An Investigation of the Gas-Solid Interface Reaction on the Surface of Ag and Ag_2S

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In order to elucidate the mechanism of the redox reaction at the gas-solid interface, the isotopic exchange between H_2S and D_2 on Ag and Ag_2S has been studied in the temperature range from 410 to 521 °C. The transfer of isotopic species between "hydrogen sulfide" [1] and "hydrogen" [1] was found to proceed by means of the reaction:

$$\text{“}H_2S\text{”}^{1)} \underset{k_i'}{\overset{k_i}{\rightleftarrows}} \text{“}H_2\text{”}^{1)} + S(ad)$$

on both surfaces. From the analysis of the kinetic data, the redox reaction rate constants, k_i and k_i', were determined as a function of the sulfur activity. It was found that k_i is inversely proportional to the sulfur activity, whereas k_i' is independent of it. The mechanism of the reaction on the surfaces of Ag and Ag_2S is discussed.

In previous works, the authors and their co-workers have kinetically studied the H_2S–D_2 exchange reaction on Cu_2S(*p*-type semiconductor),[2] β-$Fe_{1-x}S$(metallic conductor),[3] MoS_2(intrinsic semiconductor), and MnS-(*p*-type semiconductor)[4] in order to elucidate the mechanism of the redox reaction at the gas-solid interface. It was found that the activation energies and the dependence of the rate constants of the surface reaction on the sulfur activity are nearly the same for all these sulfides. Except in the case of Cu_2S, these results can not be explained by the theory proposed by Kobayashi and Wagner.[5] The mechanism proposed by the authors is that the rate-determining reaction is that between adsorbed sulfur atoms and gaseous molecules.[4]

The present work aims to study the redox reaction on Ag and Ag_2S(*n*-type semiconductor). Since the adsorption of sulfur atoms on Ag in "H_2S"–"H_2" gas mixtures, obeying a Langmuir-type adsorption isotherm, has already been reported,[6] one can confirm the validity of the theory proposed by the authors.

As the sulfur activity in the presence of both Ag and Ag_2S is 1/3.3~1/3.7 in the temperature range from 400 to 520 °C,[7] one can examine the H_2S–D_2 exchange reaction on Ag if the sulfur activity is smaller than 1/3.3~1/3.7. The sulfur activity, a_S, is defined as the pressure ratio of "hydrogen sulfide" to "hydrogen".

Experimental

Isotopic Exchange Study. The apparatus, the method of the purification of gases, and the experimental procedure were essentially the same as in previous works.[2–4] The samples were prepared as follows.

a) Ag sample: Silver powder of 99.9% purity was treated in "hydrogen" at 570 °C for 1 hour. The surface area of the powder was 2.86×10^3 cm² g⁻¹.

b) Ag_2S sample: Silver powder, treated as above, was sulfurized with a "H_2S"–"H_2" gas mixture at 570 °C until the sulfurization was completed. The surface area of the sulfide was 4.76×10^3 cm² g⁻¹.

Prior to the isotopic exchange run, the sample was equilibrated with the "H_2S"–"H_2" gas mixture, the sulfur activity of which was the same as that of the H_2S–D_2 gas mixture to be used. Therefore, the sulfur activity, a_S, was kept constant throughout the isotopic exchange run, irrespective of the change in the concentration of the isotopic species.

Results and Discussion

Isotopic Exchange Reaction. Figures 1 and 2 show the change in x_{H_2}, x_{HD}, and x_{D_2}, the mole fractions of

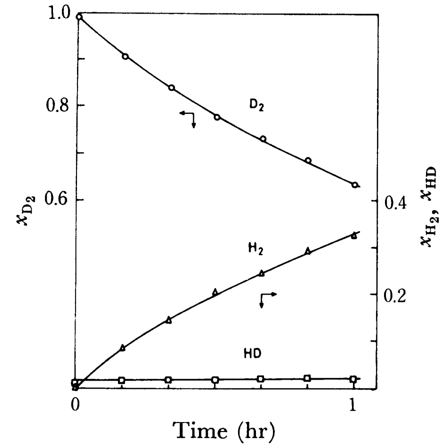

Fig. 1. Change in x_{H_2}, x_{HD}, and x_{D_2} with time. (Ag_2S, 446 °C, $P^{\circ}_{H_2S}=278$ mmHg, $P^{\circ}_{D_2}=27.8$ mmHg, $a_S=10$)

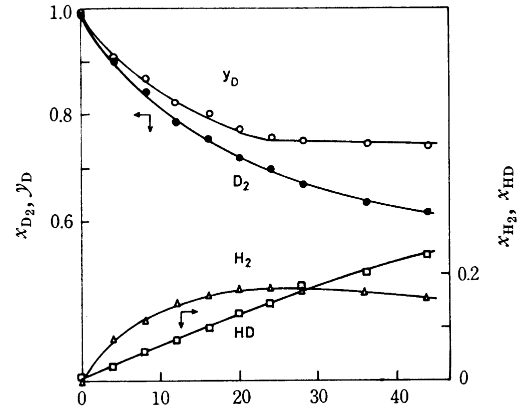

Fig. 2. Change in x_{H_2}, x_{HD}, and y_D with time. (Ag_2S, 480 °C, $P^{\circ}_{H_2S}=27.3$ mmHg, $P^{\circ}_{D_2}=81.7$ mmHg, $a_S=1/3$)

H_2, HD, and D_2 respectively, at different sulfur activities in the presence of Ag_2S. The higher range of a_S, x_{HD} remains unchanged, whereas x_{H_2} increases and x_{D_2} decreases. Thus, it may be concluded that the isotopic exchange occurs as follows:

$$H_2S + D_2 = D_2S + H_2 \tag{1}$$

This means that "H_2S" is directly converted to "H_2" by means of the reaction:

$$\text{“}H_2S\text{”} = \text{“}H_2\text{”} + S(\text{ad}) \tag{2}$$

where S(ad) represents the sulfur atom adsorbed on the surface. Reaction (2) is characterized as a redox reaction.

At $a_S = 1/3$, the HD formation becomes remarkable. However, the fraction of D in "hydrogen", $y_D (= x_{D_2} + 1/2 x_{HD})$, reaches its isotopic equilibrium value, 0.75, at the time corresponding to the maximum of x_{H_2} (Fig. 2) and then remains constant. This fact suggests that the HD formation takes place mainly by virtue of these steps:

$$H_2S = H_2 + S(\text{ad}) \tag{2'}$$

$$H_2 + D_2 = 2HD \tag{3}$$

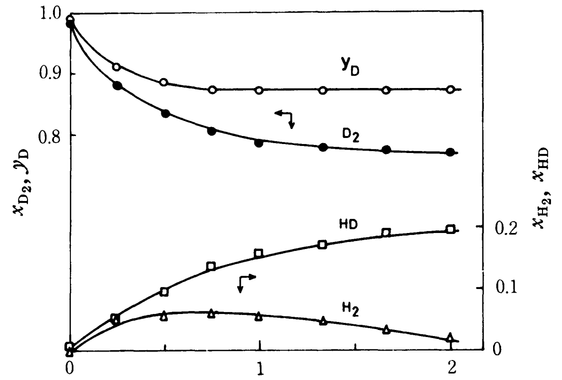

Fig. 3. Change in x_{H_2}, x_{HD}, x_{D_2}, and y_D with time. (Ag, 480 °C, $P^\circ_{H_2S} = 14.8$ mmHg, $P^\circ_{D_2} = 114.3$ mmHg, $a_s = 1/7.7$)

Figure 3 shows the change in x_{H_2}, x_{HD}, x_{D_2}, and y_D at $a_S = 1/7.7$ in the presence of Ag. The time variation of these quantities is essentially the same as in the case of Ag_2S. That is, y_D reaches its isotopic equilibrium value, 0.885, at the time corresponding to the maximum of x_{H_2}, and then it remains unchanged. Therefore, it may be concluded that the exchange reaction in the presence of Ag also proceeds *via* the (2′)—(3) steps.

One can determine k_i and k_i', the rate constants of the sulfurization and reduction of Reaction (2) respectively, by the method proposed in the previous paper.[3] Figure 4 give the plots of $\log k_i$ and $\log k_i'$ against $\log a_s$. The plots are linear. The slopes are summarized in Table 1.

Therefore, the rate equation of Reaction (2) on the surfaces of Ag and Ag_2S is expressed in the form:

$$v = kP_{\text{“}H_2S\text{”}} a_s^{-1} - k'P_{\text{“}H_2\text{”}} \tag{4}$$

The Arrhenius plots of k_i at $a_s = 1/5$ for Ag and that at $a_s = 1$ for Ag_2S are given in Fig. 5. The activation

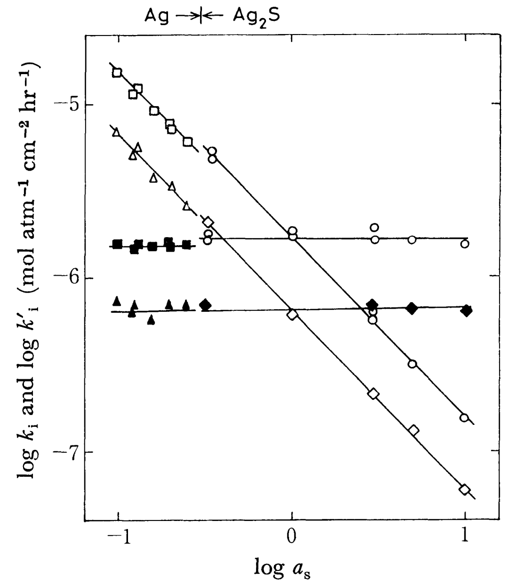

Fig. 4. Plots of $\log k_i$ and $\log k_i'$ against $\log a_s$.

Ag {□ k_i, ■ k_i', 480 °C; △ k_i, ▲ k_i', 446 °C

Ag_2S {○ k_i, ● k_i', 480 °C; ◇ k_i, ◆ k_i', 446 °C

TABLE 1. VALUES OF $(\partial \log k_i / \partial \log a_s)$ AND $(\partial \log k'_i / \partial \log a_s)$

Sample	Temperature (°C)	$(\partial \log k_i / \partial \log a_s)$	$(\partial \log k'_i / \partial \log a_s)$
Ag	480	−1.01	−0.01
	446	−1.06	−0.06
Ag_2S	480	−1.03	−0.03
	446	−1.05	−0.05

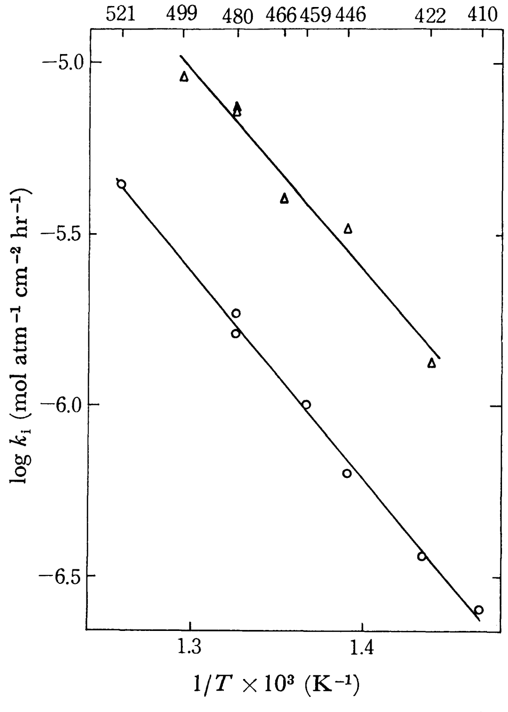

Fig. 5. Arrhenius plots for k_i at $a_s = 1$ (Ag_2S) and at $a_s = 1/5$ (Ag)

○ Ag_2S, △ Ag

TABLE 2. SUMMARY OF EXPERIMENTAL RESULTS OF H_2S–D_2 ISOTOPIC EXCHANGE STUDIES

Solid	Type of conduction	$\frac{\partial \log k_i}{\partial \log a_s}$ a)	$\frac{\partial \log k_i'}{\partial \log a_s}$ a)	Activation energy (kcal mol^{-1})
Cu_2S[2]	p-type semiconduction	−1.07	−0.07	27.8
β-$Fe_{1-x}S$[3]	metallic conduction	−0.97	0.03	26.8
MoS[4]	intrinsic semiconduction	−0.98	0.02	24.7
MnS_2[4]	p-type semiconduction	−0.95 b) ∼−0.6	0.05 b) ∼0.4	26.1
Ag_2S	n-type semiconduction	−1.03	−0.03	26.8
Ag	metallic conduction	−1.01	−0.01	27.1

a) The value at 480 °C is listed.
b) The plots of log k_i and log k'_i against log a_s are curved.

energies are 27.1 kcal mol^{-1} for Ag and 26.8 kcal mol^{-1} for Ag_2S.

Table 2 summarizes the results of the present work together with those obtained in the previous works.

Mechanism of the Surface Reaction. According to the Kobayashi-Wagner theory concerning the gas-solid interface reaction, the rate equation should be expressed as:

$$v = kP_{\text{“}H_2S\text{”}} - k'P_{\text{“}H_2\text{”}}a_s \tag{5}$$

if the solid is a metallic conductor or an intrinsic semiconductor.[3,4] As has been mentioned above, the experimental results show that the rate equation of Reaction (2) on the surface of Ag is expressed by Eq. (4). Therefore, it is evident that Eq. (5) does not hold for Ag.

Bénard and his co-workers[6] have studied the adsorption of sulfur on Ag metal in “H_2S”–“H_2” gas mixtures and found that the coverage increases from zero to a saturated value within a narrow region of log a_s as the log a_s value increases. From their results, one can conclude that the surface of silver is fully covered with sulfur atoms in the a_s and temperature ranges of the present study. In other words, θ, the fraction of the occupied adsorption sites, is independent of a_s and $(1-\theta)$ is inversely proportional to it. If the forward reaction of Eq. (2) is controlled by the transfer of sulfur atoms from “hydrogen sulfide” to the surface adsorption sites, and if the backward reaction is controlled by the removal of adsorbed sulfur atoms by “hydrogen” gas, Eq. (2) may be rewritten in this form:

$$\text{“}H_2S + \square(\text{vacant sites}) \rightleftarrows \text{“}H_2\text{”} + S(\text{ad}) \tag{6}$$

Therefore, the rate constant of sulfurization is inversely proportional to a_s, and that of the reduction is independent of it, in the a_s range studied.

The a_s dependence of the rate constants of sulfurization and reduction in the case of Ag_2S have been determined by Kobayashi and Wagner,[5] Roy and Schmalzried,[8] and Bechtold[9] by means of a solid-state electrochemical cell. Also, Takeda and his co-workers[10] employed the electrical conductivity method for the study. All the researchers other than Kobayashi and Wagner obtained the same dependence of reaction rate on a_s, as is shown in Eq. (4), and concluded that the rate-determining step was:

$$\text{“}H_2S\text{”} + 2e^- \rightleftarrows \text{“}H_2\text{”} + S^{2-}(\text{ad}) \tag{7}$$

on the basis of the Kobayashi-Wagner theory.

As has been mentioned above, the values of $(\partial \log k_i/\partial \log a_s)$ and $(\partial \log k_i'/\partial \log a_s)$ are the same for Ag and Ag_2S. Therefore, the same explanation as is the case of Ag is applicable to Ag_2S.

The activation energies and the a_s dependence of the rate constants are nearly the same for all kinds of samples studied, as is shown in Table 2. This suggests that Reaction (2) is not influenced by the electronic properties, at least not by the activity of electrons.

Summary

1) The isotopic exchange between H_2S and D_2 on Ag and Ag_2S was investigated. It was found that the isotopic exchange reaction proceeds *via* these steps:

$$H_2S + D_2 = D_2S + H_2$$
$$H_2 + D_2 = 2HD$$

2) The rate constant of the sulfurization, k_i, and that of reduction, k_i', were determined as functions of a_s and the temperature. It was found that k_i is inversely proportional to a_s, while k_i' is independent of it. The activation energies were 27.1 kcal mol^{-1} for Ag and 26.8 kcal mol^{-1} for Ag_2S.

3) The a_s dependence of the rate constants of the redox reaction on both surfaces was explained by assuming that Eq. (6) is the rate-determining step.

References

1) Terms such as “hydrogen sulfide” and “hydrogen” are used in a generic sense, irrespective of the isotopic species. The chemical symbols “H_2S” and “H_2” are employed for the chemical species of “hydrogen sulfide” and “hydrogen” respectively.

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