

## 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.<sup>1)</sup>

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<sup>2)</sup>. 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.<sup>3)</sup> (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<sup>4</sup>. The production of these substances when platinum is used as catalyst has been also reported<sup>5</sup>. 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<sup>6</sup> 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<sub>4</sub>, H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> were collected in a gas burette, and analysed by the following procedure. (1) C<sub>2</sub>H<sub>4</sub> was absorbed with bromine water. (2) H<sub>2</sub> was removed by mixing with excessive oxygen, and the mixture slowly passed through a tube containing Pd black heated to 80°C. (3) C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub> were completely burned. The ratio of these two was determined by the amount of CO<sub>2</sub> formed which was absorbed in a KOH solution. Water formed was condensed with solid CO<sub>2</sub>. 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 analysis that the products consisted mainly of carbon and hydrogen. With the wire poisoned by a run the percentages of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> 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<sub>4</sub>: 69.1%, C<sub>2</sub>H<sub>4</sub>: 0.0%, C<sub>2</sub>H<sub>6</sub>: 0.7%, H<sub>2</sub>: 30.2%.

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

CH<sub>4</sub>: 77.5%, C<sub>2</sub>H<sub>4</sub>: 0.9%, C<sub>2</sub>H<sub>6</sub>: 4.9%, H<sub>2</sub>: 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,  $\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$ , proceeds to the right with increasing temperature and CH<sub>4</sub> decreases to 0.8% at the equilibrium pressure of one atmosphere at 1100°C.<sup>7</sup> As the percentage of CH<sub>4</sub> decreases more at lower pressures, the reaction may be regarded as proceeding

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. Weaver 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)

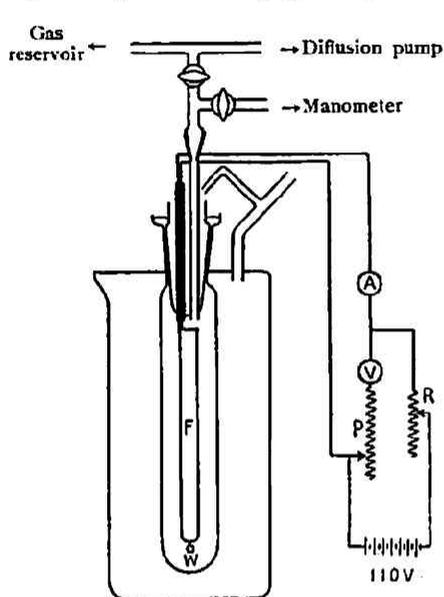


Fig. 1.

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.<sup>8)</sup> 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

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

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

Table I.  
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 I 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<sup>9)</sup> 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<sub>2</sub> 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 obtained are given in Fig. 2.

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

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.

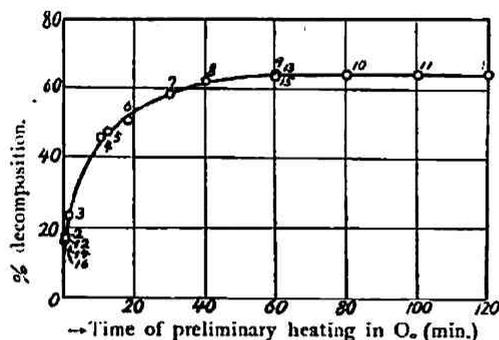


Fig. 2:—The numeral shows the experimental order. No. 1 was carried out after preliminary heating for 120 minutes. No. 2 was done successively after No. 1 without any treatment. No. 3-11 show that the activities are being recovered by increasing the time for preliminary heating. No. 12-16 show that the 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<sup>10</sup>; and it is likely that some of the carbon adsorbed

must have diffused from the surface into the interior of the metal.<sup>11</sup>

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)

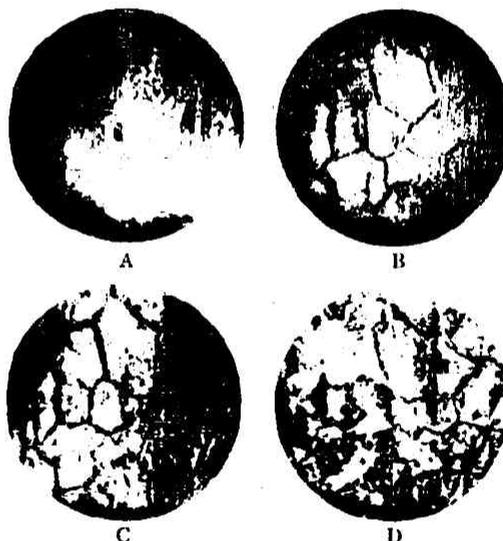


Plate 2:—Showing the initial changes caused by oxidation and by reaction using a platinum ribbon. A—polished surface before use. B—after 2 hour heating in oxygen of 10 cm. pressure at 1200°C. Grain boundaries appeared. C—after 10 minute heating in methane of 5 cm. pressure at the same temperature. Boundaries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

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<sup>12)</sup>.

### 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.<sup>8)</sup>

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

$$k_m' = 0.4343 k_m.$$

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.

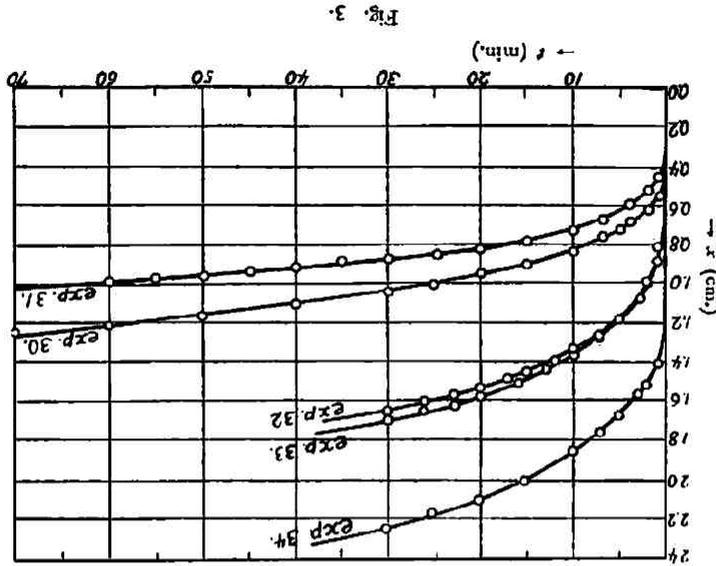


Fig. 3.

$t$	$\beta$ (mm.)	$x$ (mm.)	$k_m'$	$x/\beta$	$k$	mean $0.0245$
1	1.95	0.54	0.2098	0.5400	0.140	—
2	2.02	0.91	0.1332	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
66	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	0.028
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

$\beta_0 = 1.02 \text{ mm.}$   
 $\beta'_0 = 1.41 \text{ mm.}$   
 Expt. 30. (1200°C.). Wire 1.

Table 2.

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  $x/\beta$ .

Reactions at 1200°C.

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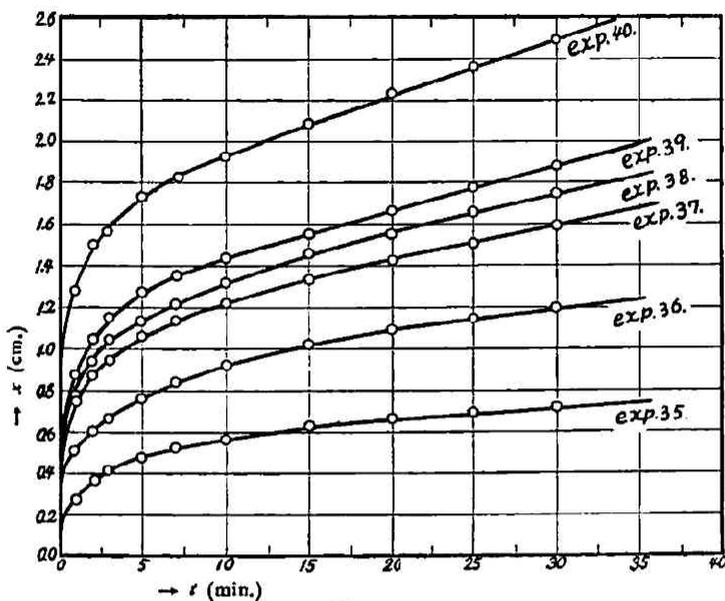


Fig. 4  
Table 3.

Expt. 35. (1200°C.), Wire 2.  
 $\rho_0 = 0.60\text{mm.}$   $\rho_0'(a) = 0.79\text{mm.}$

$t$ (min.)	$\rho'$ (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

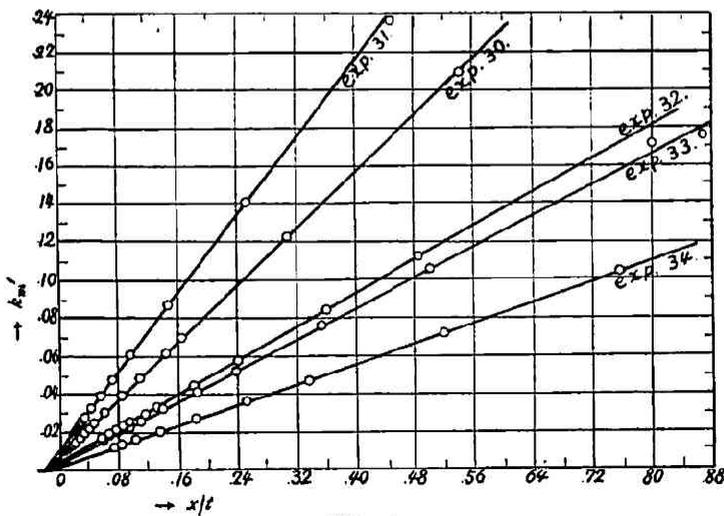


Fig. 5.

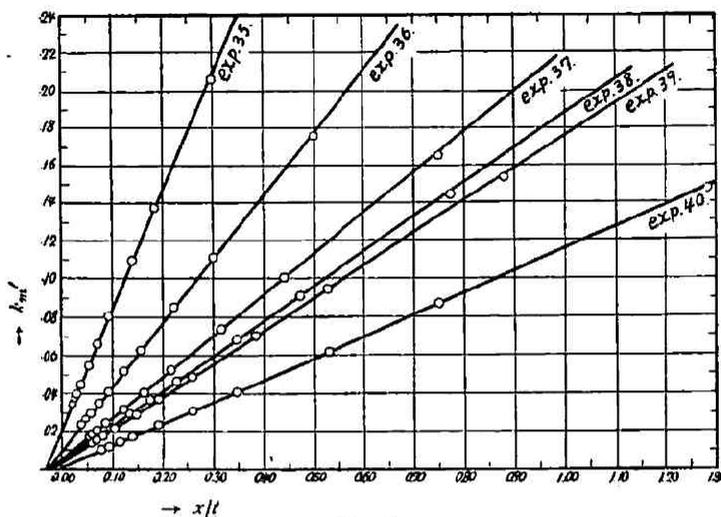


Fig. 6.

Table 4.<sup>13)</sup>

Expt. 41. (1200°C.). Wire 2.

 $r_0 = 1.25\text{mm.}$ 

$t$ (min.)	$\rho$ (mm.)	$x$ (mm.)	$k_m'$	$x/t$	$\mathcal{K}$	$k$ ( $n=1.15$ )
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<sup>14)</sup>. 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

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<sub>2</sub> (10:1); G.-M. Schwab u. E. Pietsch, *Z. physik. Chem.*, 121, 189 (1926); *Z. Elektrochem.*, 32, 430 (1926).

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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.  
 $p_0 = 1.74 \text{ mm.}$        $p_0' = 2.50 \text{ mm.}$

$t$ (min.)	$r'$ (mm.)	$x$ (mm.)	$k_m'$	$x/r'$	$k$ ( $n=1.10$ )
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 adsorption 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.	$\text{CH}_4$ (mm.)	$\text{H}_2$ (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.

 $\rho_0 = 1.59 \text{ mm.}$        $\rho'_0 = 2.31 \text{ mm.}$ 

$t$ (min.)	$\rho'$ (mm.)	$x$ (mm.)	$k_n'$	$x/t$	$k'$	$k$ ( $n = 1.13$ )
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.

 $\rho_0 = 1.93 \text{ mm.}$        $\rho'_0 = 2.31 \text{ mm.}$ 

$t$ (mm.)	$\rho'$ (mm.)	$x$ (mm.)	$k_n'$	$x/t$	$k'$	$k$ ( $n = 1.06$ )
1	2.62	0.31	0.0526	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  $A \rightarrow B + C$ , 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, 
$$\frac{dx}{dt} = \frac{k(a-x)}{1 + b_a(a-x) + b_b x + b_c x}, \quad (1)$$

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

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

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

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

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:

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

where  $n$  is a constant ( $n \geq 1$ ).

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<sup>15)</sup>.

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

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

$$kt = a^n \ln \frac{a}{a-x} - na^{n-1}x + \frac{n(n-1)}{2} \frac{a^{n-2}}{2} [a^2 - (a-x)^2] - \dots$$

$$\dots + (-1)^k \frac{n(n-1)(n-2)\dots(n-k+1)}{k!} \frac{a^{n-k}}{k} [a^k - (a-x)^k] + \dots$$

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:

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

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

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

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  $1200^\circ\text{C}$ . 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 ( $6.5 \text{ cm.}^2$ ),

so that the velocity constant  $k$  scarcely differs, 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 following report.

### 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.

The author wishes to express his hearty appreciation to Prof. S. Horiba for his continued guidance throughout this research.

This is the paper presented to Committee of Catalysis of Japan Society for the Promotion of Scientific Research.

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## THE DECOMPOSITION OF METHANE ON THE SURFACE OF PLATINUM. [II]\*

By MASAO KUBOKAWA.

In his preceding report<sup>1)</sup> the author proposed the following equation :

$$dx/dt = k(a-x)/x^n$$

to express the decomposition velocity of methane in the presence of a heated platinum wire.

In this equation,  $a$  denotes the initial amount of methane;  $x$ , the decomposed amount at time  $t$ , which should be proportional to the amount of products;  $n$ , a constant larger than 1, which the author calls the 'retardation exponent.'

It seems difficult to explain the fact that the 'retardation exponent' is larger than 1 in the equation only by a simple theory based upon Langmuir's isotherm. It was pointed out, however, that such a fact was seen not only in the decomposition of methane but in some other reactions observed by several investigators, and so it is probable that the fact has its foundation on something general in heterogeneous reactions.

### Other Reactions to which the New Equation is Applicable.

#### Decomposition of Carbon Monoxide.

[I] In the decomposition of carbon monoxide in the presence of reduced nickel it was found that in the temperature range from 240° to 300°C. and in the pressure range from 15 to 70 cm., the reaction proceeded through several stages, whose initial stage was proved to be of a retardation type presenting strong adsorption including both reversible and irreversible adsorptions of the carbon atoms, the reaction product.<sup>2)3)4)</sup>

The application of the newly proposed equation to the initial stage of this reaction showed that the 'retardation exponent' was larger than 1 in many a case, especially in the highly activated state of the catalyst fresh from reduction.

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\* This is the revised translation of the paper which appeared in *Rev. Phys. Chem. Japan*, 8, 34 (1934).

1) M. Kubokawa, *Rev. Phys. Chem. Japan*, 11, 82 (1937).  
 2) S. Horiba and T. Ri, *Rev. Phys. Chem. Japan*, 4, 73 (1930).  
 3) T. Ri, *ibid.*, 5, 41 (1931).  
 4) T. Ri, *Rec. trav.*, 51, 641 (1931).

Table 1.

Temp. °C.	Initial pressure of CO in mm.	$n$	Reference
259	425.4	1.08	Exp. 1, Catalyst I <sup>2)</sup>
251	408.0	1.01	2, V <sup>3)</sup>
251	263.2	1.05	3, V <sup>3)</sup>
251	298.2	1.01	4, V <sup>3)</sup>
264	325.1	1.85	1, VIII <sup>3)</sup>

Table 1 gives the retardation exponents calculated from the original papers. The reaction in the last example of the table proceeds, unlike others, through a retardation type till the end of the reaction. In this case it is believed that the activity of the catalyst is extremely high, and it should be noted that the retardation exponent is exceedingly large.

[II] The results obtained in the decomposition of carbon monoxide in the presence of nickel supported on silica gel<sup>6)</sup> manifest a tendency similar to the above example [I]: with the catalysts fresh from reduction, which possessed high activity, the exponents were always larger than 1, as  $n=1.03$ , or 1.04.

#### Catalytic Decomposition of Ammonia.

[I] Hinshelwood and Burk<sup>6)</sup> have investigated the decomposition of ammonia in the presence of a heated platinum wire and proposed the following equation:

$$dx/dt = k'(a-x)/x.$$

This equation has been deduced from the influence of hydrogen preliminarily mixed with ammonia. Its applicability will be known if the observed value is substituted in the following equation obtained by integration, where  $k_m'$  is a velocity constant of a unimolecular reaction in common logarithm:

$$k' = 2.303 a k_m' - x/t.$$

Table 2.  
 $a=200$  mm.  $T=1138^\circ\text{K}$

$t$ (sec.)	$x$ (mm.)	$k_m'$	$x/t$	$k'$	$k$ ( $n=1.10$ )
10	28	0.00656	2.800	0.22	—
60	56	0.00238	0.933	0.16	0.12
120	72	0.00162	0.600	0.15	0.14
240	89	0.00107	0.371	0.12	0.14
360	100	0.000836	0.278	0.11	0.14
720	120	0.000553	0.167	0.08	0.13

5) T. Ri and G. Nagamitsu, *Rev. Phys. Chem. Japan*, 9, 140 (1935).

6) C. N. Hinshelwood and R. E. Burk, *J. Chem. Soc.*, 127, 1105 (1925).

The relation between  $k_m'$  and  $x/t$  is linear as the above equation demands (Fig. 1), but, as is shown in Table 2,  $k'$  decreases as the reaction proceeds.

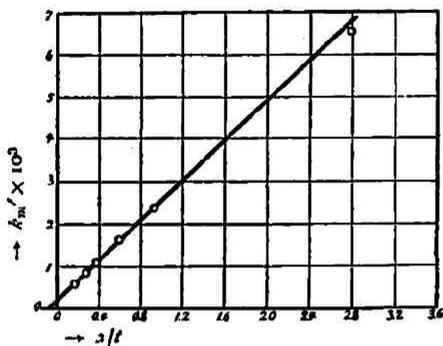


Fig. 1.

This fact has also been pointed out by Schwab and Schmidt.<sup>7)</sup>  $k$  obtained from the author's equation by putting the retardation exponent as 1.10, is quite constant as shown in the last column of Table 2.

[II] Schwab and Schmidt<sup>7)</sup> have decomposed ammonia in the presence of platinum as Hinshelwood did. The results obtained at low pressures such as 0.25–4 mm. could be explained by the above equation used by Hinshelwood, while to those obtained at relatively high pressures such as 10–300mm. a complex equation proposed by them<sup>8)</sup> was applied. Any satisfactory explanation of the equation, however, has not been given<sup>9)</sup>. The velocity constants obtained by substituting their data into the author's equation are tabulated in Table 3.

Table 3.  
 $a=350.8$  mm.  $T=1485^\circ\text{K}$

$t$ (min.)	$p$ (mm.)	$x$ (mm.)	$k_m'$	$x/t$	$k'$	(log $k''$ )	log $k$ ( $n=1.59$ )
2	502.0	151.2	0.1125	75.60	23.4	—	—
8	599.2	248.4	0.0669	31.05	23.0	(3.857)	2.170
15	629.4	278.6	0.0458	18.57	18.4	(3.888)	2.375
32	654.4	303.6	0.0272	9.49	12.5	(3.787)	2.338
66	674.0	373.2	0.0167	5.65	8.6	(3.713)	2.155
215	698.0	347.2	0.0092	1.61	5.9	(3.762)	2.190

$k'$  in Table 3 is a velocity constant putting  $n=1$ , which, as is seen, decreases as the reaction proceeds. Log  $k''$  is the logarithm of the constants obtained by their equation, which presents almost the same degree of constancy as log  $k$  calculated from the new equation putting  $n=1.59$ , which is given in the last column.

The relation between  $k_m'$  and  $x/t$  is shown in Fig. 2.

7) G.-M. Schwab u. H. Schmidt, *Z. physik. Chem.* [B], 3, 337 (1929).

8)  $-\frac{d[\text{NH}_3]}{dt} = k'' \frac{[\text{NH}_3]}{[\text{H}_2]} \cdot \frac{[\text{NH}_3]}{[\text{H}_2]([\text{H}_2] + b[\text{NH}_3])}$

9) G.-M. Schwab has put it that at high pressures chain reactions may take place. G.-M. Schwab, *Katalyse vom Standpunkt der Chemischen Kinetik*, s. 216, Berlin (1931).

10) E. Winter, *Z. physik. Chem.* [B], 13, 401 (1931).

[III] Winter<sup>10)</sup> has proposed, from the experiments on the decomposition of ammonia in the presence of iron, an equation of the same type as the author's, and derived  $n=1.5$  theoretically. He, however, dealt with the reaction velocity in the streaming methods, while we are now dealing with the reaction velocity in the closed system. Therefore, his retardation exponent has a different meaning from that of the author.<sup>11)</sup>

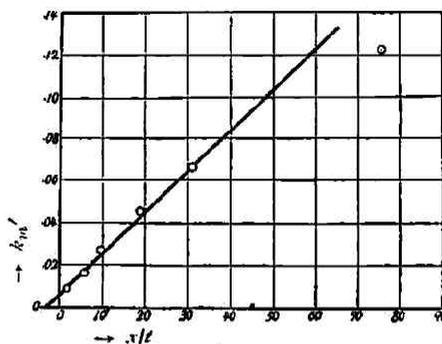


Fig. 2.

### On the Causes of Deviation from the Simple Theory.

It has been confirmed from many experimental facts that every part of the surface of a catalyst is by no means active; and that what we call the active centres distributed on the surface only takes part in a reaction, and also that there are many different kinds of active centres differing in the degree of activity.

Taylor<sup>12)</sup> has considered that the constituent atoms of those active centres are very loosely attached to the bulk of the catalyst so that their valency bounds are not completely satisfied. Schwab and Pietsch<sup>13)</sup> have mentioned that the active centres are equivalent to the phase boundaries existing on the crystal surfaces, that is, the edges and points, including spontaneous fractures and imper-

- 11) The decomposition of methane, if dealt with according to Winter, will be as follows: the methane molecules dissociate into atoms on the surface of platinum and are considered to be in equilibrium,  $\text{CH}_4 \rightleftharpoons \text{C} + 4\text{H}$ ; hence

$$\frac{[\text{C}][\text{H}]^4}{[\text{CH}_4]} = K.$$

Supposing that the adsorption of carbon by platinum is strong, the reaction velocity will be expressed by the desorption velocity of carbon atoms. Accordingly we obtain

$$\frac{dx}{dt} = k[\text{C}] = k' \frac{[\text{CH}_4]}{[\text{H}]^4}.$$

The concentration of the hydrogen atoms on the surface is considered to be proportional to the square root of the pressure of hydrogen molecules in the gas phase, and this gives

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

the initial pressure of methane being represented by  $a$ . Thus the retardation exponent becomes a stoichiometrical constant. And it seems difficult to explain the variation of the exponent under various conditions as seen later.

Moreover, in the case of the decomposition of carbon monoxide the equation becomes of a different type from that obtained experimentally.

- 12) H. S. Taylor, *Proc. Roy. Soc. [A]*, **108**, 105 (1925).  
 13) G.-M. Schwab u. E. Pietsch, *Z. physik. Chem. [B]*, **1**, 385 (1928); *ibid.*, **2**, 262 (1929); *Z. Elektrochem.*, **35**, 573 (1929).

fections of crystals. In any case, variations in degree between the most active and quite inert parts of the surface are to be expected.

In the reaction kinetics, on the other hand, a simple theory based upon Langmuir's isotherm, which was derived from the assumption that a surface consists of the atoms possessing similar adsorption capacity, is satisfactorily applicable to various kinds of reactions.<sup>14)</sup>

Though it seems possible from this that only a sort of active centre on the surface of a catalyst participates in a certain reaction, yet it proves to be contradictory when thoroughly studied<sup>15)</sup>. It should be assumed, therefore, that all the atoms on the surface whose energies are distributed almost continuously within a certain range take part in the reaction<sup>15),16)</sup>.

Suppose that various centres possessing different energies simultaneously participate in a reaction, then the reaction velocity will be treated as with a kind of centre by summing up the reaction velocities, if the reactions in these centres are of the same type. In a case where adsorption of a reaction product is strong, however, the reaction velocity in different centres should be successively dealt with. For the more active the centre is, the stronger affinity for poison it has,<sup>17)</sup> and so when poisoning is extremely intense the active centres are spoiled in order, and this makes different centres gradually take part in a reaction. Accordingly, if the reaction type in each centre differs, each type may appear in sequence as the reaction proceeds. Thus the heterogeneity of the surface of a catalyst will be proved from the kinetical standpoint. In truth this was done in the decomposition of carbon monoxide in the presence of reduced nickel.<sup>2),5),11)</sup>

Though the first stage in the above reaction which is of a retardation type seems to be represented in a kind of active centre, it is realised, as already mentioned, by both the reversible and irreversible adsorption of carbon, the latter of which signifies the formation of nickel carbide.

It has been confirmed that the irreversible adsorption of carbon takes place

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14) I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916); **40**, 1361 (1918); G.-M. Schwab u. Pietsch, *Z. Elektrochem.*, **35**, 575 (1929); G.-M. Schwab, *Ergeb. der Deut. Naturwiss.* VII. 276 (1928); *Katalyse*, Berlin (1931); C. N. Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, Oxford (1933); H. S. Taylor & E. K. Rideal, *Catalysis in Theory and Practice*, London (1926); E. K. Rideal, *Surface Chemistry*, Cambridge (1930).

15) F. H. Constable, *Proc. Roy. Soc. [A]*, **108**, 355 (1925).

16) E. Cremer u. G.-M. Schwab, *Z. physik. Chem. [A]*, **144**, 243 (1929); G.-M. Schwab, *ibid.*, [B], **5**, 406 (1929).

17) F. H. Constable, *Proc. Cambridge Phil. Soc.*, **23**, 832 (1927).

also in the decomposition of methane in the presence of platinum as a catalyst.<sup>11)</sup> It follows, therefore, that in both the reactions more than two kinds of active centres, which adsorb both reversibly and irreversibly, simultaneously take part in the reaction.

The simple theory applied to many a catalytic reaction has been derived from the assumption that the adsorption and desorption velocities of the reacting components are large compared with the reaction velocity, that is, adsorption equilibrium is always established in the course of the reaction.<sup>14)</sup>

In the case where the reaction products make reversible adsorption even in the most active centres, the adsorption equilibrium may still fail, if the adsorption is strong, and so the centres should be distinguished from other centres where adsorption equilibrium is established. Thus the reaction velocity will become that of the zero order on the active parts of the surface, because it is expressed by the desorption velocity of the reaction product.<sup>13)</sup>

It is assumed that such active parts of the surface are small in dimensions compared with the other parts where adsorption equilibrium is established. It follows, therefore, that the reaction velocity at those parts, once the parts react and are covered with products, may be negligible. And it is apparent that when the active parts make irreversible adsorption, they will be rejected from the reaction system after they have participated in the reaction.

#### Approximate Derivation of the New Velocity Equation.

In order to derive a velocity equation from the above consideration, the distribution function of the active centres possessing various adsorption capacities and activation energies should be known. And even if the distribution function is assumed, it is difficult to derive the velocity equation as it will come to be a function of time. Therefore, only two kinds of active centres were taken into consideration. Let us suppose that in the reaction,  $A \rightarrow mB + nC$ , the reaction product B or C (alone or both) adsorbs on a catalyst more strongly than the reactant A. Let  $a$  represent the initial number of mols of A;  $x$ , the number of the mols decomposed at time  $t$ ;  $\sigma$ , a fraction of the surface which participates in the reaction. Further, let us consider that though the catalytic activity of every part in the surface is uniform, there exist two parts quite different from each other in the adsorption capacity of the products.

Let  $\sigma_A$ ,  $\sigma_B$ , and  $\sigma_C$ , represent the fractions covered with A, B, and C; and

18) W. Frankenburg, *Z. Elektrochem.*, **35**, 278 (1929).

let us suppose that on these parts adsorption equilibrium is always established during the reaction. Let  $\sigma_D$  represent the fraction covered with a part of either B or C; let us suppose that on this part adsorption equilibrium is not established, and put the desorption velocity as zero for simplicity. Now equilibrium is established when the adsorption velocity of a gas on to the surface is equal to the desorption velocity; hence

$$\begin{aligned} b_A(a-x)(1-\sigma_A-\sigma_B-\sigma_C-\sigma_D) &= \sigma_A \\ mb_Bx(1-\sigma_A-\sigma_B-\sigma_C-\sigma_D) &= \sigma_B \\ nb_Cx(1-\sigma_A-\sigma_B-\sigma_C-\sigma_D) &= \sigma_C \end{aligned} \quad (1)$$

where  $b_A$ ,  $b_B$ , and  $b_C$ , are the adsorption coefficients of A, B, and C, respectively.

As the desorption velocity at  $\sigma_D$  is zero, the product remains covered and reduces the free surface area. Accordingly, let C represent a constant of proportion, and we have

$$\sigma_D = c \cdot x. \quad (2)$$

Solving (1) and (2) to find  $\sigma_A$ , the surface on which the reactant adsorbs, we obtain

$$\sigma_A = \frac{b_A(a-x)(1-cx)}{1 + b_A(a-x) + (mb_B + nb_C)x}. \quad (3)$$

It is obvious from the term  $(1-cx)$  in the numerator that the reaction velocity becomes zero when the reaction products have covered the whole active surface, and it is at this point that this equation differs from the simple equation. As  $\sigma_D$  is always smaller than 1,

$$1 - cx \approx \frac{1}{1 + cx},$$

according to binomial theorem, and Freundlich's adsorption isotherm is approximately equal to Langmuir's<sup>19)</sup>, so that

$$\frac{1}{1 + cx} \approx \frac{c'}{x^m}, \quad 0 < m < 1.$$

Adding this relation to equation (3), and omitting the terms except the term  $(mb_B + nb_C)$  as  $b_B$  or  $b_C$  is considered to be large in the denominator, we have

$$\sigma_A = \frac{c''(a-x)}{x^{m+1}}. \quad (4)$$

19) Langmuir's isotherm is expressed by  $\frac{x}{m} = \frac{ab\beta}{1+b\beta}$ , and Freundlich's by  $\frac{x}{m} = c\beta^{1/n}$ . So long as  $\beta$  does not change so much, the latter is regarded as approximately equal to the former, and this is actually seen in his experimental results. S. Iishima, *Rev. Phys. Chem. Japan*, 7, 29 (1933).

The reaction velocity is proportional to  $\sigma_A$ , so that

$$\frac{dx}{dt} = \frac{k(a-x)}{x^n}, \quad 1 < n < 2. \quad (5)$$

Here we have the newly proposed equation.

We shall derive it in different way. In the above derivation, the reaction velocity of the most active part of the surface was the same as that of other parts of the surface and it was distinguished only by the establishment of adsorption equilibrium. The most active part gives a greater reaction velocity than other centres. So let us suppose an extremely large reaction velocity, that is, the covering of the part with stable adsorption compounds even at  $t=0$ . For example, in the decomposition of methane let  $x$  represent the number of the methane molecules decomposed at a given time  $t$ , or the number of the carbon atoms formed; let  $c$  represent the number of the methane molecules decomposed at the most active part, and  $x'$ , the number of carbon atoms which retard the reaction adsorbing reversibly on less active parts, will be given by

$$x' = x - c. \quad (6)$$

From this assumption the observed reaction velocity is that for the less active parts, and so in the way similar to the former derivation we obtain

$$\begin{aligned} \frac{dx}{dt} &= \frac{k'(a-x)}{x'} \\ &= k' \frac{(a-x)}{x-c} \end{aligned} \quad (7)$$

under the condition that adsorption equilibrium is established. Integrating this, we have

$$k_m' = \frac{0.4343}{a-c} \cdot \frac{x}{t} + \frac{0.4343 k'}{a-c}, \quad (8)$$

which shows a linear relation between  $k_m'$  and  $x/t$  from whose slope  $c$  is obtained, and this leads to the calculation of the surface area of the most active part in the above mentioned assumption. Calculating  $c$  with Expt. 36 in Report I, we obtained  $c=0.22$  mm., which is equivalent to  $10^{16}$  atoms of carbon. Supposing that the specific surface of the platinum wire used is  $10^3$ <sup>20)</sup>, the total surface area is  $10^4$  cm<sup>2</sup>. As the lattice constant is  $3.9 \times 10^{-8}$  cm., the number of

20) The surface structure of the activated platinum wire used by the author was extremely fine, so that the specific surface seemed to be nearly of the order of  $10^3$  which was obtained for the chemically etched surface. see F. D. Bowden and E. A. O'connor, *Proc. Roy. Soc. [A]*, 128, 316 (1930).

atoms on the surface of platinum will be of the order of  $10^{20}$ ; hence the proportion of the most active part in the above assumption to the whole surface is  $10^{-2}$ . This result shows that the above assumption is not so absurd.

Equation (7) may be rewritten as

$$\frac{dx}{dt} = k \frac{(a-x)}{x} \cdot \frac{1}{1 - \frac{c}{x}}, \quad (9)$$

in which  $\frac{c}{x}$  is always smaller than 1, so that, by binomial theorem,

$$\frac{1}{1 - \frac{c}{x}} \approx 1 + \frac{c}{x} = 1 + \frac{\frac{x}{c}}{1 + \frac{x}{c}},$$

and from the comparison between Langmuir's and Freundlich's isotherms, we obtain

$$\frac{\frac{x}{c}}{1 + \frac{x}{c}} \approx c' x^m, \quad 0 < m < 1.$$

If we substitute these relations in equation (9) and put  $m+1=n$ , we obtain the equation

$$\frac{dx}{dt} = k \frac{(a-x)}{x^n}, \quad 1 < n < 2.$$

### Change of the Retardation Exponent under Various Conditions.

In approximate derivations of the velocity equation in the preceding section, highly active parts of the surface were taken into consideration. From this, variation of the retardation exponent is explained, though it is difficult to give a quantitative physical meaning to the retardation exponent.

#### Action of Poison.

It is considered that the more active the centres are, the less they are in number.<sup>12),13)</sup> Accordingly with relatively small amount of poison the active parts are spoiled—from the most to the less in order—leaving the centres to which the simple theory is applicable. In other words, the retardation exponent is to approach 1 with the increase of the amount of poison.

The effect of sintering is considered as similar to that of poisoning.

It was confirmed, in fact, that the exponent approached 1 when methane

21) E. A. Owen and E. L. Yates, *Phil. Mag.*, 15, 472 (1933).

was decomposed in the presence of poisoned platinum. [See Report I, p. 188].

In the decomposition of carbon monoxide in the presence of nickel fresh from reduction, the exponents always show large values as given in Expt. 1 in Table 1. After great numbers of highly active parts, however, had been poisoned by the formation of nickel carbide during Expt. 1, the exponents became smaller in Expt. 2 and so forth than in Expt. 1.

#### **Influence of Temperature.**

With the rise of temperature the inactive atoms on the surface will gradually gain energy to become active centres, and this leads to the increase in the kind of the active centres. On the other hand, the irreversible adsorption or the failure of the establishment of adsorption equilibrium on the active centres becomes remarkable with the rise of temperature. It seems probable, therefore, that the retardation exponent becomes larger. In fact this is seen in the decomposition of methane in Tables 7, 8, and 9 in Report I.

#### **Influence of Pressure.**

When the initial pressure of a reactant is low, relatively few kinds of the active parts participate in the reaction to which the simple theory may be applicable; while in the case of higher pressures, as the active parts are immediately covered with the products, the reaction velocity on the less active parts is mainly measured. Thus, the increase in pressure may lead to the failure of the establishment of adsorption equilibrium owing to the rapidity of the reaction velocity on the active parts and so the simple theory becomes inapplicable.

As for the decomposition of methane because of the narrowness of the pressure range, and as for that of carbon monoxide because of difficulty in the comparison between data, the influence of pressure on the exponent was not ascertained.

As for the decomposition of ammonia, this influence was not ascertained in the experiments of Hinshelwood and Burk,<sup>9)</sup> but in the experiments of Schwab and Schmidt<sup>7)</sup> the exponent was equal to 1 in the pressure range from 0.25 to 4mm., while it rapidly became large in the range from 10 to 300 mm., and the heat of activation increased from 44 to 140 kcal. Such a sudden increase both in the value of the exponent and in the heat of activation sufficiently suggests the change of the reaction mechanism, and yet, according to the above consideration, its explanation is possible to a certain degree. At low pressures, the reaction takes place in the highly active centres possessing the lowest heat of

activation; and at high pressures, such active centres are covered with hydrogen in an instant, so that the less active centres or the surface atoms with high heat of activation come mainly to participate in the reaction. Accordingly, the value of the average heat of activation calculated at high pressures will be larger than that at low pressures.

### Summary.

(1) It has been confirmed that the reaction velocity of catalytic reactions to be retarded by strong adsorptions of reaction products, such as\*



is expressed by the equation proposed in the preceding report.

(2) It has been discussed that the heterogeneity of the surface should be taken into consideration as one of the causes of the deviation from the simple theory, and concluded that the cause lies in the fact that either irreversible adsorption takes place or adsorption equilibrium of the reacting components is not established on highly active centres.

(3) From these considerations, the velocity equation has approximately been derived and variation of the retardation exponent under various conditions has been explained qualitatively.

The author wishes to express his sincere appreciation to Prof. S. Horiba for his continued guidance throughout this work.

This is the paper presented to Committee of Catalysis of Japan Society for the Promotion of Scientific Research.

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\* The black letters show the reaction products which are adsorbed strongly by the catalysts.