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THE DECOMPOSITION OF METHANE ON THE SURFACE OF PLATINUM. 〔I〕*

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The decomposition of methane in the presence of various kinds of catalysts has been the subject of many studies, which have been limited mostly to the discussion of equilibrium or the comparison of the catalytic activities, and very little has been touched on the kinetics of the reaction.[1]

In the present investigation the author intends to elucidate the kinetics of the reaction on the activated surface of platinum.

Experimental.

Materials.

Methane was generated by pouring hot water to aluminium carbide[2]. Impurities such as hydrogen, ethylene, acetylene, carbon dioxide, ammonia, hydrogen sulphide, and others, which might be present were removed by the procedure due to R. Schenck.[3] (1) Acetylene was absorbed by ammoniacal cuprous chloride; the solution was freshly prepared before use. (2) Ammonia and water were absorbed by pure concentrated sulphuric acid. (3) Hydrogen was removed by passing it through a pipe filled with copper oxide grains heated to 200°—230°C. (4) Carbon dioxide was absorbed by a sodium hydroxide solution. (5) Oxygen was absorbed by an alkali solution of pyrogallol. (6) Acetylene which might be produced when methane was passed over heated copper oxide was absorbed by a cuprous chloride solution. (7) The gas was completely dried with concentrated sulphuric acid and phosphorus pentoxide.

It has been mentioned that the sample purified by this procedure is very pure, and this was confirmed by the results of combustion, which showed the purity of more than 99.9%.

The electrolytic oxygen and hydrogen used were dried with concentrated sulphuric acid and phosphorus pentoxide after passing over heated asbestos. The platinum wire used as catalyst was pure commercial platinum.

Analysis of the Reaction Products.

In the case of homogeneous thermal decomposition of methane, free radicals have been

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* This paper is the revised translation of the same article in *Rev. Phys. Chem. Japan*, 6, 81–105 (1932); 8, 19–31 (1934).

[1] As to the studies made before 1930, see G. Egloff, R. E. Schaad and C. D. Lowry, *J. Phys. Chem.*, 34, 1617 (1930). Those made since 1930 will be mentioned later.

[2] M. Kubokawa, *Rev. Phys. Chem. Japan*, 6, 81 (1931).

[3] R. Schenck, *Z. anorg. Chem.*, 164, 145 (1927).

detected and hydrocarbons other than methane have been found in the products[4]. The production of these substances when platinum is used as catalyst has been also reported[5]. In the following experiment various conditions under which this formation took place were studied.

Methane was led to the heated platinum through a capillary, and in order to remove all the intermediate products out of the system, without decomposing them as much as possible, a mercury diffusion pump and an automatic Töpler pump[6] were used. The capillary used to regulate the flow of methane was of such dimensions as to make the pressure in the system 0.1—0.2 mm. The products which were assumed to consist of CH_4, H_2, C_2H_6, and C_2H_4 were collected in a gas burette, and analysed by the following procedure. (1) C_2H_4 was absorbed with bromine water. (2) H_2 was removed by mixing with excessive oxygen, and the mixture slowly passed through a tube containing Pd black heated to 80°C. (3) C_2H_6 and CH_4 were completely burned. The ratio of these two was determined by the amount of CO_2 formed which was absorbed in a KOH solution. Water formed was condensed with solid CO_2. The analytical results were accurate within 0.2%.

The composition of the reaction products was considerably varied by the treatments of the wire. When oxidations and reductions were repeated, that is the activity was increased, it was found from the anlysis that the products consisted mainly of carbon and hydrogen. With the wire poisoned by a run the percentages of C_2H_4 and C_2H_6 were increased. The comparison between the results obtained at 1200°C. is as follows:

(i) By activated wire (amount analyzed, 1.06 c.c.)

CH_4: 69.1%, C_2H_4: 0.0%, C_2H_6: 0.7%, H_2: 30.2%.

(ii) By poisoned wire (amount analyzed, 3.91 c.c.)

CH_4: 77.5%, C_2H_4: 0.9%, C_2H_6: 4.9%, H_2: 16.7%.

The latter (ii) is the composition of the gas collected, passing methane for 5 hours after one hour run with activated wire (i).

The wire used in the following experiments was activated by repeated oxidations and reductions, and thus methane could be considered to have decomposed chiefly into hydrogen and carbon.

Experimental Method and Apparatus.

The experiments were carried out in the temperature range from 900°—1300°C., using a platinum wire and heating it electrically. The pressure of methane was 1—20 mm. Hg The reaction, $CH_4 \rightleftarrows C + 2H_2$, proceeds to the right with increasing temperature and CH_4 decreases to 0.8% at the equilibrium pressure of one atomsphere at 1100°C.[7] As the percentage of CH_4 decreases more at lower pressures, the reaction may be regarded as proceeding

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[4] F. O. Rice and M. D. Dooly, *J. Am. Chem. Soc.*, **56**, 2747 (1934); L. S. Kassel, *ibid.*, **54**, 3949 (1932); **57**, 833 (1935); H. H. Storch, *ibid.*, **54**, 4188 (1932).

[5] L. Belchetz, *Trans. Farad. Soc.*, **30**, 170 (1934); L. Belchetz and E. K. Rideal, *J. Am. Chem. Soc.*, **57**, 1168 (1935).

[6] E. R. Wheaver and M. Shephard, *J. Am. Chem. Soc.* **50**, 1829 (1928).

[7] R. C. Cantelo, *J. Phys. Chem.*. **30**, 1641 (1926).

only in one direction in the present experiments. The reaction velocity was measured in terms of pressure changes. The pressure became twice as much as that of the initial at the end of the reaction, and so it was clear that the sorption of hydrogen or the effects of the vapour of grease was negligible. (Table 2, Expt. 30)

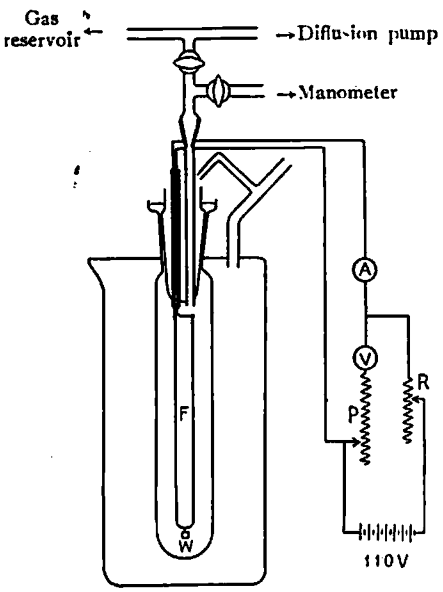

Fig. 1.

The main part of the apparatus used is shown in Fig. 1. The reaction vessel was of about 250 c.c. capacity. The pressure changes were read by means of a capillary manometer containing pure sulphuric acid obtained from Merck. Comparing it with a pyrex spring manometer, it was found that there was no effect of the vapour of the manometer liquid; the sensitivity being more than 1/50 mm.

Platinum wire, F, was 0.3 mm. in diameter, 20–70 cm. long. A relatively thick and long wire as this was used in order to enlarge the reacting surface and lessen the loss due to repeated uses. W is a glass weight.

For the measurement of the temperature an optical micro-pyrometer made by Siemens which was calibrated with a standard lamp was used. It was found that when the wire was bent and hung at regular intervals and set in the center of the vessel, about 90% of the length of the wire (except at the junctions) was at the same temperature within 10 degrees.

The temperature of the platinum wire was decreased by the formation of hydrogen in the reaction. But the temperature of the wire was maintained constant during the experiment by regulating the main resistance (R) of 50 ohm so that the voltmeter reading might coincide with that of the ammeter (A), inserting a variable resistance (P) of 10,000 ohm in series with the voltmeter (V) to reduce the reading.[8] The relation between the resistance of P and the temperature in the wire was calibrated beforehand. In this way, the regulation of the temperature was simplified.

Catalytic Activity of Platinum Wire.

Decrease in the Activity by Successive Experiments.

Ordinary platinum wire is exceedingly inactive; but repeated oxidations and reductions make it so active, causing the reaction to proceed at a measurable rate. Even an activated wire loses greater part of its activity by repeated uses. The results of the successive experiments carried out at 1200°C. are given in

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[8] cf. G.-M. Schwab u. H. Schmidt, *Z. physik. Chem.* [B], 3, 340 (1929).

Table 1. (Methane was made to react for thirty minutes each time.)

Table 1.
Decrease in the Activity by Successive Experiments.

Expt. No.	Initial pressure of methane in cm.	Final pressure in cm.	% decomp.
1	3.62	4.30	18.8
2	3.60	3.92	8.9
3	3.69	3.85	4.3
4	3.67	3.78	3.0
5	3.67	3.77	2.7
6	3.69	3.77	2.2
7	3.70	3.79	2.4

It should be noted that the decrease in the activity is great at first. As to the cause of this phenomenon, the change of the surface structure and the poisoning by the irreversible adsorption of the reaction products may both be taken into consideration. That the catalyst never loses its activity though heated for many hours in vacuum indicates that the surface structure does not change during the reaction, then the above result shows that the deactivation of the wire is caused by the poisoning effect of the reaction products.

No. 7 in Table 1 is the result obtained after one hour of high evacuation at 1200°C. after reaction (6). It is seen that the activity is scarcely recovered. It seems obvious, therefore, that the permanent poisoning is due not to hydrogen but to carbon.

Recovery of Activity by Heating in Oxygen.

Heating in oxygen enables the poisoned wire to recover its activity. In this treatment the surface structure changes, but sintering and evaporation[9] should reach equilibria after a certain time at a certain temperature, and then a certain structure should appear. Thus the following experiments were carried out to see how much time is required for heating in O_2 to obtain a constant activity at 1200°C. Methane at an initial pressure of 1.3 cm. was made to react for thirty minutes at the same temperature. And the pressure of oxygen in which the wire was treated beforehand was 10 cm.; the wire being heated for ten minutes in vacuum before each experiment with methane. The results obtaind are given in Fig. 2.

The results indicate that the activity can be recovered repeatedly; and only

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[9] The oxygen treatment causes this film of platinum oxide on the walls of the reaction vessel. Before the reaction, it was removed from the walls.

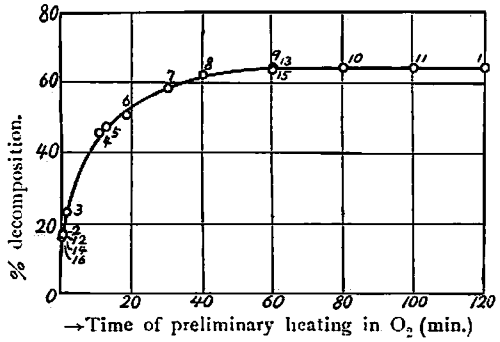

Fig. 2 :—The numeral shows the experimental order. No. 1 was carried out after preliminary heating for 120 minutes. No. 2 was done successively after No. 1 without any treatment. No. 3–11 show that the activities are being recovered by increasing the time for preliminary heating. No. 12–16 show that the activity can be recovered repeatedly.

one hour treatment with oxygen is necessary for the recovery of the activity under the above mentioned conditions. It is apparent that the larger the initial pressure of methane or the more time taken by the reaction is, the longer preliminary treatment is needed. The necessity of a long treatment in oxygen for the removal of the adsorbed carbon shows a strong combination between platinum and carbon, although the existence of platinum carbide has been denied[10]; and it is likely that some of the carbon adsorbed must have diffused from the surface into the interior of the metal.[11].

The change in surface structure during the above treatment is shown in Plates 1 and 2.

Plate 1 :—Showing the actual surface of the wire used in the experiments. Large grain boundaries as well as a fine structure of the surface are observable. (Magnified 1000 times)

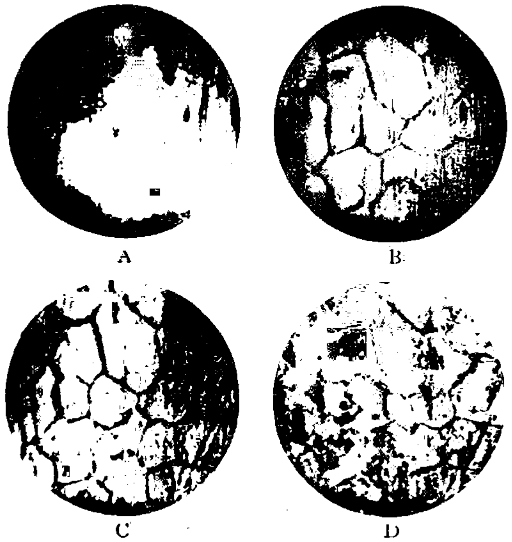

Plate 2 :—Showing the initial changes caused by oxidation and by reaction using a platinum ribbon. A—polished surface before use. B—after 2 hour heating in oxygen of 10 cm. pressure at 1200°C. Grain boundaries appeared. C—after 10 minute heating in methane of 5 cm. pressure at the same temperature. Boundaries darkened by carbon. D—afrer the same treatment as B. Showing the removal of the carbon as well as the destruction of the metal surface. (Magnified 300 times)

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[10] L. J. Collier, T. H. Harrison and W. G. A. Taylor, *Trans. Farad. Soc.*, **30**, 581 (1934).

[11] W. Hempel u. P. Rücktäschel, *Z. angew. Chem.*, **17**, 322 (1904).

The experiments were carried out in the region of negligible changes of electric resistance in the wire[12].

Measurement of the Reaction Velocity.

All the measurements were made under the same conditions of the wire. The carbon adhering on the wire was removed by heating in oxygen. Walls were cleaned mechanically, and hydrogen was admitted under the pressure of 1 cm.; and the wire was heated for five minutes at 1200°C. It was considered that by this treatment the wire adsorbed a certain quantity of hydrogen.

After methane was introduced, the wire was heated. It took about five seconds to reach a constant temperature, which was taken as $t=0$. The pressure p_0' at $t=0$ is difficult to determine by extrapolation. If p_0 denotes the initial pressure at room temperatures, p' the pressure during heating, p at room temperatures after shutting off the current, we have, according to Boyle's law,

$$p_0'=p_0\cdot\frac{p'}{p}.$$

This relation makes possible the pressure reading without cooling the wire.[8]

It is necessary for this method that the mean temperature of the reaction vessel is unchanged during the reaction. In the present pressure range, the change could be assumed to be so small as to be negligible from the following facts. (1) The extrapolated initial pressure always coincided with the calculated one. (2) The result of the analysis of the reaction velocity which was observed by the pressure reading at room temperatures after intermittent heating was the same as that observed during heating. (See Table 4.)

Let the pressure at any time be p', x the number of carbon atoms formed by the reaction is represented then,

$$x=\text{const.}\,(p'-p_0').$$

Accordingly, the number of hydrogen molecules is $2x$. If a represents the number of methane molecules before the reaction ($a=\text{const.}\ p_0'$), the velocity constant of the monomolecular reaction is expressed as follows;

$$k_m\equiv\frac{1}{t}\ln\frac{a}{a-x}=\frac{1}{t}\ln\frac{p_0'}{2p_0'-p'},$$

which will be rewritten in common logarithm as k_m', then

$$k_m'=0{,}4343\,k_m.$$

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[12] The change of the resistance at room temperatures was within 0.5%. If R_0 is assumed to be the resistance at room temperatures in $R_t=R_0(1+0.0025t)$, the change will be equivalent to the decrease of 8°C. at 1200°C.

Reactions at 1200°C.

The results obtained at 1200°C. are given in Tables 2, 3, and 4; the meaning of k and k' in the tables will be explained later. Figs. 3 and 4 show the relation between x and t, and Figs. 5 and 6 the relation between k_m' and x/t.

Table 2.

Expt. 30. (1200°C.). Wire 1.

p_0=1.02mm. p_0'=1.41mm.

t	p'(mm.)	x(mm.)	k_m'	x/t	k'	k (n=1.23)
1	1.95	0.54	0.2098	0.5400	0.140	—
2	2.02	0.91	0.1232	0.3050	0.095	0.027
4	2.08	0.67	0.0700	0.1675	0.060	0.027
5	2.13	0.72	0.0621	0.1449	0.057	0.026
7	2.17	0.76	0.0480	0.1086	0.047	0.024
10	2.24	0.83	0.0386	0.0830	0.042	0.025
15	2.21	0.90	0.0294	0.0600	0.035	0.023
20	2.36	0.95	0.0243	0.0475	0.031	0.022
25	2.41	1.00	0.0215	0.0400	0.030	0.022
30	2.46	1.05	0.0198	0.0350	0.029	0.023
40	2.53	1.12	0.0172	0.0280	0.028	0.023
50	2.58	1.17	0.0154	0.0234	0.027	0.023
60	2.62	1.21	0.0141	0.0202	0.026	0.023
60	2.66	1.25	0.0135	0.0179	0.026	0.023
80	2.69	1.28	0.0129	0.0160	0 026	0.023
90	2.72	1.31	0.0128	0.0146	0.027	0.026
100	2.74	1.33	0.0125	0.0133	0 027	0.026
110	2.76	1.35	0.0125	0.0123	0.028	0.028
120	2.77	1.36	0.0121	0.0113	0.028	0.028
140	2.78	1.37	0.0111	0.0098	0.026	0.026
160	2.79	1.38	0.0105	0.0085	0.025	0.025
180	2.79	1.38	0.0093	0.0077	0.022	0.022
200	2.80	1.39	0.0092	0.0070	0.026	0.023
						mean 0.0245

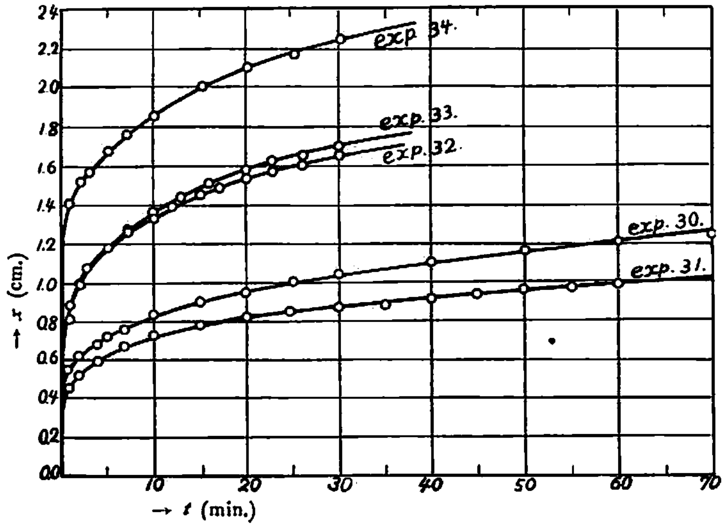

Fig. 3.

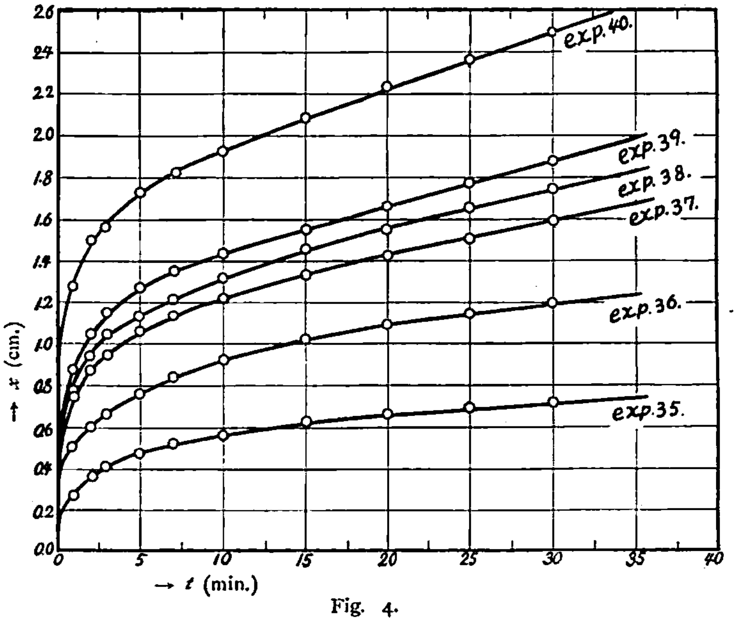

Fig. 4.

Table 3.

Expt. 35. (1200°C.). Wire 2.

p_0=0.60mm. p_0'(a)=0.79mm.

t (min.)	p'(mm.)	x (mm.)	k_m'	x/t	k'	k (n=1.16)
1	1.09	0.30	0.2074	0.300	0.077	—
2	1.16	0.37	0.1361	0.185	0.061	0.034
3	1.21	0.42	0.1098	0.140	0.060	0.036
5	1.27	0.48	0.0812	0.096	0.052	0.035
7	1.31	0.52	0.0666	0.074	0.047	0.034
10	1.35	0.56	0.0536	0.056	0.041	0.031
15	1.41	0.62	0.0445	0.041	0.040	0.032
20	1.45	0.66	0.0392	0.033	0.038	0.033
25	1.49	0.70	0.0377	0.028	0.040	0.035
30	1.51	0.72	0.0348	0.024	0.039	0.034
						0.0338

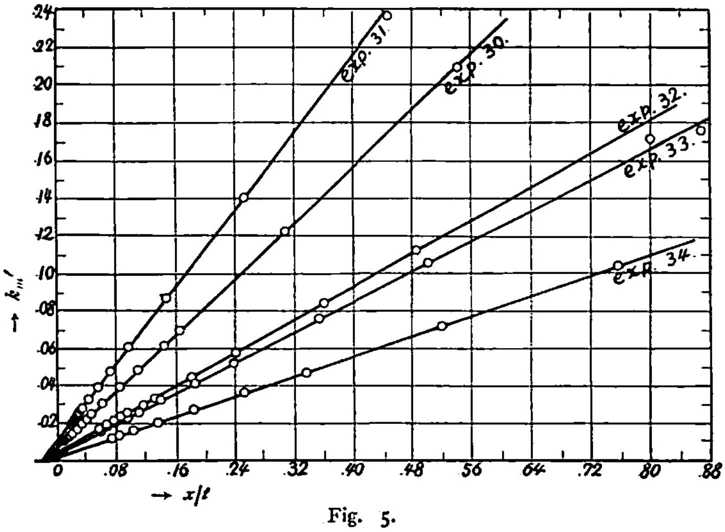

Fig. 5.

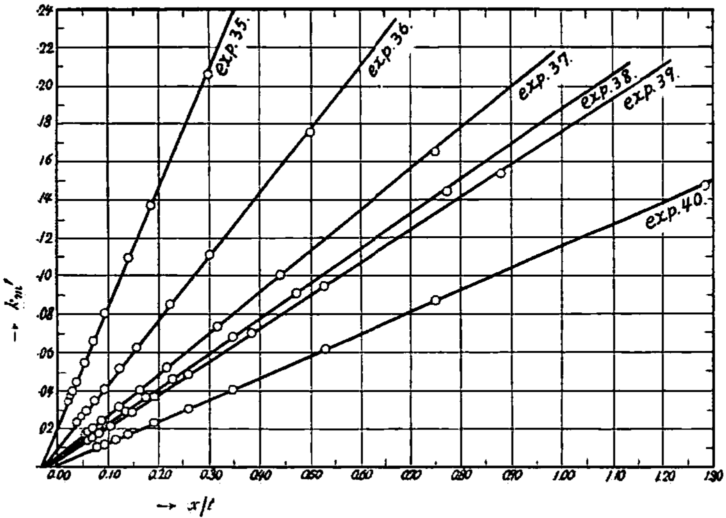

Fig. 6.

Table 4.[13]

Expt. 41. (1200°C.). Wire 2.

f_0=1.25mm.

t (min.)	p (mm.)	x (mm.)	k_m'	x/t	k'	k (n=1.15)
1	1.64	0.39	0.1623	0.390	0.097	0.019
3	1.74	0.49	0.0720	0.163	0.044	0.020
5	1.81	0.56	0.0516	0.112	0.037	0.021
7	1.87	0.62	0.0425	0.089	0.034	0.021
10	1.93	0.68	0.0341	0.068	0.030	0.021
15	2.00	0.75	0.0265	0.050	0.026	0.020
20	2.05	0.80	0.0222	0.040	0.024	0.019
25	2.10	0.85	0.0198	0.034	0.023	0.019
30	2.15	0.90	0.0184	0.033	0.023	0.021
						0.0201

As seen from the tables, k_m' is not constant but decreases as the reaction proceeds. This differs from the results on the oxide catalyst made by Schwab and Pietsch[14]. The relation between k_m' and x/t is always linear (Figs. 5 and 6). Before the kinetics of this is discussed, the results obtained under various conditions will be mentioned below.

By the Poisoned Wire. In all the experiments mentioned above the wire

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13) This experiment was carried out by a method of intermittent heating. The above mentioned method of calculating the initial pressure p_0' is not applicable if the mean temperature of the reacting system varies with pressure changes. As another method of measuring, the change of pressure p at room temperatures was read every time 20 minutes after shutting off the current in this case.

14) They have found that the reaction is of the first order on the surface of platinum coated with CaO and BaF_2 (10 : 1); G.-M. Schwab u. E. Pietsch, *Z. physik. Chem.*, **121**, 189 (1926); *Z. Elektrochem.*, **32**, 430 (1926).

was heated preliminarily in oxygen and then in hydrogen; carbon which might have adhered in the preceding experiment was removed. If this treatment was incompletely done or not at all, the reaction velocity became very small. One of the results obtained in the presence of a small quantity of adsorbed carbon is given in Table 5.

Table 5.

Expt. 42. (1200°C.). Wire 1.

p_0 = 1.74mm. p_0' = 2.50mm.

t (min.)	p'(mm.)	x (mm.)	k_m'	x/t	k (n = 1.10)
1	2.84	0.34	0.0633	0.346	—
2	3.00	0.50	0.0485	0.250	0.0047
4	3.06	0.56	0.0276	0.140	0.0050
10	3.17	0.67	0.0136	0.0670	0.0051
12	3.20	0.70	0.0119	0.0583	0.0048
15	3.24	0.74	0.0102	0.0493	0.0049
20	3.30	0.80	0.00838	0.0400	0.0047
25	3.36	0.86	0.00732	0.0344	0.0047
30	3.40	0.90	0.00647	0.0300	0.0047
40	3.50	1.00	0.00555	0.0250	0.0049
					0.00483

Effect of Added Hydrogen. The retardation caused by the irreversible adsorption of hydrogen was very slight as already mentioned. In order to see the effect of hydrogen during the reaction, the reaction velocity was measured with methane with which hydrogen was initially mixed.

The partial pressure of methane was almost the same each time. The gas was made to react for 10 minutes at 1200°C. in each experiment, and the results thus obtained are shown in Table 6. No effect of added hydrogen is seen. The analysis of the reaction velocity led to the same conclusion.

At Different Temperatures. The above experiments were all carried out at 1200°C. In the neighbourhood of 1300°C. the adsoprtion of carbon by platinum became stronger, and this made the recovery of activity very difficult. Below 1000°C. the reaction velocity became too small

Table 6.

Effects of Added Hydrogen.

Expt. No.	CH_4(mm.)	H_2(mm.)	% decomp.
43	1.09	0.00	83.5
44	1.09	0.00	83.5
45	1.13	0.01	81.4
46	1.08	0.00	83.3
47	1.15	0.71	81.7
48	1.12	1.05	83.9
49	1.10	1.08	83.0
50	1.10	2.28	82.7
51	1.10	3.02	81.5

to be measured. Such limitations in the experimental conditions rendered the measurement over a wide temperature range difficult. The results obtained at 1100°C. and 1000°C. are as follows:

Table 7.

Expt. 52. (1100°C.). Wire 2.

$p_0 = 1.59$mm. $p_0' = 2.31$mm.

t (min.)	p'(mm.)	x (mm.)	k_m'	x/t	k'	k ($n=1.13$)
1	2.88	0.57	0.1232	0.570	0.085	0.0126
2	2.95	0.64	0.0704	0.320	0.054	0.0146
3	3.02	0.71	0.0532	0.237	0.046	0.0171
5	3.09	0.78	0.0358	0.156	0.034	0.0159
7	3.14	0.83	0.0276	0.118	0.029	0.0151
10	3.21	0.90	0.0214	0.090	0.024	0.0135
						0.0148

Table 8.

Expt. 53. (1000°C.). Wire 2.

$p_0 = 1.93$mm. $p_0' = 2.31$mm.

t (mm.)	p'(mm.)	x (mm.)	k_m'	x/t	k'	k ($n=1.06$)
1	2.62	0.31	0.0626	0.310	0.023	0.0047
2	2.69	0.38	0.0391	0.190	0.018	0.0069
3	2.75	0.44	0.0306	0.147	0.016	0.0074
5	2.83	0.52	0.0222	0.104	0.014	0.0083
7	2.87	0.56	0.0172	0.080	0.012	0.0070
10	2.92	0.61	0.0133	0.061	0.010	0.0064
15	3.01	0.71	0.0105	0.047	0.009	0.0063
20	3.06	0.75	0.0085	0.038	0.007	0.0052
25	3.11	0.80	0.0074	0.032	0.007	0.0057
30	3.16	0.85	0.0066	0.028	0.007	0.0057
						0.00636

The relation between the logarithm of the reaction velocity k at each temperature and the reciprocal of the absolute temperature was linear, from which 31 kcal was obtained as the apparent heat of activation.

Discussion of Results.

In the reaction A→B+C, if the velocity of adsorption or desorption of the reacting components on the surface of a catalyst is larger than that of the reaction, the reaction velocity is expressed, according to Langmuir's adsorption isotherm,

thus,
$$\frac{dx}{dt}=\frac{k(a-x)}{1+b_a(a-x)+b_b x+b_c x}, \qquad (1)$$

where a and x are the initial and the decomposed number of molecules of the reactant respectively; b is the adsorption coefficient of each substance.

When the adsorption coefficient of the reaction products b_b or b_c is large as compared with b_a, we have

$$\frac{dx}{dt}=k'\frac{(a-x)}{x}. \qquad (2)$$

Integrating and putting $\frac{1}{t}\log\frac{a}{a-x}\equiv k_m'$,

we get

$$k_m'=\frac{0.4343}{a}\cdot\frac{x}{t}+\frac{0.4343k'}{a}. \qquad (3)$$

Now, it was observed from the above experiments that carbon was strongly adsorbed on platinum, and it is well known in other reactions, such as the decomposition of ammonia, that hydrogen was adsorbed strongly on platinum, too. Then we shall first apply the equation (3) to our reaction. The linear relation between k_m' and x/t in (3) is well satisfied as shown in Figs. 5 and 6.

On the other hand, k' which was calculated from equation (3) never became constant, decreasing as the reaction progressed, as shown in the sixth column in Tables 2, 3, 4, 7, and 8, and the fifth on Table 5. Therefore, the author proposes a new equation:

$$\frac{dx}{dt}=k\frac{(a-x)}{x^n}, \qquad (4)$$

where n is a constant ($n>1$).

First, let us compare this equation with that of (1).

In the equation (4)

(a) $n=0$: it becomes of the first order, and this shows that the adsorption of products is too feeble to cause any retardation.

(b) $0<n<1$: in this case the products cause some retardation: and the equation is an approximate equation of $\frac{dx}{dt}=k\frac{(a-x)}{1+bx}$.

(c) $n=1$: in this case the adsorption of the products is very strong, and the equation is the same with (2).

(d) $n>1$; in this case the retardation caused by the products is so strong that it can not be explained by the simple theory[15].

Thus, n represents the degree of retardation, and so it may be called the "retardation exponent".

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15) C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," p. 328, Oxford (1933).

Integrating equation (4), putting the condition that $x=0$ when $t=0$, we have

$$kt=a^n \ln \frac{a}{a-x}-na^{n-1}x+\frac{n(n-1)}{2}\,\frac{a^{n-2}}{2}\left[a^2-(a-x)^2\right]-\cdots\cdots$$
$$\cdots\cdots+(-1)^k\frac{n(n-1)(n-2)\cdots\cdots(n-k+1)}{k!}\,\frac{a^{n-k}}{k}\left[a^k-(a-x)^k\right]+\cdots\cdots$$

In this series, when n is an integer, the number of terms becomes finite; in other cases, infinite. In the present case as $\frac{a-x}{a}<1$, it is convergent; and n being a little larger than 1, the first two terms of the right side may be taken as the approximate value:

$$\frac{1}{t}\ln\frac{a}{a-x}\fallingdotseq\frac{n}{a}\cdot\frac{x}{t}+\frac{k}{a^n}.$$

The left side is the velocity constant of the first order. Let k_m' represent it in common logarithm, and we have

$$k_m'=\frac{0.4343n}{a}\cdot\frac{x}{t}+\frac{0.4343k}{a^n}, \tag{5}$$

which satisfies well all the points observed above, i. e.

(i) It represents a linear relation between k_m' and x/t.

(ii) The inclination of this straight line is larger than $0.4343/a$.

(iii) The intersection on the x/t axis is k/na^{n-1}, so that the larger the initial pressure a, the nearer it approaches to the original point. It follows, therefore, that each line which differs in initial pressure does not intersect at one point on the x/t axis. (See Figs. 5 and 6.)

If we wish to get k from equation (5), we should find n from the inclination of the straight lines in Figs. 5 and 6, and substitute it in equation (5). As seen from the last column of Tables 2, 3, 4, 5, 7, and 8, the value of k is fairly constant.

The comparison of n with k in the experiments carried out at 1200°C. is shown in the following table.

Table 9.

Wire 1. (1200°C.)				Wire 2. (1200°C.)			
Expt. No.	$a(p_0')$(mm.)	n	k	Expt. No.	$a(p_0')$(mm.)	n	k
31	1.07	1.24	0.0274	35	0.79	1.16	0.0338
30	1.41	1.23	0.0245	36	1.50	1.17	0.0366
32	2.45	1.24	0.0310	37	2.34	1.17	0.0311
33	2.60	1.23	0.0289	38	2.76	1.17	0.0320
34	4.00	1.23	0.0262	39	2.98	1.18	0.0324
				40	4.51	1.18	0.0320

n and k are constants, independent of the initial pressure of methane for the same wire. Both wire 1 and 2 have the same apparent surface areas (6.5 $\overline{\text{cm.}^2}$), so that the velocity constant k scarcely differes, but n does a little.

As to the poisoned wire, both values of n and k are smaller than those in the case of activated wire as shown in Tables 5 and 9. The change of n with that of temperature is apparent from the above table and Tables 7 and 8; when the temperature is low, n is small.

Such a change of the "retardation exponent" will be more fully discussed in connection with the discussion of equation (4) in the next number of this journal.

Summary.

The decomposition of methane has been studied in the presence of platinum wire heated electrically. The results obtained are as follows:

(1) The reaction is entirely heterogeneous, and the activity of the surface decreases rapidly in successive experiments on account of the carbon produced by the reaction.

(2) Under certain conditions the activity is recovered after the removal of the carbon by heating the wire in the atmosphere of oxygen.

(3) The analysis of the reaction velocity leads to the conclusion that the retarding effect of the reaction products makes the applicability of the simple adsorption theorem doubtful. A new equation has been proposed for the reaction velocity:

$$\frac{dx}{dt}=k\frac{(a-x)}{x^n},$$

where a is the initial amount of methane; x is the decomposed amount at time t; and n is a constant larger than one which seems to depend upon the inhomogeneity of the surface. This equation has been satisfied in several experiments in a pressure range from 0.79 to 4.51 mm. and in a temperature range from 1000° to 1200°C.

(4) Effects of the added hydrogen have not been observed.

(5) The value of 31 kcal has been obtained for the apparent heat of activation.

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