The Reduction of Zinc Oxide by Hydrogen. III. The Effect of Nitrogen on the Reduction

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The following results were obtained in the previous study of the reduction of zinc oxide by hydrogen.[1,2] The reaction proceeds independently of the hydrogen pressure. Additionally, in the presence of a large amount of zinc oxide (case 1), the reduction is not affected by the amount of zinc oxide, and the relationship between the pressure and the reaction time is linear. In the presence of a small amount (case 2), however, the relation is not linear. In the latter case, the data well satisfied Eq. 1, deduced from the assumption that the reaction rate is proportional to the surface area.

$$(p_0-p_\infty)^{1/3}-(p-p_\infty)^{1/3}=k_2(t-t_0) \qquad (1)$$

Here p_0 and p_∞ are the hydrogen pressures when the reaction starts to obey Eq. 1 and when zinc oxide is completely used up respectively. As a result, the reduction of zinc oxide was suggested to be not a surface reaction, but a consecutive one consisting of two processes, the sublimation-decomposition of zinc oxide to zinc vapor and oxygen and the subsequent reaction of oxygen and hydrogen, Further, the former process is the rate-determining step in case 2.

The thermal decomposition of zinc oxide has been known to be influenced by the third gas, i.e., nitrogen or zinc vapor.[3,4] Hence, one can expect the variation of the reaction modes, in case 2, in the presence of these gases. With this expectation the present work was carried out, using nitrogen as the third gas.

Experimental

The apparatus used for this work was the same as that used in the previous paper.[1,5] Just before the reaction started, the reaction tube was evacuated for five minutes, and then nitrogen and, finally, hydrogen were admitted at a given pressure and composition. The rate of the reduction was measured in the temperature range 690~738°C, with the amount of zinc oxide, 40.0 mg., and the pressure range of nitrogen, 0~2 cmHg. The analysis of data was made by applying Eq. 1 as in the previous work.[2] The initial pressure of hydrogen was 6.0~6.4 cmHg. Nitrogen was prepared by purifying the commercial gas in a bomb by passing it through the reduced copper heated at 500°C, through concentrated sulfuric acid and finally through magnesium perchlorate.

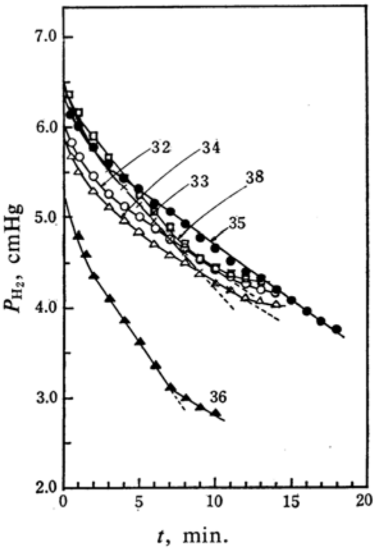

Fig. 1. The relation between residual H_2 and reaction time. Runs are shown in Table I.

Results and Discussion

The results obtained at 670°C are shown in Fig. 1. The initial amount of zinc oxide in all experiments was 40.0 mg., except for the 300 mg. in No. 35, which was done under the same conditions as No. 32. As has been mentioned above, when a large amount of zinc oxide is present, only the linear part appears in the relation between the hydrogen pressure and the reaction time.[1,2] Hence, the slope of a straight line in No. 32 can be estimated by comparing No. 32 with No. 35. From Fig. 1 and by applying Eq. 1, the specific reaction rates, k_1 and k_2, are as shown in Table I; k_1

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1) T. Imoto, Y. Harano and Y. Nishi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **84**, 115 (1963).

2) T. Imoto, Y. Harano, Y. Nishi and S. Masuda, ibid., **85**, 106 (1964).

3) E. A. Secco, *Can. J. Chem.*, **38**, 596 (1960).

4) W. J. Moore and E. L. Williams, *J. Chem. Phys.*, **63**, 1516 (1959).

5) T. Imoto, Y. Harano and A. Morishima, "The Reduction of Zinc Oxide by Carbon Monoxide. II," submitted to This Bulletin.

TABLE I. THE EFFECT OF NITROGEN ON k_1 AND k_2 AT 690°C

No.	P_{N_2} cmHg	ZnO mg.	k_1 cmHg/min.	k_2 cmHg$^{1/3}$/min.
38	0.000	40.0	0.224	0.107
36	0.340	40.0	—	0.067
33	0.526	40.0	0.184	0.056
32	0.982	40.0	0.120	0.047
35	1.040	300.0	0.120	—
34	1.470	40.0	0.105	0.029

and k_2 correspond to the reactions revealed as a straight line and a curve respectively in Fig. 1 (see also Fig. 2 in the previous report[2]). No. 38 at the zero nitrogen pressure obtained in the previous work[2] was also tabulated for the sake of comparison.

As may be seen in Table I, both k_1 and k_2 decrease with the nitrogen pressure. Moore et al.,[4] who studied the thermal decomposition of zinc oxide, found that the amount of zinc oxide decomposed in the stream of nitrogen is smaller than that in oxygen, and that it is, moreover, much smaller than would be expected from the thermodynamics by 10^{-2}. They made no reference to the reason for this. Assume that some substance retarding the sublimation-decomposition of zinc oxide is produced in the presence of nitrogen, and that the surface area of zinc oxide poisoned by the retarding substance is θ, by taking $\theta=0$ for the surface in the absence of nitrogen. Since k_2 is the specific decomposition rate of zinc oxide per unit surface area, θ at various nitrogen pressures will be given Eq. 2:

$$\theta=1-\frac{(k_2)_{P_{N_2}}}{(k_2)_{P_{N_2}=0}} \tag{2}$$

Let us assume additionally that the retarding substance is produced on the whole surface with the same probability by molecular nitrogen. Thus, at equilibrium, θ will expressed by a form similar to the Langmuir-type adsorption isotherm,[6] Eq. 3:

$$\theta=\frac{aP_{N_2}}{1+aP_{N_2}} \tag{3}$$

$$\frac{1}{\theta}=1+\frac{1}{aP_{N_2}} \tag{4}$$

TABLE II. THE RELATION BETWEEN P_{N_2} AND θ

No.	P_{N_2} cmHg	$1/P_{N_2}$ cmHg^{-1}	$\frac{(k_2)_{P_{N_2}}}{(k_2)_{P_{N_2}=0}}$	θ
38	0.000	0.00	1.000	0.000
36	0.340	2.94	0.626	0.374
33	0.526	1.90	0.523	0.477
32	0.982	1.02	0.439	0.561
34	1.470	0.68	0.271	0.729

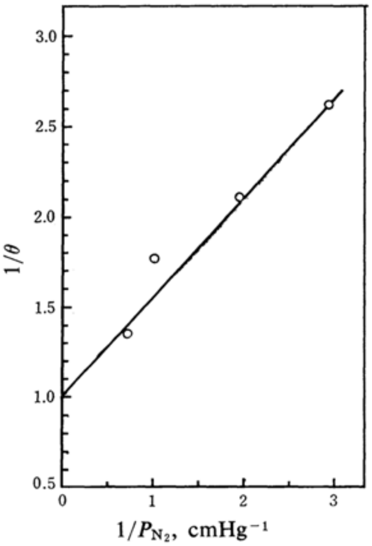

Fig. 2. $1/\theta \sim 1/P_{N_2}$ at 690°C.

θ values calculated from k_2 in Table I according to Eq. 2 are shown in Table II.

In Fig. 2, $1/\theta$ is plotted against $1/P_{N_2}$. Figure 2 shows that every value gives a good straight line, and that Eqs. 2—4, based on the above assumptions, are satisfied. $1/a$ is estimated to be 1.73 from the slope of the line in Fig. 2.

As a result, it is considered that the effect of the nitrogen molecule can be evaluated by the magnitude of a. There is another method of estimating a, even when no data of $(k_2)_{P_{N_2}=0}$ is obtained. As $(k_2)_{P_{N_2}=0}$ will be constant at a constant temperature and a constant state of the surface, the following relations are obtained from Eqs. 2 and 3:

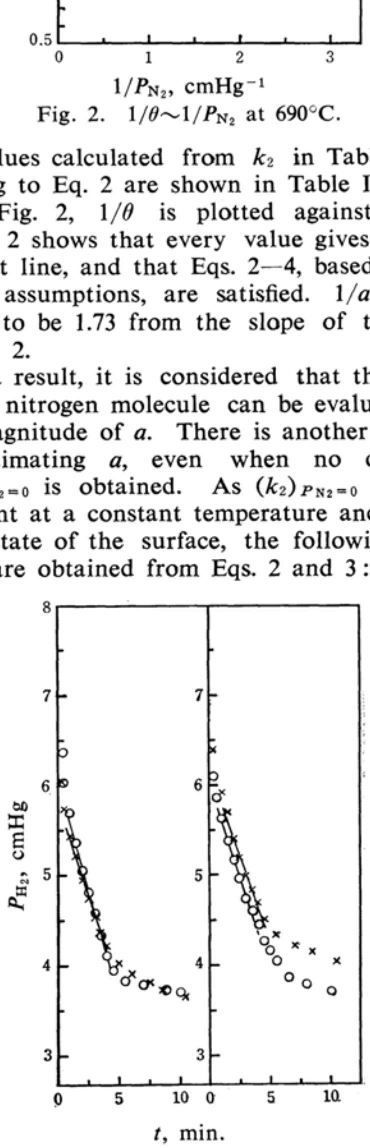

Fig. 3. $P_{H_2} \sim t$, at 714°C; P_{N_2} (cmHg) left: ○ 0.538, × 0.916; right ○ 1.480, × 1.974

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[6] I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).

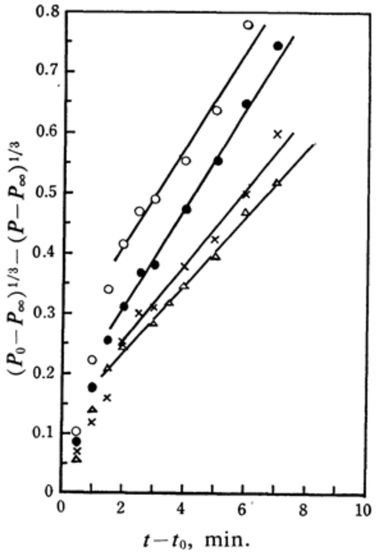

Fig. 4. Plots according to Eq. 1, at 714°C. P_{N_2} (cmHg) ○ 0.538, ● 0.916, × 1.480, △ 1.968

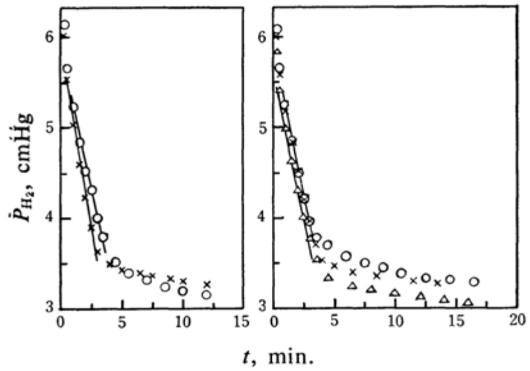

Fig. 5. P_{H_2}~t, at 738°C. P_{N_2} (cmHg): left ○ 0.000, × 0.512; right ○ 1.000, × 1.500, △ 2.000

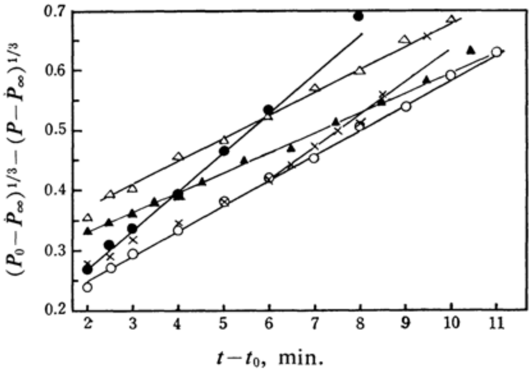

Fig. 6. Plots according to Eq. 1, at 738°C. P_{N_2} (cmHg) ● 0.000, × 0.512, ○ 1.000, △ 1.500, ▲ 2.000

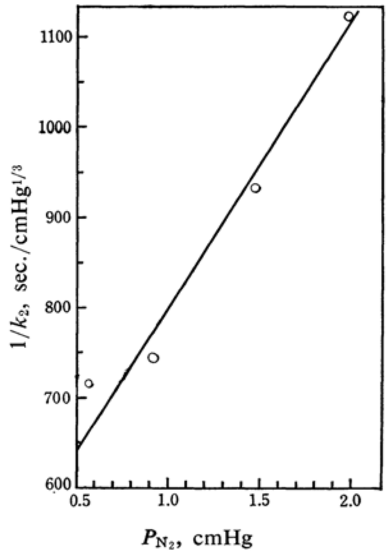

Fig. 7. Plot according to Eq. 4′, at 714°C.

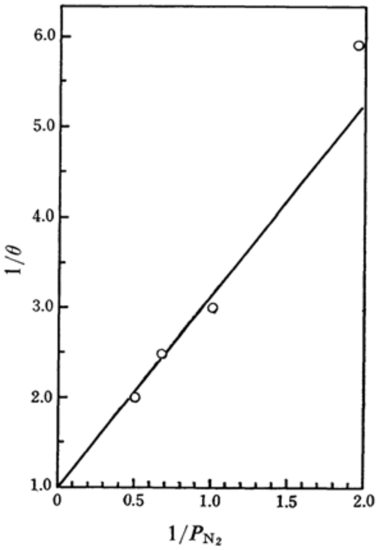

Fig. 8. Plots according Eq. 4, at 738°C.

$$1-\frac{(k_2)_{P_{N_2}}}{A}=1-\frac{1}{1+aP_{N_2}}$$

$$\frac{1}{(k_2)_{P_{N_2}}}=\frac{1}{A}-\frac{a}{A}P_{N_2} \qquad (4')$$

where A is $(k_2)_{P_{N_2}=0}$.

According to Eq. 4′, a can also be determined from the linear relation between $1/(K_2)_{P_{N_2}}$.

Results at 714 and 738°C are shown in Figs. 3—8 and Tables III and IV. Figure 7 shows the plotting according to Eq. 4′, and Fig. 8, according to Eq. 4. All values give good straight lines; from them a at 714°C and 738°C are evaluated to be 0.500 and 0.400 respectively.

TABLE III. RESULTS AT 714°C

P_{N_2} cmHg	k_2 cmHg$^{1/3}$/min.	$1/k_2$	$1/P_{N_2}$	a
0.538	0.084	11.9	1.86	0.500
0.916	0.081	12.3	1.09	
1.480	0.064	15.6	0.68	
1.968	0.053	18.9	0.51	

TABLE IV. RESULTS AT 738°C

P_{N_2} cmHg	k_2 cmHg$^{1/3}$/min.	θ	$1/P_{N_2}$	a
0	0.064	0	—	
0.512	0.053	0.17	1.95	0.400
1.000	0.043	0.33	1.00	
1.500	0.038	0.41	0.67	
2.000	0.032	0.50	0.50	

As has been mentioned above, it was found that a indicates the degree of the influence of nitrogen, and that a decreases with the temperature. It is comprehensible from the deriving principle of Eq. 3 that a corresponds to an equilibrium constant of the attraction between the substance retarding the decomposition of zinc oxide and the nitrogen in the gas phase. Therefore, the relation between $1/a$ and $1/T$ (°K^{-1}) was obtaining as shown in Fig. 9. The linearity in Fig. 9 supports the above considerations. The slope of the line gives the enthalpy of the reaction, which produces retarding substances by interaction between the surface of zinc oxide and the nitrogen molecule, as -11.5 kcal./mol.

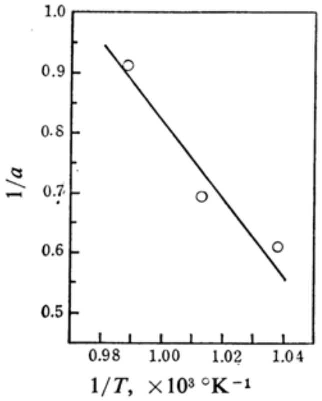

Fig. 9. $1/a$ vs. $1/T$.

As a result, it was found that nitrogen retards the reaction, the rate of which is proportional to the surface area of zinc oxide, and that the degree of the influence of nitrogen is evaluated by means of the constant, a in Eq. 3, which may be considered to reveal the equilibrium constant if the above presumption is valid. It has been reported that zinc nitride is produced by exposing the heated zinc powder in a stream of nitrogen.[7] The most probable retarding factor is the Langmuir-type chemisorption on the surface of zinc oxide —in this case, 11.5 kcal./mol. will represent the heat of chemisorption. The chemisorption of nitrogen, however, occurs only with difficulty on the normal surface of zinc oxide. The effect of nitrogen on the reduction will, however, require further studies from the point of view of the chemisortion and the surface compounds, because, as is well known,[3,4] the surface of zinc oxide submerged in the reducing gas at a high temperature has an excess of zinc, and hence its thermodynamical behavior is abnormal.

It was found that k_1 also decreases with the increase in the pressure of nitrogen (cf. from Table I). Since k_1 is the specific rate of the reaction of hydrogen and oxygen, the depressing effect of such an inert gas as nitrogen is unlikely. As has been previously reported, however, the reduction of zinc oxide is a consecutive reaction involving the decomposition of zinc oxide and the reaction of hydrogen with oxygen. Consequently, the equilibrium constant k is expected to be involved in observable k_1 generally. At present, the authors have not obtained the true rates of the reaction between hydrogen and oxygen and of the formation of zinc oxide from zinc vapor and oxygen (the specific rates are k_1° and k_{-2} respectively) under these experimental conditions; hence, the quantitative relation between k_1 and K $(=k_2/k_{-2})$ is known. At any rate, k_1 may be expressed by a function, $f(k, k_1^{\circ})=f(k_2/k_{-2}, k_1^{\circ})$. Therefore, k_1 would be affected by nitrogen, since k_2 is affected by nitrogen, as has been mentioned already.

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[7] S. Matsuura, "Aen," Maruzen (1962), p. 553.