

KINETICS OF THE SULFIDE-TO-SULFATE REACTION

A. H. Morth* and Edwin E. Smith

Engineering Experiment Station
The Ohio State University
Columbus, Ohio

A broad-based study of the sulfide-to-sulfate reaction mechanism in relation to the production of acid mine drainage is being made at The Ohio State University. This report concerns one aspect of the program; the attempt to define kinetics of the rate-determining mechanism in a chemical (rather than biological) regime.

This phase of the study was prompted by the numerous and conflicting reports on the quantitative relationship of variables on oxidation rate of pyrite, and to confirm or refute some of the beliefs that have been taken as self-evident or intuitively assumed as fact.

Two obvious items, acknowledged to influence rate of pyrite oxidation, are oxygen and water. In the absence of water and oxygen (or other effective oxidizing agent) the rate is (comparatively) zero. The role of water in the reaction, and the influence of oxygen concentration on oxidation rate have never been satisfactorily explained.

Reports of early laboratory studies (2,4,7,8,9) noted the effect of water and oxygen concentration on oxidation rates. The rate of oxidation was reported to be essentially independent of oxygen concentration (4), to be first order in respect to oxygen concentration (8); and the rate in air to be one-half that in oxygen (7).

More recent work in this laboratory (1,6) indicated that vapor phase oxidation rates varied directly with partial pressure of water and that the rate in air was approximately 35% of that in pure oxygen.

In order to reconcile these differences, an attempt was made to determine the nature of the rate-limiting mechanism and to explain the role of oxygen and water in the kinetics of pyrite oxidation.

EXPERIMENTAL

In addition to standard Warburg equipment and techniques, equipment shown in Figure 1 were used. The apparatus shown in 1A and 1B are similar in concept; 1A recirculating the vapor phase, and 1B the liquid phase, through a bed of pyrite. In each case, oxidation of pyrite was monitored by measuring the quantity of make-up oxygen required to maintain a constant pressure in the vapor space.

This type of equipment was used for several reasons: 1) to establish influence of diffusional resistances and desorption of reaction products on reaction rates, 2) to enable control of concentration of various components in the recirculating fluid, and 3) to permit periodic sampling of streams to follow build-up of reaction products.

*Present address: Monsanto Company, Indiana Orchard, Massachusetts.

Figure 1C is a modified differential Warburg unit used to determine oxidation over comparatively wide pressure ranges. It consists of two identical flasks on either arm of a manometer. The same quantity of water was added to each flask, then pyrite placed in the right-hand flask. A small amount of manometer fluid was added to the top of the mercury so that when the level was raised, the fluid filled the arms of the manometer to the desired height. To fill the system with vapor, the mercury column was lowered so that the water level was at the right-hand stopcock, the system evacuated, and then the vapor admitted through the vacuum line. The left stopcock was then closed and the mercury leveling bottle raised or lowered depending on the pressure in the system so that the water level rose half-way in the manometer. The entire assembly was agitated during liquid phase runs.

The pyrite sample used for all runs reported in this paper was a "sulfur ball" material collected from the Middle Kittanning No. 6 coal seam in Vinton County, Ohio. Several stages of float-and-sink separation on the crushed coal were used to obtain an 85% FeS_2 material. This was then carefully screened and the 70 to 100 mesh fraction used as the sample.

RESULTS

Data on liquid phase oxidation showed that flow rate of fluid through the bed had no effect on rate of oxidation. Also, the rate remained constant for the duration of the runs (one to two weeks).

Two runs were made with a column of "Amberlite" IRA-120 in series with the reactor to remove all iron from the circulating fluid. With "zero" iron in solution, the rate remained the same.

The relation between increase of iron in solution and oxygen absorbed was frequently checked and found to be approximately 3.5 moles oxygen consumed per mole of soluble iron produced. The relative ferrous-ferric ion concentration was found to vary between 85% and 95% ferrous for runs listed in Table 1.

A series of liquid phase runs were made in which oxygen concentration in the vapor space and temperature were varied. The results of these runs, together with those obtained with the ion-exchange resin in the system, are listed in Table 1.

A similar study was made using the vapor phase apparatus. As in the liquid phase runs, flow rates had no effect on rates. The rate of oxygen absorption remained constant throughout the run period which varied from several days to two weeks. Temperature and humidity of the recycled vapor were varied. The results are listed in Table 2.

Since the other oxidation units were not capable of operating over wide pressure ranges, the equipment shown in Figure 1C was constructed. Runs were made at different oxygen pressures and vapor compositions to study the effect of dissolved oxygen and nitrogen concentrations on oxidation rate. These data are shown in Table 3.

All rate data in Tables 1 and 3 were recalculated to the same reference--100 microgram oxygen per hour per gram of pyrite at 25°C and 76 cm. Hg. oxygen pressure. This was necessary in order to get consistent results from one column packing or washing to the next. The principle problem was the tendency of the sulfur ball particles to break-down during agitation. For one continuous series of runs, the change from run to run was small. But after washing or repacking, a reference run was necessary to obtain comparative rates.

INTERPRETATION OF EXPERIMENTAL RESULTS

Based on the observation that 1) flow rates of the recirculated fluid had no effect on oxygen absorption rates, 2) rates were constant throughout the test period, and 3) removal of iron from solution did not affect rates, it seems evident that reaction rates in the recirculating-type equipment, for the reaction periods used, are not influenced by diffusional resistances nor desorption of oxidation products. This conclusion is substantiated by the value of 14 Kcal. per gram-mole for the activation energy determined from an Arrhenius plot of data presented in Table 1. This value for activation energy is typical of a reaction-controlled mechanism, rather than a physically-controlled rate limiting step.

Role of Water

In studying the role of water, Kim (6) made a series of vapor phase oxidations using the equipment in Figure 1A. Over the limited temperature range studied, he observed that the rate varied linearly with absolute humidity (or partial pressure) of water in the vapor phase, apparently indicating that the rate of oxidation was first order in respect to water and suggesting that water is a reactant.

When this study was extended to cover a wider temperature range, a distinct temperature dependence was observed, as shown in Figure 2. It was also noted that in the temperature range covered by Kim, both the oxidation rate and partial pressure of water vapor (over a saturated salt solution) doubled with a 10°C temperature rise. In other words, the influence on rate observed by Kim may be interpreted as a change caused by temperature at a constant relative humidity. The runs plotted in Figure 2 are replotted as Rate vs. % Relative Humidity in Figure 3. Note that at a given value of relative humidity, the rate nearly doubles with each 10°C increase in temperature, the same as observed in liquid phase oxidation. The curves in Figure 3 are typical Type III adsorption isotherms (according to Brunauer (3), et al.) suggesting that rate may be dependent on quantity of water adsorbed.

When the isotherms of Figure 3 are extrapolated to 100% Relative Humidity and the rates thus obtained plotted together with those from the liquid phase runs (Figure 4), the similarity of temperature effect in both vapor and liquid phase oxidations is apparent.

While it is not possible to describe the role of water in all phases of the reaction, at least for the rate-limiting reaction, water is involved as a reaction medium rather than a reactant. If water were one of the reactants, the rate of reaction would level-off as the partial pressure of water approached saturation pressure (i.e., as water is no longer the limiting reactant). Instead the rate of increase is greater as water concentration nears saturation as seen in Figure 3.

Even in vapor phase oxidation, rates remain constant over long periods of time. This can be explained by products "salting-out" of a condensed liquid phase as the content of dissolved reaction products reaches saturation. This process was qualitatively observed by Birle (1) who presented photomicrographs showing the build-up of salts around the edges of pores or etch marks which contained water.

It is possible that the basic function of water is to provide a means by which the oxidation products are desorbed (dissolved) from the pyrite surface. Normal oxidation, which may occur in the dry state on clean surfaces, could be stopped by build-up of products on the "reactive sites" of pyrite. If the isotherms of Figure 3 are coincident with adsorption isotherms for water, then the rate would be directly related to the quantity of water absorbed. This relationship is now being examined.

Role of Oxygen

Possible kinetic mechanisms by which oxygen enters the rate-limiting reaction are suggested by the data presented in Table 3.

These data give a quantitative relation between oxidation rate and oxygen concentration, and indicate that the concentration of inert gas (nitrogen) affects oxidation rate.

Using procedures and modifications suggested by Hougen and Watson and others (5, 10) rate equations for different assumed mechanisms can be derived. For the type of reaction under study, simplifications can be made. It has been shown that neither desorption of products nor diffusional resistances influence the rate of reaction under the laboratory conditions used in this study. Therefore, the experimental rates can be considered "initial rates" and derivations simplified by eliminating consideration of both product composition and concentration.

It is possible to postulate a mechanism that results in a rate equation which correlates experimental data within limits of experimental error.

This proposed mechanism involves the dissociation of oxygen when adsorbed on "reactive sites" of pyrite (Reaction 2). Simultaneously, inert gas (nitrogen) can be adsorbed (Reaction 1) and compete for these "reactive sites." The rate-limiting step is the decomposition of the activated complex formed by dissociated oxygen (Reaction 3).

This mechanism can be expressed by the following reactions:



where: I = inert gas (nitrogen)

A_2 = oxygen

s = reactive site of FeS_2

As^* = activated complex of dissociated oxygen and reactive site

P = product (or products) of reaction

The rates for the individual reaction are:

$$r_1 = k_{f1} C_I (1 - \theta_A - \theta_I) - k_{r1} \theta_I \quad (4)$$

$$r_2 = k_{f2} C_A (1 - \theta_A - \theta_I)^2 - k_{r2} \theta_A^2 \quad (5)$$

$$r_3 = k_3 \theta_A^2 \quad (6)$$

where: θ_A and θ_I = fraction of total reactive sites occupied by oxygen and inert gas

C_A and C_I = concentration of oxygen and inert gas in aqueous phase

Reaction 3 is the rate-limiting step, so Reactions 1 and 2 are at equilibrium, or r_1 and $r_2 = 0$.

Then the adsorption equilibrium equations can be written:

$$K_I = \frac{k_{f1}}{k_{r1}} = \frac{\theta_I}{C_I (1 - \theta_A - \theta_I)} \quad (7)$$

$$K_A = \frac{k_{f2}}{k_{r2}} = \frac{\theta_A^2}{C_A (1 - \theta_A - \theta_I)^2} \quad (8)$$

Solving for θ_A and θ_I in terms of equilibrium constants, the rate equation may be written:

$$r_4 = \frac{k_4 K_A C_A}{(1 + \sqrt{K_A C_A} + K_I C_I)^2} = \frac{k C_A}{(1 + \sqrt{K_A C_A} + K_I C_I)^2} \quad (9)$$

Another possible mechanism results in a rate equation giving slightly poorer correlation. This assumes the formation of an activated complex by the adsorption of oxygen on single site, i. e.,





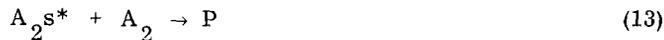
The final rate equation for this mechanism is:

$$r_{11} = \frac{kC_A}{1 + K_A C_A + K_I C_I} \quad (12)$$

Using the data for pure oxygen ($C_I = 0$) from Table 3, equations 9 and 12 were solved for "k" and " K_A ."

Plotting the data of Table 3 together with equations 9 and 12 in Figure 5 indicates that the dissociation mechanism (equation 9) is consistent with experimental data. However, it must be emphasized that this does not prove the validity of the mechanism. It merely indicates that the proposed mechanism is possible according to this set of experimental data. The single-site adsorption mechanism (equation 12), although showing greater deviation, can not be eliminated on the basis of these data.

However, other mechanisms that have been suggested can be discarded. For example, the reaction of another molecule of oxygen with the activated complex, i.e.,



is not probable since the rate equation would involve a $(C_A)^2$ term in the numerator.

The same type of analysis can be used to show that neither the physical nor chemical adsorption of oxygen can be the rate-limiting reaction. If this were the case, the initial rate would be proportional to the concentration of oxygen.

The presence of dissolved nitrogen reduces the rate of oxidation slightly as shown in Table 3. The rate data is not so consistent that a reliable value for K_I can be calculated.

Since the adsorption of oxygen occurs in an aqueous medium and since the presence of nitrogen reduces oxidation rate, it is likely that physical rather than chemical adsorption on "reactive sites" is involved. It is unusual for chemisorption to occur from highly polar solvents. Also, if oxygen were chemisorbed, nitrogen would have no effect on rate. At the same time it does not seem likely that nitrogen could compete with oxygen in an aqueous solution for physical adsorption on a relatively non-adsorptive material like pyrite.

A more critical study of the effect of nitrogen on the reaction is needed since the manner in which oxygen is adsorbed is of fundamental importance to inhibition studies. The adsorption of oxygen will have to be determined indirectly since normal procedures used to study adsorption of gases can not be used for the oxygen-water-pyrite system.

TABLE 1
LIQUID PHASE RUNS

Vapor Conc. (% O ₂)	Temp. (°C.)	Oxidation Rate*
100	20	58
100	25	100
100	30	138
100	35	215
10	25	23
26	25	47
54	25	79
79	25	85
100	25	100
100	25	102**
100	35	210**

TABLE 2
VAPOR PHASE RUNS

Temp. (°C.)	Partial Press. of Water (mm. Hg.)	% Rel. Saturation	Oxidation Rate*
25	22.8	96	85
	17.8	75	50
	12.6	53	25
	7.6	32	16
35	40.5	96	168
	31.2	75	90
	21.5	51	57
	13.1	31	33
45	69.	96	400
	53.2	75	152
	33	46	70
	22.3	31	48

**With "Amberlite"

TABLE 3
VARIABLE PRESSURE RUNS AT 25°C

Oxygen Pressure (cm. Hg.)	Nitrogen Pressure (cm. Hg.)	Liquid O ₂ Conc. (ppm.)	Oxidation Rate*
76	0	39.4	100
183	0	95	165
170	0	88	162
170	0	88	156
143	0	74	144
91	0	47	110
48	0	25	68
38	0	19.5	62
28	0	14.5	52
21.5	0	11.2	39.5
20	0	10.4	37
14	0	7.3	34
15	0	7.8	32
10	0	5.2	25
34	128	17.5	47
15	100	7.8	30.5
14	67	7.3	30
15.5	59	8.0	26.5
10	70	5.2	24.5
7.1	27	3.7	19

*Rate = Microgram oxygen, per gm. pyrite, per hour

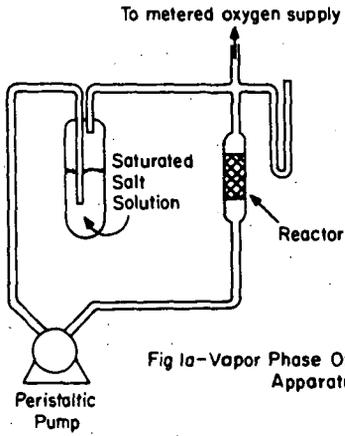


Fig 1a-Vapor Phase Oxidation Apparatus

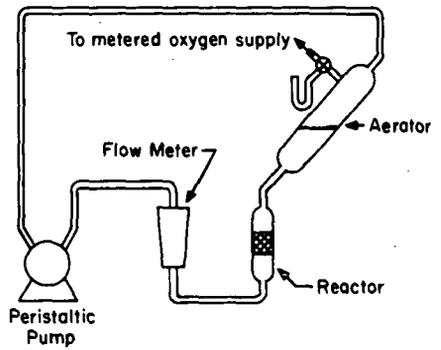


Fig 1b-Liquid Phase Oxidation Apparatus

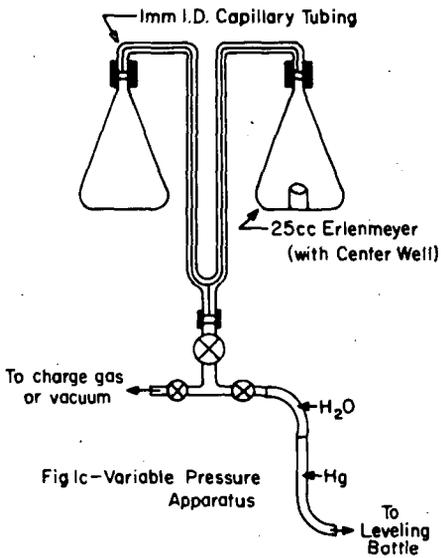


Fig 1c-Variable Pressure Apparatus

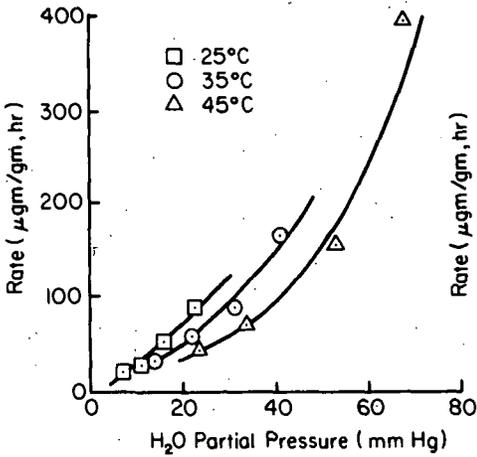


Fig 2 - Oxidation Rate vs. Partial Pressure of Water

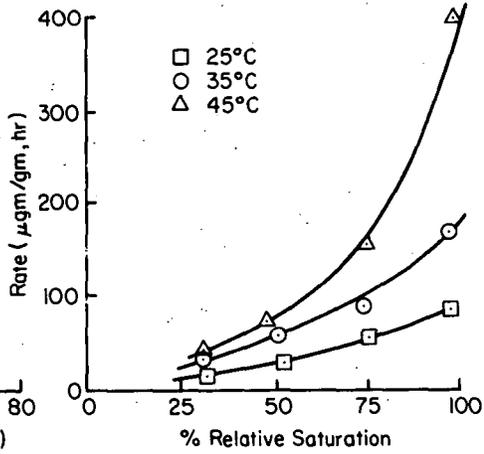


Fig 3 - Oxidation Rate vs. % Relative Saturation

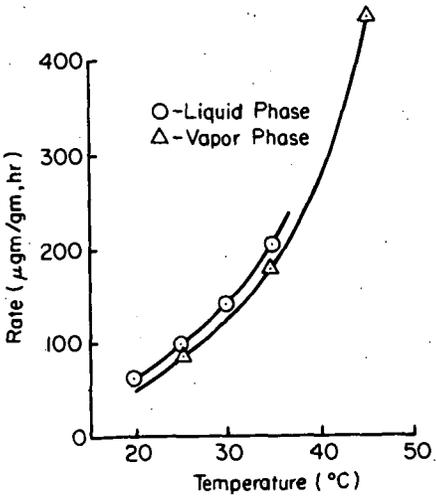


Fig 4 - Oxidation Rate vs. Temperature

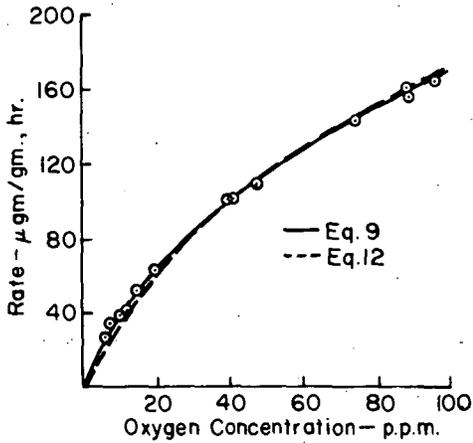


Fig 5 - Oxygen Rate vs. Oxygen Concentration in Aqueous Phase

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