# *The Thermal Decomposition of Zinc Oxide*

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In previous papers on the reduction of zinc oxide by hydrogen,[1-3] it has been suggested that the reduction is not a surface reaction, but a successive reaction consisting of the following two processes: the decomposition of zinc oxide into zinc vapor and oxygen, and the subsequent reaction of oxygen with hydrogen. Further, the former is a rate-determining step in the presence of a small amount of zinc oxide and the latter an excessive amount of it respectively.

The present work was carried out in order to obtain information of the decomposition process in the reduction and to discuss further the reduction mechanism.

As for the thermal decomposition of zinc oxide, it has been known that zinc oxide decomposes into zinc vapor and oxygen rather than subliming as zinc oxide vapor.[4,5] When Moore and Williams[6] investigated the decomposition rate in a stream of oxygen, nitrogen and zinc vapor by measuring the weight loss, they found that the rate is fastest in zinc vapor. No quantitative studies of the decomposition, however, have yet been carried out.

### Experimental

The decomposition rate was determined by using a thermobalance and a McLeod gauge. The zinc oxide used in this work was the same commercial superior product supplied by the Sakai Chemicals Co., Ltd., as was used in the previous work.

Since zinc oxide is a structure-sensitive compound and since its surface state is affected by a slight variation in the pretreatment, it was necessary to fix the standard pretreating conditions as follows: after evacuating below $10^{-5}$ mmHg for one hour at 190°C, the reaction tube was heated to the standard temperature (740°C) within half an hour, and then the reaction system was kept at 740°C for half an hour. During the heating process, the evacuation was stopped. The pressure of the oxygen evolved in this interval was estimated to be one in the initial decomposition equilibrium. Then the system was reevacuated below $10^{-5}$ mmHg and the decomposition was started. In this work, 200 min. was taken as a standard decomposition time.

### Results and Discussion

The relation between the initial amount ($w_0$) and the decomposed amount of zinc oxide after 200 min., at 740 and 780°C ($\Delta w$), is shown in Fig. 1. In Fig. 1 it can be seen that, when the amount of zinc oxide is less than 100 mg. at 740°C, the ratio ($\Delta w/w_0$) is nearly constant. On the other hand, when there is more than 100 mg. of zinc oxide, the relation deviates from linearity and the ratio is occasionally observed to be smaller than the former one. The deviation from linearity seems to take place because of the decrease in the effective surface of zinc oxide by its aggregation rather than because of the decrease in the surface of the zinc oxide lying in the lower part of the basket. Since the aggregation increases with a rise in the temperature, the deviation tends to appear in a smaller region of zinc oxide. Moreover, when pre-sintered and then crushed zinc oxide is used, the linearity appears over a wider range.

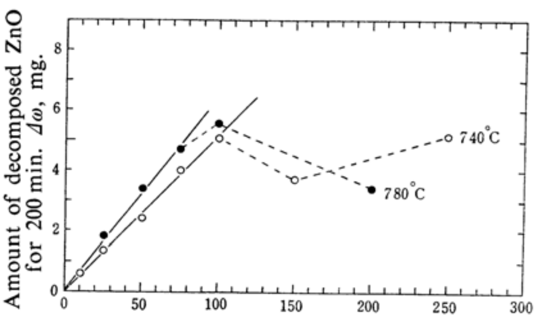

Fig. 1. The relationship between initial and decomposed amount of zinc oxide.

The decomposition ratios ($\Delta w/w_0$) at 740°C are plotted against the time for various initial amounts ($w_0$: 25, 50, 75 and 100 mg.) in Fig. 2. This figure shows that the relations between the ratio and the time are represented by an identical curve, regardless of the amount

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

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

3) T. Imoto, Y. Harano, Y. Nishi and S. Masuda, This Bulletin, **37**, 441 (1964).

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

5) L. Brewer and D. F. Mastick, *J. Chem. Phys.*, **19**, 834 (1951).

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

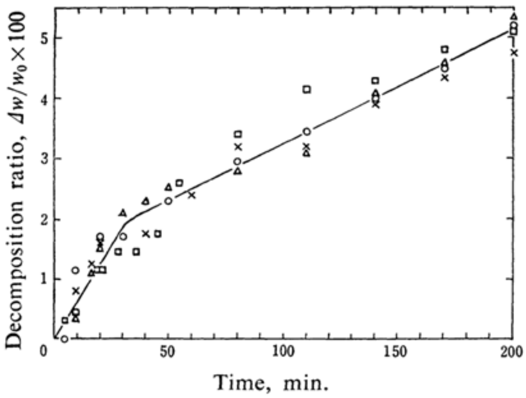

Fig. 2. The relationship between decomposition ratio and decomposition time.

| $w_0$, mg. | $w_0$, mg. | $w_0$, mg. | $w_0$, mg. |
|---|---|---|---|
| ○ 25 | × 50 | △ 75 | □ 100 |

of zinc oxide, and that in the early stages, the decomposition proceeds rapidly, but after it has proceeded for about half an hour, it proceeds at a nearly constant rate which is slower than that in the earlier part. Since the curve in Fig. 2 is nearly straight under these experimental conditions, the decomposition rate seems to be proportional to the surface area of zinc oxide.

Gray⁷⁾ investigated the sintering of zinc oxide and reported that the surface area of zinc oxide rapidly decreases in the initial half hour, but that it scarcely varies thereafter. In this work, zinc oxide was kept at a decomposition temperature for half an hour before the reaction. It is, however, still doubtful whether or not the faster decomposition stage is caused by the incompleteness of the sintering. Therefore, the following experiment was undertaken with zinc oxide which had been presintered for about two hours at the decomposition temperature in order to sinter it completely; the results obtained are shown in Fig. 3-b. From Fig. 3, it was found that the b decomposition curve has the same profile and the same slope as does the a standard curve which is identical with that in Fig. 2, and that zinc oxide also decomposes rapidly for the initial half hour. Consequently, the initial rapid decomposition seems not to be due to the variation in the surface area during the reaction.

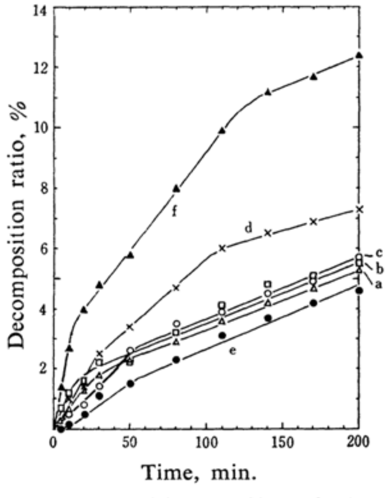

Fig. 3. Decomposition profiles of zinc oxide pretreated at various conditions (at 740°C).

△ a Standard (30 min.)
□ b Standard (200 min.)
○ c Presintered normal
× d Presintered Zn rich
● e $O_2$ treatment
▲ f $H_2$ treatment

The effect of the surface state on the decomposition rate is also shown in Fig. 3. Curves c and d show the results obtained with zinc oxide pretreated in vacuo. After sintering, the samples were exposed to air at a sintering temperature of 800°C, in case c, or cooled down to room temperature in vacuo and then exposed to admitted air, in case d. Sample c is fluffy and white, whereas sample d is coarse and gray. Such phenomena were also reported by Gray,⁷⁾ who found the surface pretreated as in sample d to be rich in zinc. Curve c is the same as the standard one (curve a), whereas curve d is different and has a longer stage of initial rapid reaction. Curves e and f show the results obtained with the sample pretreated in an atmosphere of oxygen (80 mmHg) or hydrogen (40 mmHg) respectively. In case e, the initial rapid decomposition does not appear, while in case f the reaction proceeds much faster than in the others.

The initial decomposition equilibrium pressures of oxygen in the standard experiments at 740°C are shown in Table I. In Table I, the pressure slightly fluctuates, there is, however, no difference between the samples kept at the decomposition temperature for half an hour and that kept for two hours. Assuming

TABLE I. INITIAL DECOMPOSITION PRESSURE OF OXYGEN (mmHg)

| Sample mg. | Pretreatment period at 740°C | |
|---|---|---|
| | 0.5 hr. | 2.0 hr. |
| 100 | $1.30 \times 10^{-1}$ | $1.15 \times 10^{-1}$ |
| 75 | $0.92 \times 10^{-1}$ | $1.45 \times 10^{-1}$ |
| 50 | $1.07 \times 10^{-1}$ | $1.42 \times 10^{-1}$<br>$1.30 \times 10^{-1}$ |
| 25 | $0.61 \times 10^{-1}$ | $0.99 \times 10^{-1}$ |
| 10 | $0.67 \times 10^{-1}$ | |

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7) T. J. Gray, *J. Am. Cer. Soc.*, 37, 534 (1954).

that an amount of zinc corresponding stoichiometrically to oxygen is also evolved during the pretreatment, the weight loss of zinc oxide may be calculated to be 0.07 to 0.16 mg., since the volume of the reaction vessel is 358 cc. and the volume ratio of the vessel outside and inside of the electric furnance is 1.47. If only oxygen is evolved, the weight loss would be 0.014 to 0.032 mg. From the facts that the weight loss during the above standard pretreatment was unmeasurable (less than 0.03 mg.) at 740°C and that no deposition of zinc metal on the cooler part of the reaction vessel was observed, one may say that oxygen is evolved without any accompanying evolution of zinc vapor. Therefore, the surface of the zinc oxide will be rich in zinc. Since the equilibrium decomposition pressures of oxygen in both the a and b cases were identical (cf. Table I), their surface states may also be considered to be the same. Therefore, the a and b decomposition curves (in Fig. 3) may be almost identical. On the other hand, when zinc oxide is pretreated in an atmosphere of oxygen at a higher pressure than the equilibrium pressure, no evolution of oxygen takes place, and hence, no initial rapid decomposition is observed.

As a result, it may be suggested that the fewer oxygen atoms relative to zinc atoms are involved on the surface of zinc oxide, the faster the initial reaction proceeds and the longer its rapid stage becomes. Consequently, the rate of the decomposition of zinc oxide treated by hydrogen will be very fast, since the surface has a marked deficiency of oxygen. Oxygen on the surface of the zinc oxide pretreated in vacuo will be quite scarce. On the other hand, when zinc oxide pretreated in vacuo is exposed to air at a high temperature, relatively many zinc atoms on its surface will be reoxydized and the surface will return to the original state.

Further, when the surface affected by the pretreatments has disappeared as decomposition proceeds, each sample will decompose at the same rate, regardless of the various pretreatments. Figure 3 also indicates the above suggestion.

As has been mentioned above, the pretreatment causes the surface state of zinc oxide to deviate from its stoichiometry and accelerates its initial decomposition rate. Now let us cmpare the extent of the deviation from stoichiometry with the amount of decomposition acceleration. Extraporating the linear parts of the a and b curves in Fig. 3, an intersection with the ordinate of 1.5%, is obtained. That is, the evolution of oxygen in a and b accelerates the decomposition by 1.5%. The amounts of zinc oxide which result in the non-stoichiometric state upon the evolution of oxygen, are calculated to be 0.08 to 0.02% of the initial zinc oxide, 25 to 100 mg. (assuming the non-stoichiometric substance to be zinc), and 0.16 to 0.04% (assuming, $Zn_2O$[*1]) ; hence these values are too small to explain the value of 1.5%.

Consequently, the accelerated decomposition will be caused not only by the non-stoichiometric substance, but also by the lattice defect

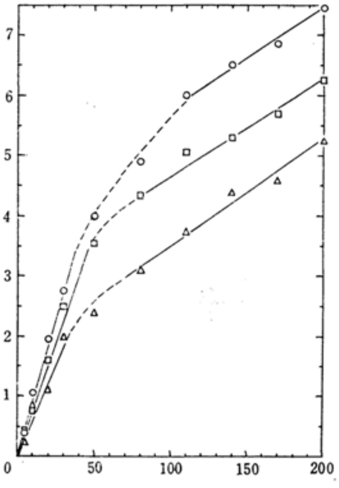

Fig. 4. The relationship between reaction rate and temperature (standard sample).

○ 820°C □ 780°C △ 740°C

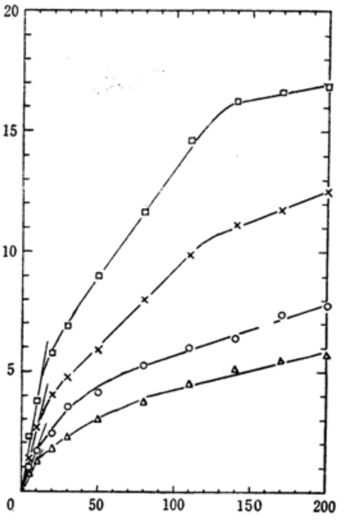

Fig. 5. The relationship between reaction rate and temperature (hydrogen pretreated sample).

□ 780°C × 740°C ○ 700°C △ 660°C

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[*1] Some investigators have suggested that, on the surface of zinc oxide in the state of oxygen deficiency, zinc suboxide, e. g., $Zn_2O$, is formed.[4,6]

TABLE II. INITIAL DECOMPOSITION RATE OF PRETREATED ZINC OXIDE BY $H_2$ (ca. 40 mmHg) AND IN VACUO ($\times 10^2$ min$^{-1}$)

| Temp. °C | Conditions of pretreatment | |
|---|---|---|
| | $H_2$ ca. 40 mmHg | in vacuo |
| 820 | | 0.094 |
| 780 | 0.411 | 0.083 |
| 740 | 0.274 | 0.066 |
| 700 | 0.198 | |
| 660 | 0.143 | |

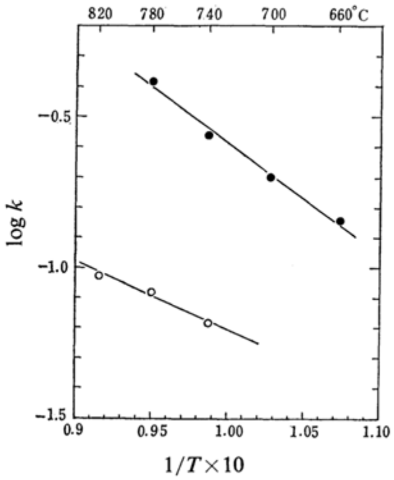

Fig. 6. Arrhenius relationships.
○ Standard ● $H_2$ treated

resulting from the lack of oxygen.

The results at various temperatures obtained with zinc oxide pretreated under standard conditions and by hydrogen are shown in Figs. 4 and 5. From Figs. 4 and 5, the initial reaction rates,[*2] which are thought to be dependent upon the pretreatments, shown in Table II are obtained. Figure 6 shows the Arrhenius plots, from which the activation energies have been found to be 9.7 and 16.6 kcal./mol. The latter value, 16.6 kcal./mol., is in good agreement with the 17.0 kcal./mol. value obtained in the previous studies[2)] of the rate of the reduction of zinc oxide by hydrogen controlled by the decomposition process of zinc oxide.

**Considerations Upon the Rate of Oxygen Evolution.**—After the decomposition had proceeded into the linear stage, as is shown in Fig. 2, the evacuation from the reaction system was stopped and the amount of oxygen which had accumulated in the system was measured. Figure 7 shows the typical curves of the accumulating rate of oxygen. Assuming that the rate of the oxygen evolution is proportional to the pressure difference of oxygen between that at the decomposition equilibrium, $P_e$, and that at time $t$, $P_{O_2}$, the rate equation may be given by Eq. 1:

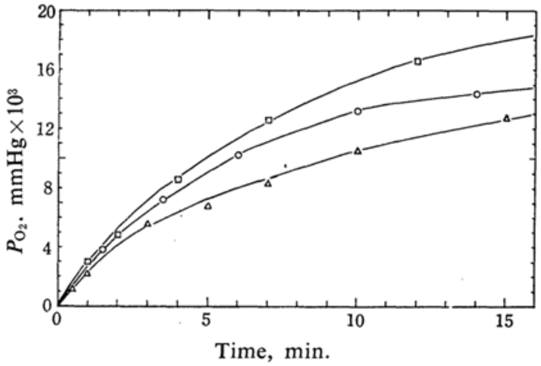

Fig. 7. Typical curves of accumulating rate of oxygen.

△ 100 mg. $P_e = 13.8\times10^{-3}$ mmHg
□ 30 mg. $P_e = 19.1\times10^{-3}$ mmHg
○ 10 mg. $P_e = 16.1\times10^{-3}$ mmHg

$$\frac{dP_{O_2}}{dt} = k_0(P_e - P_{O_2}) \qquad (1)$$

Integrating Eq. 1,

$$-\log\frac{P_e - P_{O_2}}{P_e} = k_0't \qquad (2)$$

In Fig. 8, the $\log(P_e - P_{O_2})/P_e$ obtained from Fig. 7 is plotted against the time. Figure 8 shows that every datum gives good straight lines and that Eqs. 1 and 2, based on the above assumption, are satisfied.

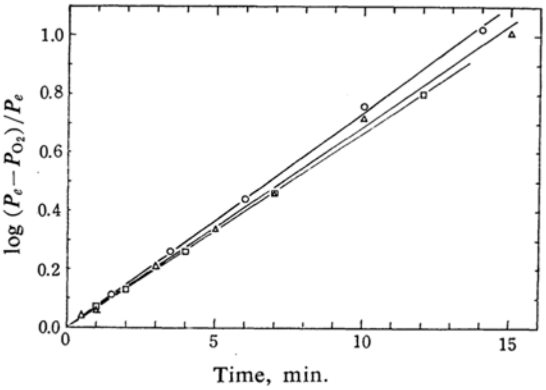

Fig. 8. $-\log(P_e - P_{O_2})/P_e$ vs. $t$.
△ 100 mg. □ 30 mg. ○ 10 mg.

The amount of zinc oxide is plotted against $k_0'$ in Fig. 9, where the $k_0'$ value is independent of the initial amounts of the zinc oxide, provided that zinc oxide is present in a larger amount. Consequently, in this region, the diffusion process of oxygen from the surface of

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[*2] The slopes of the lines in the initial reaction stage in Figs. 4 and 5 represent the initial reaction rate.

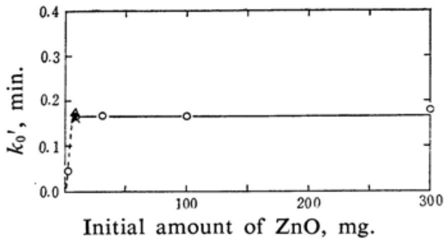

Fig. 9. The relationship between $k_0'$ and the amount of zinc oxide.
○ 700°C × 740°C △ 780°C

zinc oxide into the ambient gas is considered to be the rate-controlling step in the overall decomposition. On the contrary, at smaller amounts of zinc oxide, the decomposition rate is found to be proportional to the amount of zinc oxide; hence, the rate of the overall reaction is controlled by the decomposition process.

From the initial decomposition rate ($3.2\times 10^{-3}$ mmHg/min.) at $t=0$, $w_0=10$ mg. in Fig. 7, the rate of the weight loss is calculated to be 0.033 mg./hr. if only oxygen is evolved, and 0.17 mg./hr. if both oxygen and zinc are stoichiometrically evolved. When the above values are compared with the experimental value, 0.12 mg./hr., obtained from the slope in Fig. 2 (where $w_0$ is assumed to be 10 mg.), it may be concluded that the evolution of oxygen is predominant over the vaporization of zinc and that zinc oxide grows richer in zinc as the decomposition proceeds.

**A Comparison of the Rate Constants of the Decomposition with the Reduction by Hydrogen.**—As has been mentioned above the activation energy of the decomposition of zinc oxide is found to be in good agreement with that of the reduction by hydrogen controlled by the decomposition process. In this section, in order to discuss further the relations between these two reactions, their rate constants will be compared. The following two results, obtained at nearly the same temperature, are chosen for the comparison: at 738°C, $k_2'=0.158$ cmHg$^{1/3}\cdot$min$^{-1}$, sample 40 mg., from Ref. 2., and at 740°C, $k=0.00274$ min$^{-1}$, from Table II in this paper. The rate constant, $k_2'$, of the reduction of zinc oxide was obtained according to Eq. 3, which had been deduced from the assumption that the reduction rate is proportional to the surface area of zinc oxide:

$$(P_0-P_\infty)^{1/3}-(P-P_\infty)^{1/3}=k_2'(t-t_0) \qquad (3)$$

where

$$k_2'=k_1\left(\frac{\pi n}{3a}\right)^{1/3}\left(\frac{2}{\rho}\right)^{2/3} \qquad (4)$$

$$a=\frac{(P-P_\infty)}{w} \qquad (5)$$

where $k_1$ is the reduction rate per unit surface area in a unit of time, g./cc. min., $n$ is the number of zinc oxide particles, $w$ and $\rho$ are the mass and density of zinc oxide respectively, and $P_0$ and $P_\infty$ are the hydrogen pressures when the reduction starts to obey Eq. 3 and the zinc oxide is completely used up respectively (shown in Fig. 10). In this work, the characteristic value, $a$, defined by Eq. 5 equals 0.00947 g./(cmHg of hydrogen) at 738°C.

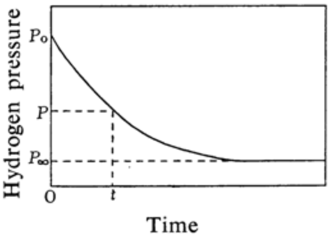

Fig. 10. The typical curve of the reduction of zinc oxide by hydrogen, which proceeds according to Eq. 3.

Since the amounts of zinc oxide is 40 mg. and since its specific surface area is 10 m$^2$/g.,*3 $n$ is calculated to be $1.2\times 10^{13}$. Therefore, from Eqs. 4 and 5, $k_1$ is given by Eq. 6:

$$k_1=k_2'\left(\frac{3a}{n\pi}\right)^{1/3}\left(\frac{\rho}{2}\right)^{2/3}$$
$$=2.85\times 10^{-6}\ \text{g./cm}^2\cdot\text{min.} \qquad (6)$$

On the other hand, in this decomposition of the pellet-type zinc oxide, the decomposed amounts in 200 min. at 780°C, $\Delta w$, were 0.6 and 0.8 mg. for the samples with the surface areas of 4.41 and 4.39 cm$^2$ respectively, and, hence, 0.7 mg. for 4.40 cm$^2$ on the average. From Fig. 1, the decomposed amount, $\Delta w$, of 0.7 mg. will be found to correspond to the initial amount $w_0$ (10 mg.) of zinc oxide powder. Therefore, the effective specific surface area for the decomposition of zinc oxide powder is 4.40 cm$^2$/10 mg. = 440 cm$^2$/g.*3 Consequently, the decomposition rate per unit of surface area in this work is 0.00274 min$^{-1}$/440 (cm$^2$/g.) $=6.23\times 10^{-6}$ g./cm$^2\cdot$min. Considering the experimental errors and the requirement of some assumptions for the comparison, the above value, $2.85\times 10^{-6}$ g./cm$^2\cdot$min., may be regarded to be in good agreement with the experimental value, $6.23\times 10^{-6}$ g./cm$^2\cdot$min.

**A Discussion of the Reverse Reaction.**—During the course of the investigation of the

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*3 There is the marked difference in the specific surface area of zinc oxide between the two samples, the one used in the decomposition, and the other in the reduction. This may be caused by the difference in particle diameter. The former contains about 30 wt.% which is larger than 250$\mu$ in particle diameter whereas in the latter only 0.03% are larger than 44 $\mu$.[1] The electron-microscope study also shows the above fact.

TABLE III. THE WEIGHT LOSS OF ZINC OXIDE AND PRESSURE CHANGE OF HYDROGEN DURING HYDROGEN PRETREATMENT

| Run No. | Temp. °C | Initial hydrogen pressure mmHg | Weight loss during hydrogen pretreatment mg. | Hydrogen pressure | |
|---|---|---|---|---|---|
| | | | | Corresponding to weight loss of ZnO mmHg | After pre-treatment mmHg |
| 69 | 740 | 32.3 | 142.0 | 76.6 | >16.8 |
| 70 | 740 | 33.1 | 140.1 | 75.6 | >16.8 |
| 71 | 740 | 32.3 | 76.00 | 41.0 | >16.8 |
| 73 | 700 | 33.1 | 67.46 | 36.4 | 28.2 |
| 74 | 700 | 30.7 | 60.75 | 32.8 | 28.9 |
| 79 | 660 | 32.3 | 24.70 | 13.3 | >17.0 |
| 80 | 660 | 31.5 | 30.90 | 16.7 | >17.0 |
| 85 | 780 | 29.1 | 121.2 | 65.5 | 16.3 |
| 87 | 780 | 29.9 | 71.39 | 35.8 | 23.8 |
| 88 | 780 | 29.1 | 59.66 | 32.2 | 25.8 |

reduction of zinc oxide by hydrogen,1-3) a deposit consisting of zinc oxide and zinc metal was observed on the cooler part of the reaction vessel. The following three reasons for zinc oxide film may be suggested.

1) The sublimed zinc oxide condenses on the cooler part of the vessel before it is reduced by hydrogen.

2) Zinc oxide decomposes into zinc vapor and oxygen, and then the reverse reaction takes place to produce the zinc oxide.

3) Zinc oxide is produced by the reaction of zinc vapor and gaseous water.

In this study of the decomposition, the zinc oxide film was not produced on the cooler part of the reduction tube. Therefore, reasons 1 and 2 above have been found to be invalid. Reason 3 was also supported by the additional observation that hydrogen, which is produced by the reaction[*4] of water and zinc, will contribute to the reduction of zinc oxide again. Table III shows the weight loss by the pretreatment of zinc oxide placed in the basket, the initial hydrogen pressure for the pretreatment, and the hydrogen pressure cooresponding to the weight loss (each value being converted at 0°C). In all the runs (except No. 79 and 80 in Table III), the hydrogen pressure corresponding to the weight loss caused by the reduction of hydrogen[*6] is found to be higher than the initial hydrogen pressure. Consequently, the hydrogen reproduced by reason 3 is suggested to reduce further the zinc oxide placed in the basket.

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[*4] Since the equilibrium constant $K$ of the reaction: $ZnO(s)+H_2 \rightleftarrows Zn(g)+H_2O(g)$ is very small[*5], the vapor pressure of wate is very low. Consequently, the reduction rate can be followed by measuring the pressure in the system as reported in Ref. 1.

[*5] $K=1.1\times10^{-3}$, $P_{H_2O}=0.85$ mmHg at 1 atm. $H_2$, 723°C
$K=2.4\times10^{-3}$, $P_{H_2O}=1.85$ mmHg at 1 atm. $H_2$, 823°C
from G. B. Taylor and H. W. Starkweather, *J. Am. Chem. Soc.*, 52, 2314 (1930).

[*6] In this case, the decomposed amount of zinc oxide is much less than the amount of zinc oxide reduced by hydrogen.