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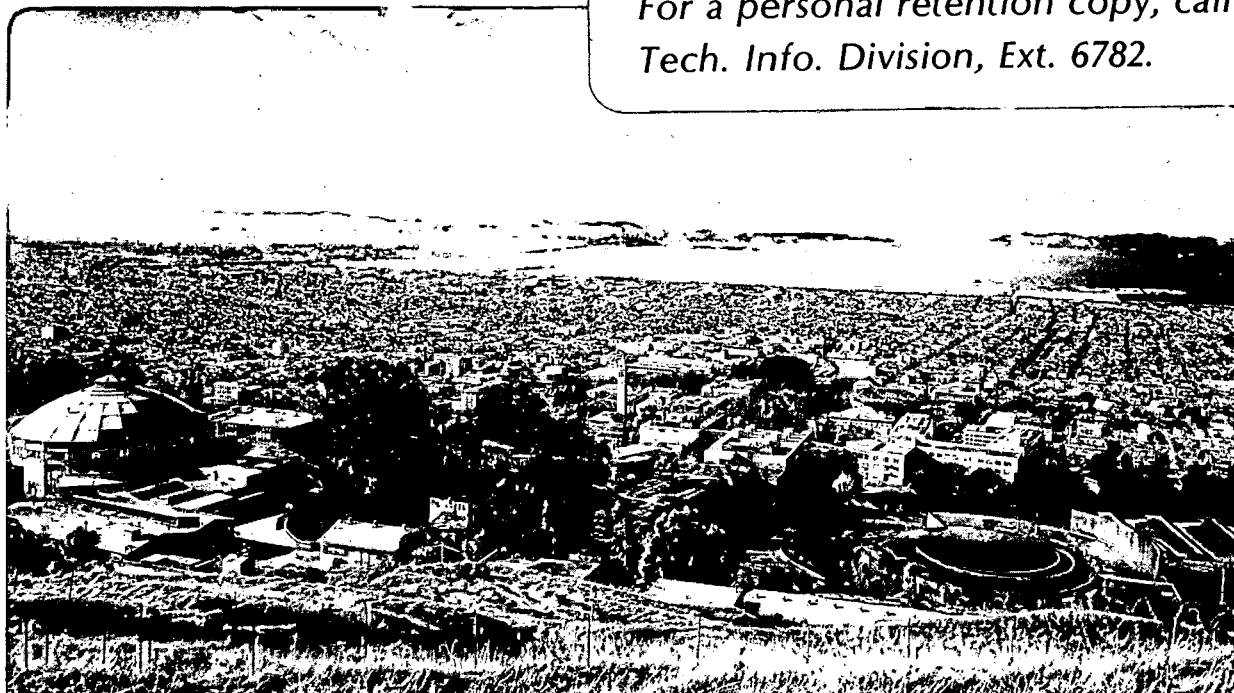# Lawrence Berkeley Laboratory

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IN THE PRESENCE OF SULFITE

Oleh Weres and Leon Tsao

January 1983

DISCLAIMER

NICKEL CATALYZED OXIDATION OF HYDROGEN SULFIDE

IN THE PRESENCE OF SULFITE

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ABSTRACT

Nickel sulfate catalyzes the reaction of hydrogen sulfide with oxygen in aqueous solution. This reaction was studied. An empirical rate expression and reaction mechanism were deduced. The rate of oxidation is independent of oxygen concentration and pH. The reaction rate is one-half order in nickel, and changes from second to first order in sulfide with increasing concentration. The oxidation reaction is an autocatalytic, free radical chain reaction. Nickel catalyzes the chain initiation step, and polysulfido radical-ions propagate the chains. Colloidal sulfur is a major reaction product that is undesirable in some applications; e.g., abatement of hydrogen sulfide emissions from geothermal powerplants. Sodium sulfite suppresses formation of colloidal sulfur by converting it to thiosulfate. Excess sulfite is converted to sulfate and trithionate.

The geothermal steam utilized by The Geysers Geothermal Power Plant of the Pacific Gas and Electric Company contains hydrogen sulfide and ammonia. Units 1 to 12 are equipped with contact condensers, and 60-75% of the H_2S dissolves in the cooling water. Ammonia increases the solubility of H_2S by converting it to HS^-. The dissolved H_2S must be destroyed before it is air-stripped in the cooling towers and emitted to the atmosphere. Oxidation with hydrogen peroxide is effective but expensive. The cooling water is saturated with atmospheric oxygen in the cooling tower; a catalyst is needed to induce reaction between the dissolved oxygen and H_2S. Nickel ion is effective, but causes the production of colloidal sulfur. In an early field test, the sulfur set into a solid, hard-to-remove scale in the cooling tower's water distribution trays (1). Formation of colloidal sulfur must be suppressed.

Snavely and Blount (2) found that nickel and cobalt are the stongest catalysts for oxidation of H_2S. At the start of the reaction there is an induction period, suggesting autocatalysis; i.e., a reaction product acts as a cocatalyst that accelerates the reaction. They theorized that this cocatalyst is a polysulfide ion. The rate of reaction is independent of oxygen concentration, and increasing the concentration of nickel hundred-fold increases the rate of reaction ten-fold. The reaction is inhibited by low pH, but the rate is independent of pH at intermediate values.

Chen and Morris (3) and Chen and Gupta (4) inferred

that the nominally uncatalyzed reaction of H_2S with oxygen is autocatalytic, and correlated good "reactivity" with a yellow color and strong UV absorption. The rate of reaction is greatest near pH 7, where formation of polysulfides and colloidal sulfur is favored. Chen and Morris (5) confirmed that nickel and cobalt are the strongest catalysts for H_2S oxidation, and reported that various organic compounds which are easily oxidized in free radical chain reactions also accelerate H_2S oxidation. Their effect on the oxidation of H_2S suggests that this is a free radical chain reaction as well.

Autocatalysis causes the chemical properties of the reaction medium to depend on its previous history. In all studies cited, sodium sulfide was added to the reaction medium, and the decline in sulfide or oxygen concentration was monitored. The gradual accumulation of the cocatalyst during the experiment strongly affects kinetic data thus obtained.

When initial sulfide concentration is < 100µM, polysulfides and colloidal S are not produced, and there is no induction period, suggesting that a different, nonautocatalytic mechanism dominates under these conditions (6,7,8). The oxidation of H_2S catalyzed by cobalt tetrasulfophthalocyanine involves yet another mechanism (9).

Steijns et al. (10,11) reported that the high temperature oxidation of gaseous H_2S over solid catalysts is autocatalytic, and involves polysulfido radicals on the surface

of the catalyst.

Our work is discussed in detail in Ref. 12, which includes a survey of relevant chemical literature, additional data, and a full description of experimental methods. Chemical and environmental problems encountered in geothermal energy utilization are surveyed elsewhere (13,14,15).

Experimental

Safety. Sodium sulfide and H_2S are poisonous and stink. Sodium sulfide stock solution was prepared in a hood, and handled outside of it in small containers only. Excess solid Na_2S and concentrated solutions were never poured down the drain. They were disposed of by reaction with excess ferric chloride solution. Spills were cleaned up promptly. The reaction flask was set up inside the hood.

Basic method. Our method allowed a steady state cocatalyst concentration and oxidation rate to be attained. One liter of "synthetic cooling water" (SCW) containing nickel sulfate was prepared in a 1-liter Erlenmeyer flask. The flask was set upon an air-driven, submersible magnetic stirrer in a water bath at 45°C. Air (0.25 1/min.), sodium sulfide solution (0.0355M; 0.45ml/min.), sodium sulfite (various conc.; 0.45ml/min.), and sulfuric acid (0.022M; 0.45ml/min.) were added continuously to the SCW, using a multi-channel persitaltic pump that was calibrated daily. The last reagent also contained nickel sulfate at triple the concentration in the SCW. Thus, H_2S was added to the SCW at

16µM/min while keeping the concentrations of oxygen and nickel constant. Addition of sodium sulfite began 20 min. after the start of the experiment, while the other reagents were added from the start. Within two hours the SCW reached chemical steady state and gathering of kinetic data began. In practice, sampling compensated for reagent addition, keeping the volume approximately constant.

The SCW resembled Geysers cooling water, but usually no thiosulfate was included. Typically, it contained 7.70mM total ammonia, 0.40mM HCO_3^-, 14.36mM boric acid, 3.65mM $SO_4^=$, and 20 or 100µM nickel sulfate. It was established that the only role of the major ions is to buffer the SCW; its exact composition does not affect the results obtained. The pH was adjusted to that desired with 1.0M NaOH at the beginning, and corrected with NaOH or H_2SO_4 as needed. Most experiments were performed at pH 7.8.

In experiments below pH 7.5, 10mM each of phosphate and maleate were added. These and other buffers slowed the development of reactivity if present from the start, but did not affect reactivity once established. The reaction was initiated at pH 7.8 without the buffer. The buffer was added at t = 60 min. as a concentrated solution prepared from maleic acid and monosodium orthophosphate, the pH of which had been adjusted to a value slightly lower than that desired in the SCW.

Determination of reactivity. To determine "reactivity", a 25 ml aliquot of SCW was pipetted into a beaker

and briefly aerated. A magnetic stirring bar was added, and the beaker was set upon a magnetic stirrer. A small amount of Na_2S solution was added using an adjustable micropipette, typically enough to introduce 70µM total sulfide. After fifteen seconds, 25 ml of sulfide antioxidant buffer was added to quench the reaction. Then electrodes (Orion Ag_2S and reference; calibrated daily) were introduced to measure the residual sulfide concentration. The fraction of the added sulfide that remains after 15s is a quantitative measure of "reactivity"; a small residual fraction indicates good reactivity, and vice-versa.

To determine the effect of varying nickel concentration, SCW was initially prepared with 100 µM Ni and reacted for two hours. Then test aliquots were removed and diluted with different amounts of preheated, nickel-free SCW to give the concentration of Ni desired. In a routine reactivity test the temperature of the test aliquot was about 35°C. To determine the effect of temperature, the temperature of the aerated test aliquot was adjusted with an ice or boiling water bath before the Na_2S was added. Typically, the oxygen concentration in the test aliquot was 3.5 to 4.0 ppm. To determine the effect of oxygen concentration, the aliquots were "aerated" with 100% N_2, air, 42/58 O_2/N_2, or 100% O_2. The O_2 concentration was then measured with a dissolved oxygen meter before adding Na_2S. To determine the effect of pH, the pH of the test aliquot was adjusted with sulfuric acid or NaOH. The pH was then measured before adding Na_2S.

Wackenroder's solution was prepared from equivalent amounts of Na_2S and Na_2SO_3. The pH of the solution was lowered to 7.3 with sulfuric acid, the solution was diluted to 0.2M total nonsulfate sulfur, and then set aside for about 30 min. to clarify.

Determination of reaction products. In these experiments, ammonium acetate and acetic acid were used in place of ammonium sulfate and sulfuric acid. To determine colloidal sulfur, the technique of Bartlett and Skoog (16) was used in modified form. Fifty ml of SCW was membrane filtered under pressure with nitrogen (Millipore type VC, 0.1μm pore size, 47mm diameter). The filter was removed from the housing and dissolved in 10 ml of 95% acetone-water. This was mixed with 15 ml of the sodium cyanide reagent. After a few minutes, a precipitate of filter material formed. This was removed with fine filter paper, and the rest of the procedure proceeded as described by Bartlett and Skoog. Thiosulfate and trithionate were determined by the method of Kelly et al. (17). Tetrathionate was never detected. Sulfate was determined gravimetrically, at the end of the experiment only. The SCW was membrane filtered as above, and boiling was avoided to reduce interference by colloidal sulfur and trithionate.

Results

Reactivity is poor at first but improves rapidly, reaching steady state in about an hour (Fig. 1). The

development of reactivity is inhibited if sodium sulfite is added from the start of the experiment (not shown). Sulfite destroys sulfur chain molecules by converting the zero valent sulfur in them to thiosulfate. However, reactivity would develop with sulfite added from the start, if the sulfide and sulfite reagents were combined before being added to the SCW. Adding this mixture to the SCW essentially produces Wackenroder's Solution, which contains polysulfides, polythionates, etc. Adding Wackenroder's solution at the beginning of an experiment accelerated the development of reactivity (Fig. 1).

Formally, the SCW was supersaturated with nickel sulfide by several orders of magnitude, but NiS did not precipitate. Buffering compounds probably retard the development of reactivity by chelating nickel, and rendering it inactive. That buffers do not affect reactivity after it has been established suggests that the nickel is tightly chelated by polysulfides.

Turbidity associated with colloidal sulfur increased rapidly during the first 20 min., but dropped rapidly after addition of Na_2SO_3 commenced, finally giving a yellow, nearly clear solution. If thiosulfate is present from the start, turbidity declines more rapidly when sulfite is added, but the development of reactivity is unaffected. However, with a sulfite:sulfide ratio = 0.5 thiosulfate has the opposite effect on turbidity (not shown); this reversal has not been explained. At pH 7.8 a minimum sulfite:sulfide

mole ratio between 0.5 and 0.75 is needed to prevent accumulation of colloidal sulfur. At pH 7.0, the minimum mole ratio needed is between 0.75 and 1.0 (not shown).

Within wide limits, there is no correlation of reactivity with either pH or sulfite:sulfide ratio. Accordingly, data generated at various values of pH and sulfite:sulfide ratio were plotted and analyzed together in Figs. 2 to 7.

With 95% confidence (Student's t test), the energy of activation is between 0.9 and 2.9 kcal; 2.4 kcal is our best estimate (Fig. 2). Reactivity does not correlate with pH between pH 5.5 and 8.5 (Fig. 3), or with oxygen concentration (Fig. 4). Lowering pH to below 5 destroys the reactivity (not shown). Probably, at low pH the cocatalyst decomposes to colloidal sulfur as do thiosulfate and the polysulfides. An apparent kinetic order in hydrogen ion or oxygen as large as ± 0.5 is excluded with confidence $> 99.9\%$.

Successfully to fit the kinetic data, it was necessary to assume that the kinetic order in nickel is one-half, and the kinetic order in sulfide decreases from two to one with increasing sulfide concentration. Eqn. (1) fits the data well:

$$\frac{d(H_2S)}{dt} = - \frac{k_2(H_2S)^2(Ni)^{0.5}}{1 + \frac{k_2}{k_1}(H_2S)} \tag{1}$$

where t is in seconds, (H_2S) and (Ni) are in moles per liter. Here (H_2S) represents the total sulfide concentration as measured with an Ag_2S electrode, and (Ni) represents the total concentration of nickel in the solution. That the concentrations of H_2S and HS^- do not appear separately is an expression of the noncorrelation of reactivity and pH. At $35^\circ C$, $k_1 = 25(moles/l)^{-0.5}s^{-1}$ and $k_2 = 3 \times 10^6 (moles/l)^{-1.5}s^{-1}$.

These values were determined by a bivariant, least-squares fit of the 158 data points in Figs. 5, 6, and 7. The data in Figs. 2, 3, and 4 were not included in this fitting procedure.

Most of the scatter in the kinetic data is associated with variation among experiments, rather than among points from a given experiment. Variations in development of reactivity appear to be responsible. Each reactivity test in Figs. 2, 4 and 6 was preceded by drastic manipulations that perturbed the population of cocatalytic molecules, and this caused considerable point scatter. Increasing nickel concentration greatly reduced point scatter (Fig. 5) by making the perturbing effects of degasing and catalysis by stray impurities relatively less important.

With no sulfite added, thiosulfate and colloidal sulfur are the main reaction products (Fig. 8). Apparently, the accumulation of colloidal sulfur is limited by its further oxidation to thiosulfate and sulfate. With sulfite:sulfide = 0.75, thiosulfate is the major reaction product with smaller yields of sulfate and trithionate, but no colloidal

sulfur (Fig. 9). Nickel concentration has no effect on product distribution (not shown). The yield of sulfate and trithionate increases with added sulfite, and colloidal sulfur is significant without sulfite only (Fig. 10). With sulfite:sulfide = 0.75, decreasing pH favors the formation of sulfate at the expense of thiosulfate, and colloidal sulfur is present only at pH 6.5 (Fig. 11).

Seventy-five to 95% of the sulfur put into the SCW was recovered. Sulfur recovery improved with increasing concentration of nickel but deteriorated with decreasing pH, suggesting that the loss of H_2S to the atmosphere is the main cause of incomplete recovery.

Discussion

Our results and conclusions are consistent with those of Snavely and Blount (2) and Chen et al. (3,4,5). A reaction mechanism consistent with the data is presented in Table 1. The reactions are approximate and may be changed somewhat without materially affecting the conclusions. Which species are protonated is not known with certainty. The exact nature of "the cocatalyst" is not known. Most probably, it is a complex mixture of polysulfides, polysulfidomonosulfonates, and the corresponding radical-ions, which interconvert and change chain length in the course of the reaction. All nickel is complexed, and this prevents the precipitation of NiS. Why the rate of reaction is independent of pH has not been explained.

Reactions (1a to d) add free radicals to the system. Reactions (1a) and (1c) are irreversible, and (1c) is rate determining. Reaction (1b) is rapid and reversible, with equilibrium constant K_{1b}. Reaction (1d) rapidly converts all HS$\cdot$ produced to relatively stable polysulfido radical-ions, and does not affect the overall rate of reaction. Reactions (2a, b, and c) are the chain propagation steps. Reactions (2b) and (2c) are rate determining. Neither (1a) nor (2a) is rate determining; therefore, the rate of reaction is independent of oxygen concentration. Reactions (5a), (5b) and (6) are side reactions which do not affect the rate of disappearance of H_2S.

An explicit rate expression may be derived. This rate expression has the same limiting behavior as the empirical rate expression Eqn. (1). In the limit $1 \ll K_{1b}(H_2S)^2$, the derived rate expression becomes:

$$\frac{d(H_2S)}{dt} = - k_1(Ni)^{0.5}(H_2S)$$

where

$$k_1 = \frac{2(k_{1c}/k_3)^{0.5}}{\frac{1}{K_{2b}} + \frac{1}{K_{2c}}}$$

In the limit $1 \gg K_{1b}(H_2S)^2$, the derived rate expression becomes

$$\frac{d(H_2S)}{dt} = - k_2(Ni)^{0.5}(H_2S)^2$$

where $k_2 = k_1(K_{1b})^{0.5}$. From the empirical values of k_1 and

k_2, we estimate $K_{1b} = 1.44 \times 10^{10} M^{-2}$.

Steijns et al. (11) postulated reactions similar to (2a, b and c) and (5a) to explain the oxidation of H_2S over solid catalysts at high temperature. The different radicals were identified with distinct ESR signals.

The major source of sulfate is sulfite oxidation. The yield of sulfate increases with added sulfite, and more sulfate is produced at pH 7.0 than at 7.8 because the rate of sulfite oxidation is greatest at pH 7 (18). Reactions (7a, b and c) are based on the mechanism for sulfite oxidation proposed by Hayon et al. (19,20). The yield of trithionate also increases with added sulfite. This is consistent with reaction (8), which was studied by Battaglia and Miller (21).

Practical application

Recently, H_2S emission abatement using iron N-hydroxyethylenediaminetriacetate (HEDTA) was successfully demonstrated at The Geysers (1). Adding SO_2 to the cooling water prevented the formation of colloidal sulfur. This reaction probably is like that catalyzed by nickel, except that iron HEDTA is a weaker catalyst.

A contact condenser steam-strips oxygen from the cooling water, rendering it anoxic between condenser and cooling tower. Reaction with oxygen-containing polysulfido radical-ions destroys H_2S, and these radical-ions are regenerated in the cooling tower. Sulfur dioxide is produced by

burning the H_2S in the condenser vent-gas, and NaOH is added to maintain pH near 7. About 90 seconds reaction time is available, and the cooling water temperature is about 48°C. Using Eqn. (1), we estimate that under these conditions 10μM nickel (0.6 ppm) would destroy 98% of the H_2S in the cooling water.

In the absence of oxygen thiosulfate and trithionate probably are the major reaction products, and little sulfate is produced. This reduces the need for NaOH to control cooling water pH. During the tests with iron HEDTA, Geysers Unit 1 stabilized at pH 6.2 without addition of NaOH (1).

Acknowledgements

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Table 1

Proposed reaction mechanism

Initiation:

$$NiS_m + O_2 \longrightarrow NiS_mO_2 \qquad (1a)$$

$$NiS_mO_2 + 2\ H_2S \longleftrightarrow (H_2S)_2NiS_mO_2 \qquad (1b)$$

$$(H_2S)_2NiS_mO_2 \longrightarrow NiS_m + 2\ HS^{\cdot} + H_2O_2 \qquad (1c)$$

$$HS^{\cdot} + S_n^{=} \longrightarrow HS^{-} + S_n^{\cdot -} \qquad (1d)$$
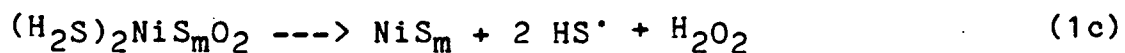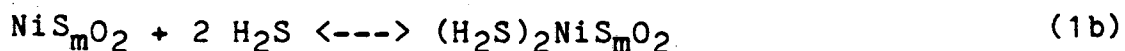
Growth of polysulfido chains:

$$S_n^{\cdot -} + O_2 \longrightarrow S_nO_2^{\cdot -} \qquad (2a)$$

$$S_nO_2^{\cdot -} + H_2S \longrightarrow S_{n+1}O^{\cdot -} + H_2O \qquad (2b)$$

$$S_{n+1}O^{\cdot -} + H_2S \longrightarrow S_{n+2}^{\cdot -} + H_2O \qquad (2c)$$

Termination:

$$R_1^{\cdot} + R_2^{\cdot} \longrightarrow R_1R_2 \qquad (3)$$
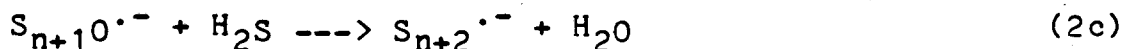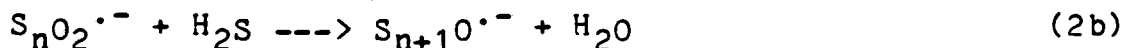
where $R_1^{\cdot}$ and $R_2^{\cdot}$ are any two radicals or radical ions.

Multiplication of polysulfido chains:

$$S_{n+m-1}^{=} + H_2S \longrightarrow S_n^{=} + S_m^{=} + 2H^{+} \qquad (4)$$
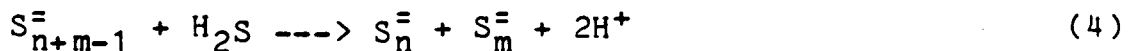
Formation of thiosulfate:

$$S_{n+1}O^{\cdot -} + O_2 \longrightarrow S_{n+1}O_3^{\cdot -} \qquad (5a)$$

$$S_{n+1}O_3^{\cdot -} + OH^{-} \longrightarrow S_{n-1}O^{\cdot -} + S_2O_3^{=} + H^{+} \qquad (5b)$$

Also:

$$S_{n+2}{}^{\cdot-} + SO_3^{=} \; \text{---}> S_{n+1}{}^{\cdot-} + S_2O_3^{=} \tag{6}$$

Formation of sulfate:

$$SO_3{}^{\cdot-} + O_2 \; \text{---}> SO_5{}^{\cdot-} \tag{7a}$$

$$SO_5{}^{\cdot-} + HSO_3^{-} \; \text{---}> SO_4{}^{\cdot-} + SO_4^{=} + H^+ \tag{7b}$$

$$SO_4{}^{\cdot-} + HSO_3^{-} \; \text{---}> SO_3{}^{\cdot-} + SO_4^{=} + H^+ \tag{7c}$$
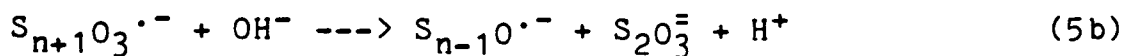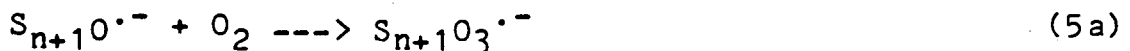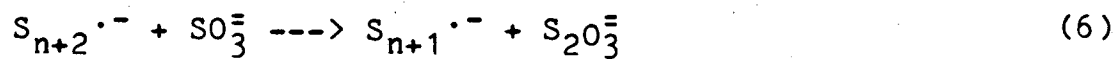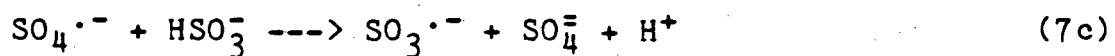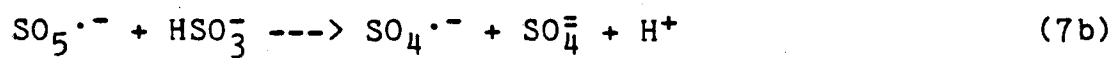
Formation of trithionate:

$$S_2O_3^{=} + 4 \; HSO_3^{-} + 2 \; H^+ \; \text{---}> 2 \; S_3O_6^{=} + 3 \; H_2O \tag{8}$$

Formation of colloidal sulfur:

$$S_{n+8}{}^{\cdot-} \; \text{---}> S_n{}^{\cdot-} + S_8 \tag{9}$$
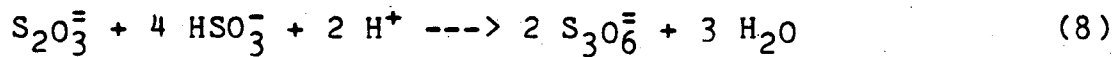
Figure captions

Fig. 1. Development of turbidity and reactivity. Sodium sulfite added from 20 minutes on; sulfite:sulfide = 0.75. Open triangles: Wackenroder's solution added at start, amounting to 400μM total nonsulfate sulfur; no sulfite added in this case. 70μM sulfide added in reactivity determinations. "Fraction H_2S remaining after 15s" is the fraction of that 70μM which remains after 15 seconds reaction time.

Fig. 2. Fraction of H_2S remaining after 15s vs. temperature. Twenty μM nickel, pH 7.9, sulfite:sulfide = 0.75. 70μM sulfide added in reactivity determinations. In Figs. 2 to 7 different symbols represent data from different experiments. The lines in these Figures were calculated using Eqn. (1) and E_a = 2.4 kcal/mole.

Fig. 3. Reactivity vs. pH. Twenty μM nickel, 62μM sulfide added in reactivity determinations.

Fig. 4. Reactivity vs. oxygen concentration.

Fig. 5. Fraction H_2S remaining after 15 seconds; 35°C and various concentrations of nickel. Vertical scale displaced between curves. "Initial sulfide" is the amount added in reactivity determinations.

Fig. 6. Effect of varying nickel concentration. SCW containing 100μM nickel diluted with varying amounts of nickel-free SCW.

Fig. 7. Effect of varying reaction time on residual H_2S.

Fig. 8. Distribution of reaction products; 20μM nickel, no sulfite, pH = 7.9.

Fig. 9. Distribution of reaction products; 100μM nickel, sulfite:sulfide = 0.75, pH = 7.8.

Fig. 10. Distribution of reaction products vs. sulfite:sulfide ratio; pH = 7.9, after 180 minutes reaction.

Fig. 11. Distribution of reaction products vs. pH; sulfite:sulfide = 0.75. Sloping dashed lines depict yield of sulfate and thiosulfate at the given pH, corrected for the contribution of the first hour of reaction at pH 7.8.
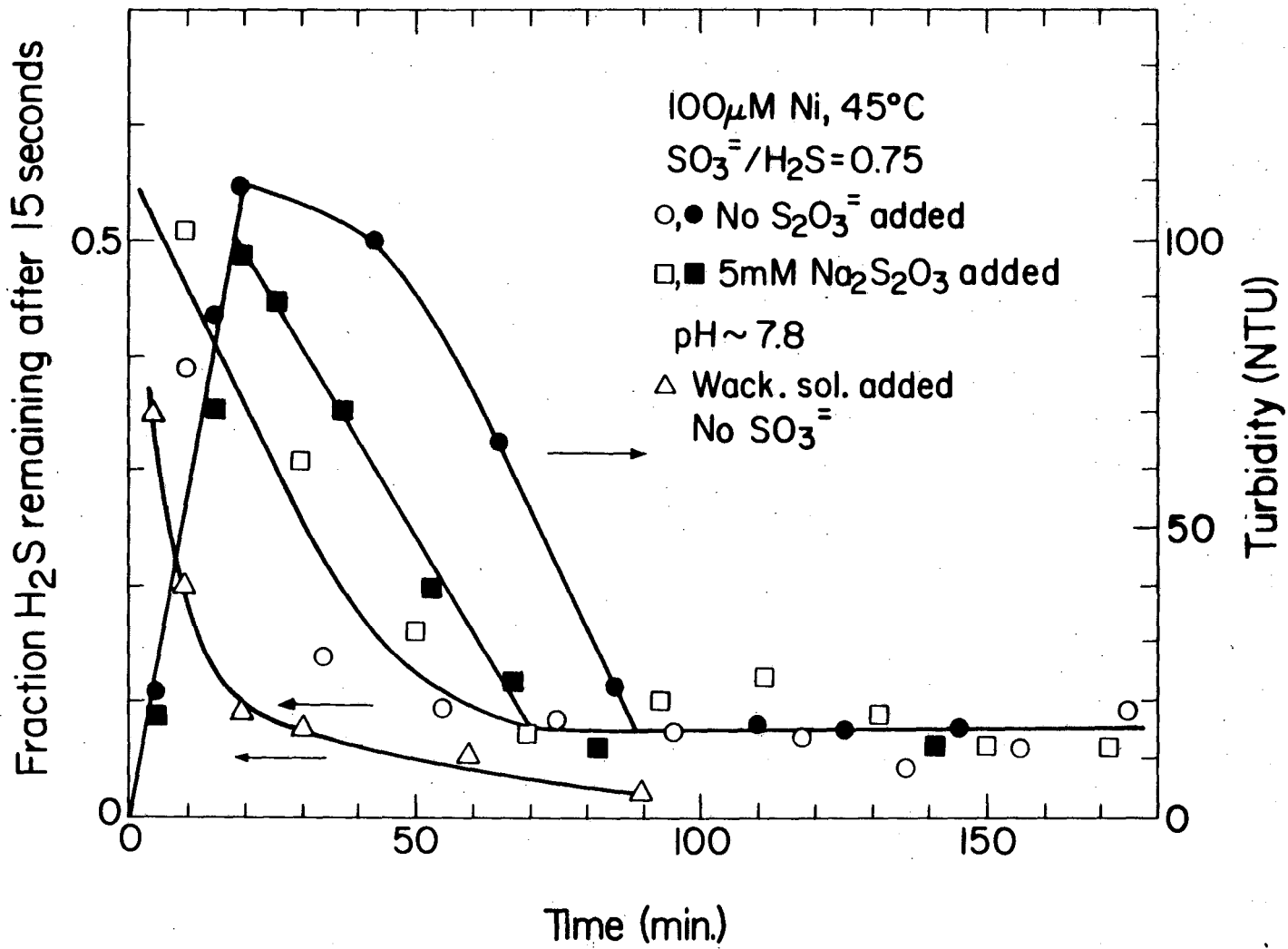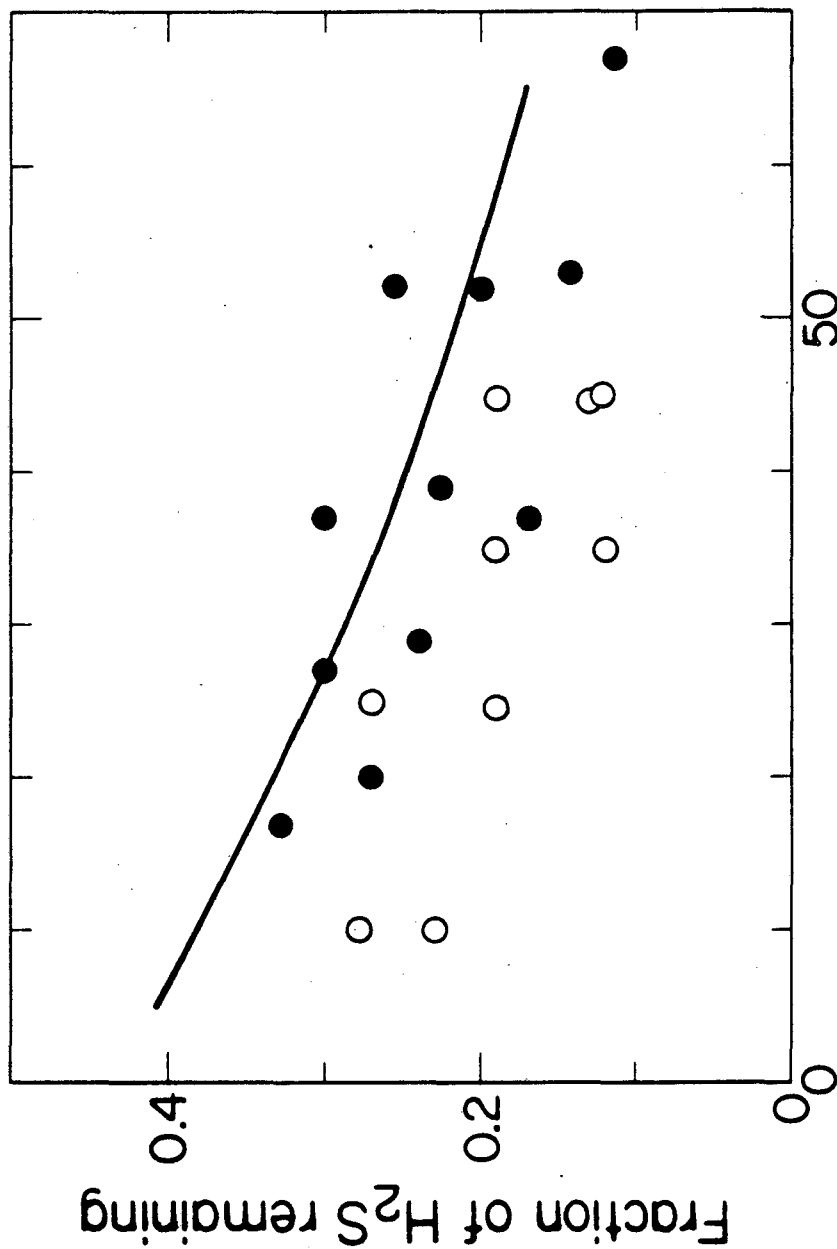
Fig. 1

RESIDUAL H$_2$S VS. TEMPERATURE

Fraction of H$_2$S remaining

Temperature (°C)

Fig. 2

XBL 825-645

RESIDUAL FRACTION VS. pH

XBL 825-659

Fig. 3

RESIDUAL FRACTION H_2S VS. (O_2)

$20\mu M$ Ni
$62\mu M$ Initial H_2S

Fraction H_2S remaining at 15s

Dissolved oxygen concentration (mg/kg)
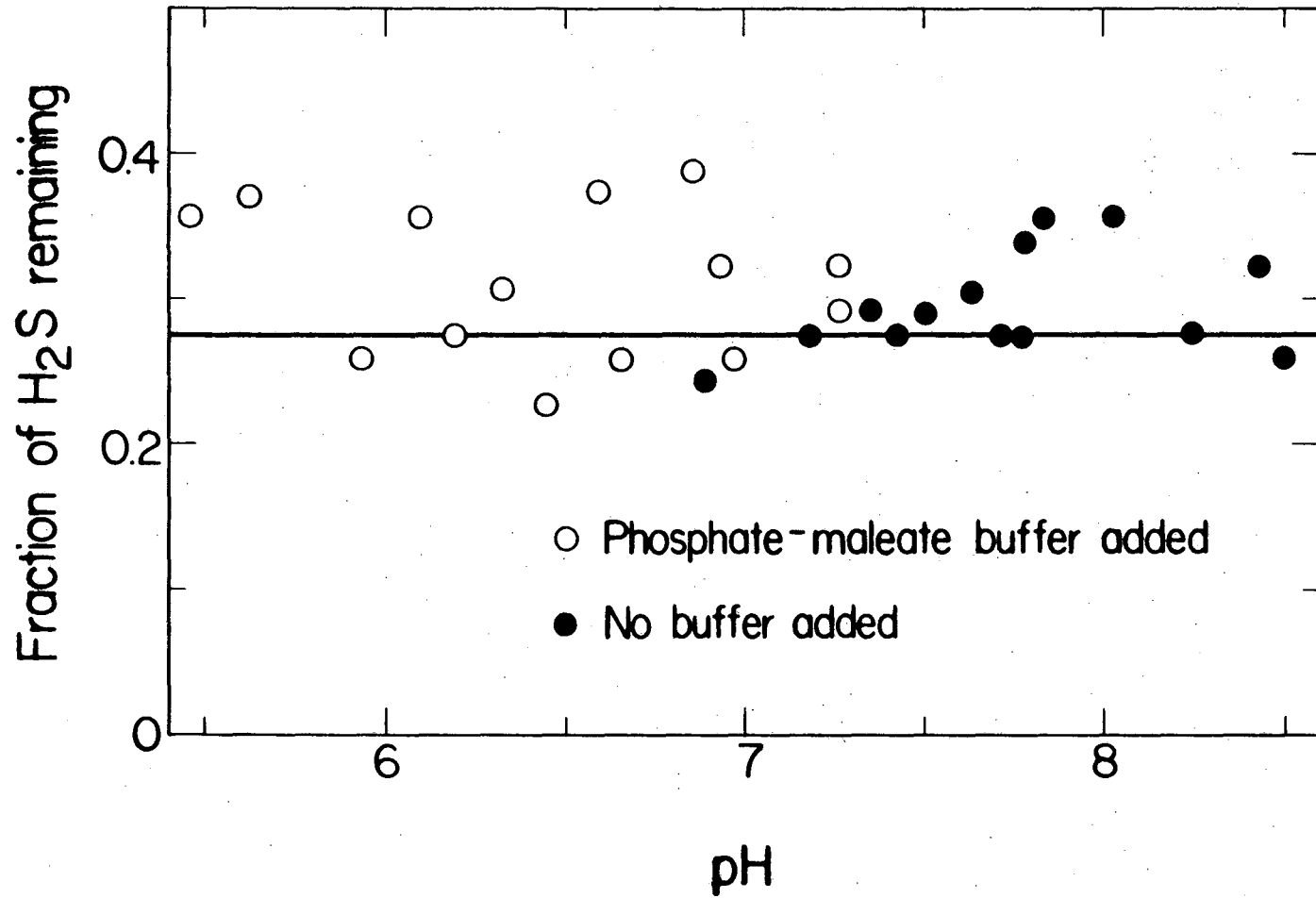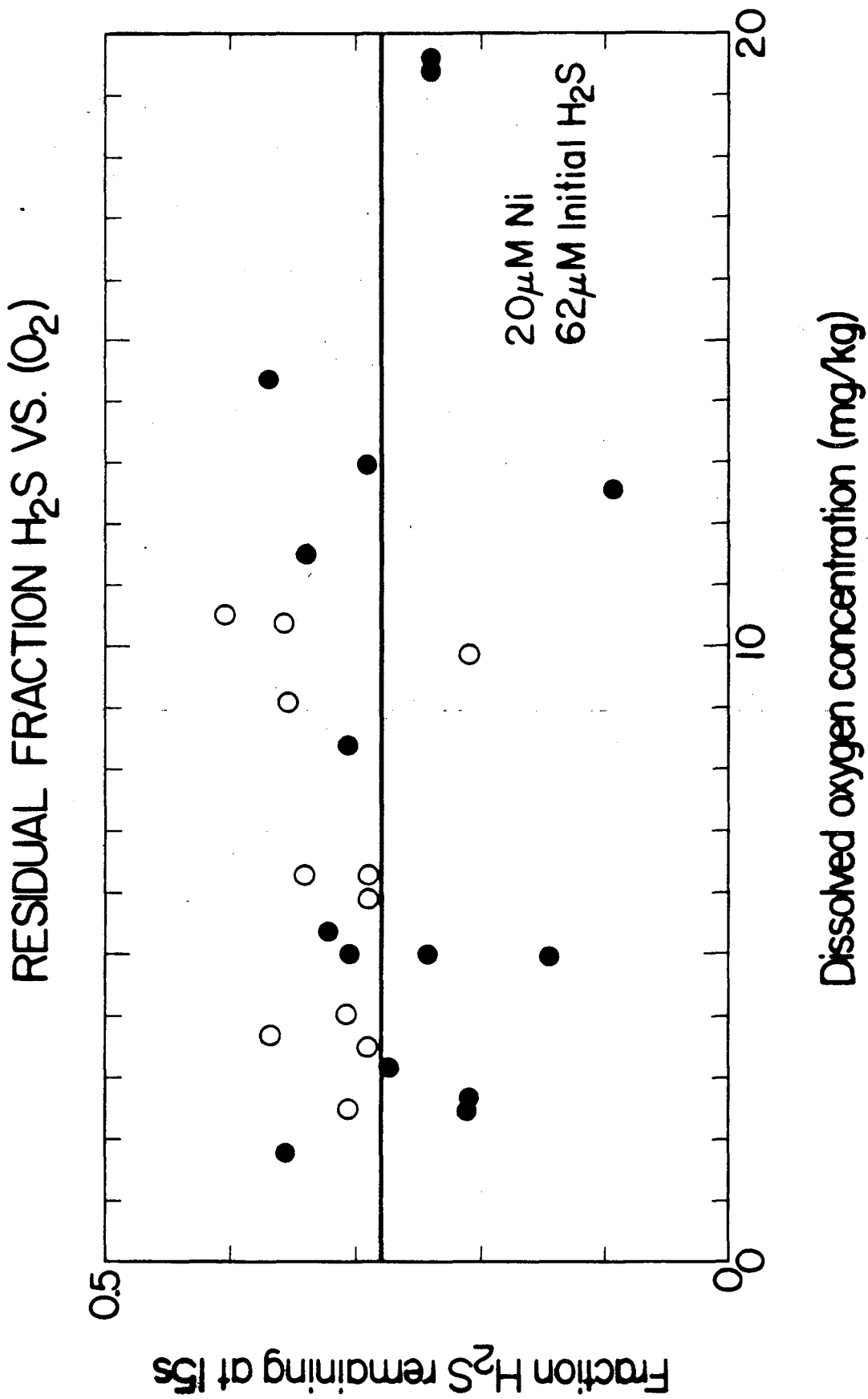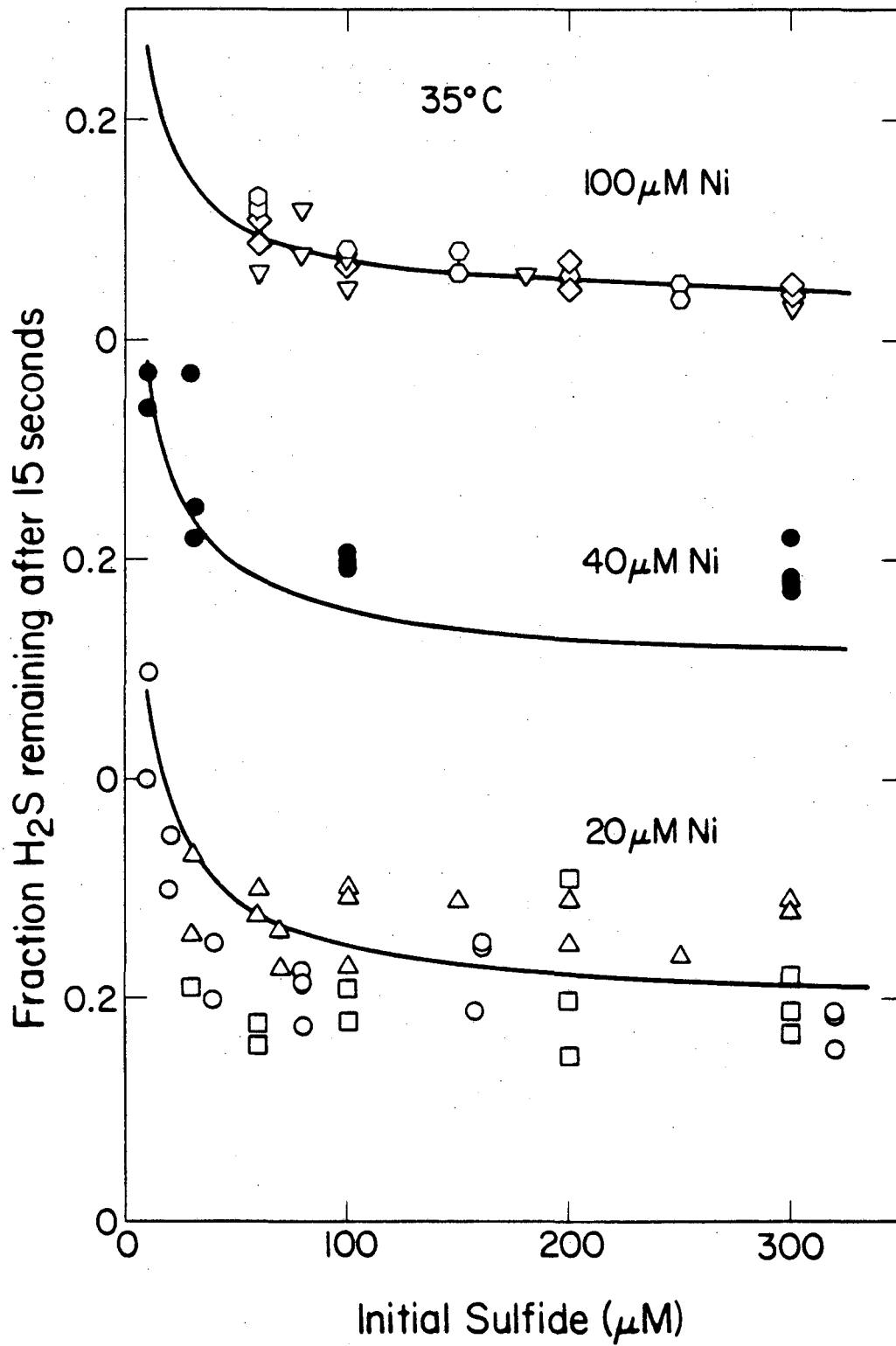
Fig. 4
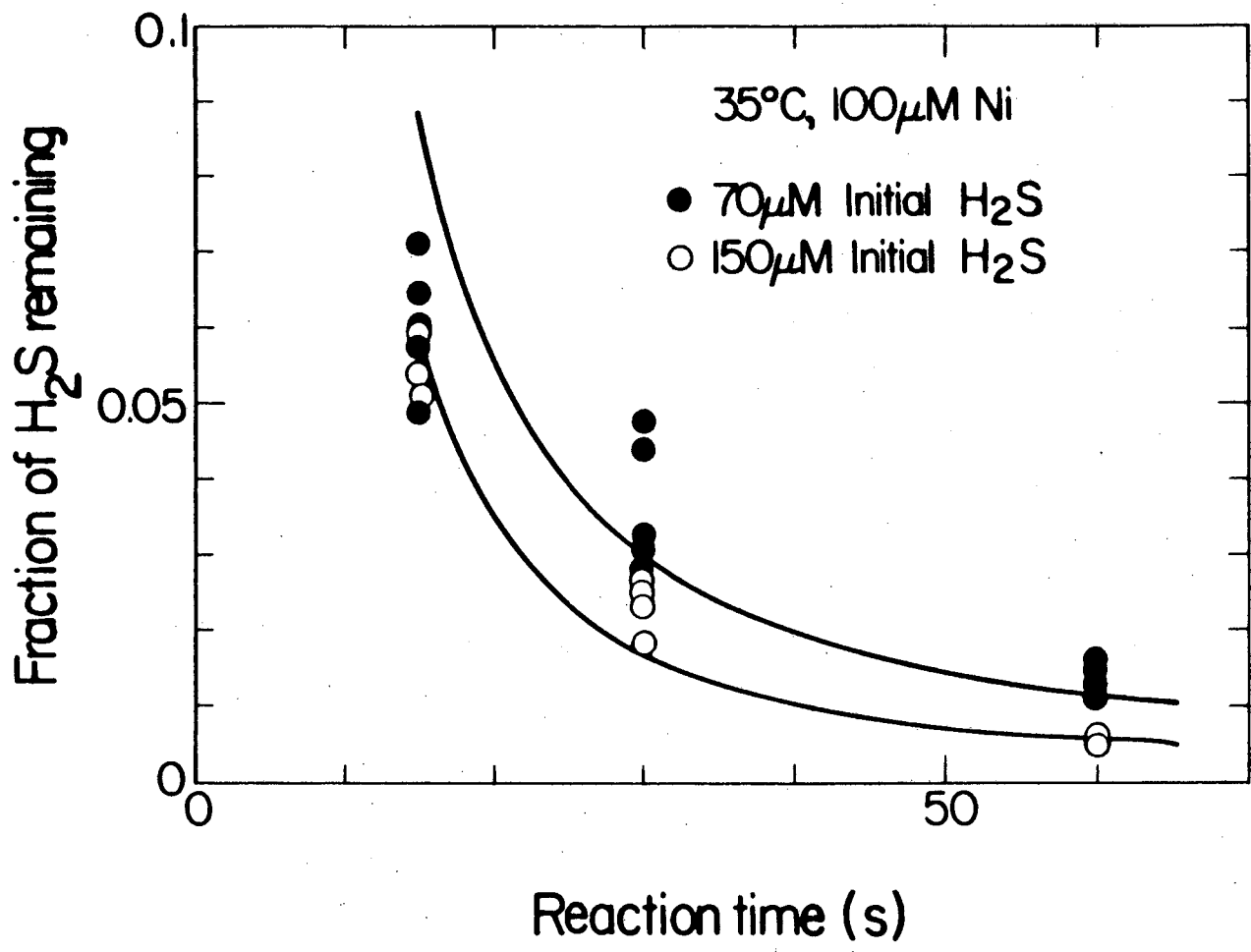
XBL 825-657

RESIDUAL VS. INITIAL H₂S

XBL 825-661

Fig. 5

Ni Varied by Dilution from $100\mu M$

35°C, t=15s

$62\mu M$ Initial H_2S

Fraction H_2S remaining

Nickel Conc. (μM)
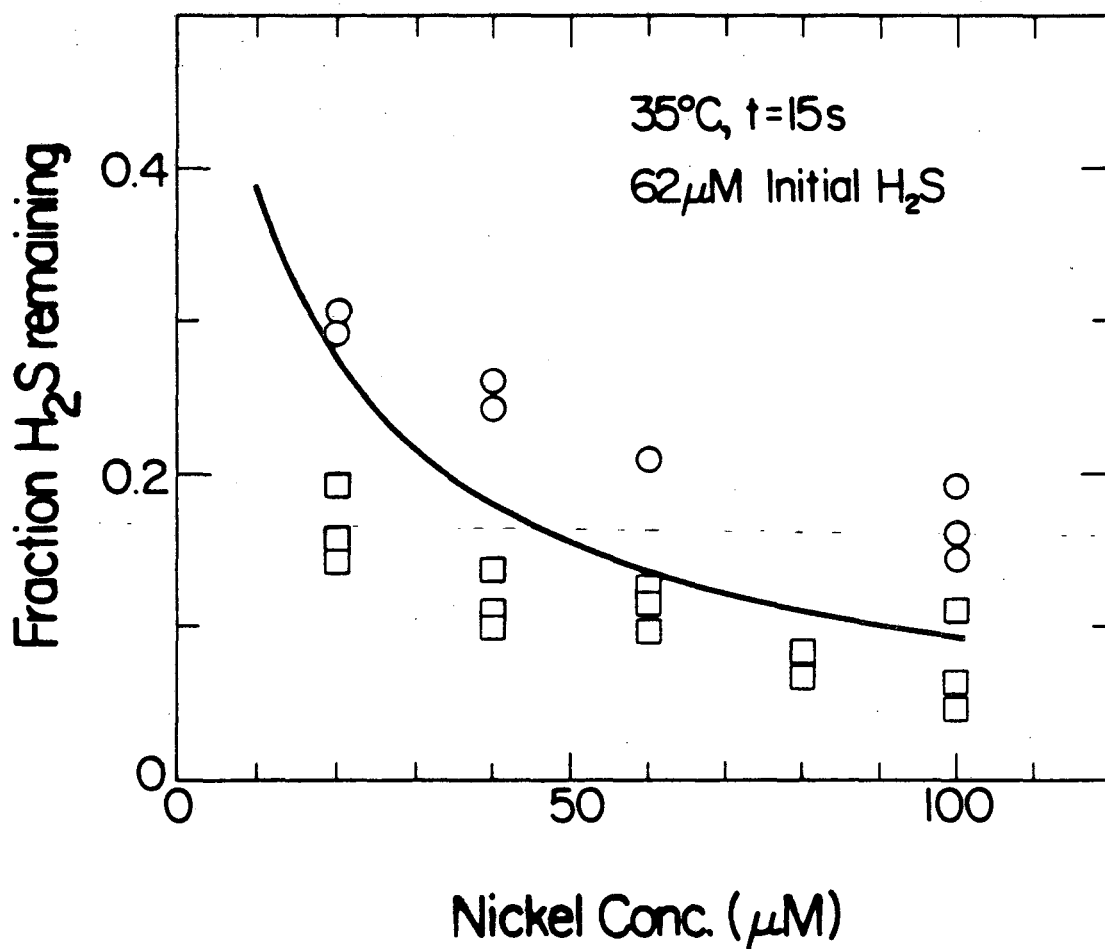
XBL 825-660

Fig. 6

RESIDUAL H₂S VS. REACTION TIME

Fig. 7

- 25 -

REACTION PRODUCT STOICHIOMETRY

45°C, 20μM Ni, pH 7.9

No Na_2SO_3

△ S(o)

○ 1/2 $S_2O_3^=$

□ 1/3 $S_3O_6^=$

◇ $SO_4^=$

⬡ ΣS

Input H_2S

Concentration as S (mM)

Time (min.)

100   200

Fig. 8

XBL 825-653

REACTION PRODUCTS

$45°C$, $100\,\mu M$ Ni, pH $= 7.8$

$Na_2SO_3/H_2S = 0.75$

△ $S^{(0)}$
○ $\frac{1}{2}S_2O_3^=$
□ $\frac{1}{3}S_3O_6^=$
◇ $SO_4^=$
○ ΣS

Input $H_2S + Na_2SO_3$

H_2S Input

Concentration as S (mM)

Time (min)
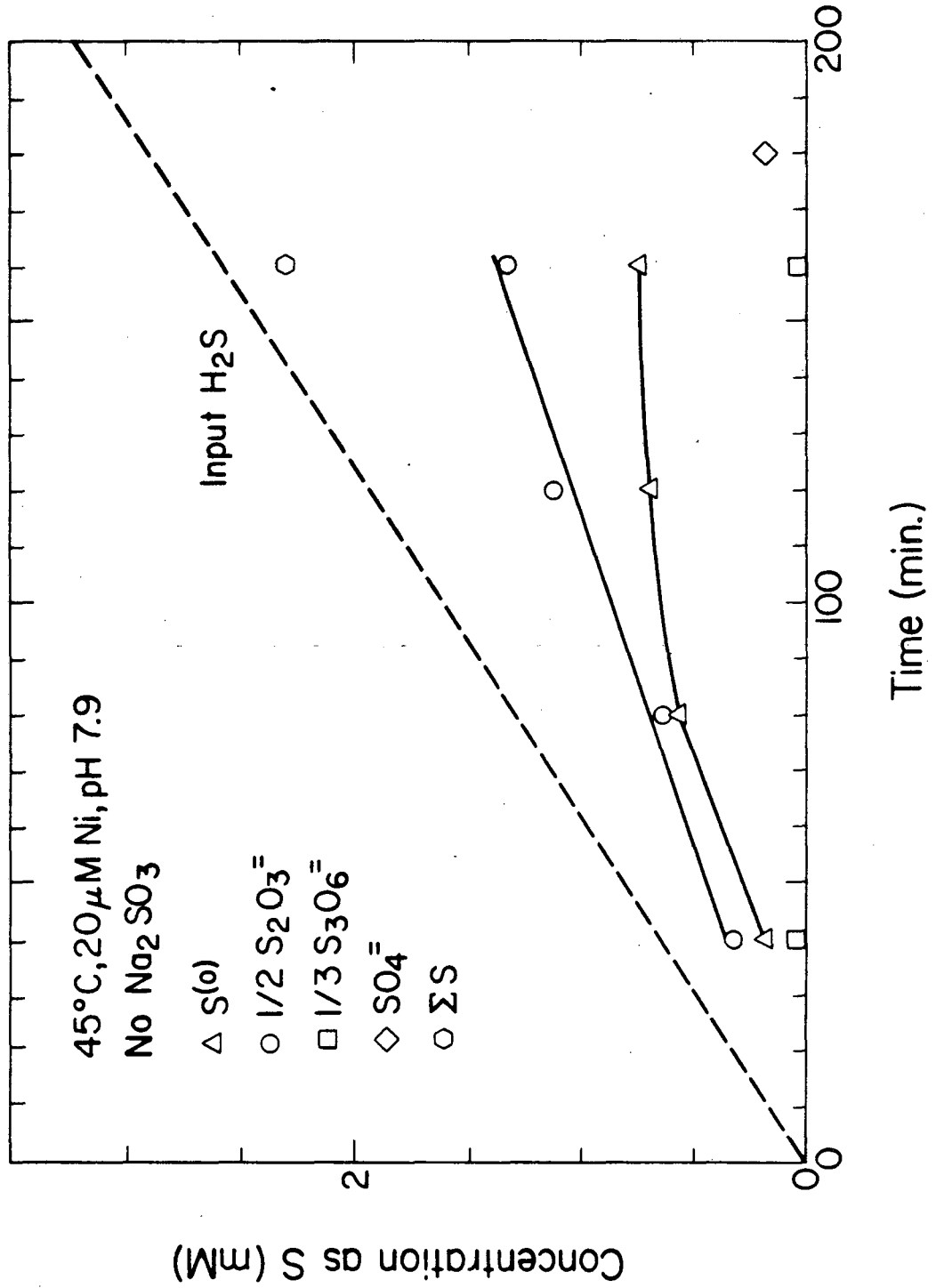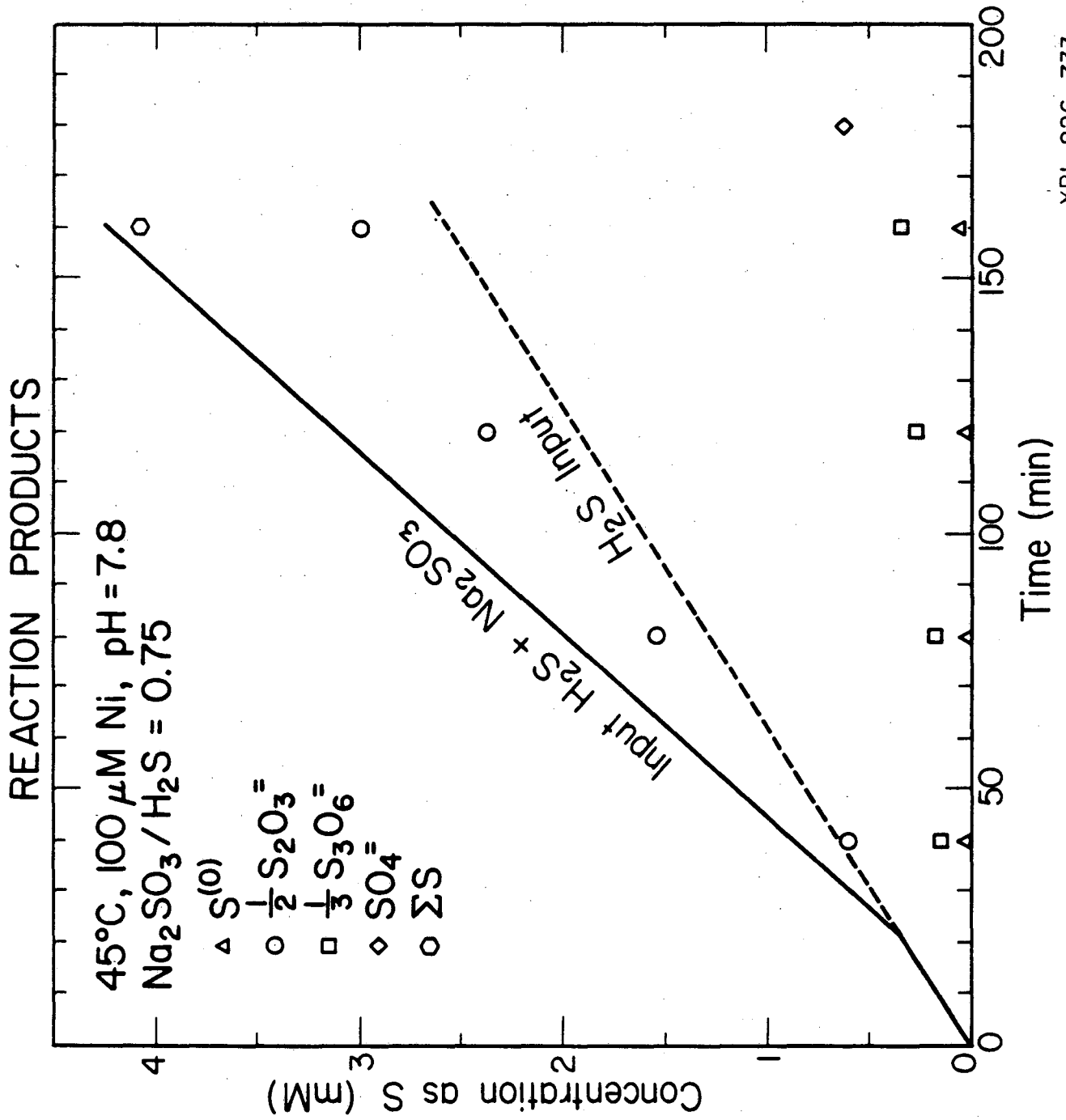
Fig. 9

XBL 826-733

PRODUCTS VS. MOLE RATIO

Fig. 10

XBL 825-652

REACTION PRODUCTS VS. pH

$45°C, 20\mu M$ Ni
$Na_2 SO_3/H_2S = 0.75, t = 180$ min.

Input $H_2S + Na_2SO_3$

$\circ \Sigma S$

Input H_2S

$1/2\ S_2O_3^{=}$

$SO_4^{=}$

$S^{(0)}$

$1/3\ S_3O_6^{=}$

Concentration as S (mM)

pH at t>60

XBL 825-651

Fig. 11