

# KINETICS AND MECHANISM OF PYRITE FORMATION AT LOW TEMPERATURES

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**ABSTRACT.** The kinetics of pyrite formation in the reaction between FeS, sulfur, and hydrogen sulfide in aqueous solution have been investigated between 20° and 50°C and at 1 atm pressure. The kinetics were followed by timed analyses of pyrite concentrations for a series of experimental runs with varying initial reactant concentrations. The rate may be described by the equations

$$d(\text{FeS}_2)/dt = k_1(\text{FeS})^2 (S)P_{\text{H}_2\text{S}}$$

or

$$d(\text{FeS}_2)/dt = k_2(\text{FeS})^2 (S) \{\Sigma\text{S}^{2-}\} \{\text{H}^+\}$$

where  $d(\text{FeS}_2)/dt$  is the rate of pyrite formation in moles liter<sup>-1</sup> sec<sup>-1</sup>,  $k_1$ , and  $k_2$  are the apparent rate constants;  $(\text{FeS})$  is the surface area of FeS in cm<sup>2</sup>;  $(S)$  is the surface area of sulfur in cm<sup>2</sup>;  $P_{\text{H}_2\text{S}}$  is the partial pressure of H<sub>2</sub>S in atm;  $\Sigma\text{S}^{2-}$  is the sum of activities of dissolved sulfide species; and  $\{\text{H}^+\}$  is the hydrogen ion activity. The apparent activation energy for the reaction is 17 kcal mole<sup>-1</sup>. The rate constant  $k_1$  varies from  $2 \times 10^{-20}$  (40°) to an estimated  $5 \times 10^{-22}$  cm<sup>6</sup> atm moles<sup>-1</sup> liter<sup>-1</sup> sec<sup>-1</sup> at 5°C;  $k_2$  varies from  $1 \times 10^{-12}$  (40°C) to  $3 \times 10^{-11}$  cm<sup>6</sup> moles<sup>-1</sup> liter<sup>-1</sup> sec<sup>-1</sup> at 5°C.

The kinetics are consistent with a mechanism involving the dissolution of both elemental sulfur and ferrous sulfide. Elemental sulfur dissolves in sulfide solutions producing polysulfide ions, and ferrous sulfide dissolves to form aqueous ferrous ions and sulfide species. Pyrite is formed directly through the reaction between aqueous ferrous ions and polysulfide ions. The nature of the polysulfide ions is unknown, but evidence is presented to suggest that larger polysulfides (for example, S<sub>8</sub>S<sup>2-</sup>) are involved.

There is a suggestion that at temperatures around 50°C the solid-solid reaction between FeS and sulfur begins to become important.

The pyrite produced through this reaction is not framboidal. The rate of pyrite formation in this chemically-controlled reaction is considerably greater than observed rates in natural sediments, which are probably transport-controlled.

## INTRODUCTION

The work of Berner (1970), Roberts, Walker, and Buchanan (1969), Rickard (1969), Hallberg (1972), and Sweeney and Kaplan (1973) has demonstrated the broad lines of the processes by which pyrite is formed at low temperatures and pressures in aqueous solutions. Generally, the reaction between an iron salt (commonly goethite in sediments) and dissolved sulfide species results in the formation of one or more of a variety of metastable ferrous or ferrous-ferric sulfides. These sulfides, which commonly consist mainly of a mixture of X-ray amorphous and crystalline compounds with the general formula, FeS, rereact with aqueous sulfide and sulfur to form FeS<sub>2</sub>. Two forms of FeS<sub>2</sub> are known, the metastable orthorhombic marcasite and the stable isometric pyrite. Marcasite tends to be formed in acid conditions and pyrite in more alkaline environments (Rickard, 1969). Most of the experimental work has not distinguished between the two minerals, although Rickard presented evidence that suggested that the form of the reactant sulfur in the reaction determined the state of the product. In the present investigation, the compound considered is pyrite. Ostroumov (1953) and Berner (1970) showed that low

temperature pyrite formation involved the addition of sulfur to metastable iron sulfides. Most investigators agree that an equation such as



would summarize the overall reaction. However, there has been considerable discussion about the detailed mechanism of the reaction. It seems widely accepted that more than one pathway occurs. Goldhaber and Kaplan (1974) have suggested that differences in sedimentary pyrite textures reflect differences in the formation processes.

Proposed reaction mechanisms can be divided into three groups:

1. *Solid state reactions.*—Pyrite may be synthesized in high temperature anhydrous systems by the reaction between an iron sulfide and elemental sulfur. The iron sulfide reactant may be mackinawite, greigite (Rickard, 1969), or pyrrhotite (Barton and Skinner, 1967). Berner (1970) has proposed that this reaction occurs at low temperatures, although Roberts, Walker, and Buchanan (1969) thought that it was probably very slow at 25°C. Lebedev, Polushkina, and Sidorenko (1971) studied iron sulfide deposits on pipeline walls from the Cheleken deposit. They observed the paragenesis: X-ray amorphous FeS  $\rightarrow$  kansite  $\rightarrow$  melnikovite  $\rightarrow$  pyrite. Kansite is synonymous with mackinawite (Milton, 1966), and melnikovite is the Russian synonym for greigite. Berner (1967) had previously shown on thermodynamic grounds that greigite was a possible intermediary in the pyritization of mackinawite. This was confirmed experimentally by Sweeney and Kaplan (1973).

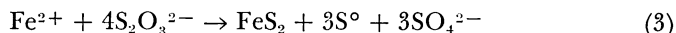
Hallberg (1972) proposed that pyrite might form through the dissociation of greigite.



The reaction had previously been shown to be thermodynamically feasible by Berner (1967).

2. *Homogeneous reactions in solution.*—Roberts, Walker, and Buchanan (1969) suggested that dissolved ferrous iron reacts directly with dissolved polysulfides to precipitate pyrite. Goldhaber and Kaplan (1974) consider it possible that this is a major pathway in sedimentary pyrite formation. They suggest that the reaction is pH dependent, since neither Roberts, Walker, and Buchanan (1969) nor Berner (1970) succeeded in forming pyrite by this reaction in alkaline solution.

Allen, Crenshaw, and Johnson (1912) produced pyrite by the reaction between dissolved ferrous iron and aqueous thiosulfate, according to the equation



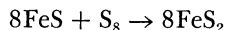
Since elemental sulfur is produced and thiosulfate thermally decomposes to  $\text{H}_2\text{S}$  and  $\text{SO}_4^{2-}$ , Berner (1970) suggested that this was actually a heterogeneous reaction.

3. *Heterogeneous reactions.*—Rickard (1969) and Skripchenko (1969) proposed that pyrite is formed by the reaction between ferrous sulfide

and aqueous polysulfide ions. The ferrous sulfide may be amorphous FeS, mackinawite, or greigite. Hallberg (1972) suggested that by this process greigite was an intermediate in pyrite formation from mackinawite.

Volkov and Ostroumov (1957) suggested that pyrite could result from the reaction between ferrous sulfide and aqueous thiosulfate. This is similar to Allen, Crenshaw, and Johnson's (1912) reaction (3), which proceeded at higher temperatures. Rickard (1969) did not obtain pyrite by this reaction at 25°C within a few weeks.

The published experimental work on pyrite formation reveals many inconsistencies. These are mainly concerned with the definition of the experimental reactants, products, and conditions. Further confusion arises from the use of basically thermodynamic approaches to draw mechanistic conclusions. For example, although elemental sulfur may be conveniently written as S° for equilibrium considerations, as in reaction (1) above, sulfur at low temperatures exists in the form of puckered, crown-shaped, eight-membered rings. Thus reactions such as (1) should be written



This is a 9th order reaction as written and is obviously mechanistically impossible.

Likewise, it has been proposed that sulfur species are critical to the pyrite formation mechanism which do not seem to exist in aqueous solutions. Berner (1962) has already commented disparagingly on the possibility of "disulphydryl iron" (Baas Becking, 1956) being an intermediary in the process. Similarly, the work of Schwarzenbach and Fischer (1960) showed that the disulfide ion, S<sub>2</sub><sup>2-</sup>, did not exist in aqueous solutions. This was subsequently confirmed by Teder (1969) and Pickering and Tobolsky (1972). The formation and reactions of the disulfide ion had previously been regarded as key processes in the formation of pyrite by direct precipitation from solution (Roberts, Walker, and Buchanan, 1969). Goldhaber and Kaplan (1974) have suggested that the precipitation process may proceed by reaction of dissolved ferrous iron with the disulfane, H<sub>2</sub>S<sub>2</sub>. However, Pickering and Tobolsky (1972) summarize recent work that indicates it is improbable that this species exists in aqueous solutions, although the possibility that it occurs in non-aqueous systems, such as crude oils, cannot be completely precluded.

Although the reaction between ferrous sulfide and elemental sulfur, in the absence of dissolved sulfide, produces pyrite rapidly at higher temperatures, it is too slow to be studied conveniently at 25°C and below (Roberts, Walker, and Buchanan, 1969). Moreover, natural sedimentary pyrite-forming systems are characterized by the presence of dissolved sulfide as well as ferrous sulfide and elemental sulfur (Berner, 1970). This paper therefore reports an attempt to determine the kinetics and mechanism of pyrite formation through reactions in low temperature systems containing aqueous sulfide, elemental sulfur, and ferrous sulfide at pH values between 7 and 8. It is believed that, because of the chemical simi-

larities between this experimental system and natural pyrite-forming environments, this is one of the major pathways for sedimentary pyrite formation.

#### METHODS

The method chosen for the study was essentially to follow the rate of formation of pyrite by analyses of the products of the reaction between FeS, sulfur, and aqueous sulfide at low temperatures and atmospheric pressure at various times. The major problem was in developing a rapid method that would give reproducible results. A long series of orientation experiments were performed for this reason.

The experimental runs were performed in 100 cc bottles into which a contact thermometer and a gas inlet and outlet system were inserted through a rubber top. This assembly was placed on a magnetic heater-stirrer. The temperature was controlled by modifying the circuitry of the heater-stirrer so that a contact thermometer could be inserted into the bottle to control the temperature during the run. Tests showed the temperature to be homogeneous throughout the bottle within  $\pm 0.5^\circ\text{C}$ , the limits of detection of the contact thermometer. Likewise no variation in temperature was observed during the runs.

Aqueous sulfide was supplied to the reaction mixture by continuous bubbling of special mixtures of  $\text{H}_2\text{S}$  and  $\text{N}_2$ , prepared for this experimentation by the AGA Laboratories in Stockholm. The sulfur used as a reactant was sublimed flowers of sulfur. It consists of almost uniform spheres of rhombic sulfur about  $20\ \mu$  in diameter. The spheres consist of agglomerates of sulfur crystals, and the texture could be described as framboidal, according to the definition of Rickard (1970).

Sedimentary ferrous sulfide consists mainly of X-ray amorphous FeS, mackinawite, or greigite, or mixtures of all three (Berner, 1970). The nature of amorphous FeS is unknown. Rickard (1969) and Sweeney and Kaplan (1973) suggested that it might be mainly poorly crystalline mackinawite, although Berner (1967) regarded it as a separate substance. Whatever its real nature, it seems to be the first formed iron sulfide in sediments. It apparently changes to crystalline mackinawite or greigite. The mackinawite-greigite transformation has been shown to be reversible (Horiuchi, 1971), and Hallberg (1972) suggested that mackinawite is not necessarily a precursor to greigite formation. However, the first-formed iron sulfide from the sulfidation of goethite (Rickard, 1974) was indistinguishable from the generally poor crystalline FeS known as amorphous FeS, which is non-magnetic and usually produces one or more mackinawite reflections on X-ray films. The ferrous sulfide used as a reactant in this experimentation was therefore amorphous FeS. This is equivalent to at least a major part of the first-formed ferrous sulfide of sediments.

FeS was produced by bubbling  $\text{H}_2\text{S}$  gas through a solution of ferrous sulfate for 18 hrs at  $40^\circ\text{C}$  in buffered solutions at  $\text{pH} = 7$  to 8. The product was examined wet, in Lindemann glass capillaries in an 11 cm Debye-Scherrer X-ray crystallographic camera. The X-ray analysis showed it to

be basically poorly crystalline FeS with a few very broad reflections indicative of mackinawite. The material was identical to that first described by Berner (1964) from a similar reaction and subsequently produced by other investigators. The FeS was examined in a scanning electron microscope. It consisted of small roughly spherical particles about  $0.02 \mu$  in mean diameter but varying up to larger sizes. Attempts had been made previously to measure the surface area by the BET method and in a Coulter-counter. These methods had indicated that most of the particles were less than  $0.5\mu$  in diameter, but that particles up to  $10\mu$  in diameter were present in very small quantities. These larger particles were assumed to be agglomerates of the smaller ones. Because of the lack of success of attempted surface area measurements with the BET method and Coulter-counter, the FeS and elemental sulfur surface areas were estimated from the microscopic measurements.

The FeS was produced in the same bottles used for the experimental runs. Where required, pH was adjusted with NaOH. The solutions were made up to volume by adding buffer solutions at the required pH. This was checked electrometrically before and after the runs. The experiments were started by adding the required amount of the elemental sulfur reactant, the solutions having reached the required temperature and sulfide concentration previously. Sampling was performed by means of 1 cc disposable syringes.

During the trial runs it was found that sampling through the rubber tops of the bottles gave divergent results, because of inhomogeneities in particle distribution in the vessels. For sampling, therefore, the rubber top with its assembly of contact thermometer and gas inlet and outlet was removed, and a self-sealing rubber top substituted. The bottle was shaken, and the samples taken through the top with the bottle inverted.

Two samples were taken from each bottle at each time interval, and each run was made with two reaction vessels. The samples were weighed and boiled immediately in concentrated HCl and in mixtures of concentrated HCl and  $\text{HNO}_3$ . These solutions were analyzed by the 2-2' dipyridyl method for total and HCl-soluble iron. For each experimental run at each time interval, two sets of analyses for each of two concurrent reactions were obtained. By this means, reproducibility of the results was confirmed.

Samples were taken initially at 15 min intervals. This was the minimum amount of time that allowed the preparation of the solutions for analysis, even with help of an assistant. Toward the end of the reaction the time intervals became longer. All the analyses were performed in quadruplicate, in order to check both the preparative method and the spectrophotometer. In effect, therefore, the final analytical result for any particular time during any run was the mean of 16 analyses. This exaggerated care was necessary to be certain of the results. Orientation studies had previously revealed a variety of possible errors in the experimentation.

The relative insolubility of pyrite in concentrated HCl has been used widely as a means of analysis for the compound when it is mixed with

other iron sulfides (Berner, 1970). Several of the products of this experimentation were in fact checked by X-ray analysis in order to determine if the method was valid and if the analyzed material was pyrite. As far as could be judged, the analytical method did reveal the quantity of pyrite present.

The kinetics were examined using initial rate theory which is described in the companion work on the kinetics and mechanism of the sulfidation of goethite (Rickard, 1974). The possibility of the kinetics being complicated by transport effects were reduced by keeping the stirring rate in the reaction vessel high and constant.

#### RESULTS

*Reaction order with respect to partial pressure of H<sub>2</sub>S, total dissolved sulfide activity, the surface areas of FeS and sulfur, and the hydrogen ion activity.*—The reaction order with respect to the individual reactants was calculated by means of initial rate theory. The results are summarized in table 1 and figures 1, 2, 3, 4, and 5.

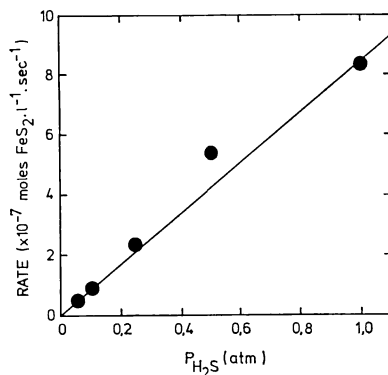


Fig. 1. Initial rate of pyrite formation versus H<sub>2</sub>S partial pressure at 40°C. The linear plot through the origin demonstrates the first order rate dependence on P<sub>H<sub>2</sub>S</sub>.

The reaction rate is first order with respect both to the partial pressure of H<sub>2</sub>S and the sulfur surface area but second order with respect to the surface area of FeS. In the pH range 7 to 8 the rate is dependent on {H<sup>+</sup>}<sup>x</sup> where x is very near zero.

The rate equation is therefore

$$d(FeS_2)/dt = k_1 (FeS)^2 (S)_{H_2S} \quad (4)$$

where  $k_1$  is the apparent rate constant, (FeS) is the FeS surface area, (S) is the sulfur surface area, and P<sub>H<sub>2</sub>S</sub> is the partial pressure of hydrogen sulfide. The effect of hydrogen ion activity is negligible since where

$$\begin{aligned} x &\rightarrow 0 \\ \{H^+\}^x &\rightarrow 1 \end{aligned}$$

TABLE 1

Experimental conditions and rate constants,  $k_1$  and  $k_2$ , for runs used in determining the reaction order with respect to  $P_{H_2S}$ , FeS and S° surface areas, total dissolved sulfide activity, hydrogen ion activity, and apparent activation energy

Run	Initial rate moles liter <sup>-1</sup> sec <sup>-1</sup>	$P_{H_2S}$ atm	pH	$\{\Sigma S^{2-}\}$	Initial FeS surface area cm <sup>2</sup>	Initial sulfur surface area cm <sup>2</sup>	T °K	$k_1$ cm <sup>3</sup> atm moles <sup>-1</sup> liter <sup>-1</sup> sec <sup>-1</sup>	$k_2$ cm <sup>6</sup> moles <sup>-1</sup> liter <sup>-1</sup> sec <sup>-1</sup>
401	$8.3 \times 10^{-7}$	1.00	7.0	$2 \times 10^{-1}$	$1.6 \times 10^5$	$1.4 \times 10^8$	313	$2.2 \times 10^{-20}$	$1.1 \times 10^{-12}$
402	$4.8 \times 10^{-7}$	0.50	7.0	$1 \times 10^{-1}$	$1.6 \times 10^5$	$1.4 \times 10^8$	313	$2.5 \times 10^{-20}$	$1.3 \times 10^{-12}$
403	$2.3 \times 10^{-7}$	0.25	7.0	$5 \times 10^{-2}$	$1.6 \times 10^5$	$1.4 \times 10^8$	313	$2.5 \times 10^{-20}$	$1.3 \times 10^{-12}$
404	$9.5 \times 10^{-8}$	0.10	7.0	$2 \times 10^{-2}$	$1.6 \times 10^5$	$1.4 \times 10^8$	313	$2.6 \times 10^{-20}$	$1.3 \times 10^{-12}$
405	$4.9 \times 10^{-8}$	0.05	7.0	$1 \times 10^{-2}$	$1.6 \times 10^5$	$1.4 \times 10^8$	313	$2.5 \times 10^{-20}$	$1.3 \times 10^{-12}$
502	$4.8 \times 10^{-7}$	1.00	7.0	$2 \times 10^{-1}$	$1.6 \times 10^5$	$7.0 \times 10^2$	313	$2.0 \times 10^{-20}$	$1.0 \times 10^{-12}$
503	$1.9 \times 10^{-7}$	1.00	7.0	$2 \times 10^{-1}$	$1.6 \times 10^5$	$3.5 \times 10^2$	313	$1.4 \times 10^{-20}$	$0.7 \times 10^{-12}$
504	$5.4 \times 10^{-8}$	1.00	7.0	$2 \times 10^{-1}$	$1.6 \times 10^5$	$1.4 \times 10^2$	313	$2.2 \times 10^{-20}$	$1.1 \times 10^{-12}$
602	$1.5 \times 10^{-7}$	1.00	7.0	$2 \times 10^{-1}$	$8.2 \times 10^4$	$1.4 \times 10^8$	313	$1.6 \times 10^{-20}$	$0.8 \times 10^{-12}$
603	$4.8 \times 10^{-8}$	1.00	7.0	$2 \times 10^{-1}$	$4.1 \times 10^4$	$1.4 \times 10^8$	313	$2.0 \times 10^{-20}$	$1.0 \times 10^{-12}$
604	$2.0 \times 10^{-8}$	1.00	7.0	$2 \times 10^{-1}$	$2.5 \times 10^5$	$1.4 \times 10^8$	313	$2.4 \times 10^{-20}$	$1.2 \times 10^{-12}$
702	$7.0 \times 10^{-7}$	1.00	7.5	$5 \times 10^{-1}$	$1.6 \times 10^5$	$1.4 \times 10^8$	313	$1.8 \times 10^{-20}$	$1.4 \times 10^{-12}$
703	$6.4 \times 10^{-7}$	1.00	8.0	$11 \times 10^{-1}$	$1.6 \times 10^5$	$1.4 \times 10^8$	313	$1.7 \times 10^{-20}$	$1.5 \times 10^{-12}$
802	$4.5 \times 10^{-8}$	1.00	7.0	$2 \times 10^{-1}$	$1.6 \times 10^5$	$1.4 \times 10^8$	323	$1.2 \times 10^{-19}$	$0.6 \times 10^{-11}$
803	$4.2 \times 10^{-7}$	1.00	7.0	$2 \times 10^{-1}$	$1.6 \times 10^5$	$1.4 \times 10^8$	305	$1.1 \times 10^{-20}$	$0.6 \times 10^{-12}$
804	$1.2 \times 10^{-7}$	1.00	7.0	$2 \times 10^{-1}$	$1.6 \times 10^5$	$1.4 \times 10^8$	293	$2.9 \times 10^{-21}$	$1.5 \times 10^{-13}$

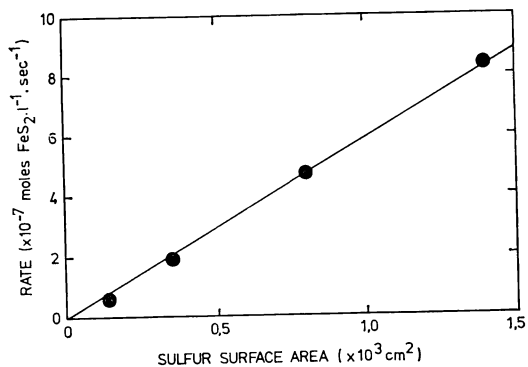
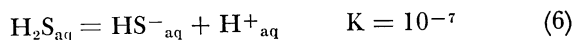


Fig. 2. Initial rate versus initial sulfur surface area at 40°C. A surface area of  $1.4 \times 10^3 \text{ cm}^2$  is equivalent to 1 g sulfur. The linear plot through the origin demonstrates the first order rate dependence on sulfur surface area.

The rate equation can be written in terms of dissolved sulfide species. In this pH range the equations describing sulfide equilibria are



and



(from standard references).

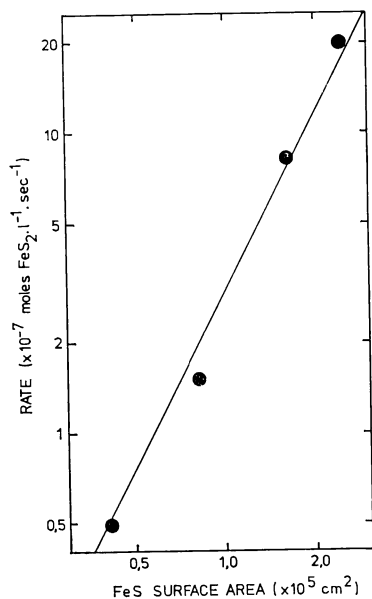


Fig. 3. Log-log plot of initial rate versus initial FeS surface area at 40°C. A surface area of  $1.6 \times 10^5 \text{ cm}^2$  is equivalent to 0.36 g FeS. The line is drawn with a slope of 2, demonstrating the second order rate dependence on FeS surface area.



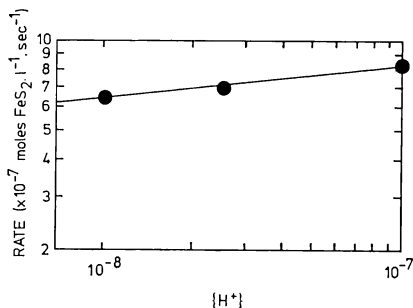


Fig. 4. Log-log of initial rate versus  $\{H^+\}$  for pH 7 to 8 at 40°C. The line is drawn with a slope of 0.1, indicating the virtual independence of the rate on pH when  $P_{H_2S}$  is taken as a rate-determining parameter.

Thus the sum of dissolved sulfide activities

$$\{\Sigma S^{2-}\} = H_2S + HS^- = P_{H_2S} \left( 10^{-1} + \frac{10^{-8}}{H^+} \right) \quad (7)$$

Since the rate is not entirely independent of  $\{H^+\}$ ,  $\{H_2S\}$ , or  $\{HS^-\}$   $\{H^+\}$  cannot be substituted for  $P_{H_2S}$  in the rate equation. The observed results are consistent with the rate being dependent on  $\{\Sigma S^{2-}\}\{H^+\}$ , since this function can be substituted for  $P_{H_2S} \{H^+\}^x$ , where  $x$  varies between 0 and 0.1 at pH = 7 to 8.

The ionic strength of the medium used in these experimental runs was about 0.2. Since  $\{\Sigma S^{2-}\}$  varied between 0.2 (at pH = 7) and 1.1 (at pH = 8) with a  $H_2S$  partial pressure of 1 atm, the activity coefficients of  $H_2S$  and  $HS^-$  will be divergent from unity and vary over that pH range. Thus the sum of the dissolved sulfide concentrations cannot be used instead of the sum of the dissolved sulfide activities.

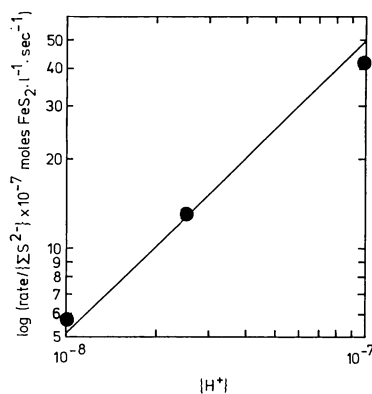


Fig. 5. Log-log plot of initial rate divided by the total dissolved sulfide activity  $\{\Sigma S^{2-}\}$  versus  $\{H^+\}$  for pH 7 to 8 at 40°C. The line is drawn with a slope of 1.0, demonstrating the first order dependence of the rate on  $\{H^+\}$ , when  $\{\Sigma S^{2-}\}$  is taken as a rate-determining parameter.

A plot of log rate  $\{S^{2-}\}$  against log  $\{H^+\}$  (fig. 5) shows that the rate is first order with respect to  $\{H^+\}$  if  $\{\Sigma S^{2-}\}$  is considered instead of  $P_{H_2S}$ . In terms of dissolved sulfide species, the rate equation becomes

$$d(FeS_2)/dt = k_2 (FeS)^2 (S)\{\Sigma S^{2-}\} \{H^+\} \quad (8)$$

where  $k_2$  is the apparent rate constant,  $\{\Sigma S^{2-}\}$  is the sum of dissolved sulfide activities, and  $\{H^+\}$  is the hydrogen ion activity.

The order-determining experimental series were all performed at a temperature of 40°C. This gave convenient rates at a temperature low enough that possible high temperature reactions would not interfere. It was possible to vary the  $H_2S$  partial pressure from 1 to as low as 0.05 atm and still obtain conveniently fast rates at 40°C. The sulfur used in the runs could be varied between 0.1 and 1 g, equivalent to a surface area variation of between 0.14 and  $1.4 \times 10^3$  cm<sup>2</sup>. However, the second order dependence on FeS surface area resulted in the rate becoming unmeasurably small below  $0.4 \times 10^5$  cm<sup>2</sup> and too rapid above  $2.46 \times 10^5$  cm<sup>2</sup>, a variation of rather less than an order of magnitude.

*Apparent rate constants for the reaction at 40°C.*—The experimental data indicate that the rate of pyrite formation from the reaction between elemental sulfur, dissolved sulfide, and FeS in aqueous solutions can be described by the equations

$$d(FeS_2)/dt = k_1 (FeS)^2 (S)P_{H_2S} \quad (4)$$

or

$$d(FeS_2)/dt = k_2 (FeS)^2 (S)\{\Sigma S^{2-}\} \{H^+\} \quad (8)$$

Values for  $k_1$  and  $k_2$  are listed for various runs in table I. The constant  $k_1$  varies between 1.4 and  $2.6 \times 10^{-20}$  cm<sup>6</sup> atm moles<sup>-1</sup> liter<sup>-1</sup> sec<sup>-1</sup> with a mean at  $2 \times 10^{-20}$ ;  $k_2$  varies between 0.7 and  $1.5 \times 10^{-12}$  cm<sup>6</sup> moles<sup>-1</sup> liter<sup>-1</sup> sec<sup>-1</sup> with a mean at  $1 \times 10^{-12}$ .

*Effect of temperature on the reaction rate.*—A series of runs were made between 20° and 50°C in order to determine the effect of temperature on the rate constant. The rate constant is related to temperature by the Arrhenius equation

$$k = Ae^{-E/RT} \quad (9)$$

where A is the frequency factor, E is the apparent activation energy or critical increment of energy for a heterogeneous reaction, R is the universal gas constant, and T is the absolute temperature. Plots of  $1/T$  against  $\log_{10}k_1$  and  $\log_{10}k_2$  are shown in figure 6. The apparent activation energy computed graphically from these data is about 17 kcal mole<sup>-1</sup>.

#### DISCUSSION

The activation energy of diffusion in solution at 25°C is usually between about 2.8 and 6.5 kcal/mole<sup>-1</sup>, depending on the solute and the solvent (for example, Burkin, 1966). Thus the apparent activation energy for a transport controlled heterogeneous reaction should be within the

same range or about 4 kcal/mole<sup>-1</sup>. The observed high apparent activation energy for the formation of pyrite demonstrates that the reaction is chemically, rather than transport, controlled under the experimental conditions used.

The reaction rate is directly proportional to the partial pressure of H<sub>2</sub>S, indicating that the presence of dissolved sulfide species is a major factor in the reaction. In fact, the rate equations demonstrate that the reactions would be very slow at these temperatures without the presence of sulfide species. This means that the direct reaction between FeS and sulfur, a process known to occur at elevated temperatures, is negligibly slow at the temperature of this experimentation.

However, sulfur is critical to the rate of reaction. Hartler, Libert, and Teder (1967) studied aspects of the rate of sulfur dissolution in aqueous sodium sulfide. They found that the rate of dissolution is approximately proportional to the specific surface of the sulfur. When polysulfide ions are not allowed to form, the reaction is close to second order with respect to total dissolved sulfide concentration. However, when polysulfide ions are formed (as in the normal situation) the reaction is first order with respect to total dissolved sulfide concentration. At the high hydroxide concentrations (0.1-1.0 m) of their experimentation, the rate was virtually independent of hydroxide concentration, being only slightly increased with increased hydroxide.

The first order dependence of the rate of pyrite formation on sulfur surface area and partial pressure of H<sub>2</sub>S found during this experimentation is thus consistent with the results of Hartler, Libert, and Teder (1967) for sulfur dissolution in sulfide solutions. However, the rate of the pyrite-forming reaction is also dependent on the pH (at constant dissolved total sulfide activities) and on the surface area of the initial ferrous sulfide.

The second order dependence on ferrous sulfide surface area is unusual. It means that if the surface area doubles the rate increases four times and indicates that ferrous sulfide is involved in more than one rate-affecting reaction.

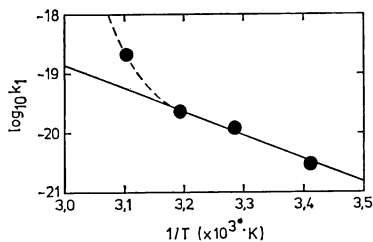


Fig. 6. Arrhenius plot of the reciprocal absolute temperature ( $1/T$ ) versus the natural logarithm of the apparent rate constant. The divergence of the point at  $1/T = 3.1$  is believed to be real and to reflect the increasing dominance of the solid-solid reaction at higher temperatures.

The reaction is first order with respect to  $\{H^+\}$  at constant  $\{\Sigma S^{2-}\}$ . This could be interpreted to indicate that dissolution of FeS is a rate-controlling step.

Dissolution of FeS would also result in the production of more dissolved sulfide. The second order dependence on FeS surface area may thus be explained with FeS dissolution as a rate-controlling step, which not only provides aqueous  $Fe^{2+}$  for further reaction but also produces more dissolved sulfide. Since the reaction rate is first order with respect to total dissolved sulfide activity, increased total dissolved sulfide increases the rate. In this interpretation, the second order dependence on FeS surface area is apparent and not real. The effect of variations of FeS surface area was examined in experimental runs, where it was assumed that all the other parameters, including total dissolved sulfide activity, were constant. Since dissolution of FeS produced more dissolved sulfide, this was not the actual case.

The proposition that FeS dissolution is a rate-controlling step provides a simple explanation for the observed kinetics, particularly the unusual second order dependence on FeS surface area. Although there are other possible explanations that could account for the rate data, these would require that FeS reacts directly in a solid form or that the dissolution rate of FeS is relatively fast and not rate-controlling.

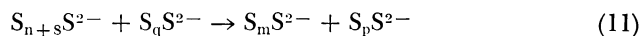
The reaction of FeS in a solid form to produce pyrite directly is not entirely consistent with the experimental observations. In particular, microscopic analyses demonstrated that the pyrite formed had a tendency to be associated closely with the sulfur rather than the FeS phase in the mixture. This feature has previously been noted by Berner (1970). Furthermore, reaction between solid FeS and a dissolved sulfur species to form pyrite directly would probably give rise to a diffusion-controlled reaction, which is not consistent with the computed apparent activation energy for the overall process.

The observed kinetics indicate that the mechanism of pyrite formation through the reaction between ferrous sulfide, sulfur, and dissolved sulfide involves dissolution of ferrous sulfide and sulfur and the subsequent reaction of dissolved iron and sulfur species to form pyrite.

According to Hartler, Libert, and Teder (1967) the dissolution of sulfur in sulfide solutions results in the formation of a mixture of different polysulfide ions. The reaction can be described by the overall equation



and



They suggest that the presence of polysulfide ions accelerates the breaking of the initially formed long open sulfur chains (11) so that ring-opening (10) or  $S_n S^{2-}$  diffusion becomes rate-determining.

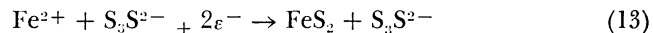
The nature of the polysulfide ions in the solution has been discussed by Schwarzenbach and Fischer (1960), Teder (1969), and Pickering and

Tobolsky (1972). These authors all report that the disulfide ion,  $SS^{2-}$ , does not exist in aqueous solution. Teder (1969) criticizes earlier work claiming the existence of this ion and demonstrates that the previous suggestion that larger ions than  $S_4S^{2-}$  do not exist in aqueous solution is also based on invalid assumptions. The above-mentioned authors further note that no evidence could be found for the presence of protonated polysulfide ions in aqueous solutions.

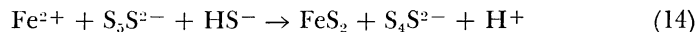
Teder (1971) provides equilibrium constants for the various possible polysulfide species at 25°C at 1 atm pressure. Thus the simple aqueous reaction



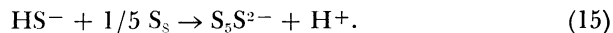
seems improbable mechanistically. The reaction between dissolved ferrous iron and larger polysulfide ions to form pyrite should involve reduction of the sulfur species, for example



It seems probable that in such a reaction the reducing agent would be a dissolved sulfide species. Thus



Berner (personal commun.) points out that this reaction is first order with respect to  $S_5S^{2-}$  since the theoretical activity product  $\{Fe^{2+}\}\{S^{2-}\}$  is constant in equilibrium with FeS. The first order dependence on  $S_5S^{2-}$  implies a first order dependence on  $\Sigma S^{2-}$  since (overall)



The measurements were made in 3 molar concentrations of an inert electrolyte and are therefore not applicable to the present experimentation. However, the data show that decreased alkalinity increases the mean size of the polysulfide ions in solution. Under the conditions used in the present experiments,  $S_4S^{2-}$  and  $S_5S^{2-}$  should be the most abundant species.

The rate of reaction is highly temperature dependent. At room temperature (that is around 20°C) the rate is eight times slower than at 40°C. This may explain many of the inconsistencies observed in the attempted experimental synthesis of pyrite in aqueous solution at room temperatures. Reference to figure 6 shows that the rate at 50°C is higher than would be expected from calculations of the apparent activation energy. It is well known that at more elevated temperatures the solid-solid reaction between sulfur and FeS to form pyrite occurs rapidly kinetically. This would mean that at higher temperatures pyrite might be formed faster than would be predicted from the heterogeneous reaction alone, due to the additional production of pyrite by the solid state reaction.

As the solid-solid reaction becomes more important with rising temperature, polysulfides become more unstable in solution. It is possible,

therefore, that the solid-solid reaction could be the dominant pathway for pyrite formation at temperatures approaching 100°C.

#### GEOLOGICAL IMPLICATIONS

Sweeney and Kaplan (1973) have demonstrated a pyrite-forming reaction sequence that involves the production of greigite,  $\text{Fe}_3\text{S}_4$ , as an intermediate. In this reaction sequence sulfurization of an initial ferrous sulfide, similar to mackinawite, in the presence of atmospheric oxygen, produces greigite and subsequently pyrite. The pyrite has a framboidal texture.

The reaction sequence studied in the present investigation did not involve atmospheric oxygen, and framboidal pyrite textures were not produced. Furthermore, there is no evidence that greigite formed during the reaction. Goldhaber and Kaplan (1974) suggest that since pyrite occurs as both framboids and single crystals in sediments, two distinct formation pathways exist. If this is the case, the present study is concerned with the formation of non-framboidal pyrite, a process that does not seem to involve greigite formation.

Some idea about the relative importance of these two processes could be obtained by measuring the percentage of total sediment pyrite occurring as framboids. In an unpublished study of pyrite from deep-sea and near shore sediments, the author has found that this percentage is highly variable, ranging from less than 1 to as much as 80 percent. The reaction examined in this experimentation is thus equivalent to one of the major pyrite-forming processes in sediments.

The rate data indicate that this chemically-controlled reaction is fast. For example, at 5°C the rate constant  $k_1 = 5 \times 10^{-22} \text{ cm}^6 \text{ atm moles}^{-1} \text{ liter}^{-1} \text{ sec}^{-1}$  or about two magnitudes lower than at 40°C. In a sediment containing 1 percent FeS and 0.01 percent sulfur with similar particle sizes to those used in this experimentation, at  $P_{\text{H}_2\text{S}} = 10^{-3}$ , the rate of the chemically-controlled reaction would be about 2 mg  $\text{FeS}_2 \text{ cm}^{-3} \text{ yr}^{-1}$ . Taking into account the low sedimentation rates usually encountered in pyrite-forming sedimentary environments, this figure is very high.

The formation of pyrite in sediments involves a series of processes, one of the main ones being the sulfidation of goethite forming FeS and sulfur, followed by the reaction investigated in this study, between FeS, sulfur, and sulfide. Reference to the companion work on the sulfidation of goethite (Rickard, 1974) demonstrates that the rate of goethite sulfidation is even faster than the rate of pyrite formation. In a chemically-controlled reaction sequence, therefore, the rate-determining step in the formation of pyrite is the production of pyrite from FeS, rather than the initial formation of the FeS from goethite.

In both studies, transport effects were nullified by keeping the agitation rate very high and constant. Qualitative investigations of this reaction sequence demonstrate that the reaction rate is considerably reduced and becomes transport controlled when the experimental systems are not agitated. In the actual sedimentary system, the agitation rate is normally

extremely low and thus the reaction should be transport-controlled. The maximum possible bacteriogenic sulfide flux is in fact lower than the rate of utilization of sulfide in both the sulfidation of goethite and formation of pyrite (Rickard, 1973). Thus the models for sedimentary pyrite formation developed by Berner (1971) and Rickard (1973), based on bacteriogenic sulfide production and diffusion as rate-limiting parameters, are consistent with the conclusions from these experimental studies.

#### CONCLUSIONS

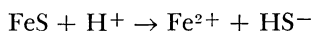
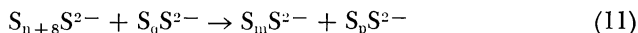
The rate of pyrite formation through the reaction between ferrous sulfide, elemental sulfur, and dissolved sulfide in aqueous solution at temperatures up to 50°C can be described by the equations

$$\text{Rate} = k_1 (\text{FeS})^2 (\text{S}) P_{\text{H}_2\text{S}} \quad (4)$$

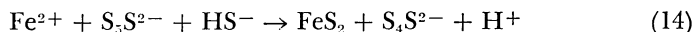
or

$$\text{Rate} = k_2 (\text{FeS})^2 (\text{S}) \{\Sigma \text{S}^{2-}\} \{\text{H}^+\} \quad (8)$$

The rate constant for equation (13),  $k_1 = 2 \times 10^{-20} \text{ cm}^6 \text{ atm moles}^{-1} \text{ liter}^{-1} \text{ sec}^{-1}$  and for equation (14),  $k_2 = 1 \times 10^{-12} \text{ cm}^6 \text{ moles}^{-1} \text{ liter}^{-1} \text{ sec}^{-1}$ , where the rate is in moles  $\text{FeS}_2 \text{ liter}^{-1} \text{ sec}^{-1}$ , the ferrous sulfide surface area (FeS), and the sulfur surface area ( $\text{S}^\circ$ ), are in  $\text{cm}^2$ , the partial pressure of  $\text{H}_2\text{S}$ ,  $P_{\text{H}_2\text{S}}$ , is in atm, and the sum of the dissolved sulfide activities  $\{\Sigma \text{S}^{2-}\}$  and hydrogen ions  $\{\text{H}^+\}$  are dimensionless. The apparent activation energy for the reaction is about 17 kcal/mole<sup>-1</sup>. The observed rate equation is consistent with a mechanism involving the dissolution of both  $\text{S}^\circ$  and FeS:



Pyrite is then produced through the direct solution reaction between dissolved ferrous and polysulfide ions, for example:



This interpretation explains all the observed features of the reaction, including the first order rate dependence on ( $\text{S}^\circ$ ),  $\{\Sigma \text{S}^{2-}\}$ , and  $\{\text{H}^+\}$  and the apparent second order rate dependence on (FeS). No detailed information about reaction (14) is available from the rate data. However, it agrees with present knowledge about the nature of dissolved polysulfide ions in solution and the large apparent activation energy for the reaction.

No evidence for the formation of iron sulfide phases other than pyrite and "ferrous sulfide" was obtained for this reaction sequence. It seems improbable that intermediate phases such as greigite,  $\text{Fe}_3\text{S}_4$ , would be formed.

The product of the reaction is non-framboidal pyrite. It has been shown that framboidal pyrite is produced by a different pathway, involving atmospheric oxygen (or ferric iron) and greigite (Sweeney and Kaplan,

1973). It is thus probable that pyrite formation in sediments involves at least two reaction pathways, giving rise to different pyrite textures. The relative importance of these two processes varies considerably in different sedimentary environments.

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