Kinetics of the Reaction between Hydrogen Sulfide and Lime Particles

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The reaction between hydrogen sulfide and lime is important, among others, as a component reaction of the hydrogen reduction of metal sulfides in the presence of lime, and in the desulfurization of fossil fuels. The results of experiments on the kinetics of this reaction are presented in this paper. The experiments were carried out in the temperature range 873 to 1073 K, using a thermogravimetric analysis technique. A "pore blocking" model was found to fit the reaction rate, which was initially rapid and leveled off at less than the complete conversion. An activation energy of 76.1 kJ/mol (18.2 kcal/g-mole) was obtained. The reaction was first order with respect to hydrogen sulfide concentration in a gaseous mixture with hydrogen. A higher initial moisture content in the calcium oxide particles resulted in a considerably higher reaction rate.

I. INTRODUCTION

In recent years, much attention has been directed to the hydrogen reduction of metal sulfides in the presence of lime as an alternative to conventional smelting.[1-7] The overall reaction in this process consists of the following successive reactions:

$$Me_xS + H_2 = x\text{Me} + H_2S \qquad [1]$$

$$CaO + H_2S = CaS + H_2O \qquad [2]$$

The role of lime in this process is two-fold: It removes H_2S, thus improving the thermodynamics of the first reaction, which has a small equilibrium constant, and it prevents the sulfur-containing gas from escaping with the effluent gas. Therefore, the reaction between hydrogen sulfide and lime is an important part of the overall process. Another example of important industrial process in which this reaction is encountered is the desulfurization of fossil fuels. Calcium oxide is also widely used to remove sulfur dioxide in combustion processes. While a substantial amount of work has been reported on the sulfation of lime, there is little information available on the kinetics of the reaction between hydrogen sulfide and lime. Gavrilova and Al'tshuler[8] studied the reaction of calcium oxide with a gas mixture of nitrogen containing 0.2 to 0.45 pct hydrogen sulfide over the temperature range 773 to 1273 K. They found that the reaction is diffusion controlled with an apparent activation energy of 13.6 to 18.8 kJ/mol. The reaction rate was retarded by steam addition, and the dissociation of hydrogen sulfide was effectively suppressed by adding hydrogen in the reacting gas. Investigations by Vestal and Johnston[9] and Pell and co-workers[10] revealed that the scavenging reaction of hydrogen sulfide by calcined dolomite is first order with respect to unreacted calcium oxide, but they reported different activation energies of 159.0 and 96.2 kJ/mol, respectively. Pell and co-workers further suggested that the reaction took place between the gas and the calcium oxide part of the dolomite, *i.e.*, magnesium oxide had little reactivity. The kinetics of this reaction was described by an adsorption model. Habashi and Mikhail[11] reported that the reaction between calcium oxide and hydrogen sulfide proceeds in accordance with Jander's parabolic rate equation and has an activation energy of 66.9 kJ/mol between 743 and 1073 K. In a recent study of Westmoreland and co-workers[12] on the reactions between hydrogen sulfide and selected metal oxides, *e.g.*, MnO, ZnO, CaO, and V_2O_3, it was suggested that all reactions were first order with respect to gas concentration and that the activation energy for the reaction of hydrogen sulfide with calcium oxide was 21.8 kJ/mol, which was obtained from initial rates between 573 and 1073 K.

Most of the investigators did not make much effort beyond the elucidation of the initial kinetics of the reaction, but this provides little information on the overall kinetic response which is required in analysis of the hydrogen reduction of metal sulfides in the presence of lime.

II. EXPERIMENTAL

Experiments were carried out in a typical thermogravimetric setup similar to the one described in Reference 13. The apparatus consisted of a recording balance (Cahn Model 1000) from one arm of which a shallow quartz tray for holding lime powder was suspended by a platinum chain into a quartz reaction tube located within a vertical tubular furnace. By means of a gas delivery system, a metered flow of gaseous reactant or an inert gas was passed through the reaction tube. The exit gas was passed through a two-stage scrubber containing zinc acetate solution to precipitate the sulfur as zinc sulfide. The gas temperature was measured by Pt-13 pct Rh/Pt thermocouples. A uniform temperature profile of ±3 K was achieved over 0.25 m length of the reaction tube. Manometers were employed to measure the pressure inside the reaction tube and the microbalance.

The helium, hydrogen, and hydrogen sulfide gases used in the experiments were supplied by Matheson Co. and were of 99.995, 99.98, and 99.5 pct minimum purity, respectively. These gases were used directly from cylinders without further purification. The calcium oxide was Mallinckrodt Analyzed Reagent Lot WCRP, which was used throughout

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this work to avoid complications which may have arisen due to the variation of reactivity of different lots.

After adjusting and calibrating the balance and the recorder, a thin layer of lime powder was spread on the quartz tray, weighed, and then suspended from one pan of the balance. The reaction tube and the tubular furnace were then placed in position, and the system was brought to the desired temperature under a steady flow of helium. The slight mass change during this heating period enabled the correction of the initial sample mass to a dry basis. Then the helium was turned off and a mixture of hydrogen and hydrogen sulfide was passed through the system. The reason for the hydrogen was to suppress the dissociation of hydrogen sulfide, which could be appreciable in the temperature range of our interest. During the reaction the microbalance was protected from hydrogen sulfide and hot gases by flushing it with helium gas. The pressure inside the reaction tube was maintained at atmospheric level.

III. EXPERIMENTAL RESULTS

A. *Characterization of the Lime Samples*

An X-ray sedimentometer (Micromeritics Model 5000D) was used to measure the particle size of the lime powder. The particle sizes of the powder ranged approximately from 2 to 30 μm with a median size of 8 μm. The surface area of lime before the reaction was measured by the BET method. The average of five measurements of the specific surface area was 4.06 (±1.4 pct) m^2/g. The true density determined by a Micromeritics Model 1310 pycnometer was 3.253 g/cm^3, which compared favorably with 3.25 to 3.38 g/cm^3 reported in the literature.[14]

The lime powder was examined using a Hitach Model 500 electron microscope. Figure 1 shows that each lime particle was composed of "crystallites" as small as 0.1 μm. Eades and Sandberg[15] also observed these crystallites in their lime samples and concluded that the actual reaction occurred on the surface of the crystallites, and the pore space and size of crystallites were the prime factors controlling the reactivity of lime. Under the scanning electron microscope, it was difficult to see any changes of the crystallite structure or size as could be expected when the molar volume of solid is increased by the conversion of calcium oxide to calcium sulfide.

Therefore, an X-ray line broadening method (using a Phillips X-ray diffractometer) was employed to determine the mean crystallite size of calcium sulfide formed after the lime powder reacted with hydrogen sulfide for about three hours at different temperatures. Calculations were made using the procedure of Rau,[16] except that the correction for instrumental line broadening was performed using Warren's equation.[17] The sizes of the CaS crystallites determined this way are listed in Table I. Compared with the mean crystallite size of lime (0.11 μm), the sizes of the product CaS crystals are somewhat greater.

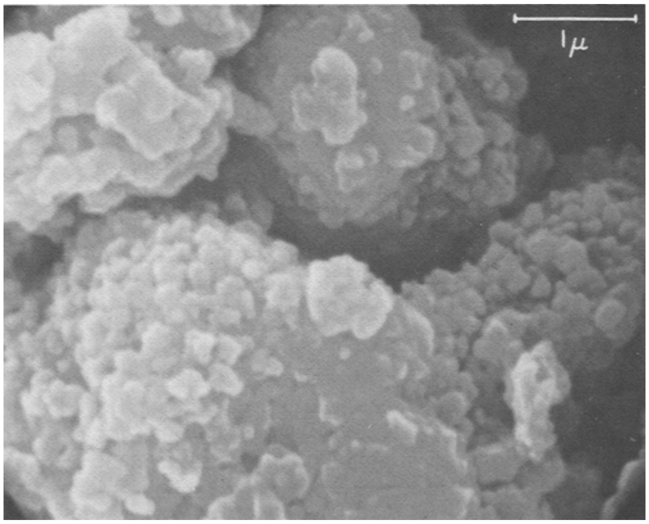

Fig. 1—Scanning electron micrograph showing the crystallites in lime particles.

B. *Kinetic Measurements*

Most experimental runs were continued for about three hours, until the sample showed no substantial further mass change. The conversion at a particular time was determined by dividing the mass change of the solid sample at the time by the theoretical maximum total mass change.

Effect of gas flow rate: The effect of gas flow rate in the range 0.52 to 1.24 dm^3 per minute (using lime powder of 46 ±1.3 mg in 3.2 pct H_2S in H_2 at 1023 K) on the reaction is shown in Figure 2. It is clear that for flow rates above 1.03 dm^3 per minute the reaction rate is independent of the gas flow rate. Thus in all the subsequent runs, a working gas flow rate of 1.24 dm^3 per minute was chosen so as to avoid any H_2S starvation and external mass transfer effects.

Effect of initial moisture content: It is well known that lime is readily hydrated upon exposure to the atmosphere, and its reactivity may be strongly influenced by the physical properties of the lime. Therefore, the effect of initial moisture content on the reaction rate of hydrogen sulfide with lime was tested. The results are shown in Figure 3. It is seen that the lime sample with a lower moisture content has a much slower rate than a sample with a higher moisture content. The initial reaction rate of a lime sample with an initial moisture content of 13.9 pct was about nine times higher than that of a sample with a moisture content of 0.9 pct. This is believed to be due to increased surface area (or porosity) of the lime crystallites resulting when they were dehydrated prior to reaction with hydrogen sulfide. To reduce the error caused by varying moisture content, all the

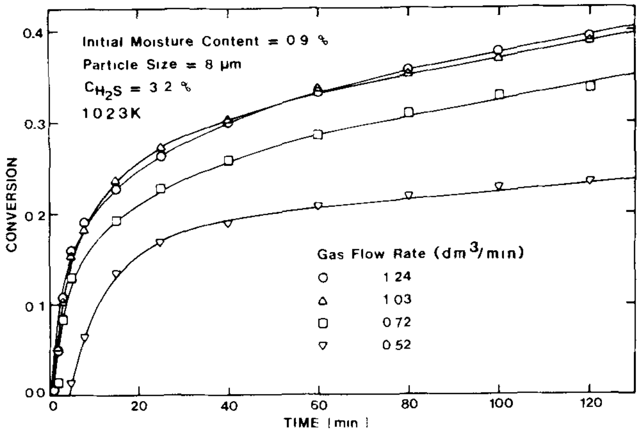

Fig 2—Effect of gas flow rate in lime powder experiments at 1023 K

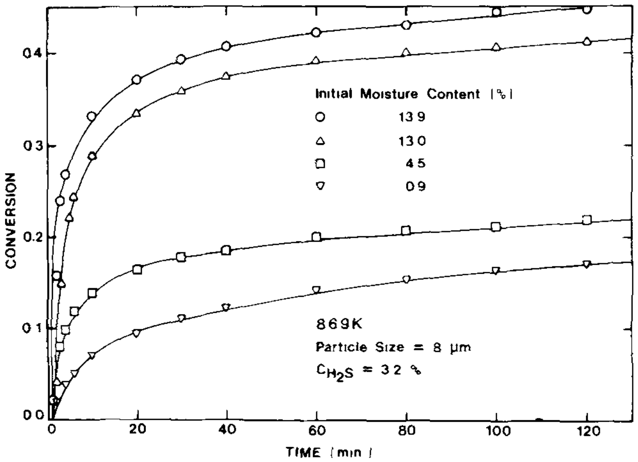

Fig. 3—Effect of initial moisture content in lime powder experiments at 869 K

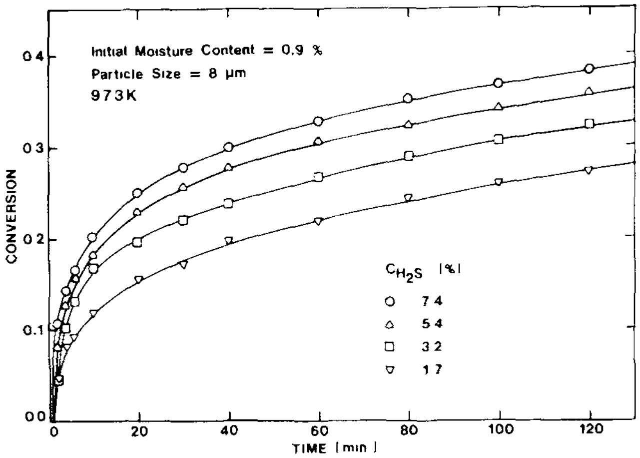

Fig. 5—Effect of hydrogen sulfide concentration in lime powder experiments at 973 K

subsequent runs were carried out by keeping the lime samples of the initial moisture content as low as possible (0.9 ±0.12 pct of the sample mass).

Effect of reaction temperature: The influence of temperature on the reaction was examined by varying the temperature in the range of 867 to 1072 K. All other experimental variables such as sample mass, gas flow rate, initial moisture content, *etc.* were nearly identical for these measurements. As shown in Figure 4, the reaction rate increases with increasing temperature. Typical conversion-time curves consist of two parts: initial region of rapid reaction followed by a period of very slow rate. These curves were reproducible within ±3.0 pct at each temperature.

Effect of hydrogen sulfide concentration: Figure 5 shows the effect of H_2S concentration on the reaction at 973 K under otherwise identical conditions. The H_2S concentration was varied between 1.7 and 7.4 vol pct in hydrogen atmosphere.

IV. INTERPRETATION OF RESULTS

In the study of the reaction of SO_2 with calcined limestone, McClellan *et al.*[18] reported that the sulfur dioxide reacted with lime crystallites to form individual crystals of $CaSO_4$. These in turn formed interlocking aggregates. On further sulfation, these crystallites covered the entire surface of the particles. The growth of adjacent crystals resulted in a tight, smooth surface as they formed larger aggregates at temperatures above 1323 K. Borgwardt[19] further found that the reaction rate of SO_2 with lime was essentially independent of particle size (less than 0.5 mm). Reaction occurred initially throughout the particle volume, and the internal diffusional resistances became significant only after the conversion of lime reached 20 pct.

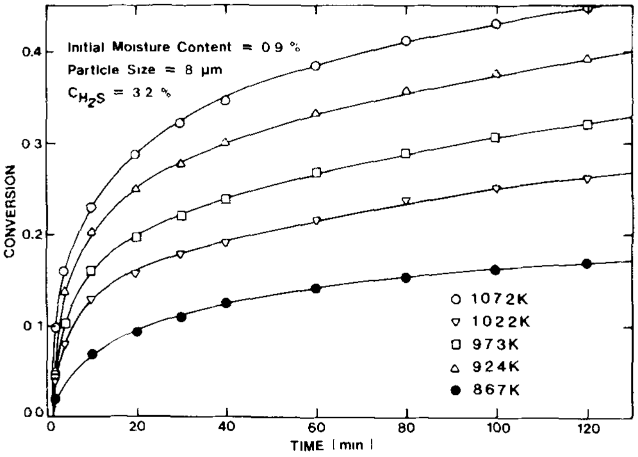

Fig. 4—Effect of reaction temperature in lime powder experiments

In the present study, the growth of crystallite size was not clearly observed under the scanning electron microscope, probably because the increase of molar volume by forming CaS (67 pct) is about one-fifth of that by forming $CaSO_4$ (302 pct). However, based upon the X-ray crystallite size data (Table I) and the results of previous investigations described above, a "pore-blocking" model was believed to be a logical choice to explain the reaction of hydrogen sulfide with lime. No other simple rate expressions tested were as satisfactory.

Pore-blocking model: Soft-burned lime, produced from the calcination of limestone, contains a theoretical porosity of 56.6 pct.[20] For such fine porous materials, a rate expression called the pore-blocking model was derived by Evans[21] based upon the reaction rate influenced by the transport of the gaseous reactant through pores. When the reaction products in a given pore set up compressional stresses in the solid, causing blockage of neighboring pores, the conversion of lime, X_D, is related to its time of exposure to the hydrogen sulfide, t, by

$$X_D = \lambda \ln(1 + k_d t/\lambda) \qquad [3]$$

where λ and k_d are constants.

Table I. Mean Crystallite Size of Sulfidation Products*

Reaction Conditions			
T (K)	Reaction Time (Min)	Crystallite Size of CaS (μm)	Conversion (Pct)
867	170	0.25	18.4
924	180	0.28	29.0
973	180	0.28	35.7
1022	185	0.13	43.0
1072	180	0.14	48.7

*The mean crystallite size of lime was about 0.11 μm

There are other models proposed for gas-solid reactions in which solid volume increases upon reaction.[22-25] They are mostly applicable for large porous pellets. For fine porous particles such as the lime used in this work, the model by Evans[21] is appropriate. An expression for H_2S/lime particle kinetics would be useful in the mathematical model for the hydrogen reduction of sulfide/lime mixtures. Therefore, the relatively simple closed-form expression of Eq. [3] is very advantageous.

Two fundamental constants indigenous to the logarithmic law are k_d, a reaction rate constant within pores, and $1/\lambda$, a proportionality constant (or pore-blocking constant) between the number of pores available and the degree of conversion. The latter constant depends only on the basic pore structure and should be independent of gas concentration. On the other hand, the former constant, related to the chemical reaction, should be influenced by temperature and gas concentration. When the reactant gas is hydrogen sulfide, k_d can be expressed as

$$k_d = d \cdot k \cdot f(C_{H_2S}) \qquad [4]$$

where d is a stoichiometry coefficient ($d = 1$ in this system), k is the rate constant, C_{H_2S} is the hydrogen sulfide concentration in the bulk, and f designates the concentration dependence.

Interpretation of the rate data: In the analysis of the experimental results, the pore-blocking model given by Eq. [1] can be tested by ascertaining whether a value of λ exists which gives a straight line at each temperature on plotting exp (X_D/λ) against t. In order to evaluate the H_2S concentration dependence of k_d, the conversion-time curves presented in Figure 5 were replotted in Figure 6 as exp (X_D/λ) against t. Using just one value of λ $(= 0.075)$, the data can be fitted by straight lines up to more than two hours of reaction where the change of reaction rates becomes insignificant. This suggests that the data obey the logarithmic law and that λ is independent of the reactant gas concentration as predicted by the model. The values of the slopes were calculated by regression analysis. In Figure 7, the values of k_d thus obtained are plotted against H_2S concentration. A straight line passing through the origin is obtained, indicating that the reaction is of first order with respect to the concentration of hydrogen sulfide in the gas phase.

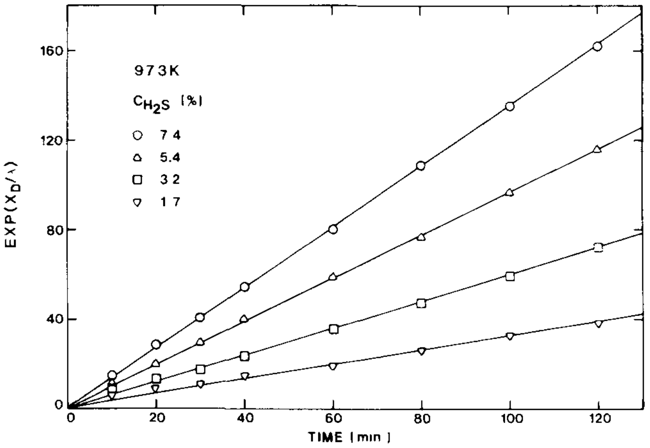

Fig 6—Plot of exp (X_D/λ) *vs* t from the results of Fig 5

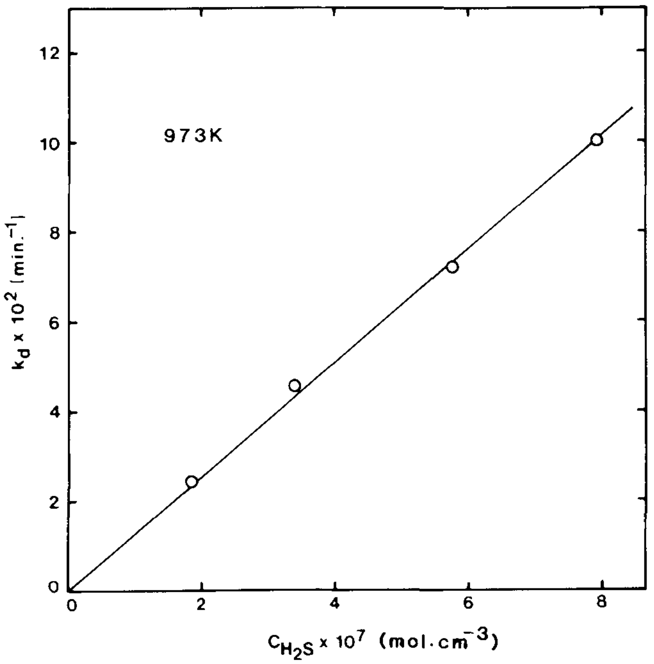

Fig. 7—Dependence of the reaction rate on hydrogen sulfide concentration from the results of Fig. 5.

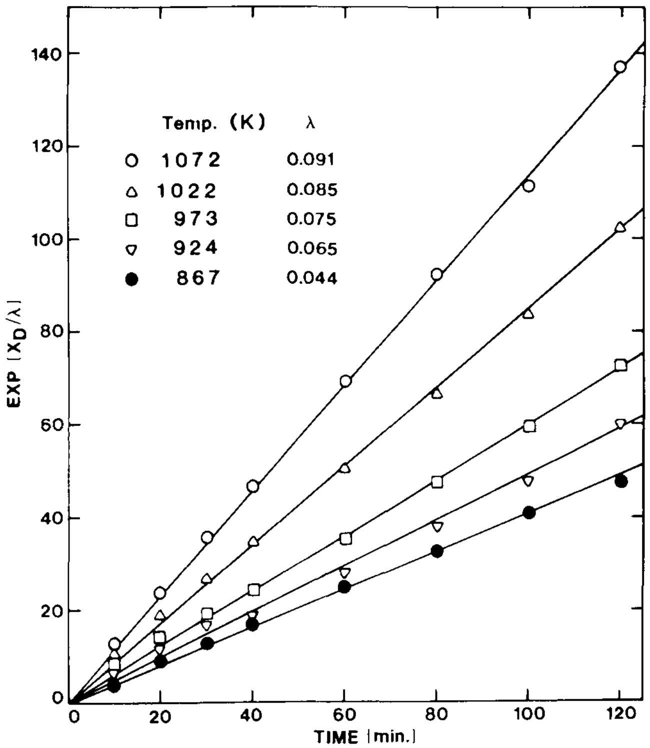

Fig. 8—Plot of exp (X_D/λ) *vs* t from the results of Fig. 4.

The results for the effect of temperature in Figure 4 are replotted in Figure 8 by using values of λ which give the best straight lines according to Eq. [3] at different temperatures. The selected values of λ thus obtained ranged from 0.044 to 0.091 and are shown in Figure 8. As shown in Figure 4, the rate of reaction at 867 K was relatively rapid during the initial stage but then markedly dropped off with time, indicating significant resistance to diffusion through the micropores of the outside layer. The chemical reaction was confined to the external crystallites of the individual particle. However, at higher temperatures, the penetration

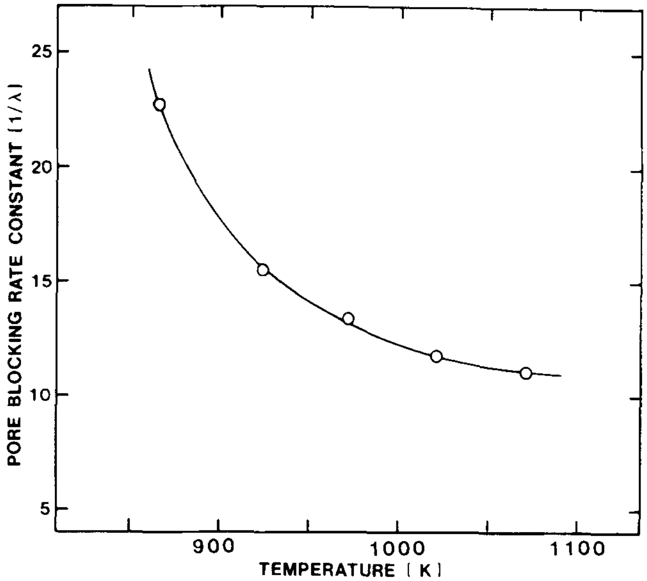

Fig. 9—Plot of pore-blocking rate constant *vs* temperature from the results of Fig. 8.

of H_2S increased, and the reaction took place within the interior structure of the particle. These phenomena can be supported indirectly by the fact that higher pore-blocking rate constants, $1/\lambda$, were obtained at lower temperatures as shown in Figure 9. As supported by the data for CaS crystallite size listed in Table I, the higher value of $1/\lambda$ would be undoubtedly associated with a somewhat larger size of CaS crystallites locally formed at the external layer of lime particles.

The rate constants at different temperatures were calculated using Eq. [4] from the slopes of each straight line in Figure 8. Figure 10 is an Arrhenius plot of the rate constants thus obtained. The slope of the straight line placed through the experimental points corresponds to an activation energy of 76.1 kJ/mol, which is in between the values of 67 and 96 kJ/mol found in the literature.[10,11] The processes affecting this activation energy are probably the chemical reaction between H_2S gas and the solid and solid-state diffusion, affected by the gasous diffusion through the pores in the solid. No attempt was made in this work to delineate definitively the relative importance of these steps. The line through these data can be expressed by the equation

$$k = 2.868 \times 10^7 \exp\left(-\frac{9160}{T}\right) \text{cm}^3/(\text{mol} \cdot \text{s}) \qquad [5]$$

for the reaction of hydrogen sulfide with lime particles of an average size 8 μm and an initial moisture content of 0.9 pct.

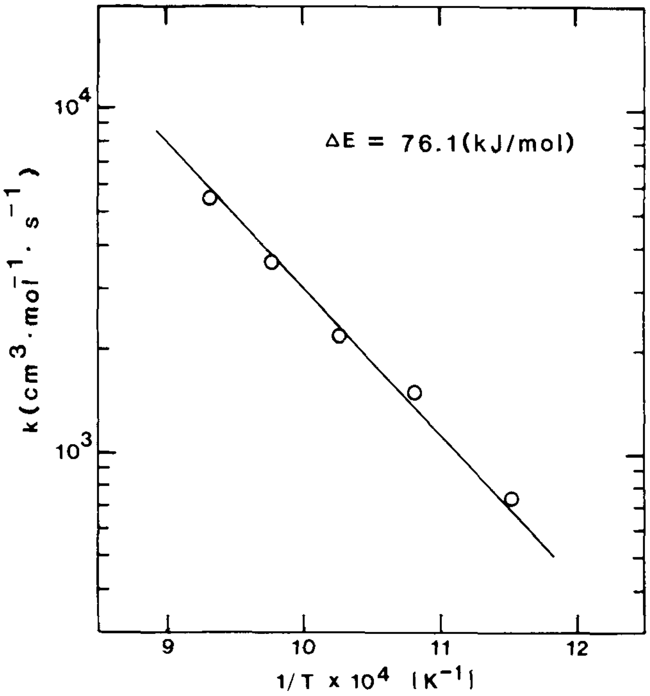

Fig. 10—Arrhenius plot of rate constants obtained from lime powder experiments.

V. CONCLUSIONS

The rate of the reaction of hydrogen sulfide with calcium oxide is initially fast, but slows down to a great extent as the reaction progresses. The pore-blocking model was applicable over the range of temperature investigated (867 to 1072 K). The reaction of lime powders with hydrogen sulfide has an activation energy of 76.1 kJ/mol. The reaction is first order with respect to hydrogen sulfide concentration. The initial moisture content in the lime has a strong influence on the reaction rate.

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