

# Intrinsic Kinetics of the Reaction between Zinc Sulfide and Water Vapor

H. Y. SOHN and DAESOO KIM

The reaction between zinc sulfide and water vapor is a component reaction in a new reaction scheme recently developed to transform zinc sulfide to zinc oxide through the use of lime and water vapor. The intrinsic kinetics of this reaction for ultrafinely ground ( $<1 \mu\text{m}$ ) ZnS particles was determined by carrying out measurements in the absence of heat- and mass-transfer effects. The reaction products were identified to be ZnO and H<sub>2</sub>S. The kinetics of the reaction can be represented by  $dX_B/dt = k_1(C_{\text{H}_2\text{O}} - C_{\text{H}_2\text{S}}/K_e)(1 - X_B)[- \ln(1 - X_B)]^{1-1/n}$ ;  $1023 < T < 1160 \text{ K}$  and  $3.94 < C_{\text{H}_2\text{O}} < 9.84 \text{ mol/m}^3$  with  $n = 1.28$  and  $k_1 = 45.3 \exp(-14600/T) \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , where  $X_B$  is the fractional conversion.

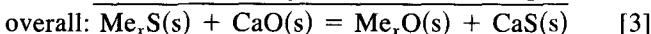
## I. INTRODUCTION

ROASTING is commonly applied to sulfide minerals to transform them into oxides for subsequent reduction by carbon or hydrogen or other extraction processes. The conventional roasting operation often suffers from the problem of sulfur dioxide emission into the environment.

A novel reaction scheme for transforming metal sulfides to the corresponding oxides has recently been developed.<sup>1,2,3</sup> In this process, metal sulfides are reacted with lime in the presence of an initial charge of steam. Steam oxidizes the sulfide to the oxide, and the hydrogen sulfide produced from this reaction further reacts with lime to form calcium sulfide and regenerates water vapor. There is *no* net consumption or generation of gaseous species. Thus, the overall reaction can be carried out in a closed system as far as the gas phase is concerned. This eliminates the possibility of emitting sulfur-containing gaseous pollutants.

Only certain metal sulfides are thermodynamically amenable to this treatment.<sup>2,3</sup> The sulfides of molybdenum, zinc, and iron are major examples. Chalcopyrite treated by this process is transformed to bornite and magnetite. A further potential application of this scheme may be to the selective oxidation of certain sulfides in mixed sulfide ores as a pretreatment prior to the separation of minerals in complex ores.

The overall reaction in this scheme consists of two gas-solid reactions, as follows:



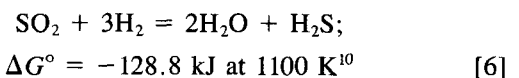
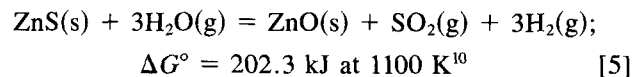
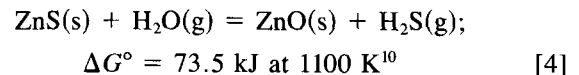
As can be seen, the reaction of a metal sulfide with water vapor is an important component in the overall reaction. A quantitative description of the rate of the overall process requires the kinetics of the two individual reactions [1] and [2]. The kinetics of reaction [2] have been studied by Habashi and Mikhail<sup>4</sup> and by Won and Sohn<sup>5</sup> as a component

reaction in the hydrogen reduction of metal sulfides in the presence of lime.<sup>6,7</sup> On the other hand, the kinetics of the reaction of metal sulfides with water vapor have not been investigated extensively. Two of the few studies reported in the literature are those by Rohrmann *et al.*<sup>8</sup> on the reaction of iron sulfide contained in pyritic copper concentrate and by Roberts and Williams<sup>9</sup> on the reaction of chalcopyrite. The latter reported that the reaction proceeded according to the shrinking-core model with a shell consisting of porous magnetite surrounding an unreacted core of bornite and chalcopyrite. From the initial rate of the reaction an activation energy of 42.3 kJ/mol was obtained. However, this study does not provide enough information on the intrinsic kinetics, since experiments were carried out under conditions in which substantial diffusional effects were present.

This paper reports the results of an investigation in which the intrinsic kinetics of the reaction between zinc sulfide and water vapor were determined in the absence of diffusional and mass-transfer effects.

## II. THERMODYNAMIC CONSIDERATIONS

When zinc sulfide is reacted with water vapor, the following reactions are likely to take place:



Both reactions [4] and [5] have a positive Gibbs free energy of reaction, indicating that the reactions are rather unfavorable. The large negative  $\Delta G^\circ$  of reaction [6], however, indicates that reaction [4] is more favorable.

In order to test which reaction actually takes place, the gaseous product of reaction between steam and ZnS was analyzed by gas chromatography and a precipitation experiment. The product gas was bubbled first through a saturated solution of lime and through cadmium sulfate and copper sulfate solutions. Only cuprous sulfide and cadmium sulfide were precipitated in the sulfate solutions. Sulfur dioxide was

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not detected in this experiment or in the analysis by a gas chromatograph. Thus, it was concluded that reaction [4] is the predominant reaction.

### III. EXPERIMENTAL

#### A. Apparatus

Figure 1 shows a schematic diagram of the apparatus used to measure the weight change upon the reaction. The apparatus consisted of a recording electrobalance, a reaction tube, a furnace, and a steam-generating unit.

A perforated platinum boat (1.2 cm × 1.2 cm) containing ultrafinely ground ZnS particles (<1 μm) of analytical grade supplied by Ventron Alfa Products was suspended in the reaction tube by a gold chain from one arm of a Cahn Model 1000 electrobalance. A metered flow of steam, nitrogen, or a mixture of the two passed through the reaction tube. The reaction tube was a 99-cm long quartz tube of 3.2 cm I.D. mounted below a 21.6-cm pyrex tube of the same diameter. The end of the quartz tube was connected to the gas-inlet pyrex tube. The bottom section of the reaction tube was filled with small pieces of fire brick to provide a packed bed for heating the inlet gas. The top end of the pyrex tube was attached to the weighing unit of the balance and sealed by an O-ring connector. Thermocouples were located in the vicinity of the platinum boat. A uniform temperature of ±1 K could be achieved in the zone where the sample was located. The output from the balance was recorded on a Linear Instruments Model 385 Strip-Chart Recorder. The steam-generating unit consisted mainly of a 500-W cylindrical steam generator and pressure regulator. Deionized water was fed into the generator through a Cole-Parmer 7103-10 oscillating pump. The flow rate of water was varied in the range 0 to 3 mL/min by the voltage applied to the pump. The flow of steam was regulated precisely by the pressure regulator consisting of a Cole-Parmer 3235 micrometric valve and one-liter flask surrounded by a

350-W heating mantle. The steam composition was verified by the metered reading of the heated flowmeter and by measuring the rate of water condensed. The pressure inside the reaction tube and the pressure regulator was measured by a mercury manometer. Other details of the experimental apparatus are given elsewhere.<sup>3</sup>

#### B. Procedure

Before each experiment the electrobalance was calibrated with standard weights. A very small amount (5 to 10 mg) of ZnS sample (Ventron Alfa Products analytical reagent) spread on a porous alumina-silica fiber was placed in the perforated platinum boat. The sample was heated to the reaction temperature in a stream of nitrogen. When a constant reaction temperature was reached, steam was turned on. The partial pressure of incoming steam was controlled by adjusting the flows of steam and nitrogen. The flow rate of steam was varied from 0.5 L/min to 2.5 L/min at 413 K. The reaction temperature was varied from 640 to 1200 K. The pressure inside the reaction tube was 38.5 Pa higher than that of the atmospheric pressure. The continuous weight change of the sample was recorded on the strip-chart recorder until no further change occurred. Additional measurements included the flow rate of steam and temperatures at different points in the proximity of the sample. At the end of the run both the furnace and steam were turned off and the sample allowed to cool under the flow of nitrogen. The reacted sample was analyzed by X-ray diffraction using copper K-alpha radiation from a Phillips Electronic Instruments X-ray Diffractometer.

### IV. RESULTS AND DISCUSSION

To determine the intrinsic kinetic parameters, the measurements should be carried out in a regime where the overall rate is controlled by chemical kinetics. In such a region, external mass transfer and the interparticle diffusion of gases

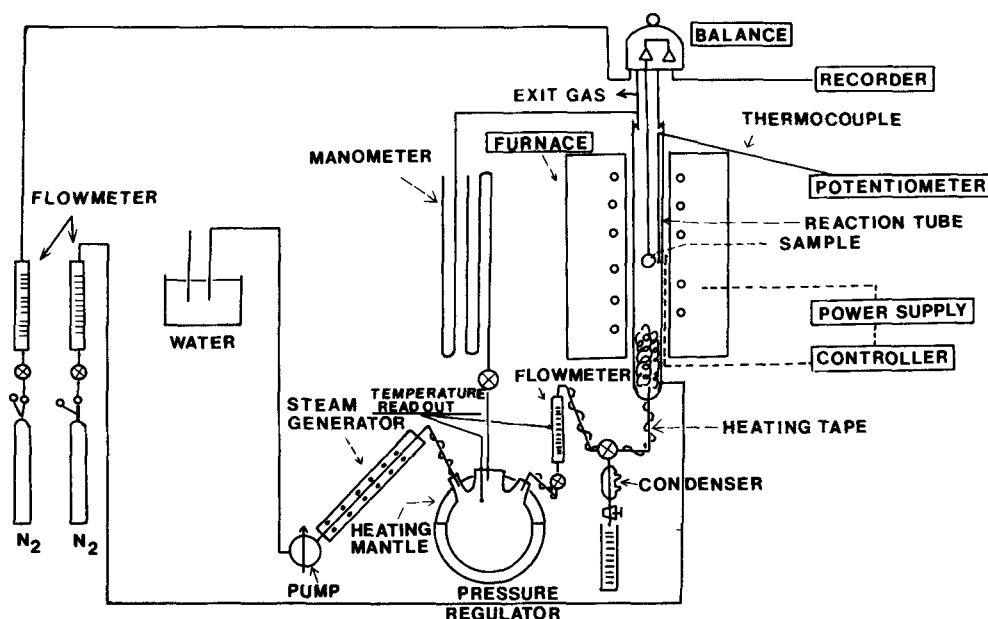


Fig. 1—A schematic diagram of the experimental apparatus.

do not play a significant role. This can be achieved by using a sufficiently high gas flow rate and a thin layer of fine powder or a thin pellet of high porosity.

### A. Effect of Steam Velocity

Equilibrium between steam and hydrogen sulfide can be attained at a very low concentration of the latter due to the positive Gibbs free energy change of reaction [4]. Hence, this reaction tends to become influenced by mass transfer at a higher gas velocity than those with a negative free-energy change. To determine the conditions where the external mass transfer does not influence the reaction rate, conversion experiments were carried out at various flow rates of steam using 10 mg of sample. Typical conversion-vs-time relationships of the reaction between steam and zinc sulfide under various flow rates of steam are given in Figure 2. It is seen that, in the range of flow rates used, the conversion data were not influenced by the variation in the steam velocity. A flow rate of 0.5 mL/min (at 293 K) was found to be sufficient to reduce the external mass-transfer resistance to a negligible level in the temperature range 1023 to 1160 K where all the runs were carried out.

### B. Effect of the Quantity of Sample

To ensure the measurements were conducted in the region where the effect of interparticle diffusion was absent, as discussed above, conversion was measured for various amounts of the solid reactant, as shown in Figure 3. The conversion rate increased as the amount of sample decreased until the solid sample reached a certain quantity (10 mg). With this amount of sample, therefore, it was concluded that the diffusional resistance through the interstices among the particles was eliminated.

### C. Effect of Reaction Temperature

Measurements were thus conducted in the absence of external mass-transport resistance and diffusional effects in the temperature range 1023 to 1160 K. Conversion-vs-time relationships are given in Figures 4(a) and (b).

### D. Effect of Steam Concentration

The concentration of steam was varied by using different flow rates of nitrogen with which the steam was mixed,

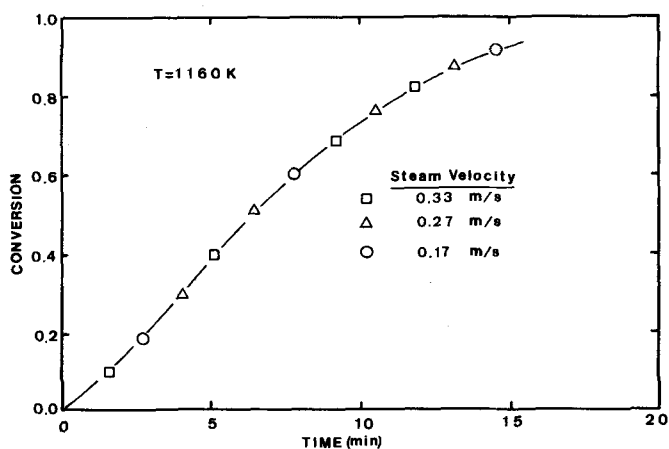


Fig. 2—Verification of the absence of external-mass-transfer effect.

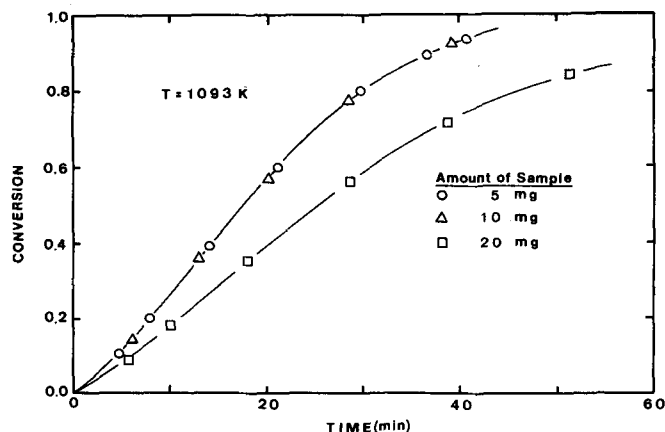
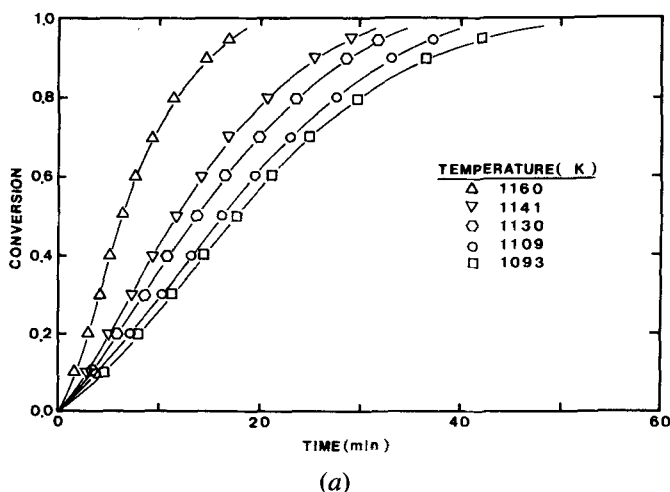
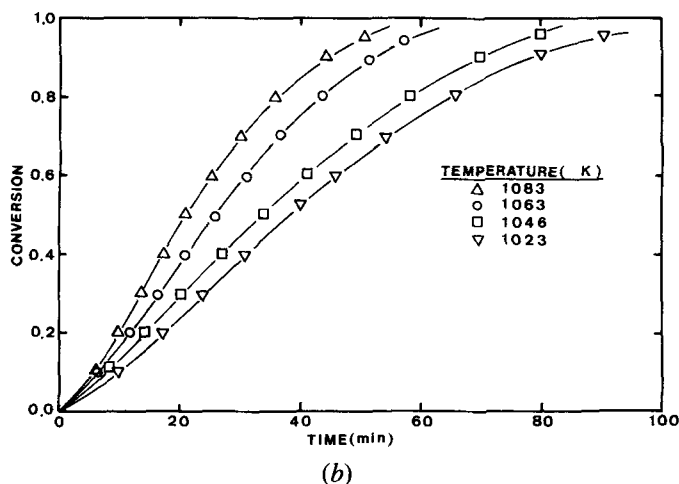


Fig. 3—Elimination of the effect of interparticle diffusion.



(a)



(b)

Fig. 4—Conversion-vs-time relationship for the reaction between steam and zinc sulfide at various temperatures ( $p_{\text{H}_2\text{O}} = 86 \text{ kPa}$ ). (a) 1160 to 1093 K. (b) 1083 to 1023 K.

maintaining the total pressure of the gas mixture constant. The effect of steam concentration on the reaction rate at various temperatures is shown in Figures 5(a) through (c).

### E. Analysis of Rate Data

For the reaction of finely-sized particles, it has been found by many investigators<sup>11-14</sup> that the reaction starts by

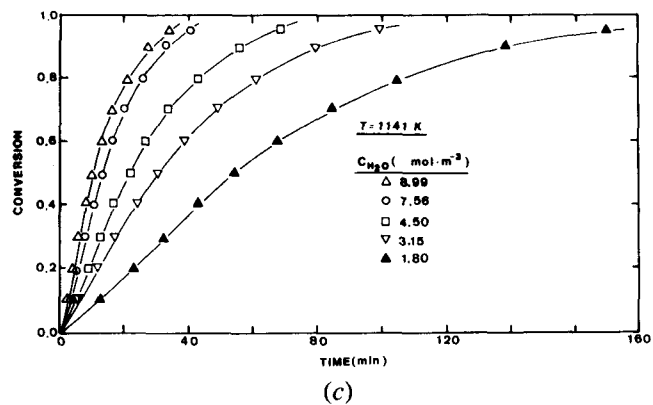
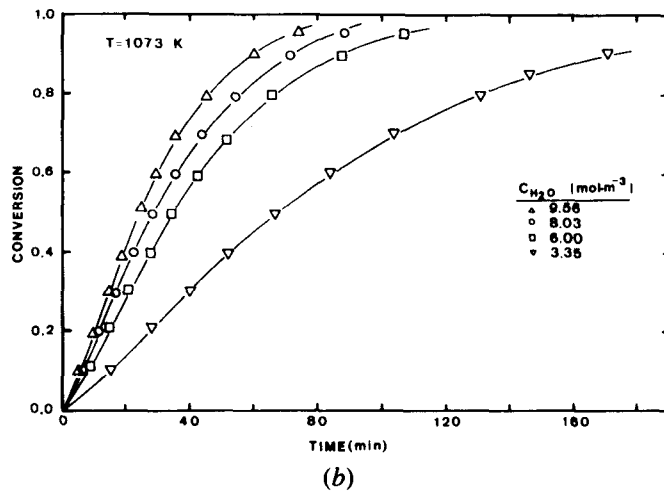
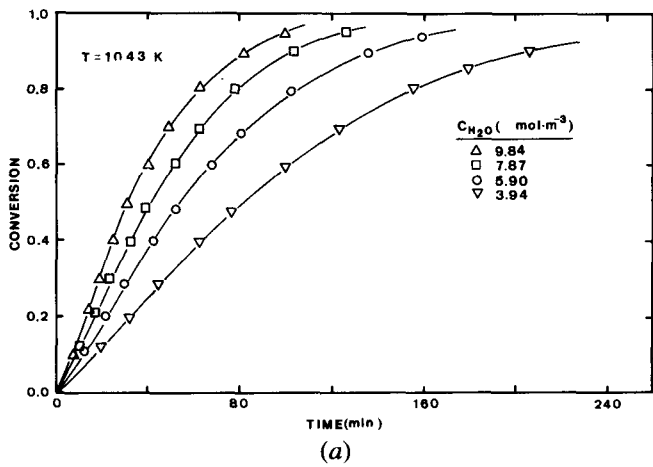


Fig. 5—Effect of steam concentration on the conversion of zinc sulfide. (a) 1043 K. (b) 1073 K. (c) 1141 K.

forming nuclei at the surface of the solid and these nuclei grow in size while new ones are formed.

The conversion-vs-time relationship for such a reaction can be described by the nucleation and growth kinetics. An often-used form of the rate expressions for this kinetics is

$$[-\ln(1 - X_B)]^{1/n} = k_b t \quad [7]$$

where  $n$  is a constant,  $X_B$  is the fractional conversion of the solid reactant, and  $k_b$  is the apparent rate constant, which can be written as

$$k_b = k_1 f(C_{H_2O}, C_{H_2S}) \quad [8]$$

In this equation,  $k_1$  is the intrinsic rate constant,  $C_{H_2O}$  and  $C_{H_2S}$  are the steam and  $H_2S$  concentrations, respectively, and  $f$  represents the dependence of the reaction rate on the gas concentrations, which is to be determined by the experi-

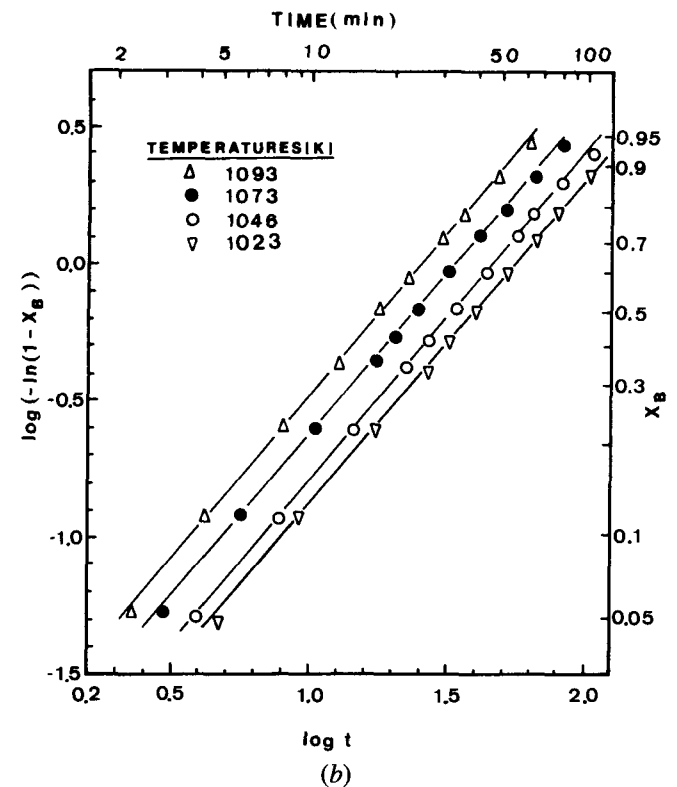
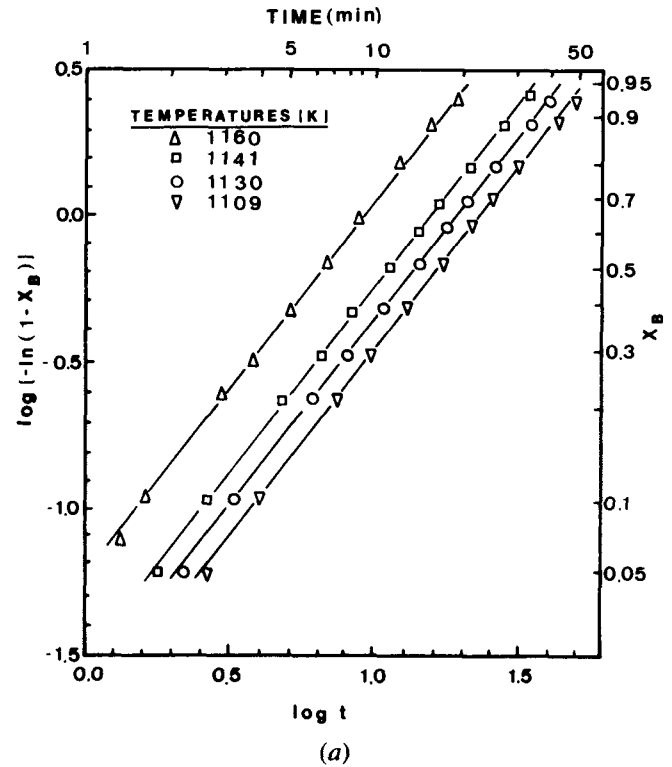


Fig. 6— $\log_{10} [-\ln(1 - X_B)]$  vs  $\log_{10} t$  for the reaction between steam and zinc sulfide at various temperatures ( $p_{H_2O} = 86$  kPa). (a) 1160 to 1109 K. (b) 1093 to 1023 K.

ment. The rate is expected to be sensitive to the concentration of the product gas  $H_2S$  because of the positive  $\Delta G^\circ$ , and hence small equilibrium constant, of the reaction. Other types of rate expressions, such as the shrinking-core and the power-law equations, were also tested, but found to be less satisfactory than the nucleation-and-growth expression.

Equation [7] indicates that, by making a linear plot between  $\log[-\ln(1 - X_B)]$  and  $\log t$ , the constants  $n$  and  $k_b$  can be determined from the slope and the intercept with  $\log t = 0$  axis, respectively. Such plots of the experimental data in Figures 4(a) and (b) are presented in Figures 6(a) and

(b). It is seen that linearity is observed over a wide range of conversion. The value of  $n$ , which is the slope of the straight line, was determined to be 1.28 from the regression analysis. This value of  $n$  perhaps suggests a one-dimensional growth of the nuclei.

Using this information, the conversion-vs-time data under various steam concentrations, shown in Figures 5(a) through (c), are replotted in terms of  $\log[-\ln(1 - X_B)]$  against  $\log t$  in Figures 7(a) through (c). To determine the dependence of the reaction rate on steam concentration, the apparent rate constant,  $k_b$ , was assumed to have the following

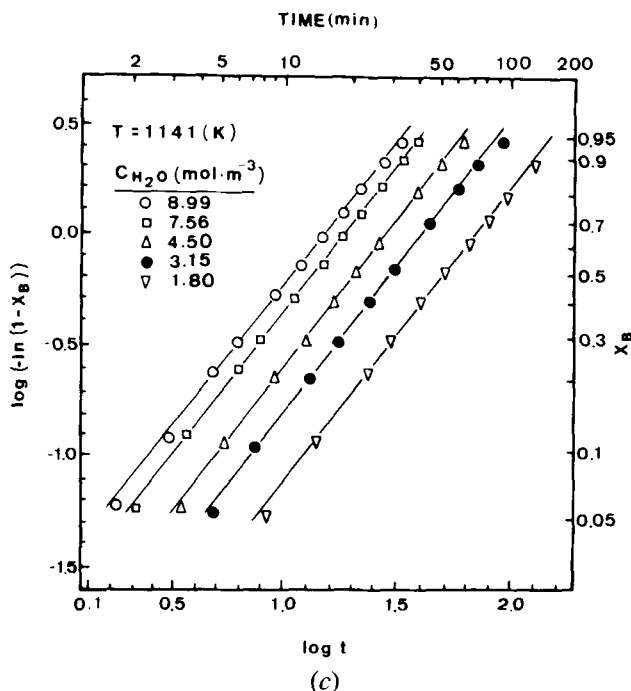
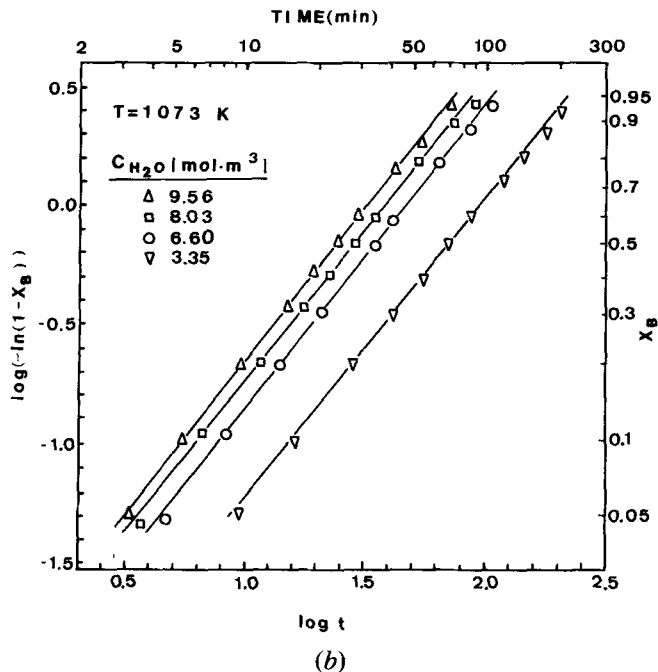
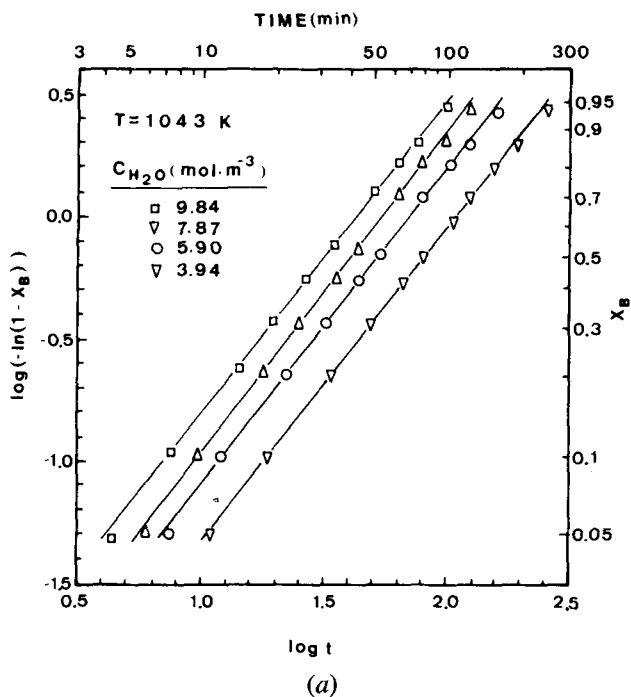


Fig. 7— $\text{Log}_{10} [-\ln(1 - X_B)]$  vs  $\text{log}_{10} t$  for the reaction between steam and zinc sulfide under various steam concentrations. (a) 1043 K. (b) 1073 K. (c) 1141 K.

relationship:

$$k_b = k_1 C_{H_2O}^m \quad [9]$$

where  $m$  is a constant. The values of  $\log(k_1 C_{H_2O}^m)$  are plotted against  $\log C_{H_2O}$  in Figure 8. The slope of the straight line, which corresponds to  $m$ , was determined to be 1 at different reaction temperatures. From this result the reaction is determined to be first order with respect to steam concentration. Although the effect of the  $H_2S$  concentration on the rate of this reaction was not determined in this work, equilibrium consideration suggests that the concentration driving force will be  $(C_{H_2O} - C_{H_2S}/K_e)$ . In view of these results, Eq. [7] can be represented as

$$[-\ln(1 - X_B)]^{1/n} = k_1(C_{H_2O} - C_{H_2S}/K_e)t \quad [10]$$

The intrinsic rate constants,  $k_1$ , were obtained from the intercepts of the straight lines with the  $\log t = 0$  axis in Figures 6(a) and (b), which correspond to  $n \log(k_1 C_{H_2O})$ .

Figure 9 is an Arrhenius plot of the rate constants obtained. The best-fit straight line through the data is represented by

$$k_1 = 45.3 \exp(-E/RT) m^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \quad [11]$$

where the activation energy,  $E$ , is  $1.22 \times 10^5 \text{ J} \cdot \text{mol}^{-1}$ .

By differentiating Eq. [10], the expression for the rate of reaction can be obtained, as follows:

$$\begin{aligned} dX_B/dt &= k_1(C_{H_2O} - C_{H_2S}/K_e)(1 - X_B) \\ &\times [-\ln(1 - X_B)]^{1-1/n} \end{aligned} \quad [12]$$

with  $n = 1.28$ .

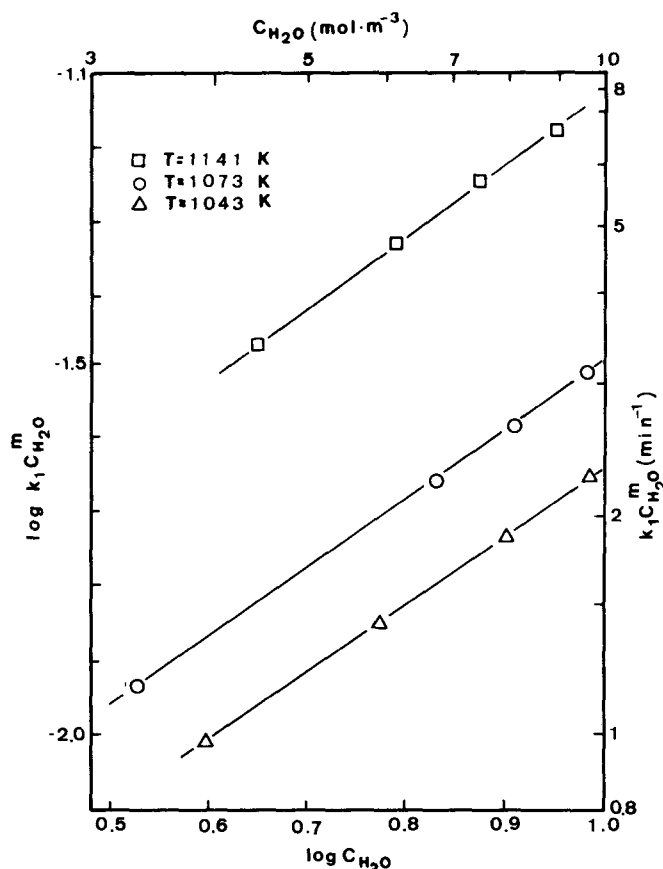


Fig. 8—Dependence of rate on steam concentration at various temperatures.

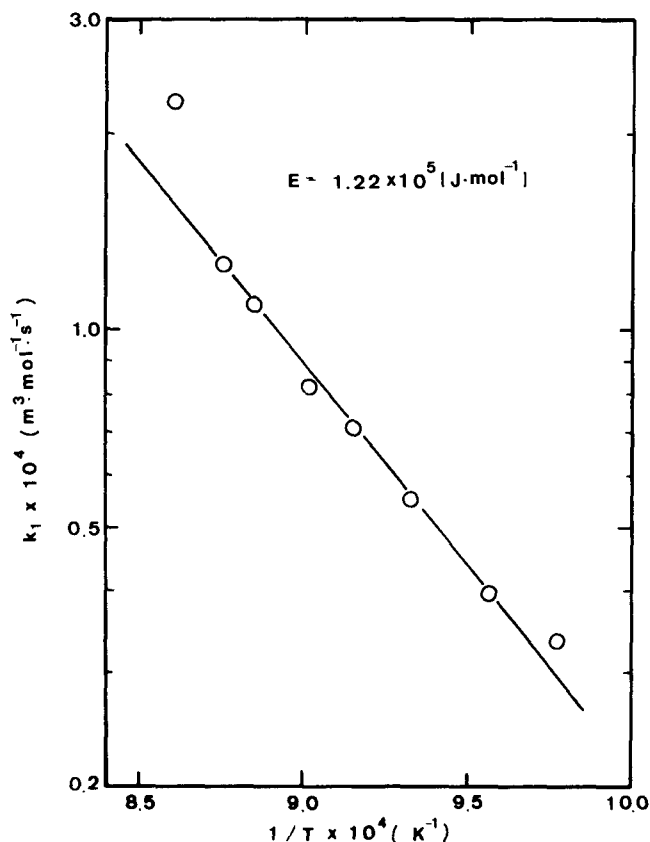


Fig. 9—Arrhenius plot of intrinsic rate constants for the reaction between steam and zinc sulfide.

## V. CONCLUSIONS

The intrinsic kinetics of the reaction between zinc sulfide and water vapor were determined by carrying out the measurements under conditions in which the effects of heat and mass transfer were eliminated. The ranges of temperature and water vapor concentration covered in the kinetics measurement were, respectively, from 1023 to 1160 K and from 3.94 to 9.84 mol/m<sup>3</sup>. The reaction products were identified to be ZnO and H<sub>2</sub>S, indicating that the reaction proceeds according to Eq. [4].

The kinetics of the reaction of ultrafine (<1 μm) ZnS particles with water vapor can be represented by Eq. [10], which gives the conversion-vs-time relationships under constant temperature and C<sub>H<sub>2</sub>O</sub>, or by Eq. [12], which represents the rate of conversion at any instance.

## ACKNOWLEDGMENTS

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