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

By MASAO KUBOKAWA.

In his preceding report[1] 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 contant 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.[2][3][4]

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**, 180 (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 II[2]
251	408.0	1.01	2, V[3]
251	263.2	1.05	3, V[3]
251	298.2	1.01	4, V[3]
264	325.1	1.85	1, VIII[3]

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[5] 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[6] 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°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

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[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. This fact has also been pointed out by Schwab and Schmidt.[7] 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.

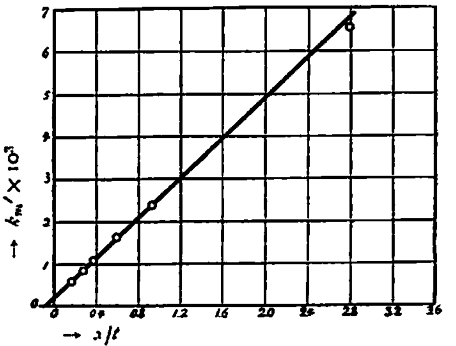

Fig. 1.

[II] Schwab and Schmidt[7] 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[8] was applied. Any satisfactory explanation of the equation, however, has not been given[9]. 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°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.

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

8) $-\frac{d[NH_3]}{dt}=k''\frac{[NH_3]}{[H_2]}\cdot\frac{[NH_3]}{[H_2]([H_2]+b[NH_3])}$

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).

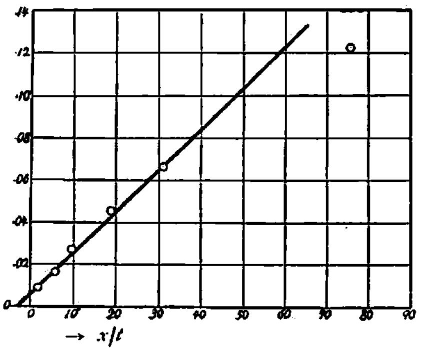

Fig. 2.

[III] Winter 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.[11]

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[12] 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[13] 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-

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[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, $CH_4 \rightleftarrows C+4H$; hence

$$\frac{[C][H]^4}{[CH_4]} = K.$$

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

$$\frac{dx}{dt} = k[C] = k'\frac{[CH_4]}{[H]^4}.$$

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 innert 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.[14]

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[15]. 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[15][16].

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,[17] 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.[2][3][4]

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.[1] 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.[14]

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.[18]

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; σ, 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 σ_A, σ_B, and σ_C represent the fractions covered with A, B, and C; and

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[18] W. Frankenburger, *Z. Elektrochem.*, **35**, 278 (1929).

let us suppose that on these parts adsorption equilibrium is always established during the reaction. Let σ_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

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

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

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

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

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

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

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 σ_D is always smaller than 1,

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

according to binomial theorem, and Freundlich's adsorption isotherm is approximately equal to Langmuir's[19], so that

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

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

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

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19) Langmuir's isotherm is expressed by $\frac{x}{m}=\frac{abp}{1+bp}$, and Freundlich's by $\frac{x}{m}=cp^{1/n}$. So long as p 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 σ_A, so that

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

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

$$x'=x-c. \tag{6}$$

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

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

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

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

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^{18} atoms of carbon. Supposing that the specific surface of the platinum wire used is 10^{3} 20), the total surface area is 10^4 $\overline{\mathrm{cm}^2}$. As the lattice constant is $3\,9\times10^{-8}$ cm., the number of

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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'conner, *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

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

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

$$\frac{1}{1-\frac{c}{x}} \doteqdot 1+\frac{c}{x}=1\Bigg/\frac{\frac{x}{c}}{1+\frac{x}{c}},$$

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

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

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

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

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.12)13) 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

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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 adsoption 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,[6] but in the experiments of Schwab and Schmidt[7] 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*

$CH_4 \rightarrow \mathbf{C} + 2\mathbf{H}_2$,	Catalysed by Pt
$2CO \rightarrow \mathbf{C} + CO_2$,	,, ,, Ni
$2NH_3 \rightarrow N_2 + 3\mathbf{H}_2$,	,, ,, Pt

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.

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The Laboratory of Physical Chemistry,
Kyoto Imperial University.

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