

THE UNIVERSITY OF CALGARY

**S-ISOTOPE FRACTIONATION DURING  
SO<sub>4</sub><sup>2-</sup> AND SO<sub>3</sub><sup>2-</sup> REDUCTION**

by

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A THESIS

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DEPARTMENT OF PHYSICS AND ASTRONOMY

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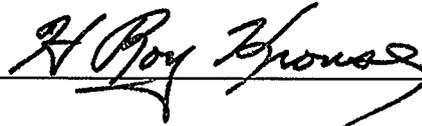
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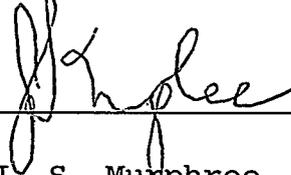
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, "S-Isotope Fractionation During  $\text{SO}_4^{2-}$  and  $\text{SO}_3^{2-}$  Reduction" submitted by Xiao Lu Wu in partial fulfilment of the requirements for the degree of Master of Science.



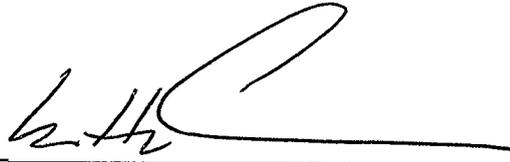
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## ABSTRACT

Sulphur isotope behavior during chemical sulphate and sulphite reductions were studied with different reducing agents at different temperatures.

During sulphate reduction by  $\text{HI-H}_3\text{PO}_2\text{-HCl}$ , the ratio of the isotope rate constants,  $k_{32}/k_{34}$ , remained constant throughout most of the reaction.  $k_{32}/k_{34}$  values of 1.0234, 1.0226 and 1.0205 at 25°C, 65°C, and 100°C respectively were obtained. The data were consistent with the initial S-O bond rupture being rate controlling as deduced by other workers. Different models of the reduction were examined. The measured data compare favourably with calculations based on the assumption of atomic masses participating in the rupture process. Sulphate reduction by  $\text{SnCl}_2$  realized smaller  $k_{32}/k_{34}$  values.

For chemical reduction of sulphite,  $k_{32}/k_{34}$  values were lower than for sulphate reduction. The data were few and quite variable consistent with the reactions not achieving steady-state. This implies that two or more reaction steps competed for rate control.

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This thesis is dedicated to my parents.

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## CHAPTER 1 Introduction

### 1.1 ISOTOPE FRACTIONATION

Differences in chemical and physical behaviour arising from differences in nuclidic masses of an element are called isotope effects. The alteration of isotope abundances in a specimen is called "isotope fractionation". The main processes producing isotope fractionation are:

1. Isotope exchange effects; 2. Kinetic isotope effects;

The term "kinetic isotope effect" refers to isotope species participating in a unidirectional conversion at different rates. It has usually referred to one step in a chemical reaction although it has been more generally used for an overall chemical reaction or even physical processes such as evaporation. Kinetic isotope effects are observed when a reaction has not gone to completion so that the product and remaining reactant do not have the same isotope composition (if the reaction is completed, the isotope composition of product will be the same as that of starting reactant).

Isotope exchange may occur between two different chemical compounds or two states of one compound. Sometimes equilibrium may be obtained for an isotope exchange reaction and an equilibrium constant defined which determines the isotope

composition of the participating molecules.

Laboratory measurements of chemical isotope effects, both equilibrium and kinetic, have developed into an extremely useful tool for the investigation of the mechanisms of chemical reactions. In addition, it has been recognized that isotope fractionation occurs in nature, so that samples of an element will have variable isotope compositions reflecting differences in their chemical, biological, and geological histories. Over the past 40 years, extensive measurements of the isotope abundance variations of hydrogen, boron, carbon, oxygen, and sulphur have aided in the solution of many geochemical problems.

## 1.2 OVERVIEW OF SULPHUR ISOTOPE FRACTIONATION IN NATURE

Sulphur has four naturally occurring stable isotopes with average abundances as follows:

$^{32}\text{S}$ : 95.02%;  $^{33}\text{S}$ : 0.75%;  $^{34}\text{S}$ : 4.21%;  $^{36}\text{S}$ : 0.02%;

$^{32}\text{S}$  and  $^{34}\text{S}$  are usually studied because of their higher abundances. Sulphur isotope compositions are normally expressed in terms of the differences, in parts per-thousand, between the  $^{34}\text{S}/^{32}\text{S}$  abundance ratios in the samples and the

$^{34}\text{S}/^{32}\text{S}$  ratio in a standard material:

$$\delta^{34}\text{S} (\text{‰}) = [ (^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{standard}} - 1 ] \times 1000 \quad 1.1$$

The standard chosen is troilite (FeS) from the Cañon Diablo meteorite. Positive and negative  $\delta^{34}\text{S}$  values mean that the sample is "enriched" and "depleted" in  $^{34}\text{S}$ , respectively, in comparison to the standard. Sulphur isotope abundance variations in nature are summarized in Figure 1.

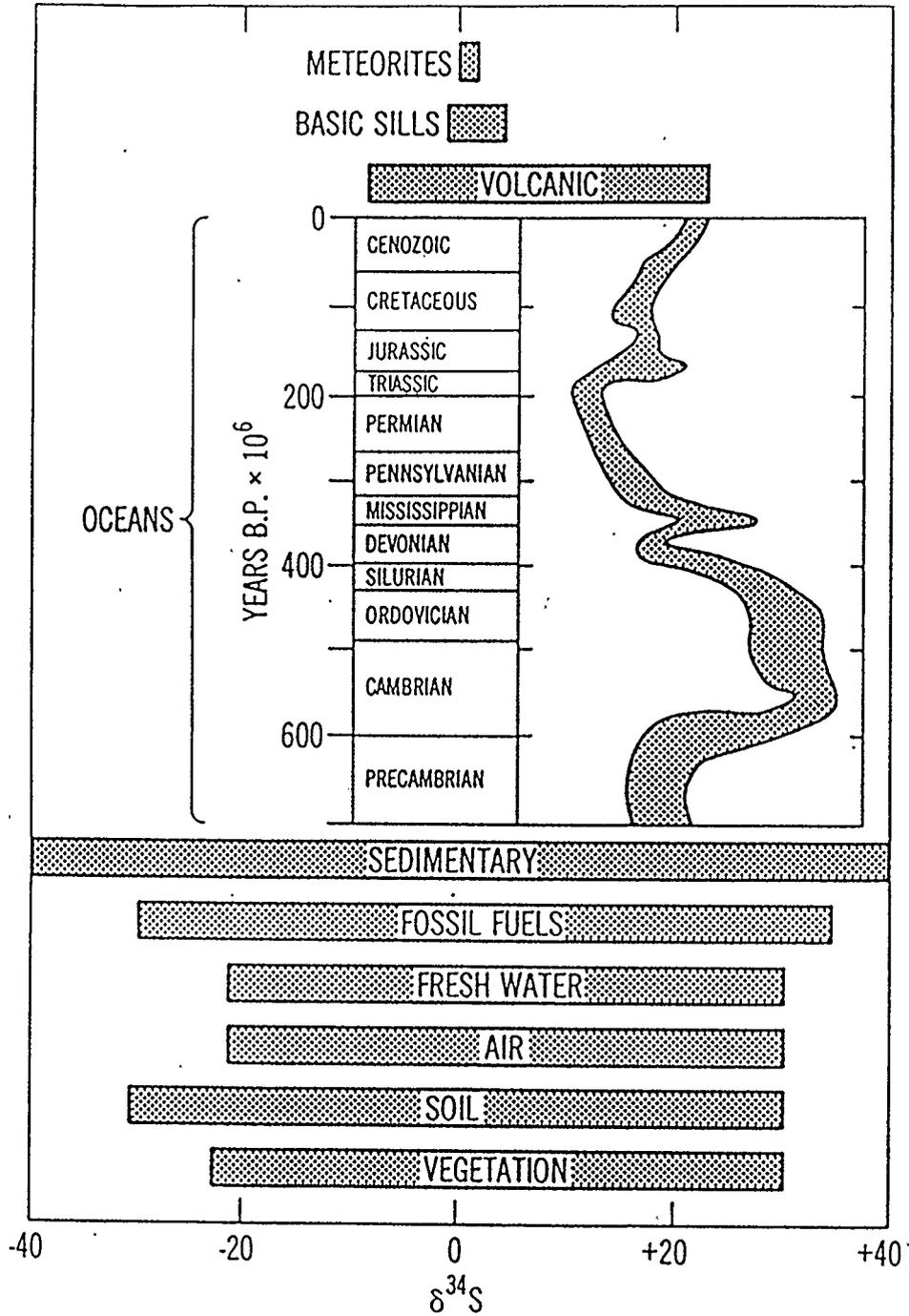


Figure 1: Sulphur isotope variations in nature (from KROUSE and TABATABAI, 1986)

A few samples fall well outside of the range. Barite concretions may have  $\delta^{34}\text{S}$  values as high as +90 ‰ (SAKAI, 1971; SHAKUR, 1982). Values for  $\delta^{34}\text{S}$  as low as -45 ‰ have been found in hydrotroilite (VESELOVSKY et al., 1969) and pyrite in cores from Deep Sea Drilling Project leg 37 (KROUSE et al., 1977). It is now well established that the large deviations of  $\delta^{34}\text{S}$  in nature are due largely to the fractionation of the sulphur isotopes in biologically mitigated reactions at low temperatures. In particular, the dissimilatory reduction of sulphate with the release of  $\text{H}_2\text{S}$  occurs with large sulphur isotope selectivities, and the turnover rates exceed those of assimilatory reduction by several orders of magnitude.

### 1.3 RELEVANCE OF $\text{SO}_4^{2-}$ REDUCTION TO NATURAL VARIATIONS IN $\delta^{34}\text{S}$ VALUES

Direct verification for sulphur isotope fractionation during  $\text{SO}_4^{2-}$  reduction in nature has been found for a number of locations. Some of these are the Cyrenaican Lakes, Africa (MACNAMARA and THODE, 1951); Texas-Louisiana Salt Domes (THODE et al, 1951); Western North American thermal springs (SASAKI and KROUSE, 1968) and stratified lakes in the Arctic (JEFFRIES and KROUSE, 1985). The wide secular variation of  $\delta^{34}\text{S}$  values in marine evaporite sulphate,  $\delta^{34}\text{S} < +10$  ‰ to  $\delta^{34}\text{S} > +35$  ‰ (Fig. 1) is believed to have resulted to a large extent from bacterial

SO<sub>4</sub><sup>2-</sup> reduction (NIELSEN & RIEKE, 1964; THODE & MONSTER, 1965; HOLSER & KAPLAN, 1966; DAVIES & KROUSE, 1975).

#### 1.4 PREVIOUS INVESTIGATION OF KINETIC ISOTOPE EFFECTS DURING SO<sub>4</sub><sup>2-</sup> REDUCTION

There is considerable debate as to the relative roles of abiotic and microbiological SO<sub>4</sub><sup>2-</sup> reduction in nature. Microbiological reduction mechanisms are very complex and involve intermediate forms such as sulphite, trithionate, and thiosulphate (see review by KROUSE and McCREADY, 1979). This thesis examines the kinetic isotope effects realized during chemical reduction of SO<sub>4</sub><sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> because SO<sub>3</sub><sup>2-</sup> is a possible intermediate. HARRISON and THODE (1957) first reported kinetic isotope effects during abiotic SO<sub>4</sub><sup>2-</sup> reduction by a HI-H<sub>3</sub>PO<sub>2</sub>-HCl mixture. The results indicated that the initial S-O bond rupture was the rate controlling step and the associated  $k_{32}/k_{34}$  was 1.022 over the temperature range 18°C to 50°C, i.e. <sup>32</sup>SO<sub>4</sub><sup>2-</sup> reacted 2.2% faster than <sup>34</sup>SO<sub>4</sub><sup>2-</sup> and no temperature dependence was observed. This study verified that chemical sulphate reduction could lead to significant sulphur isotope fractionation.

GRINENKO et al (1969) studied kinetic isotope effects during high temperature (100°C to 300°C) reduction of sulphuric

acid to  $\text{H}_2\text{S}$  with  $\text{HI-H}_3\text{PO}_2$  at  $100^\circ\text{C}$ ; to  $\text{SO}_2$  with  $\text{H}_2$  from  $138^\circ\text{C}$  to  $290^\circ\text{C}$ . The liberation of elemental  $\text{S}$  and  $\text{H}_2\text{S}$  was noted at  $290^\circ\text{C}$ . A correlation between the kinetic fractionation and temperature was found (Fig.2.).

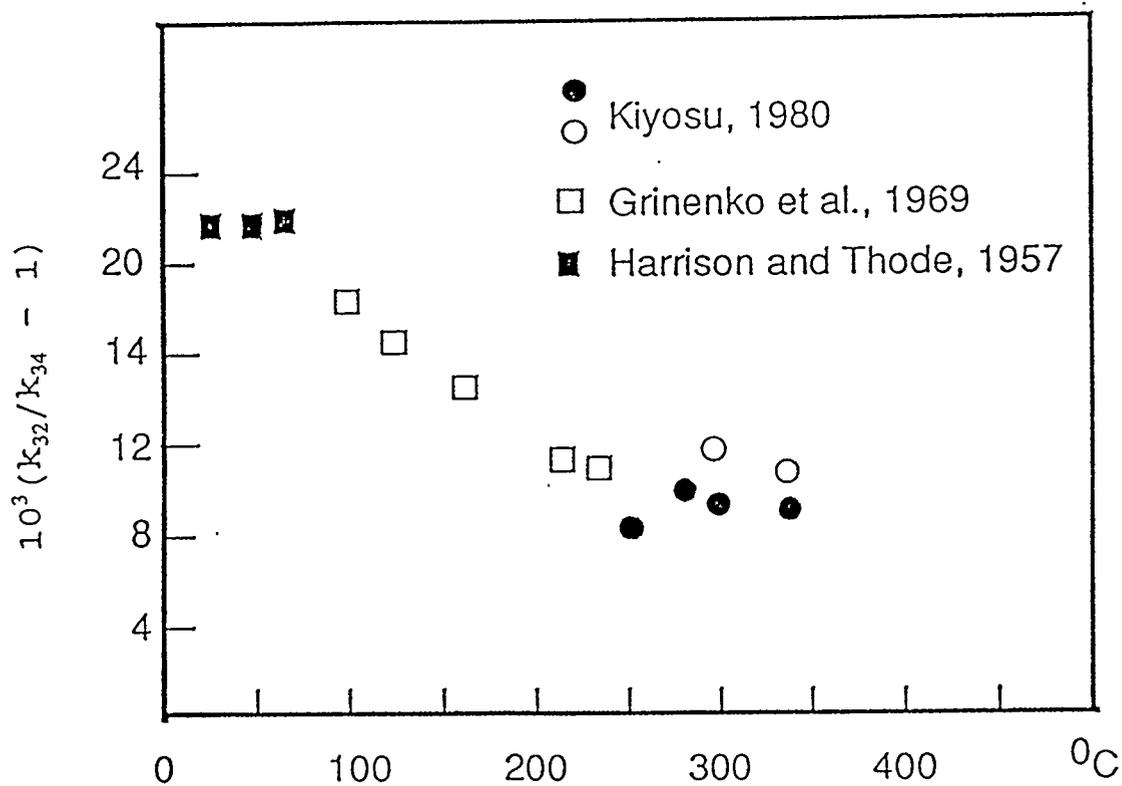


Figure 2: Dependence of  $k_{32}/k_{34}$  values on temperature during sulphate reduction.

HUSAIN and KROUSE (1978) reported isotope fractionation during the reaction of high concentrations of sulphuric acid solutions with  $H_2S$ . Produced  $SO_2$  was relatively depleted in  $^{34}S$  to the extent identified with the initial S-O bond rupture by HARRISON and THODE (1957).

KIYOSU (1980) measured  $k_{32}/k_{34}$  values during chemical reduction of sulphate by organic matter under hydrothermal conditions. He found that sulphate reduction was a first order reaction (reactant disappeared proportional to the concentration of the reactant to first order) with respect to  $SO_4^{2-}$  in the temperature range 250°C to 340°C. Dependence of kinetic fractionation on temperature was not observed within this data set but the  $k_{32}/k_{34}$  values were lower than those of HARRISON and THODE (1957). He also concluded that in this multistep reaction, the one responsible for the kinetic isotope effect was the reduction of sulphate to sulphite, consistent with the findings of HARRISON and THODE (1957).

KIYOSU and KROUSE (1990) investigated abiogenic reduction of sulphate by organic acid (acetate acid) at temperatures ranging from 241°C to 340°C. A strong temperature dependence of kinetic isotope fractionation was found (Fig. 3).

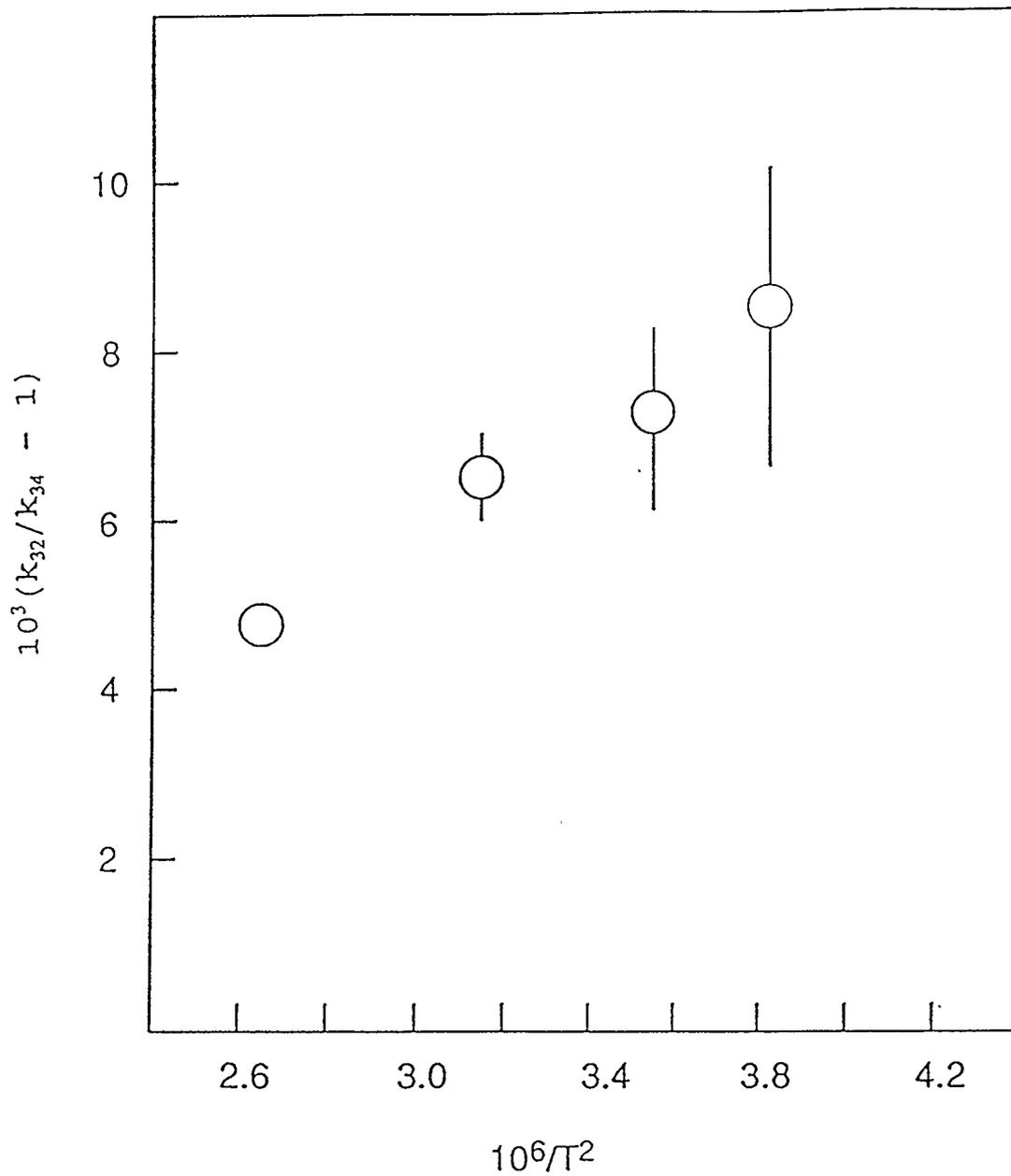


Figure 3: Temperature dependence of  $k_{32}/k_{34}$  for sulphate reduction by organic matter (KIYOSU and KROUSE, 1990).

Data on kinetic isotope effects during abiotic sulphite reduction are few. HARRISON and THODE's (1957) attempt to reduce sulphite with the same mixture they used for sulphate reduction, failed. They concluded that this was the result of generation of large amounts of elemental sulphur because of oxidation of the  $\text{H}_2\text{S}$  by product  $\text{I}_2$  before it could be reduced back to  $\text{I}^-$  by the hypophosphorous acid. In the low pH solutions consistent with many reducing agents,  $\text{SO}_2$  evolves from the reaction mixture. It may react with  $\text{H}_2\text{S}$  to produce elemental sulphur which deposits on walls throughout the system. In contrast to the above complications, sulphur isotope selectivity during bacterial  $\text{SO}_3^{2-}$  reduction has been conveniently studied with many organisms (e.g. KROUSE and McCREADY, 1975).

#### 1.5 MOTIVES FOR THE STUDY IN THIS THESIS

The findings of HARRISON and THODE (1957) are particularly important because the temperature range is relevant to many natural  $\text{SO}_4^{2-}$  reduction situations. Identification of  $k_{32}/k_{34} = 1.022$  with initial S-O bond rupture is also used to interpret sulphur isotope fractionation during microbiological sulphate reduction. This is equivalent to enquiring if one step such as the initial S-O bond rupture was decidedly slower than other steps and whether intermediates

form in the reaction (e.g. REES, 1971). However, the number of measurements by HARRISON and THODE (1957) were few, being taken only at ten percent conversion. In the work of GRINENKO et al (1969) the conversion was only five percent. Thus it is prudent to ascertain whether the ratio of the isotope rate constants remains constant throughout entire reductions.

If the interpretation of the initial S-O bond rupture being responsible for the isotope behavior is correct, how can the rupture process be best modelled? For example, are the masses of only the S and O atoms involved or does the reduced mass dependence involve fragments of participating molecules?

A closer examination of the temperature dependence of  $k_{32}/k_{34}$  is relevant in view of the large variations in isotope fractionation encountered with  $\text{SO}_4^{2-}$  reducing bacteria. It is also desirable to examine the kinetic isotope effects which result with other reducing agents in the same temperature ranges.

Since data on the isotope selectivity during  $\text{SO}_3^{2-}$  reduction are comparatively few, there is the challenge of trying to obtain such data.

## CHAPTER 2 Theoretical Background

### 2.1 ISOTOPE EXCHANGE REACTION

Isotope exchange reactions are a special case of general chemical equilibrium and can be written as



where the subscripts 1 and 2 refer to the light and heavy isotopes in molecules A and B respectively. If equilibrium is achieved, using statistical mechanics, the equilibrium constant will be equal to:

$$K = \frac{[Q_{A_2}/Q_{A_1}]^a}{[Q_{B_2}/Q_{B_1}]^b} \quad 2.2$$

where  $Q$  is total partition function of the molecules.

BIGELEISEN and MAYER(1947) showed that the equilibrium constant can be calculated directly from the ratio of reduced isotope partition functions  $Q'_2/Q'_1$ , which depend only on the vibrational frequencies of the isotope molecules. The expression is:

$$K = \frac{Q'_2}{Q'_1} = \prod_{i=1}^n \frac{u_{2i}}{u_{1i}} \frac{e^{-\frac{u_{2i}}{2}} (1 - e^{-u_{1i}})}{e^{-\frac{u_{1i}}{2}} (1 - e^{-u_{2i}})} \quad 2.3$$

Where

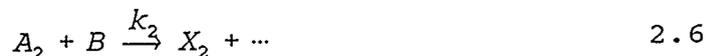
$$u_i = \frac{h\nu_i}{kT} \quad 2.4$$

$\nu_i$  is the  $i^{\text{th}}$  fundamental frequency of the molecule. The summation  $n$  is  $3N-5$  and  $3N-6$  for linear and non-linear molecules respectively where  $N$  is number of atoms in the molecule of interest.

## 2.2 KINETIC ISOTOPE EFFECTS

For unidirectional chemical reactions, the theoretical considerations are somewhat more complicated than for equilibrium isotope exchange processes. Attention must be paid to the reaction mechanism and possible intermediates involved prior to the formation of final products. Isotope fractionation in a unidirectional process results from differences in reaction rates of the different isotopic species. In a single-step, zero or first order reaction, the isotope fractionation factor between the instantaneously generated product and remaining reactant is simply given by the ratio of rate constants for the two competing isotopic reactions as follows





The lighter isotope species usually reacts with a faster rate constant, thereby relatively enriching the product in light isotopes and the remaining reactants in heavy isotopes. The theory of kinetic isotope effects (K.I.E) is based on the framework of WIGNER (1937) and EYRING (1941) who revised the transition state theory of MARCELIN (1915) with quantum statistics. One assumes that an activated complex exists between reactants and products through which the reaction passes. Molecules in the activated state are in thermal equilibrium with the reacting molecules. The overall absolute rate is then roughly equal to the concentration of molecules in the activated state times the rate constant for their passage to the final product. BIGELEISEN (1949) showed that the ratio of the isotopic rate constants is given by

$$\frac{k_1}{k_2} = \frac{K_1}{K_2} \frac{[Q_2/Q_1]}{[Q_2^*/Q_1^*]} \left( \frac{V^{*1L}}{V^{*2L}} \right) \quad 2.7$$

where  $K_1$  and  $K_2$  are transition coefficients which he assumed to be equal.  $Q_2/Q_1$  and  $Q_2^*/Q_1^*$  are the ratio of isotope partition functions for the reactants and activated complexes respectively. Each may be evaluated as

$$\prod_i^n \frac{u_{2i}}{u_{1i}} \frac{e^{-\frac{u_{2i}}{2}}}{e^{-\frac{u_{1i}}{2}}} \frac{(1 - e^{-u_{1i}})}{(1 - e^{-u_{2i}})} \quad 2.8$$

where  $u_i = hv_i/kT$  and  $v_i$  is the  $i^{\text{th}}$  fundamental frequency of the molecule. For a non-linear reactant molecule,  $n$  is  $3N-6$  where  $N$  is its number of atoms. The summation for the activated complex is over  $3n-7$  modes.  $v_{1L}^*/v_{2L}^*$ , the ratio of the two frequencies which become imaginary in the activated complex, may be evaluated in terms of the reduced masses of the activated complexes as they traverse the critical region of the reaction coordinate.

$$\frac{v_{1L}^*}{v_{2L}^*} = \sqrt{\frac{\mu_2^*}{\mu_1^*}} \quad 2.9$$

The theoretical prediction of the  $k_1/k_2$  requires precise knowledge of the form of the activated complex. Unfortunately in most cases, such information is not available. It is necessary to assume models of the activated complex. Such models are gauged by their appropriateness to the physical conditions and agreement between predictions based on them and the observed isotope effects.

Three cases will be considered according to REES and THODE (1965).

1. The activated complex is identical to the starting material, with the exception that the frequency

associated with the bond rupture is missing. Then

$$\frac{[Q_2/Q_1]}{[Q_2^*/Q_1^*]} = \frac{Q_{(v_{2L})}}{Q_{(v_{1L})}} \quad 2.10$$

where this ratio is the same as the partition function ratio for diatomic molecules with frequencies  $v_{2L}$  and  $v_{1L}$ . The effective mass ratio is evaluated as that of the reduced mass of the bond being ruptured in the activated complex.

2. The isotope partition function ratio term is very close to unity i.e. the activated complex closely resembles the reactants. This gives the lower and also the high temperature limits of  $k_1/k_2$ . Then

$$\frac{k_1}{k_2} = \left( \frac{\mu_2^*}{\mu_1^*} \right)^{\frac{1}{2}} \quad 2.11$$

3. The activated complex has some unknown structure for which the isotope partition function ratio lies between that of the starting material and unity. The extreme value of unity may be approached if in the transition state, a complicated structure is formed in which most of the vibrational frequencies are not sensitive to isotopic substitution. Then

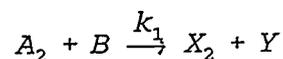
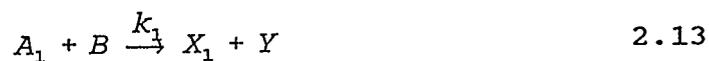
$$\frac{k_1}{k_2} = \left( \frac{Q_2}{Q_1} \right) \left( \frac{\mu_2^*}{\mu_1^*} \right)^{\frac{1}{2}} \quad 2.12$$

This approach gives an upper limit for the value of  $k_1/k_2$ .

Either mass ( $\text{SO}_3$  and O or higher masses) or atom fragments (S and O) may be tested in all three cases.

### 2.3 BEHAVIOR OF ISOTOPE COMPOSITION OF REACTION COMPONENTS

During a chemical reaction, the isotope composition of both product and reactant change. Competition between reactant isotope species can be expressed as:



at  $t=0$ ,  $A_1=A_{01}$ ,  $A_2=A_{02}$ ,  $X_1=0$ , and  $X_2=0$ .

The rates of one step first order isotopically competing reactions are given by

$$dX_1/dt = k_1(A_{01}-X_1) \quad 2.15$$

$$dX_2/dt = k_2(A_{02}-X_2) \quad 2.16$$

where subscripts 1 and 2 refer to lighter and heavier isotope species respectively.  $A_{01}$  and  $A_{02}$  are initial reactants.

$X_1$  and  $X_2$  are accumulated products. Integrating and dividing [2.15] by [2.16] yields

$$\frac{k_1}{k_2} = \frac{\ln\left(\frac{A_{01}}{A_{01}-X_1}\right)}{\ln\left(\frac{A_{02}}{A_{02}-X_2}\right)} \quad 2.17$$

The ratio of rates can be expressed in terms of  $r$  and  $f$

$$k_1/k_2 = \ln(1-f)/\ln(1-rf) \quad 2.18$$

where

$$f = (X_1 + X_2)/(A_{01} + A_{02}) \quad 2.19$$

and

$$r = (X_2/X_1)/(A_{02}/A_{01}) \quad 2.20$$

Since both of  $f$  and  $rf$  are smaller than 1, we can expand equation 2.18 as a Taylor's series. Thus we have

$$\frac{k_1}{k_2} \approx \frac{1}{r} \quad 2.21$$

equation 2.21 is equivalent to

$$\frac{k_1}{k_2} \approx \frac{X_1/X_2}{A_1/A_2} \quad 2.22$$

$A_1/A_2$  is the instantaneous ratio of the abundances of lighter and heavier isotope species in the remaining reactant. It is convenient to estimate  $k_1/k_2$  in this way.

#### 2.4 DETERMINATION OF REACTION RATE CONSTANTS

For a first order reaction, described as



the rates of disappearance of reactant and formation of product are given by

$$-dR/dt = kR \quad 2.24$$

and

$$dP/dt = k(P_{\max} - P) \quad 2.25$$

R is the concentration of reactant and P is the concentration of product.  $-dR/dt$  is equal to  $dP/dt$  if the reaction is first order.

Integration of equation 2.25 yields

$$\ln\left(1 - \frac{P}{P_{\max}}\right) = -k(t - t_0) \quad 2.26$$

or

$$P = P_{\max}(1 - e^{-k(t-t_0)}) \quad 2.27$$

For a long reaction time, P will tend to  $P_{\max}$ . For a first order reaction plotting  $\ln(1 - P/P_{\max})$  vs time will yield a straight line, the slope of which is the rate constant.

## 2.5 CALCULATION OF THE RESERVOIR $\delta^{34}\text{S}$

### 2.5-1 Calculation of $\delta^{34}\text{S}$ for Accumulated Product

In a closed system, the  $\delta$  value of accumulated product equals that of initial reactant (usually chosen as the "reference" isotope composition) when a chemical reaction

reaches to completion. Throughout the reaction, the  $\delta^{34}\text{S}$  value of the accumulated product can be computed approximately by

$$\delta^{34}\text{S} = \frac{\sum_{i=1}^n m_i (\delta^{34}\text{S})_i}{\sum_{i=1}^n m_i} \quad 2.28$$

where  $m_i$  is the mass or number of moles of the  $i^{\text{th}}$  sample sequentially removed and  $(\delta^{34}\text{S})_i$  is its isotope composition.

#### 2.5-2 Reservoir $\delta^{34}\text{S}$

If we know the initial  $\delta^{34}\text{S}$  of reactant and instantaneous  $\delta^{34}\text{S}$  of product, assuming first order reaction, we are able to compute the  $\delta^{34}\text{S}$  value of the "reservoir" (remaining reactant) using the following equation:

$$({}^{34}\text{S}/{}^{32}\text{S})_{\text{res}} = \frac{M \times ({}^{34}\text{S}/{}^{32}\text{S})_{\text{ref}} - \sum_{i=1}^k m_i \times ({}^{34}\text{S}/{}^{32}\text{S})_i}{M - \sum_{i=1}^k m_i} \quad 2.29$$

where  $({}^{34}\text{S}/{}^{32}\text{S})_{\text{res}}$  is isotope composition of reservoir.  $({}^{34}\text{S}/{}^{32}\text{S})_{\text{ref}}$  is initial isotope composition of reactant.  $M$  is the mass or number of moles of reactant and  $m_i$  is mass or number of mole of the  $i^{\text{th}}$  sample removed,  $({}^{34}\text{S}/{}^{32}\text{S})_i$  is isotope composition of  $i^{\text{th}}$  sample.

## CHAPTER 3 Experimental Methods

### 3.1 INSTRUMENTATION AND ANALYTICAL PROCEDURES

The reaction vessel and sample collectors are shown in Figs.4 and 5. The volumes of the reaction vessel and sample collector were 1000 ml and 55 ml respectively. This equipment was designed to minimize loss of gaseous products and conveniently collect samples. The temperature of a reactor could be maintained within  $\pm 1.5^{\circ}\text{C}$  using a thermocouple connected to a thermo electric controller.

#### 3.1-1 Mass Spectrometer

A Vacuum Generators Micromass 602, dual collector, gas source mass spectrometer was used to determine the sulphur isotope composition of the collected samples. Samples of  $\text{SO}_2$  can be run on this mass spectrometer with a standard deviation (essentially noise) of less than  $\pm 0.2\%$ . Reproducibility of  $\delta^{34}\text{S}$  values for different preparations from pure  $\text{Ag}_2\text{S}$  or  $\text{BaSO}_4$  is usually better than  $\pm 0.2\%$ . If the sample is small (less than 1.0 mg), higher standard deviations may result.

### 3.1-2 Basic Principles of Mass Spectrometer

A mass spectrometer analysis involves four steps:

1. Ionization of the molecules;
2. Accelerating the ions and shaping the ion beam with an electric field;
3. Deflecting the ion beam in a magnetic field;
4. Detecting the ion beams and measuring their current.

Upon leaving the source, an ion will be accelerated through an electric potential difference,  $V$ , and have kinetic energy  $E$ ;

$$E = qV = \frac{1}{2}Mv^2 \quad 3.1$$

When an ion with mass  $M$  is injected to a uniform magnetic field, it will experience a force normal to both its velocity and the magnetic field direction. According to Lorentz's law, this force is  $F = q \mathbf{V} \times \mathbf{B}$  and can be simplified to  $F = qvB$  because  $\mathbf{V}$  is normal to  $\mathbf{B}$  in the mass spectrometer used in this study.  $B$  is the magnetic flux density and  $q$  and  $v$  are the electric charge and velocity of the ion respectively. Since  $F$  is in the radial direction, it can be equated to the centripetal force required to keep an ion moving in a circular orbit of radius  $r$ . By Newton's second law  $qvB = Mv^2/r$

combining equation 3.1 gives

$$r = \left( \frac{2VM}{q} \right)^{\frac{1}{2}} B^{-1}$$

Thus, ions with different masses have orbits of different radii in the magnetic field and can be collected in different collectors.

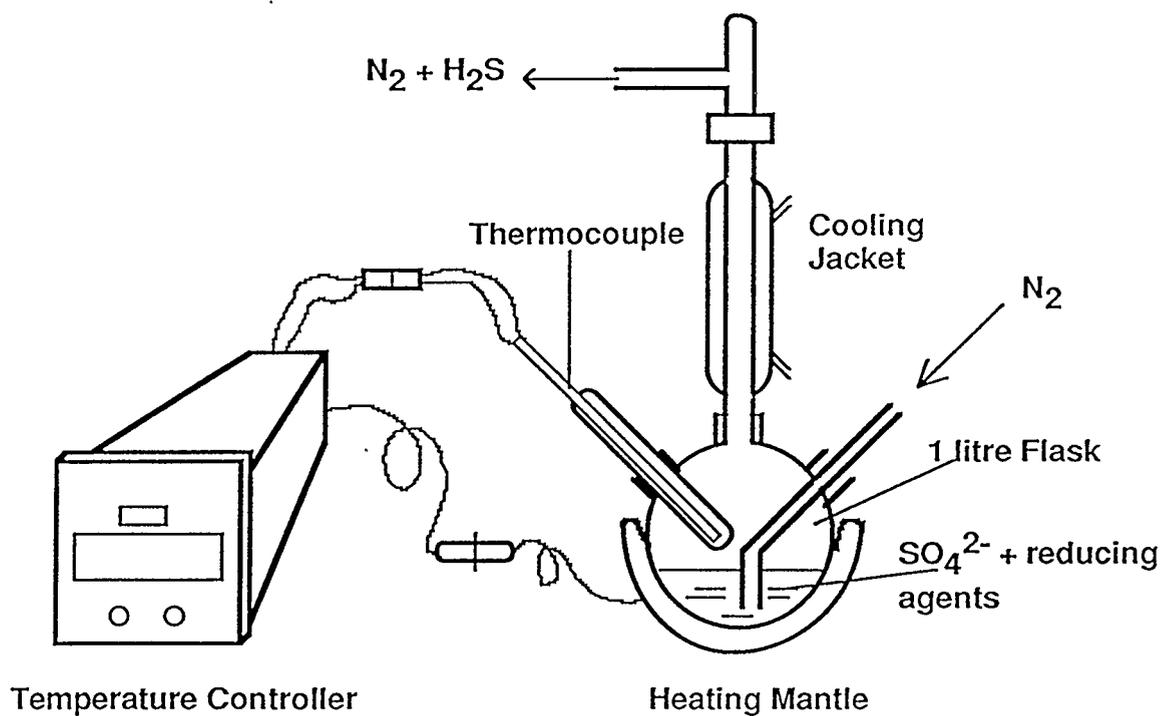


Figure 4: Reaction vessel used for sulphate and sulphite reduction studies.

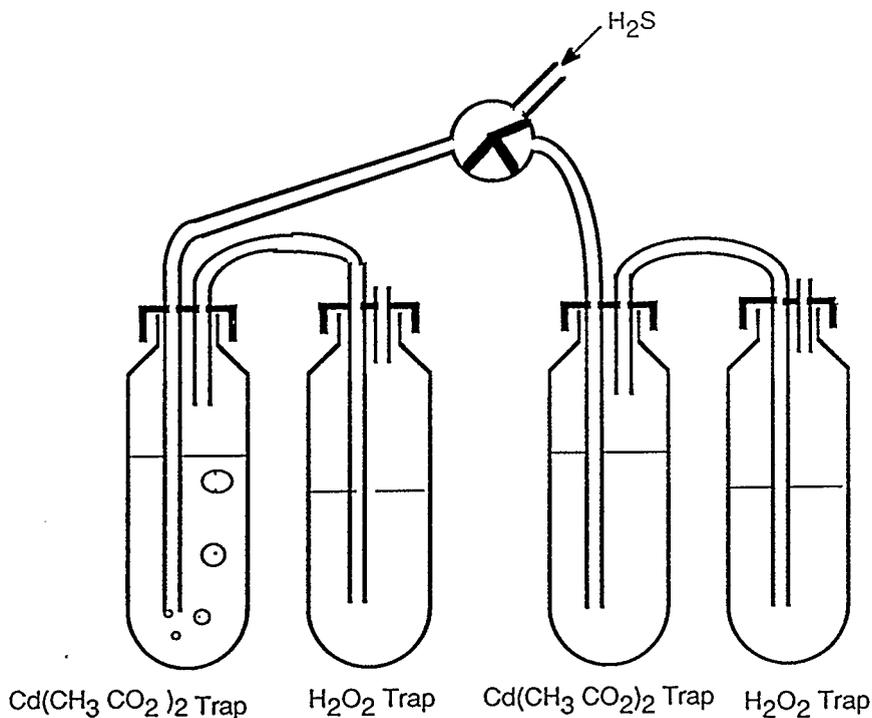


Figure 5: Sample collector for  $\text{H}_2\text{S}$  and  $\text{SO}_2$  evolved during sulphate or sulphite reduction.

### 3.1-3 Sample Preparation

Sodium sulphate or sulphite (Fisher Scientific Company) was used in these experiments. Their sulphur isotope compositions were +0.35 ‰ and +1.78 ‰ respectively. Various reducing agents were added to the reactor solution at different temperatures.  $\text{H}_2\text{S}$  product was carried by the flow of  $\text{N}_2$  to a cadmium acetate solution trap which was in turn connected to a  $\text{H}_2\text{O}_2$  trap in case any  $\text{SO}_2$  was evolved. Cold

water passed through the condenser, retained water vaporized from the reaction mixture.  $\text{H}_2\text{S}$  was precipitated as  $\text{CdS}$  in the cadmium acetate solution.  $\text{CdS}$  was then converted to  $\text{Ag}_2\text{S}$  by adding  $\text{AgNO}_3$  solution. The  $\text{Ag}_2\text{S}$  was filtered, dried, weighed, and packed with a  $\text{V}_2\text{O}_5:\text{SiO}_2$  mixture in mass ratio of 1:1 as described by UEDA and KROUSE (1987). The combustion line is illustrated in Fig.6.

$\text{Ag}_2\text{S}$  was combusted at the temperature of  $900^\circ\text{C}$ . Condensable gases were collected by a liquid  $\text{N}_2$  trap. Non-condensable gases were pumped out. A pentane- $\text{N}_2$  trap was used to separate  $\text{SO}_2$  and  $\text{CO}_2$ , the latter having a higher vapour pressure. A dry ice-ethanol slush was used to remove  $\text{H}_2\text{O}$ . The purified  $\text{SO}_2$  was then transferred to a cold finger for admission to the mass spectrometer through a capillary leak. After initial manual adjustments, the mass spectrometer operation was computer controlled. Ion current of masses 64 and 66 (mainly  $^{32}\text{S}^{16}\text{O}_2^+$  and  $^{34}\text{S}^{16}\text{O}_2^+ + ^{32}\text{S}^{16}\text{O}^{18}\text{O}$ ) were digitized and  $\delta^{34}\text{S}$  values automatically calculated. The standard deviation in  $\delta^{34}\text{S}$  value was  $< \pm 0.1 \text{ ‰}$  during the measurement of one sample.

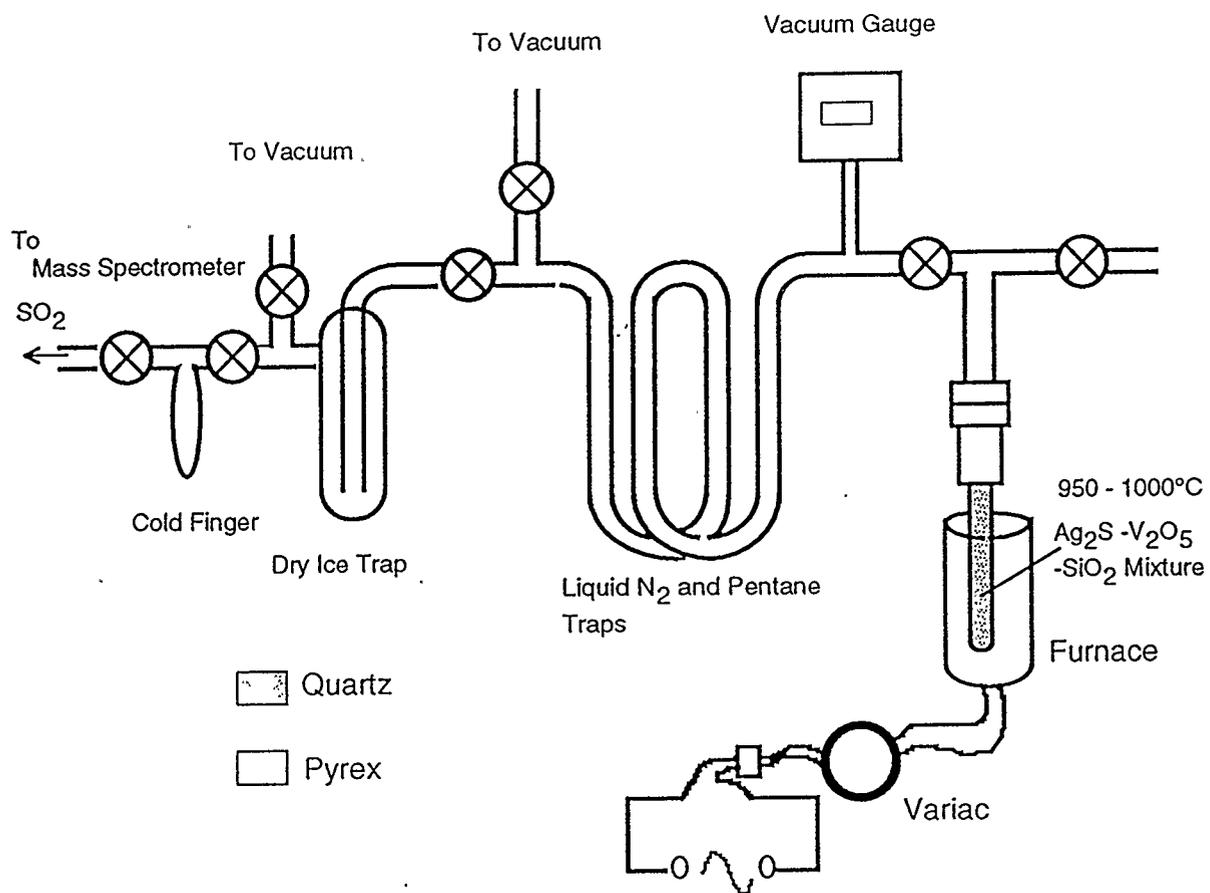


Figure 6: Combustion line for conversion of  $\text{Ag}_2\text{S}$  to  $\text{SO}_2$ .

## CHAPTER 4 Results of Reduction Experiments

### 4.1 SULPHATE REDUCTION USING THE THODE REDUCTION MIXTURE

The Thode mixture is composed of HI, H<sub>3</sub>PO<sub>2</sub>, and HCl mixed in the ratio of 4.0, 1.1, 1.6. The reduction reaction can be described as



Three reductions were carried out under the following conditions:

Experiment 1. 47ml of 0.78M Na<sub>2</sub>SO<sub>4</sub> with 50ml of the Thode reduction mixture, 25°C;

Experiment 2. 15ml of 0.47M Na<sub>2</sub>SO<sub>4</sub> with 50ml of the Thode reduction mixture, 100°C;

Experiment 3. 23ml of 0.25M Na<sub>2</sub>SO<sub>4</sub> with 40ml of the Thode reduction mixture, 65°C.

The experimental results are given in Tables 1 to 6.

Table 1. Sulphate reduction using the Thode reduction mixture at 25°C.

Isotope Fractionation

No. Reaction	Time (hours)	$\delta^{34}\text{S}$ (‰)			$k_{32}/k_{34}$ app./acc.*	
		( $\text{H}_2\text{S}$ ) <sub>M</sub>	( $\text{SO}_4^{2-}$ ) <sub>C</sub>	( $\text{H}_2\text{S}$ ) <sub>A</sub>		
1	0.12	6.5	-21.8	0.02	-21.8	1.022
2	0.37	13.5	-19.6	0.07	-20.3	1.020
3	0.52	17.5	-23.5	0.11	-21.2	1.024
4	0.57	20.5	-21.6	0.12	-21.2	1.022
5	0.76	21.5	-22.7	0.16	-21.6	1.023
6	0.86	24.5	-22.1	0.19	-21.7	1.023/1.0235
7	1.15	37.0	-22.8	0.25	-22.0	1.024
8	1.71	81.0	-22.6	0.38	-22.2	1.024
9	2.23	101.0	-23.6	0.51	-22.5	1.025
10	2.30	105.3	-22.5	0.53	-22.5	1.024
11	2.48	109.5	-22.9	0.57	-22.5	1.024
12	2.53	112.5	-22.3	0.58	-22.5	1.023
13	3.10	122.5	-22.8	0.72	-22.6	1.024/1.0235
14	3.23	127.0	-22.8	0.75	-22.6	1.024
15	3.33	128.0	-22.6	0.78	-22.6	1.024
16	3.40	131.0	-22.4	0.79	-22.6	1.024
17	3.77	136.5	-24.4	0.89	-22.7	1.026
18	4.12	145.5	-24.0	0.98	-22.9	1.026
19	4.37	151.5	-23.3	1.05	-22.9	1.025

Table 1. continued

No.	Reaction (%)	Time (hours)	$\delta^{34}\text{S}$ (‰)			$k_{32}/k_{34}$
			$(\text{H}_2\text{S})_{\text{M}}$	$(\text{SO}_4^{2-})_{\text{C}}$	$(\text{H}_2\text{S})_{\text{A}}$	app./acc.*
20	5.16	170.0	-23.4	1.25	-23.0	1.025
21	5.52	174.0	-22.6	1.34	-22.9	1.024
22	5.79	178.0	-21.6	1.41	-22.9	1.024
23	5.96	182.0	-21.0	1.45	-22.8	1.023
24	6.52	193.0	-21.3	1.59	-22.7	1.023
25	7.09	197.5	-21.5	1.73	-22.6	1.024/1.024
26	7.59	201.0	-21.0	1.85	-22.5	1.023
27	8.40	207.0	-20.9	2.06	-22.3	1.023
28	10.57	223.0	-20.8	2.61	-22.0	1.024
29	11.44	228.0	-19.3	2.83	-21.8	1.023
30	12.42	235.0	-19.3	3.08	-21.6	1.023
31	14.71	246.5	-19.8	3.70	-21.3	1.024
32	15.85	251.0	-19.0	4.01	-21.2	1.023
33	16.33	254.5	-19.3	4.14	-21.1	1.024
34	18.16	265.0	-18.2	4.65	-20.8	1.023
35	19.00	270.5	-18.6	4.89	-20.7	1.024/1.0235
36	20.29	281.5	-18.0	5.26	-20.5	1.024
37	22.05	290.0	-17.9	5.79	-20.3	1.024/1.024
38	23.58	296.0	-17.6	6.26	-20.2	1.024
39	24.59	299.5	-16.7	6.57	-20.0	1.024
40	27.44	305.5	-16.4	7.48	-19.6	1.024

Table 1. continued

No.	Reaction (%)	Time (hours)	$\delta^{34}\text{S} (\text{‰})$			$k_{32}/k_{34}$
			$(\text{H}_2\text{S})_{\text{M}}$	$(\text{SO}_4^{2-})_{\text{C}}$	$(\text{H}_2\text{S})_{\text{A}}$	app./acc.*
41	30.14	314.0	-15.1	8.36	-19.2	1.024
42	30.93	316.0	-15.1	8.63	-19.1	1.024
43	32.14	318.5	-15.0	9.05	-19.0	1.024
44	34.00	324.0	-13.7	9.70	-18.7	1.024/1.0235
45	35.85	329.0	-13.4	10.37	-18.4	1.024
46	36.89	330.0	-12.8	10.75	-18.3	1.024
47	37.82	337.	-12.1	11.10	-18.1	1.023
48	40.19	339.0	-12.3	12.04	-17.8	1.025
49	41.72	342.5	-10.8	12.64	-17.5	1.024
50	42.50	344.5	-10.7	12.96	-17.4	1.024
51	43.25	346.5	-10.5	13.27	-17.3	1.024
52	45.61	353.0	-9.6	14.28	-16.9	1.024
53	48.52	362.0	-8.2	15.56	-16.3	1.024
54	49.72	364.5	-8.4	16.14	-16.2	1.025/1.024
55	50.69	367.5	-8.3	16.63	-16.0	1.025
56	51.54	369.5	-7.7	17.06	-15.9	1.025
57	52.24	371.5	-6.5	17.40	-15.7	1.024
58	53.67	375.0	-5.6	18.12	-15.5	1.024
59	56.26	381.5	-3.9	19.44	-14.9	1.023
60	59.00	386.0	-3.3	20.97	-14.4	1.024/1.024
61	60.88	391.0	-1.4	22.08	-14.0	1.024

Table 1. continued

No.	Reaction (%)	Time (hours)	$\delta^{34}\text{S}$ (‰)			$k_{32}/k_{34}$
			$(\text{H}_2\text{S})_{\text{M}}$	$(\text{SO}_4^{2-})_{\text{C}}$	$(\text{H}_2\text{S})_{\text{A}}$	app./acc.*
62	62.25	396.0	0.1	22.88	-13.7	1.023
63	63.60	402.0	0.4	23.73	-13.4	1.023
64	67.24	409.5	1.2	26.28	-12.6	1.025
65	69.01	415.5	4.4	27.54	-12.2	1.023/1.024
66	69.78	422.5	4.7	28.14	-12.0	1.023
67	70.57	424.5	7.6	28.70	-11.8	1.021
68	72.80	433.5	8.8	30.37	-11.1	1.021
69	73.99	436.5	10.0	31.32	-10.8	1.021
70	74.66	439.0	10.4	31.88	-10.6	1.021
71	75.53	442.0	10.1	32.67	-10.4	1.022
72	76.23	445.0	11.6	33.31	-10.2	1.021
73	79.11	456.0	12.3	36.28	-9.3	1.024
74	79.51	458.0	12.3	36.76	-9.2	1.024
75	80.81	463.0	15.7	38.23	-8.8	1.022
76	81.29	465.0	14.0	38.87	-8.7	1.025/1.0235
77	82.24	469.0	15.7	40.15	-8.4	1.024
78	83.69	475.5	20.6	41.95	-7.9	1.021
79	85.38	481.5	23.7	44.14	-7.3	1.020
80	86.90	484.0	25.4	46.40	-6.7	1.020
81	87.78	488.0	27.2	47.86	-6.4	1.020
82	88.58	491.5	29.0	49.24	-6.1	1.020

Table 1. continued

No.	Reaction (%)	Time (hours)	$\delta^{34}\text{S}$ (‰)			$k_{32}/k_{34}$
			$(\text{H}_2\text{S})_M$	$(\text{SO}_4^{2-})_C$	$(\text{H}_2\text{S})_A$	app./acc.*
83	89.15	494.0	31.0	50.24	-5.8	1.019
84	90.05	498.5	32.3	51.97	-5.4	1.019/1.022
85	91.41	505.5	35.0	54.83	-4.8	1.019
86	92.33	511.0	37.5	57.06	-4.4	1.019
87	93.17	515.5	40.2	59.31	-4.0	1.018
88	93.86	519.5	42.7	61.37	-3.7	1.018
89	94.21	529.5	44.5	62.50	-3.5	1.017
90	95.60	533.0	48.3	67.59	-2.7	1.018
91	96.00	537.0	52.7	69.30	-2.5	1.016/1.019
92	96.33	540.0	54.7	70.84	-2.3	1.015
93	97.31	549.0	58.2	76.63	-1.7	1.017
94	98.01	560.0	64.5	82.49	-1.2	1.017/1.016
95	98.43	567.0	70.1	87.53	-0.9	1.016
96	98.85	583.0	77.0	94.89	-0.6	1.017
97	98.99	589.0	85.1	97.75	-0.5	1.012/1.011
98	99.13	595.0	86.7	102.56	-0.3	1.015/1.0065
99	99.25	600.6	94.3	107.26	-0.2	1.012
100	99.34	604.0	92.5	118.95	-0.1	1.024

M: measured value; C: calculated value; A: accumulated value(calculated); app.: approximate; acc.: accurate;

Table 2. Sulphate reduction using Thode reduction mixture at 25°C

Kinetics

No.	Time (hours)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
1	6.5	4.60	8.4	8.4
2	13.5	4.60	18.3	26.7
3	17.5	4.60	10.7	37.4
4	20.5	4.60	3.3	40.7
5	21.5	4.60	14.0	54.7
6	24.5	4.60	6.9	61.6
7	37.0	4.60	20.9	82.5
8	81.0	4.59	40.1	122.6
9	101.0	4.59	37.2	159.8
10	105.3	4.58	5.3	165.1
11	109.5	4.58	12.4	177.5
12	112.5	4.58	4.2	181.7
13	122.5	4.58	40.3	222.0
14	127.0	4.57	9.6	231.6
15	128.0	4.57	7.1	238.7
16	131.0	4.57	5.0	243.7
17	136.5	4.57	26.8	270.5
18	145.5	4.57	24.5	295.0
19	151.5	4.56	18.3	313.3
20	170.0	4.56	56.8	370.1
21	174.0	4.55	25.3	395.4

Table 2. continued

No.	Time (hours)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
22	178.0	4.55	19.9	415.3
23	182.0	4.55	12.2	427.5
24	193.0	4.54	39.7	467.2
25	197.5	4.54	41.3	508.5
26	201.0	4.53	35.4	543.9
27	207.0	4.53	58.4	602.3
28	223.0	4.52	155.3	757.6
29	228.0	4.49	62.3	819.9
30	235.0	4.48	70.6	890.5
31	246.5	4.47	163.9	1054.4
32	251.0	4.45	81.9	1136.3
33	254.5	4.43	34.4	1170.7
34	265.0	4.43	131.3	1302.0
35	270.5	4.41	59.9	1361.9
36	281.5	4.39	92.8	1454.7
37	290.0	4.38	125.7	1580.4
38	296.0	4.36	110.2	1690.6
39	299.5	4.34	72.5	1763.1
40	305.5	4.32	204.3	1967.4
41	314.0	4.28	193.3	2160.7
42	316.0	4.25	56.9	2217.6

Table 2. continued

No.	Time (hours)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
43	318.5	4.24	86.4	2304.0
44	324.0	4.22	133.4	2437.4
45	329.0	4.19	132.6	2570.0
46	330.0	4.16	74.4	2644.4
47	337.5	4.15	66.6	2711.0
48	339.0	4.13	170.2	2881.2
49	342.5	4.09	109.6	2990.8
50	344.5	4.07	55.7	3046.5
51	346.5	4.05	53.8	3100.3
52	353.0	4.04	169.6	3269.9
53	362.0	4.00	208.7	3478.6
54	364.5	3.94	86.0	3564.6
55	367.0	3.92	69.2	3633.8
56	369.5	3.90	61.1	3694.9
57	371.5	3.88	49.8	3744.7
58	375.0	3.87	102.6	3847.3
59	381.5	3.84	185.7	4033.0
60	386.0	3.78	196.9	4229.9
61	391.0	3.71	134.7	4364.6
62	396.0	3.67	98.1	4462.7
63	402.0	3.63	96.8	4559.5

Table 2. continued

No.	Time (hours)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
64	409.5	3.60	261.0	4820.5
65	415.5	3.49	126.4	4946.9
66	422.5	3.43	55.2	5002.1
67	424.5	3.41	56.9	5059.0
68	433.5	3.38	159.9	5218.9
69	436.5	3.30	85.1	5304.0
70	439.0	3.26	48.3	5352.3
71	442.0	3.23	62.2	5414.5
72	445.0	3.20	50.5	5465.0
73	456.0	3.17	205.9	5670.9
74	458.0	3.04	28.8	5699.7
75	463.0	3.02	93.3	5793.0
76	465.0	2.95	34.4	5827.4
77	469.0	2.93	68.0	5895.4
78	475.5	2.88	104.3	5999.7
79	481.5	2.79	121.3	6121.0
80	484.0	2.68	108.4	6229.4
81	488.0	2.57	63.6	6293.0
82	491.5	2.50	57.0	6350.0
83	494.0	2.44	40.6	6390.6
84	498.5	2.39	65.1	6455.7

Table 2. continued

No.	Time (hours)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
85	505.5	2.30	97.2	6552.9
86	511.0	2.15	66.0	6618.9
87	515.5	2.04	60.0	6678.9
88	519.5	1.92	49.8	6728.7
89	529.5	1.82	25.2	6753.9
90	533.0	1.76	99.3	6853.2
91	537.0	1.48	28.5	6881.7
92	540.0	1.39	23.7	6905.4
93	549.0	1.30	70.6	6976.0
94	560.0	0.99	50.2	7026.2
95	567.0	0.69	30.0	7056.2
96	583.0	0.45	30.4	7086.6
97	589.0	0.14	9.8	7096.4
98	595.0	0.01	10.2	7106.6
99	600.5	-0.14	8.5	7115.1
100	604.0	-0.29	6.6	7121.7

Figs. 7 and 8 illustrate the sulphur isotope fractionation and kinetics for experiment 1.

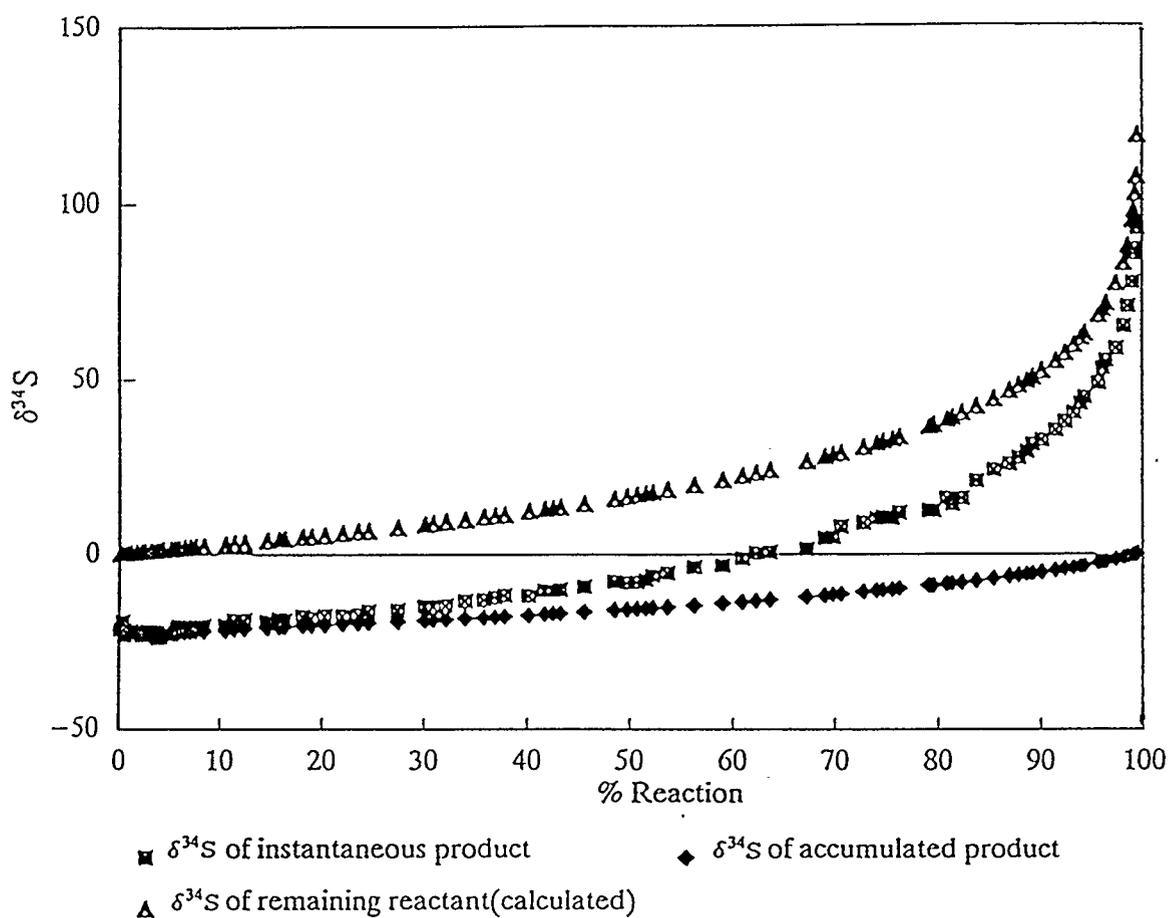


Figure 7: Isotope fractionation for experiment 1.

Reduction of sulphate with  $\text{HI-H}_3\text{PO}_2\text{-HCl}$

at 25°C.

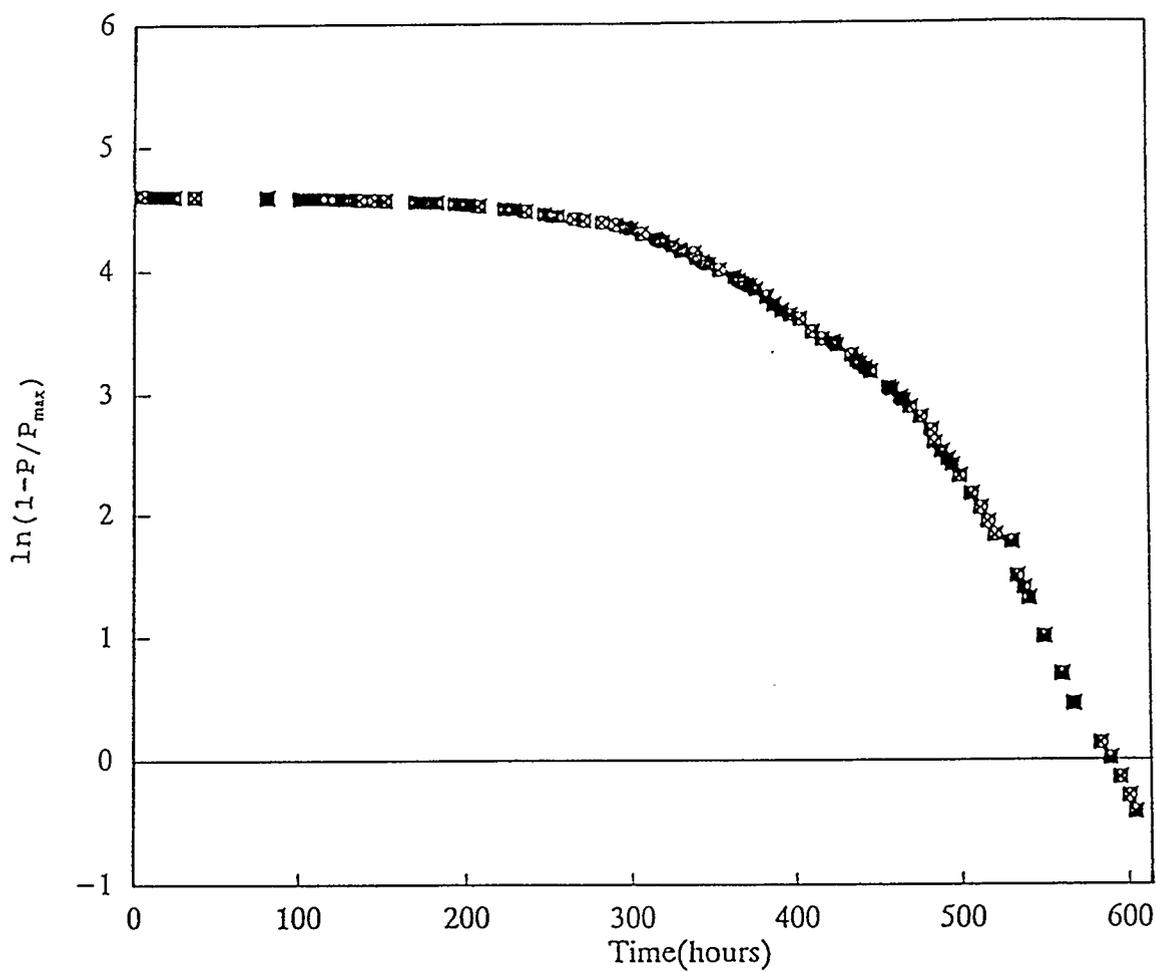


Figure 8: Kinetics for experiment 1. Reduction of sulphate with HI-H<sub>3</sub>PO<sub>2</sub>-HCl at 25°C.

Table 3. Sulphate reduction with Thode reduction mixture at 100°C.

No.	Reaction Time (%)	Time (min.)	$\delta^{34}\text{S}$ (‰)				$k_{32}/k_{34}$ app./acc.
			$(\text{H}_2\text{S})_{\text{M}}$	$(\text{SO}_4^{2-})_{\text{M}}$	$(\text{SO}_4^{2-})_{\text{C}}$	$(\text{H}_2\text{S})_{\text{A}}$	
1	7.71	0	-18.5	1.33	-18.52	/1.020	
2	11.30	5	-16.9		2.07	-18.01	/1.0195
3	16.87	10	-16.3		3.30	-17.44	n.d. /1.020
4	20.89	15	-15.4		4.25	-17.04	/1.0195
5	23.08	30	-15.0	4.6	4.79	-16.84	1.020/1.0196
6	26.16	50	-13.7		5.56	-16.47	/1.0195
7	29.73	55	-11.9	8.5	6.45	-15.92	1.021/1.0195
8	33.02	62	-11.3		7.33	-15.46	/1.0195
9	35.01	68	-10.5	9.5	7.87	-15.18	1.020/1.0195
10	37.28	76	-10.3		8.53	-14.88	/1.019
11	39.27	83	-9.9		9.13	-14.63	/1.019
12	41.06	93	-9.2	10.9	9.69	-14.39	1.020/1.020
13	42.22	103	-8.6		10.05	-14.23	/1.0194
14	43.51	115	-7.8		10.46	-14.04	/1.019
15	45.19	123	-7.7	12.9	11.02	-13.81	1.021/1.0205
16	46.90	134	-7.4		11.61	-13.57	/1.0195
17	48.81	142	-6.0		12.27	-13.28	/1.0195
18	50.55	154	-5.2	15.2	12.89	-13.00	1.021/1.019
19	52.47	165	-4.5		13.59	-12.69	/1.019
20	54.20	178	-3.9		14.25	-12.41	/1.019
21	56.26	190	-2.8		15.06	-12.06	/1.019

Table 3. continued

No.	Reaction Time (%)	Time (min.)	$\delta^{34}\text{S}$ (‰)				$k_{32}/k_{34}$ app./acc.
			$(\text{H}_2\text{S})_{\text{M}}$	$(\text{SO}_4^{2-})_{\text{M}}$	$(\text{SO}_4^{2-})_{\text{C}}$	$(\text{H}_2\text{S})_{\text{A}}$	
22	57.50	209	-2.0	16.5	15.55	-11.8	1.019/1.019
23	58.29	230	-1.7		15.88	-11.7	/1.019
24	59.10	260	-1.5		16.22	-11.57	/1.019
25	59.96	301	-0.9		16.59	-11.41	n.d./1.019
26	61.23	406	-0.8	18.0	17.16	-11.19	1.019/1.019
27	61.90	503	-0.2		17.46	-11.07	/1.019
28	62.49	621	0.2	19.7	17.74	-10.97	1.019/1.0186
29	63.14	746	0.9		18.03	-10.85	/1.019
30	64.24	1256	1.1	21.5	18.56	-10.64	1.020/1.019
31	64.81	1425	1.3		18.83	-10.54	/1.019
32	65.59	1848	2.1		19.21	-10.38	/1.019
33	68.85	2712	3.1	24.1	20.90	-9.75	1.021/1.019
34	71.90	3419	5.1		22.61	-9.11	/1.019
35	74.40	4125	7.9		24.05	-8.55	/1.0185
36	76.94	4887	10.8	33.7	25.51	-7.91	1.023/1.0185

M: measured value; C: calculated value; A: accumulated value(calculated);

n.d.: not determined;

Table 4. Sulphate reduction with Thode reduction mixture at 100°C

Kinetics				
No.	Time (min.)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
1	0	4.53	114.7	114.7
2	5	4.49	53.5	168.2
3	10	4.42	82.8	251.0
4	15	4.37	59.9	310.9
5	30	4.34	32.5	343.4
6	50	4.30	45.9	389.3
7	55	4.25	53.1	442.4
8	62	4.20	49.0	491.4
9	68	4.17	29.5	520.9
10	76	4.14	33.8	554.7
11	83	4.11	29.7	584.4
12	93	4.08	26.6	611.0
13	103	4.06	17.2	628.2
14	115	4.03	19.3	647.5
15	123	4.00	25.0	672.5
16	134	3.97	25.3	697.8
17	142	3.94	28.5	726.3
18	154	3.90	25.9	752.2
19	165	3.86	28.5	780.7
20	178	3.82	25.8	806.5
21	190	3.78	30.7	837.2
22	209	3.75	18.4	855.6

Table 4. continued

No.	Time (min.)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
23	230	3.73	11.8	867.4
24	260	3.71	12.0	879.4
25	301	3.69	12.8	892.2
26	406	3.66	18.9	911.1
27	503	3.64	9.9	921.0
28	621	3.63	8.9	929.9
29	746	3.61	9.6	939.5
30	1256	3.58	16.4	955.9
31	1425	3.56	8.4	964.3
32	1848	3.54	11.7	976.0
33	2712	3.44	48.5	1024.5
34	3419	3.34	45.4	1069.9
35	4125	3.24	37.1	1107.0
36	4887	3.14	37.8	1144.8

Figs. 9 and 10 illustrate sulphur isotope fractionation and kinetics for experiment 2.

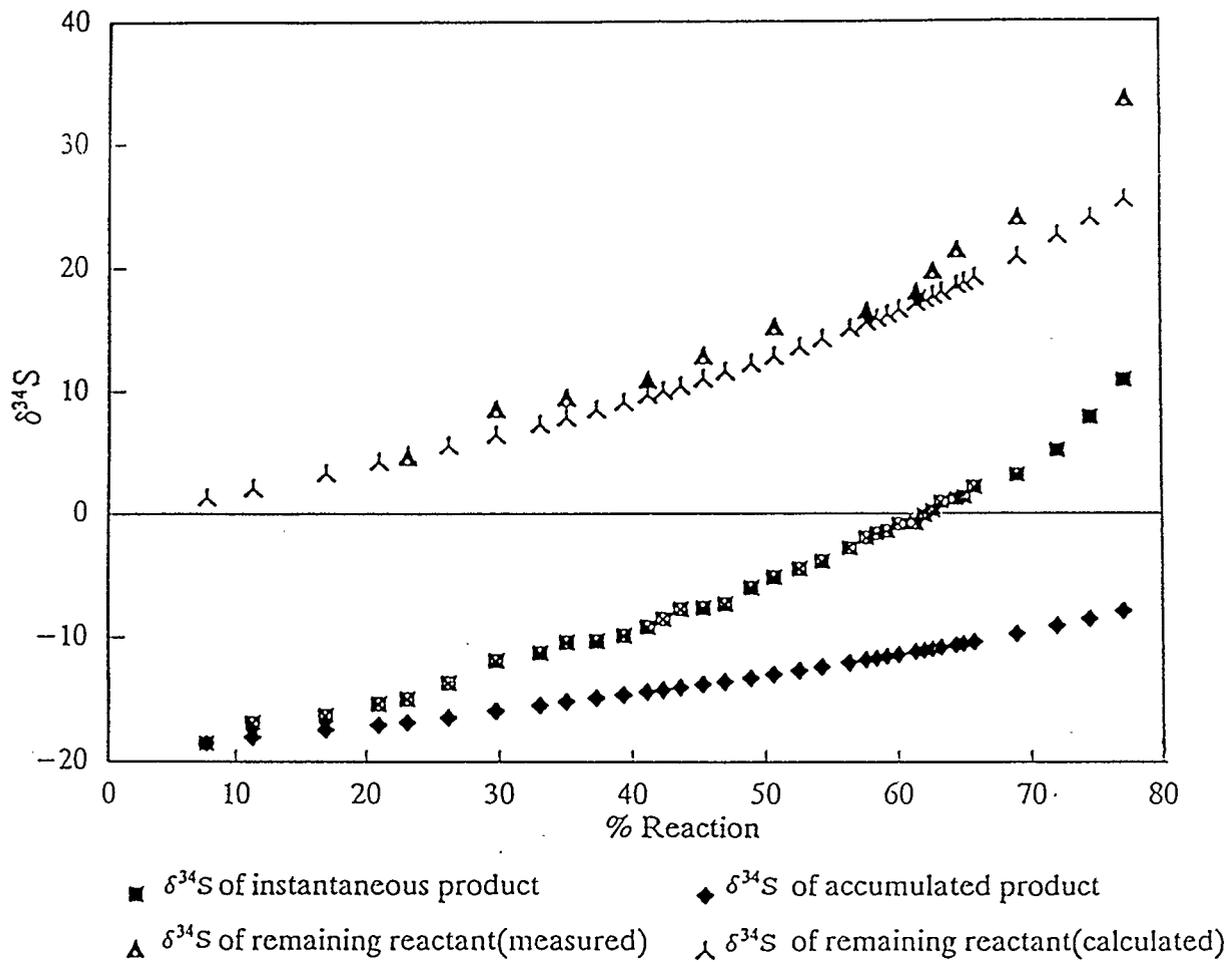


Figure 9: Isotope fractionation for experiment 2. Sulphate reduction with HI-H<sub>3</sub>PO<sub>2</sub>-HCl at 100°C.

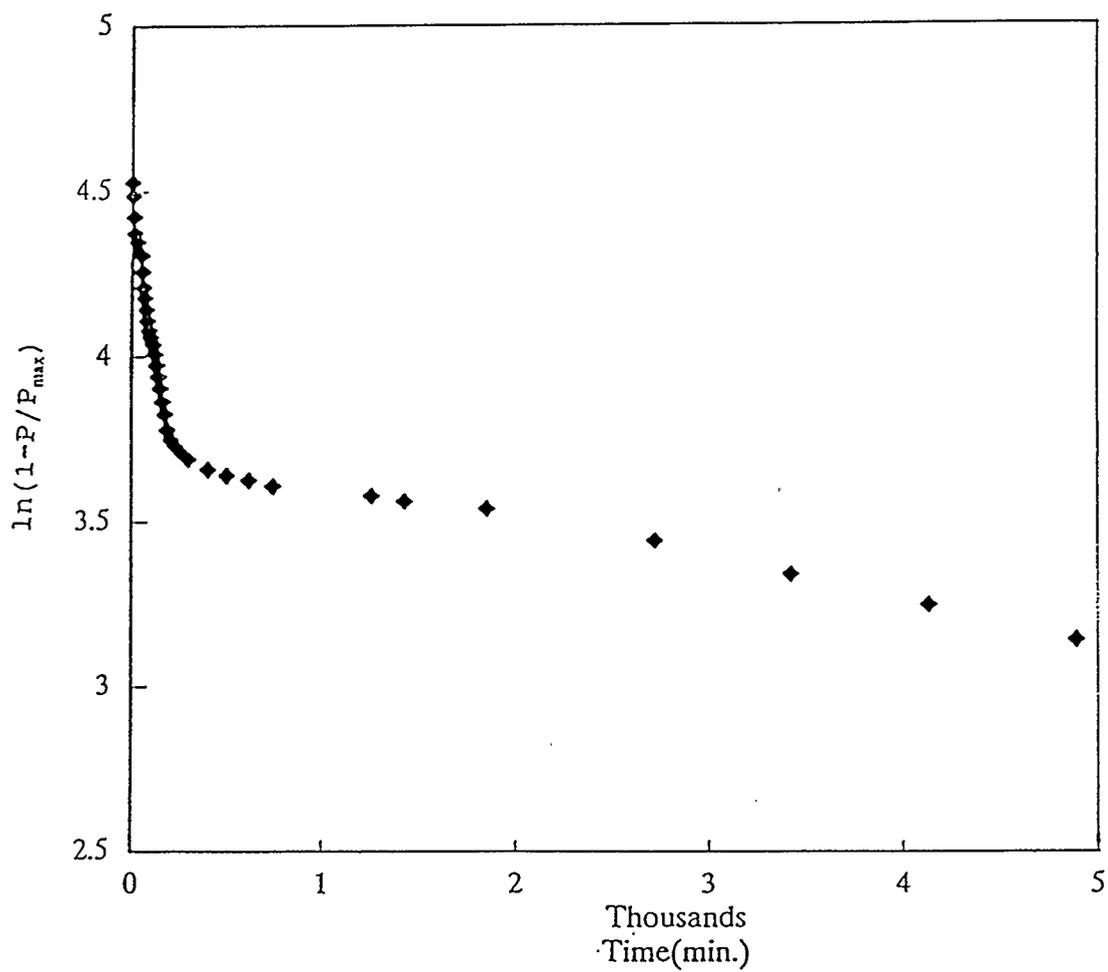


Figure 10: Kinetics for experiment 2. Sulphate reduction with  $\text{HI-H}_3\text{PO}_2\text{-HCl}$  at  $100^\circ\text{C}$ .

Table 5. Sulphate reduction using Thode reduction mixture at 65°C. Isotope fractionation

No.	Reaction Time (%)	Time (hours)	$\delta^{34}\text{S}$ (‰)				$k_{32}/k_{34}$ app./acc.
			$(\text{H}_2\text{S})_M$	$(\text{SO}_4^{2-})_M$	$(\text{SO}_4^{2-})_C$	$(\text{H}_2\text{S})_A$	
1	0.00	0.0			0.38		
2	2.51	5.5	-20.3		0.92	-20.3	/1.021
3	5.19	9.5	-21.5	1.5	1.57	-20.9	1.024/1.023
4	7.51	14.0	-21.1	1.5	2.15	-21.0	1.023/1.0225
5	10.48	24.3	-20.8	2.1	2.93	-20.9	1.023/1.0225
6	14.02	33.3	-19.7		3.88	-20.6	n.d./1.0225
7	21.13	44.3	-17.9		5.89	-19.7	/1.023
8	23.44	48.6	-16.0	4.8	6.71	-19.3	1.021/1.0226
9	32.18	51.4	-13.3	9.8	9.38	-17.7	1.023/1.022
10	36.84	54.4	-11.1	11.1	10.52	-16.9	1.022/1.022
11	42.15	56.1	-9.5		12.37	-15.9	/1.022
12	45.78	58.6	-8.9		13.67	-15.4	n.d./1.022
13	55.32	62.1	-4.4	19.9	17.60	-13.5	1.024/1.021
14	62.82	68.3	1.4		20.93	-11.7	/1.021
15	68.89	73.1	6.9	29.6	23.73	-10.1	1.023/1.020
16	74.22	76.8	11.1		26.43	-8.5	/1.019
17	79.90	80.8	17.1	37.0	31.68	-6.3	1.020/1.015
18	89.56	97.8	38.7		43.04	-1.8	/1.007
19	91.16	110.8	89.0		84.34	-0.2	/1.001

M: measured value; C: calculated value; A: accumulated value(calculated);

Table 6. Sulphate reduction using Thode reduction mixture at 65°C

Kinetic

No.	Time (hours)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
1	0.0	4.61	0.0	0.0
2	5.5	4.58	20.9	20.9
3	9.5	4.55	22.3	43.2
4	14.0	4.53	19.2	62.4
5	24.3	4.49	24.7	87.1
6	33.3	4.45	29.4	116.5
7	44.3	4.37	59.1	175.6
8	48.6	4.34	19.1	194.7
9	51.4	4.22	72.6	267.3
10	54.4	4.15	38.7	306.0
11	56.1	4.06	44.1	350.2
12	58.6	3.99	30.2	380.4
13	62.1	3.80	79.2	459.6
14	68.3	3.62	62.3	521.9
15	73.1	3.44	50.4	572.3
16	76.8	3.25	44.3	616.6
17	80.8	3.00	47.2	663.8
18	97.8	2.35	80.2	744.0
19	110.8	2.18	13.3	757.3

Figure 11 and 12 illustrate sulphur isotope fractionation and kinetics for experiment 3.

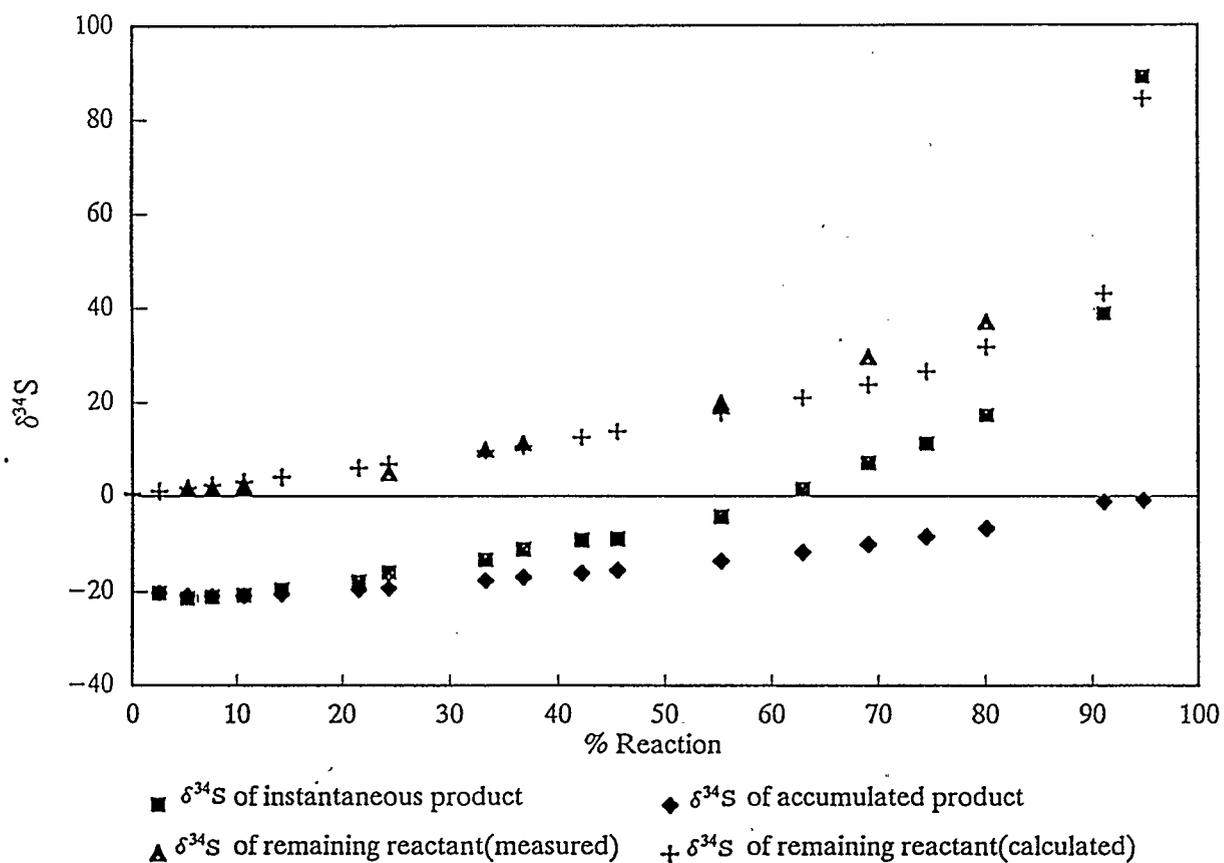


Figure 11: Isotope fractionation for experiment 3. Sulphate reduction with HI-H<sub>3</sub>PO<sub>2</sub>-HCl at 65°C.

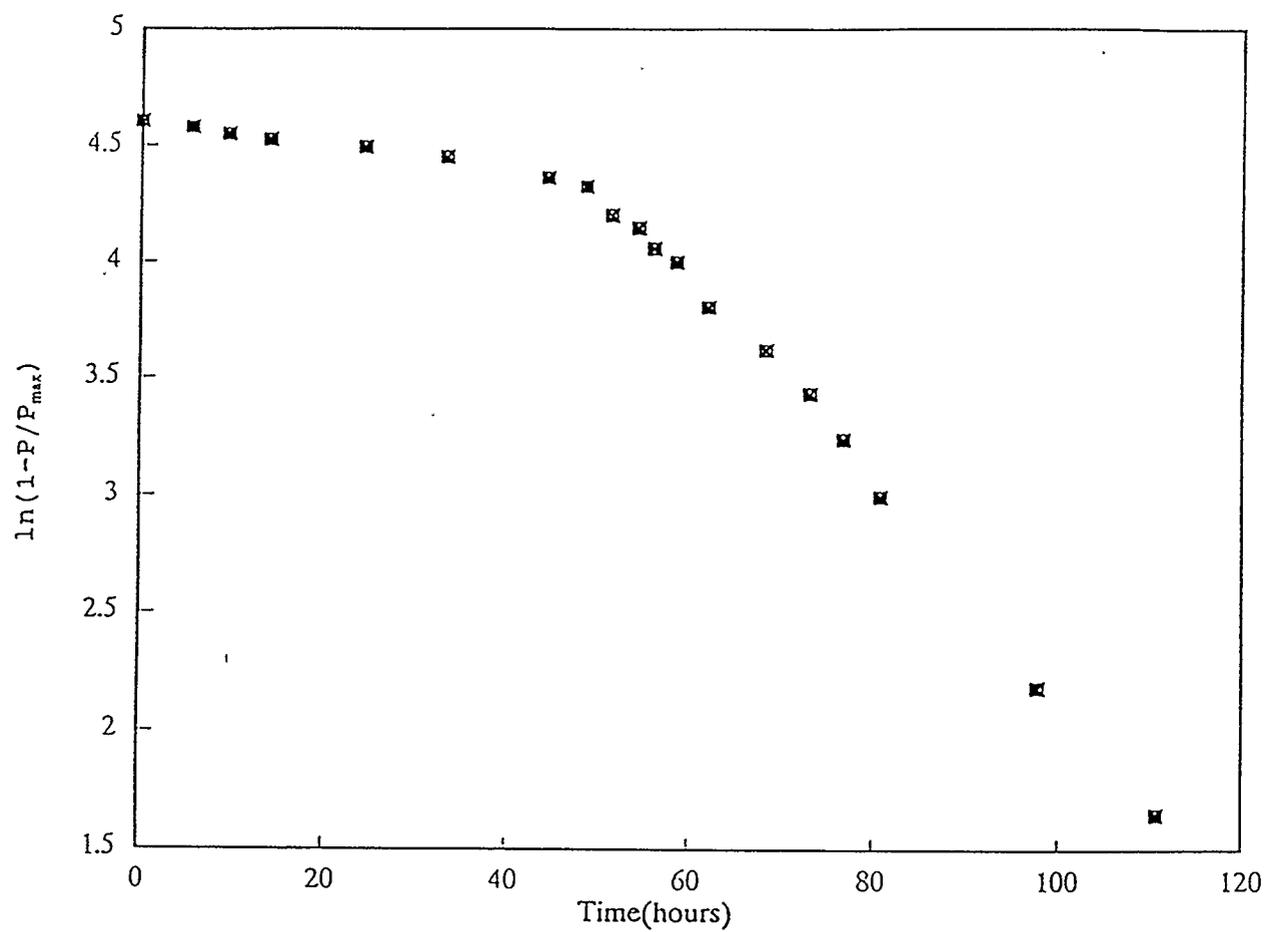


Figure 12: Kinetics for experiment 3. Sulphate reduction with HI-H<sub>3</sub>PO<sub>2</sub>-HCl at 65°C.

4.2 SULPHATE REDUCTION AT LOWER pH USING  $\text{SnCl}_2$ 

Two experiments were conducted, one at 25°C and the other at 130°C with 1.5g  $\text{H}_2\text{SO}_4$  and 10g  $\text{SnCl}_2$  powder added to 15ml of 0.14M and 0.37M  $\text{Na}_2\text{SO}_4$  respectively. No reduction was observed in the experiment at 25°C. Even at the higher temperature, the reduction proceeded very slowly. The experimental results are given in Tables 7 and 8.

Table 7. Sulphate reduction using  $\text{SnCl}_2$  at 130°C.

Isotope fractionation						
No.	Reaction(%)	Time (hours)	$\delta^{34}\text{S}$			$k_{32}/k_{34}$
			$(\text{H}_2\text{S})_M$	$(\text{SO}_4^{2-})_M$	$(\text{H}_2\text{S})_A$	app./acc.
1	1.50	0.0	-11.3	0.7	-11.30	1.012
2	1.72	11.8	-10.6	1.4	-11.21	1.012/1.012
3	2.29	29.9	-10.0	0.9	-10.91	1.011
4	2.71	57.7	-8.6		-10.55	
5	2.99	81.2	-6.5	1.1	-10.16	1.008/1.0104
6	3.54	127.7	-6.7	0.9	-9.63	1.008
7	3.89	271.2	-9.1	0.8	-9.58	1.010/1.010

M: measured value; C: calculated value; A: accumulated value (calculated);  
app.: approximate; acc.: accurate value;

Table 8. Sulphate reduction with  $\text{SnCl}_2$  at  $130^\circ\text{C}$ .

Kinetics				
No.	Time (hours)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
1	0.0	1.99	20.9	20.9
2	11.8	1.99	3.2	24.1
3	29.9	1.99	7.9	32.0
4	57.7	1.99	5.8	37.8
5	81.2	1.99	4.0	41.8
6	127.7	1.98	7.6	49.4
7	271.2	1.98	5.0	54.4

Figs. 13 and 14 illustrate sulphur isotope fractionation and kinetics for sulphate reduction by  $\text{SnCl}_2$  at  $130^\circ\text{C}$ .

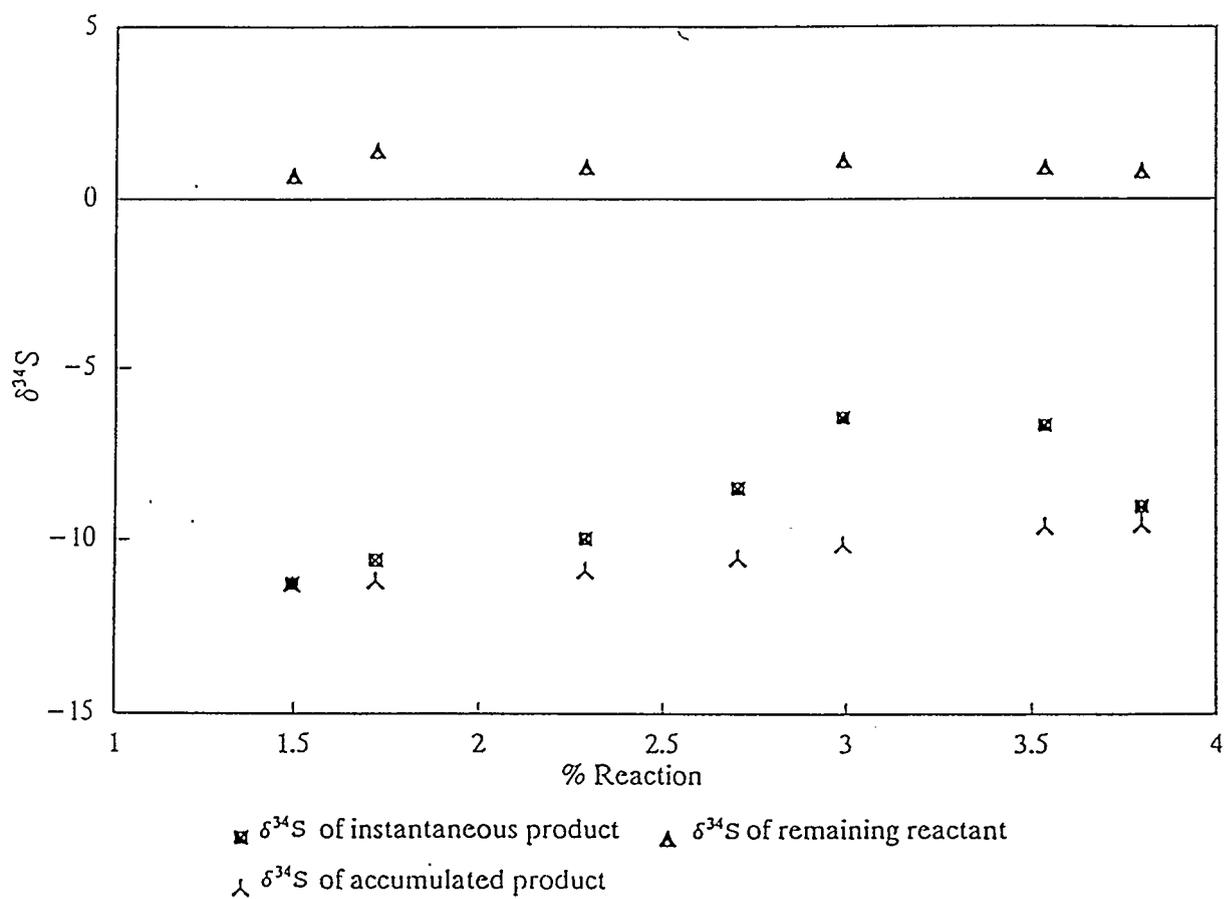


Figure 13: Isotope fractionation during sulphate reduction by  $\text{SnCl}_2$  at  $130^\circ\text{C}$ .

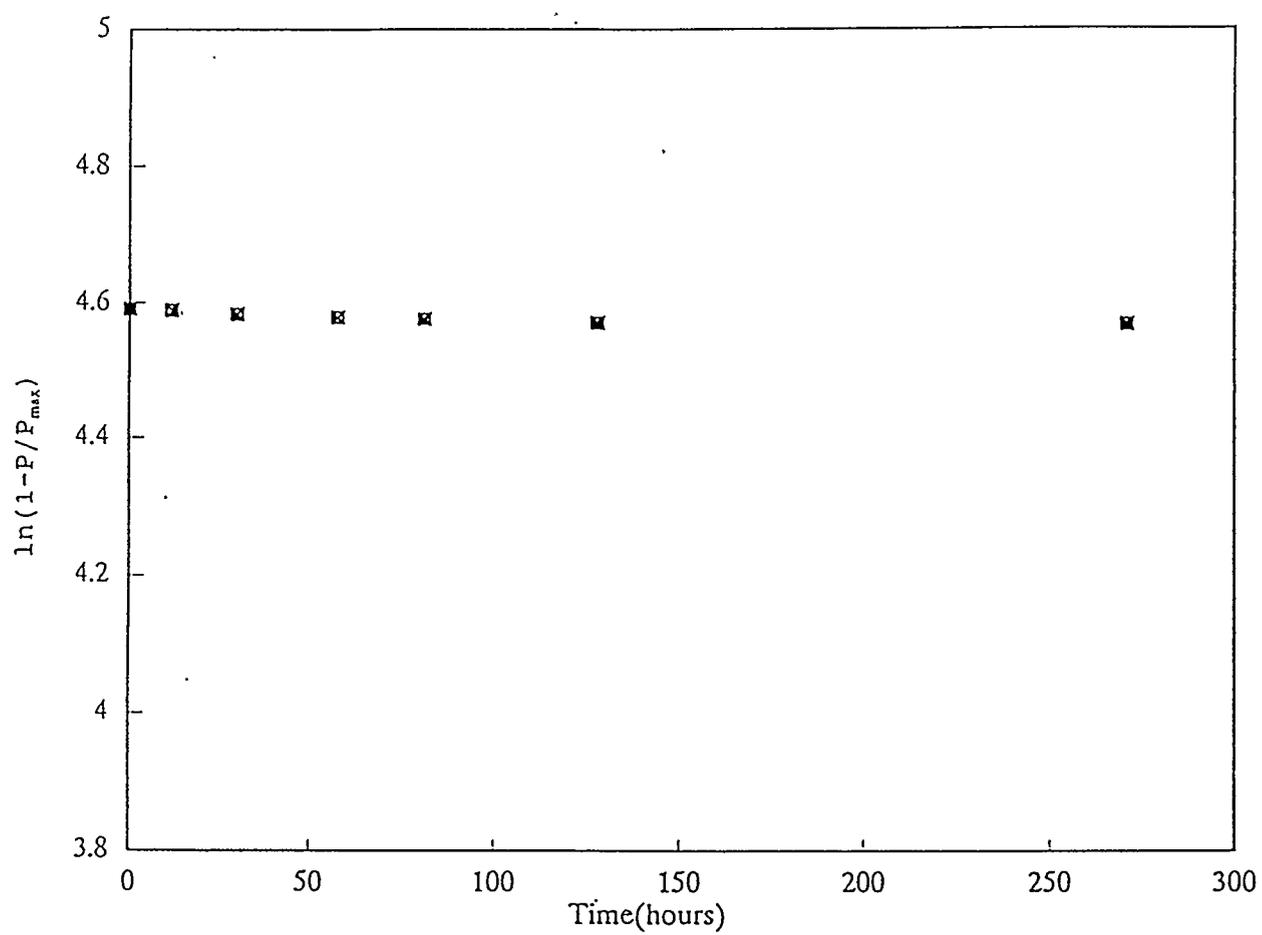


Figure 14: Kinetics during sulphate reduction  
by  $\text{SnCl}_2$  at  $130^\circ\text{C}$ .

4.3 SULPHITE REDUCTION USING A  $\text{SnCl}_2$  - ASCORBIC ACID MIXTURE

One sulphite reduction was carried out at room temperature with 57ml 0.11 M  $\text{SO}_3^{2-}$ , 35g  $\text{SnCl}_2$  and 2.5g ascorbic acid. After 18 days, only 5 samples were collected and the experiment was terminated. The isotope and kinetic data are given in Tables 9 and 10.

Table 9.  $\text{SO}_3^{2-}$  reduction by  $\text{SnCl}_2$  and ascorbic acid at 25°C.  
Isotope Fractionation

No.	Reaction(%)	Time (day)	$\delta^{34}\text{S}$ (‰)			$k_{32}/k_{34}$ app./acc.
			$(\text{H}_2\text{S})_M$	$(\text{SO}_4^{2-})_C$	$(\text{H}_2\text{S})_A$	
1	0.50	0.0	-8.1	0.04	-8.1	1.008
2	0.85	2.5	-8.5	0.08	-8.3	1.009/1.009
3	1.19	7.5	-10.6	0.12	-8.9	1.011/1.009
4	1.87	10.4	-12.1	0.22	-10.1	1.012/1.0104
5	3.24	14.4	-12.8	0.43	-11.2	1.013/1.0115

M: measured value; C: calculated value; A: accumulated value(calculated);  
app.: approximate; acc.: accurate;

Table 10.  $\text{SO}_3^{2-}$  reduction by  $\text{SnCl}_2$  and ascorbic acid: Kinetics

No.	Time (days)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
1	4.0	4.60	7.9	7.9
2	6.5	4.60	5.5	13.4
3	11.5	4.59	5.4	18.8
4	14.4	4.59	10.7	29.5
5	18.4	4.57	21.5	51.0

The isotope data are plotted in Fig.15.

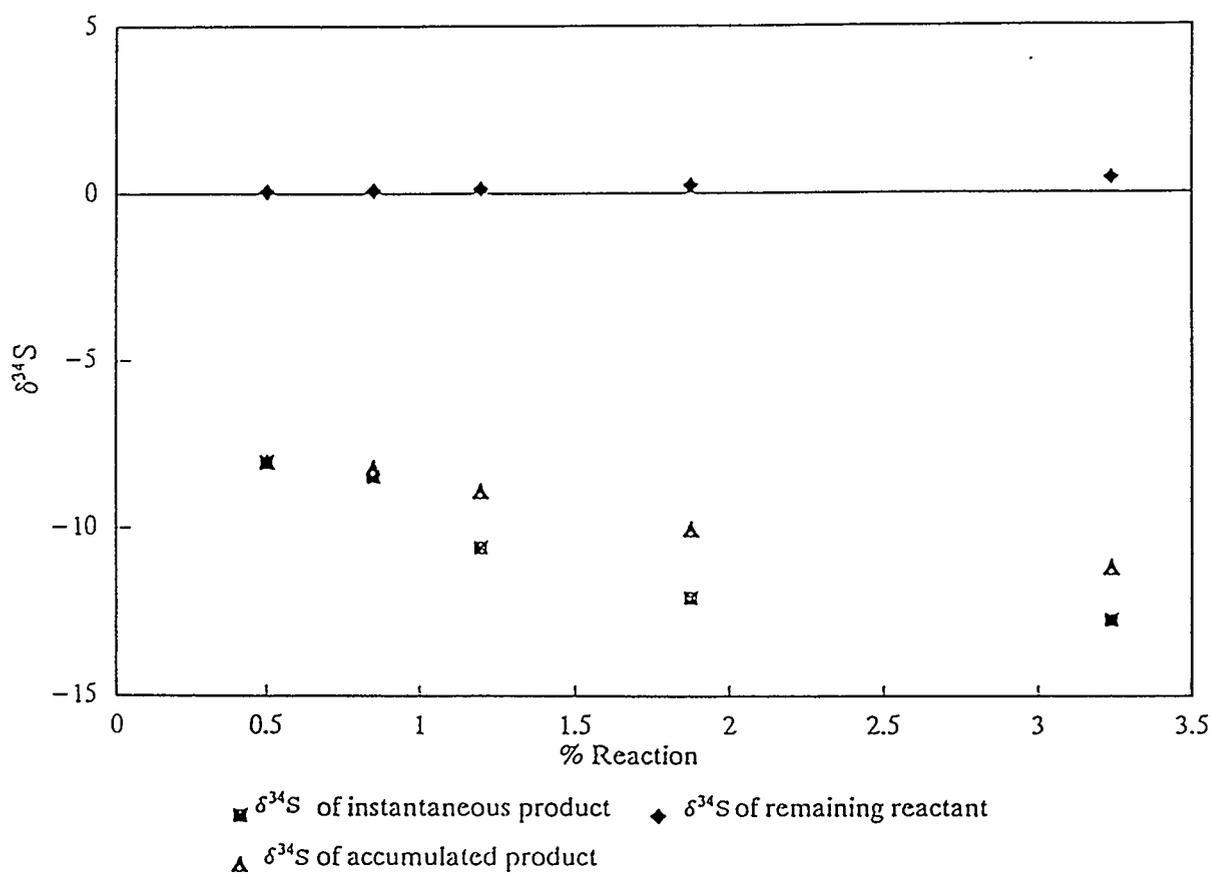


Figure 15: Isotope fractionation during  $\text{SO}_3^{2-}$  reduction with the mixture of  $\text{SnCl}_2$  and ascorbic acid at  $25^\circ\text{C}$

#### 4.4 SULPHITE REDUCTION USING $\text{SnCl}_2$

One sulphite reduction was carried out with 40ml of 0.6M  $\text{SO}_3^{2-}$  and 30g  $\text{SnCl}_2$ . The temperature of 60°C was chosen because of very slow reaction at room temperature. Isotope fractionation and kinetic data are given in Tables 11 and 12.

Table 11.  $\text{SO}_3^{2-}$  reduction with  $\text{SnCl}_2$ ,  $60^\circ\text{C}$ : Isotope fractionation

No.	Reaction(%)	Time (hour)	$\delta^{34}\text{S}$ (‰)			$k_{32}/k_{34}$
			$(\text{H}_2\text{S})_M$	$(\text{SO}_4^{2-})_C$	$(\text{H}_2\text{S})_A$	app./acc.
1	1.5	19.0	-1.6	0.06	-1.6	1.002
2	2.1	24.2	-1.6	0.08	-1.6	1.002/1.0015
3	2.3	31.5	-2.1	0.08	-1.6	1.002
4	3.0	46.0	-1.5	0.11	-1.6	1.002/1.0015
5	3.4	51.6	-1.2	0.12	-1.6	1.001
6	4.0	56.9	-1.6	0.14	-1.6	1.002/1.002
7	4.8	68.5	-1.2	0.17	-1.5	1.001
8	5.1	75.5	-0.7	0.18	-1.5	1.001
9	5.8	92.1	-0.8	0.20	-1.4	1.001
10	6.3	105.4	-1.2	0.22	-1.4	1.001
11	7.0	120.0	-1.0	0.24	-1.3	1.001/1.001
12	7.9	140.5	-1.3	0.27	-1.3	1.002
13	8.4	150.3	-1.3	0.29	-1.3	1.002
14	8.9	164.9	-1.4	0.31	-1.3	1.002
15	9.2	175.9	-1.0	0.32	-1.3	1.001
16	9.4	187.7	-0.6	0.33	-1.3	1.001
17	9.9	200.3	-0.7	0.34	-1.3	1.001
18	10.1	213.6	-0.7	0.35	-1.3	1.001/1.001
19	10.4	237.3	-1.0	0.36	-1.3	1.001
20	10.7	263.5	-1.2	0.37	-1.3	1.002
21	11.2	287.1	-1.0	0.39	-1.2	1.001

Table 11 continued

No.	Reaction(%)	Time (hour)	$\delta^{34}\text{S}$ (‰)			$k_{32}/k_{34}$
			$(\text{H}_2\text{S})_M$	$(\text{SO}_4^{2-})_C$	$(\text{H}_2\text{S})_A$	app./acc.
22	11.4	309.1	-1.1	0.39	-1.2	1.001
23	11.6	333.1	-1.0	0.40	-1.2	1.001
24	11.9	356.8	-0.5	0.41	-1.2	1.001/1.001

M: measured value; C: calculated value; A: accumulated value (calculated);

app.: approximate; acc.: accurate;

Table 12.  $\text{SO}_3^{2-}$  reduction with  $\text{SnCl}_2$ ,  $60^\circ\text{C}$ .

Kinetics				
No.	Time (hours)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
1	19.0	4.59	87.6	87.6
2	24.2	4.58	30.7	118.3
3	31.5	4.58	13.4	131.7
4	46.0	4.57	42.9	174.6
5	51.6	4.57	22.7	197.3
6	56.9	4.56	32.7	230.0
7	68.5	4.56	45.3	275.3
8	75.5	4.55	18.2	293.5
9	92.1	4.55	37.5	331.0
10	105.4	4.54	31.0	362.0
11	120.0	4.53	36.8	398.8
12	140.5	4.52	54.7	453.5
13	150.3	4.52	26.9	480.4
14	164.9	4.51	28.7	509.1
15	175.9	4.51	16.6	525.7
16	187.7	4.51	13.4	539.1
17	200.3	4.50	27.5	566.6
18	213.6	4.50	9.8	576.4
19	237.3	4.50	21.5	597.9
20	263.5	4.49	13.4	611.3
21	287.1	4.49	31.4	642.7

Table 12 continued

No.	Time (hours)	$\ln(1-P/P_{\max})$	Product (mg)	Accumulated Product (mg)
22	309.1	4.48	10.6	653.3
23	333.1	4.48	10.0	663.3
24	356.8	4.48	20.1	683.4

Figs. 16 and 17 illustrate sulphur isotope fractionation and kinetics for sulphite reduction by  $\text{SnCl}_2$  at  $60^\circ\text{C}$ .

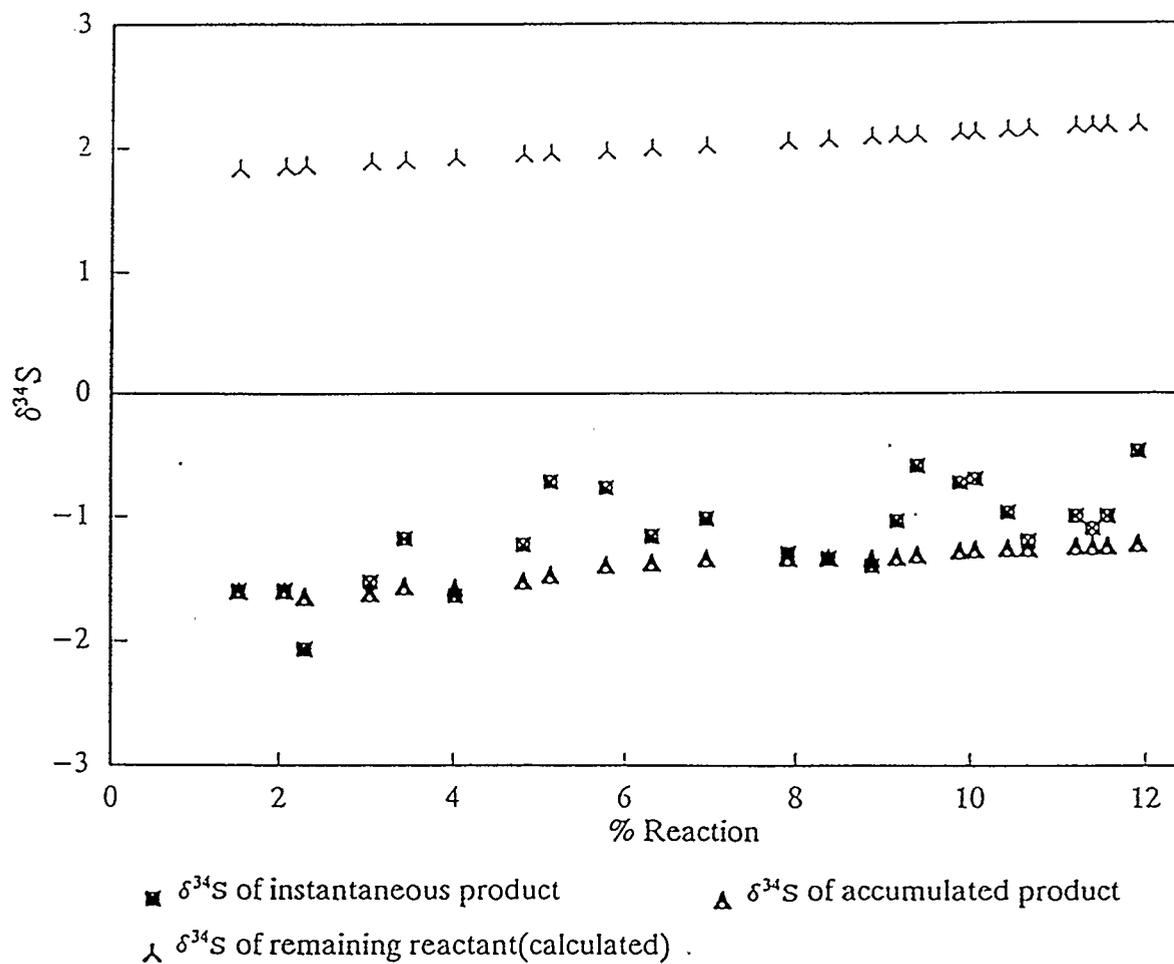


Figure 16: Isotope fractionation during  $\text{SO}_3^{2-}$  reduction with  $\text{SnCl}_2$  at  $60^\circ\text{C}$ .

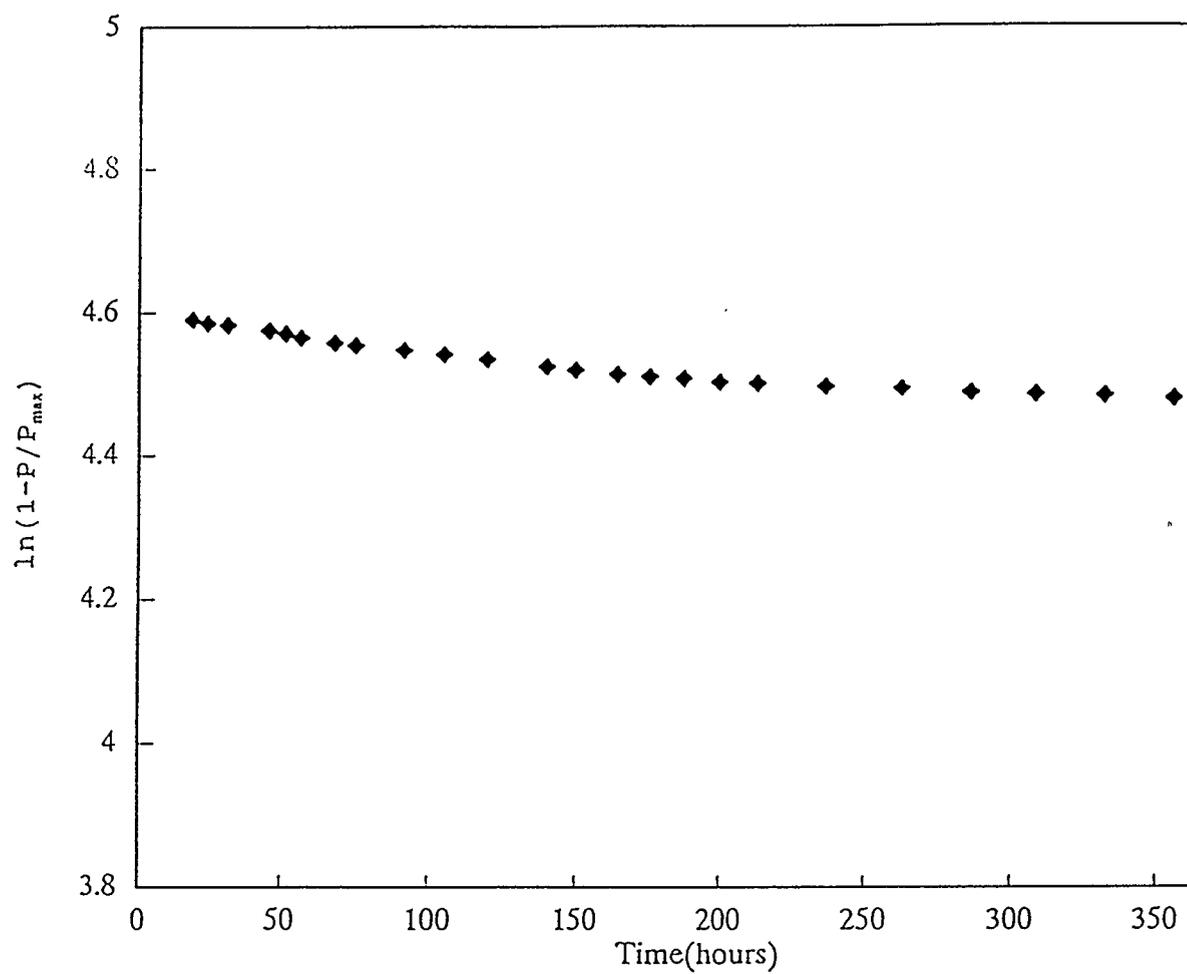


Figure 17: Kinetics during  $\text{SO}_3^{2-}$  reduction  
with  $\text{SnCl}_2$  at  $60^\circ\text{C}$ .

#### 4.5 SULPHITE REDUCTION USING THODE REDUCTION MIXTURE AND HI

In an internal report at McMaster University, MONSTER (1970) described the isotope fractionation obtained during chemical reduction of sulphite by HI to H<sub>2</sub>S. Up to 23% reduction of sodium sulphite was achieved. The average ratios of the isotope rate constants for two experiments at 0°C and 35°C were about 1.002. During the current study, Na<sub>2</sub>SO<sub>3</sub> reduction was attempted with the Thode H<sub>3</sub>PO<sub>2</sub>-HI-HCl mixture. After a few seconds, a yellow precipitate of elemental sulphur formed as reported by HARRISON and THODE (1957). An attempt was made to reduce sodium sulphite with HI alone. Elemental sulphur also formed in the reaction vessel although the process was much slower than when using the Thode reduction mixture. Because of this complication, data were not acquired.

## CHAPTER 5 Discussion

## 5.1 ERROR ANALYSIS

The experimental results presented in the previous chapter are consistent with the work done by others. However, theoretically calculated  $\delta^{34}\text{S}$  values of the remaining reactant do not agree very well with direct experimental measurements at high extents of reaction (70% reduction; e.g. Figures 9 and 11). Several factors can contribute to this discrepancy. Firstly,

$$M - \sum_i m_i$$

(where  $M$  is the number of moles of total sulphur,  $m_i$  is the number of moles of  $i^{\text{th}}$  sample) becomes small as the reaction nears completion. Errors in  $m_i$  accumulated during the course of the reaction especially when many samples were taken. Calculations for a given sample of  $\text{H}_2\text{S}$  product are subject to the errors of all previously collected samples. As the reaction nears the end, the  $\delta^{34}\text{S}$  values of unreacted reactant and instantaneous product change rapidly with extent of reaction. Therefore the error in measuring  $m_i$  and  $\sum m_i$  are very critical above 90 percent conversion. For example, in experiment 1,  $k_{32}/k_{34}$  values fell below 1.022 above 90 percent conversion. However if one equates the measured total

conversion of 99.34 to 100 percent by multiplying  $m_i$  by 1.006,  $k_{32}/k_{34}$  values increase above 1.022 as the reaction nears completion.

From the view point of stable isotope mass spectrometry, it is noted that there are larger uncertainties in the determination of the highly positive  $\delta^{34}\text{S}$  values for the product  $\text{H}_2\text{S}$  fractions collected near the end of the reduction. During the mass spectrometric measurements, the isotope composition of the sample is compared to that of a standard. If their  $\delta^{34}\text{S}$  values differ by say 10 ‰, then an uncertainty of  $\pm 0.1$  ‰ is readily achieved. However, if the difference is 100 ‰, then an uncertainty of  $\pm 0.5$  or even  $\pm 1$  ‰ is more appropriate even though the "noise" during a run may be less than  $\pm 0.1$  ‰. It is essentially a question of the "linearity" of  $\delta^{34}\text{S}$  determinations by the mass spectrometer. This can only be determined using gravimetric mixtures of separated isotopes. Although this has been done for some elements, it is not the case for sulphur.

The reduction reactor design was reasonably good and temperature fluctuations are minor compared to other errors. Although most water vapour was retained by the condenser, some did escape to the air at high temperature. This could be a problem if the isotope fractionation depended upon  $\text{SO}_4^{2-}/\text{SO}_3^{2-}$

concentration.

In summary, quoting  $k_{32}/k_{34}$  to 4 significant figures ( $\delta^{34}\text{S}$  to  $\pm 1\%$ ) is conservative at low percentage conversions but more realistic as the reaction nears 90 percent completion. Above 90 percent conversion, the errors in gravimetric data rather than stable isotope mass spectrometry increase the error in  $k_{32}/k_{34}$  considerably.

## 5.2 SULPHUR ISOTOPE FRACTIONATION DURING $\text{SO}_4^{2-}$ REDUCTION

### 5.2-1 Reduction Rate Constant

The temperature dependence of the rate constants for sulphate reduction by  $\text{HI-H}_3\text{PO}_2\text{-HCl}$  is shown in Fig. 18. This dependence can be described by the equation:

$$\log k = 1345.306/T - 9.135 \quad 5.1$$

It is noted that there is a sulphate concentration influence on the reaction order. The first order rate constant with respect to  $[\text{SO}_4^{2-}]$  increased radically to a new steady value when  $[\text{SO}_4^{2-}]$  decreased below 0.22M (Fig. 12).

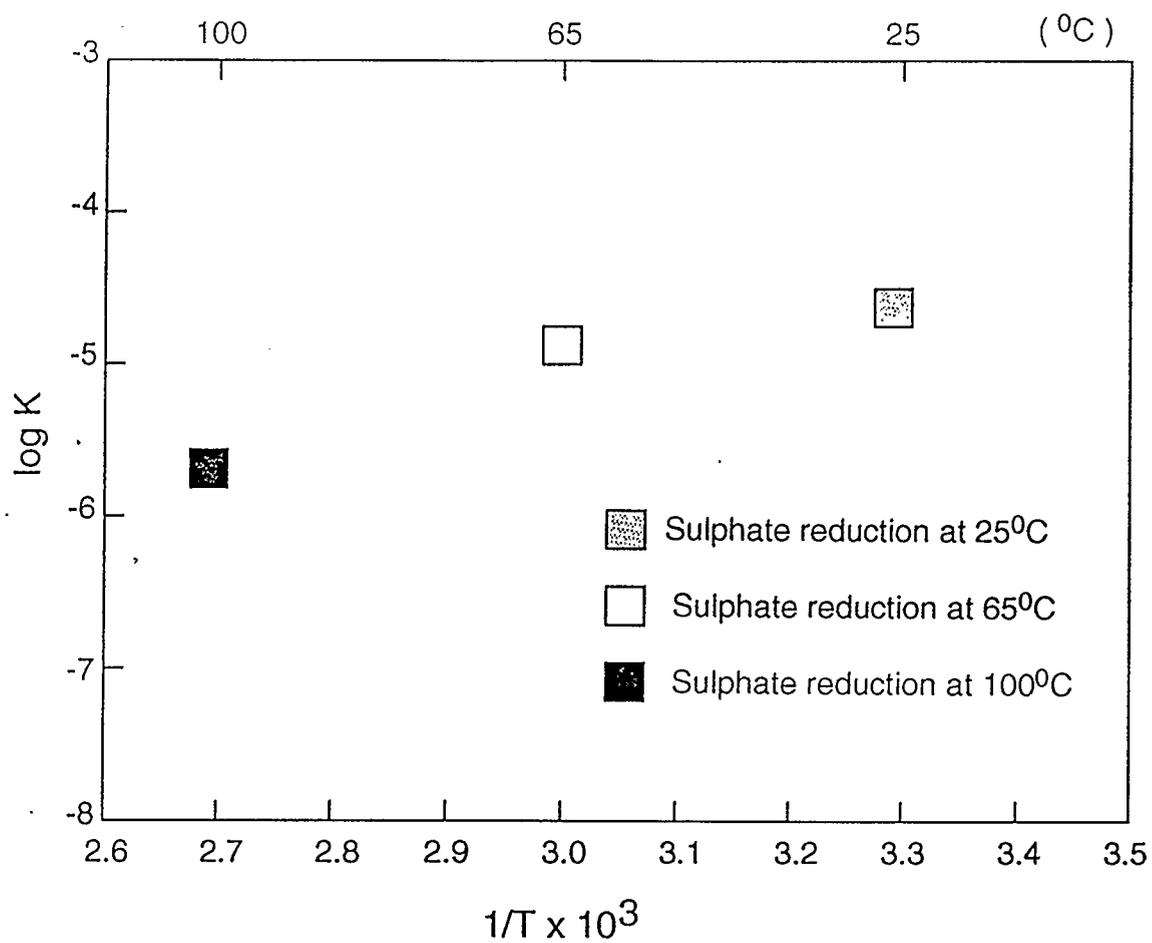


Figure 18: Temperature dependence of the rate constant for sulphate reduction by HI-H<sub>3</sub>PO<sub>2</sub>-HCl.

5.2-2 Sulphate Reduction by HI-H<sub>3</sub>PO<sub>2</sub>-HCl

In the experiment at 25°C,  $\delta^{34}\text{S}$  values of remaining reactant were not directly measured and calculated values were used to determine  $k_{32}/k_{34}$  from equation [2.22] (Table 1). More accurate  $k_{32}/k_{34}$  values based on the exact expression and data for the H<sub>2</sub>S product based on equation [2.17] are also given at some points in the reaction. The approximate and exact values agree throughout most the reaction, but there are considerable departures above 90% reduction. It is interesting to note the range of  $\delta^{34}\text{S}$  values. The remaining reactant reached +118 ‰ compared to the starting point at +0.35 ‰ and the instantaneous product measured was +92 ‰ when 99% sulphate had reacted. Usually the calculated  $\delta^{34}\text{S}$  values were lower than those experimental determined upon completion of the reaction.

It is seen that the value found by HARRISON and THODE (1957) of  $1.022 \pm 0.001$  for 10 percent conversion at 25°C is in agreement to that found with conversions of up to 90 percent in the current study (Table 13).

Table 13. Temperature dependence of  $k_{32}/k_{34}$  values during sulphate reduction by HI-H<sub>3</sub>PO<sub>2</sub>-HCl. (x) is the number of samples removed in the conversion interval.

Conversion Interval (%)	Average $k_{32}/k_{34}$	Average $k_{32}/k_{34}$	Average $k_{32}/k_{34}$
	25°C	65°C	100°C
0 -- 10	1.0237 (28)	1.0223 (4)	1.020 (1)
11 -- 20	1.0235 (8)	1.0225 (1)	1.0197 (3)
21 -- 30	1.0240 (5)	1.0228 (2)	1.0195 (3)
31 --40	1.0240 (7)	1.0220 (2)	1.0193 (4)
41 -- 50	1.0242 (6)	1.022 (2)	1.0196 (7)
51 -- 60	1.0241 (7)	1.021 (1)	1.0191 (7)
61 -- 70	1.0234 (5)	1.0205 (2)	1.0190 (8)
71 -- 80	1.0219 (8)	1.017 (2)	1.0187 (3)
81 -- 90	1.0210 (10)	1.007 (1)	
91 --100	1.0172 (16)	1.001 (1)	

It is seen in Table 13 that  $k_{32}/k_{34}$  decreases with temperature as expected theoretically but the dependence is small, being of the same order as the reproducibility of measurements.

### 5.2-3 $\text{SO}_4^{2-}$ Reduction With Stannous Chloride

In the experiment of sulphate reduction by  $\text{SnCl}_2$ , only 4% conversion was realized over a longer period than that required for completion of the reduction by  $\text{HI-H}_3\text{PO}_2\text{-HCl}$ . Nevertheless, kinetic isotope fractionation was observed with the average  $k_{32}/k_{34}$  being  $1.014 \pm 0.0023$ .

## 5.3 SULPHUR ISOTOPE FRACTIONATION DURING $\text{SO}_3^{2-}$ REDUCTION

### 5.3-1 Sulphur Isotope Fractionation during $\text{SO}_3^{2-}$ Reduction With The Mixture Of $\text{SnCl}_2$ And Ascorbic Acid

The overall sulphur isotope fractionation during sulphite reduction is small comparing with that of sulphate reduction. An average  $k_{32}/k_{34}$  of 1.0106 was found. It was observed that the isotope fractionation increased as the reaction proceeded. This suggests that two or more steps were competing for rate control and at least one had a small  $k_{32}/k_{34}$  value. Perhaps the  $k_{32}/k_{34}$  was tending towards a steady-state value consistent with S-O rupture being rate controlling. This possibility should be tested with further experiments.

### 5.3-2 Sulphur Isotope Fractionation during $\text{SO}_3^{2-}$ Reduction With $\text{SnCl}_2$ At $60^\circ\text{C}$

The extent of conversion of  $\text{SO}_3^{2-}$  to  $\text{H}_2\text{S}$  using  $\text{SnCl}_2$  at  $60^\circ\text{C}$  was only 12 percent in two weeks. In marked contrast to other experiments, the kinetic isotope effects were very small with  $k_{32}/k_{34}$  averaging 1.001. This means that a step in the reaction with very little sulphur isotope selectivity controlled the reaction.

### 5.3-3 $\text{SO}_3^{2-}$ Reduction With HI

This experiment failed because of elemental sulphur formation. A possible remedy might be to invoke a much stronger  $\text{N}_2$  flow and possibly flush out  $\text{H}_2\text{S}$  before it is oxidized to form elemental sulphur. However,  $\text{SO}_2$  might also be evolved under stronger  $\text{N}_2$  flow. Further, a reaction other than  $\text{H}_2\text{S}$  oxidation may be responsible for  $\text{S}^0$  formation.

## 5.4 COMPARISON OF EXPERIMENTAL RESULTS FOR SULPHATE REDUCTION WITH THEORETICAL MODELS

Since very little is known about the nature of the activated complex, the ratio of the isotope rate constants can not be calculated specifically. It is necessary to consider models which might approximate the physical situations.

HARRISON and THODE (1957) calculated two extreme values for the ratio of  $k_{32}/k_{34}$  during chemical sulphate reduction. The lower limit (high temperature) assumed that the activated complex resembled the starting material. Therefore there is no stretching of the S-O bond in the transition state. Then  $k_{32}/k_{34} = [m_2^*/m_1^*]$ . The  $k_{32}/k_{34}$  was evaluated as 1.010. The upper limit was made by assuming that the activated complex resembled  $\text{SO}_3^{2-}$  which is a postulated intermediate in the reaction. On this basis, the  $k_{32}/k_{34}$  was evaluated as 1.035 at 25°C. Thus HARRISON and THODE concluded that the activated complex was a structure intermediate to  $\text{SO}_4^{2-}$  and  $\text{SO}_3^{2-}$ .

As summarized in Chapter 2, REES and THODE (1965) considered another model for the reduction of  $\text{Se}^{\text{vi}}$  to  $\text{Se}^{\text{iv}}$  at 25°C in which the ratio of the isotope rate constants depended upon the isotope partition function ratio for a stretching mode frequency which might be involved in Se-O bond rupture. The normal vibrational frequencies for  $\text{SO}_4^{2-}$  are given in Table 14.

Table 14. Normal vibrational frequencies for  $^{32}\text{SO}_4^{2-}$  and  $^{34}\text{SO}_4^{2-}$  (from TUDGE and THODE, 1950).

Species	Frequencies, $\text{cm}^{-1}$ units. (Degeneracy)			
	$w_1$	$w_2$	$w_3$	$w_4$
$^{32}\text{SO}_4^{2-}$ $^{34}\text{SO}_4^{2-}$	980	451 (2)	1113.60 (3)	618.90 (3)
	980	451 (2)	1097.56 (3)	615.55 (3)

For the calculation, one component of the triply degenerate  $F_2$ -type vibration,  $w_3$ , was selected. The results of this calculation are given in Table 15. It is seen that this model agrees best with the measured value if S and O atomic masses are used for the reduced mass.

Table 15. Theoretical estimates of  $k_{32}/k_{34}$  in sulphate reduction.

Models	Reduced mass	$k_{32}/k_{34}$	
		0°C	25°C
Activated complex resembles starting material	Atomic	1.0099	1.0099
	Mass fragments	1.0020	1.0020
Ratio of partition function of activated complex equals 1	Atomic	1.1120	1.0989
	Mass fragments	1.1030	1.0900
Activated complex resembles $SO_3^{2-}$	Atomic	1.0380	1.0350
	Mass fragments	1.0300	1.0270
$(Q_2/Q_1)/(Q_2^*/Q_1^*)$ equals $(Q_2/Q_1)_{w_3}$	Atomic	1.0248	1.0186
	Mass fragment	1.0166	1.0106

## CHAPTER 6 Conclusions

Our experimental results show that the ratio of the isotope rate constants,  $k_{32}/k_{34}$ , for  $\text{SO}_4^{2-}$  reduction with HI- $\text{H}_3\text{PO}_2$ -HCl are consistently  $1.023 \pm 0.001$  up to 90% reduction conversion at 25°C. Because of the sensitivity of  $\delta^{34}\text{S}$  values to the extent of reaction above 90%, the errors are too large to specify  $k_{32}/k_{34}$  to  $\pm 0.001$  but it would seem that it does not depart radically from 1.023. Our measured  $k_{32}/k_{34}$  values agree well with HARRISON and THODE (1957) where measurements were only made at 10 percent conversion. There is a slight decrease in  $k_{32}/k_{34}$  with temperature in the range from 25°C to 100°C.

The interpretation that the initial S-O bond rupture is the rate controlling step during sulphate reduction by HI- $\text{H}_3\text{PO}_2$ -HCl has been reinforced by the current larger data set. The current theoretical calculation based on a stretching mode frequency in  $\text{SO}_4^{2-}$  and using atomic masses, agrees well with the measured  $k_{32}/k_{34}$  values.

Figure 19 summarizes the temperature dependence of  $k_{32}/k_{34}$  for sulphate reduction with different reducing agents. In some cases,  $\text{SO}_2$  was collected rather than  $\text{H}_2\text{S}$ . If the initial S-O rupture is the rate-controlling step and therefore the determiner of the overall  $k_{32}/k_{34}$ , then the final product should have no effect on the isotope behavior.

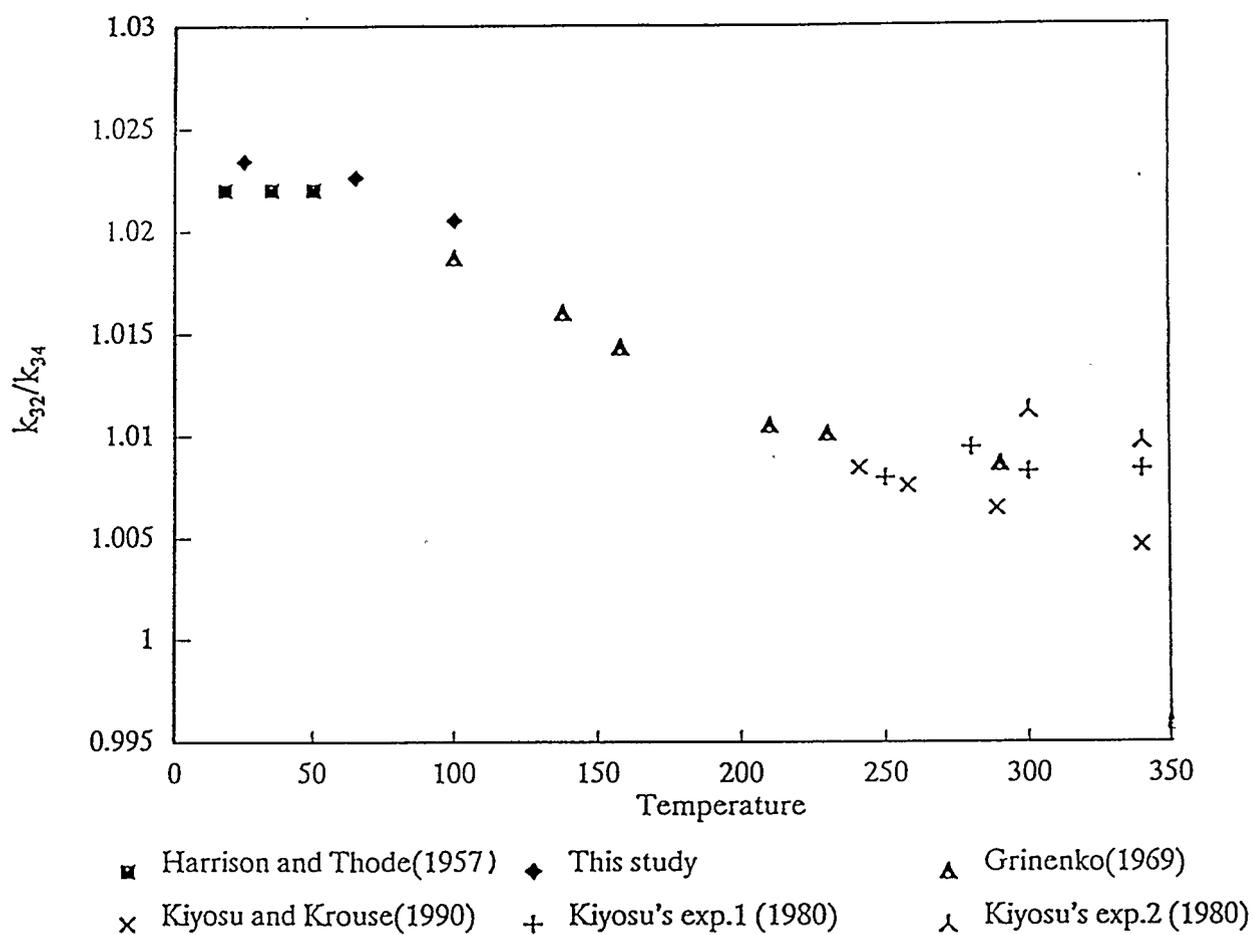


Figure 19: Temperature dependence of the ratio of the isotope rate constants,  $k_{32}/k_{34}$ , for sulphate reduction by different reducing agents.

When sulphate was reduced by  $\text{SnCl}_2$ , the measured  $k_{32}/k_{34}$  values were much smaller, near 1.010. Since the extent of reduction was only 4 percent, it is not known if the  $k_{32}/k_{34}$  values would have approached 1.023 if the reaction had proceeded further. Alternatively, another theoretical model may have to be involved to describe reduction by  $\text{SnCl}_2$ . It is seen that some of the models in Table 15 give calculated  $k_{32}/k_{34}$  values near 1.010.

$k_{32}/k_{34}$  values measured during  $\text{SO}_3^{2-}$  reduction were more variable. Interestingly, reduction with  $\text{SnCl}_2$  plus ascorbic acid gave  $k_{32}/k_{34}$  values which are almost the same as for  $\text{SO}_4^{2-}$  reduction with  $\text{SnCl}_2$  alone (1.010). In contrast, reducing  $\text{SO}_3^{2-}$  with  $\text{SnCl}_2$  alone gave  $k_{32}/k_{34}$  values near 1.001 implying that a step with negligible isotope selectivity was controlling the rate. Clearly more work is required to begin to understand the isotope systematics of  $\text{SO}_3^{2-}$  reduction. The  $\text{SO}_3^{2-}$  reduction data emphasize the undesirability of "measuring kinetic isotope effects" for only a small extent of a reaction as has been done often in the literature.

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