Sulfur Pressure Control in an H_2-Sulfur Vapor System

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(Received December 17, 1988)

Synopsis. A direct sulfur pressure control method by a N_2-sulfur vapor system was modified by using an H_2-sulfur vapor system. A ratio of H_2S/H_2 in the atmosphere was found to be controlled very well in the range from 10^{-2} to 10^{-4} only by the temperature regulation.

A direct sulfur pressure control method by using a N_2-sulfur vapor system has been recently devised and applied to the equilibrium studies of several transition metal sulfides.[1-5] However, this has disadvantage that the lower limit of partial pressure of sulfur available is restricted to 10^{-4} atm because of shortage of accuracy in determination of sulfur content. An attempt has been made to control the partial pressure of sulfur more precisely by using an H_2-sulfur vapor system under the same conditions. This note is concerned with the experimental results obtained in the H_2-sulfur vapor system.

Experimental

Sulfur Pressure Control. The apparatus used for the equilibrium study is shown schematically in Fig. 1. All this apparatus is constructed of quartz glass. The heating systems are the same ones as those described in the previous paper.[2] Several hundred grams of sulfur (purity: 99.9999%) was kept in the round-bottom reservoir. After passing
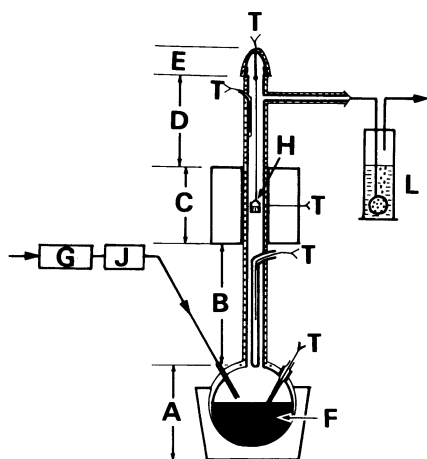

Fig. 1. Schematic diagram of apparatus. The heating systems are divided into five parts from A to E. A: Heating mantle. B: Nichrome wire (0.8 mm) is used for a winding to maintain the minimum temperature zone over the central portion of B. C: Reaction furnace. Pt-40% Rh wire (0.8 mm) is used. D: Nichrome wire (0.45 mm) is used. E: The cap is wound with Nichrome wire (0.8 mm). F: Sulfur. G: DEOXO purifier. H: Sulfide sample is suspended from the cap by strands of thin platinum wire (0.2 mm). J: Mass flow controller (SEC 310). L: NaOH solution. T: Chromel-alumel thermocouples.

hydrogen gas through the apparatus for 12 h, sulfur was heated and changed to the molten state. Prior to use, the hydrogen gas was purified using DEOXO purifier (Engelhard Co.) in order to remove oxygen and water impurities. The saturated sulfur vapor over molten sulfur was transported to the upper part of the apparatus by hydrogen gas at a constant rate (3 cm^3 of H_2/s). The central zone 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 on the wall. Only sulfur vapor equilibrated at the minimum temperature zone (width: 10 cm) was carried to the upper part of apparatus. Then the sulfur was changed to hydrogen sulfide at temperatures higher than 773 K according to the reaction of $2H_2+S_2=2H_2S$. A desired partial pressure of hydrogen sulfide was easily obtained by controlling the temperature within ±0.5 K at the minimum temperature zone. At the outlet, L, hydrogen sulfide was absorbed in 0.8 M NaOH solution (1 M=1 mol dm^{-3}) and oxidized by H_2O_2 to SO_4^{2-} ion. Finally, the sulfur content was determined gravimetrically as $BaSO_4$.

Results and Discussion

The experimental results of the sulfur pressure measurements, in terms of the amount of collected sulfur at L, are presented in Table 1 and Fig. 2. The relationship between the total amount of sulfur brought by unit volume of hydrogen and the temperature of the minimum temperature zone is given very well by the following formula (least squares treatment): $\log(W/\text{g dm}^{-3})=-4294/(T/\text{K})+7.1852$, where the amount of collected sulfur is represented as W in g. The previous experimental data obtained in the N_2-sulfur vapor system[2] are also shown in Fig. 2 for comparison. Both data exhibit very similar linear relationships except for small difference in the absolute values. This fact indicates clearly that the sulfur pressure was controlled precisely by the temperature regulation at the minimum temperature

Table 1. Relationships between the Temperature of Minimum Temperature Zone, Weight of $BaSO_4$ and the Mass Flow Rate of Sulfur

Temperature	Weight of $BaSO_4$	Mass flow rate of sulfur
K	mg h^{-1}	(g dm^{-3} of H_2)
370	2.72	3.48×10^{-5}
385	9.30	1.19×10^{-4}
386	9.88	1.26×10^{-4}
394	16.50	2.08×10^{-4}
402	23.95	3.06×10^{-4}
403	26.60	3.40×10^{-4}
413	53.68	6.78×10^{-4}
422	74.55	9.54×10^{-4}
423	88.20	1.13×10^{-3}
472	887.79	1.19×10^{-2}

is given by the following equation

$$\Delta G^\circ = -21570 + 11.79\,T. \tag{2}$$

The equilibrium of Eq. 1 is represented as follows by using the equilibrium constant K

$$\log K = -\frac{\Delta G^\circ}{RT} = \log \frac{P_{H_2S}}{P_{S_2}^{1/2}\,P_{H_2}}. \tag{3}$$

Rearranging Eq. 3, we obtain the following equation

$$\log P_{S_2} = 2\log \frac{P_{H_2S}}{P_{H_2}} + \frac{2\Delta G^\circ}{RT}. \tag{4}$$

By varying the temperature of the minimum temperature zone H_2S/H_2 ratio could be varied between 10^{-2} and 10^{-4}. The assumptions were made to calculate the sulfur pressure that the sulfur species present in the gas phase is only the diatomic molecule S_2 and that the equilibrium has been established on the reaction Eq. 1 at the high temperatures. Corresponding to the variation of H_2S/H_2, $\log P_{S_2}$ was estimated to range from -8.54 to -12.54 at 973 K.

In an application of this method iron Chevrel phase compound $Fe_{1.25}Mo_6S_{7.75}$ has been subjected to an equilibrium study at 1273 K. The rhombohedral phase of $Fe_{1.25}Mo_6S_{7.75}$ was found to be stable in the range $-7.44 < \log P_{S_2} < -5.35$.

Fig. 2. Plot of $\log(W/g\,dm^{-3})$ versus $1/T$. O: H_2-sulfur vapor system, ▲: N_2-sulfur vapor system.

zone in the selected experimental system. The slightly lower values for the data points in the H_2-sulfur vapor system may be due to incomplete transportation of sulfur. One of the possible explanations for this phenomenon may be related to the fact that the viscosity of H_2 gas is much lower than that of N_2 gas.

According to Richardson and Jeffes,[6] the free energy for the reaction

$$H_2(g) + \frac{1}{2}S_2(g) = H_2S(g) \tag{1}$$

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