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THE ELECTROCHEMICAL CHARACTERIZATION OF THE RATES OF OXIDATION OF SOLUBLE SULFIDES BY MOLECULAR OXYGEN IN AQUATIC SYSTEMS

by

Yervant Aram Demirjian

A dissertation submitted in partial fulfillment
of the requirement for the degree of
Doctor of Philosophy
(Environmental Health Sciences)
in The University of Michigan
1971

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This dissertation is dedicated to

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MY WIFE

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I. INTRODUCTION

The purpose of this investigation is to electrochemically characterize soluble sulfides, the rate of oxidation of sulfides by dissolved oxygen in aquatic systems, the effect of iron species on the oxidation rate of sulfides, and the rate of oxidation in natural waters.

MOTIVATION

When found in surface waters, reduced-sulfur compounds and related organic sulfides (1), such as mercaptans, CH_3SH and CH_3CH_2SH, are usually viewed as pollutants. Sulfides react with many metal ions within the anaerobic zone and form highly insoluble compounds, thus depleting the water of its metal ions and enriching the bottom sediments with metal deposits. The end product of oxidation of hydrogen sulfide (H_2S) in most cases is sulfate, which causes a corrosion problem with concrete structures.

From a water-pollution-control aspect, reduced sulfur compounds are toxic to most aquatic organisms, such as fish, shellfish, and larvae (2); to certain anaerobic bacteria, however, these compounds are non-toxic (3). Reduced sulfur compounds also react with dissolved oxygen (DO) and may

result in its depletion to levels which may be fatal to fish and other aquatic life (4). These compounds also have a high chlorine demand. Furthermore, even in concentrations which may not be harmful to aquatic life, they are aesthetically objectionable because of their easily detectable, unpleasant characteristic odor.

The presence of sulfides in the atmosphere is an indication of air pollution. This is true in areas where there is a sewage treatment plant, petroleum cracking plant, paper mill or tannery (4). But the sulfides themselves have a minor role in air pollution due to their rapid oxidation by the ozone present in the atmosphere. Sulfides in natural waters tend to cause an accumulation of ammonia, because when they are present ammonia does not enter the nitrification phase (5). The H_2S released may cause damage to various plant roots, e.g., in a rice field where nutrient uptake is inhibited by the H_2S (6).

Sulfides in aquatic systems may be long lasting in the presence of dissolved oxygen, thereby exerting a toxic effect on the aquatic organisms. Sulfide and oxygen may even coexist at certain concentrations (5) that are thermodynamically unfavorable for such coexistence. This phenomenon has puzzled investigators for many years.

The present author and other investigators have demonstrated in the laboratory that the rate of oxidation of sulfide in distilled water is very slow. The complete oxidation of

3-4 parts per million (ppm) of total sulfide (S_T) takes days. The oxidation rate of H_2S in the presence of oxygen in lake water, however, was found to be much faster, approximately 100 times faster than in distilled water. Due to the complexity of natural water, this higher reaction rate in lake water could have been due to a number of factors, among them the presence in natural water of trace amounts of heave metals and certain organics, which may act as promoters of the H_2S oxidation rate. This does not rule out, however, the possible existence in such water of inhibitors, such as formaldehydes, amino acids, and other organics (8).

It was determined by this author and other investigators that the oxidation of H_2S in the presence of oxygen in aquatic systems is not a simple reaction; the pathway and the reaction end product can be varied depending on the physiochemical composition of the system. Thus, the complicated oxidation pattern of H_2S by DO in such a complex system as natural waters becomes, indeed, a very difficult problem to understand. A simplified systematic approach, it seemed, would facilitate this understanding, and in this study simple experimental procedures were employed to this end. Oxidation rate studies were done on distilled water samples in the presence and the absence of iron. Then lake samples were studied by the same methods in the presence and absence of iron. The reasons for studying the effects of iron on these reactions were several. Aqueous iron has an important role

in natural waters in the limnological cycles of some key elements. Aqueous iron also is a key factor in water purification processes and in the formation of several types of industrial waters. And, finally, the abundance of iron in natural waters suggested that iron might play a role in the rapid oxidation of H_2S in such systems.

II. ENVIRONMENTAL SULFUR TRANSFORMATION

Reduced sulfur compounds come from industrial wastes such as the effluents of paper mills, tanneries, chemical plants, and gas works; from volcanic action; from hypolimnetic waters resulting from biochemical transformations involving sulfate reducing bacteria in the presence of organic matter; or from underground waters (9).

The sulfur cycle in nature consists of a complex chain of oxidation-reduction reactions in each of which many species of microorganisms take part (3).

Environmental sulfur transformation (10) can be illustrated by the schematic diagram in Figure 1. This figure shows the overall sulfur cycle in nature. Sulfur is taken up by plants largely as sulfate anions and to a lesser extent as gaseous sulfur dioxide. These sulfur compounds are transformed in the plant to reduced organic sulfur, such as in cysteine, which is a constituent of protein molecules. Unfortunately, there are not enough data to estimate the amount of sulfur bound organically in dead organic matter. As a result of bacterial action most of this sulfur is converted to sulfide from dead matter. There are not figures available for the total sulfide in soils and in the oceans.

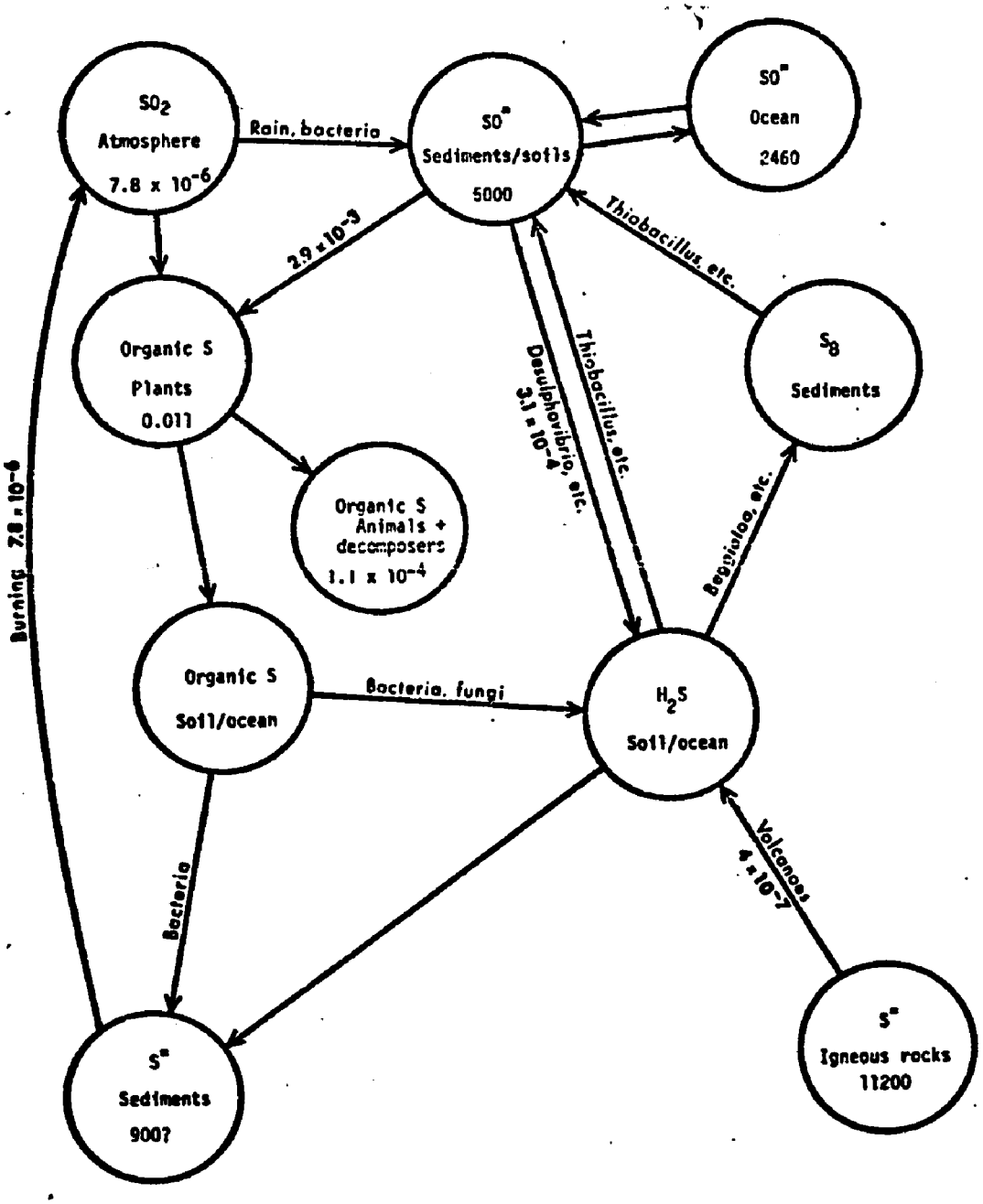


FIGURE 1. The Sulfur cycle. Numbers in boxes represent KgS per m^3; numbers attached to arrows represent KgS per year (10,52).

Sulfide to sulfate transformation can be done by many species of bacteria. Thiobacillus bacteria oxidize sulfides to sulfates in the presence of oxygen and are responsible for the production of sulfuric acid, which tends to decrease the pH of the soil. The reverse reaction is carried out by Desulfovibrio desulfuricans, which are the most common reducers of sulfur. The principal physiological property of sulfate-reducing bacteria is their growth under strictly anaerobic conditions. They derive their energy from oxidation-reduction reactions between organic matter and sulfates, as a result of which the sulfates are reduced to sulfides while the organic substances is oxidized to CO_2.

$$SO_4^{=} + 2\ C_{org} \longrightarrow S^{=} + 2\ CO_2 \quad . \qquad (1)$$

Bultin and Adams (51) have demonstrated that certain strains of sulfate-reducing bacteria can develop in the absence of organic matter, oxidizing molecular hydrogen anaerobically. This reaction is promoted by the enzyme hydrogenase:

$$4\ H_2 + SO_4^{=} \longrightarrow SO^{=} + CO_2 \qquad (2)$$

The reduction of sulfates biochemically is considered the main natural source of sulfides, which, incidentally, cause the corrosion of buried pipes, such as in oil wells and ocean floors (10).

According to Richards (5), sulfate reduction only occurs after oxygen, nitrate ions, and nitrite ions have been consumed. The mass balance of such organic decomposition by sulfate reduction can be represented by the equation:

$$(CH_2O)_{106}\ (NH_3)_{16}\ H_3PO_4 + 53\ SO_4^{=} =$$

$$106\ CO_2 + 53\ S^{=} + 16\ NH_3 + 106\ H_2O + H_3PO_4$$

The oxidation of H_2S to sulfur and further to sulfate takes place in two steps. One of these steps is oxidation by molecular oxygen, which will be described in full detail in a later part of this dissertation. The other process (1) is carried out by several types of bacteria, such as Beggiata, a pigmented sulfur bacteria. These organisms play an important role in the geographic distribution of sulfur deposits. They oxidize sulfide to sulfur in the absence of oxygen by utilizating H_2S, as a hydrogen donor, and CO_2 assimilation with light according to the following equation:

$$CO_2 + 2H_2S \longrightarrow (CH_2O) + H_2O + 2S \qquad (4)$$

Figure 2 shows examples of the different bacteria participating in the sulfur cycle (3).

Sulfides affect the physiochemical characteristics of the aquatic environment by reacting with many metal ions within the anaerobic zone and forming highly insoluble compounds (4) thus depleting the water of its metal ions and enriching the

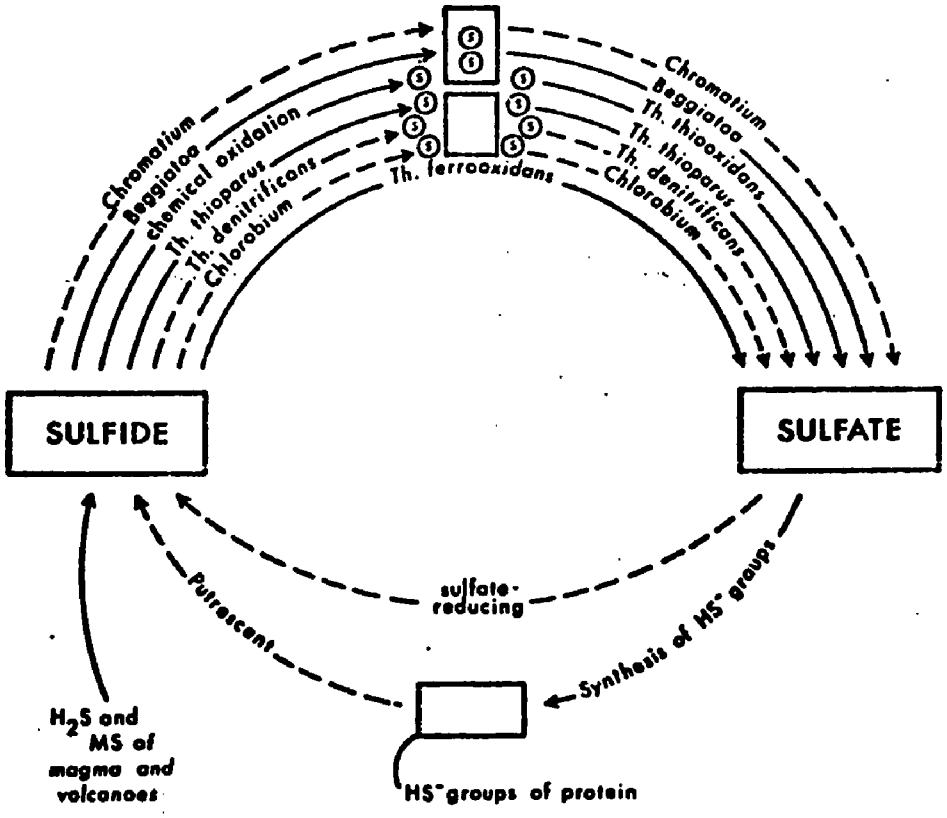


FIGURE 2. Schematic outline of the different bacteria participating in the sulfur cycle. Dotted lines indicate anaerobic microbiological process, straight lines aerobic processes (3).

bottom sediments with metal deposits. Sulfides react with dissolved oxygen and may result in its depletion to levels which may be fatal to fish and other aquatic life.

In the presence of sulfides (11), and as a result of the oxygen depletion, the redox potention (pE) of the aquatic environment tends to be lower. Table 1 shows this effect, even though at certain sulfide and oxygen concentrations both exist together, a phenomenon that is thermodynamically unfavorable and has baffled many investigators.

TABLE 1. OCCURRENCE OF DO AND SULFIDE AS A FUNCTION OF REDOX POTENTIAL (29)

Redox Potential mV	Oxygen ml/l	O_2 ug/l	$S^=$ ml/l	$S^=$ ug/l
395	5.60	498	-	-
408	7.06	628	-	-
404	6.35	565	-	-
340	1.08	96	-	-
-26	0.25	22	0.02	2
-88	0.08	7	0.67	60
-139	-	-	1.74	155
-170	-	-	3.60	320
-152	--	-	5.29	471
-144	-	-	6.15	547
-129	-	-	7.34	653

III. THERMODYNAMIC CONSIDERATIONS OF HYDROGEN SULFIDE

Hydrogen sulfide is highly soluble in water. One volume of water absorbs 4.65 volumes of H_2S at 0°C. H_2S is a very weak dibasic acid and it dissociates in two stages (12).

$$H_2S = H^+ + HS^- \qquad pK_1 = 7 \qquad (5)$$

$$HS^- = H^+ + S^= \qquad pK_2 = ? \qquad (6)$$

where pK_1 and pK_2 are the [-log] of the dissociation constant for H_2S. The pK values can be obtained from the Latimer table (24), or they can be obtained by thermodynamic calculations as follows:

$$H_2S = H^+ + HS^-$$

$$F^o_r = RT \ln K \qquad (7)$$

where

F^o_r is the free energy formation of H_2S, 9.55 Kcal.

R is the gas constant

T is the absolute temperature in °C.

Converting to the base 10 logarithm and evaluating equation (7) at 25°C, we have:

$$F^o_r = -1.364 \log K$$

or $$9.55 = -1.364 \log K$$

Solving for K, we have:

$$\log K = -7.00 \text{ and } pK = 7.00$$

The log K = -7.00, which is similar to reported values and to the experimental value shown in Figure 12. The pK_2 values are not agreed upon by all investigators. One calculated theoretical result is the following

$$HS = H^+ + S^=$$

$$F^o_r = 16.99 \text{ Kcal.}$$

at 25°C $pK_2 = 12.456$

This pK_2 value is not very close to the experimental value shown in Figure 12.

The equilibrium constant values, K, are important in the computation of the relative concentrations of H_2S, HS^-, and $S^=$ species of sulfides. The accuracy of such computations is dependent somewhat on the reliability of the equilibrium constants. The literature reports pK_1 values at 25°C that vary from 6.97 to 7.09 (13, 14). This range is in close agreement with the value of 7.00 found in this study. The reported pK_2 values at 25°C, however, vary widely from 12.90 to 15.00 (15, 16). By the potentiometric method, the experimental value for pK_2 in this work was found to be 13.00. The above pK values are corrected for dissociation constants by using the Extended Debeye-Hickel equation:

$$pK = pK' - \frac{2\sqrt{\mu}}{1+\sqrt{\mu}} \qquad (8)$$

where μ = ionic strength

$$\mu = 1/2\sum C_i z_i^2$$

where C_i = concentration of the ion

z_i = number of the electronic charges on the ion

Soluble sulfides in acidic aqueous media tend to form sulfur which is colloidal in nature and showns a Tyndall beam effect (17, 18, 19). In basic solutions soluble sulfides dissolve sulfur to form polysulfides. Most of the polysulfides are unstable in aqueous media: they are subject to rapid disproportionation. The following three equations show the disproportionation and their equilibrium relationship (17).

$$3S_2^{=} + 2H_2O \longrightarrow 2HS^- + 2OH^- + S_4^{=} \quad (9)$$

$$3S_3^{=} + H_2O \longrightarrow HS^- + OH^- + 2S_4^{=} \quad (10)$$

$$4S_4^{=} + H_2O \longrightarrow HS^- + OH^- + 3S_5^{=} \; ; \; K \quad (11)$$

$K = 4.5 \times 10^{-5}$ @ 20°C and $\mu = 0.1$

The acidity constants of each species are as follows:*

$$H_2S = H^+ + HS^- \qquad pK = 6.83 \quad (12)$$

$$HS^- = H^+ + S^{=} \qquad pK = 14.15 \quad (13)$$

$$H_2S_4 = H^+ HS_4^- \qquad pK = 3.8 \quad (14)$$

$$HS_4^- = H^+ + S_4^{=} \qquad pK = 6.3 \quad (15)$$

$$H_2S_5 = H^+ + HS_5^- \qquad pK = 3.5 \quad (16)$$

$$HS_5^- = H^+ + S_5^{=} \qquad pK = 5.7 \quad (17)$$

---

*All at $\mu = 0.1$, 20°C (17, 18)

This shows that H_2S_4 and H_2S_5 are much stronger in acidity than H_2S, and in natural pH ranges (approximately 7.00) they are more quickly ionized. Therefore, the predominant sulfide species in natural waters at pH ranges of 6.5 to 8.5 are H_2S, HS^-, $S_4^=$, and $S_5^=$.

In the system presented in this study, the oxidation of H_2S by molecular oxygen in natural water, the polysulfide formation is very negligible because the system is not favorable for sulfur formation between the pH range 6.8 to 8.75.

IV. AQUATIC CHEMISTRY OF IRON

In order to understand the behavior of iron in aquatic systems, a theoretical approach is needed in which various equilibria are assumed to be operating in controlling the species of iron. Such an over-simplification is not taken to provide conclusive evidence as to the chemistry of iron in such a complex system as natural water, but rather merely to give some insight as to which equilibria are relevant.

A. FERROUS IRON SYSTEM

Ferrous iron (Fe II) under reducing conditions in natural waters is the stable form of iron. It is found in the bottom of lakes under conditions of stagnation and in most ground waters. In waters free of carbonate and sulfide, Fe(II) can exist as $Fe(OH)_{2(s)}$. In hypolimnetic waters the concentration of sulfide species may be quite high as a result of anaerobic reduction of sulfates. Ferrous sulfide (FeS) is the predominating compound of Fe(II) over the entire range of pH encountered in the natural waters. The solubility of ferrous iron in waters free of measurable alkalinity and sulfide (20, 25) is shown in Figure 3, of ferrous iron in waters containing 5×10^{-3} M of total carbonate species in Figure 4, and

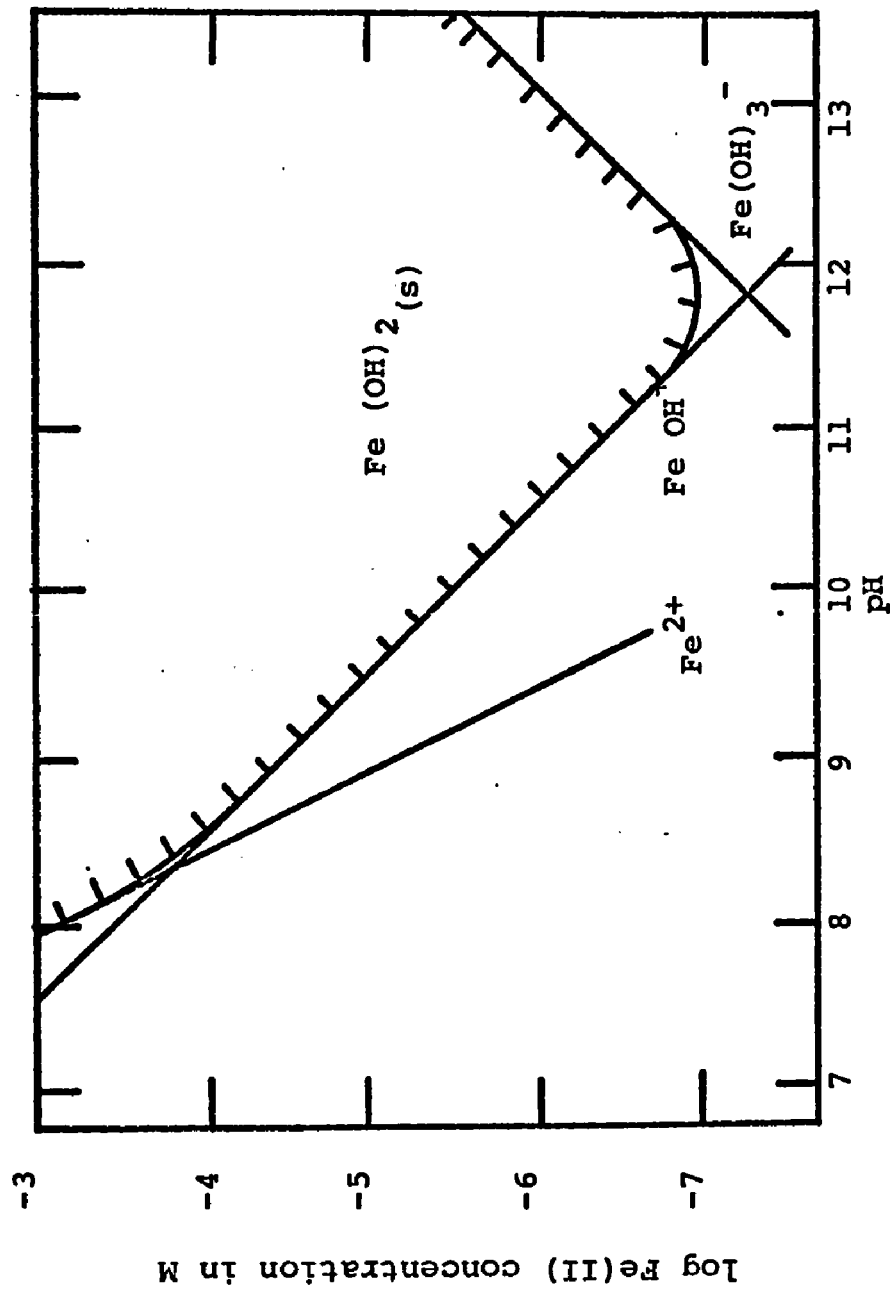


FIGURE 3. Solubility of ferrous iron in waters free of appreciable alkalinity and sulfide (20,25).

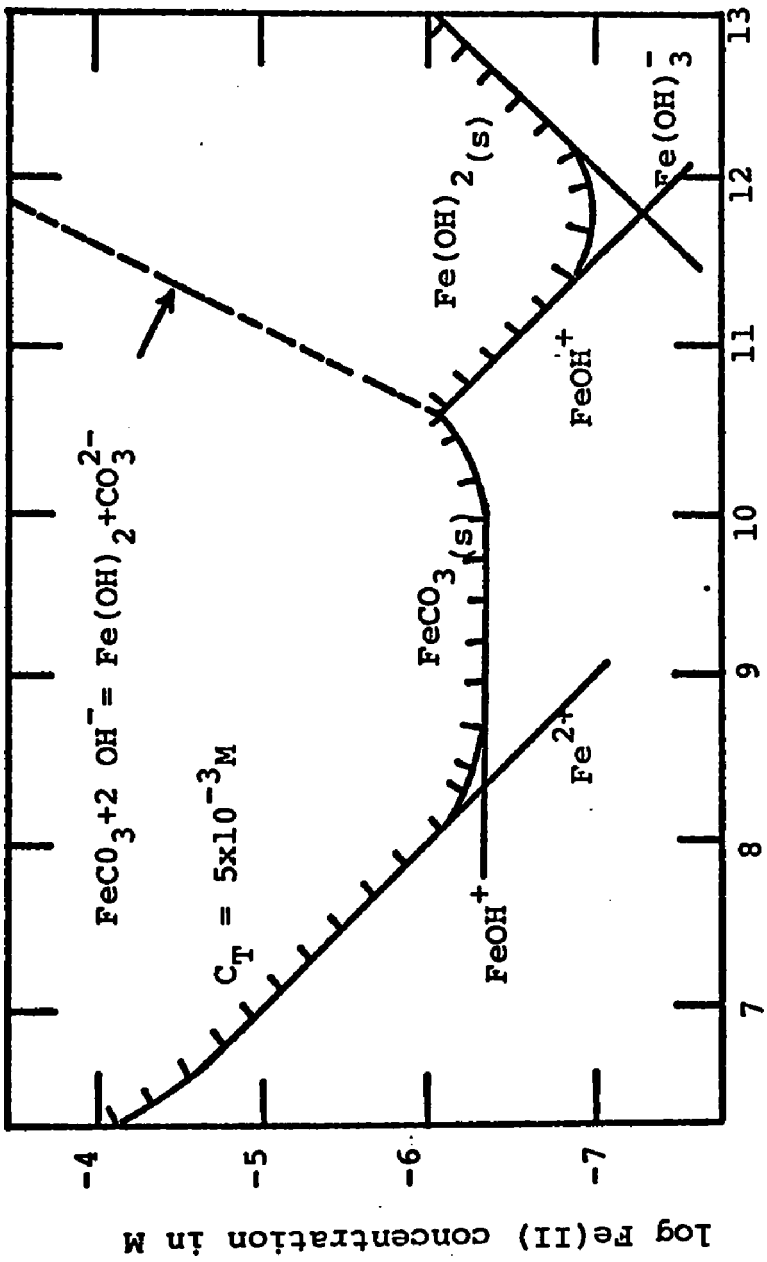


Figure 4. Solubility of ferrous iron in waters containing $5x10^{-3}$ M of total carbonate species (20,25).

of ferrous iron in waters containing 5×10^{-3} M of S_T in Figure 5. These figures show that ferrous iron solubility is governed by the solubility of its respective carbonate, hydroxide, or sulfide compounds, depending upon the composition of the water. Table 2 shows the equilibria describing the Fe(II) solubility.

B. FERRIC IRON SYSTEM

In oxygenated waters, ferric iron (Fe(III)) is the stable form of iron. In aqueous media ferric hydroxide ($Fe(OH)_3$) or ferric oxidehydroxide controls the concentration of soluble Fe(III) in natural waters. The solubility product (Ksp) of $Fe(OH)_3$ is in the range of 10^{-35} to 10^{-44} (20). In relatively high concentrations of phosphate, insoluble ferric phosphate ($FePO_4$) is the predominant species of Fe(III). Ferric phosphate is present only below pH 5. Sulfate ions and Fe(III) complexes are common in acid mine drainage, where the sulfide to sulfate oxidation is prevalent and the pH of 3 is common. Figures 6 and 7 demonstrate the solubility of ferric iron and the solubility of ferric iron in the presence of 10^{-4} M of total phosphate (20, 25). Table 3 shows equilibria describing Fe(III) solubility. In oxygenated waters, where the redox potential (pE) values are in the vicinity of the upper positive limits, ferric hydroxide is the predominant form of iron except below pH 4, where the solubility of Fe (III) increases. In the absence of oxygen--as in hypolimnetic waters, most natural ground waters, and anaerobic biological

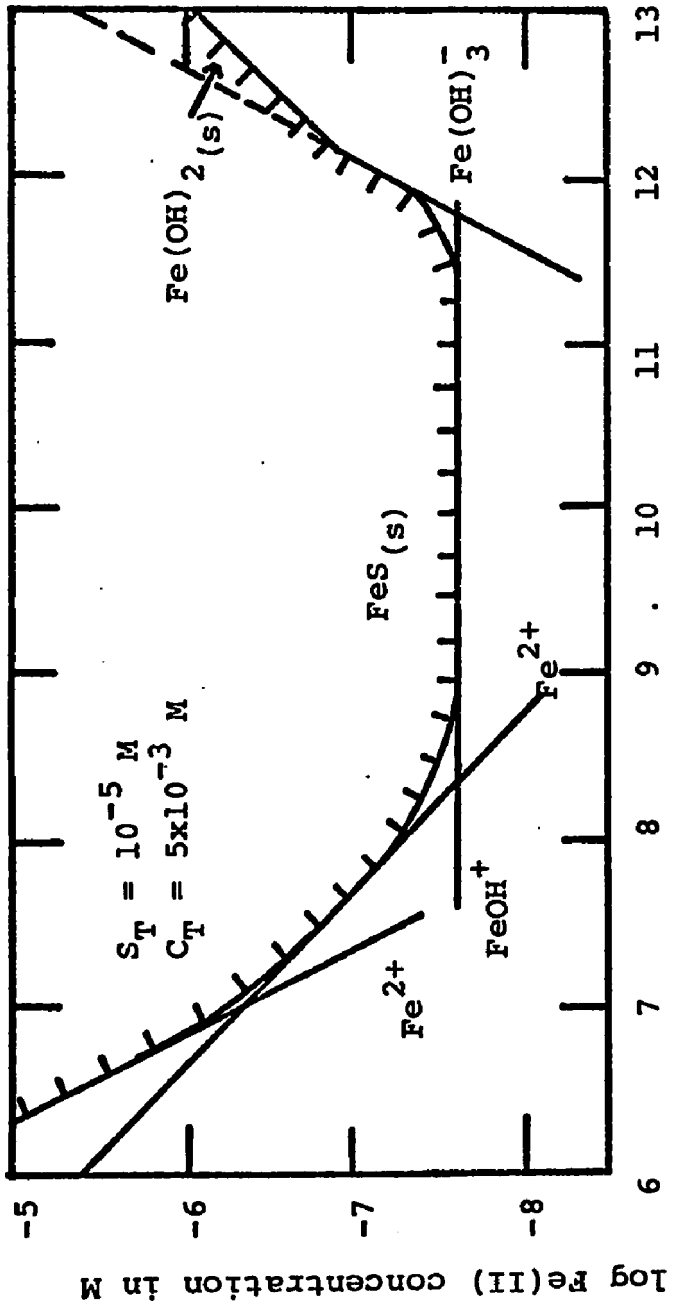


FIGURE 5. Solubility of ferrous iron in waters containing $5x10^{-3}$M of total carbonate species and 10^{-5}M of total sulfide species (20,25).

TABLE 2. EQUILIBRIA DESCRIBING Fe(II) SOLUBILITY

Equation Number	Reaction	Equilibrium Constant at 25°C	Reference
18	$Fe(OH)_{2(s)} = Fe^{+2} + 2OH^-$	8×10^{-16}	21
19	$Fe(OH)_{2(s)} = FeOH^+ OH^-$	4×10^{-10}	21
20	$Fe(OH)_{2(s)} + OH^- = Fe(OH)_3^-$	8.3×10^{-6}	22
21	$FeCO_{3(s)} = Fe^{+2} + CO_3^{-2}$	2.1×10^{-11}	23
22	$H_2CO_3 = H^+ + HCO_3^-$	4.2×10^{-7}	23
23	$HCO_3^- = H^+ + CO_3^{-2}$	4.8×10^{-11}	23
24	$FeS_{(s)} = Fe^{+2} + S^{-2}$	6×10^{-18}	28
25	$H_2S_{(aq)} = H^+ + HS^-$	1.0×10^{-7}	24
26	$HS^- = H^+ + S^{-2}$	1.3×10^{-13}	24

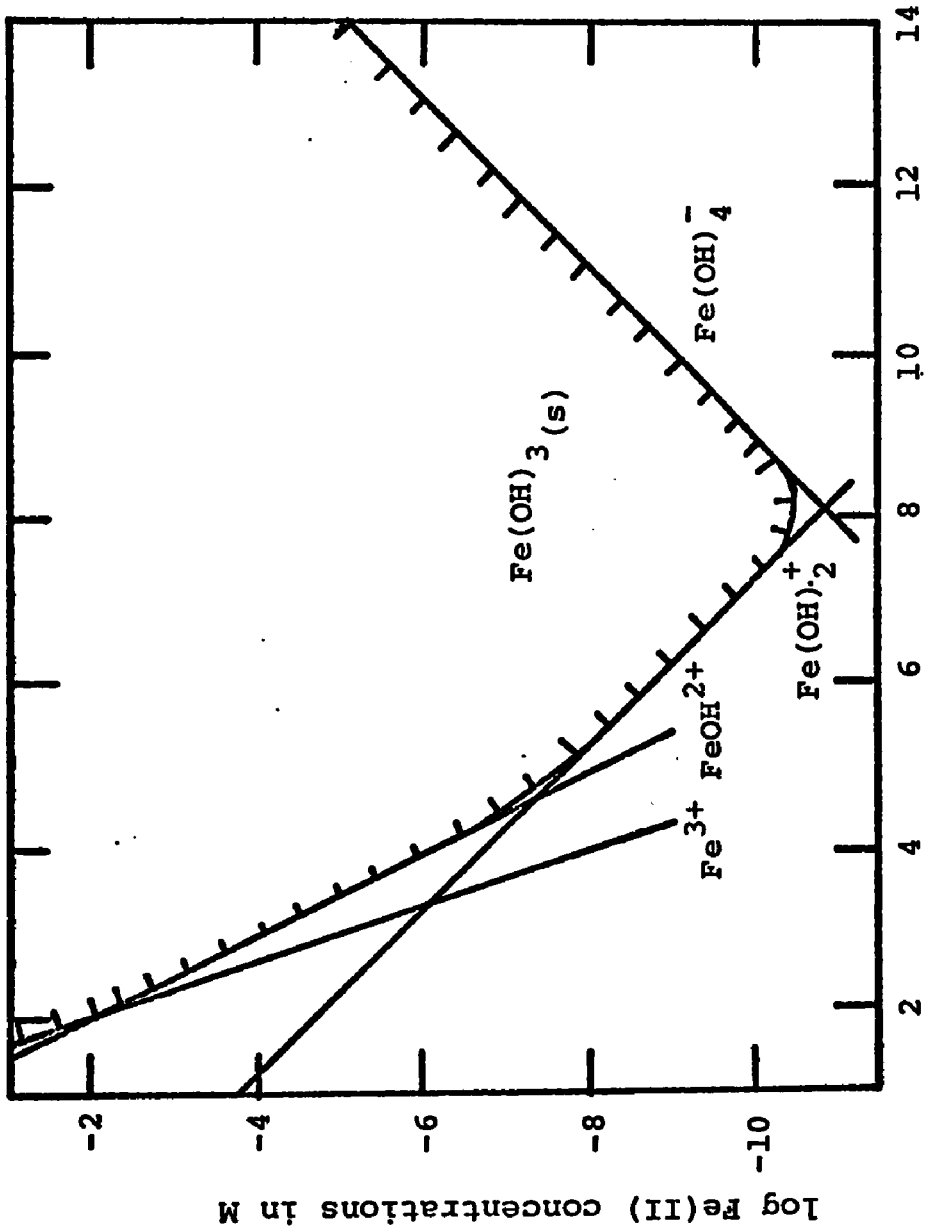


FIGURE 6. Solubility of ferric iron (20,25).

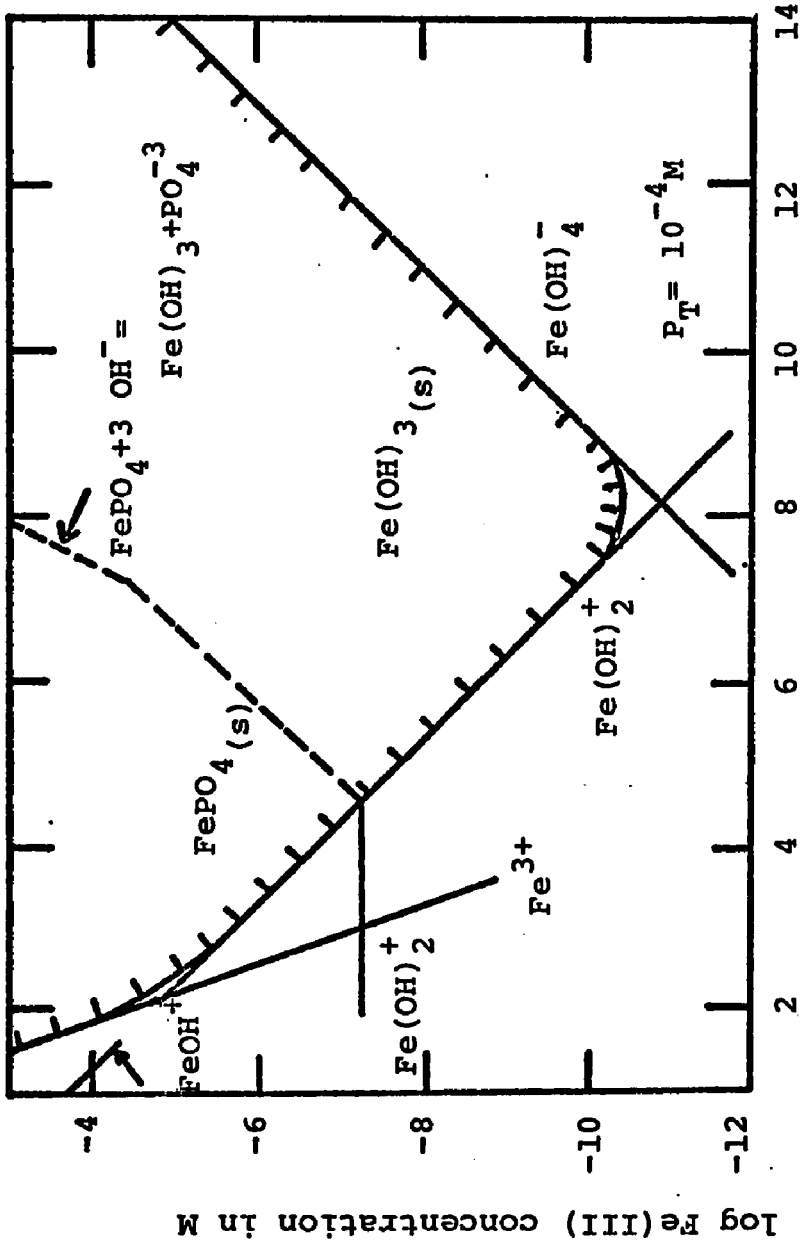


FIGURE 7. Solubility of ferric iron in the presence of 10^{-4} M of total phosphate species.

TABLE 3. EQUILIBRIA DESCRIBING Fe(II) SOLUBILITY

Equation	Reaction	Equilibrium Constant at 25°C	Reference
27	$Fe(OH)_{3(s)} = Fe^{=3} + 3OH^-$	10^{-38}	expt'l.Ch.4
28	$Fe^{+3} + H_2O = Fe(OH)^{+2} + H^+$	6.8×10^{-3}	27
27	$FeOH^{+2} + H_2O = Fe(OH)_2^+ + H^+$	2.6×10^{-5}	27
30	$Fe(OH)_{3(s)} + OH^- = Fe(OH)_4^-$	10^{-5}	28
31	$FePO_{4(s)} = Fe^{+3} + PO_4^{-3}$	10^{-24}	30
32	$H_3PO_4 = H_2PO_4^- + H^+$	7.4×10^{-3}	30
33	$H_3PO_4^- = HPO_4^{-2} + H^+$	6.4×10^{-8}	30
34	$HPO_4^{-2} = PO_4^{-3} + H^+$	5.0×10^{-13}	30

systems, such as sludge digesters--ferric iron is readily reduced by organic matter and by sulfide. The extent of reduction depends upon the pE and pH of the system. The form of resultant Fe(II) is also dependent upon the pH. The pE of such a system is in the region of the lower limits of negative pE. Figure 8 demonstrates the pE-pH diagram for iron. Concentration of soluble iron species is 10^{-5} M and alkalinity is 10^{-3} Eq-l. Equilibria for construction of the pE - pH diagram are given in Table 4.

C. FERROUS IRON OXIDATION

Ferrous iron is thermodynamically unstable in the presence of oxygen; it oxidizes to the Fe(III) form. In turn the Fe(III) formed is hydrolyzed to form a precipitate. In natural waters the cycles of phosphorous and sulfur are interrelated with the iron cycle. The rate of oxidation of Fe(II) to Fe(III) during spring and fall overturn is, therefore, partially responsible for the rate of dissolution and oxidation of sulfide and for the rate of turnover of phosphate. The oxidation of Fe(II) to Fe(III) is presented in the equation below:

$$Fe^{+2} + \tfrac{1}{4}O_2 + H^+ \rightleftharpoons Fe^{+3} + \tfrac{1}{2}H_2O \qquad (35)$$

$$Fe^{+3} + 3H_2O = Fe(OH)_{3(s)} + 3H^+ \qquad (36)$$

The rate of these reactions is dependent on DO, Fe(II), pH and $(O\overline{H})$. Stumm and Lee noticed a 100-fold increase in the

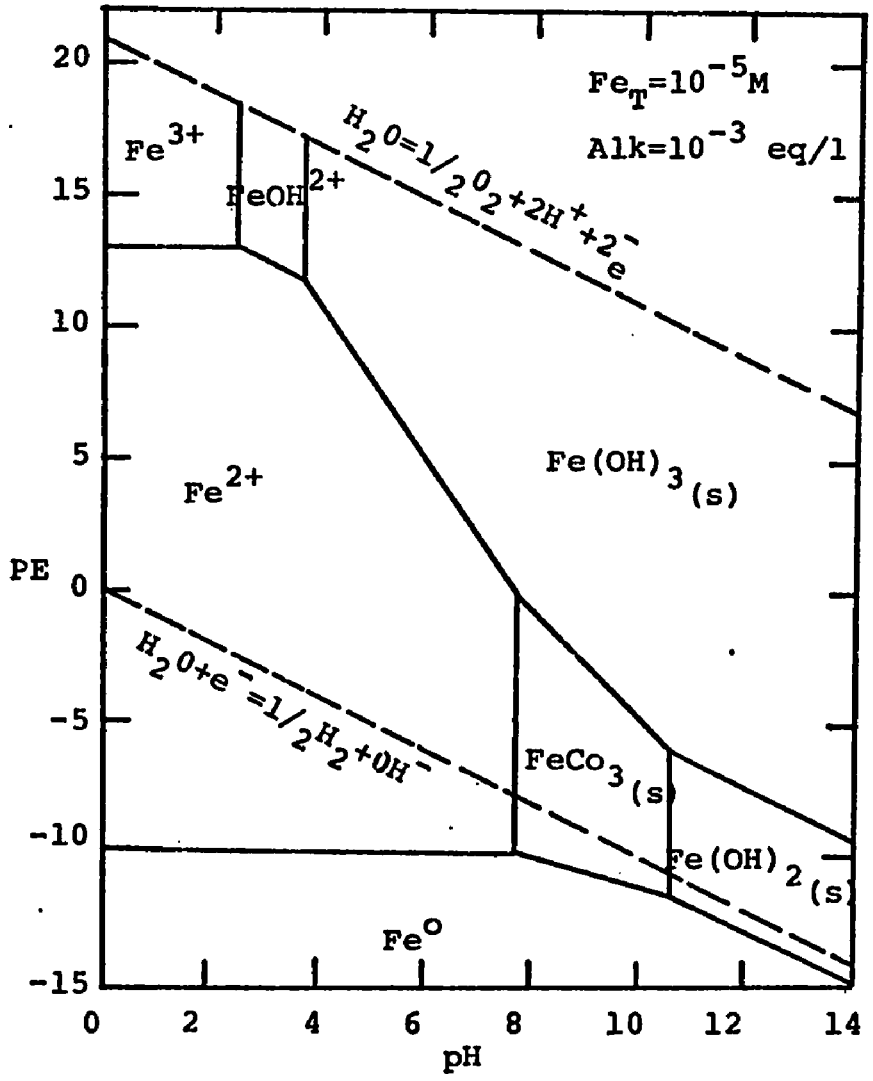


FIGURE 8. pE-pH diagram for iron concentration of soluble iron species is 10^{-5}M and alkalinity is 10^{-3} eq/l (20,25).

TABLE 4. EQUILIBRIA FOR CONSTRUCTION OF pE -pH DIAGRAM

Reaction	E^{o*} volts	pE-pH Relationship
$2H_2O = O_{2(g)} + 4H^+ + 4e^-$	-1.23	pE = 20.8-pH
$2H_2O + 2e^- = H_{2(g)} + 2OH^-$	-0.828	pE = -pH
$Fe^{+2} = Fe^{+3} + e^-$	-0.771	$pE = 13.0 - \log \frac{(Fe^{+2})}{(Fe^{+3})}$
$Fe^{+2} + H_2O = FeOH^{+2} + H^+ + e^-$	-0,914	$pE = 15.4 - pH - \log \frac{(Fe^{+2})}{(FeOH^{+2})}$
$Fe^{+2} + 2H_2O = Fe(OH)_2^+ + 2H^+ + e^-$	-1.19	$pE = 20.1 - 2pH - \log \frac{(Fe^{+2})}{(Fe(OH)_2^+)}$
$Fe^{+2} + 3H_2O = Fe(OH)_{3(s)} + 3H^+ + e^-$	-1.06	$pE = 17.9 - 3pH - \log (Fe^{+2})$
$Fe(OH)_{2(s)} + H_2O = Fe(OH)_{3(s)} + H^+ + e^-$	-0.274	pE = 4.63-pH
$FeCO_{3(s)} + 3H_2O = Fe(OH)_{3(s)} + HCO_3^- + 2H^+ e^-$	-1.08	pE = 15.3-2pH
$Fe^o = Fe^{+2} + 2e^-$	+0.440	pE = -9.93
$Fe^o + HCO_3^- = FeCO_{3(s)} - H^+ + 2e^-$	+0.440‡	pE= -5.93-1/2 pH
$Fe^o + 2H_2O = Fe(OH)_{2(s)} + 2H^+ + 2e^-$	+0.048	pE= -0.97-pH

Reaction	pK	pH Relationship
$FeCO_{3(s)} + 2H_2O = Fe(OH)_{2(s)} + H^+$	+13.6‡	$pH = 13.6 + \log (HCO_3^-)$
$Fe^{+3} + H_2O = FeOH^{+2} + H^+$	+2.17	$pH = 2.7 - \log \frac{(Fe^{+3})}{(FeOH^{+2})}$
$FeOH^{+2} + H_2O = Fe(OH)_2^+ + H^+$	+4.6	$pH = 4.6 - \log \frac{(FeOH^{+2})}{(Fe(OH)_2^+)}$
$FeCO_{3(s)} + H^+ = Fe^{+2} + HCO_3^-$	-0.09‡	$pH = 0.09 - \log (Fe^{+2}) - \log (HCO_3^-)$

*Computed from the tabulation of free energies given by Latimer (24).

+Calculated using ΔF^o $FeCO_3$=160.5 Kcal./mole, determined experimentally (20).

rate of oxidation of Fe(II) to Fe(III) for each increase of one pH unit (26). They also noticed that the carbonate-bicarbonate system has no effect on the rate of oxidation. It seems that the oxidation rate of Fe(II) to Fe(III) by oxygen is a first order reaction. In this paper, the author will attempt to quantitatively evaluate the catalytic effect of iron on sulfide oxidation by oxygen. Stumm and Lee's reactions for Fe(II) oxidation to Fe(III) were covered at pH values below 6, such as would be found in a coal mining region, where pH values of 3 are not uncommon (25). In an acidic system the oxidation of Fe(II) to Fe(III) is extremely slow. Figure 9 shows the oxygenation rate of ferrous iron as a function of pH.

D. FERRIC IRON HYDROLYSIS

Ferric iron in water generally forms the hydroxide precipitate.

$$Fe_x^{+3} + OH_y^- = Fe(OH)_{3(s)} \qquad (37)$$

The presence of sulfates, phosphates, and chlorides accelerates the rate of hydrolysis of Fe(III) (25). Freshly precipitated amorphous $Fe(OH)_3$ generally converts to α-FeOOH, α-Fe_2O_3, or β-FeOOH depending upon the conditions. In a review by Stumm of the chemistry of metal ions in aqueous solution, it is stated that an inactive amorphous material, such as colloidal sol of ferric oxidehydroxide, can be maintained for long periods of time (27).

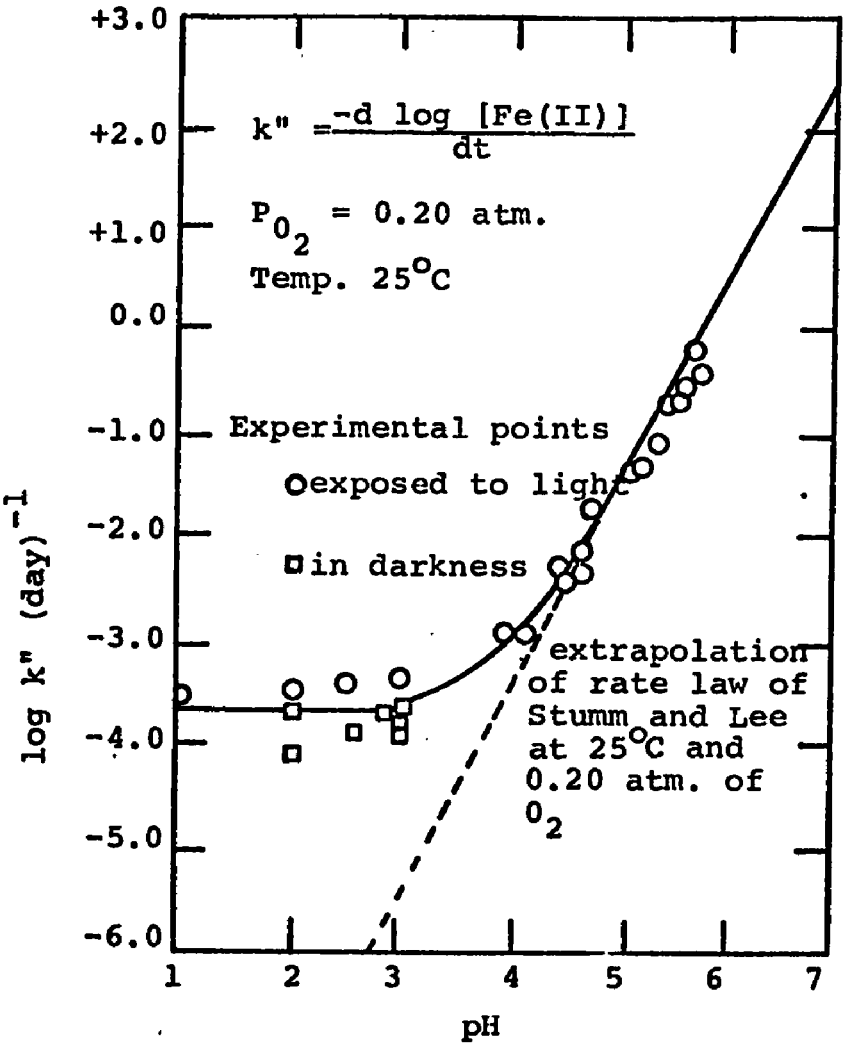


FIGURE 9. Oxygenation rate of ferrous iron as a function of pH (25).

E. PYRITE OXIDATION IN ACID MINE DRAINAGE

In order to have a better understanding of the oxidation of sulfide by molecular oxygen in the presence of iron in natural waters, a brief discussion of the oxidation of iron pyrite in coal mine drainage will now be given.

In coal mines ferrous sulfide exists as pyrite (FeS_2). When FeS_2 is exposed to air and water, sulfate and hydrogen ions are released into the water, as well as Fe(II) which in turn is oxidized to Fe(III) and $Fe(OH)_3$. The ferric iron produced can, in turn, be reduced by pyrite itself, thus completing a reaction cycle. The over-all reaction can be described as the following (25):

$$FeS_{2\,(s)} + 7/2 O_2 = H_2O = Fe^{+2} + 2SO_4^{-2} + 2H^+ \quad (38)$$

$$Fe^{+2} + 1/4\ O_2 + H^+ = Fe^{+3} + 1/2\ H_2O \quad (39)$$

$$Fe^{+3} + 3H_2O = Fe(OH)_{3\,(s)} + 3H^+ \quad (40)$$

$$FeS_{2\,(s)} + 14Fe^{+3} + 8H_2O = 15Fe^{+2} + 2SO_4^{-2} + 16H^+ \quad (41)$$

Therefore pyrite is the major source of acid mine drainage, the acidity being correlated to the amount of pyrite available in the system. One mole of pyrite will give rise to four equivalents of acidity; of this two equivalents come from sulfide oxidation and two from Fe(II) oxidation. The oxidation of FeS_2 by Fe(III) is very slow and inefficient; as an example, only 10^{-1} M of Fe(III) was reduced by 0.33 M FeS_2 in two hours (25). The microbiological oxidation of pyrite will not be discussed. Stumm (25) has stated that dissolved

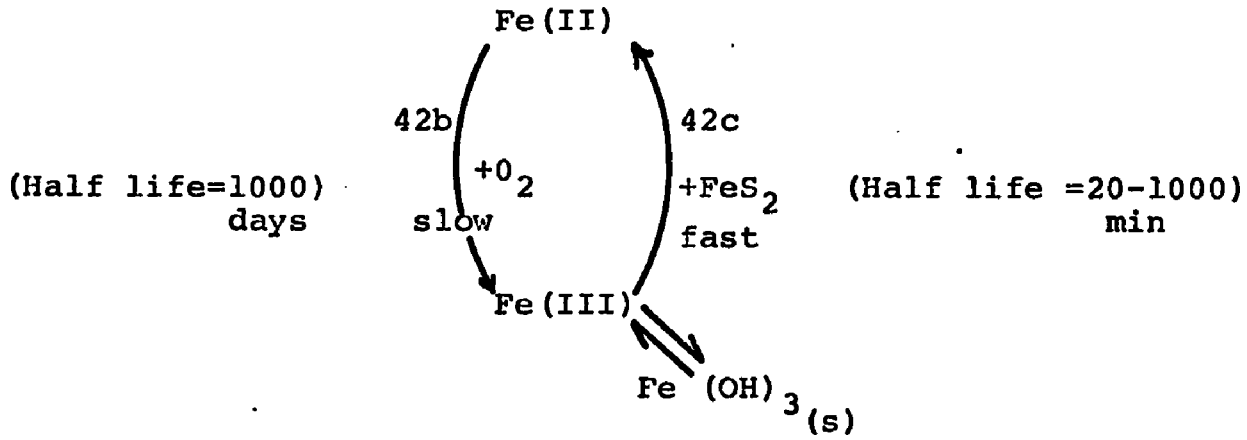
Cu^{++} and clays catalyze the oxidation of pyrite as do fine charcoal powder and fine pyrite powder; that ferric hydroxide does not catalyze the oxidation of Fe(II) and that the presence or absence of oxygen does not influence the reduction rate of Fe(III) by FeS_2.

The oxidation of pyrite is presented in the following propagation cycle.

Initiation Reaction: (25)

$$FeS_{2\,(s)} + O_2 \longrightarrow Fe(II) + S \text{ compound} \qquad (a\ 42)$$

Propagation cycle:



42d

The rate determining step is reaction 42b and it is very slow around pH 2 or 3; whereas the oxidation of FeS_2 by Fe(III) is much faster (reaction 42c). As the pH increases, the oxidation rate of Fe(II) increases and Fe(III) builds up, which increases the over-all reaction rate. In contrast to the reactions being reported in this dissertation, which involve only small concentration of iron acting as a catalyst in

systems with a pH from 7 to 8.6, acid mine-drainage reactions utilize iron as a substrate and occur around pH 2 to 3.

V. PREVIOUS WORK DONE ON OXIDATION OF HYDROGEN SULFIDE

There have been a number of studies by various investigators of the kinetics of the oxidation of sulfides by oxygen in aqueous systems. With the exception of that of Chen and Morris, however, none of the investigations has been systematic and extensive enough to lead to any firm comprehension of the system.

In 1928, Krebs measuring oxygen uptake with a manometer (28), showed that the rate of oxidation of a 0.5 M sulfide solution was increased as the alkalinity of the solution increased. He also reported the strong catalytic effect on sulfide oxidation of the transitional metal ions from $Mn^{=2}$ to Cu^{+2} in parts per million concentration. His work was confirmed by other investigators and has also been reaffirmed by this investigation. Wheatfield (5) in 1954 studied oxidation of sulfides in the Thames estuary in England, and demonstrated that the oxidation rate is increased by the presence of iron and is limited by the rate at which oxygen enters the water. Confirming his findings, it was found in the present investigation that with the addition of iron to distilled water, the rate of oxidation of sulfide increased and was dependent upon the availability of oxygen.

In 1965 E. Sowinski (7) studied the kinetics of the oxidation of sulfides as the following reaction:

$$2H_2S + O_2 \longrightarrow 2S + 2H_2O \qquad (43)$$

The oxidation was determined to be a first order reaction with respect to H_2S. At low concentrations of H_2S, e.g., 10^{-4}M, he states, his data show that the rate expression for oxygen might be second order. It appears, however, that there is little evidence to confirm this.

Stopentsev, Karpov, and Vershinina (29) in 1961 investigated the sulfide oxidation in seawater of the Black Sea and found that the reaction is first order with respect to sulfide. When the initial oxygen to sulfide ratio (DO/S_T) equals 1:2, half of the added H_2S was oxidized in 60-70 hours at 25°C. As the DO/S_T increased and if it was initially small, thiosulfate ($S_2O_3^=$) and S^o were formed and oxidation occurred in stages, first to elemental sulfur, then to sulfate. Complete oxidation was noticed when an excess of DO was available; when initial DO concentration was low with respect to H_2S, then S^o and $S_2O_3^=$ formation were favored.

According to Ostlund and Alexander (30), H_2S oxidation by O_2 in seawater is a second order reaction. When the DO was very high, they treated the reaction as a first order one. They found the decrease of sulfide to be first order reaction with a half-life of approximately 20 hours; a Ag/Ag_2S wire electrode was used for sulfide monitoring.

Cline and Richards' (31) findings suggested that the oxidation of sulfide in filtered seawater at pH 8.00 and 25°C is a complicated reaction. With H_2S concentration of $1x10^{-3}$ M and saturated DO the reaction was found to be a first order one with respect to sulfide and oxygen, and the rate constant

was found to be 2.3×10^{-1}/hour. Thirty hours were required for complete oxidation.

Avrahami and Goldring (32) studied the oxidation of sulfide in dilute solutions (1×10^{-4} M to 1×10^{-3} M) in the pH range of 11 to 13. The rate of oxidation increased with increased pH values, temperature, and oxygen concentration. The sulfide measurements were detected by ultraviolet absorption at 230 mu.

Chen and Morris (8) studied the oxidation of sulfide by O_2 in distilled water using a Warburg apparatus to monitor the oxygen uptake and measuring the sulfide by the methylene-bluemethod (33). Oxygen uptake was not, however, extensively followed. They reported the following empirical equation:

$$\text{Sulfide oxidation by } O_2\text{:} \quad \left[\frac{-d(S^{=})}{dt}\right]_{t=0} = k(\textstyle\sum S^{=})_o^{1.34} \cdot (O_2)^{0.56}$$

They also reported that the oxidation rate is pH dependent, maximum rates occurring at pH 8.50 and 11.20, that heavy metal ions, such as Ni^{+2}, Cu^{+2} and Fe^{+2}, and certain organic compounds, such as acetaldehyde, aniline, and benzyl alcohol, were accelerators, and that organics, such as EDTA, citrate, and anisole, were inhibitors. They attempted to define a reaction mechanism from among the many possibilities open to them.

As can be seen, very little thorough and systematic work was done on the oxidation of sulfide by molecular oxygen until recently, when Chen and Morris did their systematic work on

synthetic water and attempted to answer some of the pertinent questions. Some of the problems have been: (1) the difficulty of obtaining reproducible results, (2) the complexity of the reaction mechanisms, (3) the fact that there are numerous possible products, and (4) the unavailability of sulfide-sensitive and oxygen-sensitive electrodes with long enough half lives to make it economical to use them in a continuous monitoring procedure and with small enough diameters to minimize catalytic effects in ordinary-size laboratory reactors. In the present study transducers were designed and used for continuous monitoring and experiments were performed to attempt to determine the reasons for the rate of oxidation of H_2S in synthetic water being different from the rate in natural water.

VI. TECHNIQUES AND EQUIPMENT FOR ELECTROCHEMICAL CHARACTERIZATION OF SOLUBLE SULFIDES, DISSOLVED OXYGEN AND pH.

A. TECHNIQUES FOR ELECTROCHEMICAL CHARACTERIZATION OF SOLUBLE SULFIDES

There are three principal methods of measuring sulfides in aquatic environments: the titrometric or iodometric method; the colorimetric, or the methylene-blue method; and the potentiometric, or the sulfide-ion-selective electrode method. The following is a description of each method.

1. Iodometric Method (33,34)

The determination of total sulfide ($S_T = S^{2-} + HS^- + H_2S$) can be accomplished by adding an excess of standardized iodine solution ($H_2S + I_2 = S^o + 2\ HI$) and back titrating the excess with standardized thiosulfate solution (33). The determination must be done in an acidic solution due to the following interfering reaction of sulfide and iodine in basic solutions:

$$S^= + 4\ I_2 + 80\ H^- = SO_4^= + 8\ I^- + 4\ H_2O \qquad (44)$$

Because the solution must be acidic, the possibility of the loss of H_2S gas exists. To minimize this, the determination is carried out in a glass stoppered 300 ml biological oxygen demand (BOD) bottle, the bottle being unstoppered only for the addition of reagents. For the back titration with thiosulfate, a starch end point is used.

Because a concentration of about 10^{-5} M iodine is necessary to give the blue color with the indicator, a blank is necessary when working at concentrations of 10^{-3} to 10^{-4} M. The blank is determined by standardizing the iodine against the thiosulfate at high concentrations (where a blank is not necessary). The thiosulfate is then diluted to a concentration appropriate for the determination of 10^{-4} M I_2. Then a measured amount of the iodine is added to 300 ml of acifified sulfide solution and titrated with the thiosulfate. The difference between the theoretical volume of thiosulfate required for the titration and the actual amount used is the blank correction factor for the titration.

The reproducibility of the method was determined by repeating the measurement 11 times on the same solution. The standard deviation on a solution of 6.6×10^{-5} M total was 3.9×10^{-6} M, or a relative standard deviation of about 5%. Table 5 shows the statistical results of the iodometric method.

2. Colorimetric Method (Methylene-blue method) (33,34,35,36)

This method is based upon the reaction of H_2S with P-amino-dimethylaniline in the presence of ferric ion to produce methylene blue. The methylene blue is then determined photometrically. Two solutions are used in the determination:

1) One gram of P-aminodimethylaniline and 2 ml H_2SO4 diluted to one liter.
2) 31.6 grams of $Fe(NH_4)(SO_4)_2.12H_2O$ and 6.25 ml H_2SO_4 diluted to 250 ml.

TABLE 5. STATISTICAL ANALYSIS OF IODOMETRIC METHOD

Bottle Number	Meg* = S_2O_3	Meg. Total Sulfide	Normal Total Sulfide $x10^{-4}$	Dev. from mean $x10^{-4}$	Dev. Square $x10^{-12}$
1	0.0437	0.0358	1x21	0.11	121
2	0.0422	0.0363	1.23	0.09	81
3	0.0400	0.0395	1.34	0.02	4
4	0.0355	0.0440	1.49	0.17	289
5	0.0426	0.0369	1.25	0.07	49
6	0.0428	0.0367	1.24	0.08	64
7	0.0392	0.0403	1.37	0.05	25
8	0.0396	0.0399	1.34	0.03	9
9	0.0400	0.0395	1.34	0.02	4
10	0.0406	0.0389	1.32	0	0
11	0.0396	0.0399	1.35	0.03	9

*includes blank correction factor

$$\sum = 14.49 \times 10^{-4}$$

$$M = 1.32 \times 10^{-4} \qquad \sum = 655 \times 10^{-12}$$

$$\text{Standard deviation} = \sqrt{\frac{655 \times 10^{-12}}{10}} = 8 \times 10^{-6} \text{ or } 0.4 \times 10^{-5}$$

or $\pm$ 0.8×10^{05} M is the 95% confidence level.

Five milliliters of concentrated H_2SO_4 are added to 10 ml of solution I. This is then added to 100 ml of the test solution. Two milliliters of solution II are then immediately added. Fifteen minutes are allowed for full color development. The absorbance is measured at 625 mu. A reagent blank is used to set the 100% transmission level. A calibration curve is prepared by measuring the absorbance of solutions of known total sulfide concentration. It is estimated that the limit of sensitivity is about 0.1 ppm. However, with better temperature control and using a higher wavelength, a sensitivity of 0.01 ppm has been reported by other investigators (2,8). The reproducibility of the method was determined by ten analyses on the same solution. A relative standard deviation of 6% was found. Table 6 shows the statistical results of methylene blue method.

The iodometric and methylene-blue methods have these disadvantages: H_2S escapes from the test solution, and they are useless for continuous in situ measurements.

3. Potentiometric Method

Potentiometric determination of sulfides offers the advantage of continuous in situ measurements. This is particularly significant in the analysis of sulfides in natural and waste waters and is probably the only reliable method for the analysis of sulfides in hypolimnetic waters. Potentiometric measurements can be easily adapted for continuous monitoring and for the mapping of sulfide concentrations in water bodies.

TABLE 6. STATISTICAL ANALYSIS OF METHYLENE BLUE METHOD

Run Number	Absorb.	ppm*	Deviation from M	Deviation Squared $x10^{-6}$
1	0.060	0.130	0.005	25
2	0.052	0.118	0.013	169
3	0.053	0.120	0.011	121
4.	0.060	0.136	0.005	25
5	0.052	0.11	0.013	169
6	0.056	0.127		16
77	0.064	0.145	0.014	196
8	0.058	0.132	0.001	1
9	0.060	0.131	0.000	0
10	0.065	0.147	0.016	256

$M = 0.131$ $\quad \sum = 978c10^{-6}$

Standard deviation $= \sqrt{\frac{978 \times 10^{-6}}{N-1}} = 10.3 \times 10^{-3}$

relative error % $= \frac{0.0103}{0.131} \times 100 = 6\%$ for 65% confidence.

The relative error is 12% for 95% confidence.

In this part of the study the sulfide-ion-selective membrane electrode (15), Orion model 14-16; the expanded-scale pH meter, Leeds and Northrup model 7403, and a saturated calomel reference electrode (SCE) were used. The Orion electrode consists of a solid silver-sulfide membrane that separates the sample solution from an internal reference solution, which is kept at a constant silver-ion level. The difference in the silver-ion activity between the two solutions develops a potential that is dependent on the silver-ion activity in the test solution in a typical Nernstian relationship. This is described by the following equation:

$$E_c = E_{Ag^+/Ag} - E_{R.E.} + E_j \qquad (45)$$

where:

E_c = measured cell potential

$E_{Ag^+/Ag}$ = potential in the standard silver solution

$E_{R.E.}$ = potential due to the saturated calomel reference electrode

E_j = potential due to the liquid junction. In this case it is negligible since the same ionic strength was used in all solutions.

$$E_c = E^{o}_{Ag^+/Ag} + 2.3\ RT/nF\ \log a_{Ag^+} - E_{R.E.} \qquad (46)$$

where:

$2.3\ \frac{RT}{nF}$ = Nernst factor

a_{Ag^+} = The silver-ion activity in the sample solution

substituting the appropriate constans in equation (46)

$$E_c = 0.5576 + 0.059 \log a_{Ag^+} \quad (47)$$

The activity of the silver ions in the test solution is dependent on the activity of the sulfide ions. Therefore, we can calculate the activity of the sulfide ions in the test solution from the solubility product of silver sulfide.

$$a_{Ag^+} = \sqrt{Ksp/a_{s=}} \quad (48)$$

where:

Ksp = the solubility product of silver sulfide

$a_{s=}$ = the activity of sulfide ion

By substitution in equations (46) and (47)

$$E_c = 0.5576 + 0.059 \log (K_{sp}/a_{s=})^{0.5} \quad (49)$$

$$E_c = 0.5576 + \frac{0.059}{2} \log K_{sp} - \frac{0.059}{2} \log a_{s=} \quad (50)$$

$$E_c = E_1 - 0.029 \log a_s \quad (51)$$

where:

$$E_1 = 0.05576 + \frac{0.0596}{2} \log K_{sp}$$

K_{sp} is a constant that can be determined experimentally or theoretically from thermodynamic relationships.

Figure 10 illustrates the Nernstian relationship for the silver-sulfide membrane electrode. This figure represents a typical sulfide-ion-activity standardization curve at pH 13, and an ionic strength, μ of 0.1 M. The curve has a Nernstian

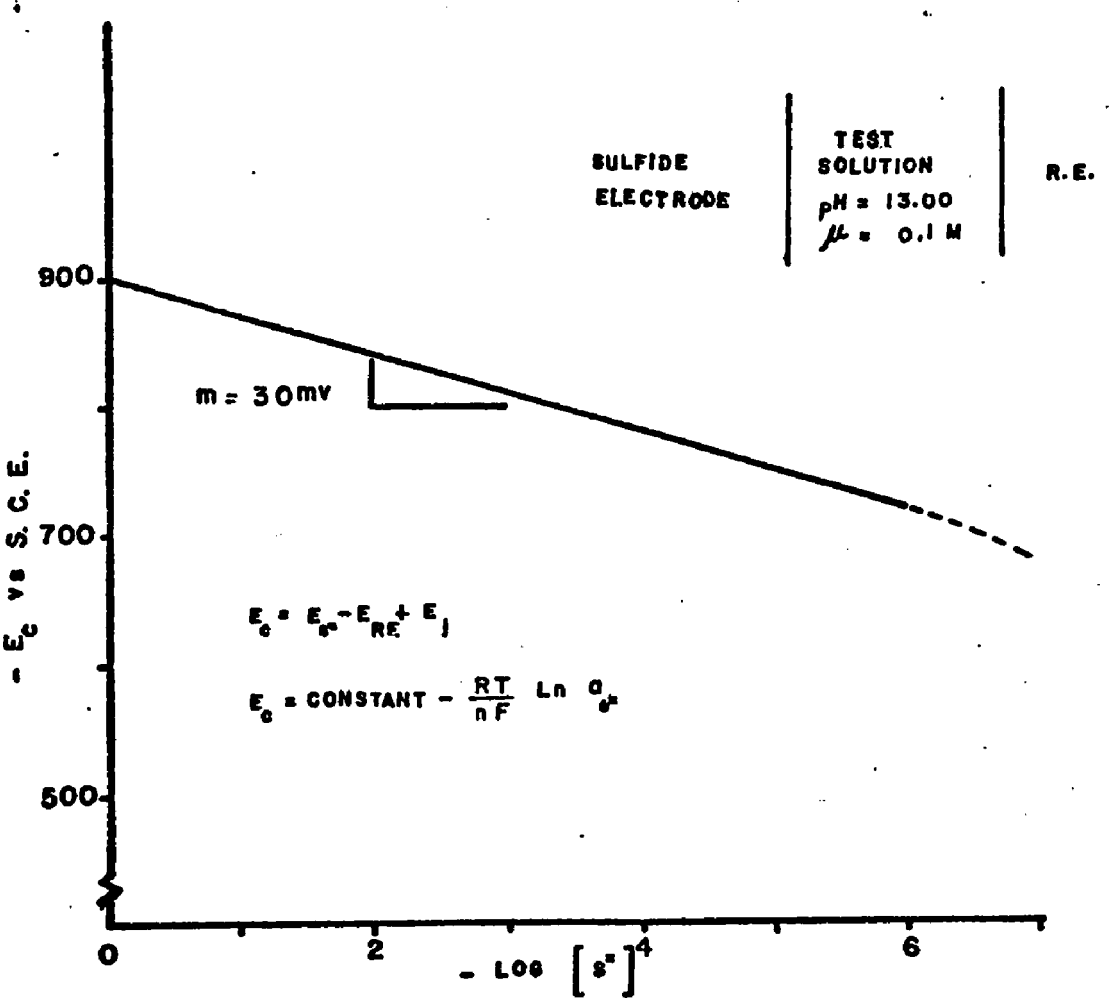


FIGURE 10. POTENTIOMETRIC MEASUREMENT OF SULFIDE ION ACTIVITY

slope which extends as low as 10^{-6} M. Below 10^{-6} M of sulfide activity the electrode potential did not follow a Nernst relationship. This was attributed, however, to the loss of sulfides during the experiment by atmospheric oxidation or by absorption on the glass wall even under extremely controlled conditions. The intercept of the curve is at -900 mv, and the reproducibility of results is + 0.5 mv, which is equal to about a 3% error.

Of particular importance in the analysis of sulfides in natural waters is the effect of the pH on free sulfides (15). Figure 11 illustrates the theoretical distribution of sulfides as a function of pH (12). The system points for the diprotic acid H_2S, taken from the literature, are $pK_1 = 7$ and $pK_2 = 13$ (9). The left part of the figure shows that H_2S is the predominating species at pH values below 6; between pH 8 and pH 13 the predominating species is the bisulfide ion, and above pH 13 the sulfide ion. On the right side of Figure 11 is a potentiometric titration diagram of hydrogen sulfide and sulfide ion by an acid or base.

The experimental results are illustrated in Figure 12. The upper part of the figure shows the effect of pH on the potential of the sulfide membrane electrode; the lower part gives the distribution of sulfide species as a function of pH. The solid lines in this figure are based on theoretical calculations of the ionic equilibria, and the points on the figure represent experimental results using the sulfide membrane electrode.

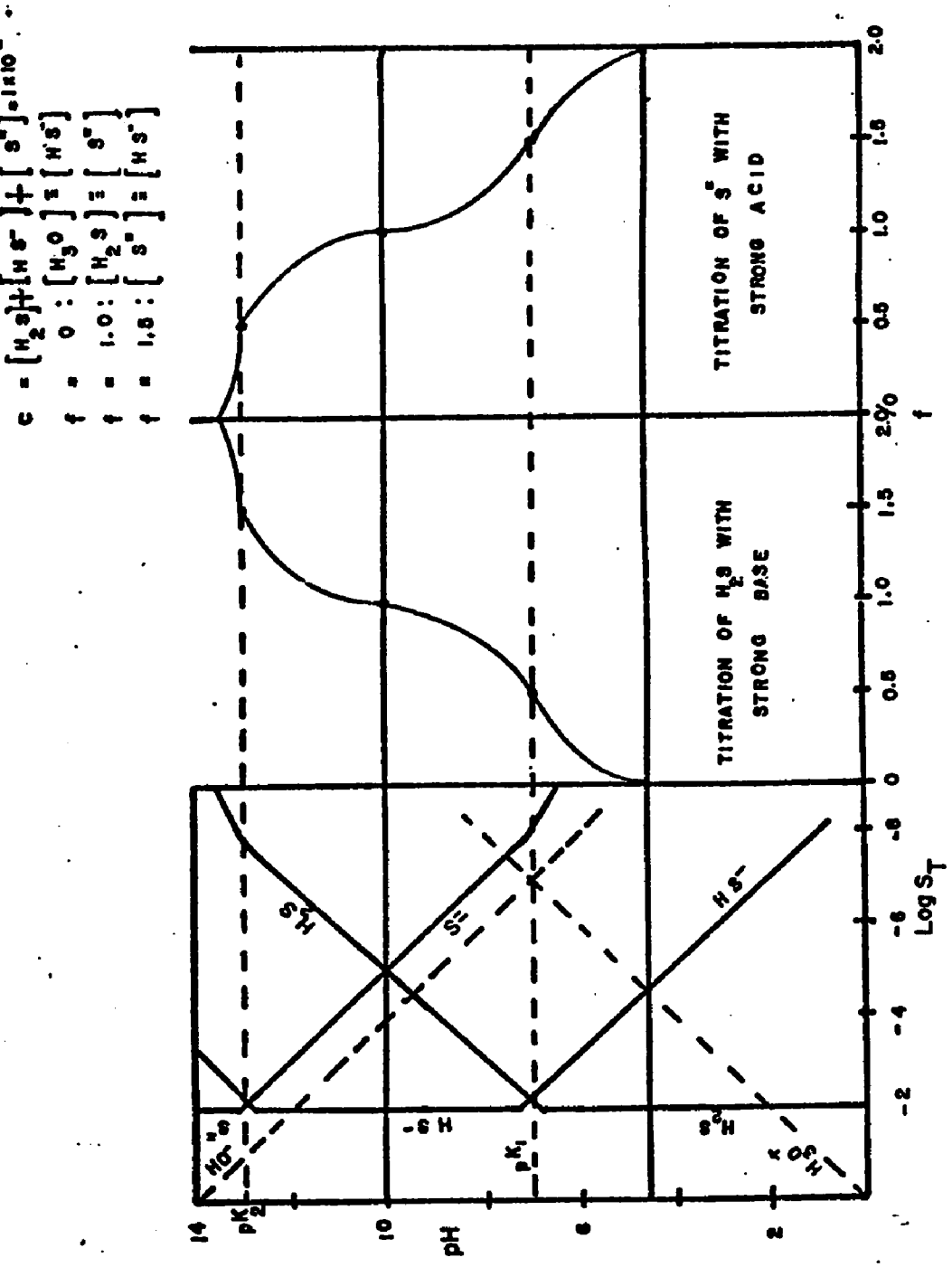


FIGURE 11. Theoretical calculated results of H_2S distribution with respect to pH.

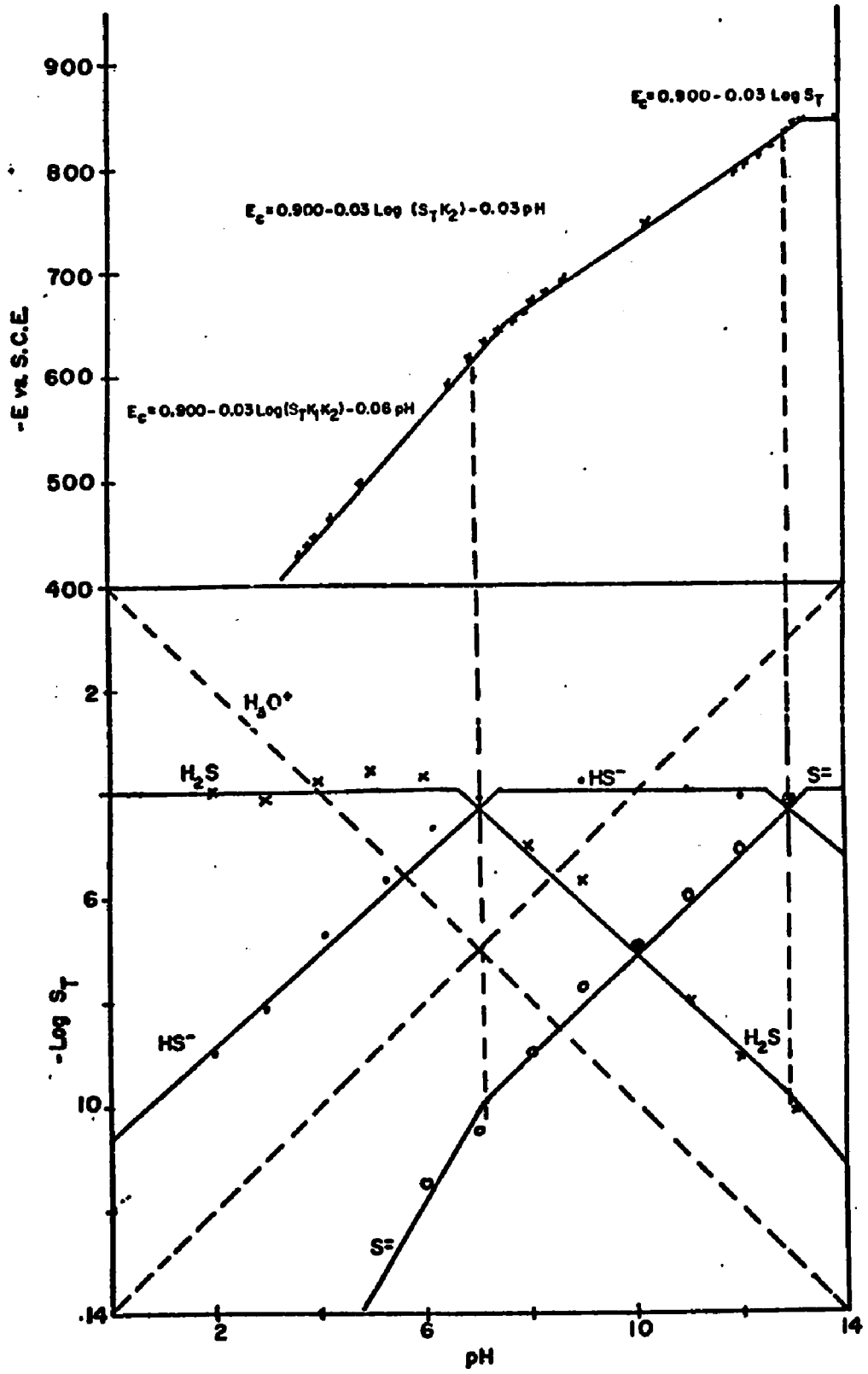


FIGURE 12. The effect of pH on the sulfide membrane electrode at constant total sulfide concentration.

Ionic strength was kept constant, approximately 0.12 M at room temperature, and corrections were done for volume change.

Examination of Figure 12 reveals that at pH values above 13 the predominating species is the sulfide ion, and the electrode potential is independent of pH, with a slope of 0. The straight line equation is calculated to be

$$E_c = 0.900 - 0.03 \log S_T \qquad (52)$$

where:

S_T is the total sulfide-ion activity in the test solution.

In the pH range between 7 and 13, the predominating species is the bisulfide ion, and the electrode potential is found to be linearly dependent on pH, with a slope of 0.03. The straight line equation is calculated to be

$$E_c = 0.900 - 0.03 \log (S_T K_2) - 0.03 \text{ pH} \qquad (53)$$

where:

K_2 is the acidity constant of

$$HS^- = S^= + H^+$$

At pH values below 7 the predominating species is H_2S and the electrode potential is found to vary linearly with pH. The slope of the straight line is calculated to be 0.06, as shown by the equation of the line

$$E_c = 0.900 - 0.03 \log (S_T K_1 K_2) - 0.06 \text{ pH} \qquad (54)$$

where:

K_1 is the acidity constant of

$$H_2S = HS^- + H^+$$

It is interesting to note that the dependence of the electrode potential on the sulfide-ion activity at various pH values can be illustrated by comparing the upper and lower portions of Figure 12.

This figure indicates the possibility of measuring sulfide-ion activity less than 10^{-20} M in solutions which are buffered with respect to the ion being measured and at concentrations of total sulfide not less than 10^{-6} M.

Figure 13 is a plot of several different -log α_o coefficients ($\alpha_o = \frac{S^=}{S_T}$), calculated from pK_2 values covering the range shown in the literature. For these plots a pK_1 value of 7 was used. Also included in Figure 13 is the experimental result. The estimated pK_2 value from this experimental result is 13, which is the same as the value for pK_2, obtained by a different method, that is shown in Figure 12.

B. IMPROVED SULFIDE-ION-SELECTIVE ELECTRODE (Solid-Junction Electrode)

The drawback in using the sulfide-ion-selective membrane electrode is that the mv response decays with time, resulting in a deviation from the Nernstian relationships and causing S_T concentration errors. The cause of this decay is not well known; one possible explanation is that metallic silver may accumulate on the surface of the electrode. In any case, it has been found that by repolishing the electrode surface with fine mesh aluminum oxide grit the performance of the sulfide electrode can be improved. The initial decay time of the Orion sulfide electrode was around 80 hours in continuously monitored

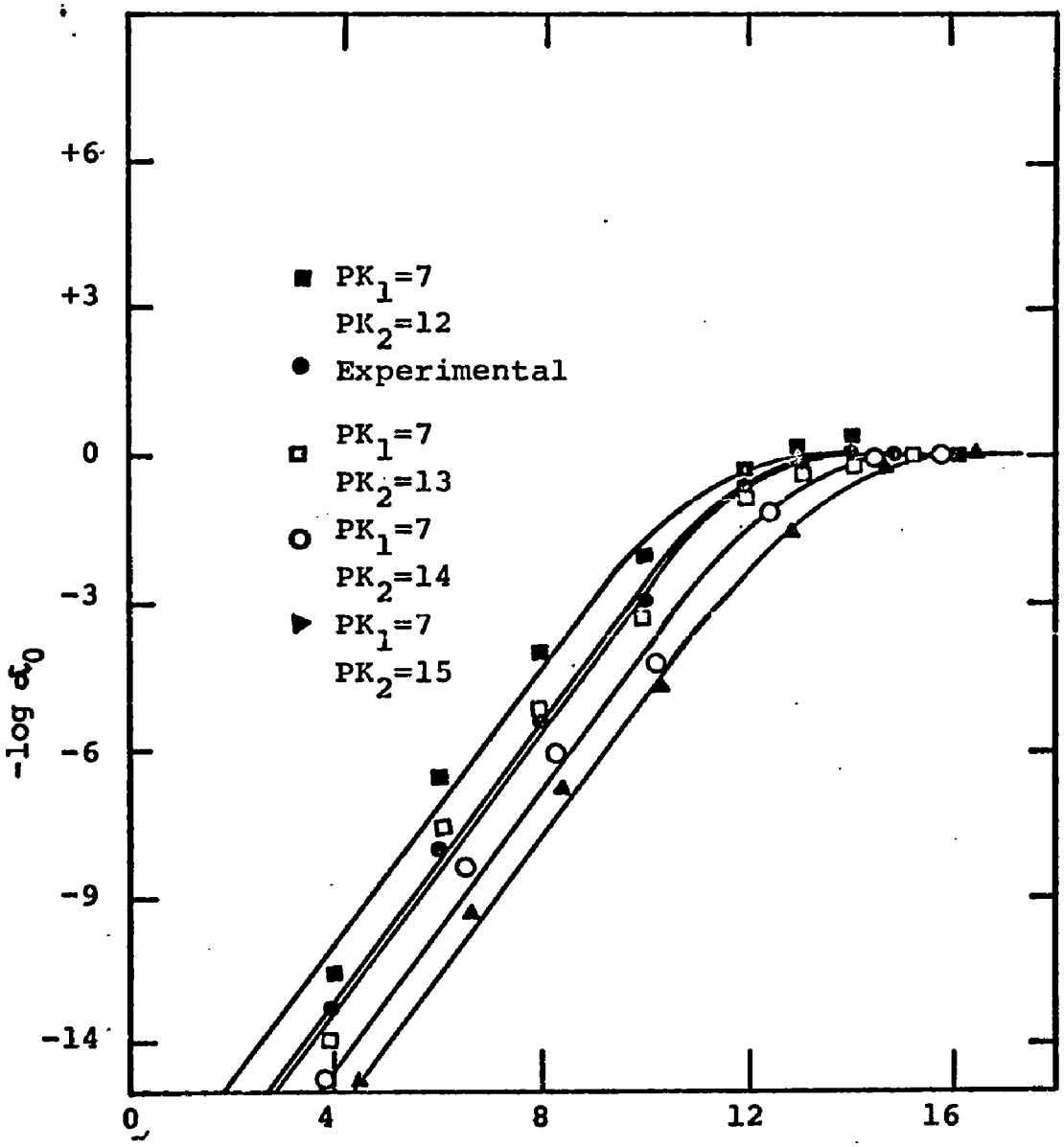


FIGURE 13. Experimental and theoretical α coefficients vs. pH for hydrogen sulfide.

experiments; after repolishing the surface of the electrode the decay time was about 40 hours in continuous usage.

It was impractical to buy several dozen sulfide electrodes at more than $200.00 each to do this kinetic study. Also, the diameter of the electrode surface of over 3/8 of an inch was thought to be large enough to cause some catalytic effect on the H_2S oxidation by DO (8). Therefore, the author of this work designed an improved sulfide-ion-selective electrode with a 1/8th inch membrane diameter, giving the surface of this electrode 1/9th the area of that of Orion in order to eliminate any catalytic effect or make it negligible. Another advantage of this new electrode is that it does not have an internal reference solution, only a 22 gauge copper wire as the electrical conductor. This electrode is used for sulfide detection in the hypolimnetic waters; it could be used as well in ocean bottoms. It is prepared under nitrogen gas and in darkness by precipitating $AgNO_3$ solution by H_2S gas, washing the Ag_2S precipitate with double glass-distilled water, air drying, pressing in a hydraulic press at pressures over 12,000 pounds, and finally connecting a copper wire and casting it in epoxy. Figure 14 illustrates the improved sulfide-ion-selective electrode, and Figure 15 demonstrates a typical calibration curve, plotting mv response against sulfide activity. The decay time of the mv response of this electrode is about 120 hours. The reference electrode used in this study was a saturated calomel electrode with a double agar salt bridge and was constructed in the laboratory.

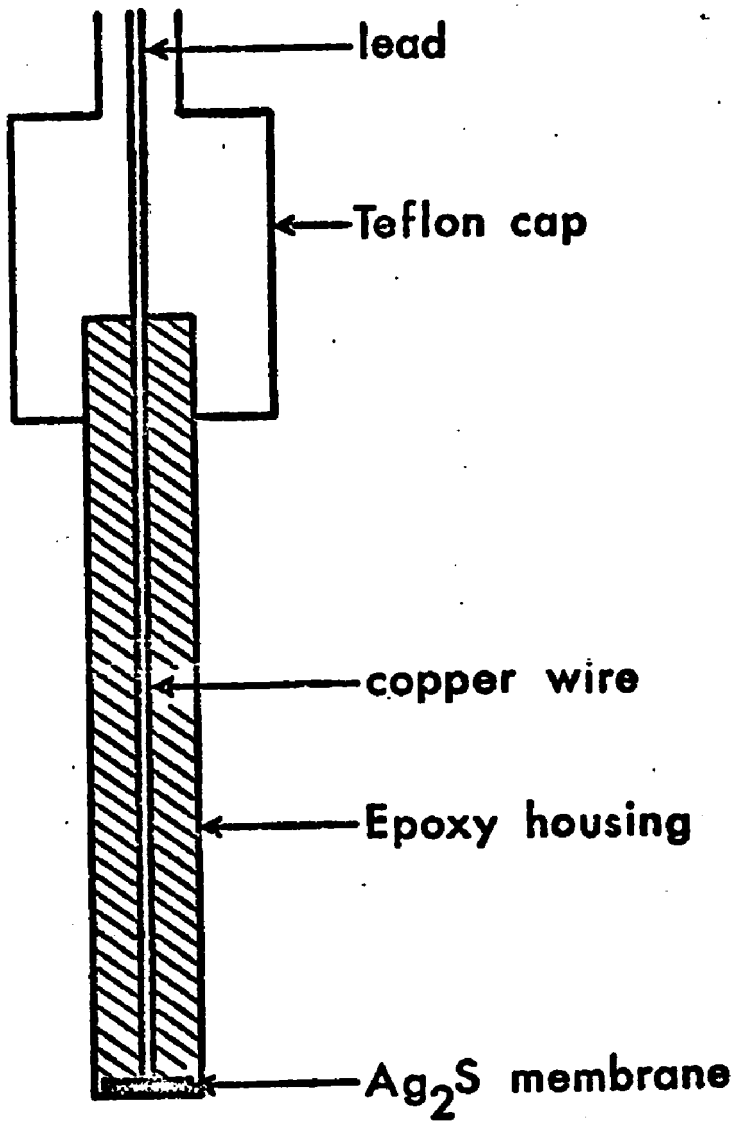


FIGURE 14. Sulfide-ion-selective solid junction membrane electrode.

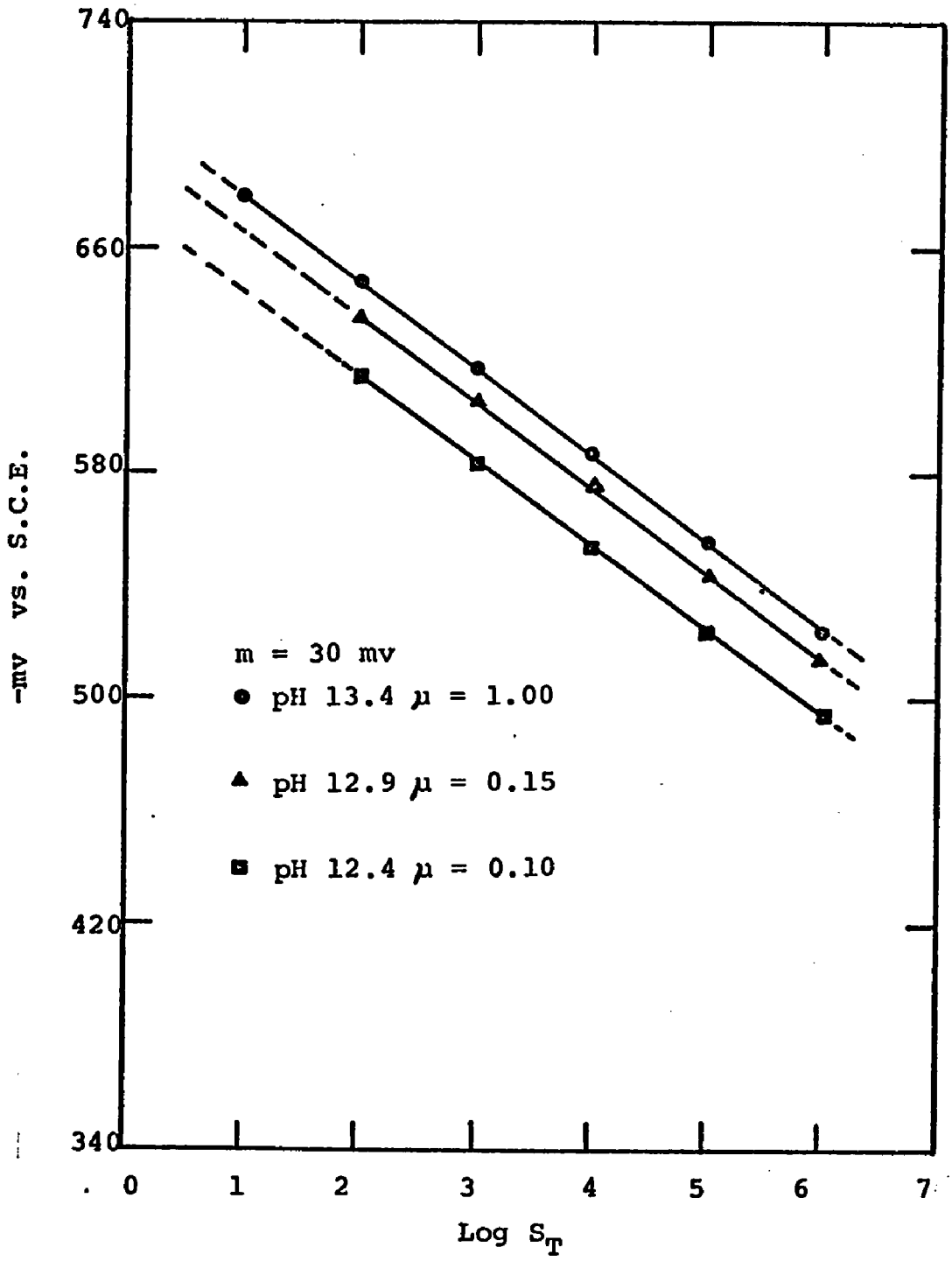


FIGURE 15. Solid junction sulfide electrode calibration

Figure 16 illustrates the salt bridge calomel reference electrode with micropore-size pore.

C. IN SITU MEASUREMENT OF TOTAL FREE SULFIDES (37)

In studying aquatic environments it is important to characterize the total sulfide activity as well as the activities of the various sulfide species. To this end it is necessary to be able to interpret the sulfide membrane electrode response not only in terms of sulfide-ion activities but also in terms of the total sulfide activity and the activity of the other sulfide species present. A simple analog circuit converter was therefore, designed which, when used with the sulfide membrane electrode and the glass electrode, gives direct measurements of total and free sulfide activities. This circuit was designed according to the following equations:

$$\log (S^{=}) = 33.78\ E_1 - 30.40 \tag{55}$$

$$\log (H^{+}) = \pm 16.89\ E_2 - 7.566 \tag{56}$$

$$+\log (HS^{-}) = -pH + pK_2 + \log (S^{=}) \tag{57}$$

$$+\log (H_2S) = -2\ pH + pK_1 + pK_2 + \log (S^{=}) \tag{58}$$

$$S_T = (H_2S) + (HS^{-}) + (S^{=}) \tag{59}$$

where:

E_1 = sulfide membrane electrode cell potential

E_2 = pH cell potential

S_T = total free-sulfide concentration.

Figure 17 shows the schematic diagram of the analog circuit with a selector knob attachment to measure total and free

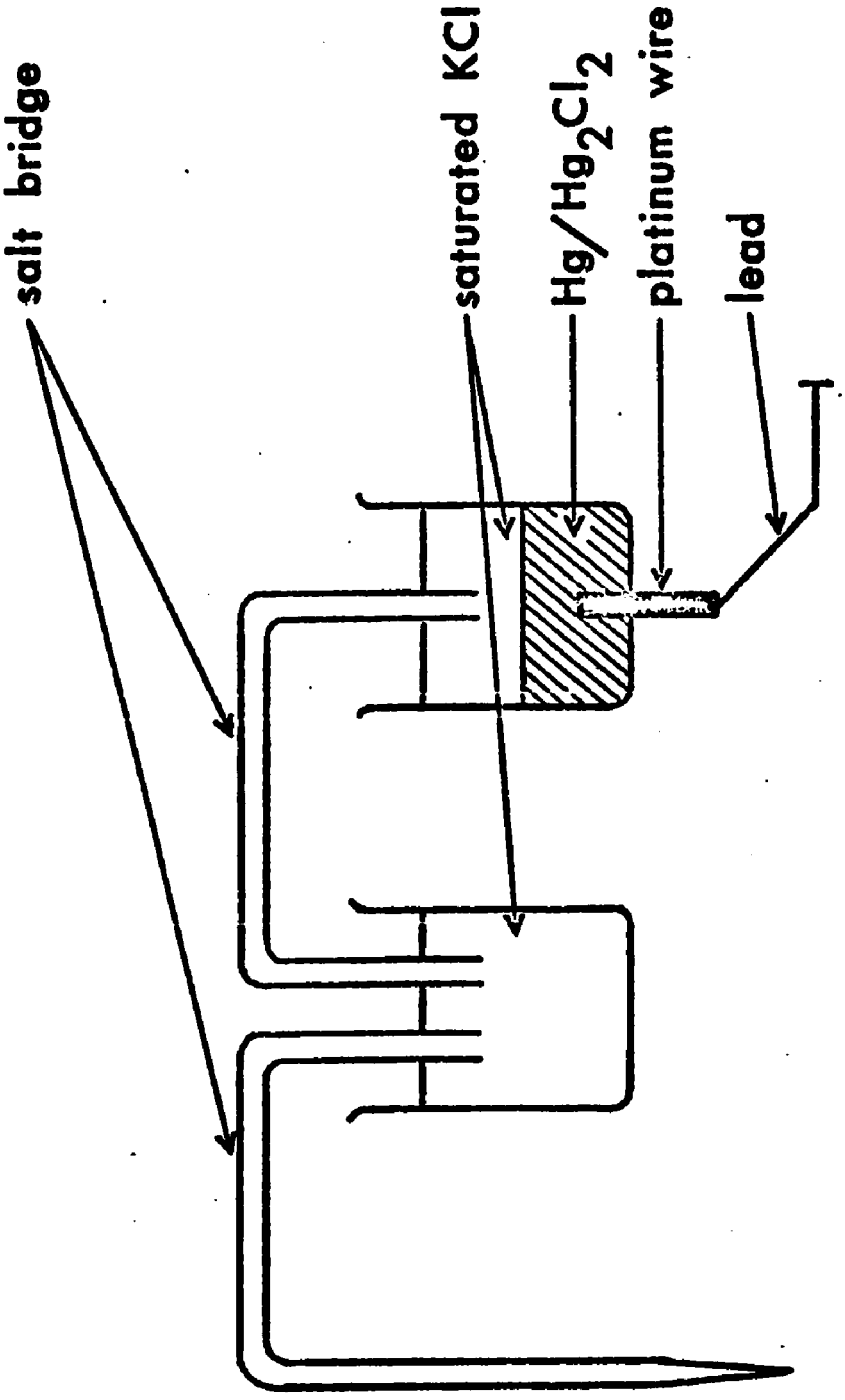


FIGURE 16. Double Junction saturated calomel electrode.

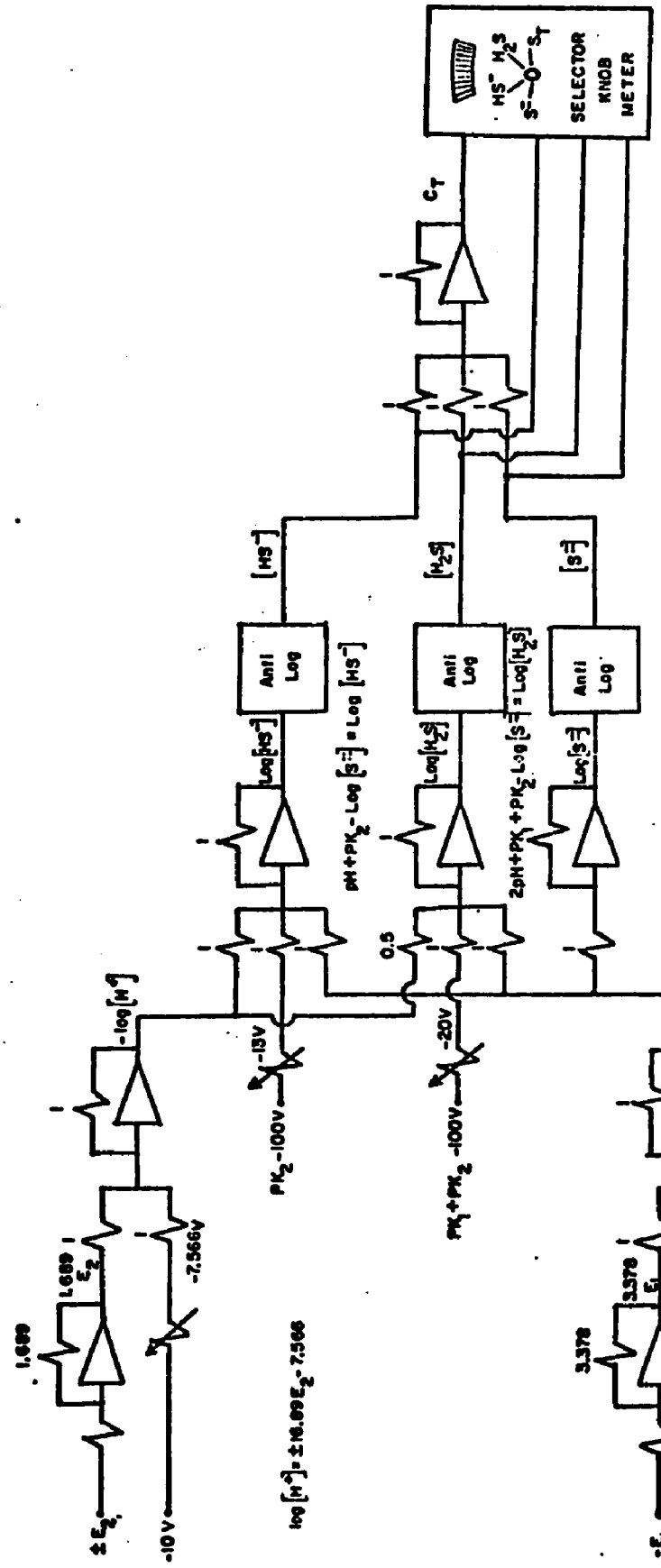


FIGURE 17. ANALOG CIRCUIT DIAGRAM FOR INSITU MEASUREMENTS OF SULFIDE ION ACTIVITY

sulfide species. The converter was made portable so that it could be used for in situ measurements in the field.

D. DISSOLVED OXYGEN ANALYSES IN PRESENCE OF SULFIDE

1. Modified Winkler Method (Iodine-Difference Method) (33,36,37)

First, the sulfide analysis is performed, and the exact amount of iodine needed to neutralize the sulfide is calculated. Then, 0.5 ml H_2SO_4 are added on top and shaken. Titration is performed with standardized $S_2O_3^=$ solution to the starch end-point. The oxygen concentration may then be calculated as follows:

$$\text{ppm } O_2 = \frac{(V_{S_2O_3} {}^{=}N_{S_2O_3}) - (V_{I_2} N_{I_2}) + (V_S^= N_S^=) \times 8000}{V_T} \qquad (60)$$

where:

$V_{S_2O_3}$ = is the volume of S_2O_3 = used in ml

$N_{S_2O_3}$ = is the normality of $S_2O_3^=$ used

V_{I_2} = is the volume of iodine in ml used

N_{I_2} = is the normality of iodine used

V_S = is the volume of sulfide in ml used

N_S = is the normality of sulfide used

V_T = is the total volume in ml

TABLE 7. STATISTICAL ANALYSIS OF OXYGEN DETERMINATION

Bottle Number	ml $S_2O_3^=$	+Blank Correction	$S_2O_3^=$	DO ppm	Deviation	Dev. Squared $x10^{-4}$
1	14.95	15.36	0.3170	8.57	0.05	25
2	14.79	15.20	0.3116	8.42	0.20	400
3	15.00	15.41	0.3184	8.42	0.01	1
4	14.98	15.39	0.3178	8.59	0.03	9
5	14.85	15.26	0.3144	8.50	0.12	144
6	15.02	15.43	0.3190	8.63	0.01	1
7	15.10	15.51	0.3210	8.68	0.06	36
8	15.29	15.70	0.3261	8.81	0.19	361
9	15.16	15.57	0.3226	8.72	0.10	100
10	15.03	15.44	0.3193	8.64	0.02	4

Mean = 9.62

$$\sum = 108 \times 10^{-4}$$

$$\sigma = \sqrt{\frac{1081 \times 10^{-4}}{10}} = 10.4 \times 10^{-2} \text{ ppm} \quad (61)$$

Thus, the 65% confidence level is 0.10 ppm, and the 95% confidence level is $\pm$0.21 ppm.

2. Method Using A Galvanic-Cell Oxygen Analyzer (GCOA)

In this study the Precision Scientific make of GCOA was used for DO analyses.

This method was described by Mancy, Okun, and Reilley (38). To avoid H_2S interference while analyzing for DO, the existing membrane is covered with a second membrane that is saturated with $Cd(NO_3)_2$. Any H_2S passing through the outer membrane is then precipitated as CdS, so that the electrode is not poisoned by sulfide. This improvement was developed by Mancy and Schmid (39). Figure 18 illustrates a typical calibration curve for the DO electrode.

E. pH MEASUREMENTS

The pH measurements were done with a Beckman Model 39004 glass electrode.

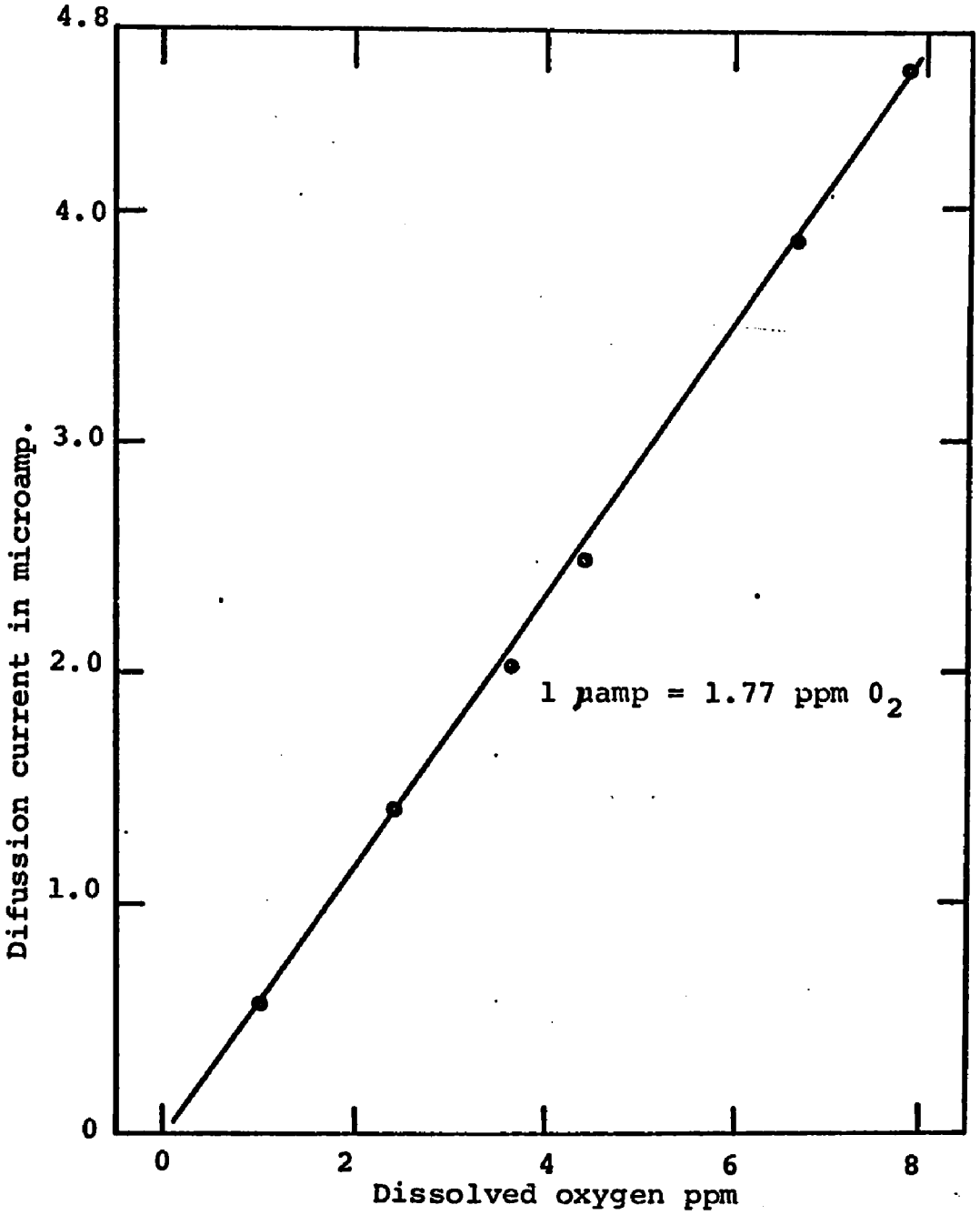


FIGURE 18. Dissolved oxygen electrode calibration.

VII. EXPERIMENTAL PROCEDURES

A. GLASSWARE CLEANING PROCEDURE

In order to achieve reproducible results in chemical reaction studies, it is necessary that a standard cleaning procedure should be adopted for all glassware used in the study in question. The steps in the standard cleaning procedure used in this work were:

1) soak in dichromate cleaning solution for several hours,
2) rinse in distilled water
3) boil in 0.1 NaOH for one hour
4) rinse in distilled water
5) boil in 0.1 N HCl for one hour
6) rinse in distilled water
7) apply a thin coating of silicone on the surface of the glassware where the solution is in contact with the glass.

After each experiment, wash the silicone coated glassware and rinse away the detergent with distilled water. Glassware treated in this manner is good only for five runs, after which all the above procedures should be repeated.

B. PROCEDURE FOR PREPARATION OF REAGENTS AND STOCK SOLUTIONS

Double glass-distilled water was used in this study, along with sodium sulfide ($Na_2S \cdot 9H_20$) analytical grade, from Baker Chemical. Stock solutions of $Na_2S \cdot 9H_20$ were prepared weekly

in oxygen free water, and before evey experiment S_T concentrations were determined using the methylene-blue method. Sulfide electrode calibrations were done before and after every experiment.

Ferrous chloride, ferric chloride, and ferrous sulfide reagents were obtained from Baker Chemical. All iron solutions were prepared fresh daily.

Synthetic water was prepared by bubbling a mixture of O_2 and N_2 through double-distilled water. In order to prevent the oxidation of sulfide from changing the pH of the solutions, this water was buffered with a borate-borax buffer to a level between pH 6.90 and pH 8.60. The ionic strength of all such water was kept at 0.01.

All of the chemicals used in these studies were analytical grade and nearly all were from Baker Chemical Company.

C. PROCEDURE FOR HANDLING NATURAL WATER

Samples of hypolimnetic water were taken into the laboratory for sulfide oxidation studies. The lake samples were treated in the following ways:

1. Sample was not filtered.
2. Sample was filtered through Whatman No. 2 paper.
3. Sample was microfiltered through a 0.45 μ pore-size membrane filter.

All samples were oxygen-saturated and sulfides were added to make the desired total sulfide concentrations. They were buffered in the same manner as were the synthetic water samples.

The lake samples were taken from Frain's Lake and Third Sister Lake. The former is located on Plymouth Road five miles northeast of Ann Arbor, Michigan, and the latter is on Liberty Road three miles west of Ann Arbor. The chemical oxygen demand (33) in these lakes was 3 to 4 ppm, and the total iron concentration was 1.2×10^{-7} M. The iron analysis was done by the phenanthroline method (33).

All organics were removed by ultraviolet (UV) irradiation, the samples being irradiated in a shallow, open Pyrex dish. After eight hours of irradiation the chemical oxygen demand was undetectable. The evaporated volume was then reconstituted by adding double distilled water.

The cations were removed from natural water by passing the water through acid-treated cation exchange resin (Dowex 50-x8, 20-50 mesh) at a rate of 500 ml per hour.

The Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} concentrations in the lake samples were below 1×10^{-8} M/l; the anodic stripping voltametry technique was employed for these heavy metal analyses (40).

D. BOD REACTOR SYSTEM PROCEDURE

At early stages of this study the reactor vessels used were biological oxygen demand (BOD) bottles. The iodometric method for total sulfide determination and the iodine difference method for DO determination were performed. The pH measurements were done before and after each run. Aliquots of the buffered sulfide solutions were siphoned into BOD bottles.

The BOD bottles were placed in a thermostatically controlled shaker-bath at 25°C. At different time intervals, for four days the BOD bottles were analyzed for total sulfide and DO titrometrically as described above. Control bottles were run at the same time with and without oxygen.

The results of BOD reactor systems were not always consistent and reproducible, due to the loss of H_2S from the bottles when acid was added for the iodometric method of S_T determinations; similarly, oxygen determinations were not very reliable. In addition, it was difficult to treat each bottle exactly the same as every other. Therefore, the BOD bottle reactor system was abandoned. The results using this system are presented, however in Appendix III. Next a continuous monitoring method for analysis, the stirred batch reactor system, was considered.

E. STIRRED BATCH REACTOR PROCEDURE

Each three-liter batch of buffered solution was prepared and saturated with oxygen at ionic strength of 0.01. Stock solution was added to make the desired total sulfide concentration. The solution was siphoned into a three-liter glass container, which was then placed into a thermostatically controlled stirred bath at 25°C. Continuous measurements were taken for sulfide ion activity by means of a sulfide electrode; for DO by the oxygen analyzer; and for pH by a glass electrode, before and after each run, using a saturated calomel electrode as the reference. The glass batch reactors were

covered with a tight plexiglas cover to assure a closed system. Figure 19 illustrates the stirred batch reactor. This reactor system was satisfactory, the results were reproducible, the experiments were simple to handle, and it was an efficient system for a kinetic study of sulfide oxidation.

F. RATE DETERMINATION PROCEDURES

The oxidation rate of sulfides by dissolved oxygen can be expressed as the rate of disappearance of sulfide or as the rate of reduction of oxygen. The S_T disappearance was measured by the improved sulfide-ion-selective electrode, using the double bridge reference electrode mentioned earlier. The mv response was recorded continuously on a stripchart recorder using Hewlett Packard Model 7100 B Autograf recorder; and the methylene-blue method of analysis was done for confirmation. Oxygen reduction was measured by a galvanic-cell oxygen analyser, the microamp (ua) response was recorded continuously on a Varion Model G-1000 strip chart recorder, and confirming measurements were done by the iodine difference method. Sulfide concentrations from 1×10^{-5} M to 1×10^{-3} M and oxygen concentrations from 1×10^{-5} M to 1×10^{-3} M were covered.

The rates of reaction were defined as the slopes of plots of change in total sulfide concentration or oxygen concentration as a function of time for the interval following the lag period. During the lag period there is little change in concentrations of reactants. In this study oxidation

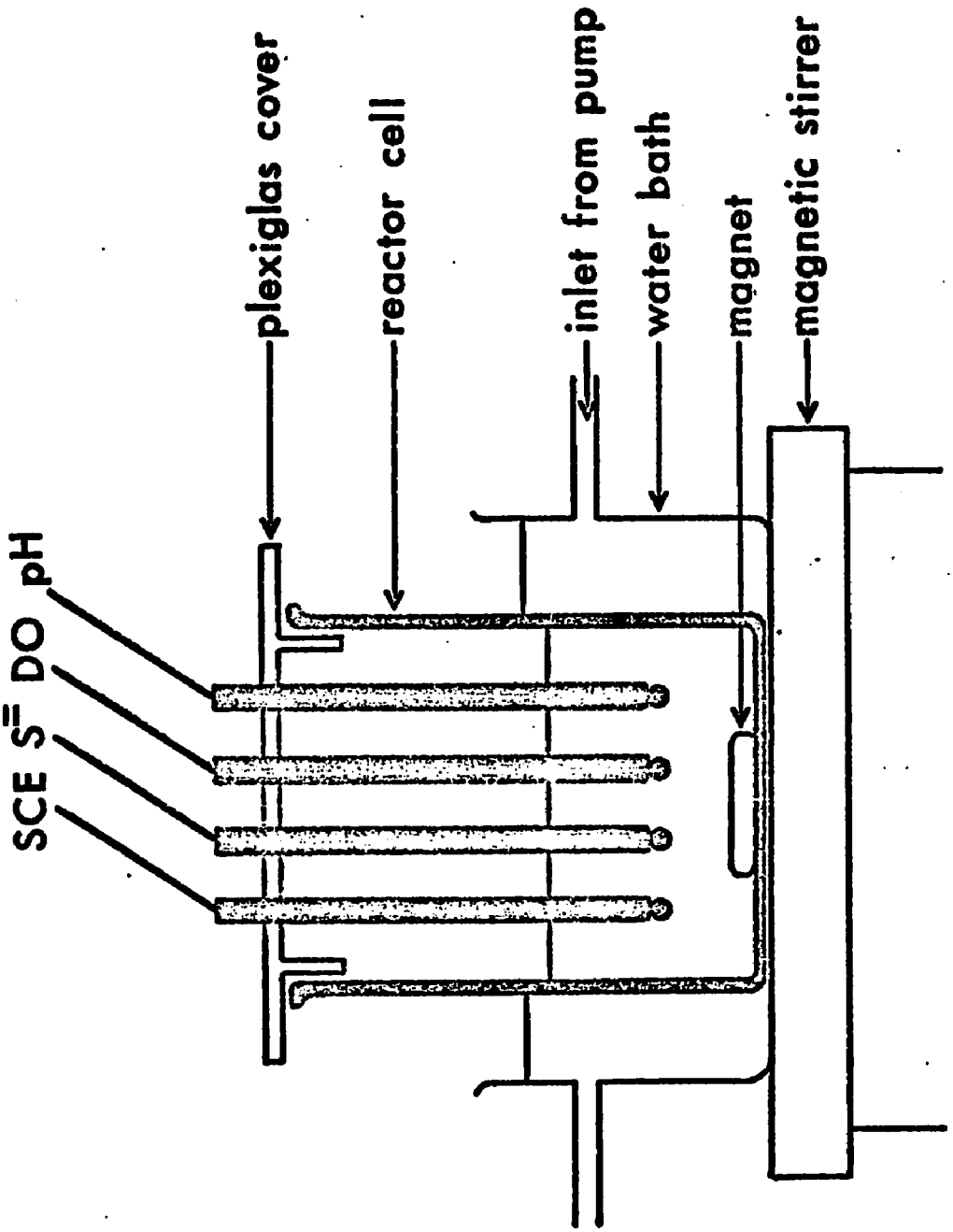


FIGURE 19. Glass Batch Reactor System.

rates were computed in order to facilitate the understanding of the mechanism of H_2S oxidation, including any catalytic effects of iron.

In general, reaction rates can be expressed as follows (41):

$$aA + bB = \text{products}$$

Thus

$$\frac{-dA}{dt} = k\, A^x B^y \ldots$$

x and y refer to the order of reaction with respect to DO and H_2S, respectively. Rate k has dimensions $(\text{conc.})^{1-n}\ (\text{time})^{-1}$. In a first order reaction k = liter/mM/day. Table 8 represents a summary of rate expressions.

The outputs of the oxygen electrode and the sulfide electrode as a function of time and pH were fed into an IBM Model 1130 computer. The rate expressions were computed as first order and second order reations and then plotted to express the rate and order of the reaction. The computer program for the rate determinations is presented in Appendix I. The computer output for the experimental data is presented in Appendix II. The rate of oxygen and sulfide disappearance is the interest of this kinetic study. Developing an empirical equation in this kind of complex reaction system would not be of great importance; furthermore, because of the numerous factors of catalytic and inhibitory elements occurring in natural waters it would be very difficult.

Table 8. Summary of Rate Expressions (42)

Order	Differential Eq.	Integrated Expression
0	$x = 0$, $y = 0$ $\quad -\frac{dA}{dt} = k_a$	$k = \frac{A_o - A}{t}$
1	$x = 1$, $y = 0$ $\quad -\frac{dA}{dt} = k_A A$	$k = \frac{1}{t} \ln \frac{A_o}{A}$
2	$x = 2$, $y = 0$ $\quad -\frac{dA}{dt} = k_A A^2$	$k = \frac{1}{t}\left(\frac{1}{A} \quad \frac{1}{A_o}\right)$
2	$x = 1$, $y = 1$ $\quad -\frac{dA}{dt} = k_A AB$	$k = \frac{a \ln (A/A_o)(B_o B)}{t\,(bA_o - aB_o)}$

Similar expressions can be written for B by substituting the appropriate values for x and y.

VIII. EXPERIMENTAL RESULTS

A. EXPERIMENTS IN SYNTHETIC SYSTEM

In these experiments double distilled water was used, and the solutions were buffered with borate at an ionic strength (u) 0.01. Sulfide oxidation was studied in the presence of oxygen at various dissolved oxygen to total sulfide ratios. The glass batch reactor procedure was used.

1. Experiments in Equal Molar Concentrations of S_T and DO at pH 8.60

Figure 20 shows semilogarithmic plots of the rate of removal of S_T and DO. When the DO to S_T concentration ratio DO/S_T was about one, the rates adhered to a typical first order reaction. The slope of the sulfide oxidation (K_{S_T}) curve was estimated to be 1.6×10^{-4}/min as a first order reaction. The slope of the DO removal curve (K_{DO}) was estimated to be 1.4×10^{-4}/min also as a first order reaction. The comparable reproducible K values were $K_{S_T} = 1.7 \times 10^{-4}$/min and $K_{DO} = 1.3 \times 10^{-4}$/min. This experiment illustrates the reproducibility of the experimental procedures using a sulfide ion selective electrode and galvanic cell oxygen analyzer. It is of interest to attempt to find the "limiting concentration levels"of S_T and DO. The limiting concentration levels being defined as the concentration levels of the reactants at which there is no appreciable reaction taking place.

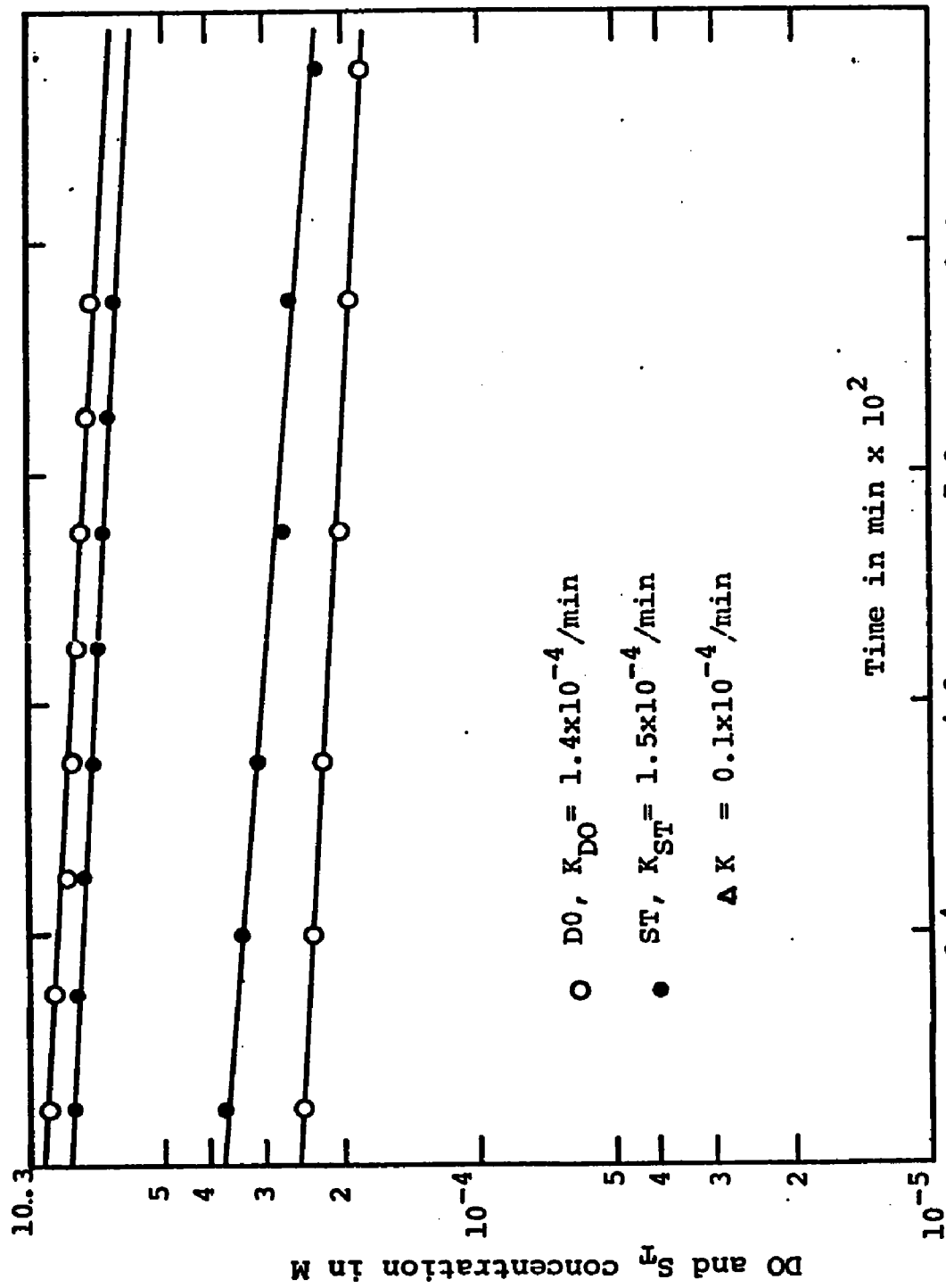


FIGURE 20. Sulfide oxidation in synthetic system at pH 8.60, $DO/_{ST}$=1 and @ 25°C.

2. Experiments in Excess of Oxygen at pH 8.60

Figure 21 illustrates the results of experiments in which the initial S_T concentration was 1.7×10^{-4} M and DO 9×10^{-4}M. The DO/S_T was about 6.4 and the pH 8.60. Semilogarithmic plots of this experiment suggest that both S_T and DO removals were first order reactions, with $K_{S_T} = 3.5 \times 10^{-4}$/min and $K_{DO} = 4.5 \times 10^{-5}$/min. As expected this experiment shows that when the $DO/_{S_T}$ was large, such as 6.4 (that is, the DO concentration is more than six times the S_T concentration), there was a significant rate increase with respect to S_T and a decrease with respect to DO, in comparison to the experiments where the DO/S_T of one. The K_{S_T} was increased by a factor of two, and the K_{DO} was decreased by a factor of three over the DO/S_T of one. When the DO/S_T was increased to about 19, the K_{S_T} was 6×10^{-3}/min, and the K_{DO} was 4.2×10^{-5}/min. Figure 22 shows the semilogarithmic plots of this experiment. These results show that as the oxygen concentration increases to greater than that of sulfide, (levels of super saturation) the oxygen consumption decreases until it reaches very slow rate. This decrease in DO consumption rate was exponential. The reverse was true for K_{S_T}: as the S_T concentration decreased with respect to DO concentration, the K_{S_T} increased rapidly. This increase in K_{S_T} was exponential. Figure 23 shows the plots of K_{S_T} and K_{DO} versus DO/S_T.

3. Experiments in Excess Sulfide at pH 8.60

Experiments were performed at total sulfide concentrations higher than those of dissolved oxygen. The conditions of the

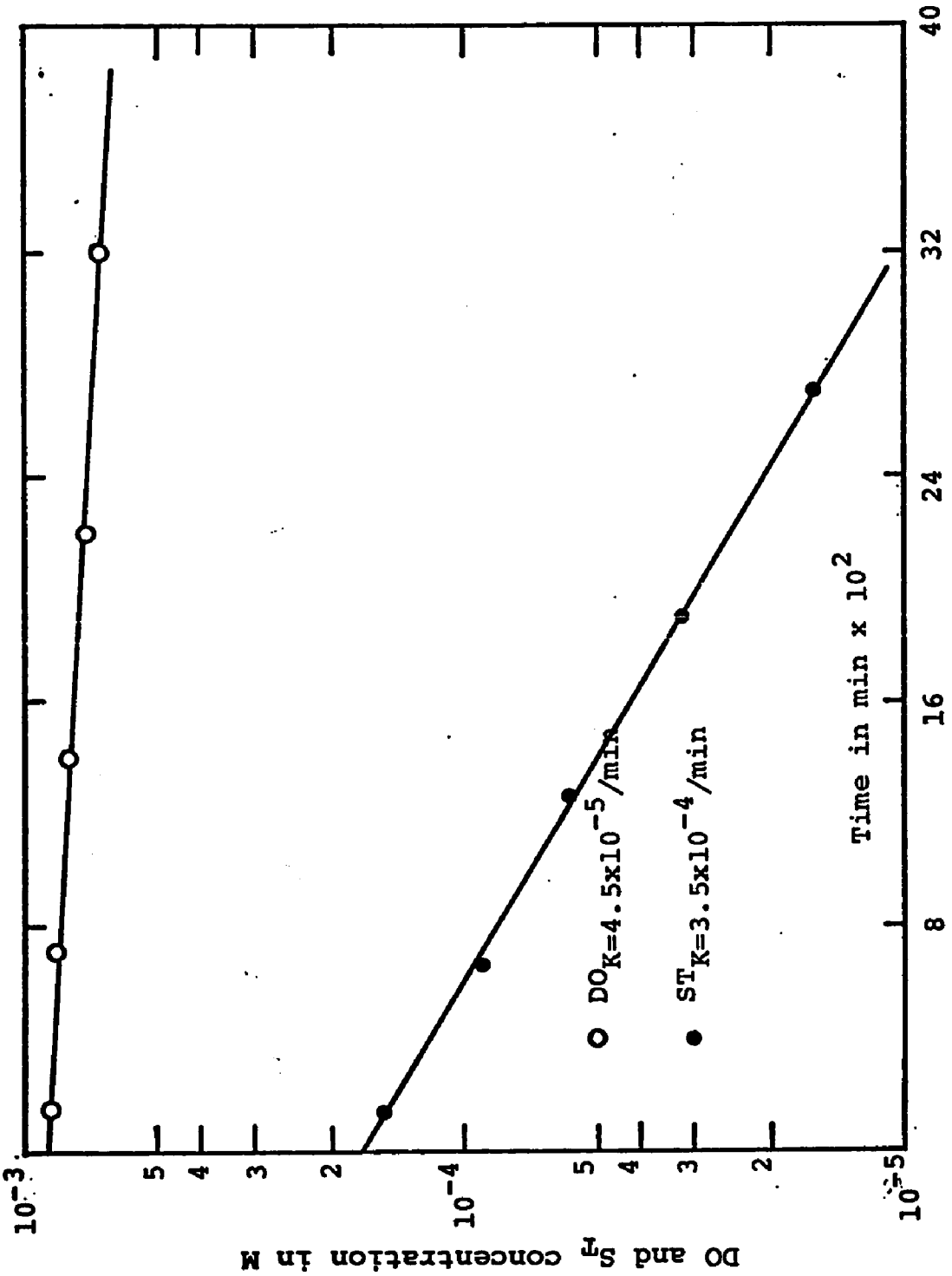


Figure 21. Sulfide oxidation in synthetic system at pH 8.60, $DO/_{ST}$ 6.4 and @ 25°C.

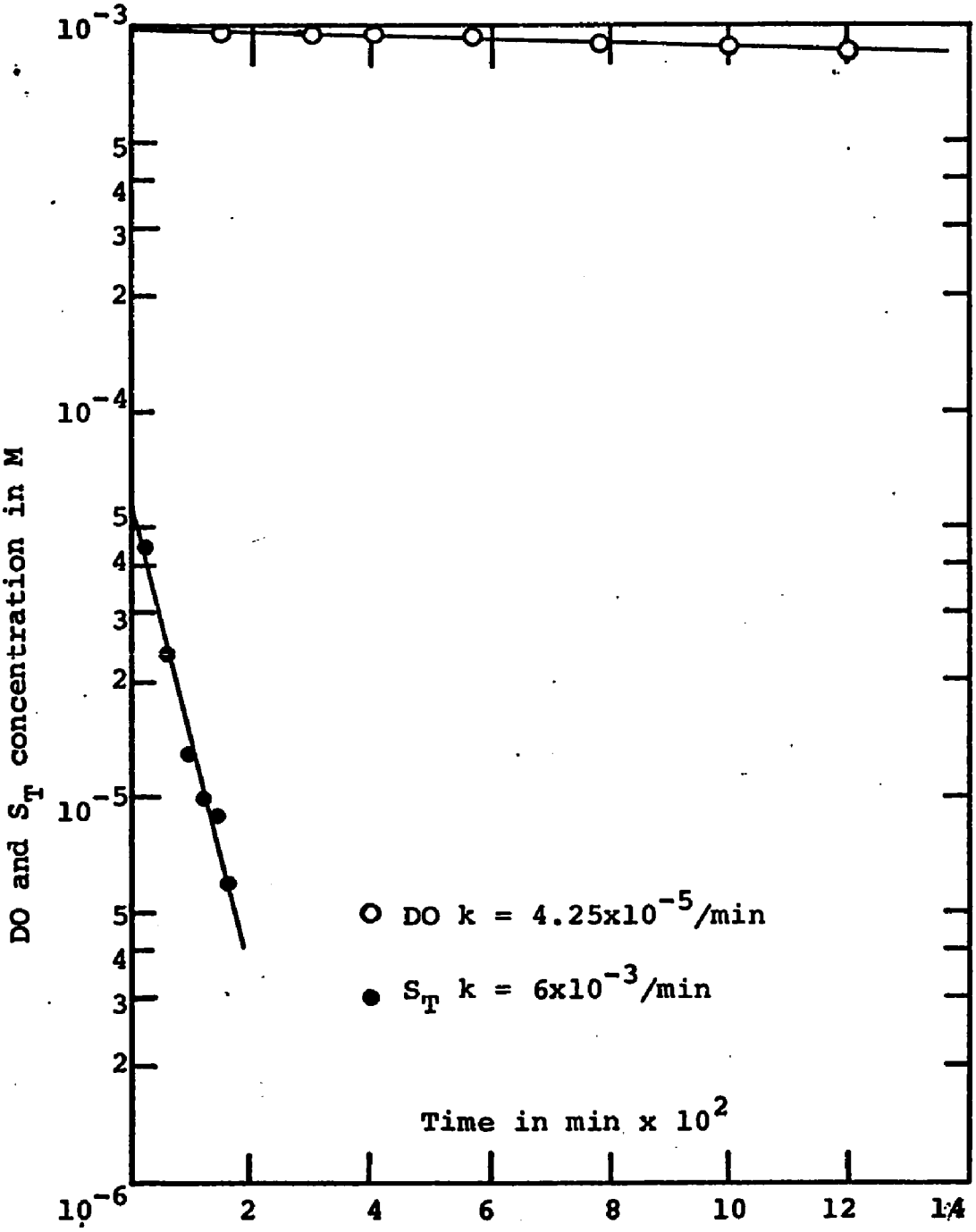


FIGURE 22. Sulfide oxidation in synthetic system at pH 8.60 DO/S_T 19 and at 25°C.

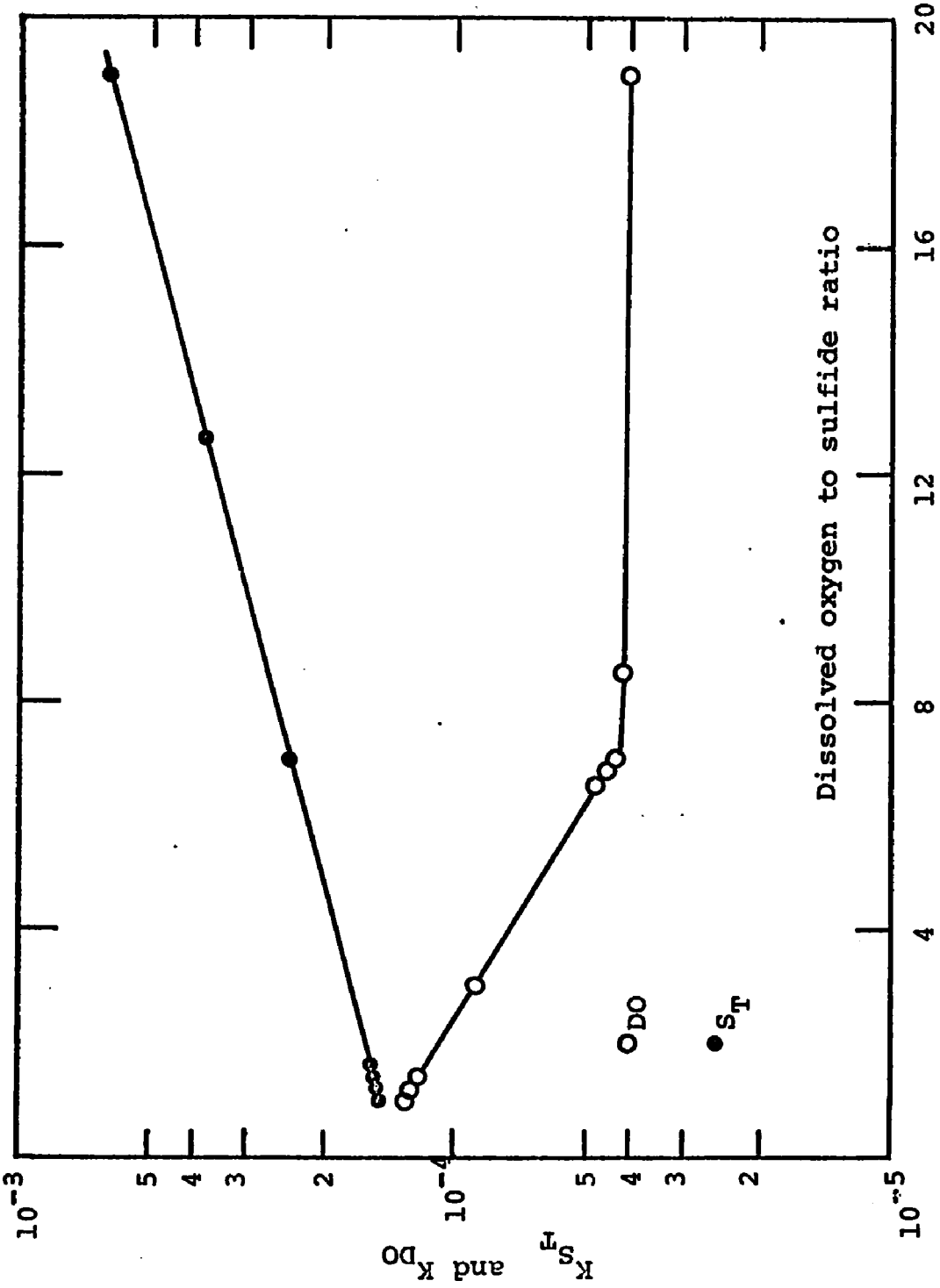


FIGURE 23. Rate constant for DO and S_T vs DO/S_T at pH 8.60 and @ 25°C.

experiments were similar to those conducted with excess oxygen. Figure 24 shows the results of a typical experiment, where the $S_T/DO = 4$. Plotted semilogarithmically, the K_{S_T} was 6.5×10^{-5}/min, and the K_{DO} was 4.5×10^{-4}/min. As expected sulfide removal by oxidation was slower than that of $S_T/DO = 1$, and the DO removal is about 3 times faster. The results of the experiment performed with $(S_T/DO) = 17.6$ are presented in Figure 25. At this ratio, the total sulfide concentration did not change to a measurable extent, and the K_{DO} was about 7.5×10^{-5}/min, which is relatively slow. The rate constant for dissolved oxygen removal was expected to be higher but on the contrary, was lower. This drop in K_{DO} at a higher $S_{T/DO}$ seems to signify that the oxygen concentration levels limit the reaction. At higher DO levels, sulfide was not very stable, and at very low oxygen concentrations, sulfide tends to be more stable.

4. Experiments at pH 7.00

Since most natural surface waters have pH values close to neutral, about 7.00, experiments were conducted at pH 7.00. Figure 26 shows the results of experiments done at pH 7.00, S_T concentration 2×10^{-4} M and DO concentration 2.4×10^{-4} M. The sulfide oxidation kinetics were second order with a rate constant ($K2_{S_T}$) of 5.5 l/M/min. The dissolved oxygen kinetics were first order with a rate constant (K_{DO}) of 3.5×10^{-5}/min. The DO/S_T was one. At 3×10^{-4} M of S_T and 1×10^{-3} M of DO the calculated $K2_{S_T}$ was 10 l/M/min, and the K_{DO} was

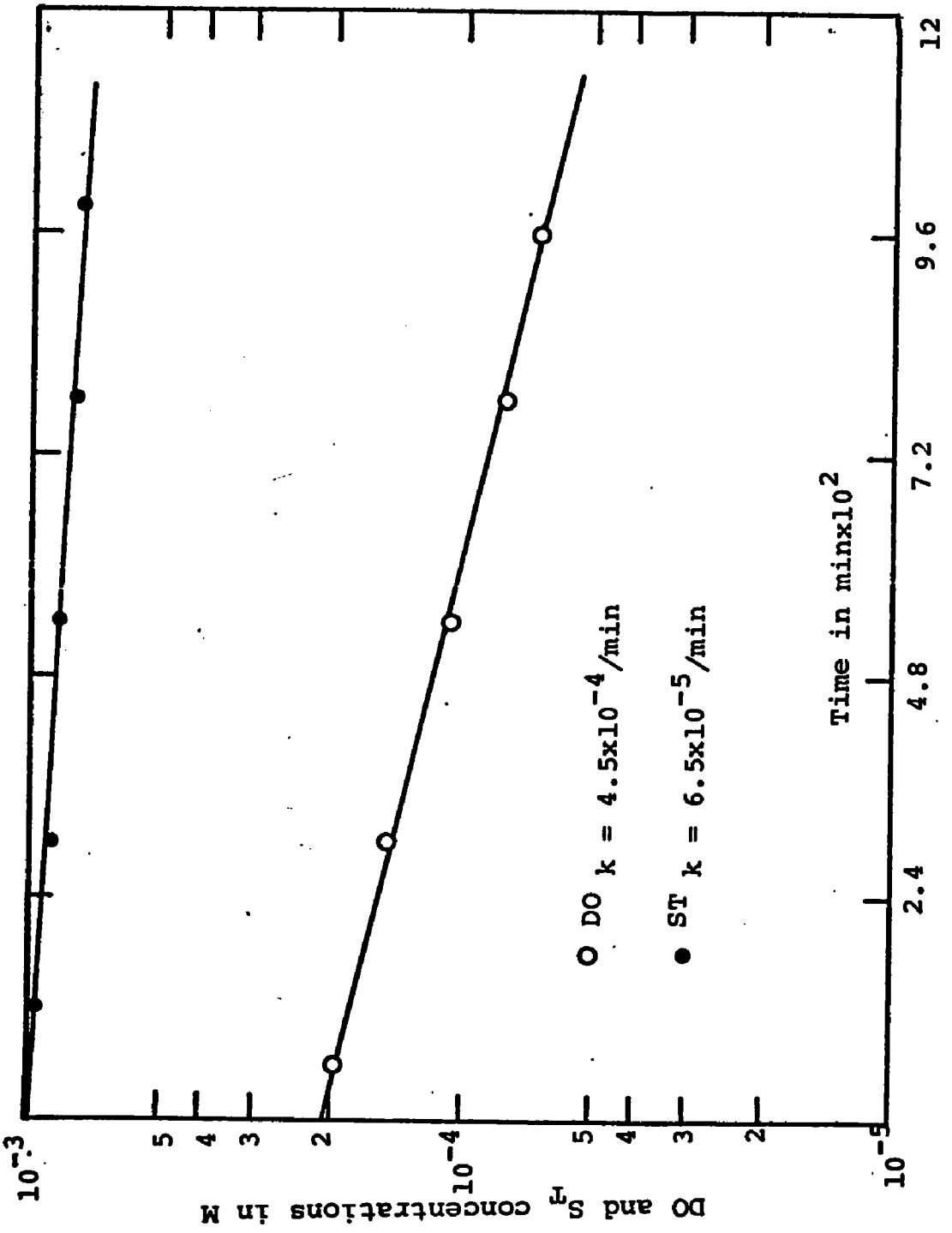


FIGURE 24. Sulfide oxidation in synthetic system at pH 8.60, $S_{T/DO}=4$, and at 25°C.

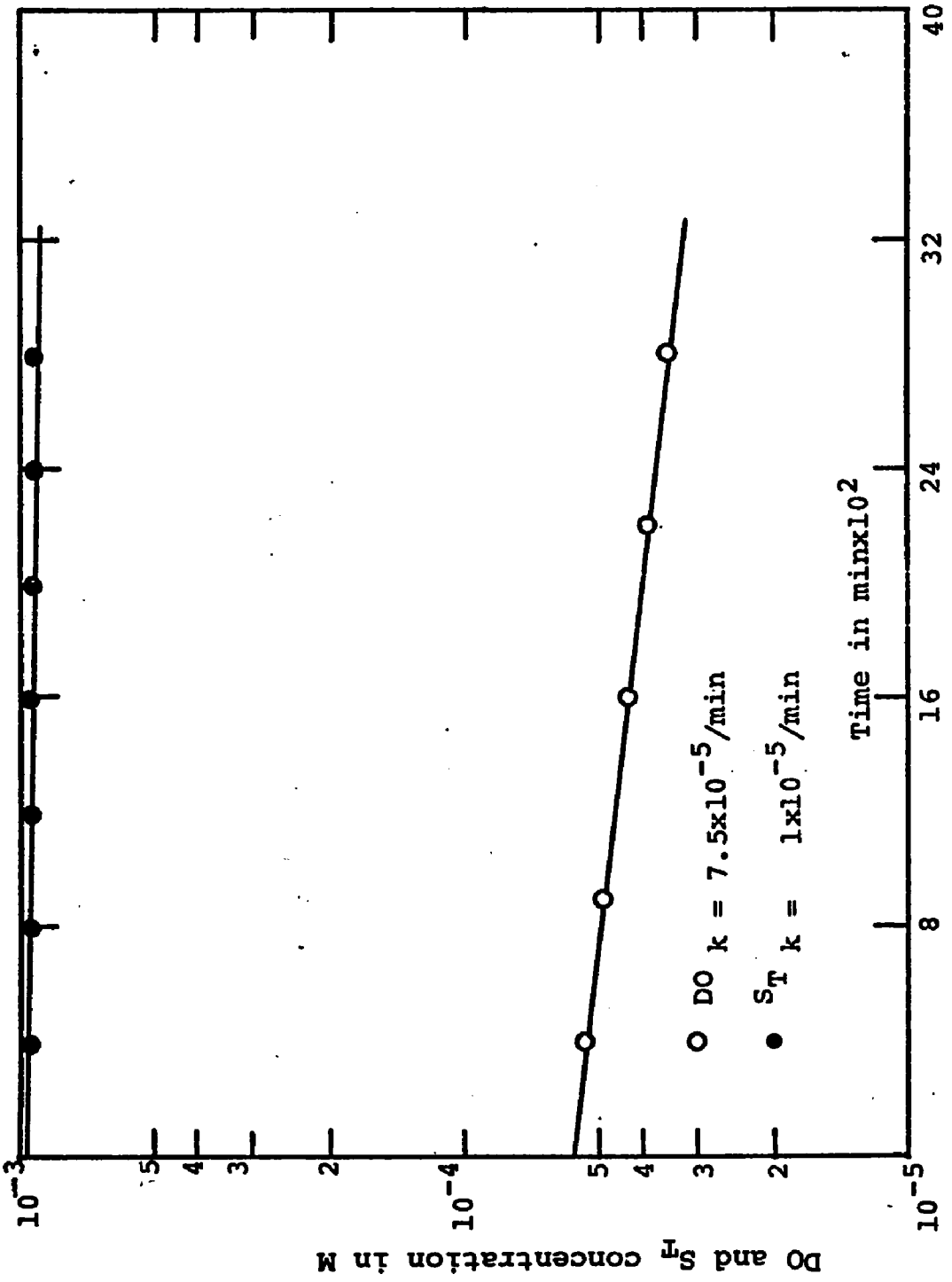


FIGURE 25. Sulfide oxidation in synthetic system at pH 8.60, $ST/_{DO}$=17.6, and at 25°C.

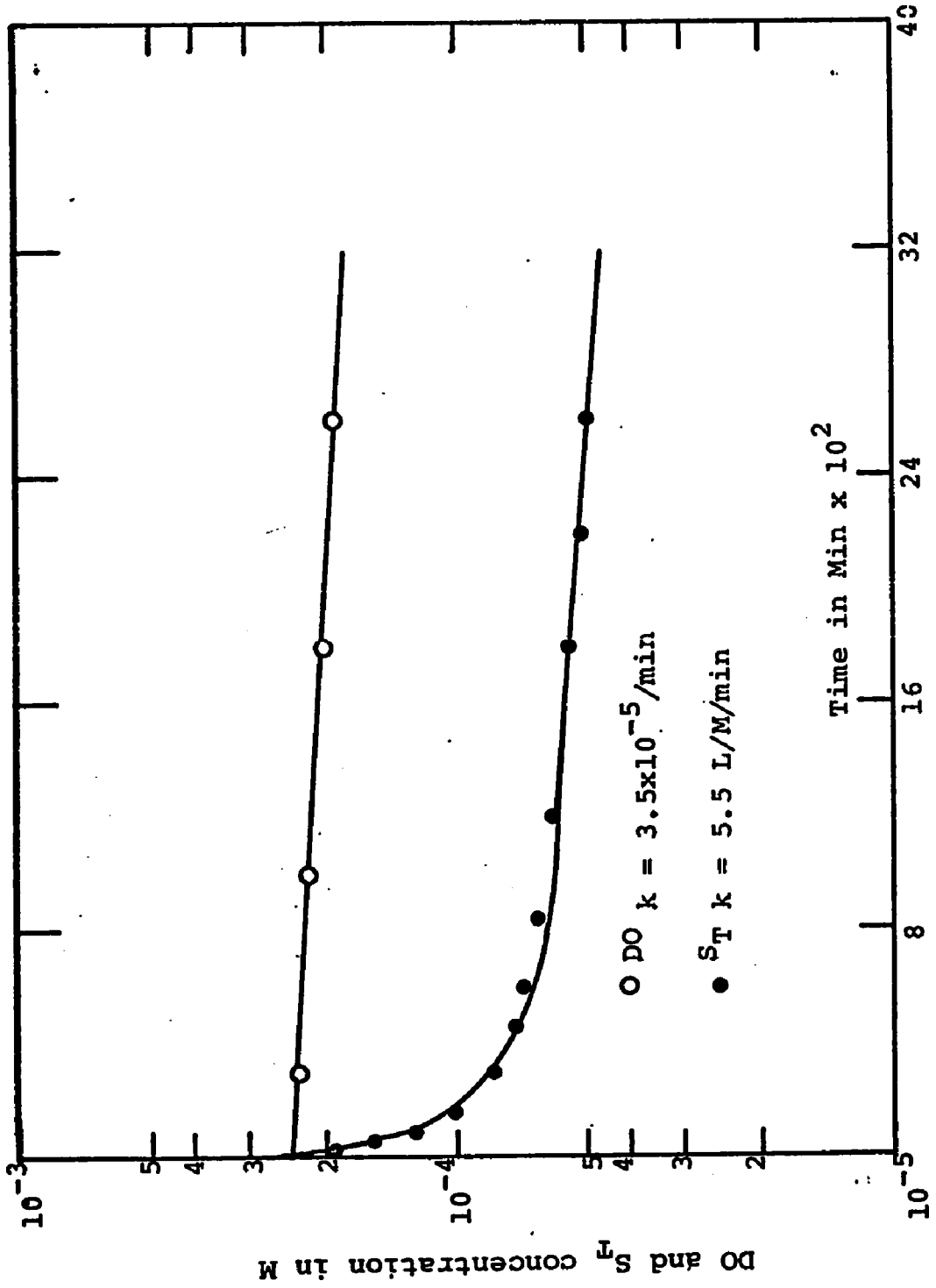


FIGURE 26. Sulfide oxidation in synthetic system at pH 7.00, $DO/S_T = 1$, and at 25°C.

3.8×10^{-5}/min; the DO/S_T was 3.33. Similarly, at DO/S_T of 33, the calculated $K2_{S_T}$ was 27.5 1/M/min, and K_{DO} was $4.\times 10^{-5}$/min. At higher DO/S_T, the sulfide oxidation rate increases, and the dissolved oxygen removal rate does not increase, it remains the same. Furthermore, at pH 7.00, the reaction rates were slower than those at pH 8.60. Table 9 shows the reaction rate constant dependency of DO/S_T at pH 7.00 and pH 8.60, including the stoichiometric relationships.

B. EXPERIMENTAL RESULTS WITH IRON PRESENT

This section of the research covers the effect of iron on the oxidation of sulfide. The study includes the effects of ferrous chloride ($FeCl_2$), ferric chloride ($FeCl_3$), ferric hydroxide ($Fe(OH)_3$) and ferric oxide (Fe_2O_3).

1. The Effect of Ferrous Chloride ($FeCl_2$) at pH 8.60

Figure 27 shows the results of the addition of ferrous chloride, 1×10^{-5} M concentration. The initial total sulfide concentration was 5.6×10^{-4} M and the dissolved oxygen concentration 9.5×10^{-4} M which is a super saturation level (not a concentration limiting factor). The DO and S_T removal are plotted semilogarithmically versus time in minutes. Ferrous iron was added through a three-way stopcok after the initial baseline reaction level was established. After 2280 minutes Fe(II) was added when the DO/S_T was 1.9. This experiment demonstrated the removal of DO and of sulfide immediately following the addition of Fe(II), 1×10^{-5} M. Part of the sulfide removal was due to ferrous sulfide precipitation (FeS),

TABLE 9. SUMMARY OF SYNTHETIC SYSTEM EXPERIMENTS

DO/S_T	pH	KST	KO_2	STOICHIOMETRY possible end product
1.14	8.60	1.6×10^{-4}	1.3×10^{-4}	$S_2O_3^=$
7.00	8.60		4.8×10^{-5}	
6.9	8.60		4.5×10^{-5}	
6.8	8.60	2.4×10^{-4}		
6.4	8.60	3.5×10^{-4}	4.5×10^{-5}	$SO_3^=$ and $S_2O_3^=$
18.77	8.60	6.00×10^{-3}	4.2×10^{-5}	$SO_3^=$
1.00	7.00	5.5 l/M/m	3.5×10^{-5}	$S_2O_3^=$
3.33	7.00	10/1/M/m	3.8×10^{-5}	$SO_3^=$
33.33	7.00	27.5 l/M/m	4.10^{-5}	$SO_4^=$
S_T/DO				
4	8.60	6.5×10^{-5}	4.5×10^{-4}	S^o sulfur
17.6	8.60	1×10^{-6}	7.5×10^{-5}	

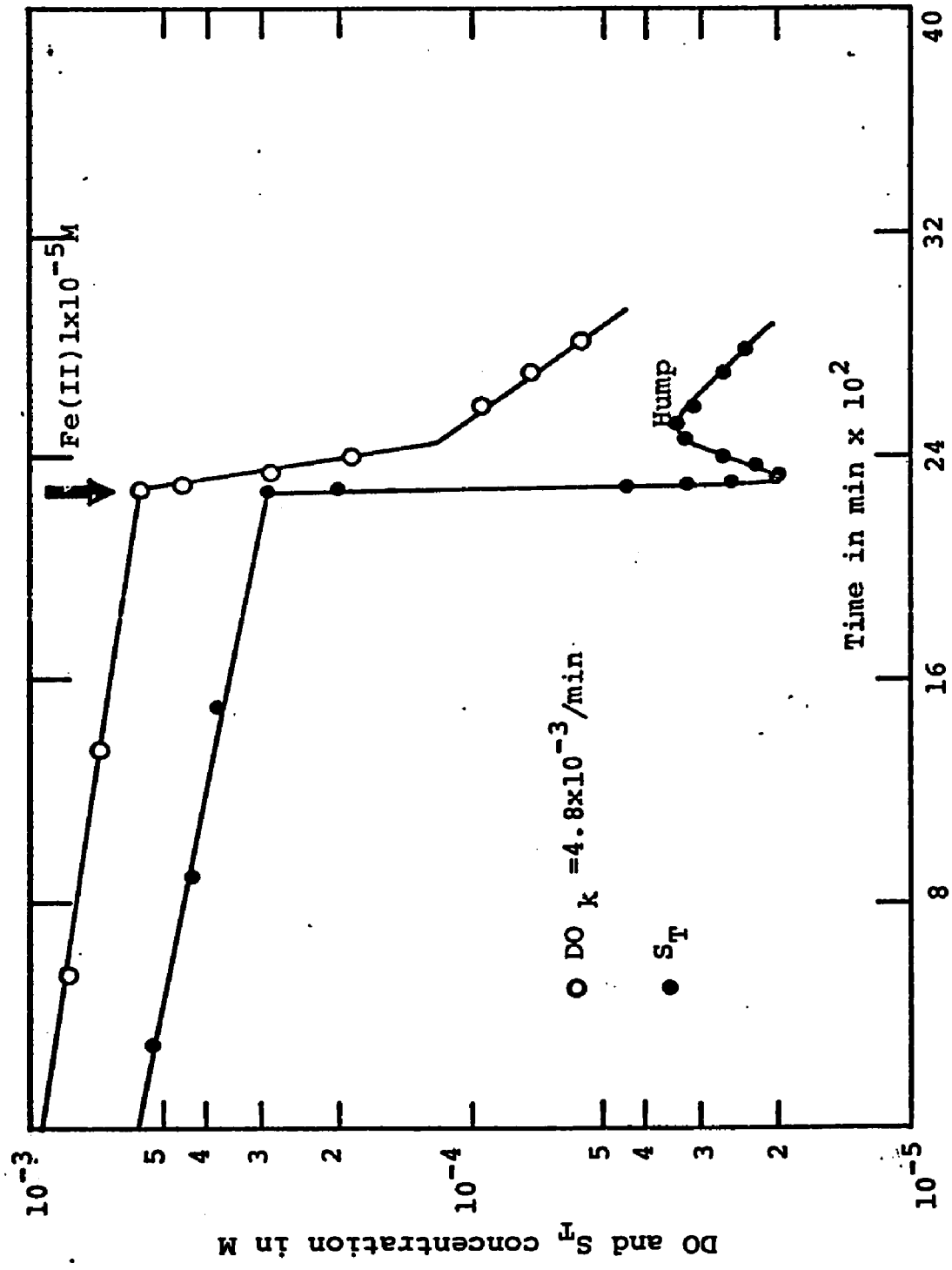


FIGURE 27. Sulfide oxidation in synthetic system at pH 8.60, DO/S_T=1.5, Fe(II) $1x10^{-5}$M and at 25°C.

1×10^{-5} M of sulfide was precipitated. The remaining sulfide $2.9\ 10^{-4}$ M was removed by oxidation with oxygen. (Stoichiometry of Fe(II) with $S^{=}$ reaction is presented in Appendix I). It appears that the S_T and DO kinetics following the addition of Fe(II), have two trends. The first trend represented by a sharp drop in S_T and DO concentrations due to precipitation of sulfide by the Fe(II) and oxidation by dissolved oxygen. The sulfide oxidation kinetics were first order with a rate constant (K_{S_T}) of 4.5×10^{-2}/min and the K_{DO} were 4.5×10^{-3}/min. The duration of this part, from the time of addition of Fe(II), was 45 min. The second part of the curve is represented by a "hump" (a parabola-shaped curve). The buildup time of the hump was about 200 min. The following explanation for the hump in the sulfide curve is proposed: in the first section, the unprecipitated sulfides were oxidized by oxygen. In the parabola-shaped curve region the precipitated ferrous sulfide began to oxidize, Fe(II) oxidized to Fe(III), and in turn Fe(III) hydrolyzed into $Fe(OH)_3$. Furthermore, accumulation of ferrous sulfide on the magnetic bar during the hump region was an indication that the precipitate was FeS. Berner has reported that FeS has magnetic property (43,44). An experiment was performed to see if the hump region was due to FeS oxidation.

Figure 28 illustrates the oxidation of FeS by DO in a system similar to that of Figure 27. A total of 1×10^{-4} M FeS was added and the DO concentration was 8.5×10^{-4} M at pH 8.60. This figure shows that the parabola-shaped curve, or

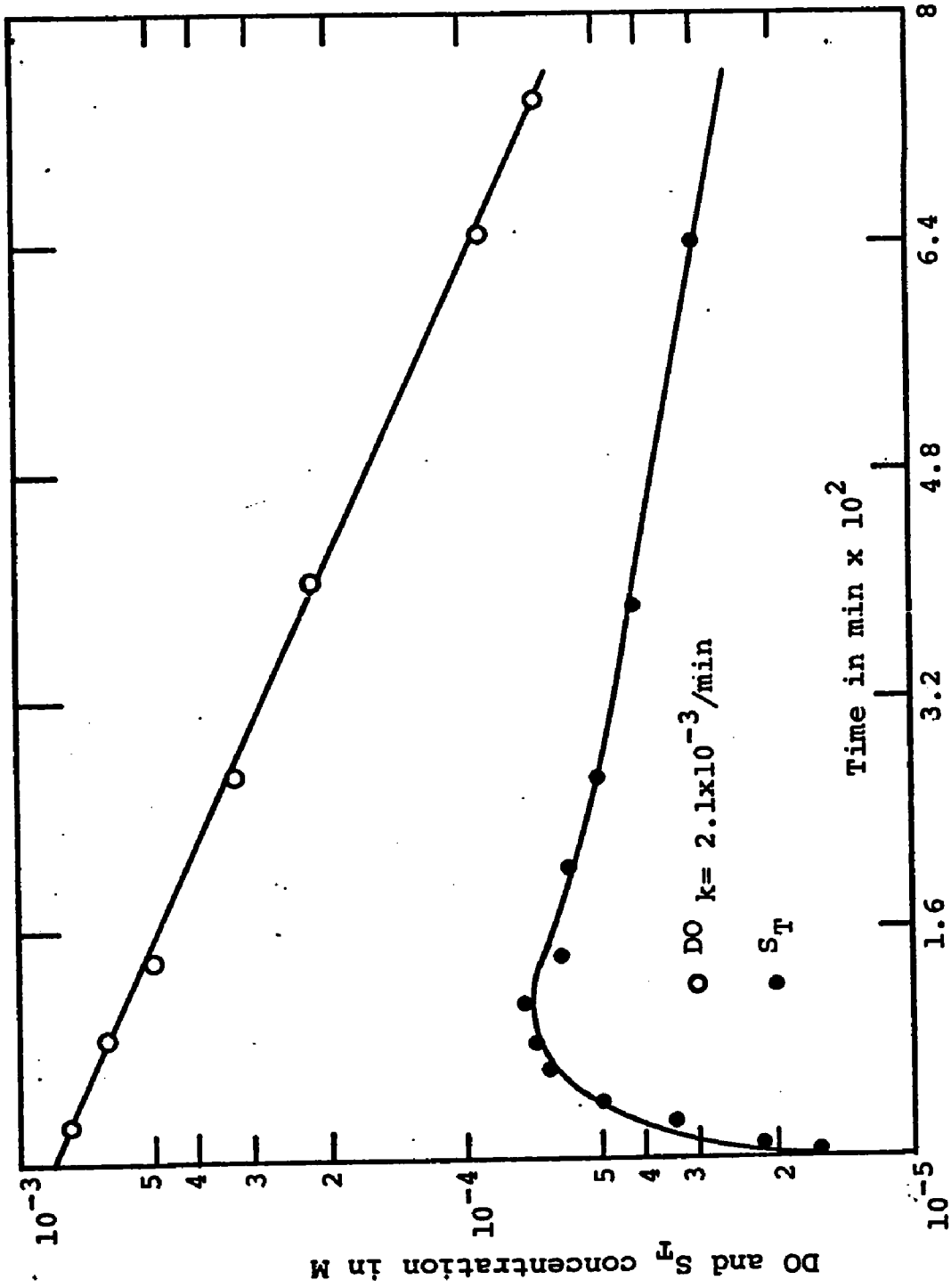


FIGURE 28. Sulfide oxidation in synthetic system at pH 8.60, FeS $1x10^{-4}$M and at 25°C.

hump, build-up was due to the Fe(II) oxidation of FeS. The chemical reactions for the oxidation by oxygen are as follows:

$$FeS \rightleftharpoons Fe^{2+} + S^{=} \quad (62)$$

$$Fe^{2+} + 1/4\ O_2\ (aq) + H^{+} \longrightarrow Fe^{3+} + 1/2\ H_2O \quad (63)$$

$$Fe^{3+} + 3\ H_2O \longrightarrow Fe(OH)_{3\,(s)} + 3H^{+} \quad (64)$$

$$8Fe^{3+} + FeS + 4H_2O \longrightarrow 9Fe^{2+} + SO_4^{2-} + 8\ H^{+} \quad (65)$$

Figure 29 shows the results of H_2S oxidation by DO in the presence of Fe(II) at 1×10^{-6} M and DO/S_T of 7.64. The initial K_{S_T} was 2.0×10^{-2}/min and the K_{DO} was 2.6×10^{-3}/min. This experiment shows that at lower concentrations of Fe(II), the catalytic effect on H_2S oxidation is less.

2. The Effect of Ferric Chloride ($FeCl_3$) at pH 8.60

Figure 30 shows the results with the addition of ferric chloride, 1×10^{-5} M concentration in a system similar to that of Figure 27. The initial S_T concentration was 4.1×10^{-4} M, and a DO concentration was 6×10^{-4}/M. Ferric iron was added after an initial baseline reaction level was established. It was added after 530 min when DO/S_T was 1.7. This figure illustrates the removal of DO and S_T immediately following the addition of Fe(III). The kinetics indicate that after the addition of Fe(III) there was a sharp drop in S_T concentration and a substantial drop in DO concentration. The $K2_{S_T}$ was 7.8×10^{-2} 1/M/min, as a second order reaction. The sharp drop in sulfide concentration was attributed to the catalytic effect of Fe(III)

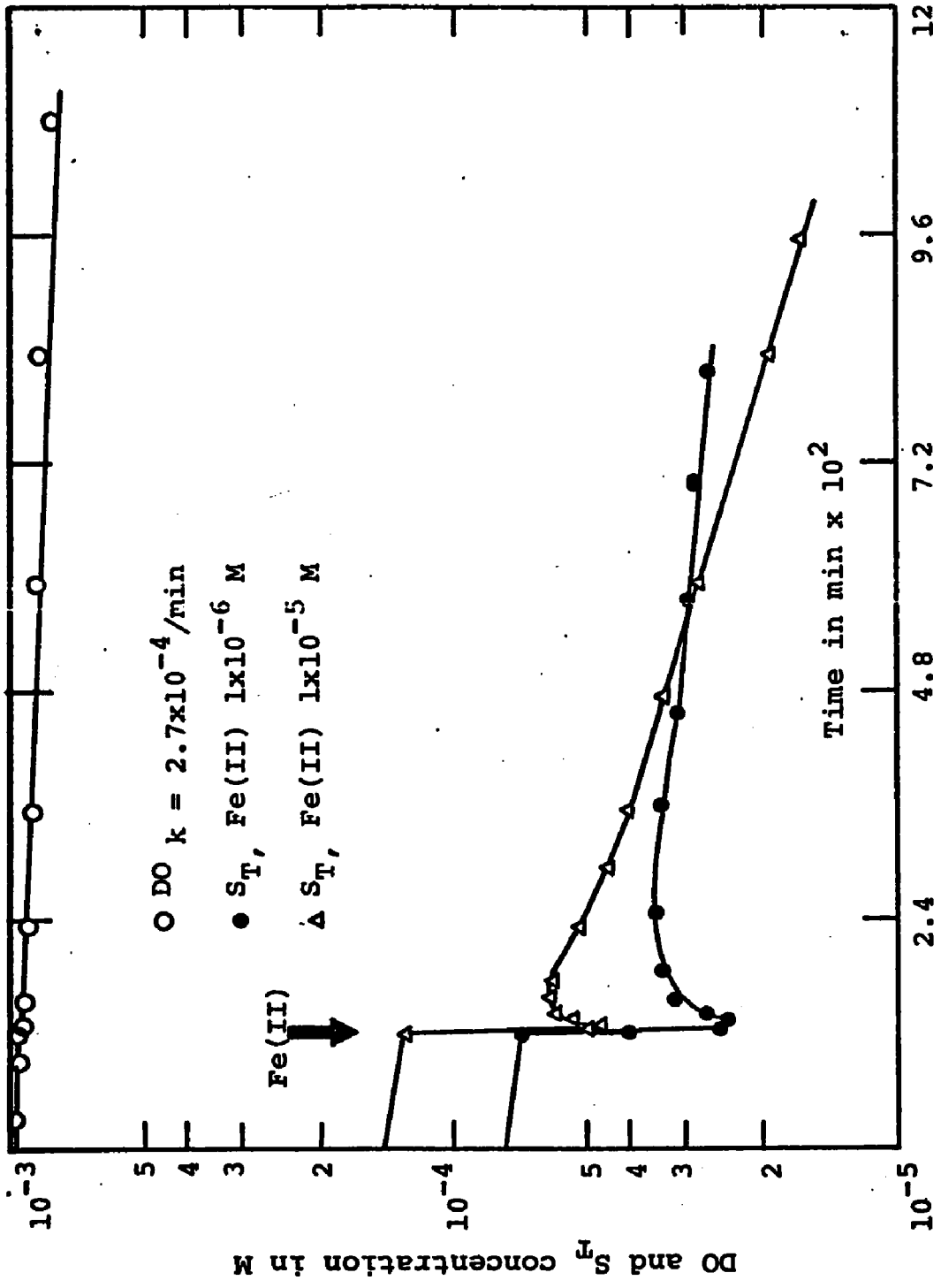


FIGURE 29. Sulfide oxidation in synthetic system at pH 8.60, $DO/S_T = 7.5$, Fe(II) 1×10^{-5}M and 1×10^{-6}M at 25°C.

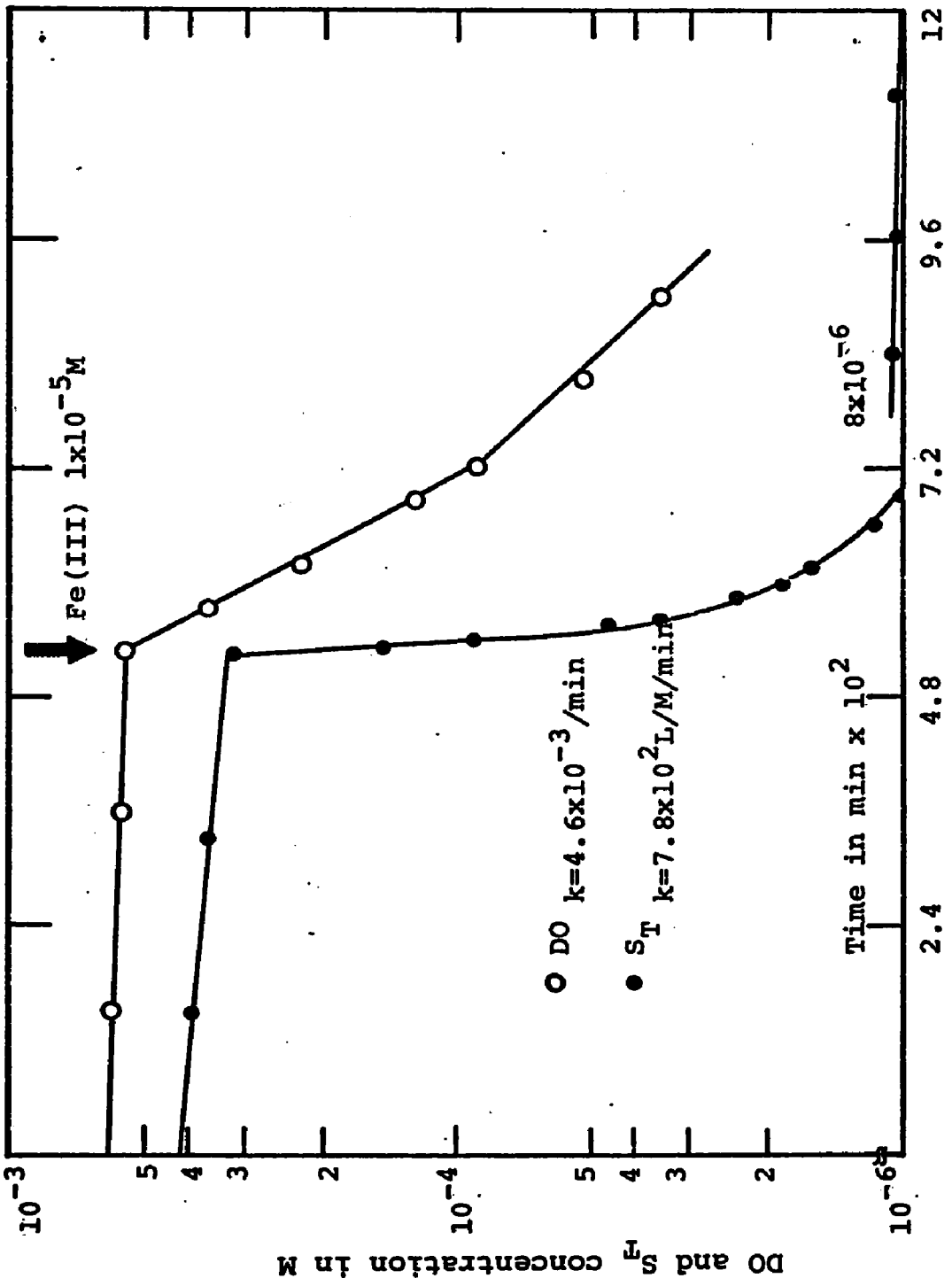


FIGURE 30. Sulfide oxidation in synthetic system at pH 8.60, DO/S_T=1.5, Fe(III) $1x10^{-5}$M, and at 25°C.

the product of Fe(III) and sulfide is instable, therefore the sulfide removal was solely due to oxidation.

The oxygen curve in Figure 30 exhibited two slopes. The first slope was the faster with a K_{DO} of 4.6×10^{-3}/min. The second slope was slower with a K_{DO} of 3.6×10^{-3}/min. The K_{DO} values in this experiment are in accordance with the corresponding values in the Fe(II) experiment.

3. The Effect of Ferric Hydroxide ($Fe(OH)_3$) at pH 8.60

Figure 31 shows the results of addition of 1×10^{-5} M ferric chloride to the sulfide system, at a DO concentration of 9.2×10^{-4} M. The reaction proceeded until all the Fe(III) was hydrolized to ferric hydroxide (about 1100 min). After 1100 min S_T to a concentration of 1.3×10^{-4} M was added. The $K2_{S_T}$ was 30 1/M/min. This indicates that the rate of sulfide oxidation is slower in the presence of $Fe(OH)_3$ than in that of Fe(II) or Fe(III). Similarly, the K_{DO} was 2.0×10^{-4}/min, this rate is also slower than in the presence of Fe(II) or Fe(III) runs. Therefore, it is evident that ferric hydroxide is not as effective a catalyst in sulfide oxidation as Fe(II) and Fe(III). Furthermore, it seems that when Fe(II) is oxidized to Fe(III), and in turn Fe(III) is hydrolyzed to $Fe(OH)_3$, the reaction rate slows down. This phenomena was observed in the Fe(II) and Fe(III) experiments (page number 79 and 81).

4. The Effect of Ferric Hydroxide and Ferrous Ion at pH 8.60

Figure 32 illustrates an experiment where Fe(III) was

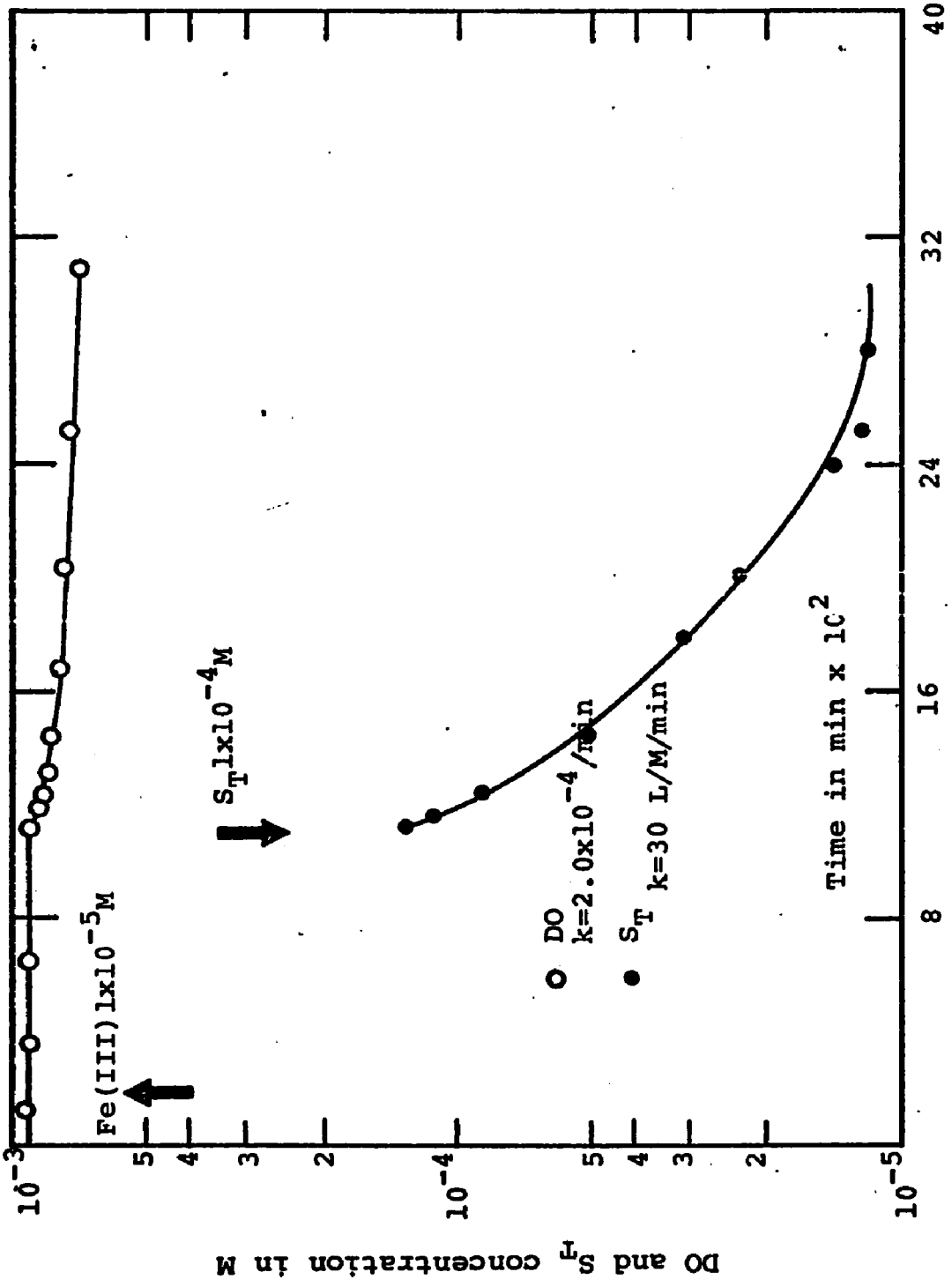


FIGURE 31. Sulfide oxidation in synthetic system at pH 8.60 $Fe(OH)_3$ $1x10^{-5}$M, and at 25oC.

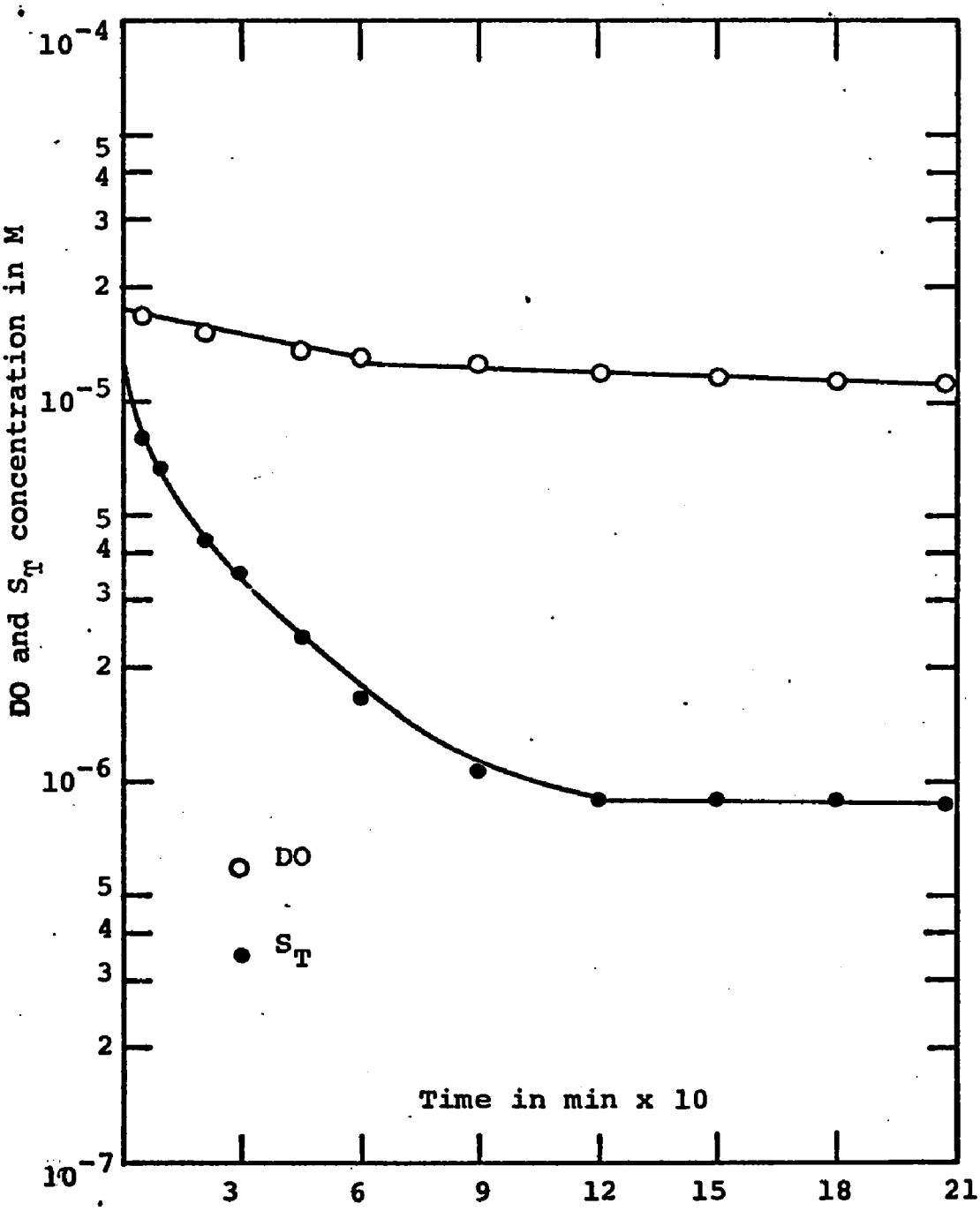


FIGURE 32. Sulfide oxidation in synthetic system at pH 8.60, $Fe(OH)_3$ $1x10^{-5}$M and Fe(II) $1x10^{-5}$M present at at 25°C.

added under conditions of oxygen saturation. After an orange-colored floculate appeared (indicates $Fe(OH)_3$), 1.28×10^{-4} M S_T was added. Following the S_T additions, 1×10^{-5} M of Fe(II) was added. The reaction rate was slower for S_T and DO removal than in experiments with Fe(II) and Fe(III). Figure 32 shows that the S_T concentration was reduced one order of magnitude in 2.5 to 3 hours compared to 10 to 15 min observed in the presence of Fe(II) and Fe(III). Also, there was no hump present as in the Fe(II) experiment. A possible explanation of this phenomenon is that $Fe(OH)_3$ may have acted as an inhibitor in the interaction of FeS catalysis in S_T oxidation, by catalytic conversion of Fe(II) to $Fe(OH)_3$. In a sense, $Fe(OH)_3$ is acting autocatalytically with Fe(II) and Fe(III).

5. <u>The Effect of Ferric Oxide (Fe_2O_3) at pH 8.60</u>

Figure 33 illustrates the results of addition of ferric oxide (1×10^{-5} M) at a DO/S_T of 2.30. The system is similar to those in Figures 30 and 31. Ferric oxide was added 465 min after the initial baseline reaction level was established. Following the kinetics after the addition of Fe_2O_3, there was a minute amount of S_T removal (may be due to some free iron presence at equilibria); the K_{S_T} was 1.37×10^{-4}/min. This rate is equal to the initial baseline reaction rate of 1.4×10^{-4}/min. It is indicative that Fe_2O_3 has no catalytic effect on sulfide oxidation by dissolved oxygen. The dissolved oxygen results are shown in Figure 33 with a K_{DO} of 1.42x 10/min. Similarly, the oxygen curve shows that there was no catalytic effect of Fe_2O_3.

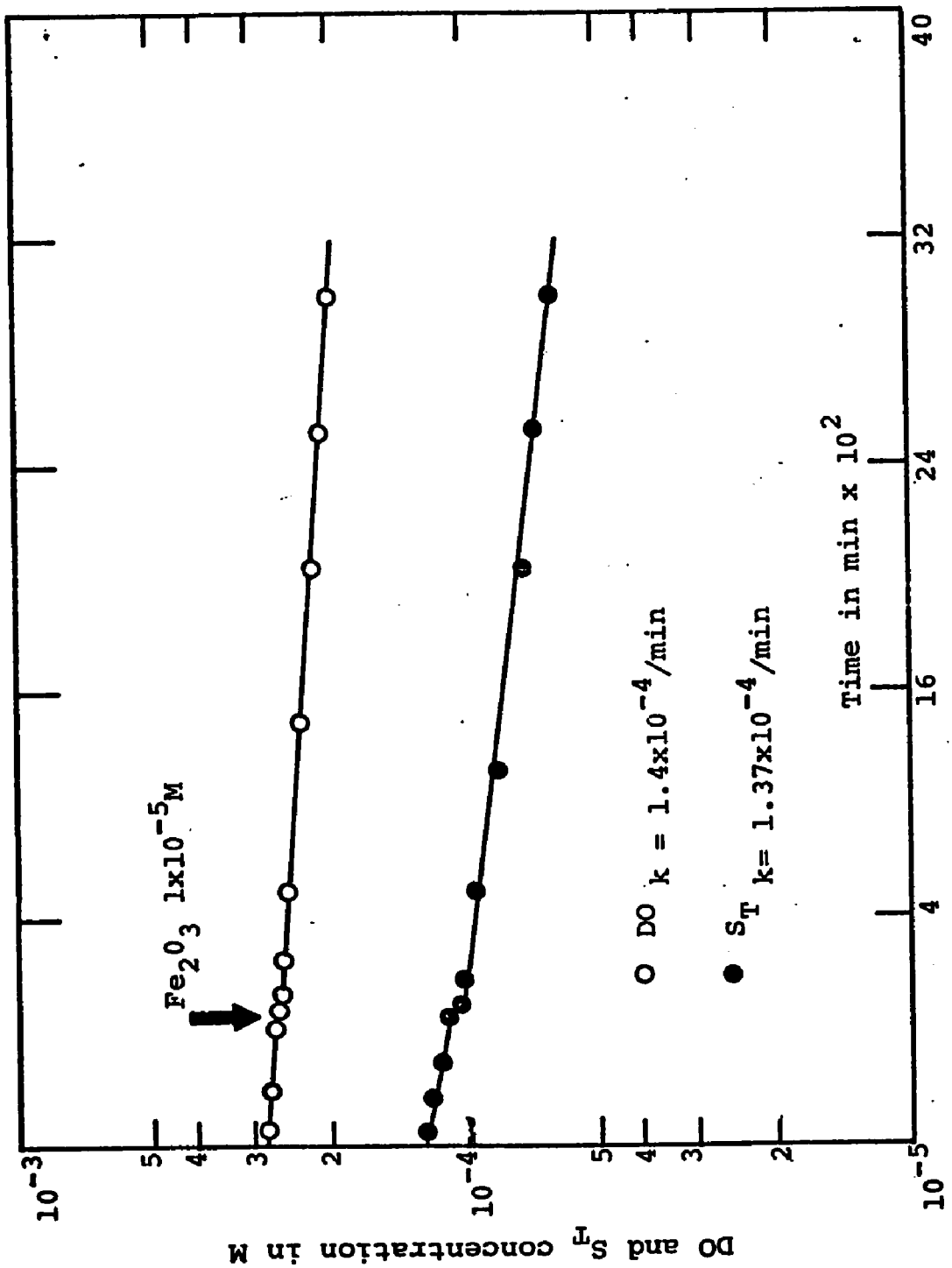


FIGURE 33. Sulfide oxidation in synthetic system at pH 8.60, DO/S_T=2.4 Fe_2O_3 $1x10^{-5}$M and at 25°C.

6. Experimental Results With Iron Present at pH 7.00

Figure 34 shows a typical experiment at 9.8×10^{-4} M DO and 2.5×10^{-4} M S_T. After the initial baseline reaction was established, 1×10^{-5} M ferrous chloride was added. The effect of Fe(II) was similar to that at pH 8.60. The time duration of the catalytic effect was about 50 min, and the duration of the hump was about 50 min. The K_{S_T} and K_{DO} were slower at pH 7.00 than at pH 8.60.

Figure 35 represents the ferric chloride results at pH 7.00 of a run similar to that of the ferrous one above. After achieving the baseline level, 1×10^{-5} M $FeCl_3$ was added to the system. The $K2_{S_T}$ following the addition of Fe(III) was 1.7×10^{2} 1/M/min and the K_{DO} was 2.2×10^{-4}/min.

The results at pH 7.00 indicate that, following the addition of Fe(II) and Fe(III), the reaction rates for K_{S_T} and K_{DO} were slower than that of at pH 8.60. In comparing the Fe(II) and Fe(III) results at pH 7.00, the rates for S_T and DO were faster in Fe(II) system, with the exception that after the hump the oxygen consumption rates were similar for Fe(II) and Fe(III). This is an indication that FeS was oxidized to Fe(III) and, in turn, Fe(III) hydrolyzed to $Fe(OH)_3$, similar to experiment at pH 8.60. Table 10 summarizes the effect of iron in H_2S oxidation by oxygen.

C. NATURAL WATER SAMPLES

Lake samples from the hypolimnion were obtained by VanDorn bottle. The samples were brought to the laboratory immediately

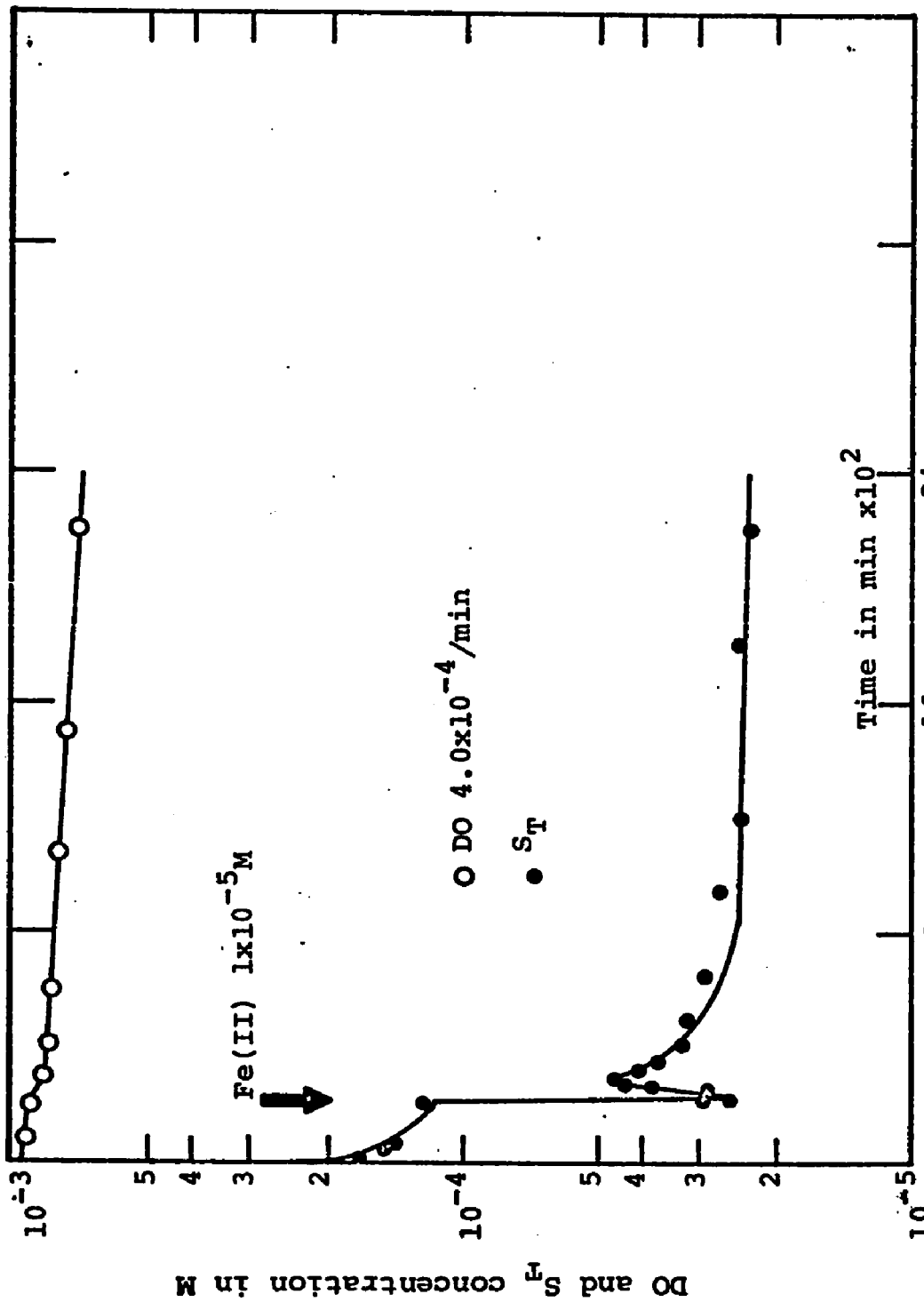


FIGURE 34. Sulfide oxidation in synthetic system at pH 7.00 DO/S_T = 7.6, Fe(II) $1x10^{-5}$M and at 25°C.

TABLE 10. SUMMARY OF SYNTHETIC SYSTEM EXPERIMENTS IN THE PRESENCE OF IRON

Iron	pH	DO/S_T	Immediately after add. of iron K2ST	Immediately after add. of iron KDO	Iron Conc. M	Hump	After hump K-volume K2ST	After hump K-volume KDO
Fe(II)	8.60	1.9	1.2×10^{3}	4.8×10^{-3}	1×10^{-5}	yes	1.0×10^{2}	2.2×10^{-3}
Fe(II)	8.60	7.64	1×10^{3}	2.0×10^{-3}	1×10^{-6}	yes	5.0×10	2.7×10^{-4}
Fe(II)	8.60	7.55	1.7×10^{3}	1.0×10^{-3}	1×10^{-5}	yes	6.2×10	1.3×10^{-4}
Fe(III)	8.60	1.7	7.8×10^{2}	4.6×10^{-3}	1×10^{-5}	no	no change	3.7×10^{-3}
Fe(III)	8.60	7.22	6.4×10^{3}	6.5×10^{-3}	2×10^{-5}	yes	1.4×10^{3}	8.0×10^{-4}
$Fe(OH)_3$	8.60	7.00	3×10	2.0×10^{-4}	1×10^{-5}	no	-	-
Fe_2O_3	8.60	2.3	1.37×10^{-4}	1.42×10^{-4}	1×10^{-5}	no	-	-
Fe(II)	7.00	7.6	4.0×10^{3}	4.0×10^{-4}	1×10^{-5}	yes	1×10^{2}	1.8×10^{-4}
Fe(III)	7.00	7.6	1.7×10^{2}	2.2×10^{-4}	1×10^{-5}	no	-	-

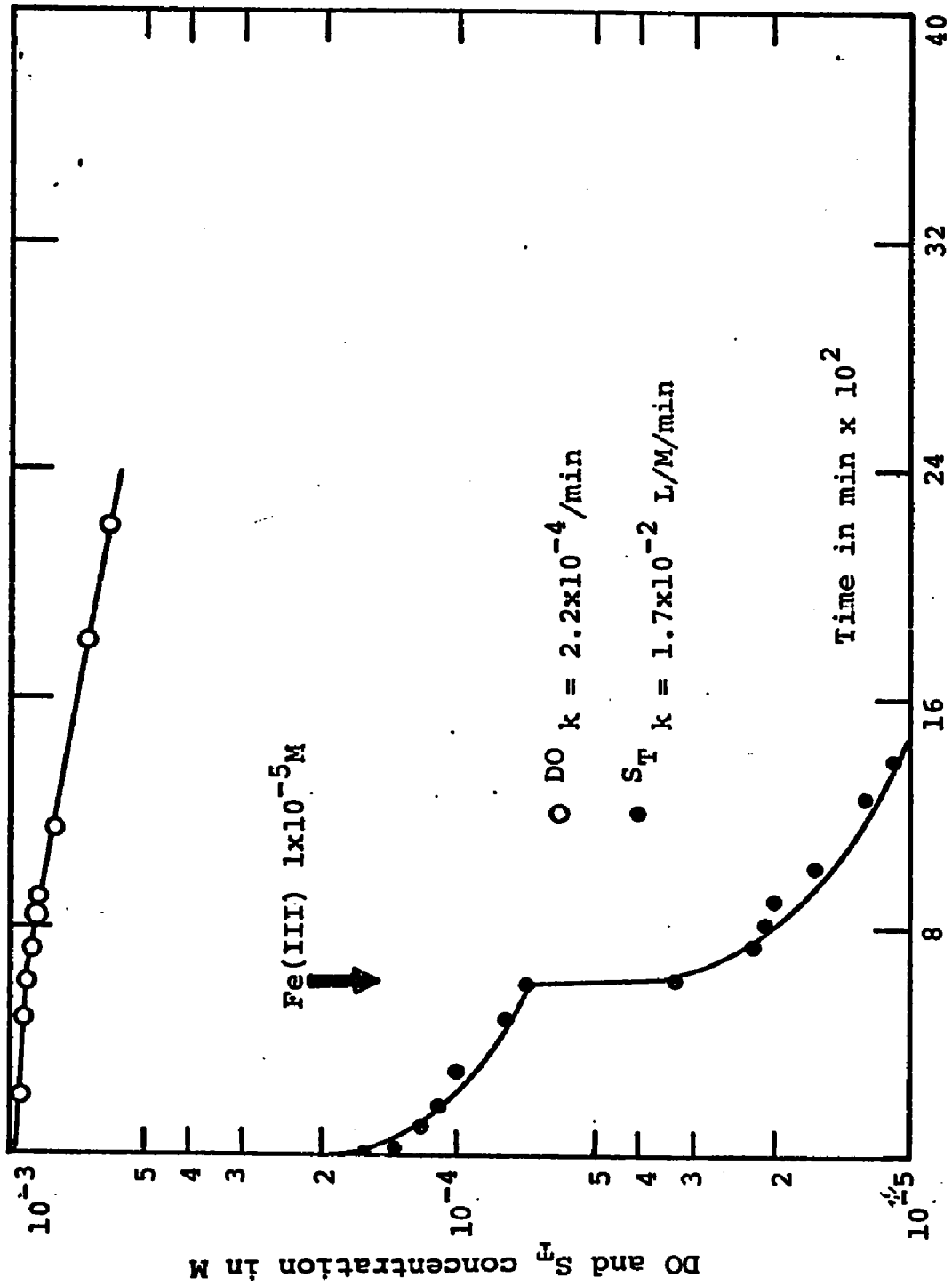


FIGURE 35. Sulfide oxidation in synthetic system at pH 7.00, Fe(III) $1x10^{-5}$M, and at 25°C.

upon collection and subjected to experimental work. The pH, S_T, total iron, DO, and COD levels were measured before the samples were filtered.

Figure 36 shows the microfiltered and Whatman filter paper results from Frain's Lake water samples. These experiments were performed at saturated oxygen levels, at pH 8.60, borate buffered, u of 0.01, and at 1×10^{-4} M of S_T concentration. These results show the reaction rates to be similar in microfiltered and Whatman paper filtered samples; and the reaction rate seems to follow as a first order reaction. The total sulfide oxidation was completed in less than 100 minutes, whereas in synthetic water, it took several days for completion. The rate of sulfide removal was 2.2×10^{-2}/min, and the DO removal was 5.0×10^{-3}/min. The sulfide removal is over 100 times faster in Frain's Lake water samples than in comparable synthetic waters. When the initial measurable S_T was completely oxidized by oxygen and the excess oxygen ceased reduction, 1×10^{-4} M sulfide was added and the oxygen resumed reduction. This is an indication that the main means of sulfide removal in lake water is by oxygen rather than microbial action.

Figure 37 presents the results from the Third Sister Lake Whatman No. 2 filtered sample experiments. The experiment was performed under identical conditions as those in Figure 36. The K_{S_T} was 1.8×10^{-2}/min, and the K_{DO} was 5.0×10^{-2}/min. The Third Sister Lake sample reaction rates were very closely correlated with the Frain's Lake samples. The lake samples studied have the same general geographic characteristics:

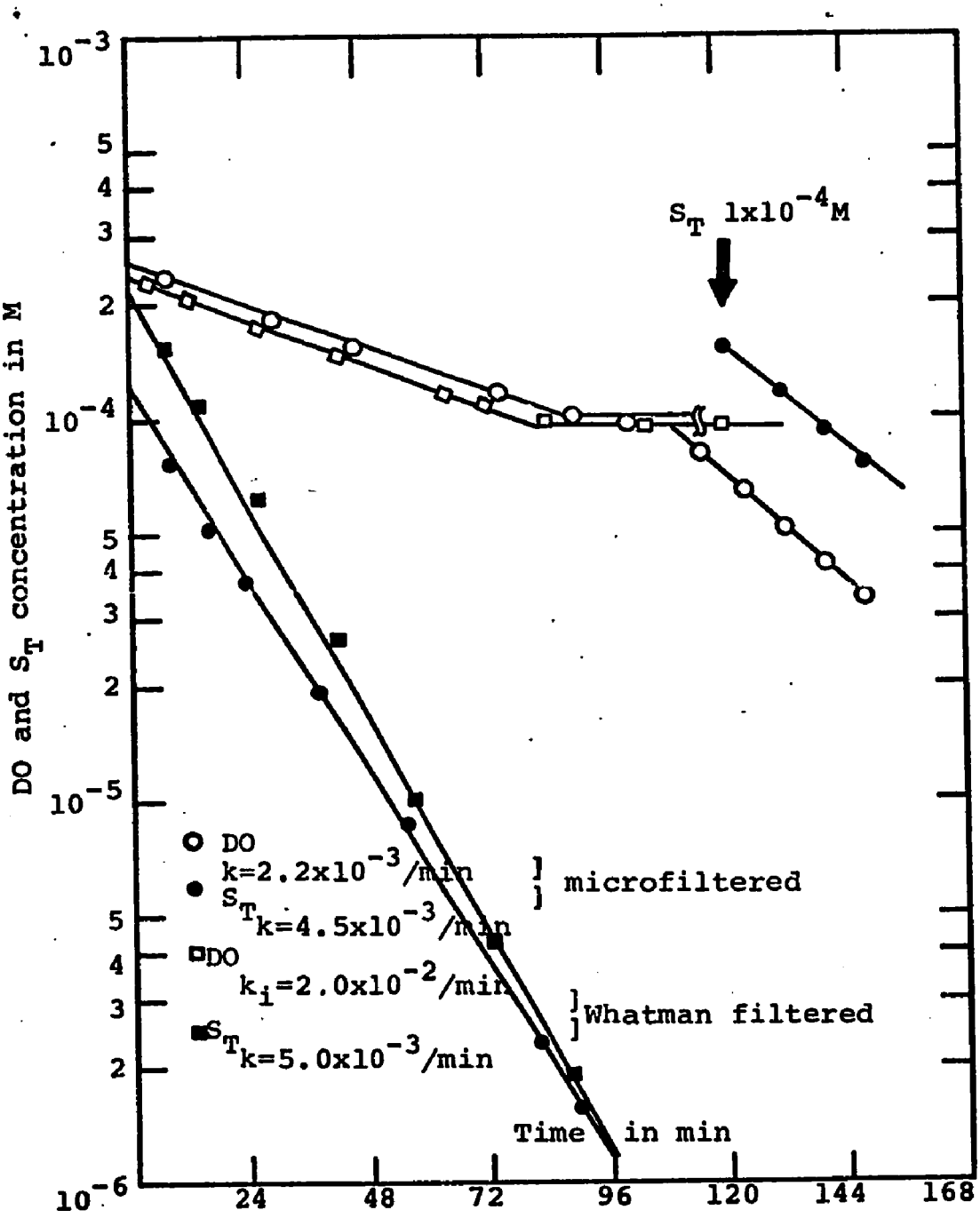


FIGURE 36. Sulfide oxidation in Frain's Lake sample at pH 8.60, $DO/_{S_T}$ =2.00 at 25°C.

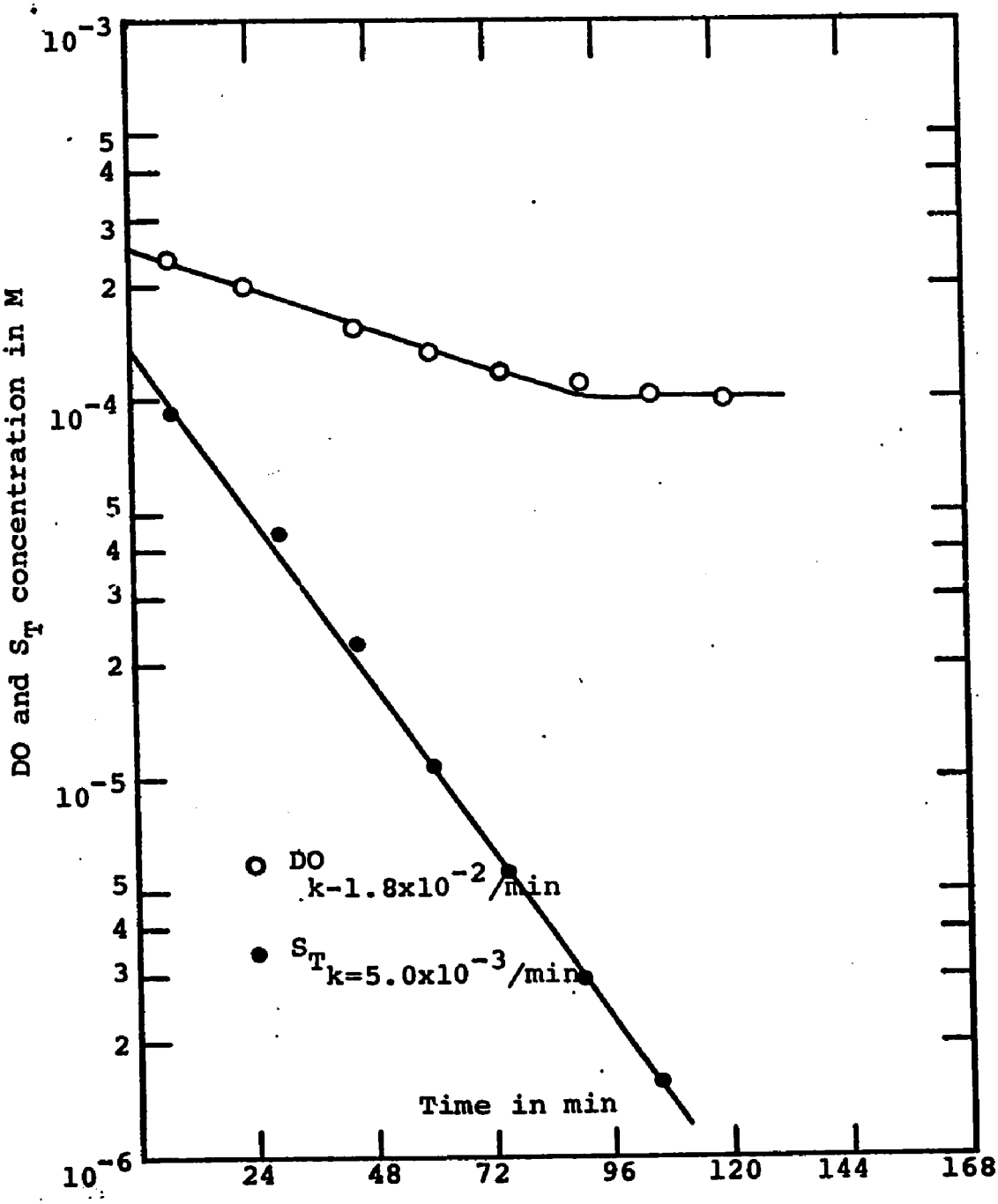


FIGURE 37. Sulfide oxidation in THird Sister Lake filtered sample at pH 8.60, DO/S_T =2 and at 25°C.

farming, fishing and recreation. However, one cannot make the general statement that most lakes behave similarly in their sulfide oxidation based on these results.

Figure 38 shows the results of the unfiltered and unbuffered Frain's Lake water experiments, the K_{S_T} was 3.9×10^{-3}/min, and the K_{DO} was 3.5×10^{-3}/min. This rate was slower than that at pH 8.60 buffered with borate -about six times slower. Completion of the reaction took over 800 min. The slower rate was expected at lower pH values. Seven was the pH of the lake sample after the addition of sulfide; an equivalent amount of HCl solution was added in order to prevent the pH change due to Na_2S addition.

Figure 39 shows the results from the sample which were microfiltered and at pH 7.00 and buffered with borate. It took over 150 min for complete sulfide-oxidation, and the rates of oxidation reaction were 1.0×10^{-2}/min for sulfide and 3.0×10^{-3}/min for DO. In buffered lake sample the reaction rate is slightly faster than in unbuffered samples. This is due to pH changes in unbuffered experiments; the final pH had changed to 6.75.

The kinetics of oxidation of H_2S by dissolved oxygen in lake water shows that the sulfide disappearance and oxygen uptake are very fast. It would be very difficult and misleading to give a simple explanation for this effect. The difficulty is due mainly to the complex chemical nature of lake waters. One way of approaching this problem of oxidation is to study the effect of a common and abundant element that is present in

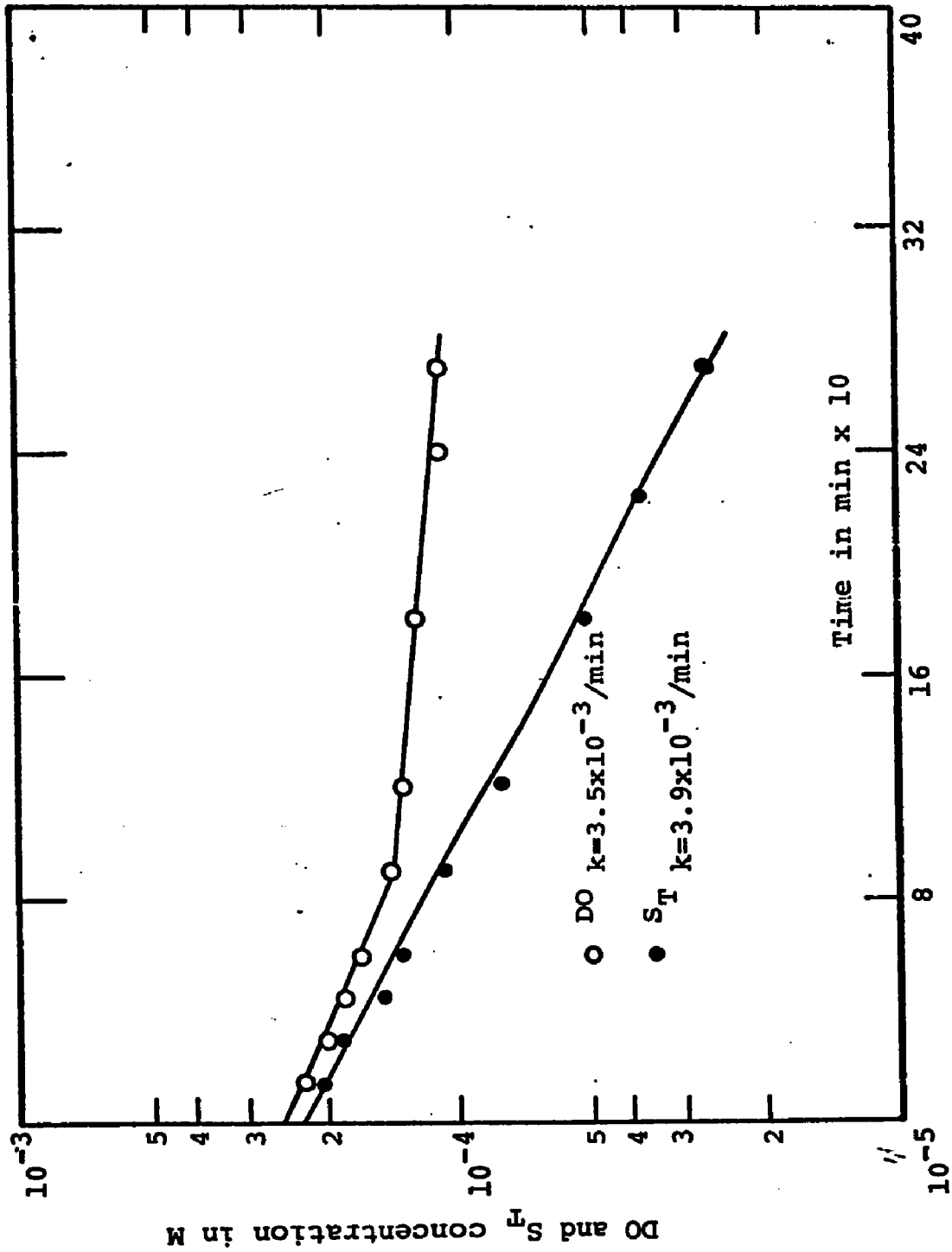


FIGURE 38. Sulfide oxidation in Frain's Lake unfiltered and unbuffered sample at 25°C.

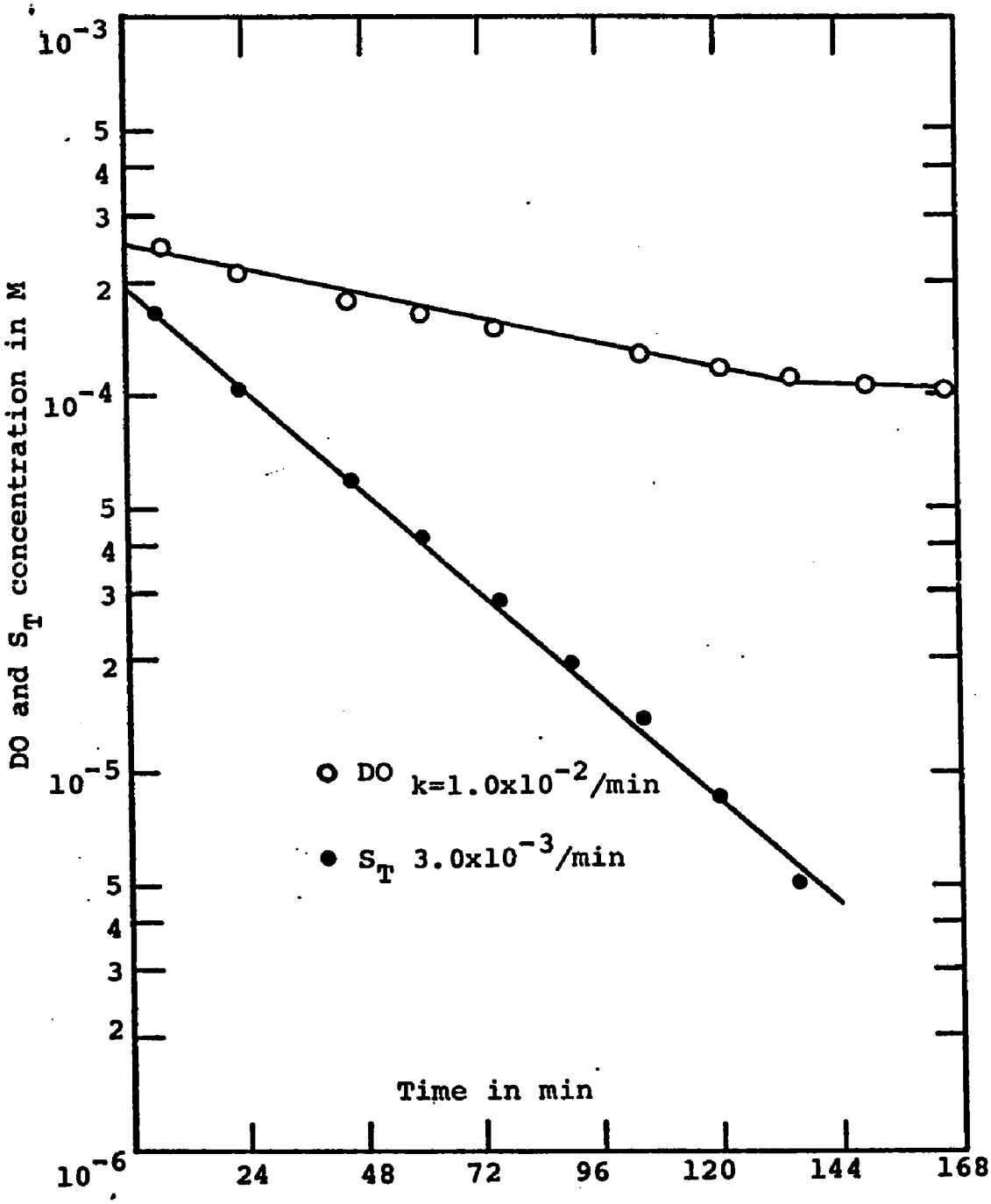


FIGURE 39. Sulfide oxidation in Frain's Lake microfiltered sample at pH 7.00, DO/S_T =1.5, and at 25°C.

lake waters: one such element is iron. In the remaining experimental results, the effect of iron on the oxidation of H_2S by O_2 in natural waters was studied.

Figure 40 shows the result of microfiltered, pH 8.60 buffered Frain's Lake sample, where Fe(II) was added to 1×10^{-5} M. The DO was at saturation and S_T was 1×10^{-4} M. The K_{S_T} was 2.0×10^{-2}/min, and K_{DO} was 5.0×10^{-3}/min. The complete oxidation of S_T took about 100 minutes. Comparing the kinetics with and without iron, there is no observable difference. On addition of iron, the precipitate of FeS immediately formed was not stable: it disappeared within a few minutes. Figure 41 shows the results of the addition of Fe(III) to a solution similar to that used in Figure 40. The K_{S_T} was 1.6×10^{-2}/min, and K_{DO} was 5.3×10^{-3}/min. The Fe(III) kinetics are similar to that of Fe(II).

In lake waters, Fe(II) and Fe(III) are not very stable. They are either being converted to $Fe(OH)_3$ very quickly or forming ligands with the organics the former being the most probable compound. Ferric hydroxide is more stable compound of iron than the ligands.

Lake water experiments were done where the organics were destroyed by ultraviolet radiation. The cations were removed by cation exchange resin, and the effect of iron studied. Figure 42 shows the result of a lake sample where organics were removed. The sample was at pH 8.60, with DO saturation, and 1×10^{-4} M S_T. The K_{S_T} in this experiment was 8.5×10^{-4}/min. Complete oxidation took over 1000 minutes. These

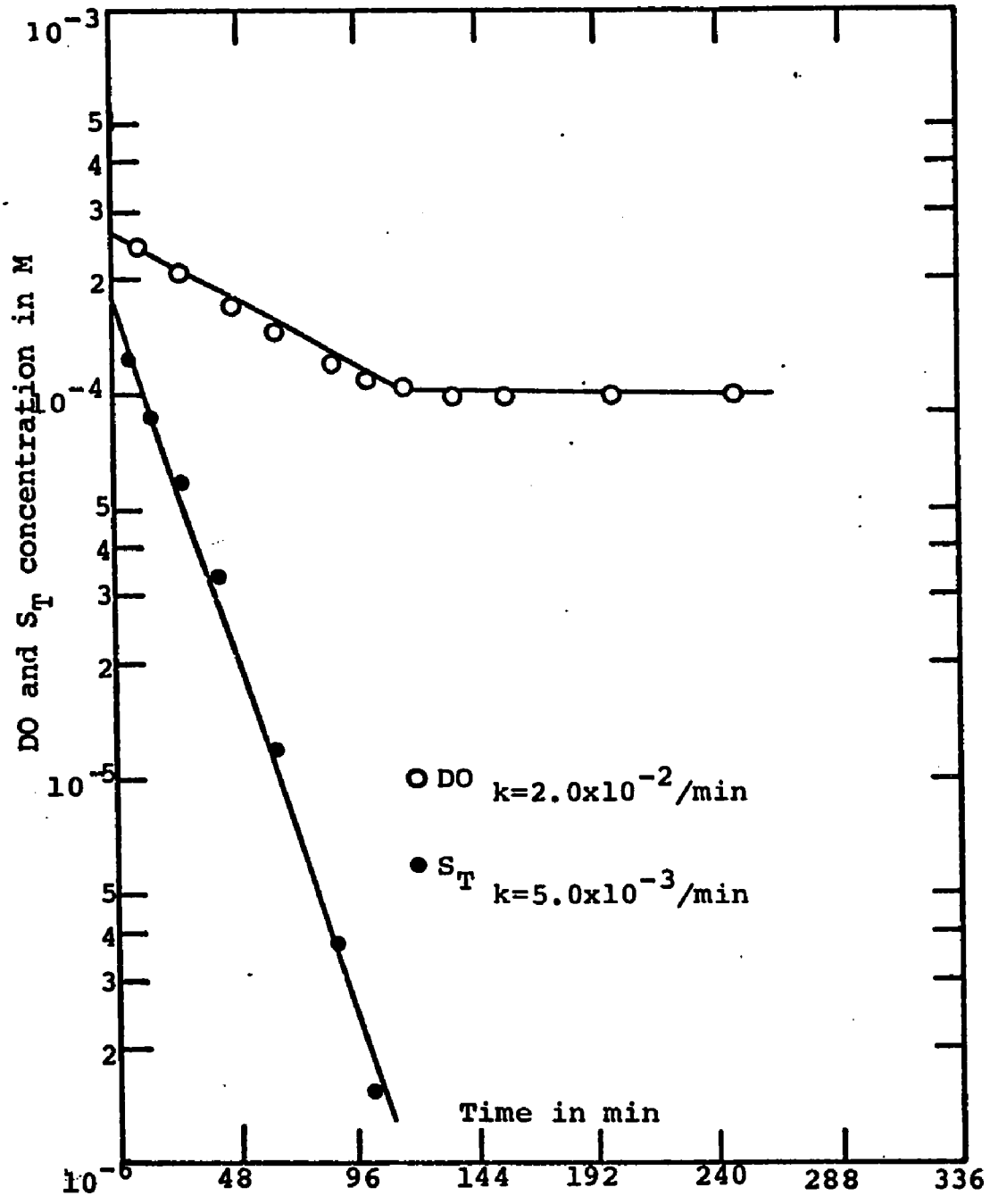


FIGURE 40. Sulfide oxidation in Frain's Lake filtered sample at pH 8.60 $DO/_{S_T}$ =1.6, Fe(II) 1x10^{-5}M and at 25°C.

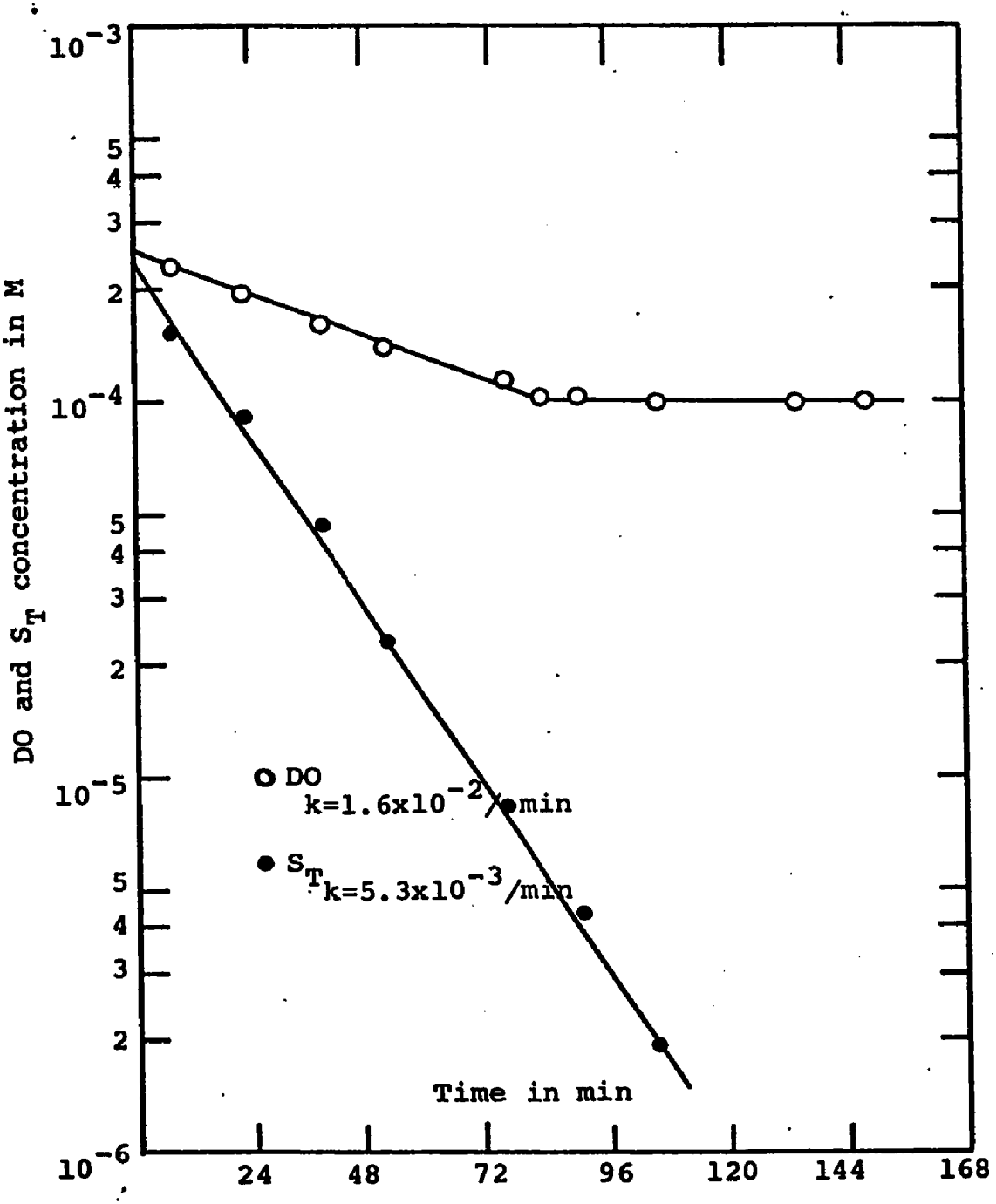


FIGURE 41. Sulfide oxidation in Frain's Lake filtered sample at pH 8.60, $DO/_{S_T}$=1.00, Fe(II) 1x10^{-5} and at 25°C.

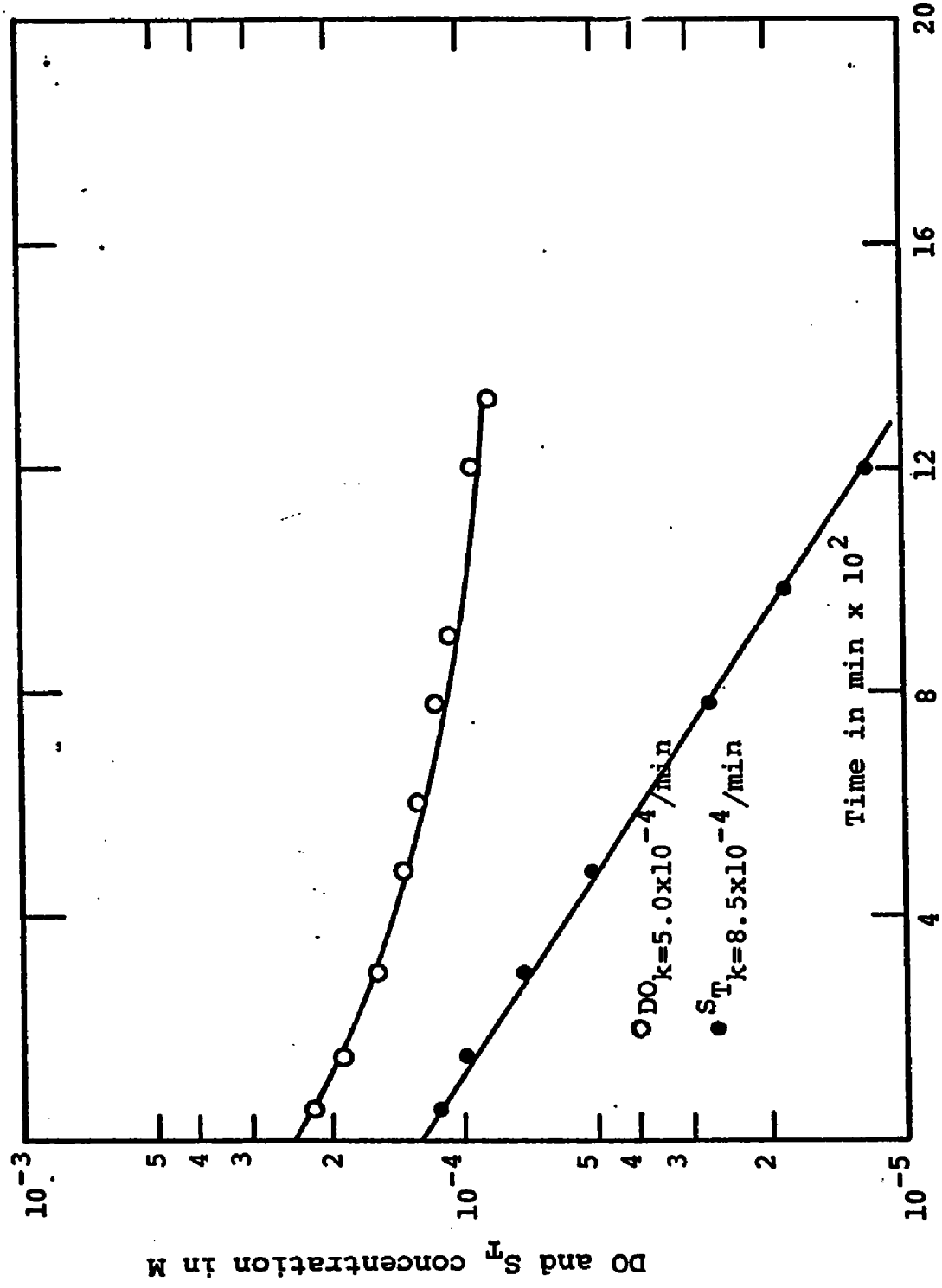


FIGURE 42. Sulfide oxidation in Fran's Lake filtered organics removed sample at pH 8.60, DO/S_T=2.0 at 25°C.

oxidation rates are slower than when organics were present. This experiment indicates that in lake water, trace amounts of organics behave as accelerators (catalysts). When 1×10^{-7} M of Fe(II) was added to the lake sample with organics removed, it did not effect the rate of H_2S oxidation. Similarly, when 1×10^{-5} M of Fe(II) was added, there was no significant change in the kinetics of the reaction. (4×10^{-5} M S_T disappearance was due to FeS precipitation and S_T oxidation). Figure 43 shows the Fe(II) effect without organics.

Figure 44 illustrates the effect of cation removal from the water under experimental conditions similar to those in which organics were removed. The kinetics show that the K_{S_T} was 1.3×10^{-4}/min, and the DO was 6×10^{-4}/min. These results point out that cations have catalytic effects on H_2S oxidation. When 1×10^{-5} M Fe(II) was added to a lake sample with cations removed, there was no significant change in the reaction rates. Figure 45 illustrates this.

Experiments were performed on lake water samples at pH 8.60 with dissolved oxygen at saturation, with S_T being 2×10^{-4} M and with cations and organisms removed. The kinetics of these natural water experiments show that these samples behave in manner similar to those of synthetic water samples under the same conditions. With the addition of iron, the general pattern remain similar also.

Table 11 shows the summary of the lake water results.

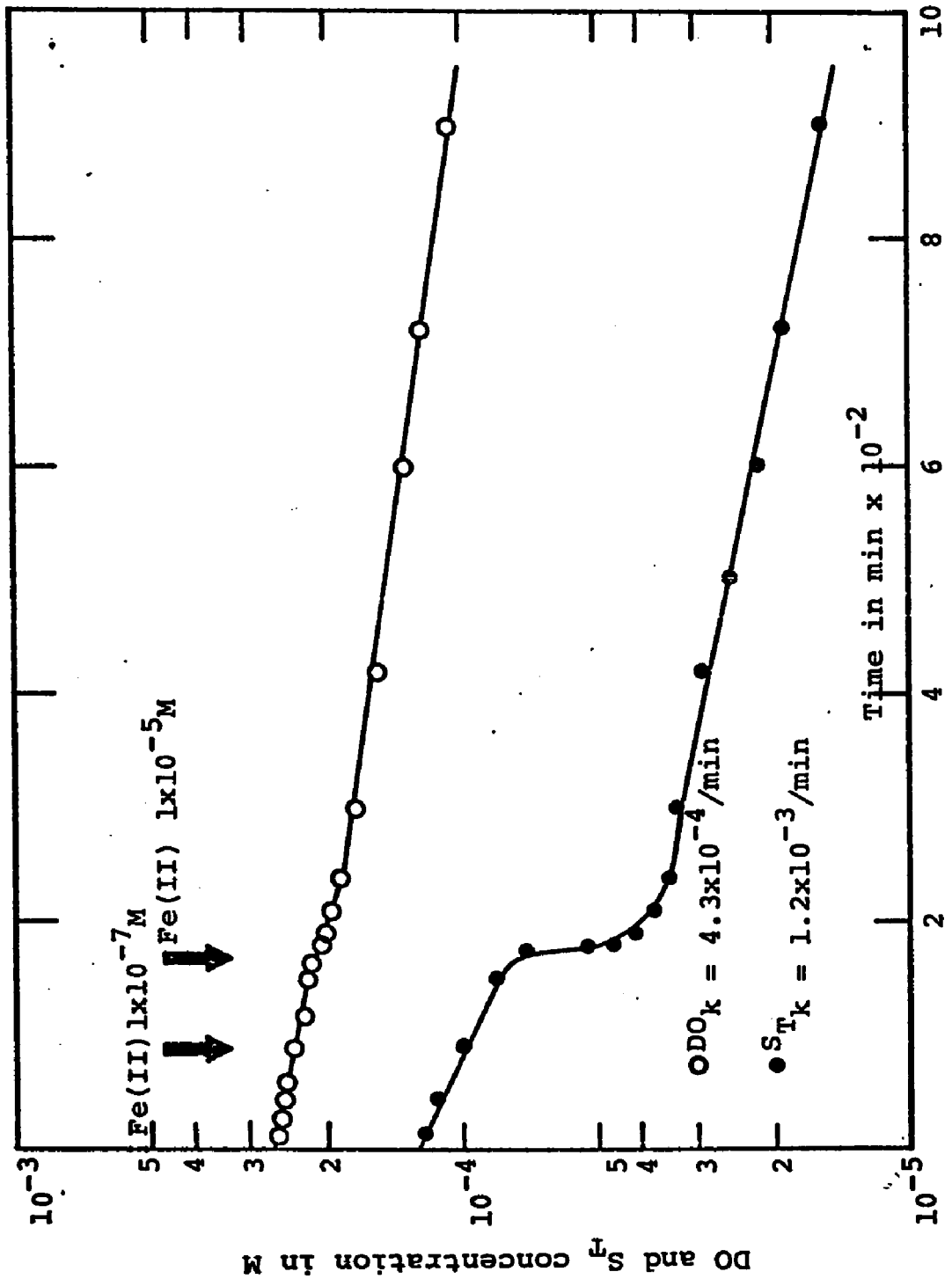


FIGURE 43. Sulfide oxidation in Frain's lake filtered organics removed sample at pH 8.60, DO/S_T =1.8, Fe(II) $1x10^{-5}$M and at 25°C.

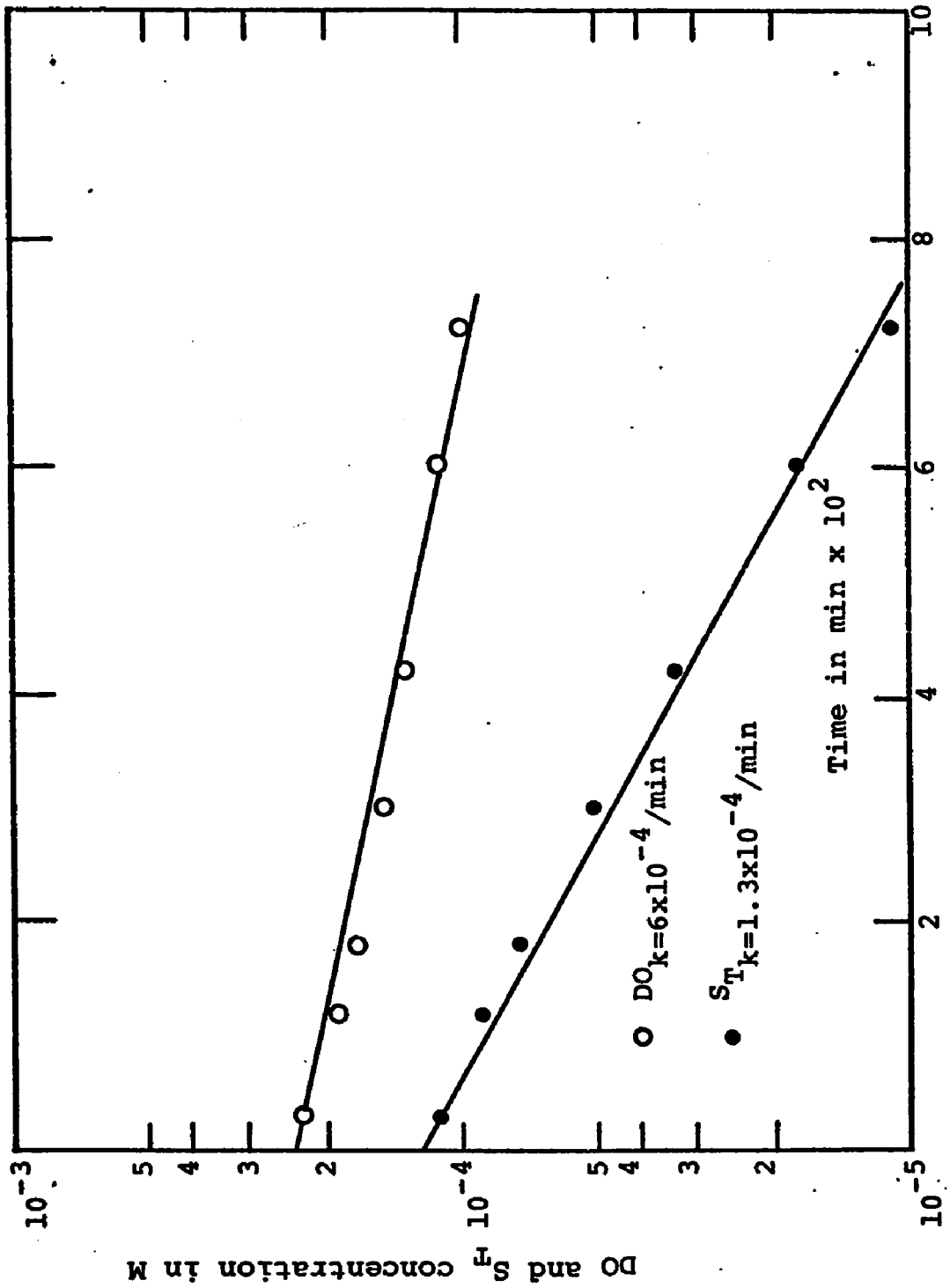


FIGURE 44. Sulfide oxidation in Fran's Lake filtered cations removed sample at pH 8.60, DO/S_T =1.8 and at 25°C.

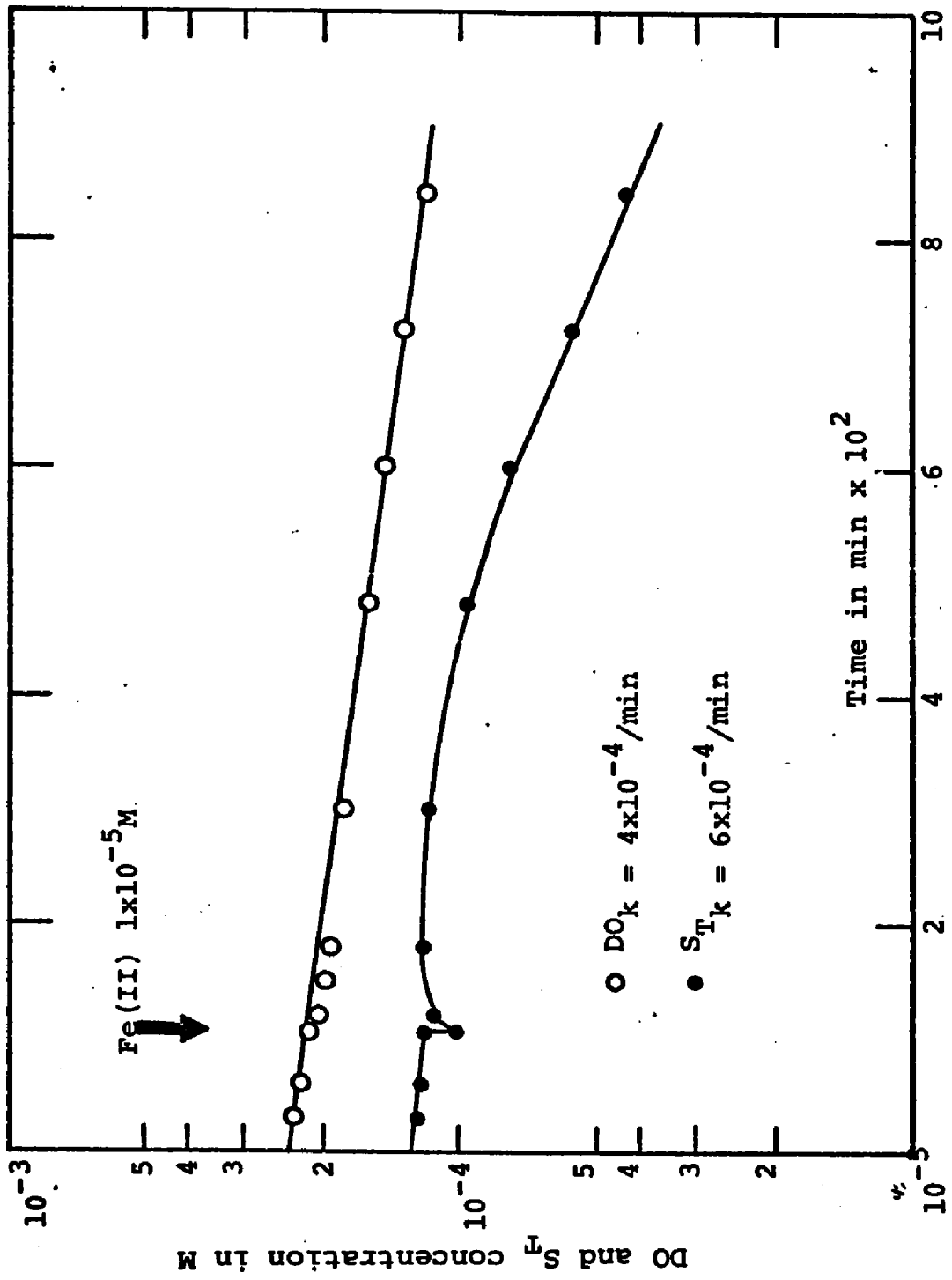


FIGURE 45. Sulfide oxidation in Fran's Lake filtered cations removed at pH 8.60, DO/S_T = 1.7, Fe(II)$x10^{-5}$ M and at 25°C.

TABLE 11. SUMMARY CF LAKE SAMPLE RESULTS

Lake	pH	Filter-ation	Organisms removed	Cations removed	Fe(II) added ($1x10^{-5}$M)	Fe(III) added ($1x10^{-5}$M)	$K_{S_T/min}$	$K_{DO/min}$	DO/S_T
Third Sister	8.60	Whatman No. 2	no	no	no	no	$1.8x10^{-2}$	$5.0x10^{-3}$	2
Frain's	8.60		no	no	no	no	$2.2x10^{-2}$	$4.5x10^{-3}$	2
"	8.60	Micro-film	no	no	no	no	$2.1x10^{-2}$	$5.0x10^{-3}$	1
"	7 (not buffered)	no	no	no	no	no	$3.5x10^{-3}$	$3.9x10^{-3}$	1
"	7 (buffered)	Micro-film	no	no	no	no	$1.0x10^{-2}$	$3.0x10^{-3}$	1.5
"	8.60	"	no	no	yes	no	$2.0x10^{-2}$	$5.0x10^{-3}$	1.6
"	8.60	"	no	no	no	yes	$1.6x10^{-2}$	$5.3x10^{-3}$	1.00
"	8.60	"	yes	no	no	no	$8.5x10^{-4}$	$8.5x10^{-4}$	2.00
"	8.60	"	yes	no	yes	no	$1.2x10^{-3}$	$4.3x10^{-3}$	2.00
"	8.60	"	no	yes	no	no	$1.3x10^{-4}$	$6.0x10^{-4}$	1.8
"	8.60	"	no	yes	yes	no	$6x10^{-4}$	$4x10^{-4}$	1.8

IX. DISCUSSION

In this study it was observed that the oxidation of H_2S in the presence of oxygen in aquatic systems is not a simple reaction. The pH dependence of the rate of oxidation of H_2S, the effect of the reaction of other impurities in the aquatic environment, and the amount of oxygen present in the system varied considerably the reaction end product.

The technique used in the electrochemical characterization of S_T and DO concentration enabled the author to pursue this study. These electrochemical measurement methods were adaptable for continuous monitoring on stripchart recorders. The improved sulfide ion selective electrode used in this study and the modified DO analyzer were evaluated by other investigators at The University of Michigan. A detailed discussion of these methods is found in Chapter VI under the potentiometric method section.

A. SYNTHETIC SYSTEMS

The results of H_2S oxidation in synthetic water indicate that the interaction between H_2S and dissolved oxygen is a very slow process. The half-life of the sulfide under the conditions shown in Figure 20 is about 60 hours; this figure is in close agreement with work done by Chen and Morris. The half-life for sulfide given by Cline and Richards is much shorter, 20 hours at $10^{o}C$. It appears that there is catalytic influence in sea water used by Cline and Richards.

1. Variation of Reaction Rate in Presence of Excess Oxygen

Studies done in excess of DO with initial oxygen concentrations ranging from 1.2 to 8 x 10^{-4} M at S_T of 0.5 to 1 x 10^{04} M, as expected, show that the sulfide oxidation rate was increasing as the DO concentration increased; and at excess oxygen concentrations, the rate of oxygen removal was decreased. The order of the reaction is a first order reaction with respect to S_T and DO in excess of DO, at pH 8.60. At pH 7.00, the reaction order seemed to be a second order with respect to DO. The K_{S_T} and K_{DO} were slower at pH 7.00 than at pH 8.60.

2. Variation of Reaction Rate with Excess Sulfide Concentrations

Studies with an initial excess of S_T ranging from 1 x 10^{-4} M to 1 x 10^{-3} M and at DO concentrations of 0.5 to 1 x 10^{-4} M as expected show that the oxygen reduction rate was increasing as the S_T increased and the sulfide oxidation rate was decreasing, and contrary to expectations, at very high S_T to DO concentration ratios, about 17, the oxygen uptake was decreased. This observation is interesting in view of the fact that at low oxygen concentrations the interaction between H_2S and O_2 is a very slow process, and this could be an explanation of the phenomenon that H_2S and O_2 may coexist, See Table 1. The reaction is first order with respect to S_T and DO at excess S_T concentrations.

3. Stoichiometry

There are two ways to estimate the mechanism by which a reaction proceeds to equilibrium or to completion. The first method is the direct and difficult approach which involves characterization of the intermediary by-products as the reaction proceeds and the determination of the products which are building up. The drawback of this method is that some of the by-products could have a short half-life, and, possibly, the concentration levels could be beyond the levels of detection. The second method is indirect: it involves calculation of the consumption of both reactants at equilibrium and determination of the equivalent amount of each consumed, correlating the equivalents to the possible intermediary or end-products. As an example, the stoichiometric calculations based on the consumption of oxygen to that of sulfide for the experiment where $DO/S_T = 1$, pH 8.7, $u = 0.01$ at 25°C, (Figure 20) follows as such:

1) Dissolved oxygen consumed: 2.43×10^{-4} M at equilibrium oxygen equivalents: $2.43 \times 10^{-4} \times 4 = 9.72 \times 10^{-4}$ M of O_2.

2) Total sulfide consumed: 2.09×10^{-4} M at equilibrium

   a) $S^{=} \longrightarrow S^{o}$, $\quad 2e = 2.09\times10^{-4}\times2 = 4.18\times10^{-4}$

   b) $2S^{=} \longrightarrow S_2O_3^{=}$ $\quad 4e = 2.09\times10^{-4}\times4 = 8.36\times10^{-4}$

   c) $S^{=} \longrightarrow SO_3^{=}$ $\quad 6e = 2.09\times10^{-4}\times6 = 12.54\times10^{-4}$

   d) $S^{=} \longrightarrow SO_4^{=}$ $\quad 8e = 2.09\times10^{-4}\times8 = 16.72\times10^{-4}$

The possible equivalent or possible product is $S_2O_3^=$ with a small amount of $SO_3^=$ or $SO_4^=$ formation, because 9.72 x 10^{-4} M of $S_2O_3^=$ formation. Therefore, the excess of O_2 consumed takes the reaction to a higher oxidation state. This calculation tells one also that the subsequent oxidation to sulfate, $SO_4^=$, is a very slow process at 25°C. These findings are confirmed by the report of industrial alkaline-sulfide bearing waste being oxidized by air; the initial product is thiosulfate (45). The stoichiometric calculations at various DO/S_T are included in Appendix I. At lower S_T concentrations, where DO/S_T is in the range of 6 to 20 at pH 8.60, the stoichiometric results show that sulfite, $SO_3^=$, and thiosulfate is formed, the former being in excess. This is indicated by the oxygen consumption ratio, which is greater than unity without an indication of lower oxidation products, such as sulfur. At a total sulfide to dissolved oxygen ratio of 4, the stoichiometrically calculated results show that sulfur is possibly the main product.

At pH 7.00 and DO/S_T of 1, the possible product is thiosulfate. The same result was found at pH 8.60. At DO/S_T of 33, there is the possibility of $SO_3^=$ and/or $SO_4^=$. Therefore, at very high DO/S_T eg. 33 the oxidation of sulfide is carried to the $SO_4^=$ formation, the more stable form of sulfur. Table 9 shows that stoichiometric results as a function of the DO/S_T. Chen and Morris reported the precipitation of sulfur is possible when the oxygen concentration is decreased to less than atmospheric equiblibrium and when the S_T concentration is above

$1x10^{-3}$ M. This investigator's findings are in agreement with Chen and Morris (8) Therefore, it is possible to conclude that at excess oxygen concentrations, sulfide oxidation proceeds to sulfite and slowly to sulfate.

At equal concentrations of S_T and DO, the reactions proceed to thiosulfate formation. At lower oxygen concentrations (below saturation) and in an excess of sulfide, the reaction proceeds to form sulfur. Thus, these findings are in agreement with the above discussion of oxygen consumption as a limiting factor. The availability of oxygen will not only determine the rate of sulfide oxidation, but also the degree of oxidation, i.e., the end products. At very low oxygen concentrations (3×10^{-5} M), there was no reaction. The formation of sulfite was puzzling in these calculations. Chen and Morris reported that sulfides act as an inhibitor in further oxidation of $SO_3^{=}$. This idea may need further investigation.

The presence of a lag period in these kinds of redox reactions, the catalytic effects of cations and organics, and the pH depndability to these reactions all indicate that a series of rapid chain reactions are taking place. Chain reactions are characterized by (1) chain initiation, (2) chain propagation and (3) chain termination. These three chain reaction characteristics may enable one to understand the kinetics and the stoichiometry of the hydrogen sulfide oxidation reaction.

In aqueous oxidation-reduction reactions, there are possibilities of electron transfer, hydrogen atom transfer and oxygen atom transfer.

It was observed that the reaction rates for S_T and DO removals were slow at acidic and faster at basic pH values. As the pH increases, the H_2S is ionized to HS^- ion. Therefore, HS^- could be the active chain initiator species of sulfide oxidation. A simple electron transfer equation could be as follows:

$$HS^- + O_2 \longrightarrow HS + O_2^- \qquad (66)$$

This hypothesis was reported by Abel (46). The HS formed by the above mechanism could combine with another O_2 and proceed in a number of possible ways. Chen and Morris proposed two ways as follows:

$$HS + O_2 \longrightarrow HSO_2^{\bullet} \qquad (67)$$

$$HS + O_2 \longrightarrow HO_2^{\bullet} + S \qquad (68)$$

The first reaction (eq. 67) will go to thiosulfate or sulfite, by-passing sulfur formation, and the second equation (eq. 68) would proceed to sulfur formation. But it would be very difficult to establish the stoichiometric relationships according to the above propagation chain mechanism in equations 67 and 68. Other investigators have established the presence of HSO_2 in aqueous solution (47,48,49). Bowers et al. (50) proposed the polysulfide catalytic effect on sulfide oxidation, but the polysulfide formation kinetics and thermodynamics are not well enough known to make a sound discussion.

From Rinker's (47,48,49) report, the probable chains termination reaction is:

$$HS\dot{O}_2 + O_2^- \longrightarrow HSO_2^- + O_2$$

The phenomenon of the H_2S and O_2 coexistence at high (S_T/DO) may be explained by the above chain reaction mechanism. Since both chain initiation and propagation require oxygen molecules, it is possible that the limited low O_2 concentrations are insufficient to carry the reaction to termination. This work needs more thorough investigation for confirmation.

A definitive reaction mechanism for a complex reaction such as H_2S oxidation is very difficult. The mechanism proposed above is without direct proof. The existence of this chain mechanism needs further intensive work to establish the basic relationships for the rate of reactions at acid and base systems, as well as the stoichiometry.

B. SYNTHETIC SYSTEMS WITH IRON

The results of H_2S oxidation in synthetic water in the presence of Fe(II) and Fe(III) indicate that the oxidation of H_2S by O_2 was very fast. This indicates that Fe(II) and Fe(III) are catalytic in sulfide oxygenations. The reaction rates are over 100 times faster than in synthetic water.

1. The Effect of Ferrous Iron

In the case of Fe(II), the reaction of H_2S with O_2 has two trends. The first trend is a sharp drop in S_T and DO

concentrations due to precipitation of sulfide by Fe(II) and oxidation by dissolved oxygen. The second trend of the curve is the "hump" (a parabola shaped curve). A Possible explanation of the hump in the sulfide curve is as follows.

The ascending portion of this parabola-shaped curve represents sulfide build-up from the oxidation of FeS. It seems that the Fe(II) and $S^{=}$ are competing for oxygen. The formation of $Fe(OH)_3$ from Fe(II) is substantiated by the appearance of an orange-colored flocculate (9). The descending portion of the hump indicates the oxidation of the freed sulfide; here the K_{S_T} and K_{DO} seem to be slower than the initial reaction rate. This slower rate can be attributed to the effect of the $Fe(OH)_3$, which is discussed below.

The build-up of sulfide concentration in the hump region is in the order of 1×10^{-5} M, which is equal to the initial FeS precipitate concentration. This equivalent relationship between Fe(II) and sulfide verifies that the ferrous sulfide is in the FeS form. Furthermore, an accumulation of FeS precipitate on the magnetic bar was an indication that precipitate was FeS. Berner has reported that FeS has magnetic property (43,44). Attempts were made to develop an x-ray diffraction pattern of FeS or other crystal compounds of iron in the region of the hump. The idea was abandoned because FeS was not stable enough in oxidizing media for x-ray filming. An <u>in situ</u> x-ray diffraction technique should be developed for this purpose, but this is beyond the scope of this study. The catalytic effect of Fe(II) was decreased

as the iron concentration decreased. It seems that FeS, acting as a catalyst in the oxidation of H_2S is autocatalytic.

2. The Effect of Ferric Iron

The effect of the addition of Fe(III) to synthetic systems showed catalysis of H_2S oxidation. Following the kinetics, after the addition of Fe(III), there was a sharp drop in S_T concentration and a substantial drop on DO concentration. The oxidation of the sulfide was the reason for the sharp drop in sulfide concentration. The product of the interaction of Fe(III) with sulfide is not a stable compound. Therefore, sulfide removal is due to oxidation. The oxygen curve in Figure 30 has two slopes. The first slope (the faster) has a rate constant with respect to DO 4.6×10^{-3}/min, as a first order reaction; and the second slope (the slower) has a rate constant of 3.6×10^{-3}/min. The K_{DO} values in this experiment are in accordance with the corresponding values in Fe(II) experiments.

The two oxygen slopes and the two sulfide slopes in the Fe(II) and Fe(III) results indicate that the iron ions converted to $Fe(OH)_3$ in the second slope region. This was indicated by an orange flocculate in the reactor. The possible chemical reactions were presented in the Fe(II) experimental results. The mechanism of action of Fe(III) as a catalyst in this study is not well understood. Among the many possible reaction possibilities are the following:

$$Fe^{3+} + S^{=} \longrightarrow FeS^{+} \qquad (69)$$

$$2Fe^{3+} + S^{=} \longrightarrow 2Fe^{2+} + S \qquad (70)$$

$$Fe^{2+} = S^{=} \longrightarrow FeS$$

Both of these reactions involve an electron transfer mechanism.

3. The Effect of Ferric Hydroxide

Ferric hydroxide is not as effective a catalyst as Fe(II) and Fe(III). When Fe(II) was added to a system where $Fe(OH)_3$ was present the catalytic effect of Fe(II) on the oxidation of H_2S was inhibited; the reaction rate for S_T oxidation and the DO uptake were slowed down to the same rate as when only $Fe(OH)_3$ was present. This indicates that $Fe(OH)_3$ acts as an autocatalyst for Fe(II) and Fe(III) conversion to $Fe(OH)_3$, and at a rate faster than when Fe(II) and Fe(III) are present alone.

4. The Effect of Ferric Oxide

In synthetic systems, ferric oxide had no catalytic effect on H_2S oxidation by molecular oxygen.

Iron experiments in synthetic water at pH 7.00 showed results similar to those at pH 8.60, with the exception that the reaction rates were slower than at pH 8.60. The iron reaction rates at pH 7.00 were expected to be slower because at similar pH values the reaction rates in the synthetic system without iron were slower than at pH 8.60.

5. Stoichiometry of Iron Sulfide Systems

At pH 8.60 and DO/S_T of 2.5 and in the presence of ferrous iron, the stoichiometric calculation shows that the reaction product is sulfate. The stoichiometric calculations are included in Appendix I. Similarly, at pH 8.60 and DO/S_T of 1.77, and in the presence of Fe(III), the reaction product was also sulfate.

The results of the ferric hydroxide system at pH 8.60 and DO/S_T of 7.00 indicate that the reaction products are sulfite and thiosulfate.

This conclusion is indicated by the amount of oxygen equivalents consumed at equilibrium, which is more than the thiosulfate equivalent and less than the sulfite equivalent. Similarly, the ferric oxide result at DO/S_T of 2.26 at pH 8.60 shows that the reaction products are sulfite and thiosulfite. These stoichimetric results of $Fe(OH)_3$ and Fe_2O_3 further indicate that they are not effective catalysts.

The calculated results at pH 7.00 for Fe(II) and Fe(III) show that the reaction product is sulfate with both iron species.

C. NATURAL SYSTEMS

So far, all the kinetic studies of hydrogen sulfide oxidation by molecular oxygen were done in synthetic water, including the effect of iron. This was done in order to elucidate the kinetics of the H_2S oxidation reaction in a complex system, such as in natural water.

Natural water is a chemically complex system. It would be very difficult to isolate and study the effects of every aqueous chemical component on the oxidation of H_2S. In order to simplify the task, the natural system was studied (1) as a whole, (2) with organics removed, (3) with cations removed, (4) with organics and cations removed; each was examined in the presence and absence of iron.

1. Filtered Lake Samples at pH 8.60

The kinetics of the lake samples filtered through a membrane filter and Whatman #2 filter paper showed no significant difference from each other. The rate of S_T oxidation was 2.2×10^{-2}/min, and DO reduction rate was about 4.5×10^{-3}/min, as a first order reaction for microfiltered samples. And the rate for S_T oxidation was 2.1×10^{-2}/min, and for DO 5×10^{-3}/min in Whatman filtered samples. The total sulfide oxidation was completed in less than 100 minutes, whereas in synthetic water, the complete oxidation required several days. After all of the measurable sulfide was oxidized by oxygen and when there was no more oxygen reduction, the addition of 1×10^{-4} M sulfide resumed oxygen reduction. This was an indication that in the lake water sulfide oxidation was due to dissolved oxygen. The results of the two different lake samples from the area of Ann Arbor, Michigan, did not show a significant difference from each other. This is not to say that most lakes behave similarly in sulfide oxidation.

2. Untreated Lake Samples

Results from unfiltered and unbuffered lake samples show that the reaction rate with respect to sulfide was 3.9×10^{-3}/min, and DO was 3.5×10^{-3}/min, as a first order reaction. The complete oxidation of sulfide took over 300 min; this slow rate is characteristic at low pH values. The pH of the untreated lake samples was about 7.00. In contrast to this, a lake sample buffered at pH 7.00 showed that the complete oxidation of H_2S took a little over 150 minutes, indicating that in buffered samples the reaction rate was about one third faster than in unbuffered samples. The reason for this difference could be that in unbuffered samples, the pH changed from 7.00 to a lower value of 6.75, even though HCl solution in amounts equivalent to Na_2S was added before the run.

The kinetics of H_2S oxidation by O_2 in lake water shows that in general the impurities in lake water are catalytic. This is not to say that one cannot find inhibitors. Chen and Morris (8) reported certain organics which behave as inhibitors for H_2S oxidation. On the other hand, the summation of the effects of impurities in the above lakes was catalytic in nature.

3. Effect of Iron on Filtered Lake Samples

To microfiltered lake samples, buffered at pH 8.60, Fe(II) was added. The rate of S_T and DO removal was 2.0×10^{-2}/min and 5.0×10^{-3}/min respectively, as a first order reaction, and the complete oxidation of S_T took about 100 minutes. This

kinetic data shows that there is no significant difference in natural water with and without iron. The FeS precipitate formed after the addition of iron was oxidized immediately. The absence of a black precipitate was an indication of this effect. The kinetics of the experiments performed with the addition of Fe(III) were similar to those done with Fe(II), as described above. It appears that the effect of Fe(II) and Fe(III) in lake water is not significant, suggesting that iron ions are not stable in natural waters. The unstability of iron in lake water could be due to the fact that iron may react in natural water to form ligands with the organics; another possibility is the Fe(II) and Fe(III) convert to insoluble $Fe(OH)_3$ form, which, being the most stable compound, would be the most favorable form of iron. The impurities in natural water act as effective catalysts in converting iron to $Fe(OH)_3$ (25).

4. Lake Samples From Which Organics Were Removed

Lake samples which were subjected to ultraviolet light to destroy the organics were buffered at pH 8.60, filtered, and the H_2S oxidation rates studied. The S_T oxidation rate was 8.5×10^{-4}/min, and DO removal was 5.0×10^{-4}/min. Complete oxidation took over 100 minutes. This experiment indicates that organics in natural water behave as catalysts to H_2S oxidation. When Fe(II) was added to the lake sample from which organics were removed, it did not effect the rate of H_2S oxidation significantly. It was observed that the

FeS formed from the addition of Fe(II) was not stable indicating its immediate conversion to $Fe(OH)_3$.

5. Lake Samples From Which Cations Were Removed

In lake samples from which cations had been removed and which had been buffered at pH 8.60 the kinetics of H_2S oxidation showed that the S_T oxidation rate was 1.3×10^{-4}/min, and the rate of DO uptake was 6×10^{-4}/min.

These results point out that cations have catalytic effects on H_2S oxidation. When 1×10^{-5} M Fe(II) was introduced to a cation-free lake sample, there was no significant change in reaction rate observed.

6. Lake Samples From Which Cations and Organics Were Removed

The kinetics of experiments performed on lake water samples with both cation and organic removed were K_{S_T} of 2.0×10^{-4}/min and K_{DO} of 1.6×10^{-4}/min. These samples were buffered to pH 8.60. The results are similar to those of parallel experiments on synthetic water samples; with the addition of iron, this similarity in the results was maintained.

In lake samples the oxidation of H_2S is a fast reaction. But when the organics or cations were removed, the oxidation reaction proceeded very slowly; this means that neither the organics nor the cations independently are effective catalysts in this oxidation reaction. However, when both organics and cations are present, the catalytic effect was much greater.

They have synergistic effects on the H_2S oxidation. On the other hand, both cations and organics were similar in their catalytic effect in converting Fe(II) and Fe(III) to $Fe(OH)_3$.

7. Stoichiometry of Natural Water Systems

At pH 8.60 and DO/S_T of 2.1, in the Frain's Lake water sample, the stoichiometric calculation shows that the reaction product is sulfate. The stoichiometric calculations for the unfiltered and unbuffered lake sample show that the reaction products are sulfur and thiosulfate. Similarly, at pH 7.00, in buffered and filtered lake samples, the reaction products were also sulfur and thiosulfate.

The results of the addition of ferrous iron to buffered lake water at 8.60 show that the reaction products are sulfur and thiosulfate. Comparable results were obtained in the presence of ferric iron. These findings indicate that the presence of iron in the lake waters does not further enhance the reaction rate of sulfide oxidation, because iron in its ionic form is not stable in a natural water environment.

X. SUMMARY AND CONCLUSIONS

The study of these kinetics data and the evaluation of the influences of external factors in the oxidation of aqueous sulfide by dissolved oxygen have provided a better picture of the realtionship between pH 7.00 and 8.60 at various oxygen/sulfide ratios to the rate of reaction. The basic information regarding the reaction rate at different pH regions elucidates the complicated behavior of sulfide-oxygen reactions in both natural water and sulfide-bearing waste water. A better understanding of the catalytic influences of iron species that affect the rate of sulfide oxidation contributes to the knowledge of the variations in this process in nature.

A stirred glass batch reactor was used for this study. An improved sulfide ion selective membrane electrode was used for following the course of sulfide oxidation as a function of time, and a galvanic cell oxygen-analyzer was used for monitoring oxygen removal. Stripchart recorders were used for continuously monitoring sulfide and oxygen removals, pH measurements were made before and after each experiment.

The stoichiometric calculations were done to correlate the possible products that could result from sulfide oxidation. Findings from the experimental observations in this study can be summarized as follows:

1. At pH 8.60 and at DO/S_T of unity, the reaction proceeds as a first order reaction with respect to S_T and DO

The first order rate expression for S_T is as follows:

$$- \frac{d_{S_T}}{dt} = k_{S_T} S_{T_o}$$

Integrated form: $k'_{S_T} = (\log S_{T_o} - \log S_T)/t_2 - t_1$

where:

$$k'_{S_T} = 2.3\ k_{S_T}$$

The k values in this experimental condition for S_T and DO were 1.6×10^{-4}/min and 1.3×10^{-4}/min, respectively.

At high DO/S_T, the reaction rate with respect to S_T was increased. This increase is exponential. The reaction rate with respect to DO decreased, and this decrease is also exponential. The reverse was observed when S_T /DO was high: the rate with respect to S_T was decreased and with respect to DO increased.

2. At pH 7.00 and at DO/S_T of unity, the reaction proceeded as a second order with respect to S_T and as a first order with respect to DO. The reaction rate for S_T was 5.5 l/M/min and for DO was 3.5×10^{-5}/min. At higher DO/S_T at pH 7.00, the reaction rate for S_T increased. The rate with respect to both S_T and DO at pH 8.60 was higher than at pH 7.00.

3. In the absence of extraneous substances, at pH 8.60 and at DO/S_T of unity, sulfide is oxidized to thiosulfate. At higher DO/S_T, sulfide is oxidized to sulfite and thiosulfate; this may indicate that sulfide is acting as an inhibitor for sulfite oxidation.

4. At higher S_T/DO and at pH 8.60, sulfide is oxidized to sulfur. The formation of polysulfides at this pH is not favored.

5. At pH 7.00 and at DO/S_T of unity, sulfide is oxidized to thiosulfate. At DO/S_T of 33.3 it is oxidized to sulfate, and at DO/S_T of 3.3 sulfite was formed.

These results show that at DO/S_T of unity and at pH 7.00 and 8.6 sulfide was oxidized to thiosulfate; at higher DO/S_T, sulfite and thiosulfate formation was favored. At high S_T/DO sulfur formation was favored. The availability of oxygen determines the rate of sulfide oxidation and the degree of oxidation. At very low DO concentrations, i.e., 3×10^{-5} M, there was no noticeable reaction occurring; this may explain the coexistance of H_2S and oxygen.

6. The sulfide oxidation reaction rate with respect to S_T was a second order and with respect to DO was a first order in the presence of Fe(II). After initial addition of Fe(II), most of the total sulfide was oxidized, and a smaller fraction of it was precipitated as FeS, 1×10^{-5} M. The formation of a hump 60 minutes after the initial addition of Fe(II), 1×10^{-5} M, is an indication of FeS precipitation. The $K_{2_{S_T}}$ was 4.5×10^{-2}/min before the hump and 1.0×10^{2} l/M/min after the hump, and the K_{DO} was 4.8×10^{-3}/min before and 2.2×10^{-3}/min after the hump. This indicates that there is a propagation cycle of ferrous iron-sulfide interaction similar to that of acid mine drainage. At lower Fe(II) con-

centrations the reaction rates were slower. At higher DO/S_T, the reaction rate with respect to sulfide was slightly higher than at near unity, and the DO rate was slower.

In the presence of Fe(III) the kinetics were similar to those with Fe(II), with the exception that there was no hump formation.

7. At pH 8.60 and in the presence of $Fe(OH)_3$, the reaction rate with respect to sulfide was 30 1/M/min, as a second order reaction and 2.0×10^{-4}/min as a first order with respect to dissolved oxygen. These results indicate that Fe(II) and Fe(III) are accelerators for the oxidation of sulfide. And $Fe(OH)_3$ and Fe_2O_3 are not as effective catalyst as Fe(II) and Fe(III).

The results at pH 7.00 for Fe(II) and Fe(III) were similar to those at pH 8.60.

8. The stoichiometric calculations indicate that in the presence of Fe(II) and Fe(III) at pH 8.60 and 7.00, sulfide was oxidized to sulfate.

9. In the presence of $Fe(OH)_3$ and Fe_2O_3 sulfide was oxidized to sulfite and thiosulfate.

10. In lake water the oxidation rate of H_2S by O_2 at pH 8.6 was very fast, 2.0×10^{-2}/min; 5.0×10^{-3}/min was the rate of DO uptake. Complete oxidation took about 100 minutes. The addition of Fe(II) and Fe(III) did not accelerate the reaction.

11. In lake water the oxidation rate at pH 7.00 was

slower than at pH 8.60. In unbuffered lake water the reaction rate was also slow.

12. In lake water with the organics removed, the oxidation of H_2S was slower than in filtered lake water at pH 8.60. The addition of Fe(II) did not effect the reaction rate significantly. The cations which remained in these samples were not effective catalysts.

13. In lake water with cations removed the oxidation of H_2S was slower than in filtered lake samples at pH 8.60. The addition of Fe(II) did not cause appreciable changes in reaction rate. Thus, organics alone are not effective catalysts, either.

14. When both cations and organics were removed from lake water, the reaction rates of H_2S oxidation were alike to that of synthetic systems. Upon addition of Fe(II) the reaction rates remained similar to those of synthetic systems with Fe(II).

15. In lake water the catalytic effect of organics and cations together is synergistic. When one is present, it has very little catalytic effect, but together they are very effective catalysts in H_2S oxidation by O_2. It is also important to notice that cations and organics in natural waters behave catalytically in converting Fe(II) and Fe(III) to $Fe(OH)_3$.

Practical Aspects of this Study

The results of this study indicate that under certain conditions sulfide and oxygen could coexist in aqueous media for long periods of time. However, it is difficult to predict the lifetime and the fate of oxidations of sulfide when ions such as iron are present in a given natural water even in the absence of biochemical activity.

When the total sulfide concentration is higher than DO levels, a large portion of sulfide is likely to form sulfur. Sulfur causes polysulfide formation. Therefore, one can predict that in the upper part of sulfide containing layers of natural and waste waters, where DO concentration is usually very low, sulfur-polysulfide interaction is the possible cycle.

At pH 700 and at S_T of 1×10^{-4} M, which is frequently the natural level, the oxidation of sulfide in atmospheric DO concentrations is very slow; the half-life, T 1/2, was over 60 hours. In the presence of iron ions and in excess of oxygen concentration, the half-life was about one hour. This study has allowed insight into the practical application of air and iron as tools in treatment of water and sulfide containing water. Water treatment which causes conversion of sulfur and uses filtration is not a satisfactory practice. It is necessary to oxidize sulfur to a higher oxidation state.

From this project, information was obtained about the improved sulfide ion selective electrodes usedin continuously

monitoring sulfide ion activity in natural waters. This electrode also can be used in monitoring sulfide ion activity in deep ocean waters, where other similar electrodes were not practical.

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APPENDIX I

Computer Program For Rate Determinations of H_2S Oxidation

```
// JOB

LOG DRIVE   CART SPEC   CART AVAIL  PHY DRIVE
  0000         1002        1002        0000
                           3002        0001

V2 M09   ACTUAL 16K  CONFIG 16K

// FOR
*LIST ALL
*ONE WORD INTEGERS
*IOCS(1403 PRINTER,2501 READER)
      REAL MV(100),LGS(100),LGHS(100),LGH2S(100)
      DIMENSION IT(100),O2(100),ST(100),COMNT(25)
      DATA PK1,PK2/7.0,13.0/
100   FORMAT(F5.3,I4,F5.3,I4)
102   FORMAT(I4,F6.2,F12.2,I4)
103   FORMAT('0',I4,3X,E10.3,4X,E10.3,3X,E10.3,5X,E10.3,4X,E10.3,4X,E10.
     23,4X,E10.3,4X,E10.3,5X,E10.3)
203   FORMAT('1MEASURE OF TOTAL SULFIDE AT PH= ',F6.3,'  FOR',I4,'  CASE
     2S WITH OXYGEN FACTOR OF  ',F5.3,10X,'RUN NO',I4)
205   FORMAT('0TIME  TOTAL SULFIDE    OXYGEN    LOG TOTAL ST    LOG OXY
     2GEN    K1 RATE ST    K1 RATE C2    K2 RATE ST    K2 RATE C2    K2
     2RATE ST02')
25    READ (8,100) PH,NDATA,OXY,NRUN
      WRITE (5,203) PH,NDATA,OXY,NRUN
      WRITE (5,205)
      IF (NDATA) 11,11,12
12    K=1
      DO 10 I =1,NDATA
      READ (8,102)IT(I),MV(I),DIV,INOX
      IF(INOX)7,7,8
8     K=I
      READ(8,500) COMNT
500   FORMAT(25A2)
      WRITE(5,206)IT(I),COMNT
206   FORMAT('0',I4,10X,'*****',4X,25A2,4X,'*****')
7     LGS(I)=(I-710+MV(I))/30.00)
      LGHS(I)=(-PH+PK2+LGS(I))
      LGH2S(I)=(-2*PH+PK1+PK2+LGS(I))
      IF(LGS(I))1,15,15
15    S=10.**LGS(I)
      GO TO 2
1     LGS(I)=-(LGS(I))
      S=1./(10.**LGS(I))
2     IF(LGHS(I))3,13,13
13    HS=10.**LGHS(I)
      GO TO 4
3     LGHS(I)=-LGHS(I)
      HS=1./10.**LGHS(I)
4     IF(LGH2S(I))5,14,14
14    H2S=10.**LGH2S(I)
      GO TO 6
5     LGH2S(I)=-LGH2S(I)
      H2S=1./10.**LGH2S(I)
6     ST(I)=S+HS+H2S
      O2(I)=(DIV*OXY*1.3561)/32000.0
      C2L=CLOG(O2(I))
      STL=CLOG(ST(I))
```

Computer Program for Rate determinations. (Cont'd.)

```
      STK=(CLOG(ST(K)/ST(I)))/(IT(I)-IT(K))
      O2K=(CLOG(O2(K)/O2(I)))/(IT(I)-IT(K))
      STK2=(ST(K)-ST(I))/(ST(I)*ST(K)*(IT(I)-IT(K)))
      C2K2=(O2(K)-O2(I))/O2(I)*O2(K)*(IT(I)-IT(K))
      CK2=(CLOG((ST(I)/ST(K))*(O2(K)/O2(I))))/((IT(I)-IT(K))*(ST(K)-O2(K
     *)))
      WRITE (6,103)IT(I),ST(I),O2(I),STL,O2L,STK,O2K,STK2,O2K2,CK2
  10  CONTINUE
  11  GO TO 25
      END
VARIABLE ALLOCATIONS
    O2(R )=00C6-0000     ST(R )=018E-00C8 COMNT(R )=01C0-0190     PV(R )=02BA-01C2     LGS(R )=0350-028A  LGMS(R )=041A-0352
  LGM2S(R )=04E0-041A     PH(R )=04E2        GXY(R )=04E4        CIV(R )=04E6        PK2(R )=04E8          PK1(R )=04EA
     S(R )=04EC           MS(R )=04EE        M2S(R )=04F0        C2L(R )=04F2        STL(R )=04F4          STK(R )=04F6
   O2K(R )=04F8        STK2(R )=04FA       O2K2(R )=04FC        CK2(R )=04FE         IT(I )=056D-050A NDATA(I )=056E
  ARUN(I )=056F          K(I )=0570          I(I )=0571        INDX(I )=0572

STATEMENT ALLOCATIONS
 100   =056F  102  =0594  103  =0599  203  =05AF  205  =05C0  500  =0625  206  =0628  25   =0650  12   =064F  8    =0670
 7     =06A8  15   =0609  1    =06E7  2    =06FC  13   =0706  3    =0714  4    =0729  14   =0733  5    =0741  6    =0756
 10    =0BE7  11   =0890

FEATURES SUPPORTED
 ONE WORD INTEGERS
 IOCS

CALLED SUBPROGRAMS
 CLOG     FAXBX    FADD     FADDX    FSUBX    FMPY     FMPYX    FDIV     FDIVX    FLD      FLDX     FSTO     FSTOX    FDVR     FLOAT
 READ2    SNED     SWRT     SCOMP    SFIO     SIOAF    SIOFX    SIOIX    SIOF     SIOI     SUBSC    PRNZ     SNR

REAL CONSTANTS
  .300000E 02=0580     .100000E 02=0582     .100000E 01=0584     .1356C0E 01=0586     .320000E 05=0588

INTEGER CONSTANTS
     8=058A       5=058B       1=058C     710=058D       2=058E

CORE REQUIREMENTS FOR
 COMMON       0  VARIABLES   1408  PROGRAM    786

END OF COMPILATION

// XEQ
```

Stoichiometry and Thermodynamics Calculations for Fe(II)

$FeS = [Fe^{2+}] + [S^{2-}] \quad K = 10^{-18}$

$K_{sp} = [Fe^{2+}]\ [S^{=}]$

Starting with $Fe_{(4)} = 1 \times 10^{-5}$ M and

$S_T = 1 \times 10^{-4}$ M

$Kp = [10^{-5}]\ [10^{-4}] = 10^{-9}$

FeS precipitate

Assume all Fe(II) FeS

Then $[FeS] = 10^{-5}$ and $[S^{=}] = 10^{-4} - 10^{-5} = 0.9 \times 10^{-4}$

$K_{sp} = 10^{-18} = [Fe^{2+}]\ [0.9 \times 10^{-4}]$

$[Fe^{2+}] - 10^{-14}$

$FeCl_2 = [Fe^{2+}] + 2\ [Cl^{-}] \quad K_{sp} = 3.6 \times 10^{-1} = [Fe^{2+}]\ [Cl^{-}]^2$

$[Fe^{2+}]\ [Cl]^2 = 10^{-14} + [2 \times 10^{-5}]^2$

$= 4 \times 10^{-24}$

Comparing 10N product with K_{sp}

therefore $FeCl_2$ does not precipitate.

Stoichiometric calculations for possible end products of H_2S oxidation by molecular oxygen. All the calculations are performed at equilibrium concentration levels, and the possible end products are underlined.

Figure 20

$S_T = 1.01 \times 10^{-3} - 0.58 \times 10^{-3} = 4.3 \times 10^{-4}$ M

$DO = 1.08 \times 10^{-3} - 0.69 \times 10^{-3} = 3.9 \times 10^{-4}$ M

Equiv. of O_2 consumed $= 3.9 \times 10^{-4} \times 4 = 15.6 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$4.3 \times 10^{-4} \times 2 = 8.6 \times 10^{-4}$ equiv. to S^o

$4.3 \times 10^{-4} \times 4 = 17.2 \times 10^{-4}$ " " $S_2O_3^=$

$4.3 \times 10^{-4} \times 6 = 25.8 \times 10^{-4}$ " " $SO_3^=$

$4.3 \times 10^{-4} \times 8 = 34.4 \times 10^{-4}$ " " $SO_4^=$

Figure 21

$S_T = 1.58 \times 10^{-4} - 0.58 \times 10^{-4} = 1.00 \times 10^{-4}$ M

$DO = 1.05 \times 10^{-3} - 0.90 \times 10^{-3} = 1.5 \times 10^{-4}$ M

Equiv. of O_2 consumed = $1.5 \times 10^{-4} \times 4 = 6.0 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$1.00 \times 10^{-4} \times 2 = 2.00 \times 10^{-4}$ equiv. of S^o

$1.00 \times 10^{-4} \times 4 = 4.00 \times 10^{-4}$ " " $S_2O_3^=$

$1.00 \times 10^{-4} \times 6 = 6.00 \times 10^{-4}$ " " $SO_3^=$

$1.00 \times 10^{-4} \times 8 = 8.00 \times 10^{-4}$ equiv. of $SO_4^=$

Figure 22

$S_T = 5.72 \times 10^{-5} - 0.48 \times 10^{-5} = 5.24 \times 10^{-5}$ M

$DO = 1.07 \times 10^{-3} - 0.986 \times 10^{-3} = 8.4 \times 10^{-5}$ M

Equiv. of O_2 consumed = $8.4 \times 10^{-5} \times 4 = 3.36 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$5.24 \times 10^{-5} \times 2 = 1.048 \times 10^{-4}$ equiv. of S^o

$5.24 \times 10^{-5} \times 4 = 2.096 \times 10^{-4}$ " " $S_2O_3^=$

$5.24 \times 10^{-5} \times 6 = 3.1 \times 10^{-4}$ " " $SO_3^=$

$5.24 \times 10^{-5} \times 8 = 4.192 \times 10^{-4}$ equiv. of $SO_4^=$

Figure 24

$S_T = 9.9 \times 10^{-4} - 7.06 \times 10^{-4} = 2.84 \times 10^{-4}$ M

$DO = 2.15 \times 10^{-4} - 0.296 \times 10^{-4} = 1.85 \times 10^{-4}$ M

Equiv. of O_2 consumed = $1.85 \times 10^{-4} \times 4 = 7.40 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$2.84 \times 10^{-4} \times 2 = 5.68 \times 10^{-4}$ equiv. of S^o

$2.84 \times 10^{-4} \times 4 = 11.36 \times 10^{-4}$ equiv. of $S_2O_3^=$

$2.84 \times 10^{-4} \times 6 = 17.04 \times 10^{-4}$ " " $SO_3^=$

$2.84 \times 10^{-4} \times 8 = 22.72 \times 10^{-4}$ " " $SO_4^=$

Figure 26

$S_T = 8.59 \times 10^{5} - 5.12 \times 10^{-5} = 3.47 \times 10^{-5}$ M

$DO = 2.28 \times 10^{-4} - 1.98 \times 10^{-4} = 3.0 \times 10^{-5}$ M

Equiv. of O_2 consumed = $3.0 \times 10^{-5} \times 4 = 1.2 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$3.47 \times 10^{-5} \times 2 = 6.94 \times 10^{-5}$ equiv. of S^o

$3.47 \times 10^{-5} \times 4 = 1.39 \times 10^{-4}$ " " $S_2O_3^=$

$3.47 \times 10^{-5} \times 6 = 2.08 \times 10^{-4}$ " " $SO_3^=$

$3.47 \times 10^{-5} \times 8 = 2.78 \times 10^{-4}$ " " $SO_4^=$

Figure 27

$S_T = 2.02 \times 10^{-4} - 0.23 \times 10^{-4} = 1.79 \times 10^{-4}$ M

$DO = 5.05 \times 10^{-4} - 0.66 \times 10^{-4} = 4.39 \times 10^{-4}$ M

Equiv. of O_2 consumed = $4.39 \times 10^{-4} = 17.5 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$1.79 \times 10^{-4} \times 2 = 3.58 \times 10^{-4}$ equiv. to S^o

$1.79 \times 10^{-4} \times 4 = 7.16 \times 10^{-4}$ " " $S_2O_3^=$

$1.79 \times 10^{-4} \times 6 = 10.74 \times 10^{-4}$ " " $SO_3^=$

$1.79 \times 10^{-4} \times 6 = 14.32 \times 10^{-4}$ " " $SO_4^=$

Figure 30

$S_T = 1.45 \times 10^{-4} - 0.16 \times 10^{-4} = 1.29 \times 10^{-4}$ M

$DO = 5.20 \times 10^{-4} - 2.31 \times 10^{-4} = 2.89 \times 10^{-4}$ M

Equiv. of O_2 consumed = $2.89 \times 10^{-4} \times 4 = 11.56 \times 10^{-4}$N

Equiv. of S_T oxidized:

$1.29 \times 10^{-4} \times 2 = 2.58 \times 10^{-4}$ equiv. to S^o

$1.29 \times 10^{-4} \times 4 = 5.16 \times 10^{-4}$ " " $S_2O_3^=$

$1.29 \times 10^{-4} \times 6 = 7.74 \times 10^{-4}$ " " $SO_3^=$

$1.29 \times 10^{-4} \times 8 = 10.32 \times 10^{-4}$ " " $SO_4^=$

Figure 31

$S_T = 1.28 \times 10^{-4} - 0.19 \times 10^{-4} = 1.09 \times 10^{-4}$ M

$DO = 9.04 \times 10^{-4} - 7.56 \times 10^{-4} = 1.48 \times 10^{-4}$ M

Equiv. of O_2 consumed = $1.48 \times 10^{-4} = 5.92 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$1.09 \times 10^{-4} \times 2 = 2.18 \times 10^{-4}$ equiv. to S^o

$1.09 \times 10^{-4} \times 4 = 4.36 \times 10^{-4}$ " " $S_2O_3^=$

$1.09 \times 10^{-4} \times 6 = 6.54 \times 10^{-4}$ equiv. to $SO_3^=$

$1.09 \times 10^{-4} \times 8 = 8.72 \times 10^{-4}$ equiv. to $SO_4^=$

Figure 33

$S_T = 1.01 \times 10^{-4} - 0.688 \times 10^{-4} = 3.22 \times 10^{-5}$ M

$DO = 2.62 \times 10^{-4} - 2.12 \times 10^{-4} = 4.0 \times 10^{-5}$ M

Equiv. of O_2 consumed: $4.0 \times 10^{-5} \times 4 = 1.6 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$3.22 \times 10^{-5} \times 2 = 6.44 \times 10^{-5}$ equiv. to S^o

$3.22 \times 10^{-5} \times 4 = 1.29 \times 10^{-4}$ " " $S_2O_3^=$

$3.22 \times 10^{-5} \times 6 = 1.932 \times 10^{-4}$ equiv. to $SO_3^=$

$3.22 \times 10^{-5} \times 8 = 2.576 \times 10^{-4}$ equiv. to $SO_4^=$

Figure 34

$S_T = 4.61 \times 10^{-5} - 2.69 \times 10^{-5} = 1.92 \times 10^{-5}$ M

DO $= 8.42 \times 10^{-4} - 7.85 \times 10^{-4} = 5.7 \times 10^{-5}$ M

Equiv. of 0_2 consumed $= 5.7 \times 10^{-5} \times 4 = 2.22 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$1.92 \times 10^{-5} \times 2 = 3.84 \times 10^{-5}$ equiv. to S^o

$1.92 \times 10^{-5} \times 4 = 7.68 \times 10^{-5}$ " " $S_2O_3^=$

$1.92 \times 10^{-5} \times 6 = 1.052 \times 10^{-4}$ " " $SO_3^=$

$1.92 \times 10^{-5} \times 8 = 1.64 \times 10^{-4}$ " " $SO_4^=$

Figure 35

$S_T = 3.16 \times 10^{-5} - 1.26 \times 10^{-5} = 1.9 \times 10^{-5}$ M

DO $= 9.11 \times 10^{-4} - 8.08 \times 10^{-4} = 1.03 \times 10^{-4}$ M

Equiv. of 0_2 consumed $= 1.03 \times 10^{-4} \times 4 = 4.12 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$1.90 \times 10^{-5} \times 2 = 3.8 \times 10^{-5}$ equiv. to S^o

$1.90 \times 10^{-5} \times 4 = 7.6 \times 10^{-5}$ " " $S_2O_3^=$

$1.90 \times 10^{-5} \times 6 = 1.14 \times 10^{-4}$ " " $SO_3^=$

$1.90 \times 10^{-5} \times 8 = 1.52 \times 10^{-4}$ " " $SO_4^=$

Figure 36

$S_T = 7.78 \times 10^{-5} - 0.16 \times 10^{-5} = 7.52 \times 10^{-5}$ M

$DO = 2.39 \times 10^{-4} - 1.63 \times 10^{-4} = 1.36 \times 10^{-4}$ M

Equiv. of 0_2 consumed = $1.36 \times 10^{-4} \times 4 = 5.44 \times 10^{-4}$ N

Equiv. of S_T ozidized:

$7.52 \times 10^{-5} \times 2 = 1.50 \times 10^{-4}$ equiv. of S^o

$7.52 \times 10^{-5} \times 4 = 3.00 \times 10^{-4}$ " " $S_2O_3^=$

$7.52 \times 10^{-5} \times 6 = 4.51 \times 10^{-4}$ " " $SO_3^=$

$7.52 \times 10^{-5} \times 8 = 6.01 \times 10^{-4}$ " " $SO_4^=$

Figure 37

$S_T = 9.24 \times 10^{-5} - 0.30 \times 10^{-5} = 8.94 \times 10^{-5}$ M

$DO = 2.39 \times 10^{-4} - 1.10 \times 10^{-4} = 1.29 \times 10^{-4}$ M

Equiv. of 0_2 consumed = $1.29 \times 10^{-4} \times 4 = 5.16 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$8.94 \times 10^{-5} \times 2 = 1.79 \times 10^{-4}$ equiv. of S^o

$8.94 \times 10^{-5} \times 4 = 3.58 \times 10^{-4}$ " " $S_2O_3^=$

$8.94 \times 10^{-5} \times 6 = 5.26 \times 10^{-4}$ " " $SO_3^=$

$8.94 \times 10^{-5} \times 8 = 8.15 \times 10^{-4}$ equiv. of $SO_4^=$

Figure 38

$S_T = 2.33 \times 10^{-4} - 0.27 \times 10^{-5} = 2.06 \times 10^{-4}$ M

$DO = 2.58 \times 10^{-4} - 1.10 \times 10^{-4} = 1.48 \times 10^{-4}$ M

Equiv. of O_2 consumed = $1.48 \times 10^{-4} \times 4 = 5.92 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$2.06 \times 10^{-4} \times 2 = 4.12 \times 10^{-4}$ equiv. of S^o

$2.06 \times 10^{-4} \times 4 = 8.24 \times 10^{-4}$ equiv. of $S_2O_3^=$

$2.06 \times 10^{-4} \times 6 = 12.36 \times 10^{-4}$ equiv. of $SO_3^=$

$2.06 \times 10^{-4} \times 8 = 16.48 \times 10^{-4}$ " " $SO_4^=$

Figure 39

$S_T = 1.74 \times 10^{-4} - 0.19 \times 10^{-4} = 1.54 \times 10^{-4}$ M

$DO = 2.60 \times 10^{-4} - 1.39 \times 10^{-4} = 1.21 \times 10^{-4}$ M

Equiv. of O_2 consumed = $1.21 \times 10^{-4} = 4.84 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$1.54 \times 10^{-4} \times 2 = 3.09 \times 10^{-4}$ equiv. of S^o

$1.54 \times 10^{-4} \times 4 = 6.18 \times 10^{-4}$ equiv. of $S_2O_3^=$

$1.54 \times 10^{-4} \times 6 = 9.24 \times 10^{-4}$ equiv. of $SO_3^=$

$1.54 \times 10^{-4} \times 8 = 12.32 \times 10^{-4}$ " " $SO_4^=$

Figure 40

$S_T = 1.43 \times 10^{-4} - 0.038 \times 10^{-4} = 1.392 \times 10^{-4}$ M

$D0 = 2.69 \times 10^{-4} - 1.22 \times 10^{-4} = 1.47 \times 10^{-4}$ M

Equiv. of 0_2 consumed = $1.47 \times 10^{-4} \times 4 = 5.88 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$1.54 \times 10^{-4} \times 2 = 3.09 \times 10^{-4}$ equiv. of S^o

$1.39 \times 10^{-4} = 4 = 5.56 \times 10^{-4}$ equiv. of $S_2O_3^=$

$1.39 \times 10^{-4} \times 6 = 8.35 \times 10^{-4}$ equiv. of $SO_3^=$

$1.39 \times 10^{-4} \times 8 = 11.12 \times 10^{-4}$ " " $SO_4^=$

Figure 41

$S_T = 1.49 \times 15^{-4} - 0.044 \times 10^{-4} = 1.446 \times 10^{-4}$ M

$D0 = 2.26 \times 10^{-4} - 1.03 \times 10^{-4} = 1.23 \times 10^{-4}$ M

Equiv. of 0_2 consumed = $1.23 \times 10^{-4} \times 4 = 4.92 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$1.44 \times 10^{-4} \times 2 = 2.88 \times 10^{-4}$ equiv. of S^o

$1.44 \times 10^{-4} \times 4 = 5.76 \times 10^{-4}$ equiv. of $S_2O_3^=$

$1.44 \times 10^{-4} \times 6 = 8.64 \times 10^{-4}$ equiv. of $SO_3^=$

$1.44 \times 10^{-4} \times 8 = 11.52 \times 10^{-4}$ " " $SO_4^=$

Figure 42

$S_T = 1.28 \times 10^{-4} - 0.10 \times 10^{-4} = 1.18 \times 10^{-4}$ M

$DO = 2.43 \times 10^{-4} - 0.87 \times 10^{-4} = 1.56 \times 10^{-4}$ M

Equiv. of O_2 consumed = $1.56 \times 10^{-4} = 6.24 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$1.18 \times 10^{-4} \times 2 = 2.36 \times 10^{-4}$ equiv. of S^o

$1.18 \times 10^{-4} \times 4 = 4.72 \times 10^{-4}$ " " $S_2O_3^=$

$1.18 \times 10^{-4} \times 6 = 7.08 \times 10^{-4}$ equiv. of $SO_3^=$

$1.18 \times 10^{-4} \times 8 = 9.44 \times 10^{-4}$ equiv. of $SO_4^=$

Figure 43

$S_T = 7.20 \times 10^{-5} - 0.70 \times 10^{-5} = 6.50 \times 10^{-5}$ M

$DO = 2.13 \times 10^{-4} - 1.0 \times 10^{-4} = 1.13 \times 10^{-4}$ M

Equiv. of O_2 consumed = $1.13 \times 10^{-4} \times 4 = 4.52 \times 10^{-4}$

Equiv. of S_T oxidized:

$6.50 \times 10^{-5} \times 2 = 1.3 \times 10^{-4}$ equiv. of S^o

$6.50 \times 10^{-5} \times 4 = 2.60 \times 10^{-4}$ " " $S_2O_3^=$

$6.50 \times 10^{-5} \times 6 = 3.90 \times 10^{-4}$ " " $SO_3^=$

$6.50 \times 10^{-5} \times 8 = 5.2 \times 10^{-4}$ " " $SO_4^=$

Figure 44

$S_T = 1.18 \times 10^{-4} - 0.45 \times 10^{-4} = 7.3 \times 10^{-5}$ M

$DO = 2.43 \times 10^{-4} - 0.78 \times 10^{-4} = 1.65 \times 10^{-4}$ M

Equiv. of O_2 consumed = $1.65 \times 10^{-4} \times 4 = 7.60 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$7.3 \times 10^{-5} \times 2 = 1.46 \times 10^{-4}$ equiv. of S^o

$7.3 \times 10^{-5} \times 4 = 2.92 \times 10^{-4}$ " " $S_2O_3^=$

$7.3 \times 10^{-5} \times 6 = 4.38 \times 10^{-4}$ " " $SO_3^=$

$7.3 \times 10^{-5} \times 8 = 6.00 \times 10^{-4}$ " " $SO_4^=$

Figure 45

$S_T = 1.20 \times 10^{-4} - 0.10 \times 10^{-4} = 1.10 \times 10^{-4}$ M

$DO = 2.18 \times 10^{-4} - 0.70 \times 10^{-4} = 1.48 \times 10^{-4}$ M

Equiv. of O_2 consumed = $1.48 \times 10^{-4} \times 4 = 5.92 \times 10^{-4}$ N

Equiv. of S_T oxidized:

$1.10 \times 10^{-4} \times 2 = 2.2 \times 10^{-4}$ equiv. of S^o

$1.10 \times 10^{-4} \times 4 = 4.4 \times 10^{-4}$ " " $S_2O_3^=$

$1.10 \times 10^{-4} \times 6 = 6.6 \times 10^{-4}$ equiv. of $SO_3^=$

$1.10 \times 10^{-4} \times 8 = 8.8 \times 10^{-4}$ equiv. of $SO_4^=$

APPENDIX II

EXPERIMENTAL DATA ON RATES OF OXIDATION OF HYDROGEN SULFIDE AT 25°C.

COMPUTER CALCULATED RESULTS OF FIGURE 20

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE C2	K2 RATE STC2
0	0.101E-02	0.108E-02	-0.299E 01	-0.296E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
30	0.974E-03	0.107E-02	-0.301E 01	-0.296E 01	0.555E-03	0.776E-04	0.128E 01	0.174E-03	0.692E 01
60	0.956E-03	0.105E-02	-0.301E 01	-0.297E 01	0.416E-03	0.156E-03	0.975E 00	0.141E-02	0.377E 01
90	0.937E-03	0.104E-02	-0.302E 01	-0.298E 01	0.370E-03	0.184E-03	0.875E 00	0.378E-02	0.270E 01
120	0.920E-03	0.102E-02	-0.303E 01	-0.299E 01	0.347E-03	0.178E-03	0.828E 00	0.656E-02	0.244E 01
150	0.902E-03	0.101E-02	-0.304E 01	-0.299E 01	0.333E-03	0.175E-03	0.803E 00	0.101E-01	0.228E 01
180	0.885E-03	0.100E-02	-0.305E 01	-0.299E 01	0.324E-03	0.187E-03	0.788E 00	0.157E-01	0.197E 01
240	0.852E-03	0.971E-03	-0.306E 01	-0.301E 01	0.312E-03	0.193E-03	0.775E 00	0.293E-01	0.171E 01
30	0.816E-03	0.673E-02	-0.308E 01	-0.217E 01	0.311E-02	-0.264E-01	0.789E 01	-0.272E-01	0.428E 03
360	0.804E-03	0.925E-03	-0.309E 01	-0.303E 01	0.277E-03	0.188E-03	0.710E 00	0.657E-01	0.130E 01
420	0.789E-03	0.896E-03	-0.310E 01	-0.304E 01	0.257E-03	0.194E-03	0.666E 00	0.937E-01	0.925E 00
540	0.759E-03	0.861E-03	-0.311E 01	-0.306E 01	0.231E-03	0.182E-03	0.609E 00	0.148E 00	0.707E 00
660	0.744E-03	0.827E-03	-0.312E 01	-0.308E 01	0.202E-03	0.176E-03	0.537E 00	0.219E 00	0.369E 00
780	0.716E-03	0.798E-03	-0.314E 01	-0.309E 01	0.192E-03	0.169E-03	0.522E 00	0.299E 00	0.335E 00
900	0.689E-03	0.775E-03	-0.316E 01	-0.311E 01	0.185E-03	0.160E-03	0.513E 00	0.385E 00	0.353E 00
1020	0.676E-03	0.757E-03	-0.316E 01	-0.312E 01	0.171E-03	0.151E-03	0.480E 00	0.471E 00	0.290E 00
1140	0.663E-03	0.734E-03	-0.317E 01	-0.313E 01	0.160E-03	0.147E-03	0.454E 00	0.582E 00	0.194E 00
1320	0.603E-03	0.717E-03	-0.321E 01	-0.314E 01	0.170E-03	0.135E-03	0.507E 00	0.725E 00	0.511E 00
1500	0.580E-03	0.694E-03	-0.323E 01	-0.315E 01	0.161E-03	0.128E-03	0.490E 00	0.905E 00	0.473E 00
1680	0.548E-03	0.670E-03	-0.326E 01	-0.317E 01	0.158E-03	0.123E-03	0.498E 00	0.111E 01	0.511E 00
1860	0.507E-03	0.647E-03	-0.329E 01	-0.318E 01	0.161E-03	0.119E-03	0.528E 00	0.134E 01	0.603E 00
2040	0.488E-03	0.630E-03	-0.331E 01	-0.320E 01	0.155E-03	0.114E-03	0.519E 00	0.157E 01	0.584E 00
2280	0.435E-03	0.607E-03	-0.336E 01	-0.321E 01	0.160E-03	0.109E-03	0.574E 00	0.192E 01	0.737E 00
2520	0.373E-03	0.578E-03	-0.342E 01	-0.323E 01	0.171E-03	0.107E-03	0.670E 00	0.237E 01	0.929E 00
2760	0.320E-03	0.561E-03	-0.349E 01	-0.325E 01	0.181E-03	0.103E-03	0.773E 00	0.276E 01	0.112E 01
2781	0.314E-03	0.555E-03	-0.350E 01	-0.325E 01	0.182E-03	0.104E-03	0.789E 00	0.285E 01	0.114E 01
2785	0.145E-03	0.520E-03	-0.383E 01	-0.328E 01	0.302E-03	0.114E-03	0.210E 01	0.324E 01	0.272E 01
2790	0.920E-04	0.497E-03	-0.403E 01	-0.330E 01	0.373E-03	0.120E-03	0.354E 01	0.354E 01	0.366E 01
2798	0.603E-04	0.451E-03	-0.421E 01	-0.334E 01	0.437E-03	0.135E-03	0.557E 01	0.422E 01	0.437E 01

COMPUTER CALCULATED RESULTS OF FIGURE 21

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE STO2
0	0.167E-03	0.107E-02	-0.377E 01	-0.297E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
30	0.164E-03	0.106E-02	-0.378E 01	-0.297E 01	0.277E-03	0.793E-04	0.385E 01	0.176E-03	0.219E 00
60	0.161E-03	0.105E-02	-0.379E 01	-0.297E 01	0.277E-03	0.795E-04	0.388E 01	0.709E-03	0.219E 00
90	*****	END OF LAG PERIOD				*****			
90	0.158E-03	0.105E-02	-0.380E 01	-0.297E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
120	0.152E-03	0.105E-02	-0.381E 01	-0.297E 01	0.555E-03	0.322E-04	0.824E 01	0.703E-04	0.585E 00
150	0.149E-03	0.104E-02	-0.382E 01	-0.298E 01	0.416E-03	0.403E-04	0.624E 01	0.352E-03	0.420E 00
180	0.143E-03	0.104E-02	-0.384E 01	-0.298E 01	0.462E-03	0.539E-04	0.706E 01	0.106E-02	0.457E 00
210	0.141E-03	0.103E-02	-0.385E 01	-0.298E 01	0.416E-03	0.608E-04	0.642E 01	0.214E-02	0.397E 00
240	0.138E-03	0.102E-02	-0.385E 01	-0.298E 01	0.388E-03	0.650E-04	0.605E 01	0.359E-02	0.362E 00
270	0.133E-03	0.102E-02	-0.387E 01	-0.298E 01	0.416E-03	0.679E-04	0.661E 01	0.541E-02	0.389E 00
300	0.130E-03	0.101E-02	-0.388E 01	-0.299E 01	0.396E-03	0.701E-04	0.636E 01	0.762E-02	0.365E 00
330	0.128E-03	0.101E-02	-0.389E 01	-0.299E 01	0.381E-03	0.717E-04	0.618E 01	0.102E-01	0.346E 00
360	0.125E-03	0.100E-02	-0.390E 01	-0.299E 01	0.370E-03	0.731E-04	0.605E 01	0.132E-01	0.332E 00
420	0.120E-03	0.999E-03	-0.391E 01	-0.300E 01	0.353E-03	0.675E-04	0.590E 01	0.182E-01	0.319E 00
480	0.116E-03	0.988E-03	-0.393E 01	-0.300E 01	0.341E-03	0.702E-04	0.582E 01	0.267E-01	0.303E 00
540	0.109E-03	0.978E-03	-0.395E 01	-0.300E 01	0.351E-03	0.700E-04	0.617E 01	0.356E-01	0.315E 00
600	0.998E-04	0.967E-03	-0.400E 01	-0.301E 01	0.392E-03	0.720E-04	0.724E 01	0.473E-01	0.357E 00
660	0.907E-04	0.959E-03	-0.404E 01	-0.301E 01	0.423E-03	0.709E-04	0.825E 01	0.585E-01	0.394E 00
720	0.840E-04	0.953E-03	-0.407E 01	-0.302E 01	0.436E-03	0.683E-04	0.886E 01	0.691E-01	0.411E 00
780	0.763E-04	0.949E-03	-0.411E 01	-0.302E 01	0.458E-03	0.647E-04	0.982E 01	0.787E-01	0.440E 00
840	0.734E-04	0.941E-03	-0.413E 01	-0.302E 01	0.444E-03	0.645E-04	0.972E 01	0.931E-01	0.424E 00
900	0.720E-04	0.935E-03	-0.414E 01	-0.302E 01	0.421E-03	0.631E-04	0.933E 01	0.106E 00	0.401E 00
960	0.706E-04	0.929E-03	-0.415E 01	-0.303E 01	0.402E-03	0.619E-04	0.899E 01	0.120E 00	0.380E 00
1020	0.693E-04	0.923E-03	-0.415E 01	-0.303E 01	0.385E-03	0.608E-04	0.871E 01	0.136E 00	0.362E 00
1140	0.642E-04	0.912E-03	-0.419E 01	-0.303E 01	0.373E-03	0.591E-04	0.881E 01	0.170E 00	0.350E 00
1260	0.595E-04	0.900E-03	-0.423E 01	-0.304E 01	0.370E-03	0.579E-04	0.924E 01	0.207E 00	0.349E 00

COMPUTER CALCULATED RESULTS OF FIGURE 22

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE STO2
0	0.572E-04	0.107E-02	-0.424E 01	-0.297E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
30	0.454E-04	0.106E-02	-0.434E 01	-0.297E 01	0.333E-02	0.391E-04	0.150E 03	0.869E-04	0.325E 01
60	0.236E-04	0.106E-02	-0.462E 01	-0.297E 01	0.638E-02	0.392E-04	0.412E 03	0.348E-03	0.626E 01
90	0.130E-04	0.105E-02	-0.488E 01	-0.297E 01	0.712E-02	0.471E-04	0.656E 03	0.946E-03	0.699E 01
120	0.101E-04	0.105E-02	-0.499E 01	-0.297E 01	0.624E-02	0.393E-04	0.673E 03	0.140E-02	0.613E 01
150	0.907E-05	0.105E-02	-0.504E 01	-0.297E 01	0.533E-02	0.393E-04	0.618E 03	0.219E-02	0.522E 01
180	0.824E-05	0.105E-02	-0.508E 01	-0.297E 01	0.467E-02	0.394E-04	0.577E 03	0.317E-02	0.457E 01
210	0.793E-05	0.104E-02	-0.510E 01	-0.297E 01	0.408E-02	0.406E-04	0.517E 03	0.445E-02	0.399E 01
240	0.763E-05	0.104E-02	-0.511E 01	-0.298E 01	0.344E-02	0.395E-04	0.473E 03	0.567E-02	0.336E 01
270	0.720E-05	0.104E-02	-0.514E 01	-0.298E 01	0.333E-02	0.396E-04	0.449E 03	0.720E-02	0.325E 01
300	0.706E-05	0.104E-02	-0.515E 01	-0.298E 01	0.302E-02	0.396E-04	0.413E 03	0.891E-02	0.295E 01
330	0.680E-05	0.103E-02	-0.516E 01	-0.298E 01	0.280E-02	0.404E-04	0.392E 03	0.110E-01	0.272E 01
360	0.667E-05	0.103E-02	-0.517E 01	-0.298E 01	0.259E-02	0.397E-04	0.367E 03	0.129E-01	0.252E 01
420	0.630E-05	0.102E-02	-0.520E 01	-0.298E 01	0.228E-02	0.398E-04	0.336E 03	0.176E-01	0.221E 01
480	0.585E-05	0.102E-02	-0.523E 01	-0.299E 01	0.206E-02	0.420E-04	0.319E 03	0.244E-01	0.199E 01
540	0.550E-05	0.101E-02	-0.525E 01	-0.299E 01	0.188E-02	0.410E-04	0.303E 03	0.302E-01	0.181E 01
660	0.520E-05	0.100E-02	-0.528E 01	-0.299E 01	0.157E-02	0.433E-04	0.264E 03	0.481E-01	0.151E 01
780	0.481E-05	0.986E-03	-0.531E 01	-0.300E 01	0.137E-02	0.451E-04	0.243E 03	0.704E-01	0.131E 01

COMPUTER CALCULATED RESULTS OF FIGURE 24

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE STO2
0	0.101E-02	0.249E-03	-0.299E 01	-0.360E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
30	0.101E-02	0.243E-03	-0.299E 01	-0.361E 01	0.000E 00	0.348E-03	0.000E 00	0.182E-03	0.458E 00
60	0.101E-02	0.238E-03	-0.299E 01	-0.362E 01	0.000E 00	0.308E-03	0.000E 00	0.649E-03	0.404E 00
90	0.998E-03	0.232E-03	-0.300E 01	-0.363E 01	0.555E-04	0.326E-03	0.127E 00	0.157E-02	0.356E 00
120	0.998E-03	0.226E-03	-0.300E 01	-0.364E 01	0.416E-04	0.338E-03	0.955E-01	0.293E-02	0.390E 00
150	0.990E-03	0.220E-03	-0.300E 01	-0.365E 01	0.555E-04	0.347E-03	0.127E 00	0.476E-02	0.383E 00
180	*****	END OF LAG PERIOD				*****			
180	0.990E-03	0.215E-03	-0.300E 01	-0.366E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
240	0.979E-03	0.204E-03	-0.300E 01	-0.368E 01	0.833E-04	0.358E-03	0.194E 00	0.654E-03	0.354E 00
300	0.979E-03	0.194E-03	-0.300E 01	-0.371E 01	0.416E-04	0.367E-03	0.973E-01	0.275E-02	0.419E 00
360	0.972E-03	0.182E-03	-0.301E 01	-0.373E 01	0.462E-04	0.397E-03	0.108E 00	0.692E-02	0.457E 00
420	0.960E-03	0.172E-03	-0.301E 01	-0.376E 01	0.555E-04	0.396E-03	0.131E 00	0.126E-01	0.438E 00
540	0.889E-03	0.149E-03	-0.305E 01	-0.382E 01	0.129E-03	0.436E-03	0.318E 00	0.337E-01	0.395E 00
660	0.889E-03	0.000E 00	-0.305E 01	-0.738E 38	0.472E-04	-0.764E-02	0.238E 00	0.221E 04	-0.997E 01
780	0.856E-03	0.000E 00	-0.306E 01	-0.738E 38	0.105E-03	-0.611E-02	0.264E 00	0.277E-04	-0.801E 01
900	0.824E-03	0.949E-04	-0.308E 01	-0.402E 01	0.111E-03	0.493E-03	0.283E 00	0.195E 00	0.492E 00
1020	0.793E-03	0.800E-04	-0.310E 01	-0.409E 01	0.115E-03	0.510E-03	0.299E 00	0.304E 00	0.509E 00
1140	0.793E-03	0.652E-04	-0.310E 01	-0.418E 01	0.100E-03	0.539E-03	0.262E 00	0.473E 00	0.565E 00
1320	0.778E-03	0.489E-04	-0.310E 01	-0.431E 01	0.921E-04	0.563E-03	0.242E 00	0.832E 00	0.608E 00
1500	0.734E-03	0.355E-04	-0.313E 01	-0.444E 01	0.984E-04	0.591E-03	0.266E 00	0.143E 01	0.635E 00
1620	0.706E-03	0.296E-04	-0.315E 01	-0.452E 01	0.101E-03	0.597E-03	0.281E 00	0.193E 01	0.638E 00

COMPUTER CALCULATED RESULTS OF FIGURE 25

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE STO2
0	0.389E-19	0.569E-04	-0.194E 02	-0.424E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
30	0.389E-19	0.566E-04	-0.194E 02	-0.424E 01	0.000E 00	0.864E-04	0.000E 00	0.102E-04	-0.151E 01
90	0.389E-19	0.561E-04	-0.194E 02	-0.425E 01	0.000E 00	0.723E-04	0.000E 00	0.774E-04	-0.127E 01
60	0.389E-19	0.564E-04	-0.194E 02	-0.424E 01	0.000E 00	0.649E-04	0.000E 00	0.307E-04	-0.113E 01
120	0.389E-19	0.559E-04	-0.194E 02	-0.425E 01	0.000E 00	0.652E-04	0.000E 00	0.124E-03	-0.114E 01
150	0.389E-19	0.555E-04	-0.194E 02	-0.425E 01	0.000E 00	0.697E-04	0.000E 00	0.208E-03	-0.122E 01
180	0.389E-19	0.552E-04	-0.194E 02	-0.425E 01	0.000E 00	0.728E-04	0.000E 00	0.314E-03	-0.127E 01
210	0.389E-19	0.549E-04	-0.194E 02	-0.426E 01	0.000E 00	0.752E-04	0.000E 00	0.442E-03	-0.132E 01
240	0.389E-19	0.545E-04	-0.194E 02	-0.426E 01	0.000E 00	0.770E-04	0.000E 00	0.594E-03	-0.135E 01
270	0.389E-19	0.542E-04	-0.194E 02	-0.426E 01	0.000E 00	0.784E-04	0.000E 00	0.768E-03	-0.137E 01
300	0.389E-19	0.539E-04	-0.194E 02	-0.426E 01	0.000E 00	0.797E-04	0.000E 00	0.967E-03	-0.139E 01
330	0.389E-19	0.535E-04	-0.194E 02	-0.427E 01	0.000E 00	0.807E-04	0.000E 00	0.118E-02	-0.141E 01
360	0.389E-19	0.532E-04	-0.194E 02	-0.427E 01	0.000E 00	0.816E-04	0.000E 00	0.143E-02	-0.143E 01
420	0.389E-19	0.528E-04	-0.194E 02	-0.427E 01	0.000E 00	0.766E-04	0.000E 00	0.183E-02	-0.134E 01
480	0.389E-19	0.525E-04	-0.194E 02	-0.427E 01	0.000E 00	0.728E-04	0.000E 00	0.229E-02	-0.127E 01
540	0.389E-19	0.518E-04	-0.194E 02	-0.428E 01	0.000E 00	0.752E-04	0.000E 00	0.301E-02	-0.132E 01
600	0.389E-19	0.515E-04	-0.194E 02	-0.428E 01	0.000E 00	0.724E-04	0.000E 00	0.359E-02	-0.127E 01
660	0.389E-19	0.510E-04	-0.194E 02	-0.429E 01	0.000E 00	0.723E-04	0.000E 00	0.437E-02	-0.127E 01
720	0.389E-19	0.505E-04	-0.194E 02	-0.429E 01	0.000E 00	0.723E-04	0.000E 00	0.522E-02	-0.127E 01
780	0.389E-19	0.501E-04	-0.194E 02	-0.429E 01	0.000E 00	0.705E-04	0.000E 00	0.600E-02	-0.123E 01
840	0.389E-19	0.498E-04	-0.194E 02	-0.430E 01	0.000E 00	0.690E-04	0.000E 00	0.683E-02	-0.121E 01
900	0.389E-19	0.491E-04	-0.194E 02	-0.430E 01	0.000E 00	0.710E-04	0.000E 00	0.813E-02	-0.124E 01
960	0.389E-19	0.484E-04	-0.194E 02	-0.431E 01	0.000E 00	0.728E-04	0.000E 00	0.955E-02	-0.127E 01
1020	0.389E-19	0.481E-04	-0.194E 02	-0.431E 01	0.000E 00	0.715E-04	0.000E 00	0.106E-01	-0.125E 01
1080	0.389E-19	0.474E-04	-0.194E 02	-0.432E 01	0.000E 00	0.733E-04	0.000E 00	0.123E-01	-0.128E 01
1200	0.389E-19	0.459E-04	-0.194E 02	-0.433E 01	0.000E 00	0.778E-04	0.000E 00	0.163E-01	-0.136E 01
1260	0.389E-19	0.452E-04	-0.194E 02	-0.434E 01	0.000E 00	0.792E-04	0.000E 00	0.185E-01	-0.139E 01

COMPUTER CALCULATED RESULTS OF FIGURE 26

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE STO2
0	0.260E-03	0.23HE-03	-0.358E 01	-0.362E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0[illegible]
15	0.215E-03	0.237E-03	-0.366E 01	-0.362E 01	0.537E-02	0.129E-03	0.523E 02	0.160E-04	-0.243[illegible] 03
30	0.192E-03	0.236E-03	-0.371E 01	-0.362E 01	0.435E-02	0.108[illegible]-03	0.449E 02	0.537E-04	-0.197E 0[illegible]
45	0.168E-03	0.236E-03	-0.377E 01	-0.362E 01	0.419E-02	0.868E-04	0.465E 02	0.969E-04	-0.190E 03
60	0.155E-03	0.235E-03	-0.380E 01	-0.362E 01	0.370E-02	0.760E-04	0.428E 02	0.151E-03	-0.168E 03
90	0.126E-03	0.234E-03	-0.389E 01	-0.362E 01	0.348E-02	0.725E-04	0.453E 02	0.325E-03	-0.158E 03
120	0.112E-03	0.233E-03	-0.394E 01	-0.363E 01	0.303E-02	0.764E-04	0.420E 02	0.610E-03	-0.137[illegible] 03
150	0.102E-03	0.232E-03	-0.399E 01	-0.363E 01	0.270E-02	0.744E-04	0.396E 02	0.931E-03	-0.122E 03
180	0.946E-04	0.231E-03	-0.402E 01	-0.363E 01	0.243E-02	0.731E-04	0.373E 02	0.132E-02	-0.109E 03
240	*****	END OF LAG PERIOD				*****			
240	0.859E-04	0.228E-03	-0.406E 01	-0.364E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000[illegible] 01
300	0.827E-04	0.227E-03	-0.408E 01	-0.364E 01	0.277E-03	0.451E-04	0.758E 01	0.859E-04	0.162E 01
360	0.796E-04	0.225E-03	-0.409E 01	-0.364E 01	0.277E-03	0.510E-04	0.773E 01	0.389E-03	[illegible].156[illegible] 01
420	0.766E-04	0.224E-03	-0.411E 01	-0.364E 01	0.277E-03	0.454E-04	0.788E 01	0.783E-03	0.162E 01
480	0.737E-04	0.222E-03	-0.413E 01	-0.365E 01	0.277E-03	0.484E-04	0.804E 01	0.149E-02	0.160E 01
600	0.709E-04	0.218E-03	-0.414E 01	-0.366E 01	0.231E-03	0.576E-04	0.683E 01	0.403E-02	0.121E 01
720	0.682E-04	0.220E-03	-0.416E 01	-0.365E 01	0.208E-03	0.329E-04	0.627E 01	0.407E-02	0.122E 01
840	0.657E-04	0.219E-03	-0.418E 01	-0.365E 01	0.194E-03	0.310E-04	0.597E 01	0.601E-02	0.114E 01
960	0.632E-04	0.218E-03	-0.419E 01	-0.366E 01	0.185E-03	0.278E-04	0.580E 01	0.778E-02	0.110[illegible] 01
1080	0.620E-04	0.217E-03	-0.420E 01	-0.366E 01	0.168E-03	0.255E-04	0.534E 01	0.973E-02	0.100E 01
1200	0.608E-04	0.216E-03	-0.421E 01	-0.366E 01	0.156E-03	0.260E-04	0.499E 01	0.130E-01	0.911E 00
1320	0.585E-04	0.215E-03	-0.423E 01	-0.366E 01	0.154E-03	0.244E-04	0.503E 01	0.155E-01	0.908E 0[illegible]
1440	0.563E-04	0.210E-03	-0.424E 01	-0.367E 01	0.152E-03	0.311E-04	0.509E 01	0.246E-01	0.851E 00
1560	0.542E-04	0.206E-03	-0.426E 01	-0.368E 01	0.151E-03	0.339E-04	0.515E 01	0.328E-01	0.822[illegible] 03
1680	0.532E-04	0.203E-03	-0.427E 01	-0.369E 01	0.144E-03	0.352E-04	0.497E 01	0.409E-01	0.765E 00
1800	0.522E-04	0.200E-03	-0.428E 01	-0.369E 01	0.138E-03	0.364E-04	0.482E 01	0.500E-01	0.716E 00
1920	0.512E-04	0.198E-03	-0.429E 01	-0.370E 01	0.133E-03	0.366E-04	0.469E 01	0.585E-01	0.680E 00
2040	0.512E-04	0.198E-03	-0.429E 01	-0.370E 01	0.129E-03	0.342E-04	0.438E 01	0.627E-01	0.635E 00
2160	0.512E-04	0.198E-03	-0.429E 01	-0.370E 01	0.117E-03	0.320E-04	0.411E 01	0.669E-01	0.595E 00

COMPUTER CALCULATED RESULTS OF FIGURE 27

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE STO2
0	0.570E-03	0.949E-03	-0.324E 01	-0.302E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
30	0.570E-03	0.943E-03	-0.324E 01	-0.302E 01	0.000E 00	0.849E-04	0.000E 00	0.167E-03	-0.224E 00
60	0.570E-03	0.935E-03	-0.324E 01	-0.302E 01	0.000E 00	0.102E-03	0.000E 00	0.810E-03	-0.270E 00
90	0.570E-03	0.932E-03	-0.324E 01	-0.303E 01	0.000E 00	0.854E-04	0.000E 00	0.152E-02	-0.225E 00
120	0.570E-03	0.924E-03	-0.324E 01	-0.303E 01	0.000E 00	0.943E-04	0.000E 00	0.300E-02	-0.248E 00
150	0.559E-03	0.917E-03	-0.325E 01	-0.303E 01	0.555E-04	0.999E-04	0.226E 00	0.499E-02	-0.117E 00
180	0.548E-03	0.910E-03	-0.326E 01	-0.304E 01	0.925E-04	0.100E-03	0.381E 00	0.729E-02	-0.217E-01
240	*****	END OF LAG PERIOD				*****			
240	0.538E-03	0.899E-03	-0.326E 01	-0.304E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
300	0.528E-03	0.877E-03	-0.327E 01	-0.305E 01	0.138E-03	0.180E-03	0.599E 00	0.136E-02	-0.116E 00
360	0.518E-03	0.858E-03	-0.328E 01	-0.306E 01	0.130E-03	0.169E-03	0.605E 00	0.516E-02	-0.840E-01
420	0.508E-03	0.847E-03	-0.329E 01	-0.307E 01	0.138E-03	0.144E-03	0.611E 00	0.997E-02	-0.147E-01
540	0.498E-03	0.827E-03	-0.330E 01	-0.308E 01	0.111E-03	0.121E-03	0.493E 00	0.235E-01	-0.276E-01
660	0.470E-03	0.802E-03	-0.332E 01	-0.309E 01	0.138E-03	0.117E-03	0.635E 00	0.454E-01	0.592E-01
780	0.453E-03	0.771E-03	-0.334E 01	-0.311E 01	0.138E-03	0.123E-03	0.648E 00	0.803E-01	0.436E-01
900	0.435E-03	0.754E-03	-0.336E 01	-0.312E 01	0.138E-03	0.115E-03	0.661E 00	0.113E 00	0.658E-01
1020	0.419E-03	0.739E-03	-0.337E 01	-0.313E 01	0.138E-03	0.108E-03	0.674E 00	0.151E 00	0.828E-01
1140	0.411E-03	0.721E-03	-0.338E 01	-0.314E 01	0.129E-03	0.106E-03	0.635E 00	0.199E 00	0.649E-01
1320	0.396E-03	0.695E-03	-0.340E 01	-0.315E 01	0.123E-03	0.103E-03	0.617E 00	0.285E 00	0.549E-01
1500	0.373E-03	0.666E-03	-0.342E 01	-0.317E 01	0.125E-03	0.103E-03	0.648E 00	0.396E 00	0.615E-01
1680	0.353E-03	0.643E-03	-0.345E 01	-0.319E 01	0.127E-03	0.100E-03	0.677E 00	0.513E 00	0.736E-01
1860	0.333E-03	0.610E-03	-0.347E 01	-0.321E 01	0.129E-03	0.103E-03	0.705E 00	0.688E 00	0.687E-01
2040	0.320E-03	0.588E-03	-0.349E 01	-0.323E 01	0.125E-03	0.102E-03	0.700E 00	0.855E 00	0.627E-01
2280	*****	FERROUS ION ADDED 1*10-5				*****			
2280	0.297E-03	0.566E-03	-0.352E 01	-0.324E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
2292	0.202E-03	0.505E-03	-0.369E 01	-0.329E 01	0.138E-01	0.412E-02	0.131E 03	0.821E-03	0.362E 02
2295	0.489E-04	0.488E-03	-0.431E 01	-0.331E 01	0.522E-01	0.427E-02	0.113E 04	0.135E-02	0.178E 03
2302	0.320E-04	0.444E-03	-0.449E 01	-0.335E 01	0.439E-01	0.479E-02	0.126E 04	0.342E-02	0.145E 03
2310	0.254E-04	0.399E-03	-0.459E 01	-0.339E 01	0.355E-01	0.504E-02	0.119E 04	0.707E-02	0.113E 03

COMPUTER CALCULATED RESULTS OF FIGURE 27 (Cont'd.)

2325	0.202E-04	0.333E-03	-0.469E 01	-0.347E 01	0.259E-01	0.512E-02	0.102E 04	0.178E-01	0.772E 02
2340	0.196E-04	0.280E-03	-0.471E 01	-0.353E 01	0.197E-01	0.487E-02	0.799E 03	0.326E-01	0.551E 02
2355	0.210E-04	0.255E-03	-0.467E 01	-0.359E 01	0.153E-01	0.461E-02	0.589E 03	0.516E-01	0.398E 02
2370	0.227E-04	0.227E-03	-0.464E 01	-0.364E 01	0.124E-01	0.439E-02	0.451E 03	0.758E-01	0.297E 02
2385	0.245E-04	0.205E-03	-0.461E 01	-0.368E 01	0.103E-01	0.419E-02	0.356E 03	0.104E 00	0.227E 02
2400	0.264E-04	0.188E-03	-0.457E 01	-0.372E 01	0.874E-02	0.397E-02	0.286E 03	0.135E 00	0.177E 02
2430	0.297E-04	0.162E-03	-0.452E 01	-0.379E 01	0.666E-02	0.362E-02	0.202E 03	0.211E 00	0.113E 02
2460	0.320E-04	0.144E-03	-0.448E 01	-0.384E 01	0.532E-02	0.329E-02	0.151E 03	0.297E 00	0.752E 01
2520	0.339E-04	0.114E-03	-0.446E 01	-0.394E 01	0.392E-02	0.289E-02	0.108E 03	0.536E 00	0.382E 01
2580	0.308E-04	0.943E-04	-0.451E 01	-0.402E 01	0.327E-02	0.259E-02	0.967E 02	0.849E 00	0.254E 01
2640	0.285E-04	0.832E-04	-0.454E 01	-0.407E 01	0.282E-02	0.231E-02	0.870E 02	0.118E 01	0.190E 01
2700	0.269E-04	0.721E-04	-0.456E 01	-0.414E 01	0.248E-02	0.213E-02	0.802E 02	0.162E 01	0.130E 01
2760	0.235E-04	0.666E-04	-0.462E 01	-0.417E 01	0.229E-02	0.193E-02	0.812E 02	0.203E 01	0.132E 01

COMPUTER CALCULATED RESULTS OF FIGURE 28

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE ST:O2
0	0.139E-03	0.910E-03	-0.385E 01	-0.304E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
60	0.137E-03	0.905E-03	-0.386E 01	-0.304E 01	0.138E-03	0.405E-04	0.230E 01	0.306E-03	0.127E 00
120	0.137E-03	0.903E-03	-0.386E 01	-0.304E 01	0.694E-04	0.204E-04	0.115E 01	0.861E-03	0.532E-01
180	0.137E-03	0.900E-03	-0.386E 01	-0.304E 01	0.462E-04	0.271E-04	0.768E 00	0.185E-02	0.249E-01
240	0.137E-03	0.900E-03	-0.386E 01	-0.304E 01	0.347E-04	0.203E-04	0.576E 00	0.246E-02	0.186E-01
300	*****	LAG PERIOD ENDED				*****			
300	0.137E-03	0.894E-03	-0.386E 01	-0.304E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
360	0.134E-03	0.890E-03	-0.387E 01	-0.305E 01	0.138E-03	0.329E-04	0.235E 01	0.245E-03	0.139E 00
420	0.129E-03	0.887E-03	-0.388E 01	-0.305E 01	0.208E-03	0.289E-04	0.359E 01	0.861E-03	0.236E 00
540	0.124E-03	0.880E-03	-0.390E 01	-0.305E 01	0.173E-03	0.290E-04	0.305E 01	0.347E-02	0.190E 00
1140	0.935E-04	0.839E-03	-0.402E 01	-0.307E 01	0.198E-03	0.333E-04	0.405E 01	0.501E-01	0.217E 00
1174	*****	FERROUS SULFIDE ADDED 1*10-5				*****			
1174	0.900E-04	0.836E-03	-0.404E 01	-0.307E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
1176	0.244E-04	0.823E-03	-0.461E 01	-0.308E 01	0.283E 00	0.332E-02	0.149E 05	0.258E-04	0.375E 03
1178	0.172E-04	0.818E-03	-0.476E 01	-0.308E 01	0.179E 00	0.233E-02	0.116E 05	0.727E-04	0.236E 03
1180	0.160E-04	0.819E-03	-0.479E 01	-0.308E 01	0.124E 00	0.200E-02	0.855E 04	0.141E-03	0.164E 03
1182	0.172E-04	0.808E-03	-0.476E 01	-0.309E 01	0.895E-01	0.184E-02	0.584E 04	0.231E-03	0.117E 03
1185	0.217E-04	0.803E-03	-0.466E 01	-0.309E 01	0.560E-01	0.159E-02	0.316E 04	0.378E-03	0.729E 02
1200	0.344E-04	0.788E-03	-0.446E 01	-0.310E 01	0.160E-01	0.993E-03	0.687E 03	0.133E-02	0.201E 02
1230	0.386E-04	0.783E-03	-0.441E 01	-0.310E 01	0.654E-02	0.511E-03	0.263E 03	0.319E-02	0.808E 01
1260	0.402E-04	0.779E-03	-0.439E 01	-0.310E 01	0.406E-02	0.359E-03	0.159E 03	0.530E-02	0.497E 01
1320	0.417E-04	0.778E-03	-0.437E 01	-0.310E 01	0.228E-02	0.215E-03	0.878E 02	0.917E-02	0.270E 01
1440	0.372E-04	0.772E-03	-0.442E 01	-0.311E 01	0.144E-02	0.129E-03	0.591E 02	0.182E-01	0.175E 01
1560	0.344E-04	0.768E-03	-0.446E 01	-0.311E 01	0.107E-02	0.948E-04	0.463E 02	0.284E-01	0.131E 01
1800	0.284E-04	0.752E-03	-0.454E 01	-0.312E 01	0.798E-03	0.733E-04	0.383E 02	0.583E-01	0.971E 00
2040	0.226E-04	0.742E-03	-0.464E 01	-0.312E 01	0.692E-03	0.598E-04	0.382E 02	0.917E-01	0.848E 00
2280	0.186E-04	0.727E-03	-0.472E 01	-0.313E 01	0.617E-03	0.549E-04	0.383E 02	0.139E 00	0.754E 00
2520	0.148E-04	0.714E-03	-0.482E 01	-0.314E 01	0.581E-03	0.506E-04	0.418E 02	0.191E 00	0.711E 00
2640	0.148E-04	0.704E-03	-0.482E 01	-0.315E 01	0.534E-03	0.507E-04	0.384E 02	0.229E 00	0.647E 00

COMPUTER CALCULATED RESULTS OF FIGURE 29

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXYGEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE STO2
0	0.127E-03	0.284E-03	-0.389E 01	-0.354E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
60	0.117E-03	0.281E-03	-0.392E 01	-0.355E 01	0.555E-03	0.757E-04	0.104E 02	0.179E-03	0.304E 01
120	0.109E-03	0.275E-03	-0.396E 01	-0.355E 01	0.555E-03	0.114E-03	0.108E 02	0.110E-02	0.279E 01
180	*****	END OF LAG PERIOD				*****			
180	0.990E-04	0.272E-03	-0.400E 01	-0.356E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
240	0.900E-04	0.269E-03	-0.404E 01	-0.356E 01	0.694E-03	0.791E-04	0.169E 02	0.179E-03	0.354E 01
300	0.833E-04	0.263E-03	-0.407E 01	-0.357E 01	0.624E-03	0.119E-03	0.158E 02	0.110E-02	0.290E 01
360	0.772E-04	0.261E-03	-0.411E 01	-0.358E 01	0.601E-03	0.107E-03	0.158E 02	0.223E-02	0.284E 01
420	0.715E-04	0.258E-03	-0.414E 01	-0.358E 01	0.590E-03	0.101E-03	0.162E 02	0.376E-02	0.281E 01
444	*****	FERCUS ICN ADDED 1*10-6				*****			
444	0.701E-04	0.256E-03	-0.415E 01	-0.359E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
450	0.253E-04	0.241E-03	-0.459E 01	-0.361E 01	0.736E-01	0.430E-02	0.419E 04	0.944E-04	0.371E 03
465	0.268E-04	0.225E-03	-0.457E 01	-0.364E 01	0.198E-01	0.267E-02	0.109E 04	0.744E-03	0.920E 02
480	0.319E-04	0.217E-03	-0.449E 01	-0.366E 01	0.949E-02	0.200E-02	0.473E 03	0.167E-02	0.401E 02
510	0.338E-04	0.212E-03	-0.447E 01	-0.367E 01	0.479E-02	0.125E-02	0.231E 03	0.355E-02	0.190E 02
540	0.338E-04	0.209E-03	-0.447E 01	-0.367E 01	0.329E-02	0.925E-03	0.159E 03	0.559E-02	0.127E 02
600	0.344E-04	0.204E-03	-0.446E 01	-0.368E 01	0.197E-02	0.629E-03	0.944E 02	0.101E-01	0.722E 01
660	0.347E-04	0.201E-03	-0.445E 01	-0.369E 01	0.141E-02	0.483E-03	0.672E 02	0.150E-01	0.497E 01
720	0.331E-04	0.197E-03	-0.447E 01	-0.370E 01	0.117E-02	0.413E-03	0.575E 02	0.212E-01	0.409E 01
780	0.319E-04	0.195E-03	-0.449E 01	-0.370E 01	0.101E-02	0.349E-03	0.507E 02	0.267E-01	0.357E 01
840	0.298E-04	0.192E-03	-0.452E 01	-0.371E 01	0.938E-03	0.313E-03	0.487E 02	0.336E-01	0.333E 01
900	0.295E-04	0.189E-03	-0.452E 01	-0.372E 01	0.822E-03	0.286E-03	0.428E 02	0.411E-01	0.287E 01
960	0.290E-04	0.188E-03	-0.453E 01	-0.372E 01	0.742E-03	0.260E-03	0.391E 02	0.479E-01	0.258E 01
1020	0.284E-04	0.186E-03	-0.454E 01	-0.372E 01	0.679E-03	0.239E-03	0.362E 02	0.551E-01	0.236E 01
1080	0.273E-04	0.183E-03	-0.456E 01	-0.373E 01	0.642E-03	0.227E-03	0.349E 02	0.644E-01	0.222E 01
1140	0.263E-04	0.180E-03	-0.457E 01	-0.374E 01	0.610E-03	0.217E-03	0.340E 02	0.746E-01	0.210E 01

COMPUTER CALCULATED RESULTS OF FIGURE 29 (Cont'd.)

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE C2	K2 RATE STC
0	0.129E-03	0.990E-03	-0.388E 01	-0.300E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
60	0.129E-03	0.985E-03	-0.388E 01	-0.300E 01	0.000E 00	0.388E-04	0.000E 00	0.319E-03	-0.450E-01
120	0.129E-03	0.985E-03	-0.388E 01	-0.300E 01	0.000E 00	0.194E-04	0.000E 00	0.639E-03	-0.225E-01
180	0.129E-03	0.985E-03	-0.388E 01	-0.300E 01	0.000E 00	0.129E-04	0.000E 00	0.958E-03	-0.150E-01
187	*****	FERROUS ION ADDED 1*10-5				*****			
187	0.129E-03	0.964E-03	-0.388E 01	-0.301E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
191	0.506E-04	0.958E-03	-0.429E 01	-0.301E 01	0.102E 00	0.598E-03	0.300E 04	0.213E-04	0.121E 03
195	0.468E-04	0.948E-03	-0.432E 01	-0.302E 01	0.552E-01	0.902E-03	0.170E 04	0.129E-03	0.650E 02
203	0.546E-04	0.946E-03	-0.426E 01	-0.302E 01	0.234E-01	0.511E-03	0.661E 03	0.233E-03	0.274E 02
210	0.590E-04	0.942E-03	-0.422E 01	-0.302E 01	0.148E-01	0.419E-03	0.401E 03	0.438E-03	0.179E 02
225	0.613E-04	0.937E-03	-0.421E 01	-0.302E 01	0.855E-02	0.318E-03	0.226E 03	0.103E-02	0.986E 01
240	0.590E-04	0.928E-03	-0.422E 01	-0.303E 01	0.644E-02	0.312E-03	0.174E 03	0.198E-02	0.735E 01
300	0.526E-04	0.917E-03	-0.427E 01	-0.303E 01	0.346E-02	0.190E-03	0.999E 02	0.553E-02	0.392E 01
360	0.451E-04	0.905E-03	-0.434E 01	-0.304E 01	0.264E-02	0.156E-03	0.835E 02	0.107E-01	0.298E 01
420	0.417E-04	0.895E-03	-0.437E 01	-0.304E 01	0.211E-02	0.138E-03	0.696E 02	0.172E-01	0.234E 01
540	0.344E-04	0.879E-03	-0.446E 01	-0.305E 01	0.162E-02	0.984E-04	0.602E 02	0.283E-01	0.183E 01
660	0.273E-04	0.864E-03	-0.456E 01	-0.305E 01	0.142E-02	0.789E-04	0.608E 02	0.409E-01	0.161E 01
780	0.234E-04	0.873E-03	-0.462E 01	-0.305E 01	0.125E-02	0.718E-04	0.587E 02	0.588E-01	0.141E 01
900	0.193E-04	0.858E-03	-0.471E 01	-0.306E 01	0.115E-02	0.709E-04	0.614E 02	0.848E-01	0.130E 01
1020	0.166E-04	0.852E-03	-0.477E 01	-0.306E 01	0.107E-02	0.639E-04	0.629E 02	0.104E 00	0.120E 01
1140	0.142E-04	0.850E-03	-0.484E 01	-0.307E 01	0.100E-02	0.570E-04	0.654E 02	0.122E 00	0.113E 01

COMPUTER CALCULATED RESULTS OF FIGURE 30

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE STO2
0	0.101E-02	0.108E-02	-0.299E 01	-0.296E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
30	0.974E-03	0.107E-02	-0.301E 01	-0.296E 01	0.555E-03	0.776E-04	0.128E 01	0.174E-03	0.692E 01
60	0.956E-03	0.105E-02	-0.301E 01	-0.297E 01	0.416E-03	0.156E-03	0.975E 00	0.141E-02	0.377E 01
90	0.937E-03	0.104E-02	-0.302E 01	-0.298E 01	0.370E-03	0.184E-03	0.875E 00	0.378E-02	0.270E 01
120	0.920E-03	0.102E-02	-0.303E 01	-0.298E 01	0.347E-03	0.178E-03	0.828E 00	0.656E-02	0.244E 01
150	0.902E-03	0.101E-02	-0.304E 01	-0.299E 01	0.333E-03	0.175E-03	0.803E 00	0.101E-01	0.228E 01
180	0.885E-03	0.100E-02	-0.305E 01	-0.299E 01	0.324E-03	0.187E-03	0.788E 00	0.157E-01	0.197E 01
240	0.852E-03	0.971E-03	-0.306E 01	-0.301E 01	0.312E-03	0.193E-03	0.775E 00	0.293E-01	0.171E 01
30	0.816E-03	0.673E-02	-0.308E 01	-0.217E 01	0.311E-02	-0.264E-01	0.789E 01	-0.272E-01	0.428E 03
360	0.804E-03	0.925E-03	-0.309E 01	-0.303E 01	0.277E-03	0.188E-03	0.710E 00	0.657E-01	0.130E 01
420	0.789E-03	0.896E-03	-0.310E 01	-0.304E 01	0.257E-03	0.194E-03	0.666E 00	0.937E-01	0.925E 00
540	0.759E-03	0.861E-03	-0.311E 01	-0.306E 01	0.231E-03	0.182E-03	0.609E 00	0.148E 00	0.707E 00
660	0.744E-03	0.827E-03	-0.312E 01	-0.308E 01	0.202E-03	0.176E-03	0.537E 00	0.219E 00	0.369E 00
780	0.716E-03	0.798E-03	-0.314E 01	-0.309E 01	0.192E-03	0.169E-03	0.522E 00	0.299E 00	0.335E 00
900	0.689E-03	0.775E-03	-0.316E 01	-0.311E 01	0.185E-03	0.160E-03	0.513E 00	0.385E 00	0.353E 00
1020	0.676E-03	0.757E-03	-0.316E 01	-0.312E 01	0.171E-03	0.151E-03	0.480E 00	0.471E 00	0.290E 00
1140	0.663E-03	0.734E-03	-0.317E 01	-0.313E 01	0.160E-03	0.147E-03	0.454E 00	0.582E 00	0.194E 00
1320	0.603E-03	0.717E-03	-0.321E 01	-0.314E 01	0.170E-03	0.135E-03	0.507E 00	0.725E 00	0.511E 00
1500	0.580E-03	0.694E-03	-0.323E 01	-0.315E 01	0.161E-03	0.128E-03	0.490E 00	0.905E 00	0.473E 00
1680	0.548E-03	0.670E-03	-0.326E 01	-0.317E 01	0.158E-03	0.123E-03	0.498E 00	0.111E 01	0.511E 00
1860	0.507E-03	0.647E-03	-0.329E 01	-0.318E 01	0.161E-03	0.119E-03	0.528E 00	0.134E 01	0.603E 00
2040	0.488E-03	0.630E-03	-0.331E 01	-0.320E 01	0.155E-03	0.114E-03	0.519E 00	0.157E 01	0.584E 00
2280	0.435E-03	0.607E-03	-0.336E 01	-0.321E 01	0.160E-03	0.109E-03	0.574E 00	0.192E 01	0.737E 00
2520	0.373E-03	0.578E-03	-0.342E 01	-0.323E 01	0.171E-03	0.107E-03	0.670E 00	0.237E 01	0.929E 00
2760	0.320E-03	0.561E-03	-0.349E 01	-0.325E 01	0.181E-03	0.103E-03	0.773E 00	0.276E 01	0.112E 01
2781	*****	FERRIC ION ADDED 1*10-5				*****			
2781	0.314E-03	0.555E-03	-0.350E 01	-0.325E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
2785	0.145E-03	0.520E-03	-0.383E 01	-0.328E 01	0.833E-01	0.700E-02	0.918E 03	0.148E-03	0.316E 03
2790	0.920E-04	0.497E-03	-0.403E 01	-0.330E 01	0.592E-01	0.530E-02	0.854E 03	0.581E-03	0.223E 03

COMPUTER CALCULATED RESULTS OF FIGURE 30 (Cont'd.)

2798	0.603E-04	0.451E-03	-0.421E 01	-0.334E 01	0.421E-01	0.530E-02	0.787E 03	0.217E-02	0.152E 03
2805	0.461E-04	0.416E-03	-0.433E 01	-0.338E 01	0.347E-01	0.520E-02	0.770E 03	0.444E-02	0.122E 03
2812	0.352E-04	0.393E-03	-0.445E 01	-0.340E 01	0.306E-01	0.483E-02	0.812E 03	0.708E-02	0.107E 03
2820	0.314E-04	0.370E-03	-0.450E 01	-0.343E 01	0.256E-01	0.451E-02	0.734E 03	0.108E-01	0.876E 02
2835	0.235E-04	0.318E-03	-0.462E 01	-0.349E 01	0.208E-01	0.447E-02	0.727E 03	0.223E-01	0.678E 02
2850	0.187E-04	0.271E-03	-0.472E 01	-0.356E 01	0.177E-01	0.449E-02	0.726E 03	0.399E-01	0.544E 02
2865	0.157E-04	0.231E-03	-0.480E 01	-0.363E 01	0.154E-01	0.452E-02	0.718E 03	0.653E-01	0.454E 02
2970	0.819E-05	0.925E-04	-0.508E 01	-0.403E 01	0.837E-02	0.411E-02	0.628E 03	0.524E 00	0.176E 02
3060	0.819E-05	0.520E-04	-0.508E 01	-0.428E 01	0.567E-02	0.368E-02	0.425E 03	0.149E 01	0.825E 01
3120	0.819E-05	0.347E-04	-0.508E 01	-0.445E 01	0.467E-02	0.355E-02	0.350E 03	0.282E 01	0.463E 01

COMPUTER CALCULATED RESULTS OF FIGURE 31

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE ST02
0	0.389E-19	0.934E-03	-0.194E 02	-0.302E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
30	0.389E-19	0.934E-03	-0.194E 02	-0.302E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
60	0.389E-19	0.934E-03	-0.194E 02	-0.302E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
90	0.389E-19	0.931E-03	-0.194E 02	-0.303E 01	0.000E 00	0.153E-04	0.000E 00	0.267E-03	-0.164E-01
120	0.389E-19	0.934E-03	-0.194E 02	-0.302E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
150	0.389E-19	0.929E-03	-0.194E 02	-0.303E 01	0.000E 00	0.138E-04	0.000E 00	0.670E-03	-0.147E-01
180	0.389E-19	0.926E-03	-0.194E 02	-0.303E 01	0.000E 00	0.192E-04	0.000E 00	0.134E-02	-0.205E-01
240	0.389E-19	0.919E-03	-0.194E 02	-0.303E 01	0.000E 00	0.289E-04	0.000E 00	0.361E-02	-0.309E-01
300	0.389E-19	0.915E-03	-0.194E 02	-0.303E 01	0.000E 00	0.301E-04	0.000E 00	0.590E-02	-0.323E-01
360	0.389E-19	0.907E-03	-0.194E 02	-0.304E 01	0.000E 00	0.349E-04	0.000E 00	0.989E-02	-0.374E-01
420	0.389E-19	0.907E-03	-0.194E 02	-0.304E 01	0.000E 00	0.299E-04	0.000E 00	0.115E-01	-0.320E-01
540	0.389E-19	0.909E-03	-0.194E 02	-0.304E 01	0.000E 00	0.220E-04	0.000E 00	0.139E-01	-0.235E-01
660	0.389E-19	0.907E-03	-0.194E 02	-0.304E 01	0.000E 00	0.190E-04	0.000E 00	0.181E-01	-0.204E-01
780	0.389E-19	0.904E-03	-0.194E 02	-0.304E 01	0.000E 00	0.179E-04	0.000E 00	0.238E-01	-0.192E-01
900	0.389E-19	0.904E-03	-0.194E 02	-0.304E 01	0.000E 00	0.155E-04	0.000E 00	0.275E-01	-0.166E-01
1020	0.389E-19	0.904E-03	-0.194E 02	-0.304E 01	0.000E 00	0.137E-04	0.000E 00	0.312E-01	-0.147E-01
1125	*****	SULFYDE ADDED 1*10-4				*****			
1125	0.128E-03	0.904E-03	-0.389E 01	-0.304E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
1140	0.116E-03	0.889E-03	-0.393E 01	-0.305E 01	0.277E-02	0.478E-03	0.523E 02	0.226E-03	0.296E 01
1170	0.112E-03	0.880E-03	-0.395E 01	-0.305E 01	0.129E-02	0.256E-03	0.249E 02	0.109E-02	0.133E 01
1200	0.907E-04	0.864E-03	-0.404E 01	-0.306E 01	0.199E-02	0.262E-03	0.429E 02	0.314E-02	0.223E 01
1230	0.872E-04	0.849E-03	-0.405E 01	-0.307E 01	0.158E-02	0.258E-03	0.347E 02	0.613E-02	0.171E 01
1260	0.824E-04	0.845E-03	-0.408E 01	-0.307E 01	0.141E-02	0.218E-03	0.320E 02	0.857E-02	0.154E 01
1320	0.748E-04	0.833E-03	-0.412E 01	-0.307E 01	0.119E-02	0.182E-03	0.284E 02	0.150E-01	0.130E 01
1380	0.693E-04	0.827E-03	-0.415E 01	-0.308E 01	0.104E-02	0.151E-03	0.259E 02	0.214E-01	0.115E 01
1440	0.642E-04	0.821E-03	-0.419E 01	-0.308E 01	0.952E-03	0.132E-03	0.246E 02	0.288E-01	0.105E 01
1560	0.500E-04	0.806E-03	-0.430E 01	-0.309E 01	0.938E-03	0.114E-03	0.279E 02	0.477E-01	0.106E 01
1680	0.389E-04	0.791E-03	-0.440E 01	-0.310E 01	0.930E-03	0.104E-03	0.321E 02	0.714E-01	0.105E 01
1800	0.309E-04	0.778E-03	-0.450E 01	-0.310E 01	0.913E-03	0.965E-04	0.362E 02	0.988E-01	0.105E 01

COMPUTER CALCULATED RESULTS OF FIGURE 31 (Cont'd.)

1920	0.265E-04	0.768E-03	-0.457E 01	-0.311E 01	0.859E-03	0.893E-04	0.375E 02	0.127E 00	0.991E 00
2040	0.227E-04	0.762E-03	-0.464E 01	-0.311E 01	0.819E-03	0.812E-04	0.394E 02	0.154E 00	0.950E 00
2160	0.191E-04	0.756E-03	-0.471E 01	-0.312E 01	0.797E-03	0.751E-04	0.428E 02	0.183E 00	0.929E 00
2280	0.161E-04	0.750E-03	-0.479E 01	-0.312E 01	0.774E-03	0.702E-04	0.469E 02	0.214E 00	0.912E 00
2400	0.141E-04	0.746E-03	-0.485E 01	-0.312E 01	0.751E-03	0.656E-04	0.494E 02	0.245E 00	0.893E 00
2520	0.123E-04	0.741E-03	-0.490E 01	-0.312E 01	0.728E-03	0.619E-04	0.525E 02	0.277E 00	0.858E 00

COMPUTER CALCULATED RESULTS OF FIGURE 32

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE STO2
0	0.128E-03	0.182E-03	-0.389E 01	-0.373E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0[illegible]
5	0.809E-04	0.171E-03	-0.409E 01	-0.376E 01	0.399E-01	0.520E-02	0.912E 03	0.562E-04	0.643E 01
10	0.667E-04	0.163E-03	-0.417E 01	-0.378E 01	0.283E-01	0.480E-02	0.718E 03	0.212E-03	0.435E 03
15	0.594E-04	0.158E-03	-0.422E 01	-0.380E 01	0.222E-01	0.411E-02	0.600E 03	0.417E-03	0.334E 03
23	0.437E-04	0.152E-03	-0.435E 01	-0.381E 01	0.202E-01	0.335E-02	0.654E 03	0.814E-03	0.313E 03
30	0.361E-04	0.146E-03	-0.444E 01	-0.383E 01	0.183E-01	0.318E-02	0.682E 03	0.134E-02	0.280E 03
45	0.246E-04	0.139E-03	-0.460E 01	-0.385E 01	0.159E-01	0.255E-02	0.729E 03	0.248E-02	0.247E 03
60	0.167E-04	0.133E-03	-0.477E 01	-0.387E 01	0.147E-01	0.225E-02	0.864E 03	0.399E-02	0.230E 03
90	0.109E-04	0.124E-03	-0.495E 01	-0.390E 01	0.118E-01	0.185E-02	0.924E 03	0.766E-02	0.184E 03
120	0.907E-05	0.121E-03	-0.504E 01	-0.391E 01	0.958E-02	0.147E-02	0.853E 03	0.110E-01	0.149E 03
150	0.907E-05	0.118E-03	-0.504E 01	-0.392E 01	0.766E-02	0.124E-02	0.682E 03	0.146E-01	0.118E 03
180	0.907E-05	0.116E-03	-0.504E 01	-0.393E 01	0.638E-02	0.107E-02	0.569E 03	0.184E-01	0.982E 02
240	0.389E-19	0.112E-03	-0.194E 02	-0.394E 01	0.646E-01	0.875E-03	0.106E 18	0.272E-01	0.117E 04
300	0.389E-19	0.112E-03	-0.194E 02	-0.394E 01	0.517E-01	0.700E-03	0.854E 17	0.340E-01	0.943E 03
360	0.389E-19	0.112E-03	-0.194E 02	-0.394E 01	0.431E-01	0.583E-03	0.712E 17	0.408E-01	0.786E 03

COMPUTER CALCULATED RESULTS OF FIGURE 33

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG CRY GEN	K1 RATE ST	K1 RATE 02	K2 RATE ST	K2 RATE 02	K2 RATE STC
0	0.127E-03	0.206E-03	-0.389E 01	-0.354E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
60	0.123E-03	0.283E-03	-0.390E 01	-0.354E 01	0.194E-03	0.753E-04	0.356E 01	0.179E-03	0.748E 00
120	0.122E-03	0.281E-03	-0.391E 01	-0.355E 01	0.138E-03	0.566E-04	0.256E 01	0.542E-03	0.516E 00
180	0.118E-03	0.280E-03	-0.392E 01	-0.355E 01	0.166E-03	0.505E-04	0.312E 01	0.109E-02	0.730E 00
240	0.115E-03	0.277E-03	-0.393E 01	-0.355E 01	0.166E-03	0.552E-04	0.316E 01	0.212E-02	0.700E 00
300	0.113E-03	0.274E-03	-0.394E 01	-0.356E 01	0.166E-03	0.597E-04	0.319E 01	0.361E-02	0.672E 00
360	*****	END OF LAG PERIOD			*****				
420	0.111E-03	0.271E-03	-0.395E 01	-0.356E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
465	0.110E-03	0.269E-03	-0.395E 01	-0.356E 01	0.555E-04	0.475E-04	0.115E 01	0.107E-03	0.498E-01
465	*****	FERRIC OXIDE ADDED 1*10-5			*****				
480	0.109E-03	0.266E-03	-0.395E 01	-0.357E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
480	0.106E-03	0.265E-03	-0.397E 01	-0.357E 01	0.777E-03	0.321E-03	0.165E 02	0.449E-04	0.287E 01
510	0.104E-03	0.263E-03	-0.397E 01	-0.357E 01	0.444E-03	0.161E-03	0.952E 01	0.203E-03	0.178E 01
540	0.103E-03	0.261E-03	-0.398E 01	-0.358E 01	0.355E-03	0.142E-03	0.768E 01	0.501E-03	0.134E 01
600	0.102E-03	0.263E-03	-0.399E 01	-0.357E 01	0.234E-03	0.537E-04	0.509E 01	0.610E-03	0.114E 01
660	0.101E-03	0.262E-03	-0.399E 01	-0.358E 01	0.188E-03	0.497E-04	0.411E 01	0.118E-02	0.872E 00
780	0.100E-03	0.258E-03	-0.399E 01	-0.358E 01	0.126E-03	0.543E-04	0.278E 01	0.340E-02	0.457E 00
900	0.957E-04	0.253E-03	-0.401E 01	-0.359E 01	0.137E-03	0.567E-04	0.309E 01	0.682E-02	0.512E 00
1020	0.935E-04	0.250E-03	-0.402E 01	-0.360E 01	0.126E-03	0.536E-04	0.286E 01	0.105E-01	0.456E 00
1140	0.866E-04	0.247E-03	-0.406E 01	-0.360E 01	0.153E-03	0.517E-04	0.367E 01	0.151E-01	0.638E 00
1320	0.849E-04	0.240E-03	-0.407E 01	-0.361E 01	0.130E-03	0.563E-04	0.312E 01	0.269E-01	0.468E 00
1500	0.802E-04	0.237E-03	-0.409E 01	-0.362E 01	0.132E-03	0.517E-04	0.325E 01	0.364E-01	0.506E 00
1680	0.787E-04	0.232E-03	-0.410E 01	-0.363E 01	0.119E-03	0.508E-04	0.296E 01	0.498E-01	0.432E 00
1860	0.757E-04	0.226E-03	-0.412E 01	-0.364E 01	0.115E-03	0.523E-04	0.294E 01	0.685E-01	0.400E 00
2040	0.748E-04	0.222E-03	-0.412E 01	-0.365E 01	0.105E-03	0.518E-04	0.270E 01	0.873E-01	0.340E 00
2280	0.726E-04	0.212E-03	-0.413E 01	-0.367E 01	0.941E-04	0.563E-04	0.257E 01	0.129E 00	0.269E 00
2520	0.688E-04	0.212E-03	-0.416E 01	-0.367E 01	0.989E-04	0.498E-04	0.264E 01	0.146E 00	0.309E 00

COMPUTER CALCULATED RESULTS OF FIGURE 34

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE G2	K2 RATE ST	K2 RATE D2	K2 RATE STG2
0	0.249E-03	0.942E-03	-0.360E 01	-0.302E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0[illegible]
15	0.190E-03	0.936E-03	-0.371E 01	-0.302E 01	0.777E-02	0.177E-03	0.822E 02	0.869E-04	0.10[illegible]E 02
30	0.170E-03	0.932E-03	-0.376E 01	-0.303E 01	0.555E-02	0.155E-03	0.624E 02	0.305E-03	0.77[illegible]E 01
45	0.160E-03	0.929E-03	-0.379E 01	-0.303E 01	0.425E-02	0.133E-03	0.493E 02	0.591E-03	0.595E 01
60	0.148E-03	0.926E-03	-0.382E 01	-0.303E 01	0.375E-02	0.122E-03	0.452E 02	0.967E-03	0.523E 01
90	0.140E-03	0.922E-03	-0.385E 01	-0.303E 01	0.277E-02	0.104E-03	0.346E 02	0.185E-02	0.[illegible]E 01
120	0.135E-03	0.917E-03	-0.386E 01	-0.303E 01	0.222E-02	0.953E-04	0.282E 02	0.301E-02	0.307E 01
150	0.130E-03	0.914E-03	-0.388E 01	-0.303E 01	0.188E-02	0.853E-04	0.245E 02	0.422E-02	0.260E 01
180	0.125E-03	0.910E-03	-0.390E 01	-0.304E 01	0.166E-02	0.825E-04	0.221E 02	0.590E-02	0.228E 01
210	*****	FERROUS IRON ADDED 1*10-5				*****			
210	0.118E-03	0.907E-03	-0.392E 01	-0.304E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0[illegible]
214	0.291E-04	0.906E-03	-0.453E 01	-0.304E 01	0.152E 00	0.172E-03	0.646E 04	0.577E-05	0.197E 04
218	0.249E-04	0.903E-03	-0.460E 01	-0.304E 01	0.843E-01	0.259E-03	0.394E 04	0.347E-04	0.10[illegible] 0[illegible]
225	0.249E-04	0.893E-03	-0.460E 01	-0.304E 01	0.449E-01	0.463E-03	0.210E 04	0.219E-03	0.564E 0[illegible]
240	0.249E-04	0.878E-03	-0.460E 01	-0.305E 01	0.224E-01	0.467E-03	0.105E 04	0.892E-03	0.279E 0[illegible]
255	0.249E-04	0.867E-03	-0.460E 01	-0.306E 01	0.149E-01	0.438E-03	0.701E 03	0.189E-02	0.184E 0[illegible]
263	0.291E-04	0.864E-03	-0.453E 01	-0.306E 01	0.114E-01	0.399E-03	0.488E 03	0.240E-02	0.140E 0[illegible]
270	0.381E-04	0.858E-03	-0.441E 01	-0.306E 01	0.819E-02	0.401E-03	0.296E 03	0.310E-02	0.987E 0[illegible]
285	0.444E-04	0.850E-03	-0.435E 01	-0.307E 01	0.566E-02	0.379E-03	0.187E 03	0.461E-02	0.669E 01
300	0.461E-04	0.842E-03	-0.433E 01	-0.307E 01	0.453E-02	0.357E-03	0.146E 03	0.628E-02	0.529E 01
330	0.411E-04	0.835E-03	-0.438E 01	-0.307E 01	0.381E-02	0.299E-03	0.132E 03	0.938E-02	0.445E 0[illegible]
360	0.366E-04	0.831E-03	-0.443E 01	-0.308E 01	0.338E-02	0.254E-03	0.125E 03	0.125E-01	0.397E 01
390	0.326E-04	0.825E-03	-0.448E 01	-0.308E 01	0.310E-02	0.228E-03	0.122E 03	0.162E-01	0.363E 01
420	0.329E-04	0.822E-03	-0.448E 01	-0.308E 01	0.264E-02	0.203E-03	0.104E 03	0.196E-01	0.309E 01
450	0.352E-04	0.821E-03	-0.445E 01	-0.308E 01	0.218E-02	0.181E-03	0.828E 02	0.279E-01	0.254E 01
480	0.352E-04	0.821E-03	-0.445E 01	-0.308E 01	0.194E-02	0.160E-03	0.736E 02	0.257E-01	0.225E 01
540	0.339E-04	0.814E-03	-0.446E 01	-0.308E 01	0.164E-02	0.143E-03	0.635E 02	0.344E-01	0.183E 01
600	0.314E-04	0.811E-03	-0.450E 01	-0.309E 01	0.147E-02	0.125E-03	0.598E 02	0.421E-01	0.170E 01
660	0.291E-04	0.806E-03	-0.453E 01	-0.309E 01	0.135E-02	0.113E-03	0.574E 02	0.510E-01	0.156E 01

COMPUTER CALCULATED RESULTS OF FIGURE 34 (Cont'd.)

720	0.285E-04	0.802E-03	-0.454E 01	-0.309E 01	0.120E-02	0.104E-03	0.520E 02	0.606E-01	0.13[illegible] 01
780	0.280E-04	0.799E-03	-0.455E 01	-0.309E 01	0.109E-02	0.965E-04	0.477E 02	0.699E-01	0.126E 01
840	0.280E-04	0.795E-03	-0.455E 01	-0.309E 01	0.992E-03	0.911E-04	0.431E 02	0.808E-01	0.114E 01
960	0.269E-04	0.785E-03	-0.456E 01	-0.310E 01	0.855E-03	0.839E-04	0.381E 02	0.106E 00	0.977E 00
1080	0.249E-04	0.778E-03	-0.460E 01	-0.310E 01	0.775E-03	0.769E-04	0.362E 02	0.131E 00	0.885E 00
1200	0.240E-04	0.773E-03	-0.461E 01	-0.311E 01	0.698E-03	0.700E-04	0.334E 02	0.155E 00	0.794E 00

COMPUTER CALCULATED RESULTS OF FIGURE 35

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE STO2
0	0.233E-03	0.955E-03	-0.363E 01	-0.301E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
15	0.158E-03	0.955E-03	-0.379E 01	-0.301E 01	0.111E-01	0.000E 00	0.133E 03	0.000E 00	0.159E 02
30	0.141E-03	0.955E-03	-0.384E 01	-0.301E 01	0.722E-02	0.000E 00	0.924E 02	0.000E 00	0.999E 01
45	0.136E-03	0.955E-03	-0.386E 01	-0.301E 01	0.518E-02	0.000E 00	0.677E 02	0.000E 00	0.717E 01
60	0.131E-03	0.955E-03	-0.388E 01	-0.301E 01	0.416E-02	0.000E 00	0.556E 02	0.000E 00	0.578E 01
90	0.123E-03	0.955E-03	-0.390E 01	-0.301E 01	0.305E-02	0.000E 00	0.421E 02	0.000E 00	0.427E 01
120	0.119E-03	0.955E-03	-0.392E 01	-0.301E 01	0.243E-02	0.000E 00	0.342E 02	0.000E 00	0.339E 01
150	0.116E-03	0.955E-03	-0.393E 01	-0.301E 01	0.199E-02	0.000E 00	0.284E 02	0.000E 00	0.276E 01
180	0.110E-03	0.955E-03	-0.395E 01	-0.301E 01	0.180E-02	0.000E 00	0.265E 02	0.000E 00	0.249E 01
240	*****	END OF LAG PERIOD				*****			
240	0.104E-03	0.955E-03	-0.398E 01	-0.301E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
300	0.100E-03	0.948E-03	-0.399E 01	-0.302E 01	0.277E-03	0.558E-04	0.625E 01	0.444E-03	0.260E 00
360	0.946E-04	0.944E-03	-0.402E 01	-0.302E 01	0.347E-03	0.449E-04	0.805E 01	0.142E-02	0.355E 01
420	0.910E-04	0.941E-03	-0.404E 01	-0.302E 01	0.324E-03	0.374E-04	0.766E 01	0.268E-02	0.339E 00
480	0.811E-04	0.933E-03	-0.409E 01	-0.302E 01	0.451E-03	0.422E-04	0.113E 02	0.541E-02	0.480E 01
540	0.751E-04	0.926E-03	-0.412E 01	-0.303E 01	0.472E-03	0.452E-04	0.123E 02	0.910E-02	0.501E 00
600	0.709E-04	0.923E-03	-0.414E 01	-0.303E 01	0.462E-03	0.415E-04	0.124E 02	0.120E-01	0.494E 00
608	*****	FERRIC IRON ADDED 1*10-5				*****			
608	0.709E-04	0.922E-03	-0.414E 01	-0.303E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
612	0.483E-04	0.920E-03	-0.431E 01	-0.303E 01	0.416E-01	0.259E-03	0.164E 04	0.884E-05	0.486E 02
616	0.329E-04	0.919E-03	-0.448E 01	-0.303E 01	0.416E-01	0.216E-03	0.203E 04	0.295E-04	0.486E 02
630	0.316E-04	0.911E-03	-0.449E 01	-0.304E 01	0.159E-01	0.237E-03	0.793E 03	0.245E-03	0.184E 02
660	0.305E-04	0.902E-03	-0.451E 01	-0.304E 01	0.705E-02	0.181E-03	0.359E 03	0.105E-02	0.806E 01
720	0.299E-04	0.889E-03	-0.452E 01	-0.305E 01	0.334E-02	0.141E-03	0.172E 03	0.364E-02	0.376E 01
780	0.282E-04	0.874E-03	-0.454E 01	-0.305E 01	0.232E-02	0.134E-03	0.123E 03	0.866E-02	0.257E 01
840	0.261E-04	0.867E-03	-0.458E 01	-0.306E 01	0.186E-02	0.115E-03	0.104E 03	0.136E-01	0.205E 01
900	0.233E-04	0.861E-03	-0.463E 01	-0.306E 01	0.165E-02	0.101E-03	0.986E 02	0.190E-01	0.182E 01
1020	0.192E-04	0.846E-03	-0.471E 01	-0.307E 01	0.137E-02	0.902E-04	0.919E 02	0.339E-01	0.150E 01
1140	0.155E-04	0.829E-03	-0.480E 01	-0.308E 01	0.123E-02	0.870E-04	0.941E 02	0.552E-01	0.135E 01

COMPUTER CALCULATED RESULTS OF FIGURE 35 (Cont'd.)

1260	0.126E-04	0.808E-03	-0.489E 01	-0.309E 01	0.115E-02	0.878E-04	0.999E 02	0.447E-01	0.124E 01
1380	0.104E-04	0.789E-03	-0.498E 01	-0.310E 01	0.107E-02	0.876E-04	0.106E 03	0.120E 00	0.116E 01
1500	0.876E-05	0.773E-03	-0.505E 01	-0.311E 01	0.101E-02	0.859E-04	0.112E 03	0.198E 00	0.109E 01

COMPUTER CALCULATED RESULTS OF FIGURE 36

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXYGEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K3 RATE ST
0	0.128E-03	0.258E-03	-0.389E 01	-0.358E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.00[illegible] 0
8	0.778E-04	0.239E-03	-0.410E 01	-0.362E 01	0.270E-01	0.416E-02	0.631E 03	0.164E-03	0.17[illegible] 0
16	0.520E-04	0.218E-03	-0.428E 01	-0.366E 01	0.244E-01	0.459E-02	0.714E 03	0.762E-03	0.15[illegible] 0
24	0.375E-04	0.199E-03	-0.442E 01	-0.370E 01	0.222E-01	0.471E-02	0.785E 03	0.184E-02	0.134[illegible] 01
30	0.276E-04	0.182E-03	-0.455E 01	-0.373E 01	0.222E-01	0.506E-02	0.947E 03	0.324E-02	0.131[illegible] 01
38	0.195E-04	0.167E-03	-0.470E 01	-0.377E 01	0.214E-01	0.496E-02	0.114E 04	0.534E-02	0.125[illegible] 01
45	0.143E-04	0.150E-03	-0.484E 01	-0.382E 01	0.211E-01	0.522E-02	0.137E 04	0.835E-02	0.121E 01
56	0.872E-05	0.137E-03	-0.505E 01	-0.386E 01	0.209E-01	0.468E-02	0.190E 04	0.126E-01	0.123[illegible] 01
75	0.347E-05	0.116E-03	-0.545E 01	-0.393E 01	0.208E-01	0.461E-02	0.373E 04	0.236E-01	0.124[illegible] 01
83	0.236E-05	0.108E-03	-0.562E 01	-0.396E 01	0.208E-01	0.456E-02	0.499E 04	0.298E-01	0.125[illegible] 01
90	0.161E-05	0.103E-03	-0.579E 01	-0.398E 01	0.211E-01	0.440E-02	0.680E 04	0.346E-01	0.124[illegible] 01
105	0.748E-06	0.953E-04	-0.612E 01	-0.402E 01	0.212E-01	0.412E-02	0.126E 05	0.464E-01	0.131E 01
120	0.286E-06	0.902E-04	-0.654E 01	-0.404E 01	0.220E-01	0.380E-02	0.289E 05	0.576E-01	0.14[illegible] 01
124	0.236E-06	0.889E-04	-0.662E 01	-0.405E 01	0.220E-01	0.375E-02	0.339E 05	0.610E-01	0.140E 01
150	0.389E-19	0.847E-04	-0.194E 02	-0.407E 01	0.[illegible]03E 00	0.322E-02	0.170E 18	0.794E-01	0.76[illegible] 01
210	0.389E-19	0.847E-04	-0.194E 02	-0.407E 01	0.738E-01	0.230E-02	0.122E 18	0.111E 00	0.54[illegible] 01
270	0.389E-19	0.847E-04	-0.194E 02	-0.407E 01	0.574E-01	0.179E-02	0.949E 17	0.143E 00	0.427E 00
330	0.389E-19	0.847E-04	-0.194E 02	-0.407E 01	0.470E-01	0.146E-02	0.777E 17	0.174E 00	0.349E 00
390	0.389E-19	0.847E-04	-0.194E 02	-0.407E 01	0.[illegible]97E-01	0.124E-02	0.657E 17	0.206E 00	0.295E 00
415	0.155E-03	0.847E-04	-0.380E 01	-0.407E 01	-0.[illegible]00E-03	0.116E-02	-0.328E 01	0.219E 00	-0.104E 00
420	0.138E-03	0.656E-04	-0.385E 01	-0.418E 01	-0.793E-04	0.141E-02	-0.137E 01	0.318E 00	-0.114E 00
428	0.114E-03	0.529E-04	-0.394E 01	-0.427E 01	0.116E-03	0.160E-02	-0.222E 01	0.429E 00	-0.114E 00
435	0.942E-04	0.444E-04	-0.402E 01	-0.435E 01	0.[illegible]06E-03	0.175E-02	0.644E 01	0.540E 00	-0.111E 00
445	0.778E-04	0.339E-04	-0.410E 01	-0.446E 01	0.486E-03	0.198E-02	0.113E 02	0.762E 00	-0.114E 00

COMPUTER CALCULATED RESULTS OF FIGURE 36 (Cont'd.)

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE G2	K2 RATE ST	K2 RATE G2	K2 RATE S1
0	0.219E-03	0.243E-03	-0.365E 01	-0.361E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
4	0.188E-03	0.270E-03	-0.372E 01	-0.364E 01	0.166E-01	0.681E-02	0.189E 03	0.631E-04	0.404E 01
8	0.155E-03	0.218E-03	-0.380E 01	-0.366E 01	0.187E-01	0.598E-02	0.235E 03	0.227E-03	0.523E 01
12	0.128E-03	0.205E-03	-0.389E 01	-0.368E 01	0.194E-01	0.616E-02	0.270E 03	0.542E-03	0.543E 01
15	0.109E-03	0.199E-03	-0.395E 01	-0.370E 01	0.199E-01	0.593E-02	0.302E 03	0.816E-03	0.581E 01
19	0.942E-04	0.188E-03	-0.402E 01	-0.372E 01	0.192E-01	0.585E-02	0.318E 03	0.115E-02	0.551E 01
27	0.618E-04	0.173E-03	-0.420E 01	-0.376E 01	0.203E-01	0.544E-02	0.430E 03	0.264E-02	0.618E 01
34	0.405E-04	0.159E-03	-0.439E 01	-0.379E 01	0.215E-01	0.545E-02	0.591E 03	0.441E-02	0.661E 01
42	0.265E-04	0.146E-03	-0.457E 01	-0.383E 01	0.218E-01	0.528E-02	0.787E 03	0.662E-02	0.672E 01
49	0.161E-04	0.135E-03	-0.479E 01	-0.386E 01	0.231E-01	0.519E-02	0.117E 04	0.951E-02	0.731E 01
57	0.101E-04	0.125E-03	-0.499E 01	-0.390E 01	0.233E-01	0.508E-02	0.164E 04	0.131E-01	0.751E 01
64	0.693E-05	0.116E-03	-0.515E 01	-0.393E 01	0.234E-01	0.500E-02	0.218E 04	0.170E-01	0.756E 01
72	0.437E-05	0.108E-03	-0.535E 01	-0.396E 01	0.236E-01	0.490E-02	0.311E 04	0.220E-01	0.767E 01
87	0.188E-05	0.995E-04	-0.572E 01	-0.400E 01	0.237E-01	0.446E-02	0.605E 04	0.306E-01	0.791E 01
102	0.808E-06	0.995E-04	-0.609E 01	-0.400E 01	0.238E-01	0.390E-02	0.120E 05	0.399E-01	0.828E 01
117	0.347E-06	0.995E-04	-0.645E 01	-0.400E 01	0.239E-01	0.332E-02	0.245E 05	0.412E-01	0.845E 01

COMPUTER CALCULATED RESULTS OF FIGURE 37

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE G2	K2 RATE ST	K2 RATE G2	K2 RATE ST
0	0.128E-03	0.273E-03	-0.389E 01	-0.356E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
8	0.924E-04	0.239E-03	-0.403E 01	-0.362E 01	0.177E-01	0.718E-02	0.376E 03	0.309E-03	0.724E 0
15	0.793E-04	0.216E-03	-0.410E 01	-0.366E 01	0.138E-01	0.679E-02	0.320E 03	0.108E-02	0.481E 0
23	0.618E-04	0.201E-03	-0.420E 01	-0.369E 01	0.137E-01	0.577E-02	0.364E 03	0.224E-02	0.559E 0
30	0.454E-04	0.180E-03	-0.434E 01	-0.374E 01	0.149E-01	0.603E-02	0.473E 03	0.424E-02	0.617E 0
45	0.227E-04	0.156E-03	-0.464E 01	-0.380E 01	0.166E-01	0.536E-02	0.801E 03	0.914E-02	0.778E 0
60	0.109E-04	0.133E-03	-0.495E 01	-0.387E 01	0.177E-01	0.518E-02	0.138E 04	0.171E-01	0.867E 0
75	0.572E-05	0.120E-03	-0.524E 01	-0.391E 01	0.179E-01	0.472E-02	0.222E 04	0.258E-01	0.914E 0
90	0.298E-05	0.110E-03	-0.552E 01	-0.395E 01	0.181E-01	0.438E-02	0.364E 04	0.364E-01	0.944E 0
105	0.161E-05	0.105E-03	-0.579E 01	-0.397E 01	0.180E-01	0.392E-02	0.582E 04	0.453E-01	0.972E 0
120	0.667E-06	0.101E-03	-0.617E 01	-0.399E 01	0.190E-01	0.357E-02	0.124E 05	0.553E-01	0.100E 0
150	0.389E-19	0.995E-04	-0.194E 02	-0.400E 01	0.103E 00	0.292E-02	0.170E 18	0.715E-01	0.69.E 0
180	0.389E-19	0.995E-04	-0.194E 02	-0.400E 01	0.862E-01	0.243E-02	0.142E 18	0.858E-01	0.574E 0
210	0.389E-19	0.995E-04	-0.194E 02	-0.400E 01	0.738E-01	0.208E-02	0.122E 18	0.100E 00	0.494E 0
232	0.161E-03	0.995E-04	-0.379E 01	-0.400E 01	-0.431E-03	0.189E-02	-0.691E 01	0.110E 00	-0.159E 0
240	0.149E-03	0.720E-04	-0.382E 01	-0.414E 01	-0.277E-03	0.241E-02	-0.462E 01	0.183E 00	-0.185E 0
255	0.109E-03	0.444E-04	-0.395E 01	-0.435E 01	0.261E-03	0.309E-02	0.507E 01	0.358E 00	-0.194E 0
270	0.808E-04	0.275E-04	-0.409E 01	-0.455E 01	0.740E-03	0.369E-02	0.169E 02	0.658E 00	-0.203E 0
285	0.667E-04	0.190E-04	-0.417E 01	-0.471E 01	0.994E-03	0.405E-02	0.251E 02	0.103E 01	-0.210E 0

COMPUTER CALCULATED RESULTS OF FIGURE 38

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE 02	K2 RATE ST	K2 RATE 02	K2 RATE ST
0	0.233E-03	0.258E-03	-0.363E 01	-0.358E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.00[illegible] 0
15	0.215E-03	0.228E-03	-0.366E 01	-0.364E 01	0.222E-02	0.352E-02	0.228E 02	0.502E-03	-0.[illegible] 0
30	0.178E-03	0.203E-03	-0.374E 01	-0.369E 01	0.388E-02	0.346E-02	0.440E 02	0.210E-02	0.16[illegible] 0
45	0.147E-03	0.182E-03	-0.383E 01	-0.373E 01	0.444E-02	0.337E-02	0.557E 02	0.486E-02	[illegible]
60	0.121E-03	0.167E-03	-0.391E 01	-0.377E 01	0.472E-02	0.314E-02	0.657E 02	0.644E-02	0.62[illegible] 0
90	0.893E-04	0.146E-03	-0.404E 01	-0.383E 01	0.462E-02	0.279E-02	0.767E 02	0.178E-01	0.74[illegible] 0
120	0.811E-04	0.135E-03	-0.409E 01	-0.386E 01	0.381E-02	0.233E-02	0.869E 02	0.281E-01	0.58[illegible] 0
180	0.532E-04	0.127E-03	-0.427E 01	-0.389E 01	0.356E-02	0.171E-02	0.805E 02	0.480E-01	0.73[illegible] 0
240	0.342E-04	0.112E-03	-0.446E 01	-0.394E 01	0.347E-02	0.150E-02	0.103E 03	0.807E-01	0.77[illegible] 0
270	0.271E-04	0.110E-03	-0.456E 01	-0.395E 01	0.345E-02	0.137E-02	0.120E 03	0.939E-01	0.624E 02

COMPUTER CALCULATED RESULTS OF FIGURE 39

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE 02	K2 RATE ST	K2 RATE 02	K2 RATE ST
0	0.128E-03	0.273E-03	-0.389E 01	-0.356E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
4	*****	END OF LAG PERIOD				*****			
4	0.174E-03	0.260E-03	-0.375E 01	-0.358E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
8	0.167E-03	0.250E-03	-0.377E 01	-0.360E 01	0.416E-02	0.432E-02	0.561E 02	0.423E-04	-0.189E 0
15	0.128E-03	0.230E-03	-0.389E 01	-0.363E 01	0.121E-01	0.470E-02	0.187E 03	0.362E-03	0.862E 0
23	0.105E-03	0.217E-03	-0.397E 01	-0.366E 01	0.114E-01	0.410E-02	0.195E 03	0.973E-03	0.846E 0
30	0.872E-04	0.203E-03	-0.405E 01	-0.369E 01	0.115E-01	0.411E-02	0.219E 03	0.188E-02	0.863E 0
45	0.594E-04	0.180E-03	-0.422E 01	-0.374E 01	0.113E-01	0.389E-02	0.270E 03	0.474E-02	0.870E 0
60	0.421E-04	0.165E-03	-0.437E 01	-0.378E 01	0.110E-01	0.351E-02	0.321E 03	0.836E-02	0.871E 0
75	0.286E-04	0.150E-03	-0.454E 01	-0.382E 01	0.110E-01	0.335E-02	0.410E 03	0.134E-01	0.893E 0
90	0.195E-04	0.139E-03	-0.470E 01	-0.385E 01	0.110E-01	0.313E-02	0.528E 03	0.192E-01	0.919E 0
105	0.138E-04	0.129E-03	-0.485E 01	-0.388E 01	0.108E-01	0.300E-02	0.658E 03	0.266E-01	0.914E 0
120	0.872E-05	0.118E-03	-0.505E 01	-0.392E 01	0.112E-01	0.293E-02	0.937E 03	0.360E-01	0.961E 0
135	0.510E-05	0.114E-03	-0.529E 01	-0.394E 01	0.117E-01	0.272E-02	0.145E 04	0.434E-01	0.104E 0
150	0.282E-05	0.108E-03	-0.554E 01	-0.396E 01	0.122E-01	0.261E-02	0.238E 04	0.534E-01	0.112E 0
165	0.128E-05	0.105E-03	-0.589E 01	-0.397E 01	0.132E-01	0.242E-02	0.481E 04	0.609E-01	0.125E 0
176	0.693E-06	0.103E-03	-0.615E 01	-0.398E 01	0.139E-01	0.231E-02	0.835E 04	0.674E-01	0.135E 0
240	0.389E-19	0.103E-03	-0.194E 02	-0.398E 01	0.663E-01	0.169E-02	0.108E 18	0.924E-01	0.751E 0
300	0.389E-19	0.105E-03	-0.194E 02	-0.397E 01	0.528E-01	0.131E-02	0.866E 17	0.112E 00	0.599E 0

COMPUTER CALCULATED RESULTS OF FIGURE 40

TIME	TOTAL SULFIDE.	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K[illegible] RATE ST
0	0.174E-03	0.283E-03	-0.375E 01	-0.354E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.00[illegible] 0
4	0.143E-03	0.269E-03	-0.384E 01	-0.357E 01	0.208E-01	0.562E-02	0.303E 03	0.625E-04	0.13 0
8	0.123E-03	0.252E-03	-0.390E 01	-0.359E 01	0.187E-01	0.644E-02	0.296E 03	0.286E-03	0.112E [illegible]
12	0.101E-03	0.240E-03	-0.399E 01	-0.361E 01	0.194E-01	0.604E-02	0.340E 03	0.618E-03	0.12[illegible] 0[illegible]
15	0.872E-04	0.233E-03	-0.405E 01	-0.363E 01	0.199E-01	0.571E-02	0.380E 03	0.929E-03	0.133E 0[illegible]
19	0.778E-04	0.223E-03	-0.410E 01	-0.365E 01	0.184E-01	0.548E-02	0.374E 03	0.146E-02	0.117E 0[illegible]
27	0.594E-04	0.207E-03	-0.422E 01	-0.368E 01	0.172E-01	0.503E-02	0.410E 03	0.281E-02	0.111E 0[illegible]
34	0.454E-04	0.193E-03	-0.434E 01	-0.371E 01	0.171E-01	0.488E-02	0.478E 03	0.449E-02	0.111E 0[illegible]
42	0.334E-04	0.180E-03	-0.447E 01	-0.374E 01	0.170E-01	0.470E-02	0.575E 03	0.687E-02	0.113E 0[illegible]
49	0.246E-04	0.169E-03	-0.460E 01	-0.377E 01	0.173E-01	0.457E-02	0.712E 03	0.939E-02	0.116E 0[illegible]
57	0.174E-04	0.156E-03	-0.475E 01	-0.380E 01	0.175E-01	0.452E-02	0.906E 03	0.131E-01	0.119E 0[illegible]
64	0.118E-04	0.146E-03	-0.492E 01	-0.383E 01	0.182E-01	0.450E-02	0.122E 04	0.171E-01	0.125E 0[illegible]
72	0.972E-05	0.137E-03	-0.505E 01	-0.386E 01	0.180E-01	0.436E-02	0.151E 04	0.216E-01	0.124E 0[illegible]
87	0.375E-05	0.122E-03	-0.542E 01	-0.391E 01	0.191E-01	0.418E-02	0.299E 04	0.323E-01	0.136E 0[illegible]
102	0.155E-05	0.112E-03	-0.580E 01	-0.394E 01	0.200E-01	0.394E-02	0.625E 04	0.442E-01	0.147E 0[illegible]
117	0.572E-06	0.105E-03	-0.624E 01	-0.397E 01	0.212E-01	0.365E-02	0.148E 05	0.558E-01	0.160E 0[illegible]
137	0.389E-19	0.101E-03	-0.194E 02	-0.399E 01	0.114E 00	0.325E-02	0.187E 18	0.696E-01	0.101E 0[illegible]
157	0.389E-19	0.995E-04	-0.194E 02	-0.400E 01	0.996E-01	0.289E-02	0.163E 18	0.825E-01	0.882E 0[illegible]
177	0.389E-19	0.995E-04	-0.194E 02	-0.400E 01	0.884E-01	0.257E-02	0.144E 18	0.930E-01	0.782E 0[illegible]
197	0.389E-19	0.995E-04	-0.194E 02	-0.400E 01	0.794E-01	0.230E-02	0.130E 18	0.103E 00	0.702E 0[illegible]
217	0.389E-19	0.101E-03	-0.194E 02	-0.399E 01	0.721E-01	0.205E-02	0.118E 18	0.110E 00	0.63[illegible] 0[illegible]

COMPUTER CALCULATED RESULTS OF FIGURE 41

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE ST
0	0.174E-03	0.263E-03	-0.375E 01	-0.357E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
8	0.149E-03	0.226E-03	-0.382E 01	-0.364E 01	0.833E-02	0.817E-02	0.119E 03	0.342E-03	0.171 0
15	0.118E-03	0.209E-03	-0.392E 01	-0.367E 01	0.111E-01	0.661E-02	0.179E 03	0.101E-02	0.509E 0
23	0.907E-04	0.192E-03	-0.404E 01	-0.371E 01	0.123E-01	0.590E-02	0.229E 03	0.222E-02	0.717 0
30	0.642E-04	0.173E-03	-0.419E 01	-0.376E 01	0.144E-01	0.603E-02	0.327E 03	0.408E-02	0.940E 0
38	0.472E-04	0.161E-03	-0.432E 01	-0.379E 01	0.149E-01	0.563E-02	0.405E 03	0.637E-02	0.103E 01
45	0.334E-04	0.150E-03	-0.447E 01	-0.382E 01	0.159E-01	0.541E-02	0.536E 03	0.892E-02	0.117E 01
53	0.227E-04	0.139E-03	-0.464E 01	-0.385E 01	0.166E-01	0.519E-02	0.719E 03	0.123E-01	0.129E 01
60	0.161E-04	0.129E-03	-0.479E 01	-0.388E 01	0.172E-01	0.515E-02	0.937E 03	0.164E-01	0.134E 01
75	0.840E-05	0.114E-03	-0.507E 01	-0.394E 01	0.175E-01	0.483E-02	0.151E 04	0.257E-01	0.142E 01
90	0.437E-05	0.103E-03	-0.535E 01	-0.398E 01	0.177E-01	0.449E-02	0.247E 04	0.365E-01	0.149E 01
105	0.195E-05	0.983E-04	-0.570E 01	-0.400E 01	0.185E-01	0.407E-02	0.481E 04	0.465E-01	0.162E 01
120	0.942E-06	0.953E-04	-0.602E 01	-0.402E 01	0.188E-01	0.368E-02	0.879E 04	0.558E-01	0.170E 01
135	0.389E-19	0.953E-04	-0.194E 02	-0.402E 01	0.115E 00	0.327E-02	0.189E 18	0.667E-01	0.126E 01

COMPUTER CALCULATED RESULTS OF FIGURE 42

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE ST
0	0.128E-03	0.243E-03	-0.389E 01	-0.361E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
15	0.125E-03	0.239E-03	-0.390E 01	-0.362E 01	0.555E-03	0.507E-03	0.100E 02	0.646E-04	0.412E 0
30	0.123E-03	0.233E-03	-0.390E 01	-0.363E 01	0.555E-03	0.643E-03	0.101E 02	0.332E-03	-0.761E 00
45	0.118E-03	0.224E-03	-0.392E 01	-0.364E 01	0.740E-03	0.786E-03	0.13PE 02	0.930E-03	-0.396E 0
60	0.114E-03	0.218E-03	-0.394E 01	-0.366E 01	0.833E-03	0.797E-03	0.158E 02	0.170E-02	0.304E 0
90	0.109E-03	0.207E-03	-0.395E 01	-0.368E 01	0.740E-03	0.771E-03	0.143E 02	0.380E-02	-0.269E 00
120	0.103E-03	0.197E-03	-0.398E 01	-0.370E 01	0.763E-03	0.768E-03	0.152E 02	0.691E-02	-0.396E-01
150	0.979E-04	0.188E-03	-0.400E 01	-0.372E 01	0.777E-03	0.742E-03	0.160E 02	0.106E-01	0.309E 0
180	0.907E-04	0.182E-03	-0.404E 01	-0.373E 01	0.833E-03	0.701E-03	0.178E 02	0.147E-01	0.114E 01
240	0.793E-04	0.169E-03	-0.410E 01	-0.377E 01	0.868E-03	0.656E-03	0.200E 02	0.255E-01	0.182E 01
300	0.734E-04	0.158E-03	-0.413E 01	-0.379E 01	0.805E-03	0.618E-03	0.193E 02	0.389E-01	0.161E 01
360	0.654E-04	0.150E-03	-0.418E 01	-0.382E 01	0.810E-03	0.581E-03	0.207E 02	0.543E-01	0.197E 01
420	0.572E-04	0.144E-03	-0.424E 01	-0.384E 01	0.833E-03	0.543E-03	0.230E 02	0.707E-01	0.251E 0.
480	0.510E-04	0.137E-03	-0.429E 01	-0.386E 01	0.833E-03	0.516E-03	0.245E 02	0.899E-01	0.274E 01
540	0.437E-04	0.133E-03	-0.435E 01	-0.387E 01	0.864E-03	0.483E-03	0.278E 02	0.108E 00	0.329E 01
600	0.389E-04	0.127E-03	-0.440E 01	-0.389E 01	0.861E-03	0.470E-03	0.297E 02	0.134E 00	0.337E 01
660	0.347E-04	0.122E-03	-0.445E 01	-0.391E 01	0.858E-03	0.450E-03	0.317E 02	0.158E 00	0.353E 01
720	0.309E-04	0.118E-03	-0.450E 01	-0.392E 01	0.856E-03	0.434E-03	0.339E 02	0.184E 00	0.365E 01
780	0.276E-04	0.115E-03	-0.455E 01	-0.393E 01	0.854E-03	0.414E-03	0.364E 02	0.210E 00	0.380E 01
840	0.246E-04	0.112E-03	-0.460E 01	-0.394E 01	0.853E-03	0.400E-03	0.390E 02	0.239E 00	0.391E 01
900	0.219E-04	0.108E-03	-0.465E 01	-0.396E 01	0.851E-03	0.388E-03	0.419E 02	0.271E 00	0.401E 01
960	0.195E-04	0.107E-03	-0.470E 01	-0.396E 01	0.850E-03	0.371E-03	0.451E 02	0.297E 00	0.414E 01
1020	0.174E-04	0.103E-03	-0.475E 01	-0.398E 01	0.849E-03	0.363E-03	0.486E 02	0.334E 00	0.421E 01
1080	0.161E-04	0.101E-03	-0.479E 01	-0.399E 01	0.833E-03	0.351E-03	0.501E 02	0.367E 00	0.417E 01
1140	0.149E-04	0.995E-04	-0.482E 01	-0.400E 01	0.818E-03	0.340E-03	0.518E 02	0.401E 00	0.413E 01
1200	0.133E-04	0.953E-04	-0.487E 01	-0.402E 01	0.819E-03	0.339E-03	0.560E 02	0.454E 00	0.415E 01
1260	0.118E-04	0.911E-04	-0.492E 01	-0.404E 01	0.820E-03	0.339E-03	0.608E 02	0.514E 00	0.416E 01
1320	0.105E-04	0.868E-04	-0.497E 01	-0.406E 01	0.820E-03	0.339E-03	0.657E 02	0.580E 00	0.416E 01

COMPUTER CALCULATED RESULTS OF FIGURE 43

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE 02	K2 RATE ST	K2 RATE 02	K2 RATE SIC2
0	0.128E-03	0.262E-03	-0.389E 01	-0.358E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
15	0.123E-03	0.259E-03	-0.390E 01	-0.358E 01	0.111E-02	0.328E-03	0.203E 02	0.450E-04	0.581E 01
30	0.118E-03	0.256E-03	-0.392E 01	-0.359E 01	0.111E-02	0.354E-03	0.207E 02	0.195E-03	0.562E 01
45	0.114E-03	0.252E-03	-0.394E 01	-0.359E 01	0.111E-02	0.397E-03	0.211E 02	0.496E-03	0.539E 01
60	0.107E-03	0.247E-03	-0.396E 01	-0.360E 01	0.124E-02	0.420E-03	0.245E 02	0.943E-03	0.616E 01
90	*****	IRON TWO ADDED 1*10-7				*****			
90	0.998E-04	0.239E-03	-0.400E 01	-0.362E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
120	0.942E-04	0.233E-03	-0.402E 01	-0.363E 01	0.133E-03	0.389E-03	0.197E 02	0.195E-03	0.317E 01
150	0.840E-04	0.224E-03	-0.407E 01	-0.364E 01	0.124E-02	0.462E-03	0.314E 02	0.948E-03	0.565E 01
165	0.793E-04	0.220E-03	-0.410E 01	-0.365E 01	0.133E-02	0.480E-03	0.345E 02	0.155E-02	0.610E 01
173	*****	IRON TWO ADDED 2*10-5				*****			
173	0.720E-04	0.213E-03	-0.414E 01	-0.366E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
177	0.530E-04	0.209E-03	-0.427E 01	-0.367E 01	0.333E-01	0.217E-02	0.124E 04	0.172E-04	0.219E 0
180	0.463E-04	0.207E-03	-0.433E 01	-0.368E 01	0.273E-01	0.187E-02	0.109E 04	0.458E-04	0.179E 0
195	0.405E-04	0.203E-03	-0.439E 01	-0.369E 01	0.113E-01	0.100E-02	0.490E 03	0.245E-03	0.730E 0
210	0.375E-04	0.199E-03	-0.442E 01	-0.370E 01	0.765E-02	0.843E-03	0.345E 03	0.589E-03	0.480E 0
240	0.347E-04	0.188E-03	-0.445E 01	-0.372E 01	0.472E-02	0.819E-03	0.222E 03	0.193E-02	0.279E 0
300	0.334E-04	0.175E-03	-0.447E 01	-0.375E 01	0.242E-02	0.671E-03	0.126E 03	0.569E-02	0.137E 0
360	0.321E-04	0.165E-03	-0.449E 01	-0.378E 01	0.137E-02	0.600E-03	0.919E 02	0.117E-01	0.895E 0
420	0.298E-04	0.156E-03	-0.452E 01	-0.380E 01	0.155E-02	0.546E-03	0.796E 02	0.192E-01	0.70-E 01
480	0.276E-04	0.148E-03	-0.455E 01	-0.382E 01	0.145E-02	0.518E-03	0.727E 02	0.290E-01	0.595E 01
540	0.241E-04	0.139E-03	-0.461E 01	-0.385E 01	0.129E-02	0.503E-03	0.750E 02	0.416E-01	0.557E 01
600	0.215E-04	0.133E-03	-0.466E 01	-0.387E 01	0.122E-02	0.480E-03	0.763E 02	0.551E-01	0.525E 01
660	0.188E-04	0.127E-03	-0.472E 01	-0.389E 01	0.119E-02	0.464E-03	0.806E 02	0.712E-01	0.516E 01
720	0.164E-04	0.122E-03	-0.478E 01	-0.391E 01	0.117E-02	0.440E-03	0.858E 02	0.867E-01	0.516E 01
780	0.138E-04	0.116E-03	-0.485E 01	-0.393E 01	0.118E-02	0.434E-03	0.962E 02	0.108E 00	0.529E 01
840	0.114E-04	0.112E-03	-0.494E 01	-0.394E 01	0.119E-02	0.419E-03	0.110E 03	0.129E 00	0.549E 01
900	0.872E-05	0.108E-03	-0.505E 01	-0.396E 01	0.126E-02	0.408E-03	0.138E 03	0.152E 00	0.600E 01
960	0.680E-05	0.101E-03	-0.516E 01	-0.399E 01	0.130E-02	0.410E-03	0.169E 03	0.185E 00	0.628E 01

COMPUTER CALCULATED RESULTS OF FIGURE 44

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE ST/O2
0	0.118E-03	0.243E-03	-0.392E 01	-0.361E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 00
15	0.114E-03	0.237E-03	-0.394E 01	-0.362E 01	0.111E-02	0.765E-03	0.219E 02	0.978E-04	0.276E 01
30	0.112E-03	0.228E-03	-0.395E 01	-0.364E 01	0.833E-03	0.909E-03	0.166E 02	0.473E-03	-0.606E 01
45	0.107E-03	0.220E-03	-0.396E 01	-0.365E 01	0.925E-03	0.970E-03	0.188E 02	0.115E-02	-0.355E 01
60	0.103E-03	0.213E-03	-0.398E 01	-0.366E 01	0.972E-03	0.939E-03	0.201E 02	0.202E-02	0.260E 00
90	0.979E-04	0.201E-03	-0.400E 01	-0.369E 01	0.925E-03	0.921E-03	0.198E 02	0.461E-02	0.319E-01
120	0.907E-04	0.192E-03	-0.404E 01	-0.371E 01	0.972E-03	0.847E-03	0.216E 02	0.771E-02	0.103E 01
150	0.824E-04	0.184E-03	-0.408E 01	-0.373E 01	0.105E-02	0.807E-03	0.247E 02	0.117E-01	0.194E 01
180	0.748E-04	0.173E-03	-0.412E 01	-0.376E 01	0.111E-02	0.816E-03	0.273E 02	0.176E-01	0.236E 01
240	0.618E-04	0.161E-03	-0.420E 01	-0.379E 01	0.118E-02	0.749E-03	0.323E 02	0.300E-01	0.344E 01
300	0.510E-04	0.150E-03	-0.429E 01	-0.382E 01	0.122E-02	0.698E-03	0.372E 02	0.452E-01	0.419E 01
360	0.413E-04	0.139E-03	-0.438E 01	-0.385E 01	0.127E-02	0.669E-03	0.438E 02	0.651E-01	0.489E 01
420	0.334E-04	0.133E-03	-0.447E 01	-0.387E 01	0.130E-02	0.622E-03	0.511E 02	0.844E-01	0.549E 01
480	0.270E-04	0.125E-03	-0.456E 01	-0.390E 01	0.133E-02	0.603E-03	0.593E 02	0.111E 00	0.586E 01
540	0.223E-04	0.118E-03	-0.465E 01	-0.392E 01	0.134E-02	0.578E-03	0.672E 02	0.136E 00	0.611E 01
600	0.177E-04	0.112E-03	-0.475E 01	-0.394E 01	0.137E-02	0.560E-03	0.798E 02	0.171E 00	0.651E 01
660	0.141E-04	0.105E-03	-0.485E 01	-0.397E 01	0.140E-02	0.548E-03	0.946E 02	0.209E 00	0.682E 01
720	0.105E-04	0.995E-04	-0.497E 01	-0.400E 01	0.145E-02	0.539E-03	0.119E 03	0.253E 00	0.734E 01
780	0.872E-05	0.932E-04	-0.505E 01	-0.403E 01	0.145E-02	0.534E-03	0.136E 03	0.306E 00	0.734E 01
900	0.454E-05	0.783E-04	-0.534E 01	-0.410E 01	0.157E-02	0.547E-03	0.235E 03	0.462E 00	0.821E 01

COMPUTER CALCULATED RESULTS OF FIGURE 45

TIME	TOTAL SULFIDE	OXYGEN	LOG TOTAL ST	LOG OXY GEN	K1 RATE ST	K1 RATE O2	K2 RATE ST	K2 RATE O2	K2 RATE ST.2
0	0.128E-03	0.243E-03	-0.389E 01	-0.361E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
30	0.125E-03	0.233E-03	-0.390E 01	-0.363E 01	0.277E-03	0.643E-03	0.503E 01	0.332E-03	-0.316E 0
60	0.123E-03	0.224E-03	-0.390E 01	-0.364E 01	0.277E-03	0.589E-03	0.508E 01	0.124E-02	-0.27[illegible]E 0
105	*****	IRON TWO ADDED 1*10-5				*****			
105	0.120E-03	0.218E-03	-0.391E 01	-0.366E 01	0.000E 00	0.000E 00	0.000E 00	0.000E 00	0.000E 0
107	0.101E-03	0.207E-03	-0.399E 01	-0.368E 01	0.375E-01	0.108E-01	0.779E 03	0.222E-04	0.274E 0
109	0.103E-03	0.206E-03	-0.398E 01	-0.368E 01	0.166E-01	0.606E-02	0.342E 03	0.501E-04	0.10[illegible]E 0
113	0.109E-03	0.204E-03	-0.395E 01	-0.368E 01	0.520E-02	0.348E-02	0.104E 03	0.115E-03	0.177E 0
120	0.114E-03	0.203E-03	-0.394E 01	-0.369E 01	0.166E-02	0.203E-02	0.326E 02	0.238E-03	-0.381E 01
150	0.118E-03	0.199E-03	-0.392E 01	-0.370E 01	0.185E-03	0.882E-03	0.355E 01	0.940E-03	-0.716E 01
180	0.120E-03	0.194E-03	-0.391E 01	-0.371E 01	0.000E 00	0.653E-03	0.000E 00	0.195E-02	-0.677E 01
300	0.118E-03	0.180E-03	-0.392E 01	-0.374E 01	0.427E-04	0.427E-03	0.821E 00	0.901E-02	-0.395E 01
360	0.112E-03	0.175E-03	-0.395E 01	-0.375E 01	0.130E-03	0.367E-03	0.258E 01	0.134E-01	-0.243E 01
480	0.960E-04	0.161E-03	-0.401E 01	-0.379E 01	0.266E-03	0.352E-03	0.570E 01	0.270E-01	-0.876E 0
600	0.778E-04	0.148E-03	-0.410E 01	-0.382E 01	0.387E-03	0.338E-03	0.926E 01	0.509E-01	0.496E 0
720	0.572E-04	0.133E-03	-0.424E 01	-0.387E 01	0.528E-03	0.347E-03	0.149E 02	0.852E-01	0.186E 01
840	0.429E-04	0.120E-03	-0.436E 01	-0.391E 01	0.612E-03	0.349E-03	0.204E 02	0.129E 00	0.270E 0
1020	0.265E-04	0.103E-03	-0.457E 01	-0.398E 01	0.719E-03	0.352E-03	0.321E 02	0.220E 00	0.377E 0
1200	0.167E-04	0.847E-04	-0.477E 01	-0.407E 01	0.783E-03	0.375E-03	0.469E 02	0.376E 00	0.429E 0
1380	0.101E-04	0.699E-04	-0.499E 01	-0.415E 01	0.843E-03	0.347E-03	0.705E 02	0.590E 00	0.469E 0
1560	0.540E-05	0.593E-04	-0.526E 01	-0.422E 01	0.927E-03	0.388E-03	0.121E 03	0.850E 00	0.554E 01
0	0.389E-19	0.000E 00	-0.194E 02	-0.738E 38	-0.147E 00	0.348E-01	-0.244E 18	-0.500E-05	-0.187E 0

APPENDIX III

BIOLOGICAL OXYGEN DEMAND BOTTLE REACTOR

SYSTEM RESULTS

pH 8.1 $S_T = \log a_1 = 4.10$

First order with respect to S_T LOG $a_1/a_2 = k\ (t_2-t_1)$

time in hrs.	t	log a_1/a_2	kx 10^{-2} hr^{-1}
12.25	12.00	0.165	1.4
24.1...	23.85	0.197	1.0
36.5	36.25	0.594	1.5
51.6	51.35	0.631	1.2
73.0	72.75	0.731	1.0

As second order $a_1-a_2/a_1a_2 = k(t_2-t_1)$

kx 10^{-2} 1/moles/hr.
3.0
2.0
6.0
5.0
5.0

First order with respect to oxygen DO = log a = -3.703

log a_1/a_2	kx 10^{-3} hr^{-1}
0.07	6.0
0.162	6.7
0.221	6.0
0.218	4.0
0.363	5.0

As second order $a_1-a_2/a_1a_2 = k(t_2-t_1)$

kx 10^{1} 1/moles/hr
7.4
9.7
9.2
6.0
9.0

pH 9.00 S_T = log a_1= -3.651

First order with respect to S_T^* Log $a_1/a_2 = k(t_2-t_1)$

t	log a_1/a_2	k x 10^{-3} hr^{-1}
2.6	0.024	9.2
4.9	0.052	11.0
7.5	0.059	8.0
21.6	0.240	11.0
44.2	0.258	6.0
70.1	0.279	4.0

As second order $a_1-a_2/a_1a_2 = k\ (t_2-t_1)$

k x 10^1 1/moles/hr.
7.0
8.7
7.0
11.0
6.5
4.3
2.5

First order with respect to oxygen DO = log a_1= -3.6

DO = log $a_1/a_2 = k(t_2-t_1)$

log a_1/a_2	k x 10^{-2} hr^{-1}
0.035	1.5
0.085	1.7
0.103	1.37
0.488	2.23
1.041	2.4

As second order $a_1-a_2/a_1a_2 = k\ (t_2-t_1)$

k x 10^2 1/moles/hr.
1.4
2.0
1.6
4.3
10.0

pH 13.00 $S_T = \log a_1 = 4.015$

First order with respect to S_T^* $\log a_1/a_2 = k(t_2-t_1 0)$

t	$\log a_1/a_2$	$k \times 10^{-2}$ hr^{-1}
4.2	0.04	1.74
10.8	0.077	1.85
24.3	0.221	1.72
48.8	0.303	1.35
78.4	0.467	0.9

As second order $a_1-a_2/a_1a_2 = k(t_2-t_1)$

$k \times 10^2$ 1/moles/hr.
1.95
2.3
2.45
2.3
2.1
1.67

First order with respect to oxygen DO = $\log a_1/a_2 = k(t_2-t_1)$

$\log a_1 = -3.64$

$\log a_1/a_2$	$k \times 10^{-2}$ hr^{-1}
0.047	1.1
0.100	0.92
0.167	0.70
0.291	0.60
0.323	0.46
0.290	0.30

As second order $a_1-a_2/a_1a_2 = k(t_2-t_1)$

$k \times 10^2$ 1/moles/hr.
1.15
1.05
0.80
0.80
0.60
0.36