dia. 2.0 cm. Spark gap 2.0 cm. Spark voltage 47,000 volts.

Gas velocity c.c. / hour	Percentage of decomposed ethane	Percentage of gaseous products calculated for decomposed ethane				Ratios of products					
		C_2H_2	C_2H_4	H_2	CH_4	$\frac{C_2H_2}{H_2}$	$\frac{C_2H_4}{H_2}$	$\frac{CH_4}{H_2}$	$\frac{C_2H_4}{C_2H_2}$	$\frac{CH_4}{C_2H_2}$	$\frac{CH_4}{C_2H_4}$
519	64.1	70.7	14.3	226.4	19.2	0.31	0.06	0.09	0.20	0.27	1.34
546	61.1	69.1	15.5	211.2	17.2	0.33	0.07	0.08	0.22	0.25	1.10
750	56.7	66.4	17.4	217.6	16.2	0.31	0.07	0.07	0.26	0.24	0.93
834	48.2	66.7	24.7	209.2	17.9	0.32	0.12	0.09	0.37	0.27	0.73
843	52.9	64.6	23.7	217.0	17.6	0.30	0.11	0.08	0.37	0.27	0.74
1022	52.5	65.8	19.5	208.8	17.8	0.32	0.09	0.09	0.30	0.27	0.91
1290	49.7	62.2	24.9	198.9	17.2	0.31	0.13	0.09	0.40	0.28	0.69
1434	50.4	61.5	20.2	201.2	16.8	0.31	0.10	0.08	0.33	0.27	0.83
1505	47.4	66.5	26.5	217.5	17.2	0.31	0.12	0.08	0.40	0.26	0.65
1688	48.5	63.1	26.7	197.7	16.7	0.32	0.14	0.08	0.42	0.26	0.63
1693	44.2	66.7	25.7	221.5	18.1	0.30	0.12	0.08	0.39	0.27	0.70
1966	45.6	59.4	24.5	184.9	16.2	0.32	0.13	0.09	0.41	0.27	0.66
2228	39.1	61.7	30.3	192.8	15.7	0.32	0.16	0.08	0.49	0.25	0.52
2662	37.8	64.4	28.1	206.5	16.9	0.31	0.14	0.08	0.44	0.26	0.60
3247	39.8	62.3	26.8	194.5	15.3	0.32	0.14	0.08	0.43	0.26	0.57

* The total percentage of all the gaseous products become greater than 300%, indicating that, among the products, many higher hydrocarbons, such as propane and butane, are formed during the decomposition of the methane. For this reason we understand that the percentages of decomposed ethane must be really more abundant than the represented value for its behavior contrast with methane.

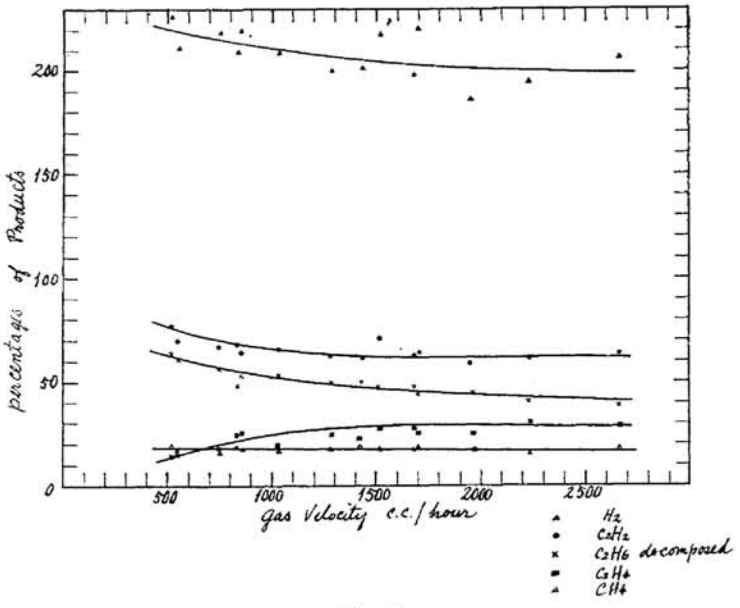

Fig. 5.

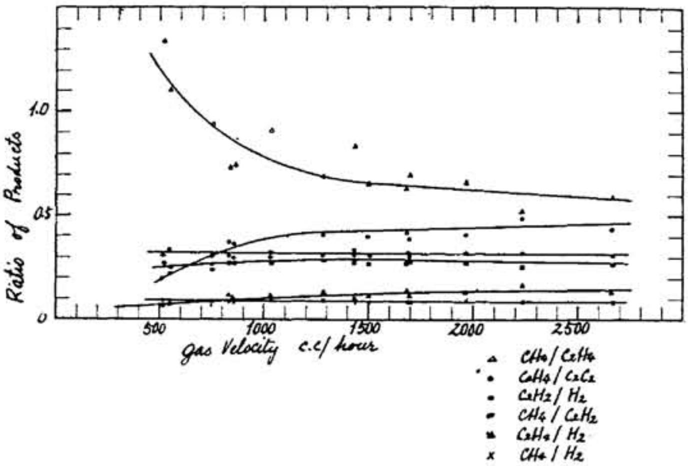

Fig. 6.

When reference is made to the investigation by Lind⁽¹⁾ for the decomposition of propane and butane by the action of α-radiation, the production of the higher hydrocarbons such as benzene in the writer's case is suspected with a great possibility, and further investigation into this interesting subject will surely be fruitful of results.

Conclusions.

Several stream experiments were carried out with methane, ethylene and ethane at varying spark voltages and at different gas velocity.

Considering the experimental results, the radicals ($-CH_3$), ($=CH_2$), ($\equiv CH$) and ($\equiv C$), are supposed to be formed temporarily from methane differing in the yield according to the strength of the electric current, and the rate of the gas velocity, and these radicals, polymerising with one another or combining with activated hydrogen, would produce ethane, ethylene, acetylene, methane and carbon. The polymerisation of the radical ($\equiv CH$), into acetylene is favorable under the experimental conditions, and the formation of benzene or higher hydrocarbons is in full force or promising.

In conclusion, the writer's thanks are due to Director Vice-Admiral S. Kishimoto, for permission to publish these results, and also he is desirous

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(1) *J. Am. Chem. Soc.*, **48** (1926), 2335.

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