

AN ABSTRACT OF THE THESIS OF

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Title: THE ELECTROCHEMICAL OXIDATION OF AQUEOUS
SULFUR DIOXIDE SOLUTIONS AT A GLASSY CARBON
ELECTRODE

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Abstract approved: _____
Dr. Harry Freund

Heretofore the electrochemical oxidation of aqueous SO_2 has been studied primarily at platinum and gold electrodes. The electrodes exhibit poor reproducibility and have limited the study of the S(IV) system to a very narrow set of conditions where meaningful results could be obtained.

The problem of reproducibility was minimized in this work by using a non-metallic "glassy carbon" electrode.

Stationary electrode polarography offered a versatile means of studying the electrode mechanism. The pH, total S(IV) concentration, and scan rate were varied systematically and the corresponding behavior of the system was studied.

The results indicated that the electrooxidation of aqueous SO_2 conforms to a chemical reaction preceding an irreversible charge

transfer. The preceding chemical reaction could involve the dissociation of bisulfite ions, producing sulfite ions that finally undergo the electron transfer reaction.

It was suggested that this electrochemical system degenerates to an uncomplexed irreversible charge transfer at higher pH's. A value for $(1-\alpha)n_a$ of $.66 \pm .02$ was obtained and verified using different approaches in handling the available data. A heterogeneous rate constant, \vec{k}_s , of $4.9 \pm 3.0 \times 10^{-10}$ cm/sec was calculated, indicating the degree of irreversibility of this reaction.

An overall n value intermediate between one and two was calculated. To explain this it was suggested that the S(IV) electrooxidation involves two mechanisms that are occurring simultaneously. The first involves a direct two electron transfer, while the second involves a one electron transfer followed by a radical reaction to form dithionate.

It was recommended that controlled potential coulometry be employed to obtain more reliable n values. This technique has not been used in studying the S(IV) electrooxidation thus far because of the problem of electrode surface contamination. It was felt that this problem would be minimized using glassy carbon and that this technique could therefore be used successfully.

The Electrochemical Oxidation of Aqueous Sulfur Dioxide
Solutions at a Glassy Carbon Electrode

by

Bruce Edward Warden

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TABLE OF CONTENTS

<u>Chapter</u>	<u>Page</u>
I. INTRODUCTION	1
General	1
Oxidation of Sulfite Solutions	2
Electrochemical Oxidation of Sulfite Solutions	5
Intent of Research	10
Glassy Carbon Electrode	12
Stationary Electrode Polarography	13
Reversible Charge Transfer	13
II. EXPERIMENTAL	23
Reagents	23
Potassium Ferrocyanide Solutions	23
Sodium Sulfite Solutions	23
Britton and Robinson Buffers	23
Apparatus	24
The Indicator Electrode	24
The Cell	29
Instrumentation	31
Experimental Procedure	33
Stationary Electrode Polarography	33
Chronoamperometric Determination of Diffusion Coefficients	34
III. EXPERIMENTAL RESULTS AND DISCUSSION	36
IV. CONCLUSIONS	66
BIBLIOGRAPHY	69
APPENDIX: Analysis of Sulfite or SO ₂ Solutions	73

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. The eight cases for stationary electrode voltammetry.	20
2. Summary of voltammetric results at pH = 1.8.	38
3. Summary of voltammetric results at pH = 2.8.	39
4. Summary of voltammetric results at pH = 4.0.	40
5. Summary of voltammetric results at pH = 5.5.	41
6. Summary of voltammetric results at pH = 7.0.	42
7. Summary of voltammetric results at pH = 8.4.	43
8. Summary of voltammetric results at pH = 10.1.	44
9. Diffusion coefficient of S(IV) at various pH's.	63

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Voltammetric cell assembly.	30
2. Theoretical potential shift versus pH at 25° C.	50
3. Experimental half peak potential versus pH at a constant scan rate of .033 v/sec and constant concentration of S(IV).	51
4. Anodic current-voltage curves for S(IV) at various pH's.	54
5. Peak current versus the square root of scan rate at pH 4.0 and 10.1.	57
6. Log of current versus $E - E^{\circ}$ at pH 10.1, 3.16 mM S(IV).	60

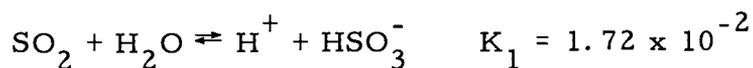
THE ELECTROCHEMICAL OXIDATION OF AQUEOUS SULFUR DIOXIDE SOLUTIONS AT A GLASSY CARBON ELECTRODE

I. INTRODUCTION

General

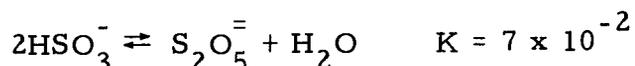
Sulfur dioxide has been studied extensively. Most of its physical properties have been characterized and can be found in various references (9, 17, 33). The use of sulfur dioxide in paper processes and production of sulfuric acid are well known. With the recent increased emphasis on pollution, the recovery and recycling of exhaust gases containing sulfur dioxide has become an active area of research (33, p. 68).

Sulfur dioxide will dissolve in water to form solutions of approximately 1 M concentration. The SO_2 hydrolyzes to sulfurous acid, H_2SO_3 , although the latter's existence as a molecular species is now considered doubtful (33, p. 10-18). The hydration of SO_2 and its accompanying ionization are among the most rapid reactions known (33, p. 13). The bisulfite and sulfite ions are well known and the equilibrium constants involving their ionization have been determined by several investigators (10). They are:





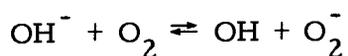
It is also known that at higher concentrations of bisulfite ion (approaching 10^{-2} M), dimerization takes place and pyrosulfite ion is formed. The equilibrium has been studied and reported (7).



The formal charge on sulfur in the aqueous SO_2 system is +4. It has long been known that in aqueous solution, sulfur(IV) is oxidized by various oxidizing agents to sulfur(VI). In fact, sulfite has been used as an "oxygen scavenger" in systems where dissolved molecular oxygen is objectionable (33, Ch. 2).

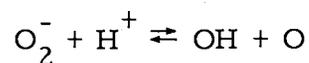
Oxidation of Sulfite Solutions

Several investigators have studied the oxidation of sulfur(IV) by dissolved oxygen (1, 19, 33). The most extensive studies have been carried out by Abel and coworkers (1). It was proposed that dissolved oxygen and hydroxide ions react to form radical species which react with the sulfur(IV) species. The reaction is initiated by the formation of the hydroxyl radical,

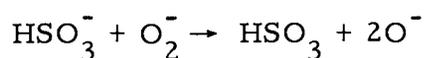
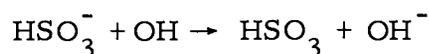
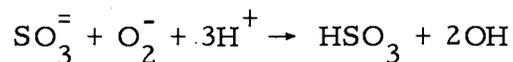
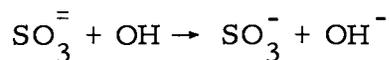


The aqueous oxygen ion reacts with more oxygen or with protons

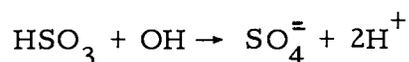
forming more hydroxyl radicals.



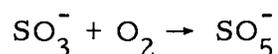
All of these radicals react with the sulfite or bisulfite ions forming intermediates, i. e. ,



The second step of the reaction may involve another radical reaction such as,



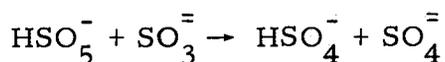
Another mechanism which has received much attention is the classical Hammett scheme (19). This mechanism involves a free radical chain reaction in which the free radical SO_3^- is formed and reacts with oxygen,



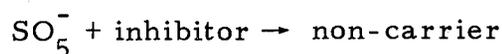
The powerful oxidizing agent HSO_5^- may be formed by the interaction of the radical SO_5^- with bisulfite ion



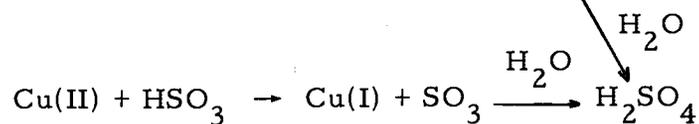
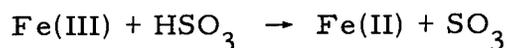
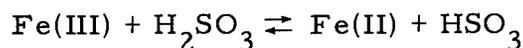
Sulfate ion may then be formed by the following reaction:



In the presence of inhibitors, the radical SO_5^- may oxidize the inhibitor thereby terminating the chain process



In cases where transition metal ions are the oxidants, mechanisms have been proposed with direct electron transfer between S(IV) and the oxidant. The products formed are sulfate and dithionate. A general mechanism was proposed by Higginson (20) and applied to a S(IV):Fe(III):Cu(II) system. The S(IV) species gives up 1 electron to the oxidant and forms a free radical. The free radical either dimerizes to dithionate or reacts with another metal ion giving up a second electron and ultimately forming sulfate. The general scheme for this system in a highly acid medium was as follows.



The Cu(II) acted as a catalyst. It was pointed out that HSO_3^- and $\text{SO}_3^{=}$ ions could be involved in the same scheme, with different free radicals involved as intermediates.

Electrochemical Oxidation of Sulfite Solutions

The anodic oxidation of aqueous SO_2 solutions has received relatively little attention. The work that has been done is restricted primarily to studies at supposedly inert metal electrodes (Pt and Au).

In the early 1900's, the anodic oxidation of sulfite to dithionate was studied and proposed as another means of producing dithionate commercially (12, 13, 15).

The first significant investigation of the electrooxidation of sulfite solutions was carried out by Glasstone and Hickling on platinum electrodes (16). The apparent primary concern was the determination of the factors that affect the yield of dithionate during electrolysis. Their results indicated that pH 8 is the most efficient acidity for dithionate formation. Although the yield falls off at both ends of the pH scale, it was shown to be lowest in acid solutions (less than 4% efficient at pH 1). Glasstone and Hickling proposed that the actual oxidation of sulfite resulted from a chemical reaction with electrolytically generated hydrogen peroxide. Their experiments consisted of electrolyzing a sulfite solution and analyzing the resulting solution for sulfate and dithionate (the proposed products). The suggestion was

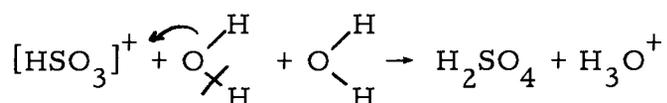
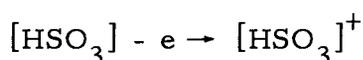
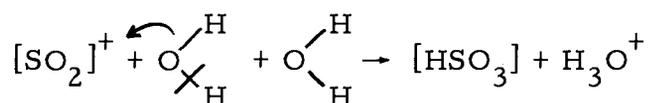
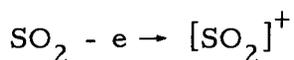
based primarily on the observation that dithionate production was greatly reduced when catalysts for hydrogen peroxide decomposition were added. Their argument was that dithionate could only be produced by H_2O_2 whereas sulfate could be produced by oxidation of sulfite with either H_2O_2 or its decomposition product, O_2 .

Bassett and Henry (5) objected to this interpretation on the basis that the reaction between hydrogen peroxide and sulfite produces little if any dithionate. These workers concluded that the electrochemical process was purely electron transfer. They suggested a mechanism similar to the homogeneous oxidation of sulfite. The SO_3^- ion surrenders either one or two electrons to the solid metal of the positive electrode instead of to a metal ion. If two SO_3^- ions each lose one electron and collide immediately after that event, a dithionate ion results. If, however, SO_3^- loses both electrons, sulfate is formed.

No further work was reported on the electrochemistry of the aqueous sulfite system until 1953, when Rozental' and Veselovskii (31) chose sulfite in 0.5F H_2SO_4 as one of several systems to investigate in order to determine the mechanism and kinetics of anodic processes at platinum electrodes. Using a rotating wire electrode, fairly reproducible limiting currents were obtained once an electrode had been "activated" by repeated voltage scans between 0.3 and 1.5 v (vs NHE). A chemical oxidation step between the oxide film on the anode and the dissolved sulfur dioxide was suggested. This was

based on the observation that the anodic oxide wave was enhanced with the introduction of sulfite. Differential capacitance and surface resistance data were later presented in support of this mechanism (8).

Shlygin and coworkers (6, 7, 22) disagreed with the oxide mechanism and suggested that the oxidation in acid solution involves direct electron transfer with a possible parallel oxidation process operating in the potential region where oxygen evolution occurs. They referred to the direct electron transfer as being an electron-radical process. The following scheme was proposed.



To support this mechanism, polarization curves were obtained (22). Small constant current steps were applied to a platinum electrode and the resulting potentials were recorded. It is noted that no concern was taken for preconditioning of the electrode. In .1F H_2SO_4 a 1 N sodium sulfite solution was oxidized and a curve was observed well before the presence of oxygen. This was strong evidence that the

mechanism is a direct electron transfer. They also proposed that it is $\text{SO}_2(\text{H}_2\text{O})$ and not HSO_3^- or $\text{SO}_3^{=}$ that undergoes the electron transfer. To prove this the same experiment was carried out in a basic solution (1 N KOH) in which little or no $\text{SO}_2(\text{H}_2\text{O})$ would be present. No wave occurred until after the formation of oxygen which indicated that the HSO_3^- and $\text{SO}_3^{=}$ ions were not capable of direct electron transfer but could be oxidized by the O_2 formed at higher potentials.

It is difficult to accept this conclusion since the data presented are not clear. Certainly an inactive electrode (which is likely without proper preconditioning) would produce the same results.

Seo and Sawyer (32) used voltammetric and chronopotentiometric techniques to study this S(IV) system at both platinum and gold electrodes. Before any meaningful results could be obtained a complete preconditioning process of the electrode was established. The most reproducible results were obtained in .1 F H_2SO_4 .

From voltammetric curves it was established that the oxidation of aqueous SO_2 at platinum and gold electrodes is similar and occurs by two mechanisms. Two waves were observed. The first wave occurred at potentials less positive than that required for oxide formation and therefore was ascribed to a pure electrochemical electron transfer process. The second wave occurred in the potential region for oxide formation and was interpreted as an enhancement of the oxide formation. It was suggested that this probably represents a

chemical reaction between the anodically formed oxide and sulfite species. This process seems to be in line with what Veselovskii had reported earlier.

Voltammetry was used primarily as a qualitative tool. It was noted, however, that the peak current was proportional to the concentration of the S(IV) species in the millimolar range.

Chronopotentiometric data provided some insight into the mechanism of the first process. The fact that no reverse wave was observed with current reversal indicated a totally irreversible process. From the constancy of $i\tau^{1/2}$ data the process was assumed to be diffusion controlled. The Sand equation was therefore applicable and upon using a value of $2 \times 10^{-5} \text{ cm}^2/\text{sec}$ for the diffusion coefficient, as given by Kolthoff and Miller (23), an n value of 2 was calculated.

Seo and Sawyer (32) applied a constant current and recorded the potential of the working electrode as a function of time. $E_{t=0}$ could be obtained by extrapolation of the potential-time curve to $t = 0$. A plot of $\log i$ vs $E_{t=0}$ gives a straight line with a slope equal to $-\frac{.059}{(1-\alpha)n_a}$ and an intercept proportional to the heterogeneous rate constant, k_s . From such data a $(1-\alpha)n_a$ value of .92 was reported. $(1-\alpha)$ is referred to as the transfer coefficient and can be thought of as a symmetry factor. It is usually given a value of .5. The value of n_a was therefore two, indicating that the rate determining step also involved two electrons. A heterogeneous rate constant of

5×10^{-13} cm/sec was reported for the reaction at a platinum electrode in .1 F H_2SO_4 , giving an indication of the irreversibility of the process.

In conclusion, the data was consistent with the direct oxidation of dissolved SO_2 to a S(VI) species which in turn reacts with water to form sulfate.

Work was done at pH's up to 5 in an attempt to identify the sulfur species undergoing oxidation. The authors make a weak attempt to show that the reacting species is actually SO_2 , in agreement with Shlygin, but admit that the results were too erratic to reach a more definitive conclusion.

The most recent work reported on the sulfite electro-oxidation is by Comtat and Maheng (11). They concerned themselves primarily with the region in which there appears to be a chemical reaction between the adsorbed oxygen on platinum and the sulfite species. Theoretical models were postulated to fit observed i - E curves based on adsorption theory.

Intent of Research

The electrochemical oxidation of aqueous SO_2 has been studied using various techniques and with varying degrees of sophistication. Experiments have ranged from examination of the electrochemical products to galvanostatic, voltammetric, and chronopotentiometric

techniques. In all cases the system has only been studied under a narrow set of conditions, and therefore only a partial picture can be uncovered.

One of the major problems in all of the earlier work has been the lack of an electrode that will give reproducible results. A logical step would be to consider an electrode material which is non-metallic in nature, since the problem of oxide formation should not be present. To this end, the electrode used in this study will be glassy carbon.

In recent years stationary electrode polarography has been developed both in theory and practice and has proven to be a most versatile technique to unravel mechanistic problems. The S(IV) system offers an excellent opportunity to utilize this new technique. Likewise, SEP can supply new and valuable data which will help in understanding the electrochemical oxidation of S(IV) more clearly.

It will therefore be the intent of this research to study the electrochemical oxidation of aqueous SO_2 at a glassy carbon electrode using stationary electrode polarography, and to supply a body of information which will aid in characterizing the system and the electrode reaction(s). The system will be studied by systematically varying the pH, total S(IV) concentration, and applied potential scan rate, and observing the corresponding behavior of the system under these varied conditions.

Glassy Carbon Electrode

There have been various carbon type electrodes introduced in the past decade. Among these, "glassy carbon" appears to be the most attractive. This material was first introduced by Yamada and Sato (37). An extensive review of its preparation, structure, properties, and uses is given by Noda, Yamada, and Inogaki (38). It is impervious, is highly resistant to chemical attack, and is obtainable in a relatively pure state. It is called "glassy carbon" because of its similarity to glass, both in appearance and conchoidal surface of fracture.

Glassy carbon was first considered as an electrochemical indicator electrode in 1965 by Zittel and Miller (26). They reported that the electrode had a very wide usable potential range. Reproducibility was excellent with the systems that they had studied. Since then, glassy carbon has been used in anodic stripping techniques involving analysis of Ag and Cu (24). It was also used in the study of the oxidation of organic systems (21). Recently, Alder (3) has studied some 30 different materials, ranging from metals to semiconductors, as possible electrodes for anodic voltammetry. It was concluded that glassy carbon was one of the best, offering excellent reproducibility and needing very little care.

Stationary Electrode Polarography

Stationary electrode polarography (or rapid scan voltammetry) is similar to ordinary polarography but differs in one very important way. While polarography functions in two dimensions of current and potential, rapid scan voltammetry adds the dimension of time.

It was only in the mid 1960's that the qualitative and quantitative aspects of this technique were compiled and elucidated in a series of papers by Shain and coworkers (27, 28, 35, 36).

This work will draw on the diagnostic criteria set forth by Nicholson and Shain (28) for interpretation of results. It is therefore necessary to consider their work in some detail. In order that a foundation be laid for understanding Nicholson's results, an introduction to the theory of rapid scan voltammetry follows. The simple case for the uncomplicated reversible charge transfer will be summarized, with no intention of a thoroughly rigid development, but simply an overview of the ideas and method of attack employed.

Reversible Charge Transfer

1. Introduction. Experimentally one applies a voltage, that varies linearly with time, to a microelectrode in an unstirred solution containing a low concentration of an electroreducible or oxidizable substance with a high concentration of an unreactive electrolyte. The

applied voltage can be of various waveforms such as a sawtooth or triangular wave. The corresponding current produced is monitored.

There are three modes of mass transfer possible in the process just described: electrical migration, convection, and diffusion. To simplify the theory, it is necessary to eliminate, or at least minimize, the first two processes so that only diffusion need be considered. Migration occurs when a current through a solution is carried by ions of the electroactive species. This is minimized experimentally by using a large excess of supporting electrolyte. Convection is minimized by not stirring the solution and by isolating the cell from mechanical vibration and thermal gradients. Diffusion arises from the normal thermal agitation of molecules, resulting in a net movement whenever a concentration gradient is present. This last process has been studied thoroughly and is described best by Fick's laws of diffusion.

The final current function arrived at in theory has been normalized, that is, the effects of scan rate, diffusion coefficients, concentration of depolarizer, electrode area, and number of electrons have been removed, leaving only the general shape of the current-potential function. It was necessary to do this in order to make the theory as general as possible, although it is often hard to relate one's experimental results to the normalized data.

The theory is developed considering a reduction reaction and it

will be presented in that fashion here.

2. The Initial and Boundary Conditions. Consider the following electrode reaction:



to take place at the surface of an electrode where diffusion is the only mode of mass transfer. Also, assume the electron transfer process is fast and reversible. Fick's laws will then govern the movement of species in the solution. The flux of the chemical species is given by Fick's 1st law.

$$\text{Flux g-mole/cm}^2 \text{ sec} = \frac{\partial N_O}{A dt} = D_O \left(\frac{\partial C_O}{\partial x} \right)_x \quad (2)$$

Since the process is reversible

$$D_O \left(\frac{\partial C_O}{\partial x} \right)_x = -D_R \left(\frac{\partial C_R}{\partial x} \right)_x \quad (3)$$

Fick's 2nd law can be written as

$$\left(\frac{\partial C_O}{\partial t} \right)_x = D_O \left(\frac{\partial^2 C_O}{\partial x^2} \right)_x \quad (4)$$

$$\left(\frac{\partial C_R}{\partial t} \right)_x = D_R \left(\frac{\partial^2 C_R}{\partial x^2} \right)_x \quad (5)$$

In order to calculate a theoretical model for stationary electrode

polarography, certain initial and boundary conditions have to be chosen. They are:

For $t = 0, x \geq 0$:

$$C_O = C_O^*; \quad C_R = C_R^* \cong 0 \quad (6)$$

For $t \geq 0, x \rightarrow \infty$:

$$C_O \rightarrow C_O^*, \quad C_R \rightarrow 0 \quad (7)$$

For $t > 0, x = 0$:

$$D_O \left(\frac{\partial C_O}{\partial x} \right)_{x=0} = -D_R \left(\frac{\partial C_R}{\partial x} \right)_{x=0} \quad (3a)$$

$$\frac{C_O}{C_R} = \exp \left[\frac{nF}{RT} (E - E^0) \right] \quad (8)$$

C_O and C_R are the concentrations of substances O and R, x is the distance from the electrode, t is the time, C_O^* and C_R^* are the bulk concentrations of O and R, D_O and D_R are the diffusion coefficients, n is the number of electrons, E is the applied potential of the electrode, E^0 is the formal electrode potential, and R , T , and F have their usual significance.

The necessary assumptions involved in Equations (1) and (2) were already stated. Equation (3) is a material balance expression equating rates of arrival and removal of material from the electrode

interface. Equations (4) and (5) assume semi-infinite linear diffusion, rapid equilibrium between O and R compared to diffusion rates, the solubility of O and R in the solution, and only diffusion as the mode of mass transfer. Equation (6) assumes homogeneous spatial distribution of O and R at the start of the experiment. Equation (7) implies that the cell is physically large enough that further extension would produce no observable effect on the process under consideration. Equation (8) is the Nernst relationship between potential and chemical equilibrium. This also implies a reaction rate much faster than the mass transfer rate.

3. Solutions and Results. For rapid scan voltammetry, the potential in Equation (8) is a function of time, given by

$$\begin{aligned} 0 < t \leq \lambda & \quad E = E_i - vt \\ t \geq \lambda & \quad E = E_i - 2v\lambda + vt \end{aligned}$$

where E_i is the initial potential, v is the scan rate in volts/sec, and λ is the time at which the scan is reversed (called switching potential).

If we substitute this into Equation (8), we obtain an abridged boundary condition:

$$C_O/C_R = \theta S(\lambda, t) \quad (9)$$

where

$$\theta = \exp[(nF/RT)(E_i - E^0)]$$

and

$$S(\lambda, t) = \begin{cases} e^{-at} & \text{for } t \leq \lambda \\ e^{-2a\lambda+at} & \text{for } t \geq \lambda \end{cases}$$

and $a = nFv/RT$.

For the cathodic scan only, t is always less than λ , and Equation (9) reduces to

$$C_O/C_R = \theta e^{-at}.$$

Nicholson and Shain continue on by applying Laplace transforms and combining the boundary and initial conditions to arrive at an integral equation which is then solved by numerical methods with the aid of a computer to give a current function versus a normalized potential in terms of $(E - E_{1/2})/n$. Further details can be found in Nicholson's thesis and its Appendices (29).

A table of current function vs normalized potential is constructed and from this table various relationships which characterize the system can be derived.

The current function, when multiplied by ordinary parameters of the electrode process, gives the current as a function of applied potential in the real world. The current equation is:

$$i = nFA\sqrt{aD_O} C_O^* \sqrt{\pi} x(at)$$

or

$$i = 602n^{3/2} A\sqrt{D_O v} C_O^* \sqrt{\pi} (at)$$

where n = the total number of electrons involved in the reaction,
 A = electrode area in cm^2 , D_O = diffusion coefficient for the reactant
 in cm^2/sec , v = the scan rate in volts/sec, C_O^* is the reactant con-
 centration in g-moles/l, and $a = nFv/RT$.

The development has dealt with the simple case of reversible charge transfer. Other cases, involving kinetic limitations and prior and post chemical reactions have been developed in an analogous manner by Nicholson and Shain. The final integral equations arrived at to describe a particular system were the result of modifications made in the diffusion equations and also the equations involving the initial and boundary conditions were either changed or altered. Out of the solution to these integral equations, current functions were tabulated as a function of a normalized potential. The diagnostic criteria arising from these current function tables is of much practical value in characterizing an unknown electrochemical system.

Nicholson presented the uncomplicated charge transfer situations (reversible and irreversible) together with various coupled chemical reactions as a series of eight cases. These are summarized in Table 1. Petcoff provides an excellent review of these eight cases (30).

Table 1. The eight cases for stationary electrode voltammetry.

Case	Reaction	Description
I	$O + ne \rightleftharpoons R$	Uncomplicated reversible charge transfer
II	$O + ne \xrightarrow{k} R$	Uncomplicated irreversible charge transfer
III	$Z \xrightleftharpoons[k_b]{k_f} O$ $O + ne \xrightleftharpoons{k} R$	Preceding reversible chemical reaction, reversible charge transfer
IV	$Z \xrightleftharpoons[k_b]{k_f} O$ $O + ne \xrightarrow{k} R$	Preceding reversible chemical reaction, irreversible charge transfer
V	$O + ne \rightleftharpoons R$ $R \xrightleftharpoons[k_b]{k_f} Z$	Reversible charge transfer followed by a reversible chemical reaction
VI	$O + ne \rightleftharpoons R$ $R \xrightarrow{k_f} Z$	Reversible charge transfer followed by an irreversible chemical reaction
VII	$O + ne \rightleftharpoons R$ $R + Z \xrightarrow{k_f} O$	Catalytic reaction with reversible charge transfer
VIII	$O + ne \xrightarrow{k} R$ $R + Z \xrightarrow{k_f} O$	Catalytic reaction with irreversible charge transfer

Throughout the discussion, reference will be made to Cases II and IV which involve a totally irreversible charge transfer (both the uncomplicated situation and the situation in which a chemical reaction precedes the electron transfer).

The term irreversibility should be clarified. If the electron transfer rate is much faster than the rate of mass transfer during an electrode reaction, then a polarogram of the reaction is said to be reversible. If the electron transfer rate is slow enough to affect the shape of the wave (due to the overpotential needed to accelerate the electron transfer rate), then a condition of quasi-reversibility occurs. Finally, if the electron transfer rate is very slow, it will be the limiting factor for all scan rates, and the reaction is said to be totally irreversible. Case II and IV are concerned with a totally irreversible system.

Perhaps the easiest test for total irreversibility is to run a cyclic scan and observe whether or not a wave occurs during the reverse scan. If there is no reverse wave, then the system can be considered totally irreversible. If it is quasi-reversible, a wave will appear, but its peak will be displaced from the potential at the peak of the forward scan wave.

The effects of adsorption on polarographic waves should be mentioned, for the effects are often similar to electron-transfer phenomena and might easily cause misinterpretation of data. According to

Wopschall and Shain (35, 36), two general situations can occur: the product or reactant can be weakly adsorbed, or they can be strongly adsorbed.

Wopschall warns that the presence of adsorption is not always easy to detect. Strong adsorption is usually obvious, but weak adsorption can easily be mistaken for coupled chemical reactions or capacitive current. Two characteristics of adsorption enable its detection. The first is the behavior with scan rate.

The adsorbed material is usually a relatively fixed amount giving a fixed charge flow. At fast scan rates, adsorption can predominate. A plot of i_p versus the square root of scan speed will deviate from a straight line and begin curving upwards at higher scan rates. For a purely adsorptive peak, i_p/v is almost constant.

The second characteristic of adsorption enabling its detection is its dependence upon concentration. While i_p/C^* is constant for many processes, this ratio will usually increase with decreasing concentration when adsorption is present.

II. EXPERIMENTAL

Reagents

Potassium Ferrocyanide Solutions

A 0.0100 F potassium ferrocyanide solution was prepared by dissolving 0.4216 grams of ACS reagent grade $K_4Fe(CN)_6 \cdot 3H_2O$ in 1.0 M KCl, previously deaerated for half an hour, and brought up to the mark with a 100 ml volumetric flask. The solution was used immediately upon preparation to obtain effective surface area data.

Sodium Sulfite Solutions

A stock solution was prepared by dissolving 2.9180 grams of ACS reagent grade anhydrous Na_2SO_3 in distilled water, previously deaerated for half an hour, and brought up to the mark with a 100 ml volumetric flask. The stock solution was stored in a glass container kept stoppered except when drawing solution. The solution was standardized each day before use by a simple iodometric titration as outlined in Appendix 1.

Britton and Robinson Buffers

In order to study the aqueous sulfur dioxide system under a wide range of pH's, a versatile wide range buffer system is desired.

One of the most useful buffers for this purpose is the Britton and Robinson buffer. It has a range from pH 1.8-12.0, and it consists of a mixture of phosphoric, boric, and acetic acids to which varying amounts of NaOH are added to adjust the pH to a desired level. The ionic strength of this buffer changes noticeably as the pH is varied. Fregoni (14) made an in depth study of this system and supplied the necessary information to maintain the ionic strength at a constant level by adding an appropriate amount of KCl.

The ionic strength in this research was held constant at 1.0.

Apparatus

The Indicator Electrode

1. The Material. Glassy carbon is one of a host of glass-like carbons that are commercially available. All of these glass-like carbons have nearly identical properties, the only difference being in the exact preparation of the material. They all start with a thermo-setting resin such as furfuryl alcohol or phenolformaldehyde. The resin is formed to the desired shape by various techniques and allowed to dry. It is then put through a thermal carbonization process, and the charred material resulting is the glasslike carbon.

The two types of glass-like carbons thus far cited in the electrochemical literature are glassy carbon and vitreous carbon. Glassy

carbon is available in various grades from the Tokai Electrode Mfg. Co. Ltd., Japan. They also have a subsidiary in the United States called International Carbon Corporation.¹ Vitreous carbon is manufactured by Vitreous Carbons Ltd., England. The material is available in the United States through the Beckwith Carbon Corporation.²

Both of these electrode materials have been used in this laboratory and as would be expected, they show qualitatively very similar electrochemical characteristics. However, the data reported in this thesis pertain only to glassy carbon. The grade of glassy carbon used was GC-20 and was in the form of a rod.

2. Construction of the Electrode. A small hole, one mm in diameter and one mm deep, is drilled in both ends of a 2 mm diameter brass rod that is 4 mm in length. At one end a small length of glassy carbon rod (.9 mm diam.) is soldered. At the other end of the brass rod, a copper wire is soldered which is extended upwards 8 inches. This assembly is then centered inside a glass tube (7 mm ID), which has been coated with resin release, and the whole assembly is cast with a commercially available polyester casting resin. Once the resin has set up, it shrinks away from the glass tubing, leaving a rod. The end of the rod is ground down roughly until the glassy carbon

¹Address: 245 Park Ave., New York, N. Y. 10017.

²Address: 16140 Raymer St., Van Nuys, Calif. 91406

surface is flush with the resin. The surface is then ground with various grades of silicon carbide powder and finally with 600 grit SiC paper. A well defined planar surface is established with a geometric area of $.0063 \pm .0010 \text{ cm}^2$. The surface area was determined by rotating the electrode and measuring the diameter of the glassy carbon rod at various positions with a Bausch and Lomb 7x comparator with .1 mm reticles. Taking an average of the readings, an area was then computed. The resistance between the electrode surface and the wire lead was measured with a Fairchild DVM (Model 7050) and found to be less than one ohm.

3. Conditioning of the Electrode. After grinding the surface of electrode with 600 grit SiC paper, it was placed in a buffered solution at pH 7 with mM sulfite present. The voltammetric wave was observed. The wave continually shifted, rapidly at first and much more slowly with time until after a period of time ranging between 5 hours to a day, the wave observed was reproducible. The i_p was considerably higher at first, indicating that more surface area was available at the beginning. The same observations were made when the electrode was kept in distilled water between runs and even when it was kept in the open air, although in the latter case it was a much slower process and the wave never completely stabilized. This might have been caused by contamination of the electrode surface being in the air.

This "aging" phenomenon observed could be the result of a reorientation of the surface molecules after grinding, which would give a different double layer structure as well as surface area until an equilibrium had been reached.

It was noted that once this "aging" had taken place, no other preconditioning was needed. Results were very reproducible from run to run as well as from day to day.

When a run was made and the electrode washed with distilled water and then another run made, the two waves observed were reproducible in most cases to the width of the pen trace. Monitoring the same wave (oxidation of SO_2 at pH 7) over a period of a week, the i_p/C values varied by 5%. The peak and half peak potentials varied by about the same amount. This degree of reproducibility was never accomplished with a platinum electrode, even with elaborate preconditioning techniques.

The electrode was stored in distilled water when not in use.

4. Effective Surface Area of the Electrode. To ascertain the effective working area of the electrode, the oxidation of $\text{Fe}(\text{CN})_6^{4-}$, as $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ in 1 M KCl was studied chronoamperometrically. A constant potential was applied to the electrode, which was well anodic of the polarographic peak for the reaction, and the resulting current decay curve was monitored. If the measured current is controlled by semi-infinite linear diffusion, the following equation can be

used:

$$A = \frac{it^{1/2} \pi^{1/2}}{nFCD^{1/2}} \quad (10)$$

where:

A = electrode area, cm^2

i = current, amp

t = time, sec

n = g mole \bar{e} / g mole reactant

F = faraday, coulombs / g mole $^{-}$

C = concentration, g moles / ml

D = diffusion coefficient, cm^2/sec

In order for this to be the case, an electrode must really be shielded. Adams (2, p. 43-61) showed, however, that this condition is approached by simply using an electrode in which the surface of the electrode is flush with its insulating boundary. The $it^{1/2}$ product will not be constant, but will increase slightly with time. One simply has to extrapolate back to $it^{1/2}$ at $t = 0$ in order to use working Equation (10). Another assumption that must be made is that the iron species be related to the sulfite species of interest so that the effective surface area for both is the same.

The effective surface area was calculated from four different runs and was determined to be $.0073 \text{ cm}^2$ with an average deviation of $.0005$. This is compared to the geometric area of $.0063 + .0010 \text{ cm}^2$.

It is not surprising that the effective area is larger, since the electrode surface is rough. Adams shows that as one increases the roughness of the surface, the effective area goes from being less than the geometric area to as much as 20% larger (2, p. 58).

The Cell

A diagram of the cell used in this work is given in Figure 1. It is a modification of the conventional H-cell design. The working electrode compartment is separated from the reference electrode compartment by a coarse frit and a saturated KCl agar bridge, while it is separated from the auxiliary electrode compartment by a fine frit. Efficient deaeration of the solution is accomplished by passing prepurified nitrogen through the fine frit at the bottom of the working compartment. Nitrogen can also be passed over the top of the solution by diverting the flow of nitrogen, via a two-way stopcock, through an opening at the top of the cell compartment. This allows one to keep a nitrogen atmosphere over the anolyte at all times. The working compartment is small enough so that 5 ml of solution will fill it up to the top of the frits.

Platinum gauze, dipped in 1 M KCl, served as the auxiliary electrode.

The reference electrode was a saturated calomel electrode and was constructed according to Meites (25, p. 63), but scaled down to

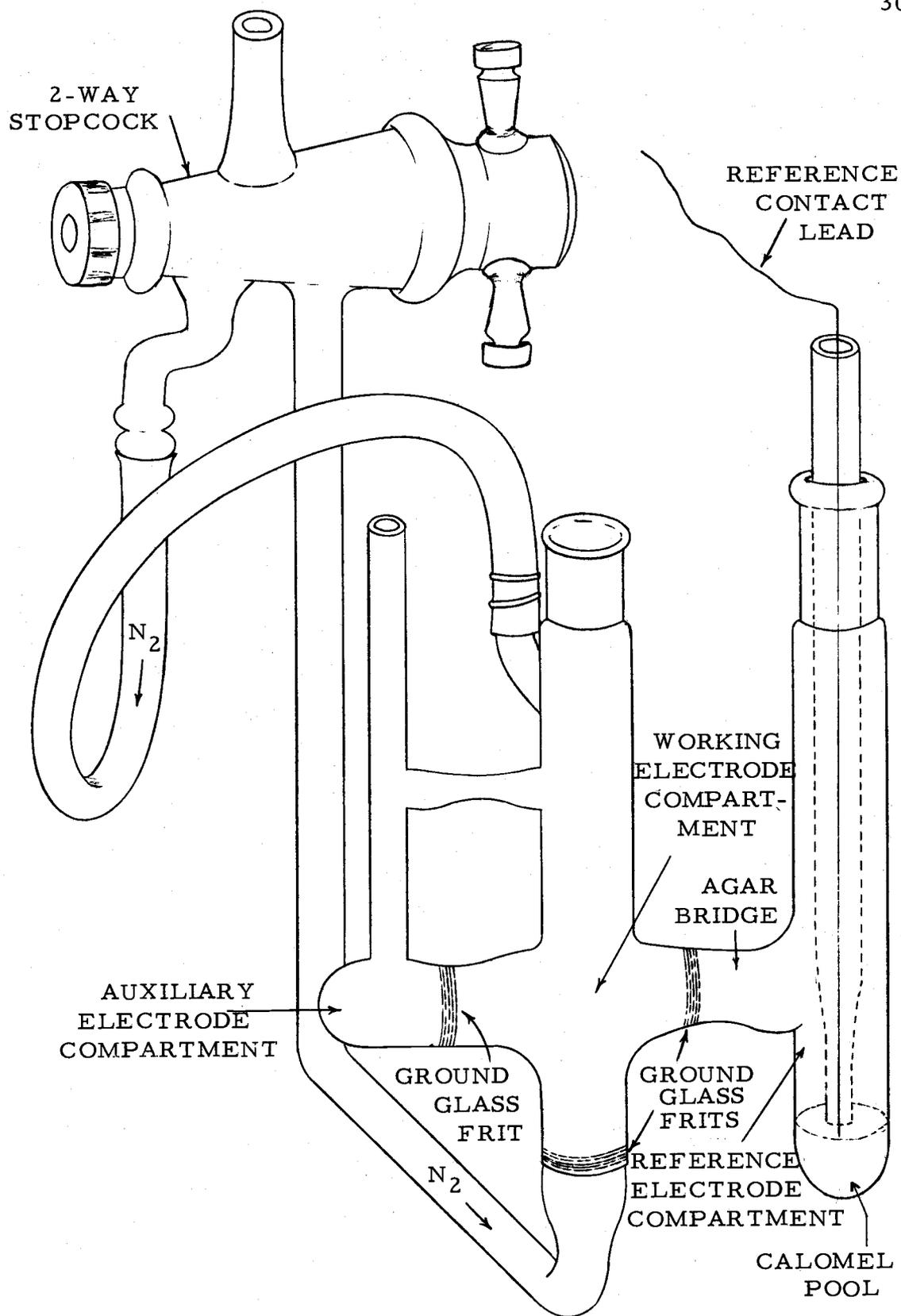


FIGURE 1. VOLTAMMETRIC CELL ASSEMBLY.

comply with the size of the reference compartment. The agar bridge was also constructed by following Meites instructions. The reference compartment was sealed and contact was made by dipping a platinum wire, sealed in glass tubing, into the calomel pool.

The cell resistance was measured to be 100 ohms, using a typical a. c. bridge measurement. An a. c. signal (1 KHz, 1 volt p to p) was applied between the working and auxiliary electrodes, and a null was established using a Heathkit impedance bridge. A Tektronix oscilloscope (Type 564) was used to observe the null.

Instrumentation

The versatile Heath Polarographic Unit was used for both voltammetric and chronoamperometric work. It consists of: Heath Operational Amplifiers (EUW-19B); Heath Chopper Stabilizers (EUA-19-4); and the Heath Polarographic Module (EUA-19-2).

The unit offers a range of potential scan rates from .05 v/min to 2 v/min. It also allows one to dial in a desired constant potential which can be applied across the cell. Scan rates from .2-2 v/min were calibrated and found to be very stable over a long period of time. For faster scan rates the Chemtrix Polarographic Time Base (Type 205) was used. This time base was connected to the Heath unit via auxiliary input jacks and used in place of the Heath potential scan for scan rates of .1, .2, and .5 v/sec. These were also calibrated and

found to be stable. For scan rates up to 10 v/sec the Chemtrix Polarographic Time Base was used with the Chemtrix current to voltage amplifier (Type 300). The trace was displayed on a tektronix storage oscilloscope (Type 564).

One minor modification was made. A .0047 uf capacitor was placed in parallel with the feedback resistor of the current to voltage operational amplifier of the Heath unit. The capacitor had the effect of attenuating the a. c. gain thereby reducing the a. c. noise in the signal. Runs were made both with and without the capacitor with the only noticeable difference being a major reduction in the noise level.

A Varian X-Y Plotter (Model F-80) was used as the recording instrument. The X axis monitored the potential applied between the working and reference electrodes, while the Y axis monitored the output signal from the Heath unit, which was proportional to the current flowing at any time. The X-Y Plotter also has its own time base which was calibrated and used in the chronoamperometric work. The input impedance to the X-Y Plotter is finite (2 megohms) and it was necessary to use only the 10 v output jack of the Heath unit. This has an output impedance of less than one ohm as compared to the 100 mv output jack which offers an output impedance of a megohm.

Temperature control was maintained by using a Blue M-Microtrol constant temperature bath. The temperature of the cell was maintained at $25 \pm .1^{\circ}\text{C}$.

pH measurements were taken with a Beckman Zeromatic pH Meter using the Beckman glass electrode and SCE. Standard buffer solutions, made from Coleman certified buffer tablets (good to $\pm .01$ pH at 25°C), were used for calibration of the instrument.

Experimental Procedure

Stationary Electrode Polarography

The temperature and ionic strength of the system were held constant throughout this work, while the pH, total SO₂ concentration, and potential scan rate were varied in a systematic fashion.

First, the working cell compartment was thoroughly cleaned by flushing with distilled water. Then 5 ml of a buffer, whose pH had been measured, was delivered to the cell by means of a calibrated pipet. The solution was deaerated with prepurified nitrogen for 5 minutes to remove all oxygen. Background curves were taken at the glassy carbon electrode in this electrolyte at all the various potential scan rates (3.32-500 mv/sec). Then 10 μ l of the standardized sulfite solution were introduced into the cell using a 100 μ l syringe³ (accurate to ± 1 μ l). The solution was stirred by means of a rod pushed up and down. Voltammetric waves were then obtained for the SO₂ species at

³Hamilton Co., No. 710.

increasing potential scan rates. Once all the scans had been run, 15 more μl of the sulfite solution were added to the cell, making a total of 25 μl of the sulfite species. Again the scans were made. This procedure was repeated adding 50 μl and then 75 μl of the sulfite solution to the cell. Once all the runs had been made, the solution was sucked out and the cell thoroughly flushed out with distilled water. The same procedure was followed for various pH's by simply changing the buffer solution used as the electrolyte.

Chronoamperometric Determination of Diffusion Coefficients

If the SO_2 system is controlled by semi-infinite linear diffusion, then Equation 10, which is used to determine electrode area can also be applied in determining an unknown diffusion coefficient if everything else in the equation is known. The following procedure was adopted for obtaining the necessary data.

A potential is selected which is well past the peak observed for the electrode reaction at a particular pH. This potential is dialed in on the Heath unit. The Varian X-Y plotter is used in the Y-time mode with a time base of 5 sec/in. The current-decay curve produced by applying a constant potential across the cell is thus recorded.

Five ml of a buffer are delivered to the cell using a 5 ml pipet. The solution is deaerated for 5 minutes and then a background i-t

curve is obtained. Then 75 μl of the standardized sulfite solution are added to the cell using the 100 μl syringe and the solution is stirred. Then the i-t curve is obtained.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Before any quantitative studies were attempted on this system, a general qualitative picture was obtained by observing cyclic fast scan polarograms at pH 7.0. Only one wave corresponding to the oxidation of the S(IV) species was observed, with no cathodic wave observed for the reverse scan. The wave shifted anodically with increasing scan rate. One can reach a general conclusion in comparing the above observations with Nicholson's various cases, that the reaction appears to be a totally irreversible charge transfer, which is in agreement with Sawyer's conclusions.

However, the chemical system comprising the S(IV) species is complex, as already mentioned, and at least three distinct S(IV) species are present in solution, any or all of which may react at the electrode surface to produce a polarographic wave. The kinetic parameters such as $(1-\alpha)n_a$ and k_s (the heterogeneous rate constant), as well as the overall number of electrons involved in the reaction, n , have been reported at rather specific conditions, at a platinum electrode. The results do not appear to be conclusive.

In order to get a more complete picture of the behavior of this S(IV) system, the pH, total S(IV) concentration, and scan rates were varied systematically as described in the experimental section and the corresponding peak potentials, half peak potentials, and peak

currents were recorded.

The results are presented in Tables 2-8. All of the results are listed in an attempt to provide as complete a body of data as possible. The background was always subtracted from the experimental curve to give a corrected curve from which recorded values were taken. The peaks observed, especially at the lower pH's were very rounded and therefore the peak potentials could be read to no better than ± 20 mv. The peak currents could be read much more accurately and the corresponding half peak potentials (E_p at $i_p/2$) are therefore much more reliable.

It is of interest to note that the peak current is directly proportional to the concentration of the S(IV) species in solution at all pH's at concentrations from .5 to 6 millimolar. The peak current is also directly proportional to the square root of the scan rate up to the fastest scan rate presented of .5 v/sec.

From Tables 2-8, it is seen that the half peak potential is a function of the pH. As the pH increases, the half peak potential appears at less anodic potentials, indicating that the oxidation becomes easier. A shift is no longer observed at pH's above 7.

To explain this, let us assume that only the SO_3^- species is involved in the electron transfer reaction. The following general scheme can be proposed:

Table 2. Summary of voltammetric results at pH = 1.8.

Scan Rate v/sec	Conc. mM S(IV)	E_p Volts vs SCE	$E_{p/2}$ Volts vs SCE	i_p μ_a
.51	1.14	.950	.755	3.24
	3.40	.975	.728	13.75
	6.70	1.025	.770	23.55
.10	1.14	.855	.683	2.09
	3.40	.885	.678	6.64
	6.70	.995	.710	11.75
.033	.46	.800	.565	.61
	1.14	.825	.630	1.30
	3.40	.888	.658	4.00
	6.70	.935	.700	7.32
.0167	.46	.800	.595	.42
	1.14	.830	.624	.98
	3.40	.875	.655	2.90
	6.70	.920	.680	5.70
.0083	.46	.775	.580	.32
	1.14	.818	.608	.77
	3.40	.875	.638	2.40
	6.70	.900	.665	4.48
.0033	.46	.800	.562	.26
	1.14	.850	.591	.67
	3.40	.865	.634	1.77
	6.70	.905	.642	3.71

Table 3. Summary of voltammetric results at pH = 2.8.

Scan Rate v/sec	Conc. mM S(IV)	E_p Volts vs SCE	$E_{p/2}$ Volts vs SCE	i_p μ_a
.51	.38	.838	.645	1.76
	.92	.882	.685	2.48
	2.84	.895	.674	9.90
	5.40	.945	.706	18.40
.20	.38	.805	.616	1.15
	.92	.845	.620	2.18
	2.84	.870	.640	7.00
	5.40	.905	.670	13.10
.10	.38	.745	.600	.65
	.92	.795	.590	1.69
	2.84	.845	.630	5.00
	5.40	.870	.645	9.50
.033	.38	.745	.522	.50
	.92	.782	.570	.98
	2.84	.820	.588	3.02
	5.40	.849	.617	5.90
.0167	.38	.732	.535	.34
	.92	.780	.550	.76
	2.84	.810	.582	2.30
	5.40	.832	.600	4.60
.0083	.38	.725	.513	.28
	.92	.795	.542	.61
	2.84	.800	.570	1.83
	5.40	.820	.580	3.68
.0033	.38	.732	.505	.20
	.92	.772	.510	.37
	2.84	.835	.571	1.42
	5.40	.960	.575	3.13

Table 4. Summary of voltammetric results at pH = 4.0.

Scan Rate v/sec	Conc. mM S(IV)	E_p Volts vs SCE	$E_{p/2}$ Volts vs SCE	i_p μ_a
.51	.56	.765	.522	2.24
	1.14	.777	.590	3.10
	3.40	.840	.648	11.90
	6.68	.930	.615	22.75
.10	.46	.690	.460	.94
	1.14	.740	.524	1.60
	3.40	.765	.535	5.65
	6.68	.850	.560	11.20
.033	.46	.675	.465	.54
	1.14	.690	.490	.98
	3.40	.740	.505	3.48
	6.68	.815	.532	6.85
.0167	.46	.665	.450	.42
	1.14	.687	.468	.78
	3.40	.715	.486	2.69
	6.68	.790	.514	5.40
.0083	.46	.668	.438	.32
	1.14	.690	.452	.65
	3.40	.740	.485	2.14
	6.68	.785	.498	4.35
0.0033	.46	.677	.424	.24
	1.14	.690	.440	.53
	3.40	.735	.460	1.59
	6.68	.805	.495	3.45

Table 5. Summary of voltammetric results at pH = 5.5.

Scan Rate v/sec	Conc. mM S(IV)	E_p Volts vs SCE	$E_{p/2}$ Volts vs SCE	i_p μ_a
.51	.45	.715	.460	1.80
	1.13	.700	.496	4.00
	3.31	.725	.524	15.00
	6.52	.763	.495	21.55
.20	.45	.687	.440	1.47
	1.13	.675	.450	3.05
	3.31	.700	.464	8.60
	6.52	.735	.470	14.00
.10	.45	.625	.427	1.00
	1.13	.640	.428	2.14
	3.31	.674	.428	6.25
	6.52	.724	.434	10.00
.033	.45	.550	.385	.60
	1.13	.575	.398	1.28
	3.31	.623	.397	3.80
	6.52	.690	.402	6.58
.0167	.45	.525	.365	.39
	1.13	.565	.377	1.04
	3.31	.600	.382	2.88
	6.52	.672	.392	5.10
.0083	.45	.525	.352	.33
	1.13	.550	.363	.83
	3.31	.625	.380	2.26
	6.52	.665	.384	4.00
.0033	.45	.550	.337	.25
	1.13	.575	.354	.65
	3.31	.650	.350	1.70
	6.52	.735	.380	3.44

Table 6. Summary of voltammetric results at pH = 7.0.

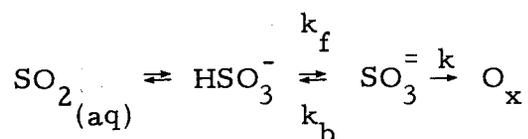
Scan Rate v/sec	Conc. mM S(IV)	E_p Volts vs SCE	$E_{p/2}$ Volts vs SCE	i_p μ_a
.51	1.02	.525	.355	2.30
	3.04	.525	.347	9.80
	6.00	.575	.375	19.80
.10	.41	.426	.280	.95
	1.02	.430	.300	1.04
	3.04	.482	.318	4.96
	6.00	.550	.335	11.20
.033	.41	.375	.276	.42
	1.02	.425	.296	.71
	3.04	.450	.293	3.08
	6.00	.500	.311	6.33
.0167	.41	.387	.266	.29
	1.02	.400	.278	.60
	3.04	.435	.285	2.30
	6.00	.500	.300	4.84
.0083	.41	.370	.225	.22
	1.02	.405	.257	.56
	3.04	.435	.275	1.82
	6.00	.495	.286	3.85
.0033	.41	.400	.245	.13
	1.02	.400	.255	.42
	3.04	.450	.273	1.35
	6.00	.525	.280	2.98

Table 7. Summary of voltammetric results at pH = 8.4.

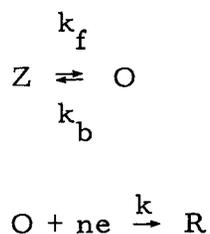
Scan Rate v/sec	Conc. mM S(IV)	E_p Volts vs SCE	$E_{p/2}$ Volts vs SCE	i_p μ_a
.51	.44	.550	.365	1.84
	1.08	.511	.337	4.48
	3.22	.508	.339	13.00
	6.34	.530	.350	18.85
.20	.44	.512	.338	1.33
	1.08	.488	.337	3.02
	3.22	.480	.325	8.84
	6.34	.512	.337	13.25
.10	.44	.462	.315	.78
	1.08	.474	.334	2.06
	3.22	.462	.310	6.18
	6.35	.483	.318	9.70
.033	.44	.410	.290	.44
	1.08	.427	.308	1.20
	3.22	.425	.284	3.76
	6.34	.460	.297	6.08
.0167	.44	.400	.273	.38
	1.08	.410	.287	.97
	3.22	.408	.270	2.71
	6.34	.440	.283	4.68
.0083	.44	.381	.258	.30
	1.08	.402	.278	.76
	3.22	.400	.266	2.00
	6.34	.416	.270	3.64
.0033	.44	.380	.250	.22
	1.08	.400	.258	.56
	3.22	.400	.255	1.44
	6.34	.450	.194	2.81

Table 8. Summary of voltammetric results at pH = 10. 1.

Scan Rate v/sec	Conc. mM S(IV)	E_p Volts vs SCE	$E_{p/2}$ Volts vs SCE	i_p μ_a
.51	1.08	.462	.345	3.80
	3.16	.488	.358	11.60
	6.20	.481	.350	25.25
.20	.43	.438	.320	1.36
	1.08	.450	.338	2.35
	3.16	.470	.342	8.24
	6.20	.458	.335	17.85
.10	.43	.437	.315	1.04
	1.08	.447	.317	2.35
	3.16	.450	.324	6.48
	6.20	.447	.319	12.92
.033	.43	.400	.304	.46
	1.08	.405	.295	1.26
	3.16	.421	.300	3.88
	6.20	.410	.290	7.75
.0167	.43	.387	.283	.41
	1.08	.388	.280	1.02
	3.16	.402	.284	2.94
	6.20	.398	.280	5.83
.0083	.43	.375	.270	.31
	1.08	.383	.268	.74
	3.16	.392	.278	2.26
	6.20	.382	.273	4.50
.0033	.43	.360	.258	.22
	1.08	.374	.255	.56
	3.16	.380	.265	1.69
	6.20	.378	.260	3.28



Nicholson's Case IV involves a chemical reaction preceding an irreversible charge transfer. In this case the electroactive species is produced by a homogeneous first order (or pseudo first order) chemical reaction.



According to Nicholson, the resulting χ function arrived at by solving the integral expression for this system is quite complex.

$$\begin{aligned} \chi(\text{bt}) = & \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \left[\frac{(\sqrt{\pi})^j}{\sqrt{(j-1)!}} \prod_{i=1}^{j-1} \left(1 + \frac{\sqrt{1}}{K\sqrt{\ell/b+i}} \right) \right] \\ & \times \exp \left[- \frac{j a n F}{RT} (E - E^0 + \frac{RT}{a n F} \ln \frac{\sqrt{\pi D} \text{O}}{k_s} - \frac{RT}{a n F} \ln \frac{K}{K+1}) \right] \end{aligned}$$

Three distinct limiting situations can be recognized which allow one to reduce this complex function to simpler terms. These limiting cases are describable in terms related to the scan rate, rate constants, and equilibrium constant.

The first term is b , which is defined by:

$$b = nFv/RT$$

The second term is l , which is the sum of the forward and reverse rate constants for the chemical reaction:

$$l = k_f + k_b$$

The last term involves the first two plus the equilibrium constant K , for the preceding chemical reaction.

$$\psi = \sqrt{b/Kv}$$

For the first limiting situation, l/b is very small, i. e., the scan rate is much faster than the chemical reaction rate. The resulting wave has the same shape as Case II (uncomplexed irreversible charge transfer); its potential is unaffected by the kinetic complication, and the magnitude of the current is a function of the equilibrium concentration of O, which depends on K .

The other two limiting cases can be obtained by first assuming that l/b is large. Then, if ψ is small, the wave is again that for Case II, except that the potential at which the wave occurs is shifted by the equilibrium constant. The term describing the shift is

$$-\frac{RT}{\alpha n_a F} \ln \frac{K}{K+1}.$$

Finally, for large ψ , the wave flattens out and both the potential and magnitude of the current become independent of scan rate.

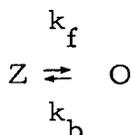
Nicholson points out that there is a wide range between these last two limiting cases, and he solved the χ function for several intermediate ψ values.

The first limiting case in which l/b is small certainly would not apply to the S(IV) system, since acid dissociations are considered extremely fast and l would be very large.

The second limiting case in which l/b is large and ψ is small seems much more likely. As already mentioned, the potential at which the wave appears is affected by the term

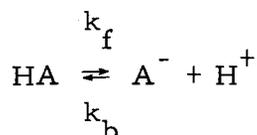
$$-\left(\frac{RT}{anF}\right) \ln \frac{K}{K+1}$$

It is noted that K is the equilibrium constant for a first order chemical reaction



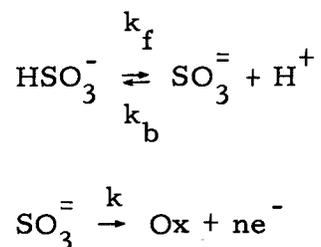
where $K = \frac{[O]}{[Z]}$ and the species, O , undergoes a further electrochemical reaction.

For an acid dissociation the reaction is first order, in the forward direction and pseudo first order in the reverse direction if the system is buffered.



Nicholson's K would only apply if $[H^+]$ were held constant, so that the ratio $\frac{[A^-]}{[HA]}$ would be fixed by the equilibrium constant. Clearly, Nicholson's K is a function of pH for the S(IV) system and must be modified to apply.

The following model will be considered:



According to Nicholson's treatment,

$$K = \frac{[\text{SO}_3^{=}]}{[\text{HSO}_3^-]}$$

The actual K_a is:

$$K_a = \frac{[H^+][\text{SO}_3^{=}]}{[\text{HSO}_3^-]} = 6.4 \times 10^{-8}$$

It follows that

$$K = K_a / [H^+]$$

Substituting this new value for K into the expression

$-(RT/F) \ln \frac{K}{K+1}$ gives:

$$-(RT/F) \ln \frac{K_a}{K_a + [H^+]}$$

which is applicable to this system (αn_a was left out to normalize the expression).

If the acid concentration is much less than K_a , the above term falls to zero and there should be no more shift. At high acid concentrations the above term would reduce to

$$-(RT/F)(\ln K_a + \text{pH})$$

which predicts a linear shift with pH.

A theoretical plot of pH versus $-(RT/F) \ln K_a / K_a + [H^+]$ (at 25°C) is shown in Figure 2. A value for αn_a (or $(1-\alpha)n_a$ in this case) of 1 was assumed. A linear shift with pH is noted up to pH 6.5 with a slope of $-.059 \text{ v/pH}$. At higher pH's the potential approaches a constant value.

This is in good agreement with the experimental results. Figure 3 shows a plot of $E_{p/2}$ vs pH at constant scan rate and concentration of S(IV) species. At the lower pH's a linear shift is observed with a least squares slope ranging from $-.060$ to $-.075 \text{ v/pH}$, the slope increasing as the concentration of the S(IV) species was increased. At higher pH's (above 7), the $E_{p/2}$ values remain fairly constant, which is consistent with the theory.

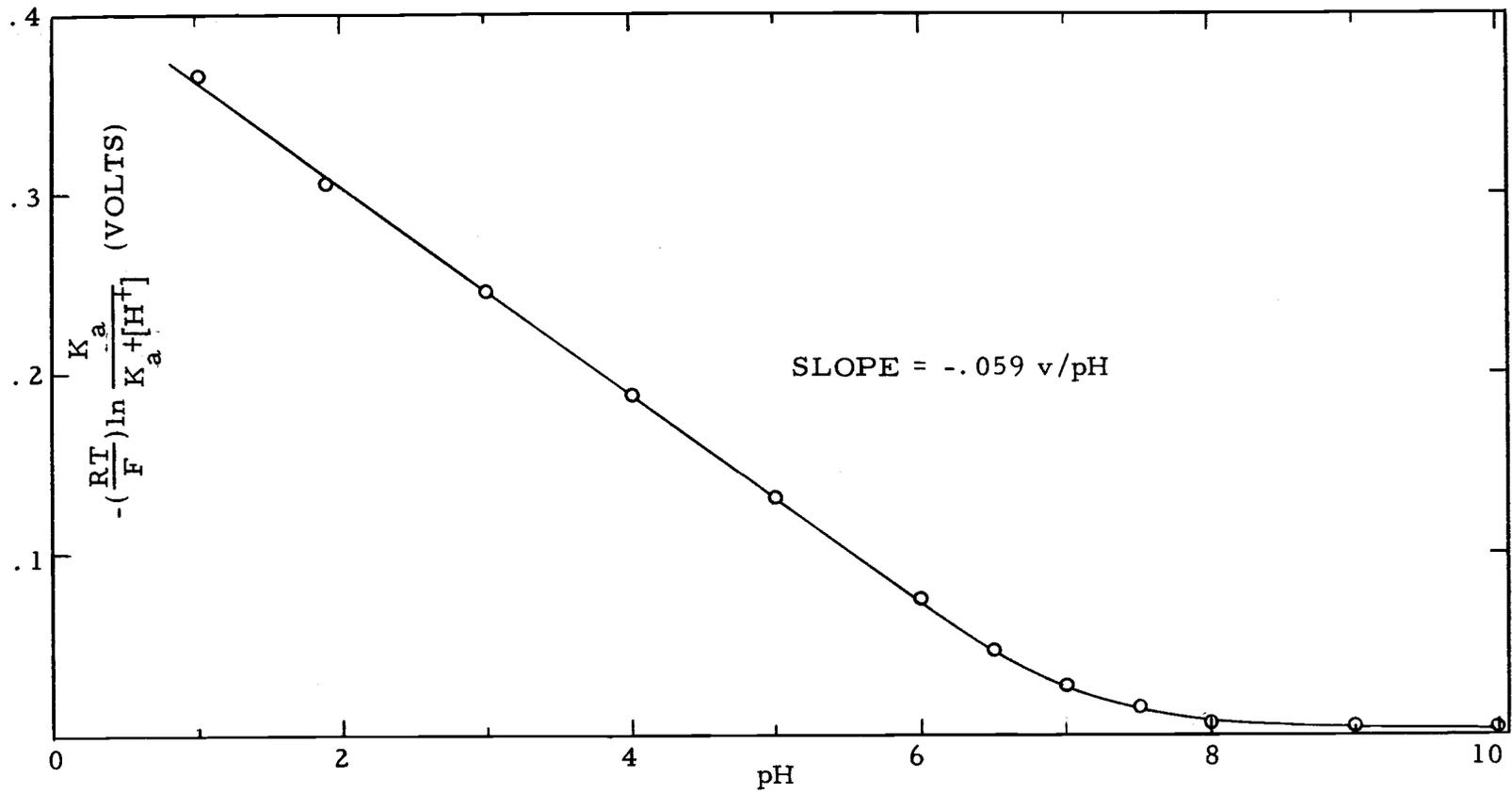


FIGURE 2. THEORETICAL POTENTIAL SHIFT VERSUS pH AT 25°C.

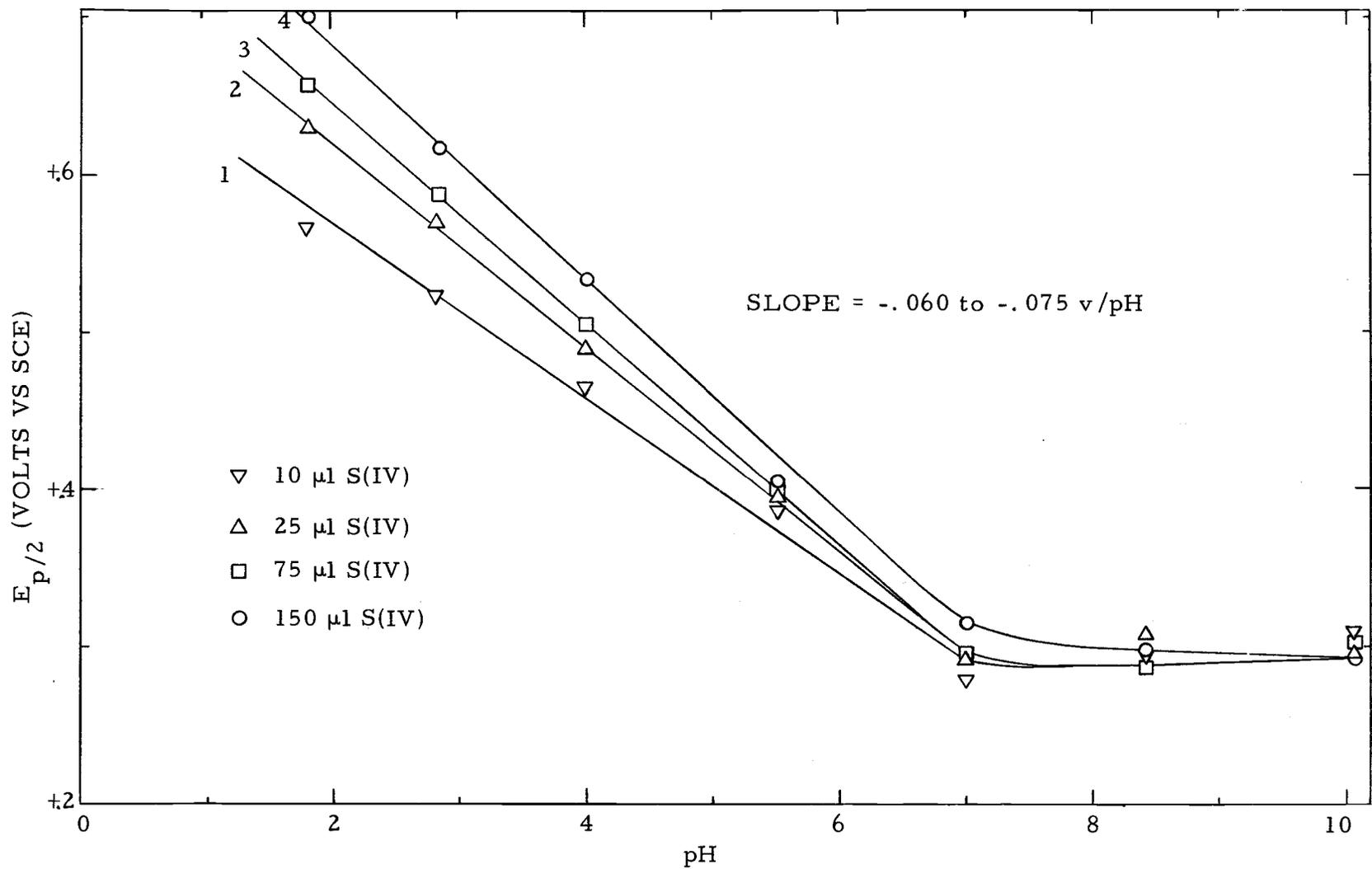
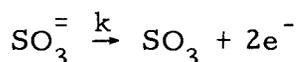


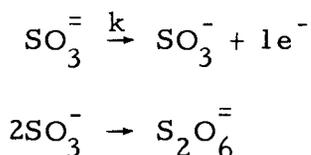
FIGURE 3. EXPERIMENTAL HALF PEAK POTENTIAL VERSUS pH AT A CONSTANT SCAN RATE OF .033 v/sec AND CONSTANT CONCENTRATION OF S(IV).

The fact that the slope is increasing with increasing concentration of S(IV) species indicates that $(1-\alpha)n_a$ is changing and suggests that possibly the mechanism of the electrode reaction is changing.

At the lowest concentration (around .5 mM S(IV)) the slope agrees very well with the slope calculated for a $(1-\alpha)n_a$ value of 1. If the transfer coefficient, $(1-\alpha)$, could be assumed to be .5, then n_a would be two. This would be in line with the following reaction.



As the slope increases $(1-\alpha)n_a$ decreases and suggests that possibly there is an interfering reaction. For example, the following reaction might be taking place.



The second reaction is more likely to occur at higher concentrations of $\text{SO}_3^{\cdot-}$, since more SO_3^- radicals could be formed and the chance for the simultaneous collision of two of these radicals to form dithionate would increase.

A decrease in $(1-\alpha)n_a$ with increasing concentration of S(IV) would explain the anodic shift at a constant pH with increasing concentration of S(IV). It would also explain why the peak becomes more

rounded with increasing concentration of S(IV).

That little or no shift is seen in $E_p/2$ with increase in the S(IV) concentration at higher pH values indicates that the process in which dithionate is formed reaches a maximum efficiency at a certain level of SO_3^- . Both of the above mechanisms are applicable at the higher pH's.

Examination of Figure 4 shows that at pH's less than 7, the waves appear to have the same shape. As the pH is increased above 7, the peak becomes sharper and the slope of the wave increases. Further, in examining Tables 2-8 it is seen that i_p/C (at constant v) remains constant as the pH is varied, except at pH 10.1. The i_p/C values at this pH appear to be much higher than experimental error can account for.

As the kinetic parameter, ψ , approaches zero, the shape of the wave is identical to the uncomplexed case. However, as ψ moves away from zero the wave begins to flatten out and the peak becomes rounded, until it reaches the limiting case where ψ is very large, in which case an S shaped wave is observed. In this limit, the potential of the wave and magnitude of the current are independent of the scan rate. This is clearly not applicable to this system. However, an intermediate value of ψ does appear probable.

Let us look closely at the kinetic parameter, ψ

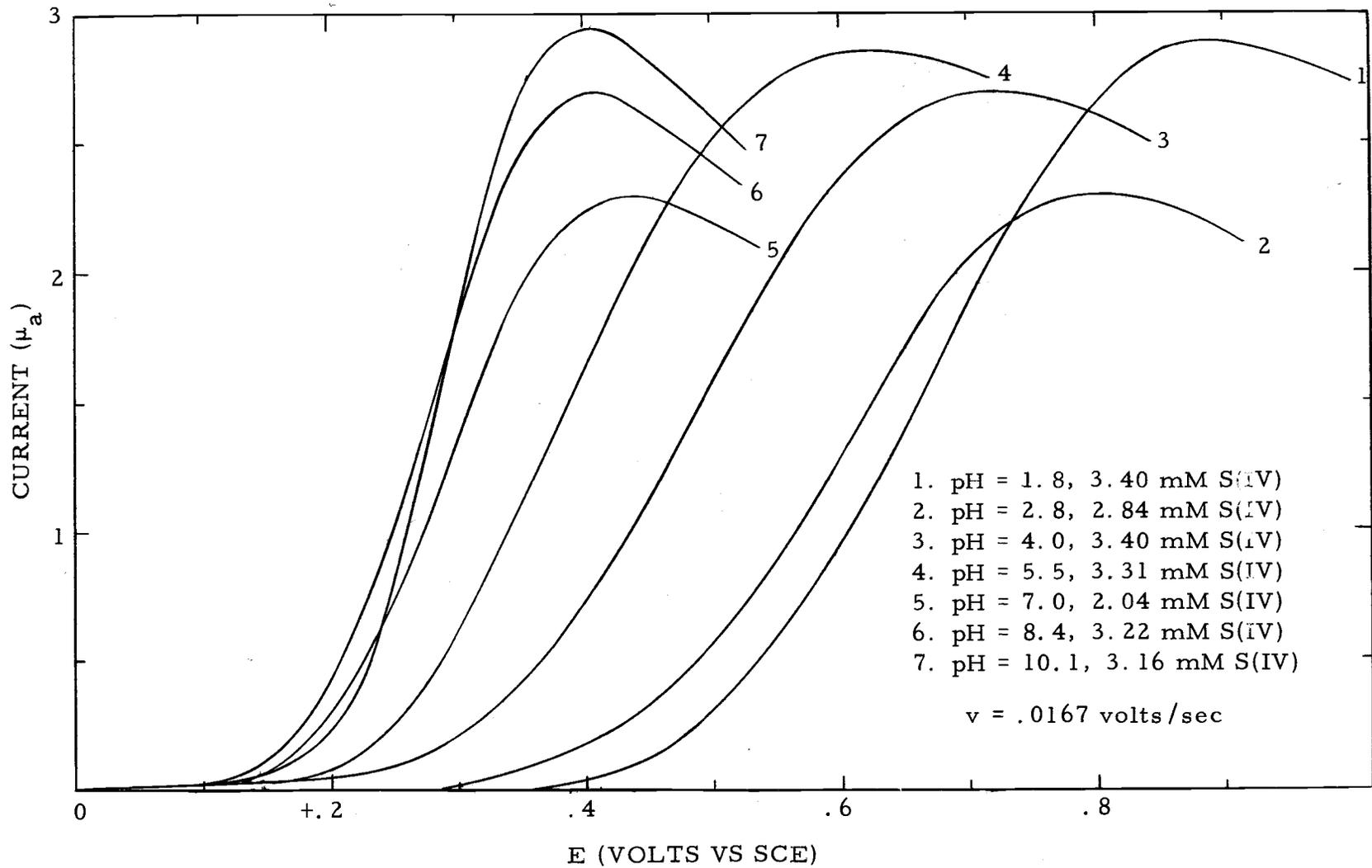


FIGURE 4. ANODIC CURRENT-VOLTAGE CURVES FOR S(IV) AT VARIOUS pH's.

$$\psi = \sqrt{b}/K\sqrt{t}$$

but $K = K_a/[H^+]$ for this system. Also, l must be modified, i.e., $l_a = k_f + k_b[H^+]$. Therefore the new ψ is

$$\psi_{\text{new}} = \sqrt{b}[H^+]/K_a \sqrt{k_f + k_b[H^+]}$$

This would indicate that at higher acid concentrations the kinetic parameter, ψ_{new} , should be a factor. For a weak acid $k_b \gg k_f$ and l_a will therefore equal $k_b[H^+]$. As the pH is increased, the product $k_b[H^+]$ will approach k_f and eventually $k_b[H^+] \ll k_f$ and l_a will equal k_f .

ψ_{new} should decrease slowly as the pH increases. A pH will be reached when the denominator will remain constant and the numerator will continue to decrease. Certainly as the hydrogen ion concentration becomes much less than K_a , ψ_{new} would approach zero. At pH 10.1 this apparently is the case and one notes experimentally that the peak is sharper and that the peak current has increased.

ψ also shows that since b is proportional to the scan rate, ψ should increase with scan rate. This means that the peak should begin approaching a plateau and the magnitude of the current should decrease markedly. This effect was not observed for scan rates as high as .5 v/sec. This is still another indication that the ψ_{new} must be small for this system.

In order to show that ψ_{new} is a factor at the lower pH's and can therefore influence the shape of the waves, potential scan rates up to 10 v/sec were used to study the system at pH 4 and 10.1. The total S(IV) concentration was held constant during the runs.

A plot of i_p vs $v^{1/2}$ is shown in Figure 5. This shows that the current falls off at the higher scan rates at pH 4.0, which supports a chemical complication. At pH 10.1, the current remains proportional to \sqrt{v} , even at the higher scan rates. Qualitatively, the waves at pH 4 become more drawn out with higher scan rates and the peak was becoming noticeably more rounded. However, as one would expect, the shape of the waves at pH 10.1 did not seem to be affected by the scan rate, which is in line with the uncomplexed Case II.

If we assume that at pH 10.1 we have an uncomplexed irreversible charge transfer (Case II), we can obtain quantitative values for the kinetic parameters of the electrode reaction: $(1-\alpha)n_a$, k_s , and n .

Nicholson provides the following equation which offers a quantitative means for calculating $(1-\alpha)n_a$ values.

$$(E_{p/2})_2 - (E_{p/2})_1 = \frac{RT}{\alpha n_a F} \ln \sqrt{v_1/v_2} \quad (11)$$

This equation is written for a cathodic reaction. It is a simple

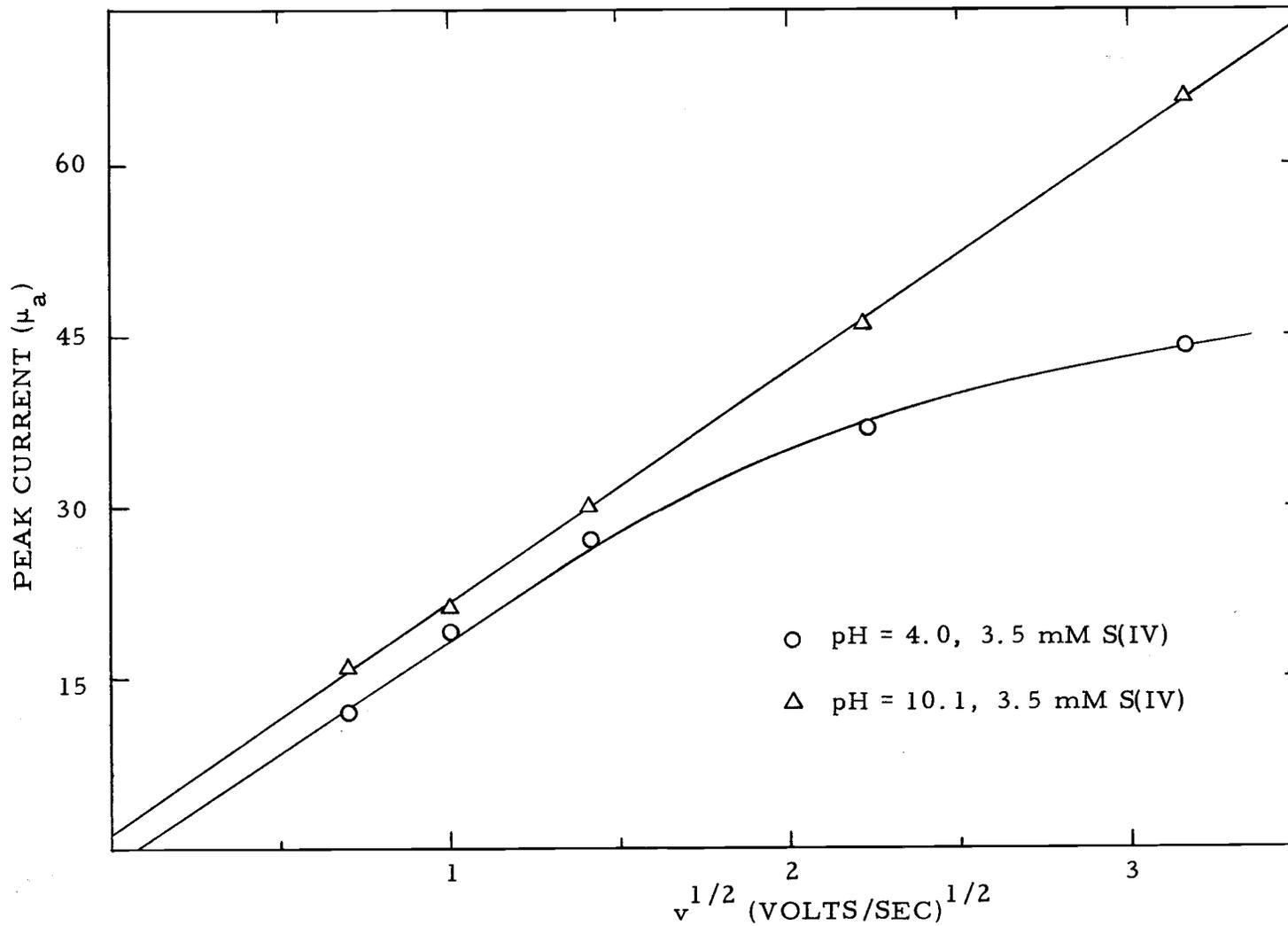


FIGURE 5. PEAK CURRENT VERSUS THE SQUARE ROOT OF SCAN RATE AT pH 4.0 AND 10.1.

matter to apply it to an anodic reaction.

$$(E_{p/2})_2 - (E_{p/2})_1 = - \frac{RT}{(1-\alpha)n_a F} \ln \sqrt{v_1/v_2} \quad (12)$$

$$= \frac{RT}{(1-\alpha)n_a F} \ln (v_2/v_1)^{1/2} \quad (13)$$

$$= \frac{RT}{2F} \frac{1}{(1-\alpha)n_a} \ln \frac{v_2}{v_1} \quad (14)$$

At 25°C, Equation (14) reduces to the following:

$$(E_{p/2})_2 - (E_{p/2})_1 = \frac{.0295}{(1-\alpha)n_a} \log \frac{v_2}{v_1} \quad (15)$$

where $(E_{p/2})_2$ = the half peak potential at scan rate v_2 .

Applying Equation (15) to the experimental results in Table 8, a $(1-\alpha)n_a$ value of $.66 \pm .02$ was calculated.

The equation derived by Reinmuth for describing the foot of an irreversible wave (29) offers another means of obtaining a $(1-\alpha)n_a$ value as well as a value for \bar{k}_s . Nicholson warns that the equation is valid for only the first 10% of the wave. The working equation for a reduction reaction is:

$$i = nFAC_O^* \bar{k}_s \exp\left[-\frac{\alpha n F}{RT} (E - E^0)\right] \quad (16)$$

i is the current flowing at the foot of the wave in amps,

$n = \text{g-moles } e^- / \text{g-mole reactant}$, C_O^* is the bulk concentration of the reducible species in moles/cm³, \vec{k}_s is the formal heterogeneous rate constant, E is the applied potential in volts, and E^0 is the standard electrode potential for the electrochemical couple. Equation (16) can be written to apply to an anodic reaction,

$$i = nFAC_R^* \vec{k}_s \exp\left[\frac{(1-a)n}{RT} (E-E^0)\right] \quad (17)$$

Then at 25°C, Equation (17) can be rewritten

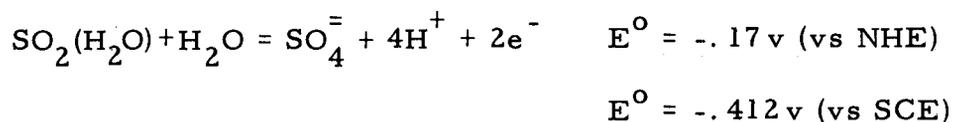
$$\log i = \log nFAC_R^* \vec{k}_s + 17.0(1-a)n_a (E-E^0) \quad (18)$$

Thus a plot of $\log i$ versus $(E-E^0)$ will yield a slope equal to $17.0(1-a)n_a$ and an intercept proportional to \vec{k}_s . Such a plot is given in Figure 6. The data were taken from curve 7, Figure 4.

A least squares fit gives a straight line with a slope of 11.08 and an intercept of -13.45.

From the slope, a $(1-a)n_a$ value of .65 was calculated and is in excellent agreement with the value calculated previously.

A standard electrode potential for the sulfate-sulfite system in acid solutions can be found in most handbooks:



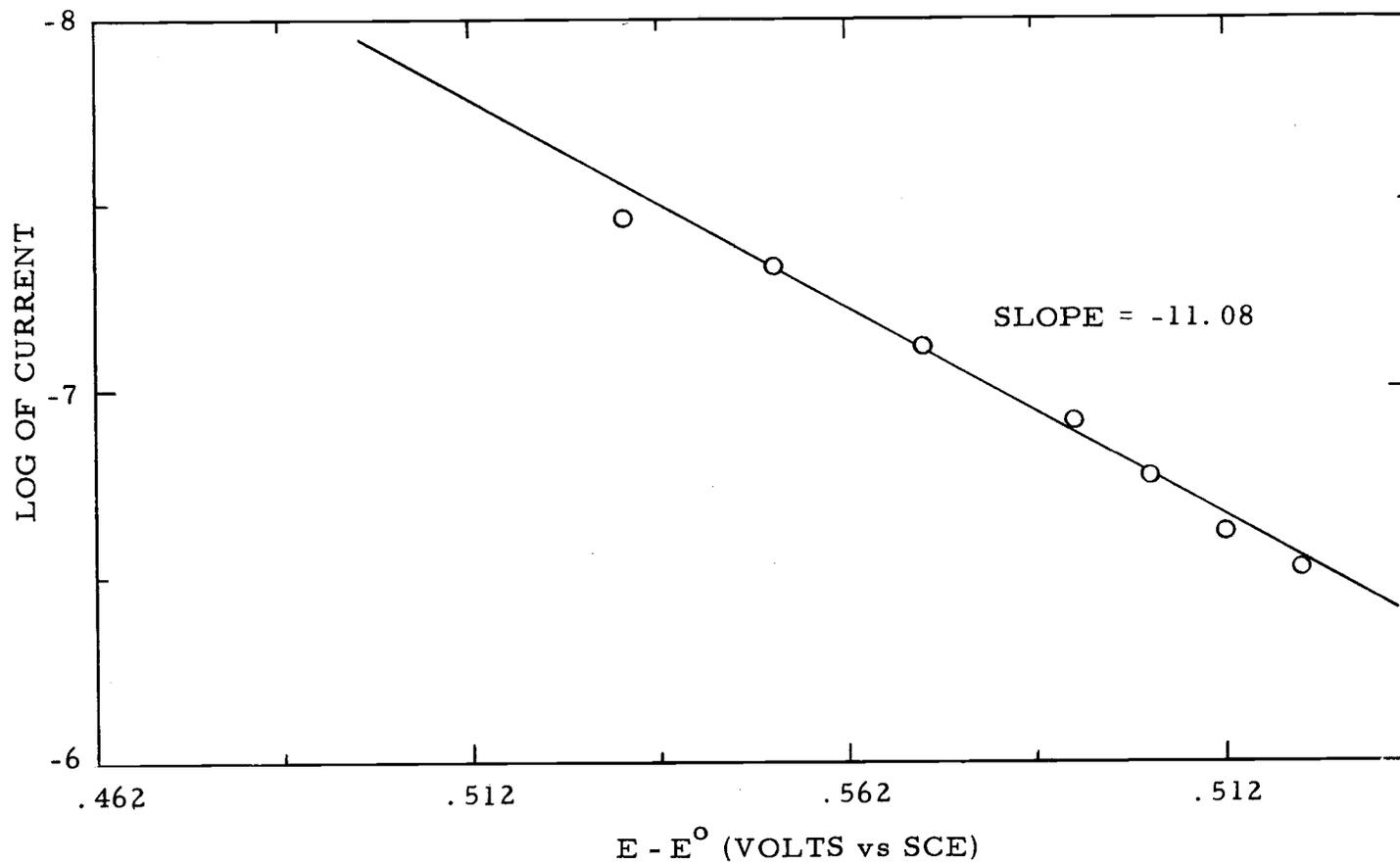


FIGURE 6. LOG OF CURRENT VERSUS $E - E^0$ AT pH 10.1, 3.16 mM S(IV).

Using the value for $E^0 = -.412$ v (vs SCE), a \vec{k}_s value of 7.9×10^{-10} cm/sec was obtained from the intercept.

Nicholson derived a useful equation which provides yet another means of obtaining $(1-\alpha)n_a$ and \vec{k}_s values.

$$i_p = 0.227 n F A C_R^* \vec{k}_s \exp\left[\frac{(1-\alpha)n F}{RT} (E_{p/2} - E^0)\right] \quad (19)$$

where i_p = peak current in amps, and $E_{p/2}$ is the potential in volts at which the current is equal to half the peak current. Equation (19) can be rewritten (at 25°C):

$$\log i_p = \log (.227 n F A C_R^* \vec{k}_s) + 17.0(1-\alpha)n_a (E_{p/2} - E^0) \quad (20)$$

If one plots $\log i_p$ versus $(E_{p/2} - E^0)$ for varying scan rates, a straight line should result with a slope proportional to $(1-\alpha)n_a$ and an intercept proportional to \vec{k}_s .

Taking data from Table 8, a $(1-\alpha)n_a$ value of .59 was calculated from the slope. This is lower than the values obtained previously.

The \vec{k}_s value, calculated from the intercept, was 1.8×10^{-10} cm/sec. This is compared to 7.0×10^{-10} cm/sec as calculated from Reinmuth's equation. These values are in good agreement and offer a quantitative measure of the degree of irreversibility of this electrochemical reaction.

It is of interest to know the diffusion coefficient, D , of the species involved in the electron transfer in the particular medium in which it is carried out. Kolthoff and Miller reported a value of $2.0 \times 10^{-5} \text{ cm}^2/\text{sec}$ for the diffusion coefficient of "dissolved SO_2 " at a mercury electrode in .1 F H_2SO_4 . This value was used by Sawyer in his calculations. One cannot be certain that the species undergoing the reduction reaction (as reported by Kolthoff and Miller) is the same species undergoing the electrooxidation. The diffusion coefficients therefore could differ even in the same medium. Furthermore, the Britton and Robinson buffer system used in this work offers a much different solution environment.

Therefore, it was necessary to determine D values at all the various pH's. Chronoamperometry provides a direct means for obtaining such values. The working equation along with its basic assumptions has already been considered.

$$D^{1/2} = \frac{it^{1/2} \pi^{1/2}}{nFAC}$$

It should be re-emphasized that the equation holds only if there is diffusion control. For this reason the applied potential was sufficiently past E_p , that the driving force imposed diffusion control on the system. Table 9 summarizes the calculated diffusion coefficients at the various pH's.

Table 9. Diffusion coefficient of S(IV) at various pH's.

pH	D (cm ² /sec)
1.8	7.34 ± .30 x 10 ⁻⁶
2.8	6.50 ± .52 x 10 ⁻⁶
4.2	8.60 ± .68 x 10 ⁻⁶
5.5	9.05 ± .48 x 10 ⁻⁶
7.0	7.45 ± .20 x 10 ⁻⁶
8.4	7.39 ± .51 x 10 ⁻⁶
10.1	8.05 ± .38 x 10 ⁻⁶

An n value of 2 was assumed in calculating the D values. Three runs were made at each pH.

The diffusion coefficient does not appear to change drastically as the pH is changed. This would support the idea that the reacting species is the same throughout. The small deviations could be due simply to the changing buffer medium.

It is noted that the D values obtained are much lower than the values reported previously. This might suggest that in fact a different species is involved in this electrode reaction. If this is the case, the Sawyer's calculations could be in error.

Assuming that Case II applies at pH 10.1, an overall n value can be calculated for this reaction by applying the following equation given by Nicholson.

$$i_p = 602n((1-\alpha)n_a)^{1/2} AD^{1/2} v^{1/2} C^* (.4958) \quad (21)$$

where i_p is the observed peak current in amps, n = g-moles of electrons/g-mole reactant, A is the electrode area in cm^2 , D is the diffusion coefficient in cm^2/sec , v is the scan rate in volts/sec, C^* is the bulk concentration of the reactant in moles/l, and .4958 is the value of $\chi(bt)\sqrt{\pi}$ at the peak.

The following values were substituted into Equation (21):

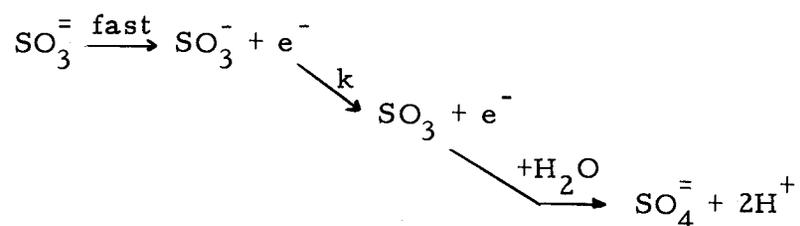
$$(1-\alpha)n_a = .66, \quad A = 7.35 \times 10^{-3} \text{ cm}^2, \quad D = 8.05 \times 10^{-6} \text{ cm}^2/\text{sec}, \\ v = 8.3 \times 10^{-3} \text{ v/sec}, \quad C^* = 3.16 \times 10^{-3} \text{ M}, \quad \text{and } i_p = 2.26 \times 10^{-6} \text{ amps.}$$

An n value of 1.5 was calculated. Other experimental values from Table 8 were substituted into Equation (21) and n values ranging from 1.3 to 1.7 were obtained.

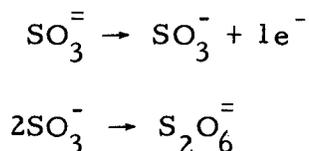
This method of obtaining an n value is somewhat unreliable since many of the parameters used in the equation are associated with a considerable error (i. e., $(1-\alpha)n_a$, A , D , and i_p).

A value for n , intermediate between one and two would lend support to the suggestion that two mechanisms are actually involved in the electrochemical oxidation of sulfite solutions.

The first mechanism involves a two electron transfer,



while the second mechanism involves a one electron transfer



Coulometric experiments at controlled potential should be run to verify an n value. Such experiments have never been attempted in studying the electrooxidation of the S(IV) system, primarily because platinum and gold have been the electrode materials and a changing surface activity over a period of time becomes a problem. Glassy carbon should offer an excellent opportunity for such an experiment to be carried out successfully. Only when a reliable n value is established can one propose a mechanism with reasonable certainty.

Electron paramagnetic resonance studies have been reported on simple oxy radicals such as OH, O_2^{\ominus} , SO_2^{\ominus} , and SO_3^{\ominus} (34). Recently, thin layer electrochemistry has been coupled with EPR to study intermediates in electrochemical reactions (4). If the intermediate(s) in this reaction could be detected by this method, a much better understanding of the mechanism would result.

IV. CONCLUSIONS

Although it has been postulated that dissolved SO_2 is the actual species undergoing a direct electron transfer at gold and platinum electrodes, this does not appear to be true in this case. Evidence points to the sulfite species (SO_3^-) as undergoing the electron transfer at a glassy carbon electrode (in the potential range in which this work was concerned) and that this is coupled with a chemical complication from the aqueous SO_2 system itself (i. e. , Nicholson's Case IV).

If the potential scan rate were made fast enough, a limiting current would be observed. This current would be limited only by the preceding chemical reaction and directly proportional to $K(k_f+k_b)^{1/2}$. In this case the reaction could be the dissociation of bisulfite. A means would therefore be available for obtaining values for the rate constants associated with this weak acid dissociation. The data obtained indicates that scan rates exceeding 10 v/sec will be needed to attain this limiting condition.

The observed anodic shift in $E_{p/2}$ with increasing S(IV) concentration at the lower pH's is explained in part as being due to a changing electrode mechanism.

The diffusion coefficient for the S(IV) species in the Britton and Robinson buffer system appears to be much less than the value reported by Kolthoff and Miller. This might suggest that in fact,

another species is involved in this reaction other than dissolved SO_2 .

It was suggested that this electrochemical system degenerates to the uncomplexed irreversible charge transfer (Case II) at higher pH's. A value for $(1-\alpha)n_a$ of $.66 \pm .02$ was obtained and verified using different approaches in handling the available data. A heterogeneous rate constant, \bar{k}_s , of $4.9 \pm 3.0 \times 10^{-10}$ cm/sec was calculated, indicating the degree of irreversibility of this reaction.

Finally, an intermediate n value between one and two was calculated for this reaction. This is consistent with the suggestion that the reaction involves two mechanisms that are occurring simultaneously. The first involves a direct two electron transfer, while the second involves a one electron transfer followed by a radical reaction to form dithionate ($\text{S}_2\text{O}_6^{=}$).

Further experiments would help to elucidate the mechanism for this reaction.

Galvanostatic measurements would offer another means for obtaining the heterogeneous rate constant, as well as offering $(1-\alpha)n_a$ values. It would be extremely valuable to be able to separate $(1-\alpha)$ from n_a , although such a method does not appear to be available.

Controlled potential coulometry is needed to establish an n value for this reaction. It appears that glassy carbon would allow such experiments to be carried out successfully without contamination of the surface as is the case with the noble metals.

It is very likely that free radical ions are involved as intermediates in this reaction, as is the case in the homogeneous oxidation of aqueous SO_2 . If such intermediates could be detected by employing techniques such as EPR coupled with a thin layer electrochemical cell, a much better understanding of the mechanism would result.

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APPENDIX

ANALYSIS OF SULFITE OR SO₂ SOLUTIONS

Ref: Schroeter, L. C., "Sulfur Dioxide," Pergamon Press, N. Y., 1966, pp. 169-171.

Reagents: 0.05 M sodium thiosulfate, standardized by some method beforehand.

Potassium iodate, reagent grade with a min. assay of 99.8%.

Potassium iodide solution, about 0.1 M.

Concentrated sulfuric acid, reagent grade.

Starch indicator solution.

Equipment: Balance capable of measuring to nearest 0.1 mg.

A 50 ml buret.

Volumetric pipets, 1 ml, and as needed.

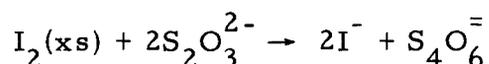
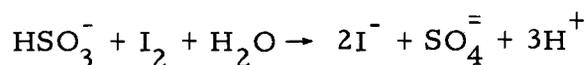
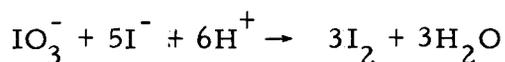
A magnetic stirrer with Teflon coated stirring bar.

Beakers, graduated cylinders, wash bottle etc.

Procedure: Dry the potassium iodate to constant weight at 100° C.

Dissolve the accurately weighed potassium iodate (0.10-0.13 g) in 10-15 ml of distilled water and add 2 ml of concentrated sulfuric acid. While stirring, add 15 ml of 0.1 M potassium iodide solution. (The solution will immediately turn dark brown and solid iodine particles will form.) Immediately pipet into this solution the aliquot sample of the sulfite or sulfur dioxide solution. Titrate with standardized sodium thiosulfate solution until the color of the sample solution is a faint yellow, then add 2 ml of starch indicator and titrate to the point where the color changes from violet to colorless.

Reactions involved:



Calculation formulas:

$$\text{wt. KIO}_3 (0.998) \left(\frac{1 \text{ mole KIO}_3}{214.01 \text{ g KIO}_3} \right) \left(\frac{3 \text{ moles I}_2}{1 \text{ mole KIO}_3} \right)$$

$$= \text{total moles of I}_2 \text{ produced} = \text{wt. KIO}_3 \times 0.01399$$

$$\text{Vol. Na}_2\text{S}_2\text{O}_3 \frac{\# \text{ moles Na}_2\text{S}_2\text{O}_3}{1000 \text{ ml}} \frac{1 \text{ mole I}_2}{2 \text{ mole Na}_2\text{S}_2\text{O}_3}$$

= number of moles I₂ which did not react with the sulfite or sulfur dioxide.

To find the concentration of the sulfur dioxide (sulfite) solution, take the difference of the number of moles of iodine, calculated above, to obtain the number of moles of iodine which reacted with the sulfite. Then calculate the concentration

$$\frac{(\text{Tot. moles I}_2 - \text{moles I}_2 \text{ titrated})}{\text{Vol. in ml of sulfite solution}} \left(\frac{1 \text{ mole SO}_3^-}{1 \text{ mole I}_2} \right) \left(\frac{1000 \text{ ml}}{1 \text{ l.}} \right)$$

= concentration of sulfite solution in moles SO₃²⁻ per liter.