*Magnetochemical Investigation on Thermal Decomposition of Silver Oxide**

By Shōtaro TOBISAWA

(Received April 20, 1959)

The thermal decomposition of silver oxide in oxygen under atmospheric pressure, was investigated by Lewis[1], and was found to follow the equation $dx/dt = kx(1-x)$, where x is the fraction of silver produced. His result was confirmed by Hood and Murphy[2]. On the other hand, it was found by Garner and Reeves[3] that the decomposition in vacuo did not hold Lewis' equation but gave the equation $\sqrt[3]{p} = kt - C$ for the initial part of the decomposition, where p is the pressure of oxygen evolved with the progress of decomposition. The rates of thermal decompositions of the type A (solid)→B (solid) + C (gas) have been interpreted in terms of the formation and growth of nuclei by many investigators[4]. It may, therefore, be considered that the formation and growth of nuclei depend on the origins of silver oxide and also on the experimental conditions under which the decompositions are carried out.

All the previous work on the kinetics of the decomposition of silver oxide had been carried out by measuring the pressures of the oxygen gas evolved. Although this pressure-method is the most common for kinetic measurements of solid decomposition, it is undesirable for an accurate

---

* Presented before the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.

[1] G. N. Lewis, *Z. physik. Chem.*, **52**, 310 (1905); *J. Am. Chem. Soc.*, **28**, 139 (1906).

[2] G. C. Hood and G. W. Murphy, *J. Chem. Educ.*, **26**, 169 (1949).

[3] W. E. Garner and L. W. Reeves, *Trans. Faraday Soc.*, **50**, 254 (1954).

[4] W. E. Garner, "Chemistry of the Solid State", Butterworths Scientific Publications, London (1955), p. 213.

measurement of the reaction rate on account of the existence of a considerable space from a reaction chamber to a piece of equipment for pressure measurement. The present author has constructed a recording magnetic balance of Hirone's type[5] with many improvements. This balance has been used continuously with very high sensitivity for many hours and as a thermal balance without magnetic field. By using it as the magnetic balance, the kinetics of the decomposition of silver oxide can be investigated by the measurement of change in magnetic susceptibility, due to the oxygen gas evolved. By using it as the thermal balance, the kinetics can be studied by the measurement of the loss in weight with the progress of decomposition. In the case of magnetic balance, silver oxide was charged into a small bulb and was sealed after being evacuated. The pressure of oxygen in contact with the undecomposed silver oxide became higher as the reaction proceeded. However, in the case of thermal balance, the sample was packed in an open bulb and the decomposition was carried out under costant reduced pressure.

The purpose of the present work is to show the results of kinetic measurements obtained under the above two experimental conditions, together with the measurements of the magnetic susceptibility of silver oxide and of metallic silver produced by the complete decomposition of silver oxide.

Experimental

Materials.—In the present work, four samples were used. Samples A and B were guaranteed reagents of the Kanto Chemical Co. Ltd., and of Kahlbaum, respectively. Silver carbonate contained in the above samples could easily be converted into silver oxide by heating under vacuum according to the equation, $Ag_2CO_3=Ag_2O+CO_2$. Samples C and D were obtained by heating the samples A and B at 250°C for an hour under the vacuum of 10^{-5} mmHg, respectively. This treatment was carried out before each measurement.

Apparatus.—The magnetic balance was operated by the Faraday method, because this method is convenient to measure the change in magnetic susceptibility of the reaction system at high temperatures. As indicated in Fig. 1a, a small bulb of fused quartz was suspended in the position giving the maximum value of $H\cdot\partial H/\partial x$, which was determined from Fig. 2. Here H is the field strength and $\partial H/\partial x$ is its gradient along the vertical line passing through the center of the gap between the pole pieces. The bulb 4 mm. high could be held within the error of about one per cent of the maximum value of $H\cdot\partial H/\partial x$.

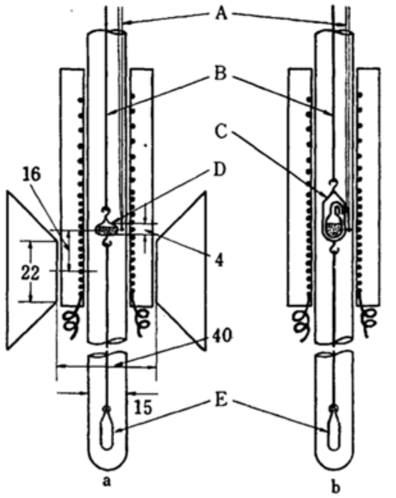

Fig. 1. Positions of sample bulbs in the magnetic balance a and the thermal balance b, showing in mm. unit.
A: $P_t-P_t\cdot Rh$ (13%) thermocouple (0.3 mm. in diameter)
B: Fused quartz rod (1.2 mm. in diameter)
C: Fused quartz basket
D: Fused quartz bulb (ca. 0.10 cc. in volume)
E: Weight of copper

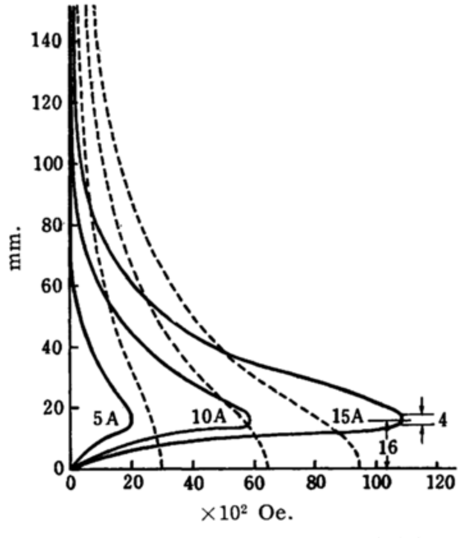

Fig. 2. Diagram of H (---) and $H\cdot\partial H/\partial x$ (—). The origin is the middle point between two centers of pole pieces.

The recorder used here could plot three values, the magnetic forces acting on a bulb containing a sample, the temperatures of a sample, and the currents supplied to an electromagnet, on a chart at regular intervals of 15 sec., respectively. The

---

[5] T. Hirone, S. Maeda and N. Tuya, *Rev. Sci. Instr.*, **25**, 516 (1954); *Sci. Rep. Res. Inst. Tohoku Univ.*, **A6**, 67 (1954).

magnetic force could be indicated by the current which was proportional to the force, and was calibrated by the magnetic susceptibility of the empty bulb of fused quartz in each measurement. The susceptibility of the fused quartz was -0.46×10^{-6} units per gram[6], and it scarcely depended on temperature at all. The full scale of the recording chart was 10 milliamp. The apparatus was modulated to make it possible to indicate changes of 0.1 milliamp. corresponding to -0.58×10^{-6} e. m. u. in magnetic susceptibility, on a recording chart. The temperature scale of the recorder was calibrated by using the freezing points of four Kahlbaum reagents: tin, zinc, antimonium and silver. Each measurement was carried out in the constant magnetic field of 8250 Oersteds.

When the balance was used as a thermal balance, the recorder could give the losses in weight and the corresponding temperatures of the sample. One millimeter on the recording chart corresponded to 0.015 mg. A sample was packed in the bulb shown in Fig. 1b and was thermally decomposed under the constant pressure of 50 mmHg.

Results

Decomposition Temperature.—The decomposition temperature of silver oxide was determined by the above two methods by raising the temperature at constant rate, 200°C per hour. The results obtained by means of the thermal balance, are shown in Figs. 3 (for the samples A and B) and 4 (for the samples C and D). The first losses in weight for the samples A and B occur at 148°C and the second ones at 372°C. The first losses in weight for the samples C and D are negligibly small and the second ones occur at 354°C.

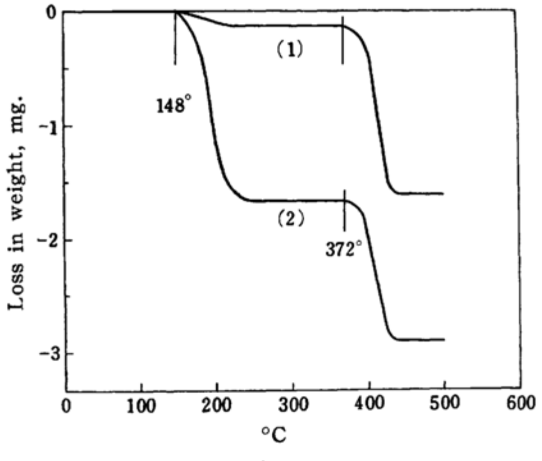

Fig. 3. Loss in weight-temperature curves. (1) Sample A (wt. 20.0 mg.); (2) Sample B (wt. 20.0 mg.).

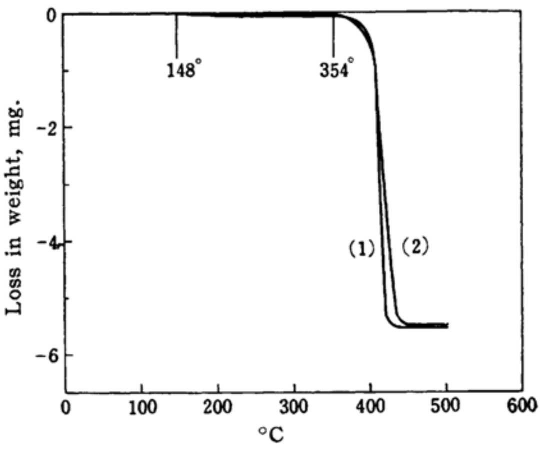

Fig. 4. Loss in weight-temperature curves. (1) Sample C (wt. 80.0 mg.); (2) Sample D (wt. 80.0 mg.).

The curves of magnetic susceptibility against temperature for the reaction system are given in Fig. 5. The sample used in each measurement was about 50 mg. and was sealed in a bulb after being evacuated for several hours under a vacuum of 10^{-5} mmHg. The curves for the samples A and B deflect obviously toward the paramagnetic sides owing to the paramagnetism of oxygen gas evolved at the decomposition at 372°C. The curve of the sample C shown in a broken line in Fig. 5, indicates that the silver oxide decomposes at 354°C. All the samples treated with heating under evacuation, decomposed at the same temperature. It is apparent from the magnetic measurements that the first losses at 148°C are not due to oxygen gas.

Moisture had no responsibility for the loss in weight at 148°C, because each sample was freed from moisture by evacuation. A preliminary qualitative analysis of carbon dioxide with barium hydroxide solution, showed that the silver oxide was partly converted into silver carbonate. The first loss in weight at 148°C in Fig. 3 is, therefore, due to the thermal decomposition of silver carbonate contained in the sample. The negligibly small amount of loss in weight in Fig. 4 can be ascribed to the decomposition of silver carbonate which had been formed by combining the silver oxide with carbon dioxide in air, within two hours or so before the beginning of the measurement. From the above experimental results, it

---

6) S. S. Bhatnagar and K. N. Mathur, "Physical Principles and Applications of Magnetochemistry", Macmillan & Co., Ltd., London (1935), p. 354.

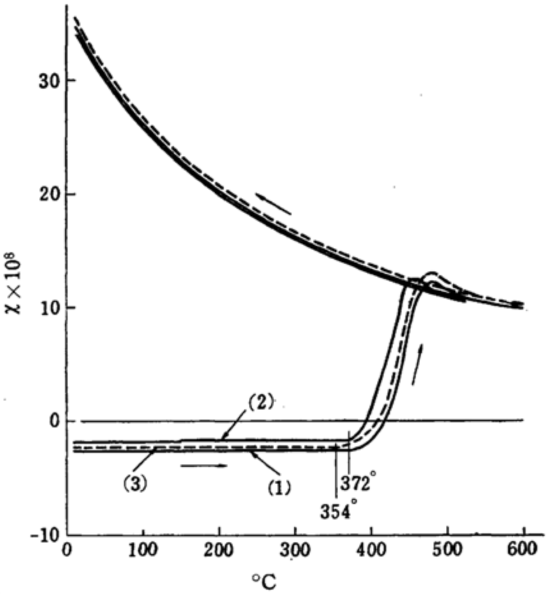

Fig. 5. Magnetic susceptibility-temperature curves.
(1) Sample A (wt. 50.0 mg.); (2) Sample B (wt. 50.0 mg.); (3) Sample C (wt. 49.3 mg.).

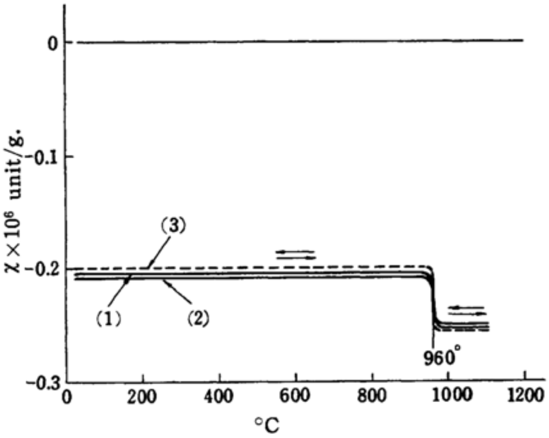

Fig. 6. Magnetic susceptibility-temperature curves.
(1) Metallic silver obtained from sample A;
(2) Metallic silver obtained from sample B;
(3) Kahlbaum silver metal.

is found that the decomposition temperature of silver oxide is apparently affected by silver carbonate contained in the oxide.

Magnetic Susceptibilities of Metallic Silver and Silver Oxide.—In order to know whether paramagnetic or ferromagnetic impurity was present in the samples A and B, the magnetic susceptibilities of metallic silver obtained by the complete decomposition, were measured. In addition, the susceptibility of Kahlbaum silver was measured. The curves obtained are shown in Fig. 6. The magnetic susceptibilities of metallic silver produced by the decomposition of the samples A and B were -0.21×10^{-6} units per gram and that of Kahlbaum silver was -0.20×10^{-6} units per gram at room temperature. The curves in Fig. 6 show that the magnetic susceptibility of metallic silver is independent of temperature below 1100°C, except for a slight increase at the melting point. These facts indicate that no magnetic impurities are involved in either sample, and that the metallic silver is normally diamagnetic and takes no supercooling. The curve obtained by Honda7) shows that the magnetic susceptibility of metallic silver increases with increasing temperature. On the other hand, Selwood8) mentioned that the magnetic susceptibility of metallic silver was almost independent of temperature.

The magnetic susceptibility of silver oxide from which carbon dioxide was removed, was -0.48×10^{-6} units per gram at room temperature. It was less than the value of -0.58×10^{-6} units per gram9), reported previously.

Kinetic Measurements.—(1) Photo. 1 is an example of the chart obtained by means of the thermal balance, showing the losses in weight and the corresponding temperatures. In each measurement a required constant temperature could be obtained within a few minutes. Curves of the loss in weight (x) against time (t) at 380, 390, 400 and 410°C for 80 mg. of the sample D are shown in Fig. 7. It was ascertained that the rate of decomposition held neither

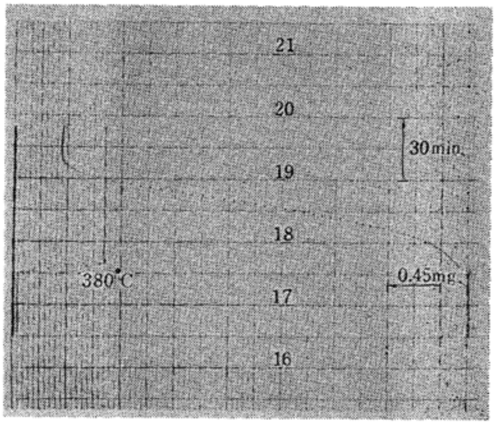

Photo. 1. An example of chart obtained by means of the thermal balance.

---

7) K. Honda, *Ann. Physik*, **32**, 1027 (1910).
8) P. W. Selwood, "Magnetochemistry", 2nd Ed., Interscience Publishers, New York (1956), p. 362.
9) See reference 8, p. 214.

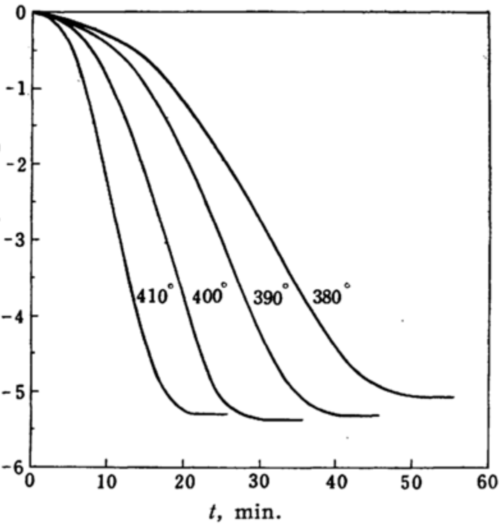

Fig. 7. Loss in weight-time curves for sample D.

Lewis' equation nor that of Prout-Tompkins[10]. The validity of the equation, $\sqrt[3]{x}=kt-C$, presented by Garner et al. for the initial part of the decomposition, was examined by plotting $\sqrt[3]{x}$ against t in Fig. 8. The values of k were obtained from the figure. The activation energy of 29.4 kcal. per mole was estimated from the slope of line which was obtained by plotting $\log k$ against $1/T$. The activation energies reported for this decomposition are as follows: 31.8[1] 35~36[11], 10.5[12] and 45.6~46.2 kcal. per mole[2].

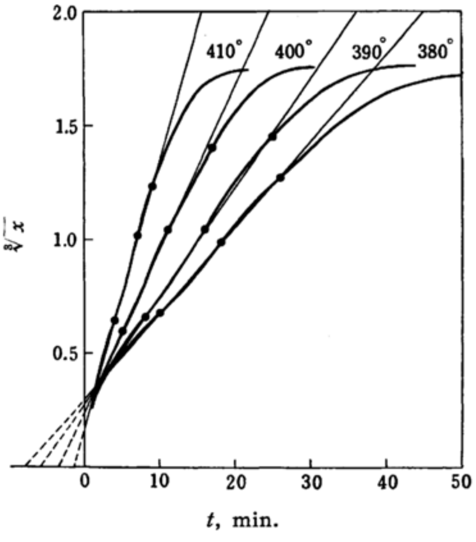

Fig. 8. Curves obtained according to Garner's equation.
●: Inflection point.

(2) Examining in detail the plots in Fig. 8, it is seen that these plots show the curves with several inflection points. The plots of dx/dt against t are shown in Fig. 9. The time was calculated by setting zero time at the point where the half of

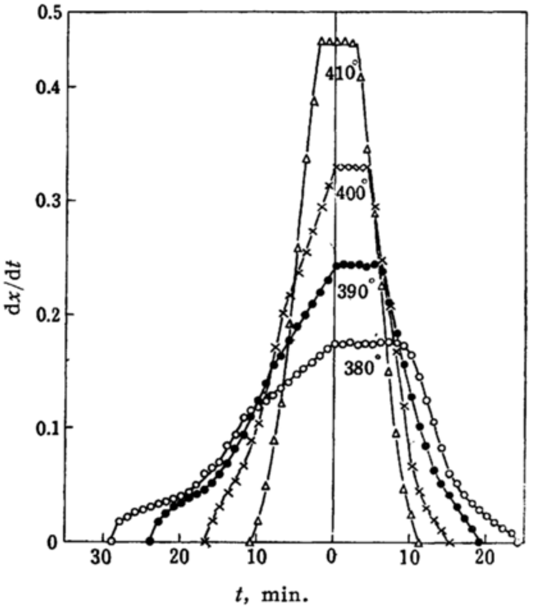

Fig. 9. Plots of dx/dt against time for sample D.

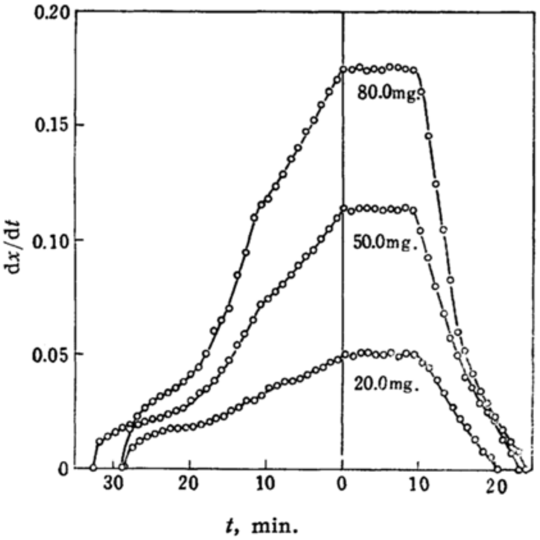

Fig. 10. Plots of dx/dt against time for sample D at 380°C.

---

10) E. G. Prout and F. C. Tompkins, *Trans. Faraday Soc.*, **40**, 488 (1944).

11) A. F. Benton and L. C. Drake, *J. Am. Chem. Soc.*, **28**, 139 (1906).

12) M. M. Pavlyuchenko and E. Gurevich, *Zhur. Obshchei Khim.*, **21**, 467 (1951); *Chem. Abstr.*, **45**, 5006 (1951).

TABLE I. VALUES FOR α AND β

Stage	380°C		390°C		400°C		410°C	
	α	β	α	β	α	β	α	β
1	1.72×10^{-2}	0.39	1.74×10^{-2}	0.52	1.75×10^{-2}	0.83	1.79×10^{-2}	1.44
2	0.09×10^{-2}	1.65	0.16×10^{-2}	1.65	0.42×10^{-2}	1.65	1.32×10^{-2}	1.65
3	0.81×10^{-2}	0.91	0.79×10^{-2}	1.09	2.29×10^{-2}	0.95	3.76×10^{-2}	1.13
4	1.77×10^{-1}	0	2.45×10^{-1}	0	3.30×10^{-1}	0	4.42×10^{-1}	0
5	1.44×10^{12}	− 7.50	3.69×10^{11}	− 7.50	1.61×10^{7}	− 5.00	6.63×10^{4}	− 3.64
6	1.35×10^{23}	−14.14	2.95×10^{28}	−18.14	1.15×10^{20}	−14.14	1.95×10^{16}	−12.00

silver oxide was decomposed. All the curves in Fig. 9 indicate that the rate of decomposition varies discontinuously, and that the period constant rate is recognized in the curve. The plots of dx/dt against t obtained for 20, 50 and 80 mg. of the sample D at the same temperature, 380°C, are given in Fig. 10. The figure shows that the period of constant rate is not affected by the difference in weight of sample. By plotting $\log dx/dt$ against $\log t$ in Fig. 11, the breaking points become very distinctive. The curve for the whole course of the decomposition can be divided into several linear parts. Each linear part can be represented by the equation $\log dx/dt = \log \alpha + \beta \log t$ or $dx/dt = \alpha t^{\beta}$. The estimated values for α and β from Fig. 11 are listed in Table I. The value of α depends on temperature except in the case of the first stage, and β also varies with temperature except in the cases of the certain stages.

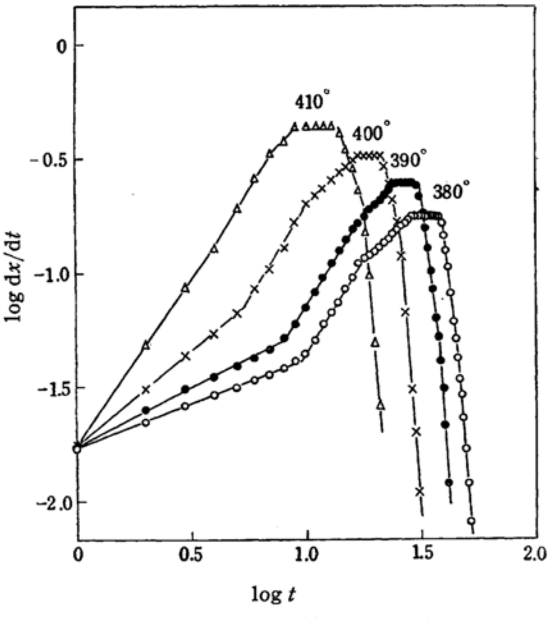

Fig. 11. Plots of $\log dx/dt$ against $\log t$ for sample D.

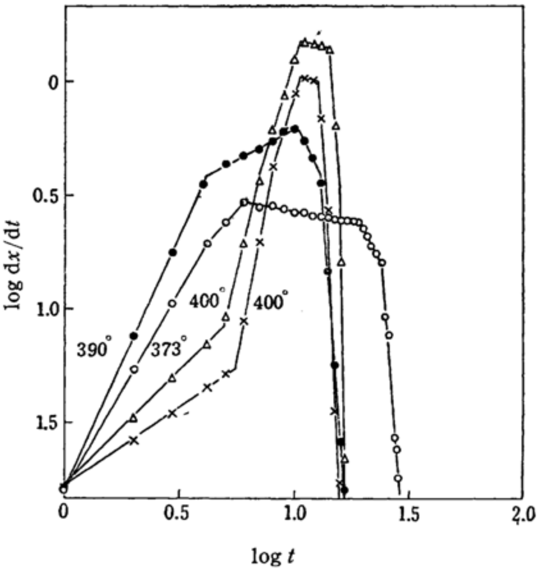

Fig. 12. Plots of $\log dx/dt$ against $\log t$ for sample C (wt. 80.0 mg.).
—△—: wt. 150.0 mg.

As indicated in Fig. 12, the curves of $\log dx/dt$ against $\log t$ for the sample C can also be divided into several linear parts for the whole course of the decomposition, as found in the case of sample D.

(3) In the magnetic measurements, the balance was modulated to make it possible to indicate only the change of paramagnetic nature with very high sensitivity. Thus, the small values of diamagnetic susceptibilities of silver oxide and of metallic silver produced by decomposition could be neglected. To determine the weight of oxygen gas evolved in the bulb, the value of paramagnetic susceptibility obtained under a constant temperature was compared with the theoretical value calculated from Van Vleck's equation[13]. In each experiment, the estimated weight of oxygen gas evolved in the bulb at the end of the experiment, was in good agreement with the difference between an initial

---

[13] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities", Oxford University Press, London (1932), p. 266.

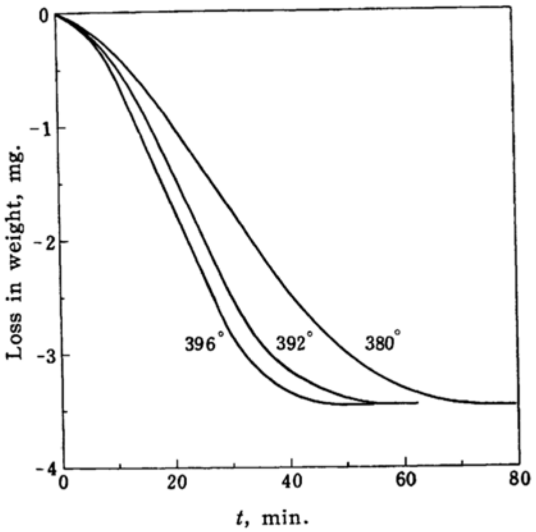

Fig. 13. Loss in weight-time curves for sample D.

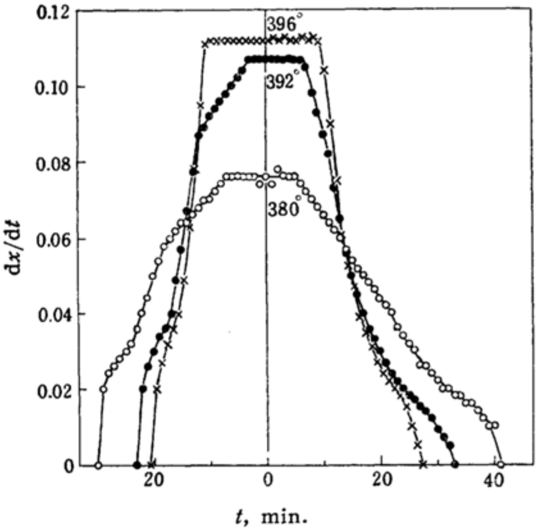

Fig. 14. Plots of dx/dt against time for sample D.

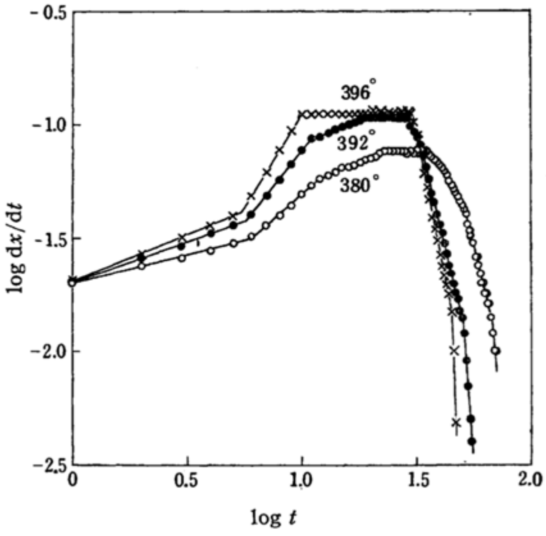

Fig. 15. Plots of log dx/dt against log t for sample D.

weight of bulb containing a sample and the one containing the residue obtained by removing the oxygen gas evolved in the bulb. In every measurement, the sample used was about 50 mg., and the temperature of the sample was controlled similarly as in the case of the thermal balance. The curves of x against t for the sample D at 380, 392 and 396°C, and the curves of dx/dt against t are shown in Figs. 13 and 14, respectively. The rate of decomposition is represented by the curves with the period of constant rate, as found in the case of the thermal balance. From the plots of log dx/dt against log t in Fig. 15, it is apparent that the curves can be divided into the several linear parts. The equation $dx/dt=\alpha' t^{\beta'}$ can, therefore, be applied to the result obtained under the condition in which the sample is decomposed in contact with the evolved gas. The estimated values for α' and β' are given in Table II. The value of α' depends on temperature except for the first stage, β' also varies with temperature except for certain stages. These features are similar to those found in the

TABLE II. VALUES FOR α' AND β'

Stage	380°C		392°C		396°C	
	α'	β'	α'	β'	α'	β'
1	2.00×10^{-2}	0.26	2.03×10^{-2}	0.35	2.04×10^{-2}	0.42
2	0.65×10^{-2}	0.88	0.42×10^{-2}	1.26	$\left[0.29\times10^{-2}\right.$	$\left[1.61\right.$
3	2.04×10^{-2}	0.42	3.80×10^{-2}	0.34	$\left[0.29\times10^{-2}\right.$	$\left[1.61\right.$
4	0.76×10^{-1}	0	1.07×10^{-1}	0	1.12×10^{-1}	0
5	4.10	−1.12	7.95×10	−1.95	$\left[3.93\times10^{7}\right.$	$\left[-5.09\right.$
6	9.04×10	−1.95	$\left[3.76\times10^{6}\right.$	$\left[-4.35\right.$	3.93×10^{7}	−5.09
7	4.34×10^{6}	−4.10	$\left[3.76\times10^{6}\right.$	$\left[-4.35\right.$	$\left[3.93\times10^{7}\right.$	$\left[-5.09\right.$
8	5.01×10^{18}	−10.70	1.10×10^{22}	−13.40	3.38×10^{39}	−24.40

experimental results obtained by the thermal balance.

It was noteworthy that several breaking points appear on the curve in each constant temperature, in spite of the entirely different origins and experimental conditions. This fact shows that fresh potential sites at which nuclei can be formed, are created at intervals as the reaction proceeds. It may be considered that the formation of fresh potential sites is due to a strain which is induced by the reaction product at a surrounding undecomposed portion when the reaction product grows to a certain magnitude.

Summary

(1) It was found, by means of the thermal and magnetic balance, that the decomposition temperatures of silver oxide and of silver oxide containing silver carbonate are 354 and 372°C, respectively.

(2) The magnetic susceptibilities of metallic silver obtained by the decomposition and of silver oxide are -0.21×10^{-6} and -0.48×10^{-6} units per gram at room temperature, respectively. Metallic silver is normally diamagnetic from room temperature to 1100°C.

(3) Under the present experimental conditions, the rate of decomposition is represented by the equation $dx/dt=a_it^{b_i}$ for the whole course of the decomposition, where i is the subscript for each stage, and generally both a_i and b_i depend on the temperature. It is considered that nuclei are created at intervals as the reaction proceeds.

The author wishes to express his sincere gratitude to Professor Y. Nomura for his suggestions regarding this work and for his helpful advice during the course of the construction of the apparatus.

Department of Chemistry
Defense Academy
Yokosuka