Equilibrium Study of the Fe–V–S System by Thermogravimetry

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An equilibrium study of the Fe–V–S system was carried out in the range of $\log(P_{S_2}/\text{atm}) = -4$ to -0.8 at temperatures between 723 and 1093 K. The gravimetric method was employed by making use of a quartz spring balance. The partial pressure of sulfur was controlled in an N_2-sulfur vapor system by temperature regulation. The partial pressure of S_2 was calculated from the thermodynamic data, taking account of the existence of different molecular species: S_2 through S_8. Three kinds of ternary sulfides with different Fe/V ratios were used as starting material. The P_{S_2}-T-X relation was established through *in situ* measurements at high temperatures. It was found that the Fe–V–S system has an extensive ternary solid solution with the NiAs type of fundamental structure.

The compounds in the Fe–V–S system have not received much attention in the past, because they seem to occur in nature rather infrequently. Only the synthetic FeV_2S_4 compound, which is related to the ternary transition metal chalcogenides MM'_2S_4(M=Fe, Co,Ni; M'=Ti,V; X=S,Se), has recently been studied by solid state physicists, who reported its structural, magnetic and electrical properties.[1–4] However, very few studies have been published on the thermochemical aspects needed to determine the ternary phase relations in the Fe–V–S system.

Much information has now been obtained on the phase relations and crystal structures in the binary systems Fe–S[5] and V–S.[6] Vanadium sulfides, where the sulfur atoms are in hexagonal close packing, form the B8 (NiAs-type) structure at the composition VS, and the C6 ($Cd(OH)_2$-type) structure at VS_2. Within the composition limits VS–VS_2, structures intermediate between the B8 and C6 types are formed due to the removal of metal atoms from every second metal layer in the B8 structure. At lower temperatures, the vanadium vacancies are ordered within alternate metal layers, giving rise to ordered superstructures such as monoclinic V_3S_4(nonreduced space group I2/m referred to the fundamental NiAs-type cell) and monoclinic V_5S_8 (nonreduced space group F2/m).[7] With increasing temperature, the homogeneity ranges within those structures tend to be broadened. On the other hand, iron sulfides do not show the complete transition between the B8 and C6 structure types. The composition Fe_7S_8 is the stable limit of the B8 structure in the Fe–S system. When the number of metal vacancies increases beyond that in Fe_7S_8, a different structure type, such as cubic FeS_2(space group Pa3), becomes stable.

Accordingly, it is expected that the Fe–V–S system contains complicated ternary solid solutions based on the NiAs-type fundamental structure. In the solid solution, one end member is iron sulfide, FeS_x (NiAs-type) in the compositional range FeS–Fe_7S_8, while the other is one of the vanadium sulfides, such as VS_x (NiAs-type) in the compositional range VS–V_7S_8, V_3S_4 (distorted NiAs-type), or V_5S_8 (distorted NiAs-type). In order to clarify the behavior of ternary sulfides of the Fe–V–S system, it is important to determine in detail at high temperatures the phase relations and the compositional stability of the ternary solid solutions included in the system. Thus, the purpose of the present investigation was to establish the equilibrium diagrams of the sulfur-rich portion of the Fe–V–S system from the thermochemical viewpoint.

The equilibrium study was carried out mainly with a gravimetric method by making use of a quartz spring balance at 773—1093 K. The partial pressure of sulfur was controlled in an N_2–sulfur vapor system only by temperature regulation. The present paper is concerned with the calculation of the partial pressure of S_2 at specimen temperature in the employed experimental system and the P_{S_2} (equilibrium sulfur pressure)-T (temperature)-X (composition) relations of the Fe–V–S system at high temperatures.

Experimental

Materials. Reagent grade $VOSO_4 \cdot 3H_2O$ was mixed in ethanol with a reagent grade $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in an agate mortar in desired quantitites. The mixture was dried, put in a quartz boat, and heated in an H_2S atmosphere at 1323 K for 4 h. The sulfide powder thus synthesized was quenched to room temperature and was used as the starting material. Prior to the experiments, the composition of the powder samples was determined by colorimetric methods for vanadium and ion and by weight-loss on oxidation to $xFe_2O_3 \cdot yV_2O_5$ at 873 K for sulfur. Fe/(Fe+V) ratios of the synthesized sulfides were in good agreement with those of mechanical mixtures of source materials within the accuracy of ±0.5%. The over-all errors involved in the chemical analysis were ±0.2% by weight.

Sulfur Pressure Control. A direct sulfur pressure control method was employed in the equilibrium studies. The principal procedure is similar to that described by Wakihara *et al.*[8] The apparatus used for the equilibrium runs is shown schematically in Fig. 1. All this apparatus was constructed of quartz glass. The heating system was divided into five parts in order to keep each portion of the apparatus at the desired temperature. Nichrome wire (0.8 and 0.45 mm) and Pt–40%Rh wire (0.8 mm) were wound directly outside the quartz assembly as shown in Fig. 1 and fixed with an alumina cement. The temperatures of five portions of the system were controlled by chromel-alumel thermocouples.

Five hundred grams of guaranteed reagent grade sulfur was kept in the round-bottom reservoir A (2 dm³). After passing nitrogen gas through the apparatus for 12 h, the sulfur was heated at 673 K and changed to the molten state by means of the heating mantle. Prior to use, the nitrogen gas was purifired by means of an MCN-005 type gas purifier

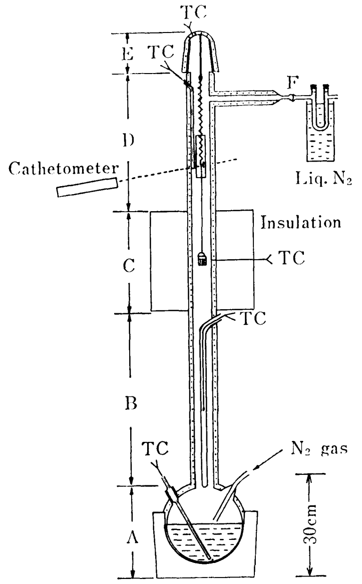

Fig. 1. Schematic diagram of apparatus.
Heating systems. A: The round-bottom reservoir is heated by means of heating mantle. B: Nichrome wire (0.8 mm) is used for a winding to maintain the minimum temperature zone over the central portion of B. C: The reaction chamber is wound with Pt-40%Rh wire coil (0.8 mm). The uncertainty in temperature is within ±3 K. D: The spring chamber is wound with Nichrome wire coil (0.45 mm). E: The cap is wound with Nichrome wire coil (0.8 mm). TC: Chromel-alumel thermocouples.

(Japan Pure Hydrogen Co.) in order to remove oxygen and water impurities. The saturated sulfur vapor over the molten sulfur was transported to the upper part of the apparatus by nitrogen gas at a constant rate (2 cm^3 of N_2/s). The central zone (width: 10 cm) of part B was held at the minimum temperature in all this apparatus so that the transported sulfur vapor from the reservoir became supersaturated and excess sulfur was condensed at this zone. Only the sulfur vapor which equilibriated at the minimum temperature zone was carried to the reaction chamber C. Thus, a desired partial pressure of sulfur was obtained by controlling the temperature within ±0.5 K at the minimum temperature zone. The upper portions, D and E, were also heated at higher temperatures than that of the minimum temperature zone so as to avoid any condensation of sulfur in the course of passing the atmosphere. At the outlet, F, sulfur was collected into a U-tube cooled by liquid nitrogen, and the weight of sulfur was measured for the calculation of partial pressure of S_2.

Thermogravimetry. For study of equilibrium experiments, a gravimetric method was employed, in which the elongation of a McBain balance could be followed by means of a cathetometer. The spring balance manufactured from a quartz glass fiber has the sensitivity of 67 mm per g weight at room temperature. The balance was suspended from a solid hook of a quartz rod in the center of the cap E. About 1 g of sulfide powder sample was placed in a quartz crucible (diameter: 16 mm, length: 16 mm, and weight: 280 mg) suspended from the top of the spring by strands of thin gold wire (0.2 mm). The length of the wire was adjusted in order that the crucible might be situated in the middle of the reaction chamber C. In order to observe the target visually, the spring chamber D was equipped with a transparent window (12×2.5 cm), which was not covered by the cement. A fluorescent lamp gave illumination from the rear side of the window. By making use of a quartz reference rod, the elongation of the spring was measured with the aid of a travelling microscope. The error in composition of sulfide specimens was estimated to be ±0.002 or sulfur to metal ratios, because the weighing could be read accurately to 0.2 mg, which corresponded to 0.001 cm of the smallest scale division.

Equilibrium was judged to be attained when the sample weight was constant. For log P_{S_2} of -2 and above, three hours were sufficient to attain equilibrium. For log P_{S_2} less than -3, twelve hours were found to be sufficient. The composition of the sulfide was calculated from the weight loss of the sample, assuming iron and vanadium to be involatile.

Besides the measurements described above, some supplemental experiments were carried out in order to examine the X-ray powder diffraction patterns of sulfides. A sample was placed in the crucible suspended from the cap E with a long platinum wire (0.2 mm) into the apparatus. After equilibrium was attained, the crucible was lifted up to the upper portion of the apparatus, taken out, and quenched in liquid nitrogen. Sulfides thus obtained were identified by using an X-ray diffractometer set up for Ni-filtered CuK_α radiation. The measurement was carried out at a goniometer scanning speed of 0.5° min^{-1}.

Results and Discussion

Calculation of Partial Pressure of S_2. The experimental results of the sulfur pressure measurements, in terms of the weight of collected sulfur at F, are presented in Table 1. The relationship between the weight of sulfur transported by unit volume of nitrogen and the temperature of the minimum temperature zone is given very well by the following formula (least squares treatment): $\log (w/\mathrm{mg\,dm^{-3}}) = -3787\frac{1}{T/\mathrm{K}} + 9.281$. This linear relationship indicates that the sulfur pressure was controlled precisely by the temperature regulation at the minimum temperature zone in the selected experimental system.

According to Rau *et al.*,[9] sulfur vapor contains molecular species from S_2 to S_8 at high temperatures below 1173 K. Therefore, it is necessary to calculate the partial pressure S_2 while considering the equilibrium between the different molecular species from S_2 to S_8.

TABLE 1. RELATIONSHIPS BETWEEN THE MASS FLOW RATE OF SULFUR AND THE TEMPERATURE OF THE MINIMUM TEMPERATURE ZONE

Temperature (K)	Mass flow rate of sulfur (mg/dm^3 of N_2)
403	0.763
424	2.164
426	2.653
471	16.907
505	61.753
536	164.360
567	398.730

The partial pressure of S_2 at the specimen temperature was computed in the following way from the thermodynamic data of Rau *et al.* Assumptions were made that the sulfur vapor behaved ideally as a perfect gas and that a steady state of mass flow was set up in the experimental system. Then, P_{S_2} is given by the following equation:

$$P_{S_2} = \frac{m_2}{n+\sum_{i=2}^{8} m_i}, \tag{1}$$

where m_i and n are the number of moles of the sulfur vapor species S_i and of nitrogen, respectively, in the mass flow of gas for a given time interval t. A perfect gas obeys the following relations:

$$PV = (n+m_2+m_3+\cdots+m_8)RT, \tag{2}$$

and

$$P_{S_i} = m_iRT. \tag{3}$$

Substituting for m_i from Eq. 3 into Eq. 1, and rearranging, we obtain the following equation:

$$1 - \sum_{i=2}^{8} P_{S_i} = \frac{32.064\,n}{W}\sum_{i=2}^{8} iP_{S_i}, \tag{4}$$

where W represents the total amount of sulfur collected at the outlet within a time interval t. The equilibria connecting the various molecular species with S_2

$$S_i = (i/2)S_2 \tag{5}$$

are given by the equilibrium constant K_i

$$K_i = P_{S_2}^{i/2}/P_{S_i}. \tag{6}$$

Therefore, substitution of values of the equilibrium constant K_i into Eq. 4 through Eq. 6 yields the following expression as a function of P_{S_2}:

$$(2A+1)X^2 + \sum_{i=3}^{8}\frac{iA+1}{K_{S_i}}X^i - 1 = 0, \tag{7}$$

where $A=\frac{32.064n}{W}$ and $X=P_{S_2}^{1/2}$. Prior to the calculation of P_{S_2}, the equilibrium constant K_i was computed from the thermodynamic data of Rau *et al.* According to Eq. 7, the partial pressures of S_2, which were in equilibrium with the specimens, were calculated in the iterative Newton method from the data in Table 1. The physically meaningful value for P_{S_2} was selected. Values of log P_{S_2} are drawn in Fig. 2 as a function of the temperature at the minimum temperature zone with the specimen temperature as a parameter. The results for each given series are tied together by a smooth curve, which shows that the logarithmic values of P_{S_2} ranged from -4 to -0.8, corresponding to the change of temperature from 373 to 573 K. The uncertainty of log P_{S_2} was estimated to be ± 0.02 or less throughout the experimental range. From those smooth curves, the correction of P_{S_2} for specimen temperature could be made with sufficient accuracy. It will be seen that for specimen temperatures below 1000 K and also for values of log P_{S_2} higher than -2, the correction is not negligible.

Composition vs. P_{S_2} *Diagrams in the Fe–V–S System.* Representative selections of ternary sulfides in the Fe–V–S system (Fe/(Fe+V) mole ratios=0.05, 0.26, 0.35, respectively) have been subjected to an equilibrium study by the thermogravimetry. The experimental results of the investigation are shown graphically in Figs. 3—5. The isotherms drawn in Figs. 3—5 give the variation of equilibrium sulfur pressure P_{S_2} in relation to the composition of sulfides. The abscissa and ordinate are sulfur to metal ratio $(S/(Fe+V)=X)$ and log P_{S_2}, respectively. Also, the phases as revealed by X-ray diffraction of the quenched specimens are given in the figures together with those judged from results of *in situ* measurements.

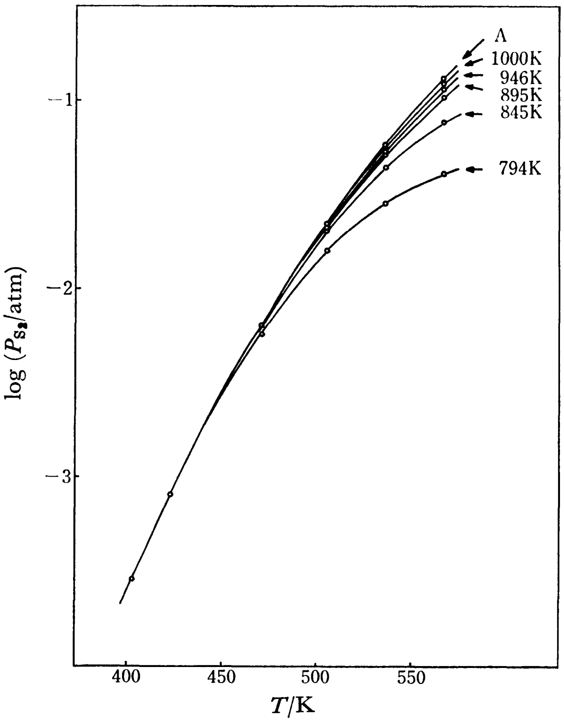

Fig. 2. Log P_{S_2} curve as a function of the temperature at the minimum temperature zone with the specimen temperature as a parameter.
A: Theoretical value, which is deduced from calculation of P_{S_2} on the basis of the assumption that sulfur vapor consists of only S_2 species.

Figure 3 shows isotherms of the ternary sulfide with composition $Fe_{0.05}V_{0.95}S_x$. The composition covered between $Fe_{0.05}V_{0.95}S_{1.33}$ and $Fe_{0.05}V_{0.95}S_{1.60}$. Two discontinuities are found in the composition-P_{S_2} diagrams for 895 K in this region. One is in the range d—e $(1.45 \leq X \leq 1.46)$, and the other in the range f—g $(1.55 \leq X \leq 1.56)$. The horizontal isotherm described above represents a two-phase equilibrium. It becomes narrower and eventually vanishes with increasing temperature.

From Fig. 3, it is evident that the specimens at 895 K contain three phases: A, B, C. The tangent to the isothermal curves approaches gradually to a vertical line at the specific compositions of a $(X=1.33)$ and c $(X=1.60)$ in the phase A and C regions, respectively. At the same time, the sulfur pressure changes rapidly. Judging from this feature of the isotherms, it can be suggested that the A and C phases correspond to (Fe+V) : S=3 : 4 and (Fe+V) : S=5 : 8 phases, respectively. The sulfur-rich limit of the former extends to the com-

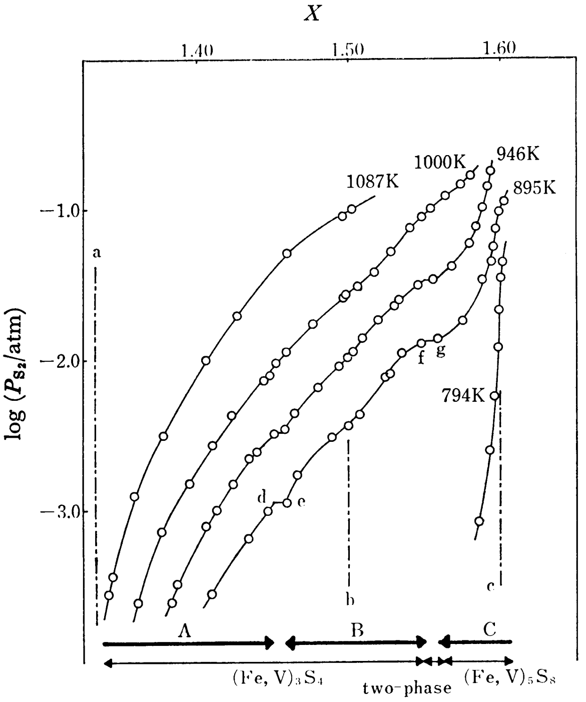

Fig. 3. P_{S_2}-composition (S/(Fe+V)=X) isotherms of $Fe_{0.05}V_{0.95}S_x$. Results of powder phase identifications are shown in lower part of figure together with results of phase identifications by thermogravimetry. a: $(Fe_{0.05}V_{0.95})_3S_4$, b: $(Fe_{0.05}V_{0.95})_2S_3$, c: $(Fe_{0.05}V_{0.95})_5S_8$.

position of $X=1.45$ and the metal-rich limit of the latter to $X=1.56$, where the isotherm becomes horizontal at 895 K. Within the phase B region ($1.46<X<1.55$), however, rapid change in the pressure at a specific composition is not observed. Instead, at the composition $X=1.50$ the curvature changes. A relatively small change in the pressure causes an appreciable variation of the composition, suggesting the flatness of the free energy surface. As evident in the curves for 1000 and 1087 K, the phases exhibit large mutual solubilities with increasing temperature.

A few remarks should be made here regarding the powder X-ray diffraction patterns of the quenched specimens. In contrast to the *in situ* observations described above, only two phases were detected in the range $1.33 \leqq X \leqq 1.60$. Their X-ray powder patterns were similar to those of V_3S_4 and V_5S_8, respectively, in the V–S system. This suggests that Fe can substitute for V in both V_3S_4 and V_5S_8 phases due to the formation of ternary solid solutions. In the range, $1.55 \leqq X \leqq 1.56$, a mixture of (Fe, V)$_3$S$_4$ and (Fe,V)$_5$S$_8$ patterns was obtained.

In the range, $1.45<X<1.55$, however, no mixture was obtained in the X-ray powder diffraction pattern; this result is inconsistent with the observation in Fig. 3. This is considered to originate from the difficulties that the phase in the range $1.46<X<1.55$ can hardly be distinguished from the (Fe,V)$_3$S$_4$ phase by X-ray powder analysis, due to the similarity of crystal structure. In fact, both phases show a large mutual solubility with increasing temperature (above 1000 K in Fig. 3). The unknown phase, B, may be inferred to be (Fe,V)$_2$S$_3$ phase, on the analogy of sesquisulfide V_2S_3, from a study of the V–S system.[10,11] In the present study, therefore, the phase described above is designated as the (Fe,V)$_2$S$_3$ phase for convenience throughout the paper.

Figure 4 shows isotherms with the composition $Fe_{0.264}V_{0.736}S_x$, richer in Fe than that in Fig. 3. The region covered experimentally lies between the composition $Fe_{0.264}V_{0.736}S_{1.333}$ and $Fe_{0.264}V_{0.736}S_{1.520}$. Two phases, A and B, exist in this range. Rapid increase of the pressure is observed near the stoichiometric compositions, $(Fe_{0.264}V_{0.736})_3S_4$ and $(Fe_{0.264}V_{0.736})_2S_3$. This indicates the existence of extensive ternary solid solutions such as (Fe,V)$_3$S$_4$ and (Fe,V)$_2$S$_3$, one end member of which is one of vanadium sulfides such as V_3S_4 and V_2S_3.

Again, the X-ray powder diffraction of the quenched specimen exhibits no difference between the two phases.

Figure 5 shows isotherms with the composition $Fe_{0.349}V_{0.651}S_x$. Within the present experimental pressure range, a large change in the pressure is observed only near the composition, $X=1.33$, in the phase A region. Therefore, it is considered that this phase is included in the region of the solid solution of the (Fe,V)$_3$S$_4$ phase.

As shown in Figs. 3—5, within the present experimental temperatures and Fe/V ratios, the features of isotherms depend upon compositions and temperature. With respect to isotherms, it is found that the sulfur content in the ternary sulfide which is equilibriated at the respective P_{S_2} values decreases with increasing Fe/V ratio.

This indicates that the equilibrium sulfur pressure of sulfides in the Fe–V–S system increases with decreasing vanadium content, when the S/(Fe+V) ratio is held

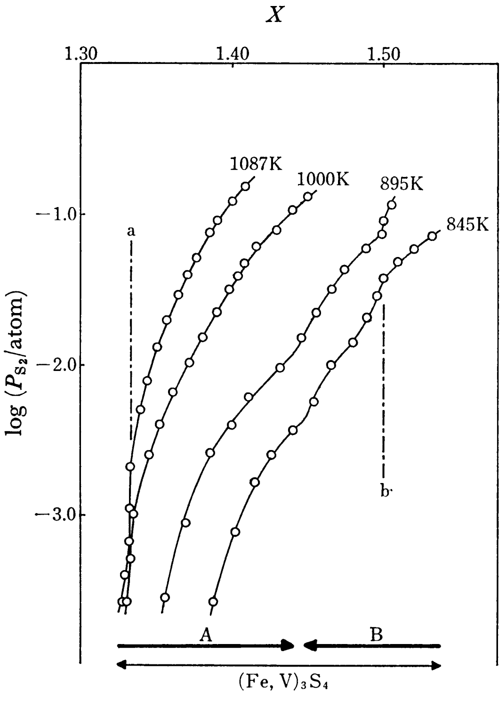

Fig. 4. P_{S_2}-composition isotherms of $Fe_{0.264}V_{0.736}S_x$. a: $(Fe_{0.264}V_{0.736})_3S_4$, b: $(Fe_{0.264}V_{0.736})_2S_3$.

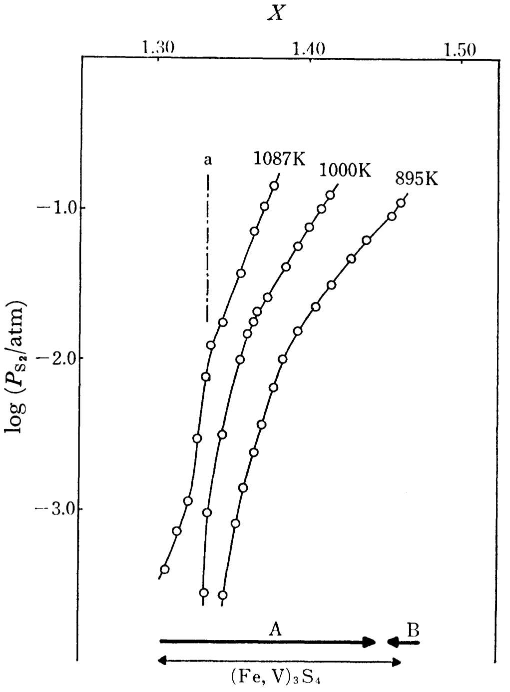

Fig. 5. P_{S_2}-composition isotherms of $Fe_{0.349}V_{0.651}S_x$.
a: $(Fe_{0.349}V_{0.651})_3S_4$.

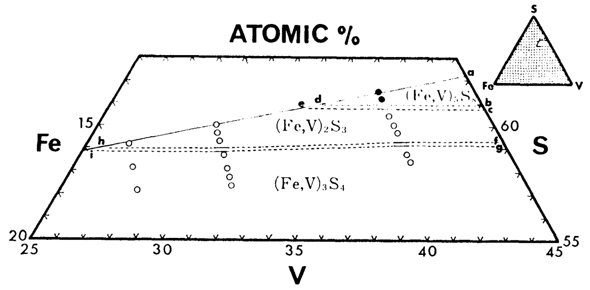

Fig. 6. Tentative phase diagram of the sulfur-rich portion of the Fe–V–S system for 895 K.
Two-phase fields are represented as follows
Area b-c-d-e: $(Fe,V)_5S_8+(Fe,V)_2S_3$, and Area f-g-h-i: $(Fe,V)_2S_3+(Fe,V)_3S_4$.
Phase identifications of quenched specimens by X-ray powder diffraction method are shown as follows
○: monoclinic V_3S_4-type structure,
●: monoclinic V_5S_8-type structure.

constant. From the experimental results described before, it is concluded that within the range Fe/(Fe+V) =0.05, 0.26, and 0.35, solid solution phases of $(Fe,V)_3S_4$, $(Fe,V)_2S_3$, and $(Fe,V)_5S_8$ are found and that the mutual solubility increases with increasing temperature (Figs. 3—5).

The tentative isothermal phase diagram in the sulfur-rich portion of the Fe–V–S system for 895 K was constructed on the basis of the results of thermogravimetry. The phase relations and their compositional limits are summarized in Fig. 6.

The iron-rich limits of solid solution phases such as $(Fe,V)_5S_8$ and $(Fe,V)_2S_3$ are determined by a smooth fitting of data points which are obtained under the highest sulfur pressure condition ($\log(P_{S_2}/\mathrm{atm})=-0.95$) in this study. This boundary is drawn approximately as a straight line. The extension of this line intersects the boundary line, V–S, at the point a, whose composition is given as about 62.2 atomic % of sulfur. This value is in good agreement with that of the sulfur-rich limit of V_5S_8 phase ($VS_{1.64}$) which was reported by Saeki *et al.*[12] However, phase relations outside the line showing the iron-rich limits of solid solutions could not be determined owing to the limitation of the direct sulfur pressure control method and are omitted in Fig. 6.

With experimental data obtained in this study and with the homogeneity range of the compounds from the V–S system, as previously determined by De Vries and Jellinek[6] for V_5S_8 phase and by Nakahira *et al.*[11] for V_2S_3 and V_3S_4 phases, it was possible to draw two-phase fields. The boundaries of two-phase fields which show discontinuity of isotherms are represented as dotted lines nearly in parallel with the FeS–VS join. As shown in Fig. 6, two-phase mixtures of $(Fe,V)_5S_8+(Fe,V)_2S_3$ and $(Fe,V)_2S_3+(Fe,V)_3S_4$ are found in the range of S/(Fe+V) atomic ratios, 1.55—1.56 and 1.44—1.45 or 1.45—1.46, respectively.

Judging from the behavior of the iron-rich limits of solid solution fields, it was expected that the monoclinic $(Fe,V)_3S_4$ phase was stable over a wide compositional range. With the aid of a supplemental experiment using iron-rich ternary sulfides, the phase boundary of $(Fe,V)_3S_4$ was confirmed to be reached to the position of about 0.30 Fe/(Fe+V) ratio. Some representative unit-cell dimensions of quenched specimens in the $(Fe,V)_3S_4$ phase field are listed in Table 2. It is indicated that the axial dimensions, especially of the a- and c-axis, change smoothly with corresponding variations in Fe composition. From the results mentioned above, it is concluded that stoichiometric FeV_2S_4, as reported by many investigators, is not a specific ternary phase, but is included in the $(Fe,V)_3S_4$ solid solution fields.

The author is at present extending the present work to the iron-rich portion of the composition triangle of FeS–VS–S.

The author wishes to express his hearty thanks to Professor Mitsuoki Nakahira of Okayama College of Science for his encouragement and helpful discussions throughout this study.

Table 2. Unit-cell dimentions of $(Fe,V)_3S_4$ solid solution

Composition	a(Å)	b(Å)	c(Å)	β(°)	Volume (Å³)
$Fe_{0.05}V_{0.95}S_{1.39}$	5.860±3	3.285±2	11.355±1	91.97	218.5
$Fe_{0.26}V_{0.74}S_{1.38}$	5.855±2	3.291±1	11.297±5	91.94	217.5
$Fe_{0.35}V_{0.65}S_{1.39}$	5.848±2	3.291±1	11.237±5	91.95	216.2

References

1) B. L. Morris, R. H. Plovnick, and A. Wold, *Solid State. Commun.*, **7**, 291 (1969).

2) S. Muranaka and T. Takada, *Bull. Inst. Chem. Res., Kyoto Univ.*, **51**, 287 (1973).

3) S. Muranaka and T. Takada, *J. Solid State Chem.*, **14**, 291 (1975).

4) M. Cheverton and A. Sapet, *C. R. Acad. Sci., Paris*, **261**, 298 (1965).

5) G. Kullerud and H. S. Yoder, *Econ. Geol.*, **54**, 533 (1959).

6) A. B. De Vries and F. Jellinek, *Rev. Chim. Miner.*, **11**, 624 (1974).

7) I. Kawada, M. Nakano-Onoda, M. Ishii, M. Saeki, and M. Nakahira, *J. Solid State Chem.*, **15**, 246 (1975).

8) M. Wakihara, T. Uchida, and M. Taniguchi, *Mater. Res. Bull.*, **11**, 973 (1976).

9) H. Rau, T. R. N. Kutty, and J. R. F. Guedes de Carvalho, *J. Chem. Thermodyn.*, **5**, 833 (1973).

10) J. Tudo, *Rev. Chim. Miner.*, **2**, 53 (1965).

11) M. Nakahira, K. Hayashi, M. Nakano-Onoda, and K. Shibata, "Proc. 8th Int. Symp. on the Reactivity of Solids," ed by J. Wood *et al.*, Plenum Press, New York (1977), pp. 397—401.

12) M. Saeki, M. Nakano, and M. Nakahira, *J. Cryst. Growth*, **24/25**, 154 (1974).