79. The Formation of the Reaction Nuclei in the Reduction of Cupric Oxide by Hydrogen.

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When there occurs a reaction between a gas and a solid, it is readily admitted that the surface condition of the solid—the crystal structure etc.—has a great influence upon the reaction. On the other hand, it has been well known that in a heterogeneous catalytic reaction, the surface condition causes a variation of the catalytic activity of a solid catalyst. From these facts it is expected that there exist some relations between the catalytic activity of a solid and the reaction involved. In order to elucidate such relations with respect to copper, the author has followed the velocity of reduction of cupric oxide by hydrogen, by removing the water produced from the system by cooling it with dry ice and measuring statically the change in hydrogen pressure. It was found that the reaction proceeded autocatalytically and the velocity reached maximum after a certain lapse of time[1]. The velocity formulae differ from each other in the courses before and after the velocity maximum. To the first part, the following empirical formula

$$\frac{dx}{dt}=K_0x^{\frac{2}{3}}(a-x) \tag{1}$$

is applied, where a is the initial pressure of hydrogen, x the decrease in hydrogen pressure and K_0 a constant. In the latter part the velocity is much greater than that in the formula (1).

The reaction in the first part may be assumed to proceed as follows: (1) There occurs a reaction between adsorbed hydrogen and cupric oxide at the interface of reduced copper as the reaction nucleus and cupric oxide. (2) In the beginning of the reaction, the nuclei on the cupric oxide crystal are small in number, and they are never in contact with one another[2]. (3) The progress of the reaction is proportional to the velocity of the growth of the nuclei and there is no change in their number. From these assumptions is derived the reaction velocity formula

$$\frac{dx}{dt}=k_0N_0^{\frac{1}{3}}x^{\frac{2}{3}}(a-x) \tag{2}$$

where k_0 is the constant and N_0 the number of the reaction nuclei at first. Assuming $k_0N_0^{\frac{1}{3}}=K_0$, the formula (2) becomes identical with the formula (1), and the variations in K_0 according to the change of the

1) S. Hasegawa, Rev. Phys. Chem. Japan, **17** (1943), 49.
2) S. Roginsky und E. Schulz, Z. physik. Chem. A, **138** (1928), 21.

reaction temperature, the heat treatment of cupric oxide or the addition of the reduction product, reduced copper, can be well explained by these assumptions.

In the following it is intended to show that in the latter part of this reaction the increase of velocity is due to the formation of reaction nuclei.

Experimental Results.

The results obtained at 160°, 180°, 200°, 240° and 280°C are graphically shown taking $\log \frac{dx}{dt} - \log x^{\frac{2}{3}}(a-x)$ as the ordinate and

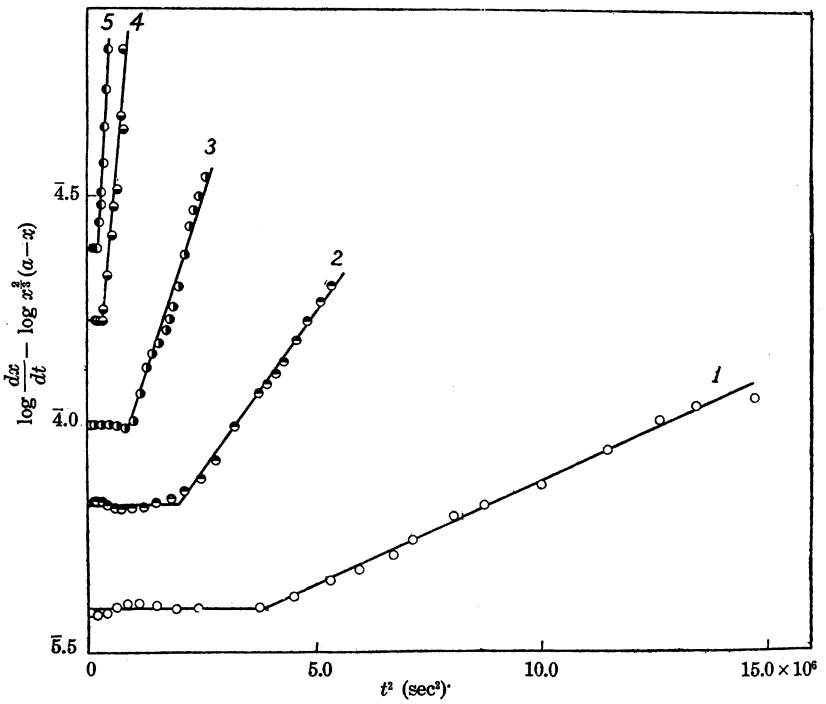

Fig. 1. $\log \frac{dx}{dt} - \log \left[x^{\frac{2}{3}}(a-x)\right] \sim t^2$ curves at different temperatures; 1, 160°; 2, 180°; 3, 200°; 4, 240°; 5, 280°C.

t^2 as the abscissa. As seen in the figure the curve consists of the two parts—a straight line parallel to the abscissa and an inclining straight one. Let the point where the former horizontal line intersects the abscissa be $\log K_0$, the inclination of the latter straight line be $0.4343\varkappa'$ and the time when the two straight lines intersect each other be τ, then the following velocity formulae can be obtained:

$$\frac{ax}{dt} = K_0 x^{\frac{2}{3}}(a-x) \qquad (1)$$

for the first part of the reaction, and

$$\frac{dx}{dt}=K_0e^{\varkappa'(t^2-\tau^2)}x^{\frac{2}{3}}(a-x) \qquad (3)$$

for the second part. And it happened that τ is equal to the time for the velocity to reach a maximum. In comparison of (1) and (3), it is seen that (3) does not radically differ from (1), but it is nothing but (1) with the correction term $e^{\varkappa'(t^2-\tau^2)}$.

The results obtained under various experimental conditions are summarized in the following table.

TABLE 1.

Exp. Group	Exp. No.	Reaction temp. (°C)	Initial pressure (mmHg)	Treatment	$0.4343\varkappa'$	$0.4343\varkappa'\tau^2$
I	1	160	175.6	Cupric oxide was oxidized before every experiment at 300° C.	4.36×10^{-8}	0.139
	2	180	175.2		1.34×10^{-7}	0.166
	3	200	176.9		3.25×10^{-7}	0.151
	4	240	175.0		9.00×10^{-7}	0.134
	5	280	176.6		1.57×10^{-6}	0.141
II	6	180	115.0	„	2.02×10^{-7}	0.220
	7	„	175.2		1.45×10^{-7}	0.216
	8	„	234.5		1.11×10^{-7}	0.223
III	9	180	175.2	No treatment.	1.45×10^{-7}	0.216
	10	„	178.2	Heated at 797° C for 2 hours.	1.20×10^{-7}	0.941
	11	„	176.3	Heated at 797° C for 5 hours.	6.59×10^{-8}	1.094
IV	12	180	178.8	Oxidized before experiment.	1.88×10^{-7}	0.431
	13	„	177.9	Unoxidized and performed immediately after Exp. No. 12.	5.84×10^{-7}	0.148
	14	„	178.1	Unoxidized and performed immediately after Exp. No. 13.	6.41×10^{-7}	0.130

Cupric oxide used was prepared by adding potassium hydroxide solution to that of cupric nitrate and heating the precipitate at 847° C for 5 hours.

I. With rising temperature, $\varkappa'$ becomes larger, while $\varkappa'\tau^2$ is constant independent of the reaction temperature.

II. The higher the initial pressure is, the smaller is $\varkappa'$, while $\varkappa'\tau^2$ remains unchanged.

III. In the case of the heat treatment of the sample, the longer the heating is, the smaller is $\varkappa'$ and larger is $\varkappa'\tau^2$.

IV. In the case of the sample which has been repeatedly used without being oxidized, i. e. without removing the reduced copper produced in the preceding experiment, the larger the amount of the reduced copper is, the larger is $\varkappa'$ and the smaller is $\varkappa'\tau^2$.

For all the reaction under the above mentioned conditions the

formulae (1) and (3) are applicable to the first part and the second part respectively.

Considerations.

The comparison of (2) and (3) leads to the following formula for the second part:

$$\frac{dx}{dt}=k_0N_0^{\frac{1}{3}}e^{\varkappa'(t^2-\tau^2)}x^{\frac{2}{3}}(a-x) \tag{4}$$

It is probably due to the failure of some of the above assumptions that the formula for the first part cannot be applied to the second part and it is necessary to make a correction by $e^{\varkappa'(t^2-\tau^2)}$.

As it is improbable that the reaction mechanism suddenly changes in its course, the assumption (1) may be valid for the whole reaction. If against the assumption (2) there occurs a contact between the nuclei, the reaction velocity of this part is to be proportional only to hydrogen pressure and independent of the reacted quantity. But the fact is that the formula (3) is applicable to this part. And once a contact happens to take place between the nuclei, the reaction must proceed in first order and not autocatalytically. But the experimental results are contrary to such expectations: when the sample is used without being reoxidized, the reaction proceeds also autocatalytically and the formulae (1) and (3) are applicable, too. Accordingly, the assumption (2) can also be applied to the second part. The assumption (3) supposes that the number of the nuclei does not change; but in fact it should be properly considered that new nuclei are formed during the course of the reaction[3] It can be deduced that the correction $e^{\varkappa'(t^2-\tau^2)}$ in the formula (4) should never be made for k_0, x, and $a-x$, but only for N_0. The number of the nuclei does not change so far as τ, but after the lapse of τ it increases according to

$$N=N_0e^{\varkappa(t^2-\tau^2)} \tag{5}$$

And the increase in the number of the nuclei needs an induction period τ. The mechanism of the increase of nuclei cannot be discussed merely with the above results, but it may be supposed that the increase will start after the surface has reached to a certain state. The presence of the induction period gives an interesting suggestion that it plays an important rôle in the formation of the nucleus.

In the formula (5), the terms $e^{\varkappa\tau^2}$ and $e^{\varkappa t^2}$ are considered to represent the surface condition of cupric oxide at τ and t respectively. It is found that at different reaction temperatures the values of $\varkappa$ and τ differ, but $\varkappa\tau^2$ remains constant. Such is also the case with different initial pressures. In these cases, the number of nuclei N_0 can be regarded as equal, namely, the surface condition of cupric oxide is the

3) E. Topley and J. Hume, Proc. Roy. Soc. A, **120** (1928), 211.
J. Hume and J. Colvin, Phil. Mag., **8** (1929), 589.
Proc. Roy. Soc. A, **125** (1929), 635.
A. Wischin, ibid., **172** (1939), 314.

same at the start of the reaction. Therefore, $\varkappa\tau^2$ is expected from the formula (5) to be equal at the time when the number of the nuclei begins to increase. On the contrary, when the decrease in the number of the nuclei N_0 is caused by heating, $e^{\varkappa\tau^2}$ should become larger in order to reach the same state. And the enlargement of N_0 by the addition of reduced copper should lead to the reduction of $e^{\varkappa\tau^2}$. In fact, as seen in the table, these expectations are satisfied with the experimental results.

$\varkappa$ is proportional to the velocity constant of the nuclei formation. Therefore, the apparent activation energy of the formation can be obtained from the changes of $\log \varkappa$ with reaction temperature. Experimental results give 14 kcal as its value.

In conclusion it is the author's pleasant duty to acknowledge the scrupulously conscientious care with which Professor S. Horiba has had the goodness to guide him throughout this work.