The Partial Molar Quantity of the Sulfur of the Compounds in the Fe–V–S System

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Synopsis. An equilibrium study of the Fe–V–S system was carried out under controlled sulfur-pressure conditions. Partial molar enthalpies of the sulfur of the compounds in the Fe–V–S system were calculated on the basis of the P_{S_2}–T–X relations, which were established at temperatures between 520 and 814 °C.

The phase relations in the portion of the FeS–VS–S composition triangle have recently been clarified.[1-4] It has been found that the Fe–V–S system has extensive solid-solution phases, such as $(Fe,V)_{1-x}S$ and $(Fe,V)_3S_4$, which have a lattice intermediate between the NiAs-type and the $Cd(OH)_2$ lattice. However, no thermodynamic data on the ternary compounds of Fe–V–S have yet been reported. This note will be concerned with the partial molar enthalpy of sulfur, $\Delta\bar{H}_S$, which can be derived from the thermochemical data of compounds in the Fe–V–S system.

Experimental

The sulfide samples with the desired atomic Fe:V ratios were synthesized by heating mechanical mixtures of reagent-grade $VOSO_4 \cdot 3H_2O$ and $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in an H_2S atmosphere at 1050 °C for 4 h; they were then used as the starting materials. The equilibrium study was carried out by means of thermogravimetry, using a quartz spring balance. The general experimental procedures, the apparatus, and the chemical analyses are the same as those described in the previous paper.[1]

Results and Discussion

The experimentally determined P_{S_2} (equilibrium sulfur pressure)–T(temperature)–X(composition) relations, which had been reported in three preceding publications,[1,3,4] were used in the computation of the activities and the partial molar enthalpies.

Under the experimental conditions employed, the vapor phase in equilibrium with iron vanadium sulfides contains various molecular species of sulfur from S_2 to S_8. In such a case, according to Geffken *et al.*,[5] the activity of sulfur, a_S, can be given by

$$a_S = \left(\frac{P_{S_n}}{P_{S_n}^{\circ}}\right)^{1/n}, \quad (1)$$

where the subscript, n, indicates the number of atoms in a molecule. If the reference state of sulfur is chosen as 0.5 S_2 (g), where the S_2 (g) is considered to be an ideal gas at a pressure of 1 atm at the given temper-

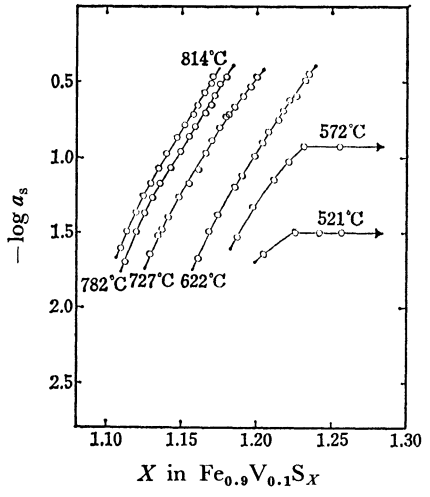

Fig. 1. The relation of log a_S with composition, X in $Fe_{0.90}V_{0.10}S_X$.

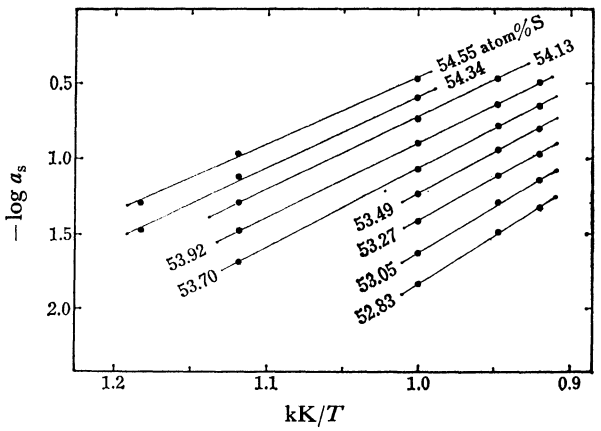

Fig. 2. The relation of log a_S with $1/(T/\mathrm{K})$.

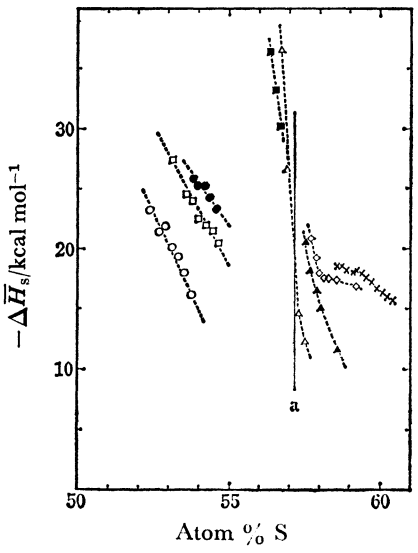

Fig. 3. $\Delta\bar{H}_S$ of compounds in the Fe–V–S system as function of composition. The stoichiometric Fe+V:S=3:4 composition is designated as the symbol a. ○: Fe:V=1:0, □: Fe:V=9:1, ●: Fe:V=4:1, ■: Fe:V=3:2, △: Fe:V=1:1, ▲: Fe:V=7:13, ◇: Fe:V=13:37, ×: Fe:V=1:19.

ature,[6] the activity of sulfur is expressed by:

$$\log a_S = 0.5 \log P_{S_2}. \quad (2)$$

The partial molar enthalpies can be computed from the Gibbs-Helmholtz equation[7] by using the activity data as follows:

$$\Delta\bar{H}_S = -4.574\, T^2 \frac{d \log a_S}{dT}. \quad (3)$$

Figure 1 shows a typical example of the isotherms of $Fe_{0.90}V_{0.10}S_X$, where the activity of sulfur is calculated according to Eq. 1. Figure 2 represents the log a_S versus the reciprocal temperature relations, which are derived from the experimental data shown in Fig. 1. It is found that the data points lie on a straight line for a given composition in the range from 52.8 to 54.5 atom% S. This suggests that the Gibbs-Helmholtz equation holds in the relation of log a_S with $1/T$ under the experimental temperature conditions. From the slopes of these straight lines, the partial molar enthalpies of the sulfur of $Fe_{0.90}V_{0.10}S_X$ were calculated by the least-squares method. The calculated partial molar enthalpies are plotted in Fig. 3 as a function of the composition, together with those of other samples. The $\Delta\bar{H}_S$ of $Fe_{0.90}V_{0.10}S_X$ increases linearly from -27.5 to -20.5 kcal/mol (1 cal=4.184 J) in the compositional range from 53.1 to 54.6 atom% S.

As is evident in Fig. 3, $\Delta\bar{H}_S$ varies with the composition of the iron vanadium sulfides. It can be concluded that (1) $\Delta\bar{H}_S$ decreases with an increase in the V/Fe ratio when the sulfur content is held constant and (2) $\Delta\bar{H}_S$ increases with an increase in the sulfur content when the V/Fe ratio is held constant.

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