# *Studies on the Reduction Processes of Germanium Dioxide by Hydrogen*

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## Introduction

Two methods of obtaining a metallic germanium are known, namely the one is by the reduction of germanium tetrachloride with metallic zinc in gas phase[1] which is known as the duPont process, and the other by the reduction of germanium dioxide by hydrogen[1,2]. The latter process is superior to the former for obtaining a highly pure germanium because its product is less contaminated with impurities.

In general, the reaction between metal oxide and hydrogen have been well studied by many workers, but as there have been few papers on the reduction of germanium dioxide, we have made a study of this problem.

## Experimental Procedure

A study of the rate of the reduction of germanium dioxide may be pursued by measuring the weight decrease of the oxide in hydrogen at intervals of the reduction. The measuring apparatus consists of a vertical quartz tube and a quartz spring balance suspended at one end of a rod in the tube. The rod can be moved vertically to bring a sample dish to the hot zone of the tube kept at a desired temperature. The decrease in weight of the oxide can be estimated by reading the shrinkage of the spring by means of a cathetometer.

The sensitivity of the spring balance is calibrated by weighing the weight of 0 to 500 mg. to determine the weight-elongation relationship. From the experiment, it was found that the relationship is shown by

$$W \text{ mg.} = 1.53 \times 10^2 \times l \text{ cm.}$$

Germanium dioxide has three crystal structures, i.e., tetragonal rutile type, hexagonal $\alpha$-quartz type, and amorphous[3]. It was desirable to ex-

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[1] H.C. Torrey and C.A. Whitmer, "Crystal Rectifiers", McGrow-Hill (1948), Chap. 10.

[2] A.P. Thompson and J.R. Musgrave, *J. of Metals*, 4, 1132 (1952).

[3] Otto H. Johnson, *Chem. Rev.*, **51**, 431 (1952).

amine the reduction process on each of the above three crystal types, but unfortunately tetragonal rutile type crystal could be prepared by neither heat treatment nor any other processes which might be expected. The samples are highly pure germanium dioxide made by "Otavi Meinen und Eisenbarn Gesellschaft", Germany, and the crystal structure was hexagonal α-quartz type by an X-Ray analysis.

The amorphous type structure was prepared by fusing the crystalline germanium dioxide.

## Experimental Results

A known weight of hexagonal α-quartz type germanium dioxide was placed on the sample dish and the weight decrease was measured as the temperature increased at a constant velocity of 5.3°/min. in the hydrogen stream. Curves I and II in Fig. 1 show the temperature-time and weight decrease-time relationship respectively. These curves show that the reduction occurs at about 450°C.

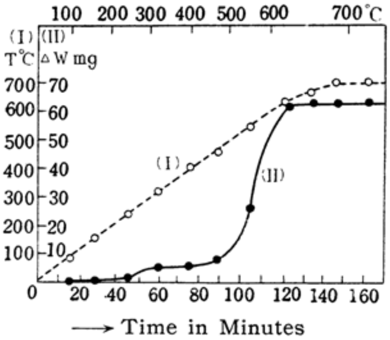

Fig. 1. Curve (I) Temperature-Time relationship. Curve (II) Weight decrease-Time relationship.

**Hexagonal α-quartz Type Germanium Dioxide.**—About 180 mg. of hexagonal α-quartz type germanium dioxide was placed in the apparatus and the absorbed water was removed by heating at 300°C for about thirty minutes in the stream of dry hydrogen, then the sample dish was pulled up above the heating zone and then it was pushed down to the heating zone of the furnace kept at a desired temperature. The reaction temperatures which we studied were 450, 500 and 600°C and the flow velocity of hydrogen was varied from 50 cc./min. to 210 cc./min. The results are shown in Fig. 2.

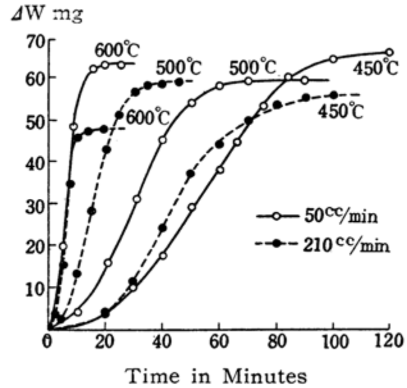

Fig. 2. Reaction curves with different temperature and hydrogen flow rate. (crystalline germanium dioxide)

**Amorphous Germanium Dioxide.**—*Preparation of Amorphous Germanium Dioxide.*—The hexagonal type germanium dioxide used in the previous experiment was melted at 1300°C and a glossy transparent mass was obtained which was shown to be amorphous by the X-ray analysis. This mass was crushed to the same size as the crystalline sample. The reaction curves are shown in Fig. 3. In the case of the amorphous sample the reaction type was represented by the first order reaction and showed no distinct induction period.

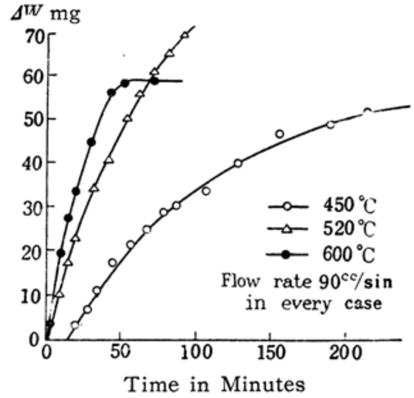

Fig. 3. Reaction curves with different temperatures. (amorphous germanium dioxide)

## Consideration of the Results of the Experiment

**a) Hexagonal α-quartz Type Germanium Dioxide.**—This reaction has an autocatalytic phenomena as shown in Fig. 2 and the reaction velocity of this kind is ordinarily shown as follows[4].

$$\mathrm{d}x/\mathrm{d}t = Kx^n(a-x) \qquad (1)$$

$x$: product at a time $t$. $a$: initial amount.
$K$: const. $n$: const.

The exponential factor $n$ in (1) is a topochemical factor and is varied by the surface condition of solid phase and by the number of the reaction centers on the surface of the crystal, and can be determined by the following method.

Eq. (1) is differentiated by $t$.

$$\mathrm{d}^2x/\mathrm{d}t^2 = K\{(nx^{(n-1)}(a-x) - x^n\}$$

at the maximum of the reaction velocity curve

$$\mathrm{d}^2x/\mathrm{d}t^2 = 0 \text{ then, } nx^{(n-1)}(a-x) - x^n = 0$$

as $x \neq 0$ during the reaction,

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[4] K. Kawakita, *Proc. of Phys. Chem. Japan*, **14**, 79 (1940).

$$x=an/(n+1) \qquad (2)$$

As the value of $x$ at the maximum of $dx/dt$ can be obtained from the experiment, the value of $n$ can be determined. Relations between $dx/dt$ and $t$ can be obtained graphically from Fig. 2 and are shown in Fig. 4. Since time $t$ at the maximum of $dx/dt$ is determined from this figure, the corresponding value of $x$ is found from Fig. 2. On the other hand, $x$ at the completion of reaction, which equals $a$, is known from the experiment. The corresponding values are calculated by inserting these values in Eq. (2).

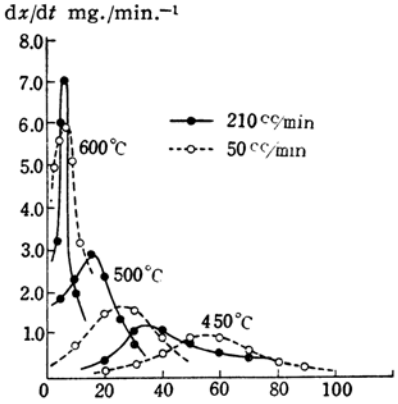

Fig. 4. Reaction velocity and time relationship at different temperatures.

The values of $n$ vary indefinitely from 0.4 to 2.2 corresponding to the reaction temperature and hydrogen flow rates. This is caused by the formation of reaction nuclei and their rate of propagation, which are concerned with the formation and evaporation of germanium monoxide. The faster the hydrogen flow rate, the more the evaporation of monoxide becomes appreciable as shown in Table I and the $n$ values become more irregular. But in the case of 50 cc./min. because the formation of monoxide is limited, the $n$ values become constant, independent of temperature and may be taken as unity as shown in Table II.

TABLE I

DEVIATION OF WEIGHT DECREASE FROM CALCULATED VALUE

| Temp. °C | Flow Rate cc./min. | Weight Decrease $\Delta W$ Calculated mg. | Weight Decrease $\Delta W$ Found mg. | Difference mg. | Percent of Deviation against Calculated Value |
|---|---|---|---|---|---|
| 450 | 50 | 71.2 | 75.0 | −3.8 | −5.3 |
| | 210 | 54.7 | 60.0 | −5.2 | −9.5 |
| | 50 | 62.2 | 64.0 | −1.8 | −2.8 |
| 600 | 90 | 59.9 | 64.0 | −4.1 | −6.8 |
| | 210 | 45.7 | 52.0 | −6.3 | −13.7 |

Then Eq. (1) becomes rather simple and is shown by:

$$dx/dt=Kx(a-x).$$

Dissolving this differential equation

$$\ln x/(a-x)=aKt+C$$

when $\ln x/(a-x)$ is plotted against $t$, the inclination of the curve shows $aK$, from which $K$ is obtained as shown in Fig. 5 and listed in Table II.

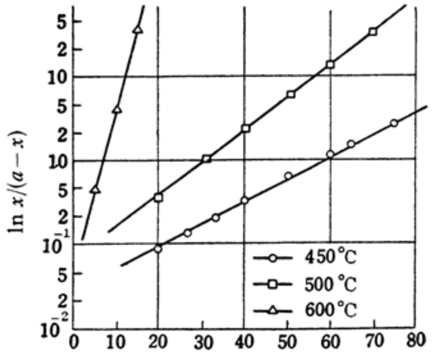

Fig. 5. Determination of reaction velocity constant $k$ at flow velocity 50 cc/min.

From these data, the apparent activation energy is calculated and is found to be 18.3 kcal./mol. for the gas flowing velocity of 50 cc./min. as shown in Fig. 7.

TABLE II

$n$ AND $K$ VALUES CORRESPONDING WITH DIFFERENT TEMPERATURES AT FLOW RATE OF 50 cc./min.

| Reaction Temp. °C | $n$ | $K$ (min.⁻¹ mol.⁻¹) |
|---|---|---|
| 450 | 0.80 | 11.7 |
| 500 | 1.22 | 21.7 |
| 600 | 1.13 | 105 |

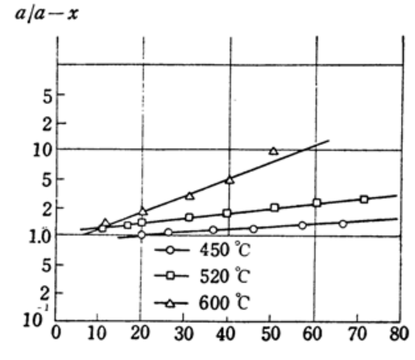

Fig. 6. Determination of reaction velocity constant $k$ with different temperatures (amorphous germanium dioxide)

**b) Reduction of Amorphous Germanium Dioxide.**—In the case of crystalline germanium dioxide, the maximum of d$x$/d$t$ exists at about one third of the whole reaction process, but in this case, the reaction velocity is represented by a rate equation of ordinary first order reaction. If d$x$/d$t$ is plotted against $t$ it is clear that it is corresponding to $n=0$ in Eq. (1) as is shown in Fig. 6.

In this case, the reaction equation is represented by

$$dx/dt=K(a-x) \text{ then, } \ln a/(a-x)=Kt.$$

From this equation we can obtain the values of $K$.

$$K\ (450°C)=0.0096\ \text{min.}^{-1}$$
$$K\ (520°C)=0.016\ \text{min.}^{-1}$$
$$K\ (600°C)=0.604\ \text{min.}^{-1}$$

From these values the apparent activation energy is shown to be 15.2 kcal./mol.

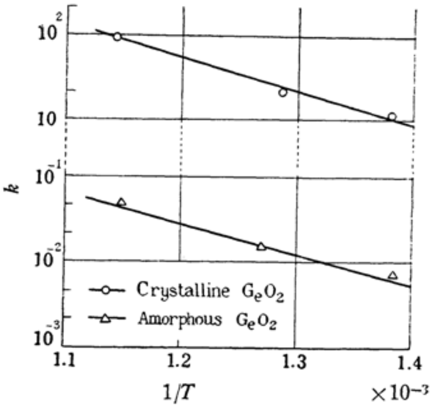

Fig. 7. Determination of apparent activation energy of reduction of crystalline and amorphous germanium dioxides.

The gas-solid reactions discussed above, are ordinarily considered to follow the following five steps and the slowest process among them determines the reaction velocity[5].

(1) Collision of hydrogen gas on the surface of germanium dioxide.

(2) Adsorption of hydrogen gas.

(3) Reaction on the surface.

(4) Desorption of products from the surface.

(5) Diffusion of products from surface to the gas phase.

Since the reaction process of (1) and (5) are diffusional ones, the observed activation energy must be very small, and judging from the observed activation energy, these processes will not play a predominant rôle in the whole reaction.

The process of (3) is rather complicated and the following four reactions must be considered[6,7,8,9].

(1) $GeO_2+2H_2=Ge+2H_2O$
(2) $GeO_2+H_2=GeO+H_2O$
(3) $GeO+H_2=Ge+H_2O$
(4) $Ge+GeO_2=2GeO$

The observed reaction rate will be the superposition of these four reactions.

Reaction (1) is the most common reduction reaction of metal oxide and the reactions (2) and (3) seem to be the transition steps of the reduction process. In the case of germanium dioxide, reactions of (2) and (3) can not be neglected, because the observed weight decrease in the reduction is greater than the calculated values from the initially weighed germanium dioxide according to reaction (1). This discrepancy can not be explained without considering the evaporation of germanium monoxide produced by the reaction (2). For this reason the formation of germanium monoxide will be genuine, but the period during which the evaporation of this material occurs is limited to the beginning of the reaction, and since the surface of the grain of germanium oxide is immediately covered with germanium metal by the reaction (3), further evaporation of monoxide is prevented by the germanium metal film. On the contrary, in the case of amorphous germanium dioxide, no more weight decrease is observed than that which was calculated and this fact seems to be owing to the difficulty of reaction (2) because of the different surface condition, and the fact that the reaction (1) will be the predominant process.

It is clear from Eq. 1 that the greater the value of $n$, the longer the induction period which should be observed, also that the value of $n$ reprsents the surface conditions and the rate of propagation of reaction nuclei on the surface. The two different reaction types described above on crystalline and amorphous germanium oxides with hydrogen will be explained considering this factor $n$. This difference seemed to be caused by the differences of the surface conditions; namely that the crystalline germanium dioxide has many crystal edges which act as active centers. At the beginning, the reaction occurs from such points and the reaction propagates to other parts of the surface and thus the main reaction occurs after some induction period. During the induction period, the reaction (2)

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[5] N. F. Mott and R. W. Gurney, "Electronic processes in Ionic Crystals", Oxford at the Clarendon Press (1950), Chap. 8.

[6] Les. Brawer, *Chem. Rev.*, **52**, 1 (1953).

[7] R. B. Bernstein and D. Cubicciotti, *J. Am. Chem. Soc.*, **73**, 4112 (1951).

[8] Meller. "Comprehensive treatise in Inorganic and Physical Chemistry", Vol. 7, p. 265.

[9] W. Bues u. H. V. Wartenberg, *Z. f. anorg. u. allgem. Chem.*, **266**, 281 (1951).

become appreciable. On the other hand, the surface of the amorphous germanium dioxide has a more uniform character point to point and has same chances of starting a reaction, so that a sufficient number of nuclei form at once at the beginning of the reaction and the main reaction occurs without occuring reaction (2).

Reaction (4) occurs on the contact surface during the reduction process between the germanium produced and the remaining germanium dioxide. But since this is solid-solid reaction, its velocity is small enough to be neglected in this case.

## Conclusion

The reduction process of germanium dioxide and the hydrogen system were studied for the crystalline and amorphous germanium dioxides. In the case of the crystalline dioxide, the reduction process had autocatalytic action and its velocity was represented by the formula $dx/dt=Kx(a-x)$. On the other hand, in the case of amorphous germanium dioxide the process showed no distinct induction period and followed the first order reaction type. This difference seemed to be owing to the differences of surface conditions of crystalline and amorphous germanium dioxides and was well represented by the value of topochemical factor $n$ in Eq. (1).

The activation energies of reduction process of crystalline and amorphous germanium dioxide were found to be 18.3 kcal./mol. and 15.2 kcal./mol. respectively. This reduction process seemed to be rather complicated, and we must consider some reactions belonging to the $GeO_2$-$GeO$-$Ge$ system, but we treated the reaction under the assumption that the $GeO_2+2H_2=Ge+2H_2O$ was the main process as the first order approximation.

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