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Isotopic Exchange between Hydrogen Sulfide and Deuterium on the Surface of Cuprous Sulfide

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The isotopic exchange between H_2S and D_2 has been followed in the temperature range 425—525°C on a cuprous sulfide specimen. At high sulfur activities of Cu_2S, the predominant reaction is $H_2S+D_2=H_2+D_2S$, and at moderate sulfur activities the same reaction is predominant in the initial period. Analysis of kinetic data shows that the exchange reaction is first order. From the first-order rate constant, k_i, the rate constant of sulfidation of Cu_2S by "hydrogen sulfide"* and k_i', the rate constant of reduction of Cu_2S by "hydrogen"* are determined. It is shown that k_i is inversely proportional to the sulfur activity of Cu_2S and that k_i' is independent of it. Dependence of k_i and k_i' on sulfur activity is interpreted on the basis of a theory proposed by Kobayashi and Wagner. The formation of HD becomes remarkable as the sulfur activity of Cu_2S decreases. This finding shows that the reaction, $H_2S+D_2=HD+HDS$, becomes appreciable with the decrease in sulfur activity.

Oxidation and sulfidation of metals and reduction of oxides and sulfides at high temperatures implies the reaction at the gas-solid interface as an elementary step. Since not only gaseous reactants but also species in the solid phase take part in the reaction at the gas-solid interface, it is necessary to determine the reaction rate as a function of the activity of reactants in the solid phase as well as the partial pressure of reactant gases in order to discuss the reaction mechanism.

Kobayashi and Wagner[1] have constructed solid-state electrochemical cells, such as $Ag|AgI|Ag_2S|Pt$ and $Cu|CuI|Cu_2S|Pt$, and determined the rate of reduction of Cu_2S and Ag_2S by H_2 as a function of the sulfur activity, using the coulometric titration technique. They have proposed a new theory for interpreting the dependence of reaction rate on the

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[*1] Terms such as "hydrogen" and "hydrogen sulfide" are used in a generic sense, irrespective of isotopic species.

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

sulfur activity of sulfides and discussed the reaction mechanism.

On the basis of the theory proposed by Kobayashi and Wagner, several kinetic studies[2-5] have been carried out on the reaction at the gas-solid interface. As to experimental technique, the isotopic exchange method and the chemical relaxation method have been developed in addition to the coulometric titration technique.

In the present work, the isotopic exchange between H_2S and D_2 on the surface of Cu_2S is studied, and the rate of sulfidation of Cu_2S by H_2S and the rate of reduction of the sulfide by H_2 are determined as a function of the sulfur activity of Cu_2S.

From the result, the mechanism of reaction on the surface of Cu_2S is discussed.

Experimental

Apparatus. The apparatus is shown in Fig. 1. A is a Cu_2S specimen placed in a reaction vessel B, which is heated by an electric furnace C. A magnetic pump D and valves E are used for circulating the gas mixture in the reaction system in the direction indicated by arrows. M is a mercury manometer. F is used to collect a small portion of gas. G is a U-shaped glass trap for the separation of "hydrogen sulfide" from "hydrogen". H is a bulb to transfer samples of gas to a mass spectrometer. I, J, and K are reservoirs for purified D_2, H_2S, and H_2, respectively, and L a reservoir for gas mixtures of H_2S and D_2.

Materials. *a) Purification of* H_2. Hydrogen of commercial grade was passed through paradium-asbestos catalyser heated at 450°C to convert the trace of oxygen into water vapor. The gas was then dried by means of a tube filled with desiccating agent $Mg(ClO_4)_2$ and stored in a gas reservoir.

b) Purification of D_2. Heavy water supplied by the Showa Denko Co. was electrolysed in a U-shaped electrolytic cell equipped with a diaphragm of sintered glass. Impurity oxygen was removed in the same way as in the purification of H_2. A typical composition of deuterium gas was 96% D_2, 3.1% HD and 0.9% H_2.

c) Purification of H_2S. Hydrogen sulfide gas, 99.9% pure, was passed through a desiccating tube of $Mg(ClO_4)_2$ and condensed in a trap cooled by liquid nitrogen. The trap then was evacuated to remove uncondensed gaseous impurities and the condensed hydrogen sulfide was evaporated by removing liquid nitrogen.

d) Preparation of Cu_2S *Specimen.* A copper specimen, 9.0 cm long and 4.2 cm wide, was taken from a high purity copper sheet with thickness 0.22 mm. After being polished with a 1000-emery paper, the specimen was cleaned by petroleum ether and stored in a desiccator. The finished copper specimen was then folded and placed in a pyrex tube. High purity sulfur with an amount 5% more than that necessary for the formation of stoichiometric cuprous sulfide was added to the tube. After evacuation, the tube was sealed and placed in a furnace heated at 400°C to let copper react with sulfur to form Cu_2S. After the completion of sulfidation, the specimen was annealed in a H_2S-H_2 gas mixture.

Experimental Procedure. Prior to the isotopic exchange reaction, a H_2S-H_2 gas mixture, the sulfur activity of which was the same as that of a H_2S-D_2 gas mixture to be used in the isotopic exchange reaction, was admitted to the reaction vessel and the Cu_2S specimen was kept in the atmosphere for a period until equilibrium was attained between the Cu_2S specimen and the H_2S-H_2 gas mixture. The H_2S-H_2 gas mixture

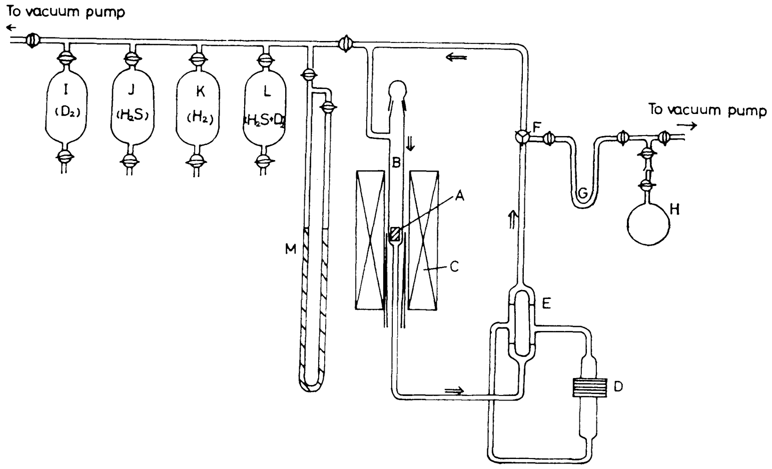

Fig. 1. Apparatus for the isotopic exchange experiment
A Cu_2S specimen, B reaction vessel, C furnace, D magnetic pump, E valves, F sampling tube, G U-shaped trap, H sampling bulb for mass-spectroscopic analysis, I—L gas reservoirs, M mercury manometer

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2) H. J. Grabke, *Ber. Bunsenges. Physik. Chem.*, **69**, 48 (1965).

3) H. J. Grabke, *ibid.*, **70**, 664 (1966).

4) S. Stotz, *ibid.*, **70**, 37 (1966).

5) E. Bechtold, *ibid.*, **69**, 328 (1965).

was removed and a H_2S-D_2 gas mixture was introduced into the reaction system and circulated by a circulation pump.

Small portions of the mixture were collected in F, and then expanded to G. After "hydrogen sulfide" in the U-shaped tube G was frozen out with liquid nitrogen around the trap, "hydrogen" was transferred to the bulb H to be analyzed by means of a mass-spectrometer.

Results and Discussion

Blank Experiment. In order to investigate whether or not the isotopic exchange reaction between D_2 and H_2S occurs in the absence of Cu_2S, a blank experiment has been carried out at various temperatures. No exchange was observed below 525°C, and about 5% of the initial amount of D_2 was found to have exchanged after 3 hr of reaction at 575°C. Thus the experiment was carried out below 525°C.

Change in Mole Fractions of H_2, HD and D_2 with Time. From the data of mass-spectroscopic analysis, mole fractions of H_2, HD and D_2 were calculated, where the mole fraction is the number of moles of a specific kind of hydrogen divided by the total number of moles of "hydrogen." The mole fractions are denoted by x_{H_2}, x_{HD} and x_{D_2}.

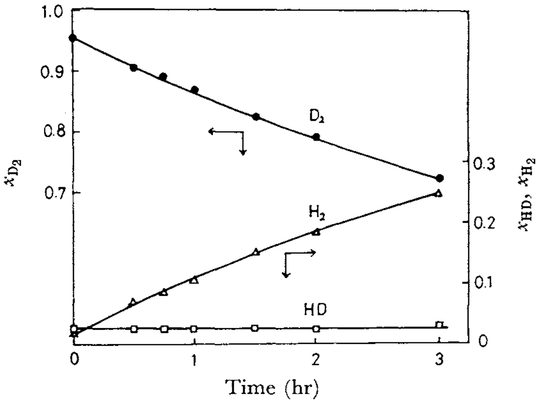

Fig. 2. Change in x_{D_2}, x_{HD} and x_{H_2} with time. (478°C, $P^{\circ}_{H_2S}=160$ mmHg, $P^{\circ}_{D_2}=20$ mmHg, $a_S=4$)

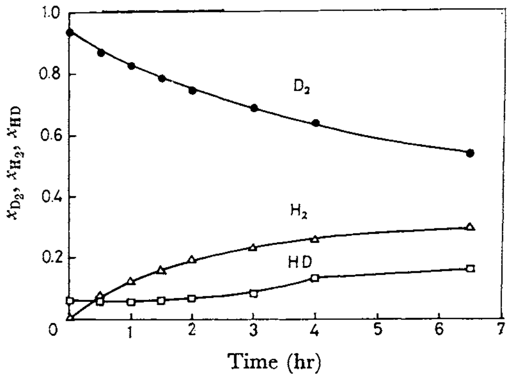

Fig. 3. Change in x_{D_2}, x_{DH} and x_{H_2} with time. (478°C, $P^{\circ}_{H_2S}=20$ mmHg, $P^{\circ}_{D_2}=20$ mmHg, $a_S=1$)

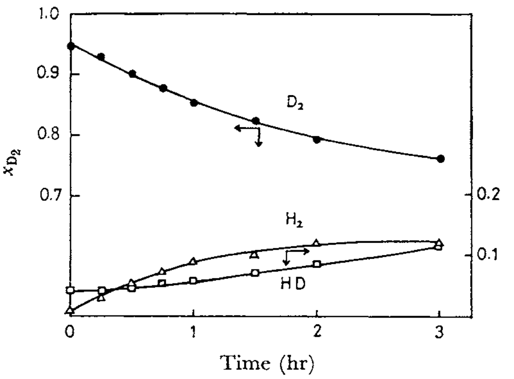

Fig. 4. Change in x_{D_2}, x_{HD} and x_{H_2} with time. (478°C, $P^{\circ}_{H_2S}=40$ mmHg, $P^{\circ}_{D_2}=160$ mmHg, $a_S=1/4$)

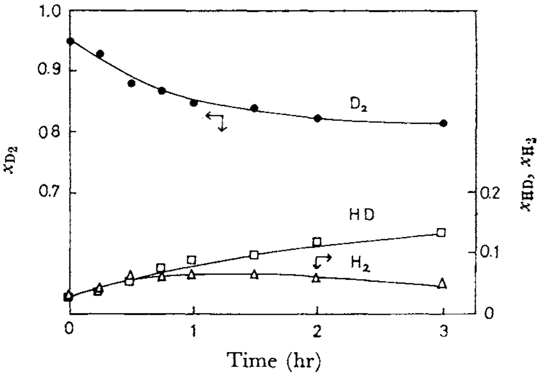

Fig. 5. Change in x_{D_2}, x_{HD} and x_{H_2} with time. (478°C, $P^{\circ}_{H_2S}=40$ mmHg, $P^{\circ}_{D_2}=400$ mmHg, $a_S=1/10$)

Figures 2 to 5 give the plots of x_{H_2}, x_{HD} and x_{D_2} against time at different sulfur activities. The sulfur activity, a_S, was defined as the pressure ratio of "hydrogen sulfide" to "hydrogen." Figure 2 shows the change in x_{H_2}, x_{HD} and x_{D_2} with time in the case where a_S is 4. As seen from the figure, x_{HD} remains unchanged, whereas x_{H_2} increases and x_{D_2} decreases. Thus, the predominant exchange reaction is

$$H_2S + D_2 = D_2S + H_2 \qquad (1)$$

This reaction proceeds *via* the sulfidation of Cu_2S by H_2S and the reduction by H_2 as follows:

$$H_2S = H_2 + \text{"S(a)"} \qquad (2)$$

$$D_2 + \text{"S(a)"} = D_2S \qquad (3)$$

where "S(a)" denotes sulfur atoms or ions on the surface of Cu_2S. Accordingly, the rate of sulfidation of Cu_2S by H_2S can be obtained from the kinetic of reaction (1).

The change in mole fractions of H_2, HD, and D_2 at $a_S=1$ is given in Fig. 3. x_{HD} is constant during the initial period of reaction and then increases with time. As seen in Fig. 4, the change in mole fractions with time at $a_S=1/4$ is similar to that at $a_S=1$, but the initial period where x_{HD} is constant is shorter. At $a_S=1/10$, the formation of HD is remarkable. HD would be formed by the reaction

$$H_2S + D_2 = HDS + HD \qquad (4)$$

Reaction (4) probably proceeds *via* steps,

$$H_2S = H(a) + HS(a) \qquad (5)$$

$$D_2 = 2D(a) \qquad (6)$$

$$H(a) + D(a) = HD \qquad (7)$$

$$HS(a) + D(a) = HDS$$

where H(a), D(a), HS(a) represent H, D and HS adsorbed on the surface of Cu_2S.

It is noteworthy that the mechanism of reaction at the gas-solid interface changes with the activity of reactants in the solid phase.

Order of Reaction and Rate Constants of Sulfidation and Reduction. According to McKay's law,[6] the rate of isotopic exchange is first order regardless of the individual forward or reverse reactions. If only reaction (1) occurs and the reaction obeys McKay's law, the rate of exchange per unit area of Cu_2S specimen is given by the equation

$$\frac{\dot{n}_{D_2}}{A} = k_i P_{D_2S} - k_i' P_{D_2} \qquad (9)$$

or

$$\frac{\dot{n}_{H_2}}{A} = k_i P_{H_2S} - k_i' P_{H_2} \qquad (10)$$

where A is the apparent surface area of Cu_2S specimen, n_{H2} and n_{D2} are, respectively, numbers of moles of H_2 and D_2 in the reaction system at the time of t, k_i is the rate constant of sulfidation of Cu_2S by "hydrogen sulfide" and k_i' is the rate constant of reduction of Cu_2S by "hydrogen."

Let us solve Eq. (9). The equation is rewritten as

$$\frac{\dot{n}_{D_2}}{A} = \frac{RT}{V}(k_i n_{D_2S} - k_i' n_{D_2}) \qquad (11)$$

where V is the dead volume of the reaction system. Since only reaction (1) is assumed to occur, $n^{\circ}_{D_2}$, the number of moles of D_2 at the beginning of reaction, is equal to the sum of n_{D_2} and n_{D_2S} at the time of t, thus

$$n^{\circ}_{D_2} = n_{D_2} + n_{D_2S} \qquad (12)$$

Insertion of Eq. (12) into Eq. (11) yields

$$\frac{\dot{n}_{D_2}}{A} = \frac{RT}{V}\{k_i n^{\circ}_{D_2} - (k_i + k_i')n_{D_2}\} \qquad (13)$$

At equilibrium $n_{D_2}=0$, accordignly,

$$\frac{n^{e}_{D_2}}{n^{\circ}_{D_2}} = \frac{k_i}{k_i + k_i'} \qquad (14)$$

where $n^{e}_{D_2}$ represents the number of moles of D_2 at equilibrium. Inserting Eq. (14) into Eq. (13), we obtain

$$\dot{n}_{D_2} = -\frac{ART}{V}(k_i + k_i')(n_{D_2} - n^{e}_{D_2}) \qquad (15)$$

Integration of Eq. (15) yields

$$-\log\frac{n_{D_2} - n^{e}_{D_2}}{n^{\circ}_{D_2} - n^{e}_{D_2}} = \frac{ART(k_i + k_i')}{2.303V}t \qquad (16)$$

By replacing n_{D_2}, $n^{\circ}_{D_2}$ and $n^{e}_{D_2}$ by x_{D_2}, $x^{\circ}_{D_2}$ and $x^{e}_{D_2}$, respectively, Eq. (16) is rewritten as

$$-\log\frac{x_{D_2} - x^{e}_{D_2}}{x^{\circ}_{D_2} - x^{e}_{D_2}} = \frac{ART(k_i + k_i')}{2.303V}t \qquad (17)$$

If we denote the slope of the polt of $-\log\{x_{D_2} - x^{e}_{D_2})/(x^{\circ}_{D_2} - x^{e}_{D_2}\}$- against t by α, we have

$$\alpha = \frac{ART(k_i + k_i')}{2.303V} \qquad (18)$$

k_i and k_i' are represented by the following equations.

$$k_i = \frac{2.303\alpha V}{ART}\frac{x^{e}_{D_2}}{x^{\circ}_{D_2}} \qquad (19)$$

and

$$k_i' = \frac{2.303\alpha V}{ART}\left(1 - \frac{x^{e}_{D_2}}{x^{\circ}_{D_2}}\right) \qquad (20)$$

Therefore, if α is determined experimentally, k_i and k_i' can be calculated by Eqs. (19) and (20).

The solution of Eq. (10) has a form

$$-\log\frac{x^{e}_{H_2} - x_{H_2}}{x^{e}_{H_2} - x^{\circ}_{H_2}} = \frac{ART(k_i + k_i')}{2.303V}t \qquad (21)$$

The slope of the plot of $\log\{(x^{e}_{H_2} - x_{H_2})/(x^{e}_{H_2} - x^{\circ}_{H_2})\}$ *vs.* t. is the same that of the plot of $\log\{(x_{D_2} - x^{e}_{D_2})/(x^{\circ}_{D_2} - x^{e}_{D_2})\}$ *vs.* t. Therefore, it is also possible to calculate the values of k_i and k_i' from the data for H_2.

The plot of $\log\{(x_{D_2} - x^{e}_{D_2})/(x^{\circ}_{D_2} - x^{e}_{D_2})\}$ *vs.* t for the data given in Fig. 2 is shown in Fig. 6. In this figure the plot of $\log\{(x^{e}_{H_2} - x_{H_2})/(x^{e}_{H_2} - x^{\circ}_{H_2})\}$ *vs.* t

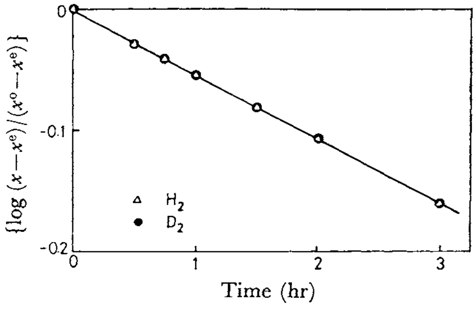

Fig. 6. Plot of $\log\{(x-x^{e})/(x^{\circ}-x^{e})\}$ *vs.* t for the data given in Fig. 2.
(478°C, $P^{\circ}_{H_2S}=160$ mmHg, $P^{\circ}_{D_2}=40$ mmHg, $a_S=4$)

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[6] H. A. C. McKay, *Nature*, **142**, 997 (1938).

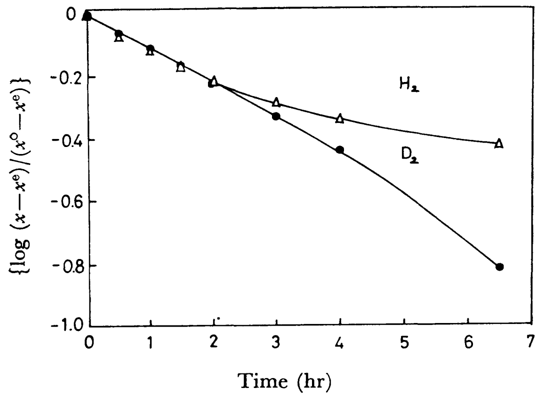

Fig. 7. Plot of $\log\{(x-x^e)/(x^\circ-x^e)\}$ *vs.* *t* for the data given in Fig. 3.
(478°C, $P^\circ_{H_2S}$=20mmHg, $P^\circ_{D_2}$ =20 mmHg, a_S=1)

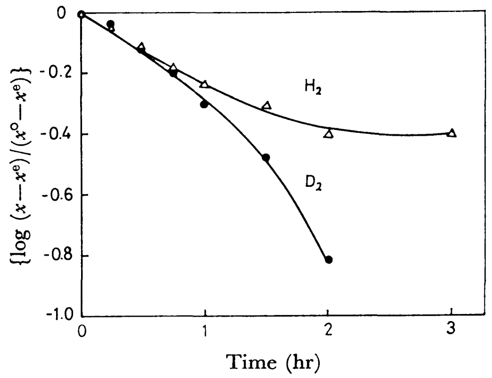

Fig. 8. Plot of $\log\{(x-x^e)/(x^\circ-x^e)\}$ *vs.* *t* for the data given in Fig. 4.
(478°C, $P^\circ_{H_2S}$=40 mmHg, $P^\circ_{D_2}$ =160 mmHg, a_S= 1/4)

Table 1. Values of k_i and k_i'

Temp. (°C)	$P^\circ_{H_2S}$ (mmHg)	$P^\circ_{D_2}$ (mmHg)	a_S	observed $k_i\times10^9$ $\frac{\text{mol}}{\text{atm cm}^2\cdot\text{sec}}$	observed $k_i'\times10^9$ $\frac{\text{mol}}{\text{atm cm}^2\cdot\text{sec}}$	mean $k_i\times10^9$ $\frac{\text{mol}}{\text{atm cm}^2\cdot\text{sec}}$	mean $k_i'\times10^9$ $\frac{\text{mol}}{\text{atm cm}^2\cdot\text{sec}}$
525	20	20	1	5.40	4.89	5.82 ±0.34	5.33 ±0.31
	40	40	1	5.82	5.50		
	80	80	1	6.42	5.59		
500	80	80	1	4.02	3.94		
478	160	40	4	0.591	2.31	0.655±0.064	2.52 ±0.21
	320	80	4	0.719	2.73		
	40	20	2	1.18	2.32	1.24 ±0.08	2.46 ±0.16
	80	40	2	1.20	2.36		
	133	66	2	1.36	2.69		
	20	20	1	3.01	2.92	2.57 ±0.27	2.53 ±0.24
	20	20	1	2.71	2.64		
	33	33	1	2.41	2.37		
	40	40	1	2.76	2.71		
	80	80	1	2.30	2.26		
	80	80	1	2.25	2.29		
	20	41	1/2	5.08	2.76	5.92 ±0.21	2.93 ±0.31
	27	54	1/2	5.70	2.67		
	90	180	1/2	6.20	3.36		
	21	82	1/4	13.0	2.97		
450	40	40	1	0.836	0.868	0.919±0.058	0.929±0.043
	80	80	1	1.000	0.990		
425	40	40	1	0.538	0.521	0.507±0.014	0.523±0.015
	73	73	1	0.507	0.493		

is also given. $x^e_{D_2}$ and $x^e_{H_2}$ are calculated by the equations

$$x^e_{D_2} + x^e_{H_2} = 1 \tag{22}$$

$$\frac{x^e_{D_2}}{x^e_{H_2}} = \frac{P^\circ_{D_2}}{P^\circ_{H_2S}} \tag{23}$$

where $P^\circ_{D_2}$ and $P^\circ_{H_2S}$ are the partial pressures of D_2 and H_2S at the beginning of reaction, respectively. Both plots are straight and coincide well with each other.

Similar plots for the data given in Fig. 3 and

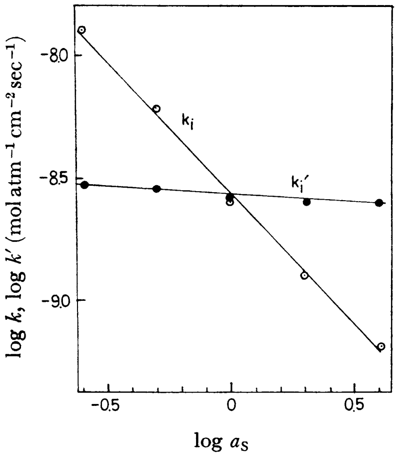

Fig. 9. Plots of $\log k_i$ and $\log k_i'$ against $\log a_S$.

Fig. 4 are shown in Fig. 7 and Fig. 8, respectively. McKay's law holds in the initial period where x_{HD} remains constant, and the straight line portion for D_2 well agrees with that for H_2.

The values of k_i and $k_{i'}$ calculated by Eqs. (19) and (20) are listed in Table 1. It is seen from the table that the value of k_i is the same irrespective of the total pressure, if the values of a_S is the same.

Dependence of k_i and $k_{i'}$ on a_S. Figure 9 gives the plot of $\log k_i$ *vs.* $\log a_S$ and that of $\log k_{i'}$ *vs.* $\log a_S$. Both plots are linear. The slope for the former plot is -1.07 and that for the latter is -0.07. Such dependence of k_i and $k_{i'}$ on a_s is explained on the basis of the theory by Kobayashi and Wagner as follows.

The reaction between H_2S and H_2 on the surface of Cu_2S proceeds by the following parallel reactions

$$H_2S \rightleftarrows H_2 + S \tag{24 A}$$

$$H_2S + e^- \rightleftarrows H_2 + S^- \tag{24 B}$$

$$H_2S + 2e^- \rightleftarrows H_2 + S^{2-} \tag{24 C}$$

where e^- denotes electrons in Cu_2S, and S, S^- and S^{2-} are adsorbed sulfur atoms, monovalent sulfur ions and divalent sulfur ions, respectively.

Assuming that adsorbed sulfur atoms and sulfur ions are in equilibrium with those in bulk of cuprous sulfide, we obtain the following rate equations:

$$\left(\frac{\dot{n}_{H_2}}{A}\right)_A = k_1 P_{H_2S} - k_1' P_{H_2} a_S \tag{25 A}$$

$$\left(\frac{\dot{n}_{H_2}}{A}\right)_B = k_2 P_{H_2S} a_e - k_2' P_{H_2} a_{S^-} \tag{25 B}$$

$$\left(\frac{\dot{n}_{H_2}}{A}\right)_C = k_3 P_{H_2S} (a_e)^2 - k_3' P_{H_2} a_{S^{2-}} \tag{25 C}$$

where a_S, a_S^-, a_S^{2-} and a_e represent the activities of respective species. The first terms on the right side are the rate of sulfidation of Cu_2S and the second ones are the rate of reduction.

There are also several equilibrium relationships in solid phase. They are:

$$S^- \rightleftarrows S + e^-$$

$$\frac{a_S a_e}{a_{S^-}} = K_1 \tag{26}$$

$$S^{2-} \rightleftarrows S + 2e^-$$

$$\frac{a_S (a_e)^2}{a_{S^{2-}}} = K_2 \tag{27}$$

Moreover, for cuprous sulfide, we have

$$(a_{Cu})^2 a_S = K_3 \tag{28}$$

According to Wagner and Wagner[7] the activity of cuprous ions in cuprous sulfide is independent of the composition of Cu_2S. Hence

$$a_{Cu} = K_4' a_{Cu^+} a_e = K_4 a_e \tag{29}$$

From Eqs. (28) and (29), we obtain

$$a_e = K_5 (a_S)^{-1/2} \tag{30}$$

Combination of Eqs. (26), (27) and (30) yields

$$a_{S^-} = K_6 (a_S)^{1/2} \tag{31}$$

$$a_{S^{2-}} = K_7 \tag{32}$$

Inserting Eqs. (30), (31) and (32) into Eqs. (25 A), (25 B) and (25 C), we obtain

$$\left(\frac{\dot{n}_{H_2}}{A}\right)_A = k_1 P_{H_2S} - k_1' P_{H_2} a_S \tag{33 A}$$

$$\left(\frac{\dot{n}_{H_2}}{A}\right)_B = k_2 K_5 P_{H_2S} (a_S)^{-1/2} - k_2' K_6 P_{H_2} (a_S)^{1/2} \tag{33 B}$$

$$\left(\frac{\dot{n}_{H_2}}{A}\right)_C = k_3 K_5^2 P_{H_2S} (a_S)^{-1} - k_3' K_7 P_{H_2} \tag{33 C}$$

These equations are summarized into a generalized formula

$$\frac{\dot{n}_{H_2}}{A} = v_{ox} - v_{red} = k P_{H_2S} (a_S)^{-m/2} - k' P_{H_2} (a_S)^{n/2} \tag{34}$$

or

$$\frac{\dot{n}_{H_2}}{A} = k P_{H_2S} (a_e)^m - k' P_{H_2} (a_e)^{-n} \tag{35}$$

where m and n are constants characteristic of reaction mechanism, namely,

$m=0$, $n=2$ for mechanism (24 A)
$m=1$, $n=1$ for mechanism (24 B)
$m=2$, $n=0$ for mechanism (24 C)

From a comparison of Eq. (34) with Eq. (9) or (10) we obtain

$$k_i = k(a_S)^{-m/2} \tag{36}$$

$$k_i' = k'(a_S)^{n/2} \tag{37}$$

As mentioned already, the slope of the plot of $\log k_i$ *vs.* $\log a_S$ is -1.07 and that of the plot of $\log k_{i'}$ *vs.* $\log a_S$ is -0.07. It is thus concluded that m is 2 and n is 0. This result shows that mechanism (24 C) prevails in this case.

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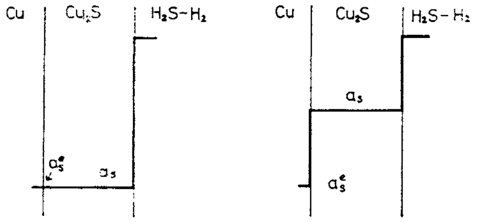
[7] J. B. Wagner and C. Wagner, *J. Chem. Phys.*, **26**, 1597 (1957).

TABLE 2. COMPARISON OF DATA OF ISOTOPIC EXCHANGE WITH THAT OF COPPER SULFIDATION

Temp. (°C)	k_L^0 $\frac{\text{mol}}{\text{atm cm}^2\cdot\text{sec}}$	a_S^e	$k_i(1)$ $\frac{\text{mol}}{\text{atm cm}^2\cdot\text{sec}}$	$k_i(a_S^e)$ $\frac{\text{mol}}{\text{atm cm}^2\cdot\text{sec}}$
500	5.93×10^{-7}	1.78×10^{-4}	3.94×10^{-9}	2.21×10^{-5}
450	2.22×10^{-7}	1.12×10^{-4}	0.919×10^{-9}	8.21×10^{-6}

Comparison of the Data of the Isotopic Exchange with That of Copper Sulfidation. The authors[8] have studied the sulfidation of Cu by H_2S and H_2S-H_2 gas mixtures and found that; (1) the reaction obeys the linear rate law, (2) the linear rate constant is proportional to the partial pressure of H_2S, and (3) the linear rate constant is nearly independent of the partial pressure of hydrogen. The findings show that the sulfidation of Cu by H_2S is mainly controlled by the reaction at the gas sulfide interface. k_L^0, the linear rate constant at 1 atm of H_2S, is listed in the second column of Table 2.



(a) (b)

Fig. 10. Schematic representations of distribution of sulfur activity during the sulfidation of copper.

If the reaction at the gas-sulfide interface is much slower than the reaction at the metal-sulfide interface and the diffusion of materials across the sulfide, the sulfur activity would drop at the gas-sulfide interface appreciably, because a large driving force is needed at the interface to advance the reaction. In an ideal case, the sulfur activity at the gas-sulfide interface is equal to the sulfur activity in coexistence of Cu and Cu_2S, as schematically shown in Fig. 10(a). In this case, the rate of sulfidation of Cu by H_2S should be equal to k_i at a_S^e. The fifth column in Table 2 gives the estimated k_i values at a_S^e, assuming that the relationship between k_i and a_S found in the present work holds down to a_S^e. The calculated k_i value at a_S^e is about two orders higher than the observed linear rate constant k_L^0 in magnitude.

A possible explanation for this discrepancy is as follows. If the reaction at the metal-sulfide interface is as slow as the reaction at the gas-sulfide interface, the sulfur activity also drops at the metal-sulfide interface as shown in Fig. 10(b). Accordingly, a_S, the sulfur activity of Cu_2S at the gas-sulfide interface, is higher than a_S^e, and the k_i value at a_S is smaller than that at a_S^e. Further experiment is needed to elucidate the cause of the discrepancy.

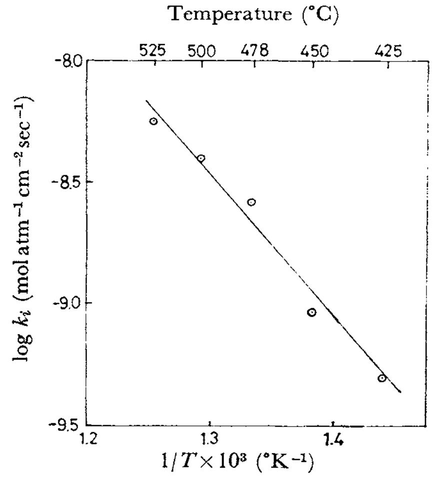


Fig. 11. Arrhenius plot for k_i at $a_S=1$.

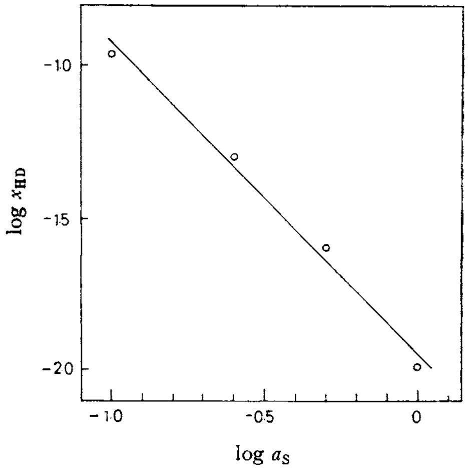


Fig. 12. Relationship between x_{HD} and a_S at 15% conversion of D_2. (478°C)

The Arrhenius plot of k_i at $a_S=1$ is given in Fig. 11. Activation energy determined from the slope is 27.8 kcal/mol. On the other hand, the activation energy of sulfidation of Cu in H_2S is 21.3 kcal/mol. In the latter case, the sulfur activity of Cu_2S surface would change with tempera-

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[8] M. Takeda, K. Fueki and T. Mukaibo, *J. Electrochem. Soc. Jap.*, **36**, 95 (1968).

ture. The difference in the activation energy might be due to the difference in the temperature dependence of sulfur activity on Cu_2S surface.

Formation of HD. As already mentioned, the formation of HD becomes remarkable as the sulfur activity of Cu_2S decreases. Figure 12 shows the relationship between the sulfur activity of Cu_2S and the mole fraction of HD at the time where 15% of the initial amount of D_2 has been exchanged. Correlation between the formation of HD and the sulfur activity is evident. However, because of the lack of adequate kinetic data, detailed discussion on the mechanism of formation of HD is difficult for the time being.

Summary

(1) The isotopic exchange between H_2S and D_2 on Cu_2S was investigated as a function of temperature and a_S, the sulfur activity of Cu_2S.

(2) It was found that when a_S is high the exchange reaction $H_2S+D_2=H_2+D_2S$ is predominant and the formation of HD is small. It was also found that when a_S is low the formation of HD proceeds after an initial period of reaction.

(3) The rate of exchange reaction $H_2S+D_2=H_2+D_2S$ was found to obey McKay's law, and the first-order rate constants were obtained. k_i, the rate constant of sulfidation of Cu_2S by H_2S, and k_i', the rate constant of reduction of Cu_2S by H_2 were calculated from the first-order rate constants.

(4) Both plots of $\log k_i$ *vs.* $\log a_S$ and $\log k_i'$ *vs.* $\log a_S$ were linear. The slope of the former plot was -1.07 whereas that of the latter was -0.07.

(5) Based on the theory proposed by Kobayashi and Wagner, the predominant reaction mechanism for the reaction $H_2S+D_2=H_2+D_2S$ was discussed.

(6) Activation energy was found to be 27.8 kcal/mol.

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