[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, U. S. BUREAU OF MINES]

Pyrolysis of Methane Flowing Through a Porcelain Tube in the Region 1000°[1]

BY ALVIN S. GORDON[2]

The reaction between methane and steam at temperatures between 1000 and 1100° has been investigated,[3] using a porcelain reaction vessel in a flowing system. It was found that steam does not attack methane directly, but rather the carbon or highly carbonaceous material which results from the decomposition of methane. It seemed worth while to investigate the decomposition of methane at the same temperature and pressure conditions and in the absence of steam. Kassel[4] made an exhaustive study of methane decomposition in the range between 700 and 800° and sub-atmospheric pressure, using a static system of quartz. He also used a sillimanite vessel and did not report appreciable difference in decomposition rate. Kassel found that the first portion of the reaction was first order and homogeneous, with hydrogen depressing the rate. There was an induction period of indeterminate origin. Wheeler and Wood[5] used a static system and found that quartz chips gave an initial decomposition-rate increase at 700° and sub-atmospheric pressure. In a flowing system, increase in quartz surface had no effect. The same authors reported in another paper[6] that, in a flowing system up to 1050°, no appreciable difference in rate of decomposition was observed with quartz and porcelain tubes. Holliday and Excell[7] found that hydrogen was somewhat soluble in quartz, the solubility increasing with temperature. They also reported that hydrogen slowed the velocity of decomposition of methane.

Apparatus, Materials and Procedure

The essential parts of the apparatus have previously been described[8]: a platinum-rhodium furnace 24″ long surrounded a McDaniel porcelain combustion tube, 1″ o. d. × $^3/_4$″ i. d. × 30″ long, the porcelain tubing extending beyond the furnace about 3 inches at each end. A 2-mm. Pyrex capillary was sealed to the small-diameter end and a 29/42 Pyrex ground-glass joint to the other. Two closely fitting porcelain tubes, faced with porcelain discs at the ends, were inserted into the combustion tube; the space between these inserts determined the volume of the reaction cell. The temperature was measured by two platinum–platinum-rhodium thermocouples, one cemented at each end of the reaction cell to the outer porcelain surface.

Purification of methane from a cylinder involved removal of ethane and higher hydrocarbons by passage through an activated charcoal trap at Dry-Ice temperature and of hydrogen, through a cupric oxide tube at about 300°. This gas was dried and passed through a flowmeter into the furnace. From the furnace the gases were led into a collection bottle filled with nearly saturated sodium chloride solution, constructed so that the gases discharged at atmospheric pressure. The rate of displacement of the salt solution was measured to determine the exit velocity of the gases.

During the investigation it was noted that the products of decomposition which covered the surface slowed down the reaction; after run 257 these products were burned off with oxygen after every few experiments. The rate was reproducible within 5–10% by this method; *e. g.*, runs 318 and 319 are reproduced to about 8%.

The gas analyses for each experiment were made by a mass spectrometer (under the supervision of Dr. R. A. Friedel). Most of the analyses were done in duplicate; percentages of hydrocarbons present in tenths of a per cent. could be reproduced within ten per cent., whereas methane could be reproduced within one-tenth per cent. Nitrogen reproducibility was quite erratic. These analyses were used to determine the methane percentage decomposed on an original volume basis. To obtain this value, hydrocarbon products with a molecular weight higher than benzene were calculated as carbon. Since naphthalene, anthracene, phenanthrene and pyrene were identified by their ultraviolet spectra, this assumption introduced an error. Benzene was present in very small percentage, so that these products, presumably formed from benzene, will probably be present in small percentage. From the percentages of hydrocarbons in the exit gas, the percentage of methane decomposed on an original volume basis was calculated.

Benton's[9] equation for reaction in a flowing system with change in volume was used in treating these data. It is assumed, in deriving this equation, that the diffusion was small compared to the linear velocity. For small percentage of decomposition, even a large diffusion effect will not give a large error in using the above equation.

The rate of decomposition was assumed to be first order, and the specific rate constant was calculated from the equation

$$k = \frac{V_0}{V_b}\left(g \ln \frac{1}{1 - F} - (g - 1) F\right)$$

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(3) A. S. Gordon, unpublished results.

(4) Kassel, THIS JOURNAL, **54**, 3949 (1932).

(5) Wheeler and Wood, *Fuel*, **9**, 567 (1930).

(6) Wheeler and Wood, *ibid.*, **7**, 535 (1928).

(7) Holliday and Excell, *J. Chem. Soc.*, 1066 (1929).

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TABLE I

KINETIC DATA AT 1007° THROUGH 1075° OF METHANE DECOMPOSITION IN A PORCELAIN TUBE

Pressure = 1 atm., $S:V$ = 2.47

Run	Methane decomposed, %	$\bar{t}$,[a] sec.	T, °C.	"k"[b]	Products of methane decomposition, per cent. exit volume						
					C_2H_4	C_2H_2	C_2H_6	C_3H_6	$CH_3—C≡CH$	H_2	C_6H_6
191	1.27	0.288	1007	0.044	0.11	0.04	0.09	0.02	0.02	1.91	0.00
190	1.54	.364	1007	.043	.13	.05	.09	.02	.02	2.36	.00
189	2.40	.533	1007	.046	.22	.09	.09	.03	.04	3.74	.00
188	3.69	.724	1007	.052	.34	.16	.11	.05	.06	5.69	.01
187	7.36	1.130	1007	.068	.65	.36	.12	.06	.07	11.41	.03
186	8.70	1.329	1007	.069	.80	.40	.11	.07	.07	13.51	.02
185	9.82	1.454	1007	.071	.91	.41	.09	.06	.07	15.28	.01
180	10.54	1.499	1007	.074	.87	.39	.10	.07	.05	16.56	.01
193	1.27	0.219	1033	.058	.13	.05	.09	.02	.03	1.87	.00
194	1.74	.299	1033	.059	.18	.07	.10	.02	.04	2.59	.00
195	2.39	.347	1033	.069	.26	.12	.12	.04	.05	3.50	.00
196	3.10	.402	1033	.078	.37	.18	.11	.04	.07	4.53	.00
197	6.28	.632	1033	.103	.72	.37	.12	.07	.09	9.44	.00
198	7.42	.671	1033	.115	.81	.45	.11	.07	.11	11.10	.02
200	10.88	.893	1033	.107	1.08	.62	.10	.08	.10	16.35	.04
211	14.39	1.293	1033	.120	1.27	.65	.10	.08	.08	21.53	.08
212	16.91	1.516	1033	.122	1.36	.68	.11	.09	.06	25.32	.04
215	2.29	0.184	1053	.125	0.31	.08	.12	.03	.07	3.15	.02
216	2.37	.202	1053	.118	.32	.09	.13	.03	.06	3.28	.01
218	2.74	.232	1053	.119	.37	.14	.12	.04	.06	3.85	.01
219	3.72	.255	1053	.129	.49	.22	.13	.05	.12	5.22	.02
221	4.30	.334	1053	.131	.55	.27	.13	.06	.12	6.07	.03
222	5.68	.399	1053	.146	.69	.37	.12	.07	.12	8.25	.03
256	6.61	.431	1053	.158	.75	.34	.14	.05	.11	9.89	.03
255	8.22	.495	1053	.173	.88	.42	.13	.06	.11	12.32	.05
223	9.66	.571	1053	.177	.98	.65	.14	.08	.14	14.25	.07
224	3.96	.162	1075	.250	.49	.25	.15	.03	.11	5.67	.02
225	4.15	.166	1075	.254	.51	.26	.14	.02	.11	6.02	.02
226	4.80	.190	1075	.259	.60	.30	.12	.05	.12	7.00	.02

[a] $\bar{t}$ = average time of contact of methane in reaction cell. [b] "k" = first-order constant (sec.$^{-1}$).

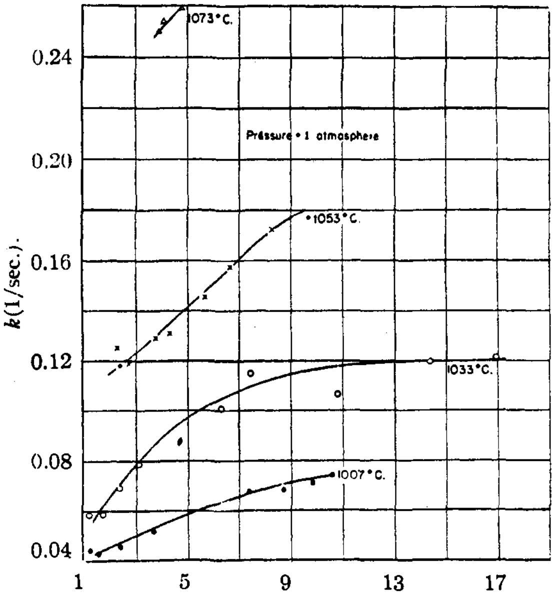

Fig. 1.--First-order constants against percentage of methane decomposed at various temperatures.

where

k = first-order specific rate constant (1/second)
V_o = velocity (cc./second) of the gases entering the reaction cell
V_b = volume of the reaction cell (cc.)
$g = \dfrac{\text{gaseous moles formed from methane decomposed}}{\text{moles methane decomposed}}$
F = fraction of methane decomposed

Results and Discussion

Effect of Product Gases on the Pyrolysis

Referring to the data in Table I, which have been plotted in Fig. 1, it may be seen that the first-order constant always tended to increase with increasing decomposition of methane at each of the temperatures studied. It may be shown[9a] that increase of first-order constants with time indicates a less-than-first-order reaction or an autocatalytic reaction. To test the latter hypothesis, small percentages of the product gases were added to the methane entering the reaction vessel. When 0.72%

(9a) If k_T is the true constant and k_1 is the first-order constant

$$-\frac{d(CH_4)}{dt} = k_1(CH_4) = k_T(CH_4)^T$$

$$k_T = k_1\,(CH_4)^{1-T}$$

since k_1 increases with time, T must be less than 1 so that $(CH_4)^{1-T}$ will decrease correspondingly with time in order to keep k_T constant.

TABLE II

EFFECT OF SMALL PERCENTAGES OF PRODUCT GASES ON THE DECOMPOSITION OF METHANE AT 1007°

Pressure = 1 atm., $S:V$ ratio = 2.47.

Run	Methane decomposed, %	$\bar{t}$,[a] sec.	"k"[b]	Product gases, per cent. exit volume						
				C_2H_4	C_2H_2	C_2H_6	C_3H_6	$CH_3—C{\equiv}CH$	H_2	C_6H_6
				0.72% of Acetylene						
265	3.11	0.281	0.115	0.52	0.24	0.12	0.06	0.10	4.67	0.02
266	3.45	.281	.124	.52	.25	.12	.06	.12	5.20	.04
267	5.50	.476	.122	.74	.30	.12	.07	.10	8.47	.07
268	5.82	.482	.129	.80	.34	.12	.08	.11	8.95	.05
269	8.37	.707	.131	1.01	.41	.12	.08	.10	12.95	.09
270	8.42	.723	.130	1.03	.42	.13	.08	.09	12.99	.09
301	2.49	.160	.159	0.40	.29	.13	.03	.10	3.82	.01
				1.00% of Ethylene						
303	3.41	0.290	0.121	0.86	0.28	0.14	0.08	0.12	5.88	0.02
309	3.25	.291	.116	.85	.31	.12	.08	.11	5.99	.03
304	4.95	.434	.119	.98	.37	.13	.09	.12	8.40	.02
306	6.64	.547	.128	1.06	.44	.12	.09	.09	11.17	.04
307	6.72	.556	.127	0.99	.44	.13	.08	.10	11.54	.05
				2.08% of Hydrogen						
314	1.64	0.275	0.063	0.33	0.10	0.11	0.04	0.06	4.54	0.00
315	3.09	.467	.070	.49	.18	.11	.06	.08	6.87	.02
316	5.24	.731	.740	.68	.28	.08	.05	.09	10.45	.03
				Decomposition of Pure Methane at 1007°						
318	1.39	0.279	0.050	0.08	0.02	0.10	0.02	0.03	2.15	0.00
319	1.51	.279	.054	.12	.02	.07	.01	.01	2.49	.00
320	2.57	.473	.055	.23	.06	.08	.02	.04	4.17	.00
321	4.41	.738	.061	.40	.14	.10	.05	.07	6.95	.03

[a] $\bar{t}$ = average time of contact of methane in the reaction cell. [b] "k" = first-order constant (sec.$^{-1}$).

of acetylene was in the entering gas, as the results in Table II show, 2 to 2.5 times as much methane decomposed in the same time as when no acetylene was present, even after as much as 8.5% of methane had been decomposed. With the smallest contact time (0.16 second) only 0.29% of acetylene appears in the exit gas when 0.72% of acetylene was in the in-gas, and the temperature was 1007°. After a short time in the reaction cell, even though the percentage of acetylene was quite small, it had a large catalytic effect on the decomposition rate of methane. Because the percentage of ethylene in the exit gas in the study with acetylene in the in-gas was increased somewhat over the percentage observed for pure methane, the decomposition was studied with about 1% of ethylene in the in-gas. As may be seen in Table II, the ethylene in the exit gas was never less than 0.85%. For about the same contact time, the percentages of methane decomposed were in the same range, whether acetylene or ethylene was added to the in-gas. If the shorter of the comparable contact times was examined, it was seen that, with acetylene in the in-gas (average of runs 265 and 266), 0.52% of ethylene and 0.25% of acetylene appeared in the exit gas; when the contact time was 0.281 second, 3.28% of methane was decomposed. On the other hand, with ethylene in the in-gas (average of runs 303 and 309), 0.86% of ethylene and 0.30% of acetylene were in the exit gas when the contact time was 0.291 second; 3.33% of methane was decomposed in these experiments. These data showed that increasing the percentage of ethylene has little, if any, effect on the rate of decomposition. For longer contact times, comparisons between ethylene and acetylene in the in-gas were not possible because the percentages of ethylene and acetylene in the exit gas were so nearly the same.

It may be noted that the percentage of acetylene in the exit gas increased with increasing percentage of methane decomposed; since acetylene was a catalyst for the decomposition of methane, the reaction was autocatalytic.

It was of some interest to examine the possible reactions of acetylene as a catalyst in this reaction. If the primary products of methane pyrolysis were methyl radicals and hydrogen atoms, these atoms of hydrogen probably formed hydrogen molecules by reaction with methane molecules before any appreciable reverse reaction with methyl radicals occurred. On the other hand, the primary products may have been methylene radicals and hydrogen molecules, as suggested by Kassel,[4] so that the reverse reaction would be with hydrogen molecules. For both mechanisms, the concentration of hydrogen molecules would determine the reverse-reaction velocity. In the early stages of the reaction, acetylene could react with hydrogen, preventing the reverse reaction to reform methane, and a percentage of methane equal to the acetylene percentage could be decomposed, which is not enough to account for the large observed effect. If acetylene should react with the free radicals, not enough methane would be decomposed to account for the large observed effect. It was thought possible that acetylene attacked methane directly, yielding ethylene and a methylene radical. The methylene reacted with methane to form ethane, which decomposed to ethylene and then acetylene, setting up a chain reaction. Another possibility was that only one hydrogen atom was removed from the methane by acetylene, forming a C_2H_3 and CH_3 radical, the C_2H_3 reacting with another methane molecule to form ethylene and a second CH_3 radical. The above mechanism required the percentage of ethylene to be increased over the normal percentage in the exit gas. This increase of ethylene percentage was noted.

Kassel[4] studied the effect of the addition of hydrogen on the velocity of decomposition at 760° in a static system and found that 10% or more of hydrogen greatly retarded the reaction. The effect of hydrogen was studied in the present investigation at 1007° by adding 2.01% hydrogen to the reactant gas. As seen in Table II, there was a 20 to 30% increase in reaction rate over that of the untreated gas when between 1.64 to 3.09% of methane was decomposed. More ethylene and acetylene appeared in the exit gas for the same percentage of methane decomposed in these experiments than when there was no hydrogen in the reactant gas. Thus there was a greater catalysis of the decomposition.

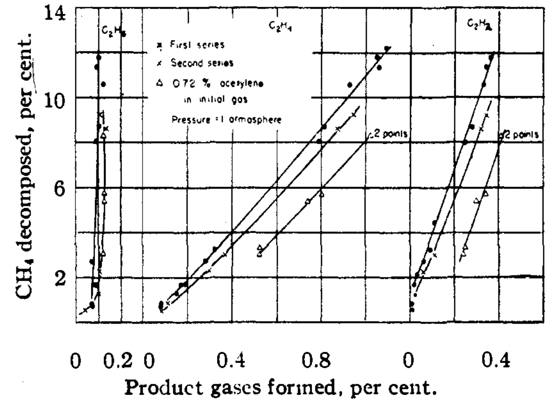

Fig. 2.—Gases formed from methane decomposed at 1007°.

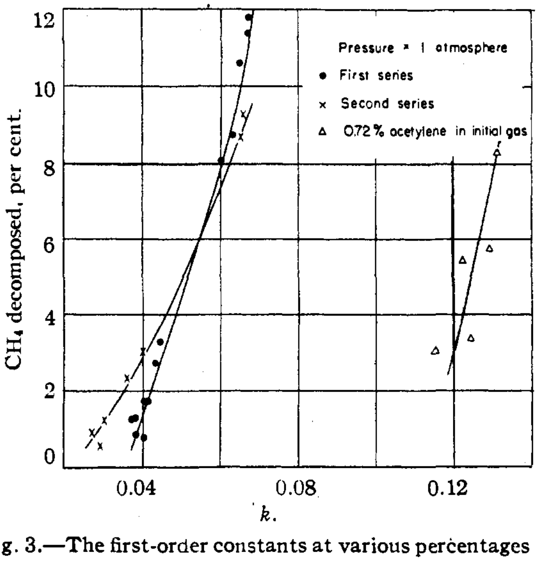

Fig. 3.—The first-order constants at various percentages of methane decomposed at 1007°.

It was hard to account for the difference in the effect of hydrogen in Kassel's paper and the present work, because the experimental conditions were different. The increase in acetylene catalysis when hydrogen was in the entering gas could more than compensate for a hydrogen retardation effect.

Effect of Surface on the Pyrolysis

If a series of runs with successively greater decomposition of methane at 1007° was followed, without any cleansing of the reaction vessel, by a similar series of successively greater decomposition, the first-order constants were smaller in the second series for the same percentage of methane decomposed. At the same time, the percentages of ethylene and acetylene were greater in the second series. These data are plotted in Figs. 2 and 3. Since the catalytic effect of acetylene was greater in the second series, the higher reaction constants must be viewed as the larger effect of surface, the surface being partly poisoned in the second series by decomposition products. Results obtained when the porcelain tube was cleansed with oxygen, *e. g.*, runs 318–321, Table II, show that the velocity of methane decomposition was greatest in this case. To compare the effect of surface and product gases at an equally active surface, the surface was cleansed with oxygen after every few runs.

The effect of increased surface : volume ratio was studied by inserting three porcelain tubes $^3/_8$-inch o. d. by 2 inches length by $^1/_{32}$-inch wall thickness (to get a large surface increase with small volume decrease) into the reaction cell. The results of experiments at 1007 and 1033° are reported in Table III. Results of experiments without any additional surface are included for comparison. It was seen that, at comparable times of contact, between two and three times as much methane was decomposed in the same time when the extra surface was present as in the normal decomposition of methane. From the results in Table III, it was seen that the concentration of ethylene or acetylene or both (since the concentration of one always influences the other) was relatively increased by increases $S:V$ ratio at very low concentrations of these gases, and relatively decreased with increased $S:V$ ratio when a small concentration of ethylene and acetylene had been built up. Thus the surface catalyzes the decomposition of ethylene and acetylene.

The effect of surface was not quantitative be-

TABLE III

EFFECT OF SURFACE:VOLUME RATIO ON THE DECOMPOSITION OF METHANE

Pressure = 1 atm.

Run	Methane decomposed, %	$\bar{t}$,[a] sec.	$S:V$,[b] cm.$^{-1}$	T, °C.	Product gases, per cent. exit volume C_2H_4	C_2H_2	C_2H_6	C_3H_6	$CH_3—C\equiv CH$	H_2	C_6H_6
277	3.62	0.235	9.52	1007	0.22	0.03	0.10	0.02	0.01	6.15	0.00
278	3.62	.236	9.52	1007	.23	.03	.08	.03	.01	6.19	.00
279	3.78	.273	9.52	1007	.29	.04	.11	.04	.02	6.24	.00
280	3.85	.276	9.52	1007	.30	.03	.08	.04	.02	6.44	.00
281	5.97	.462	9.52	1007	.40	.06	.05	.07	.02	10.09	.00
282	6.02	.480	9.52	1007	.36	.06	.08	.04	.02	10.22	.00
283	8.07	.693	9.52	1007	.39	.08	.07	.04	.02	13.79	.00
284	8.14	.694	9.52	1007	.41	.07	.05	.04	.03	13.93	.00
318	1.39	.279	2.47	1007	.08	.02	.10	.02	.03	2.15	.00
319	1.51	.279	2.47	1007	.12	.02	.07	.01	.01	2.49	.00
320	2.57	.473	2.47	1007	.23	.06	.08	.02	.04	4.17	.00
321	4.41	.738	2.47	1007	.40	.14	.10	.05	.07	6.95	.03
358	4.32	.208	9.52	1033	.42	.09	.12	.05	.05	6.76	.01
359	4.39	.209	9.52	1033	.43	.08	.10	.05	.04	7.01	.00
344	3.10	.154	9.52	1033	.36	.07	.12	.04	.04	4.73	.01
322	1.42	.210	2.47	1033	.15	.03	.07	.02	.02	2.17	.02
323	1.52	.211	2.47	1033	.15	.03	.08	.02	.02	2.37	.00
324	3.27	.383	2.47	1033	.37	.13	.11	.05	.08	4.89	.02
325	3.99	.438	2.47	1033	.51	.16	.10	.06	.10	5.81	.02
0.72% of Acetylene in the Reactant Gas											
285	4.81	0.268	9.52	1007	0.51	0.22	0.10	0.06	0.08	8.20	0.01
286	5.06	.266	9.52	1007	.50	.21	.10	.05	.08	8.44	.02
287	8.58	.495	9.52	1007	.61	.20	.07	.05	.05	14.53	.03
288	8.66	.486	9.52	1007	.60	.20	.07	.06	.05	14.73	.02
289	11.37	.722	9.52	1007	.64	.21	.07	.05	.03	19.21	.02

[a] $\bar{t}$ = average time of contact of methane in reaction cell. [b] $S:V$ = surface:volume ratio in reaction cell.

cause, in the effort to make the porcelain wall thickness as small as possible to get a large increase in area with a small increase in volume, a much more porous structure results than is present in the porcelain of the reaction cell. Thus these reported values err on the high side for the effect of macro-measured surface.

The effect of surface probably was quite high, and there was therefore a large but indeterminate effect of the large $S:V$ ratio (67.5) in the annular entrance and exit spaces, since the temperature varies; the effects compared at constant contact time are not affected by this correction.

The results of increased $S:V$ ratio on the rate of decomposition of methane containing 0.72% of acetylene, keeping contact time as near constant as possible, may be compared in Tables II and III. They show that the larger $S:V$ ratio increases the decomposition velocity, the effect decreasing with increasing contact time. The acetylene content of the exit gases built up faster with time for the smaller $S:V$ ratio; its effect counterbalanced the $S:V$ ratio effect, and the difference in per cent. of methane decomposed between the larger and smaller $S:V$ ratios became smaller.

At the shortest contact time studied, the acetylene in the exit gas was about the same for the two different $S:V$ ratios. Since the acetylene in the in-gas was also the same, it seemed reasonable to assume that the acetylene contents were not too different at any point in the reaction vessel. The effect of acetylene alone, $S:V$ ratio alone, and the two acting simultaneously was obtained by subtracting the normal methane decomposed at the same contact time from the value of methane decomposed when one or both of the above effects were present in addition. Using the average values of the duplicate experiments reported in Tables II and III, the following resulted:

Methane Decomposed, Per cent. Acetylene + $S:V$	Acetylene	$S:V$
4.94	3.28	3.82
subtracting the average of the normal methane decomposition (1.45) from each of these values		
3.49	1.83	2.37

Adding the effect of acetylene and $S:V$ and comparing with acetylene plus $S:V$, it was seen that the sum of the separate values was 0.71 per cent. *greater* than the effect of the two combined. This was evidence for no interaction of surface and acetylene, which pointed to a homogeneous catalysis by acetylene. For the longer contact times the above procedure could not be employed because the acetylene percentage in exit gases was quite different for the two $S:V$ ratios.

The products of reaction besides those mentioned include propene, methyleneacetylene, benzene, naphthalene, pyrene and anthracene. There

TABLE IV

EFFECT OF NITROGEN AND STEAM ON THE DECOMPOSITION OF METHANE AT 1007° AND $S:V = 2.47$

Pressure = 1 atm.

Run	Methane decomposed, %	$\bar{t}$,[a] sec.	N_2 in inlet gas, %	H_2O in inlet gas %	Product gases, per cent. exit volume C_2H_4	C_2H_2	C_2H_6	C_3H_6	$CH_3—C{\equiv}CH$	H_2	C_6H_6
318	1.39	0.279	..	..	0.08	0.02	0.10	0.02	0.03	2.15	0.00
319	1.51	.279	..	..	.12	.02	.07	.01	.01	2.49	.00
320	2.57	.473	..	..	.23	.06	.08	.02	.04	4.17	.00
321	4.41	.738	..	..	.40	.14	.10	.05	.07	6.95	.03
310[b]	2.12	.406	52.6	..	.08	.05	.05	.02	.03	1.53	.02
311[b]	2.77	.543	52.6	..	.16	.05	.03	.00	.02	2.27	.00
312[b]	3.43	.648	52.6	..	.19	.09	.05	.02	.04	2.62	.00
380	1.17	.246	..	50	.10	.02	.11	.03	.01	2.11	.01
381	1.16	.245	..	50	.12	.01	.08	.02	.01	2.22	.00

[a] $\bar{t}$ = average time of contact of methane in reaction cell. [b] There is 0.05% ethane in the inlet gas.

was always less than 0.01% of propane, or butadiene, contrary to the experience of Hague and Wheeler,[10] who found butadiene in the products from the decomposition of methane in a flowing system at 950° in quartz, from which they concluded that benzene was formed with butadiene as an intermediate. The results in this research indicated no stable 4-carbon intermediate. If the naphthalene is formed from benzene, it is presumably made in a two-step reaction with acetylene or ethylene, or both.

Propene and methylacetylene were observed as products in the decomposition of methane. These compounds could form by the reaction of free methylene radicals and ethylene to give propene, which dehydrogenates to methylacetylene, or alternatively acetylene could react with methylene to give methylacetylene. The question of whether methylene, methyl or both are the primary radicals of methane decomposition has not been definitely answered. Barrow, Pearson and Purcell[11] reviewed the question and concluded that both may be present. Eltenton[12] used a mass spectrometer to detect the free radicals from methane decomposition and reported that only methyl radicals were detected.

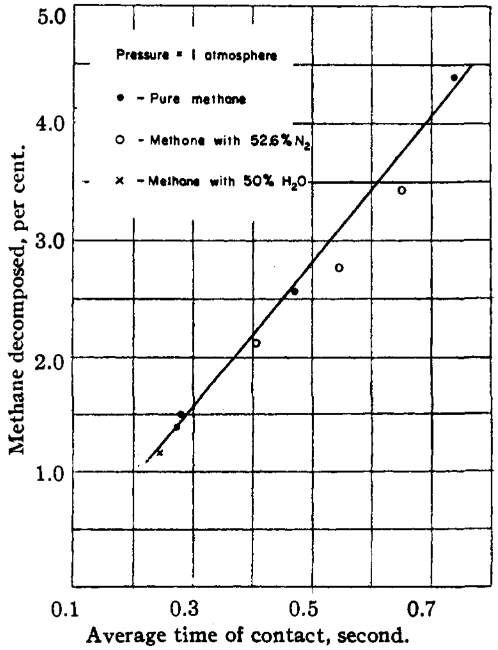

Fig. 4.—Percentage of methane decomposed *vs.* average time of contact at 1007° and $s/v = 2.47$.

Three tubes of quartz were added to the reaction cell with quartz surface:volume of reaction cell = 10.24. At 1007°, there was only an increase from 1.45% of methane decomposed, with no extra surface, to 1.97% of methane decomposed for the added quartz surface at about the same average time of contact. Part of the above increase may be explained by the increased time spent in the entrance and exit annular spacing, since the volume of these tubes necessitated about a 30% decrease in velocity through the reaction cell to keep the contact time stationary. Thus quartz surface had a minor effect on the reaction velocity.

The effect of porcelain surface when 30% of methane was decomposed was investigated at 1033°. For the same contact time, the decomposition of methane when the $S:V$ ratio = 6.94 was *less* than the decomposition of methane when the $S:V$ ratio = 2.47. Thus, surface had a large effect on the decomposition velocity only in the early stages of the decomposition, and this may account for the small effect of porcelain over quartz surface previously reported.

The average time of contact here was over four seconds. About 1% of carbon monoxide was found in the exit gas, owing to the slow reaction between methyl or some intermediate and porcelain. A similar result with much larger carbon monoxide was reported previously by Bone and Coward.[13]

The result of percentages of the methane decomposed in passage through the furnace, with

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(10 Hague and Wheeler, *J. Chem. Soc.*, **363** (1929).

(11) Barrow, Pearson, and Purcell, *Trans. Faraday Soc.*, **35**, 880 (1939).

(12) Eltenton, *J. Chem. Phys.*, **10**, 403 (1942).

(13) Bone and Coward, *J. Chem. Soc.*, **93**, 1197 (1908).

pure methane and with methane diluted about 1:1 with nitrogen and with steam, were shown in Table IV and plotted in Fig. 4. A straight line was drawn through the four points for pure methane decomposition; the three points with nitrogen fell reasonably close to this line and the two almost identical points with steam fell on the line. Since the first-order "constants" for pure methane over this range of contact times increased some 36%, these plotted results were quite interesting because they indicated a first-order decomposition. It may be noted in Table IV that the percentages of acetylene in the exit gas for the same percentage of methane decomposed were not very different for these various cases. One possible way the observed results may be explained was by assuming that, in the rate of decomposition of methane, the effect of surface and of acetylene depended on the concentration of methane to the first power; the acetylene and surface may be to any power. Kassel[4] has already shown the homogeneous decomposition to be first order at somewhat lower temperatures.

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Summary

The decomposition of methane has been studied in a porcelain tube at temperatures between 1007 and 1075°. The following observations were made:

1. Within this range the first-order reaction constants increased with increasing decomposition.
2. There was a catalytic effect of acetylene, probably homogeneous, which accounts for (1), since the percentage of acetylene increased with increasing percentage of decomposition.
3. There was probably no effect of ethylene on the decomposition of methane.
4. There was a large catalytic effect of surface in the early stages of the reaction which disappeared by the time 30% of the methane was decomposed.
5. No induction period was found.
6. In the early stages of the decomposition, 50% nitrogen or steam in the entering gas resulted in about the same percentage of decomposition of the methane for equal contact time.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Effect of Activator Concentration on the Infrared-Sensitive Phosphor, Strontium Sulfide–Samarium, Europium[1]

BY KENNETH F. STRIPP AND ROLAND WARD

The recognition by Urbach[2] that the double activator principle permits long storage of energy in infrared-sensitive phosphors at room temperatures led to the development of his Standard VI phosphor. This material was originally prepared by heating a mixture containing approximately 70% strontium sulfide, 25% strontium sulfate and 5% calcium fluoride to which samarium and europium salts had been added. It has been shown[3] that the strontium sulfate and calcium fluoride constitute the flux for this phosphor and that the sulfate may cause some oxidation to occur.

In attempts to simplify the composition of these phosphors, it was found that satisfactory fluxing could be obtained with strontium chloride. The only complication which this flux may cause is the introduction of chloride ions. The lattice constants from pure strontium sulfide and from strontium sulfide fluxed with strontium chloride were the same within experimental error, indicating a very limited solubility of the chloride in the sulfide. The luminescent characteristics of phosphors prepared in this way appeared to be much more consistent than those obtained by the Lenard procedure so that it was thought worthwhile to undertake a more critical determination of the optimum concentrations of the activators.

Experimental

(a) The Preparation and Measurement of Samples.—Pure strontium sulfate obtained by precipitation from purified strontium nitrate solution[4] was reduced to the sulfide by heating in silica glass boats to constant weight in a stream of dry hydrogen or hydrogen sulfide. The products were white powders which showed neither fluorescence nor phosphorescence on exposure to ultraviolet radiation.

Strontium chloride solution was purified by a procedure

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(1) This work was carried out at the Polytechnic Institute of Brooklyn under Contract NObs 28370 with the Bureau of Ships.

(2) F. Urbach, D. Pearlman and H. Hemmendinger, *J. Optical Soc. Am.*, **36**, 372 (1946).

(3) W. Primak, R. K. Osterheld and R. Ward, THIS JOURNAL, **69**, 1283 (1947).

(4) A. L. Smith, R. D. Rosenstein and R. Ward, *ibid.*, **69**, 1725 (1947).