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# Kinetics of the Reaction at the Silver–Silver Sulfide Interface

Junichiro Mizusaki, Kazuo Fueki, and Takashi Mukaibo

*Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

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The reaction rate at the Ag/$Ag_2S$ interface was determined as a function of silver activity of $Ag_2S$ in the temperature range 215—400 °C. The silver activity of $Ag_2S$ at the interface was measured electrochemically by means of an Ag/AgI electrode. The reaction rate was measured by the direct sulfurization method (Wagner's pellet method) and by Rickert's method using Ag/AgI/$Ag_2S$/Pt cell. The rates obtained by the two methods were in good agreement. It was found that this is a first-order reaction with respect to the activity of sulfur in $Ag_2S$ and that the rate equation is given by

$$v = 1.0\times10^4\ \{\exp(-18000/RT)\}a_S\ \mathrm{eqv\ cm^{-2}\,s^{-1}} \qquad \text{(i)}$$

The following reaction mechanism prevails at the interface.

$$2\mathrm{Ag(Ag)} + \mathrm{S(Ag_2S)} \longrightarrow 2\mathrm{Ag^+(Ag_2S)} + \mathrm{S^{2-}\,(Ag_2S)} \qquad \text{(ii)}$$

Solid state reactions such as oxidation or sulfurization of metals or formation of spinels involve a solid–solid interface reaction as an elementary process. Because of the fact that the rate of reaction at a solid–solid interface is much higher than that of diffusion in a solid phase, the solid–solid interface reaction has not been studied kinetically yet. However, a few systems have been found recently in which the solid–solid interface reaction has an effect on the overall reaction rate.

Rickert and his co-workers showed that the sulfurization of silver is a mixed controlled reaction of three elementary processes, *i.e.*, reaction at the Ag/$Ag_2S$ interface, diffusion in $Ag_2S$, and reaction at the $Ag_2S$/S(g) interface. They tried to measure the reaction rate at the Ag/$Ag_2S$ interface quantitatively by the coulometric titration method.[1–3] Schmalzried and his collaborators studied the formation of spinels,

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[1] H. Rickert, *Z. Phys. Chem.*, *N. F.*, **23**, 355 (1960).

[2] H. Rickert and C. D. O'Briain, *ibid.*, **31**, 71 (1962).

[3] H. Rickert and K. H. Tostmann, *Werkstoffe und Korrosion* **21**, 965 (1970).

such as $ZnAl_2O_4$, from their constituent oxides, and discussed the influence of the reactions at the $ZnO/ZnAl_2O_4$ and $ZnAl_2O_4/Al_2O_3$ boundaries on the overall reaction rate.[4,5] Leute and Kalb investigated the interdiffusion for the system (Hg, Cd)Te/(Hg, Cd)Se, and discussed the influence of the interface reaction in the initial stage.[6] In these investigations, however, no quantitative treatment was performed.

The present study was undertaken to investigate the reaction at the $Ag/Ag_2S$ interface kinetically.

## Experimental

In order to obtain the reaction rate as a function of the silver activity of silver sulfide at the solid-solid interface, the direct sulfurization method (Wagner's pellet method[1,7]) and Rickert's coulometric titration method[2] were used.

*Direct Sulfurization Method.* A schematic diagram of the experimental arrangement is shown in Fig. 1. The sulfurization rate of silver by liquid sulfur was determined from the growth rate of the sulfide layer. The silver activity of silver sulfide at the interface was measured electrochemically with an Ag/AgI electrode. The rate equation was determined from the sulfurization rate and silver activity at the interface.

The essential part of the apparatus for the direct sulfurization method is shown in Fig. 2. A silver cylinder (10 mm in diameter) with a small hole (1.5 mm in diameter) along its axis was fabricated from a silver rod (99.9% pure). The surface in contact with the $Ag_2S$ pellet was polished with No. 1000 emery papers and 0.3 $\mu$ alumina polishing powder. A compact silver sulfide rod (10 mm in diameter) prepared by direct sulfurization of the silver rod was sliced into pellets about 0.5 mm in thickness. The pellets were also polished to attain good contact with the silver cylinder. Sulfur of reagent grade was purified several times by distillation.

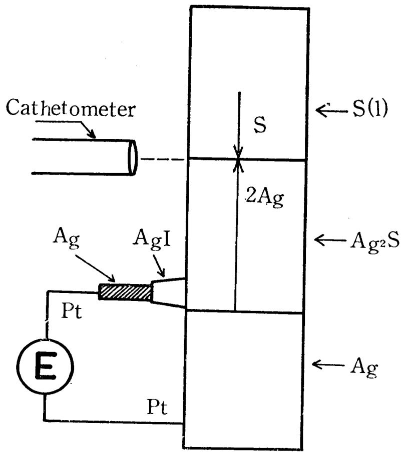

Fig. 1. Schematic diagram of direct sulfurization method.

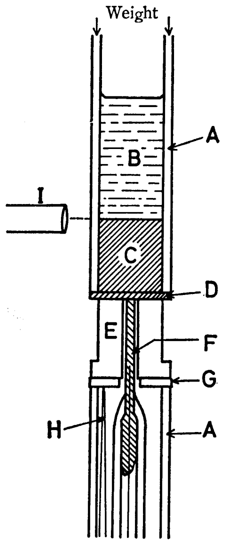

Fig. 2. Apparatus for direct sulfurization method.
(A) Pyrex tube (B) Liquid sulfur
(C) $Ag_2S$ formed (D) $Ag_2S$ pellet
(E) Ag cylinder (F) Ag/AgI electrode
(G) Pt electrode (H) Thermocouple
(I) Cathetometer

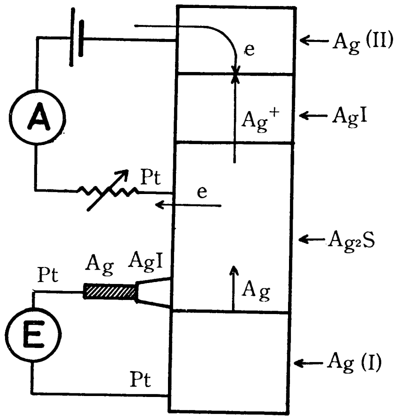

Fig. 3. Schematic diagram of coulometric titration method.

The Ag/AgI electrode consisting of a silver wire (0.2 mm in diameter) and silver iodide of reagent grade was assembled in a small alumina tube of 1.2 mm in outer diameter. The electrode was placed in the hole of the silver cylinder with its upper edge in contact with the $Ag_2S$ pellet near the $Ag/Ag_2S$ interface. A pyrex tube, with inner diameter 6—8 mm was used to press the $Ag_2S$ pellet and to hold liquid sulfur in it. In order to assure good contact between the cylinder and the $Ag_2S$ pellet, a pressure of about 3 kg/cm$^2$ was applied by a spring or weight through the pyrex tube.

An electric furnace was constructed by winding nichrome wires around the pyrex tube in order to follow the growth of $Ag_2S$ layer continuously from the outside by means of a cathetometer. The reaction temperature was controlled by an electric controller within $\pm 1$ °C. Measurements were performed in purified nitrogen atmosphere.

*Coulometric Titration Method.* The coulometric titration method was originated by Rickert and O'Briain.[2] The principle is schematically shown in Fig. 3. When a potential difference is given between Ag(II) and $Ag_2S$, silver is removed from $Ag_2S$ to Ag(II) in the form of $Ag^+$ ions and electrons. Namely, $Ag^+$ ions are transported through the AgI pellet since silver iodide is a pure ionic conductor, and electrons are removed from $Ag_2S$ to Ag(II) through a Pt wire. The rate of silver removal can thus be measured as an electric current by means of an ammeter A. As silver

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[4] H. Schmalzried, *Ber. Dtsch. Keram. Ges.*, **42**, 11 (1965).
[5] C. A. Duckwitz and H. Schmalzried, *Z. Phys. Chem., N. F.*, **76**, 173 (1971).
[6] V. Leute and A. Kalb, *J. Phys. Chem. Solids*, **33**, 417 (1972).
[7] C. Wagner, *Z. Phys. Chem., B*, **21**, 25 (1933).

is removed from $Ag_2S$ to Ag(II), an equivalent amount of silver goes into the $Ag_2S$ pellet across the Ag(I)/$Ag_2S$ interface. When a steady state is established, the rate of reaction at the Ag(I)/$Ag_2S$ interface is equal to that of removal of silver from the $Ag_2S$ pellet. The silver activity of silver sulfide is measured electrochemically by means of an Ag/AgI electrode. An $Ag_2S$ pellet of about 2 mm in thickness was used. The AgI pellet was prepared by pressing silver iodide powder of reagent grade in a die under the pressure of 7 t/cm². The pellet was 10 mm in diameter and about 7 mm in thickness. The electric furnace and other experimental apparatus were almost the same as those used in the direct sulfurization method.

## Results

*Direct Sulfurization Method.* A typical result is shown in Fig. 4. $E$(mV) is the potential drop at the Ag/$Ag_2S$ interface and $x$(mm) the thickness of the silver sulfide layer formed. The reaction rate $v$(eqv cm$^{-2}$ s$^{-1}$) was calculated by the graphical differentiation of $x$-time curves. The silver activity of $Ag_2S$, $a_{Ag}$, is related to $E$ as follows:

$$\log a_{Ag} = -\frac{EF}{2.3RT} \tag{1}$$

where $F$ is the Faraday constant. The activity of metallic silver is taken as unity.

The plots of $\log v$ *vs.* $\log a_{Ag}$ were obtained at 250, 300, 340, and 400 °C by the direct sulfurization method.

*Coulometric titration method.* Fig. 5 shows the time dependence of $E$ when silver was removed from $Ag_2S$ to Ag(II) at constant currents. The reaction rate $v$(eqv cm$^{-2}$ s$^{-1}$) was calculated from the electric current and the area of the Ag/$Ag_2S$ interface. We see that the steady state was attained in a short time when the reaction rate was high.

The plots of $\log v$ *vs.* $\log a_{Ag}$ are given by open circles and solid lines in Fig. 6. Circles show the experimental average values. Empirical solid lines were calculated by the method of least-squares, bars showing the standard deviation from the solid line. The slope of the line is −1.9±0.3, −2.1±0.3, −2.3±0.3, and −2.2±0.6 for the temperatures 215, 250, 300, and 350 °C, respectively. Because of the difficulty in attaining a reproducible good contact between silver and silver sulfide, scattering of the experimental values could not be noticeably reduced.

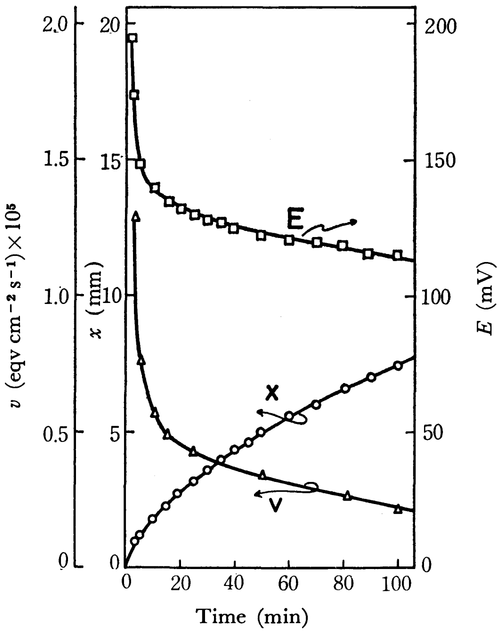

Fig. 4. Change of $E$, $v$, and $x$ with time at 300 °C; direct sulfurization method.

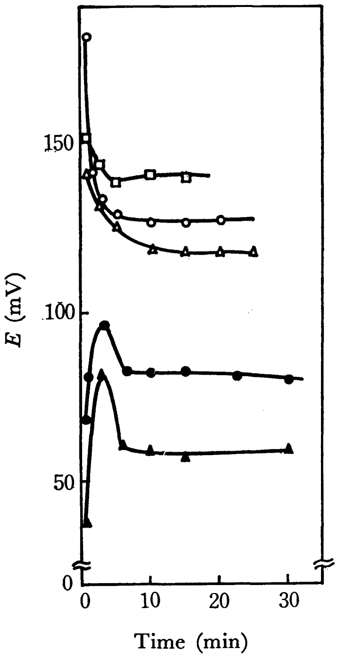

Fig. 5. Change of $E$ with time at 300 °C; coulometric titration method.

□: 4.0×10⁻⁶ eqv cm⁻² s⁻¹ ○: 2.0×10⁻⁶ eqv cm⁻² s⁻¹
△: 1.0×10⁻⁶ eqv cm⁻² s⁻¹ ●: 2.0×10⁻⁷ eqv cm⁻² s⁻¹
▲: 1.0×10⁻⁷ eqv cm⁻² s⁻¹

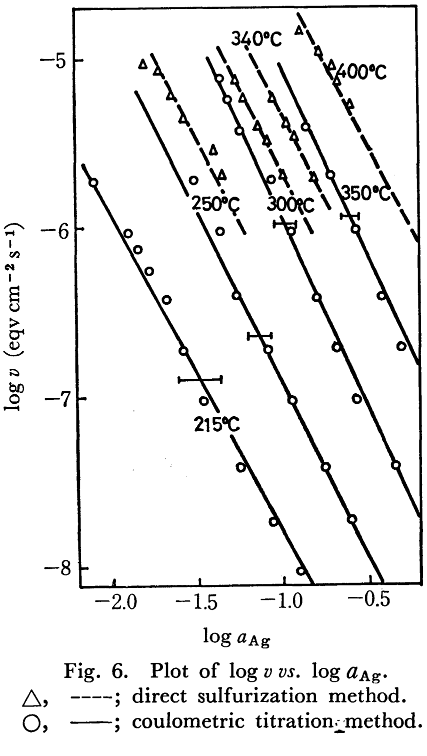

Fig. 6. Plot of $\log v$ *vs.* $\log a_{Ag}$.

△, ----; direct sulfurization method.

○, ——; coulometric titration method.

The results obtained by both methods are in fairly good agreement (Fig. 6).

Rickert and his co-workers showed that the relation between log $v$ *vs.* log $a_{Ag}$ is not linear at 220 and 300 °C, but we found a linear relation.

## Discussion

*Mechanism.* Kobayashi and Wagner[8] studied the reduction of $Ag_2S$ by $H_2$ at 300 °C and obtained the rate of reduction at the gas-solid interface as a function of $a_S$. They proposed three mechanisms wherein S, $S^-$, $S^{2-}$, and electrons are reactants in solid phase. If the same reactants take part in the reaction between silver and $Ag_2S$, the transfer of silver atom from metal sulfide would proceed by the most predominant of the following three mechanisms.

$$2Ag(I) + S(II) \rightarrow Ag_2S(II) \tag{2.A}$$

$$2Ag(I) + S^-(II) \rightarrow Ag_2S(II) + e^-(II) \tag{2.B}$$

$$2Ag(I) + S^{2-}(II) \rightarrow Ag_2S(II) + 2e^-(II) \tag{2.C}$$

where (I) denotes the metal phase, (II) the sulfide phase, and $e^-$ is electron.

The corresponding rate equations for these mechanisms are

$$v_A = K_A[a_{Ag}(I)]^2 a_S - K_A' a_{Ag_2S} \tag{3.A}$$

$$v_B = K_B[a_{Ag}(I)]^2 a_{S^-} - K_B' a_{Ag_2S} a_{e^-} \tag{3.B}$$

$$v_C = K_C[a_{Ag}(I)]^2 a_{S^{2-}} - K_C' a_{Ag_2S}(a_{e^-})^2 \tag{3.C}$$

Since the reaction proceeds under the condition far from equilibrium in our case the reverse reactions can be neglected.

The silver activity of metal phase is unity and thus the rate equations (3.A)—(3.C) are rewritten as

$$v_A = k_A a_S \tag{4.A}$$

$$v_B = k_B a_{S^-} \tag{4.B}$$

$$v_C = k_C a_{S^{2-}} \tag{4.C}$$

According to Wagner[9], $a_{Ag_2S}$ and $a_{Ag}$ of $\alpha$-$Ag_2S$ are constant irrespective of nonstoichiometry of the sulfide, *viz.*,

$$a_{Ag_2S} = \text{const} \tag{5}$$

$$a_{Ag^+} = \text{const} \tag{6}$$

Assuming the chemical equilibria between species in $\alpha$-$Ag_2S$, we obtain

$$Ag = Ag^+ + e^-$$

$$a_{Ag^+} a_{e^-} = K_1 a_{Ag} \tag{7}$$

$$S^{2-} = S + 2e^-$$

$$a_S(a_{e^-})^2 = K_2 a_{S^{2-}} \tag{8}$$

$$S^- = S + e^-$$

$$a_S a_{e^-} = K_3 a_{S^-} \tag{9}$$

$$2Ag + S = Ag_2S$$

$$a_{Ag_2S} = K_4(a_{Ag})^2 a_S \tag{10}$$

Where $K_1$, $K_2$, $K_3$, and $K_4$ are equilibrium constants.

From Eqs. (5)—(10), we get

$$a_S \propto (a_{Ag})^{-2} \tag{11}$$

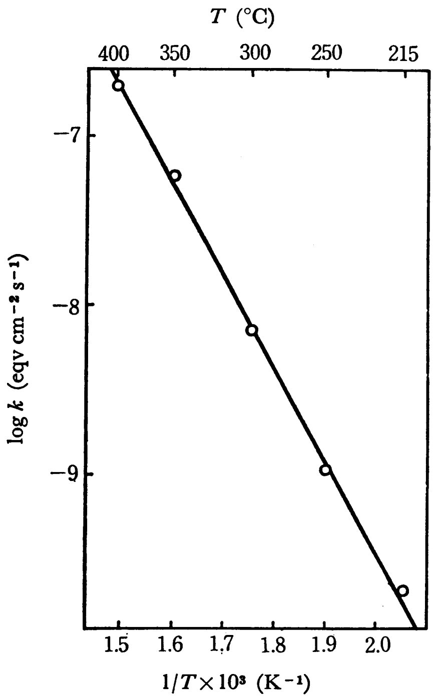

Fig. 7. Arrhenius plot of *k*.

$$a_{S^-} \propto (a_{Ag})^{-1} \tag{12}$$

$$a_{S^{2-}} \propto (a_{Ag})^0 \tag{13}$$

Thus, Eqs. (4.A)—(4.C) are expressed in the form

$$v = k(a_{Ag})^n \tag{14}$$

where $n=-2$ for mechanism (A), $n=-1$ for mechanism (B) and $n=0$ for mechanism (C).

We found that $n$ varies from $-1.9$ to $-2.3$. Thus, it is concluded that $n$ is $-2$ and that mechanism (A) prevails for the reaction at the Ag/$Ag_2S$ interface.

*Rate Constants.* The logarithms of the rate constants for each temperature can be obtained from extrapolation of the lines (Fig. 6) to the ordinate log $a_{Ag}=0$. Figure 7 shows the Arrhenius plot of $k$, which is expressed by

$$k = 251 \exp(-25000/RT) \quad \text{eqv cm}^{-2}\,\text{s}^{-1} \tag{15}$$

Therefore the rate equation is

$$v = 251\{\exp(-25000/RT)\,(a_{Ag})^{-2}\}\text{eqv cm}^{-2}\,\text{s}^{-1} \tag{16}$$

If the activities of sulfur of $Ag_2S$ under reaction and in equilibrium with Ag are expressed in terms of $a_S$ and $a_S{}^0$, respectively, we have

$$a_S(a_{Ag})^2 = a_S{}^0 \tag{17}$$

Hence

$$(a_{Ag})^{-2} = \frac{a_S}{a_S{}^0} \tag{18}$$

Substituting (18) into (16) we have

$$v = 251\{\exp(-25000/RT)\}(a_S/a_S{}^0)\ \text{eqv cm}^{-2}\,\text{s}^{-1} \tag{19}$$

According to Kiukkola and Wagner[10] the standard free energy of formation of $Ag_2S$, $\Delta G^0$, is

$$\Delta G^0 = -7.04 - 0.00735\,T \quad \text{kcal/mol} \tag{20}$$

$\Delta G^0$ is related to $a_S{}^0$ as follows.

$$\Delta G^0 = RT \ln a_S{}^0 \quad \text{kcal/mol} \tag{21}$$

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[8] H. Kobayashi and C. Wagner, *J. Chem. Phys.*, **26**, 1609 (1957).

[9] C. Wagner, *ibid.*, **21**, 1819 (1953).

[10] K. Kiukkola and C. Wagner, *J. Electrochem. Soc.*, **104**, 379 (1957).

Eq. (19) can be written as

$$v = 1.00\times 10^4\{\exp(-18000/RT)\}a_S \text{ eqv cm}^{-2}\text{s}^{-1} \qquad (22)$$

## Summary

(I) The solid–solid interface reaction between silver and silver-sulfide was investigated kinetically by the direct sulfurization and coulometic titration methods.

(2) The reaction rate was determined as a function of $a_S$, silver activity of silver-sulfide, at 215—400 °C.

The rate equation is

$$v = 1.00\times 10^4\{\exp(18000/RT)a_S\} \text{ eqv cm}^{-2}\text{s}^{-1}$$

(3) The reaction mechanism was discussed on Kobayashi-Wagner's theory. The following mechanism was found to be predominant.

$$2\text{Ag(Ag)} + \text{S(Ag}_2\text{S)} \rightarrow 2\text{Ag}^+\text{(Ag}_2\text{S)} + \text{S}^{2-}\text{(Ag}_2\text{S)}$$