

## Note

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### The reaction of H<sub>2</sub>S with CaO and its role in the reduction of sulfides by H<sub>2</sub>

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(Received 24 May 1976)

Calcium oxide was found to accelerate the reduction of copper sulfides by H<sub>2</sub><sup>1,2</sup>. For example, at 800°C in the presence of the stoichiometric amount of CaO reduction of Cu<sub>2</sub>S was complete in an hour while in absence of CaO only traces of Cu were formed under similar conditions. This enhancing effect was attributed to the strong affinity of CaO for H<sub>2</sub>S which is formed during reduction according to the equations:



The equilibrium constant for reaction (1) at 800°C is  $3 \times 10^{-3}$  while for reaction (2) it is  $1.7 \times 10^3$ . Therefore, the equilibrium constant for the overall reaction:



is 5.1, thus the reduction is thermodynamically favored.

The utilization of CaO as an aid in the reduction of other sulfides and especially PbS was next investigated. It is known that PbS can be readily reduced to Pb by H<sub>2</sub> at about 750°C; but, at that temperature the volatility of PbS is appreciable and leads to inconvenient operation<sup>3</sup>. Reduction of PbS in the liquid and vapor phase was considered by other investigators<sup>4,5</sup> but the temperature required had to be above 1000°C. If CaO enhances the reduction of PbS in a similar way to the case of Cu<sub>2</sub>S then it might be possible to conduct the reaction at a lower temperature, (e.g., 400°C) at which Pb is already molten and the volatility of PbS is negligible.

Contrary to expectation, the presence of CaO was found to inhibit the reduction of PbS. Thus in absence of CaO, reduction was 26% complete in 100 min at 600°C, 55% at 650°C, and 80% at 700°C. In presence of CaO, on the other hand, no reduction took place below 650°C, and only traces of Pb formed at 700°C. Ford and Fahim<sup>6</sup> studied the reduction of Co<sub>9</sub>S<sub>8</sub> by H<sub>2</sub> in presence of CaO by noting the change in weight of the mixture using a thermobalance. They found that at a gas

flow-rate of  $200 \text{ ml min}^{-1}$  an appreciable amount of  $\text{H}_2\text{S}$  representing as much as 10% of the sulfur in the sample escaped from the system without reaction with the lime and, therefore, they recommended using low  $\text{H}_2$  flow for an effective CaO role although this will result in a lower reduction rate. In the case of chalcopyrite, this phenomenon was not observed in our laboratory. It became evident, then, that for a better understanding of the role of CaO in the reduction of sulfides it was necessary to study the kinetics of the reaction of CaO with  $\text{H}_2\text{S}$  on which little is known<sup>7-9</sup>. Gabrilova and Altshuler<sup>7</sup> who were the only researchers to investigate this reaction found that the absorption of  $\text{H}_2\text{S}$  by CaO is slow. Contacting a gas mixture containing 0.3%  $\text{H}_2\text{S}$  and the balance  $\text{N}_2$  with a static bed of CaO at  $700^\circ\text{C}$  for 50 min at  $2.13 \text{ m sec}^{-1}$  gas flow-rate, resulted in 71% absorption of  $\text{H}_2\text{S}$ . At  $500^\circ\text{C}$  the absorption was 55% after 1 h, other conditions being equal. They also found that at  $1000^\circ\text{C}$ , the rate increased linearly with increasing gas flow-rate; the highest linear flow-rate permissible in their apparatus was  $2.13 \text{ m sec}^{-1}$ . They suggested that the reaction was diffusion-controlled through the boundary layer. This was confirmed when they studied the effect of temperature in the range 500 to  $1000^\circ\text{C}$  and found an activation energy of 3.3 to  $4.5 \text{ kcal mol}^{-1}$ . In the present study, emphasis was therefore laid on eliminating the effect of diffusion through the boundary layer so that conclusions could be drawn regarding the reaction mechanism.

Reagent grade CaO was heated at different temperatures in  $\text{H}_2\text{S}$  atmosphere in a thermogravimetric analysis unit. The TG instrument was a Fisher 10-560-100 assembly with a Cahn RG electrobalance. The heating system consisted of a vertical tube furnace connected to the model 360 linear temperature programmer which provides linear heating rates. The recorder was a Honeywell Elektronik 19. The sample was about 8 mg. The effect of gas flow-rate was studied at  $470$  and  $800^\circ\text{C}$  using undiluted  $\text{H}_2\text{S}$ . Results are shown in Fig. 1; they show that the boundary layer diffusion barrier can be overcome at a gas flow-rate of 40 and  $70 \text{ ml min}^{-1}$  at  $470$  and  $800^\circ\text{C}$ , respectively. Therefore, all tests were conducted at a gas flow-rate of  $70 \text{ ml min}^{-1}$ .

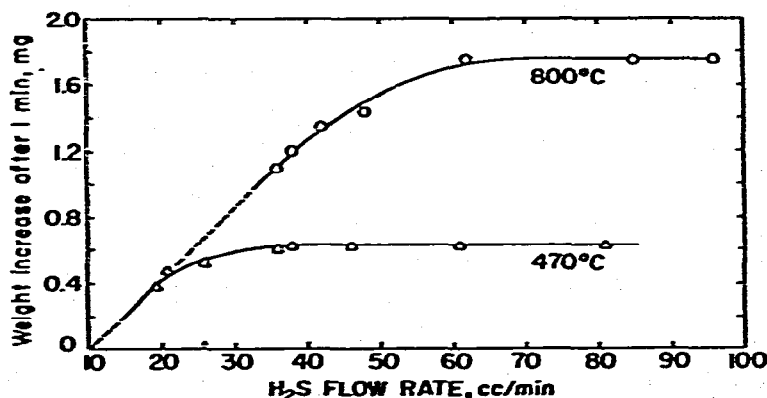


Fig. 1. Effect of  $\text{H}_2\text{S}$  flow-rate on its reaction with CaO.

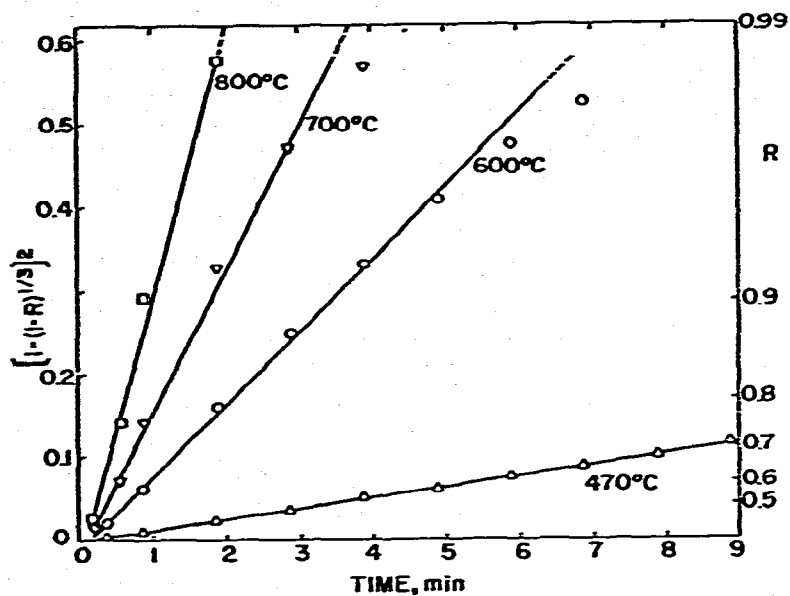


Fig. 2. Plot of fraction reacted versus time according to Jander's equation.

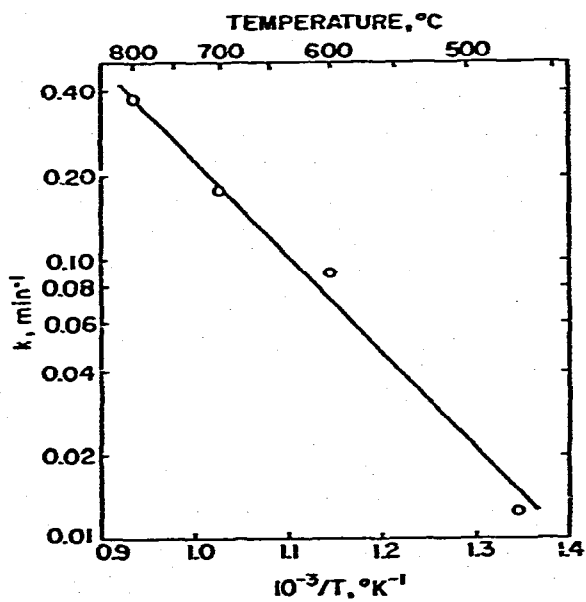


Fig. 3. Arrhenius plot for the reaction:  $\text{H}_2\text{S} + \text{CaO} \rightarrow \text{CaS} + \text{H}_2\text{O}$ .

Data of isothermal tests fitted Jander's equation:

$$[1 - (1 - R)^{1/3}]^2 = kt \quad (4)$$

where  $R$  is the fraction reacted in time  $t$ , and  $k$  is the rate constant, as shown in Fig. 2. This indicates that the reaction is diffusion-controlled. Other plots were tried but did not yield a straight line. The plot of  $\log k$  versus  $1/T$  yielded a straight line (Fig. 3) from which the activation energy of the process was calculated to be  $16 \text{ kcal mol}^{-1}$ . This value is typical for gaseous diffusion through the product layer.

An explanation for the different behavior of CaO during the reduction of  $\text{Cu}_2\text{S}$  and PbS can be as follows. Although the absorption of  $\text{H}_2\text{S}$  by CaO is thermodynamically highly favorable, yet kinetically especially below  $500^\circ\text{C}$ , it is a slow reaction that is governed by diffusion. If the rate of formation of  $\text{H}_2\text{S}$  according to:



is slower than that of its reaction with CaO, the partial pressure of  $\text{H}_2\text{S}$  surrounding the sulfide particle will be lower than the equilibrium concentration and therefore the reduction will proceed. This seems to be the case in the reduction of  $\text{Cu}_2\text{S}$  by  $\text{H}_2$ . On the other hand, if the rate of reduction of sulfide is higher than that of the reaction of  $\text{H}_2\text{S}$  with CaO, the partial pressure of  $\text{H}_2\text{S}$  surrounding the sulfide particle will approach the equilibrium concentration and the reaction will stop. This is probably the case with PbS.

#### ACKNOWLEDGEMENT

The authors acknowledge with thanks the financial support granted by the Canadian National Research Council.

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