An Investigation of a Surface Reaction between Pyrrhotite and the Hydrogen–Hydrogen Sulfide Mixture

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The isotopic exchange between H_2S and D_2 has been studied in the temperature range from 480 °C to 551 °C on a pyrrhotite specimen. The isotopic exchange reaction proceeded *via* these steps:

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

From the analysis of the kinetic data, the rate constant of the sulfurization of $Fe_{1-x}S$ by "hydrogen sulfide,"[1] k_i, and that of reduction by "hydrogen,"[1] k_i', were determined. It was found that k_i is inversely proportional to the sulfur activity of $Fe_{1-x}S$, a_S, and that k_i' is independent of it. It was found that the rate equation for the sulfurization of $Fe_{1-x}S$ in the "hydrogen"–"hydrogen sulfide" gas mixture could be expressed in the form of $v=kP_{\text{"}H_2S\text{"}}a_S^{-1}-k'P_{\text{"}H_2\text{"}}$.[1] A possible mechanism of the reaction at the surface of $Fe_{1-x}S$ is discussed.

For the elucidation of the mechanism of the gas-solid interface reaction, it is necessary to determine the reaction rate as a function of the activity of chemical species in a solid as well as the partial pressure of the reactant gases. Such a study was first carried out by Kobayashi and Wagner[2] for the reduction of silver sulfide by "hydrogen." Several methods have been developed on the same basis of the theory proposed by them and have been applied to oxide and sulfide systems.[3–7]

The present work aims to study the reaction at the interface between β-$Fe_{1-x}S$ and a "hydrogen"–"hydrogen sulfide" gas mixture by using the isotopic exchange method.

Experimental

$Fe_{1-x}S$ Specimen. An iron specimen was taken from a Ferrovac E sheet (0.05 mm thick). After being polished with 1000-emery paper and cleaned by petroleum ether, it was sulfurized in a gas mixture of hydrogen sulfide and hydrogen at 580 °C. As the $Fe_{1-x}S$ was fragile, it could not be used in the form of "foil" through many runs. Therefore, it was crushed lightly and the powder larger than 170 mesh was used as a sample. The surface area was 133.3 $cm^2\,g^{-1}$.

Isotopic Exchange Method. The apparatus, the method of the purification of gases, and the experimental procedure were essentially the same as in the isotopic exchange experiment on Cu_2S.[7] As the pyrrhotite sample was a powder, a Pyrex glass reaction vessel with a G3 filter (Fig. 1) was used, and the temperature was measured at a position near the sulfide sample.

The isotopic exchange was carried out after the chemical equilibrium had been reached between the sulfide and the "hydrogen"–"hydrogen sulfide" gas mixture. Therefore, a_S, the sulfur activity of the solid, defined as the pressure ratio of "hydrogen sulfide" to "hydrogen," was kept constant throughout the isotopic exchange run, irrespective of the change in the concentration of isotopic species.

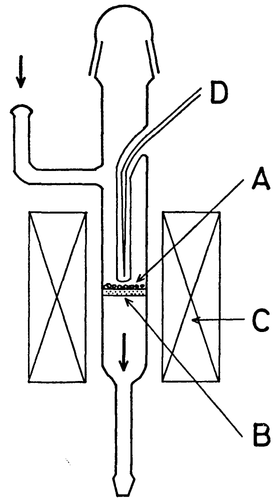

Fig. 1. Reaction vessel for the isotopic exchange experiment.
A $Fe_{1-x}S$ specimen B G3 filter
C furnace D Thermocouple

A blank test showed that, in the absence of $Fe_{1-x}S$, no exchange occurred below 528 °C, whereas a little exchange did occur at 551 °C. No deposition of sulfur occurred at the cold portions of reaction vessel over all the temperature and gas composition ranges studied.

Results and Discussion

Isotopic Exchange Reaction. Figures 2–4 give the change in x_{H_2}, x_{HD}, and x_{D_2}, the mole fractions of H_2, HD, and D_2 respectively, at different sulfur activities.

The following two mechanisms are possible for the formation of H_2 and HD. In the first mechanism, H and D atoms are formed by the dissociation of H_2S and D_2 *via* (1a) and (1b):

$$H_2S \rightleftharpoons HS(ad) + H(ad) \quad (1a)$$
$$D_2 \rightleftharpoons 2\,D(ad) \quad (1b)$$

where H(ad), D(ad), and HS(ad) represent H, D,

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[1] Terms such as "hydrogen" and "hydrogen sulfide" 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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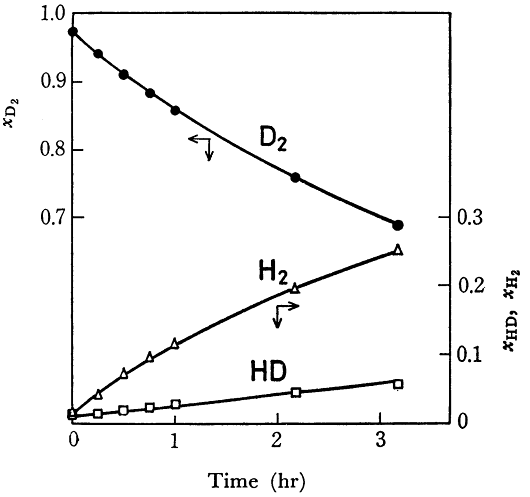

Fig. 2. Change in x_{D_2}, x_{HD} and, x_{H_2} with time. (551 °C, $P^0_{H_2S}=123.6$ mmHg, $P^0_{D_2}=30.9$ mmHg, $a_S=4$).

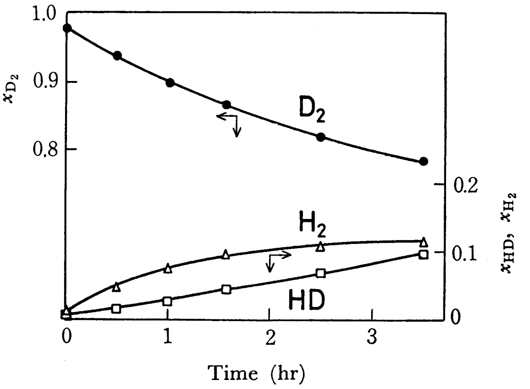

Fig. 3. Change in x_{D_2}, x_{HD}, and x_{H_2} with time. (551 °C, $P^0_{H_2S}=17.6$ mmHg, $P^0_{D_2}=70.4$ mmHg, $a_S=1/4$).

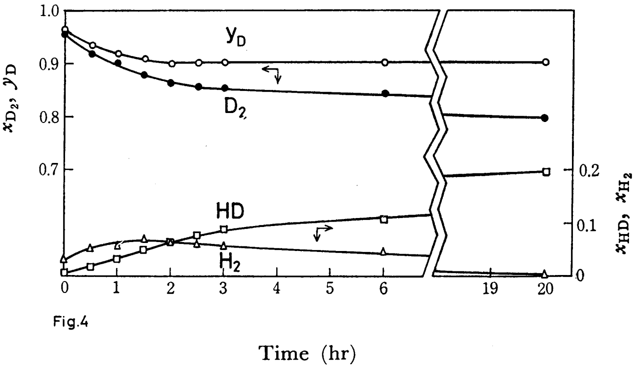

Fig. 4. Change in y_D, x_{D_2}, x_{HD}, and x_{H_2} with time. (551 °C, $P^0_{H_2S}=12.5$ mmHg, $P^0_{D_2}=125$ mmHg, $a_S=1/10$).

and HS adsorbed on the surface of $Fe_{1-x}S$. Then, H_2 and HD are formed by these reactions:

$$D(ad) + H(ad) \rightleftharpoons HD \tag{1c}$$

$$H(ad) + H(ad) \rightleftharpoons H_2 \tag{1d}$$

In the second mechanism, H_2S is directly converted to H_2, giving a sulfur atom to the lattice site on $Fe_{1-x}S$

$$H_2S \rightleftharpoons H_2 + S(lattice) \tag{2a}$$

The (2a) reaction is characterized as the redox reaction or as the two atom-direct exchange reaction. Then, H_2 and D_2 react to form HD:

$$H_2 + D_2 \rightleftharpoons 2\,HD \tag{2b}$$

As may be seen from Figs. 2—4, the rate of HD formation was smaller than that of H_2 in the initial period, and the formation of HD became remarkable only after the concentration of H_2 became high. These facts suggest that the (2a) and (2b) mechanisms are more predominant than (1a)—(1d). The second mechanism may also be confirmed as follows.

Let us define y_D, the fraction of D in "hydrogen," by:

$$y_D = x_{D_2} + \frac{1}{2}x_{HD} \tag{3a}$$

and y_H, the fraction of H in "hydrogen," by:

$$y_H = x_{H_2} + \frac{1}{2}x_{HD} \tag{3b}$$

At $a_s=1/10$, y_D decreases with time during the initial period, but it reaches a constant value at the time corresponding to the maximum of x_{H_2}; thereafter it remains unchanged, while x_{H_2}, x_{HD}, and x_{D_2} are still changing. When the value of a_s is 1/10, the ratio of H to D is also 1/10. Thus, after the isotopic equilibrium is attained between "hydrogen" and "hydrogen sulfide," the ratio of y_H to y_D is 1/10; *i. e.*, y_D is 0.909. Figure 4 shows that the constant value of y_D is equal to 0.909 within the limits of experimental error. The results clearly show that the H to D ratio attains equilibrium at the time x_{H_2} reaches its maximum and that, thereafter, only relative changes of x_{H_2}, x_{HD}, and x_{D_2} occur. That is, these results mean that H_2 and HD are formed by the mechanisms of (2a)—(2b) and not by (1a)—(1d).

At the beginning of the reaction, only H_2S and D_2 exist in the gas phase of the reaction system. Because the exchange reaction proceeds *via* (2a) and (2b), the amount of H in "hydrogen" at any time represents the amount of H transported from "hydrogen sulfide" to "hydrogen" *via* (2a). Similarly, the amount of D in "hydrogen sulfide" represents the amount of D transported from "hydrogen" to "hydrogen sulfide" *via* (2a). Accordingly, the change in the amount of D in "hydrogen" with time is given by this equation:

$$\frac{1}{A}\frac{dn_D}{dt} = \frac{RT}{V}(k_i n_D' - k_i' n_D) \tag{4}$$

where A is the surface area of $Fe_{1-x}S$, where k_i and k_i' are the rate constant of sulfurization and reduction respectively (mol atm^{-1} cm^{-2} hr^{-1}), and where V is the volume of the reaction system. n_D and n_D' are defined as follows:

$$n_D = n_{D_2} + \frac{1}{2}n_{HD} = n_{\text{“}H_2\text{”}}y_D \tag{5}$$

$$n_D' = n_{D_2S} + \frac{1}{2}n_{HDS} = n_{\text{“}H_2S\text{”}}y_D' \tag{6}$$

where n_{D_2}, n_{HD}, n_{D_2S}, and n_{HDS} represent the number of moles of D_2, HD, D_2S, and HDS respectively. $n_{\text{“}H_2\text{”}}$ and $n_{\text{“}H_2S\text{”}}$ are the number of moles of "hydrogen" and "hydrogen sulfide" respectively. y_D' is defined in the same manner as in the case of (3a) for "hydrogen sulfide."

At the beginning of the reaction:

$$n_{\mathrm{D}} + n_{\mathrm{D}}' = n_{\mathrm{D}}^{\mathrm{o}} = n_{\text{“H}_2\text{”}} x_{\mathrm{D}_2}^{\mathrm{o}} = n_{\text{“H}_2\text{”}} y_{\mathrm{D}}^{\mathrm{o}} \tag{7}$$

The insertion of Eq. (7) into Eq. (4) yields:

$$\frac{\mathrm{d}n_{\mathrm{D}}}{\mathrm{d}t} = \frac{ART}{V}[k_i n_{\mathrm{D}}^{\mathrm{o}} - (k_i + k_i')n_{\mathrm{D}}] \tag{8}$$

After the isotopic equilibrium between “hydrogen” and “hydrogen sulfide” has been attained, $\mathrm{d}n_{\mathrm{D}}/\mathrm{d}t=0$ and $n_{\mathrm{D}}=n_{\mathrm{D}}^{\mathrm{e}}$; *i.e.*,

$$\frac{\mathrm{d}n_{\mathrm{D}}}{\mathrm{d}t} = \frac{ART}{V}[k_i n_{\mathrm{D}}^{\mathrm{o}} - (k_i + k_i')n_{\mathrm{D}}^{\mathrm{e}}] = 0 \tag{9}$$

Accordingly,

$$\frac{n_{\mathrm{D}}^{\mathrm{e}}}{n_{\mathrm{D}}^{\mathrm{o}}} = \frac{k_i}{k_i + k_i'} \tag{10}$$

By integrating Eq. (8) and using Eq. (10), we obtain:

$$-\log \frac{n_{\mathrm{D}} - n_{\mathrm{D}}^{\mathrm{e}}}{n_{\mathrm{D}}^{\mathrm{o}} - n_{\mathrm{D}}^{\mathrm{e}}} = \frac{ART}{2.303\,V}(k_i + k_i')t \tag{11}$$

By replacing n_{D}, $n_{\mathrm{D}}^{\mathrm{o}}$, and $n_{\mathrm{D}}^{\mathrm{e}}$ by y_{D}, $y_{\mathrm{D}}^{\mathrm{o}}$, and $y_{\mathrm{D}}^{\mathrm{e}}$ respectively, Eq. (11) can be rewritten as:

$$-\log \frac{y_{\mathrm{D}} - y_{\mathrm{D}}^{\mathrm{e}}}{y_{\mathrm{D}}^{\mathrm{o}} - y_{\mathrm{D}}^{\mathrm{e}}} = \frac{ART}{2.303\,V}(k_i + k_i')t \tag{12}$$

Figures 5—7 show the plot of $\log\{(y_{\mathrm{D}} - y_{\mathrm{D}}^{\mathrm{e}})/(y_{\mathrm{D}}^{\mathrm{o}} - y_{\mathrm{D}}^{\mathrm{e}})\}$ *vs.* t for the data given in Figs. 2—4 respectively. The plots are linear irrespective of the HD formation. If we denote the slope of the plot of $-\log\{(y_{\mathrm{D}} - y_{\mathrm{D}}^{\mathrm{e}})/(y_{\mathrm{D}}^{\mathrm{o}} - y_{\mathrm{D}}^{\mathrm{e}})\}$ against t by α, k_i and k_i' can be represented by the following equations:

$$k_i = \frac{2.303\,V}{ART}\alpha\frac{y_{\mathrm{D}}^{\mathrm{e}}}{y_{\mathrm{D}}^{\mathrm{o}}} \tag{13}$$

$$k_i' = \frac{2.303\,V}{ART}\alpha\left(1 - \frac{y_{\mathrm{D}}^{\mathrm{e}}}{y_{\mathrm{D}}^{\mathrm{o}}}\right) \tag{14}$$

The k_i and k_i' calculated by Eqs. (13) and (14) using α were independent of the total pressure.

Figure 8 gives the plots $\log k_i$ and $\log k_i'$ against $\log a_{\mathrm{s}}$. Both plots are linear at 551 °C and 480 °C. The slopes of $\log k_i$ *vs.* $\log a_{\mathrm{s}}$ are -1.00 for 551 °C and -0.97 for 480 °C. The slopes of $\log k_i'$ *vs.* $\log a_{\mathrm{s}}$ are 0.00 and 0.03 respectively.

The Arrhenius plot of k_i at $a_{\mathrm{s}}=1$ is given in Fig. 9. The activation energy determined from the slope is 26.8 kcal mol^{-1}.

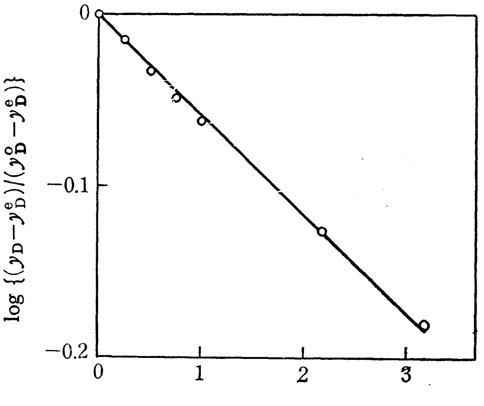

Fig. 5. Plot of $\log\{(y_{\mathrm{D}} - y_{\mathrm{D}}^{\mathrm{e}})/(y_{\mathrm{D}}^{\mathrm{o}} - y_{\mathrm{D}}^{\mathrm{e}})\}$ *vs.* t for the data given in Fig. 2.

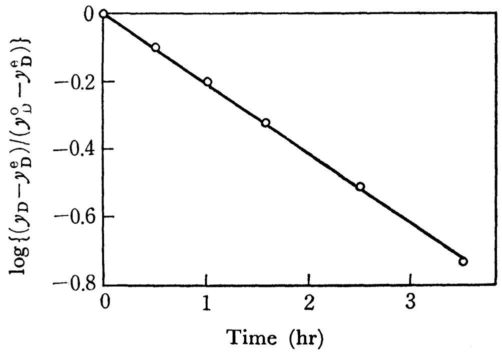

Fig. 6. Plot of $\log\{(y_{\mathrm{D}} - y_{\mathrm{D}}^{\mathrm{e}})/(y_{\mathrm{D}}^{\mathrm{o}} - y_{\mathrm{D}}^{\mathrm{e}})\}$ *vs.* t for the data given in Fig. 3.

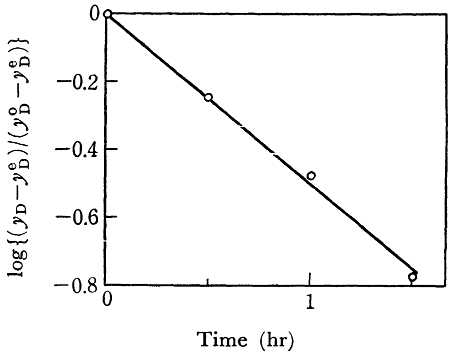

Fig. 7. Plot of $\log\{(y_{\mathrm{D}} - y_{\mathrm{D}}^{\mathrm{e}})/(y_{\mathrm{D}}^{\mathrm{o}} - y_{\mathrm{D}}^{\mathrm{e}})\}$ *vs.* t for the data given in Fig. 4.

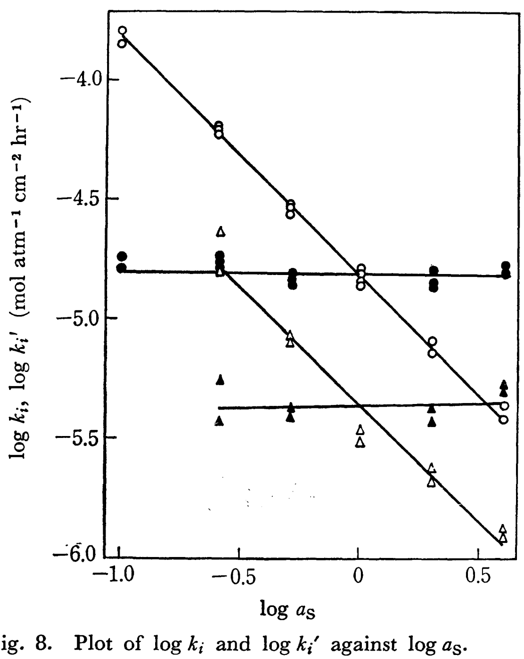

Fig. 8. Plot of $\log k_i$ and $\log k_i'$ against $\log a_{\mathrm{S}}$.
○ k_i, ● k_i' } 551 °C △ k_i, ▲ k_i' } 480 °C

Reaction Mechanism of Sulfurization. From the results of this study, the rate of redox reaction proceeding *via* (2a) can be expressed by this equation:

$$v = k_i P_{\text{“H}_2\text{S”}} - k_i' P_{\text{“H}_2\text{”}} = kP_{\text{“H}_2\text{S”}} a_{\mathrm{S}}^{-1} - k' P_{\text{“H}_2\text{”}} \tag{15}$$

where k and k' are constants.

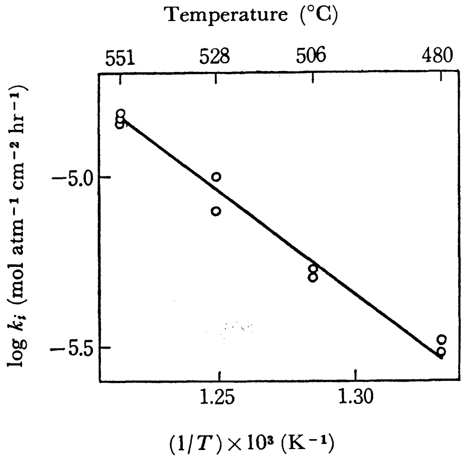

Fig. 9. Arrhenius plot for k_i at $a_S=1$.

Kobayashi and Wagner considered that e^-, S, S^-, and S^{2-} are reactants in Ag_2S and proposed the following three mechanisms for the reduction of Ag_2S by "hydrogen":

$$\text{``H}_2\text{''} + S \rightleftharpoons \text{``H}_2\text{S''} \qquad (16A)$$

$$\text{``H}_2\text{''} + S^- \rightleftharpoons \text{``H}_2\text{S''} + e^- \qquad (16B)$$

$$\text{``H}_2\text{''} + S^{2-} \rightleftharpoons \text{``H}_2\text{S''} + 2\,e^- \qquad (16C)$$

where S, S^-, and S^{2-} are sulfur atom, mono-, and divalent sulfur ions respectively and where e^- is an electron. They showed that the rate equations for (16A) to (16C) can be expressed in a general formula:

$$v = k'P_{\text{``H}_2\text{''}}a_S{}^{m-} - kP_{\text{``H}_2\text{S''}}a_e^{m} \qquad (17)$$

where m is integers characteristic of the reaction mechanism.

Let us first discuss the mechanism of the redox reaction on the pyrrhotite surface by the Kobayashi-Wagner mechanism.

Pyrrhotite is known as a semiconductor below the Néel temperature. However, the temperature coefficient of the conductivity is negative in the temperature range of this study, *i. e.*, above the Néel temperature[8–10], and the conductivity is independent of a_s.[10] As the conductivity is ~10^3 mho-cm, we can conclude that β-$Fe_{1-x}S$ is a compound of metallic conduction. The metallic conduction is due to a half-filled narrow d-band. If the ratio of S to Fe changes, the number of electrons in the d-band also changes. However, we can expect that the Fermi level of electron will not be influenced because the density of the state of the narrow d-band is very high. Accordingly, we can assume that the activity of the electron, a_e, is nearly constant over the whole experimental range of a_s, *i. e.*,

$$a_e \cong \text{const.} \qquad (18)$$

Among e^-, S, S^-, and S^{2-}, the following equilibrium relationships exist:

$$S^- \rightleftharpoons S + e^- \qquad (19A)$$

$$S^{2-} \rightleftharpoons S + 2\,e^- \qquad (19B)$$

i. e.

$$a_{S^-} \propto a_S \qquad (20A)$$

$$a_{S^{2-}} \propto a_S \qquad (20B)$$

Therefore, for mechanisms (16A) to (16C), the rate equation of the sulfurization reaction of the pyrrhotite should be expressed in this form:

$$v = kP_{\text{``H}_2\text{S''}} - k'P_{\text{``H}_2\text{''}}a_S \qquad (21)$$

This dependence of the reaction rate on a_s does not agree with the results observed in this study.

Next, les us consider the Fe atom as a reactant in sulfide. In this case, the reaction mechanism is:

$$\text{``H}_2\text{S''} + \text{Fe(sulfide)} \rightleftharpoons \text{``H}_2\text{''} + \text{FeS} \qquad (22)$$

and the rate equation is:

$$v = kP_{\text{``H}_2\text{S''}}a_{Fe} - k'P_{\text{``H}_2\text{''}}a_{FeS} \qquad (23)$$

Since the activity of $Fe_{1-x}S$ is nearly constant, irrespective of nonstoichiometry,[11]

$$a_{Fe} = \text{const}\cdot a_S{}^{-1} \qquad (24)$$

The insertion of Eq. (24) into Eq. (23) yields:

$$v = kP_{\text{``H}_2\text{S''}}a_S{}^{-1} - k'P_{\text{``H}_2\text{''}} \qquad (25)$$

Therefore, it may be concluded that Eq. (22) is a possible mechanism for the redox reaction on the pyrrhotite surface.

Summary

(1) The isotopic exchange between H_2S and D_2 on $Fe_{1-x}S$ was investigated as a function of the temperature and of a_s, the sulfur activity of $Fe_{1-x}S$.

(2) It was found that the isotopic exchange reaction proceeds *via*:

$$H_2S + D_2 \rightleftharpoons D_2S + H_2$$

$$H_2 + D_2 \rightleftharpoons 2\,HD$$

(3) The rate equation for the sulfurization of $Fe_{1-x}S$ in the "hydrogen"-"hydrogen sulfide" gas mixture was

$$v = kP_{\text{``H}_2\text{S''}}a_S{}^{-1} - k'P_{\text{``H}_2\text{''}}$$

The activation energy was 26.8 kcal mol^{-1}.

(4) The reaction mechanism of redox reaction was discussed.

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