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Kinetics of the Reaction at the Silver Sulfide-Liquid Sulfur Interface

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The reaction rate, v, at the $Ag_2S/S(l)$ interface was determined as a function of the silver activity a_{Ag} in Ag_2S utilizing a solid-state electrochemical cell, $Ag/AgI/Ag_2S/Pt$. The rate equation was found to be expressed by $v=k(a_{Ag})^2-k'$. On the basis of the theory by Kobayashi and Wagner, the rate-controlling step of the $Ag_2S/S(l)$ interface reaction is concluded to be $S^-(ad)+e \rightarrow S^{2-}(ad)$. The overall reaction rate of silver sulfidization by liquid sulfur can be well explained by the mixed control of a three-step reaction; the $Ag_2S/S(l)$ interface reaction, the diffusion of silver ions in Ag_2S, and the Ag/Ag_2S interface reaction.

Alpha-AgI is an ionic conductor, the conductivity of which is as high as that of aqueous ionic solutions. This extraordinarily high conductivity is due to the special crystal structure. Also, silver chalcogenides, Ag_2X, have high ionic and electronic conductivities due to their structure and non-stoichiometry. Therefore, several electrochemical investigations have been carried out using α-AgI as an electrolyte and silver chalcogenides as electrodes. The silver activity in solid Ag_2X can be determined by emf measurements using an electrochemical cell, $Ag/AgI/Ag_2X$. Conversely, when a constant voltage is applied to the cell, the silver ions flow through AgI and the electrons, through the outer circuit. As a result, silver atoms are transferred from Ag to Ag_2X or in the reverse direction, the rate of silver transfer can be measured as the electric current. When the equilibrium is established between Ag and Ag_2X under an applied constant voltage, the silver activity in Ag_2X has a constant value corresponding to the applied voltage. Therefore, the silver activity in Ag_2X can be controlled by the voltage applied to the cell.

So far, various thermodynamical and kinetic measurements have been done by means of the $Ag/AgI/Ag_2X$ cell. For example, the non-stoichiometric ranges and phase relations of Ag–S,[1,2] Ag–Se[3,4] and Ag–Te[5] systems have been investigated by the coulometric titration technique, and kinetic studies have been carried out on solid-solid[6,7] and gas-solid[8–11] interface reactions.

Electrochemical methods in which the $Ag/AgI/Ag_2X$ cell is employed give interesting results which cannot be obtained by other methods for the investigation of solid-state reactions. The present work aims to study the $Ag_2S/S(l)$ interface reaction kinetically using the $Ag/AgI/Ag_2S$ cell.

Experimental

Materials. A silver rod was prepared by melting silver powder (99.99% purity) and casting it in a silica tube, 10 mm in inner diameter. The rod was cut into pellets 10 mm thick, and a hole, 1.5 mm in diameter, was drilled along the axis of each pellet. Silver sulfide was prepared by the sulfidization of silver with liquid sulfur. One end of a glass tube, 10 mm in outer diameter and 8 mm in inner diameter, was finished as flat as possible, placed in contact with a silver pellet, and pressed by a weight. Then, sulfur purified by vacuum distillation was dropped into the glass tube to react the sulfur with silver at 200 °C. Since the lower end of the tube was so flat that leakage of liquid sulfur could be avoided. Silver sulfide grown in the glass tube was taken out and sliced into pellets 2—3 mm thick. Each pellet was pressed under a pressure of 5 t/cm^2 and polished to a thickness of about 1 mm. Silver iodide pellets, 10 mm thick were prepared by pressing AgI powder under a pressure of 5 t/cm^2.

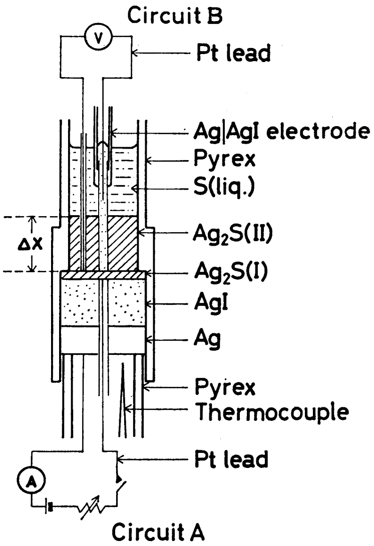

Fig. 1. Apparatus for the measurement of the rate of $Ag_2S/S(l)$ interface reaction.

Kinetic Study on the $Ag_2S/S(l)$ Interface Reaction. The apparatus and technique employed in the present study were generally similar to those used by Mizusaki and his co-investigators[12] for their investigation of the $Ag_2Se/Se(l)$ interface reaction. However, an improvement was made in the apparatus, since the dissociation pressure of Ag_2S is higher than that of Ag_2Se.[13] As is shown in Fig. 1, two glass tubes, one of which was 13 mm in inner diameter, the other being 10 mm in inner diameter, were joined. Three pellets of Ag, AgI, and $Ag_2S(I)$, 10 mm in diameter, were assembled and pressed with the joined glass tube. Since AgI tends to deform plastically, the pressing resulted in a close contact between the AgI pellet and the inner wall of the glass tube. Thus, the vaporization of sulfur from Ag_2S could be prevented. The end surface of the glass tube was finished as flat as possible so that liquid sulfur could be held in the tube without leakage when the end was placed in contact with the $Ag_2S(I)$ pellet. The Ag/AgI electrode in a small alumina tube, 1.5 mm in outer diameter, was placed in the glass tube so that the tip could be brought to contact with the surface of the $Ag_2S(I)$ pellet. The reaction rate was measured as an electric current flowing through the outer circuit A, by means of an ammeter, while the potential difference between the $Ag_2S(I)$ pellet and Ag was determined by means of potentiometer.

Rate Measurement of the Reaction between Silver and Liquid Sulfur. The same apparatus and technique as used by Mizusaki and his co-investigators[12] were employed for the measurement. A silver cylinder, 8 mm in diameter, and a Ag_2S pellet, 10 mm in diameter, were assembled and pressed with a glass tube, 10 mm in outer diameter. Then, sulfur was dropped into the glass tube, and the change in the thickness of the Ag_2S pellet was followed with time by means of a cathetometer.

Observation of the Ag_2S Surface with SEM. After the sulfidization, the liquid sulfur was poured out and the residual sulfur on the surface of Ag_2S was dissolved with CS_2. The surface of the Ag_2S thus obtained was examined by means of an SEM.

Results and Discussion

Observation on the Ag_2S Surface by Means of SEM. Observation of the surface of Ag_2S by means of SEM revealed that the surface of Ag_2S is always compact, regardless of the experimental conditions, as is shown in Fig. 2.

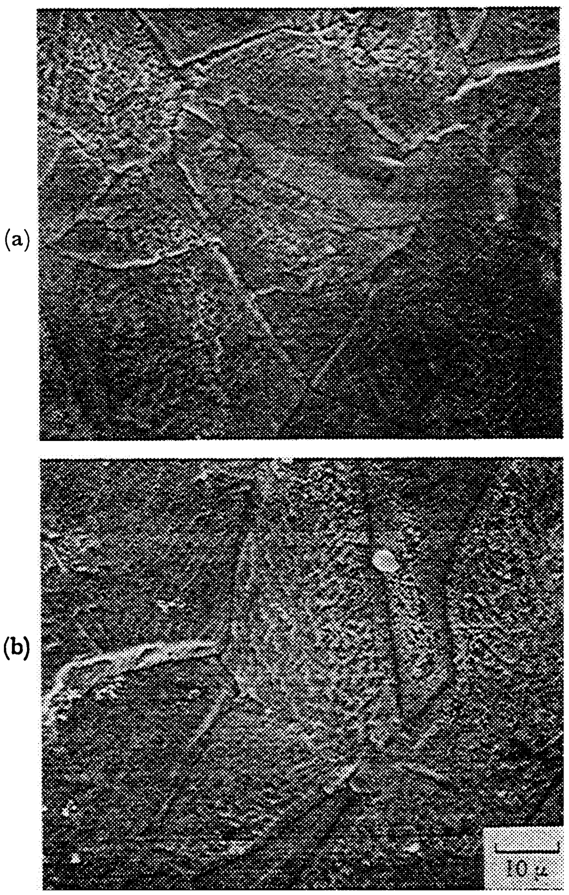

Fig. 2. SEM photographs of the surface of Ag_2S at the $Ag_2S/S(l)$ interface. (185 °C)
(a): $I A^{-1} = 1080$ mA cm^{-2} (b): $I A^{-1} = 192$ mA cm^{-2}

Results of a Kinetic Study of the $Ag_2S/S(l)$ Interface Reaction. When the circuit A is open, $Ag_2S(I)$ is in equilibrium with the liquid sulfur, and the potential difference, E°, appearing in the circuit B gives the standard free energy formation of Ag_2S by means of the following relation,

$$E^\circ = -\Delta G^\circ/2F, \tag{1}$$

where F is Faraday's constant. If metallic silver is taken as the standard state, the silver activity, a^*_{Ag}, in Ag_2S equilibrated with liquid sulfur is represented by the equation

$$a^*_{Ag} = \exp(-F\cdot E^\circ/R\cdot T). \tag{2}$$

When the switch is turned on and a constant current, I, is allowed to flow in, the silver ions are transported from the Ag electrode to the $Ag_2S(I)/S(l)$ interface through AgI and $Ag_2S(I)$, while the electrons flow from the Ag electrode to the $Ag_2S/S(l)$ interface through the outer circuit and $Ag_2S(I)$. The silver ions and electrons arriving at the $Ag_2S(I)/S(l)$ interface react with liquid sulfur to form $Ag_2S(II)$ in the glass tube at a constant rate. Accordingly, the Ag/AgI electrode used for the measurement of the potential difference is buried in the $Ag_2S(II)$ layer. If the area of the $Ag_2S/S(l)$ interface is represented by A, the reaction at the $Ag_2S/S(l)$ interface proceeds at a rate of $I/2F\cdot A$ and a potential difference is produced at the $Ag_2S(II)/S(l)$ interface. If the silver activity in $Ag_2S(II)$ at the $Ag_2S/S(l)$ interface and that in $Ag_2S(I)$ at the tip of Ag/AgI electrode are designated by a'_{Ag} and a_{Ag} respectively, and if the thickness of $Ag_2S(II)$ layer is Δx, the following relations are obtained:

$$E' - E = \frac{I\cdot\Delta x}{\sigma_{Ag^+}\cdot A}, \tag{3}$$

$$E' = -\frac{2.303R\cdot T}{F}\log a'_{Ag}, \tag{4}$$

$$E = -\frac{2.303R\cdot T}{F}\log a_{Ag}, \tag{5}$$

where σ_{Ag^+} is the ionic conductivity of Ag^+ ions in Ag_2S. In Eq. 3, σ_{Ag^+} is assumed to be independent of the silver activity in Ag_2S.[14]

Figure 3 shows the plot of E *vs.* Δx at 200 °C. Since $I/\sigma_{Ag^+}A$ is constant under a constant current, I, E' is determined from the intercepts of the ordinate with the

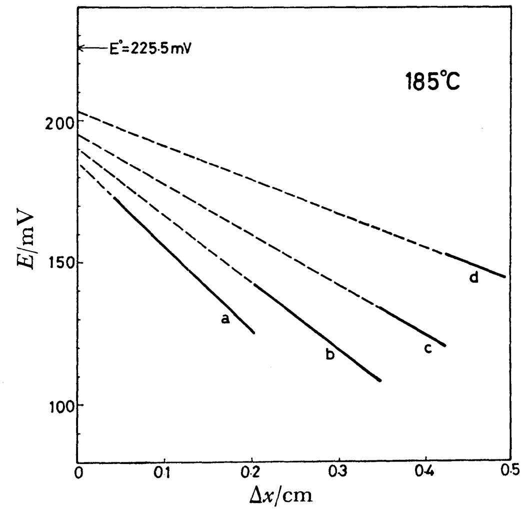

Fig. 3. Plots of E *vs.* Δx.
a: $I A^{-1} = 1080$ mA cm^{-2}, b: $I A^{-1} = 880$ mA cm^{-2},
c: $I A^{-1} = 660$ mA cm^{-2}, d: $I A^{-1} = 440$ mA cm^{-2}.

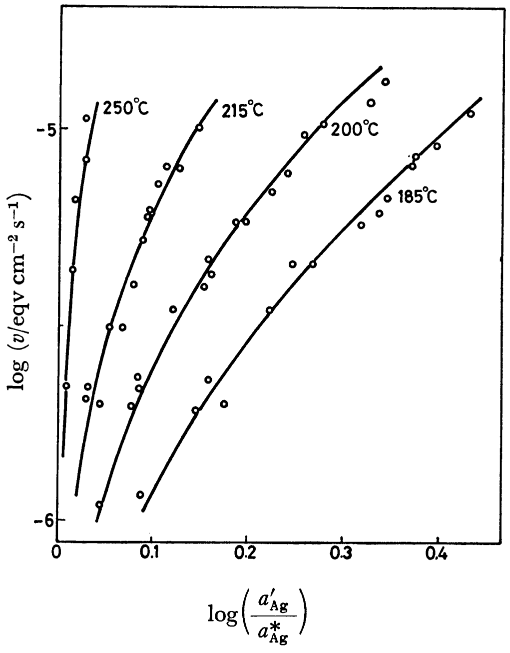

Fig. 4. Plots of log v *vs.* $\log(a'_{Ag}/a^*_{Ag})$.

extrapolated lines. The $E°$ measured in the present work is shown by an arrow. It is in good agreement with that obtained by Kiukkola and Wagner.[5] The potential difference, $E°-E'$, gives the driving force of the Ag_2S/S(l) interface reaction.

Figure 4 shows the relationship between the reaction rate and a'_{Ag}/a^*_{Ag}. The logarithm of a'_{Ag}/a^*_{Ag} is equivalent to $(E°-E')/2.303\ R\cdot T$.

Kinetics of the $Ag_2S/S(l)$ Interface Reaction. Kobayashi and Wagner[8] studied the kinetics of the reduction of Ag_2S by H_2 and found that the rate of reduction at the gas-solid interface depends not only on the partial pressure of the reacting gases, but also on the activity of the reacting chemical species in solid. A similar dependence of the surface reaction rate on the activity of the reacting chemical species was observed in redox reactions between CO_2 or CO and metal oxides, such as FeO,[15,16] Fe_3O_4,[15] and CoO,[17] and in redox reactions between H_2S or H_2 and metal sulfides.[18,19] From these results, it is concluded that the dependence of the reaction rate on the activity of the reacting chemical species in solids would be like that for the gas-solid interface reactions. In the case of the Ag_2S/S(l) interface reaction, the reaction rate was found to depend on the silver activity of Ag_2S at the Ag_2S/S(l) interface, as is shown in Fig. 4. So, it is expected that a mechanism similar to that of the gas-solid interface reaction would be operative in the present interface reaction.

According to Gee's[20] study, the molecular species of liquid sulfur are S_8 and S_6 with a cyclic structure and polymeric sulfur in the temperature range of the present investigation. They are in equilibrium with each other. At the Ag_2S(II)/S(l) interface, S_x molecule would adsorb and dissociate in the following way:

$$S_x(l) = xS(ad). \tag{6}$$

Since the density of liquid sulfur is several thousand times that of sulfur vapor, it is considered that the surface of Ag_2S is saturated with adsorbed sulfur and that the surface concentration of S(ad) is constant.

The process whereby S(ad) is reduced to S^{2-}(ad) must be

$$S(ad) + e \longrightarrow S^-(ad), \tag{7}$$

$$S^-(ad) + e \longrightarrow S^{2-}(ad). \tag{8}$$

Since S(ad) is in equilibrium with S(l), a_s(ad) is equal to a_s(l). Moreover, it is assumed that S^{2-}(ad) is in equilibrium with the S^{2-} ion in Ag_2S and that equilibria are established among chemical species, Ag, Ag^+, e, S, S^-, and S^{2-}, in Ag_2S. As the activity of Ag^+, a_{Ag^+} is constant regardless of the composition of Ag_2S,[1] the activity of the respective species depends on a'_{Ag} as follows:

$$a_e \propto a'_{Ag}, \tag{9}$$

$$a_{Ag^+},\ a_{S^{2-}} = \text{const.} \tag{10}$$

a) If Reaction 7 is rate-controlling,

$$v_1 = \overrightarrow{k}_1 a_S(ad)a_e - \overleftarrow{k}_1 a_{S^-}(ad). \tag{11}$$

The a_s(ad) activity is equal to a_s(l) and is independent of a'_{Ag}. Since a preliminary equilibrium is established in Eq. 8,

$$\frac{a_{S^{2-}}(ad)}{a_{S^-}a_e} = K_2, \tag{12}$$

that is

$$a_{S^-} = \frac{a_{S^{2-}}(ad)}{K_2}(a_e)^{-1}. \tag{13}$$

The $a_{s^{2-}}$(ad) activity is equal to $a_{s^{2-}}$ in the Ag_2S bulk; therefore,

$$a_{S^-} \propto {a'_{Ag}}^{-1}. \tag{14}$$

Thus, Eq. 11 can be rewritten in the form

$$v_1 = k_1 a'_{Ag} - k_{-1}(a'_{Ag})^{-1}. \tag{15}$$

b) If Reaction 8 is rate-controlling,

$$v_2 = \overrightarrow{k}_2 a_{S^-}(ad)a_e - \overleftarrow{k}_2 a_{S^{2-}}(ad). \tag{16}$$

Assuming that equilibrium is kept for Reaction 7, we obtain

$$\frac{a_{S^-}(ad)}{a_S(ad)a_e} = K_1. \tag{17}$$

Thus,

$$a_{S^-}(ad) = K_1 a_S(ad)a_e \propto a'_{Ag}. \tag{18}$$

Accordingly,

$$v_2 = k_2(a'_{Ag})^2 - k_{-2}. \tag{19}$$

As may be noticed from Eqs. 15 and 19, the rate equations have the general expression,

$$v = \overrightarrow{k}(a'_{Ag})^m - \overleftarrow{k}(a'_{Ag})^{-n}, \tag{20}$$

where $m=1$ and $n=1$ when the $S(ad) + e \rightarrow S^-(ad)$ reaction is slow, and $m=2$ and $n=0$ when the $S^-(ad) + e \rightarrow S^{2-}(ad)$ reaction is slow. When the equilibrium is established between Ag_2S and liquid sulfur, v in Eq. 20 is zero; therefore,

$$\overrightarrow{k}(a^*_{Ag})^m = \overleftarrow{k}(a^*_{Ag})^{-n}. \tag{21}$$

The insertion of Eq. 21 into Eq. 20 gives

$$v = \overrightarrow{k}(a^*_{Ag})^m\left\{\left(\frac{a'_{Ag}}{a^*_{Ag}}\right)^m - \left(\frac{a'_{Ag}}{a^*_{Ag}}\right)^{-n}\right\}$$
$$= k\left\{\left(\frac{a'_{Ag}}{a^*_{Ag}}\right)^m - \left(\frac{a'_{Ag}}{a^*_{Ag}}\right)^{-n}\right\}. \quad (22)$$

A curve-fitting calculation using data for 185 °C and 200 °C in Fig. 4 showed that a set of $m=2$ and $n=0$ gives a better agreement between the calculated and observed values than a set of $m=1$ and $n=1$. It is concluded that the $S^-(ad)+e \rightarrow S^{2-}(ad)$ reaction is rate-controlling for the $Ag_2S/S(l)$ interface reaction.

In the case of $m=2$ and $n=0$, Eq. 22 is rewritten as

$$v = k\left\{\left(\frac{a'_{Ag}}{a^*_{Ag}}\right)^2 - 1\right\}. \quad (23)$$

Figure 5 shows the plot of log v *vs.* log $\{(a'_{Ag}/a^*_{Ag})^2-1\}$. The data for each temperature fall on a straight line. From the intercept of the ordinate with the plotted lines, we can calculate the rate constant, k. Figure 6 shows the Arrhenius plot for k. The Arrhenius equation is

$$k = 1.22\times10^7 \exp\left(\frac{-26900}{RT}\right) \quad (\text{eqv cm}^{-2}\ \text{s}^{-1}) \quad (24)$$

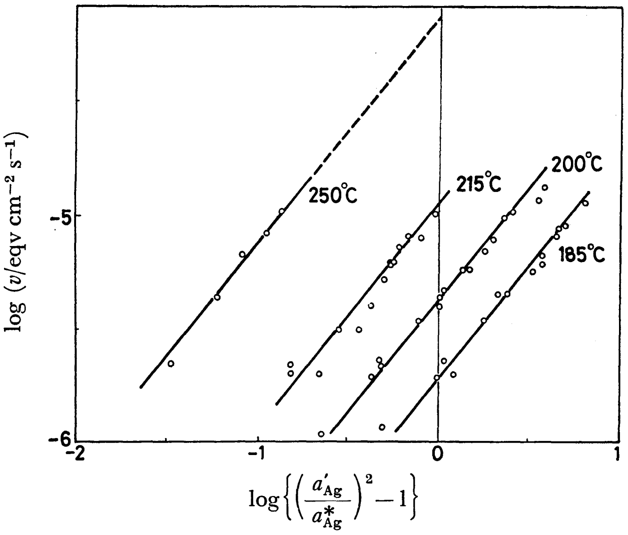

Fig. 5. Plots of log v *vs.* $\log\{(a'_{Ag}/a^*_{Ag})^2-1\}$.

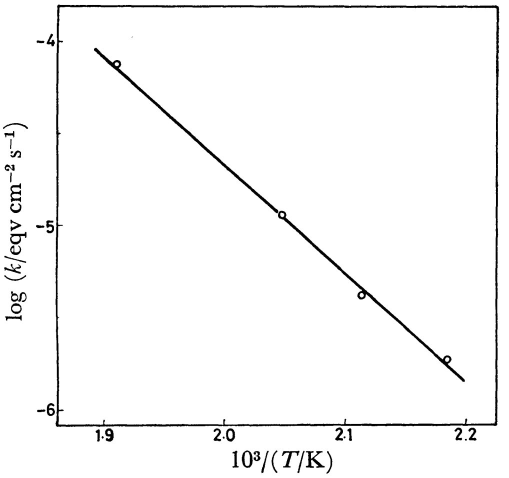

Fig. 6. Arrhenius plot of k.

Driving Forces of the Three Steps of Silver Sulfidization. The reaction of metal tarnishing consists of three elementary steps:

1) Reaction at the metal/scale interface,

2) diffusion of electrons and ions through the growing scale, and

3) reaction at the gas (or liquid)/scale interface.

If one of these steps is rate-controlling, the driving force, that is, the difference in the silver chemical potential of the step, is equal to that of the over-all reaction. If two or three steps are simultaneously slow, the driving force of the over-all reaction is divided into two or three parts.

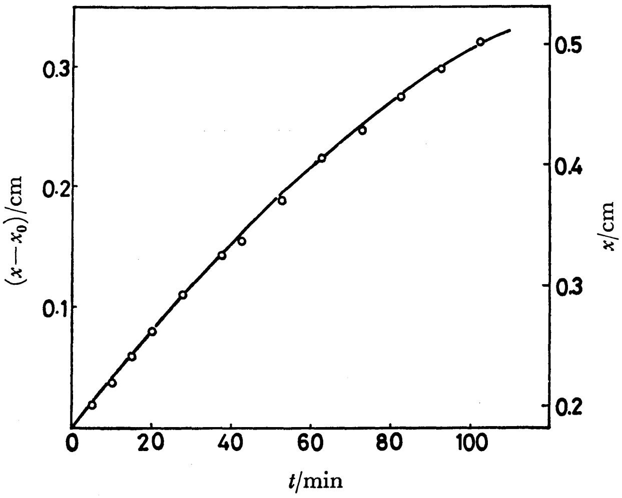

Fig. 7. Plot of x or $x-x_0$ *vs.* time.

Mizusaki and his co-investigators[12] have determined the distribution of the chemical potential of silver in a growing Ag_2Se layer in the selenization of silver, and have found that Ag_2Se and Se(l) are actually in chemical equilibrium during the reaction. In the present study, the difference in the silver chemical potential across the $Ag_2S/S(l)$ interface was observed during the sulfidization. This finding suggests that the sulfidization of silver is mixed-controlling. Therefore, the driving force for each reaction step was calculated from the sulfidization curve given in Fig. 7. In this figure, x is the total thickness of the Ag_2S layer and $x-x_0$ is the increase in the thickness of the Ag_2S layer. The over-all reaction rate is calculated by the graphical differentiation of the curve. The ionic conductivity of Ag_2S is calculated from Eq. 3 and the gradient of the straight lines in Fig. 2. Thus,

$$\sigma\cdot T = 3.8\times10^4 \exp\left(\frac{-2900}{RT}\right) \quad (\text{ohm}^{-1}\ \text{cm}^{-1}\ \text{K}). \quad (25)$$

The value agrees with the result obtained by means of the four-probe conductivity measurement.[21]

If the silver activity of Ag_2S at the Ag/Ag_2S interface is denoted by a''_{Ag}, the logarithm of silver activity ratio (a'_{Ag}/a''_{Ag}) is

$$\log\left(\frac{a'_{Ag}}{a''_{Ag}}\right) = \frac{I\cdot xF}{\sigma_{Ag^+}\cdot A\cdot R\cdot T}$$
$$= \frac{vx\cdot F^2}{\sigma_{Ag^+}\cdot R\cdot T}. \quad (26)$$

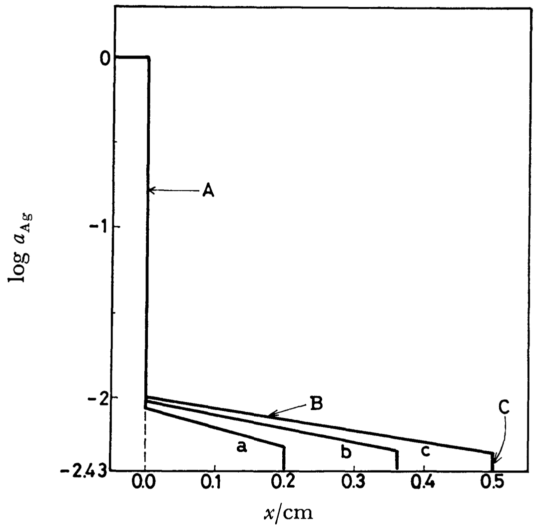

Fig. 8. Distribution of log a_{Ag} during the reaction at 200 °C.
a: $t=0$ min. b: $t=50$ min. c: $t=100$ min.
A: Potential difference at Ag/Ag_2S interface.
B: Potential difference in Ag_2S layer.
C: Potential difference at Ag_2S/S(l) interface.

The activity ratio (a'_{Ag}/a^*_{Ag}) at the Ag_2S/S(l) interface is obtained from the relation of v *vs.* log (a'_{Ag}/a^*_{Ag}) in Fig. 4. Since the reaction rate, v, can be obtained from Fig. 7, and since log a^*_{Ag} is calculated by means of Eq. 2, the distribution of the chemical potential of silver in the Ag_2S layer during the sulfidization can be drawn. Figure 8 shows the plots of log a_{Ag} against x. Evidently, the over-all reaction is mixed-controlling by means of three reaction steps. From Fig. 8 we can estimate the chemical potential difference at the Ag/Ag_2S interface during the reaction. The result is in good agreement with the result of the electrochemical measurement carried out by Mizusaki and his co-investigators.$^{7)}$

Summary

(1) The Ag_2S/S(l) interface reaction was investigated kinetically. The rate equation was found to be represented by

$$v = 1.22\times 10^7 \exp\left(\frac{-26900}{RT}\right)\left\{\left(\frac{a'_{Ag}}{a^*_{AG}}\right)^2 - 1\right\}.$$
$$(\text{eqv cm}^{-2}\ \text{s}^{-1})$$

It was also concluded that the reaction step,

$$S^-(\text{ad}) + e \longrightarrow S^{2-}(\text{ad}),$$

is rate-controlling.

(2) The driving forces of the Ag_2S/S(l) interface reaction and the diffusion of the silver ions in Ag_2S were quantitatively determined. In the initial stage of sulfidization, the over-all reaction was mixed-controlled by means of three step reactions: Ag_2S/S(l) interface reaction, diffusion, and Ag/Ag_2S interface reaction.

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