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PROJECT STATUS REPORT

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GRANT NUMBER AND TITLE

Biological Conversion of Synthesis Gas
U. S. Department of Energy No.: DE-FG21-90MC27225

GRANT PERIOD

September 4, 1990 - September 3, 1993

Task 1. Test Plan

Task has been completed.

Task 2. Culture Development

The anaerobic, photosynthetic bacterium *Rhodospirillum rubrum* has been chosen for catalysis of the biological water gas shift reaction. In addition, two other anaerobic, photosynthetic bacteria, *Chlorobium thiosulfatophilum* and *Chlorobium phaeobacteroides*, have been evaluated as candidates for H_2S conversion to elemental sulfur. Growth and H_2S uptake studies in the presence of basal medium indicated that *C. thiosulfatophilum* is a much superior organism. *C. phaeobacteroides* showed sporatic growth at best, with growth always slower than *C. thiosulfatophilum*. Also, when *C. phaeobacteroides* experienced slow growth, no H_2S consumption was observed. *C. thiosulfatophilum* always showed superior growth and H_2S uptake, and thus will be selected as the bacterium for H_2S conversion to elemental sulfur.

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Task 3. Mass Transfer/Kinetic Studies

The growth of cells on CO_2 and H_2S by *C. thiosulfatophilum* is evaluated, as well as the uptake of both H_2S and COS by the bacterium. COS is utilized indirectly by the bacterium after chemical reaction of COS with water to form CO_2 and H_2S. A rate expression for H_2S disappearance into butyl rubber stoppers has been developed, as well as the stoichiometry and rate expression for COS reaction with water.

INTRODUCTION

The anaerobic, photosynthetic bacterium *Chlorobium thiosulfatophilum* has been chosen from among several bacteria for its ability to convert H_2S to elemental sulfur. The bacterium utilizes CO_2 as its carbon source and operates at the mesophilic temperature of 37°C. The bacterium requires tungsten light for growth and compounds such as H_2S, elemental sulfur or H_2 as a source of reducing power. Of these latter three compounds, H_2S as sulfide is the preferred source of reducing power, with H_2 and elemental sulfur utilized only when sulfide has been depleted from the medium. The organism is also capable of indirectly utilizing COS, since COS reacts with water to form CO_2 and H_2S by the equation (Thompson *et al.*, 1935):

$$COS + H_2O \rightarrow CO_2 + H_2S \tag{1}$$

Thus, the H_2S formed by Equation (1) is utilized by *C. thiosulfatophilum* following the reaction of COS and water.

The purpose of this report is to present kinetic information on the rate of growth of *C. thiosulfatophilum*, as well as the rate of uptake of both H_2S

and COS. Information on process yields, stoichiometry and methods to compensate for H_2S loss to rubber septa in the batch reactors are presented and discussed.

GROWTH OF C. THIOSULFATOPHILUM IN THE PRESENCE OF H_2S

As was mentioned previously, *C. thiosulfatophilum* utilizes CO_2 as a carbon source, but also requires tungsten light and a source of reducing power such as H_2S, H_2 or elemental sulfur for growth. In the presence of H_2S, the sulfide is converted to elemental sulfur during growth.

To illustrate this interdependence of light, carbon source and reducing power a plot of the natural log of the ratio of the cell concentration compared to the initial cell concentration as a function of time is shown in Figure 1 for various initial H_2S levels. This plot should yield straight lines for each initial H_2S level, the slopes of these lines corresponding to the specific growth rate, μ, for each H_2S concentration. However, as is noted in Figure 1, essentially a single straight line is obtained for all of the H_2S levels. This result indicates that something other than H_2S is limiting the reaction. In this case, it is obvious that H_2S and CO_2 are present in excess and that the light intensity is limiting cell growth. It is thus expected that a Monod relationship for specific growth rate as a function of light intensity will be obtained.

The cell production by *C. thiosulfatophilum* as a function of the total sulfide concentration (H_2S (g), H_2S (l) and related species) is plotted in Figure 2 in order to determine the yield of cells from sulfide. As is noted, a single straight line is obtained for all of the initial H_2S levels, at least until H_2S is depleted from the system. When all of the H_2S is depleted from the medium, the culture continues to grow, utilizing elemental sulfur as the source of reducing power. This onset of elemental sulfur utilization is represented in Figure 2 by the vertical cell production data for each initial H_2S level.

As is noted in Figure 2, a cell yield on sulfide of 9.2 mg cells/mmol sulfide is obtained. This yield is greater than typical yields of cells from glucose by the yeast *Saccharomyces cerevisiae*, where a yield of 5.4-9.0 mgcells/mmol glucose is obtained.

A determination of Monod kinetics for H_2S uptake by *C. thiosulfatophilum* was not possible due to difficulties in following the various sulfur species and the problem associated with sulfur disappearance into the rubber septa sealing the batch reactors.

LOSS OF H_2S INTO RUBBER SEPTA

Previous studies with H_2S uptake by various species of chlorobia have generated data which are difficult to quantify and model since H_2S is known to diffuse through the rubber septa sealing the batch reactors. Although H_2S disappearance into butyl rubber is relatively small in comparison to H_2S uptake by the bacteria, it would be helpful if the average amount of H_2S leaving the batch system through the stopper could be quantified.

If a first order rate of disappearance of H_2S (both gas and liquid species) is assumed, the following equation may be written:

$$-\frac{d(\text{sum } H_2S)}{dt} = k\ P^{G}_{H_2S} \tag{2}$$

In Equation (2), $-\frac{d(\text{sum } H_2S)}{dt}$ represents the rate of disappearance of all sulfur species into the butyl rubber stoppers, $P^{G}_{H_2S}$ represents the gas phase partial pressure of H_2S and k represents the first order rate constant.

Equation (2) may be integrated to yield:

$$- \Delta \text{ (sum } \Delta \text{ } H_2S) = k \int_o^t P_{H_2S}^{G} \, dt \qquad (3)$$

Thus a plot of - Δ (sum Δ H_2S) as a function of $\int_o^t P_{H_2S}^{G}$ should yield a straight line with a slope k if the disappearance can indeed be represented by a first order relationship.

Figure 3 shows such a plot for two initial H_2S levels in water (no culture), housed in serum stoppered batch reactors. As is noted, a reasonable straight line can be fitted through the data. The slope of this line, k, is 0.0470 mmol/atm•h. This relationship can now be used to correct experimental data for H_2S disappearance through the butyl rubber stoppers.

INDIRECT COS UPTAKE BY C. THIOSULFATOPHILUM

As was mentioned previously, COS undergoes a chemical reaction with water to produce H_2S and CO_2 by the equation:

$$COS + H_2O \rightarrow CO_2 + H_2S \qquad (1)$$

Thompson *et al.* (1935) studied the reaction and showed that the kinetics of the reaction could be described by a first order irreversible rate expression over a temperature range of 15-40°C. They showed that the rate constant varied with temperature by the equation:

$$k = 1.06 \times 10^{12} \, e^{-22710/RT} \qquad (4)$$

where k is the first order rate constant, sec^{-1};

R is the ideal gas constant, 1.987 cal/gmole°C; and

T is the absolute temperature, °K.

At 37°C, the rate constant is thus calculated as 0.37 h^{-1}.

C. thiosulfatophilum can utilize COS indirectly, by utilizing the H_2S produced by the chemical reaction in Equation (1). If this is a satisfactory process, it will eliminate the need for an additional organism (such as *Rhodospirillum rubrum* or *Peptostreptococcus productus*) for COS degradation.

Figures 4-9 show cell growth, gas phase COS uptake and gas phase production and uptake profiles for indirect COS utilization by *C. thiosulfatophilum*. Two experiments were performed: one with 0.2, 0.9 and 0.6 mmol of COS initially; and one with 0.3, 0.5 and 0.8 mmol of COS initially.

In examining the cell concentration profiles of Figures 4 and 5, it is seen that typical cell concentration profiles are obtained even though COS is utilized by an indirect route. It also appears that the lag phase is slightly larger for the highest initial COS levels.

Figures 6 and 7 present gas phase COS concentration profiles for the two experiments. Also shown in each figure are the results of an experiment using the highest COS level (0.6 mmol and 0.8 mmol, respectively) and no culture. As is noted in the two figures, the rate of disappearance of COS from the batch reactors, as determined from the slopes of the COS concentration profiles, is identical with and without culture regardless of the initial COS level. This result indicates that the rate limiting step in COS uptake is the reaction of COS with water by Equation (1). Thus, the actual uptake of COS does not depend upon the initial concentration of COS, at least until the initial COS level reaches very high inhibitory levels.

Figures 8 and 9 show gas phase H_2S production (by the chemical reaction) and uptake profiles for the two experiments for *C. thiosulfatophilum*. As in

Figures 6 and 7, profiles without culture are also shown at the highest initial COS levels. As is noted in Figures 8 and 9, the profiles without culture showed the gradual accumulation of H_2S with time. The production of H_2S by Equation (1) is indeed a relatively slow reaction. As is noted in the experimental runs with culture, the H_2S produced by the chemical reaction was not immediately consumed by the culture. Consumption did not occur due to the low initial cell density. It should be remembered that H_2S is required for growth. There was no evidence that COS could be directly utilized by *C. thiosulfatophilum*. There is also some evidence to suggest that COS may even be inhibitory to the growth of the bacterium and its ability to utilize COS.

Figure 10 shows a plot of the increased total sulfur (COS (g), H_2S (g), total sulfide species) profiles for the data without culture in Figures 6-9. It is assumed in this plot that all COS in the liquid phase had been converted to H_2S. As is noted in the figure, one experiment showed essentially constant total sulfur, while the other experiment showed that the total sulfur content decreased slightly with time.

Figure 11 shows the same profile as in Figure 10 now corrected for H_2S disappearance into the stopper by the results of Figure 3. As is noted in Figure 11, now one set of data shows increasing total sulfur with time, while the other data set shows essentially constant total sulfur with time. Obviously, sulfur is not always lost to the stoppers, thus complicating the correction for H_2S disappearance.

Figure 12 utilizes the same data to determine the actual experimental stoichiometry of Equation (1). According to Equation (1), a slope of 1.0 should result when H_2S production (corrected for disappearance into the stoppers) is plotted against COS consumption. As is noted in Figure 12, a slope of 0.94 mol/mol is attained, thereby verifying the stiochiometry of Equation (1).

The kinetics of the chemical reaction in Equation (1) may also be determined from the data of Figures 6-9. The rate of disappearance of COS from the gas and liquid phases may be written as:

$$-\frac{d}{dt}\left(n^{G}_{COS} + n^{L}_{COS}\right) = k_t \cdot C^{L}_{COS} \cdot V_L = k_t \cdot \frac{P_{COS}}{H} \cdot V_L \tag{5}$$

Assuming that $k_t << K_L a$, $P^{L}_{COS} = P^{G}_{COS}$ at equilibrium

Therefore,

$$-\frac{d}{dt}\left(\frac{P^{G}_{COS} \cdot V_G}{RT} + \frac{P^{G}_{COS} \cdot V_L}{H}\right) = k_t \frac{P^{G}_{COS}}{H} \cdot V_L \tag{6}$$

Thus, a plot of $-\left(\frac{1}{V_L}\right)\frac{d}{dt}\left[P^{G}_{COS}\left(\left(\frac{H}{RT}\right)V_G + V_L\right)\right]$ as a function of P^{G}_{COS} should yield a straight line of slope k_t. In this plot,

$$\frac{H}{RT} = \frac{55.10}{0.08206 \cdot (273.15 + 30)} = 2.215 \text{ (dimensionless)}$$

Such a plot is shown in Figure 13. As is noted, a rate constant of 0.243 h^{-1} is attained, which compares well with the values of 0.144 h^{-1} at 30°C or 0.339 h^{-1} at 37°C obtained by Thompson *et al*. (1935). Smith (1990) obtained a value of 0.25 h^{-1} under the exact same experimental conditions as the experiment in Figure 13.

Task 4. Bioreactor Studies

Experiments are underway in continuous stirred tank and trickle bed reactors using *R. rubrum* for water gas shift biocatalysis. Experiments are in the planning stages utilizing *C. thiosulfatophilum* for H_2S/COS removal and conversion to elemental sulfur.

Task 5. Limiting Conditions/Scale-up

Experiments are being planned to measure the effects of physical properties (viscosity, density, surface tension, etc.) of the fermentation medium on the measurement of the mass transfer coefficient. Correlations from the literature will be modified as needed in calculating the mass transfer coefficient in continuous systems.

Task 6. Economic Evaluations

No work was scheduled on this task during the reporting period.

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LITERATURE CITED

1. Thompson, H. W., C. F. Kearton and S. A. Lamb, "The Kinetics of the Reaction Between Carbonyl Sulphide and Water," *J. Chemical Society*, Part II, 1935.

2. Smith, K. D., "The Biological Removal of Carbonyl Sulfide from Coal Derived Synthesis Gas Streams," M.S. Thesis, University of Arkansas, 1990.

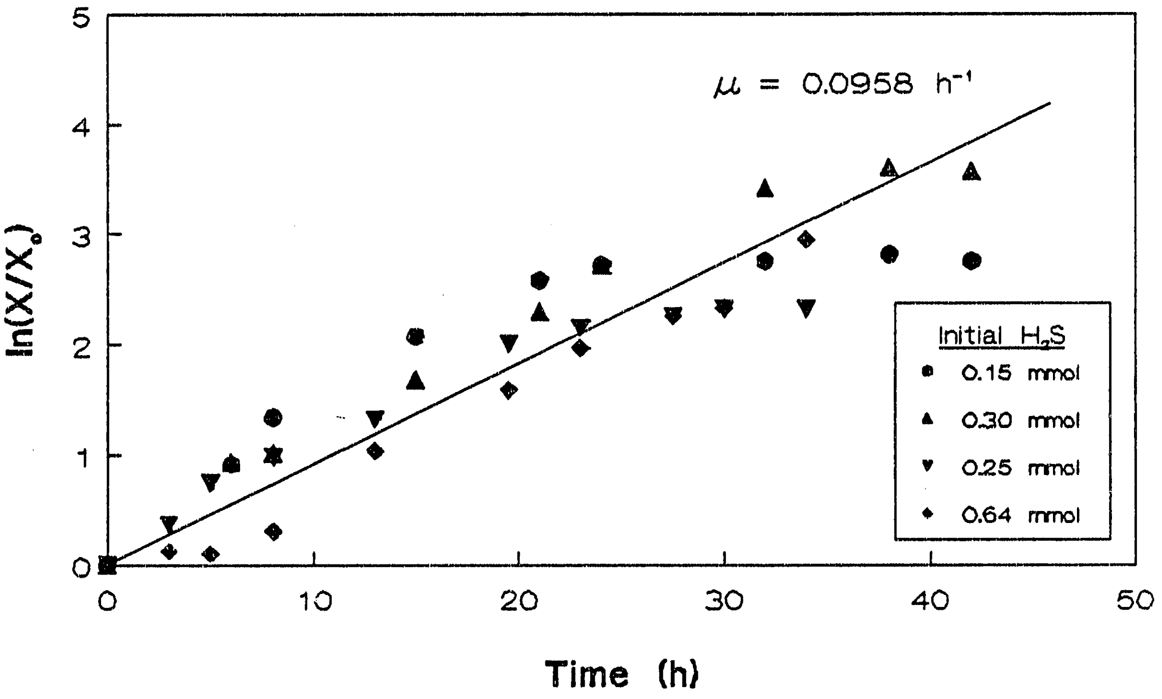

Figure 1. Determination of the Specific Growth Rate of *C. thiosulfatophilum* at Various Initial H_2S Levels.

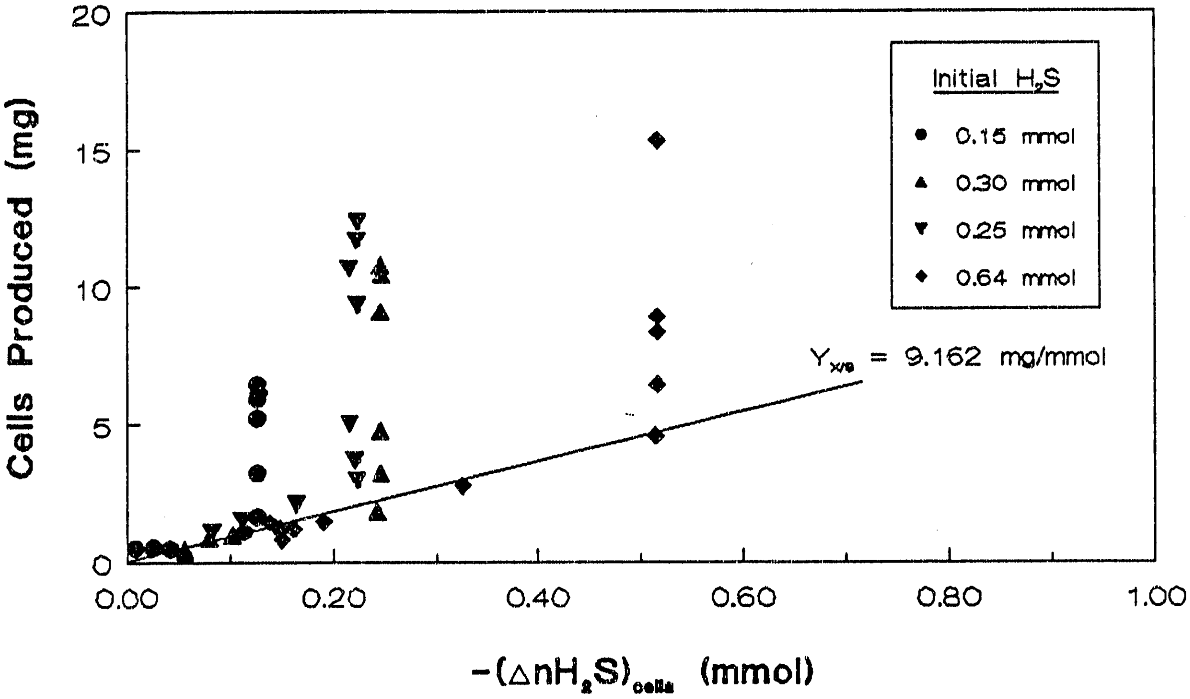

Figure 2. Cell Production by *C. thiosulfatophilum* as a Function of Sulfide Consumption.

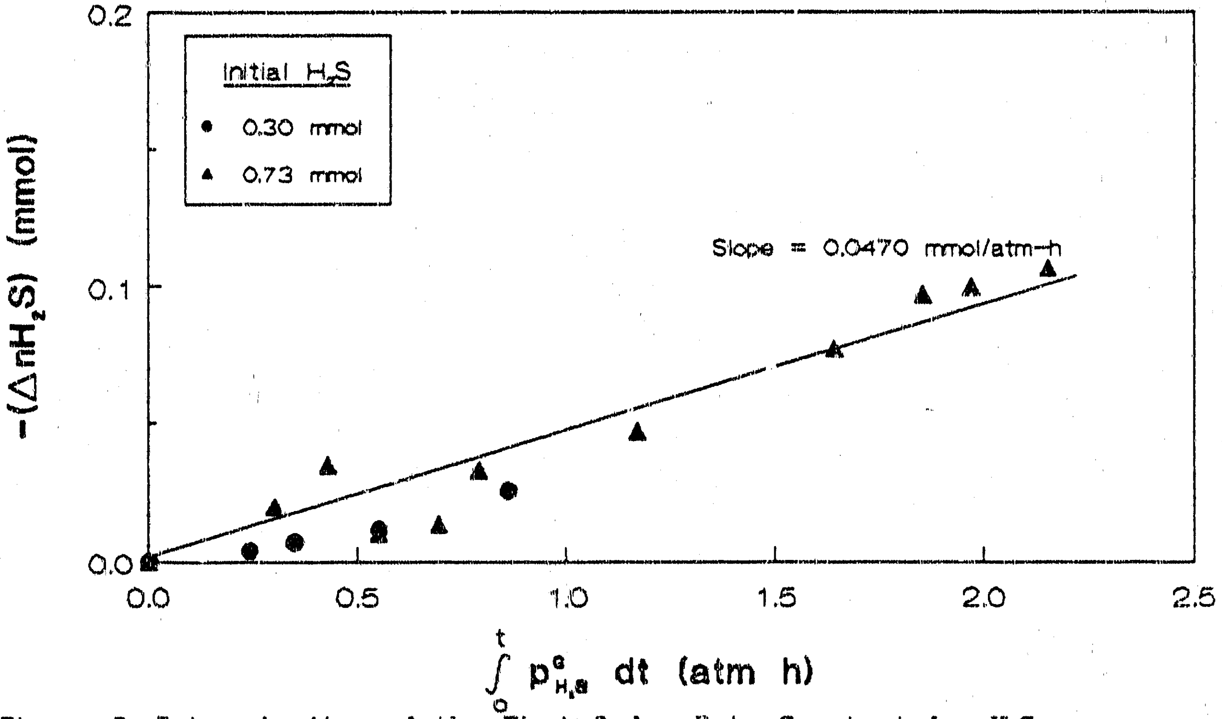

Figure 3. Determination of the First Order Rate Constant for H_2S Disappearance into Butyl Rubber Septa.

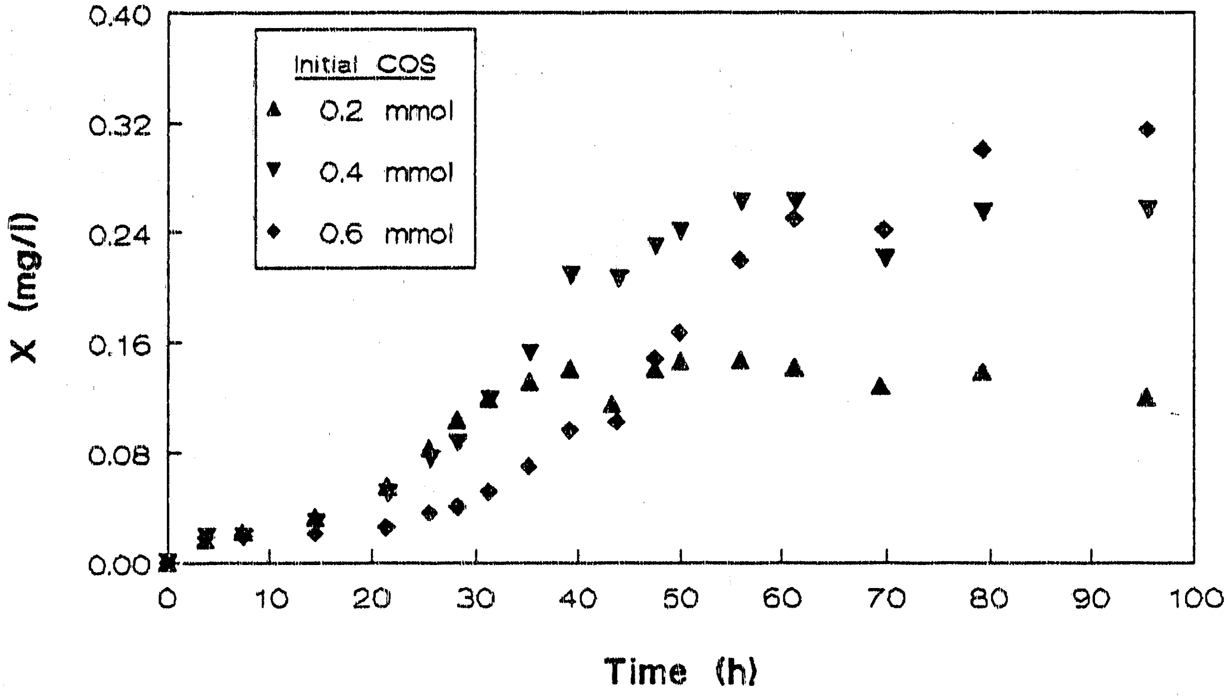

Figure 4. Cell Concentration Profiles for the Indirect Uptake of COS by *C. thiosulfatophilum* (Experiment 1).

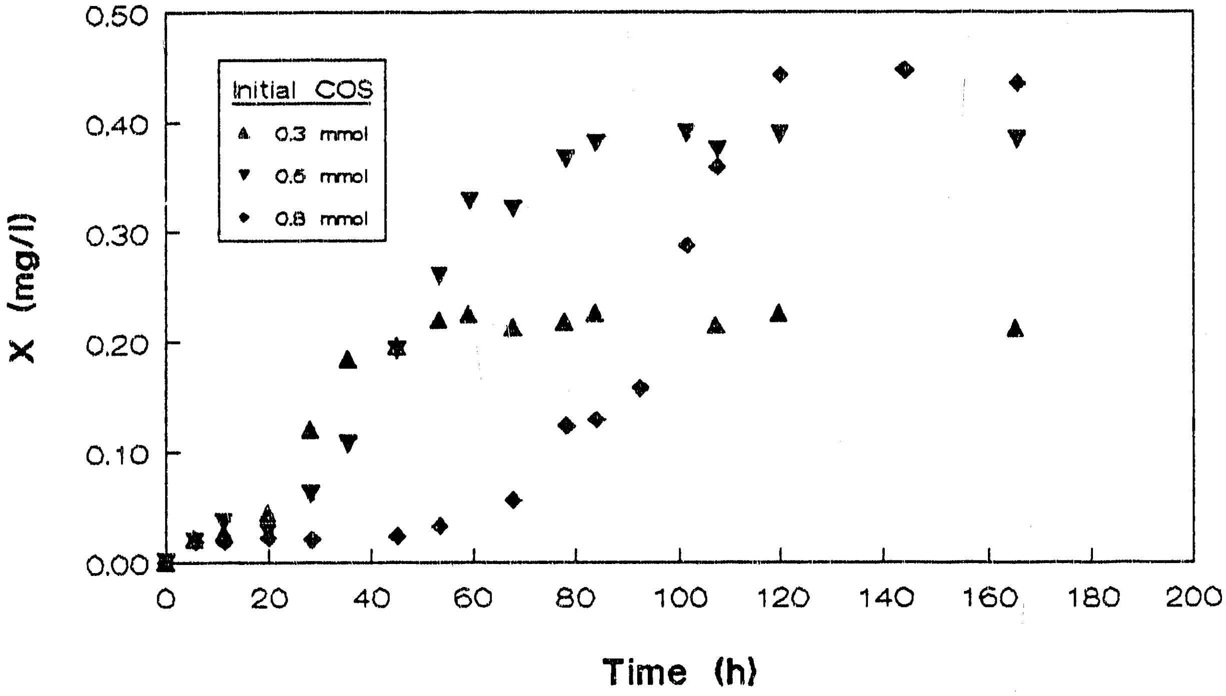

Figure 5. Cell Concentration Profiles for the Indirect Uptake of COS by *C. thiosulfatophilum* (Experiment 2).

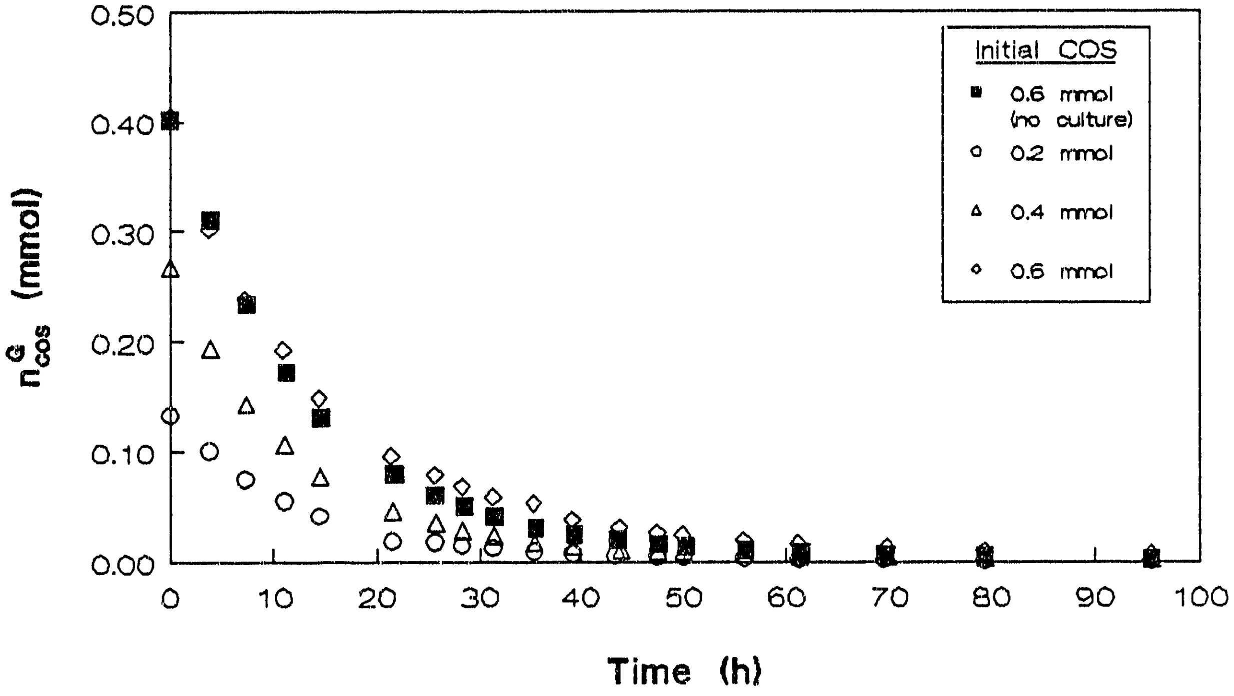

Figure 6. Gas Phase COS Uptake Profile for *C. thiosulfatophilum* (Experiment 1).

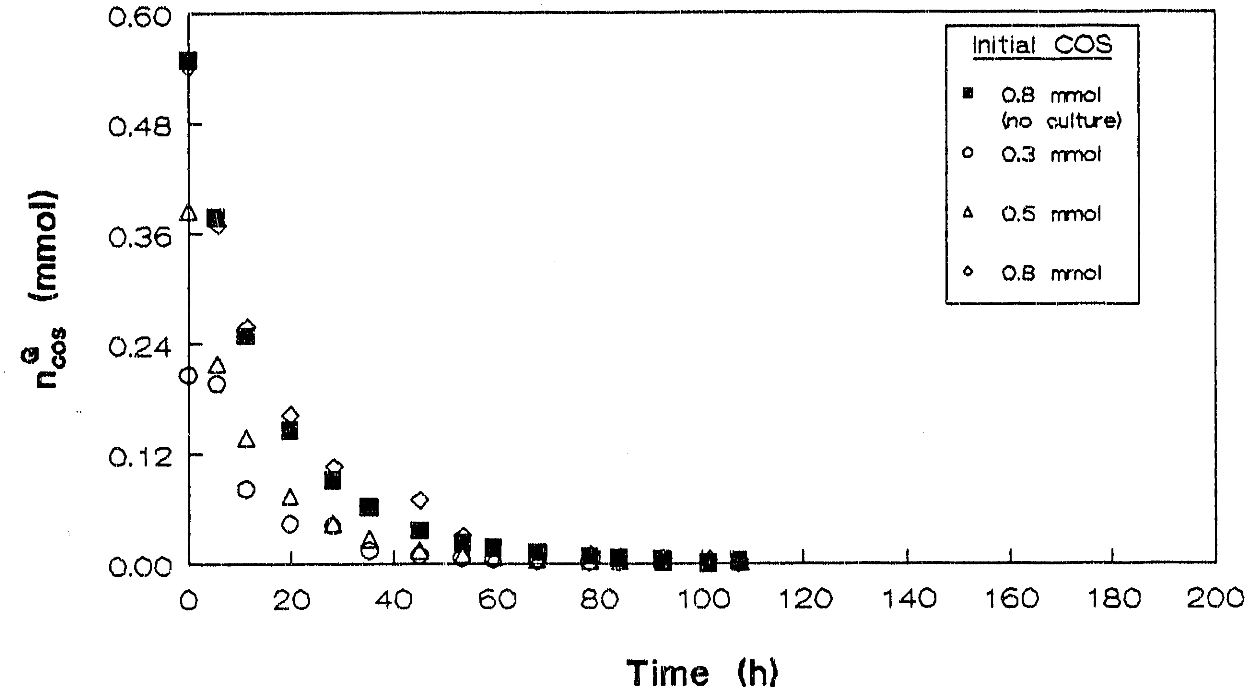

Figure 7. Gas Phase COS Uptake Profile for *C. thiosulfatophilum* (Experiment 2).

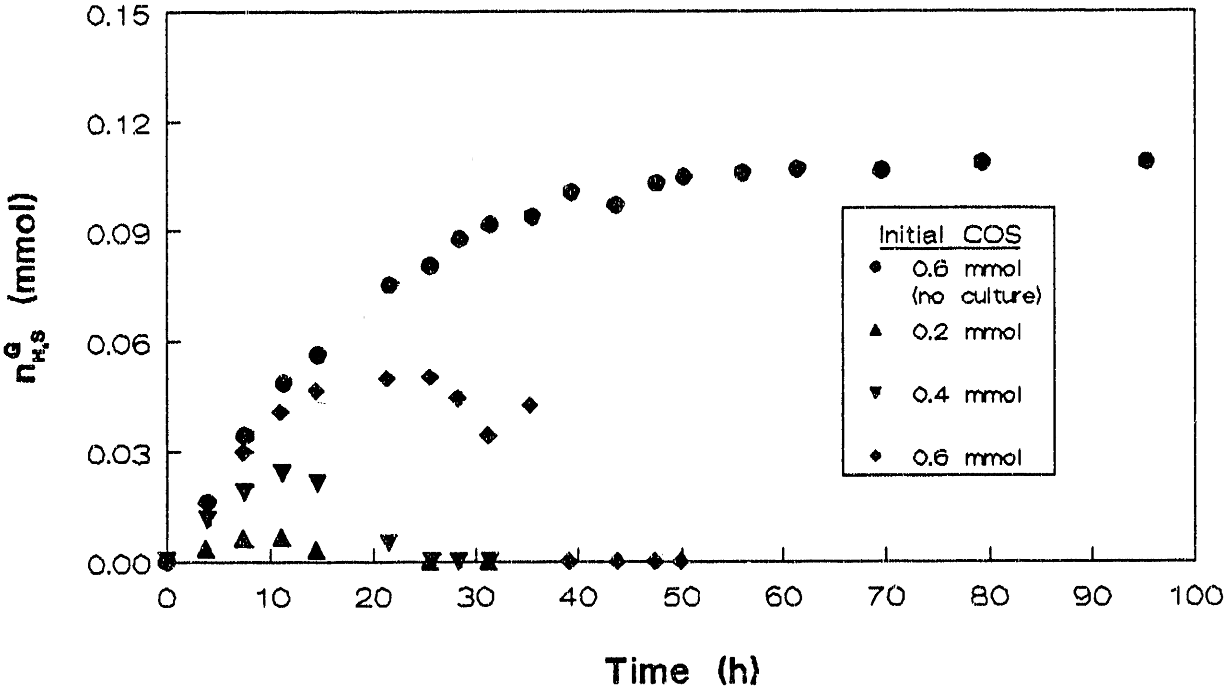

Figure 8. Gas Phase H_2S Production (from COS) and Uptake Profile by *C. thiosulfatophilum* (Experiment 1).

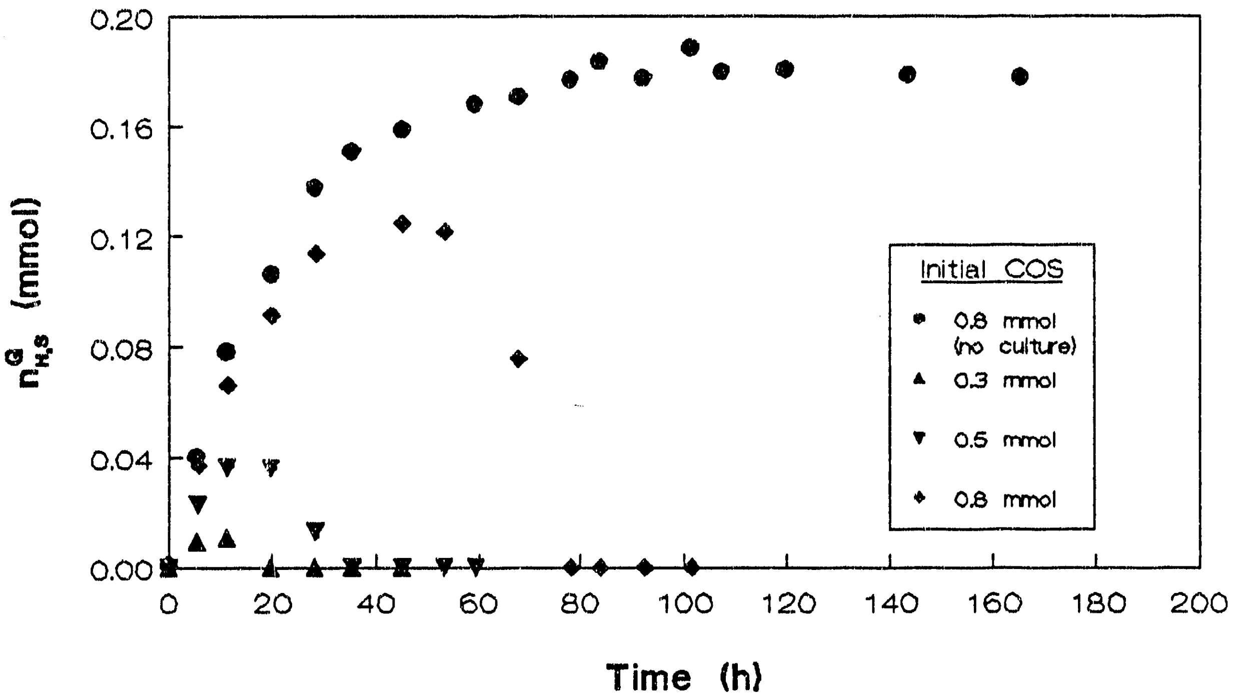

Figure 9. Gas Phase H_2S Production (from COS) and Uptake Profile by *C. thiosulfatophilum* (Experiment 2).

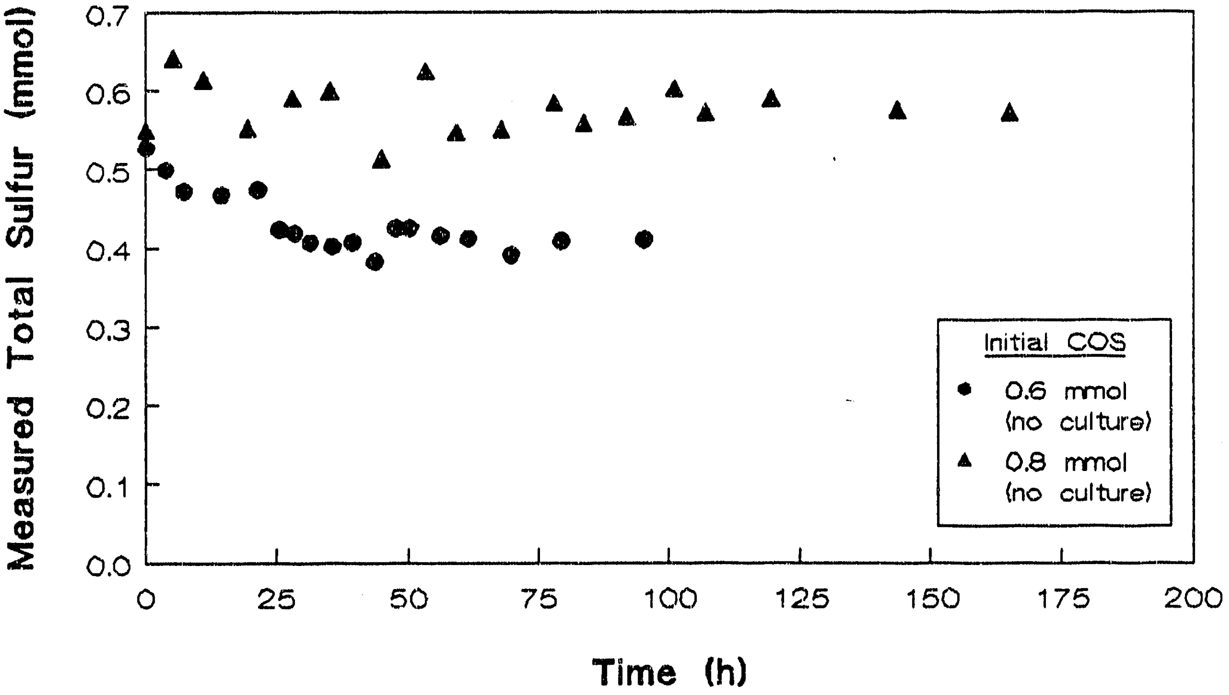

Figure 10. Measured Total Sulfur Profile without Culture for COS Conversion to H_2S.

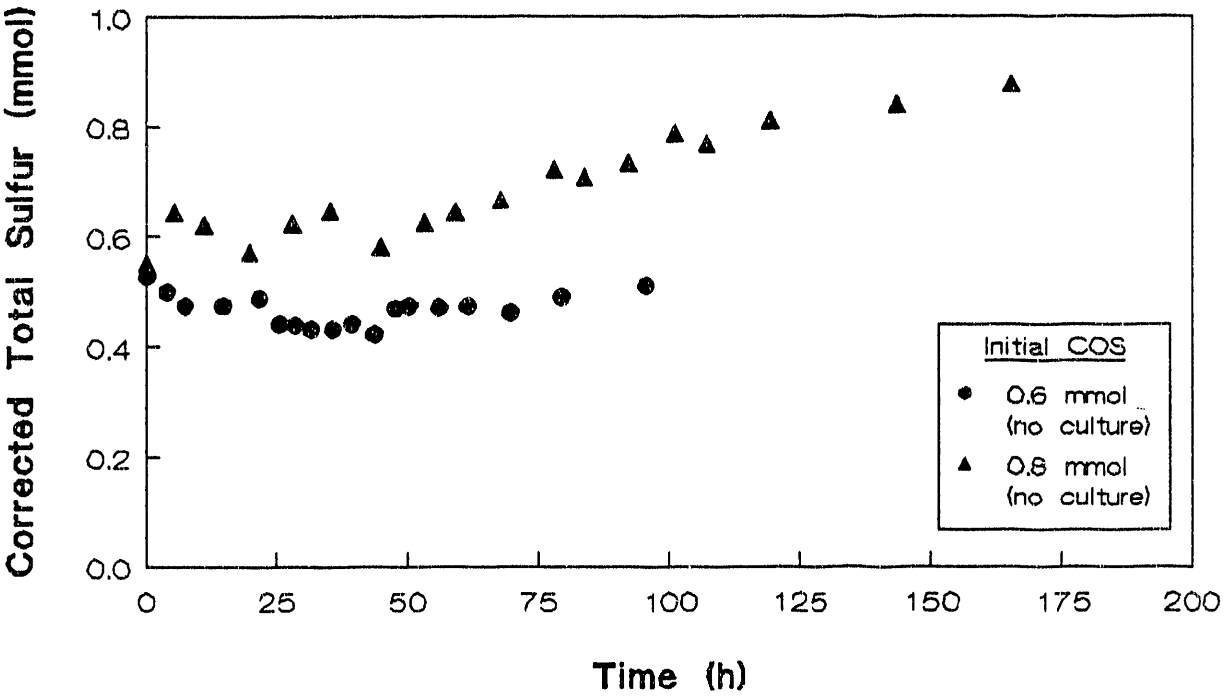

Figure 11. Measured Total Sulfur Profile without Culture for COS Conversion to H_2S (Corrected for H_2S Disappearance into Rubber Stopper).

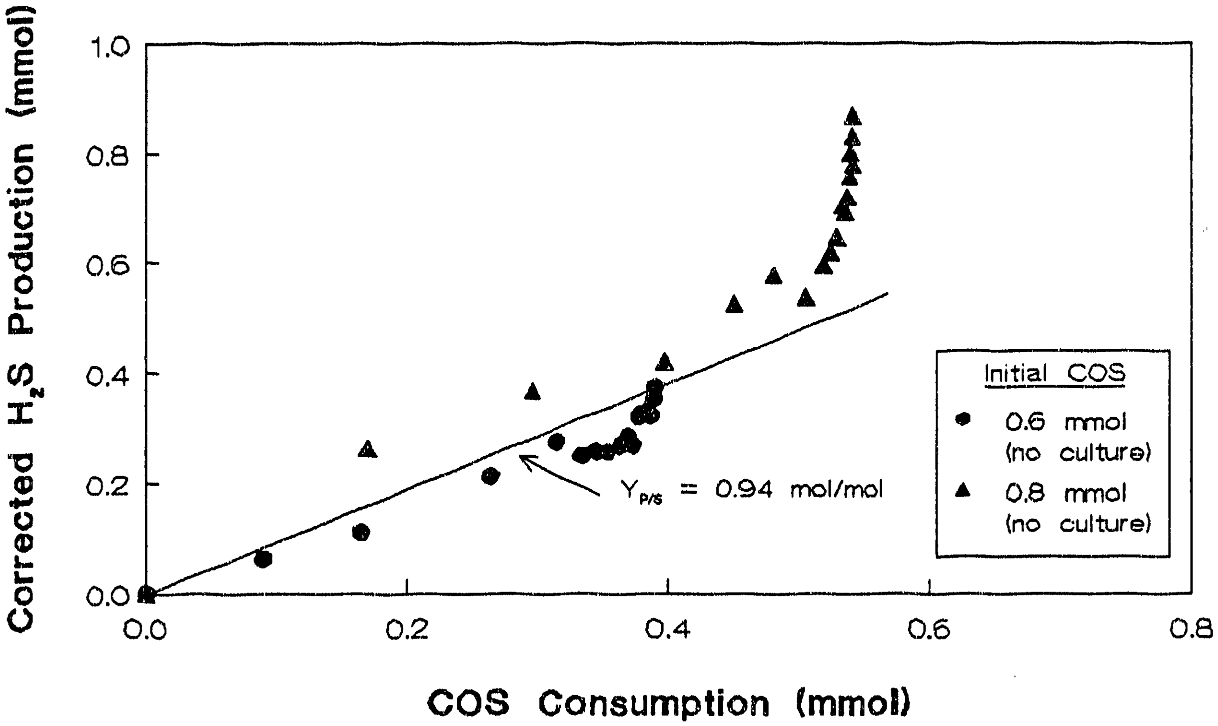

Figure 12. Determination of Stoichiometry for Equation (1).

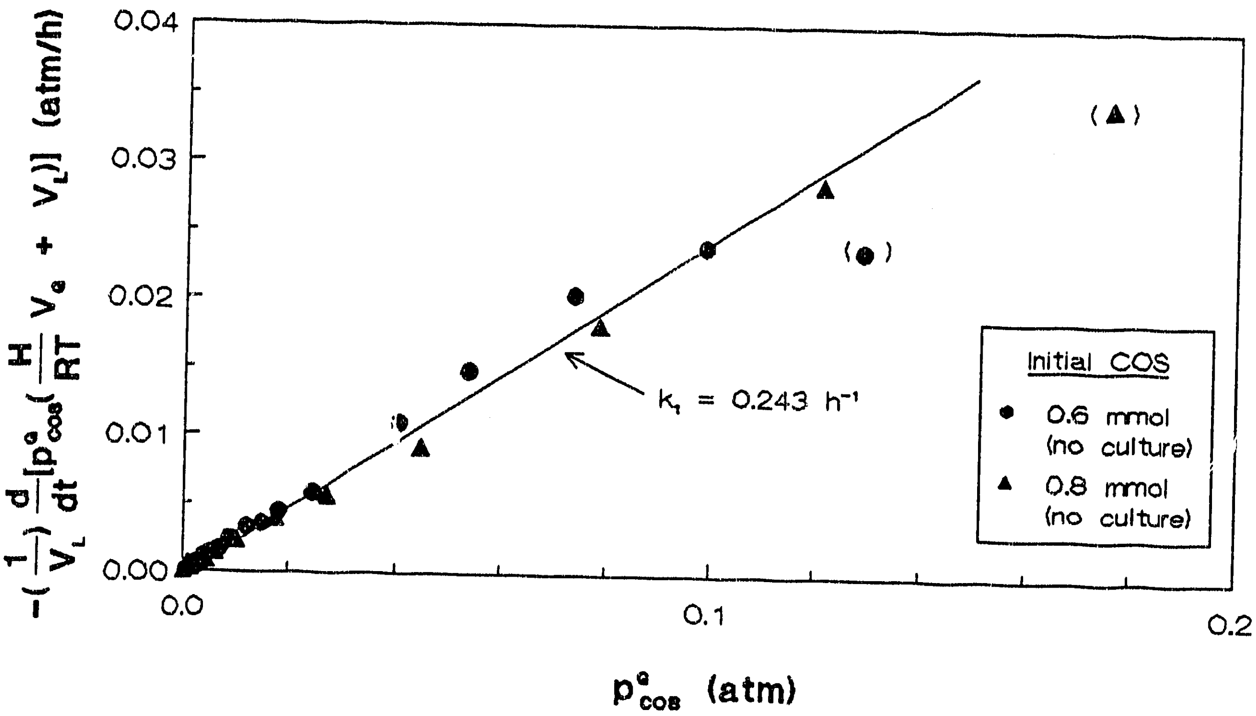

Figure 13. Determination of the First Order Reaction Rate Constant for the Reaction: $COS + H_2O \rightarrow H_2S + CO_2$.

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