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Equilibrium Study of Iron Vanadium Sulfides in the Iron-rich Portion of the Composition Triangle of FeS–VS–S

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An equilibrium study of a part of the Fe–V–S system at sections with atomic Fe:V ratios of 1:0, 9:1, and 4:1 was carried out by means of thermogravimetry. The thermochemical data which were obtained in the range of $\log(P_{S_2}/\text{atm}) = -4$ to -0.8 at temperatures between 520 and 814 °C are presented. The compositional limits of the univariant assemblage of $Fe_{1-\delta}S$–FeS_2–$(Fe,V)_3S_4$ were determined at 570 °C on the basis of X-ray analyses of the quenched specimens. The rate of FeS_2 formation under the experimental conditions employed was studied qualitatively from the point of view of the sulfidation kinetics of iron vanadium sulfides.

The results of equilibrium studies of the ternary compounds of Fe–V–S with the constant V/(Fe+V) ratio in the range of 0.29 to 1 were presented in earlier publications.[1–3] The author wishes to report in this paper the experimental results for a further series of samples with the V/(Fe+V) ratios of 0.20, 0.10, and 0. In this part of the Fe–V–S system, the following compounds are included: the hexagonal $(Fe,V)_{1-\delta}S$ solid solution, the monoclinic $(Fe,V)_3S_4$ solid solution, and the cubic FeS_2 (pyrite). With respect to the phase relations, it is known that the ternary univariant assemblage, which is composed of a three-phase mixture of FeS_2, the $(Fe,V)_3S_4$ solid solution, and $Fe_{1-\delta}S$, is stable over wide compositional ranges at 570 °C.[2] However, the compositional data on the phase boundary of the univariant assemblage have not yet been determined precisely in detail.

The primary aims of this study were to obtain the thermochemical data of iron vanadium sulfides under equilibrium conditions and to determine the phase relations and its compositional limits in detail. Considerable attention has been focussed on the determination of the univariant field of FeS_2–$Fe_{1-\delta}S$–$(Fe,V)_3S_4$ s.s.–vapor. In this connection, the sulfidation kinetics of iron vanadium sulfides was examined in order to obtain fundamental knowledge on the rate of FeS_2 formation under the experimental conditions employed.

The main thermochemical study was carried out with a gravimetric method by using a quartz spring balance at temperatures between 500 and 814 °C. The sulfur pressure in the N_2–sulfur vapor system was controlled by temperature regulation. The present paper is concerned with the P_{S_2} (equilibrium sulfur pressure)-T (temperature)-X (composition) relations, the phase relations, and the sulfidation rate of iron vanadium sulfides in the case of FeS_2 formation.

Experimental

Materials. Sulfide samples with atomic Fe : V ratios of 9 : 1 and 4 : 1 were synthesized by heating the mechanical mixtures of reagent-grade $VOSO_4\cdot3H_2O$ and $FeSO_4\cdot(NH_4)_2SO_4\cdot6H_2O$ in an H_2S atmosphere at 1050 °C for 4 h. The iron sulfide samples were synthesized by means of a direct reaction from the elements. The iron powder (99.99%) and sulfur powder (99.9999%) were used for preparation. The mixture in desired quantities was sealed in an evacuated silica tube, heated at high temperatures, and quenched in water. Two samples with different compositions were used for the study of the Fe–S system. One was $FeS_{1.12}$, which had been synthesized at 800 °C for a week. The other was $FeS_{2.01}$, which had been heated at first at 450 °C for a week and then homogenized at 600 °C for a week. These artificial sulfides were used as the starting materials for the equilibrium study.

General Procedure. The equilibrium study of iron vanadium sulfide was carried out by both thermogravimetry and the rigid tube, quench-type, annealing experiment at temperatures between 520 and 814 °C. The general experimental procedures, the apparatus, and the methods of the chemical analyses and of the phase identification of quenched specimens are the same as those described in previous papers.[1–2]

Results and Discussion

Composition versus P_{S_2} *Diagram in an Iron-rich Portion of the Composition Triangle of FeS–VS–S.* The results of equilibrium studies of the Fe–V–S system at sections with atomic Fe:V ratios of 4:1, 9:1, and 1:0 are shown graphically in Figs. 1—3. The isothermal curves are drawn by a smooth fitting of data points which represent the relation of the equilibrium sulfur pressure, P_{S_2}, to the composition of the sulfides (X=S/(Fe+V)) at the selected temperature. Also, the phase relations which were revealed by the X-ray diffraction of the quenched specimens are given in Table 1 and Figs. 1—3. Below, a solid solution will be abbreviated as

Table 1. Results of X-ray identification of the specimens quenched from 570 °C

Composition		Time/h	Products
Fe/(Fe+V)	S/(Fe/V)		
1.000	1.120	720	$Fe_{1-\delta}S$ (hexagonal:3c)
	1.150	90	$Fe_{1-\delta}S$
	1.170	90	$Fe_{1-\delta}S+FeS_2$
0.900	1.146	182	$(Fe_{0.90}V_{0.10})_{1-\delta}S$
	1.168	144	$(Fe,V)_{1-\delta}S+(Fe,V)_3S_4$
	1.220	109	$(Fe,V)_{1-\delta}S+(Fe,V)_3S_4$
	1.230	109	$Fe_{1-\delta}S+(Fe,V)_3S_4+FeS_2$
	1.750	111	$Fe_{1-\delta}S+FeS_2+(Fe,V)_3S_4$
	1.800	111	$FeS_2+(Fe,V)_3S_4$
0.800	1.146	182	$(Fe_{0.80}V_{0.20})_{1-\delta}S$
	1.160	95	$(Fe,V)_{1-\delta}S+(Fe,V)_3S_4$
	1.216	109	$(Fe,V)_{1-\delta}S+(Fe,V)_3S_4$
	1.500	1536	$(Fe,V)_3S_4+FeS_2+Fe_{1-\delta}S$
	1.550	127	$FeS_2+(Fe,V)_3S_4$

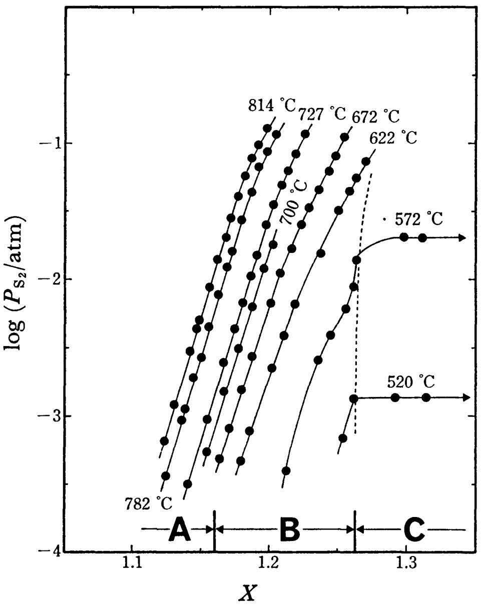

Fig. 1. P_{S_2}-composition (X=S/(Fe+V)) isotherm of $Fe_{0.80}V_{0.20}S_X$. Phase identifications of quenched specimens by X-ray powder diffraction method are shown in lower part of figure as follows A: $(Fe_{0.80}V_{0.20})_{1-\delta}S$. B: $(Fe,V)_{1-\delta}S$+$(Fe,V)_3S_4$ s.s. C: $Fe_{1-\delta}S$+FeS_2+$(Fe,V)_3S_4$ s.s. The dashed line indicates the phase boundary of the univariant field.

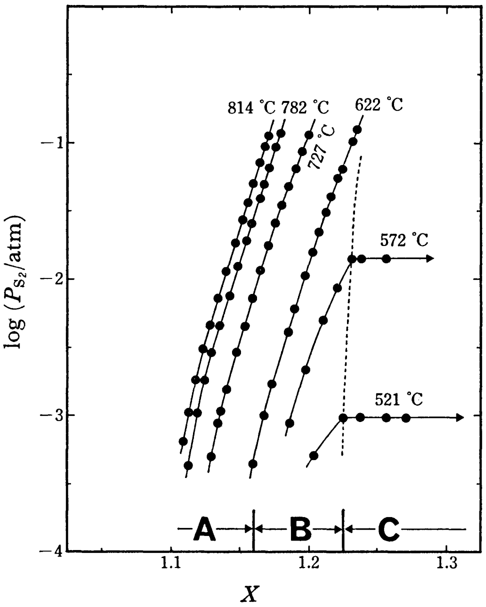

Fig. 2. P_{S_2}-composition isotherms of $Fe_{0.90}V_{0.10}S_X$. A: $(Fe_{0.90}V_{0.10})_{1-\delta}S$. B: $(Fe,V)_{1-\delta}S$ s.s.+$(Fe,V)_3S_4$ s.s.. C: $Fe_{1-\delta}S$+FeS_2+$(Fe,V)_3S_4$ s.s.

s.s. for convenience.

Figure 1 shows isotherms with the composition of $Fe_{0.80}V_{0.20}S_X$, where X ranges between 1.12 and 1.32. As listed in Table 1, the following phase relations are obtained at 570 °C: $(Fe_{0.80}V_{0.20})_{1-\delta}S$ phase, a two-phase mixture of $(Fe,V)_{1-\delta}S$ s.s. and $(Fe,V)_3S_4$ s.s., and a three-phase mixture of FeS_2, $Fe_{1-\delta}S$, and $(Fe,V)_3S_4$ s.s. in the compositional ranges of $X<1.16$, $1.16\leqq X<1.263$, and $1.263\leqq X<1.55$ respectively.

As is shown in Fig. 1, the isothermal curves for 814, 782, 727, and 700 °C exhibit continuous and gradual changes in the sulfur pressure with the composition. Although the sulfur-rich limit of the hexagonal $(Fe_{0.80}V_{0.20})_{1-\delta}S$ phase was determined to be about $X=1.16$ from the X-ray measurements of the quenched specimens, no characteristic curvature change in the isotherms is observed at $X=1.16$. This behavior of the isotherms seems to be indicative of the existence of a high-temperature phase, as has been reported previously.2,3) There is the possibility that the homogeneity range of the $(Fe_{0.80}V_{0.20})_{1-\delta}S$ becomes broadened with an increase in the temperature and that its sulfur-rich limit has a composition with a value higher than $X=1.16$.

With respect to the isotherms for 572 and 520 °C, an abrupt change in the slope is observed at the composition of about $X=1.262$. In the compositional range of $X>1.262$, the isotherms become horizontal due to the formation of FeS_2, as has been discussed previously.2) On the basis of the phase relations which were determined from the X-ray studies of the quenched specimens, it is suggested that the horizontal parts of the isotherms mean a univariant field of the Fe–V–S system, where $Fe_{1-\delta}S$, FeS_2, and $(Fe,V)_3S_4$ s.s. coexist at equilibrium.

Figure 2 shows the isothermal curves of the composition of $Fe_{0.90}V_{0.10}S_X$, where X ranges from 1.11 to 1.31. The phase relations obtained at 570 °C are as follows: $(Fe_{0.90}V_{0.10})_{1-\delta}S$ phase, a two-phase mixture of $(Fe,V)_{1-\delta}S$ and $(Fe,V)_3S_4$ s.s., and a three-phase mixture of $Fe_{1-\delta}S$, FeS_2, and $(Fe,V)_3S_4$ s.s., in the compositional ranges of $X<1.16$, $1.16\leqq X<1.23$, and $1.23\leqq X<1.75$ respectively.

The isothermal curves of $Fe_{0.90}V_{0.10}S_X$ are similar in shape to that of $Fe_{0.80}V_{0.20}S_X$ except that the entire curves are shifted to the sulfur-poor side with regard to the composition. As is evident in Fig. 2, no curvature changes are observed in the isotherms for 814, 782, and 727 °C at the sulfur-rich phase boundary of $(Fe_{0.90}V_{0.10})_{1-\delta}S$. It is noted that the isotherms for 521 and 572 °C become horizontal due to the FeS_2 formation at $X=1.225$ and $X=1.230$ respectively. However, no such change is observed in the isotherm for 622 °C in the present experimental compositional range. This suggests that the sulfur-poor limits of the three-phase field recedes toward the sulfur-rich side with an increase in the temperature.

Figure 3 shows the isotherms of the binary compound, FeS_X, where X lies in the range from 1.07 to 1.25. In this compositional range, only two phases were detected by the X-ray powder diffraction of the quenched specimens (Table 1). One is the hexagonal $Fe_{1-\delta}S$ (pyrrhotite), whose X-ray diffraction patterns exhibit 3c-type supper structure lines4) in addition to the fundamental reflection lines of the NiAs type, while the other is the cubic FeS_2 (pyrite). The following phase relations were confirmed at 570 °C: the $Fe_{1-\delta}S$ phase, and a two-phase mixture of $Fe_{1-\delta}S$ and FeS_2, in the compositional ranges of $X<1.16$ and $X\geqq1.16$ respectively.

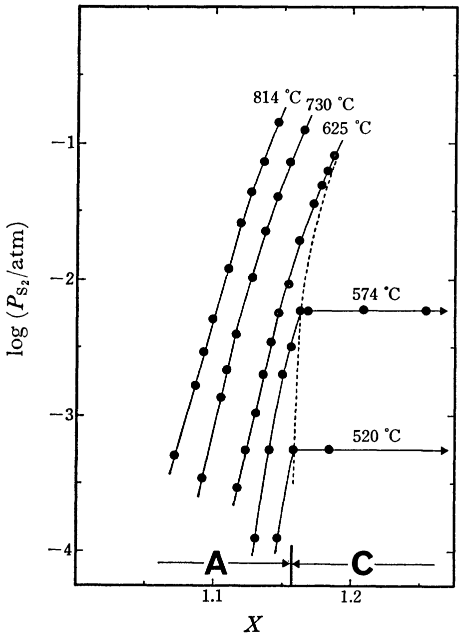

Fig. 3. P_{S_2}-Composition isotherms of FeS_X. A: $Fe_{1-\delta}S$. C: $Fe_{1-\delta}S+FeS_2$. The phase boundary of $Fe_{1-\delta}S$ is represented as the broken line.

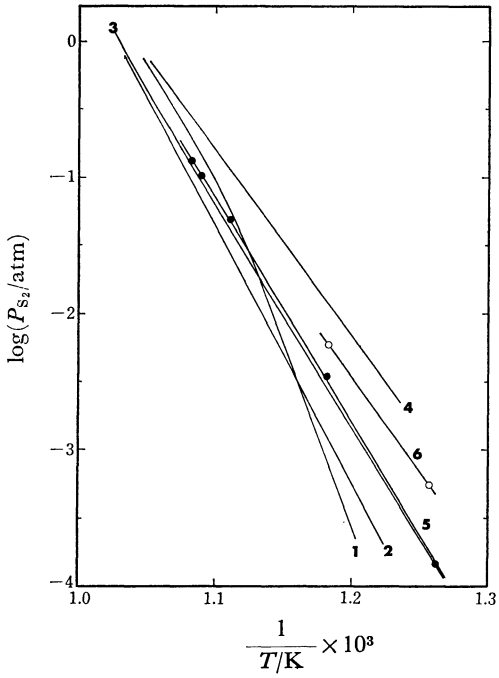

Fig. 4. The relation of decomposition pressure of FeS_2 with the inverse temperature. 1: Allen and Lombard (1917). 2: Rosenqvist (1954). 3: Toulmin and Barton (1964). 4: D'Or (1931). 5: Present work; ● decomposition pressure of FeS_2. 6: Present work; ○ sulfur pressure in the case of FeS_2 formation, as is seen in Fig. 3.

TABLE 2. RELATION OF THE DECOMPOSITION PRESSURE OF PYRITE TO THE TEMPERATURE

Temp / °C	$-\log(P_{S_2}/\text{atm})$
520	3.84
574	2.47
620	1.47
628	1.31
646	0.99
652	0.88

With respect to the isotherm feature, it is noted that the horizontals associated with a two-phase equilibrium of $Fe_{1-\delta}S$ and FeS_2 appear at the compositions of $X=1.155$ and $X=1.160$ for 520 and 574 °C (Fig. 3). However, the isotherm for 625 °C does not show such horizontals in the range of $X<1.19$. Those results indicate that the homogeneity range of the $Fe_{1-\delta}S$ phase tends to be broadened to the sulfur-rich side with an increase in the temperature.

A few remarks should be made here regarding the equilibrium sulfur pressure of a two-phase mixture of $Fe_{1-\delta}S$ and FeS_2. For example, in the experiments for 574 and 520 °C, the sulfur pressure was controlled to bring the composition to a higher sulfur content than at the beginning of that series. The sulfidation of the specimens proceeded with an increase in the sulfur pressure, and isotherms became horizontal in a two-phase field due to the considerable increase in the sulfur content in the solids, associated with the FeS_2 formation. In this case, however, the values of the sulfur pressure at the horizontal parts of the isotherms are not regarded as truly resulting from a two-phase equilibrium of $Fe_{1-\delta}S$ and FeS_2, because a slightly higher sulfur potential than the equilibrium one is needed on the formation of FeS_2 in order to supply the activation energy of the reaction of $Fe_{1-\delta}S$ with sulfur vapor. Therefore, it is designated here as the upper limit of the equilibrium sulfur pressure.

The relation of the decomposition pressure of FeS_2 to temperature was examined in order to determine the lower limits of the equilibrium sulfur pressure of $Fe_{1-\delta}S$–FeS_2 mixtures. Experiments were carried out by thermogravimetry using $FeS_{2.01}$ as the starting material. When a significant weight loss of specimens was observed within the time interval of 30 min at the selected temperature and pressure, it was judged that FeS_2 begins to decompose to $Fe_{1-\delta}S$ and sulfur vapor. The experimental results are listed in Table 2 and shown in Fig. 4, together with the results reported by other investigators.$^{5-8)}$ The data points obtained in this study are well represented by the following equation (least-squares treatment): $\log(P_{S_2}/\text{atm}) = -16477/(T/\text{K})+16.96$, where 1 atm=101.325 kPa. This result is in good agreement with that of Toulmin and Barton,$^{5)}$ as is shown in Fig. 4. The upper limit of the equilibrium sulfur pressure which was obtained on the sulfidizing specimens (Fig. 3) is given in Fig. 4 for comparison.

The true equilibrium value probably lies within the range between the upper and lower limits of sulfur pressure at a given temperature. The difference in the sulfur pressure between the formation and the reduction of FeS_2 is about $0.25=\log(P_{S_2}/\text{atm})$ at 574 °C. It may be considered that this discrepancy is derived from the sluggishness of the reaction rate of

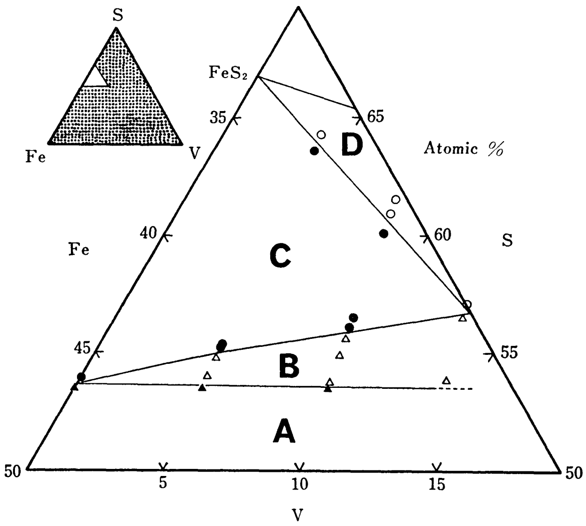

Fig. 5. Tentative phase diagram of the iron-rich portion of the composition triangle of FeS–VS–S at 570 °C. Phase relations are represented as follows. ▲: $(Fe,V)_{1-\delta}S$ s.s. △: $(Fe,V)_{1-\delta}S$ s.s.+$(Fe,V)_3S_4$ s.s. ●: $Fe_{1-\delta}S+FeS_2+(Fe,V)_3S_4$ s.s. ○: $FeS_2+(Fe,V)_3S_4$ s.s.

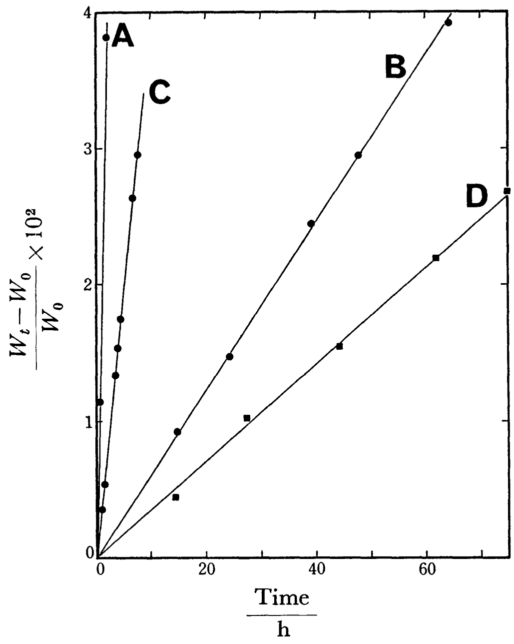

Fig. 6. The relation of the weight gain of the sample with time.

the formation or the reduction of FeS_2 under the present experimental conditions. On the assumption that the true equilibrium sulfur pressure of the $Fe_{1-\delta}S$–FeS_2 mixture is halfway between the upper and lower limits, the Gibbs free energy of the $[2/(1-2\delta)]Fe_{1-\delta}S+S_2=[2(1-\delta)/(1-2\delta)]FeS_2$ reaction was calculated in the temperature range of 520—580 °C: $\Delta G^\circ_T=-67100+68.5\,T\,\mathrm{cal_{th}}$, where $1\ \mathrm{cal_{th}}=4.184\ \mathrm{J}$.

The Tentative Phase Diagram at 570 °C. The tentative isothermal phase diagram in the iron-rich portion of the composition triangle FeS–VS–S was constructed on the basis of the results of both thermogravimetry and rigid-tube, annealing, quench-type experiments. The phase relations and phase boundaries are shown in Fig. 5.

With respect to the Fe–S binary system, the sulfur-rich limit of $Fe_{1-\delta}S$ is determined to be 46.3 atom% Fe at 570 °C (Fig. 3). This value is in good agreement with the sulfur-rich limit of $Fe_{1-\delta}S$ (46.2 atom% Fe), which was reported by Arnold.[9] As is shown in Fig. 6, it is assumed that the $Fe_{1-\delta}S$ and $V_{1-\delta}S$ phases form a complete $(Fe,V)_{1-\delta}S$ solid solution (A region) at 570 °C. The sulfur-rich phase boundary of the $(Fe,V)_{1-\delta}S$ field is extended nearly parallel with the line joining FeS–VS from the Fe–S side to the V–S side in the $0\leqq V/(Fe+V)<0.3$ range.

The univariant field (C region) is determined by a smooth fitting of data points. The sulfur-poor boundary of the univariant field recedes progressively toward sulfur-poor compositions with an increase in the Fe content; its limits are 55.1 and 55.9 atom% S in the sections with atomic Fe:V ratios of 9:1 and 4:1 respectively. On the other hand, the sulfur-rich boundary of the univariant field is shifted progressively toward a sulfur-rich composition with an increase in the Fe content; its limits are about 63.9 and 60.6 atom% S in the sections with atomic Fe:V ratios of 9:1 and 4:1 respectively. It should be noted that the sulfur-rich boundary line intersects the line joining Fe–S at the composition of FeS_2.

The two-phase fields (B region) of $(Fe,V)_3S_4$ and $(Fe,V)_{1-\delta}S$ are present in the middle part between the A and C regions. However, the compositional relation of $(Fe,V)_{1-\delta}S$ to the coexisting $(Fe,V)_3S_4$ has not been determined in this study.

Sulfidation Kinetics of Iron Vanadium Sulfides. In a series of reports,[1–3] the phase relations and P_{S_2}-X-T relations of the Fe–V–S system have been presented without any particular regard for the reaction kinetics. In general, it is well known that the time required for equilibriation increases with the decrease in the temperature with respect to the phase equilibria. Therefore, it may be suggested that the thermochemical data reported in this series are perhaps somewhat less accurate at lower temperatures, such as 520 °C, because the establishment of the equilibrium could not be checked precisely. It is necessary to obtain experimental data on the sulfidation kinetics of iron vanadium sulfides in order to have a comprehensive understanding of the Fe–V–S system at lower temperatures.

In the course of the equilibrium study of the Fe–V–S system, the sulfidation rate was examined supplementally. Considerable attention has been focussed on the rate of FeS_2 formation in the univariant field (FeS_2–$Fe_{1-\delta}S$–$(Fe,V)_3S_4$ s.s.–vapor). The sulfidation kinetics of powder samples were determined by means of thermogravimetry.

The variation in the sample weight with time was examined along the horizontal parts of the isotherms (Figs. 1—3) in order to ascertain the sulfidation rate of the sulfide powder. The composition at the sulfur-poor limit of the horizontal line was selected as the starting composition in the sulfidation experiments. About 300 mesh and 1 g of powder samples were used.

The degree of the weight gain of the sample is shown in Fig. 6 for periods up to 80 h. The experimental results may be represented well as the following linear relation: $W_t=W_0(1+\alpha t)$, where α, t, W_t, and W_0 denote the gain in the sample weight per a unit of time, time/h, the sample weight at time $t=t$, and $t=0$ respectively. As a first approximation, it can be proposed that the slope of the linear equation, α, is related to the rate of FeS_2 formation. From Fig. 6, the following values are obtained for the slopes of Lines A, B, C, and D: for $FeS_{1.156}$, $\alpha_A=1.98\times 10^{-2}$/h at 520 °C and $P_{S_2}=10^{-2.08}$, and $\alpha_B=0.06\times 10^{-2}$/h at 520 °C and $P_{S_2}=10^{-3.26}$, for $FeS_{1.161}$, $\alpha_C=0.40\times 10^{-2}$/h at 574 °C and $P_{S_2}=10^{-2.22}$, and for $Fe_{0.90}V_{0.10}S_{1.225}$, $\alpha_D=0.04\times 10^{-2}$/h at 520 °C and $P_{S_2}=10^{-3.02}$. It should be noted that sulfidation rate of $Fe_{1-\delta}S$ (pyrrhotite) at 520 °C increases with an increase in the sulfur pressure in the P_{S_2} range from $10^{-3.26}$ to $10^{-2.08}$. On the basis of the assumption that the P_{S_2} values of Experiments B, C, D are very close to the equilibrium values at a given temperature, the following conclusions are obtained: (1) the sulfidation rate of $Fe_{1-\delta}S$ increases with an increase in the temperature, and (2) there is the tendency for the FeS_2 formation to be inhibited by the presence of vanadium in sulfides.

The over-all reaction rate of pyrrhotite for FeS_2 formation was calculated according to the $FeS_x+yS_2=FeS_2$ sulfidation reaction, where x and y are 1.156 and 0.422 respectively at 520 °C. In this case, the sulfidation rate was represented by the following equation; $-d[P]/dt=K_{obsd}[P]$ where [P] is the concentration of FeS_x with the composition at the sulfur-rich limit and where K_{obsd} is the apparent first-order rate constant. From the experimental results, the following K_{obsd} values were obtained from the slopes in the first-order plots in a region of low conversion ($0.87<P/P_0\leqq 1$): $K_A=1.98\times 10^{-5}$/s, $K_B=6.26\times 10^{-7}$/s, and $K_C=4.13\times 10^{-6}$/s. The activation energy of FeS_2 formation was calculated to be 191.6 kJ/mol by using values of K_B and K_C according to the Arrhenius equation. This value is much larger than that of the sulfidation of Fe metal (113.0 kJ/mol) under the sulfur pressure of 1 atm, which was reported by Narita and Nishida.[10] The reaction mechanism of iron vanadium sulfides on the sulfidation process could not be clarified in this study. Further detailed studies of the sulfidation kinetics will be necessary for a comprehensive understanding of the Fe–V–S system.

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