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MAGNETIC RESONANCE SPECTROSCOPY

D.A. Horner
(Ph.D. Thesis)

August 1984

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THE KINETICS OF OXYGEN EXCHANGE BETWEEN BISULFITE
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NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Ph.D. Thesis

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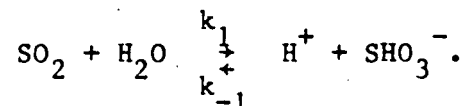
The Kinetics of Oxygen Exchange between Bisulfite Ion and Water
as Studied by Oxygen-17 Nuclear Magnetic Resonance Spectroscopy

By

David Allen Horner

ABSTRACT

The nuclear magnetic relaxation times of oxygen-17 have been measured in aqueous sodium bisulfite solutions in the pH range from 2.5 to 5 as a function of temperature, pH, and S(IV) concentration, at an ionic strength of 1.0 m. The rate law for oxygen exchange between bisulfite ion and water was obtained from an analysis of the data, and is consistent with oxygen exchange occurring via the reaction



The value of k_{-1} was determined, and is in essential agreement with the results of a previous determination by relaxation measurements.

Direct spectroscopic evidence was found for the existence of two isomers of bisulfite ion: one with the proton bonded to the sulfur (HSO_3^-) and the other with the proton bonded to an oxygen (SO_3H^-). (The symbol SHO_3^- in the above chemical equation refers to both isomeric forms of bisulfite ion.) The relative amounts of the two isomers were determined as a function of temperature, and the rate and mechanism of oxygen exchange between the two was investigated. One of the two

isomers, presumably SO_3H^- , exchanges oxygens with water much more rapidly than does the other.

A two-pulse sequence was developed which greatly diminished the solvent peak in the NMR spectrum. This pulse sequence allowed accurate measurements of the linewidth of the solute peak to be made.

Mathematical expressions were derived for the linewidth of the solute peak in the presence of chemical exchange of nuclei between the solvent and solute environments.

ACKNOWLEDGEMENTS

I wish to express my heartfelt gratitude to Professor Robert E. Connick for his guidance throughout the course of this work and my entire graduate career. His helpful advice, careful explanations, and seemingly inexhaustible patience have been greatly appreciated. I leave Berkeley with a deep sense of respect for him, and feel fortunate to have served my scientific apprenticeship under his tutelage.

Thanks are also due to Rudi Nunlist and Rich Mazzarisi for their assistance with and maintenance of the NMR spectrometers. Their help speeded the experimental work immeasurably.

This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the United States Department of Energy under Contract No. DE-AC03-76SF00098.

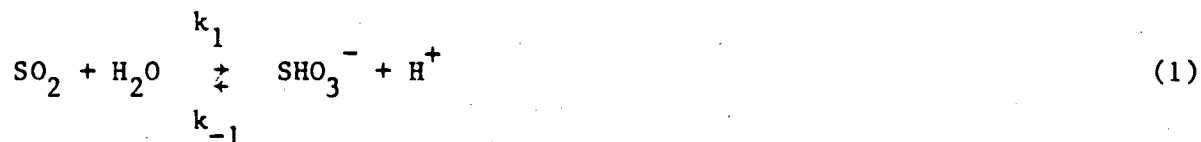
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INTRODUCTION

When sulfur dioxide dissolves in water it retains its molecular structure as SO_2 . Although the resulting solution is acidic, the undissociated free acid H_2SO_3 has never been shown to exist;¹⁻⁵ in order to ionize to bisulfite ion and hydrogen ion the sulfur dioxide must react with a water molecule. The first and second ionizations of sulfur dioxide are represented as



and



(The symbol SHO_3^- refers to all isomeric forms of bisulfite ion.)

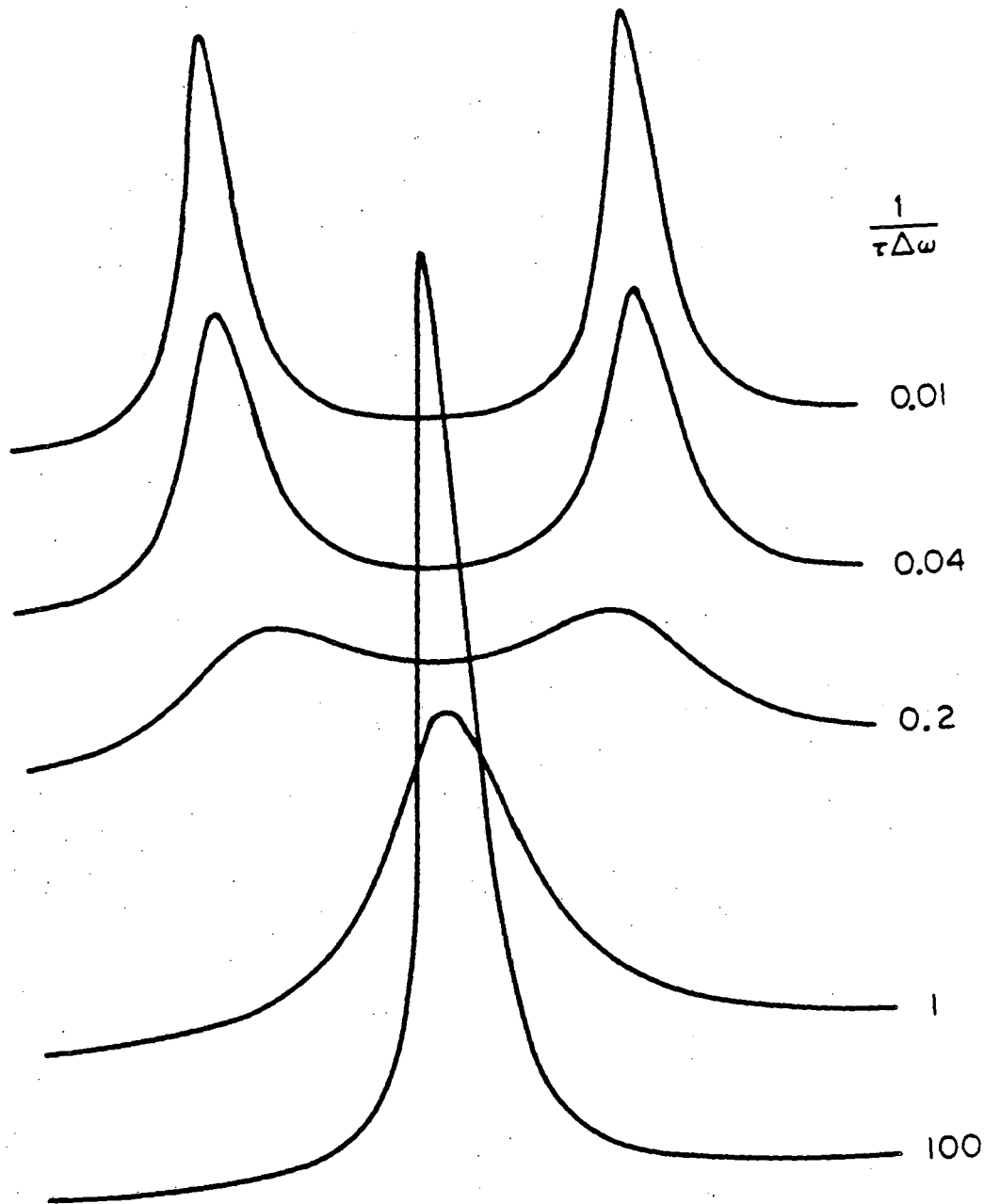
Previous investigators^{6,7} have apparently measured the rate of reaction 1, but their values of k_{-1} differ by more than a factor of 30, and thus are not in good agreement. The present study was undertaken to redetermine the rate of reaction 1. It was also hoped that information could be gained concerning the rate and mechanism of the dimerization of bisulfite ion⁸ to produce the species $\text{S}_2\text{O}_5^{2-}$:



In the course of the study, evidence was obtained of the existence in solution of two isomers of bisulfite ion, one having the proton bonded to the sulfur and the other having the proton bonded to an oxygen. The equilibrium concentration ratio of the two isomeric forms was determined, and the kinetics of the transformation of one form to the other was studied.

Since reactions 1, 2, and 3 as well as the isomerization of bisulfite ion involve oxygen exchange among the S(IV) species and between the S(IV) species and water, the rates and mechanisms of these reactions may be obtained from a study of the kinetics of the exchange of oxygen between the various species in the aqueous $\text{SO}_2 - \text{SHO}_3^- - \text{SO}_3^{2-}$ system. It was recognized several years ago⁹ that the oxygen exchange processes in this system could be studied using oxygen-17 nuclear magnetic resonance (NMR) spectroscopy. In the present work, information about oxygen exchange processes was derived from the widths, positions and number of peaks in the ^{17}O NMR spectra of bisulfite solutions. These spectral features are all sensitive to the rates of the exchange reactions (see Figure 1). Rate laws and Arrhenius parameters of the corresponding rate constants were obtained from the dependence of the half widths of the NMR peaks upon the experimental variables of temperature, pH, and S(IV) concentration, which affect the magnitudes of the pseudo first order rate constants for oxygen exchange between sites having different resonance frequencies or relaxation times.¹⁰

Preliminary experiments indicated that ^{17}O NMR could best be employed to study the $\text{SO}_2 - \text{SHO}_3^- - \text{SO}_3^{2-}$ system in the region between pH 3 and pH 5. This is because the chemical exchange between bisulfite ion and water is not rapid enough to cause coalescence of the S(IV) and



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Figure 1

water resonances throughout the entire region, yet is not so slow that the linewidths of the peaks are insensitive to the rate of that exchange process. The ionic strength of the solutions was chosen to be near that of one of the earlier studies to ensure meaningful comparison of results.

One of the problems which arose very early in this work concerned the presence of the large solvent (water) resonance in the ^{17}O NMR spectrum. It was desirable to study the broadening of the S(IV) peaks in the spectrum, because a reaction which exchanges oxygens between two species, such as reaction 1, which exchanges oxygens between bisulfite ion and water, increases (in the slow exchange limit) the linewidths of the two peaks by amounts which are inversely proportional to the concentrations of the corresponding chemical species. However, the chemical shifts of the S(IV) peaks were small enough to place these resonances on a "wing" of the water resonance. The location of the solute peaks on a wing of the solvent peak, together with inevitable small inaccuracies in the phase adjustment of the spectrum, precluded accurate measurement of the half widths of the solute resonances. A pulse sequence was developed which all but eliminated the solvent peak from the spectrum, and mathematical expressions were derived for the linewidth of the remaining solute peak in the presence of chemical exchange with the solvent.

EXPERIMENTAL PROCEDURE

Sample Preparation

Analytical reagent grade sodium metabisulfite, sodium chloride, hydrochloric acid, and sodium hydroxide from the Mallinckrodt Chemical Company were used without further purification unless otherwise noted.

Aqueous solutions of bisulfite and sodium chloride were prepared by dissolving weighed amounts of sodium metabisulfite and sodium chloride in 3.00 ml of water. In most cases the sodium chloride was dried in a 110°C oven and cooled in a desiccator prior to weighing. The water used in the preparation of samples for oxygen-17 NMR measurements was enriched to circa 50 mole percent oxygen-17 and 40 percent oxygen-18, with natural abundance hydrogen and deuterium. It was obtained from Monsanto Research Corporation's Mound Facility in Miamisburg, Ohio, and purified in the manner described below. Proton NMR samples were prepared with ordinary distilled water.

The pH of each solution was measured with a Beckman Altex model 531164 combination pH electrode and an Orion Research model 601A digital meter. They were calibrated using standard buffer solutions of pH 4 and 7. Adjustments of the pH were made by adding small amounts of 6M HCl or 6M NaOH to the bisulfite solutions.

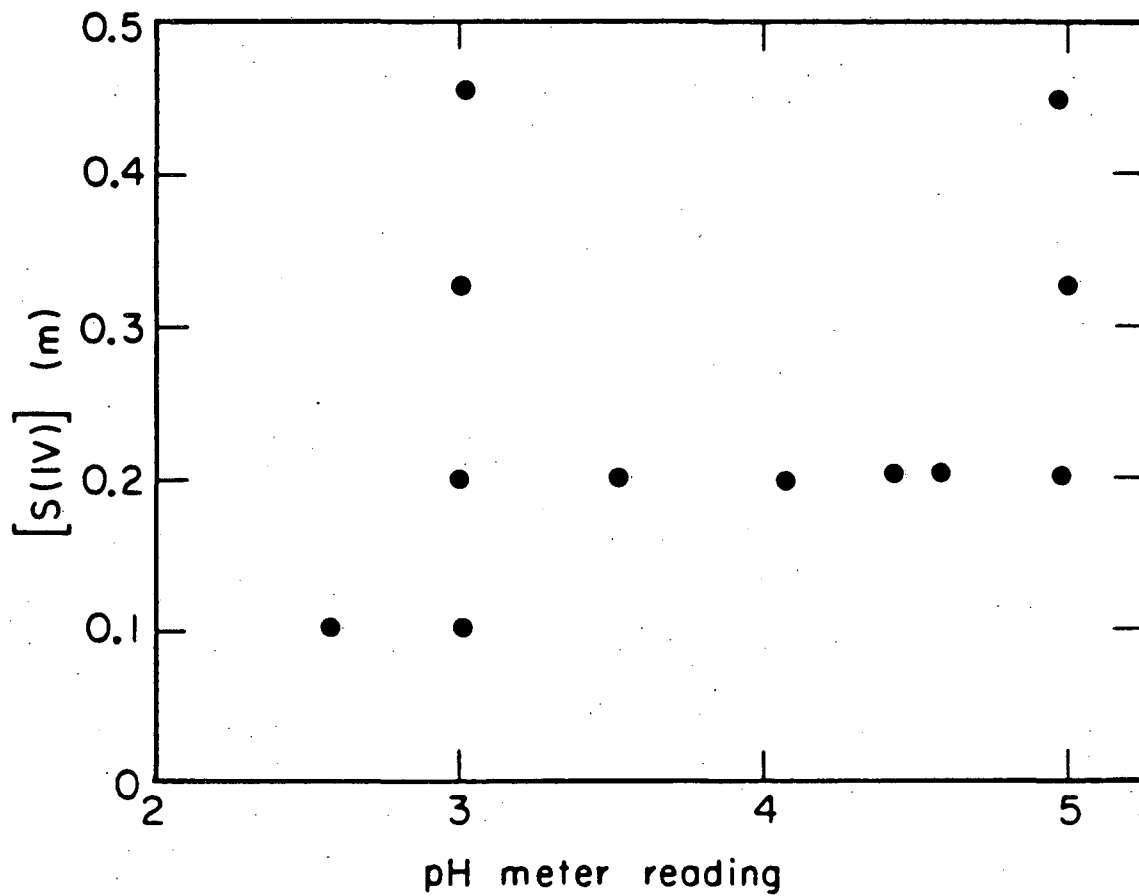
Several precautions were taken to exclude oxygen from the bisulfite solutions and prevent the oxidation of aqueous bisulfite ion by molecular oxygen. Following the weighing of sodium bisulfite and sodium chloride, all reagents were transferred to a glove bag, which was then sealed and flushed with nitrogen for about thirty minutes. Nitrogen was

then bubbled through the water for 15 minutes, followed by an additional 5 minutes of flushing the glove bag. The water used to rinse the electrode and in some cases the HCl and NaOH solutions had also had nitrogen bubbled through them prior to being placed inside the glove bag. In the glove bag the salts were dissolved in water transferred by pipet, the pH adjustment was made, and the solution was transferred to a thin-walled glass NMR sample tube, which was then sealed with a pressure cap and paraffin film. The solutions were stored in the glove bag under a nitrogen atmosphere.

Due to its high cost and limited availability, it was necessary to recover the oxygen-17 enriched water from the bisulfite solutions after NMR measurements were made, so that the water could be used in later samples. Recovery and purification were accomplished by three successive vacuum distillations. Prior to the second distillation the solution was made basic by the addition of a small amount of sodium hydroxide to prevent the production of SO_2 by the disproportionation of bisulfite, and the subsequent distillation of the SO_2 .

The compositions of the various bisulfite solutions are shown in Figure 2. Enough sodium chloride was present in each solution to give an ionic strength of 1.0 m at 25°C.

Some discussion of the units in which the S(IV) concentration is expressed in Figure 2 (and elsewhere in this work) is appropriate. The total volume of any of the bisulfite solutions was not known, so molarity could not be used as a unit of concentration for S(IV). The number of moles of S(IV) and the volume of H_2O used in preparing each solution were known, so knowledge of the density of the water would allow the concentration of S(IV) to be expressed in terms of moles of



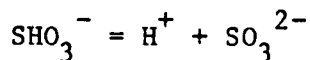
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Figure 2

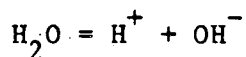
S(IV) per kg of H₂O. This traditional definition of molality was thought to be unsatisfactory for the present work, which involved the use of ¹⁷O enriched water, because it yields different concentrations of S(IV) for two solutions prepared in exactly the same manner save for the use of water having different mole fractions of the oxygen isotopes. Since the chemical behavior of two such solutions would be expected to be nearly identical, their differing concentrations in units of moles of S(IV) per kg of H₂O would be somewhat misleading. It was decided, therefore, to employ a unit of concentration which would yield equal S(IV) concentrations for solutions prepared using an equal number of moles of S(IV) and equal volumes of water, and would correspond to the traditional definition of molality if the water used were of normal isotopic composition. The unit chosen, moles of S(IV) per 55.5 moles of H₂O, is called "molality" and abbreviated by the symbol "m" throughout this dissertation.

In the course of interpreting the NMR data it was necessary to know the concentrations of various species in the bisulfite solutions. It was also necessary to know the concentrations of the ionic species in order to determine the amount of NaCl needed to bring the ionic strength of each solution up to 1.0 m. Therefore, the concentrations of SO₂(aq), bisulfite ion, SO₃²⁻, S₂O₅²⁻, H⁺, Cl⁻, and Na⁺ which were contributed by the sodium metabisulfite, water and added HCl or NaOH in each solution were calculated from the known S(IV) and hydrogen ion concentrations using the following equilibrium quotients,¹¹ appropriate for conditions of 25°C and ionic strength 1.0 m:





$$\log_{10} K_2 = -6.34$$



$$\log_{10} K_w = -13.79,$$

and the equilibrium quotient, K_d , for the dimerization of bisulfite ion to produce metabisulfite. The latter was estimated for an ionic strength of 1.0 M from the work of Connick, Tam, and von Deuster¹² by first obtaining the equilibrium quotient at $[\text{Na}^+] = 5.0 \text{ M}$ and a particular concentration of S(IV) by interpolation, and then extrapolating the result to an ionic strength of 1.0 M using their plot of $\log K_d$ vs. $\mu^{1/2}$, assuming that the slope of the curve is independent of the S(IV) concentration. Calculated values of K_d ranged from 0.081 to 0.084. The equilibrium quotients are given in units of molarity; all were assumed to have the same values in units of molality.

The calculation of concentrations at 25°C required the use of the hydrogen ion concentration of each solution, which was calculated using the pH meter reading, assumed to be $-\log_{10}(a_{\text{H}^+})$, and an estimated value of the activity coefficient. The value of the mean activity coefficient of 0.01 M HCl in 1 m NaCl,¹³ equal to 0.754, was considered to be a reasonable substitute for the unknown activity coefficient of H^+ in the bisulfite solutions because the ionic strength of each solution was 1.0 m, and the primary salts present were NaCl (with a concentration of at least 0.5 m), and the 1-1 salt NaHSO_3 .

After the calculations for 25°C had established the exact amount of added HCl or NaOH in each solution, calculations of concentrations, including that of hydrogen ion, at temperatures other than 25°C were

made after first correcting the values of the equilibrium quotients K_1 , K_2 , and K_w for changes in temperature using the tabulated enthalpies of reaction -4, -3, and 13.55 kcal/mole,¹¹ respectively. The enthalpy values apply to solutions of lower ionic strengths than those in this study, and are given only for a temperature of 25°C, but they were used in lieu of better values and were assumed (out of necessity) to be temperature independent. The small temperature dependence of K_d was ignored.¹²

NMR Measurements

Oxygen-17 nuclear magnetic resonance spectra were obtained with the use of a pulse NMR spectrometer consisting in part of a Cryomagnet Systems 4.7 Tesla superconducting magnet, a homebuilt receiver and transmitter, a Nicolet Instrument Corporation 293A⁺ programmable pulser, a Nicolet Instrument Corporation 1180 Data System, and a broadband, multinuclear probe built for 10 millimeter (outside diameter) sample tubes. All experiments were run without a field-frequency lock on samples spinning at roughly 20 revolutions per second. No vortex plugs were used inside sample tubes, an omission which had no observable effect upon oxygen-17 linewidths. Data in the form of digitized free induction decays were stored on a magnetic disk. Data analyses were performed on the Fourier transforms of the free induction decays.¹⁴ The NTCFT computer program of Nicolet Technology Corporation was employed for data acquisition and analysis.

Sample temperature was controlled during the oxygen-17 experiments

by passing a flow of nitrogen gas, initially at a temperature below the desired sample temperature, through a heater and thence past the sample. An electronic relay device connected to both the heater and a thermocouple located directly below the sample provided regulation of the temperature by switching off the heater whenever the temperature measured by the thermocouple exceeded a preset value.

Because of the poor thermal contact between the thermocouple and the sample, it was known that the thermocouple potential, while useful for the purpose of temperature regulation, was an inaccurate measure of the temperature of the sample. Therefore, the chemical shift difference between the proton NMR peaks of an ethylene glycol sample contained in a sealed capillary placed within the large sample tube was used as the measure of the temperature of the bisulfite solution. The temperature dependence of the chemical shift difference of the ethylene glycol peaks has been determined by several workers; in this work the calibration curve used was that of Kaplan, Bovey, and Cheng.¹⁵ Although the water in the bisulfite sample contributes a much larger proton NMR signal than the ethylene glycol, the peaks of the latter were large enough and located far enough away from the water peak to be easily seen.

Since the proton frequency of 201 MHz was outside the tunable range of the broadband probe's observation coil circuit (and because, even if the proton frequency were accessible, it would have been inconvenient to retune the circuit every time a temperature measurement was desired) the ethylene glycol proton NMR signal was obtained by pulsing and observing with the decoupler coil, which was tuned to 201 MHz. Both the output of the frequency synthesizer and the necessary hardware changes within the transmitter and receiver of the spectrometer were computer controlled,

simplifying the task of changing between the oxygen-17 and proton frequencies.

The decoupler coil contained a slightly larger volume than the oxygen-17 observation coil which was enclosed by it; it was assumed that the temperature obtained from the proton NMR spectrum was an accurate measure of the temperature of that portion of the sample within the oxygen-17 observation coil. The calibration curve used has an estimated uncertainty of ± 0.9 degrees. The temperature was regulated to ± 0.2 degrees.

At each temperature the procedure followed was to set the temperature and allow 30 minutes for stabilization, shim the z , z^2 , and z^3 magnetic field gradients on the proton NMR signal of the sample, measure the temperature, acquire the NMR data, and measure the temperature again.

A small number of proton NMR spectra were acquired for purposes other than temperature measurement (using samples other than those used in the ^{17}O measurements). These spectra were obtained with the instrument described previously, in which the multinuclear probe had been replaced by a proton probe which accepted 5 mm (outside diameter) sample tubes.

The transverse relaxation time of the oxygen-17 in the water of each bisulfite solution was determined by fitting a Lorentz lineshape equation to the water peak in a spectrum obtained by acquiring between 200 and 6000 free induction decays following 5 μsec (17°) pulses in a 4K data file, using quadrature phase detection, a spectral width of 62500 Hz (31250 Hz on each side of the pulse frequency), and Bessel filters with the 3 dB point set at 31250 Hz. A long delay time of approximately

200 μsec between the end of the pulse and the beginning of data acquisition eliminated rolling baselines caused by pulse breakthrough. Because the use of phase correction which varies linearly with frequency was also undesirable, the exact length of this delay was set equal to a time at which the free induction decay signal arising from the water was in phase with the signal arising from the bisulfite,¹⁶ i.e. the inverse of the frequency difference between the water and bisulfite peaks plus the time taken by the signal to reach the computer.¹⁷ Fourier transformation of the free induction decay was preceded by its multiplication by an exponential function and the addition of zeroes at its end to improve the signal to noise ratio and spectral appearance, respectively, in the frequency domain. The amount of line broadening produced by exponential multiplication was subtracted from the linewidth obtained from the Lorentzian curve fit to give the true linewidth. Magnetic field inhomogeneity produced no detectable line broadening in a room temperature sample of acidified water.

A two-pulse excitation sequence ($\theta_x - \tau - \theta_x$ -acquire; $\theta < 45^\circ$) was used to suppress the strong signal arising from the solvent water magnetization and allow accurate measurement of the widths of the bisulfite peaks. In this pulse sequence the frequency of the pulse (and thus the frequency of the rotating frame of reference) is set equal to the Larmor frequency of the nuclei in the solvent site. The first pulse, applied along the (+x)-axis of the rotating frame, causes all spins to precess about this axis, tilting the magnetization in the yz-plane toward the y-axis. During the time τ the solute magnetization precesses in the rotating frame with a frequency $\nu_{\text{solute}} - \nu_{\text{solvent}}$, while the solvent magnetization remains oriented in the yz-plane. The

length of time τ between the pulses is set equal to half the inverse of the difference in frequency between the solute and solvent peaks, i.e. the time required for the solute magnetization to precess one-half cycle in the rotating frame, after which it is again oriented in the yz-plane, but 180° out of phase with the solvent magnetization. The second pulse, applied along the (-x)-axis, tilts the solvent magnetization back to the z-axis, but tilts the solute magnetization further toward the xy-plane. Because only the component of magnetization in the xy-plane is detected by the spectrometer, the solvent magnetization does not contribute to the subsequent free induction decay.

Probably because of the occurrence of a non-negligible amount of relaxation and chemical exchange during the time between pulses, it was found necessary to make small adjustments to the length of the second pulse, the wait time between pulses, and the radio frequency of the pulses, in order to find the combination which produced the greatest diminution in the height of the water peak. The optimal settings for the oxygen-17 spectra occurred when the second pulse was slightly shorter than the first, and the time between pulses was a bit less than half the inverse of the frequency difference of the water and bisulfite peaks, and resulted in a reduction in height of the water peak of up to a factor of 1000. After the acquisition of the free induction decay, the width of the bisulfite peak was determined in the same manner as the width of the water peak in the one-pulse spectrum.

Measurements of the longitudinal relaxation times of oxygen-17 in the water of the bisulfite solutions were carried out using an inversion recovery pulse sequence¹⁸ (180° - τ - θ -acquire; $\theta < 90^\circ$), in which the phase of the θ pulse is shifted by 180° each time the pulse sequence is

repeated. The alternation of the phase of the θ pulse eliminates the effects upon the T_1 measurement of transverse magnetization produced by imperfections in the 180° pulse.¹⁹ The time between repetitions of the pulse sequence was greater than six times T_1 to allow the magnetization to decay to its equilibrium value prior to each inverting pulse. T_1 was determined by fitting the amplitude of the water peak at ten different values of τ to the expression

$$A(\tau) = A(\infty) \left\{ 1 - (1 + W)e^{-\tau/T_1} \right\},$$

where

$A(\tau)$ = amplitude of water peak at time τ ,

τ = time between 180° and θ pulses,

and W is a parameter which compensates for the fact that the z -component of the magnetization at the end of the 180° pulse is smaller in absolute magnitude than M_0 , due to pulse imperfections.²⁰ For a perfect 180° pulse, W equals one. Typical values of W were between 0.75 and 0.79.

The chemical shift scale was chosen to be such that the water resonance in the NMR spectrum of each solution had a chemical shift of zero. (It should be noted that the absolute chemical shift of the water may vary from solution to solution due to chemical exchange effects.) The chemical shifts of the S(IV) peaks in the ^{17}O NMR spectra were determined by subtracting the frequency of the H_2O peak in the one-pulse spectrum from the frequency of the S(IV) peak in the two-pulse spectrum which had been recorded immediately before or after the one-pulse spectrum, and are reported in units of parts per million, with downfield shifts being positive.

In order to compare the population of ^{17}O in one chemical environment to its population in another the areas of the peaks in the NMR spectra were measured (see Results and Discussion for measurement methods). The area of a peak in the NMR spectrum is proportional to the magnitude of the corresponding transverse magnetization (i.e. the transverse magnetization of the ^{17}O in the chemical environment which corresponds to the peak) which exists at the beginning of data acquisition. Because the preacquisition delay times and the time between pulses (in the two-pulse experiment) were not short in comparison to the ^{17}O relaxation times it was necessary to correct the areas for the effect of relaxation which occurred prior to the beginning of data acquisition. The mathematical expressions used for correcting the peak areas will now be derived.

The peak areas measured in the one-pulse spectra are in error because the transverse component of magnetization in each chemical environment decays between the end of the pulse²¹ and the beginning of data acquisition. The relationship between the magnitude of the transverse magnetization in environment i , $M_{xy(i)}$, at the beginning of data acquisition to that at the end of the pulse is

$$M_{xy(i)}(t_d) = M_{xy(i)}(0)\exp[-t_d/(T_2)_i],$$

where t_d = the time between the end of the pulse²¹ and the beginning of data acquisition,

$(1/T_2)_i$ = the half-width at half-height of peak i , i.e. the transverse relaxation rate constant for ^{17}O in environment i ,

and where it has been assumed for simplicity that the ^{17}O in each environment relaxes exponentially. The measured area ratio of the two peaks is $M_{xy(i)}(t_d)/M_{xy(j)}(t_d)$, and the true population ratio is the ratio of the magnitudes of the transverse magnetizations at the end of the pulse, given by the expression

$$\frac{M_{xy(i)}(0)}{M_{xy(j)}(0)} = \frac{M_{xy(i)}(t_d)}{M_{xy(j)}(t_d)} \exp\{t_d\left[\left(\frac{1}{T_2}\right)_i - \left(\frac{1}{T_2}\right)_j\right]\}.$$

The ratios of the measured areas of the two S(IV) peaks in the two-pulse spectra are not equal to the corresponding ^{17}O population ratios because of relaxation occurring both during the time between pulses and during the preacquisition delay. To analyze the effect of relaxation upon the peak areas it is necessary to consider what happens to the magnetization of each environment during each part of the two-pulse sequence.

The first pulse, P_1 , rotates all magnetizations about the x-axis of the rotating frame of reference. (This is an approximation. The pulse frequency is close to the H_2O frequency, but is far enough away from the S(IV) frequencies that the effective field, H_{eff} , is not equal to H_1 for all environments.²²) The angle through which the magnetization vectors are tipped about the x-axis due to the first pulse is

$$\theta_1 = \gamma H_1 t_{P1} = \frac{\pi}{2} \frac{t_{P1}}{t_{90^\circ}},$$

where t_{P1} is the length of the first pulse and t_{90° is the length of a 90° pulse. At the end of the first pulse the components of the magnetization of environment i are

$$\begin{aligned}M_{xi} &= 0, \\M_{yi} &= M_1(\sin \theta_1), \\M_{zi} &= M_1(\cos \theta_1),\end{aligned}$$

where M_1 is the magnitude of the equilibrium magnetization of environment 1.

During the time τ between pulses longitudinal and transverse relaxation occur and the transverse magnetizations precess in the rotating frame, so that at the end of the time between pulses

$$\begin{aligned}M_{zi} &= M_1 \{1 - (1 - \cos \theta_1) \exp[-\tau/(T_1)_i']\}, \\M_{xy(i)} &= M_1(\sin \theta_1) \exp[-\tau/(T_2)_i'],\end{aligned}$$

where $(T_1)_i'$ and $(T_2)_i'$ are the longitudinal and transverse relaxation times, respectively, of ^{17}O in environment 1 during the time between pulses. For simplicity it will be assumed that after the time τ the transverse magnetization of each S(IV) environment is aligned along the (-y)-axis, and the H_2O transverse magnetization is aligned along the y-axis. This is not a bad assumption, because in the actual experiments the frequency of the rotating frame (i.e. the pulse frequency) was close to the H_2O frequency, and the time τ was chosen to be about equal to half the precessional period of the S(IV) magnetization in the rotating frame.

The second pulse, P2, rotates the magnetization about the x-axis by an angle

$$\theta_2 = \frac{\pi}{2} \frac{t_{P2}}{t_{90^\circ}},$$

in a direction opposite to the direction of the rotation produced by the first pulse. The relationship of the magnitude of the xy-component of the magnetization in S(IV) environment i at the end of the pulse to its magnitude at the beginning of the pulse is

$$M_{y1}(\text{final}) = [M_{z1}(\text{initial})](\sin \theta_2) + [M_{y1}(\text{initial})](\cos \theta_2).$$

Therefore, the magnitudes of the transverse components of the magnetization of S(IV) environment i at the end of the second pulse are

$$\begin{aligned} M_{x1} &= 0, \\ M_{y1} &= M_i \{1 - (1 - \cos \theta_1) \exp[-\tau/(T_1)_i']\} (\sin \theta_2) \\ &\quad + M_i (\sin \theta_1) (\cos \theta_2) \exp[-\tau/(T_2)_i']. \end{aligned}$$

During the delay time t_d between the end of the pulse²¹ and the beginning of data acquisition both relaxation and precession occur, so the magnitude of the transverse component of magnetization in S(IV) environment i at the beginning of data acquisition is

$$\begin{aligned} M_{xy(i)} &= M_i \exp[-t_d/(T_2)_i] \{ \sin \theta_2 (1 - (1 - \cos \theta_1) \exp[-\tau/(T_1)_i']) \\ &\quad + (\sin \theta_1) (\cos \theta_2) \exp[-\tau/(T_2)_i'] \}, \end{aligned}$$

where $(T_2)_i$ is the time constant for the decay of transverse magnetization in S(IV) environment i during the preacquisition delay.

Based upon the foregoing discussion, a reasonable estimate of the population ratio (M_i/M_j) of ¹⁷O in the two S(IV) environments can be obtained from the ratio of the peak areas in the two-pulse spectrum

using the expression

$$\frac{M_i}{M_j} = \frac{M_{xy(i)} \exp\{t_d/(T_2)_i\} \{A_j(\sin \theta_2) + (\sin \theta_1)(\cos \theta_2)\exp[-\tau/(T_2)_j']\}}{M_{xy(j)} \exp\{t_d/(T_2)_j\} \{A_i(\sin \theta_2) + (\sin \theta_1)(\cos \theta_2)\exp[-\tau/(T_2)_i']\}}$$

where $A_i = 1 - (1 - \cos \theta_1)\exp[-\tau/(T_1)_i']$,

$M_{xy(i)}/M_{xy(j)}$ = the ratio of the area of S(IV) peak i to that of S(IV) peak j in the two-pulse spectrum,

$$\theta_1 = (\pi/2)(t_{p1}/t_{90^\circ}),$$

$$\theta_2 = (\pi/2)(t_{p2}/t_{90^\circ}),$$

t_{p1} , t_{p2} = the lengths of the first and second pulses of the two-pulse sequence, respectively,

t_{90° = the length of a 90° pulse

τ = the time interval between the two pulses,

t_d = the length of the interval between the time the first part of the free induction decay arrives at the computer and the time at which data acquisition begins,

$(T_2)_i$ = the time constant for the decay of transverse magnetization in S(IV) environment i during the preacquisition delay,

$(T_2)_i'$ = the time constant for the decay of the transverse magnetization in S(IV) environment i during the time between the two pulses,

$(T_1)_i'$ = the time constant for the decay of the longitudinal magnetization in S(IV) environment i during the time between the two pulses.

In general $(T_2)_i$, the time constant for the decay of transverse

magnetization in S(IV) environment i during the preacquisition delay, is not equal to $(T_2)'_i$, the time constant for decay of transverse magnetization during the time between pulses, because only during the latter time does the water magnetization have a large transverse component. Due to chemical exchange effects the relaxation of the ^{17}O in the S(IV) environments depends upon the orientation of the water magnetization (see Appendices A and B). However, it is believed that in the pH and temperature regions in which two S(IV) peaks are visible (and in which this correction to the areas is being applied) the exchange with water occurs slowly enough to cause the pseudo first order rate constant for the exchange reaction to be small compared to the frequency difference between the water peak and S(IV) peak i , making it reasonable to assert that $(T_2)_i \approx (T_2)'_i$ and to set $(1/T_2)_i$ equal to the half-width at half height of peak i .

The results of the inversion recovery experiments indicate that the longitudinal relaxation time of the ^{17}O in each S(IV) environment is about equal to the measured longitudinal relaxation time in water, $(T_1)_{\text{H}_2\text{O}}$ (see Results and Discussion). Therefore, for the purpose of correcting the peak areas, $(T_1)'_i$ and $(T_1)'_j$ were set equal to the measured value of the longitudinal relaxation time of water in the bisulfite solutions. The error introduced into the peak area ratios by this substitution was less than 5%.

RESULTS AND DISCUSSION

Description and Interpretation of Spectra

Several peaks were observed in the oxygen-17 spectra: a large peak due to the oxygen-17 in water, and 1 or 2 much smaller peaks located between 170 and 200 ppm downfield from the water. The widths and chemical shifts of the peaks, as well as the number of peaks seen, were found to be dependent upon the pH, temperature, and concentration of S(IV) (see Figures 3 and 4). The half-width at half-height ($1/T_2$) of the water peak was found to be greater than the measured value of $1/T_1$, and grew as the S(IV) concentration was increased. The difference between $1/T_2$ and $1/T_1$, shown in Figure 5, became greater with increasing temperature and decreasing pH in samples at or above pH 3.5.²³

In the spectra of samples having pH values of 3.6 or less, one peak appeared in addition to the water peak, and was located between 175 and 178 ppm downfield from the latter. (The exact position was a function of temperature.) This peak broadened with increases in temperature, pH, or S(IV) concentration. Two peaks also were seen in the spectra of samples with a pH of 5, but they were separated by about 193 ppm. The resonance at 193 ppm broadened with increases in temperature, and at low temperatures also broadened with increasing S(IV) concentration, while at high temperature line narrowing was observed with increasing S(IV) concentration. Since this peak was observed only in the samples with pH equal to 5, no observation can be made about the acidity dependence of its linewidth.

Between pH 4 and 4.5, two overlapping peaks were observed downfield

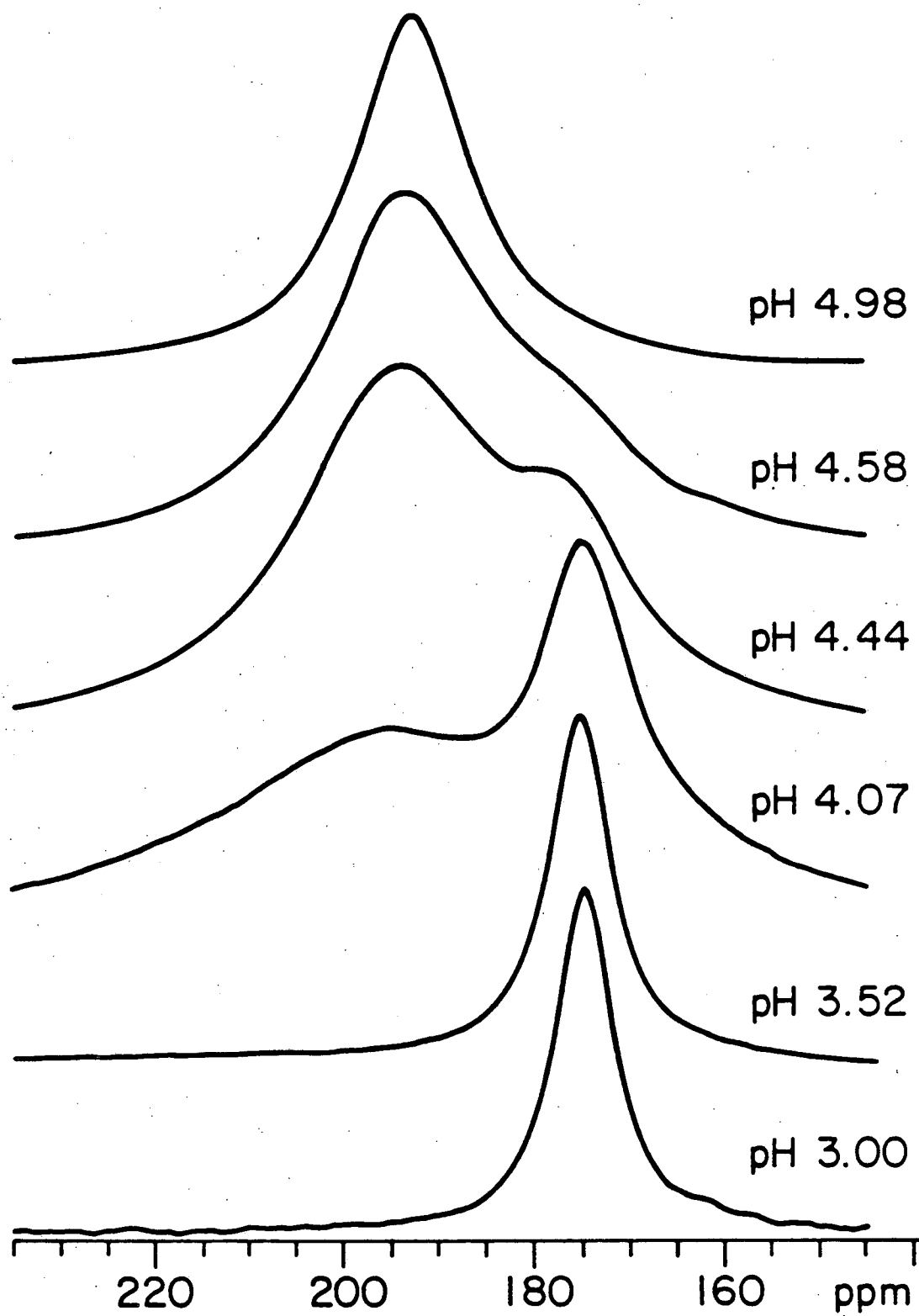


Figure 3

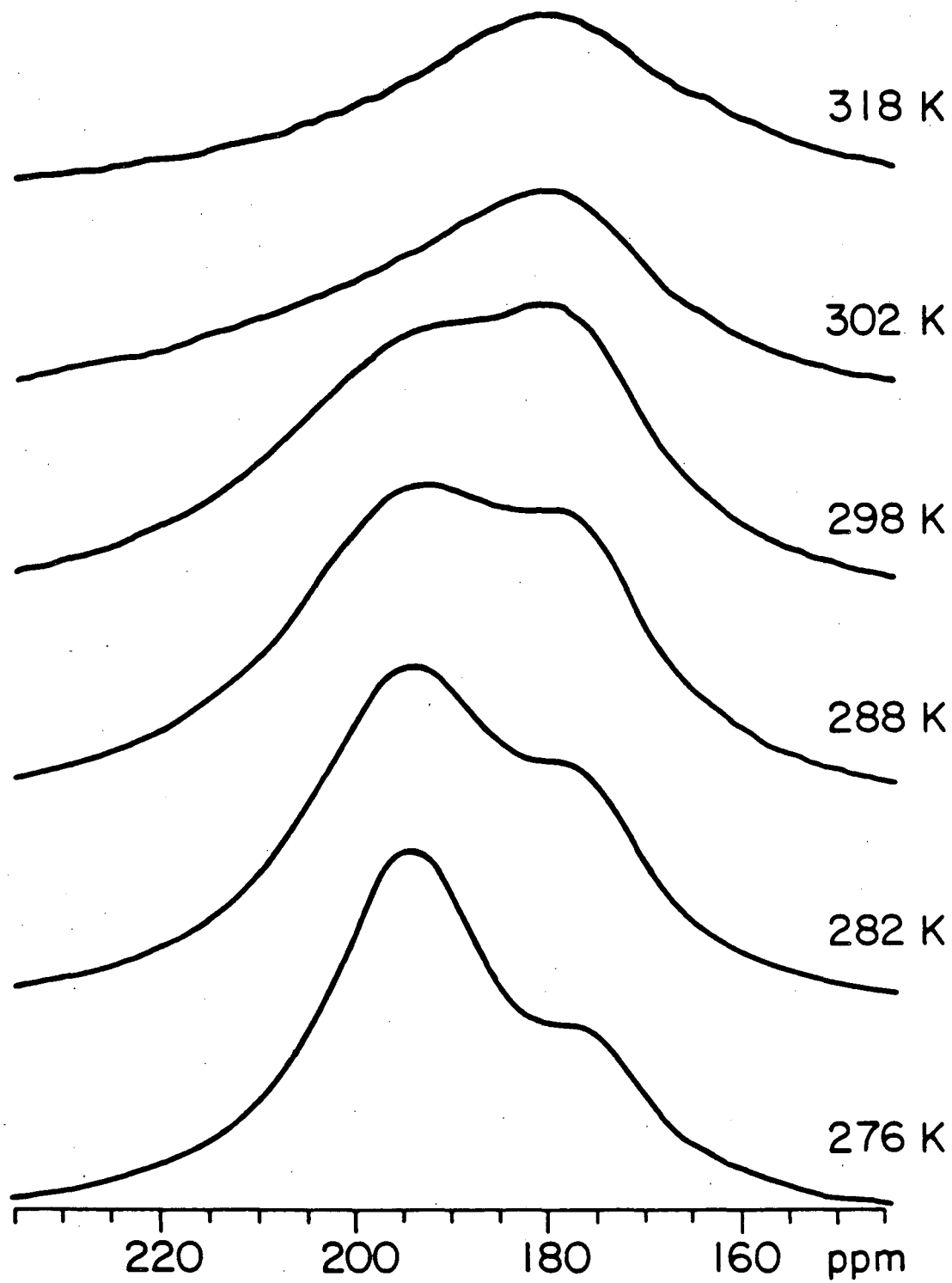
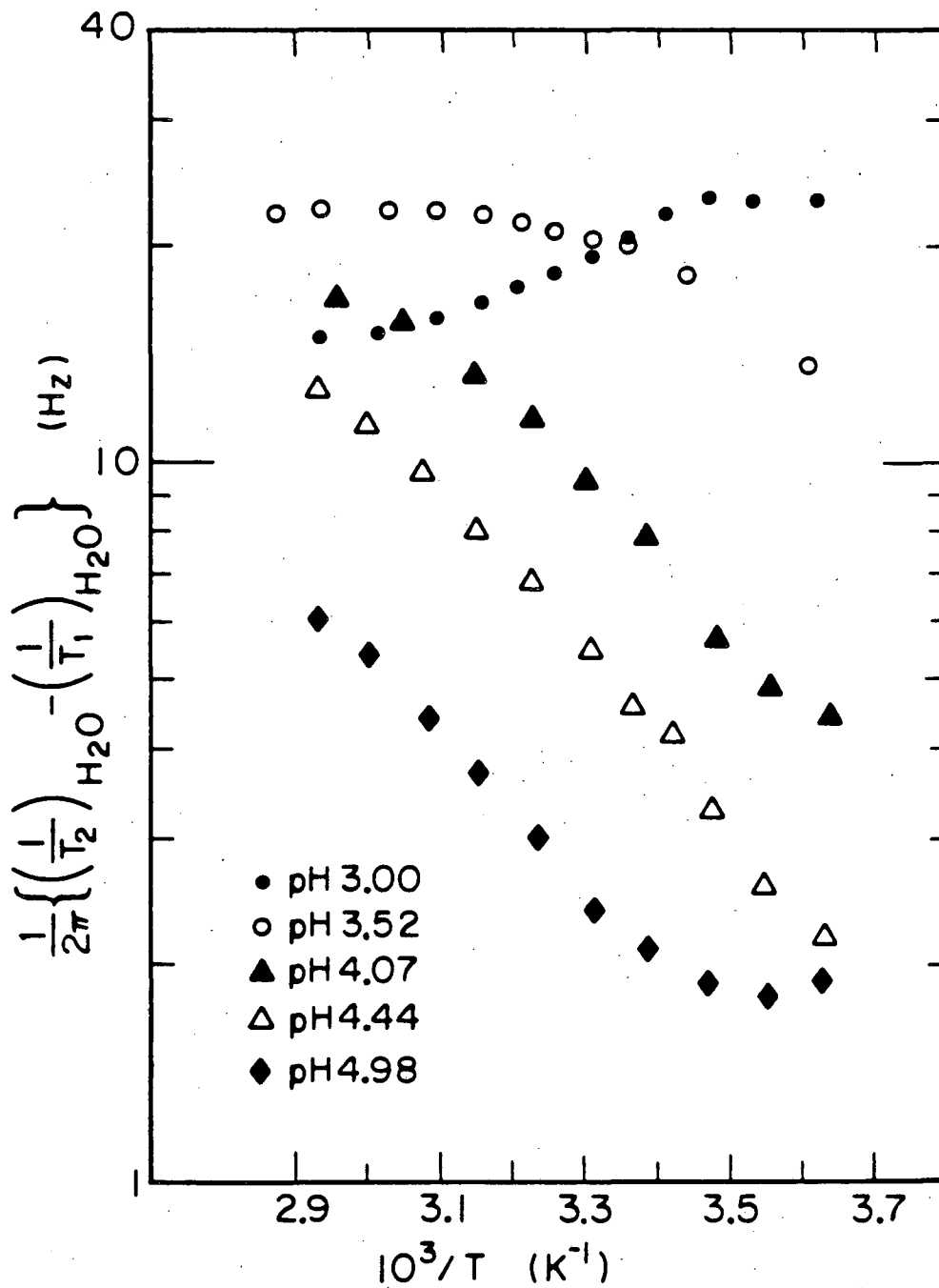


Figure 4



from the water resonance: one at roughly 195 ppm and one between 175 and 180 ppm. The use of a spectrum simulation computer program allowed rough values of the widths and areas of the peaks to be obtained, showing that the peak at 195 ppm narrowed and the one between 175 and 180 ppm broadened as the pH was increased, and that the ratio of the area of the former to that of the latter was about 5 to 10. As the temperature was increased from 0°C to 70°C, both increased in width, but the one at 195 ppm broadened to the extent that it was difficult to see at the highest temperatures (see Figure 4).

In the spectra of the sample having a pH of 4.58, three peaks were observed, but only below room temperature, and even then the two overlapping peaks were indistinct, with the upfield one appearing as a shoulder on the peak at 195 ppm. As the temperature was raised, this remaining distinction disappeared as the lines broadened, and one observed only the water peak and a broad resonance whose maximum moved upfield to 183 ppm at 60°C.

The changes in appearance of the spectrum which take place when the acidity, temperature, and S(IV) concentration are varied indicate that chemical exchange is occurring between several different species in the solution. The finite widths of the spectral lines arise from the nuclear magnetic relaxation of oxygen-17 which in solutions containing no paramagnetic species is caused by quadrupole coupling interrupted by molecular tumbling;²⁴ it can also be contributed to by exchange of oxygen atoms between chemically different environments. Although the contribution to $1/T_2$ from chemical exchange can be an increasing or decreasing function of temperature, depending upon whether the system is close to the slow or fast exchange limit, the rate of quadrupolar

relaxation is expected to be proportional to the rotational correlation time, which is, in turn, proportional to the coefficient of viscosity of the solution divided by the absolute temperature.²⁵ The quadrupolar relaxation rate should therefore decrease as the temperature rises. It is also expected that because of rapid rotational reorientation, the transverse and longitudinal relaxation times will be equal.²⁵ The observation of nonequality of $1/T_2$ and $1/T_1$ of the water, and the increase with temperature of the widths of the other resonances thus cannot be explained by a relaxation mechanism involving only quadrupole coupling, but must also include chemical exchange effects.

Unless the rotational correlation times are altered by changes in acidity and S(IV) concentration, the effects of these changes upon the linewidths must be due to chemical exchange, with pseudo first order rate constants which are functions of the concentrations of hydrogen and bisulfite ions. Because, as will be seen, the longitudinal relaxation times of the water are independent of these concentrations (at the low concentrations used in this work), the rotational correlation times probably do not vary significantly in the solutions studied.

At least a partial interpretation of the spectrum is necessary before rate constants can be determined. Based on the behavior of the small peaks downfield from water, it is believed that there are two chemical species giving rise to resonances at 195 ppm and between 175 and 178 ppm, which exchange oxygen atoms at a rate which increases with pH, causing the two peaks to coalesce at pH 5. Using the observed area ratio in the spectra of solutions between pH 4 and 4.5, a position for the coalesced peak of 192 to 193 ppm is calculated, agreeing with the position of the peak in the spectra of solutions of pH 5. An increased

rate of exchange with increasing basicity is also consistent with the observed pH dependence of the width of the peak located at 175-178 ppm.

If there are two resonances downfield from water that are coalescing at pH 5 but distinct at lower pH values, then the peak at 195 ppm displays a seemingly incongruous broadening as the acidity is increased. Both this broadening and the broadening of the water peak can be explained by the existence of oxygen exchange between water and the chemical species corresponding to the 195 ppm peak, which increases in rate with decreasing pH. The 195 ppm species is then involved in two chemical exchange processes, the rates of which have opposite pH dependences. As the acidity is varied the chemical exchange with water must have the greater effect upon the change in linewidth. At pH values of 3.5 and less, the exchange with water is presumably so rapid that the consequent broadening of the resonance at 195 ppm makes it difficult to see.

Although the peak at 193 ppm in the spectra of solutions at pH 5 appears to arise from the coalescence of two peaks which have an area ratio of between 5 and 10 at slightly higher acidities, it does not necessarily follow that its area must be 6 to 11 times that of the small peak in the spectra of the low pH samples, because the concentrations of the S(IV) species in aqueous solutions are pH dependent. However, if the peaks are identified with particular chemical species then the peak area ratios can be predicted from the concentrations calculated using known stability constants, and compared with the actual area ratios to confirm or contradict the interpretation of the behavior of the peaks in the 170-200 ppm region.

To identify the small peaks, the concentration of oxygen atoms in

the chemical species corresponding to the peaks at 193 ppm and 175-178 ppm were determined from the spectra containing only two resonances by evaluating the peak areas, using the water peak as an internal standard.²⁶ The height and width of each resonance were measured, since the area of a Lorentzian line is proportional to the product of its height and width.

The linewidth and height of the water peak were taken from the Lorentzian curve fitting mentioned in the Experimental Procedure section. The curve fitting program required a flat baseline, and so could not be used for an accurate determination of the linewidth and height of the small downfield peak, which was located on a wing of the water peak in the one-pulse spectrum. Therefore, the width of the line was taken from the curve fitting of the peak in the two-pulse spectrum. It is shown in Appendix B that the linewidths are equal in the two spectra.

The height of the small peak in the one-pulse spectrum was then determined in the following manner: the wing of the water peak was approximated by a non-horizontal straight line in the region of the small downfield peak. From the slope of this line and the linewidth obtained from the two-pulse spectrum, the difference in the height of the peak at the frequencies $\omega_0 + 1/T_2$ and $\omega_0 - 1/T_2$ was calculated (ω_0 is the location of the peak maximum), as well as the length of the line segment connecting the trace at the two frequencies. The line segment which had this length and the same slope as the baseline was located and drawn on the recorded spectrum. The height of the peak was taken to be twice the vertical distance from the midpoint of the line segment to the trace of the peak.

The use of this method for determining the height of the small peak requires that its shape in the one-pulse spectrum be Lorentzian, because its width was determined from the two-pulse spectrum, in which it always has a Lorentzian shape (see Appendix B). Because in all the spectra used to measure the peak areas the half-width at half-height of the small peak was less than one-tenth of the frequency difference between it and the water peak, it was assumed that to a good approximation the slow exchange limit obtained, in which the spectrum is a superposition of Lorentzian lines.

The peak areas were corrected for the effect of signal decay occurring during the finite delay time between the end of the pulse and the beginning of data acquisition (see Experimental Procedure).

Table 1 shows the results of the determination of peak areas, from which several features stand out. Calculations of the concentrations of the various chemical species show that over 90% of the S(IV) is present in these solutions in the form of bisulfite ion, while SO_2 , $\text{S}_2\text{O}_5^{2-}$, and SO_3^{2-} account for no more than 3%, 7%, and 3%, respectively. In all of these species the number of oxygen atoms per sulfur atom is either 2, 2.5, or 3. It is seen that the area of the peak at 193 ppm is so large that it can be accounted for only by assigning this peak to bisulfite ion.

The bisulfite ion concentration is too large to account for the area of the resonance at 175-178 ppm. (The area of the 175-178 ppm peak is dependent upon the temperature, but this fact does not affect the conclusions reached in this section. The temperature dependence of the area will be treated in more detail later.) However, the area seems too great to assign the peak to SO_2 , $\text{S}_2\text{O}_5^{2-}$, or SO_3^{2-} , and the chemical

Table 1
 Variation of S(IV) Peak Area with S(IV) Concentration and
 Acidity in ^{17}O NMR Spectra of Sodium Bisulfite Solutions
 in Which Only One S(IV) Peak Appears

$[\text{S(IV)}]^{a,b}$	pH meter reading	S(IV) peak chemical shift, ppm	$\frac{\text{area S(IV) peak}}{\text{area H}_2\text{O peak}} \times \frac{55.5}{[\text{S(IV)}]}^c$
0.201	4.98	193	3.24 ± 0.07
0.449	4.97	191-193	3.05 ± 0.04
0.101	3.01	175-178	0.50 ± 0.08
0.199	3.00	175-178	0.42 ± 0.06
0.456	3.02	173-177	0.42 ± 0.06

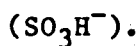
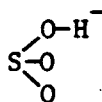
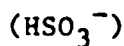
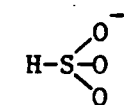
^aThe S(IV) was added as $\text{Na}_2\text{S}_2\text{O}_5$.

^bThe S(IV) concentration is expressed in units of moles of S(IV) per 55.5 moles of H_2O , referred to elsewhere in this work by the term "molality" (see Experimental Procedure).

^cThe values are the average of results taken from spectra recorded between 0° and 30°C , and include a correction for the signal decay which occurred during the pre-acquisition delay time (see Experimental Procedure).

shift relative to water is smaller than what would be expected for SO_2 or SO_3^{2-} .⁹ An additional argument against assigning the peak to $\text{S}_2\text{O}_5^{2-}$ is that its area increases in proportion to the total S(IV) concentration, while in solutions containing most S(IV) in the form of bisulfite ion the $\text{S}_2\text{O}_5^{2-}$ concentration is roughly proportional to the square of the S(IV) concentration.

Having ruled out other options, it appears necessary to assign the peaks at 175-178 ppm and 195 ppm to the two isomers of bisulfite ion, which have the structures



The HSO_3^- structure is known to exist because it is identified by its H-S vibrations in the Raman spectrum; positive but less incontrovertible evidence supports the existence of SO_3H^- .²⁷ The question of which particular isomer should be assigned to each peak will be addressed later. Until then, the two NMR species will be called "195 ppm bisulfite ion" and "175 ppm bisulfite ion" in reference to their oxygen-17 chemical shifts.

Over the pH range from 3 to 5 the total bisulfite ion concentration changes very little, so the same must be true of each of the two isomers. Given the fact that at the intermediate pH values where both are observed the two S(IV) peaks have an intensity ratio between 5 and 10, one predicts that the coalesced peak located at 193 ppm in the spectra of pH 5 solutions should have an area between 6 and 11 times as

great as that of the S(IV) peak at 175-178 ppm in the pH 3 spectra. A value of 7.50 ± 0.75 is calculated from the data in Table 1; this is within the predicted range, and stands as additional confirmation of the interpretation of the spectra.

The proposition that oxygen exchange occurs between water and the 195 ppm bisulfite ion was suggested by the observation that the corresponding lines in the ^{17}O NMR spectrum broaden with increasing acidity. The following comparison of the widths of the lines in the intermediate pH range supports this thesis.

In the case of chemical exchange between two sites, A and B, if the pseudo first order rate constants are much smaller than the frequency separation between the resonances (the slow exchange limit) then the widths of the lines, $(1/T_2)_A$ and $(1/T_2)_B$, are²⁸

$$\left(\frac{1}{T_2}\right)_A = \frac{1}{T_{2A}} + \frac{1}{\tau_{AB}} \quad \text{and} \quad \left(\frac{1}{T_2}\right)_B = \frac{1}{T_{2B}} + \frac{1}{\tau_{BA}},$$

where $1/T_{2A}$ = the "natural linewidth" of site A, that is, the value the linewidth would have in the absence of chemical exchange,

and $1/\tau_{AB}$ = the pseudo first order rate constant for chemical exchange from site A to site B,

with analogous definitions for $1/T_{2B}$ and $1/\tau_{BA}$.

The pseudo first order rate constants are connected by the relation

$$\frac{\tau_{BA}}{\tau_{AB}} = \frac{p_B}{p_A},$$

where p_A and p_B are the mole fractions of the observed nucleus (e.g.

oxygen-17) in sites A and B, respectively. Since the ratio of the area of peak B to that of peak A is equal to p_B/p_A , it is seen that the amount of line broadening due to chemical exchange is inversely proportional to the area of the peak. Although the spectra in the intermediate pH range are more accurately described by three site exchange than by two site exchange, and the widths of the two S(IV) peaks are not negligible compared to their frequency difference, it is still expected that the broadening of the individual lines can give a crude measure of the pseudo first order rate constants.

Although the exchange between the two forms of bisulfite ion causes broadening of both the peak at 195 ppm and the one between 175 and 178 ppm, the amount of broadening of the latter should be about 6.5 times that of the former because of the population difference. Since the former is wider than the latter between pH 4 and 4.5, most of the broadening of the 195 ppm peak must come from sources other than chemical exchange between the two forms of bisulfite ion. As a very rough approximation its width was set equal to the pseudo first order rate constant for chemical exchange with water. (The natural linewidth was ignored, but was not a large fraction of the total linewidth). The rate constant for exchange from water to the 195 ppm bisulfite ion was approximated by setting it equal to the extra broadening of the water peak, $1/T_2 - 1/T_1$.

Given the fact that most of the S(IV) in the solutions exists in the form of bisulfite ion, of which about 87% is the 195 ppm isomer (according to the data in Table 1), the ratio of the population of oxygen-17 in 195 ppm bisulfite ion to its population in water in 0.20 M solutions is calculated to be about 0.010. The ratio of estimated rate

constants obtained from the line broadening of the 195 ppm and water peaks in the spectra of the 0.20 m solution of pH 4.44 was found to be 130 ± 10 . It is concluded that oxygen exchange is occurring between the water and the isomer of bisulfite ion which has its resonance 195 ppm downfield from the water resonance. Both the anomalous temperature dependence of $1/T_2 - 1/T_1$ of water which is shown by the pH 3 solution in Figure 5, and the high temperature behavior of $1/T_2 - 1/T_1$ of water in the pH 3.5 solution, are probably attributable to exchange which is so rapid that the water peak has coalesced with the 195 ppm peak, resulting in exchange narrowing of the coalesced resonance as the temperature rises.

Analysis of the Broadening of the 175-178 ppm S(IV) Peak

After it was learned that oxygen exchange occurs between the two isomers of bisulfite ion and between at least one of these isomers and water, the broadening of the peak located at 175-178 ppm was studied to determine whether the 175 ppm bisulfite ion exchanges oxygen with water at an appreciable rate, and to determine the rate and mechanism of the oxygen exchange between the two isomers of bisulfite ion.

In studying the broadening of the spectral lines to obtain pseudo first order rate constants, the system must, in general, be treated as one involving three site chemical exchange. However, at and below pH 3.5 the exchange between water and the 195 ppm bisulfite ion is not only rapid enough to coalesce the two peaks, as discussed previously, but is also substantially more rapid than exchange between either of these

species and the 175 ppm bisulfite ion. This is known because the width of the peak located at 175-178 ppm, which must be less than or roughly equal to the pseudo first order rate constant for oxygen exchange from 175 ppm bisulfite ion to the 195 ppm site and water, is less than one tenth of the frequency difference between the 195 ppm site and water, while the pseudo first order rate constant for oxygen exchange from 195 ppm bisulfite ion to water must be greater than or roughly equal to this frequency difference in order to bring about coalescence of the 195 ppm and water resonances. Under these conditions the broadening of the 175-178 ppm peak can be analyzed using the two site chemical exchange formalism with oxygen exchange occurring between 175 ppm bisulfite ion and a site comprised of both water and 195 ppm bisulfite ion.

The linewidth of the 175-178 ppm peak can be easily measured in the two-pulse spectrum, but in order to obtain quantitative rate information the relationship between the linewidth and the pseudo first order rate constant for exchange into the other site must be known. Through the following examination of the physical processes which occur during the two-pulse experiment this relationship is deduced. (A rigorous mathematical derivation is given in Appendix B.)

The first pulse of the two-pulse sequence²⁹ tips the magnetization vector of the sample toward the xy-plane of the rotating frame of reference. In the time between the two pulses the 175 ppm bisulfite ion magnetization precesses in the rotating frame relative to the water magnetization, while the 195 ppm bisulfite ion magnetization precesses with the water magnetization due to the rapid exchange between the latter two sites. After the second pulse has tipped the water and 195 ppm bisulfite ion magnetization back to the z-axis, only the 175 ppm

bisulfite ion magnetization has a nonzero component in the xy-plane.

After the end of the second pulse the magnetization decays to its equilibrium orientation along the z-axis. If the 175 ppm bisulfite ion did not exchange oxygens with the other species then its transverse magnetization would decay exponentially with a first order rate constant equal to $1/T_2(175)$, the natural linewidth of the peak in the NMR spectrum. However, the 175 ppm bisulfite ion magnetization is the sum of the individual magnetic moments of the oxygen-17 nuclei in that isomer, and chemical exchange replaces these nuclei with nuclei from the combined water/195 ppm bisulfite ion site; $1/\tau_{175}$ is the pseudo first order rate constant for oxygen exchange out of the 175 ppm bisulfite ion site. Because all the solutions were dilute enough to make the oxygen-17 population in the 175 ppm and 195 ppm sites much smaller than in water, almost all of the oxygen-17 which exchanges into the 175 ppm bisulfite ion site had been in the combined water/195 ppm site at the end of the second pulse; the magnetic moments of these nuclei have random xy-components. The nuclei in the 175 ppm site which exchange into the water/195 ppm site do eventually exchange back into the former, but spend a long enough time in the latter to lose all phase coherence with the nuclei still in the 175 ppm site because the lifetime of an oxygen nucleus in the water/195 ppm site, τ_{H_2O} , is much greater than $1/\Delta\omega$, the inverse of the frequency difference between the two sites (i.e. $1/[175 \times \omega_0 \times 10^{-6}]$). This is the result of the diluteness of the solution and the large frequency difference between the two sites; since

$$\tau_{H_2O} = \tau_{175} \frac{[H_2O]}{3[(SHO_3^-)_{175}]}$$

the diluteness of the solution ensures that $\tau_{H_2O} \gg 1/\Delta\omega$ if τ_{175} is not much less than $1/\Delta\omega$. The existence of the peak at 175-178 ppm with a linewidth at least 10 times smaller than $\Delta\omega$ is proof that τ_{175} is not less than $1/\Delta\omega$, since otherwise this peak would be coalesced with the water/195 ppm bisulfite ion peak. With respect to transverse magnetization the water and 195 ppm site therefore act as a pool of relaxed oxygen-17 which can exchange into the 175 ppm bisulfite ion site. For every oxygen-17 nucleus which exchanges out of the 175 ppm bisulfite ion site, one completely relaxed oxygen-17 nucleus enters from the water/195 ppm site.

The transverse relaxation rate of the 175 ppm bisulfite ion oxygen-17 is thus augmented, over the value it would have in the absence of chemical exchange, by the rate at which nuclei in the 175 ppm site can be replaced by nuclei which are completely relaxed; consequently the first order rate constant for the decay of the transverse magnetization, $\{(1/T_2)_{175}\}$, is given by

$$\left(\frac{1}{T_2}\right)_{175} = \frac{1}{T_{2(175)}} + \frac{1}{\tau_{175}} \quad (2-1)$$

Fourier transformation of the free induction decay yields the peak at 175-178 ppm with a half width at half height of $(1/T_2)_{175}$.

The rate law for oxygen exchange processes involving the 175 ppm bisulfite ion can now be investigated by examining the behavior of the width of the peak as a function of pH, temperature, and concentration of S(IV) species. Figure 6 shows the linewidth of the peak at 175-178 ppm at pH 3 as a function of the concentration of S(IV) at various temperatures. It is seen that the linewidth is a linear function of the

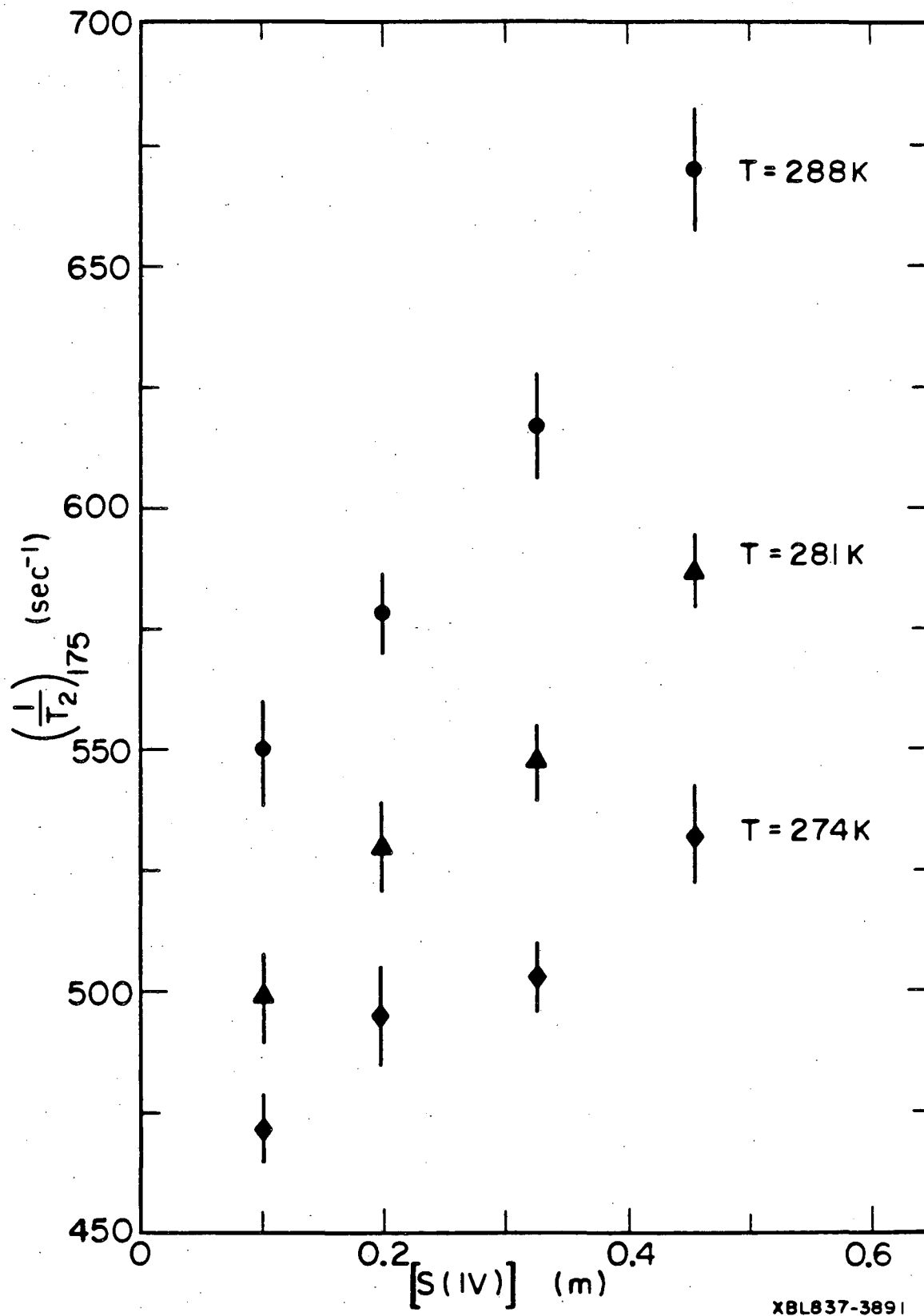


Figure 6a

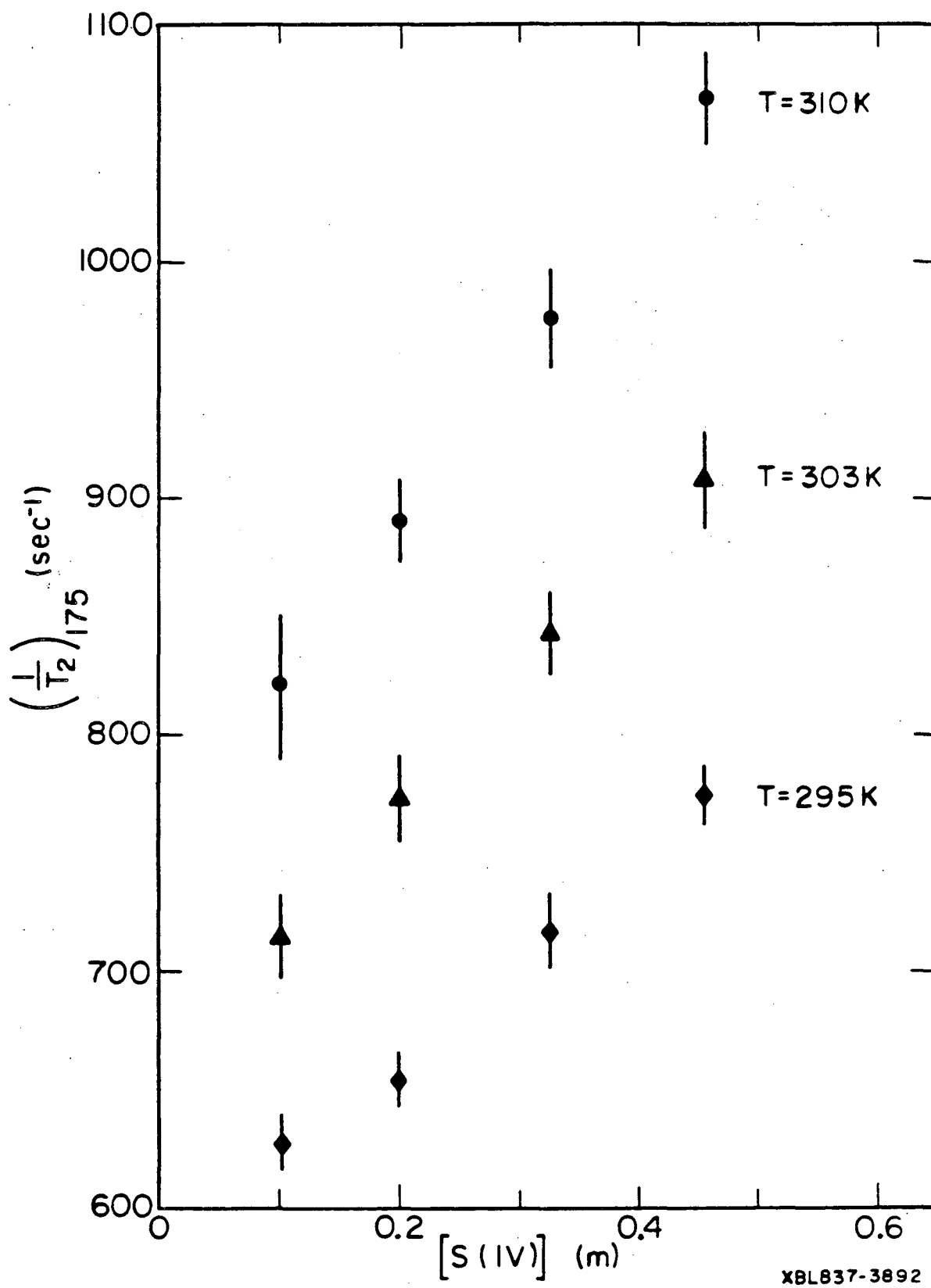
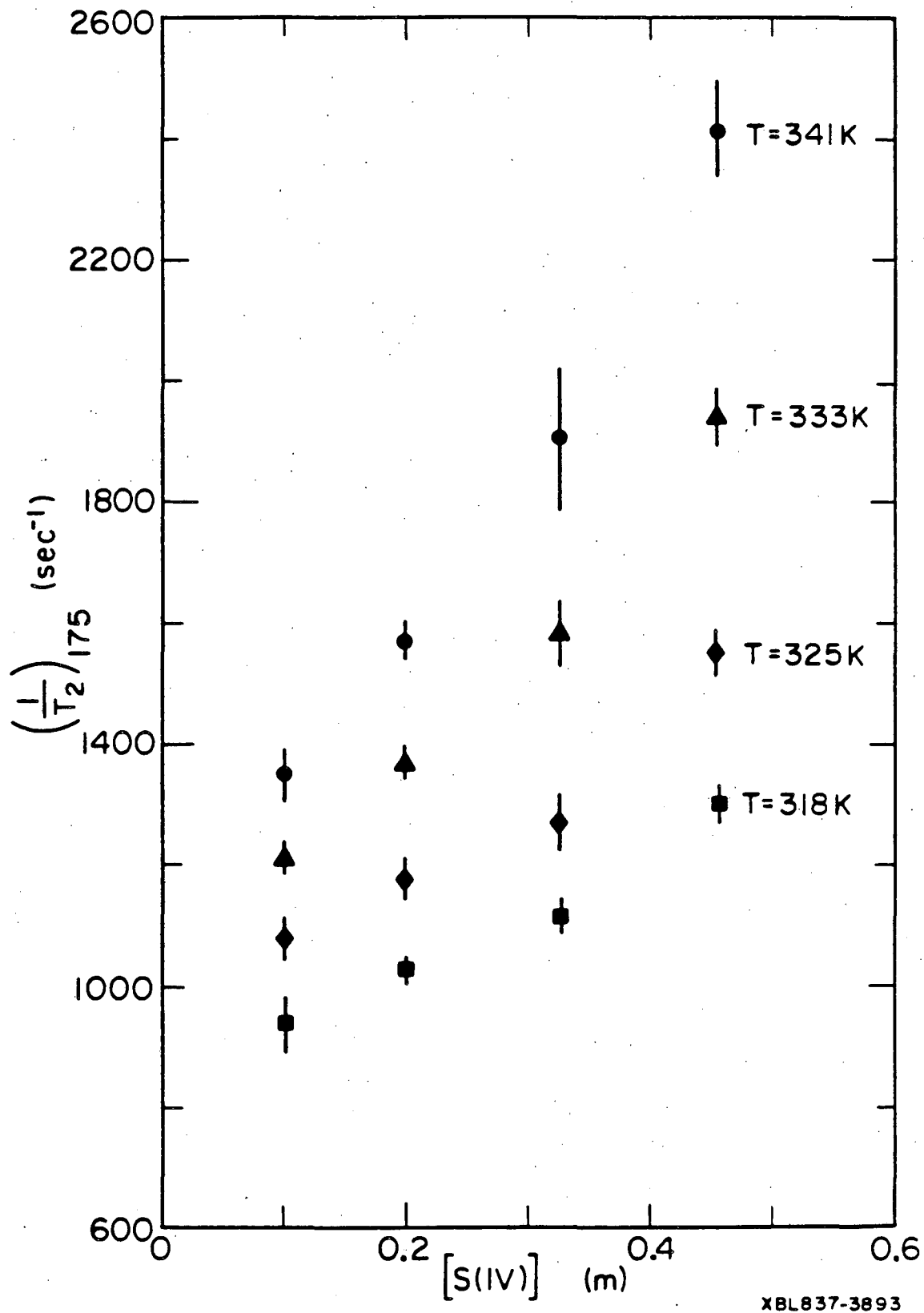


Figure 6b



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Figure 6c

S(IV) concentration with a nonzero intercept. Since the natural linewidth, $1/T_2(175)$, is not expected to vary significantly as the S(IV) concentration is changed, the dependence of the linewidth upon the S(IV) concentration requires that the pseudo first order rate constant, $1/\tau_{175}$, be either first order in S(IV) or the sum of two terms, one of which is first order in S(IV), and the other zero order in S(IV).

Extrapolation of the data in Figure 6 shows that even as the S(IV) concentration approaches zero, the linewidth becomes greater as the temperature increases. Therefore, $1/\tau_{175}$ must contain a term which is zero order in S(IV) in order to account for the temperature dependence of the linewidth at very small concentrations of S(IV). As $[S(IV)]$ approaches zero the linewidth of the peak at 175-178 ppm becomes equal to its natural linewidth plus the zero order term of $1/\tau_{175}$ (if it exists), but only the latter is expected to increase with temperature; the natural linewidth should decrease as the temperature is raised.

To determine the hydrogen ion dependence of the pseudo first order rate constant for oxygen exchange out of the 175 ppm bisulfite ion site, a comparison was made of the linewidth of the peak at 175-178 ppm in the oxygen-17 NMR spectra of four samples: those with $[S(IV)] = 0.10$ m and pH 2.58 and 3.01, and the two with $[S(IV)] = 0.20$ m and pH values of 3.00 and 3.52. At a S(IV) concentration of 0.10 m, changing the pH from 2.58 to 3.01 increased the linewidth only slightly, ranging from an increase of about 10 sec^{-1} or less below room temperature to 50 to 100 sec^{-1} between 50° and 70°C . However, at $[S(IV)] = 0.20$ m the change from pH 3.00 to 3.52 produced an increase in linewidth of about 200 sec^{-1} at the lowest temperatures to 700 sec^{-1} at the highest temperatures. These data indicate that at least one of the terms in

$1/\tau_{175}$ is of some negative order in hydrogen ion, and since the change in pH was very similar at the two S(IV) concentrations, the significantly greater pH effect observed for the more concentrated solutions suggests, but does not prove, that the term in the pseudo first order rate constant which is first order in S(IV) has an inverse dependence upon the hydrogen ion concentration. However, there may also be a term in $1/\tau_{175}$ which is zero order in S(IV) and increases in magnitude with decreasing hydrogen ion concentration.

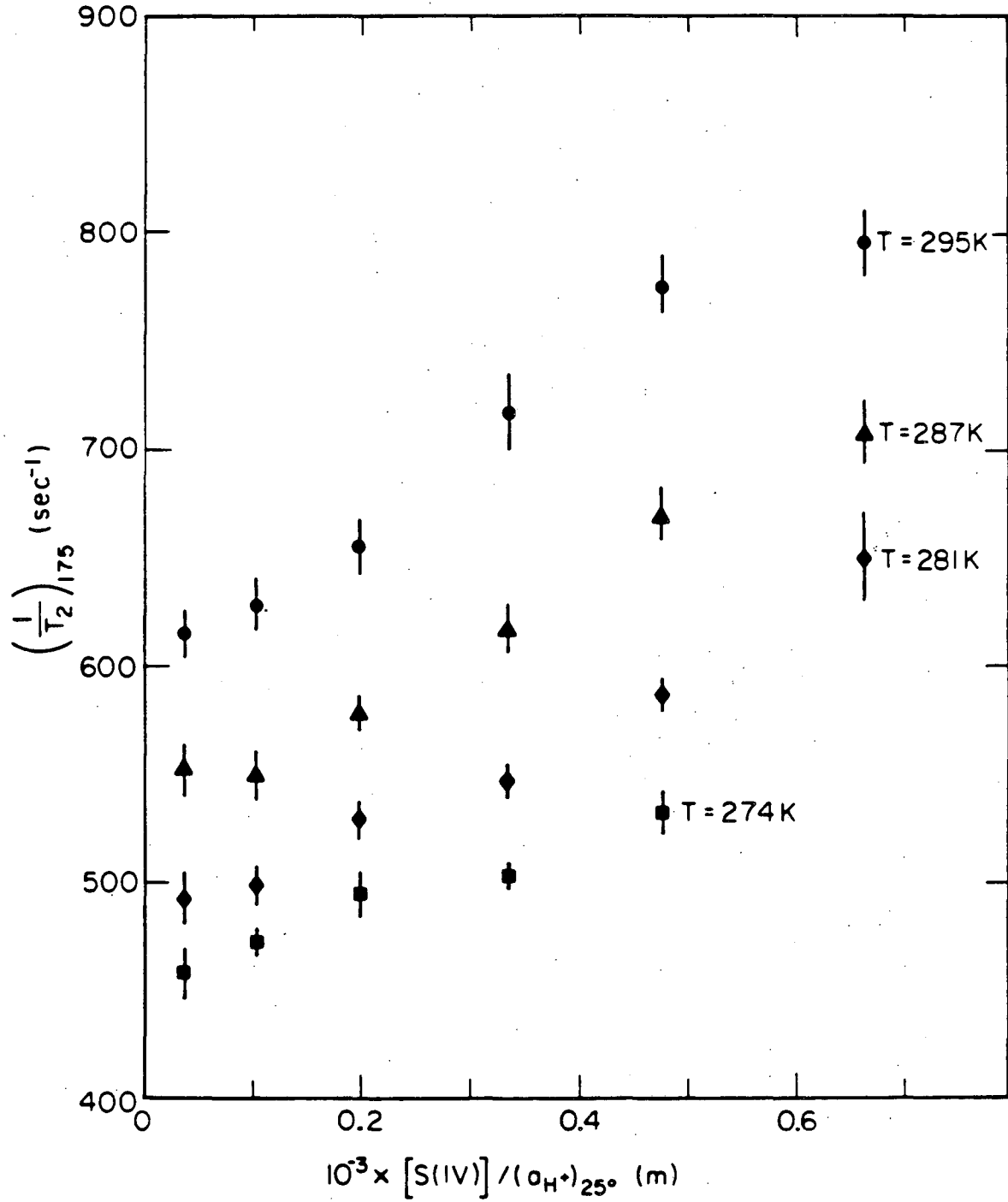
Even if $1/\tau_{175}$ contains a term which is zero order in S(IV) and a function of pH, it can be shown that at pH 3, $1/\tau_{175}$ contains a sizable term which is independent of both [S(IV)] and $[H^+]$. By extrapolation of the 274 K data in Figure 6 to [S(IV)] = 0 one obtains an upper limit to the natural line width of the 175 ppm resonance of about 450 sec^{-1} at 274 K. Since the natural linewidth decreases as the temperature is raised, it must be less than 450 sec^{-1} at 341 K. The total linewidth at 341 K and very small S(IV) concentration is about 1050 sec^{-1} , which means that the term in $1/\tau_{175}$ which is zero order in S(IV) must be greater than 600 sec^{-1} at 341 K. Since the change in linewidth which occurred in going from pH 2.58 to pH 3.01 was only $50\text{-}100 \text{ sec}^{-1}$ at high temperature, of which some may be due to the pH dependence of the term in $1/\tau_{175}$ which is first order in S(IV), the [S(IV)]-independent term in $1/\tau_{175}$ must be between order 0 and -0.2 in H^+ .

Given the small pH dependence of the term in $1/\tau_{175}$ which is zero order in S(IV), it is seen that the term which is first order in S(IV) must be of some negative order in H^+ to account for the comparatively large increase in linewidth of the 175-178 ppm peak as the pH changes from 3.00 to 3.52. For the moment it will be assumed that $1/\tau_{175}$

contains no significant terms which are independent of $[S(IV)]$ and dependent upon $[H^+]$, allowing the pH dependence of the term which is first order in $S(IV)$ to be determined. If this term is of order -1 in H^+ , that is, if the functional form of the pseudo first order rate constant is $1/\tau_{175} = N + Q[S(IV)]/[H^+]$, then a plot of $(1/T_2)_{175}$ vs. $[S(IV)]/a_{H^+}$ should be a straight line if the activity coefficient of each species is essentially the same in all six solutions at any given temperature. Such an assumption about the activity coefficients is probably not a bad one, because the ionic strength is the same in each solution, with sodium chloride replacing sodium bisulfite. Replacing a_{H^+} by its value at $25^\circ C$, $(a_{H^+})_{25^\circ}$, merely expands or contracts the abscissa scale.

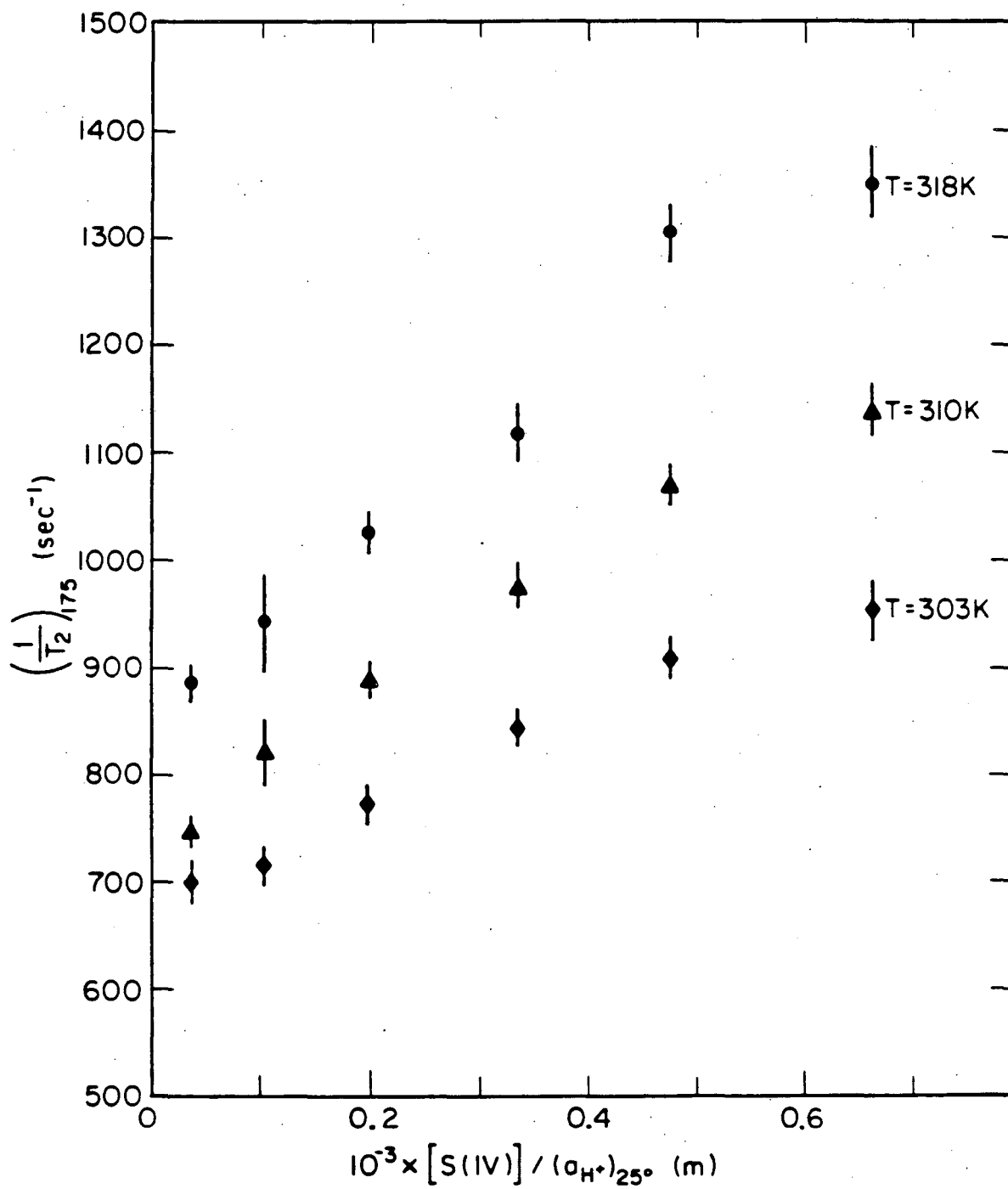
Plots of $(1/T_2)_{175}$ vs. $[S(IV)]/(a_{H^+})_{25^\circ}$ are shown in Figure 7 for several temperatures, using $1/T_2$ values of the 175-178 ppm peak in the spectra of the solutions having pH values ranging from 2.58 to 3.52. The points exhibit systematic deviations from straight line character. Similar graphs with $[S(IV)]/[(a_{H^+})_{25^\circ}]^{0.5}$ or $[S(IV)]/[(a_{H^+})_{25^\circ}]^{1.5}$ as the abscissa show a greater deviation from linearity.

Since there appears to be no linear function of one variable which satisfactorily fits the data, it is necessary to consider the possibility that the rate law contains more than two terms. However, to be consistent with the plots of Figure 6 any such rate law must reduce to a linear function of $[S(IV)]$ under conditions of constant pH. In many of the plots of Figure 7 a line drawn through only the middle four points (which correspond to pH 3.0 solutions of various $S(IV)$ concentrations) passes below the point having an abscissa of 0.038 (pH 2.58, $[S(IV)] = 0.10$ m) and above the point having an abscissa of 0.662



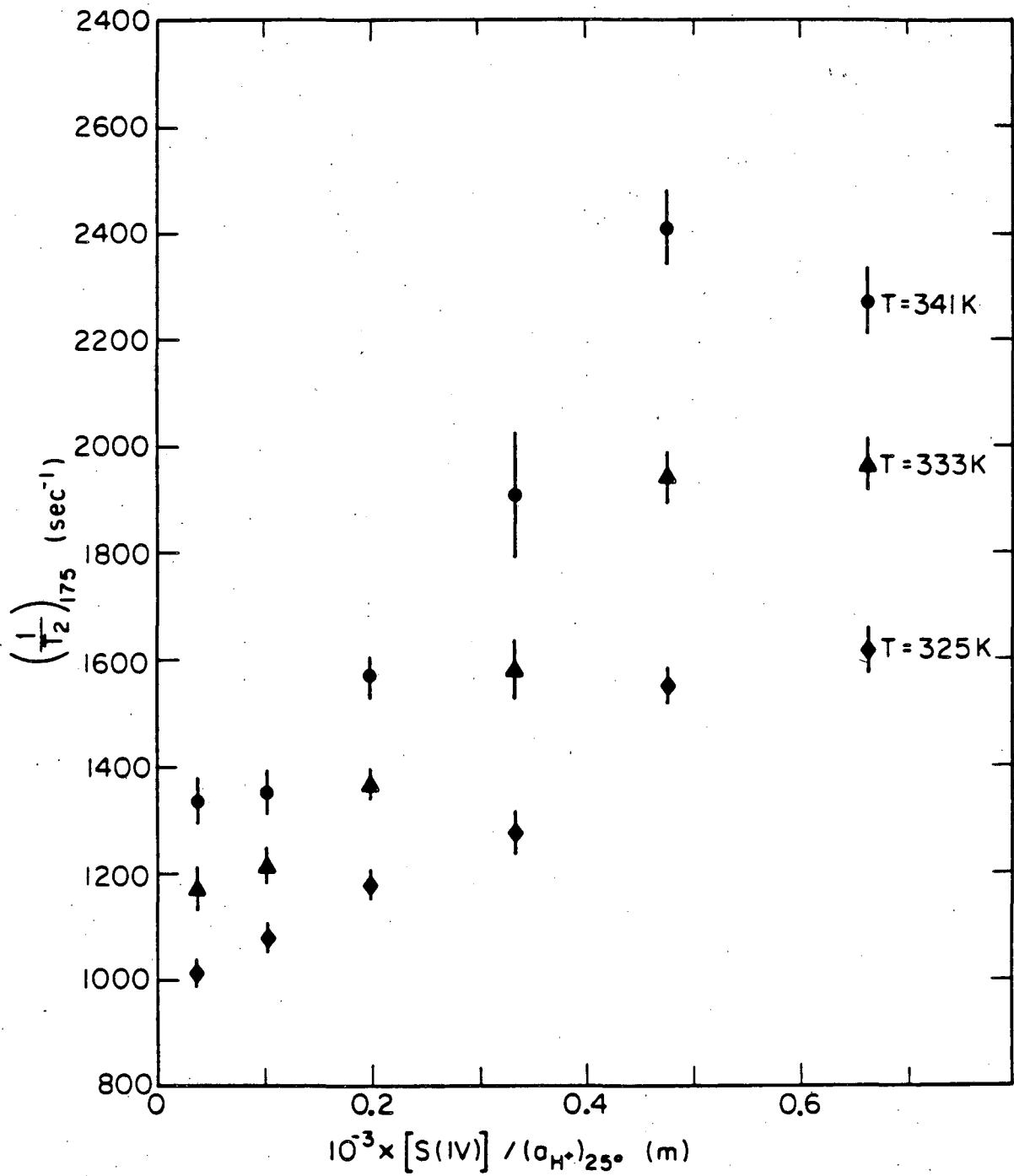
XBL 837-3903

Figure 7a



XBL837-3902

Figure 7b



XBL837-3901

Figure 7c

(pH 3.52, $[S(IV)] = 0.20$ m). If it is assumed that two of the terms in $1/\tau_{175}$ are $N + Q[S(IV)]/[H^+]$, then the locations of the outside points of Figure 7 indicate that an additional term such as $R[SHO_3^-]$ or $R'[H^+]$ may be a significant part of the pseudo first order rate constant.

Before proceeding further, the assumed second term in $1/\tau_{175}$, $Q[S(IV)][H^+]^{-1}$, will be rearranged, because it is desirable to replace the factor $[S(IV)]$ with the concentration of one of the actual species in the solution. Bisulfite ion is the species chosen, because it is the only one whose concentration remains nearly fixed in proportion to $[S(IV)]$ over the ranges of pH and S(IV) concentration which were studied. The second term in $1/\tau_{175}$ is therefore rewritten as

$$Q \frac{[S(IV)] [SHO_3^-]}{[SHO_3^-] [H^+]},$$

where $[SHO_3^-]$ is the sum of the concentrations of the two isomers of bisulfite ion. The factor $[H^+]$ can be removed from the denominator and a rate law indicative of a simpler mechanism can be obtained by replacing $[SHO_3^-]/[H^+]$ with $[SO_3^{2-}]/K_2$, where K_2 is the equilibrium quotient for the dissociation of bisulfite ion, a replacement which yields

$$\frac{1}{\tau_{175}} = N + Q'[SO_3^{2-}], \quad (2-2)$$

where

$$Q' = Q \frac{[S(IV)]}{[SHO_3^-] K_2}.$$

To determine whether either of the two terms $R[SHO_3^-]$ or $R'[H^+]$ is

suitable as the additional term in equation 2-2 the functions

$$\left(\frac{1}{T_2}\right)_{175} = N' + Q'[\text{SO}_3^{2-}] + R[\text{SHO}_3^-] \quad (2-3)$$

and

$$\left(\frac{1}{T_2}\right)_{175} = N' + Q'[\text{SO}_3^{2-}] + R'[\text{H}^+], \quad (2-4)$$

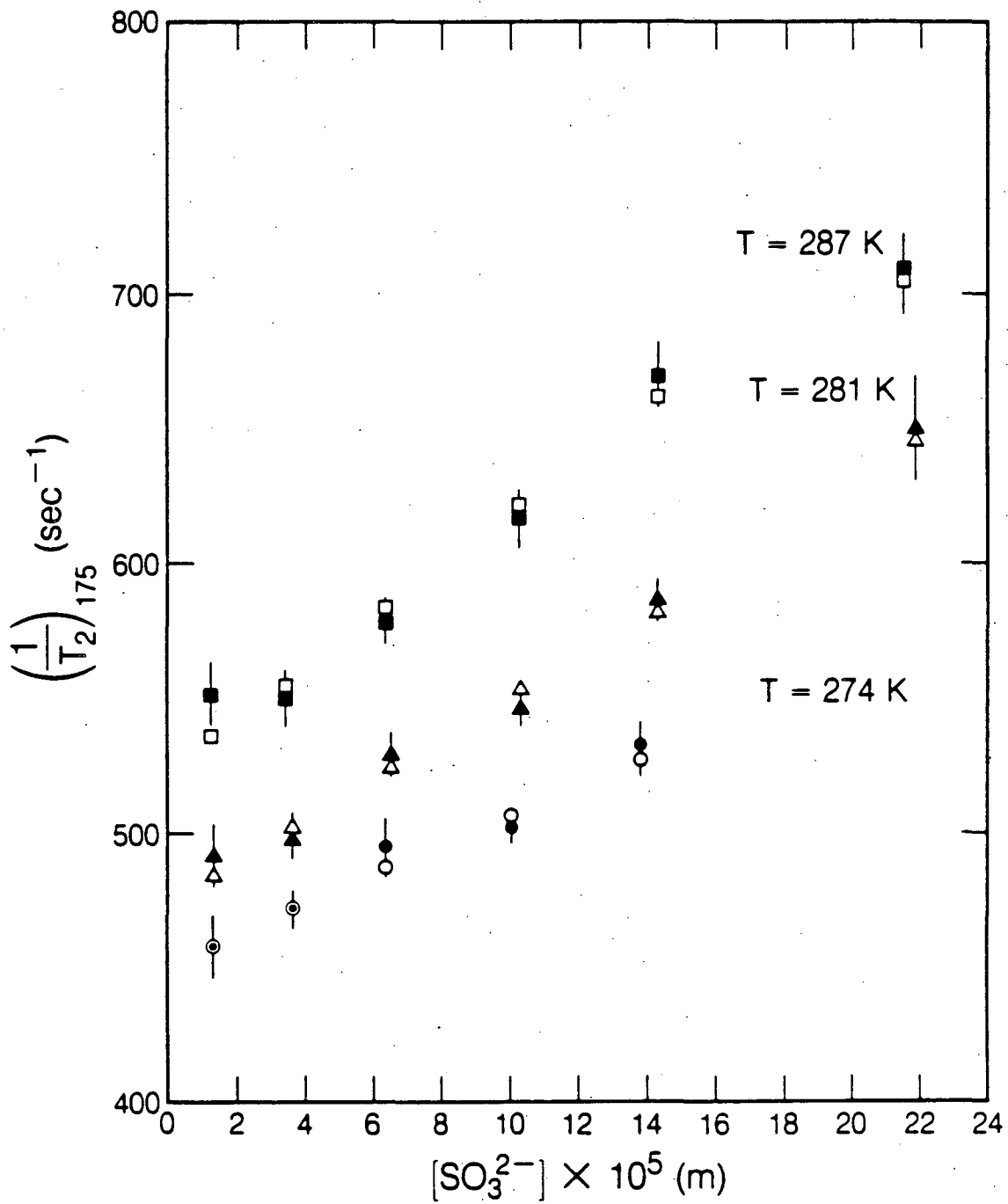
where

$$N' = \frac{1}{T_2(175)} + N \quad (2-5)$$

and N is defined by equation 2-2, were fit to the data of Figure 7 by the method of weighted linear least squares.³⁰ The concentrations of SO_3^{2-} , SHO_3^- , and H^+ used were those calculated for each solution by the method outlined in the Experimental Procedure section. It was found that function 2-4 could not be made to fit the data well, but it was possible to obtain a good fit with function 2-3. Figure 8 shows plots, with $[\text{SO}_3^{2-}]$ as the abscissa, of both experimental values of $(1/T_2)_{175}$ and those obtained from the least squares fitting of function 2-3. It is concluded that the pseudo first order rate constant for exchange of oxygens out of the 175 ppm site into the water/195 ppm site is

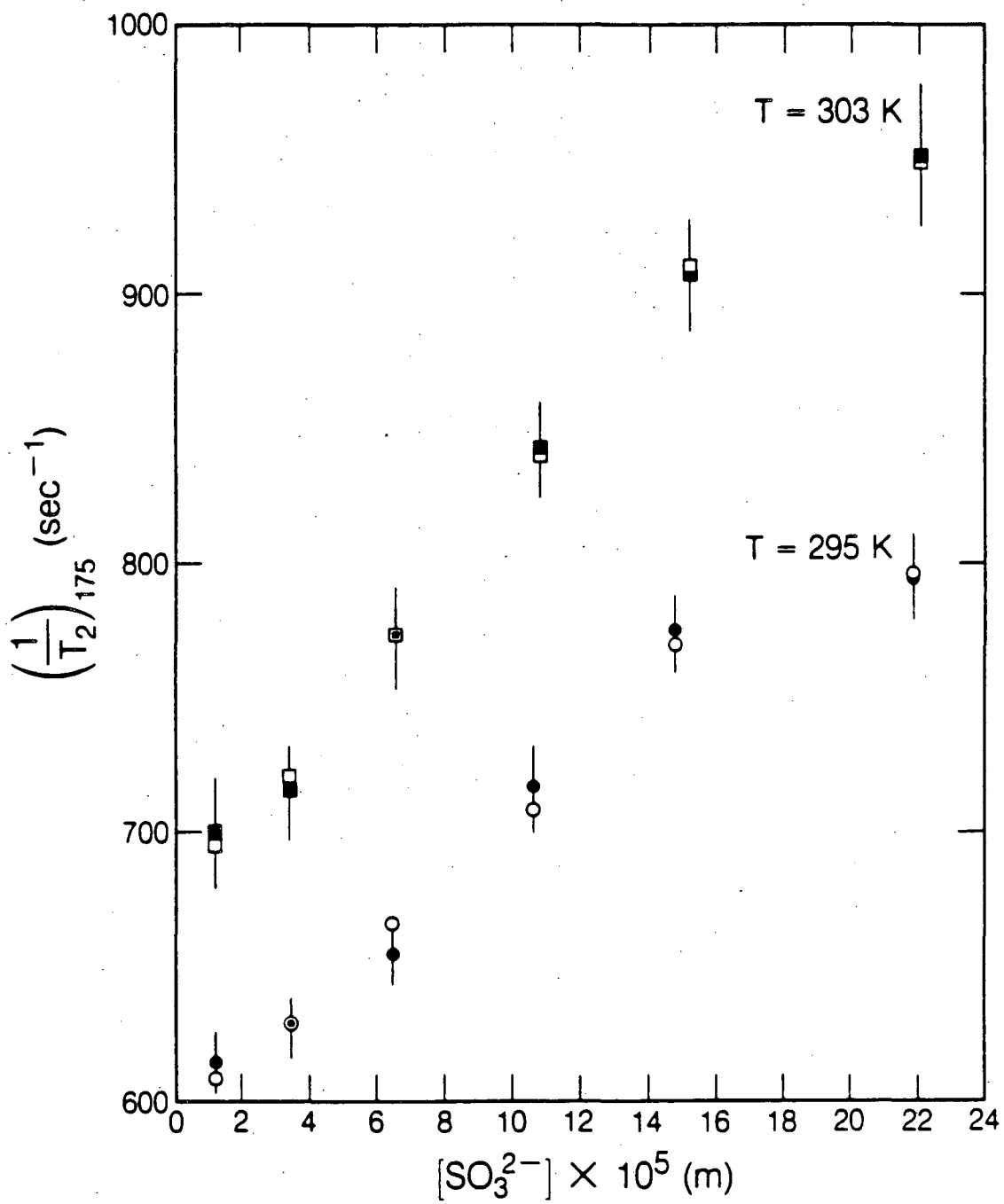
$$\frac{1}{\tau_{175}} = N + Q'[\text{SO}_3^{2-}] + R[\text{SHO}_3^-]. \quad (2-6)$$

The functional form of $1/\tau_{175}$ can be accounted for by a mechanism which will be given shortly. Although the contribution of chemical exchange to the relaxation in the 175 ppm site occurs through exchange of oxygens between that site and water (the latter acting as a pool of relaxed oxygens), $1/\tau_{175}$ can be derived from a mechanism in which oxygens are transferred from the 175 ppm bisulfite ion to any of the



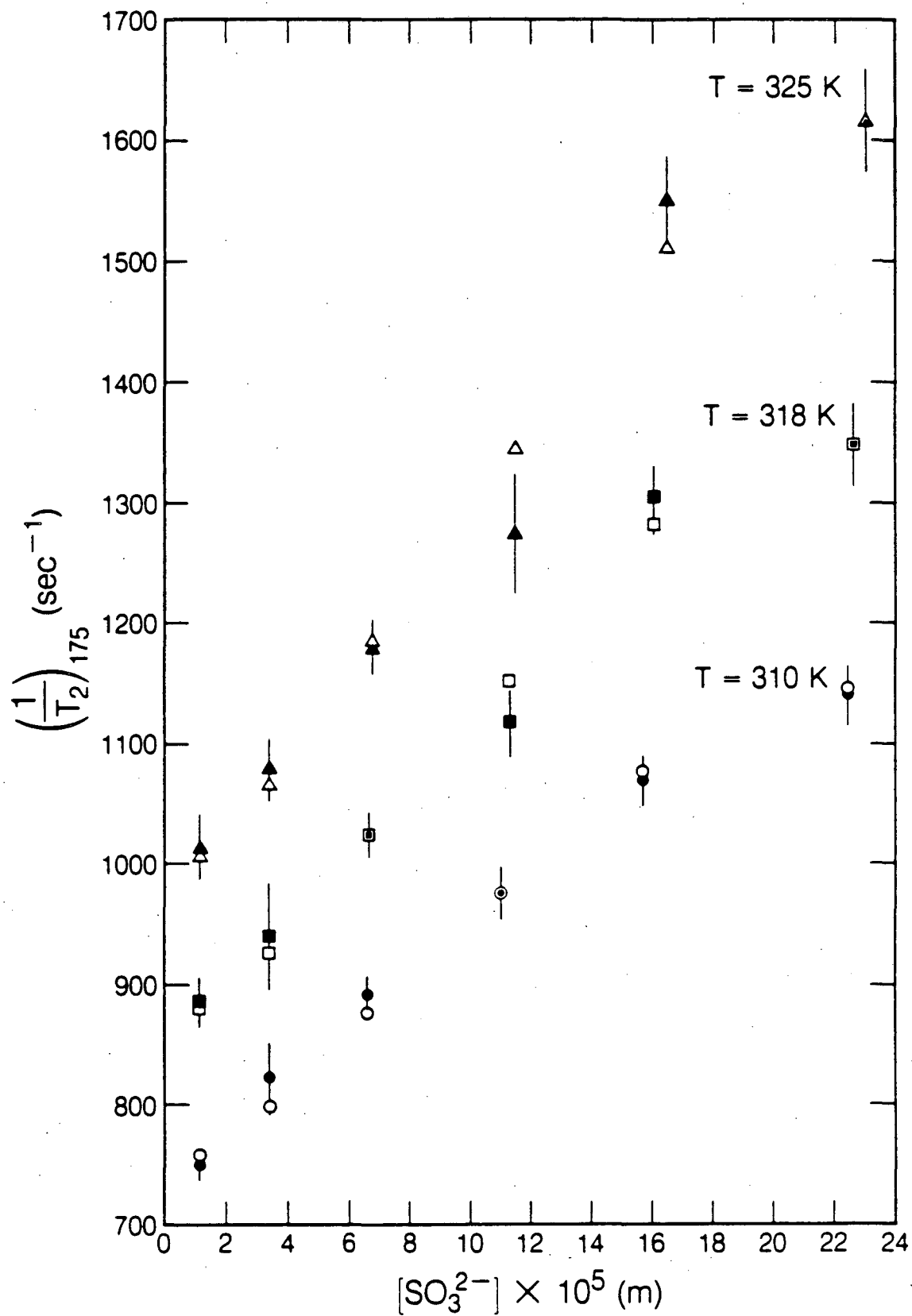
XBL 848-7809A

Figure 8a



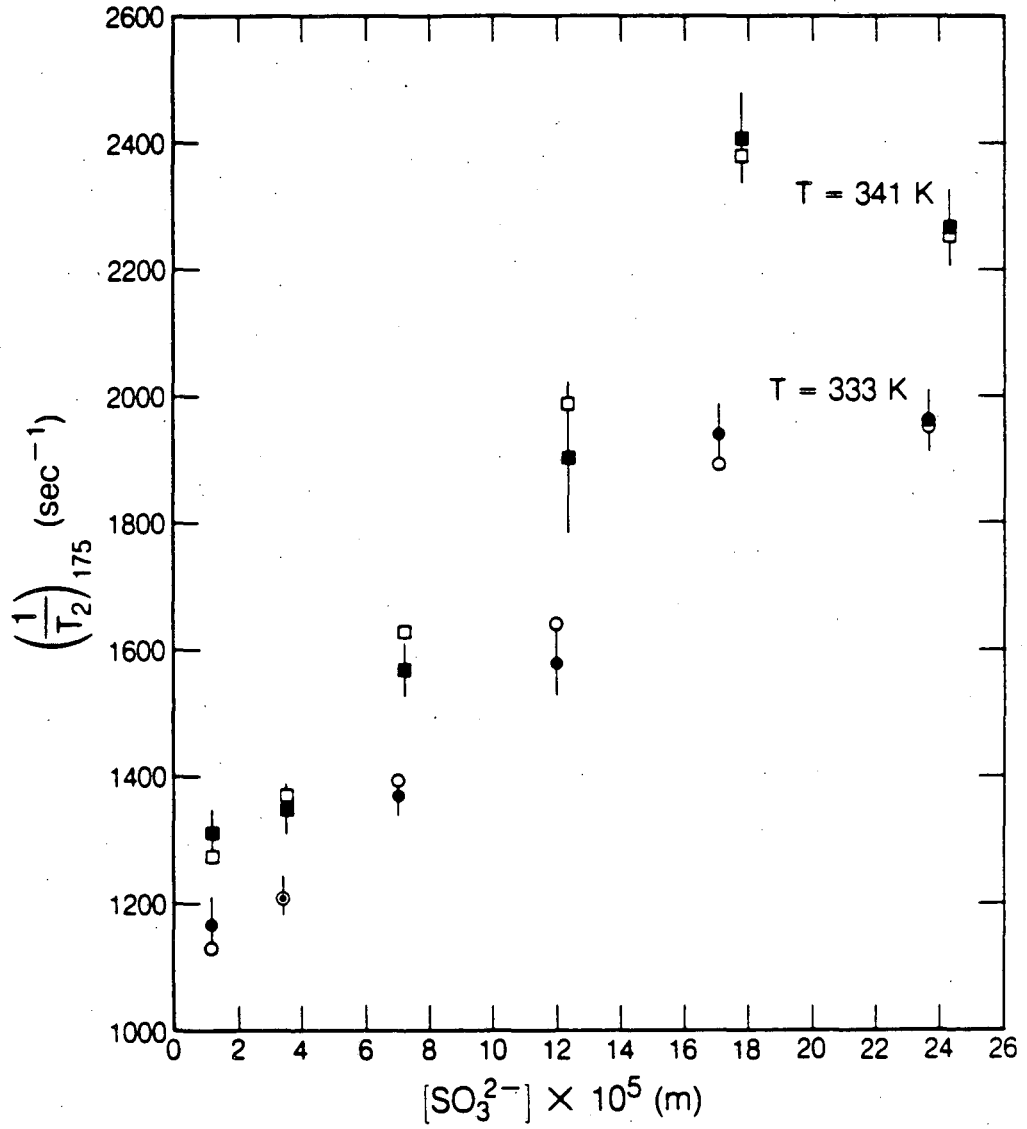
XBL 848-7808A

Figure 8b



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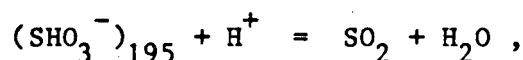
Figure 8c



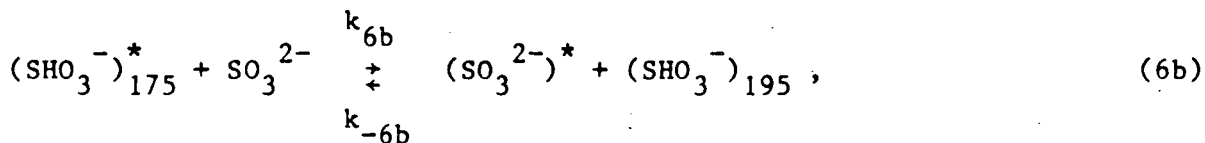
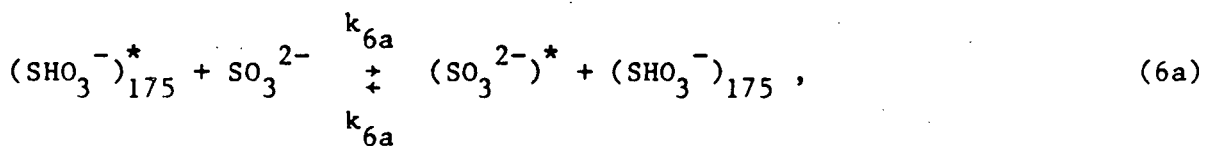
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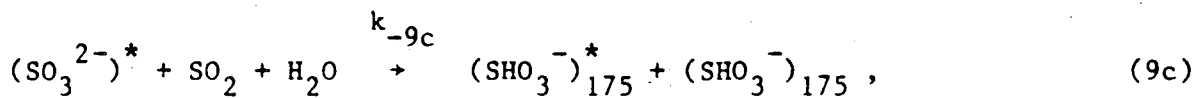
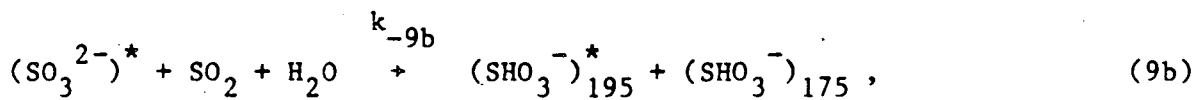
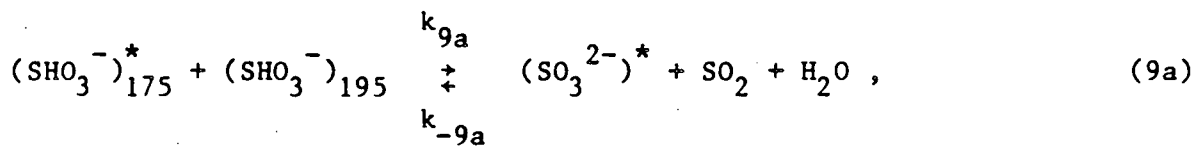
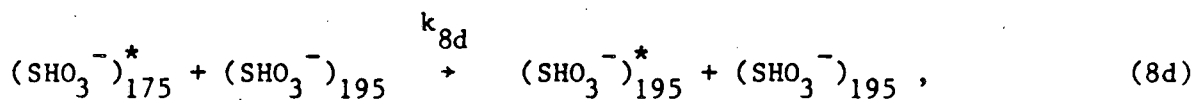
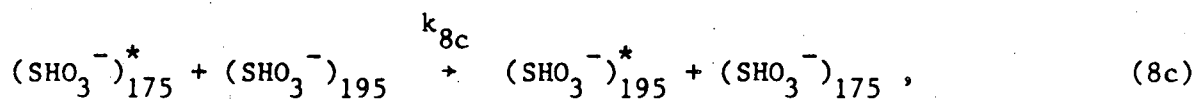
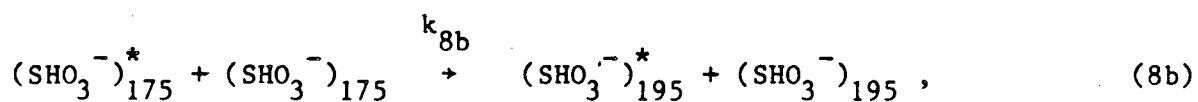
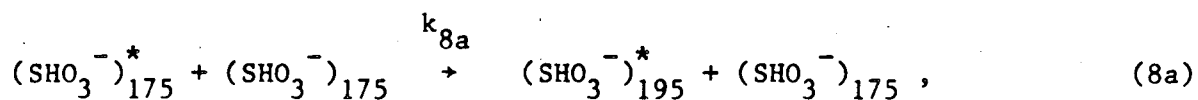
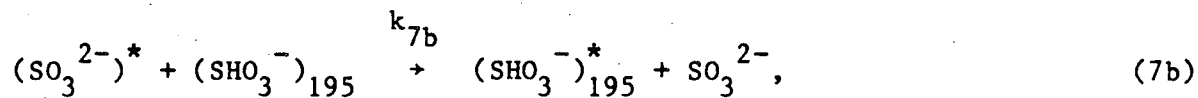
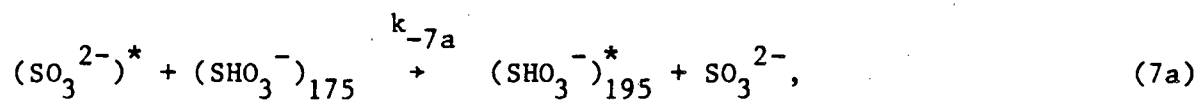
Figure 8d

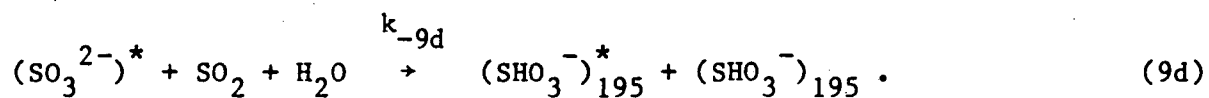
three species H_2O , 195 ppm bisulfite ion, or SO_2 , because virtually all oxygens which reach 195 ppm bisulfite ion and SO_2 are transferred to water rather than 175 ppm bisulfite ion. This is known from the fact that oxygen exchange between the 175 ppm and 195 ppm sites occurs much more slowly (at and below pH 3.5) than exchange between the 195 ppm site and water, and from the results of the next section, in which it is found that the exchange between 195 ppm bisulfite ion and water occurs primarily through the reaction



below (and possibly above) pH 4.5. The proposed mechanism, which exchanges oxygen atoms between the two isomers of bisulfite ion both directly and via sulfite ion, is

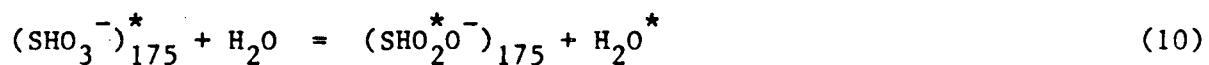




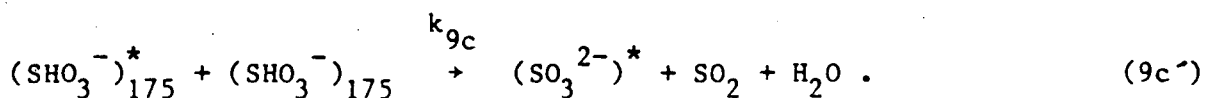
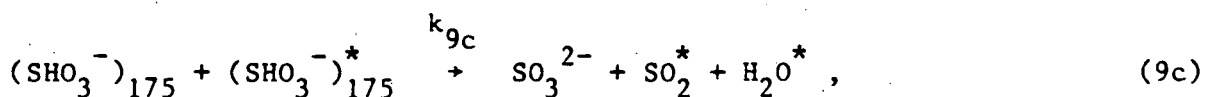
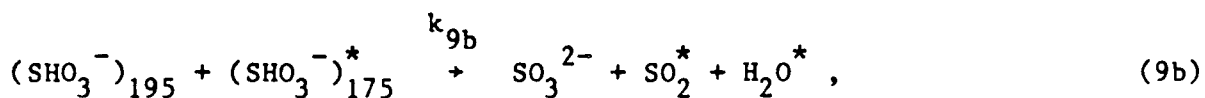


Note that reaction 6b is identical to reaction 7a, and $k_{6b} = k_{-7a}$. The reaction has been written twice, once with the label on the 175 ppm bisulfite ion and the other time with the label on the sulfite ion, to explicitly show that the reaction affects the concentrations of both labelled 175 ppm bisulfite ion and labelled sulfite ion.

Before continuing with a discussion of the mechanism of reactions 4-9 it is necessary to explain the reason for the omission from the mechanism of several steps which are consistent with various terms of $1/\tau_{175}$. The reaction



is consistent with the constant term in $1/\tau_{175}$, but was excluded because it was considered mechanistically improbable. The following reactions are consistent with the $R[\text{SHO}_3^-]$ term of $1/\tau_{175}$:



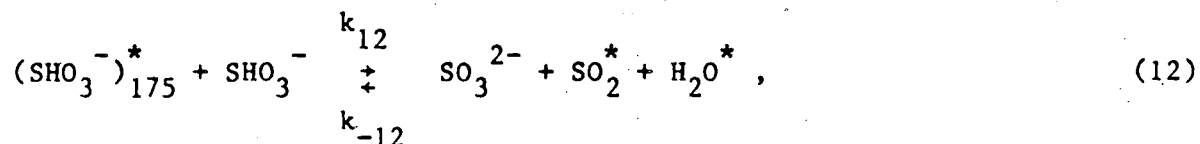
The rationale behind the omission of these steps is related to the absence from $1/\tau_{175}$ of a term which is first order in hydrogen ion.

Such a term could arise from the reaction



For reasons which will soon be explained, reaction 11 is believed to proceed much more rapidly under the present experimental conditions than either of the analogous reactions 9b or 9c. Since $1/\tau_{175}$ contains no significant contribution from reaction 11 it should also, therefore, have no noticeable contributions from reactions 9b and 9c. Furthermore, since the rates of reactions 9c and 9c' are identical, and since both contribute equal amounts to $1/\tau_{175}$, reaction 9c' is also unimportant. If reaction 11 is much more rapid than reactions 9b and 9c under the present experimental conditions then reactions 9b, 9c, and 9c' may reasonably be omitted from the mechanism by which oxygen is exchanged from 175 ppm bisulfite ion to the combined water/195 ppm site.

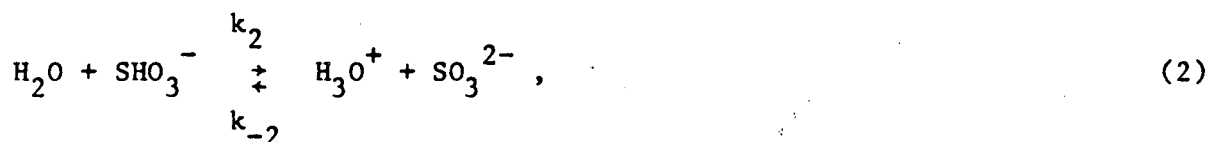
To compare the rate of reaction 11 to those of 9b and 9c it is convenient to define the composite reaction



in which oxygen is transferred to water and sulfur dioxide from 175 ppm bisulfite ion by its reaction with either isomer of bisulfite ion. It may be shown that

$$k_{12}[\text{SHO}_3^-] = k_{9b}[(\text{SHO}_3^-)_{195}] + 2k_{9c}[(\text{SHO}_3^-)_{175}] , \quad (2-7)$$

from which it is seen that if reaction 11 is more rapid than reaction 12, it is more rapid than both reactions 9b and 9c. In reactions 11 and 12 the 175 ppm bisulfite ion acts as a base by accepting protons from the acids H_3O^+ and SHO_3^- . The relative rates of reactions 11 and 12 should thus be very similar to the relative rates of the two acid-base reactions



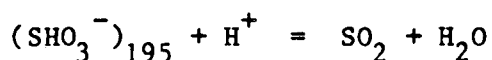
in which water (the base) accepts protons from the acids H_3O^+ and SHO_3^- . The value at 298 K of the second order rate constant k_{13} is known to be^{31,32} $1.1 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$. An upper limit to the value of the pseudo first order rate constant k_2 may be obtained using the relationship $k_2 = k_{-2}K_2$, a value of K_2 equal to $4.6 \times 10^{-7} \text{ M}$, and an upper limit to k_{-2} of $1 \times 10^{11} \text{ M}^{-1}\text{sec}^{-1}$, a value appropriate for a diffusion controlled reaction between a hydrogen ion and a negatively charged base.³³ It is found that $k_2 < 4.6 \times 10^4 \text{ sec}^{-1}$ at 298 K. The relationship between the rates of reactions 13 and 2 is

$$\frac{\text{rate of reaction 13}}{\text{rate of reaction 2}} = \frac{k_{13}[\text{H}^+][\text{H}_2\text{O}]}{k_2[\text{SHO}_3^-]} \quad (2-8)$$

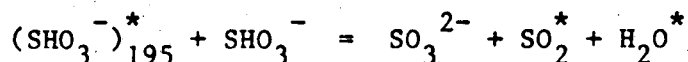
The conditions of the present work for which this ratio takes its smallest value occur at pH 5 and $[\text{S(IV)}] = 0.45 \text{ m}$, in which case the ratio has a value of at least 300. Reaction 13 is much more rapid than

reaction 2, and thus reaction 11 is expected to be considerably more rapid than reaction 12, in the pH and concentration ranges of this study.

Another reason for believing that reaction 11 is much more rapid than reaction 12 arises from the analysis, to be presented in the next section, of the broadening of the water peak in the ^{17}O NMR spectra of the bisulfite solutions, from which it is found that the reaction



transfers oxygen nuclei from 195 ppm bisulfite ion to water much more rapidly than the reaction



below pH 4.5. The relationship between the rates of these two reactions should be very similar to that between reactions 11 and 12, to which they are analogous.

(The omission of reactions 9b and 9c and the retention of 9a is also consistent with the future identification of 175 ppm bisulfite ion and 195 ppm bisulfite ion as HSO_3^- and SO_3H^- , respectively. The latter would be expected to react more easily with a proton donor to produce sulfur dioxide and water.)

Returning now to the mechanism of reactions 4 through 9, it is seen that the net reaction which occurs is

$$(\text{SHO}_3^-)_{175}^* \xrightarrow{(\tau_{175,195})^{-1}} (\text{SHO}_3^-)_{195}^*$$

for which the corresponding rate law is

$$-\frac{d[(\text{SHO}_3^-)_{175}^*]}{dt} = \frac{1}{\tau_{175,195}} [(\text{SHO}_3^-)_{175}^*]. \quad (2-9)$$

Since the proposed mechanism contains no reactions which exchange oxygen atoms directly between 175 ppm bisulfite ion and water at an appreciable rate, $1/\tau_{175}$, which is defined as the pseudo first order rate constant for exchange of oxygen atoms between 175 ppm bisulfite ion and the combined water/195 ppm bisulfite ion site, is equal to $1/\tau_{175,195}$, the pseudo first order rate constant for oxygen exchange from the 175 ppm site to the 195 ppm site.

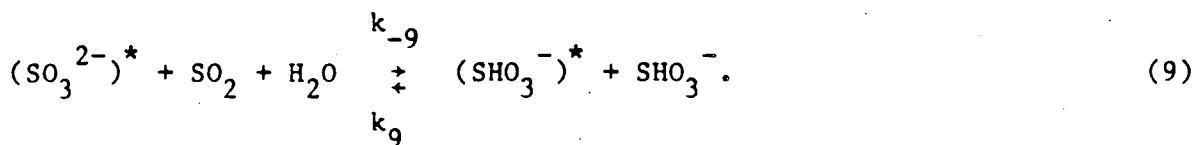
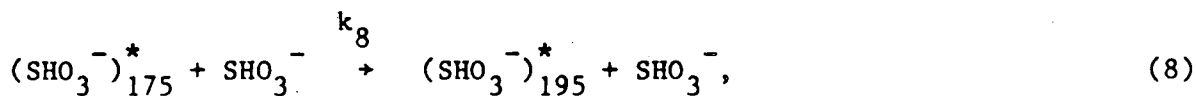
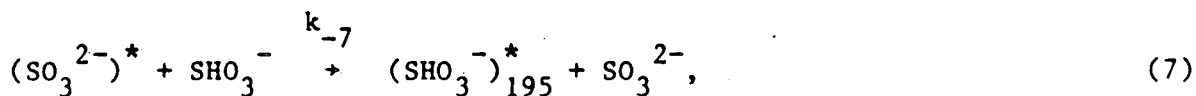
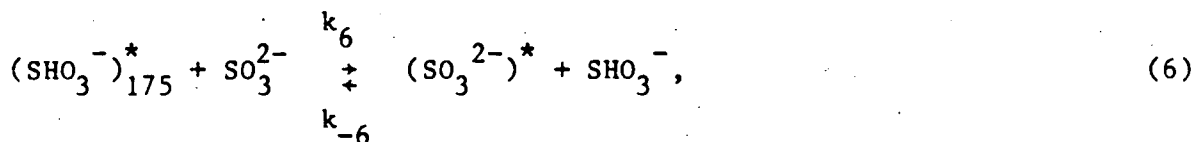
The expression for $1/\tau_{175}$ in terms of the rates of reactions 4 through 9 is obtained by deriving from the mechanism an expression for $d[(\text{SHO}_3^-)_{175}^*]/dt$, from which $[(\text{SO}_3^{2-})^*]$ is eliminated through the use of the steady state approximation. (The steady state approximation is valid for $(\text{SO}_3^{2-})^*$ because its concentration is very small compared to the concentrations of $(\text{SHO}_3^-)_{195}^*$ and $(\text{SHO}_3^-)_{175}^*$ in the acidic solutions for which the experimental rate law was determined.) If the subsequent expression for $d[(\text{SHO}_3^-)_{175}^*]/dt$ is then rearranged to the same form as equation 2-9, $1/\tau_{175}$ is obtained by inspection, since it is the coefficient of $[(\text{SHO}_3^-)_{175}^*]$. According to the suggested oxygen exchange mechanism

$$\frac{1}{\tau_{175}} = (k_{8a} + 2k_{8b})[(\text{SHO}_3^-)_{175}] + (k_{8c} + k_{8d})[(\text{SHO}_3^-)_{195}] + D,$$

where

$$D = \frac{\{k_4 + (k_{6a} + k_{6b})[SO_3^{2-}] + k_{9a}[(SHO_3^-)_{195}]\} \{k_{-7a}[(SHO_3^-)_{175}] + k_{-7b}[(SHO_3^-)_{195}] + k_{-5}[H^+] + (k_{-9b} + k_{-9d})[SO_2]\}}{\{(k_{6a} + k_{-7a})[(SHO_3^-)_{175}] + (k_{-6b} + k_{-7b})[(SHO_3^-)_{195}] + (k_{-4} + k_{-5})[H^+] + (k_{-9a} + k_{-9b} + k_{-9c} + k_{-9d})[SO_2]\}} \quad (2-10)$$

Although $1/\tau_{175}$ in 2-10 does not have the functional form of the experimental rate law (2-6), there are several limiting conditions under which it does reduce to a simple linear expression in $[SO_3^{2-}]$ and $[SHO_3^-]$. Before considering these it is convenient to define three reactions which are combinations of reactions 6a and 6b; 7a and 7b; 8a, 8b, 8c, and 8d; 9a, 9b, 9c, and 9d: they are



Reaction 6 as written and the reverse of reaction 7 express the formation of either isomer of bisulfite ion by the reaction of 175 ppm bisulfite ion with sulfite ion and 195 ppm bisulfite ion with sulfite ion, respectively, and reaction 8 expresses the transformation of one isomer to the other via hydrogen transfer between two bisulfite ions. It is clear that

$$k_6 = k_{6a} + k_{6b} \quad \text{and}$$

$$k_{-9} = k_{-9a} + k_{-9b} + k_{-9c} + k_{-9d} ,$$

and it is not difficult to show that

$$k_{-6}[\text{SHO}_3^-] = k_{6a}[(\text{SHO}_3^-)_{175}] + k_{6b}[(\text{SHO}_3^-)_{195}] ,$$

$$k_{-7}[\text{SHO}_3^-] = k_{7a}[(\text{SHO}_3^-)_{175}] + k_{7b}[(\text{SHO}_3^-)_{195}] ,$$

and

$$k_8[\text{SHO}_3^-] = (k_{8a} + 2k_{8b})[(\text{SHO}_3^-)_{175}] + (k_{8c} + k_{8d})[(\text{SHO}_3^-)_{195}] ,$$

where

$$[\text{SHO}_3^-] = [(\text{SHO}_3^-)_{175}] + [(\text{SHO}_3^-)_{195}] .$$

Substitution of these composite rate constants into 2-10 yields

$$\frac{1}{\tau_{175}} = k_8 [\text{SHO}_3^-]$$

$$+ \frac{\{k_4 + k_6[\text{SO}_3^{2-}] + k_{9a}[(\text{SHO}_3^-)_{195}]\} \{k_{-5}[\text{H}^+] + k_{-7}[\text{SHO}_3^-] + (k_{-9b} + k_{-9d})[\text{SO}_2]\}}{k_{-4}[\text{H}^+] + k_{-5}[\text{H}^+] + k_{-6}[\text{SHO}_3^-] + k_{-7}[\text{SHO}_3^-] + k_{-9}[\text{SO}_2]}$$

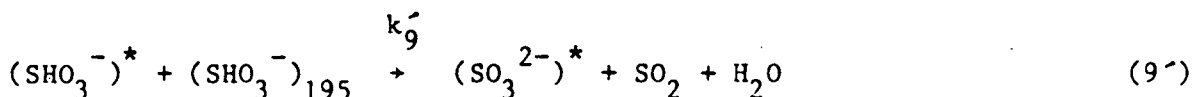
(2-11)

A comparison of the value of $k_{-9}[\text{SO}_2]$ to that of $(k_{-4} + k_{-5})[\text{H}^+]$ shows that the former makes a relatively small contribution to the denominator of the second term of the right side of equation 2-11, and can therefore be neglected. Since $[\text{SO}_2] = [\text{H}^+][\text{SHO}_3^-]/K_1$, the term $k_{-9}[\text{SO}_2]$ is greatest in comparison to $(k_{-4} + k_{-5})[\text{H}^+]$ at high S(IV) concentrations. Therefore, the comparison was made for the most concentrated solution used in this work, for which $[\text{S(IV)}] = 0.456 \text{ m}$, $[\text{H}^+] = 0.0013 \text{ m}$, and $[\text{SO}_2] = 0.013 \text{ m}$ at 298 K.

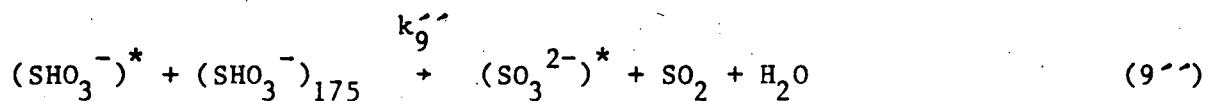
The upper limit to the value of $k_{-9}[\text{SO}_2]$ was determined using the formula

$$k_{-9}[\text{SO}_2] = k_9 \frac{K_1}{K_2} [\text{SO}_2] \quad (2-12)$$

and an upper limit to k_9 , estimated in the following manner. The relationship between k_9 and the rate constants of the reactions

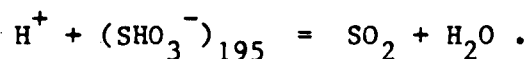


and



$$\text{is } k_9 = \frac{1}{[\text{SHO}_3^-]} \{k_9' [(\text{SHO}_3^-)_{195}] + k_9'' [(\text{SHO}_3^-)_{175}]\} . \quad (2-13)$$

It is known that 195 ppm bisulfite ion exchanges oxygens with water much more rapidly than does 175 ppm bisulfite ion, and it is found in the next section that this exchange between 195 ppm bisulfite ion and water occurs primarily through the reaction



Since this reaction, which involves addition of a proton to 195 ppm bisulfite ion, occurs much more rapidly than the analogous reaction between hydrogen ion and 175 ppm bisulfite ion, and since reactions 9' and 9'' differ from these reactions only in that bisulfite ion, rather than H_3O^+ , is the proton donor, it is reasonable to assume that $k_9' \gg k_9''$. Since the 195 ppm bisulfite ion is also the more abundant of the two isomers, equation 2-13 reduces to

$$k_9 = k_9' \frac{[(\text{SHO}_3^-)_{195}]}{[\text{SHO}_3^-]} . \quad (2-14)$$

An upper limit to k_9' was obtained from the analysis of the water peak broadening, presented in the next section, which yields information about oxygen exchange from 195 ppm bisulfite ion to water. Although no

evidence was found for an exchange process which is second order in bisulfite ion, which would have been found if reaction 9' proceeded at an appreciable rate, the uncertainties in the data were great enough that such a second order exchange process would be unrecognizable if $k_9' < 4500 \text{ M}^{-1}\text{sec}^{-1}$ (i.e. if the contribution to $1/\tau_{195, \text{H}_2\text{O}}$ from reaction 9' was less than 300 sec^{-1} at $[\text{S(IV)}] = 0.2 \text{ m}$ and 298 K). Using this as an upper limit to k_9' and a value of $[(\text{SHO}_3^-)_{195}]/[\text{SHO}_3^-]$ equal to 0.83 (the evaluation of which will be discussed later in this section), it is found from 2-12 and 2-14 that

$$k_{-9}[\text{SO}_2] < 4.5 \times 10^6 \text{ sec}^{-1} \quad (2-15)$$

for the solution which is 0.456 m in S(IV) and 0.0013 m in H^+ .

A lower limit to the value of $(k_{-4} + k_{-5})[\text{H}^+]$ can be found if the rate constant for the reaction



is estimated. Reaction 14 is also either reaction 4 or reaction 5, and belongs to the class of reactions involving proton addition to one of the oxygens of the conjugate base of an inorganic oxyacid. These reactions are known to occur extremely rapidly; their bimolecular rate constants have values of at least $5 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$.⁴ It seems reasonable to assume that the rate constant k_{-14} is also greater than $5 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$, and may be nearly equal to the rate constant for $\text{SO}_4^{2-} + \text{H}^+ \rightarrow \text{SO}_4\text{H}^-$, about $1 \times 10^{11} \text{ M}^{-1}\text{sec}^{-1}$.

Since k_{-14} is equal to either k_{-4} or k_{-5} we have

$$(k_{-4} + k_{-5})[H^+] > k_{-14}[H^+] , \quad (2-16)$$

and for the solution in which $[S(IV)] = 0.456 \text{ m}$ and $[H^+] = 0.0013 \text{ m}$,

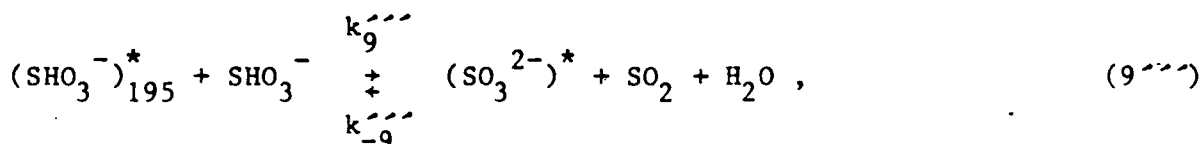
$$(k_{-4} + k_{-5})[H^+] > 6.5 \times 10^7 \text{ sec}^{-1} . \quad (2-17)$$

Combining inequalities 2-15 and 2-17 gives

$$(k_{-4} + k_{-5})[H^+] > 14 \{k_{-9}[SO_2]\} \quad (2-18)$$

for the solution in which $[S(IV)] = 0.456 \text{ m}$ and $[H^+] = 0.0013 \text{ m}$. In all the other solutions from which $1/\tau_{175}$ was determined the ratio of $(k_{-4} + k_{-5})[H^+]$ to $k_{-9}[SO_2]$ is even greater than in the 0.456 m solution. It is therefore reasonable to neglect the contribution of $k_{-9}[SO_2]$ in the denominator of the second term of $1/\tau_{175}$ (equation 2-11).

Given the negligible contribution of $k_{-9}[SO_2]$ to the denominator of the second term of $1/\tau_{175}$, equation 2-11 can be made to reduce to the experimentally determined rate law only if $(k_{-9b} + k_{-9d})[SO_2]$ makes an insignificant contribution to the numerator of the second term of $1/\tau_{175}$. It is almost certainly true that $k_{-5}[H^+]$ is much larger than $(k_{-9b} + k_{-9d})[SO_2]$, in which case the latter can be neglected in the numerator of the second term of $1/\tau_{175}$ in equation 2-11. To show this we define the reaction



which is the composite of reactions 9b and 9d. Since

$k_{-9b} + k_{-9d} = k_{-9'}$, and since all the reactions occur under equilibrium conditions, it follows that

$$\frac{(k_{-9b} + k_{-9d})[SO_2]}{k_{-5}[H^+]} = \frac{k_{9''}[SHO_3^-]}{k_5} \quad (2-19)$$

In both reactions 5 and 9'' the 195 ppm bisulfite ion donates a proton to a base; in reaction 5 the base is water, in reaction 9'' bisulfite ion (either isomer). However, reaction 5 is a simple proton transfer reaction, while reaction 9'' involves additional bond breaking in the base. Because the mechanism of reaction 9'' is more complicated than that of reaction 5, and because the concentration of water is much larger than that of bisulfite ion, we expect the ratio given in equation 2-19 to be much less than one. This allows us to neglect the contribution of $(k_{-9b} + k_{-9d})[SO_2]$ in equation 2-11.

If the contributions of $k_{-9}[SO_2]$ and $(k_{-9b} + k_{-9d})[SO_2]$ are neglected, then equation 2-11 reduces to the experimentally determined rate law if at least one of the following three statements is true:

$$k_{-5}[H^+] + k_{-7}[SHO_3^-] \gg k_{-4}[H^+] + k_{-6}[SHO_3^-], \quad (2-20a)$$

$$k_{-5}[H^+] \gg k_{-7}[SHO_3^-] \quad \text{and} \quad (2-20b)$$

$$k_{-4}[H^+] + k_{-5}[H^+] \gg k_{-6}[SHO_3^-] + k_{-7}[SHO_3^-],$$

$$k_{-7}[\text{SHO}_3^-] \gg k_{-5}[\text{H}^+] \quad \text{and} \quad (2-20c)$$

$$k_{-6}[\text{SHO}_3^-] + k_{-7}[\text{SHO}_3^-] \gg k_{-4}[\text{H}^+] + k_{-5}[\text{H}^+].$$

If inequality 2-20a is true then sulfite ion reacts to form 195 ppm bisulfite ion much more rapidly than it reacts to form 175 ppm bisulfite ion. In such a case the rate limiting steps within the group of reactions 4, 5, 6, 7, and 9 are those through which oxygens are transferred from the 175 ppm bisulfite ion to sulfite ion, and $1/\tau_{175}$ reduces to

$$\frac{1}{\tau_{175}} = k_4 + k_6[\text{SO}_3^{2-}] + k_{9a}[(\text{SHO}_3^-)_{195}] + k_8[\text{SHO}_3^-] \quad (2-20a \text{ true}). \quad (2-21a)$$

The physical interpretation of inequality 2-20b is that if true, it states that bisulfite ions are formed much more rapidly by the reaction of sulfite ion and hydrogen ion than by the reaction of sulfite ion and bisulfite ion, and specifically that the 195 ppm bisulfite ion isomer is formed much more rapidly by the sulfite ion - hydrogen ion reaction than by hydrogen transfer from bisulfite ion to sulfite ion. In this case

$$\frac{1}{\tau_{175}} = \{k_4 + k_6[\text{SO}_3^{2-}] + k_{9a}[(\text{SHO}_3^-)_{195}]\} \left\{ \frac{k_{-5}}{k_{-4} + k_{-5}} \right\} + k_8[\text{SHO}_3^-] \quad (2-20b \text{ true}). \quad (2-21b)$$

Inequality 2-20c is the converse of 2-20b, and causes $1/\tau_{175}$ to reduce to

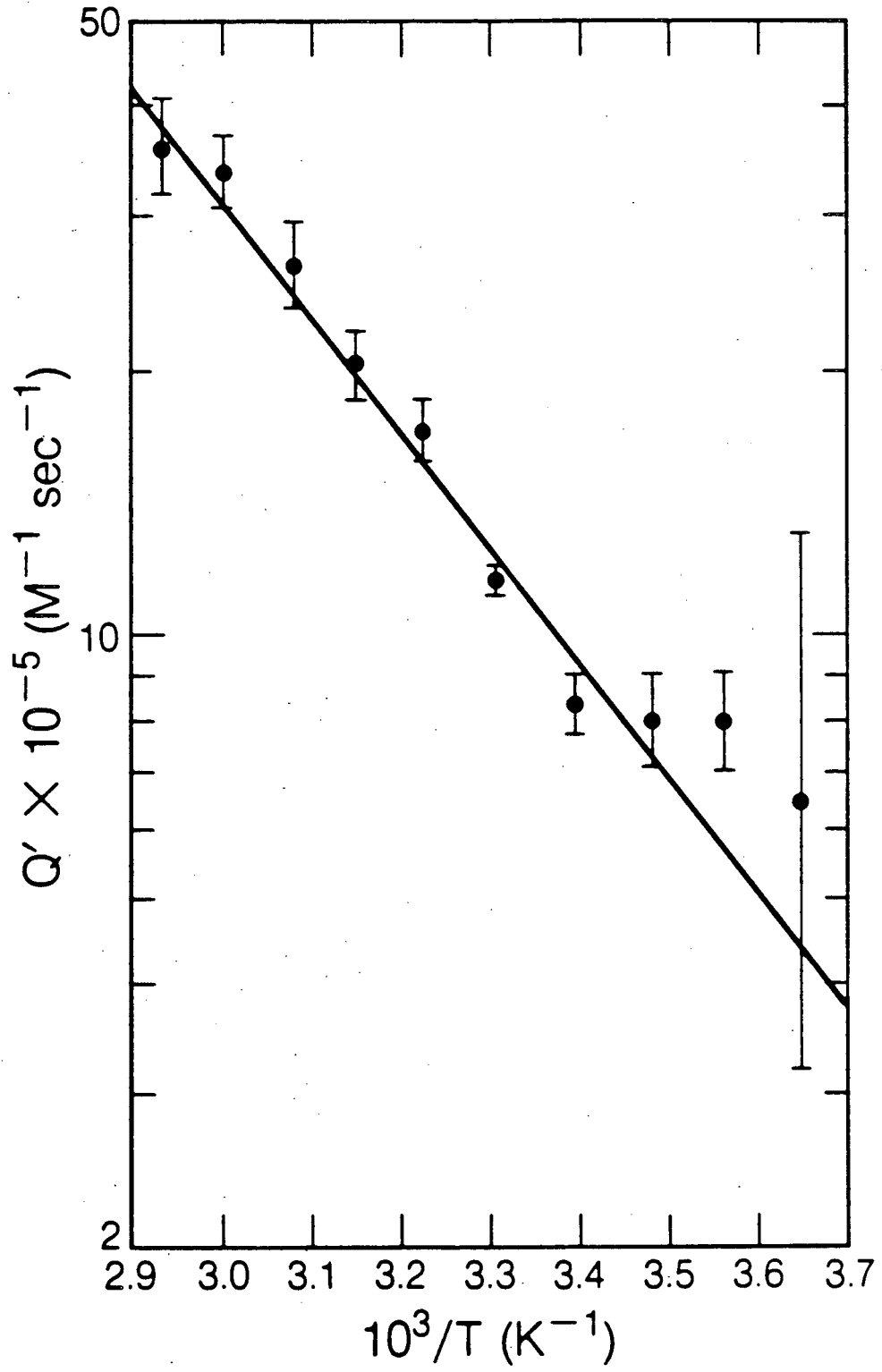
$$\frac{1}{\tau_{175}} = \{k_4 + k_6[\text{SO}_3^{2-}] + k_{9a}[(\text{SHO}_3^-)_{195}]\} \left\{ \frac{k_{-7}}{k_{-6} + k_{-7}} \right\} + k_8[\text{SHO}_3^-]$$

(2-20c true).

(2-21c)

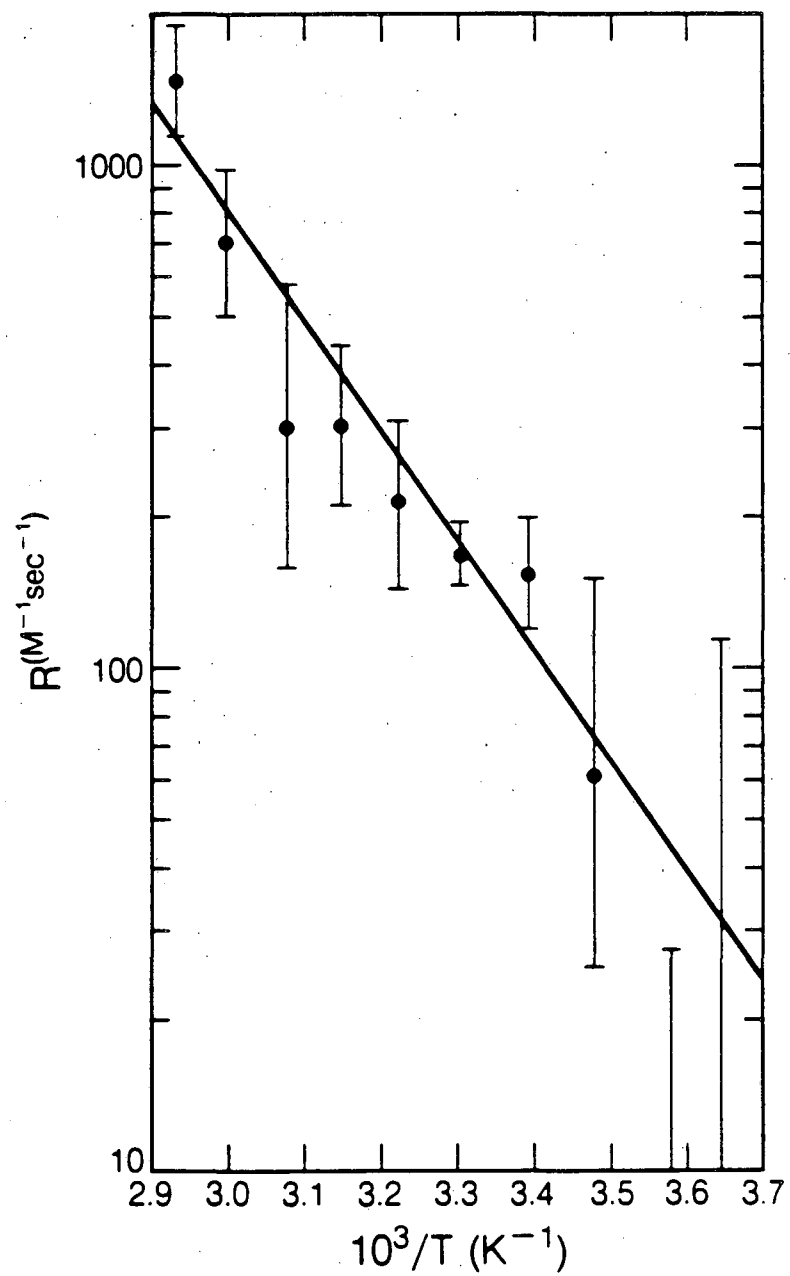
Of the three inequalities in 2-20, only the third seems implausible. Inequality 2-20c is most likely false because the magnitude of $(k_{-4} + k_{-5})[\text{H}^+]$ relative to $(k_{-6} + k_{-7})[\text{SHO}_3^-]$ should be very similar to that of $k_{13}[\text{H}^+][\text{H}_2\text{O}]$ relative to $k_2[\text{SHO}_3^-]$. It was shown earlier that $k_{13}[\text{H}^+][\text{H}_2\text{O}]$ was much larger than $k_2[\text{SHO}_3^-]$. Further evidence that 2-20c is false is provided by the magnitude of the ratio of k_{-4} to k_{-6} , obtained from the experimental data. To see this it is necessary to evaluate the constants N and Q' of equation 2-6.

The values of Q' , R , and $1/T_2(175) + N$ were obtained from the aforementioned least squares fitting of 2-3 to the linewidth data of the solutions at and below pH 3.5. The values of Q' , R , and $1/T_2(175) + N$ obtained thereby are shown in Figures 9, 10, and 11, respectively. At 298 K the value of Q' is about $1.1 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$. A value of N can be estimated by noting that $1/T_2(175)$ is expected to decrease as the temperature rises, and thus its maximum value is given by the low temperature value of $1/T_2(175) + N$, about 450 sec^{-1} . The natural linewidth of water decreases by a factor of two in going from 274 K to 298 K due to a decrease in the rotational correlation time (see Figure 12); it was assumed that $1/T_2(175)$ does the same. From this estimate of $1/T_2(175) < 225 \text{ sec}^{-1}$ at 298 K the data of Figure 11 yield an estimated value of N between 395 and 620 sec^{-1} at 298 K.



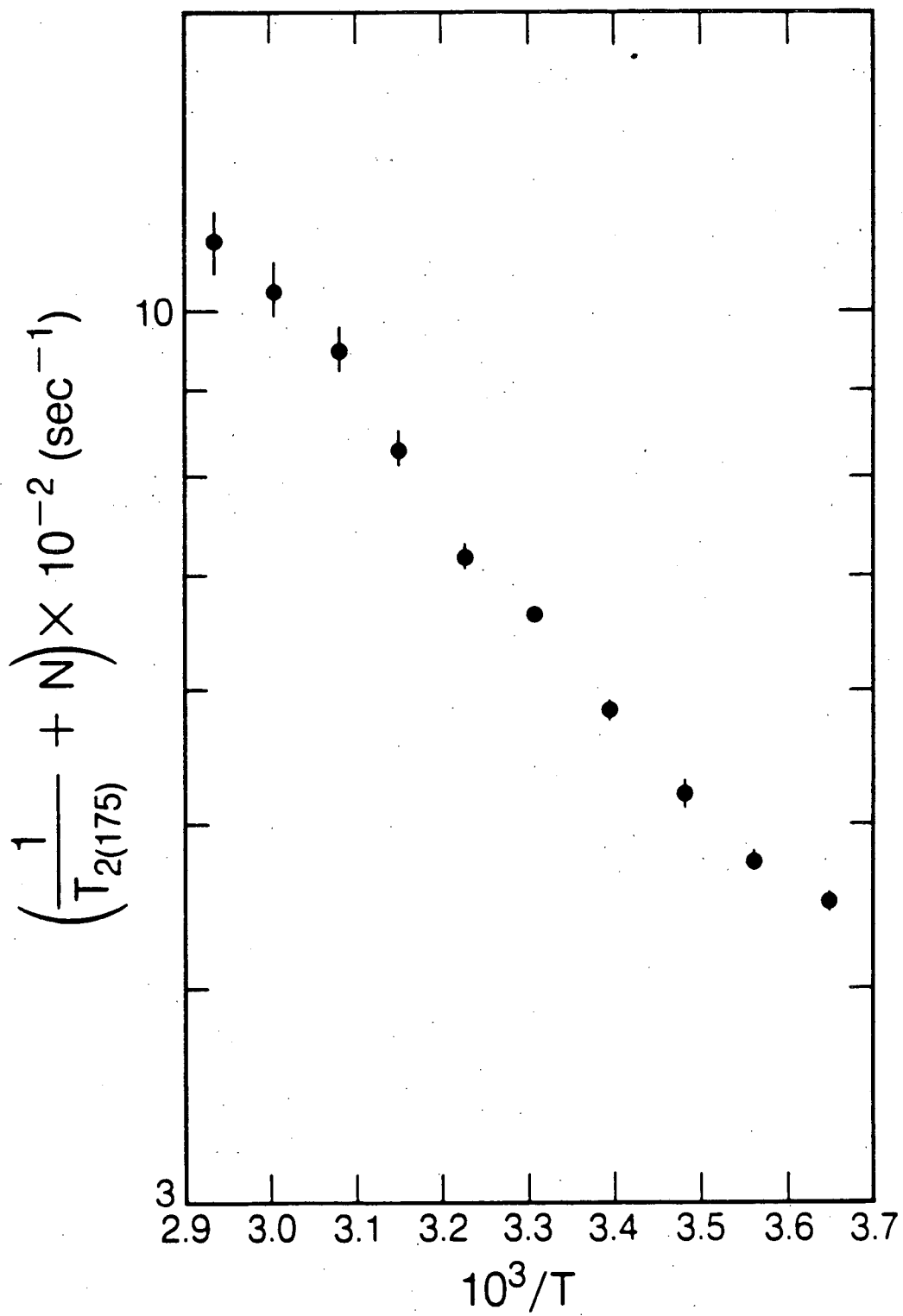
XBL 848-7813

Figure 9



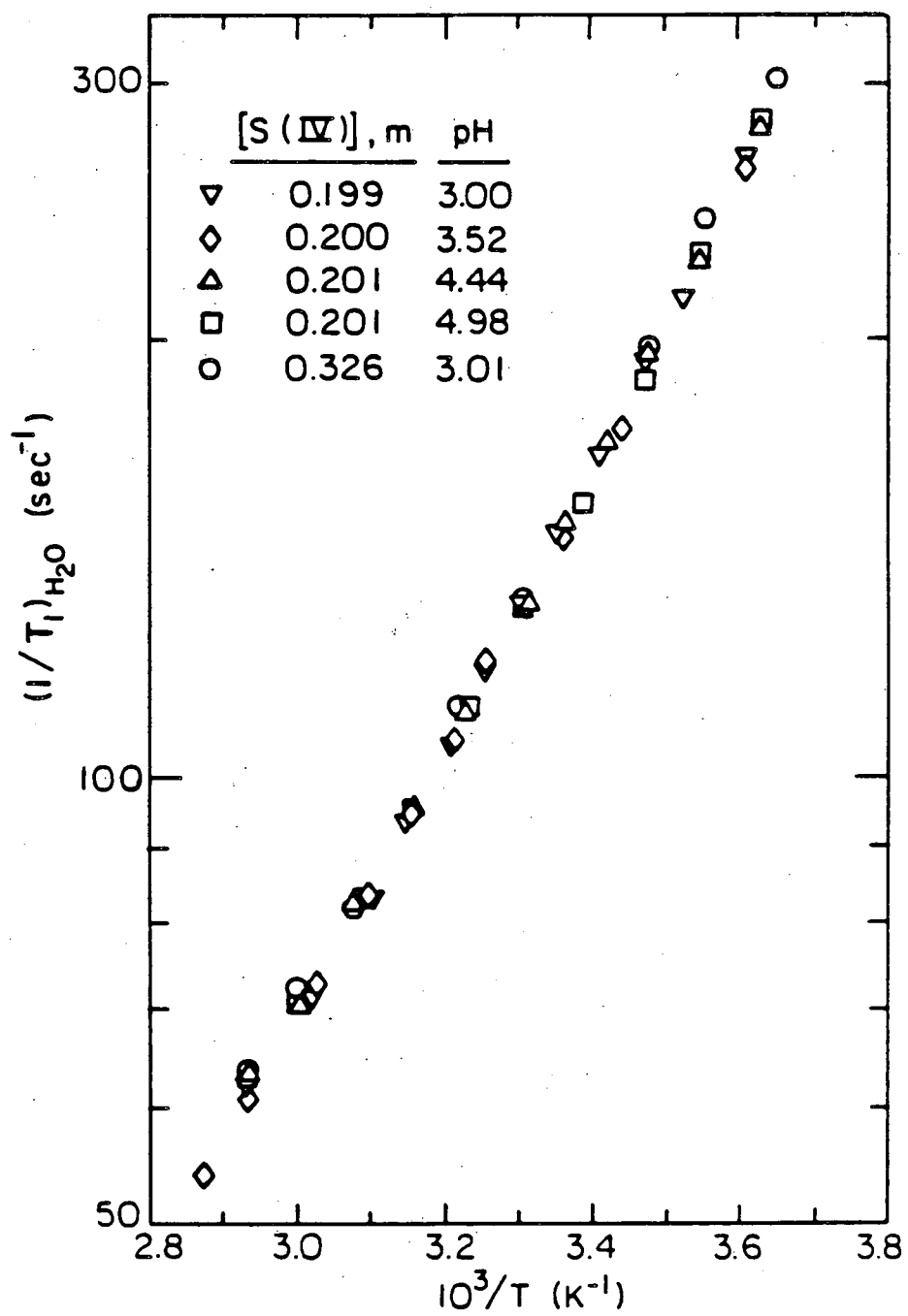
XBL 848-7812

Figure 10



XBL 848-7815

Figure 11



XBL 838-6081

Figure 12

Regardless of which of the limiting cases given by 2-20 may be true, the relationship between N and Q' is

$$\frac{N}{Q'} = \frac{k_4}{k_6}.$$

If both sides of the equation are multiplied by $[H^+]/[SHO_3^-]$, and if the substitutions $k_4 = k_{-4}K_4$, $k_6 = k_{-6}K_6$, and $K_4/K_6 = K_2$ are made, this equation can be rearranged to give

$$\frac{1}{K_2} \frac{N}{Q'} \frac{[H^+]}{[SHO_3^-]} = \frac{k_{-4}[H^+]}{k_{-6}[SHO_3^-]}. \quad (2-22)$$

The right side of this equation is the ratio of two of the terms in inequalities 2-20a, 2-20b, and 2-20c. Substitution of the values $K_2 = 10^{-6.34}$ M, $Q' = 1.1 \times 10^6$ M⁻¹sec⁻¹, 395 sec⁻¹ < N < 620 sec⁻¹, 0.10 M < $[SHO_3^-]$ < 0.42 M, and $[H^+] = 0.0013$ M (values appropriate for the pH 3 bisulfite solutions from which $1/\tau_{175}$ was determined) into the left side of 2-22 yields

$$2 < \frac{k_{-4}[H^+]}{k_{-6}[SHO_3^-]} < 16.$$

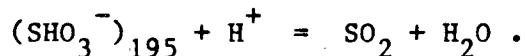
Given both this relationship between $k_{-4}[H^+]$ and $k_{-6}[SHO_3^-]$, and the likelihood that k_{-5}/k_{-7} is about equal to k_{-4}/k_{-6} due to the similarity of the two pairs of reactions, it is concluded that inequality 2-20c is probably false in the pH range in which $1/\tau_{175}$ was determined.

Before continuing with the interpretation of $1/\tau_{175}$, it is necessary to digress and discuss the evaluation of the equilibrium quotient for the reaction.

$$(\text{SHO}_3^-)_{175} = (\text{SHO}_3^-)_{195} \cdot \quad (15)$$

The equilibrium quotient K_{15} was determined using the areas of the peak at 175-178 ppm in the pH 3 solutions and the coalesced peak at 193 ppm in the pH 5 solutions. If the only S(IV) species present in the solutions were HSO_3^- and SO_3H^- , then the quantity $\{[(\text{SHO}_3^-)_{175}] + [(\text{SHO}_3^-)_{195}]\} / [(\text{SHO}_3^-)_{175}]$ would be given by the ratio of the area of the 193 ppm peak at pH 5 to the area of the 175-178 ppm peak at pH 3. However, between 3 and 10% of the S(IV) in each of the solutions is present in the form of SO_3^{2-} , $\text{S}_2\text{O}_5^{2-}$, and SO_2 , the ^{17}O resonances of which could perhaps be coalesced with the resonance of one of the isomers of bisulfite ion, creating the possibility that the areas of the 175-178 ppm and 193 ppm peaks are not proportional to the 175 ppm bisulfite ion and total bisulfite ion concentrations, respectively. It was therefore necessary to make some assumption concerning which S(IV) species contribute to the areas of the two peaks. It was assumed that the area of the peak at 175-178 ppm is due only to 175 ppm bisulfite ion, while the area of the peak at 193 ppm arises from all the S(IV) species due to coalescence of the SO_2 and $\text{S}_2\text{O}_5^{2-}$ resonances with the 195 ppm bisulfite ion resonance and the coalescence, at pH 5, of the SO_3^{2-} resonance with those of both 175 ppm bisulfite ion and 195 ppm bisulfite ion. The assignment of the SO_3^{2-} oxygen population to either the 175 ppm or the 195 ppm site is unimportant at low pH because the concentration of SO_3^{2-} is very small at high acidity. The results of the analysis of the broadening of the water peak will show that the SO_2 and 195 ppm bisulfite ion resonances have coalesced over the entire pH range studied due to the rapid oxygen exchange which occurs through the

reaction



Results from the ^{17}O NMR spectra of two very concentrated bisulfite solutions ($[\text{S(IV)}] > 4 \text{ m}$), in which the $\text{S}_2\text{O}_5^{2-}$ concentration is large enough to make a significant contribution to peak areas, indicate that at high concentrations the $\text{S}_2\text{O}_5^{2-}$ and bisulfite ion resonances are coalesced. (The pH meter readings of the two solutions were 3.2 and 4.5.) It was assumed that the $\text{S}_2\text{O}_5^{2-}$ and the 195 ppm bisulfite ion resonances are also coalesced at lower S(IV) concentrations.

The assumption that the SO_3^{2-} contributes to the area of the 193 ppm peak at pH 5 is justified by the coalescence of the 175 ppm and 195 ppm resonances at that acidity. The increase with pH of the oxygen exchange rate between 175 ppm bisulfite ion and 195 ppm bisulfite ion, which produces the coalescence of the 175 ppm and 195 ppm resonances at pH 5, is a consequence of the increase with pH of the rate of reaction 6. The necessary condition for coalescence of two resonances is that the sum of the pseudo first order rate constants for oxygen exchange between the two sites be much larger than the difference between the precessional frequencies in the two sites. Since SO_3^{2-} is the intermediate in the oxygen exchange occurring via reaction 6, the rate of which is large enough to coalesce the 175 ppm and 195 ppm resonances at pH 5, and because the differences between the precessional frequency in the sulfite environment (corresponding to 235 ppm⁹) and those of the 175 ppm bisulfite ion and 195 ppm bisulfite ion are no more than a factor of three greater than the frequency difference between the 175

ppm and 195 ppm environments, the SO_3^{2-} resonance is coalesced with those of 175 ppm bisulfite ion and 195 ppm bisulfite ion at pH 5, and thus contributes to the area of the coalesced peak located at 193 ppm.

Because the areas of the S(IV) peaks were measured using the area of the water peak as an internal standard, and because it has been assumed that the area of the 175-178 ppm peak is due only to 175 ppm bisulfite ion, the equilibrium quotient for reaction 15 could be evaluated by converting the area of the peak at 175-178 ppm to a 175 ppm bisulfite ion concentration and comparing this concentration to the calculated total concentration of bisulfite ion (i.e. the sum of the concentrations of the two isomers) for the solution. However, it was thought best to use the area of the 193 ppm bisulfite peak as a measure of the total concentration of bisulfite ion, in the hope that any systematic error inherent in the determination of peak areas would be at least partially cancelled by the use of area measurements to obtain both the 175 ppm bisulfite ion concentration and the total bisulfite ion concentration.

The equilibrium quotient K_{15} was evaluated using the formula

$$K_{15} = \frac{\text{area corresponding to total } \text{SHO}_3^- \text{ concentration at pH 3}}{\text{area of 175-178 ppm peak at pH 3}} - 1.$$

The area corresponding to the total bisulfite ion concentration at pH 3 was obtained using the area of the 193 ppm peak at pH 5 in the following manner. The concentrations of SHO_3^- , SO_2 , SO_3^{2-} , and $\text{S}_2\text{O}_5^{2-}$ were calculated for the pH 5 solutions, after which the fraction of the 193 ppm peak area due to bisulfite ion was determined. Because the concentration of bisulfite ion changes slightly over the pH range from 3

to 5 at constant S(IV) concentration, the area corresponding to the total bisulfite ion concentration at pH 3 is not equal to the area corresponding to the total bisulfite ion concentration at pH 5. There were also slight differences between the bisulfite ion concentrations of the pH 3 and pH 5 solutions due to the fact that the S(IV) concentration was not exactly the same in every solution. Therefore, the area corresponding to the total bisulfite ion concentration in the pH 3 solution was obtained by multiplying the area corresponding to the total bisulfite ion concentration in the pH 5 solution by the ratio of the calculated bisulfite ion concentration at pH 3 to that calculated at pH 5. To minimize error in this ratio arising from error in the estimated value of the equilibrium quotient for the dimerization of bisulfite ion (which was used in calculating the bisulfite ion concentrations), the 193 ppm peak area obtained from the pH 5 solution was used to determine an area corresponding to the total bisulfite concentration only for a pH 3 solution of similar S(IV) concentration.

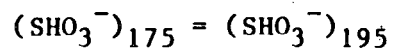
The values of the parameters used in the calculation of K_{15} are listed in Table 2 together with the resulting values of the equilibrium quotient. Figure 13 shows a plot of $\log(K_{15})$ vs. $1/T$. A nonweighted linear least squares treatment of the data yields

$$\ln K_{15} = (-3.232 \pm 0.527) + (1438 \pm 151)/T \quad (2-23)$$

as the equation of the best straight line through the points, with a covariance of slope and intercept of -79.7. From the values of the slope and intercept one obtains $\Delta H_{15} = -2.9 \pm 0.3$ kcal/mole and $\Delta S_{15} = -6 \pm 1$ cal K^{-1} mol $^{-1}$.

Table 2

Values of Parameters Used in the Calculation of K_{15} , the Equilibrium Quotient for the Reaction



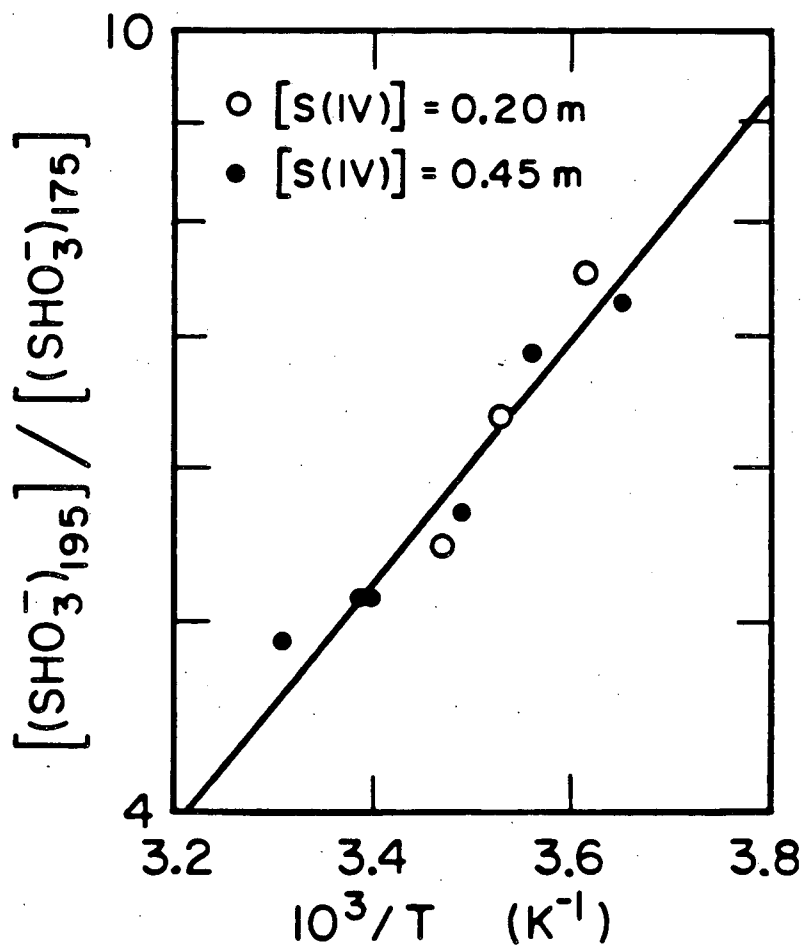
[S(IV)],m	pH meter reading	S(IV) peak chemical shift, ppm	$\frac{[\text{SHO}_3^- \text{ oxygens}]^a}{[\text{total S(IV) oxygens}]}$	T, °C	$[\text{SHO}_3^-], \text{m}^a$	$\frac{\text{area S(IV) peak}}{\text{area H}_2\text{O peak}} \times 55.5^b$	K_{15}^c
0.201	4.98	193	0.945	2-29	0.189	0.65 ± 0.01	
0.199	3.00	175-178	-	3.7	0.188	0.0719	7.52
"	"	"	-	10.6	0.188	0.0830	6.37
"	"	"	-	15.2	0.188	0.0946	5.46
0.449	4.97	191-193	0.919	1-29	0.408	1.37 ± 0.02	
0.456	3.02	173-177	-	1.1	0.416	0.155	7.28
"	"	"	-	7.7	0.416	0.163	6.86
"	"	"	-	13.9	0.416	0.191	5.69
"	"	"	-	21.4	0.415	0.211	5.06
"	"	"	-	21.9	0.415	0.211	5.06
"	"	"	-	29.3	0.415	0.217	4.89

Table 2 (cont.)

^aCalculated using literature values of equilibrium quotients, as explained in the text.

^bIncludes a correction for the effect of signal decay which occurred during the preacquisition delay time (see Experimental Procedure).

^cSee text for method used to calculate K_{15} .



XBL837-3898

Figure 13

Returning now to the interpretation of $1/\tau_{175}$, it will be shown that the assumptions that either inequality 2-20a or inequality 2-20b is true and that k_{-14} is at least $5 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ allows the evaluation of the rate constant for the reaction



(where HSO_3^- is the isomer of bisulfite ion in which the proton is bonded to the sulfur atom) and the determination of an upper limit to the value of k_6 .

It is apparent that if inequality 2-20a is true then $1/\tau_{175}$ is given by 2-21a, and

$$N = k_4 = K_4 k_{-4} \quad (2-20a \text{ true}). \quad (2-24)$$

The equilibrium quotient K_4 was calculated using the formula

$$K_4 = K_2 \left\{ 1 + \frac{[(\text{SHO}_3^-)_{195}]}{[(\text{SHO}_3^-)_{175}]} \right\}. \quad (2-25)$$

The ratio of bisulfite ion concentrations is equal to K_{15} , which at 298 K is 4.9 ± 0.1 , from which one obtains $K_4 = (2.7 \pm 0.1) \times 10^{-6}$. Since the value of N is between 395 and 620 sec^{-1} at 298 K, the value of k_{-4} is approximately $2 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. This is much smaller than the assumed value for k_{-14} , so the association $k_{-4} = k_{-16}$ and $k_{-5} = k_{-14}$ is made, identifying 175 ppm bisulfite ion and 195 ppm bisulfite ion as HSO_3^- and SO_3H^- , respectively. The value of k_6 is equal to Q^- ; at 298 K this is $1.1 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$. Since $k_{-5} \gg k_{-4}$ it is also quite likely that

$k_{6b} \gg k_{6a}$, because reactions 6a and 6b are homologous to reactions 4 and 5. If this is true, then $k_{6b} \approx k_{6b} + k_{6a} = k_6$. Finally, R is given by

$$R = k_8 + k_9 \left(1 + \frac{1}{K_{15}}\right)^{-1} \quad (2-20a \text{ true}). \quad (2-26)$$

If inequality 2-20b is true, $1/\tau_{175}$ is given by 2-21b, and

$$N = k_4 \left(\frac{k_{-5}}{k_{-4} + k_{-5}}\right) = K_4 \left(\frac{1}{k_{-4}} + \frac{1}{k_{-5}}\right)^{-1} \quad (2-20b \text{ true}). \quad (2-27)$$

Using $395 \text{ sec}^{-1} < N < 620 \text{ sec}$, $K_4 = 2.7 \times 10^{-6} \text{ M}$, and a value for either k_{-4} or k_{-5} of $5 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, it is found that the smaller of k_{-4} and k_{-5} has a value of approximately $2 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at 298 K. This value is assigned to k_{-16} because k_{-14} is believed to be at least $5 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, but it is not known on the basis of this result how to assign the peaks at 175-178 ppm and 195 ppm. It should be noted that the right side of 2-27 reduces to $K_4 k_{-16}$ because (as has just been shown) either $k_{-5} \gg k_{-4}$ or $k_{-4} \gg k_{-5}$. The expression for Q' is

$$Q' = k_6 \left(\frac{k_{-5}}{k_{-4} + k_{-5}}\right) = k_6 \left(1 + \frac{k_{-4}}{k_{-5}}\right)^{-1} \quad (2-20b \text{ true}). \quad (2-28)$$

Depending upon which of the two inequalities $k_{-4} \gg k_{-5}$, $k_{-5} \gg k_{-4}$ is true, Q' is equal to either $k_6 k_{-5}/k_{-4}$ or k_6 . By similar reasoning, R is given by either

$$R = k_8 + k_9 \left(\frac{k_{-5}}{k_{-4}}\right) \left(1 + \frac{1}{K_{15}}\right)^{-1} \quad (2-20b \text{ true; } k_{-4} \gg k_{-5}), \quad (2-29)$$

or

$$R = k_8 + k_9 \left(1 + \frac{1}{K_{15}}\right)^{-1} \quad (2-20b \text{ true, } k_{-5} \gg k_{-4}). \quad (2-30)$$

The consequences of the validity of either 2-20a or 2-20b can be summarized briefly. In either case, if $k_{-14} > 5 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, then $N = K_4 k_{-16}$. If inequality 2-20a is true then 195 ppm bisulfite ion and 175 ppm bisulfite ion are assigned to SO_3H^- and HSO_3^- , respectively, and $Q' = k_6$, and is probably equal to k_{6b} . R is given by equation 2-26. If inequality 2-20b is true then either $\{k_{-5} \gg k_{-4}, Q' = k_6, \text{ and } R \text{ is given by 2-30}\}$ or $\{k_{-4} \gg k_{-5}, Q' = k_6 k_{-5}/k_{-4}, \text{ and } R \text{ is given by 2-29}\}$, but it is not known to which isomers of bisulfite ion the ^{17}O NMR peaks at 175-178 ppm and 195 ppm should be assigned from these data alone. (Additionally, it is probably true that k_6 is about equal to either k_{6a} or k_{6b} , the former being the case if $k_{-4} \gg k_{-5}$ and the latter if $k_{-5} \gg k_{-4}$.)

Upon the basis of the foregoing analysis it is believed that plots of $\log N$ vs. $1/T$ and $\log Q'$ vs. $1/T$ should be linear, because both N and Q' are products of rate constants and equilibrium quotients. (Since Arrhenius plots of rate constants and equilibrium quotients are expected to be linear, an Arrhenius plot of a product of rate constants and equilibrium quotients should be linear also.) The $\log Q'$ vs. $1/T$ data of Figure 9 were therefore subjected to a weighted linear least squares analysis, from which the temperature dependence of Q' was found to be

$$\ln Q' = (24.02 \pm 0.82) + (-3024 \pm 250)/T, \quad (2-31)$$

with a covariance of the slope and intercept of $\ln Q'$ vs. $1/T$ of -204.

The expected linearity of a plot of $\log N$ vs. $1/T$ was used to evaluate both N and $1/T_2(175)$ from the values of $N + 1/T_2(175)$ which are shown in Figure 11. The slight curvature of that graph is presumably due to the term $1/T_2(175)$. Since the values of $1/T_2(175)$ were not known, it was assumed that $1/T_2(175)$ was proportional to $1/T_2(H_2O)$. Because the solutions were of low viscosity the rotational correlation time of the water molecules should be rapid enough to bring about "extreme narrowing",²⁵ causing $1/T_2(H_2O)$ to become equal to $1/T_1(H_2O)$, shown in Figure 12.³⁴ On the basis of the expected Arrhenius behavior of N and the assumed proportionality of $1/T_2(175)$ and $1/T_1(H_2O)$, the function

$$N + \frac{1}{T_2(175)} = \exp\left\{a + \frac{b}{T}\right\} + c \frac{1}{T_1(H_2O)} \quad (2-32)$$

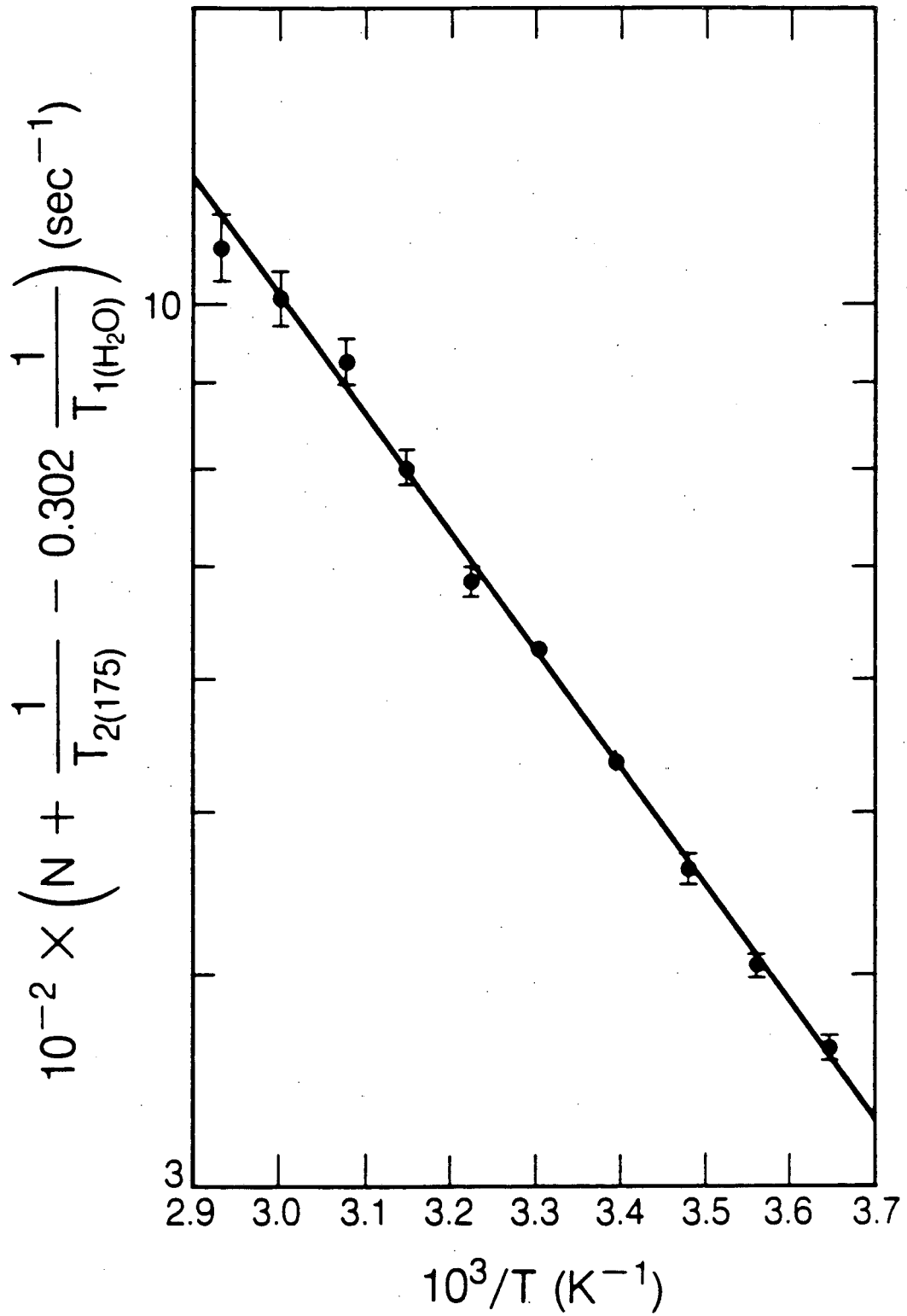
was fit to the data of Figures 11 and 12 using a weighted nonlinear least squares computer program.³⁵ It was found that

$$\frac{1}{T_2(175)} = (0.30 \pm 0.07) \frac{1}{T_1(H_2O)} \quad (2-33)$$

and

$$\ln N = (11.767 \pm 0.283) + (-1614 \pm 90)/T, \quad (2-34)$$

with a covariance of -25.5 between the two constants of 2-34. A plot of $\log \{N + 1/T_2(175) - 0.30[1/T_1(H_2O)]\}$ vs. $1/T$ (i.e. $\log N$ vs. $1/T$) is shown in Figure 14 along with the straight line corresponding to the log



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Figure 14

N values of equation 2-34.

Using the expression $N = K_4 k_{-16}$, the value of k_{-16} at 298 K is found to be $(2.1 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$.

Although equations 2-26, 2-29, and 2-30 do not require a plot of $\log R$ vs. $1/T$ to be linear, the data of Figure 10 were fit to a linear function for the purpose of calculating values of $1/\tau_{175}$ from equation 2-6. (Values of $1/\tau_{175}$ are needed in the calculation of $1/\tau_{195, \text{H}_2\text{O}}$ from the water peak linewidth data.) The points at the lowest two temperatures were not used in the least squares analysis because they correspond to negative values of R . The results of the weighted linear least squares analysis of the eight highest temperature points is

$$\ln R = (21.78 \pm 1.70) + (-5023 \pm 528)/T, \quad (2-35)$$

with a covariance of -898 between the slope and y-intercept of $\ln N$ vs. $1/T$.

Analysis of the Broadening of the Water Peak

Although it would be desirable to study the broadening of the bisulfite peak located at 195 ppm in order to obtain the rate law for oxygen exchange between 195 ppm bisulfite ion and water, it is not feasible to do this. There are no spectra in which the peak at 195 ppm is both visible and not overlapped by the peak at 175-178 ppm, making accurate determination of the linewidths impossible. The fitting of the lineshape to a superposition of two Lorentzian curves or to a more

complex expression which includes the effect of oxygen exchange between the two forms of bisulfite is inherently inaccurate because the preacquisition delay in the two-pulse sequence introduces phase differences between the two S(IV) peaks.

Fortunately, information on the oxygen exchange between the 195 ppm bisulfite ion and water can also be obtained by analyzing the broadening of the water peak. The broadening of the water peak in excess of its natural linewidth is due to the transverse relaxation of the magnetic moments of the oxygen-17 nuclei in water which occurs through exchange of oxygen into the 195 ppm site, where the oxygen-17 magnetic moments precess at a different frequency. After chemical exchange back into the water takes place the oxygen-17 magnetic moments in the water site have lost some phase coherence.

Because the oxygen nuclei which have been exchanged from the water into the 195 ppm site can occasionally exchange into the 175 ppm bisulfite ion and thence back into the 195 ppm bisulfite ion before returning to the water, a three site chemical exchange formalism must be used to treat the broadening of the water peak. The problem is simplified, however, by the results of the previous section, which show that direct exchange of oxygen between the water and 175 ppm bisulfite ion occurs very slowly compared to the rates of the other exchange processes, and may therefore be neglected in the following data analysis. Because all the solutions studied were dilute enough to cause the population of oxygen in water to be much greater than in either isomer of bisulfite ion, the treatment of Swift and Connick³⁶ is applicable to the present case and gives as a good approximation

$$\left(\frac{1}{T_2}\right)_{H_2O} = \frac{1}{T_{2(H_2O)}} + \frac{P_{195}}{P_{H_2O}} \frac{1}{\tau_{195,H_2O}} - \frac{P_{195}}{P_{H_2O}} \left(\frac{1}{\tau_{195,H_2O}}\right)^2 \frac{A}{A^2 + B^2},$$

(3-1)

where

$$A = \frac{P_{175}}{P_{195}} \frac{1}{\tau_{175,195}} \frac{\left(\frac{1}{T_{2(175)}}\right)^2 + \frac{1}{T_{2(175)}} \frac{1}{\tau_{175,195}} + (\Delta\omega_{175})^2}{\left(\frac{1}{T_{2(175)}} + \frac{1}{\tau_{175,195}}\right)^2 + (\Delta\omega_{175})^2} + \frac{1}{\tau_{195,H_2O}} + \frac{1}{T_{2(195)}},$$

$$B = \Delta\omega_{195} + \frac{P_{175}}{P_{195}} \left(\frac{1}{\tau_{175,195}}\right)^2 \frac{\Delta\omega_{175}}{\left(\frac{1}{T_{2(175)}} + \frac{1}{\tau_{175,195}}\right)^2 + (\Delta\omega_{175})^2},$$

and the symbols have the following meanings:

$\left(\frac{1}{T_2}\right)_{H_2O}$ = the half width at half height of the water peak,

$\frac{1}{T_{2(i)}}$ = the natural linewidth of the peak corresponding to site i,
i.e. the linewidth the peak would have in the absence of chemical exchange,

$\frac{1}{\tau_{i,j}}$ = the pseudo first order rate constant for the exchange of oxygen
from site i to site j,

p_i = the fraction of ^{17}O nuclei which are in site i , and

$\Delta\omega_i$ = the precession frequency of the oxygen-17 nuclei in site i in the absence of chemical exchange minus the spectral frequency at which the water peak has its maximum height. (This is not the exact definition of $\Delta\omega_i$ given by Swift and Connick, but is a good approximation because the chemical shifts of the S(IV) peaks relative to water are large in comparison to the half width of the water peak.)

The pseudo first order rate constant for oxygen exchange between the 195 ppm site and water can be evaluated using equation 3-1, because all the other quantities in the equation are known or can be estimated fairly accurately. In the previous section $1/T_2(175)$ was determined to be equal to $0.3(1/T_1)_{\text{H}_2\text{O}}$. The choice of values for the other quantities requires some explanation.

Because the value of $1/\tau_{195,\text{H}_2\text{O}}$ which is obtained by solving equation 3-1 is a function of the linewidth of the water peak minus its natural linewidth, and because the water peak is not greatly broadened by the chemical exchange with the dilute 195 ppm bisulfite ion, broadening of the water peak arising from magnetic field inhomogeneity cannot be ignored as it was in the analysis of the broadening of the 175-178 ppm S(IV) peak. To obtain an estimate of the amount of inhomogeneous broadening the half width at half height of the water peak at various temperatures in a 1 m NaCl solution was compared to the values of $1/T_1$ obtained from the same solution. Although T_2 is expected to be equal to T_1 , the linewidth was greater than $1/T_1$ by an average of

$2.9 \pm 0.8 \text{ sec}^{-1}$ over the entire temperature range, with no apparent temperature dependence. The linewidth in excess of $1/T_1$ is presumably due to magnetic field inhomogeneity. It was assumed that field inhomogeneity also broadened the water peak in the spectra of each bisulfite solution by an extra $2.9 \pm 0.8 \text{ sec}^{-1}$, so this amount was subtracted from the measured linewidths to obtain values of $(1/T_2)_{\text{H}_2\text{O}}$.

The values of p_{175}/p_{195} and $p_{195}/p_{\text{H}_2\text{O}}$ required for solving equation 3-1 were determined from peak areas at several temperatures for each S(IV) solution. First, p_{175}/p_{195} and $(p_{175} + p_{195})/p_{\text{H}_2\text{O}}$ were evaluated; from these quantities $p_{195}/p_{\text{H}_2\text{O}}$ was calculated.

In the calculations of p_{175}/p_{195} and $p_{195}/p_{\text{H}_2\text{O}}$ it was assumed that the resonances of $\text{S}_2\text{O}_5^{2-}$, SO_2 , and SO_3^{2-} are coalesced with that of the 195 ppm bisulfite ion. The assumption of the coalescence of the $\text{S}_2\text{O}_5^{2-}$ and SO_2 resonances with the 195 ppm bisulfite ion resonance has been discussed in the previous section. The validity of the assumption of coalescence of the SO_3^{2-} and 195 ppm bisulfite ion resonances rests upon the argument, yet to be made, that the peak at 195 ppm should be assigned to SO_3H^- . Since the concentration of SO_3H^- is much greater than that of SO_3^{2-} in the pH range studied, the necessary condition for coalescence of the two resonances is that the pseudo first order rate constant for oxygen exchange from SO_3^{2-} to SO_3H^- be much larger than the frequency difference between the two peaks ($\Delta\omega = 2\pi \times [235 - 195] \times 27$, where 235 and 195 are the chemical shifts of sulfite ion⁹ and 195 ppm bisulfite ion, respectively, and 27 is the Larmor frequency of ^{17}O in MHz.) The exchange between SO_3H^- and SO_3^{2-} via reaction 14 is rapid enough to meet this condition throughout the pH range studied, but it is also true that reaction 6 is sufficiently rapid to coalesce the

resonances of 175 ppm bisulfite ion and SO_3^{2-} throughout this pH range, and reaction 16 is rapid enough to coalesce the HSO_3^- and SO_3^{2-} resonances at the low pH values. Since SO_3^{2-} is in rapid exchange with both isomers of bisulfite ion it is not necessarily correct to assign all of the SO_3^{2-} oxygen population to the 195 ppm site. However, in this case such an assignment can be made because k_{-14} is much greater than k_{-16} . If it is assumed that 195 ppm bisulfite ion is SO_3H^- it follows that k_{-7} is substantially larger than k_{-6} , because reactions 6 and 7 are similar to reactions 16 and 14: SO_3^{2-} accepts a proton from the acid SHO_3^- in reactions 6 and 7 and from the acid H_3O^+ in reactions 16 and 14. The pseudo first order rate constants for oxygen exchange from SO_3^{2-} to 195 ppm bisulfite ion are therefore much larger than those for exchange from SO_3^{2-} to 175 ppm bisulfite ion, in which case it is probably a very good approximation to assign all of the SO_3^{2-} oxygen population to the 195 ppm site.

Because $\text{S}_2\text{O}_5^{2-}$, SO_2 , and SO_3^{2-} are present in all the S(IV) solutions and are believed to have resonances which contribute to the oxygen population of the 195 ppm site, the quantity p_{175}/p_{195} is less than K_{15}^{-1} , to which it is related according to the expression

$$\frac{p_{175}}{p_{195}} = \left\{ (K_{15} + 1) \frac{[\text{total S(IV) oxygens}]}{[\text{SHO}_3^- \text{ oxygens}]} - 1 \right\}^{-1}. \quad (3-2)$$

For use in this equation the ratio of the total concentration of oxygen in S(IV) species to the concentration in only bisulfite ion was determined from the calculated concentrations of the S(IV) species in each solution, and K_{15} was calculated from equation 2-23.

The quantity $p_{195}/p_{\text{H}_2\text{O}}$ was calculated using the equation

$$\frac{P_{195}}{P_{H_2O}} = \left(\frac{P_{175} + P_{195}}{P_{H_2O}} \right) \left(1 + \frac{P_{175}}{P_{195}} \right)^{-1}. \quad (3-3)$$

The quantity $(P_{175} + P_{195})/P_{H_2O}$ is the ratio of the concentration of oxygens in all S(IV) species to the concentration in H_2O , and was obtained for each solution from the calculated concentrations of the various S(IV) species and an H_2O concentration of 55.5 m.

It has been argued previously that the natural linewidth of the water peak, $1/T_2(H_2O)$, should be equal to $1/T_1(H_2O)$ in the bisulfite solutions studied, and therefore could be obtained from the plot of longitudinal relaxation rate constants in Figure 12. It was tacitly assumed that the rate constant for longitudinal relaxation of ^{17}O in the water of the bisulfite solutions (the quantity which was actually measured) is equal to $1/T_1(H_2O)$, the rate constant which would be measured if no chemical exchange occurred. The validity of this assumption will now be addressed. For the moment the presence of 175 ppm bisulfite ion will be neglected. The measured longitudinal relaxation rate constant for water, $(1/T_1)_{H_2O}$, is a function of $1/\tau_{195,H_2O}$, and has a value which varies from $1/T_1(H_2O)$ to the weighted average of the two different rate constants which would be measured for the longitudinal relaxation of 195 ppm bisulfite ion and water in the absence of chemical exchange, i.e.

$$\left(\frac{1}{T_1} \right)_{H_2O} = \frac{P_{195}}{T_1(195)} + \frac{P_{H_2O}}{T_1(H_2O)}, \quad (3-4)$$

as the value of $1/\tau_{195,H_2O}$ increases from zero to being much greater than the difference between $1/T_1(195)$ and $1/T_1(H_2O)$.²⁸ In the latter

case the measured longitudinal relaxation rate constant in the 195 ppm site is also given by equation 3-4. Measurements of $(1/T_1)_{H_2O}$ in solutions of various acidities showed that the variations in pH which produce large changes in the linewidth of the water peak have no observable effect upon $(1/T_1)_{H_2O}$. Inspection of the spectra taken for the T_1 measurements revealed that the water and S(IV) magnetizations each went through a null at about the same time after the 180° pulse, indicating that the longitudinal relaxation time of ^{17}O is roughly the same in the water and the S(IV) environments. From these observations it is concluded that either $1/\tau_{195,H_2O}$ is large enough to cause $(1/T_1)_{H_2O}$ to be given by equation 3-4, or that $1/T_{1(195)}$ is so close to $1/T_{1(H_2O)}$ that the variations in $(1/T_1)_{H_2O}$ produced by large changes in $1/\tau_{195,H_2O}$ cannot be detected. In the latter case $(1/T_1)_{H_2O}$ is equal, to a very good approximation, to $1/T_{1(H_2O)}$, and in the former case is given by equation 3-4. (The results of this section will show that the former situation probably holds in most, and the latter in all, of the experimental conditions of this work.)

Even if $(1/T_1)_{H_2O}$ is given by equation 3-4, there is evidence that $1/T_{1(195)}$ is close enough to $1/T_{1(H_2O)}$ to cause $(1/T_1)_{H_2O}$ to be very nearly equal to $1/T_{1(H_2O)}$. Because it is likely that $1/T_{1(195)} = 1/T_{2(195)}$, an estimate of an upper limit to the former can be obtained from the width of the S(IV) peak in the pH 5 solutions, in which the 175 ppm bisulfite ion and 195 ppm bisulfite ion exchange oxygens so rapidly that only a single coalesced S(IV) peak is seen at 193 ppm. The half width at half height of this peak must be at least

$$\left(\frac{P_{175}}{P_{175} + P_{195}} \right) \left(\frac{1}{T_{2(175)}} \right) + \left(\frac{P_{195}}{P_{175} + P_{195}} \right) \left(\frac{1}{T_{2(195)}} \right), \quad 37$$

and is probably greater, both because coalescence is probably not complete at pH 5, and because exchange with water also broadens the line, as is evident from the fact that the 193 ppm peak width increases as the temperature is raised. The maximum value of the weighted average of $1/T_{2(175)}$ and $1/T_{2(195)}$ is thus the width of the narrowest S(IV) peak observed at pH 5, 1020 sec^{-1} (observed in the ^{17}O NMR spectrum of the 0.449 m solution at 1.1°C). Using $p_{175}/(p_{175} + p_{195}) = 0.11$ and $1/T_{2(175)} = 90 \text{ sec}^{-1}$, the latter obtained from $1/T_{2(175)} = 0.3[1/T_{1(\text{H}_2\text{O})}]$, it is calculated that $1/T_{2(195)}$ (equal to $1/T_{1(195)}$) is no greater than 1130 sec^{-1} at 1.1°C (and is smaller at higher temperatures). The values of $(1/T_1)_{\text{H}_2\text{O}}$ obtained from the 0.20 m bisulfite solutions (Figure 12), in which $p_{195}/p_{\text{H}_2\text{O}} \approx 0.0096$, are therefore no more than about 11 sec^{-1} (3.7%) greater than $1/T_{1(\text{H}_2\text{O})}$ at 1.1°C . If it is assumed for simplicity that $1/T_{1(195)}$ is proportional to $(1/T_1)_{\text{H}_2\text{O}}$, then $(1/T_1)_{\text{H}_2\text{O}}$ is no more than 3.7% greater than $1/T_{1(\text{H}_2\text{O})}$ at each temperature. A similar calculation shows that if $1/T_{1(195)}$ is less than $1/T_{1(\text{H}_2\text{O})}$ then $(1/T_1)_{\text{H}_2\text{O}} - 1/T_{1(\text{H}_2\text{O})}$ would be less than 1% of $1/T_{1(\text{H}_2\text{O})}$.

It is likely that $1/T_{1(195)}$ is actually less than 1130 sec^{-1} , and the difference between $(1/T_1)_{\text{H}_2\text{O}}$ and $1/T_{1(\text{H}_2\text{O})}$ is under 3.7% of $1/T_{1(\text{H}_2\text{O})}$. The longitudinal relaxation rate constant of ^{17}O in the water of a 1 m NaCl solution was measured at various temperatures, and within experimental uncertainty was found to have the same values as the longitudinal relaxation rate constant of the ^{17}O in the water of the bisulfite solutions, showing no systematic deviation from a curve drawn through the points of Figure 12. Although the value of $1/T_{1(\text{H}_2\text{O})}$ in the 1 m NaCl solution is not necessarily the same as in the bisulfite

solutions, it is probably not much different in the two, since the bisulfite solutions contain more than 0.5 m NaCl. It would be fortuitous if $1/T_{1(H_2O)}$ were different in the 1 m NaCl solution than in the bisulfite solutions but $1/T_{1(195)}$ was just the right magnitude to cause $(1/T_1)_{H_2O}$ to have the same value in the two solutions. It is more likely that $1/T_{1(H_2O)}$ is about the same in the two types of solutions, and $1/T_{1(195)}$ is close enough to $1/T_{1(H_2O)}$ to cause no noticeable difference in the measured longitudinal relaxation rate constant for ^{17}O in water. The systematic error which is introduced by using values of $(1/T_1)_{H_2O}$ in place of $1/T_{1(H_2O)}$ is therefore probably less than the random error associated with a value of $(1/T_1)_{H_2O}$ obtained from a curve drawn through the points of Figure 12. It is concluded that within experimental uncertainty $1/T_{1(H_2O)} = (1/T_1)_{H_2O}$. The population of 175 ppm bisulfite ion is small enough, and $1/T_{1(175)}$ close enough to $(1/T_1)_{H_2O}$ to cause any effect of 175 ppm bisulfite ion upon $(1/T_1)_{H_2O}$ to be unnoticeable.

On the basis of the foregoing discussion it is also reasonable to assume that

$$\frac{1}{T_{2(195)}} = \left(\frac{1}{T_1}\right)_{H_2O} \pm 100\%. \quad (3-5)$$

Because the analysis of the broadening of the 175-178 ppm S(IV) peak led to the conclusion that 175 ppm bisulfite ion does not exchange oxygen directly with water at an appreciable rate, the pseudo first order rate constant for exchange of oxygen out of the 175 ppm site is equal to $1/\tau_{175,195}$, the pseudo first order rate constant for exchange of oxygen from the 175 ppm site to the 195 ppm site, and therefore

(see 2-6)

$$\frac{1}{\tau_{175,195}} = N + Q[\text{SO}_3^{2-}] + R[\text{SHO}_3^-] \quad (3-6)$$

Actually, this statement is not necessarily true for all of the bisulfite solutions, because inequality 2-20, the satisfaction of which is required to cause $1/\tau_{175,195}$ to take the form given by equation 3-6, is possibly not true over the entire pH range studied. It has been argued previously, however, that if 2-20a is true below pH 3.5 then $k_{-5} \gg k_{-4}$ and $k_{-7} \gg k_{-6}$, causing 2-20a to be true at all acidities and S(IV) concentrations. It was also implied that if the rate constant for the reaction



is at least $5 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ at 298 K, then 2-20a is true if 195 ppm bisulfite ion is SO_3H^- . This assignment of the S(IV) peaks in the ^{17}O NMR spectrum will be assumed for now; the results of the analysis of the broadening of the H_2O peak will be used to argue that 195 ppm bisulfite ion is, in fact, SO_3H^- .

It is also possible that even if inequality 2-20a is true $1/\tau_{175,195}$ is not given by equation 3-6 at the higher pH values, because the steady state approximation was applied to the concentration of $(\text{SO}_3^{2-})^*$ in the derivation of the expression for $1/\tau_{175,195}$ from the proposed oxygen exchange mechanism. At the higher pH values the concentration of SO_3^{2-} is not negligible compared to the concentration of 175 ppm bisulfite ion, invalidating the use of the steady state

approximation. However, this complication was ignored because it was found that $1/\tau_{175,195}$ had very little effect upon the values of $1/\tau_{195,H_2O}$ obtained from equation 3-1 at high pH.

From equation 3-6, $1/\tau_{175,195}$ was evaluated at several temperatures for each bisulfite solution using values of N, Q', and R calculated from equations 2-34, 2-31, and 2-35, respectively, and concentrations of SO_3^{2-} and SHO_3^- calculated as described previously.

In order to solve equation 3-1 for $1/\tau_{195,H_2O}$ it was also necessary to know the values of $\Delta\omega_{175}$ and $\Delta\omega_{195}$, the difference between the precession frequency of oxygen-17 in the 175 ppm and 195 ppm sites, respectively, and the spectral frequency of the water peak maximum. (It was desired to use values more accurate than the approximate values 175 ppm and 195 ppm.) For the bisulfite solutions of pH 3.5 and below the values of $\Delta\omega_{175}$ were measured directly from the spectra, in which only one S(IV) peak appeared. At pH 4 and above $\Delta\omega_{175}$ could not be measured accurately either because the peak at 195 ppm overlapped the one at 175 ppm or because the two S(IV) peaks had coalesced, leaving no peak at 175 ppm to measure. The values of $\Delta\omega_{175}$ for the solutions of pH 4 and above were therefore estimated from the values of $\Delta\omega_{175}$ at pH 3.5 and below by a method which will now be explained.

At pH 3.5 and below $\Delta\omega_{175}$ exhibited no great dependence upon acidity, but was noticeably dependent upon temperature and bisulfite concentration, as is shown in Figure 15 for two representative samples. It is believed that the temperature dependence is not attributable to chemical exchange, but that the concentration dependence is. If the absolute resonance frequency of the 175 ppm bisulfite ion is independent of concentration, the measured frequency difference between

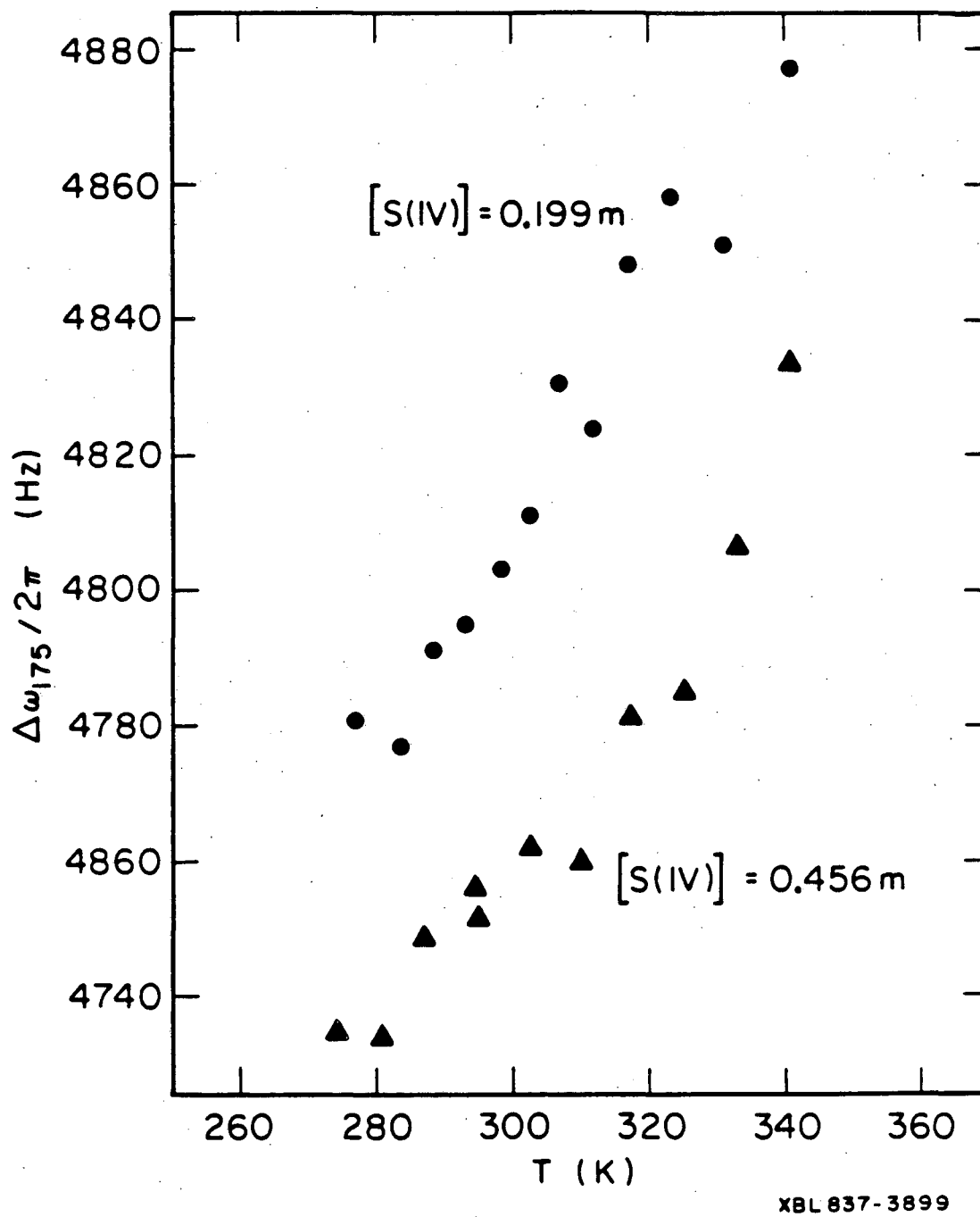


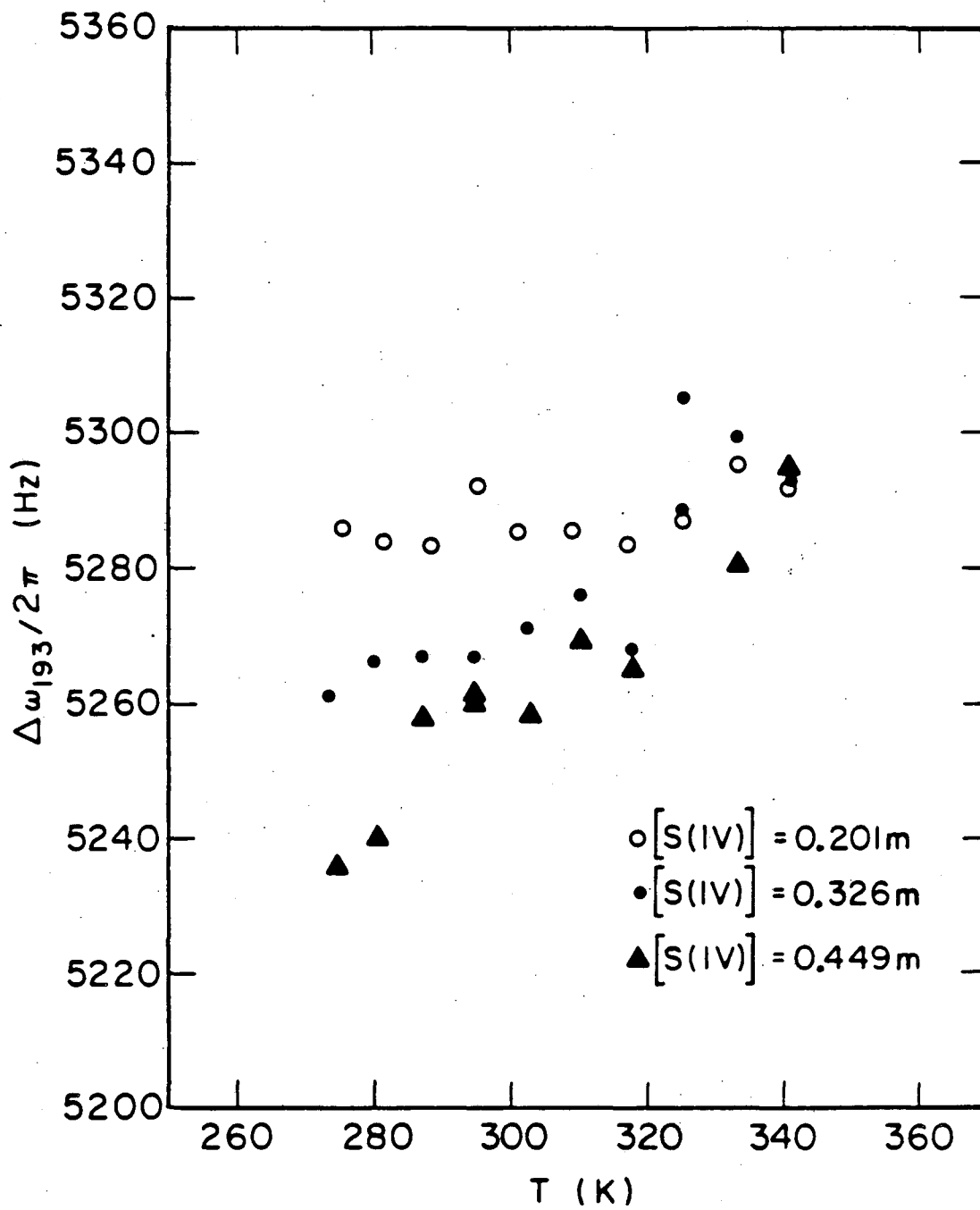
Figure 15

the peak at about 175 ppm and the water peak would be expected to decrease as the bisulfite concentration rises because the water resonance and the 195 ppm resonance are coalesced, and the combined water/195 ppm peak has an absolute frequency equal to $(p_{195}\omega_{195} + p_{H_2O}\omega_{H_2O})/(p_{195} + p_{H_2O})$, which is closer to ω_{175} than is ω_{H_2O} . The decrease in $\Delta\omega_{175}$ of $320 \pm 60 \text{ sec}^{-1}$ which is observed in going from a 0.20 m bisulfite solution to one which is 0.456 m in S(IV) is consistent with this interpretation. Since the 195 ppm resonance and the water resonance are not coalesced at high pH, the values of $\Delta\omega_{175}$ were estimated for the solutions above pH 4 by extrapolating the pH 3 shift data to $[S(IV)] = 0$, resulting in a value for $\Delta\omega_{175}$ equal to 250 sec^{-1} plus the value of $\Delta\omega_{175}$ in the solution of pH 3 and $[S(IV)] = 0.20 \text{ m}$. (For the extrapolation, $\Delta\omega_{175}$ was assumed to decrease by 320 sec^{-1} in going from the 0.20 m solution to the 0.456 m solution.)

Because $\Delta\omega_{175}$ and p_{175}/p_{195} are known, $\Delta\omega_{195}$ at pH 5 could be determined from the position of the coalesced S(IV) peak at pH 5, which has a chemical shift of

$$\Delta\omega_{193} = (p_{195}\Delta\omega_{195} + p_{175}\Delta\omega_{175})/(p_{175} + p_{195}). \quad (3-7)$$

The temperature dependence of the chemical shift of the coalesced peak at the nominal frequency of 193 ppm is shown in Figure 16 for the three solutions of pH 5. The observed variation of the slope of $\Delta\omega_{193}$ vs. T with concentration of S(IV) is a bit puzzling; although the chemical shift of the coalesced S(IV) peak is expected to be dependent upon temperature due to the fact that $\Delta\omega_{175}$ is a function of temperature, the slope of $\Delta\omega_{175}$ vs. T at pH 3 is independent of concentration. Over the



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Figure 16

temperature range studied $\Delta\omega_{175}$ changes by about 600 sec^{-1} , and therefore should cause a concomitant change in $\Delta\omega_{193}$ of about 80 sec^{-1} . Such an effect is consistent with the data from the 0.20 m solution, but a much greater variation in $\Delta\omega_{193}$ is observed in the 0.326 and 0.449 m solutions. It may be that there is a large temperature dependence in the precession frequency of ^{17}O in $\text{S}_2\text{O}_5^{2-}$, which is assumed to be part of the 195 ppm site and has a concentration proportional to the square of the bisulfite ion concentration. Although the veracity of this explanation is at best uncertain, it will be used in the calculation of $\Delta\omega_{195}$ at various S(IV) concentrations for lack of a better alternative.

The value of $\Delta\omega_{195}$ was determined in the following manner: at pH 5 $\Delta\omega_{195}$ was calculated from $\Delta\omega_{193}$, $\Delta\omega_{175}$, and p_{175}/p_{195} using equation 3-7. If it is assumed that the ^{17}O precession frequency in the 195 ppm site is independent of pH then $\Delta\omega_{195}$ changes with pH for the same reason as does $\Delta\omega_{175}$, that is, because the absolute frequency of the water peak changes with pH as it coalesces with the peak at 195 ppm. (Although the 195 ppm peak has coalesced with the water peak at low pH, $\Delta\omega_{195}$ is not zero, because it is defined as the difference between the precession frequency of the ^{17}O nuclei which are actually present in the 195 ppm site minus the frequency of the water peak maximum.) Therefore, for solutions above pH 4, $\Delta\omega_{195}$ was given a value equal to its value at pH 5 and similar S(IV) concentration, and at pH 3.5 and below $\Delta\omega_{195}$ was assigned a value equal to that at pH 5 and similar S(IV) concentration minus 125,250,400, and 570 sec^{-1} for the solutions of S(IV) concentrations 0.10, 0.20, 0.325, and 0.456 m, respectively. (The subtraction is required by the change in frequency of the water peak.

The calculation of the value of $\Delta\omega_{195}$ at low pH from its value at a similar S(IV) concentration at high pH, rather than just any S(IV) concentration, was necessary because $\Delta\omega_{195}$ is concentration dependent.)

It should be noted that the assumption of the pH independence of the ^{17}O precession frequency in the 195 ppm site is not strictly true due to the variation with pH of the concentrations of SO_2 and SO_3^{2-} , the resonances of which have different frequencies and are coalesced with the 195 ppm resonance. However, because the SO_2 and SO_3^{2-} contribute only a small fraction of the ^{17}O population in the 195 ppm site the effect of changes in acidity upon the ^{17}O precession frequency in that site is small; the difference between $\Delta\omega_{195}$ at pH 3 and pH 5 and $[\text{S(IV)}] = 0.20 \text{ m}$ due to differences in the concentrations of SO_2 and SO_3^{2-} (with chemical shifts of 520 and 235 ppm, respectively⁹) was estimated to be less than 4 ppm. Because such a change in $\Delta\omega_{195}$ had only a small effect upon the calculated values of $1/\tau_{195, \text{H}_2\text{O}}$ (changing them by less than 0.2%) it was ignored.

The values of $1/\tau_{195, \text{H}_2\text{O}}$ were determined for each sample at several temperatures by rearranging equation 3-1 to yield a quadratic equation in $1/\tau_{195, \text{H}_2\text{O}}$ (cubic terms are also obtained, but cancel each other), and finding the solutions to the equation after having substituted in the appropriate values of the parameters $(1/T_2)_{\text{H}_2\text{O}}$, $1/T_2(\text{H}_2\text{O})$, $1/T_2(195)$, $1/T_2(175)$, P_{175} , P_{195} , $P_{\text{H}_2\text{O}}$, $\Delta\omega_{175}$, $\Delta\omega_{195}$, and $1/\tau_{175, 195}$. For each set of parameters there are two solutions for $1/\tau_{195, \text{H}_2\text{O}}$; in some cases both are real and positive. Two real, nonnegative solutions can exist because the water peak can have the same linewidth for two values of $1/\tau_{195, \text{H}_2\text{O}}$ on opposite sides of the point of maximum broadening of the water resonance. The choice of one of the solutions

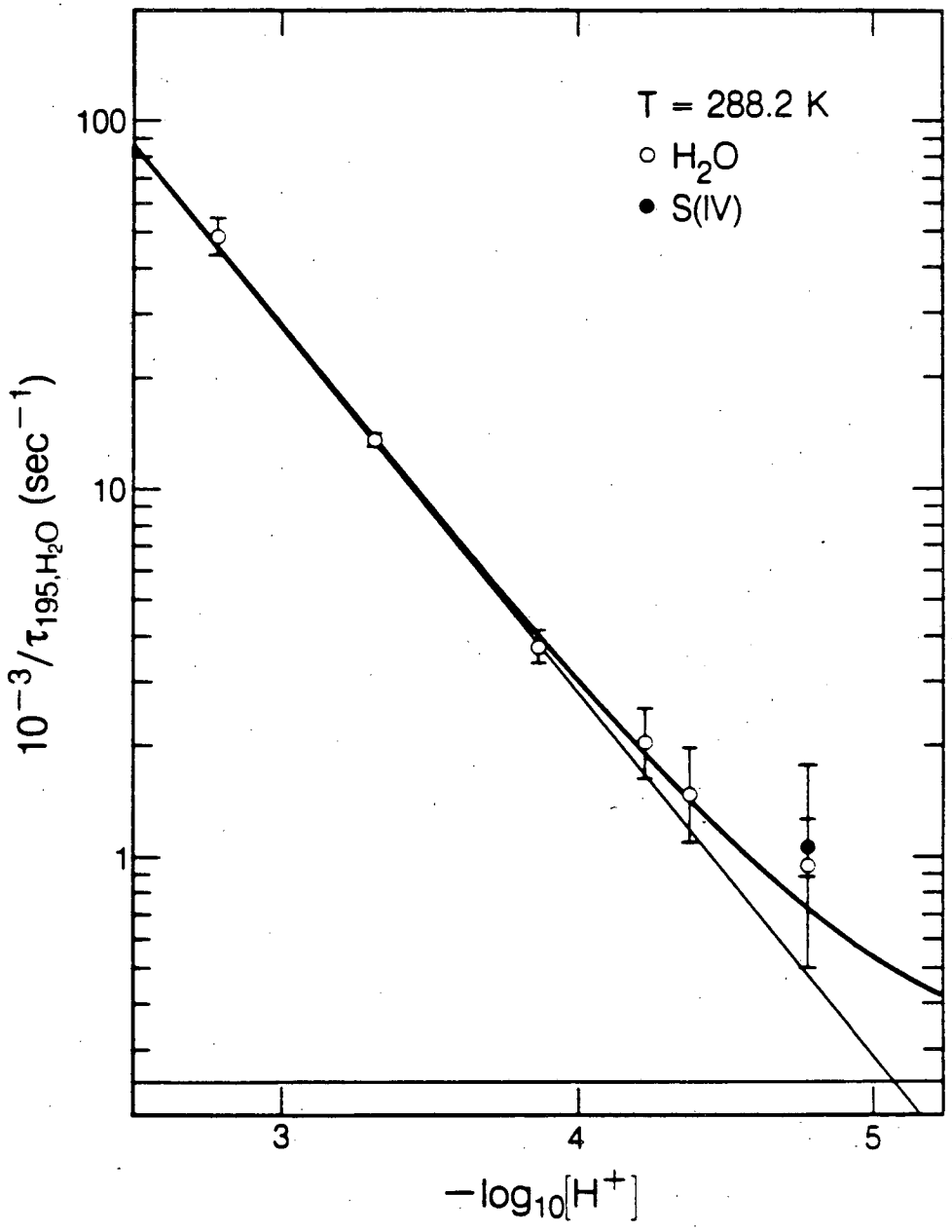
as the correct one was made by referring to the temperature dependence of $(1/T_2)_{H_2O} - (1/T_1)_{H_2O}$ (see Figure 5), using the fact that as the temperature is raised and the rate of oxygen exchange increases, $(1/T_2)_{H_2O} - (1/T_1)_{H_2O}$ increases on the slow exchange side of the point of maximum broadening and decreases on the fast exchange side. Very near the coalescence point it was not possible to determine $1/\tau_{195,H_2O}$ accurately because it was not known which of the two solutions to equation 3-1 was correct.

After calculating the values of $1/\tau_{195,H_2O}$, the pseudo first order rate constant for oxygen exchange from the 195 ppm site to water, the dependence of $1/\tau_{195,H_2O}$ upon the concentrations of H^+ and S(IV) was determined. The dependence upon $[H^+]$ was found at several temperatures by plotting the logarithm of $1/\tau_{195,H_2O}$ vs. $-\log_{10}[H^+]$ for solutions which were 0.2 m in S(IV), as shown in Figures 17-22. The pseudo first order rate constant appears to be first order in H^+ at high acidity, and changes to a smaller, nonintegral order at lower acidities. It was assumed that the transition to lower order with respect to H^+ was due to a term in $1/\tau_{195,H_2O}$ which is independent of $[H^+]$. Proceeding from this assumption, the data at each temperature were fit to a function of the form

$$\frac{1}{\tau_{195,H_2O}} = A + B[H^+] ,$$

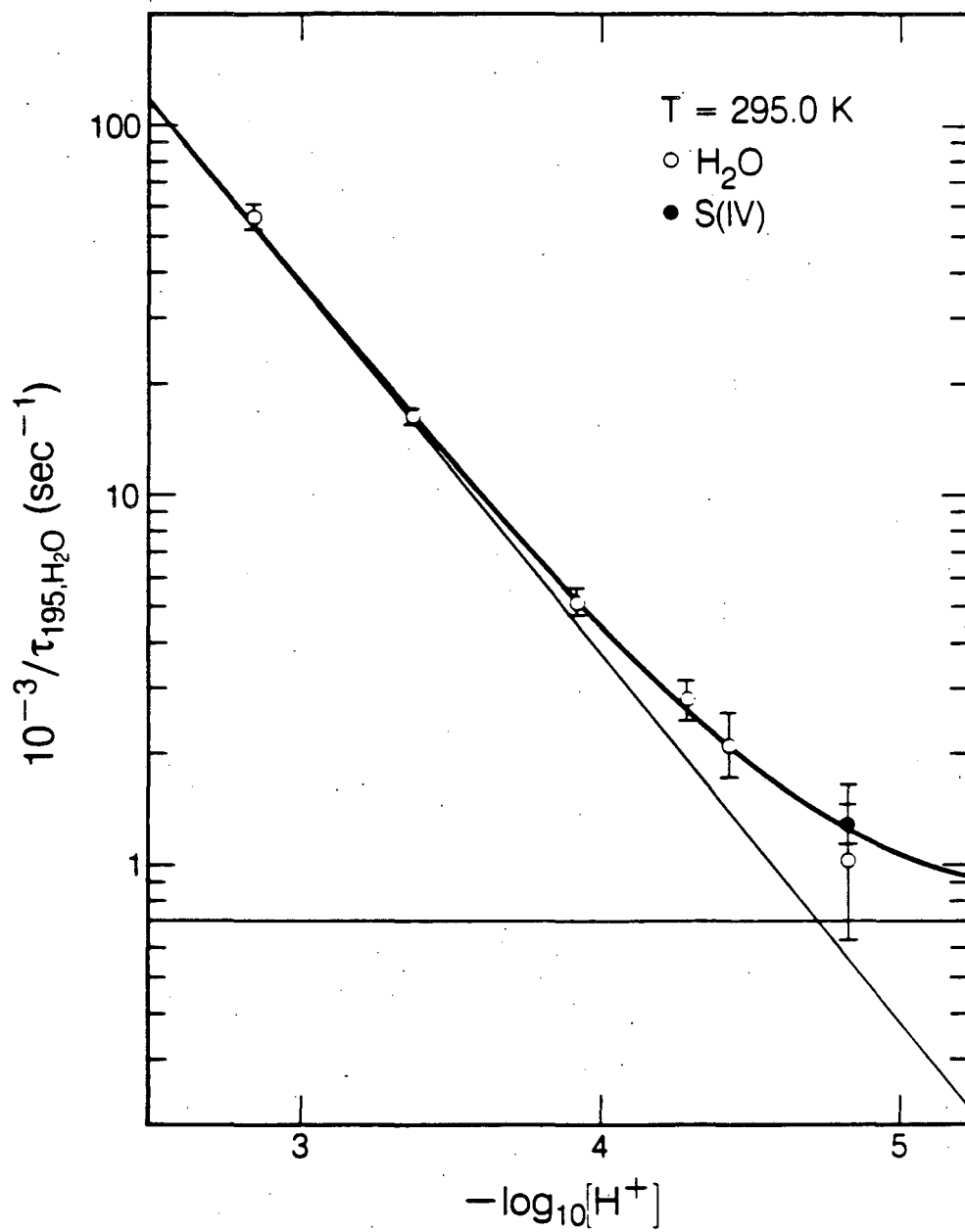
and the values of A and B were determined by the method of weighted linear least squares. The functions corresponding to the best fits of the data are represented by the smooth curves in Figures 17-22.

It is of some concern that the values of $1/\tau_{195,H_2O}$ obtained from



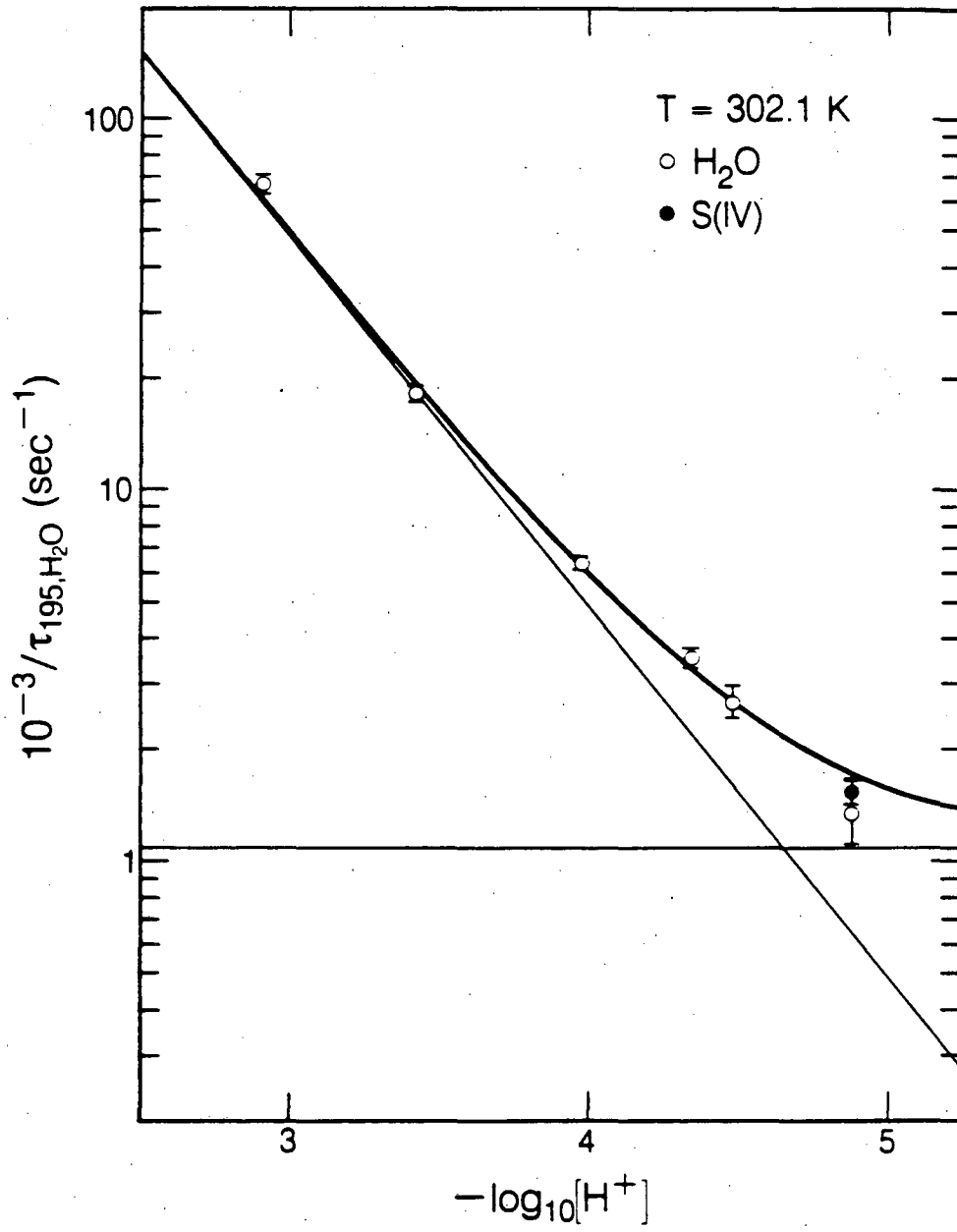
XBL 848-7820

Figure 17



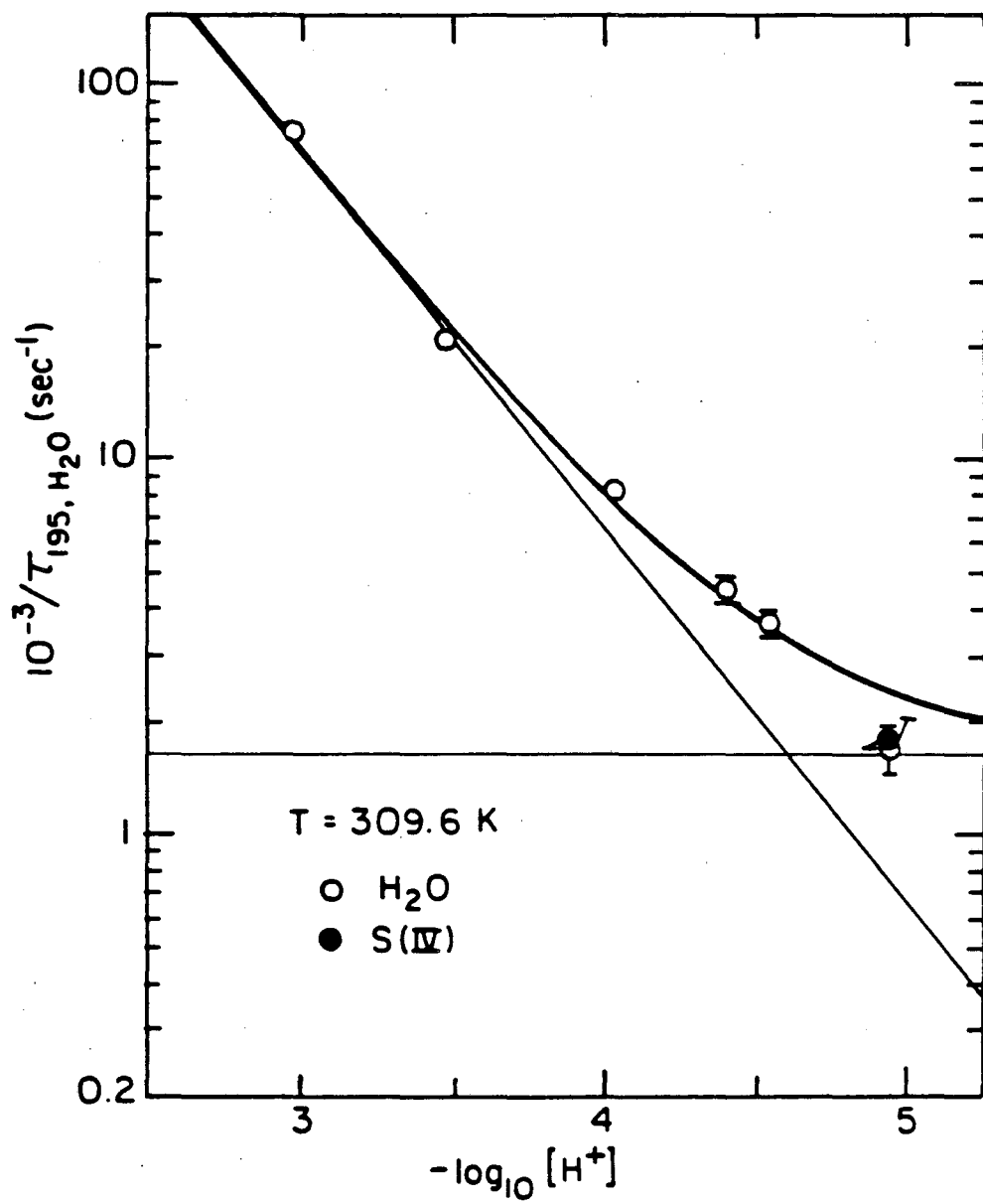
XBL 848-7816

Figure 18



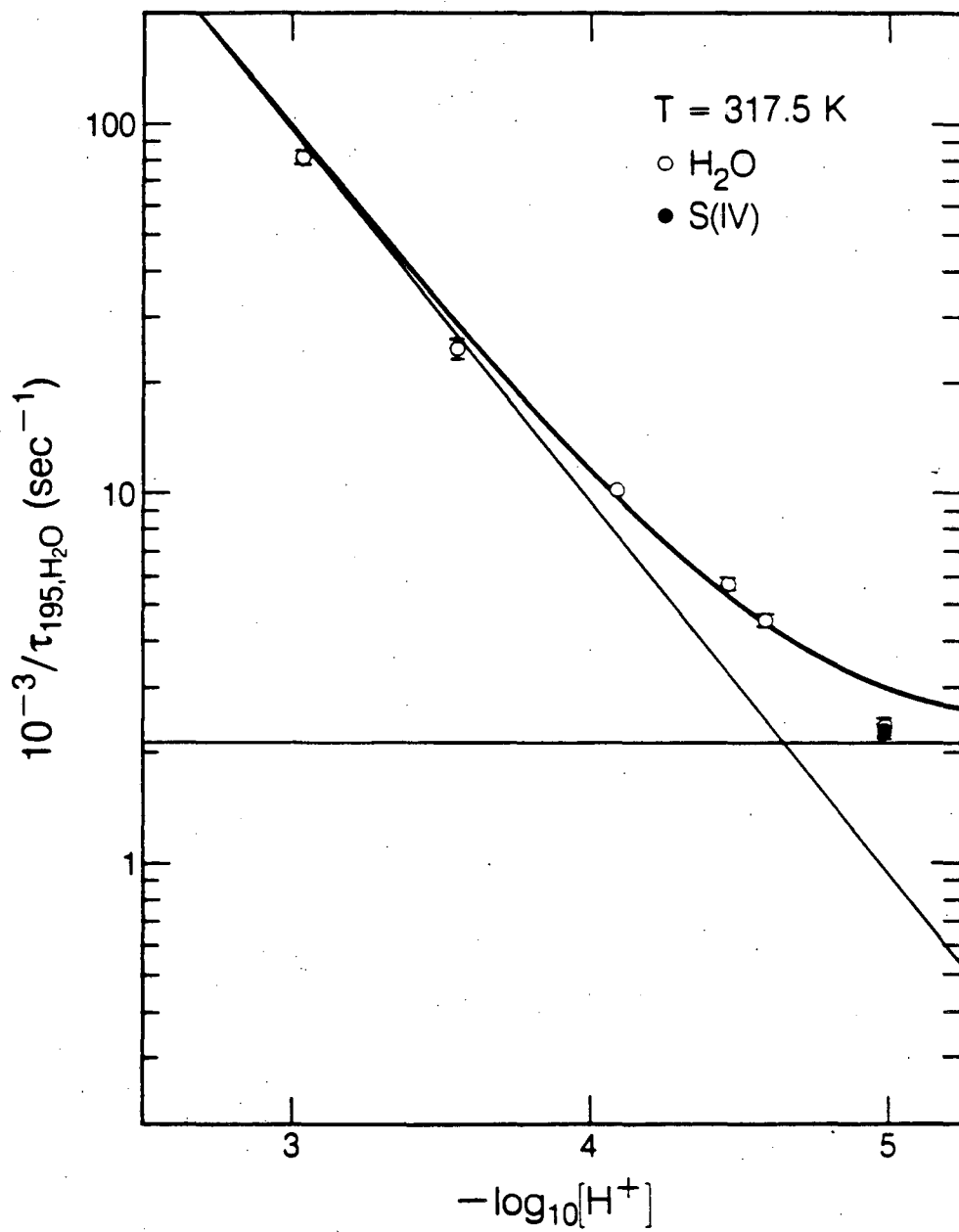
XBL 848-7821

Figure 19



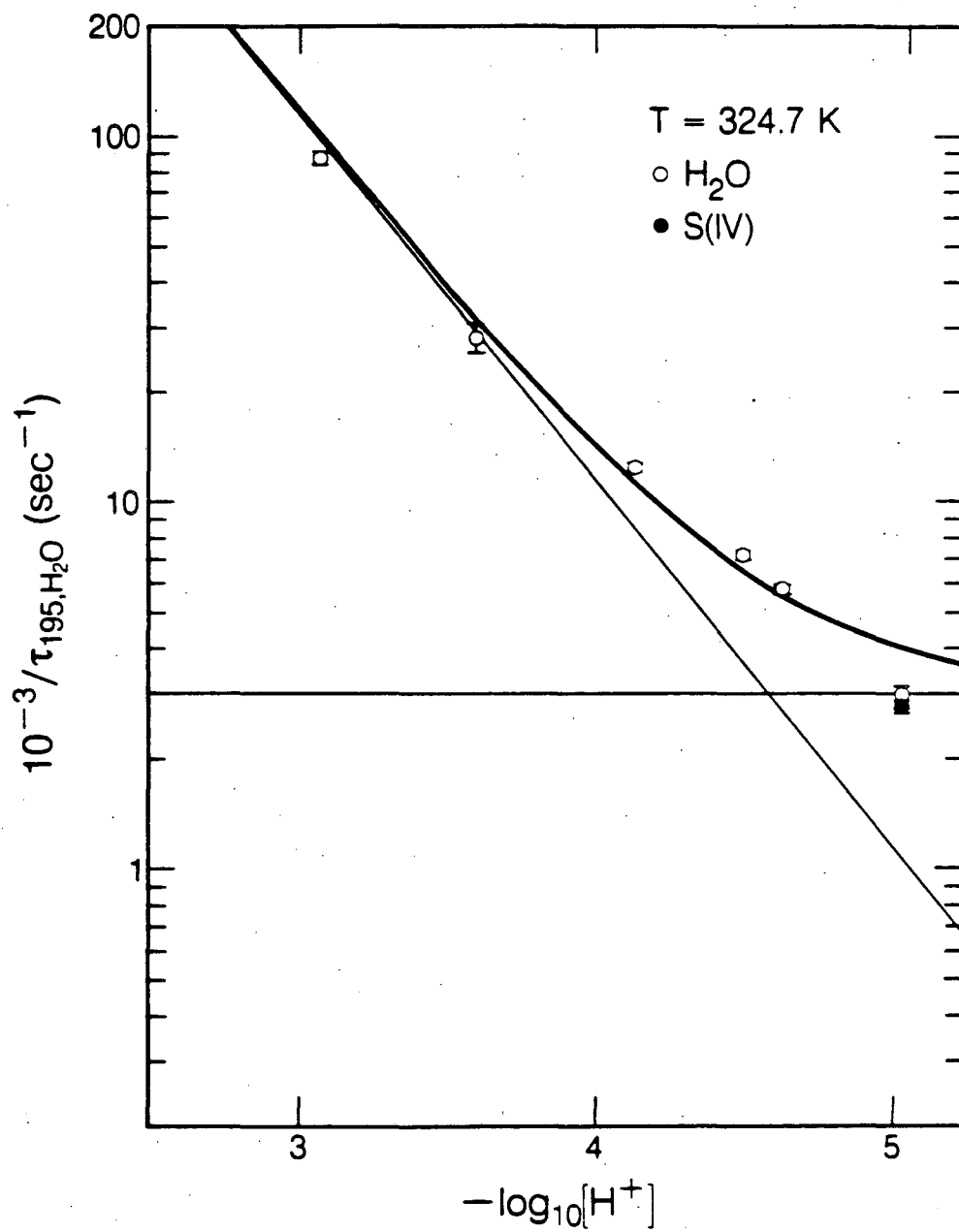
XBL 838-6143

Figure 20



XBL 848-7819

Figure 21



XBL 848-7822

Figure 22

the broadening of the water peak of the pH 5 sample show a systematic deviation from the curves. As a way of checking to see if a systematic error was introduced into the calculation of $1/\tau_{195, H_2O}$, the values at pH 5 were recalculated using the broadening of the coalesced S(IV) peak (located at 193 ppm) rather than the broadening of the water peak. It was thought that if two independent calculations of $1/\tau_{195, H_2O}$ produced the same result then the values could be considered to be reliable.

The determination of $1/\tau_{195, H_2O}$ from the broadening of the S(IV) peak in the pH 5 solution requires the use of an analytic expression for the linewidth of the peak. This expression is obtained by noting that the oxygen exchange between the two forms of bisulfite ion is sufficiently rapid to coalesce the 175 ppm and 195 ppm peaks, while the exchange between bisulfite ion and water is in the slow exchange limit, as evidenced by the fact that the half width at half height of the S(IV) peak is much smaller than the frequency difference between the water peak and the S(IV) peak. Based on the results of the previous section, direct oxygen exchange between the 175 ppm bisulfite ion and water is excluded. In the absence of exchange with water, the linewidth of the coalesced S(IV) peak would be given to a good approximation by³⁸

$$\begin{aligned} \left(\frac{1}{T_2}\right)_{S(IV)} = & \frac{P_{195}}{P_{175} + P_{195}} \frac{1}{T_2(195)} + \frac{P_{175}}{P_{175} + P_{195}} \frac{1}{T_2(175)} \\ & + \frac{P_{175}P_{195}}{(P_{175} + P_{195})^2} \frac{(\Delta\omega_{195} - \Delta\omega_{175})^2}{\frac{1}{\tau_{175,195}} + \frac{1}{\tau_{195,175}}} \end{aligned} \quad (3-8)$$

Since there does exist slow exchange of oxygen between the 195 ppm

bisulfite ion and water, the coalesced S(IV) peak should be broadened by an additional amount equal to the pseudo first order rate constant for exchange from the combined 175 ppm/195 ppm site to the water site,³⁹ i.e. by an amount equal to

$$\frac{P_{195}}{P_{175} + P_{195}} \frac{1}{\tau_{195, H_2O}}$$

For the case of interest, in which there is simultaneous fast oxygen exchange between the two forms of bisulfite ion and slow exchange between the 195 ppm bisulfite ion and water, we therefore have for the linewidth of the S(IV) peak located at 193 ppm

$$\begin{aligned} \left(\frac{1}{T_2}\right)_{S(IV)} = & \frac{P_{195}}{P_{175} + P_{195}} \frac{1}{\tau_{195, H_2O}} + \frac{1}{P_{175} + P_{195}} \left(\frac{P_{175}}{T_{2(175)}} + \frac{P_{195}}{T_{2(195)}} \right) \\ & + \frac{P_{175}P_{195}}{(P_{175} + P_{195})^2} \frac{(\Delta\omega_{195} - \Delta\omega_{175})^2}{\frac{1}{\tau_{175, 195}} \left(1 + \frac{P_{175}}{P_{195}}\right)}, \end{aligned} \quad (3-9)$$

where the substitution

$$\frac{1}{\tau_{195, 175}} = \frac{1}{\tau_{175, 195}} \frac{P_{175}}{P_{195}}$$

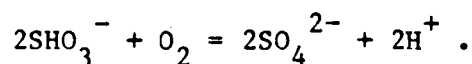
has been made.

After rearrangement, equation 3-9 may be used to evaluate $1/\tau_{195, H_2O}$, because all the other quantities in the equation are known. The values of $1/\tau_{195, H_2O}$ which were obtained using equation 3-9 and the S(IV) peak linewidth data are plotted in Figures 17-22. It is

seen that these values are in good agreement with those determined using the water peak linewidth data and equation 3-1, leading to the conclusion that there is no significant systematic error in the calculation of the pseudo first order rate constant.

The agreement between the two methods of calculating $1/\tau_{195, H_2O}$ is gratifying, but leaves unsolved the problem of the deviation of the pH 5 points from the curves of Figures 17-22. The data could perhaps be fit better by a function of the form $1/\tau_{195, H_2O} = C[H^+]^{0.5} + D[H^+]$, but such a rate law is difficult to rationalize mechanistically. It was thought necessary to examine the possibility that the deviations observed in Figures 17-22 are not of the pH 5 points from the curves of $1/\tau_{195, H_2O} = A + B[H^+]$, but rather are deviations of the points between pH 4 and 5 from the straight line corresponding to $1/\tau_{195, H_2O} = B[H^+]$. In other words, it was suspected that the A term in $1/\tau_{195, H_2O}$ does not actually exist, but appears to because the abscissa or ordinate values (or both) of some of the points in Figures 17-22 are actually too large.

A systematic error in the calculated hydrogen ion concentration of a solution, and the consequent deviation of its corresponding point from a plot of $B[H^+]$ vs. $-\log_{10}[H^+]$, would result if some of the bisulfite ion in the solution were oxidized by dissolved O_2 after the pH of the solution was measured:



Between pH 3 and 5 the $SO_2 - SHO_3^- - SO_3^{2-}$ system is near an equivalence point, and therefore the pH would be very sensitive to H^+ produced by the oxidation reaction. It is known that some oxidation occurred in

every solution because a small SO_4^{2-} peak could be seen at 164 ppm in the ^{17}O NMR spectra. Because oxygen exchange between sulfate ion and water is very slow, and because the water and the S(IV) species were enriched in ^{17}O , the appearance of a sulfate peak in the spectrum is evidence of oxidation of (^{17}O enriched) bisulfite ion.

In order to determine the amount of bisulfite ion which had oxidized the relative areas of the SO_4^{2-} and S(IV) peaks in the spectra of the 0.2 m solutions were determined with the aid of a computer generated curve analysis, with care being taken to correct the areas for the effect of signal decay which occurred during the preacquisition delay time. For the pH 5 solution, in which the coalesced S(IV) peak is due to ^{17}O in all the S(IV) species, the peak area ratio is nearly proportional to the ratio of the amounts of SO_4^{2-} and S(IV) present in the solution, and for the cases in which the measured S(IV) peak was the peak at 175-178 ppm the area ratio is proportional to the ratio of the concentrations of SO_4^{2-} and 175 ppm bisulfite ion. It was found that roughly 0.3% of the S(IV) had oxidized in each of the 0.2 m solutions. The change in hydrogen ion concentration resulting from this amount of oxidation is not negligible, producing a change of about 0.15 unit in the abscissa value of the pH 4 solution, but does not cause the points in Figures 17-22 to lie more closely upon a line of slope -1. In fact, because the effect of the oxidation upon $-\log_{10}[\text{H}^+]$ is greatest near the equivalence point of the sulfurous acid (located at $-\log_{10}[\text{H}^+] = 3.9$) the curvature of the plot is actually made more severe, and the pH 5 point lies even further away from a smooth curve drawn through the others. It was necessary to conclude that oxidation is not a satisfactory explanation for the deviation of the high pH points in

Figures 17-22 from the straight lines corresponding to $1/\tau_{195, H_2O} = B[H^+]$.

Having noted that oxidation of S(IV) did occur in the sample solutions and that the extent of oxidation was great enough to significantly affect the hydrogen ion concentration of each, one must ask whether this oxidation occurred before or after the pH measurement was made. Unfortunately, the answer is uncertain because it is not known exactly how much oxygen remained in the glove bag during the preparation of each solution. After the pH measurement the sample was immediately placed in an NMR sample tube, which was then sealed. Thus only oxygen inside the sample tube would be able to participate in the oxidation reaction after the pH measurement. Since the volume of the sample was 3 ml and that of the enclosed airspace above the sample about 8 ml, the air in the glove bag and sample tube would need to contain about 0.3% oxygen in order to account for the oxidation, after the pH measurement, of 0.3% of the S(IV) in the 0.2 m solutions. The necessary oxygen concentration does not seem unbelievably large, so it is possible that some significant amount of oxidation occurred after the pH measurement. However, no decisive statement on this matter can be made with the amount of information available.

Since it could not be established in a completely satisfactory manner whether or not the data in Figures 17-22 actually should be fit by the function $1/\tau_{195, H_2O} = A + B[H^+]$, the data analysis was carried out as if this function is the correct form of $1/\tau_{195, H_2O}$, though with some lingering doubts, particularly because the fitted curves deviate systematically from the pH 5 points by more than would be expected from the estimated experimental uncertainty.

The [S(IV)] dependence of the coefficients in the expression $1/\tau_{195, H_2O} = A + B[H^+]$ was determined through examination of the variation of $1/\tau_{195, H_2O}$ with changing S(IV) concentration in solutions of pH 3 and pH 5. It is evident from Figures 17-22 that the $[H^+]$ independent term in $1/\tau_{195, H_2O}$ is insignificant at pH 3, so any variation in $1/\tau_{195, H_2O}$ with changing S(IV) concentration at that pH can be attributed to the S(IV) dependence of the coefficient B. The calculated values of $1/\tau_{195, H_2O}$ for solutions of pH 3 and various S(IV) concentrations are found in Table 3; it is apparent that the coefficient B is zero order in S(IV).

The [S(IV)] dependence of the coefficient A was studied using the data from pH 5 solutions, since A contributes a larger fraction of $1/\tau_{195, H_2O}$ at lower acidities. Because the contribution of the $[H^+]$ dependent term in $1/\tau_{195, H_2O}$ cannot be ignored at pH 5 the value of A in each case was calculated using the formula

$$A = \frac{1}{\tau_{195, H_2O}} - B[H^+] \quad (3-10)$$

Values of A at three different S(IV) concentrations and several temperatures are listed in Table 4. The values of B used in the calculation were those obtained from the fitting of the data shown in Figures 17-22. The calculation was performed twice for each solution at every temperature by using both the value of $1/\tau_{195, H_2O}$ obtained from the water peak broadening and the value determined from the (coalesced) S(IV) peak linewidth. The results show that A, the term in $1/\tau_{195, H_2O}$ which is independent of the concentration of H^+ , is also not a function of the S(IV) concentration. It is therefore concluded that $1/\tau_{195, H_2O}$

Table 3

Effect of S(IV) Concentration, at pH 3 and Various Temperatures, upon the Pseudo First Order Rate Constant for Oxygen Exchange to Water from the Site with an Oxygen-17 NMR Chemical Shift of 195 ppm

<u>$-\log_{10}[\text{H}^+]^{\text{a}}$</u>	<u>[S(IV)] (m)</u>	<u>$10^{-3} \times 1/\tau_{195, \text{H}_2\text{O}} (\text{sec}^{-1})$</u>					
		<u>288 K</u>	<u>295 K</u>	<u>302 K</u>	<u>309 K</u>	<u>317 K</u>	<u>325 K</u>
2.89	0.101	50 ± 10	50 ± 10	61 ± 7	69 ± 7	77 ± 6	80 ± 5
2.88	0.199	49 ± 5	56 ± 4	67 ± 4	75 ± 4	82 ± 3	87 ± 3
2.89	0.326	47 ± 5	58 ± 3	64 ± 3	71 ± 3	76 ± 2	82 ± 3
2.90	0.456	46 ± 3	49 ± 4	61 ± 1	69 ± 3	74 ± 2	76 ± 2

^aValues given are for 25°C, and were calculated by the method explained in the Experimental Procedure section.

Table 4

Effect of S(IV) Concentration, at pH 5 and Various Temperatures,
upon the $[H^+]$ Independent Term in the Pseudo First Order Rate Constant
for Oxygen Exchange to Water from the Site with an Oxygen-17 NMR
Chemical Shift of 195 ppm

T (K)	[S(IV)] (m) ^a	$-\log_{10}[H^+]^b$	$1/\tau_{195,H_2O} - B[H^+] \text{ (sec}^{-1}\text{)}^c$	
			<u>H₂O data^d</u>	<u>S(IV) data^e</u>
288	0.201	4.78	500 ± 600	600 ± 200
	0.327	4.80	500 ± 300	500 ± 200
	0.449	4.77	500 ± 200	500 ± 200
295	0.201	4.83	500 ± 500	700 ± 200
	0.327	4.86	600 ± 300	600 ± 200
	0.449	4.82	700 ± 200	700 ± 200
302	0.201	4.89	700 ± 300	900 ± 100
	0.327	4.91	800 ± 200	800 ± 100
	0.449	4.89	1200 ± 100	900 ± 100
309	0.201	4.94	1000 ± 300	1100 ± 100
	0.327	4.96	1100 ± 200	1100 ± 100
	0.449	4.93	1500 ± 100	1200 ± 100

Table 4 (cont.)

T (K)	[S(IV)] (m) ^a	$-\log_{10}[\text{H}^+]$ ^b	$1/\tau_{195,\text{H}_2\text{O}} - B[\text{H}^+]$ (sec ⁻¹) ^c	
			<u>H₂O data^d</u>	<u>S(IV) data^e</u>
317	0.201	4.99	1400 ± 200	1400 ± 100
	0.327	5.01	1500 ± 100	1300 ± 100
	0.449	4.98	2000 ± 100	1600 ± 100
325	0.201	5.04	1900 ± 200	1700 ± 200
	0.327	5.06	2000 ± 200	1800 ± 200
	0.449	5.03	2300 ± 200	2100 ± 200

^aThe concentrations of SHO_3^- at the three S(IV) concentrations were calculated to be 0.19, 0.30, and 0.41 m at all temperatures.

^bCalculated by method described in Experimental Procedure section.

^cThe functional form of $1/\tau_{195,\text{H}_2\text{O}}$ was assumed to be

$$1/\tau_{195,\text{H}_2\text{O}} = A + B[\text{H}^+].$$

^dCalculated using value of $1/\tau_{195,\text{H}_2\text{O}}$ determined from H₂O peak linewidth.

^eCalculated using value of $1/\tau_{195,\text{H}_2\text{O}}$ determined from S(IV) peak linewidth.

is given by

$$\frac{1}{\tau_{195, H_2O}} = A + B[H^+] \quad (3-11)$$

Oxygen exchange mechanisms which are consistent with equation 3-11 will now be suggested. It is first necessary to note that the experimental rate law for oxygen exchange between the 195 ppm site and water is

$$\text{oxygen exchange rate} = \frac{1}{\tau_{195, H_2O}} [O_{195}] ,$$

where $[O_{195}]$ is the concentration of oxygen atoms in the 195 ppm site. In the pH and concentration ranges studied $[O_{195}]$ is nearly proportional to the concentration of bisulfite ion, and not proportional to the concentrations of other sulfur species, so mechanisms will be chosen which produce a rate law which is first order in bisulfite ion.

The term $B[H^+]$ in $1/\tau_{195, H_2O}$ can be explained by the one step mechanism.



from which it is deduced that B and k_{-17} are related by the expression

$$k_{-17} = \frac{B[O_{195}]}{[(\text{SHO}_3^-)_{195}]} \quad (3-12)$$

If it is assumed that SO_3^{2-} , SO_2 , $\text{S}_2\text{O}_5^{2-}$, and $(\text{SHO}_3^-)_{195}$ are all part of the 195 ppm site then the ratio $[O_{195}]/[(\text{SHO}_3^-)_{195}]$ is slightly greater

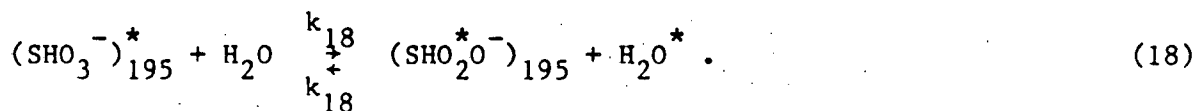
than 3 for the solutions of interest; the exact value was determined at several temperatures and pH values using the calculated concentrations of the S(IV) species and the value of K_{15} , and was found to range from 3.14 to 3.16.

A plot of $\log k_{-17}$ vs. $1/T$ is shown in Figure 23 along with a straight line representing the weighted linear least squares fit of the data. The temperature dependence of k_{-17} is given by

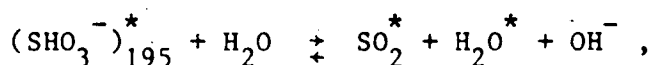
$$\ln k_{-17} = (30.91 \pm 0.25) + (-3637 \pm 75)/T, \quad (3-13)$$

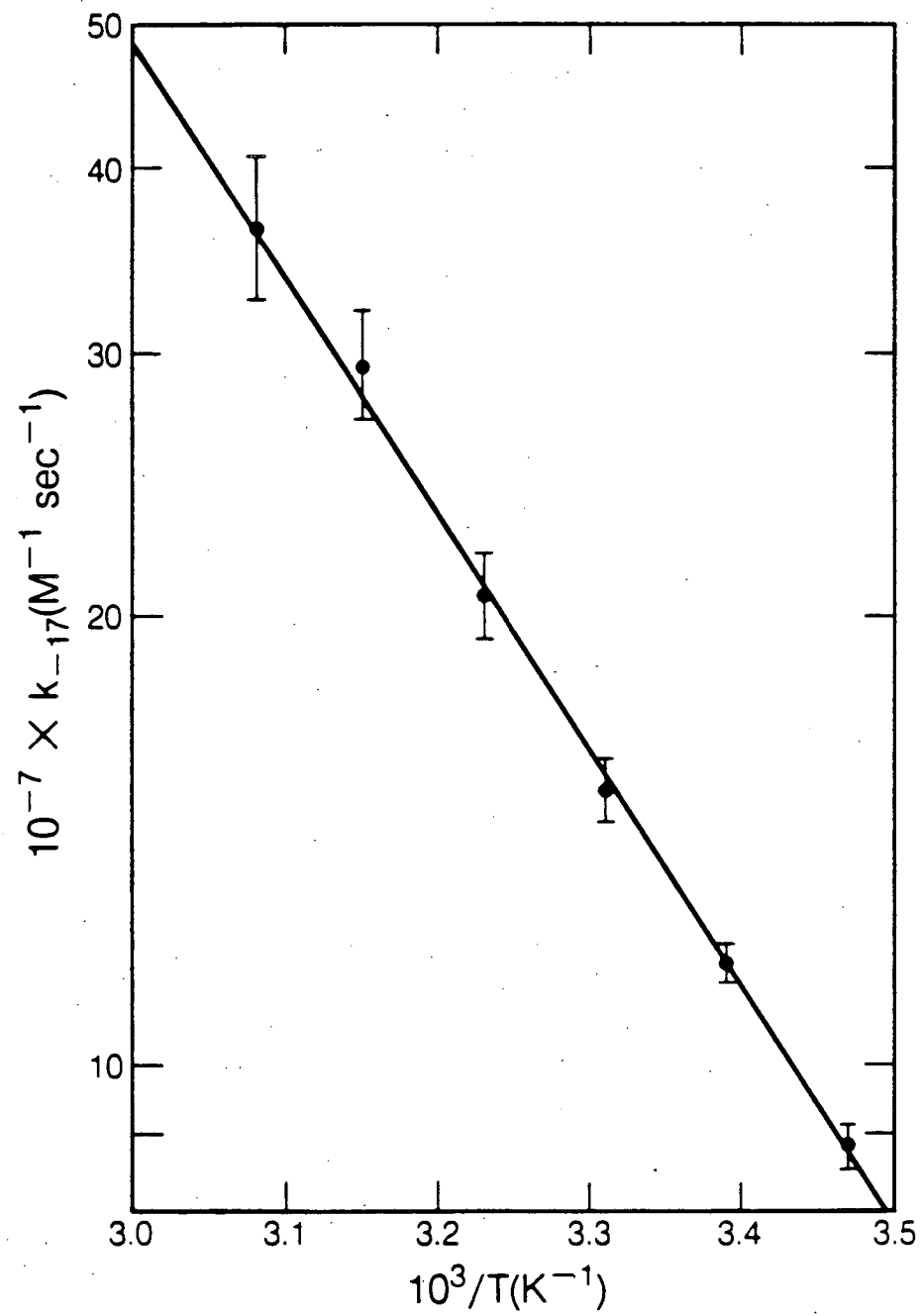
with a covariance between the slope and y-intercept of -19.0. The value of k_{-17} at 25°C is $(1.33 \pm 0.01) \times 10^8 \text{ M}^{-1}\text{sec}^{-1}$.

The constant term in $1/\tau_{195, \text{H}_2\text{O}}$ is consistent with the following single step mechanism:



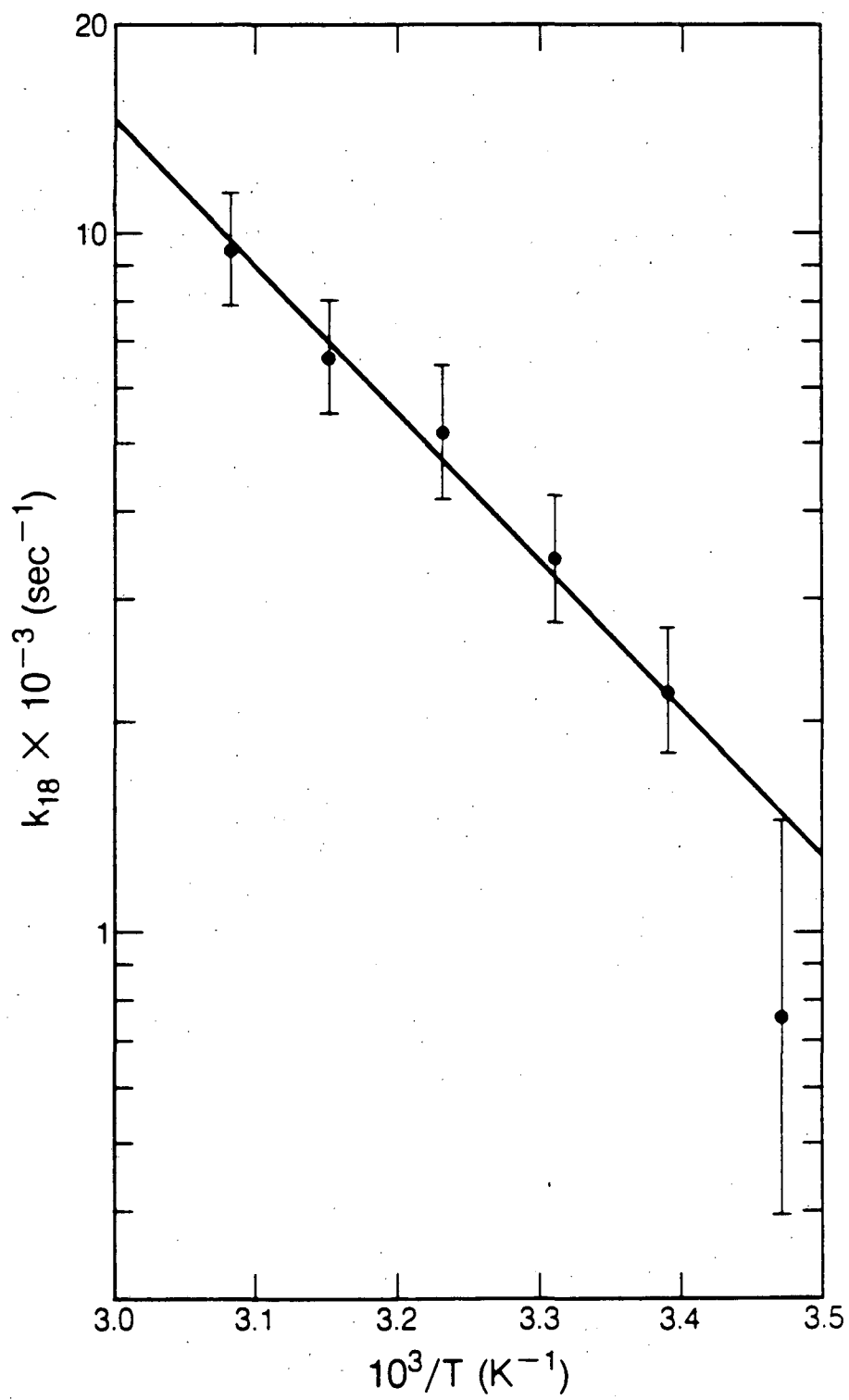
This mechanism is most plausible if the 195 ppm bisulfite ion is the SO_3H^- isomer, since it is easy to visualize the water oxygen forming a bond with the sulfur atom as the H-O group of the bisulfite ion moves away from the sulfur atom and extracts a hydrogen from the entering water. On the other hand, the hydrogen atom in the HSO_3^- isomer hinders the water molecule in its approach to the sulfur atom. (Another mechanism which can account for the constant term in $1/\tau_{195, \text{H}_2\text{O}}$ is





XBL 848-7816

Figure 23



XBL 848-7817

Figure 24

which is analogous to reaction 17. However, this mechanism is unreasonable because the pseudo first order rate constant for the forward reaction is so large ($3A = 2500 \text{ sec}^{-1}$ at 25°C) that the rate of the reverse reaction would need to exceed that of a diffusion controlled reaction in order to maintain equilibrium.)

The relationship between k_{18} and A is

$$k_{18} = A \frac{[O_{195}]}{[(\text{SHO}_3^-)_{195}]} \quad (3-14)$$

Values of k_{18} were determined at several temperatures using values of $[O_{195}]/[(\text{SHO}_3^-)_{195}]$ obtained in the manner outlined previously. The results are plotted as $\log k_{18}$ vs. $1/T$, shown in Figure 24. The weighted linear least squares fit of the data yields

$$\ln k_{18} = (23.98 \pm 1.49) + (-4802 \pm 462)/T, \quad (3-15)$$

with a covariance between the slope and y-intercept of -688. At 25°C k_{18} is equal to $2600 \pm 200 \text{ sec}^{-1}$.

It has been assumed in much of the preceding data analysis that the SO_2 resonance in the ^{17}O NMR spectrum is coalesced with that of the 195 ppm bisulfite ion. The validity of this assumption can now be investigated, because it depends upon the rate of reaction 17, which brings about oxygen exchange between 195 ppm bisulfite ion and SO_2 . In order for the two resonances to coalesce, the sum of the two pseudo first order rate constants for oxygen exchange must be much greater than the difference in resonance frequency of the two sites, i.e.

$$\frac{1}{\tau_{(\text{SHO}_3^-)_{195}, \text{SO}_2}} + \frac{1}{\tau_{\text{SO}_2, (\text{SHO}_3^-)_{195}}} \gg \left| [\omega_{\text{SO}_2}] - [\omega_{(\text{SHO}_3^-)_{195}}] \right| . \quad (3-16)$$

The frequency difference is calculated to be $5.5 \times 10^4 \text{ sec}^{-1}$ using the formula $\Delta\omega = 2\pi \times 27 \times (520 - 195)$, where 27 is the Larmor frequency of ^{17}O in MHz and 520 and 195 are the chemical shifts in ppm of aqueous sulfur dioxide⁹ and 195 ppm bisulfite ion, respectively. Because reaction 17 transfers oxygens from 195 ppm bisulfite ion to SO_2 twice as rapidly as to water, and because the concentration of oxygen atoms in the 195 ppm site is nearly equal to the concentration of those in 195 ppm bisulfite ion at the S(IV) concentrations used in this work, we have

$$\frac{1}{\tau_{(\text{SHO}_3^-)_{195}, \text{SO}_2}} \approx 2B[\text{H}^+] , \quad (3-17)$$

where $B[\text{H}^+]$ is the pseudo first order rate constant for oxygen exchange from the 195 ppm site to water via reaction 17. Because the pseudo first order rate constant for oxygen exchange from site X to site Y must (at equilibrium) be related to the pseudo first order rate constant for exchange from Y to X by the ratio of oxygen populations of the two sites, we also have

$$\frac{1}{\tau_{\text{SO}_2, (\text{SHO}_3^-)_{195}}} \approx 2B[\text{H}^+] \frac{3[(\text{SHO}_3^-)_{195}]}{2[\text{SO}_2]} . \quad (3-18)$$

Addition of equations 3-17 and 3-18 followed by elimination of $[SO_2]$ and $[(SHO_3^-)_{195}]$ by use of the expressions for K_1 and K_{15} yields

$$\frac{1}{\tau_{(SHO_3^-)_{195}, SO_2}} + \frac{1}{\tau_{SO_2, (SHO_3^-)_{195}}} = 2B[H^+] \left\{ 1 + \frac{3K_1}{2[H^+] \left(\frac{1}{K_{15}} + 1 \right)} \right\} .$$

(3-19)

A calculation using 25°C values of $B = 3.7 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$, $K_1 = 10^{-1.34} \text{ M}$, and $K_{15} = 4.9$ gives a value of $4 \times 10^6 \text{ sec}^{-1}$ for the sum of the two pseudo first order rate constants over the entire pH range used in this work. This value is about 70 times greater than $\Delta\omega$, verifying the assumption of coalescence of the SO_2 and 195 ppm bisulfite ion resonances throughout the pH range of this work.

In evaluating $1/\tau_{195, H_2O}$ from the measured water peak linewidths and equation 3-1 it was necessary to know the value of the natural linewidth of the water peak, $1/T_2(H_2O)$, which was assumed to be equal to $1/T_1(H_2O)$. The argument that this quantity was equal to the measured longitudinal relaxation rate constant of the ^{17}O in water, $(1/T_1)_{H_2O}$, was dependent upon the magnitude of $1/T_1(195)$ being close to that of $1/T_1(H_2O)$. A check on the earlier conclusions can be made now that values of $1/\tau_{195, H_2O}$ are known. Assuming, as before, that $1/T_1(195)$ is equal to $1/T_2(195)$, values of $1/T_1(195)$ can be calculated using equation 3-9, linewidths of the coalesced S(IV) peak at pH 5, and values of $1/\tau_{195, H_2O}$ obtained from the water peak broadening data and equation 3-1. Because the difference between $1/T_1(H_2O)$ and $1/T_1(195)$ is greatest at low temperature, a calculation of $1/T_1(195)$ was carried out for the $[S(IV)] = 0.20 \text{ m}$, pH 5 solution at 288 K, for which $(1/T_2)_{S(IV)} = 1260$

sec^{-1} , $1/T_2(175) = 57.5 \text{ sec}^{-1}$, $p_{175}/p_{195} = 0.16$, $(\Delta\omega_{195} - \Delta\omega_{175}) = 3300 \text{ sec}^{-1}$, $1/\tau_{175,195} = 5150 \text{ sec}^{-1}$, and $1/\tau_{195,H_2O} = 930 \text{ sec}^{-1}$. The calculated value of $1/T_1(195)$ (assumed to be equal to $1/T_2(195)$) is 270 sec^{-1} . Since the measured value of $(1/T_1)_{H_2O}$ is 190 sec^{-1} at 288 K, and the maximum difference between $(1/T_1)_{H_2O}$ and $1/T_1(H_2O)$ is given by equation 3-4, $(1/T_1)_{H_2O}$ and $1/T_1(H_2O)$ differ by no more than about 0.8 sec^{-1} at 288 K. This is less than the experimental uncertainty in the measured longitudinal relaxation rate constant, so the use of $(1/T_1)_{H_2O}$ in place of $1/T_1(H_2O)$ appears to be justified. These results also confirm equation 3-5.

Comparison with Previous Work

The results of the present work can be compared to those of two previous studies, both of which evaluated rate constants for the reaction of bisulfite ion and hydrogen ion to produce sulfur dioxide and water (reaction 1). Eigen, Kustin, and Maass⁶ studied the frequency dependence of the attenuation of sound waves in sulfur dioxide solutions of relatively high acidity ($\text{pH} < 2$) and an ionic strength of 0.1 m. The absorption of sound by the solutions was presumed to produce shifts in the equilibrium of reaction 1. Although Eigen and coworkers were not measuring oxygen exchange rates, their results are comparable to those of oxygen exchange studies, and set a lower limit to the rate of oxygen exchange between bisulfite ion and water, because reaction 1 does bring about oxygen exchange between these two species. Betts and Voss⁷ studied the kinetics of oxygen exchange between sulfite ion and water in

alkaline solutions ($\text{pH} > 8$) of ionic strength 0.9 M by measuring the rate of appearance or disappearance of oxygen-18 in the sulfite ion of aqueous sulfite solutions containing ^{18}O enriched water or sodium sulfite, respectively. The rate was studied as a function of the sulfite ion concentration and the pH. Betts and Voss also reported a rate constant for the dimerization reaction (reaction 3).

Although Eigen, Kustin, and Maass interpreted their sound absorption data in terms of the relaxation to equilibrium values of the concentrations of the species in solution via reaction 1, their data must be reinterpreted in light of the findings of the present work regarding the two isomers of bisulfite ion. The 175 ppm bisulfite ion reacts with hydrogen ion to produce sulfur dioxide and water at a rate which is so low that it was undetectable in the present work, and at the acidities at which Eigen, Kustin, and Maass worked the equilibration between the two isomers of bisulfite ion (reaction 15) occurs much more slowly than the reaction in which water and sulfur dioxide are formed from 195 ppm bisulfite ion and hydrogen ion (reaction 17). Under these conditions it would be expected that the relaxation which occurs via reaction 17 is largely uncoupled from that occurring via reaction 15. It can be shown that the relaxation time measured by Eigen and coworkers is given to a very good approximation by

$$\tau_{\text{II}} = \{k_{-17}([\text{H}^+] + [(\text{SHO}_3^-)_{195}] + K_{17})\}^{-1} \quad (4-1)$$

Assuming this to be the proper interpretation of the measurements of Eigen, Kustin, and Maass, the data of those workers were used to evaluate k_{-17} from equation 4-1. The value of K_{17} was obtained from the

relationship $K_{17} = K_1 \{1 + (1/K_{15})\}^{-1}$, and is equal to 0.014. (No attempt was made to correct K_{15} for ionic strength effects.) The data of Eigen and coworkers yields a value for k_{-17} of $(2.2 \pm 0.2) \times 10^8$ $M^{-1} \text{sec}^{-1}$ at 20°C .

To allow meaningful comparison of the results of the various studies the value of k_{-17} determined from the data of Eigen, Kustin, and Maass was corrected to the ionic strength of the present work, and the value of k_{-17} from this work was used to calculate a corresponding value of k_{-1} . The value of k_{-1} was calculated from the expression

$$k_{-1} = k_{-17} \left(\frac{1}{K_{15}} + 1 \right)^{-1} . \quad (4-2)$$

The ionic strength correction was made using the relationship

$$(k_{-17})_{\mu=1.0} = (k_{-17})_{\mu=0.1} \left\{ \frac{(\gamma_{\text{H}^+} \gamma_{\text{SHO}_3^-})_{\mu=1.0}}{(\gamma_{\text{H}^+} \gamma_{\text{SHO}_3^-})_{\mu=0.1}} \frac{(\gamma^\ddagger)_{\mu=0.1}}{(\gamma^\ddagger)_{\mu=1.0}} \right\} , \quad (4-3)$$

The choice of values of the activity coefficients requires some explanation.

The mean ionic activity coefficient of H^+ and SHO_3^- was estimated at $\mu = 0.1$ m and $\mu = 1.0$ m by calculating its value in the 0.140 m solution of Eigen, Kustin, and Maass and the 0.20 m, pH 5 solution of this work using Pitzer's equations.⁴⁰ It was assumed that the ionic strength of the solution of Eigen and coworkers was adjusted to 0.1 m with sodium chloride. The ionic interaction parameters used in the calculation were those suggested by Rosenblatt.⁴¹ Rosenblatt did not

include estimates of the interaction parameters of the $\text{H}^+\text{-SHO}_3^-$, $\text{H}^+\text{-S}_2\text{O}_5^{2-}$, and $\text{H}^+\text{-SO}_3^{2-}$ pairs; their values were assumed to be equal to the parameters of $\text{H}^+\text{-HSO}_4^-$, $\text{H}^+\text{-SO}_4^{2-}$, and $\text{H}^+\text{-SO}_4^{2-}$, respectively. Because the values of the ionic interaction parameters involving S(IV) species were uncertain, the effect of different choices of interaction parameters upon the calculated activity coefficient was also investigated. As might be expected for solutions in which the major ionic species are Na^+ and Cl^- , the calculated value was not very sensitive to changes in the interaction parameters involving S(IV) species, with one exception. The choice of $\text{Na}^+\text{-SHO}_3^-$ interaction parameters did have a noticeable effect upon the mean ionic activity coefficient of H^+ and SHO_3^- in the 0.2 m solution. The value of the activity coefficient in that solution ranged from 0.66 to 0.76, and depended upon whether the $\text{Na}^+\text{-SHO}_3^-$ interaction parameters were taken to be equal to those for the $\text{Na}^+\text{-ClO}_3^-$, $\text{Na}^+\text{-ClO}_4^-$, or $\text{Na}^+\text{-HCO}_3^-$ pairs. The calculated value of the mean ionic activity coefficient of H^+ and SHO_3^- was 0.79 in the solution of Eigen and coworkers. The values of the mean ionic activity coefficient of H^+ and SHO_3^- were therefore taken to be 0.71 ± 0.05 and 0.79 at $\mu = 1.0$ m and $\mu = 0.1$ m, respectively. (These values are very similar to 0.754 and 0.792, the measured values of the mean ionic activity coefficient of 0.01 M HCl in solutions of 0.99 m and 0.09 m NaCl, respectively.¹³⁾

The activity coefficient of the activated complex, γ^\ddagger , was not known, but the ratio of its values at the two ionic strengths may be estimated by noting that the activated complex can be thought of as an uncharged but polar nonelectrolyte whose activity coefficient changes as the salt content of the solution increases. Since NaCl was the major

component of the 0.2 m solutions of this work and the solutions of Eigen and coworkers, it was thought that the activity coefficient of the activated complex should be about equal to the activity coefficient of a polar nonelectrolyte in a sodium chloride solution if the structure of the nonelectrolyte is similar to that of the activated complex. The activity coefficients of acetic acid, chloroacetic acid, dichloroacetic acid,⁴² and sulfur dioxide⁴³ have values near unity in 0.1 m NaCl, and are greater by 10 to 50 percent in 1.0 m NaCl solutions. Assuming that the activity coefficients of these substances are similar to that of the activated complex of reaction 17, the ratio $(\gamma^\ddagger)_{\mu=0.1}/(\gamma^\ddagger)_{\mu=1.0}$ was taken to be equal to 0.79 ± 0.12 .

The comparison of the rate constants for reactions 1 and 17 as well as a listing of Betts and Voss' rate constant for reaction 3 and the value of k_{18} from this work are found in Table 5. (The small uncertainties associated with the results of the present work are due to the small uncertainties in the slopes and intercepts of the lines obtained in the least squares curve fitting of the data in Figures 23 and 24. Systematic errors could have an appreciable effect on the reported values of the rate constants, especially if such errors were present in the values of $(1/T_2)_{H_2O}$ and $1/T_2(H_2O)$.) The results of the present work are in moderately good agreement with those of Eigen, Kustin, and Maass. The fact that Eigen and coworkers made no mention of reaction 18 is not a source of disagreement, for they would not have observed an effect due to reaction 18 using relaxation methods because relaxation methods cannot detect exchange reactions. There are several points of disagreement between the results of this work and those of Betts and Voss. The two values of k_{-1} differ by about a factor of 20

Table 5

Comparison of Rate Constants Obtained in This Study with Those
Determined by Other Workers

$$\text{H}^+ + \text{SHO}_3^- \xrightleftharpoons{k_{-1}} \text{SO}_2 + \text{H}_2\text{O}$$

<u>k_{-1} ($\text{M}^{-1} \text{sec}^{-1}$)</u>	<u>Reference</u>	<u>Temperature ($^{\circ}\text{C}$)</u>	<u>Ionic Strength</u>
$(2.5 \pm 0.3) \times 10^9$	7	24.7	0.9 M
$(1.098 \pm 0.009) \times 10^8$ ^a	This work	24.7	1.0 m
2×10^8 ^b	6	20	0.1 m
$(9.15 \pm 0.08) \times 10^7$ ^a	This work	20.0	1.0 m

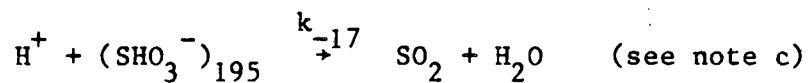
^aCalculated from value of k_{-17} using equation 4-2.

^bThe value reported in reference 6 was given to only one significant figure, and contained no estimate of experimental uncertainty.

$$2\text{SHO}_3^- \xrightleftharpoons{k_3} \text{S}_2\text{O}_5^{2-} + \text{H}_2\text{O}$$

<u>k_3 ($\text{M}^{-1} \text{sec}^{-1}$)</u>	<u>Reference</u>	<u>Temperature ($^{\circ}\text{C}$)</u>	<u>Ionic Strength</u>
700 ± 200	7	24.7	0.9 M

Table 5 (cont.)

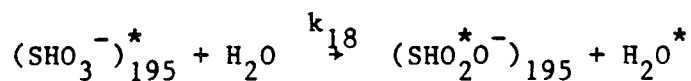


k_{-17} ($\text{M}^{-1} \text{sec}^{-1}$)	Reference	Temperature ($^{\circ}\text{C}$)	Ionic Strength
$(2.2 \pm 0.2) \times 10^8$ ^d	6	20	0.1 m
$(1.4 \pm 0.3) \times 10^8$ ^e	6	20	1.0 m
$(1.086 \pm 0.009) \times 10^8$	This work	20.0	1.0 m

^c $(\text{SHO}_3^-)_{195}$ is the isomer of bisulfite ion whose oxygen-17 NMR signal is located 195 ppm downfield from water. This isomer is believed to be SO_3H^- .

^dCalculated from the data of reference 6 using equation 4-1.

^eCalculated from the value of k_{-17} at $\mu = 0.1$ m using equation 4-3.



k_{18} (sec^{-1})	Reference	Temperature ($^{\circ}\text{C}$)	Ionic Strength
2600 ± 200	This work	25.0	1.0 m

and may, in fact, really differ by a factor of 60, because Betts and Voss' reported values are inexplicably smaller, by a factor of 3, than those calculated from their data using their equation 10.

For a reaction which involves the breaking of a sulfur-oxygen bond the experimental values of k_{-1} seem surprisingly large, and Betts and Voss' incredibly so; their value is very nearly equal to that of a diffusion controlled reaction. The great magnitude of Betts and Voss' rate constant argues in favor of the results of the present work and that of Eigen, Kustin, and Maass. It may be that a catalytic impurity was present in Betts and Voss' solutions. The reaction between hydrogen ion and bicarbonate ion to produce carbon dioxide and water (analogous to reaction 1) is known to be susceptible to both heterogeneous⁴⁴ and homogeneous⁴⁵ catalysis. The term in Betts and Voss' rate law which they attributed to oxygen exchange from sulfite ion to water via bisulfite ion and reaction 1 is

$$\text{oxygen exchange rate} = k[\text{H}^+]^2[\text{SO}_3^{2-}] \quad (4-4)$$

To be consistent with equation 4-4 the catalyst would probably have to react with bisulfite ion (to break one of the sulfur-oxygen bonds) in place of hydrogen ion, and would be required to have a concentration proportional to that of hydrogen ion. Since the rate of the step involving the catalyst must not exceed the rate of a diffusion controlled reaction, the magnitude of the constant in equation 4-4 requires that the concentration of the catalyst be at least as large as that of hydrogen ion. However, it cannot be stated with any certainty whether such a catalyst actually was present in Betts and Voss'

solutions.

Betts and Voss' data allowed them to determine the rate constant for the dimerization of bisulfite ion (reaction 3). The corresponding term in the rate law for oxygen exchange between bisulfite ion and water, when written in terms of the major species in acidic solutions, is

$$\text{oxygen exchange rate} = k_3[\text{SHO}_3^-]^2, \quad (4-5)$$

and contributes to $1/\tau_{195, \text{H}_2\text{O}}$ a term which is first order in bisulfite ion. Using their value of k_{-3} one calculates that $1/\tau_{195, \text{H}_2\text{O}}$ has a value of 170 sec^{-1} under conditions of 25°C and $[\text{S(IV)}] = 0.2 \text{ m}$. No dependence of $1/\tau_{195, \text{H}_2\text{O}}$ upon the concentration of S(IV), almost all of which existed in the form of bisulfite ion, was observed in the present work. The data of Table 4 seem to exhibit a slight S(IV) dependence, but this was considered insignificant in light of the large uncertainties associated with the tabulated values, which make it difficult to detect a [S(IV)] dependent contribution to $1/\tau_{195, \text{H}_2\text{O}}$ as small as that predicted from Betts and Voss' results. The results of the present work are therefore not inconsistent with Betts and Voss' value for the rate constant of the dimerization reaction.

The value of k_{18} obtained in this work is inconsistent with the observations of Betts and Voss. If the oxygen exchange rate law corresponding to reaction 18 is written in terms of $[\text{H}^+]$ and $[\text{SO}_3^{2-}]$ one obtains

$$\text{rate} = \frac{k_{18}}{K_2} \frac{1}{\left(1 + \frac{1}{K_{15}}\right)} [\text{H}^+][\text{SO}_3^{2-}] . \quad (4-6)$$

If the values of the constants and values of $[\text{H}^+]$ and $[\text{SO}_3^{2-}]$ appropriate for Betts and Voss' solutions are substituted into equation 4-6 it is found that the predicted oxygen exchange rate is about 0.4 M sec^{-1} at 25°C and pH 9.5. This indicates that reaction 18 should be the dominant oxygen exchange mechanism in the pH range in which Betts and Voss' work was carried out, yet not only did those workers observe oxygen exchange rates much slower than those predicted by equation 4-6, their experimental rate law was second order in H^+ . An unsuccessful attempt was made to find an oxygen exchange mechanism which would yield a rate law which has the form of 4-6 in the acidic region and changes over to second order in H^+ in alkaline solutions. This casts further doubt upon the very existence of the $[\text{H}^+]$ independent term in $1/\tau_{195, \text{H}_2\text{O}}$, from which k_{18} was determined.

The rate constant of reaction 1, which according to the results of this work is only a factor of 1000 smaller than the rate constant of a diffusion controlled reaction, stands in marked contrast to that of the analogous reaction



which has a value equal to $6 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$.⁴⁶ Although both reactions involve the breaking of a C-O or S-O bond there is a large difference in activation energy, which may be due to the fact that little atomic rearrangement is necessary for the remaining O-S-O portion of the bisulfite ion to attain the bent SO_2 structure compared to the amount

required in transforming the O-C-O remnant of the bicarbonate ion to the linear CO₂ structure. It is also possible, as suggested by Eigen, Kustin, and Maass, that the exchange of oxygen between bisulfite ion and water occurs via the HSO₃⁻ isomer, which for some reason can react with hydrogen ion to release water much more rapidly than the SO₃H⁻ or bicarbonate ion, in which the first hydrogen is bound to an oxygen atom. However, as will be seen shortly, it is believed that it is the SO₃H⁻ isomer, rather than HSO₃⁻, which exchanges oxygen directly with water.

The Two Isomers of Bisulfite Ion

The oxygen-17 NMR spectra of bisulfite solutions provide the most convincing evidence to date for the existence of two isomers of bisulfite ion, HSO₃⁻ and SO₃H⁻. In addition, as has been discussed previously, analysis of the ¹⁷O spectra led to evaluation of the equilibrium quotient, enthalpy change, and entropy change for the isomerization reaction



These were determined to be $K_{15} = 4.9 \pm 1$ at 298 K, $\Delta H_{15} = -2.9 \pm 0.3$ kcal mol⁻¹, and $\Delta S_{15} = -6 \pm 1$ cal K⁻¹ mol⁻¹. However, the identification of each of the isomers with one of the two peaks in the NMR spectrum has not yet been made (although the results of this section were anticipated several times in assuming that the 195 ppm bisulfite

ion is SO_3H^-).

The experimental data, unfortunately, allow no direct identification of the two S(IV) peaks, so the association of each peak with a particular isomer will be made on the basis of which assignment provides the best rationale for the great disparity between the abilities of the two isomers to exchange oxygen with water. It was found in this work that one of the isomers of bisulfite ion reacts with hydrogen ion to form sulfur dioxide and water at a rate which is close to that of a diffusion controlled reaction, while the reaction of the other isomer with hydrogen ion is so slow that it was undetectable. (The rate constant of the former reaction, k_{-17} , is $1.1 \times 10^8 \text{ M}^{-1}\text{sec}^{-1}$. The upper limit to the rate constant of the latter reaction is estimated to be $2 \times 10^5 \text{ M}^{-1}\text{sec}^{-1}$.) The SO_3H^- isomer offers the simplest mechanism for the reaction with hydrogen ion; the incoming hydrogen ion need only attack the oxygen on which the bisulfite hydrogen is located, and then rupture of the sulfur-oxygen bond yields water and sulfur dioxide. On the other hand, the mechanism involving HSO_3^- is more complicated because it requires the bisulfite hydrogen to migrate from the sulfur to an oxygen atom.

Not only does the reaction of H^+ and HSO_3^- involve a more complicated mechanism than the reaction of H^+ and SO_3H^- , but the necessary breaking of the S-H bond in the former case involves a nonnegligible amount of activation energy. It was found in this work that the rate constant for the formation of HSO_3^- from SO_3^{2-} and H^+ is $2.1 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at 298 K. (Strictly speaking, the data only allow one to say that this is the rate constant for either the reaction in which HSO_3^- is formed, or the reaction in which SO_3H^- is formed, from SO_3^{2-}

and H^+ . However, the assumption that the rate constant for the latter is at least $5 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ resulted in the measured rate constant being assigned to the reaction in which HSO_3^- is formed. The results of this assumption are in qualitative agreement with the situation in phosphorous acid, in which the hydrogen atoms bound to the oxygen atoms of the acid exchange between the acid and water much more rapidly than the hydrogen atom bound to phosphorous.⁴⁷⁾ If equilibrium quotients for reactions 14 and 16 are calculated using the values of K_2 and K_{15} , and rate constants for the dissociation of HSO_3^- and SO_3H^- are then calculated, it is found that the rate constant for dissociation of HSO_3^- is 50 to 100 times smaller than the rate constant for dissociation of SO_3H^- if the latter is 195 ppm bisulfite ion, and 1000 to 2000 times smaller if the latter is 175 ppm bisulfite ion. Thus the HSO_3^- dissociates less readily even if the other isomer is thermodynamically more stable.

Given the relatively simple mechanism of the reaction between SO_3H^- and hydrogen ion to produce sulfur dioxide and water, and the difficulty of breaking the S-H bond in HSO_3^- , the great difference in the observed rates of exchange of oxygen between the two isomers of bisulfite ion and water can best be rationalized if SO_3H^- is 195 ppm bisulfite ion and HSO_3^- is 175 ppm bisulfite ion.

There is one experimental test which may be carried out to attempt to verify the assignments of the 175 ppm bisulfite ion and 195 ppm bisulfite ion to HSO_3^- and SO_3H^- , respectively. Assuming that the assignment is correct, the HSO_3^- protons exchange relatively slowly with the protons in water. Since the exchange can occur either directly or via hydrogen transfer from HSO_3^- to SO_3H^- followed by rapid transfer

from SO_3H^- to water, the reactions which exchange hydrogen ions between HSO_3^- and water are just those which exchange oxygen atoms between HSO_3^- and SO_3H^- , reactions 4 through 9. Consequently the pseudo first order rate constant for hydrogen exchange from HSO_3^- to water is equal to $1/\tau_{175,195}$. The HSO_3^- should therefore produce a distinct peak in the proton NMR spectrum if $1/\tau_{175,195}$ is several times less than the difference between the precessional frequency of the protons in HSO_3^- and water. The observation of such a peak would confirm the assignment of the peaks in the ^{17}O spectrum.

Several attempts were made to find the HSO_3^- resonance in proton NMR spectra of bisulfite solutions. The HSO_3^- peak is expected to be most narrow in solutions for which $1/\tau_{175,195}$ is small, that is, in solutions of high acidity and low S(IV) concentration. However, the decrease in peak width obtained by using low S(IV) concentrations is offset by the concomitant diminution of peak area. No HSO_3^- peak was observed in proton NMR spectra of a 0.2 m sodium bisulfite solution of pH 3, nor in the spectra of 0.2, 0.4, and 1 m solutions of pH 2, even when the two-pulse sequence was employed to suppress the water peak and the temperature was lowered to near 0°C to decrease $1/\tau_{175,195}$. It was thought that a distinct, though broad, HSO_3^- peak could have been seen had it been located at least 2 ppm away from the water peak.

In an attempt to increase the chemical shift of the HSO_3^- proton relative to those in water, two solutions were prepared which contained dysprosium chloride in addition to the sodium bisulfite. The rare earth ions are known to shift the ^1H NMR water resonance a great deal without introducing excessive line broadening.⁴⁸ The effect of Dy^{3+} upon the HSO_3^- proton resonance is not known, but it was hoped that the chemical

shift produced by Dy^{3+} would be sufficiently different in HSO_3^- and water, and the line broadening of the HSO_3^- resonance small enough, to enable observation of the HSO_3^- resonance. Spectra were acquired of solutions which were 0.4 and 1 m in S(IV), 0.02 m in DyCl_3 , and had a pH of 2. The Dy^{3+} shifted the water resonance 4.0 ppm downfield relative to its position in the spectrum of pure water, but again, no other peak was observed in either the one or the two-pulse spectra.

The identification of 175 ppm bisulfite ion and 195 ppm bisulfite ion as HSO_3^- and SO_3H^- , respectively, is believed to be correct even though no proton NMR signal could be observed for the 175 ppm bisulfite ion. But the proton NMR spectra provide no certain evidence for this conclusion because the chemical shift of the proton in HSO_3^- is not known.

Oxygen Exchange between Bisulfite Ion and $\text{S}_2\text{O}_5^{2-}$

It has been mentioned previously that measurements of the H_2O and S(IV) peak areas in the ^{17}O NMR spectra of a very concentrated bisulfite solution (S(IV) = 4.7 M, pH = 4.5) indicated that the $\text{S}_2\text{O}_5^{2-}$ and SHO_3^- resonances were coalesced at high S(IV) concentrations. Since it has been concluded that the elementary reaction



was not an important mechanism for oxygen exchange between bisulfite ion and water in the 0.2 m solutions, a question which naturally arises is

whether reaction 3 can account for the observed coalescence of the $S_2O_5^{2-}$ and SHO_3^- resonances at high S(IV) concentrations, or whether a reaction such as



must be invoked. (Both SO_2 and SO_3^{2-} exchange oxygen atoms rapidly with SO_3H^- .) An attempt was made to answer this question by estimating the frequency difference, $\Delta\omega$, between the bisulfite ion resonance and the $S_2O_5^{2-}$ resonance, and comparing it to the estimated maximum value of $1/\tau_{SHO_3^-, S_2O_5^{2-}} + 1/\tau_{S_2O_5^{2-}, SHO_3^-}$, the sum of the two pseudo first order rate constants for oxygen exchange between bisulfite ion and $S_2O_5^{2-}$ via reaction 3. If reaction 3 is to account for the observation of a single maximum in the S(IV) peak of the ^{17}O NMR spectrum of the 4.7 M solution then the sum of the two pseudo first order rate constants must be greater than $\Delta\omega$.

The value of $\Delta\omega_{SHO_3^-, S_2O_5^{2-}}$ was estimated from the chemical shift of the S(IV) peak in three solutions of different S(IV) concentrations: 0.201 m, 0.800 m and 4.7 M. In the spectrum of each solution only one S(IV) peak appeared. The pH and S(IV) concentration were large enough in each solution to cause rapid exchange between the two isomers of bisulfite ion, and the resultant coalescence of their resonances. Peak area measurements showed that the $S_2O_5^{2-}$ and SHO_3^- resonances were coalesced in the 4.7 M solution; they were assumed to be coalesced in the more dilute solutions. As has been shown previously, the SO_2 and SO_3^{2-} resonances are coalesced with that of SHO_3^- . The chemical shift of the S(IV) peak relative to that of water was found to be different in

the three solutions. Because the chemical shift, $\delta_{S(IV)}$, of the coalesced S(IV) peak is the weighted average of the chemical shifts of each of the S(IV) species, i.e.

$$\delta_{S(IV)} = (p_{SHO_3^-})(\delta_{SHO_3^-}) + (p_{S_2O_5^{2-}})(\delta_{S_2O_5^{2-}}) + (p_{SO_3^{2-}})(\delta_{SO_3^{2-}}) + (p_{SO_2})(\delta_{SO_2}), \quad (6-1)$$

the concentration dependence of the S(IV) chemical shift presumably arises from the changes in the relative amounts of the various S(IV) species as the total S(IV) concentration is varied. (In equation 6-1 it was assumed for simplicity that the 5 oxygens in $S_2O_5^{2-}$ are made equivalent through some exchange process. If they are not, $\delta_{S_2O_5^{2-}}$ should be replaced by the weighted average of the chemical shifts of the 5 oxygens.) Since the chemical shifts of SO_3^{2-} and SO_2 are known to be 235 and 520 ppm, respectively⁹, the chemical shifts of the S(IV) peaks in the three solutions can be used to find $\delta_{SHO_3^-}$ and $\delta_{S_2O_5^{2-}}$ if the concentrations of the various S(IV) species in each of the solutions are known. The frequency difference between the SHO_3^- and $S_2O_5^{2-}$ resonances may then be evaluated.

The concentrations of SHO_3^- , $S_2O_5^{2-}$, SO_3^{2-} , and SO_2 , and from them the fractions of oxygen-17 present in each S(IV) site, were calculated in the manner described in the Experimental Procedure section. In the calculation for the 4.7 M solution the values used for pK_1 , pK_2 , pK_w , and K_d were 1.72, 6.36, 14.18, and 0.293, respectively. Although the 4.7 M solution has an ionic strength of about 6 M, the values chosen for pK_1 , pK_2 , and pK_w are those for a solution of ionic strength 3.0¹¹

because the values at higher ionic strength have not been measured. The mean ionic activity coefficient of H^+ and SHO_3^- was used for the hydrogen ion activity coefficient, and was calculated from Pitzer's equations, as discussed previously. Because the activity coefficient of hydrogen ion in solutions of high S(IV) concentration is greatly dependent upon the ionic interactions involving S(IV) species, for which the parameters are not known, the calculated value of the activity coefficient is quite uncertain. At 25°C its value is 0.9 ± 0.2 . However, this uncertainty in the activity coefficient turns out to have a negligible effect upon the calculated value of the frequency difference between the SHO_3^- and $S_2O_5^{2-}$ resonances. The concentrations of the S(IV) species calculated for each of the solutions, as well as the chemical shift of the S(IV) peak in the ^{17}O NMR spectrum of that solution, are listed in Table 6.

After the fractions of ^{17}O in each S(IV) site were calculated the ^{17}O chemical shifts of SHO_3^- and $S_2O_5^{2-}$ were determined by first rearranging equation 6-1 to give

$$\frac{1}{P_{S_2O_5^{2-}}} \{ \delta_{S(IV)} - (P_{SO_3^{2-}})(\delta_{SO_3^{2-}}) - (P_{SO_2})(\delta_{SO_2}) \} = (\delta_{SHO_3^-}) \frac{P_{SHO_3^-}}{P_{S_2O_5^{2-}}} + (\delta_{S_2O_5^{2-}}), \quad (6-2)$$

which has the form $y = mx + b$, where m and b are $\delta_{SHO_3^-}$ and $\delta_{S_2O_5^{2-}}$, respectively. A plot of

$$\frac{1}{P_{S_2O_5^{2-}}} \{ \delta_{S(IV)} - (P_{SO_3^{2-}})(\delta_{SO_3^{2-}}) - (P_{SO_2})(\delta_{SO_2}) \} \text{ vs. } \frac{P_{SHO_3^-}}{P_{S_2O_5^{2-}}}$$

Table 6

Calculated Compositions of Sodium Bisulfite Solutions
Containing 0.201 m, 0.800 m, and 4.66 M S(IV), and the Chemical Shift
of the S(IV) Peak in the Oxygen-17 NMR Spectra of Those Solutions

	<u>Solution "J"</u>	<u>Solution "6"</u>	<u>Solution "4"</u>
[S(IV)]	0.201 m	0.800 m	4.66 M
[NaCl]	0.787 m	0	0
pH meter reading	4.98	5.13	4.50
[SHO ₃ ⁻] ^a	0.189 m	0.689 m	2.1 M
[SO ₂] ^a	6.2×10 ⁻⁵ m	1.6×10 ⁻⁴ m	0.004 M
[S ₂ O ₅ ²⁻] ^a	2.9×10 ⁻³ m	0.040 m	1.3 M
[SO ₃ ²⁻] ^a	6.2×10 ⁻³ m	0.032 m	0.03 M
ionic strength ^b	1.0 m	0.90 m	6.0 M
¹⁷ O chemical shift ^c of S(IV) peak	193 ppm	190 ppm	180 ppm

^aCalculated in the manner described in the text.

^bDetermined from calculated concentrations.

^cChemical shift relative to H₂O. Downfield shifts are positive.

for the three solutions did yield a straight line, a result which supports the interpretation of the concentration dependence of the chemical shift of the S(IV) peak. The chemical shifts of SHO_3^- and $\text{S}_2\text{O}_5^{2-}$, equal to the slope and y-intercept of the line, respectively, were found to be 193 ± 1 ppm and 164 ± 9 ppm, respectively, with a covariance of -3.9 between the two values. The difference in chemical shift between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ is thus equal to 29 ± 9 ppm, assuming that the five oxygens in $\text{S}_2\text{O}_5^{2-}$ have the same chemical shift. (More precisely, 29 ppm is the difference between the weighted average of the chemical shifts of the two isomers of bisulfite ion and the weighted average of the chemical shifts of the five $\text{S}_2\text{O}_5^{2-}$ oxygens.)

The values of $1/\tau_{\text{SHO}_3^-, \text{S}_2\text{O}_5^{2-}}$ and $1/\tau_{\text{S}_2\text{O}_5^{2-}, \text{SHO}_3^-}$ were estimated from the broadening of the water peak in the 4.7 M solution in a manner which will be described shortly. Oxygen-17 NMR spectra of this solution were acquired at 24.4 MHz⁴⁹ at a number of temperatures between -15°C and 50°C . The S(IV) peak exhibited a single maximum throughout this temperature range, so the pseudo first order rate constants were estimated at the low temperatures to provide the most severe comparison of their magnitudes to that of $\Delta\omega_{\text{SHO}_3^-, \text{S}_2\text{O}_5^{2-}}$.

The first step in estimating the pseudo first order rate constants for oxygen exchange between bisulfite ion and $\text{S}_2\text{O}_5^{2-}$ was to obtain from the broadening of the water peak a value of $1/\tau_{\text{H}_2\text{O}, \text{S(IV)}}$, the pseudo first order rate constant for oxygen exchange from water to the S(IV) species. It was assumed that $1/\tau_{\text{H}_2\text{O}, \text{S(IV)}} + 1/\tau_{\text{S(IV)}, \text{H}_2\text{O}}$ was much less than $\Delta\omega_{\text{H}_2\text{O}, \text{S(IV)}}$, in which case the linewidth of the water peak, $(1/T_2)_{\text{H}_2\text{O}}$, is given to a good approximation by

$$\left(\frac{1}{T_2}\right)_{\text{H}_2\text{O}} = \frac{1}{T_{2(\text{H}_2\text{O})}} + \frac{1}{\tau_{\text{H}_2\text{O},\text{S(IV)}}} \quad (6-3)$$

(Since the chemical shift of the S(IV) peak in the 4.7 M solution was 180 ppm, the value of $\Delta\omega_{\text{S(IV)},\text{H}_2\text{O}}$ is equal to 28000 sec^{-1} . The value of $1/\tau_{\text{H}_2\text{O},\text{S(IV)}} + 1/\tau_{\text{S(IV)},\text{H}_2\text{O}}$ obtained through the use of equation 6-3 was found to be less than 0.05 times $\Delta\omega_{\text{S(IV)},\text{H}_2\text{O}}$ below 5°C , so the use of equation 6-3 was considered to be justified in the temperature range from -15°C to 5°C .) A plot of $\log(1/T_2)_{\text{H}_2\text{O}}$ vs. $1/T$ is shown in Figure 25. The values of $1/\tau_{\text{H}_2\text{O},\text{S(IV)}}$ were obtained from these data by assuming that the linewidth that the water peak would have in the absence of chemical exchange, $1/T_{2(\text{H}_2\text{O})}$, was proportional to the values of $1/T_1$ measured in the 0.2 m solutions (Figure 12). The proportionality constant C was then adjusted until a plot of

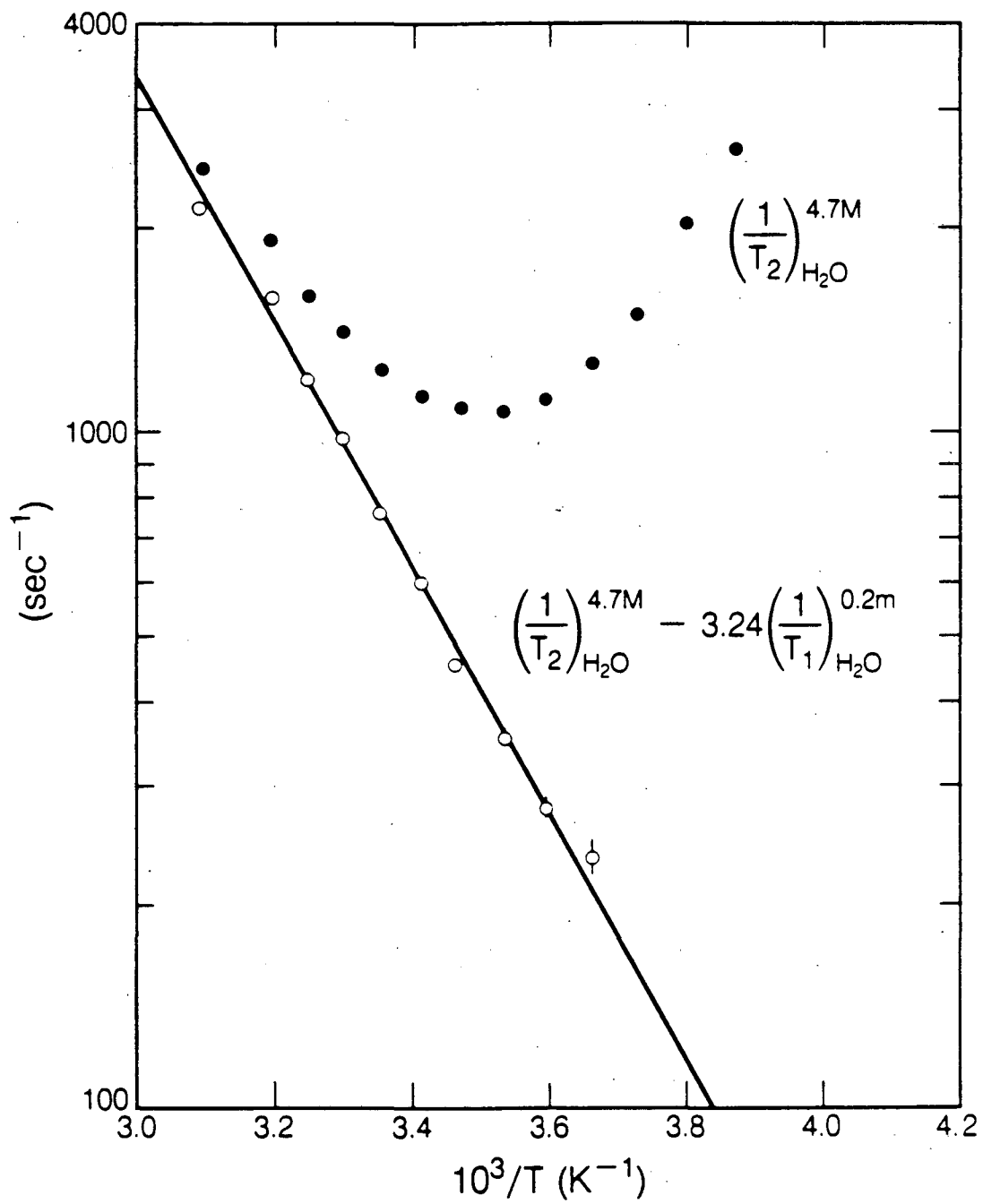
$$\log\left\{\left(\frac{1}{T_2}\right)_{\text{H}_2\text{O}}^{4.7\text{M}} - C\left(\frac{1}{T_1}\right)_{\text{H}_2\text{O}}^{0.2\text{m}}\right\} \text{ vs. } \frac{1}{T}$$

showed the linear behavior expected of a plot of $\log\{1/\tau_{\text{H}_2\text{O},\text{S(IV)}}\}$ vs. $1/T$ (Figure 25). The proportionality constant was found to be equal to 3.24. Assuming that the ordinate values of the semilogarithmic plot shown in Figure 25 are equal to $1/\tau_{\text{H}_2\text{O},\text{S(IV)}}$, it is found that

$$\frac{1}{\tau_{\text{H}_2\text{O},\text{S(IV)}}} = 277 \pm 18 \text{ sec}^{-1} \quad \text{at } 278 \text{ K, and} \quad (6-4a)$$

$$\frac{1}{\tau_{\text{H}_2\text{O},\text{S(IV)}}} = 120 \pm 11 \text{ sec}^{-1} \quad \text{at } 263 \text{ K.} \quad (6-4b)$$

The second step in the estimation of $1/\tau_{\text{SHO}_3^-}$, $\text{S}_2\text{O}_5^{2-}$ and



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Figure 25

$1/\tau_{\text{S}_2\text{O}_5^{2-}, \text{SHO}_3^-}$ is the evaluation of $1/\tau_{\text{SHO}_3^-, \text{H}_2\text{O}}$ from $1/\tau_{\text{H}_2\text{O}, \text{S(IV)}}$.

The relationship between these two quantities is

$$\frac{1}{\tau_{\text{SHO}_3^-, \text{H}_2\text{O}}} = \frac{P_{\text{S(IV)}}}{P_{\text{SHO}_3^-}} \frac{P_{\text{H}_2\text{O}}}{P_{\text{S(IV)}}} \frac{1}{\tau_{\text{H}_2\text{O}, \text{S(IV)}}} \quad (6-5)$$

The ratio $P_{\text{H}_2\text{O}}/P_{\text{S(IV)}}$ is equal to the ratio of the areas of the water peak and the S(IV) peak in the ^{17}O NMR spectrum of the 4.7 M solution, and was found to be equal to 3.7 ± 0.2 . (This value agrees well with the one determined from the calculated concentrations of the S(IV) species.) The ratio $P_{\text{S(IV)}}/P_{\text{SHO}_3^-}$ is the inverse of the fraction of S(IV) oxygens which are in bisulfite ions; its calculated value is 2.0 at both temperatures. These values, together with those of $1/\tau_{\text{H}_2\text{O}, \text{S(IV)}}$, yield

$$\frac{1}{\tau_{\text{SHO}_3^-, \text{H}_2\text{O}}} = 2050 \pm 170 \text{ sec}^{-1} \quad \text{at 278 K, and} \quad (6-6a)$$

$$\frac{1}{\tau_{\text{SHO}_3^-, \text{H}_2\text{O}}} = 888 \pm 95 \text{ sec}^{-1} \quad \text{at 263 K.} \quad (6-6b)$$

The values of $1/\tau_{\text{SHO}_3^-, \text{H}_2\text{O}}$ given above are not entirely due to reaction 3. They contain contributions from all reactions which exchange oxygen atoms between bisulfite ion and water. An upper limit to the contribution from reaction 3 was found by subtracting from the above values the contribution from reaction 1, i.e. subtracting $k_{-1}[\text{H}^+]/3$. The hydrogen ion concentration was obtained from the measured pH of the 4.7 M solution, 4.50, and the calculated mean ionic

activity coefficient of H^+ and SHO_3^- , 0.9 ± 0.2 , which was assumed to be equal to the hydrogen ion activity coefficient. Values of k_{-1} at 278 K and 263 K were calculated using equation 4-2 after first correcting k_{-17} for the high ionic strength of the 4.7 M solution using an equation analogous to equation 4-3, and a mean ionic activity coefficient of H^+ and SHO_3^- equal to 0.71 ± 0.05 in the 0.2 m solutions (in which k_{-17} was determined) and 0.9 ± 0.2 in the 4.7 M solution. Because the activity coefficient of the activated complex in the concentrated solution was not known, it was assumed to be equal to its value at the lower ionic strength (approximately unity). This is not necessarily a good assumption, and introduces an unknown and possibly large amount of systematic error into the ionic strength correction.

After subtracting the contribution of reaction 1 from the value of $1/\tau_{SHO_3^-, H_2O}$, the upper limit to $1/\tau_{SHO_3^-, S_2O_5^{2-}}$ may be obtained. Since reaction 3 exchanges 5 oxygen atoms between bisulfite ion and $S_2O_5^{2-}$ for every one exchanged between bisulfite ion and water, $1/\tau_{SHO_3^-, S_2O_5^{2-}}$ is equal to 5 times the contribution of reaction 3 to the value of $1/\tau_{SHO_3^-, H_2O}$. The estimated value of the pseudo first order rate constant for oxygen exchange from bisulfite ion to $S_2O_5^{2-}$ via reaction 3 is therefore

$$\frac{1}{\tau_{SHO_3^-, S_2O_5^{2-}}} < 5750 \pm 1500 \quad \text{at 278 K, and} \quad (6-7a)$$

$$\frac{1}{\tau_{SHO_3^-, S_2O_5^{2-}}} < 2190 \pm 770 \quad \text{at 263 K.} \quad (6-7b)$$

From the relationship

$$\frac{1}{\tau_{S_2O_5^{2-}, SHO_3^-}} = \frac{p_{SHO_3^-}}{p_{S_2O_5^{2-}}} \frac{1}{\tau_{SHO_3^-, S_2O_5^{2-}}} \quad (6-8)$$

and a value of $p_{SHO_3^-}/p_{S_2O_5^{2-}}$ equal to 1.0 for the 4.7 M solution, we obtain

$$\frac{1}{\tau_{S_2O_5^{2-}, SHO_3^-}} + \frac{1}{\tau_{SHO_3^-, S_2O_5^{2-}}} < 11500 \pm 3000 \quad \text{at 278 K, and} \quad (6-9a)$$

$$\frac{1}{\tau_{S_2O_5^{2-}, SHO_3^-}} + \frac{1}{\tau_{SHO_3^-, S_2O_5^{2-}}} < 4400 \pm 1500 \quad \text{at 263 K.} \quad (6-9b)$$

It is quite possible that some systematic error was introduced into the upper limits given in inequality 6-9 by the subtraction of $k_{-1}[H^+]/3$ (the contribution of reaction 1) from the values of $1/\tau_{SHO_3^-, H_2O}$. In the calculation of the hydrogen ion concentration it was assumed that the pH meter reading was equal to the activity of hydrogen ion in the 4.7 M solution. However, at such high ionic concentrations the change in electrical potential across the junction of the sample solution and the reference electrode's 4 M KCl solution would be expected to have a significant effect upon the pH meter reading, and cannot be ignored.

A rough estimate of the liquid junction potential, E_L , was obtained from the Henderson equation⁵⁰ for the junction potential between two solutions (labelled "a" and "b"):

$$E_L = \frac{RT}{F} \frac{\sum_i \frac{u_i}{z_i} (c_i^b - c_i^a)}{\sum_i u_i (c_i^b - c_i^a)} \ln \frac{\sum_i u_i c_i^a}{\sum_i u_i c_i^b}, \quad (6-10)$$

where u_i = the mobility of ion i ;
 z_i = the charge number of ion i (with algebraic sign retained);
 c_i^a = the concentration of ion i in solution a , expressed in equivalents rather than moles;
 R = the gas constant;
 F = the Faraday constant.

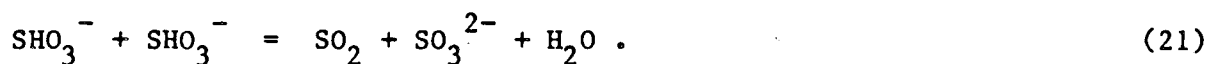
The concentrations in the 4.7 M S(IV) solution are $[\text{Na}^+] = 4.7$ M, $[\text{SHO}_3^-] = 2.1$ M, and $[\text{S}_2\text{O}_5^{2-}] = 1.3$ M ($c_{\text{S}_2\text{O}_5}^a = 2.6$ M). The equivalent conductances of the ions were used for the ionic mobilities, to which they are proportional.⁵¹ The equivalent conductances of ClO_4^- and SO_4^{2-} were substituted for those of SHO_3^- and $\text{S}_2\text{O}_5^{2-}$, respectively, since the latter were not known. Although the conductances of K^+ and Cl^- were available at high concentrations, those of Na^+ , ClO_4^- , and SO_4^{2-} were not, so the limiting equivalent conductances were used for all ions. These are equal to 73.5, 76.3, 50.1, 68.0, and 79.8 for K^+ , Cl^- , Na^+ , ClO_4^- , and SO_4^{2-} , respectively.⁵² Although the ionic concentrations are large, the calculated value of E_L is fortuitously very small, 6×10^{-6} volt. This junction potential would have a negligible effect upon the pH meter reading. However, the large uncertainties in the equivalent conductances, as well as the fact that the approximations used in the derivation of equation 6-10 are invalid at high ionic strength, cast

much doubt upon the calculated value of E_L . Unfortunately, because the calculated value of E_L is both very uncertain and fortuitously small, one is hesitant to use it as even a rough estimate of the true liquid junction potential.

As a check upon the values of the upper limits given in inequalities 6-7 and 6-9, an upper limit to $1/\tau_{\text{SHO}_3^-, \text{S}_2\text{O}_5^{2-}}$ was calculated from the broadening of the water peak in the spectrum of the 0.800 M solution at 278 K in a manner similar to the calculation leading to inequality 6-7. The measured linewidth of the water peak in that spectrum was $325 \pm 16 \text{ sec}^{-1}$, from which one eventually obtains an estimated upper limit to $1/\tau_{\text{SHO}_3^-, \text{S}_2\text{O}_5^{2-}}$ of $7600 \pm 2200 \text{ sec}^{-1}$. This value is roughly equal to the one given in inequality 6-7a for the 4.7 M solution, suggesting that the upper limits given in inequalities 6-7 and 6-9 are not excessively large.

As stated earlier, if reaction 3 is to account for the observation of a single maximum in the S(IV) peak of the ^{17}O NMR spectra of the 4.7 M solution, then the sum of the two pseudo first order rate constants for oxygen exchange between bisulfite ion and $\text{S}_2\text{O}_5^{2-}$ must be at least as large as $\Delta\omega$, the difference between the ^{17}O precessional frequency in the SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ sites. The chemical shift difference between the two sites was found to be $29 \pm 9 \text{ ppm}$, which corresponds to a precessional frequency difference of $4400 \pm 1400 \text{ sec}^{-1}$ at the magnetic field strength used in acquiring the spectra of the 4.7 M solution. Comparison of this value with those given in inequalities 6-9a and 6-9b does not, unfortunately, lead to an unambiguous conclusion concerning whether reaction 3 is rapid enough to cause coalescence of the SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ resonances in the spectra of the 4.7 M solution.

It is not unlikely that the upper limits given in inequality 6-9 contain a sizeable contribution from the reaction



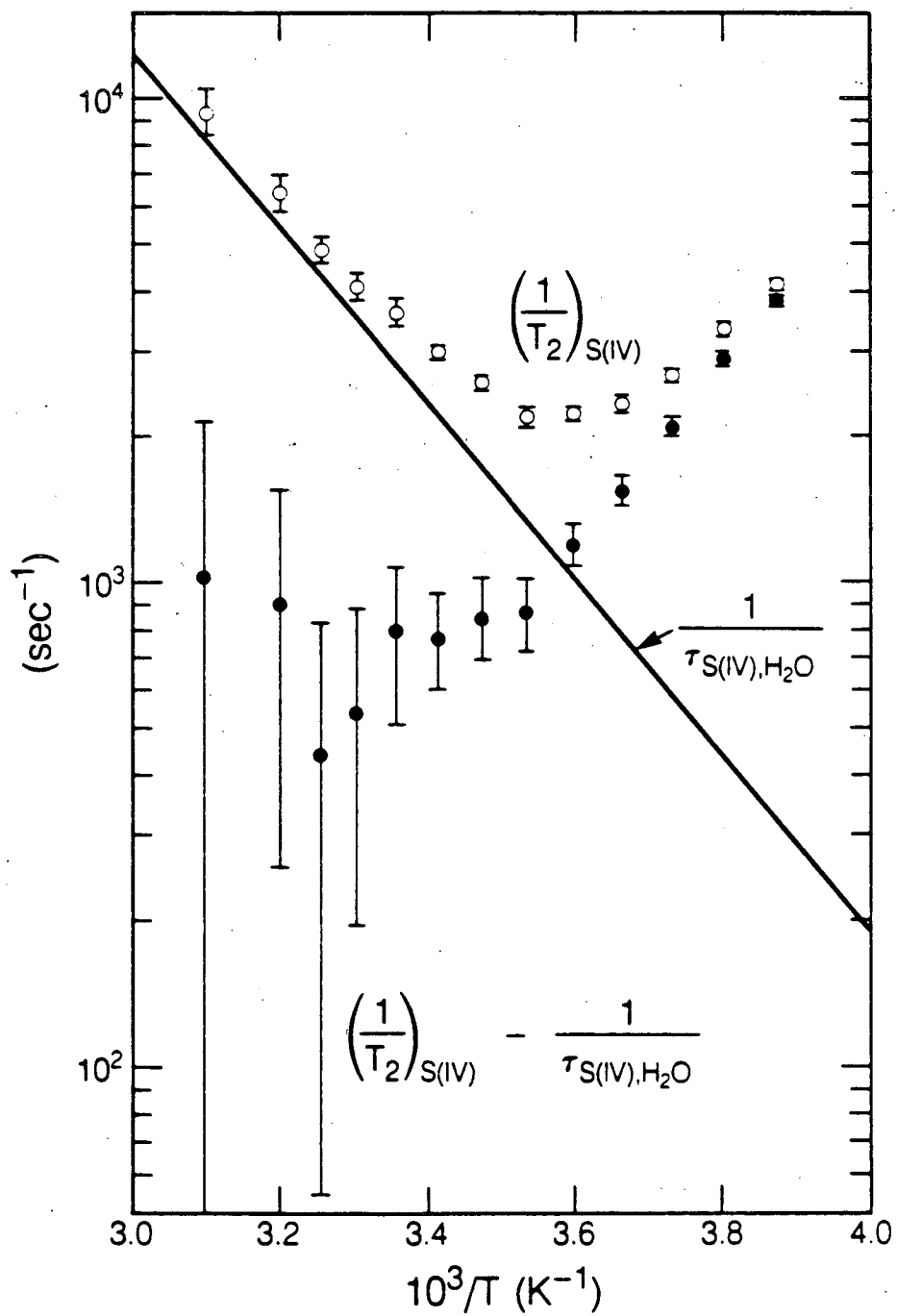
The contribution of reaction 21 was not subtracted from the values of $1/\tau_{\text{SHO}_3^-, \text{H}_2\text{O}}$, and was thus carried into the values given in inequality 6-9. If reaction 21 is more rapid than reaction 3 (as would be expected due to the simpler mechanism of reaction 21) then the upper limits in inequality 6-9 should be reduced by at least a factor of two. However, even halving the upper limits does not exclude reaction 3 from being rapid enough to coalesce the SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ resonances.

The values given in inequality 6-9 set upper limits to the pseudo first order rate constants for oxygen exchange between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ which occurs via paths which also exchange oxygen between S(IV) species and water. Although the above results do not definitely require the existence of other paths to account for the coalescence of the SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ resonances, such paths may exist. In particular, dissociation of SHO_3^- followed by reaction 20 would bring about oxygen exchange between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ without concomitant oxygen exchange between SHO_3^- and water if SO_2 could be produced from SHO_3^- by some process that does not lead to oxygen exchange with water. One such route by which SO_2 might be produced is the transfer of oxygens between the " SO_2 " and " SO_3 " ends of $\text{S}_2\text{O}_5^{2-}$, followed by dissociation of $\text{S}_2\text{O}_5^{2-}$ into sulfur dioxide and sulfite ion. Another would be through the momentary formation of the symmetrical, oxygen bridged isomer of $\text{S}_2\text{O}_5^{2-}$.

From the width of the S(IV) peak in the spectra of the 4.7 M

solution we can obtain rough estimates of upper and lower limits to the pseudo first order rate constants for oxygen exchange between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ by all processes, including those which do not exchange oxygens between S(IV) species and water. If the lower limit to the sum of the pseudo first order rate constants is larger than the upper limit given in inequality 6-9 (the latter being an upper limit to the sum of the pseudo first order rate constants for oxygen exchange via processes which also exchange oxygens with water) then we can say that there must exist processes which exchange oxygens between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ but not between S(IV) species and water.

The temperature dependence of the half width at half height of the S(IV) peak, i.e. $(1/T_2)_{\text{S(IV)}}$, is shown in Figure 26. At high temperatures the peak broadens with increasing temperature due to oxygen exchange between the S(IV) and water environments. Because the width of the S(IV) peak is several times less than the frequency difference between the S(IV) and water peaks it is not a bad approximation to treat the system as being in the slow exchange limit, in which case $(1/T_2)_{\text{S(IV)}}$ is the sum of two terms: the pseudo first order rate constant for oxygen exchange from the S(IV) site to water and a second term whose value is equal to the linewidth which the S(IV) peak would have in the absence of exchange with water. The second term is affected by chemical exchange between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$. If the exchange between the two species is extremely rapid then the second term in $(1/T_2)_{\text{S(IV)}}$ will be equal to the weighted average of the natural linewidths corresponding to these two species, but if the exchange is not rapid enough to cause complete exchange narrowing then the term will be larger than the weighted average of the natural linewidths, and will also be a



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Figure 26

function of the pseudo first order rate constants for oxygen exchange between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$. (Chemical exchange between other S(IV) species has a negligible effect upon the width of the S(IV) peak because all species other than SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ are present in low concentrations.)

The second term in $(1/T_2)_{\text{S(IV)}}$, which contains the information about chemical exchange between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$, was evaluated by subtracting from $(1/T_2)_{\text{S(IV)}}$ the pseudo first order rate constant for oxygen exchange from the S(IV) site to water, $1/\tau_{\text{S(IV),H}_2\text{O}}$. The latter quantity was determined from the broadening of the water peak in the spectra of the 4.7 M solution, as described previously. Both $1/\tau_{\text{S(IV),H}_2\text{O}}$ and the difference between $(1/T_2)_{\text{S(IV)}}$ and $1/\tau_{\text{S(IV),H}_2\text{O}}$ are shown in Figure 26. It is found that the S(IV) linewidth in the absence of chemical exchange between S(IV) species and water is

$$\left(\frac{1}{T_2}\right)_{\text{S(IV)}} - \frac{1}{\tau_{\text{S(IV),H}_2\text{O}}} = 1200 \pm 110 \text{ sec}^{-1} \quad \text{at 278 K, and} \quad (6-11a)$$

$$\left(\frac{1}{T_2}\right)_{\text{S(IV)}} - \frac{1}{\tau_{\text{S(IV),H}_2\text{O}}} = 2940 \pm 140 \text{ sec}^{-1} \quad \text{at 263 K.} \quad (6-11b)$$

Since the frequency difference between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ is known, the S(IV) linewidth in the absence of oxygen exchange with water may be used to estimate the pseudo first order rate constants for exchange between the SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ environments if the natural linewidths of the SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ resonances are known also. In the 0.2 m solutions the natural linewidth of SHO_3^- was found to be roughly equal to that of

water. For the 4.7 M solution we make the assumptions

$$\log\left\{\frac{1}{T_2(\text{SHO}_3^-)}\right\} = \log\left\{\frac{1}{T_2(\text{H}_2\text{O})}\right\} \pm \log 2 \quad \text{and} \quad (6-12a)$$

$$\log\left\{\frac{1}{T_2(\text{S}_2\text{O}_5^{2-})}\right\} = \log\left\{\frac{1}{T_2(\text{H}_2\text{O})}\right\} \pm \log 2, \quad (6-12b)$$

that is, the natural linewidths of SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ are assumed to be within a factor of 2 of the natural linewidth of water. The natural linewidth of the water resonance in the 4.7 M solution was found earlier to be 840 sec^{-1} at 278 K and 1900 sec^{-1} at 263 K.

The upper and lower limits to the pseudo first order rate constants for oxygen exchange between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ were estimated using the fact that the linewidth of the S(IV) peak should decrease as the rate of chemical exchange between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ increases, and approaches a limit equal to the weighted average of the natural linewidths of the SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ resonances. The upper limits to the pseudo first order rate constant are those values which produce the linewidths given in 6-11 when the natural linewidths of SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ are allowed to take their maximum values of 1680 sec^{-1} at 278 K and 3800 sec^{-1} at 263 K. Since the weighted averages of the maximum natural linewidths are greater than the values given in 6-11 we can set no upper limit to the pseudo first order rate constants for oxygen exchange between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$.

The lower limits to the pseudo first order rate constants are those values which produce the linewidths given in 6-11 when the natural linewidths of SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ are set at their minimum values of 420

sec^{-1} at 278 K and 300^{-1} at 263 K. Using these values of $1/T_2(\text{SHO}_3^-)$ and $1/T_2(\text{S}_2\text{O}_5^{2-})$, the previously determined values of $\Delta\omega_{\text{SHO}_3^-, \text{S}_2\text{O}_5^{2-}}$ and $P_{\text{SHO}_3^-}/P_{\text{S}_2\text{O}_5^{2-}}$, and various trial values of $1/\tau$, simulated spectra of a two site, chemically exchanging system were generated by a computer, and the linewidths were compared to the experimentally determined values of $(1/T_2)_{\text{S(IV)}} - 1/\tau_{\text{S(IV), H}_2\text{O}}$ (equation 6-11). By this method the lower limits were set to the pseudo first order rate constants for oxygen exchange between SHO_3^- and $\text{S}_2\text{O}_5^{2-}$ by all processes:

$$\left(\frac{1}{\tau_{\text{S}_2\text{O}_5^{2-}, \text{SHO}_3^-}} + \frac{1}{\tau_{\text{SHO}_3^-, \text{S}_2\text{O}_5^{2-}}} \right)_{\text{total}} > 7000 \text{ sec}^{-1} \quad \text{at 278 K,} \quad (6-13a)$$

$$\left(\frac{1}{\tau_{\text{S}_2\text{O}_5^{2-}, \text{SHO}_3^-}} + \frac{1}{\tau_{\text{SHO}_3^-, \text{S}_2\text{O}_5^{2-}}} \right)_{\text{total}} > 3000 \text{ sec}^{-1} \quad \text{at 263 K.} \quad (6-13b)$$

Comparison of inequalities 6-9 and 6-13 shows that the data do not require the existence of paths of oxygen exchange between bisulfite ion and $\text{S}_2\text{O}_5^{2-}$ which do not also exchange oxygen between S(IV) species and water, such as the previously discussed mechanism involving reaction 20, the transfer of oxygen between the SO_2 and SO_3 ends of $\text{S}_2\text{O}_5^{2-}$, and the momentary formation of the symmetrical, oxygen bridged isomer of $\text{S}_2\text{O}_5^{2-}$. Unfortunately, we conclude that neither the broadening of the water peak nor that of the S(IV) peak allow the mechanism of oxygen exchange between bisulfite ion and $\text{S}_2\text{O}_5^{2-}$ to be determined with certainty. However, regardless of whether scrambling of the $\text{S}_2\text{O}_5^{2-}$ oxygens or formation of the symmetrical, oxygen bridged isomer of $\text{S}_2\text{O}_5^{2-}$ occur, and even if reaction 3 proceeds at an appreciable rate, reaction

20 seems quite plausible mechanistically, and may very well be a major route for the dimerization of bisulfite ion.

Appendix A: Derivation of the Lineshape Equation for a Two Site,
Chemically Exchanging System in the Pulse NMR Experiment

In this appendix an expression for the height of the frequency domain signal in the pulse NMR experiment is derived. The system under consideration is one in which there are two chemically distinct sites, A and B, between which the nuclei can exchange. The approach used is an extension of the work of Leigh⁵³ and of Gupta, Pitner, and Wasylishen.⁵⁴ The solution is applicable to any pulse sequence, the exact form of the signal height as a function of frequency being determined by boundary conditions, i.e. the state of the magnetization of the system at the end of the pulse sequence.

To make the results of this appendix of more practical value, the effects of two common experimental parameters are also included. These parameters are t_d , the time delay between the arrival of the free induction decay signal at the computer and the beginning of data acquisition, and the phase angle θ , which expresses the amount of dispersion present in the spectrum. (For a perfectly phased spectrum $\theta = 0$, and the spectrum is pure absorption.)

The derivation of the lineshape equation has three distinct parts. First, the equation for the time domain signal, i.e. the free induction decay, is derived. Next, the Fourier transform of this expression is found. This is the general lineshape equation. Finally, boundary conditions are applied to obtain the lineshape equation for the experiment of interest.

The starting point for the derivation is the set of modified Bloch equations⁵⁵ for the time dependence of the transverse magnetization of

the system. For the special case of no rf field ($H_1 = 0$), a condition which holds during the free induction decay, we have

$$\begin{bmatrix} \dot{u}_A \\ \dot{u}_B \\ \dot{v}_A \\ \dot{v}_B \end{bmatrix} = \begin{bmatrix} -1/\tau_{2A} & 1/\tau_B & \omega'_A & 0 \\ 1/\tau_A & -1/\tau_{2B} & 0 & \omega'_B \\ -\omega'_A & 0 & -1/\tau_{2A} & 1/\tau_B \\ 0 & -\omega'_B & 1/\tau_A & -1/\tau_{2B} \end{bmatrix} \begin{bmatrix} u_A \\ u_B \\ v_A \\ v_B \end{bmatrix} \quad (A-1)$$

The symbols have the following meanings:

u_A, v_A = the components of the nuclear magnetization in site A which are in phase and out of phase, respectively, with the effective rotating component of a reference rf field having a frequency equal to the frequency of the pulse (this rf field is equivalent to the reference signal present in the receiver).

$\omega'_A = \omega_A - \omega_r$, where ω_A is the precessional frequency of the nuclei in site A and ω_r is the angular frequency of the reference signal. (ω'_A is equivalent to the quantity $-\Delta\omega_A$ in the notation of references 53 and 55.)

$1/\tau_{2A} = 1/T_{2A} + 1/\tau_A$, where T_{2A} is the transverse relaxation time the nuclei in site A would have in the absence of chemical exchange, and

$1/\tau_A$ = the pseudo first order rate constant for the exchange of nuclei out of site A into site B.

Similar definitions apply for u_B , v_B , ω'_B , $1/\tau_{2B}$, $1/T_{2B}$, and $1/\tau_B$. It should be noted that the "rotating frame" is defined by a reference signal having the same frequency as the pulse.

Equation A-1 can be simplified while preserving the phase relationship between u and v by defining

$$\begin{aligned} g_A &= u_A - iv_A, \\ g_B &= u_B - iv_B, \\ \alpha_A &= 1/T_{2A} - i\omega'_A, \text{ and} \\ \alpha_B &= 1/T_{2B} - i\omega'_B, \end{aligned} \tag{A-2}$$

whereupon equation A-1 becomes

$$\begin{bmatrix} \dot{g}_A \\ \dot{g}_B \end{bmatrix} = \begin{bmatrix} -\alpha_A - 1/\tau_A & 1/\tau_B \\ 1/\tau_A & -\alpha_B - 1/\tau_B \end{bmatrix} \begin{bmatrix} g_A \\ g_B \end{bmatrix}. \tag{A-3}$$

The goal is to solve equation A-3 to express $g = g_A + g_B$ as a function of time; this is the equation for the free induction decay.

Equation A-3 can be solved by first defining

$$\tilde{A} = \begin{bmatrix} -\alpha_A - 1/\tau_A & 1/\tau_B \\ 1/\tau_A & -\alpha_B - 1/\tau_B \end{bmatrix} \text{ and } \tilde{g} = \begin{bmatrix} g_A \\ g_B \end{bmatrix}, \tag{A-4}$$

which allows equation A-3 to be rewritten as

$$\frac{d}{dt} \vec{g} = \tilde{A} \cdot \vec{g} \quad (\text{A-5})$$

The solutions to equation A-5 are of the form⁵⁶

$$\vec{g} = \vec{x} e^{\lambda t}, \quad (\text{A-6})$$

where \vec{x} is an eigenvector of the matrix operator \tilde{A} with eigenvalue λ ,
i.e.

$$(\tilde{A} - \lambda \tilde{I}) \vec{x} = 0. \quad (\text{A-7})$$

(\tilde{I} is the identity matrix.) Nontrivial ($\vec{x} \neq 0$) solutions exist only if

$$\det (\tilde{A} - \lambda \tilde{I}) = 0. \quad (\text{A-8})$$

The solutions of equation A-5 are found by solving equation A-8 for λ , then substituting each of these values of λ into equation A-7 and solving it for \vec{x} . (Note, however, that for each value of λ the corresponding vector \vec{x} is determined only to within a multiplicative constant. This constant must be determined from boundary conditions.)

The general solution of equation A-5 is

$$\vec{g} = \sum_j c_j \vec{x}_j \exp(\lambda_j t), \quad (\text{A-9})$$

where the index j designates the solution corresponding to a particular eigenvalue λ_j , and the coefficients c_j are to be determined by boundary

conditions. For the case of interest the matrix \tilde{A} has two eigenvalues, and equation A-9 therefore has two terms. In general the λ_j are complex numbers; the real part of λ_j describes the rate of transverse relaxation of the magnetization, and the imaginary part the frequency of oscillation of the magnetization with respect to the reference signal.

From equation A-9 one obtains expressions for the transverse components of the nuclear magnetization in sites A and B as functions of time:

$$g_A = \sum_{j=1}^2 c_j (x_j)_1 \exp(\lambda_j t) , \quad \text{and} \quad (\text{A-10a})$$

$$g_B = \sum_{j=1}^2 c_j (x_j)_2 \exp(\lambda_j t) . \quad (\text{A-10b})$$

Since \bar{x}_j is determined to within a multiplicative constant, the vector components $(x_j)_1$ and $(x_j)_2$ are not independent of each other. Using equation A-7, the relationship between them is found to be

$$(x_j)_2 = \tau_B \left[\alpha_A + \frac{1}{\tau_A} + \lambda_j \right] (x_j)_1 = \left\{ \tau_A \left[\alpha_B + \frac{1}{\tau_B} + \lambda_j \right] \right\}^{-1} (x_j)_1 . \quad (\text{A-11})$$

If we define

$$a_j = \frac{(x_j)_2}{(x_j)_1} , \quad (\text{A-12})$$

then equation A-10 becomes

$$g_A = \sum_{j=1}^2 c_j (x_j)_1 \exp(\lambda_j t) , \quad (\text{A-13a})$$

$$g_B = \sum_{j=1}^2 c_j a_j (x_j)_1 \exp(\lambda_j t) . \quad (\text{A-13b})$$

The total time domain signal, g , is equal to $g_A + g_B$. We thus have

$$g(t) = \sum_{j=1}^2 R_j \exp(\lambda_j t) , \quad (\text{A-14})$$

in which the quantity R_j is defined by

$$R_j = c_j (1 + a_j) (x_j)_1 . \quad (\text{A-15})$$

The R_j are constants which must be determined from the boundary conditions of the particular experiment.

Equation A-14 is the mathematical expression for the free induction decay. Only the values of λ_j and R_j need be known in order to specify completely the time behavior of the transverse magnetization of the system. For the case under consideration, the matrix \tilde{A} has two eigenvalues, which are determined by solving equation A-8. They are

$$\lambda_j = - \left(\frac{1}{2}\right) \left[\alpha_A + \frac{1}{\tau_A} + \alpha_B + \frac{1}{\tau_B} \right] + (-1)^j \left(\frac{1}{2}\right) \left\{ \left[\alpha_A + \frac{1}{\tau_A} - \alpha_B - \frac{1}{\tau_B} \right]^2 + \frac{4}{\tau_A \tau_B} \right\}^{1/2}$$

$$\text{with } j = 1, 2. \quad (\text{A-16})$$

Since the real part of λ_j expresses the rate of decay of the magnetization, and the imaginary part of λ_j its frequency of oscillation, it is convenient to adopt the following notation for the

real and imaginary parts of λ_j :

$$\lambda_j = -\left(\frac{1}{T_2}\right)_j + i\omega_j, \quad (\text{A-17})$$

that is, $\left(\frac{1}{T_2}\right)_j = -\text{Re } \lambda_j$ and $\omega_j = \text{Im } \lambda_j$

The equation for the signal amplitude as a function of frequency is the Fourier transform of $g(t)$. However, the Fourier transform calculated by the computer of a pulse NMR spectrometer is altered by the existence of a delay between the time the signal reaches the computer and the moment that data acquisition begins. The relationship between the time as measured by the computer, t' , the real time, t , and the delay time, t_d , is

$$t' = t - t_d. \quad (\text{A-18})$$

Equation A-14 may be rewritten as

$$g(t_d + t') = \sum_{j=1}^2 R_j \exp[\lambda_j(t_d + t')] \quad (\text{A-19})$$

to incorporate explicitly the distinction between the "real time" and the "computer time". The frequency domain signal calculated by the computer is

$$\begin{aligned} f(\omega) &= \int_0^{\infty} g(t_d + t') \exp(-i\omega t') dt' \\ &= - \sum_{j=1}^2 R_j \left(\frac{1}{\lambda_j - i\omega} \right) \exp(\lambda_j t_d). \end{aligned} \quad (\text{A-20})$$

(In evaluating the integral at its upper limit use was made of the fact that the real part of λ_j is negative. This causes the contribution from the upper limit to vanish.) Using the definitions given in equation A-17, we may rewrite equation A-20 as

$$f(\omega) = \sum_{j=1}^2 R_j \exp\left\{\frac{-t_d}{(T_2)_j}\right\} \frac{(T_2)_j - i(\omega - \omega_j)[(T_2)_j]^2}{1 + [(T_2)_j]^2 (\omega - \omega_j)^2} \exp(i\omega_j t_d) . \quad (\text{A-21})$$

Equation A-21 expresses the lineshape of the frequency domain spectrum.

To illustrate the evaluation of the R_j from boundary conditions and to clarify the meaning of equation A-21, the lineshape equation for a standard one-pulse experiment will be derived. The "boundary conditions" are always taken to be the conditions at the end of the pulse sequence. In this example, we assume that a perfect 90° pulse has been applied along an arbitrary direction in the x-y plane of the rotating frame of reference. At $t = 0$ (immediately after the pulse) we have

$$g(0) = g_A(0) + g_B(0) = iM_0 e^{i\theta} , \quad (\text{A-22})$$

where M_0 is the magnitude of the magnetization immediately before the pulse (and immediately after a perfect 90° pulse), and is equal to $M_{0A} + M_{0B}$, and θ is the angle between the axis along which the pulse was applied and the x-axis of the rotating frame, i.e. θ is the phase difference between the pulse signal and the reference signal. If the pulse and reference signals are not in phase then the magnetization will

not be aligned along the y-axis of the rotating frame at the end of the pulse. From equation A-3 we obtain

$$\dot{g}(t) = \dot{g}_A(t) + \dot{g}_B(t) = -\alpha_A g_A(t) - \alpha_B g_B(t), \quad (\text{A-23})$$

and at $t = 0$,

$$\dot{g}(0) = -ie^{i\theta} [\alpha_A M_{0A} + \alpha_B M_{0B}] \quad (\text{A-24a})$$

$$= -ie^{i\theta} [\alpha_A p_A M_0 + \alpha_B p_B M_0]. \quad (\text{A-24b})$$

(p_A and p_B are the fractions of nuclei in sites A and B, respectively.)

The R_j are determined by substituting equations A-22 and A-24b into the expressions for $g(0)$ and $\dot{g}(0)$ obtained from equation A-14:

$$g(0) = R_1 + R_2, \quad (\text{A-25})$$

$$\dot{g}(0) = R_1 \lambda_1 + R_2 \lambda_2, \quad (\text{A-26})$$

a substitution which yields

$$R_1 = \frac{-iM_0 (\lambda_2 + \alpha_A p_A + \alpha_B p_B)}{\lambda_1 - \lambda_2} \exp(i\theta) \quad \text{and} \quad (\text{A-27a})$$

$$R_2 = \frac{+iM_0 (\lambda_1 + \alpha_A p_A + \alpha_B p_B)}{\lambda_1 - \lambda_2} \exp(i\theta). \quad (\text{A-27b})$$

It is convenient to separate the factor $e^{i\theta}$ from the rest of R_j by the definition

$$R_j' = R_j \exp(-i\theta) . \quad (\text{A-28})$$

With the substitution of equation A-28, equation A-21 becomes

$f(\omega) =$

$$\sum_{j=1}^2 \left\{ \exp\left(\frac{-t_d}{(T_2)_j}\right) \frac{[\text{Re } R_j'] (T_2)_j + [\text{Im } R_j'] (\omega - \omega_j) [(T_2)_j]^2}{1 + [(T_2)_j]^2 (\omega - \omega_j)^2} \exp[i(\theta + \omega_j t_d)] \right\}$$

$$+ i \sum_{j=1}^2 \left\{ \exp\left(\frac{-t_d}{(T_2)_j}\right) \frac{[\text{Im } R_j'] (T_2)_j - [\text{Re } R_j'] (\omega - \omega_j) [(T_2)_j]^2}{1 + [(T_2)_j]^2 (\omega - \omega_j)^2} \exp[i(\theta + \omega_j t_d)] \right\}$$

(A-29)

It is illuminating to consider the special case of no chemical exchange between sites A and B. For the moment it will also be assumed that both t_d and θ are equal to zero. In the case of no chemical exchange both $1/\tau_A$ and $1/\tau_B$ are equal to zero. Substitution of these values into equation A-16 yields

$$\lambda_1 = -\alpha_A = -\frac{1}{T_{2A}} + i\omega_A' \quad (\text{no chemical exchange}) \quad (\text{A-30a})$$

$$\lambda_2 = -\alpha_B = -\frac{1}{T_{2B}} + i\omega_B^r \quad (\text{no chemical exchange}). \quad (\text{A-30b})$$

Substitution of these expressions and equation A-28 into equation A-27 yields

$$R_1^r = ip_A M_0 = iM_{0A} \quad (\text{no chemical exchange}), \text{ and} \quad (\text{A-31a})$$

$$R_2^r = ip_B M_0 = iM_{0B} \quad (\text{no chemical exchange}), \quad (\text{A-31b})$$

and substitution of equations A-17, A-30, and A-31 into A-29 gives the lineshape equation for the case of no chemical exchange:

$$f(\omega) = \sum_{k=A,B} \frac{M_{0k}(\omega - \omega_k^r)(T_{2k})^2}{1 + (T_{2k})^2(\omega - \omega_k^r)^2} + i \sum_{k=A,B} \frac{M_{0k}T_{2k}}{1 + (T_{2k})^2(\omega - \omega_k^r)^2}$$

$$(\text{no chemical exchange; } \theta = \tau_d = 0). \quad (\text{A-32})$$

Equation A-32 shows that the imaginary part of the frequency domain signal is made up of two pure absorption curves, one corresponding to the A resonance and the other to the B resonance. The imaginary part of the properly phased spectrum therefore corresponds to the "out of phase" signal of continuous wave NMR, and is just the familiar absorption spectrum of a two site, nonexchanging system. The real part of the signal is the dispersion spectrum.

The effect of improper phasing of the spectrum or the existence of a nonzero delay time can be seen by again substituting equations A-17,

A-30, and A-31 into A-29 without setting θ and t_d equal to zero. One obtains

$f(\omega) =$

$$\sum_{k=A,B} \exp\left(\frac{-t_d}{T_{2k}}\right) \left\{ \frac{M_{0k}(\omega - \omega_k^-)(T_{2k})^2}{1 + (T_{2k})^2 (\omega - \omega_k^-)^2} \cos(\theta + \omega_k^- t_d) \right. \\ \left. - \frac{M_{0k} T_{2k}}{1 + (T_{2k})^2 (\omega - \omega_k^-)^2} \sin(\theta + \omega_k^- t_d) \right\} \\ + i \sum_{k=A,B} \exp\left(\frac{-t_d}{T_{2k}}\right) \left\{ \frac{M_{0k} T_{2k}}{1 + (T_{2k})^2 (\omega - \omega_k^-)^2} \cos(\theta + \omega_k^- t_d) \right. \\ \left. + \frac{M_{0k}(\omega - \omega_k^-)(T_{2k})^2}{1 + (T_{2k})^2 (\omega - \omega_k^-)^2} \sin(\theta + \omega_k^- t_d) \right\}$$

(no chemical exchange).

(A-33)

Improper phasing ($\theta \neq 0$) mixes the absorption and dispersion modes in amounts which are constant across the entire spectrum. A nonzero delay time also alters the phasing of the spectrum, but the amount of dispersion mixed into each absorption signal, and vice versa, varies with the frequency of the resonance. The phase of a peak located right at the reference frequency ($\omega_k^- = 0$) is not altered at all by the time delay. The time delay also results in diminished peak heights due to

the exponential factor in equation A-33. (This is the direct consequence of the decay of the time domain signal which occurs during the delay time.) As with the phase effect, the peak height diminution is not the same for the two resonances, but depends upon their respective relaxation times. These effects are familiar to users of pulse NMR.

The effect of chemical exchange upon the lineshape can be understood by examining equation A-29. If chemical exchange occurs between sites A and B then R_1' and R_2' are complex, not pure imaginary as in the no exchange case, because λ_1 and λ_2 will deviate from the values given by equation A-30. For the case $\theta = t_d = 0$, equation A-29 shows that complex R_j' lead to a lineshape expression whose real and imaginary parts are made up of a superposition of absorption and dispersion curves. According to equation A-29 the imaginary (out of phase) portion of the signal, shown in Figure 1, is made up of an absorption and dispersion centered at ω_1 and an absorption and dispersion centered at ω_2 . Note, however, that ω_1 and ω_2 are functions of $1/\tau_A$ and $1/\tau_B$, and are exactly equal to ω_A' and ω_B' only if there is no chemical exchange.

As Figure 1 shows, the amplitude of that portion of the absorption spectrum located between the two peaks grows as the chemical exchange rate increases from zero. (The absorption spectrum corresponds to the imaginary part of the lineshape expression.) This phenomenon is connected with the increasing contribution of the two dispersion curves to the imaginary part of the lineshape expression. It can easily be shown, for example, that the real parts of R_1' and R_2' are of opposite sign in the slow exchange limit, for which $\lambda_1 = -\alpha_A - 1/\tau_A$ and $\lambda_2 = -\alpha_B - 1/\tau_B$.²⁸ (The values of the R_j' are obtained from equation

A-27.) This results in the positive portions of the dispersion curves (one curve centered at ω_1 and the other at ω_2) being located in the region between the two peaks.

Appendix B: The NMR Lineshape of a Two Site, Chemically Exchanging System in the Special Case of a Dilute Solution in which the Two-Pulse Selective Excitation Sequence has Eliminated the Solvent Signal

In this work a two-pulse sequence was used to suppress the NMR signal arising from the solvent of a dilute solution in order to observe clearly the signal arising from the solute (see Experimental Procedure). The half width at half height of the solute resonance was used to determine the rate of oxygen exchange between the solute and the solvent. It was assumed, on the basis of physical arguments, that under the experimental conditions of this work the chemical exchange increased the half width at half height of the solute resonance by an amount equal to the pseudo first order rate constant for oxygen exchange from the solute site to the solvent site. In this appendix an expression will be derived for the lineshape obtained in the two-pulse experiment, and it will be shown that the assumption concerning the halfwidth of the solute peak is correct. Understanding this appendix requires familiarity with Appendix A.

The lineshape for the two-pulse experiment is obtained as a special case of the general lineshape for two site chemical exchange. The time dependence of the magnetization in the rotating frame is (equation A-14)

$$g(t) = \sum_{j=1}^2 R_j \exp(\lambda_j t) , \quad (\text{B-1})$$

and the lineshape in the frequency domain is given by (equation A-21)

$$f(\omega) = \sum_{j=1}^2 R_j \frac{(T_2)_j - i(\omega - \omega_j)[(T_2)_j]^2}{1 + [(T_2)_j]^2 (\omega - \omega_j)^2}, \quad (\text{B-2})$$

where

$$g = u - iv,$$

$$\lambda_j = -\left(\frac{1}{2}\right)\left[\alpha_A + \frac{1}{\tau_A} + \alpha_B + \frac{1}{\tau_B}\right] + (-1)^j \left(\frac{1}{2}\right)\left\{\left[\alpha_A + \frac{1}{\tau_A} - \alpha_B - \frac{1}{\tau_B}\right]^2 + \frac{4}{\tau_A \tau_B}\right\}^{1/2},$$

$$1/(T_2)_j = -\text{Re } \lambda_j,$$

$$\omega_j = \text{Im } \lambda_j,$$

R_1, R_2 are constants to be determined from boundary conditions,

$$\alpha_A = 1/T_{2A} - i\omega'_A,$$

$$\omega'_A = \omega_A - \omega_{\text{reference}} = \omega_A - \omega_{\text{pulse}},$$

α_B and ω'_B have definitions analogous to those of α_A and ω'_A , and

$u, v, 1/T_{2A}, 1/T_{2B}, 1/\tau_A, 1/\tau_B, \omega_A,$ and ω_B have their usual meanings (stated in Appendix A).

For simplicity it has been assumed that t_d , the time interval between the arrival of the free induction decay signal at the computer and the

beginning of data acquisition, is equal to zero.

Since the R_j are complex it is helpful to rewrite equation B-2 in the following form:

$$f(\omega) = \sum_{j=1}^2 \frac{[\text{Re } R_j](T_2)_j + [\text{Im } R_j](\omega - \omega_j)[(T_2)_j]^2}{1 + [(T_2)_j]^2 (\omega - \omega_j)^2} + i \sum_{j=1}^2 \frac{[\text{Im } R_j](T_2)_j - [\text{Re } R_j](\omega - \omega_j)[(T_2)_j]^2}{1 + [(T_2)_j]^2 (\omega - \omega_j)^2} \quad (\text{B-3})$$

The imaginary part of the frequency domain signal corresponds to the absorption mode lineshape, but this lineshape is not solely a superposition of absorption curves; it also contains contributions from dispersion curves due to the presence of chemical exchange. (In the absence of chemical exchange R_j is pure imaginary, causing the imaginary part of $f(\omega)$ to consist of two absorption curves and no dispersion.)

The imaginary part of the signal is made up of an absorption curve and a dispersion centered at ω_1 and an absorption curve and a dispersion curve centered at ω_2 .

Although the imaginary part of $f(\omega)$ contains contributions from both absorption and dispersion curves, the phase of the spectrum can be adjusted to make the imaginary part of $f(\omega)$ consist of an absorption curve and a dispersion curve centered at ω_1 and an absorption curve only at ω_2 (or vice versa). Phasing of the spectrum is accomplished by multiplying $f(\omega)$ by the function $e^{-i\phi}$, in which ϕ is a variable phase

angle. The new lineshape function is then

$$\begin{aligned}
 f'(\omega) &= f(\omega)e^{-i\phi} \\
 &= \sum_{j=1}^2 \left\{ \frac{[-(\text{Re } R_j)\sin\phi + (\text{Im } R_j)\cos\phi](\omega - \omega_j)[(T_2)_j]^2}{1 + [(T_2)_j]^2 (\omega - \omega_j)^2} \right. \\
 &\quad \left. + \frac{[(\text{Re } R_j)\cos\phi + (\text{Im } R_j)\sin\phi](T_2)_j}{1 + [(T_2)_j]^2 (\omega - \omega_j)^2} \right\} \\
 &\quad + i \sum_{j=1}^2 \left\{ - \frac{[(\text{Re } R_j)\cos\phi + (\text{Im } R_j)\sin\phi](\omega - \omega_j)[(T_2)_j]^2}{1 + [(T_2)_j]^2 (\omega - \omega_j)^2} \right. \\
 &\quad \left. + \frac{[(\text{Im } R_j)\cos\phi - (\text{Re } R_j)\sin\phi](T_2)_j}{1 + [(T_2)_j]^2 (\omega - \omega_j)^2} \right\}. \tag{B-4}
 \end{aligned}$$

If ϕ is chosen such that $\tan\phi = -(\text{Re } R_2)/(\text{Im } R_2)$, then the imaginary part of $f'(\omega)$ will contain an absorption curve centered at ω_2 but no dispersion curve at that location. (In practice the choice of ϕ is made empirically.)

It will be shown that in a dilute solution in which A is the solvent and B the solute, and in which chemical exchange is not rapid enough to coalesce the A and B resonances, λ_2 is given to a good approximation by

$$\lambda_2 = - \left(\frac{1}{T_{2B}} + \frac{1}{T_B} \right) + i\omega_B', \tag{B-5}$$

from which we obtain

$$\left(\frac{1}{T_2}\right)^2 = \frac{1}{T_{2B}} + \frac{1}{\tau_B} \quad \text{and} \quad \omega_2 = \omega_B' . \quad (\text{B-6})$$

Therefore, the NMR spectrum of a dilute solution in which the A and B resonances are not coalesced may be phased to yield an absorption peak centered at ω_B' with a half width at half height equal to $1/T_{2B} + 1/\tau_B$. This is the sought after result concerning the linewidth of the solute peak.

Before proving that $\lambda_2 = -(1/T_{2B} + 1/\tau_B) + i\omega_B'$ for the system of interest, the relative sizes of the peaks at ω_1 and ω_2 will briefly be considered. The foregoing discussion applies to all pulse sequences; even the spectrum obtained in the standard one-pulse experiment may be phased to yield an absorption peak at ω_B' with linewidth $1/T_{2B} + 1/\tau_B$. The advantage of the two-pulse selective excitation sequence for chemical exchange studies lies in its suppression of the solvent resonance, thereby allowing the linewidth of the solute peak to be measured accurately. In terms of the formalism of this appendix, the two-pulse sequence greatly increases the ratio of $|R_2|$ to $|R_1|$ relative to its value in the one-pulse experiment.

The constants R_1 and R_2 are determined from the conditions at the end of the pulse sequence. We assume that at the end of the second pulse the A (solvent) magnetization has been returned to the z-axis of the rotating frame, and the B (solute) magnetization is located in the y-z plane of the rotating frame and has a transverse component of magnitude M_B . (The orientation of the B magnetization at the end of the second pulse has been chosen such that no x component of magnetization

exists. The lineshape function derived for this case differs only in phase from lineshape functions corresponding to other initial x-y orientations of the B magnetization.) The initial conditions are therefore

$$g(0) = iM_B \quad \text{and} \quad (B-7)$$

$$\dot{g}(0) = -i\alpha_B M_B, \quad (B-8)$$

the latter obtained from the modified Bloch equations (equation A-3) with $\dot{g} = \dot{g}_A + \dot{g}_B$, $g_A(0) = 0$, and $g_B(0) = iM_B$. From equation B-1 we may also write

$$g(0) = R_1 + R_2 \quad \text{and} \quad (B-9)$$

$$\dot{g}(0) = R_1 \lambda_1 + R_2 \lambda_2. \quad (B-10)$$

Combining equations B-7 through B-10 yields

$$R_1 = \frac{-iM_B(\lambda_2 + \alpha_B)}{\lambda_1 - \lambda_2}, \quad (B-11a)$$

$$R_2 = \frac{+iM_B(\lambda_1 + \alpha_B)}{\lambda_1 - \lambda_2}. \quad (B-11b)$$

If there is no chemical exchange then $\lambda_1 = -\alpha_A$ and $\lambda_2 = -\alpha_B$, from which it follows that $R_1 = 0$. Thus, as would be expected, the two-pulse

spectrum contains no signal at ω_1 in the absence of chemical exchange.

(The solvent site acquires transverse magnetization only if chemical exchange occurs.) It can be shown that at low rates of exchange $|R_2|$ is much greater than $|R_1|$, meaning that the peak at ω_2 (the solute peak) is the dominant peak in the spectrum. However, as the rate of exchange increases the ratio $|R_2|/|R_1|$ decreases, and the height and area of the solvent peak grow in relation to the height and area of the solute peak.

It will now be shown that $\lambda_2 = -(1/T_{2B} + 1/\tau_B) + i\omega_B'$ in the NMR spectrum of a dilute solution in which chemical exchange is not rapid enough to coalesce the A and B resonances, in which B is the solute and A the solvent. The condition of no coalescence may be stated as

$$|\Delta\omega_{AB}| \equiv |\omega_A' - \omega_B'| > \frac{1}{\tau_A} + \frac{1}{\tau_B} \quad (\text{B-12})$$

(the one-pulse NMR spectrum of a two site system contains only a single maximum when inequality B-12 is false, hence the reference to coalescence), and the meaning of "dilute solution" is $[B] \ll [A]$, which is equivalent to

$$\frac{1}{\tau_B} \gg \frac{1}{\tau_A} . \quad (\text{B-13})$$

The condition of no coalescence is appropriate for the two-pulse sequence, because if $1/\tau_A + 1/\tau_B$ were larger than or on the order of $\Delta\omega_{AB}$ then the A and B magnetizations would remain together, rather than move apart, during the interval between the two pulses, the second pulse would return both magnetization vectors to the z-axis, and both the solvent peak and the solute peak would be suppressed. For all cases of

interest, therefore, inequality B-12 is true.

To derive the limiting expression for λ_2 it is helpful to separate the exact expression for λ_j into its real and imaginary parts:^{28,53}

$$-\operatorname{Re} \lambda_j = \frac{1}{2} \left(\frac{1}{\tau_{2A}} + \frac{1}{\tau_{2B}} \right) - (-1)^j \left\{ \frac{G + (G^2 + H^2)^{1/2}}{2} \right\}^{1/2}, \quad (\text{B-14})$$

$$\operatorname{Im} \lambda_j = \frac{\omega_A' + \omega_B'}{2} - (-1)^j \left\{ \frac{(G^2 + H^2)^{1/2} - G}{2} \right\}^{1/2}, \quad (\text{B-15})$$

where

$$G = \frac{1}{4} \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}} \right)^2 + \frac{1}{\tau_A \tau_B} - \frac{1}{4} (\Delta\omega_{AB})^2,$$

$$H = -\frac{1}{2} \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}} \right) (\Delta\omega_{AB}),$$

$$\frac{1}{\tau_{2A}} = \frac{1}{T_{2A}} + \frac{1}{\tau_A}, \quad \frac{1}{\tau_{2B}} = \frac{1}{T_{2B}} + \frac{1}{\tau_B},$$

$$\Delta\omega_{AB} = \omega_A' - \omega_B' = \omega_A - \omega_B.$$

By straightforward algebraic manipulation we may express $G^2 + H^2$ as

$$\begin{aligned} G^2 + H^2 &= \left\{ \frac{1}{4} \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}} \right)^2 - \frac{1}{\tau_A \tau_B} + \frac{1}{4} (\Delta\omega_{AB})^2 \right\}^2 + \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}} \right)^2 \left(\frac{1}{\tau_A \tau_B} \right) \\ &= c^2 + ab \end{aligned} \quad (\text{B-16})$$

or in the form

$$\begin{aligned}
G^2 + H^2 &= \left\{ \frac{1}{4} \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}} \right)^2 + \frac{1}{\tau_A \tau_B} + \frac{1}{4} (\Delta\omega_{AB})^2 \right\}^2 - \left(\frac{1}{\tau_A \tau_B} \right) (\Delta\omega_{AB})^2 \\
&= d^2 - bf,
\end{aligned} \tag{B-17}$$

where

$$a = \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}} \right)^2, \quad b = \frac{1}{\tau_A \tau_B}, \quad f = (\Delta\omega_{AB})^2,$$

$$c = \frac{1}{4} \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}} \right)^2 - \frac{1}{\tau_A \tau_B} + \frac{1}{4} (\Delta\omega_{AB})^2,$$

$$d = \frac{1}{4} \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}} \right)^2 + \frac{1}{\tau_A \tau_B} + \frac{1}{4} (\Delta\omega_{AB})^2.$$

Equation B-16 is used in the derivation of $-\text{Re } \lambda_j$, B-17 in the derivation of $\text{Im } \lambda_j$.

The Limiting Form of $-\text{Re } \lambda_2$

Starting from equation B-16, we obtain

$$\begin{aligned}
(G^2 + H^2)^{1/2} &= (c^2 + ab)^{1/2} \\
&= c \left(1 + \frac{ab}{c^2} \right)^{1/2} \\
&= c \left\{ 1 + \left(\frac{1}{2} \right) \left(\frac{ab}{c^2} \right) - \left(\frac{1}{2} \right)^2 \left(\frac{1}{2!} \right) \left(\frac{ab}{c^2} \right)^2 + \left(\frac{1}{2} \right)^2 \left(\frac{3}{2} \right) \left(\frac{1}{3!} \right) \left(\frac{ab}{c^2} \right)^3 - \dots \right\} \\
&= c + \left(\frac{1}{2} \right) \left(\frac{ab}{c} \right) - \left(\frac{1}{2} \right)^2 \left(\frac{1}{2!} \right) \left(\frac{a^2 b^2}{c^3} \right) + \left(\frac{1}{2} \right)^2 \left(\frac{3}{2} \right) \left(\frac{1}{3!} \right) \left(\frac{a^3 b^3}{c^5} \right) - \dots
\end{aligned} \tag{B-18}$$

(The square root of $1 + ab/c^2$ has been expanded in a Taylor series.)

Using the fact that $G + c = a/2$, we next write

$$\begin{aligned} & \frac{G + (G^2 + H^2)^{1/2}}{2} \\ &= \frac{G + c}{2} + \left(\frac{1}{2}\right)^2 \left\{ \left(\frac{ab}{c}\right) - \left(\frac{1}{2}\right)\left(\frac{1}{2!}\right)\left(\frac{a^2 b^2}{c^3}\right) + \left(\frac{1}{2}\right)\left(\frac{3}{2}\right)\left(\frac{1}{3!}\right)\left(\frac{a^3 b^3}{c^5}\right) - \dots \right\} \\ &= \frac{a}{4} \left\{ 1 + \frac{b}{c} \left[1 - \left(\frac{1}{2}\right)\left(\frac{1}{2!}\right)\left(\frac{ab}{c}\right) + \left(\frac{1}{2}\right)\left(\frac{3}{2}\right)\left(\frac{1}{3!}\right)\left(\frac{ab}{c}\right)^2 - \dots \right] \right\}. \end{aligned} \quad (\text{B-19})$$

The square root of the above quantity is expanded in a Taylor series:

$$\begin{aligned} & \left\{ \frac{G + (G^2 + H^2)^{1/2}}{2} \right\}^{1/2} \\ &= \frac{a^{1/2}}{2} \left\{ 1 + \left(\frac{1}{2}\right)x - \left(\frac{1}{2}\right)^2 \left(\frac{1}{2!}\right)x^2 + \left(\frac{1}{2}\right)^2 \left(\frac{3}{2}\right)\left(\frac{1}{3!}\right)x^3 - \dots \right\}, \end{aligned} \quad (\text{B-20})$$

where

$$x = \frac{b}{c} \left\{ 1 - \left(\frac{1}{2}\right)\left(\frac{1}{2!}\right)\left(\frac{ab}{c}\right) + \left(\frac{1}{2}\right)\left(\frac{3}{2}\right)\left(\frac{1}{3!}\right)\left(\frac{ab}{c}\right)^2 - \dots \right\}. \quad (\text{B-21})$$

Finally, we arrive at the expression for $-\text{Re } \lambda_2$:

$$\begin{aligned} -\text{Re } \lambda_2 &= \frac{1}{2} \left(\frac{1}{\tau_{2A}} + \frac{1}{\tau_{2B}} \right) - \left\{ \frac{G + (G^2 + H^2)^{1/2}}{2} \right\}^{1/2} \\ &= \frac{1}{\tau_{2B}} - \frac{a^{1/2}}{4} \left\{ x - \left(\frac{1}{2}\right)\left(\frac{1}{2!}\right)x^2 + \left(\frac{1}{2}\right)\left(\frac{3}{2}\right)\left(\frac{1}{3!}\right)x^3 - \left(\frac{1}{2}\right)\left(\frac{3}{2}\right)\left(\frac{5}{2}\right)\left(\frac{1}{4!}\right)x^4 + \dots \right\} \\ &= \frac{1}{\tau_{2B}} \left\{ 1 - \frac{1}{4} \frac{a^{1/2}}{1/\tau_{2B}} \left[x - \left(\frac{1}{2}\right)\left(\frac{1}{2!}\right)x^2 + \left(\frac{1}{2}\right)\left(\frac{3}{2}\right)\left(\frac{1}{3!}\right)x^3 - \dots \right] \right\}. \end{aligned} \quad (\text{B-22})$$

Equation B-22 is exact.

The right side of equation B-22 reduces to $1/\tau_{2B}$ (to a good approximation) if

$$x < 1 \quad \text{and} \quad \frac{1}{4} \frac{a^{1/2}}{1/\tau_{2B}} x \ll 1. \quad (\text{B-23})$$

The conditions of B-23 are equivalent to

$$\frac{ab}{c^2} < 1 \quad \text{and} \quad \frac{b}{c} < 1 \quad \text{and} \quad \frac{1}{4} \frac{a^{1/2}}{1/\tau_{2B}} \frac{b}{c} \ll 1. \quad (\text{B-24})$$

We now examine the conditions of validity of each of the inequalities of B-24.

Starting from the definition of ab/c^2 , we have

$$\begin{aligned} \frac{ab}{c^2} &= \frac{\left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}}\right)^2 \left(\frac{1}{\tau_A \tau_B}\right)}{\left\{ \frac{1}{4} \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}}\right)^2 - \frac{1}{\tau_A \tau_B} + \frac{1}{4} (\Delta\omega_{AB})^2 \right\}^2} \\ &= \frac{\frac{1}{\tau_A \tau_B}}{\frac{\left\{ \frac{1}{4} (\Delta\omega_{AB})^2 - \frac{1}{\tau_A \tau_B} \right\}^2}{\left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}}\right)^2} + \frac{1}{16} \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}}\right)^2 - \frac{1}{2} \left(\frac{1}{\tau_A \tau_B}\right) + \frac{1}{8} (\Delta\omega_{AB})^2}. \end{aligned} \quad (\text{B-25})$$

The right side of equation B-25 has in it three quantities which can vary independently: $1/(\tau_A \tau_B)$, $(\Delta\omega_{AB})^2$, and $(1/\tau_{2A} - 1/\tau_{2B})^2$. We wish to show that ab/c^2 is no greater than 1 under the conditions given by inequalities B-12 and B-13. We proceed by finding the value of

$(1/\tau_{2A} - 1/\tau_{2B})^2$ which causes the right side of equation B-25 to take its maximum value (with respect to $[1/\tau_{2A} - 1/\tau_{2B}]^2$), then finding the relationship between $1/(\tau_A \tau_B)$ and $(\Delta\omega_{AB})^2$ necessary to make this maximum value no greater than 1. The right side of equation B-25 is at a maximum with respect to $(1/\tau_{2A} - 1/\tau_{2B})^2$ when

$$\left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}}\right)^2 = 4 \left| \frac{1}{4}(\Delta\omega_{AB})^2 - \frac{1}{\tau_A \tau_B} \right|, \quad (\text{B-26})$$

in which case equation B-25 becomes

$$\left(\frac{ab}{c^2}\right)_{\max} = \frac{\frac{1}{\tau_A \tau_B}}{\left| \frac{1}{8}(\Delta\omega_{AB})^2 - \frac{1}{2}\left(\frac{1}{\tau_A \tau_B}\right) \right| + \frac{1}{8}(\Delta\omega_{AB})^2 - \frac{1}{2}\left(\frac{1}{\tau_A \tau_B}\right)}. \quad (\text{B-27})$$

According to equation B-27 the maximum value of ab/c^2 is infinite if $(\Delta\omega_{AB})^2 < 4[1/(\tau_A \tau_B)]$. The quantity ab/c^2 will be less than or equal to one for all values of $(1/\tau_{2A} - 1/\tau_{2B})^2$ only if

$$(\Delta\omega_{AB})^2 > 8 \frac{1}{\tau_A \tau_B}. \quad (\text{B-28})$$

Inequality B-28 is met by the combination of inequalities B-12 and B-13, which are true for the system under consideration.

We next determine whether b/c is less than or equal to one. The quantity b/c is given by

$$\frac{b}{c} = \frac{\frac{1}{\tau_A \tau_B}}{\frac{1}{4} \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}} \right)^2 - \frac{1}{\tau_A \tau_B} + \frac{1}{4} (\Delta\omega_{AB})^2}, \quad (\text{B-29})$$

and reaches a local maximum with respect to $(1/\tau_{2A} - 1/\tau_{2B})^2$ when the latter quantity is equal to either zero or $4/(\tau_A \tau_B) - (\Delta\omega_{AB})^2$. The restrictions imposed in making ab/c^2 less than or equal to one have already excluded positive values of $4/(\tau_A \tau_B) - (\Delta\omega_{AB})^2$. We therefore limit our consideration to the local maximum at which $(1/\tau_{2A} - 1/\tau_{2B})^2$ is equal to zero. This gives

$$\left(\frac{b}{c}\right)_{\max} = \frac{\frac{1}{\tau_A \tau_B}}{\frac{1}{4} (\Delta\omega_{AB})^2 - \frac{1}{\tau_A \tau_B}}. \quad (\text{B-30})$$

From equation B-30 it is seen that the ratio b/c is less than or equal to one if inequality B-28 is true.

The quantity $\frac{1}{4} \frac{a^{1/2} b}{1/\tau_{2B} c}$ may be written

$$\frac{1}{4} \frac{a^{1/2} b}{1/\tau_{2B} c} = \frac{\frac{1}{\tau_A \tau_B}}{4 \left(\frac{1}{\tau_{2B}} \right) \left\{ \frac{1}{4} \left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}} \right) + \frac{\frac{1}{4} (\Delta\omega_{AB})^2 - \frac{1}{\tau_A \tau_B}}{\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}}} \right\}}, \quad (\text{B-31})$$

and is at a maximum with respect to $(1/\tau_{2A} - 1/\tau_{2B})$ when

$$\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}} = \pm \left\{ (\Delta\omega_{AB})^2 - 4 \frac{1}{\tau_A \tau_B} \right\}^{1/2}, \quad (\text{B-32})$$

which yields

$$\left| \frac{1}{4} \frac{a^{1/2}}{1/\tau_{2B}} \frac{b}{c} \right|_{\max} = \frac{\frac{1}{\tau_A \tau_B}}{2 \left(\frac{1}{\tau_{2B}} \right) \left\{ (\Delta\omega_{AB})^2 - 4 \left(\frac{1}{\tau_A \tau_B} \right) \right\}^{1/2}}. \quad (\text{B-33})$$

Because $1/\tau_{2B} = 1/T_{2B} + 1/\tau_B$ we may write

$$\left| \frac{1}{4} \frac{a^{1/2}}{1/\tau_{2B}} \frac{b}{c} \right|_{\max} < \frac{\frac{1}{\tau_A}}{2(\Delta\omega_{AB}) \left\{ 1 - \frac{4}{(\Delta\omega_{AB})^2} \left(\frac{1}{\tau_A \tau_B} \right) \right\}^{1/2}}. \quad (\text{B-34})$$

Since we are interested in situations in which inequality B-28 is true, (i.e. in which ab/c^2 and b/c are less than or equal to 1) we may substitute inequality B-28 into equation B-34 to obtain

$$\left| \frac{1}{4} \frac{a^{1/2}}{1/\tau_{2B}} \frac{b}{c} \right|_{\max} < \frac{\frac{1}{\tau_A}}{2^{1/2} (\Delta\omega_{AB})}. \quad (\text{B-35})$$

Therefore

$$\left| \frac{1}{4} \frac{a^{1/2}}{1/\tau_{2B}} \frac{b}{c} \right| \ll 1 \quad \text{if}$$

$$(\Delta\omega_{AB})^2 > 8 \frac{1}{\tau_A \tau_B} \quad \text{and} \quad \frac{1}{\tau_A} \ll 2^{1/2} (\Delta\omega_{AB}). \quad (\text{B-36})$$

We may summarize our results by saying that

$$\text{if } (\Delta\omega_{AB})^2 > 8 \frac{1}{\tau_A \tau_B} \quad \text{and} \quad 2^{1/2}(\Delta\omega_{AB}) \gg \frac{1}{\tau_A} \quad (\text{B-37})$$

then to a good approximation

$$- \text{Re } \lambda_2 = \frac{1}{T_{2B}} + \frac{1}{\tau_B} \quad (\text{B-38})$$

The inequalities in B-37 are sufficient requirements for the validity of equation B-38, and are met by the conditions which hold for the two-pulse spectrum of a dilute solution, inequalities B-12 and B-13.

The Limiting Form of $\text{Im } \lambda_j$

We expand the right side of equation B-15 by following a procedure similar to that used in the expansion of the right side of equation B-14, the difference being that we start with $G^2 + H^2$ in the form given by equation B-17. This procedure yields

$$\text{Im } \lambda_j = \frac{\omega'_A + \omega'_B}{2} - (-1)^j \left(\frac{f}{2}\right)^{1/2} \left\{ 1 - \frac{y}{2} - \left(\frac{1}{2}\right)^2 \left(\frac{1}{2!}\right) y^2 - \left(\frac{1}{2}\right)^2 \left(\frac{3}{2}\right) \left(\frac{1}{3!}\right) y^3 - \dots \right\} \quad (\text{B-39})$$

where

$$y = \frac{b}{d} \left\{ 1 + \left(\frac{1}{2}\right) \left(\frac{1}{2!}\right) \left(\frac{bf}{d^2}\right) + \left(\frac{1}{2}\right) \left(\frac{3}{2}\right) \left(\frac{1}{3!}\right) \left(\frac{bf}{d^2}\right)^2 + \left(\frac{1}{2}\right) \left(\frac{3}{2}\right) \left(\frac{5}{2}\right) \left(\frac{1}{4!}\right) \left(\frac{bf}{d^2}\right)^3 + \dots \right\}, \quad (\text{B-40})$$

and the quantities b, d, and f have the meanings given in equation B-17. Since $f^{1/2} = \Delta\omega_{AB}$, equation B-40 yields the following exact expressions for $\text{Im } \lambda_1$ and $\text{Im } \lambda_2$:

$$\text{Im } \lambda_1 = \omega_A' - z, \quad (\text{B-41})$$

$$\text{Im } \lambda_2 = \omega_B' + z, \quad (\text{B-42})$$

where

$$z = \frac{\Delta\omega_{AB}}{4} \left\{ y + \left(\frac{1}{2}\right)\left(\frac{1}{2!}\right)y^2 + \left(\frac{1}{2}\right)\left(\frac{3}{2}\right)\left(\frac{1}{3!}\right)y^3 + \left(\frac{1}{2}\right)\left(\frac{3}{2}\right)\left(\frac{5}{2}\right)\left(\frac{1}{4!}\right)y^4 + \dots \right\} \quad (\text{B-43})$$

and y is given by equation B-40.

It will be shown that z (which is equal to zero in the absence of chemical exchange) is small in comparison to $|\Delta\omega_{AB}|$ under the conditions given in B-12 and B-13. Since $|\Delta\omega_{AB}| = \omega_B'$ in the two-pulse experiment, $\text{Im } \lambda_2$ is given to a good approximation by ω_B' . The correction term z is not necessarily small compared to ω_A' because the latter quantity is a frequency of precession in the rotating frame, not the laboratory frame. Since the pulse frequency is chosen to be near ω_A the quantity ω_A' is nearly equal to zero. Depending upon the application it may or may not be acceptable to neglect the correction term. However, in the case of the two-pulse experiment the important point seems to be whether z is significant in comparison to $\Delta\omega_{AB}$, thereby producing a noticeable change in the position of one peak relative to the other.

The ratio $z/\Delta\omega_{AB}$ is given by

$$\frac{z}{\Delta\omega_{AB}} = \frac{1}{4} \left\{ y + \binom{1}{2} \binom{1}{2!} y^2 + \binom{1}{2} \binom{3}{2} \binom{1}{3!} y^3 + \binom{1}{2} \binom{3}{2} \binom{5}{2} \binom{1}{4!} y^4 + \dots \right\}, \quad (\text{B-44})$$

and is much less than one if

$$\frac{bf}{d^2} < 1 \quad \text{and} \quad \frac{1}{4} \frac{b}{d} \ll 1. \quad (\text{B-45})$$

From the definitions of b , d , and f it is easy to show that bf/d^2 is always less than or equal to one. The quantity $b/4d$ may be written as

$$\frac{1}{4} \frac{b}{d} = \frac{\frac{1}{\tau_A \tau_B}}{\left(\frac{1}{\tau_{2A}} - \frac{1}{\tau_{2B}}\right)^2 + \frac{4}{\tau_A \tau_B} + (\Delta\omega_{AB})^2}. \quad (\text{B-46})$$

The maximum value of $b/4d$ with respect to $(1/\tau_{2A} - 1/\tau_{2B})^2$ is

$$\left(\frac{1}{4} \frac{b}{d}\right)_{\max} = \frac{\frac{1}{\tau_A \tau_B}}{\frac{4}{\tau_A \tau_B} + (\Delta\omega_{AB})^2}. \quad (\text{B-47})$$

Comparison of equation B-47 with inequalities B-12 and B-13 shows that under conditions of a dilute solution in which the A and B resonances are not coalesced, $b/4d$ is much less than 1. We have thus shown that under these conditions $z/\Delta\omega_{AB}$ is much less than 1, and therefore

$$\omega_2 \equiv \text{Im } \lambda_2 = \omega_B' \quad \text{and} \quad \left(\begin{array}{l} \text{if inequalities} \\ \text{B-12 and B-13 true} \end{array} \right) \quad (\text{B-48})$$

$$\omega_1 - \omega_2 = \text{Im } \lambda_1 - \text{Im } \lambda_2 = \Delta\omega_{AB}.$$

Appendix C: Experimental Data

This appendix contains the data obtained from ^{17}O NMR spectra. All spectra except those of solution 4 were acquired at an rf frequency of 27.377 MHz. The spectra of solution 4 were acquired at 24.416 MHz. The symbols used in the tables of data have the following meanings:

$(\frac{1}{T_2})_{\text{H}_2\text{O}}^*$ = the measured half width at half height of the water peak. The measured value includes broadening arising from magnetic field inhomogeneity.

$(\frac{1}{T_2})_{\text{S(IV)}}^*$ = the measured half width at half height of the S(IV) peak. This quantity was measured in spectra in which only one S(IV) peak appeared. It includes broadening arising from magnetic field inhomogeneity.

$(T_1)_{\text{H}_2\text{O}}$ = the longitudinal relaxation time of the oxygen-17 in the water of the solution.

$\Delta\nu_{\text{S(IV)},\text{H}_2\text{O}}$ = the spectral frequency of the S(IV) peak minus the spectral frequency of the water peak of the same solution. This quantity was measured in spectra in which only one S(IV) peak appeared.

Table C-1

Experimental Data: 1 m NaCl Solution

solution composition: 0.1749 g NaCl, 3.00 ml H₂O

measured pH = 2.46 (pH adjusted with HCl)

T	$\left(\frac{1}{T_2}\right)_{\text{H}_2\text{O}}^*$	$\left(\frac{1}{T_1}\right)_{\text{H}_2\text{O}}$
(°C)	(sec ⁻¹)	(sec ⁻¹)
1.7	292	289.2 ± 0.2
8.0	236	232.6 ± 0.2
14.5	195	190.8 ± 0.2
21.6	160	157.2 ± 0.1
28.9	134	130.9 ± 0.2
38.3	109	106.6 ± 0.1
47.7	91	88.5 ± 0.1
57.1	77	74.6 ± 0.1
66.5	66	63.8 ± 0.1

Table C-2

Experimental Data: Solution 4

solution composition: 5.0018 g $\text{Na}_2\text{S}_2\text{O}_5$, enough H_2O to make total volume

11.3 ml

measured pH = 4.50

T	$\left(\frac{1}{T_2}\right)_{\text{H}_2\text{O}}^*$	$\left(\frac{1}{T_2}\right)_{\text{S(IV)}}^*$
(°C)	(sec ⁻¹)	(sec ⁻¹)
-15	2630 ± 10	4184 ± 87
-10	2023 ± 13	3380 ± 130
-5	1497 ± 7	2692 ± 75
0	1264 ± 8	2350 ± 100
5	1116 ± 5	2240 ± 72
10	1072 ± 7	2220 ± 110
15	1082 ± 5	2596 ± 103
20	1136 ± 4	2999 ± 96
25	1237 ± 7	3630 ± 230
30	1401 ± 8	4100 ± 270
35	1581 ± 8	4890 ± 290
40	1915 ± 13	6430 ± 570
50	2441 ± 18	9350 ± 1020

Table C-3

Experimental Data: Solution E

solution composition: 0.0567 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.1395 g NaCl , 3.00 ml H_2O

measured pH = 3.00 (pH adjusted with 6M HCl)

T	$(\frac{1}{T_2})_{\text{H}_2\text{O}}^*$	$(\frac{1}{T_1})_{\text{H}_2\text{O}}$	$(\frac{1}{T_2})_{\text{S(IV)}}^*$	$\Delta\nu_{\text{S(IV),H}_2\text{O}}$
($^{\circ}\text{C}$)	(sec^{-1})	(sec^{-1})	(sec^{-1})	(Hz)
3.7	414.7 \pm 0.6	268.5 \pm 0.2	510 \pm 8	4781
10.6	361.9 \pm 0.6	214.4 \pm 0.1	549 \pm 8	4777
15.2	335.5 \pm 0.6	193.4 \pm 0.3	587 \pm 7	4791
20.0	304.1 \pm 0.6	167.4 \pm 0.1	636 \pm 7	4795
25.0	274.6 \pm 0.6	147.2 \pm 0.1	708 \pm 8	4803
29.5	252.6 \pm 0.6	131.0 \pm 0.1	773 \pm 14	4811
34.1	232.5 \pm 0.6	119.8 \pm 0.2	842 \pm 9	4831
38.9	215.5 \pm 0.6	105.6 \pm 0.2	945 \pm 16	4824
43.7	200.4 \pm 0.4	94.9 \pm 0.1	1013 \pm 11	4848
50.4	183.5 \pm 0.4	83.0 \pm 0.2	1155 \pm 14	4858
58.2	167.8 \pm 0.4	71.0 \pm 0.4	1337 \pm 25	4851
67.8	157.1 \pm 0.3	61.5 \pm 0.1	1571 \pm 41	4877

Table C-4

Experimental Data: Solution F

solution composition: 0.0570 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.1407 g NaCl , 3.00 ml H_2O

measured pH = 3.52 (pH adjusted with 6M HCl)

T (°C)	$(\frac{1}{T_2})^*_{\text{H}_2\text{O}}$ (sec ⁻¹)	$(\frac{1}{T_1})_{\text{H}_2\text{O}}$ (sec ⁻¹)	$(\frac{1}{T_2})^*_{\text{S(IV)}}$ (sec ⁻¹)	$\Delta\nu_{\text{S(IV),H}_2\text{O}}$ (Hz)
4.3	349.4 ± 0.1	261.5 ± 0.1	---	4817
17.6	290.3 ± 0.1	174.3 ± 0.3	738 ± 11	4808
24.7	272.1 ± 0.1	147.2 ± 0.2	846 ± 13	4823
29.3	259.6 ± 0.1	133.5 ± 0.1	953 ± 14	4834
34.0	249.4 ± 0.1	120.2 ± 0.6	1069 ± 16	4838
38.6	241.9 ± 0.1	106.3 ± 0.2	1179 ± 22	4840
43.5	235.0 ± 0.1	96.0 ± 0.5	1312 ± 16	4866
50.1	224.9 ± 0.1	83.7 ± 0.3	1555 ± 29	4880
57.8	214.3 ± 0.1	72.8 ± 0.3	1875 ± 35	4879
67.7	203.6 ± 0.1	60.5 ± 0.5	2268 ± 51	4908
75.4	194.8 ± 0.1	54.0 ± 0.5	2826 ± 75	4924

Table C-5

Experimental Data: Solution I

solution composition: 0.0574 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.1387 g NaCl , 3.00 ml H_2O

measured pH = 4.44 (pH adjusted with 6M NaOH)

T	$\left(\frac{1}{T_2}\right)_{\text{H}_2\text{O}}^*$	$\left(\frac{1}{T_1}\right)_{\text{H}_2\text{O}}$
($^{\circ}\text{C}$)	(sec^{-1})	(sec^{-1})
2.8	294.1 \pm 1.1	280.4 \pm 0.1
8.9	243.2 \pm 0.9	226.7 \pm 0.1
14.6	213.6 \pm 0.9	196.3 \pm 0.2
19.4	194.8 \pm 0.3	170.4 \pm 0.1
24.4	177.2 \pm 0.5	148.8 \pm 0.1
29.3	165.9 \pm 0.8	131.0 \pm 0.1
36.9	153.3 \pm 0.6	110.5 \pm 0.1
44.4	145.8 \pm 0.7	95.1 \pm 0.1
52.0	142.6 \pm 0.5	82.3 \pm 0.1
60.1	141.4 \pm 0.4	70.2 \pm 0.1
68.3	142.0 \pm 0.5	62.8 \pm 0.1

Table C-6

Experimental Data: Solution J

solution composition: 0.0573 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.1379 g NaCl , 3.00 ml H_2O

measured pH = 4.98 (pH adjusted with NaOH)

T (°C)	$(\frac{1}{T_2})_{\text{H}_2\text{O}}^*$ (sec ⁻¹)	$(\frac{1}{T_1})_{\text{H}_2\text{O}}$ (sec ⁻¹)	$(\frac{1}{T_2})_{\text{S(IV)}}^*$ (sec ⁻¹)	$\Delta\nu_{\text{S(IV)},\text{H}_2\text{O}}$ (Hz)
2.7	292.8 ± 0.8	281.8 ± 0.1	1128 ± 8	5286
8.7	240.0 ± 0.7	229.0 ± 0.1	1176 ± 6	5284
15.2	201.1 ± 0.6	188.4 ± 0.1	1262 ± 5	5283
22.2	169.0 ± 0.4	154.8 ± 0.1	1385 ± 6	5292
28.7	148.3 ± 0.4	133.5 ± 0.2	1532 ± 9	5285
36.1	130.7 ± 0.3	111.6 ± 0.1	1730 ± 10	5285
43.9	118.8 ± 0.4	95.4 ± 0.1	2020 ± 15	5283
51.6	110.0 ± 0.4	82.4 ± 0.1	2322 ± 20	5287
60.1	104.3 ± 0.4	70.9 ± 0.1	2752 ± 20	5295
67.8	101.2 ± 0.4	62.5 ± 0.1	3201 ± 47	5292

Table C-7

Experimental Data: Solution K

solution composition: 0.0565 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.1398 g NaCl , 3.00 ml H_2O

measured pH = 4.07

T	$(\frac{1}{T_2})_{\text{H}_2\text{O}}^*$
(°C)	(sec ⁻¹)
2.2	313.5 ± 0.4
8.2	262.6 ± 0.3
14.3	230.0 ± 0.4
22.6	203.6 ± 0.4
29.9	188.5 ± 0.4
37.3	181.0 ± 0.3
44.9	176.6 ± 0.4
55.4	174.7 ± 0.4
65.1	171.5 ± 0.6

Table C-8

Experimental Data: Solution L

solution composition: 0.0579 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.1401 g NaCl , 3.00 ml H_2O

measured pH = 4.58 (pH adjusted with 6M NaOH and 6M HCl)

T	$\left(\frac{1}{T_2}\right)_{\text{H}_2\text{O}}^*$
(°C)	(sec^{-1})
1.4	302.8 ± 0.6
8.0	247.6 ± 0.4
14.4	209.9 ± 0.4
22.3	177.8 ± 0.4
22.4	179.1 ± 0.3
29.7	157.7 ± 0.3
37.4	145.1 ± 0.3
44.9	136.3 ± 0.3
52.6	131.9 ± 0.3
62.1	130.7 ± 0.4

Table C-9

Experimental Data: Solution Q

solution composition: 0.0287 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.1572 g NaCl , 3.00 ml H_2O

measured pH = 2.58 (pH adjusted with 6M HCl)

T ($^{\circ}\text{C}$)	$\left(\frac{1}{T_2}\right)_{\text{H}_2\text{O}}^*$ (sec^{-1})	$\left(\frac{1}{T_2}\right)_{\text{S(IV)}}^*$ (sec^{-1})	$\Delta\nu_{\text{S(IV)}, \text{H}_2\text{O}}$ (Hz)
0.6	368.2 \pm 0.6	455 \pm 11	4763
7.3	295.9 \pm 0.6	493 \pm 9	4776
13.8	243.8 \pm 0.5	549 \pm 10	4785
21.3	200.4 \pm 0.5	607 \pm 12	4795
21.4	206.1 \pm 0.5	622 \pm 14	4802
29.0	166.5 \pm 0.4	699 \pm 20	4804
36.9	141.4 \pm 0.4	749 \pm 12	4823
44.5	122.5 \pm 0.4	886 \pm 16	4835
52.4	108.1 \pm 0.4	1031 \pm 24	4857
60.0	96.8 \pm 0.4	1168 \pm 38	4878
67.4	88.0 \pm 0.8	1336 \pm 47	4856

Table C-10

Experimental Data: Solution R

solution composition: 0.0289 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.1579 g NaCl , 3.00 ml H_2O

measured pH = 3.01 (pH adjusted with 6M HCl)

T (°C)	$(\frac{1}{T_2})_{\text{H}_2\text{O}}^*$ (sec ⁻¹)	$(\frac{1}{T_2})_{\text{S(IV)}}^*$ (sec ⁻¹)	$\Delta\nu_{\text{S(IV),H}_2\text{O}}$ (Hz)
1.1	372.6 ± 0.6	472 ± 6	4778
7.8	317.3 ± 0.5	499 ± 8	4784
14.3	272.1 ± 0.6	552 ± 8	4796
21.6	231.8 ± 0.6	635 ± 10	4806
21.7	234.4 ± 0.8	630 ± 11	4805
29.1	199.2 ± 0.5	711 ± 13	4815
36.7	172.8 ± 0.5	821 ± 27	4820
44.5	151.4 ± 0.4	941 ± 45	4839
52.1	136.3 ± 0.3	1095 ± 21	4848
59.7	125.7 ± 0.5	1213 ± 28	4870
67.3	115.6 ± 0.6	1352 ± 40	4883

Table C-11

Experimental Data: Solution S

solution composition: 0.1301 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.0939 g NaCl , 3.00 ml H_2O

measured pH = 3.02 (pH adjusted with 6M HCl)

T (°C)	$\left(\frac{1}{T_2}\right)_{\text{H}_2\text{O}}^*$ (sec ⁻¹)	$\left(\frac{1}{T_2}\right)_{\text{S(IV)}}^*$ (sec ⁻¹)	$\Delta\nu_{\text{S(IV),H}_2\text{O}}$ (Hz)
1.1	639.6 ± 1.4	532 ± 6	4735
7.7	580.6 ± 1.1	587 ± 3	4734
13.9	526.5 ± 1.3	664 ± 3	4749
21.4	471.9 ± 1.1	775 ± 4	4756
21.9	481.3 ± 1.4	798 ± 6	4751
29.3	415.3 ± 1.6	908 ± 5	4762
36.9	371.3 ± 1.2	1069 ± 8	4760
44.6	342.4 ± 1.1	1304 ± 7	4781
52.3	321.1 ± 1.2	1578 ± 28	4785
60.1	304.1 ± 0.9	1942 ± 25	4806
67.7	294.1 ± 0.9	2410 ± 44	4834

Table C-12

Experimental Data: Solution T

solution composition: 0.1280 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.0879 g NaCl , 3.00 ml H_2O

measured pH = 4.97 (pH adjusted with 6M NaOH)

T	$(\frac{1}{T_2})^*_{\text{H}_2\text{O}}$	$(\frac{1}{T_2})^*_{\text{S(IV)}}$	$\Delta\nu_{\text{S(IV),H}_2\text{O}}$
(°C)	(sec^{-1})	(sec^{-1})	(Hz)
1.1	320.4 ± 0.7	1019 ± 5	5236
7.5	261.4 ± 0.6	1037 ± 2	5240
14.1	218.7 ± 0.4	1114 ± 3	5258
21.9	184.7 ± 0.6	1278 ± 3	5260
22.0	187.2 ± 0.9	1270 ± 2	5261
29.4	170.9 ± 0.8	1505 ± 7	5258
37.0	157.7 ± 0.6	1814 ± 15	5269
44.9	153.3 ± 0.9	2187 ± 24	5265
52.5	146.4 ± 0.5	2675 ± 16	5289
60.2	150.2 ± 0.4	3268 ± 55	5280
67.8	157.7 ± 0.5	3986 ± 41	5294

Table C-13

Experimental Data: Solution U

solution composition: 0.0930 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.1170 g NaCl , 3.00 ml H_2O

measured pH = 3.01 (pH adjusted with 6M HCl)

T (°C)	$(\frac{1}{T_2})^*_{\text{H}_2\text{O}}$ (sec ⁻¹)	$(\frac{1}{T_1})_{\text{H}_2\text{O}}$ (sec ⁻¹)	$(\frac{1}{T_2})^*_{\text{S(IV)}}$ (sec ⁻¹)	$\Delta\nu_{\text{S(IV),H}_2\text{O}}$ (Hz)
0.8	536.6 ± 1.0	303.2 ± 0.3	501 ± 4	4758
8.1	478.8 ± 1.0	242.1 ± 0.1	550 ± 5	4760
14.5	430.4 ± 1.5	197.0 ± 0.3	621 ± 6	4772
21.0	377.6 ± 1.1	---	711 ± 8	4771
21.5	---	---	723 ± 16	--
29.1	331.8 ± 0.9	132.0 ± 0.1	838 ± 8	4782
36.8	295.9 ± 1.1	111.9 ± 0.2	974 ± 13	4791
44.6	282.1 ± 2.9	---	1118 ± 23	4794
52.5	245.7 ± 1.1	81.9 ± 0.2	1304 ± 45	4812
60.4	230.0 ± 0.9	71.6 ± 0.1	1600 ± 46	4830
68.0	217.4 ± 0.6	63.2 ± 0.1	1930 ± 110	4839

Table C-14

Experimental Data: Solution V

solution composition: 0.0932 g $\text{Na}_2\text{S}_2\text{O}_5$, 0.1156 g NaCl , 3.00 ml H_2O

measured pH = 5.00 (pH adjusted with 6M NaOH and 6M HCl)

T ($^{\circ}\text{C}$)	$\left(\frac{1}{T_2}\right)^*_{\text{H}_2\text{O}}$ (sec^{-1})	$\left(\frac{1}{T_2}\right)^*_{\text{S(IV)}}$ (sec^{-1})	$\Delta\nu_{\text{S(IV),H}_2\text{O}}$ (Hz)
0.4	314.9 \pm 0.6	1020 \pm 3	5261
7.0	255.2 \pm 0.6	1024 \pm 7	5266
14.0	211.9 \pm 0.4	1076 \pm 7	5267
21.4	179.0 \pm 0.4	1197 \pm 6	5267
29.2	156.0 \pm 0.5	1384 \pm 9	5271
36.9	140.0 \pm 0.4	1641 \pm 14	5276
44.7	130.1 \pm 0.7	1956 \pm 39	5268
52.5	124.7 \pm 0.7	2383 \pm 55	5305
60.5	123.0 \pm 0.6	2843 \pm 63	5299
68.2	124.7 \pm 0.7	3220 \pm 200	5293

CAPTIONS FOR FIGURES

- Figure 1
p. 3
- Calculated NMR lineshapes showing the effect of chemical exchange of the observed nucleus between two equally populated sites A and B. The natural linewidths of the two peaks, $1/T_{2A}$ and $1/T_{2B}$, are each equal to $|\omega_A - \omega_B|/15.6$, where ω_A and ω_B are the precessional frequencies of the nuclei in sites A and B, respectively. The quantity $1/\tau$ is the pseudo first order rate constant for exchange of nuclei from one site to the other.
- Figure 2
p. 7
- Compositions of the sodium bisulfite solutions upon which the ^{17}O NMR experiments were performed. The values on the abscissa are numbers read from a pH meter which was connected to the pH electrode immersed in each solution at room temperature.
- Figure 3
p. 23
- Traces of a portion of the ^{17}O NMR spectrum of sodium bisulfite solutions of various acidities, showing how the number of peaks in the spectrum as well as the widths and chemical shifts of the peaks are dependent upon the pH of the solution. The S(IV) concentration of each solution was 0.20 moles of S(IV) per 55.5 moles of H_2O , and the temperature of each solution was between 4 and 10°C . The term "pH" refers to the common logarithm of the reciprocal of the room temperature activity of hydrogen ion as

measured by a pH meter. The ^{17}O spectra were recorded at a radio frequency of 27.377 MHz using the two-pulse sequence described in the Experimental Procedure section. The chemical shift scale was chosen so that the water peak in the one-pulse spectrum of each solution had a chemical shift of zero. Downfield shifts are positive. The vertical expansion is not the same for different traces.

Figure 4
p. 24

Traces of a portion of the ^{17}O NMR spectrum of a sodium bisulfite solution of $[\text{S(IV)}] = 0.201 \text{ m}$ and for which the room temperature pH meter reading was 4.44, showing how the peaks broadened as the temperature was raised. The ^{17}O spectra were recorded at a radio frequency of 27.377 MHz using the two-pulse sequence described in the Experimental Procedure section, and the chemical shift scale was chosen so that the water peak in the one-pulse spectrum at each temperature had a chemical shift of zero. Downfield shifts are positive. The vertical expansion is not the same for different traces.

Figure 5
p. 25

Temperature dependence of the difference between $1/T_2^*$ and $1/T_1$ of the ^{17}O in the water of sodium bisulfite solutions of $[\text{S(IV)}] = 0.20 \text{ m}$ and various concentrations of H^+ . $(1/T_2^*)_{\text{H}_2\text{O}}$ is the measured half width at half height of the water peak, and includes broadening due to magnetic field inhomogeneity (estimated to be $0.5 \pm 0.1 \text{ Hz}$). The term pH refers to the common logarithm of the reciprocal of the

room temperature activity of hydrogen ion as measured by a pH meter.

Figure 6 Dependence of the half width at half height of the
pp. 39-41 bisulfite peak at 175 ppm upon the concentration of
S(IV). Data at each temperature were obtained from the
same set of four sodium bisulfite solutions. At 25°C the
ionic strength of each solution was 1.0 m, and the activity
of H^+ as measured by a pH meter ranged from 9.6×10^{-4} to
 1.00×10^{-3} m.

Figure 7 Dependence of the half width at half height of the
pp. 45-47 bisulfite peak located at 175 ppm upon the concentration of
S(IV) divided by the room temperature activity of H^+ . Data
at each temperature were obtained from the same set of six
sodium bisulfite solutions. (At the lowest temperature
data were obtained from only five of the six solutions.)
At 25°C the ionic strength of each solution was 1.0 m, and
the common logarithm of the activity of H^+ as measured by a
pH meter was -2.58, -3.01, -3.00, -3.01, -3.02, and -3.52
for the solutions having abscissa values of 0.038, 0.103,
0.199, 0.334, 0.447, and 0.662, respectively.

Figure 8 Dependence of the half width at half height of the
pp. 50-53 bisulfite peak located at 175 ppm upon the concentration of
 SO_3^{2-} . Data at each temperature were obtained from the
same set of six sodium bisulfite solutions. (At the lowest

temperature data were obtained from only five of the six solutions.) At 25°C the ionic strength of each solution was 1.0 m, and the common logarithm of the activity of H^+ as measured by a pH meter was, in order of increasing abscissa value, -2.58, -3.01, -3.00, -3.01, -3.02, and -3.52. The solid symbols and error bars represent the experimental data. Also shown (as open symbols) are points obtained from the weighted linear least squares fit of the data to the function $(1/T_2)_{175} = N' + Q' [SO_3^{2-}] + R [SHO_3^-]$.

Figure 9
p. 70

Arrhenius plot of Q' . The ordinate values were obtained from the weighted linear least squares fitting of the data of Figure 7 to the function $(1/T_2)_{175} = N' + Q' [SO_3^{2-}] + R [SHO_3^-]$, where $(1/T_2)_{175}$ is the half width at half height of the peak located at 175 ppm in the oxygen-17 NMR spectra of the bisulfite solutions. The straight line represents the weighted linear least squares fit of the points.

Figure 10
p. 71

The logarithm of R plotted versus the reciprocal of the absolute temperature. The ordinate values were obtained from the weighted linear least squares fitting of the data of Figure 7 to the function $(1/T_2)_{175} = N' + Q' [SO_3^{2-}] + R [SHO_3^-]$, where $(1/T_2)_{175}$ is the half width at half height of the peak located at 175 ppm in the oxygen-17 NMR spectra of the bisulfite solutions. The points at the two highest temperatures have negative values of R, and therefore have no loci on the semilog plot. However, the corresponding

error bars extend to positive values of R , as shown. The straight line represents the weighted linear least squares fit of the eight highest temperature points.

Figure 11 p. 72 The logarithm of $\{1/T_2(175) + N\}$ plotted as a function of the reciprocal of the absolute temperature. The quantity $1/T_2(175)$ is the natural linewidth of the peak located at 175 ppm in the ^{17}O NMR spectra of the bisulfite solutions. The quantity N is that term in the pseudo first order rate constant for oxygen exchange out of the 175 ppm environment which is independent of both pH and S(IV) concentration. The ordinate values were obtained from the weighted linear least squares fitting of the data of Figure 7 to the function $(1/T_2)_{175} = N' + Q'[\text{SO}_3^{2-}] + R[\text{SHO}_3^-]$, where $(1/T_2)_{175}$ is the half width at half height of the peak at 175 ppm, and N' is equal to $1/T_2(175) + N$.

Figure 12 p. 73 Values of $1/T_1$ of the ^{17}O in water as a function of the reciprocal of the absolute temperature for several bisulfite solutions. The total concentration of S(IV) ranged from 0.20 to 0.33 m, and the pH ranged from 3 to 5. Enough NaCl was present in each solution to bring the ionic strength up to 1.0 m.

Figure 13 p. 81 Temperature dependence of the equilibrium quotient for the reaction $(\text{SHO}_3^-)_{175} = (\text{SHO}_3^-)_{195}$, where the subscripts 175 and 195 identify the two isomers of bisulfite ion by their

^{17}O NMR chemical shifts (in ppm) relative to water. The equilibrium quotient was determined at an ionic strength of 1.0 m for S(IV) concentrations of 0.20 and 0.45 m. The straight line represents the linear least squares fit of the data.

Figure 14 Values of the quantity $N + 1/T_2(175) - 0.302(1/T_1)_{\text{H}_2\text{O}}$ as a
p. 86 function of the absolute temperature. The ordinate values are assumed to be equal to N. The straight line represents the least squares fit of these points, and was obtained through a weighted nonlinear least squares computer analysis of the data of Figure 11, as explained in the text.

Figure 15 The temperature dependence of the exact chemical shift of
p. 99 the peak located at ca. 175 ppm downfield from the water peak in the ^{17}O NMR spectra of two sodium bisulfite solutions of pH 3. The chemical shift values are given relative to the shift of the water peak. The spectra were recorded at a radio frequency of 27.377 MHz. The compositions of the two solutions were [S(IV)] = 0.199 m, pH = 3.00, μ = 1.00 m; and [S(IV)] = 0.456 m, pH = 3.02, μ = 1.04 m, where "pH" refers to the common logarithm of the reciprocal of the room temperature activity of hydrogen ion as measured by a pH meter.

Figure 16
p. 101

The temperature dependence of the exact chemical shift of the peak located at ca. 193 ppm downfield from the water peak in the ^{17}O NMR spectra of three sodium bisulfite solutions of pH 5. The chemical shift values are given relative to the shift of the water peak. The spectra were recorded at a radio frequency of 27.377 MHz. The compositions of the three solutions were $[\text{S(IV)}] = 0.201 \text{ m}$, $\text{pH} = 4.98$, $\mu = 1.00 \text{ m}$; $[\text{S(IV)}] = 0.326 \text{ m}$, $\text{pH} = 5.00$, $\mu = 1.01 \text{ m}$; and $[\text{S(IV)}] = 0.449 \text{ m}$, $\text{pH} = 4.97$, $\mu = 0.99 \text{ m}$, where "pH" refers to the common logarithm of the reciprocal of the room temperature activity of hydrogen ion as measured by a pH meter.

Figures
17-22
pp.
105-110

The pseudo first order rate constant for exchange of ^{17}O from the 195 ppm environment to water plotted as a function of $-\log_{10}[\text{H}^+]$, for six different sodium bisulfite solutions of $[\text{S(IV)}] = 0.20 \text{ m}$ and ionic strength 1.0 m. Data acquired at six different temperatures are shown in Figures 17-22. The open circles represent $1/\tau_{195, \text{H}_2\text{O}}$ values obtained by analysis of the broadening of the water peak in the ^{17}O NMR spectra of the solutions. For the solution of highest pH, $1/\tau_{195, \text{H}_2\text{O}}$ was also evaluated from the width of the S(IV) peak located about 193 ppm downfield from the water peak. This datum is represented by the solid dot. The smooth curve in each plot represents the weighted linear least squares best fit of the H_2O data to the expression $1/\tau_{195, \text{H}_2\text{O}} = A + B[\text{H}^+]$. The horizontal line is

a plot of A vs. $-\log_{10}[\text{H}^+]$, and the diagonal line is a plot of B[H^+] vs. $-\log_{10}[\text{H}^+]$.

Figure 23 The logarithm of k_{-17} plotted as a function of the absolute
p. 122 temperature. k_{-17} is the rate constant for the reaction in
which sulfur dioxide and water are formed from hydrogen ion
and the isomer of bisulfite ion which has an oxygen-17 NMR
signal located 195 ppm downfield from that of water. The
straight line represents the weighted linear least squares
fit of the data.

Figure 24 The logarithm of k_{18} plotted as a function of the absolute
p. 123 temperature. k_{18} is the rate constant for the reaction in
which an oxygen atom is exchanged between water and the
isomer of bisulfite ion which has an oxygen-17 NMR signal
located 195 ppm downfield from that of water. The straight
line represents the weighted linear least squares fit of
the data.

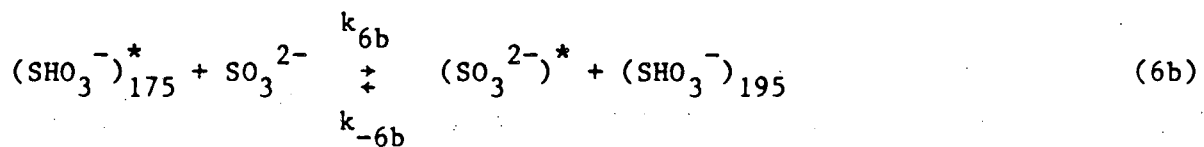
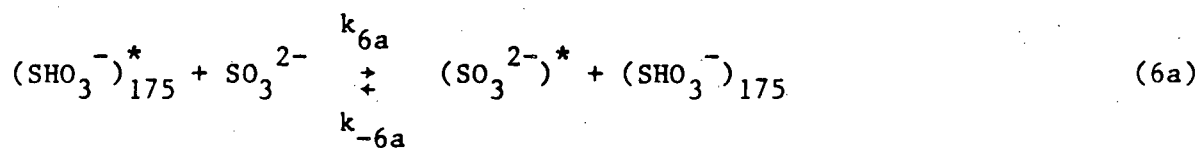
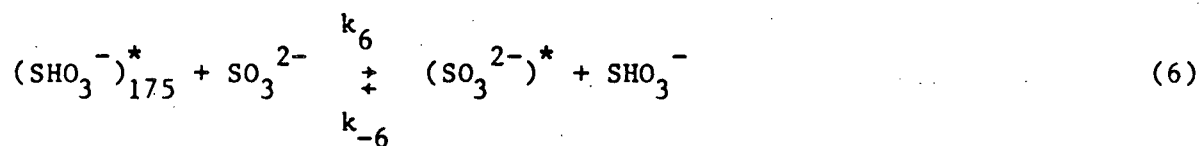
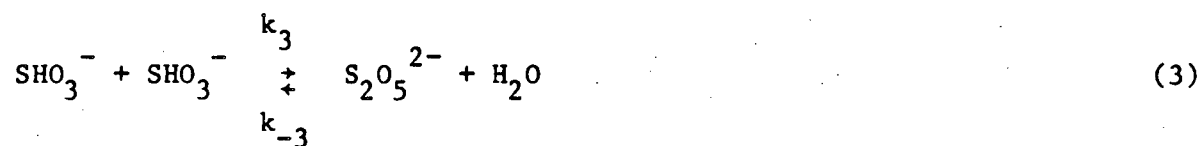
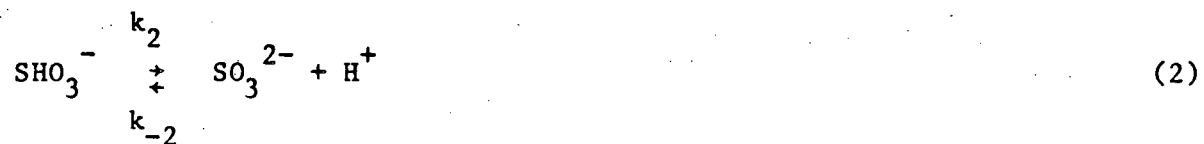
Figure 25 The temperature dependence of two functions:
p. 148 ● - the half width at half height of the water peak in the
 ^{17}O NMR spectrum of a 4.7 M sodium bisulfite solution
of pH 4.5;
○ - the half width at half height of the water peak in the
 ^{17}O NMR spectrum of the 4.7 M sodium bisulfite solution
minus 3.24 times the longitudinal relaxation rate
constant of ^{17}O in the water of 0.2 m sodium bisulfite

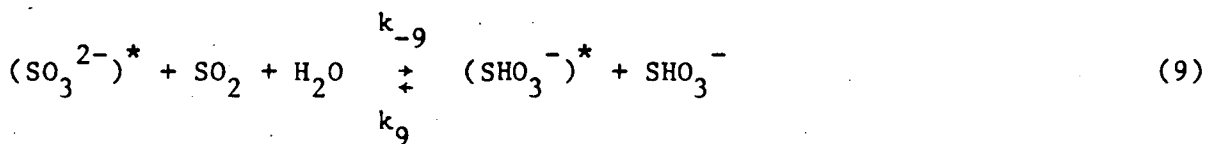
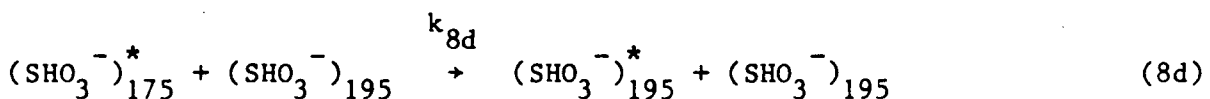
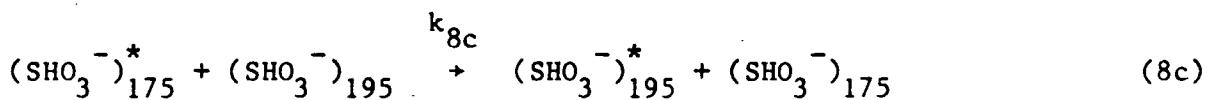
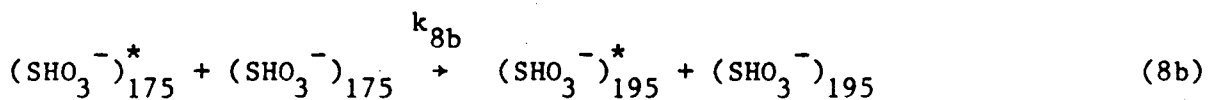
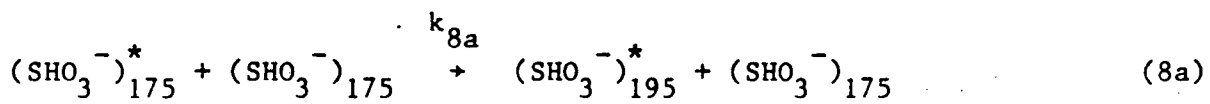
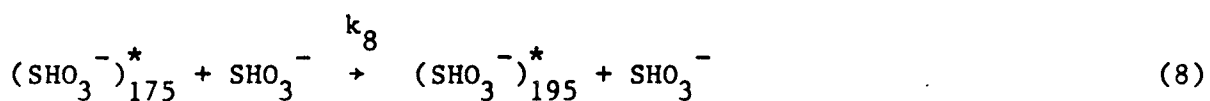
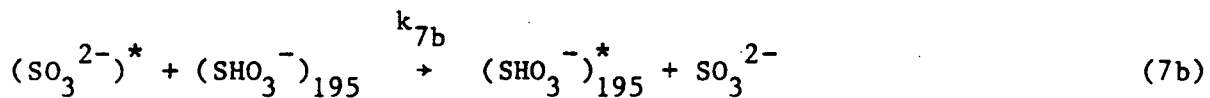
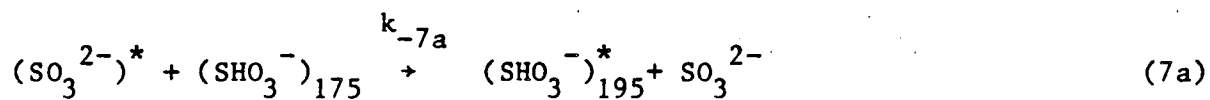
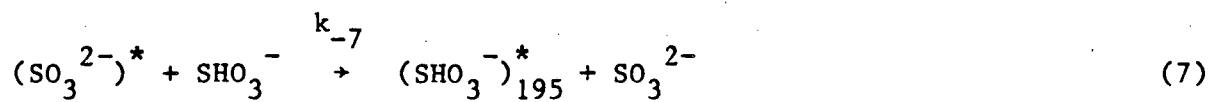
solutions. The ordinate values are assumed to be equal to $1/\tau_{\text{H}_2\text{O},\text{S(IV)}}$, the pseudo first order rate constant for oxygen exchange from water to S(IV) species. The straight line represents the weighted linear least squares fit of the data.

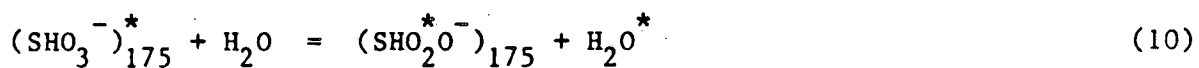
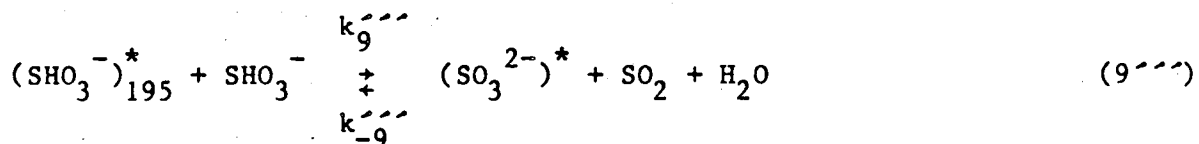
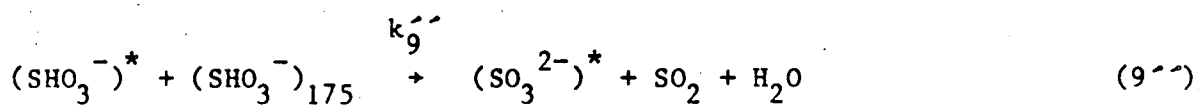
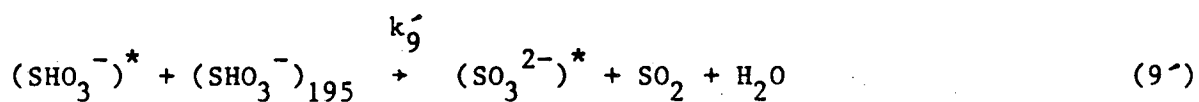
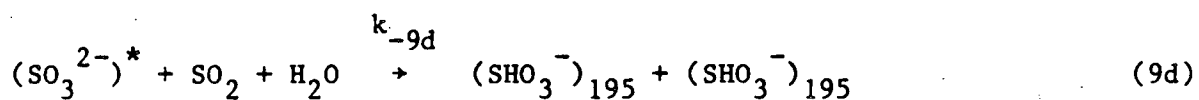
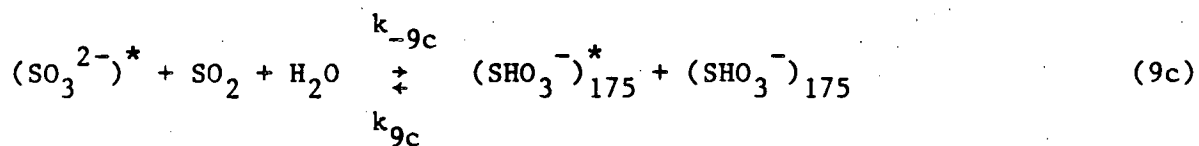
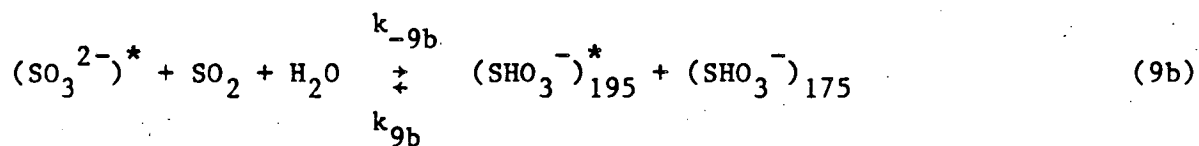
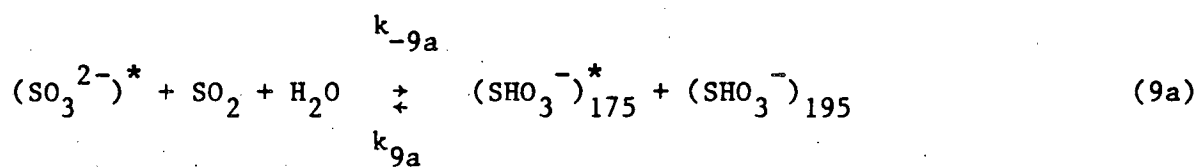
- Figure 26 The temperature dependence of three functions:
p. 156 ○ - the half width at half height of the S(IV) peak in the ^{17}O NMR spectrum of a 4.7 M sodium bisulfite solution of pH 4.5;
solid line - the pseudo first order rate constant for oxygen exchange from the S(IV) site to water in the 4.7 M solution, determined from the broadening of the water peak;
● - the difference between the above two quantities. This difference is assumed to be equal to the half width at half height which the S(IV) peak would have in the absence of oxygen exchange between S(IV) species and water.

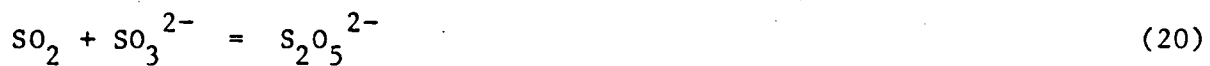
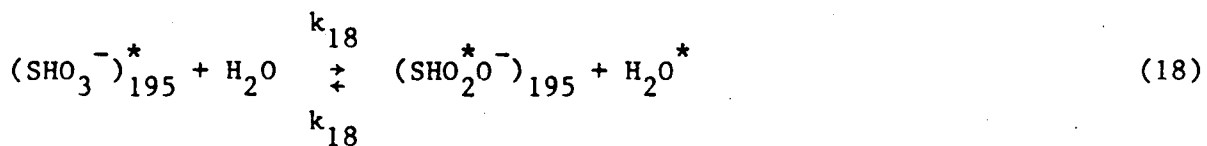
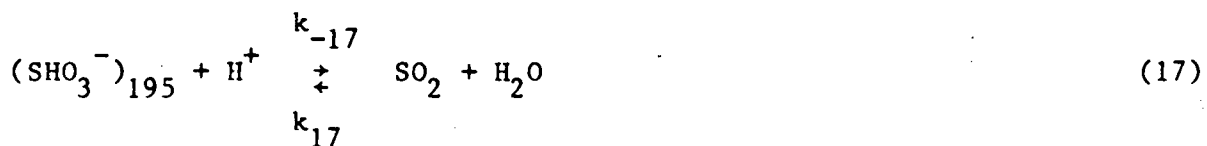
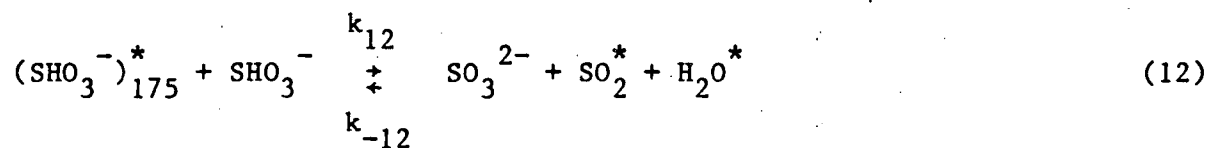
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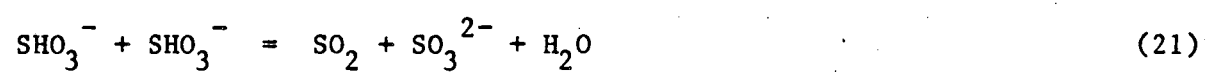
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p. 31 Acidity in ^{17}O NMR Spectra of Sodium Bisulfite Solutions in
Which Only One S(IV) Peak Appears
- Table 2 Values of Parameters Used in the Calculation of K_{15} , the
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79-80 $(\text{SHO}_3^-)_{175} = (\text{SHO}_3^-)_{195}$
- Table 3 Effect of S(IV) Concentration, at pH 3 and Various
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118-119 First Order Rate Constant for Oxygen Exchange to Water from
the Site with an Oxygen-17 NMR Chemical Shift of 195 ppm
- Table 5 Comparison of Rate Constants Obtained in This Study with
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- Table 6 Calculated Compositions of Sodium Bisulfite Solutions
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Chemical Shift of the S(IV) Peak in the Oxygen-17 NMR
Spectra of Those Solutions

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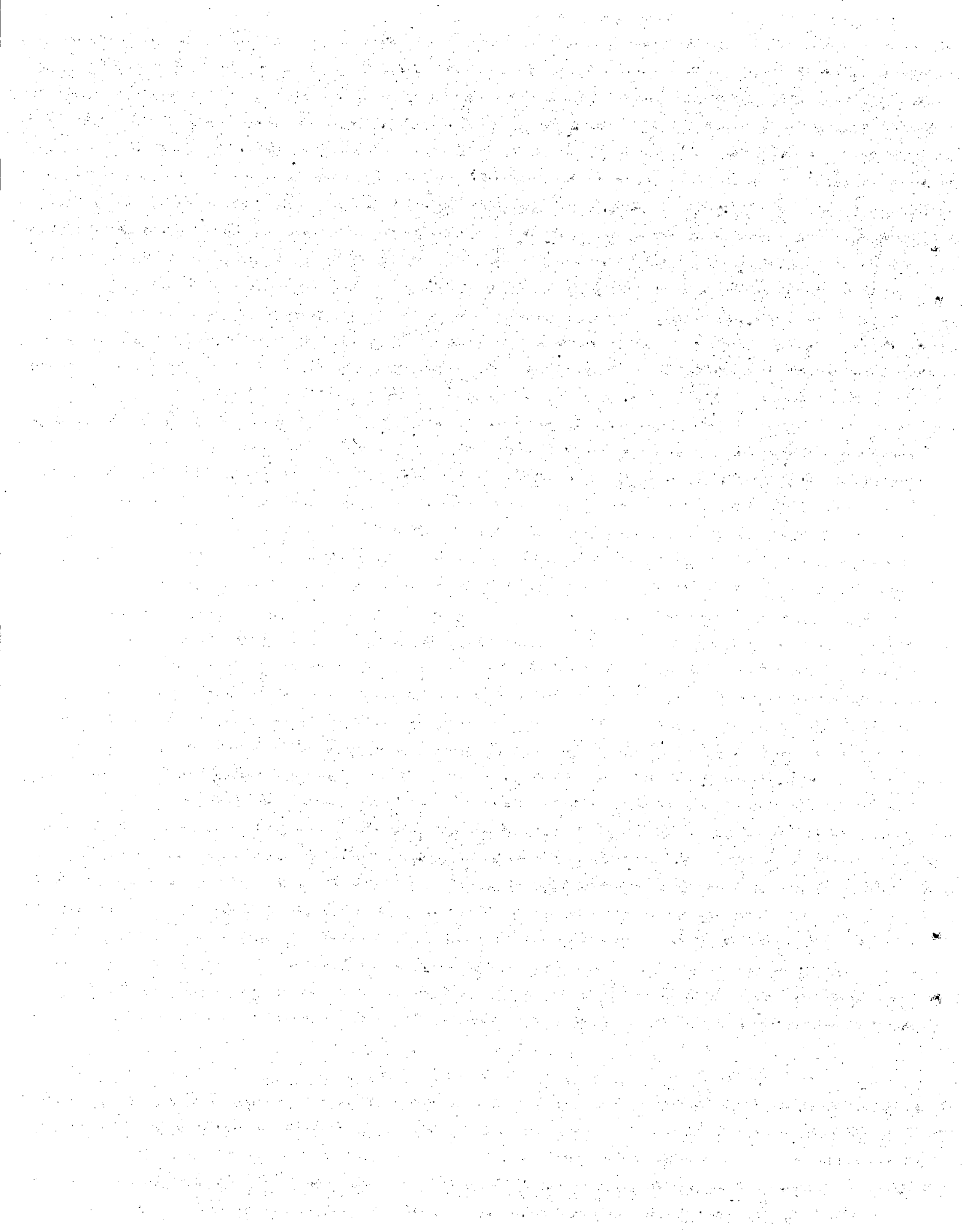
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17. Using the facts that the frequency of a component of the free induction decay is the frequency of precession with respect to the pulse frequency, and all components of the free induction decay are of the same phase when the signal first arrives at the computer, the time taken by the signal to reach the computer was determined experimentally by finding the delay time for which the water peak had the same phase in several spectra taken with different pulse frequencies.
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22. Reference 14, p. 11.
23. The term "pH" shall often be used in this dissertation to refer to the number read from the pH meter (see Experimental Procedure), although the quantity measured by the electrode and meter is probably closer to $-\log_{10}[a(\text{H}^+)]$. When "pH" is meant to refer to $-\log_{10}[\text{H}^+]$ it will be stated explicitly.
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30. The author is indebted to Mike Wagner for the weighted linear least squares computer program.
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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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