SULFUR DIOXIDE TRANSPORT THROUGH AQUEOUS SOLUTIONS

Thesis by

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In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1979

(Submitted January 5, 1979)

ACKNOWLEDGEMENTS

Congratulations are due to my advisor, Dr. Sheldon K. Friedlander, who once went to the board during a group seminar and outlined in 30 seconds the boundary layer method that turned out to be a major contribution in this work. I hope that this type of insight has rubbed off on me during my stay at Cal Tech. I am sure that Dr. Friedlander would second this idea, and for this reason, I record his immortal words "You can't calculate everything."

Shawn Golden deserves a special round of applause for giving up many Saturdays to type most of the thesis and to make a seemingly endless number of revisions. In case you lost count, Shawn, my advisor approved the fourth draft.

For their technical input and occasional wit, I thank Larry McClellan, Peter McMurry, Rick Flagan, Cliff Davidson, Jim Ouimette, Art Stelson, Fernando Cadena, Howard Liljestrand, James Pankow, Dan Rader, and Don Kuehne. As my office mate, Don has been reasonable, pleasant, and, at times, alot of laughs. I advise Don, however, to do his next office mate a favor by getting an FM stereo receiver to replace his transistor radio.

An invaluable part of my education has come from Mr. Elton Daly, the machine shop supervisor. I appreciate his patience, insight, and skill. His ability to transform my chicken-scratch drawings into the finished product is truly amazing.

Much of the nitty-gritty machining on my apparatus was done by Joe Fontana, Rich Eastvedt, and Dave Byrum. Their helpfulness and skill are appreciated.

Many other people involved in support services have been friendly and helpful. These include Roderick Casper, Jeanne Tatro, Katie Foley, Rayma Harrison, Gunilla Hastrop, Helen Fabel, Elaine Granger, Joan Matthews, Adelaide Massengale, Jennifer Burkhart, and Bonnie Sherburn.

I thank Bill Croasmun, John Wolfskill, Frank Brown, and the other members of the Wednesday noon Bible Study for the many insights into the Word of God that we have discussed throughout the years. May I Tim. 6:11 characterize your lives.

My parents have had a piece in this work, too. I appreciate many aspects of the environment they provided in the past and the pride and confidence in me that they continue to have.

Many friends at Lake Avenue Congregational Church have contributed fun, care, spiritual wisdom, and great examples of godliness. Foremost among these are Kent Tucker, Bruce Leafblad, Ray Ortlund, Nathan Gates, Dewey Cass, Bob Decker, David Kattenhorn, Ben and Gini Downing, and Steve and Mary Anne Cunningham. You guys are beautiful.

The one who has shared with me the whole experience is my precious and beautiful wife, Linda. I love you. Thank you for all of your kindness, encouragement, love and perseverance. You have grown so much in the last four years, and I appreciate that, too. Let us go hard after God together.

And Lord, You have been beautiful. Thank You for everything: the strength for certain times, the joy for others, good health, a good mind, a godly wife, a good church, and, mostly, the ability to know You through your Son, Jesus Christ. I hope You will be pleased with my understanding and presentation of the microcosm of your universe discussed in this thesis.

ABSTRACT

A theory for the rate of SO_2 transport through aqueous solutions has been developed based on measurements of the steady-state flux of SO_2 through aqueous films of known composition. Conditions in most of the experiments were typical of flue gas desulfurization (FGD) scrubbers.

Aqueous films, in the form of agar gels or soaked polyethylene filters, were mounted in a diffusion cell. Humidified nitrogen with a known mole fraction of SO_2 ($y_{SO_2,o}$) flowed through one side of the cell. Clean, humidified N_2 flowed through the other side, sweeping away SO_2 passing through the films. Films of water and solutions of neutral and alkaline sodium salts (0.1-2.0M NaCl, 10^{-3}-3.0M NaOH, $NaHSO_3$, or Na_2SO_3) were studied with $y_{SO_2,o} = 10^{-4}$, $2\cdot10^{-4}$ $5\cdot10^{-4}$, and 10^{-3}.

In alkaline solutions, the transport by sulfur-containing ions was up to 1300 times larger than the contribution of dissolved SO_2 molecules. The chemical reactions of SO_2 that form these ions have previously been regarded as instantaneous (i.e., at equilibrium). Equilibrium theory, however, overpredicts the observed flux through alkaline solutions by up to a factor of seven. A new non-equilibrium boundary layer analysis (NEBLA) has been developed to account for this deviation. This analysis treats the boundary layers as regions where the conversion from molecular SO_2 to sulfur-containing

ions (and vice-versa) is frozen. The NEBLA is the first analysis to predict the flux for a system that has non-linear kinetics and is far from the limits of both zero and instantaneous chemical reactions.

For water and NaCl solutions, data agreed with an analytical expression for the flux based on the equilibrium approximation. This expression accounts for the (diffusion-induced) potential gradient. The potential gradient increases the effective diffusivity of HSO_3^- by approximately 73%. With this assist, HSO_3^- is responsible for 80% to 95% of the net flux. The agreement of the water and neutral solution data with equilibrium theory shows that the deviation from equilibrium in the alkaline solutions is a pH effect.

Data on chemical speciation and equilibrium, activity, diffusion, and reaction rate coefficients for aqueous SO_2 solutions are incomplete. The experiments with water and NaCl solutions assisted in the choice of reaction rate and activity coefficients; unmeasured equilibrium and diffusion coefficients were estimated theoretically.

Because the transport theory has been developed for a one-dimensional film, it can be most easily adapted to the film model that is employed in the absorption literature. In this way, the theory can be used to predict absorption rates of SO_2 in FGD scrubbers and by bodies of water, rain, plumes, lung mucus, and plants.

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LIST OF SYMBOLS

Symbol Definition

a_i -- activity of species i

$\mathring{a}_i$ -- activity coefficient parameter (eq. A-14)

A -- cross-sectional area of aqueous film

A -- parameter from Debye-Huckel theory (eq. A-14)

A^{z-} -- anion of neutral salt

b_i -- activity coefficient parameter (eq. A-14)

B -- parameter from Debye-Huckel theory (eq. A-14)

$\bar{B}$ -- contribution of potential gradient to the flux (eq. 3.24)

B_M, B_A -- parameters in Bromley activity coefficient model (eqs. D-2,3)

C_i -- concentration of species i (mole/liter)

C_A -- "total alkalinity" in lime/limestone scrubbers

C_o -- concentration of non-volatile species added to film (eq. 3.13)

C* -- characteristic value of H_3O^+ concentration in boundary layer near x = 1

$\tilde{C}$ -- arbitrary concentration used in non-dimensionalizing (eq. 3.9)

D_{eff} -- effective binary salt diffusivity (eq. 3.25)

D_i -- diffusion coefficient of species i

D_i' -- diffusion coefficient modified to account for potential gradient (eqs. 3.49a,b)

$D^*_{HSO_3^-}$ -- effective (enhanced) diffusivity of HSO_3^- (eq. 3.35)

Da -- Damkohler number (eq. 5.7)

F -- Faraday's constant (eq. 3.6)

LIST OF SYMBOLS (Cont.)

Symbol Definition

F -- facilitation factor (eq. 5.1)

F_{SS} -- facilitation factor derived from perturbation analysis of Suchdeo and Schultz (1974a)

H_{SO_2} -- Henry solubility coefficient (eq. 3.4)

I -- ionic strength (eq. A-45)

k_1, k_{-1} -- forward and reverse rate coefficients for the hydrolysis of SO_2 (eq. 1.1)

k_F, k_R -- forward and reverse rate coefficients for reaction 3.88

K -- equilibrium coefficient (Table 3.1)

L -- thickness of aqueous film

$\underline{m}$ -- effective Henry solubility coefficient (eq. 2.18)

m_i -- molal concentration of species i

M_d -- molar flow rate through downstream side of cell

M_u -- molar flow rate through upstream side of cell

M^{z+} -- cation of neutral salt

n_i -- number of atoms of type "i" in a given chemical species

N_i -- flux of species i

N_{H_2O} -- flux of SO_2 through water films

N_o -- flux of SO_2 in absence of chemical reactions

Na_{tot} -- total alkaline sodium concentration

P_o -- arbitrary pressure used in non-dimensionalizing

P_{tot} -- total pressure

LIST OF SYMBOLS (Cont.)

Symbol Definition

PG_1 -- defined by eq. 3.26a; for use in potential gradient analysis

PG_2 -- defined by eq. 3.26b; for use in potential gradient analysis

Q_i -- volumetric flow rate (cm^3/sec)

r_i -- rate of production of species i by homogeneous chemical reaction

R -- universal gas constant

S_T -- total dissolved sulfur (eq. C-1)

T -- temperature

U_i -- parameter for calculating activity coefficient (eq. A-14)

x -- distance variable in aqueous film

x_o -- arbitrary fixed point in film (eq. 3.18)

y_m -- mole fraction SO_2 indicated by Meloy sulfur analyzer

$y_{SO_2,o}$, $y_{SO_2,1}$ -- mole fraction SO_2 in gas phase at $x = 0$ and $x = 1$

z_i -- algebraic charge on species i

z^- -- algebraic charge on anion of neutral salt

z^+ -- algebraic charge on cation of neutral salt

Subscripts

A -- anion

bl -- boundary layer theory (NEBLA)

eq -- equilibrium theory

LIST OF SYMBOLS (Cont.)

Symbol — Definition

Subscripts, cont.

i -- any species

j -- sulfur-containing species

j' -- sulfur-containing species other than $SO_2(aq)$

k -- sodium-containing species

M -- cation

n -- any species

NV -- a non-volatile species

Superscripts

o -- infinite dilution

$\hat{}$ -- a dimensional variable or parameter

Greek Symbols

β -- approach to equilibrium (eq. 5.8)

γ -- activity coefficient (eq. A-14)

δ_o -- boundary layer thickness near $x = 0$ (eq. 3.76)

δ_1 -- boundary layer thickness near $x = 1$ (eq. 3.92)

ε -- void volume fraction of filter matrix (eq. 4.1)

ε -- molar absorptivity (Chapter 2)

λ_i -- conductivity (eq. 2.13)

μ -- solution viscosity

μ_o -- solution viscosity at infinite dilution

ν^- -- number of atoms of anion in one molecule of neutral salt

LIST OF SYMBOLS (Cont.)

Symbol Definition

Greek Symbols, cont.

ν^+ -- number of atoms of cation in one molecule of neutral salt

ρ_{gel} -- density of agar gel

τ -- tortuosity of filter matrix (eq. 4.2)

τ_D -- characteristic diffusion time

τ_R -- characteristic reaction time

ϕ -- enhancement factor; F + 1 (eq. 5.1)

Φ -- electric field potential (eq. 3.6)

CHAPTER 1: INTRODUCTION

Sulfur dioxide transport in aqueous solutions is an old topic that is receiving renewed interest in connection with environmental problems. Rouelle (1744, 1754) appears to have been the first to record the use of aqueous solutions for absorbing SO_2. He found that rags soaked in potassium hydroxide could indicate the presence of SO_2 in the atmosphere. Since that time, many investigators have studied the properties of aqueous solutions of SO_2.

A fundamental understanding of SO_2 transport depends on chemical speciation and thermodynamic, reaction rate, and diffusion coefficient studies. Information in these areas has been growing since the early 1900's but is still incomplete. Thus, early work on SO_2 absorption and transport lacked information necessary for the development of a fundamental theory.

In the last five years a few fundamental studies have been done. These are reviewed in section 2.5.2.2. However, a complete theory for SO_2 transport in aqueous solutions is lacking. Significant unknowns, outlined in section 1.1, remain.

The goals of this work are to develop a complete theory for this transport process and to test the theory under experimental conditions typical of several applications.

1.1 Objectives and Strategy

1.1.1 Chemical Speciation

To devise a fundamental transport theory, it is necessary to know what species exist in aqueous SO_2 solutions. Substantial information on chemical speciation has been developed in the literature (section 2.1). Many species, however, that are likely to exist in aqueous SO_2 solutions have not yet been looked for. Most of these species are ion pairs. These can be important in alkaline SO_2 solutions, particularly divalent cation systems like lime/limestone- or magnesium-based scrubbing solutions. The significance of these species to the transport process has not been recognized previously.

Also, the species $S_2O_5^{=}$ and $HS_2O_5^{-}$, which have been identified in solution, have been omitted from previous transport studies. In the chemical speciation area, the objective is to include in the theory all possible species. The intent is to be complete and to show how to deal with more complex solutions.

1.1.2 Equilibrium and Activity Coefficients

Equilibrium coefficients serve two roles in the transport theory. First, they help identify what species are important. Second, many reactions in the SO_2 system are instantaneous and are therefore at local equilibrium. Here the coefficients provide quantitative relationships among the species involved.

Thermodynamic data in the literature are limited. For the reactions among the species identified in SO_2/H_2O solutions, equilibrium coefficients have been measured. For the species that are likely to exist but have not been identified, no equilibrium data exist. One objective, therefore, is to provide equilibrium coefficients for reactions that have not been studied.

Since this study deals with highly non-ideal solutions, selection of a reasonable activity coefficient model is important.

1.1.3 Chemical Reaction Kinetics

If no chemical reactions occurred in aqueous SO_2 solutions, the transport would reduce to Fickian diffusion of dissolved SO_2 molecules. Chemical reactions give the system its complexity by forming sulfur-containing species which assist the transport of SO_2. These species are called "carriers" in the facilitated transport literature. The rates of the reactions determine the importance of the carriers.

Few data on chemical reaction rates exist for aqueous SO_2 solutions. The reaction that has been studied is

$$SO_2(aq) + 2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_3O^+ + HSO_3^- \qquad (1.1)$$

Conflicting literature values for k_1 range over eight orders of magnitude (section 2.3). Theoretical flux predictions developed in this thesis would differ by up to four orders of magnitude if the entire range of k_1 values in the literature were used.

Previous SO_2 transport studies have assumed all reactions to be instantaneous. The value of k_1 has therefore been unimportant. This study shows that the instantaneous approximation can lead to serious errors in predicting the transport rate. The value of k_1 is therefore needed. A goal of this study is to resolve the conflict in k_1 values.

1.1.4 Diffusion Coefficients

Values for diffusion coefficients are needed for a quantitative transport theory. Some diffusion coefficients have been measured (section 2.4); others must be estimated. Also, the effect of solution viscosity on the diffusivities must be established. Sections 3.1 and 4.5.2 address these topics.

1.1.5 General Transport Theory

Because conservation of mass

$$\nabla \cdot N_i = r_i \qquad (1.2)$$

applies to each species, a theory for the rate of SO_2 transport in aqueous solutions could be written in terms of an arbitrary number of species with the various equilibrium, activity, rate, and diffusion coefficients as parameters. In principle, the simultaneous second-order, non-linear, differential equations could be solved numerically.

Such an approach is unjustified for this system because of the unknowns that have been discussed. The numerical problem itself would be difficult. There are at least 15 species in some aqueous SO_2 solutions. Also, several of the chemical reactions are proton exchanges. These are generally much faster than other reactions so that the differential equations may prove to be stiff. Therefore, in developing the transport theory, all complexities of the problem will be retained except ones that would require numerical solution of differential equations.

Schultz, Goddard, and Suchdeo (1974) have reviewed facilitated transport and given analytical techniques for calculating the flux of any number of species through a film when each species obeys Fick's law. For non-linear kinetics, the techniques are asymptotic expansions valid in the limit of either fast or slow chemical reactions. In the present system, many species are ions so that the flux expression (eq. 3.6) must include the Fickian term and the potential gradient. Nonetheless, the expression for the flux of SO_2 through an arbitrary aqueous film can be reduced by reasonable approximations to a linear combination of concentration differences, similar to eq. I.3.47 of Schultz, Goddard, and Suchdeo. These differences are not known exactly. For SO_2/H_2O and SO_2/neutral salt solutions, an equilibrium approximation allows the differences to be computed. Because the equilibrium approximation and the asymptotic analyses of Schultz, Goddard, and Suchdeo fail in alkaline SO_2 solutions, a new non-equilibrium boundary layer analysis (NEBLA) is developed.

The equilibrium approximation is not new in facilitated transport literature. The NEBLA, however, is the first analysis that predicts the flux for systems that are far removed from both the fast and slow reaction regimes. When applied to aqueous SO_2 solutions, the NEBLA brings out the non-equilibrium aspects of the transport process. The discovery of significant non-equilibrium effects in the SO_2 system is one of the major contributions of this work.

1.1.6 Experiments -- Testing Theory

Experimental testing of the theory is necessary because the physico-chemical data for aqueous SO_2 solutions are incomplete and approximations are made in solving the equations that govern the transport rate. The experiment measures the steady-state flux of SO_2 through an aqueous film of known composition (Chapter 4). When the partial pressures of SO_2 in the gas phases above and below the film are known and when the film thickness is known, the observed flux can be compared to the theoretical flux.

The aqueous films are either pure water, neutral salt solutions (0.1-2.0M NaCl), or alkaline salt solutions with $10^{-3}M \leq Na_{tot} \leq 3.0M$, where Na_{tot} is the total sodium concentration added to the film as NaOH, $NaHSO_3$, or Na_2SO_3. The quantity Na_{tot} is equal to the acid neutralizing capacity (ANC) that is often employed in the literature of water chemistry (Stumm and Morgan, 1970). Partial pressures of SO_2 range from 100ppm to 1000ppm (total pressure $\sim$744mm Hg). The partial pressures of SO_2 and the alkaline solution concentrations are typical of flue gas desulfurization scrubbers.

1.2 Applications

1.2.1 Flue Gas Scrubbing

Flue gas desulfurization (FGD) scrubbers that operate with aqueous solutions are the primary application. Design of a scrubber from fundamental principles requires an expression for the enhancement factor, ϕ. (The enhancement factor is the absorption rate divided by the absorption rate in the absence of chemical reactions.) Because a fundamental understanding that would allow ϕ to be calculated has been unavailable, existing scrubbers have been designed empirically. Much operating experience now exists. A fundamental understanding of SO_2 transport, however, can assist the design of second-generation processes and optimization of existing processes.

Some scrubbers are gas-phase controlled. Lime/limestone scrubbers, however, are liquid-phase controlled (Corbett, et al., 1977). Second-generation processes based on citrate and phosphate buffering solutions also have liquid-phase resistance (Aul, et al., 1977). Many processes have a varying degree of liquid-phase control that depends on operating conditions (Ayer, 1977, 1978).

Some studies (section 2.5.2.2) derive expressions for the enhancement factor. Various approximations are involved, however, that are not necessary and that are sometimes seriously wrong. The fundamentals expressed in this study avoid these approximations and assumptions. Since the theory is developed for a one-dimensional aqueous film, the fundamentals can be adapted most easily to the film model that is employed in scrubber design and absorption literature.

1.2.2 Droplet Absorption -- Rain and Plumes

Rain droplets and aqueous droplets in cooling tower and power-plant plumes absorb atmospheric or source-related SO_2. In these examples, transport of SO_2 in aqueous solutions is involved. These uptake processes have been discussed at the Dubrovnik conference (Husar, 1978). Although the fundamentals in this study have been expressed in terms of a one-dimensional film, application to the spherical geometry would be straightforward.

1.2.3 Bodies of Water, Plants, Lung Mucus

Sulfur dioxide in the atmosphere or in plumes contacts bodies of water and plants and is also inhaled. Liss (1971) and Brimblecombe and Spedding (1974) discuss absorption in sea water. The process seems to be gas-phase controlled for atmospheric SO_2 concentrations (5-20ppb). The liquid phase may be important if a plume with $\sim$20ppm SO_2 were blowing over a body of water (e.g., if an industrial source is sited near water).

Liss used the analysis of Hoover and Berkshire (1969) to arrive at the conclusion of gas-phase control. This analysis, however, is approximate. Equation 31 in Hoover and Berkshire's paper was integrated with the assumption that the quantity τ is constant. Their equation 17 shows τ is a function of the pH. Therefore their analysis applies only when the pH in the liquid film is only slightly affected by the absorbing gas. They test their theory with CO_2 which is a relatively weak acid-gas in comparison to SO_2. Therefore, this analysis may not be applicable to SO_2 absorption. Hence, the liquid-phase fundamentals shown in this study have a contribution to absorption by bodies of water.

Plant fluids and lung mucus are dilute aqueous solutions of macromolecules and other solutes. Absorption of SO_2 by these fluids can be treated approximately by ignoring the solutes. In most SO_2 inhalation studies (Amdur, 1966; Speizer and Frank, 1966; Frank et al., 1967; Ichioka, 1972), the nose and throat have absorbed 99% of the inhaled SO_2. Only 1% penetrated to the lung. These studies, however, used SO_2 concentrations (1-800ppm) that are well above atmospheric levels. Strandberg (1964) has shown that 60% penetrates to the lung when the SO_2 concentration is 50ppb. This penetration is shown to be part of a trend toward higher penetration at lower SO_2 concentrations. Deep penetration into the lung therefore is likely for atmospheric SO_2 levels.

1.3 Summary and Overview

The transport of SO_2 in aqueous solutions has much practical significance. The theory developed and tested here will explain the fundamentals of this process.

Previous work with SO_2 is discussed in Chapter 2, and the unknowns remaining to be solved by this study become clear. In Chapter 3, the transport theory is explained. Problems of chemical speciation, equilibrium and diffusion coefficients are dealt with, and the complex nature of the aqueous solutions being studied becomes evident. The theory is derived for an arbitrary aqueous SO_2 solution. Approximations are applied to each type of solution (pure water, neutral and alkaline salt). The NEBLA is discussed last as it addresses the most complex solutions and is the most complex analysis.

The apparatus used to test the theories is described in Chapter 4. The experimental program is explained, and each part of the program is shown to fulfill a particular role in testing the theories.

Chapter 5 discusses in order the results of the pure water and neutral and alkaline solution experiments. The pure water data help resolve the problem of the kinetics of reaction 1.1. A simple expression for the flux (Chapter 3) is verified. Viscosity and activity effects are discussed in the context of the neutral salt data. The theory derived for neutral salt solutions is also shown to be adequate.

Compared to pure water, alkaline solutions show up to a factor of 28 increase in the transport rate. The flux, however, is far from that predicted by equilibrium theory. The NEBLA is shown to explain these effects and to predict the flux nearly quantitatively.

CHAPTER 2: LITERATURE REVIEW

The literature review gives the known physico-chemical data for aqueous SO_2 solutions and identifies gaps where this information is incomplete. Studies of absorption and transport are also discussed. Many of the problems with previous studies are brought out, and the role of the present work becomes clear.

Discussions and criticisms of controversial points and contradictory data are also presented. The nature of dissolved SO_2 molecules is discussed, and the existence of H_2SO_3 is rejected. Best values of the thermodynamic and transport properties are selected from available data. The review summarizes in a single reference source much pertinent information on SO_2 in aqueous solutions.

2.1 Chemical Speciation

Table 2.1 shows the species that have been identified in SO_2/H_2O solutions by various researchers. Absorption peaks in the UV, IR, and Raman spectra are also given. Early studies by Wright (1914), Garrett (1915), and Getman (1926) identified most of the species in SO_2/H_2O solutions. Later studies have added more detail and precision to the UV, IR, and Raman spectra. The works of Simon and Waldmann (1955, 1956) and Eriksen and Lind (1972) are important contributions.

Table 2.1

Chemical Species in SO_2/H_2O Solutions

Species	Absorption Peaks			References
	UV(nm)	IR(cm^{-1})	Raman(cm^{-1})	
SO_2(aq)	276	1152-57 1332-34	524,1152, 1330	Wright (1914) Garrett (1915) Getman (1926) Rao (1944) Simon & Waldmann(1956) Falk & Giguere(1958) Jones & McLaren(1958) Scoggins (1970) Eriksen & Lind(1972) Huss & Eckert(1977)
HSO_3^-	190-215		457,587, 709,1019, 1089,1129, 2532	Simon & Waldmann (1955,1956) Eriksen & Lind(1972) Hayon, et al. (1972)
$S_2O_5^=$	255-57		420,1049	Bailey & Baly(1922) Simon and Waldmann (1956) Golding (1960) Arkhipova (1971) Hayon et al.(1972) Bourne,et al.(1974)
$SO_3^=$	185		966	Simon and Waldmann (1955);Hayon, et al. (1972)
$HS_2O_5^-$	suggested as a possible species			Simon and Waldmann (1955) Falk & Giguere(1958)

Debate has occurred during the past 65 years over the nature of the species SO_2(aq) which absorbs at 276nm (UV). Some researchers claim this species is "sulphurous acid" (H_2SO_3). Others say this species is an uncombined SO_2 molecule dissolved in water (much like dissolved CO or NO). Unfortunate nomenclature has contributed to the confusion. For example, a paper by Falk and Giguere (1958) that argues for uncombined SO_2 molecules is entitled "On the Nature of Sulphurous Acid."

Initially, Wright (1914) argued that SO_2 in aqueous solution "consists to a large extent of uncombined gas molecules." He based his conclusion on the observation that gaseous SO_2 molecules and SO_2 in water have only slightly different UV absorption spectra. Later researchers (Garrett, 1915; Bailey and Baly, 1922; Campbell and Maass, 1930; Morgan and Maass, 1931; DeMaine, 1956) appealed to the existence of H_2SO_3 to explain their results. No spectroscopic absorption bands attributable to H_2SO_3 were identified, however.

Bhagavantam (1930) and Gerding and Nijveld (1936) demonstrated that the Raman spectra of aqueous SO_2 is very close to that of gaseous SO_2.

The question intrigued Falk and Giguere (1958) who looked for H_2SO_3 by infrared spectroscopy. They showed that aqueous SO_2 has the same absorption peaks as liquid

SO_2 and that solid SO_2 at -190°C has the same spectra as an equimolar H_2O-SO_2 solution frozen at -190°C. The conclusion was therefore that H_2SO_3 does not exist in liquid or condensed phases.

These studies show that SO_2 molecules in aqueous solution exist in a state equivalent to dissolved O_2 or N_2 molecules. Thus, present understanding is that H_2SO_3 does not exist as a stable species in aqueous SO_2 solutions It is recommended that the notation $SO_2(aq)$ be adopted for SO_2 molecules dissolved in water, and the term "sulphurous acid" be used only colloquially.

Species other than those listed in Table 2.1 can exist in alkaline SO_2 solutions (e.g., in an Na_2SO_3 solution, ion pairs like $NaSO_3^-$ may exist). Such species have not been reported in the literature. Therefore, speciation information is incomplete. The lack of information on speciation for alkaline SO_2 solutions presents an unknown that is addressed by this work. Alkaline solutions are important in several applications, and a fundamental study of the nature of these solutions would be valuable.

2.2 Equilibrium Coefficients

In aqueous solution, the independent equilibria among the species of Table 2.1 are

$$SO_2(aq) + 2H_2O \rightleftharpoons H_3O^+ + HSO_3^- \qquad (2.1)$$

$$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^= \qquad (2.2)$$

$$2HSO_3^- \rightleftharpoons S_2O_5^= + H_2O \qquad (2.3)$$

$$S_2O_5^= + H_3O^+ \rightleftharpoons HS_2O_5^- + H_2O \qquad (2.4)$$

Also, an equilibrium between gaseous SO_2 and aqueous SO_2 exists

$$SO_2(g) \rightleftharpoons SO_2(aq) \qquad (2.5)$$

There are no reported values for the equilibrium coefficient of reaction 2.4. Equilibrium coefficients for the other reactions are

$$K_{1,a} = \frac{a_{H_3O+}a_{HSO_3^-}}{a_{SO_2}a_{H_2O}^2} \qquad (2.6)$$

$$K_{2,a} = \frac{a_{H_3O+}a_{SO_3^=}}{a_{HSO_3^-}a_{H_2O}} \qquad (2.7)$$

$$K_{3,a} = \frac{a_{S_2O_5^=}a_{H_2O}}{a^2_{HSO_3^-}} \tag{2.8}$$

$$H_{SO_2,a}a_{SO_2} = y_{SO_2}P_{tot} \tag{2.9}$$

Here $K_{i,a}$ are the thermodynamic equilibrium coefficients, and $H_{SO_2,a}$ is the Henry solubility coefficient (gas phase assumed ideal).

Equilibrium coefficients are often based on molar concentrations and on molal concentrations. An example is

$$K_{1,c} = \frac{C_{H_3O^+}C_{HSO_3^-}}{C_{SO_2}} \tag{2.10}$$

In the tables that follow, the subscript a refers to the thermodynamic equilibrium coefficient, the subscript c to the coefficient based on molar concentrations, and the subscript m to the coefficient based on molal concentrations.

Tables 2.2a)-d) report the published data for K_1, K_2, K_3 and H_{SO_2}. Ionic strength and temperature are listed when known. Best values of K_1, K_2, K_3, and H_{SO_2} are listed in Table 2.3. Huss and Eckert's (1977) recent study is the most precise and careful measurement of $K_{1,a}$. Their value of $K_{1,a}$ disagrees with several values near 0.0172 mole/1. The authors point out that

Table 2.2a

Literature Values of K_1

Coefficient	Value	Conditions	Reference
$K_{1,c}$	0.0174 $\frac{\text{mole}}{\ell}$	25°C	Kerp & Bauer (1907)
$K_{1,c}$	0.0174 "	25°C	Lindner (1912)
$K_{1,c}$	0.0173 "	25°C	Campbell & Maass (1930)
$K_{1,c}$	0.0174 "	25°C	Morgan & Maass (1931)
$K_{1,a}$	0.0139 "	25°C	Britton and Robinson (1932)
$K_{1,a}$	0.0130 "	25°C	Johnstone and Leppla (1934)
$K_{1,a}$	0.0172 "	25°C	Tartar and Garretson (1941)
$K_{1,c}$	0.0407 "	25°C, 1 molal $NaClO_4$	Nilsson, et al. (1958)
$K_{1,m}$	0.0427 $\frac{\text{mole}}{\text{kg}}$	25°C, 1 molal $NaClO_4$	"
$K_{1,c}$	0.0162 $\frac{\text{mole}}{\ell}$	25°C, 3.5 molal $NaClO_4$	"
$K_{1,m}$	0.0191 $\frac{\text{mole}}{\text{kg}}$	25°C, 3.5 molal $NaClO_4$	"
$K_{1,c}$	0.0139 $\frac{\text{mole}}{\ell}$	25°C, $I=10^{-2}$ M	Ellis & Anderson (1961)
$K_{1,c}$	0.0170 "	25°C, I=0.1 M	Eigen, et al. (1961)
$K_{1,a}$	0.0129 "	25°C	Rabe & Harris (1963)
$K_{1,a}$	0.0114 "	25°C	Wang & Himmelblau (1964)
$K_{1,c}$	0.0180 "	25°C, $I \simeq 1.0$ M	"
$K_{1,a}$	0.0142 "	25°C	Deveze & Rumpf (1964)
$K_{1,c}$	0.0171 "	25°C, $I \simeq 10^{-4}$ M	Beilke & Lamb (1975)
$K_{1,a}$	0.0139 "	25°C	Huss & Eckert (1977)

Table 2.2b

Literature Values of K_2

Coefficient	Value	Conditions	Reference
$K_{2,c}$	$1.66 \cdot 10^{-9}\ \frac{\text{mole}}{\ell}$	25°C	Britton and Dodd (1931)
$K_{2,c}$	$1.82 \cdot 10^{-8}$ "	25°C	Britton and Robinson (1931)
$K_{2,c}$	$1.023 \cdot 10^{-7}$ "	25°C	Britton and Robinson (1932)
$K_{2,a}$	$6.24 \cdot 10^{-8}$ "	25°C	Tartar and Garretson(1941)
$K_{2,c}$	$4.37 \cdot 10^{-7}$ "	25°C,1M $NaClO_4$	Frydman, et al. (1958)
$K_{2,m}$	$4.57 \cdot 10^{-7}\ \frac{\text{mole}}{\text{kg}}$	25°C,1M $NaClO_4$	"
$K_{2,c}$	$3.72 \cdot 10^{-7}\ \frac{\text{mole}}{\ell}$	25°C,3.5M $NaClO_4$	"
$K_{2,m}$	$4.37 \cdot 10^{-7}\ \frac{\text{mole}}{\text{kg}}$	25°C,3.5M $NaClO_4$	"
$K_{2,a}$	$7.08 \cdot 10^{-8}\ \frac{\text{mole}}{\ell}$	25°C	Sillen (1964)
$K_{2,c}$	$2.82 \cdot 10^{-7}$ "	25°C,1M Na_2SO_4	"
$K_{2,a}$	$6.31 \cdot 10^{-8}$ "	25°C	Hayon, et al.(1972)

Table 2.2c

Literature Values of K_3

Coefficient	Value	Conditions	Reference
$K_{3,c}$	0.07 ℓ/mole	20°C	Golding (1960)
$K_{3,c}$	2.0 "	22°C, I=0.3 M	Arkhipova and Chistyakova (1971)
$K_{3,a}$	0.068ǂ "	20°C	Hayon, et al. (1972)
$K_{3,c}$	0.34 "	25°C, I=2.0 M	Bourne, et al. (1974)
	0.22 "	" I=0.9 M	"
	0.175 "	" I=0.5 M	"
	0.115 "	" I=0.1 M	"
	0.086 "	" I=0.01M	"
$K_{3,a}$	0.076 "	25°C	"

ǂCalculated using Golding's molar absorptivity.

Table 2.2d

Literature Values of Henry Coefficient, H_{SO_2}

Coefficient	Value	Conditions	Reference
$H_{SO_2,c}$	$0.802\ \frac{\ell\,atm}{mole}$	25°C	Campbell and Maass (1930)
$H_{SO_2,m}$	$0.794\ \frac{kg\ atm}{mole}$	25°C, $I<10^{-3}M$	Johnstone and Leppla (1934)
$H_{SO_2,c}$	$0.935\ \frac{\ell\,atm}{mole}$	25°C, 1M $NaClO_4$	Nilsson, et al. (1958)
$H_{SO_2,c}$	$0.870\ \frac{\ell\,atm}{mole}$	25°C, 3.5M $NaClO_4$	Frydman, et al. (1958)
$H_{SO_2,a}$	$0.833\ \frac{kg\ atm}{mole}$	25°C	Rabe and Harris (1963)
$H^{\ddagger}_{SO_2,x}$	0.0332	25°C, $I<10^{-3}M$	Hales and Sutter (1973)

$$^{\ddagger}H_{SO_2,x}C_{SO_2} = \frac{P_{SO_2}}{RT}$$

Table 2.3

Best Values of Equilibrium and Henry Coefficients, 25°C

Coefficient	Value	pK	Comment
$K_{1,a}$	0.014 mole/ℓ	1.854	Fair literature consensus; based on Huss and Eckert(1977)
$K_{2,a}$	$6.24\cdot10^{-8}\ \frac{\text{mole}}{\ell}$	7.205	Fair literature consensus; based on Tartar and Garretson (1941)
$K_{3,a}$	0.076 ℓ/mole	1.119	Good literature consensus; based on Bourne, et al.(1974)
$H_{SO_2,a}$	$0.81\ \frac{\ell\text{atm}}{\text{mole}}$		Strong literature consensus

an unusually low mean activity coefficient for the H_3O^+, HSO_3^- ion pair is implied if the value $K_{1,a} = 0.0172$ mole/l is accepted.

To measure K_1, Huss and Eckert used conductance and spectroscopic techniques. Previous investigators had not used spectroscopy. Huss and Eckert employ more recent theoretical and computational techniques for obtaining K_1 from the conductance data (Bury, et al., 1969; Rosenbrock, 1960). Their K_1 value determined spectroscopically agrees with the value from the conductance data to within 1%. Huss and Eckert report $K_{1,a} = (1.39 \pm 0.02)\cdot 10^{-2}$ mole/l. The value 0.014 mole/l has been chosen for Table 2.3.

Table 2.2b shows considerable variation among values of K_2. The first three values, however, are from older studies (1920's) in which electrodes were used that did not have a well-established standard potential (tungsten, antimony-antimony oxide, glass). The glass electrode had the best established standard potential. The coefficient determined with this electrode (Britton and Robinson, 1932) agrees best with recent measurements of $K_{2,a}$. Also, the ionic strength for several of the studies is high; these studies report $K_{2,c}$ and $K_{2,m}$, not $K_{2,a}$.

Measurements of $K_{2,a}$ (Tartar and Garretson, 1941; Sillen, 1964; Hayon, et al., 1972) are consistent. Tartar and Garretson's value of $K_{2,a} = 6.24 \cdot 10^{-8}$ mole/l is chosen as the best value since their study is a careful one that has been substantiated by Hayon, et al. (1972).

Values of $K_{3,a}$ indicated by Table 2.2c are in good agreement except for Arkhipova and Chistyakova's value. There is a plausible explanation for the disagreement. Arkhipova and Chistyakova used spectroscopy to determine K_3. In this technique, the raw UV absorption data give the product of the equilibrium coefficient, K_3, times the molar absorptivity, ε. The best values of $K_{3,a}$ and are computed from these data by a least square analysis. Arkhipova and Chistyakova found $K_3 \cdot \varepsilon = 7962$, $K_3 = 2$ l/mole, and $\varepsilon = 3981$ mole/l. Golding however reports $\varepsilon = 143$ mole/l. If one uses Golding's ε value, the $K_3 \cdot \varepsilon$ product reported by Arkhipova and Chistyakova gives $K_3 = 0.072$ l/mole. This value agrees with the other literature values. Thus, the spurious K_3 value may result from incorrect data analysis rather than incorrect data.

Literature data then are in good agreement on the value of $K_{3,a}$. The most thorough study is that of Bourne, et al. (1974), and their value $K_{3,a} = 0.076$ l/mole is chosen as the best value.

There is good agreement among reported values of the Henry coefficient. Two values in Table 2.2d are at higher ionic strengths. Averaging the four other values (note $H_xRT = H_c$) yields $H_{SO_2,a} = 0.81$ l-atm/mole. This value is chosen for Table 2.3.

2.3 Chemical Reaction Kinetics

Few rate coefficients for the chemical reactions in aqueous SO_2 solutions have been measured. The rate of dissociation of H_2O has been measured by Eigen and DeMayer (1963). It is so rapid that it can be regarded as instantaneous for the purposes of this study.

The only other reaction in the SO_2/H_2O system that has been studied is

$$SO_2(aq) + 2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_3O^+ + HSO_3^- \qquad (2.11)$$

This reaction (the hydration or hydrolysis of SO_2) is extremely important in the transport of SO_2 through aqueous solutions.

Values of k_1 shown in Table 2.4 range over eight orders of magnitude. The dimensions of k_1 are time^{-1} because the hydrolysis is pseudo first-order. A reliable value of k_1 is needed because the rate of hydrolysis determines the extent to which sulfur-containing ions assist the transport. A goal of this research is to resolve this rate coefficient discrepancy.

Table 2.4

Rate Coefficient of Reaction

$$SO_2(aq) + 2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_3O^+ + HSO_3^-$$

k_1 sec^{-1}	Conditions	Reference
>250 (estimated)	20°C, dilute	Saal (1928)
1.62	11.2°C, dilute	Phipps (1947)
4.09 (extrapolated)	25°C	" "
$3.4 \cdot 10^6$	20°C, I = 0.1 M	Eigen,et al.(1961)
$3.17 \cdot 10^{-2}$	25°C	Wang & Himmelblau(1964)
>0.2	25°C	Beilke & Lamb (1975)
>16	∿0°C, dilute	Harrison, personal communication (1976)

In the absence of data, all reactions in the system other than reaction 2.11 are assumed to be instantaneous. This approximation is reasonable since ionic reactions in general are fast. The proton-transfer reactions in the system are usually diffusion-controlled (Eigen and DeMaeyer, 1963).

One important reaction

$$2HSO_3^- \rightleftarrows S_2O_5^= + H_2O \tag{2.12}$$

may not be instantaneous because $S_2O_5^=$ contains a S-S bond (Golding, 1960). The reaction mechanism therefore must involve more than a simple proton transfer or ion pair dissociation.

2.4 Diffusion Coefficients

Data on diffusion coefficients for species in aqueous SO_2 solutions are scarce. The exceptions are H_3O^+ and $SO_2(aq)$. Available data are given in Tables 2.5a,b,c with methods and conditions of measurement. Values of D_i can be obtained from conductivity data since the conductivity, λ_i, is related to the diffusivity by (Newman, 1973)

$$D_i = \frac{RT\lambda_i}{|z_i|F^2} \tag{2.13}$$

Table 2.5a

Literature Values of Diffusion Coefficient of H_3O^+

$10^5 \cdot D_{H_3O^+}$ $cm^2 sec^{-1}$	Technique/Conditions	Reference
9.277	Conductivity, 25°C, $I \simeq 0$	Morgan and Maass (1931)
9.297	25°C, $I \simeq 0$	MacInnes, et al. (1932)
9.308	25°C, $I \simeq 0$	Robinson and Stokes (1965)
9.312	Conductivity, 25°C, $I \simeq 0$	Newman (1973)

Table 2.5b

Literature Values of Diffusion

Coefficient of $SO_2(aq)$

$10^5 \cdot D_{SO_2}$ cm^2sec^{-1}	Technique/Conditions	Reference
2.04	Polarography, 25°C, pH≃1	Kolthoff and Miller (1941)
1.62, 1.83, 2.08, 2.33, 2.59	Diaphragm cell; 20°, 25°, 30°, 35°, 40°C	Peaceman (1951)
1.46	Wetted-wall tower, absorption of pure SO_2 into water, 20°C	Lynn, et al. (1955)
1.40	Absorption of pure SO_2, 20°C	Groothius and Kramers (1955)
1.41	Jet absorption of pure SO_2, 20°C	Toor and Chiang (1959)
1.48	Packed column absorption, pure SO_2, 20°C	Norman and Sammak (1963)
1.44	Packed column absorption, pure SO_2, 20°C	Takeuchi and Namba (1964)
1.46	Radioactive tracer, 20°C, pH≃1	Eriksen (1967)
1.44	Jet absorption, pure SO_2, 20°C	Hetherington (1968)
1.27	Radioactive tracer, 21°C, 3.5 M $NaClO_4$	Eriksen (1969)
1.64	25°C	Bengtsson (1974); quoted by Rochelle and King (1977)

Table 2.5c

Literature Values of Diffusion Coefficients of HSO_3^- and $SO_3^=$

Species	$10^5 \cdot D_i cm^2 sec^{-1}$	Technique/Conditions	Reference
HSO_3^-	1.47	Conductivity, 25°C, $2 \cdot 10^{-3}$M $NaHSO_3$	Washburn(1926)
	1.38	Conductivity, 25°C	Campbell and Maass(1930)
	1.23‡	Radioactive Tracer, 25°C 1 M NH_4HSO_3	Eriksen(1967)
	1.49*	Radioactive Tracer, 22°C $I \simeq 0$	Eriksen(1967)
		Radioactive Tracer, 29°C	Eriksen(1967)
	0.67	2 M $LiHSO_3$	"
	0.98	2 M $NaHSO_3$	"
	1.26	2 M $KHSO_3$	"
	1.17	2 M NH_4HSO_3	"
	0.75	21°C, 3.5 M $NaClO_4$	Eriksen(1969)
$SO_3^=$	0.710	Radioactive Tracer, 25°C 1 M $(NH_4)_2SO_3$	Eriksen(1967)
	0.50	Radioactive Tracer, 21°C 3.5 M $NaClO_4$	Eriksen(1969)

$$^{\ddagger}D_{HSO_3^-} = 6.315 \cdot 10^{-3} cm^2 sec^{-1} \exp\left(\frac{-1862\ K}{T}\right) \quad 295\ K \le T \le 309\ K$$

$$^{*}D_{HSO_3^-} = 1.49 \cdot 10^{-5} cm^2 sec^{-1} - 4.08 \cdot 10^{-6} C^{1/2} cm^2 sec^{-1} \ell^{1/2} mole^{-1/2}$$

at 22°C (C = NH_4HSO_3 concentration)

where F is Faraday's constant. Some of the D_i values in Tables 2.5b,c are computed from eq. 2-13.

Diffusion coefficients vary with solution viscosity and with the solutes present in solution. Therefore, in finding best values, it is desirable to extrapolate to infinite dilution. Adjustments can be made when the coefficients are to be used for concentrated solutions.

Table 2.6 shows the recommended D_i^o values for 25°C. Choice of $D^o_{H_3O^+}$ is easy since reported values agree. The value in Table 2.6 is the average of the four values in Table 2.5a.

Choice of a best value for $D^o_{SO_2}$ is not as easy. Most investigators calculated D_{SO_2} from the absorption rate of SO_2 into water. Penetration theory was used as the model for data analysis. In every case, the ionization of SO_2 to HSO_3^- was not accounted for or discussed, and this sheds doubt on the validity of the reported D_{SO_2} values. All of the absorption studies, however, were done with pure SO_2. In water exposed to 1 atm. of SO_2, HSO_3^- is only 11% of the total dissolved sulfur at 20°C. Therefore, the neglect of the ionization is unimportant.

Another point is that an SO_2/H_2O solution exposed to one atmosphere of SO_2 at 20°C has a pH of 0.85 or an ionic strength (I) of 0.14M. Therefore, the studies do

Table 2.6

Recommended Values of Diffusion Coefficients
Infinite Dilution, 25°C

Species	$10^5 \cdot D_i^o$ $cm^2 sec^{-1}$	Comments
H_3O^+	9.30	Strong literature consensus
SO_2(aq)	1.60	Good literature consensus; estimated from data at 20°C; see text
HSO_3^-	1.47	Based on Eriksen (1967), Washburn (1926), Campbell and Maass (1930)
$SO_3^=$	1.10	Estimated; see text

not give D_{SO_2} at infinite dilution even though pure water is the absorbing medium.

Since most data are at 20°C, extrapolating to 25°C is another problem. Only Peaceman (1951) gives a temperature dependence for D_{SO_2}. He reports a 12% increase in D_{SO_2} from 20°C to 25°C. This increase is significantly larger than the 2% increase that is predicted if D is assumed proportional to T (Stokes-Einstein).

Given these difficulties, averaging all of the 20°C data and assuming a 10% increase to extrapolate to 25°C and to infinite dilution seems reasonable. The value $D^o_{SO_2} = 1.6 \cdot 10^{-5} cm^2 sec^{-1}$ achieved by this method agrees with Bengtsson's value. Kolthoff and Miller's value is neglected since it disagrees significantly with the other values.

For $D^o_{HSO_3^-}$, Eriksen (1967, 1969) is the prime authority. None of his data, however, are at infinite dilution. The value at 22°C shown in Table 2.5c is deduced by extrapolating his data to infinite dilution. If $D_{HSO_3^-}$ is assumed proportional to the temperature (Stokes-Einstein), then his value at 22°C becomes $D^o_{HSO_3^-} = 1.51 \cdot 10^{-5} cm^2 sec^{-1}$ at 25°C.

Since the conductivity data are from old studies, it was decided to average them and to count this average as one value. Eriksen's 25°C value is then averaged with this one value yielding $D^o_{HSO_3^-} = 1.47 \cdot 10^{-5} cm^2 sec^{-1}$.

The only data for $D^{o}_{SO_3^=}$ are for concentrated solutions. Extrapolating to infinite dilution presents a problem. Molecular weight considerations predict $D^{o}_{SO_3^=} \simeq D^{o}_{HSO_3^-}$. Table 2.5c shows, however, that $D_{SO_3^=} = 0.58 \cdot D_{HSO_3^-}$ in 1M NH_4^+ solution and $D_{SO_3^=} = 0.67 \cdot D_{HSO_3^-}$ in 3.5M $NaClO_4$. A reasonable estimate therefore is obtained by averaging these ratios

$$D^{o}_{SO_3^=} = D^{o}_{HSO_3^-}\left[\frac{1 + 0.58 + 0.67}{3}\right] = 1.1 \cdot 10^{-5}\ cm^2 sec^{-1} \qquad (2.14)$$

This recommended value is shown in Table 2-6.

No diffusion coefficient data exist for $S_2O_5^=$, $HS_2O_5^-$ or other species in alkaline SO_2 solutions ($NaSO_3^-$, etc.). This lack of data represents an unknown that is addressed in Chapter 3.

2.5 Mass Transfer with Chemical Reaction and SO_2 Transport Studies

The contributions of the present work to the general topic of mass transfer with chemical reaction and to SO_2 transport in particular become clear in this section. By discussing the general topic first, the similarities in the principles that have evolved in absorption literature and facilitated transport literature can be described.

2.5.1 Mass Transfer with Chemical Reaction

Absorption studies in the chemical engineering literature have developed extensively the principles of mass transfer with chemical reaction (Sherwood, Pigford, and Wilke, 1975; Danckwerts, 1970; Astarita, 1967). Although absorption generally occurs into highly turbulent fluids, standard absorption models (film, penetration, surface renewal) propose a stagnant layer at the gas-liquid interface.

Equations governing the absorption are

$$D_i \frac{d^2 C_i}{dx^2} = -r_i \tag{2.15}$$

for the film model and

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + r_i \tag{2.16}$$

for the penetration and surface renewal models. Equation 2.15 or 2.16 applies to each species involved in a given absorption process. Because analytical solutions to eqs. 2.15,16 are available only for simple forms of r_i (e.g., linear kinetics), complex processes such as CO_2 absorption into NaOH or amine solutions have been approached by simplifying the full, multicomponent, non-linear reaction schemes into forms that can be treated analytically (Danckwerts and Sharma, 1966; Astarita and Gioia, 1965; Hikita, Asai, and Takatsuka, 1976). Progress in the field is presently in the area of developing solutions to eqs. 2.15,16 for more complex forms of r_i (Hikita and Asai, 1976; Wellek, Brunson, and Law, 1978).

Further understanding of mass transfer with chemical reaction has developed in the biological literature under the heading of "carrier-mediated" transport. Osterhout (1940) established the concept of carrier-mediated transport by demonstrating that quiacol would carry Na^+ and K^+ across a non-aqueous layer of quiacol. As the concept was applied to more systems, the "bucket brigade" model and versions thereof (Wilbrandt and Rosenberg, 1961) were developed to explain the phenomenon. In this model, the species passing through the film or membrane attaches to a carrier molecule on one side of the film. The (stationary) carrier passes the penetrant to a neighboring carrier molecule, and this process is repeated until the penetrant reaches the other side of the film.

Wang (1961) and Fatt and LaForce (1961) proposed that in the oxygen/hemoglobin system, oxyhemoglobin (HbO_2) was not stationary but underwent Brownian diffusion. These researchers countered Scholander's proposal (1960) that the observed augmentation of O_2 transport through blood could be explained by a "bucket brigade" involving hemoglobin. Friedlander and Keller (Keller, 1964; Friedlander and Keller, 1965; Keller and Friedlander, 1966) resolved the controversy by showing that the O_2/Hb system could be treated quantitatively by considering O_2, Hb, and HbO_2 to be undergoing simultaneous diffusion and reversible reaction. Analytical problems caused by the non-linear rate expression were avoided by the use of the affinity function (Friedlander and Keller, 1965).

When Friedlander and Keller showed that the concepts of simultaneous diffusion and chemical reaction (long the mainstay of chemical engineering absorption literature) applied to some biological systems, facilitated transport became a new dimension of mass transfer with chemical reaction. Studies of CO_2 transport through aqueous films (Ward and Robb, 1967; Otto and Quinn, 1971; Suchdeo and Schultz, 1974a), of NO transport through formamide films containing Fe^{++} (Ward, 1970), of O_2 transport through aqueous cobaltodihistidine films (Bassett and Schlutz, 1970), and of simultaneous O_2 and CO_2 transport in hemoglobin solutions (Ulanowicz and Frazier, 1970) showed that complex systems could be treated quantitatively by considering simultaneous diffusion and reversible reaction. These and other studies (Kruezer and Hoofd, 1970; Goddard, et al., 1970; Smith, Meldon, and Colton, 1973; Suchdeo and Schultz, 1974b) developed a variety of approximate analytical tools for solving equations typical of facilitated transport systems.

In reviewing facilitated transport, Schultz, Goddard, and Suchdeo (1974) unified all of the analytical approaches to equations with the form

$$D_i \frac{d^2 C_i}{dx^2} = -r_i \tag{2.17}$$

and generalized the results to include any number of species and any functional form for r_i. The flux of any volatile species through a film was shown to be a linear combination of concentration differences. When r_i is non-linear, these differences can be computed only by approximate (asymptotic) methods that are valid when the chemical reactions are either fast or slow.

For some aqueous SO_2 solutions, the potential gradient is significant, and the governing differential equations are different from eq. 2.17. Also, the asymptotic analyses given by Schultz, Goddard, and Suchdeo fail to explain the flux of SO_2 through alkaline solutions because the system is far from the limits of fast and slow chemical reactions.

Since eqs. 2.17 and 2.15 are identical (except for boundary conditions), the approach shown by Schultz, Goddard, and Suchdeo applies to absorption problems. This fact has not been appreciated by those in the absorption field, presumably because absorption originated in chemical engineering and facilitated transport originated in biology. Because the equations that govern SO_2 transport reduce to equations like 2.17 for many solutions of practical interest, the fundamentals expressed in this study can be used to predict absorption rates of SO_2.

New analyses for facilitated systems have not appeared since the review of Schultz, Goddard, and Suchdeo. The principles, however, have been applied to a number of systems of practical interest (Donaldson and Quinn, 1975; Meldon, Smith, and Colton, 1977; Matson, Herrick, and Ward, 1977; Lander and Quinn, 1978).

2.5.2 SO_2 Transport Studies

Two subdivisions of previous studies of SO_2 transport in aqueous solutions provide a convenient format. The first is older absorption studies. These are concerned with data correlation rather than a fundamental interpretation of the absorption process ("phenomenological studies"). The second subdivision consists of more recent studies that take a mechanistic approach to understanding the transport process ("fundamental studies").

2.5.2.1 Phenomenological studies

Sims (1861) first reported the capacity of water for absorbing SO_2. Absorption rates in processing equipment, however, were not studied until the 1920's. Several investigators (Halsam, et al., 1923, 1924; Cantelo, et al., 1927; Adams 1933; Hixon, 1935) used pure water in packed or spray towers to absorb either pure SO_2 or burner gas emissions (20% SO_2). Data were correlated with the film model. Although no attempts were made to relate the liquid film coefficient to fundamentals, the liquid film was shown to control the absorption rate.

Johnstone and co-workers (Johnstone and Keyes, 1935; Dobry, 1935; Krebs, 1937; Johnstone and Singh, 1937; Johnstone, 1937; Johnstone and Blankmeyer, 1938; Johnstone and Kleinschmidt, 1938; Johnstone and Singh, 1940; Johnstone and Silcox, 1947) studied SO_2 absorption in a variety of aqueous media including concentrated $NaHSO_3$, NaOH, $NaOH/H_2O_2$, and sodium acetate solutions. The gas phases were generally 2000-8000ppm SO_2 in air. The absorption was shown to be gas-phase controlled when suitably alkaline solutions were used (e.g., > 0.5M NaOH). As a result, these studies mostly ignored the liquid-phase transport.

The exception was Krebs (1937) who varied the pH of the absorbing solution in a wetted wall apparatus. Liquid-film resistance was important when the pH of the absorbing solution was less than 5. His thesis contains a qualitative discussion of the fundamentals of the transport in the liquid phase.

The unfavorable economics of the processes studied by Johnstone led to the development of other FGD processes in the 60's and 70's. It is known (Corbett, et al., 1977; Aul, et al., 1977) that the liquid phase controls or influences absorption rates in many modern FGD scrubbers, including lime/limestone systems.

When Higbie's penetration theory arose, several investigators interpreted SO_2 absorption with it. This theory contains a concentration difference in the liquid phase which provides the driving force for the absorption. Disagreement as to the proper driving force for SO_2 absorption led to a controversy over the rate of SO_2 hydrolysis (eq. 2.11).

Whitney and Vivian (1949) absorbed pure SO_2 into water in a packed tower. They assumed the concentration difference in the penetration theory to be based on the concentration of $SO_2(aq)$. Data were successfully correlated under this assumption, indicating that the chemical reaction of SO_2 with water was unimportant. Hence Whitney and Vivian concluded that ". . . the hydrolysis rate may be so slow as to be inconsequential with respect to the diffusion rate." This result was similar to the result of their chlorine absorption study (Whitney and Vivian, 1947).

Lynn and coworkers (1955), Toor and Chiang (1959), and Norman and Sammak (1963) also measured absorption rates of pure SO_2 into water and correlated their data with the penetration theory. These investigators, however, assumed the driving force to be based on the total concentration of dissolved sulfur ($SO_2(aq)$, HSO_3^-, etc.). This assumption is tantamount to assuming that the hydrolysis reaction is instantaneous. Therefore, when the data agreed with the penetration theory combined with this "instantaneous" assumption, these investigators concluded that the hydrolysis reaction was extremely fast.

Studies of the rate of hydrolysis (section 2.3) exacerbated this controversy. Wang and Himmelblau's (1964) data agreed with Whitney and Vivian's conclusion. The data of Eigen, et al. (1961) supported Lynn, et al., Toor and Chiang, and Norman and Sammak.

A possible explanation for the disagreement lies in the partial pressures of SO_2 used in these investigations. Since 0.1 to 1.0 atmosphere of SO_2 was employed, only 10% to 30% of the total dissolved sulfur would be in ionic forms (mostly HSO_3^-) even if the hydrolysis was instantaneous. The difference between a slow and an instantaneous reaction therefore can be lost in experimental error and uncertainty in the value of the diffusion coefficient of SO_2.

Hetherington (1968) addressed this problem directly. In his experiment, however, the slow reaction model differed from the instantaneous reaction model by only 7% (see Tables 8.2 and 8.3 of his thesis). Within experimental error, there is no difference between an instantaneous reaction and a slow reaction, and his conclusion that the reaction is instantaneous is unjustified.

A goal of the present work is to obtain data on a system for which the difference between a slow and fast reaction is more than a factor of 10. In this way, a clear distinction between the kinetic extremes can be achieved.

2.5.2.2 Fundamental studies

Thomas's study (1964) provides a transition to a more mechanistic approach to SO_2 transport. Sulfur dioxide was absorbed into water from a 5% to 15% mixture of SO_2 in air. The two-film theory was applied for the data analysis. Thomas considered the hydrolysis in a clear, valid manner. His eq. 19 assumes that the diffusion coefficients of all sulfur-containing species are equal. In pure water, this assumption is poor because the potential gradient enhances the diffusivity of HSO_3^- (section 3.2.2). Thomas ignores the potential gradient. Under the partial pressures of SO_2 studied, the HSO_3^- contributes a maximum of 1/3 of the total dissolved sulfur. Therefore the equal diffusivity assumption was not serious, and data were successfully correlated with the two-film theory.

Radioactive tracer studies by Eriksen (1967, 1969) yielded valuable diffusion coefficient data (section 2.4). Several approximations and simplifications are present in his work. First, the only species considered in solution were $SO_2(aq)$, HSO_3^-, and $SO_3^=$. (Note his eq. 7a, 1969, is eventually replaced by eq. 8). Several species were therefore ignored (section 3.1). Also, all chemical reactions were assumed to be instantaneous. The length scale in his study (3mm) justifies this approximation no matter if Wang and Himmelblau or Eigen are right about the magnitude of k_1 (section 2.3). The kinetic question therefore remained unaddressed.

Eriksen omitted the potential gradient by appealing to the high ionic strength of his solutions. The neutral salt studies reported here, however, indicate that the potential gradient is as important in neutral salts as it is in pure water (section 5.2). Eriksen's tracer solutions had no pH gradients. The present study shows significant pH effects (section 5.3). Therefore, although Eriksen's study is sound, it leaves unanswered several important questions.

Onda, et al., (1971) absorbed pure SO_2 into solutions of NaOH and Na_2SO_3. Results were interpreted with an instantaneous, irreversible reaction model. Only SO_2(aq), HSO_3^-, and $SO_3^=$ were considered to exist in solution. The potential gradient was approximately accounted for.

In general, this is a sound study. The instantaneous reaction theory however is not always valid (section 5.3). Because pure SO_2 was absorbed, enhancement factors were no larger than 1.2 (Figure 8 of Onda, et al., 1971). Under partial pressures of SO_2 of practical interest (100-5000 ppm), instantaneous reaction theory predicts enhancement factors as large as 10^4. Such large enhancement factors, however, are not observed in the present study.

Using penetration theory as a basis, Rochelle and King (1977) developed an approximate theory for SO_2 absorption into lime/limestone slurries. Instantaneous reactions were assumed, and the potental gradient was ignored. The complex chemistry of the lime/limestone system was lumped into a "total alkalinity" term denoted by C_A. An effective Henry solubility coefficient, $\underline{m}$, was also defined as

$$\underline{m} = \frac{\text{partial pressure of } SO_2}{\text{total dissolved sulfur}} \tag{2.18}$$

The expression for the enhancement factor derived with these approximations was used to generate an equation for the removal of SO_2 by a scrubber. This equation was integrated by assuming C_A and m to be constant. Although Rochelle recognized that m is not constant, he estimated that it varies by a factor of 2 over the height of the scrubber. A factor of 10, however, is more reasonable (Appendix C). Also, C_A is not a constant. Nonetheless, some scrubber data are successfully correlated by choosing two unknown parameters (Figure 7 of Rochelle and King, 1977).

Rochelle's thesis (Rochelle, 1977) has appeared as EPRI report no. FR 463 SR. It contains further information.

In a study similar to Onda's, Hikita, et al., (1977) absorbed pure SO_2 into concentrated NaOH and Na_2SO_3 solutions and interpreted the data with an instantaneous reaction-plane model. Enhancement factors no larger than 4 were observed since pure SO_2 was absorbed. Non-equilibrium aspects of the SO_2 transport system were not found, and partial pressures of practical interest were not studied.

A nearly exact model for SO_2 absorption into water was given by Hikita and coworkers (1978). This model included an accounting of the potential gradient and assumed instantaneous hydrolysis of SO_2. Data agreed well with the model. Pure SO_2 was used in the experiments, however. Since only 11% of the total dissolved sulfur exists in ionic forms when the partial pressure of SO_2 is one atmosphere, the conditions studied did not represent a severe test of the theory. Enhancement factors no larger than 1.3 were observed.

Teramoto, et al., (1978) have examined the more complex problem of simultaneous SO_2 and CO_2 absorption. This situation is relevant to scrubbers since the CO_2 partial pressure in power-plant stack gases is about 0.1 atmosphere.

2.6 Applications and Related Topics

Many areas of practical interest involve absorption and transport of SO_2 in aqueous solutions. These and related topics are listed below with references that provide a good introduction to the literature in a given area.

1) Solubility of SO_2 in aqueous media -- Rowland and Abdulsattar (1978), Abdulsattar, Sridhar, and Bromley (1977), Oestreich (1976)
2) Flue gas desulfurization -- Ayer (1978), Biondo (1977), Rochelle (1977)
3) SO_2 absorption by natural waters -- Husar (1978), Brimblecombe and Spedding (1974), Hales (1972)

4) Lung mucous absorption -- Hickey (1976), Bell (1976)
5) Vegetation absorption -- Babich and Stotzky (1978), Crittend and Read (1978), Hocking and Hocking (1977)
6) SO_2 transport in polymer membranes -- Kuehne (1979), Felder, Spence, and Ferrell (1975)
7) General chemistry of SO_2 -- Zipp (1974), Rooney, et al. (1973), Peone (1971), Schroeter (1966)

CHAPTER 3: THEORY

3.1 Chemical Speciation; Equilibrium and Diffusion Coefficients

Chemical species, equilibria, and equilibrium coefficients in SO_2/Na^+ aqueous solutions[‡] are shown in Table 3.1. Species omitted in previous SO_2 transport studies are $S_2O_5^=$, $NaHSO_3$, $NaS_2O_5^-$, $Na_2S_2O_5$, $NaSO_3^-$, Na_2SO_3, $HS_2O_5^-$, $H_2S_2O_5$, and NaOH. Equilibrium calculations predict these species to account for two-thirds of the total dissolved sulfur when $Na_{tot} = 3M$. When $Na_{tot} = 0.5M$, these species account for about 15% of the dissolved sulfur. Hence, they must be included in discussions of concentrated alkaline solutions.

In Table 3.1, coefficients K_1-K_4 and K_{12} are taken from the literature, and coefficients K_5-K_{11} are estimated from the Fuoss equation (Fuoss, 1958). This calculation is approximate since the ion diameter, $\underline{a}$, appearing in the Fuoss equation is uncertain for some of the species. Values of $\underline{a}$ are given by Klotz and Rosenberg (1972). Reasonable values for the species of interest can be obtained by comparison with similar species listed by Klotz and Rosenberg.

Diffusion coefficients have been measured for several species (section 2.4). Unmeasured coefficients (D_j) can be

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[‡] Na^+ added to solutions as NaOH, $NaHSO_3$, Na_2SO_3, or $Na_2S_2O_5$

Table 3.1 Species, Equilibria, and Equilibrium Coefficients (25°C) for the $SO_2/Na^+/H_2O$ System

Reaction	Equilibrium Coefficient		Reference
	Symbol	Value	
$SO_2+2H_2O \rightleftarrows H_3O^++HSO_3^-$	K_1	0.014 mole/ℓ	Huss and Eckert (1977)
$HSO_3^-+H_2O \rightleftarrows H_3O^++SO_3^=$	K_2	$6.24 \cdot 10^{-8}$ mole/ℓ	Tartar and Garretson (1941)
$2HSO_3^- \rightleftarrows S_2O_5^=+H_2O$	K_3	0.076 ℓ/mole	Bourne, et al. (1974)
$2H_2O \rightleftarrows H_3O^++ OH^-$	K_4	$1.008 \cdot 10^{-14}\ \frac{\text{mole}^2}{\ell^2}$	MacInnes (1932)
$NaHSO_3 \rightleftarrows Na^++HSO_3^-$	K_5	3.00 mole/ℓ	Fuoss estimate (see text)
$NaS_2O_5^- \rightleftarrows Na^++S_2O_5^=$	K_6	0.19 mole/ℓ	" "
$Na_2S_2O_5 \rightleftarrows Na^++NaS_2O_5^-$	K_7	0.19 mole/ℓ	" "
$NaSO_3^- \rightleftarrows Na^++SO_3^=$	K_8	0.19 mole/ℓ	" "
$Na_2SO_3 \rightleftarrows Na^++NaSO_3^-$	K_9	0.19 mole/ℓ	" "
$HS_2O_5^-+H_2O \rightleftarrows H_3O^++S_2O_5^=$	K_{10}	0.0104 mole/ℓ	" "
$H_2S_2O_5+H_2O \rightleftarrows H_3O^++HS_2O_5^-$	K_{11}	10 mole/ℓ	" "
$NaOH \rightleftarrows Na^++OH^-$	K_{12}	5.04 mole/ℓ	Moelwyn-Hughes (1972)

Note: Coefficients K_1-K_4 are chosen as the best available data from several literature sources. See Table 2.3.

estimated from measured ones (D_i) by the Stokes-Einstein relation:

$$\frac{D_j}{D_i} = \left(\frac{MW_i}{MW_j}\right)^{1/3} \tag{3.1}$$

Here, MW_i is the molecular weight of the ith species. In calculating D_j, it is reasonable to use $D_i = D_{SO_2}$ for j = uncharged species, $D_i = D_{HSO_3^-}$ for j = univalent species, and $D_i = D_{SO_3^=}$ for j = divalent species. Diffusion coefficients at infinite dilution, 25°C, calculated in this way are shown with measured coefficients in Table 3.2.

For SO_2/neutral salt solutions or SO_2/H_2O solutions, the complex physical chemistry (Table 3.1) is unnecessary. The important species in these solutions under the conditions of the present study are $SO_2(aq)$, H_3O^+, HSO_3^-, and the cation and anion of the neutral salt. Appropriate simplifications will be applied for these solutions (sections 3.2.3.1,2). The complex model will be used only for the alkaline solutions.

3.2 SO_2 Transport Through an Aqueous Film

Figure 3.1 is a schematic diagram of an aqueous film, exposed to a gas phase at each boundary, that contains pure water or a neutral or alkaline salt (e.g.,

Table 3.2

Diffusion Coefficients, Infinite Dilution, 25°C

Species	$10^5 \cdot D_i^o$ cm^{2}sec^{-1}	Source
H_3O^+	9.30	Best available data[‡]
OH^-	5.26	Newman (1973)
HSO_3^-	1.47	Best available data[‡]
$S_2O_5^=$	1.00	Calculated
$SO_3^=$	1.10	Best available data[‡]
SO_2(aq)	1.60	"
Na^+	1.33	Newman (1973)
$NaHSO_3$	1.40	Calculated
$NaS_2O_5^-$	0.87	"
$Na_2S_2O_5$	1.10	"
$NaSO_3^-$	1.00	"
Na_2SO_3	1.30	"
$HS_2O_5^-$	0.90	"
$H_2S_2O_5$	1.20	"
NaOH	1.87	"

[‡] From literature review; Tables 2.5 and 2.6.

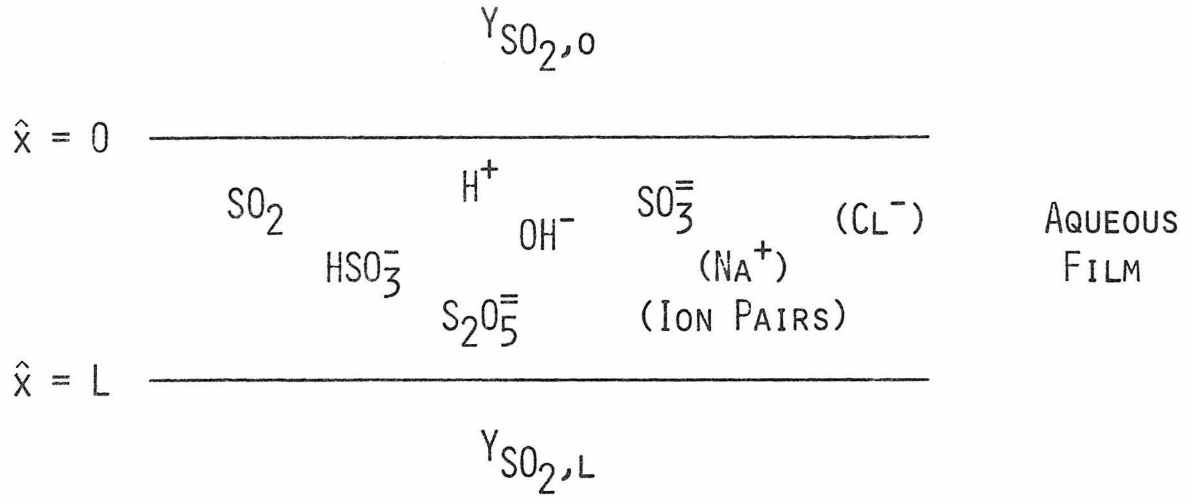


FIGURE 3.1 -- Physical System - Aqueous film, exposed to SO_2, with or without a neutral or alkaline salt. The goal of theory is to predict flux of SO_2 through film.

NaCl, NaOH, $NaHSO_3$). Each gas phase has a total pressure of one atmosphere and is a mixture of N_2 and SO_2 humidified to prevent evaporation of the film. The gas phase on the $\hat{x} = 0$ side (upstream side) contains an SO_2 mole fraction symbolized by $y_{SO_2,o}$. On the downstream side, $y_{SO_2,1}$ is defined similarly. Species present in the film, discussed in the previous section, are shown.

When $y_{SO_2,o} > y_{SO_2,1}$, SO_2 passes through the film from $\hat{x} = 0$ to $\hat{x} = L$. The goal of the theory is to predict the flux of SO_2 (moles per unit area per unit time) through the film under steady conditions given any $y_{SO_2,o}$, $y_{SO_2,1}$, and the concentrations of any salts in the aqueous film.

3.2.1 General Results

Equations for this system are

Conservation of mass (each species)

$$\frac{dN_i}{dx} = r_i \tag{3.2}$$

boundary conditions

$$N_{NV} = 0 \qquad x = 0,1 \tag{3.3}$$

$$c_{SO_2}(0) = \frac{y_{SO_2,o}P_{tot}}{\gamma_{SO_2}H_{SO_2}} \qquad c_{SO_2}(1) = \frac{y_{SO_2,1}P_{tot}}{\gamma_{SO_2}H_{SO_2}} \tag{3.4a,b}$$

Electroneutrality

$$\sum_i z_i C_i = 0 \qquad (3.5)$$

Flux expression

$$N_i = -D_i \frac{dC_i}{dx} - z_i D_i C_i \frac{F}{RT} \frac{d\Phi}{dx} \qquad (3.6)$$

Reaction mechanisms

$$r_i = r_i(T,P,C_n) \qquad (3.7)$$

Equation 3.3 states that non-volatile species (ions, ion pairs) have zero flux at the boundaries. The technique for solving for the SO_2 flux does not require explicit rate expressions to be written. Therefore, the reaction rates (eq. 3.7) are simply denoted as functions of the temperature, pressure, and species concentrations.

Parameters and variables in eqs. 3.2-7 have been non-dimensionalized by

$$N_i = \frac{L\hat{N}_i}{D^o_{SO_2}\tilde{C}} \qquad (3.8)$$

$$C_i = \frac{\hat{C}_i}{\tilde{C}} \qquad (3.9)$$

$$x = \frac{\hat{x}}{L} \tag{3.10}$$

$$r_i = \frac{L^2 \hat{r}_i}{D^o_{SO_2} \tilde{C}} \tag{3.11}$$

$$D_i = \frac{\hat{D}_i}{D^o_{SO_2}} \tag{3.12a}$$

$$H_{SO_2} = \frac{\hat{H}_{SO_2} P_o}{\tilde{C}} \tag{3.12b}$$

$$P_{tot} = \frac{\hat{P}_{tot}}{P_o} \tag{3.12c}$$

The hatted symbols have dimensions. The concentration $\tilde{C}$ is an arbitrary characteristic concentration, and P_o is an arbitrary reference pressure.

When a sodium salt is added to the film in a concentration $\hat{C}_o$, conservation of sodium yields the following integral constraint:

$$\int_0^1 \left(\sum_k n_k C_k\right) dx = C_o \tag{3.13}$$

k = sodium-containing species

Here n_k is the number of sodium atoms in the kth sodium-containing species. Similar constraints apply to any non-volatile substances added to the film.

If there are N species in solution other than H_2O, eqs. 3.2-7 define N+1 equations for N+1 unknowns (N concentrations plus the potential gradient, $\frac{d\Phi}{dx}$). The system is not overspecified when eq. 3.13 applies since not all of the equations for the sodium-containing species are independent (see Goddard, et al., 1970). Thus, the concentration profile of SO_2(aq), $C_{SO_2}(x)$, can in principle be found. The desired (non-dimensional) flux, N_{SO_2}, is given by

$$-D_{SO_2} \frac{dC_{SO_2}}{dx}\bigg|_{x=0} = N_{SO_2} = -D_{SO_2} \frac{dC_{SO_2}}{dx}\bigg|_{x=1} \qquad (3.14)$$

Although an analytical solution for $C_{SO_2}(x)$ has not been found, significant progress in determining the flux can be made. Defining n_j as the number of sulfur atoms in the jth sulfur-containing species, conservation of sulfur requires

$$\sum_j n_j r_j = 0 \qquad (3.15)$$

(subscript j refers only to sulfur-containing species).

Substituting r_j from eq. 3.3 and integrating yields

$$\sum_j n_j N_j = \text{constant} \equiv A_{SO_2} \tag{3.16}$$

where A_{SO_2} is some (unknown) constant. Since at $x = 0$, $N_j = 0$ for $j \neq SO_2$, and since $n_{SO_2} = 1$, the constant A_{SO_2} must be N_{SO_2}.

Hence, eq. 3.6 in eq. 3.16 yields

$$N_{SO_2} = -\frac{d}{dx}\left(\sum_j n_j D_j C_j\right) - \frac{F}{RT}\frac{d\Phi}{dx}\left(\sum_j z_j n_j D_j C_j\right) \tag{3.17}$$

where the D_j are assumed constant. One more integration gives

$$N_{SO_2} = \frac{1}{x-x_o}\sum_j n_j D_j [C_j(x_o) - C_j(x)] - \frac{1}{x-x_o}\frac{F}{RT}\int_{x_o}^{x}\frac{d\Phi}{dx}\left(\sum_j z_j n_j D_j C_j\right)dx \tag{3.18}$$

or

$$N_{SO_2} = \sum_j n_j D_j [C_j(0) - C_j(1)] - \frac{F}{RT}\int_0^1 \frac{d\Phi}{dx}\left(\sum_j z_j n_j D_j C_j\right)dx \tag{3.19}$$

The absence of an electric current in the film implies

$$\sum_i z_i N_i = 0 \tag{3.20}$$

Substituting eq. 3.6 into eq. 3.20 gives

$$-\frac{F}{RT}\frac{d\Phi}{dx} = \frac{\frac{d}{dx}\left(\sum_i z_i D_i C_i\right)}{\sum_i z_i^2 D_i C_i} \tag{3.21}$$

Therefore eqs. 3.18,19 become

$$\begin{aligned} N_{SO_2} &= \frac{1}{x-x_o}\sum_j n_j D_j [C_j(x_o) - C_j(x)] \\ &+ \frac{1}{x-x_o}\int_{x_o}^{x} \frac{\sum_j z_j n_j D_j C_j}{\sum_i z_i^2 D_i C_i}\frac{d}{dx}\left(\sum_i z_i D_i C_i\right)dx \end{aligned} \tag{3.22}$$

and

$$\begin{aligned} N_{SO_2} &= \sum_j n_j D_j [C_j(0) - C_j(1)] \\ &+ \int_0^1 \frac{\sum_j z_j n_j D_j C_j}{\sum_i z_i^2 D_i C_i}\frac{d}{dx}\left(\sum_i z_i D_i C_i\right)dx \end{aligned} \tag{3.23}$$

Although eqs. 3.22,23 have been derived for an aqueous SO_2 solution, similar equations would apply for any number of volatile species (CO_2, NH_3, H_2S, etc.) undergoing transport simultaneously. The subscript j would refer to a given species just as it refers to "SO_2" in eqs. 3.22,23.

Equations 3.22,23 hold for an arbitrary aqueous SO_2 solution since nothing has been assumed about what the sulfur-containing species are. Although these equations are not explicit statements of the flux in terms of known quantities, they will prove useful for calculating N_{SO_2}.

3.2.2 Role of the Potential Gradient

The potential gradient poses a difficulty in the analysis because it gives rise to the term

$$\bar{B} = \int_0^1 \frac{\sum_j z_j n_j D_j C_j}{\sum_i z_i^2 D_i C_i} \frac{d}{dx}\left(\sum_i z_i D_i C_i \right) dx \qquad (3.24)$$

in eqs. 3.22,23. Analyses of facilitated transport reviewed by Schultz, Goddard, and Suchdeo (1974) have omitted the potential gradient. It has been included by others in various contexts (Meldon, Smith, and Colton, in press; Brian, 1961; Vinograd and McBain, 1941).

Because the concentration profiles are unknown, $\bar{B}$ cannot be computed without numerical solution of the differential equations. In the following discussion, certain limiting cases will be considered.

In a solution that has a concentration gradient of a single salt, the anion (A^{z-}) and cation (M^{z+}) attempt to diffuse at different rates when the diffusivities of A^{z-} and M^{z+} are different. A minute charge separation occurs, and a potential gradient is set up. (Electroneutrality remains an accurate approximation--see section 76 of Newman, 1973.) The effect of the potential is to speed up the ion with the smaller diffusivity and slow down the ion with the larger diffusivity, causing each to move with the same effective diffusivity. This "binary salt" diffusivity is given by

$$D_{eff} = \frac{(z^+ - z^-)D^+D^-}{z^+D^+ - z^-D^-} \tag{3.25}$$

where D^+ and D^- are the diffusivities of the cation and anion (Nernst, 1888).

Aqueous SO_2/Na^+ solutions behave as single salt solutions under some conditions. When $Na_{tot} < 0.05M$, Na^+, HSO_3^-, and H_3O^+ are the important ions. Defining

$$PG_1 \equiv \frac{D_{Na+}C_{Na+}}{D_{HSO_3^-}C_{HSO_3^-}} \tag{3.26a}$$

and

$$PG_2 \equiv \frac{D_{H_3O+}C_{H_3O^+}}{D_{HSO_3^-}C_{HSO_3^-}} \tag{3.26b}$$

$\bar{B}$ becomes

$$\bar{B} = -\int_0^1 \frac{1}{PG_2 + PG_1 + 1} \frac{d}{dx}[D_{HSO_3^-} C_{HSO_3^-} (PG_2 + PG_1 - 1)]dx \quad (3.27)$$

Consider solutions in which

$$\frac{C_{H_3O^+}}{C_{HSO_3^-}} \simeq 1 \quad (3.28)$$

(e.g., SO_2/H_2O solutions). Then,

$$PG_2 \simeq \frac{D_{H_3O^+}}{D_{HSO_3^-}} \quad (3.29)$$

Because electroneutrality requires

$$C_{Na^+} + C_{H_3O^+} = C_{HSO_3^-} \quad (3.30)$$

eq. 3.28 implies

$$\frac{C_{Na^+}}{C_{HSO_3^-}} << 1 \quad (3.31)$$

which implies

$$PG_1 << 1 \quad (3.32)$$

Using eqs. 3.29,32 in eq. 3.27, eq. 3.23 becomes

$$N_{SO_2} = \sum_j n_j D_j^* [C_j(0) - C_j(1)] \qquad j = SO_2(aq),\ HSO_3^- \tag{3.33}$$

with

$$D^*_{SO_2} = D_{SO_2} \tag{3.34}$$

and

$$D^*_{HSO_3^-} = \frac{2D_{H_3O+}D_{HSO_3^-}}{D_{H_3O+} + D_{HSO_3^-}} = 1.727 D_{HSO_3^-} \quad \text{at } 25°C \tag{3.35}$$

Hence, when eq. 3.28 applies, aqueous SO_2/Na^+ solutions behave as a "binary salt" consisting of H_3O^+ and HSO_3^- (compare eq. 3.35 to eq. 3.25). The potential gradient enhances the diffusivity of HSO_3^- by a factor of 1.727 (25°C).

Now consider solutions in which

$$PG_2 << 1 \tag{3.36}$$

(e.g., sufficiently concentrated alkaline solutions). When eq. 3.36 holds, then

$$\frac{C_{H_3O^+}}{C_{HSO_3^-}} << 1 \tag{3.37}$$

so that

$$\frac{C_{Na^+}}{C_{HSO_3^-}} \simeq 1 \tag{3.38}$$

and

$$PG_1 \simeq \frac{D_{Na^+}}{D_{HSO_3^-}} \tag{3.39}$$

Using eqs. 3.36,39 in eq. 3.27, eq. 3.23 becomes

$$N_{SO_2} = \sum_j n_j \tilde{D}_j [C_j(0) - C_j(1)] \qquad j = SO_2(aq),\ HSO_3^- \tag{3.40}$$

with

$$\tilde{D}_{SO_2} = D_{SO_2} \tag{3.41a}$$

and

$$\tilde{D}_{HSO_3^-} = \frac{2D_{Na+}D_{HSO_3^-}}{D_{Na+} + D_{HSO_3^-}} \simeq D_{HSO_3^-} \tag{3.41b}$$

Hence, when eq. 3.36 holds, aqueous SO_2/Na^+ solutions behave as a "binary salt" of Na^+ and HSO_3^- ions. Because

$$D_{Na+} \simeq D_{HSO_3^-} \tag{3.42}$$

the potential gradient has no effect when eq. 3.36 is satisfied, and eq. 3.40 can be written

$$N_{SO_2} = \sum_j n_j D_j [C_j(0) - C_j(1)] \qquad j = SO_2(aq),\ HSO_3^- \tag{3.43}$$

Equilibrium composition calculations (Appendix A) provide approximate ranges where eqs. 3.28 and 3.36 are valid. Tables 3.3 and 3.4 show that eq. 3.28 is satisfied when $Na_{tot} \lesssim 10^{-3}M$ and that eq. 3.36 is satisfied when $Na_{tot} \gtrsim 3 \cdot 10^{-2}M$.

When $Na_{tot} > 0.05M$, the system cannot be treated by considering only Na^+, HSO_3^-, and H_3O^+, and the complete sum

$$\sum_i z_i D_i C_i$$

in $\bar{B}$ must be considered. Electroneutrality requires

$$\sum_i z_i C_i = 0 \tag{3.44}$$

so that

$$\bar{D} \sum_i z_i C_i = 0 \tag{3.45}$$

where $\bar{D}$ is an arbitrary, characteristic diffusivity.

Table 3.3

$\frac{c_{H_3O^+}}{c_{HSO_3^-}}$ in dilute $SO_2/Na^+/H_2O$ solutions

T = 25°C

P_{tot} = 744 mm Hg

$Na^+ \frac{mole}{\ell}$	$10^6 \cdot y_{SO_2}$ 1000	500	200	100
0	1	1	1	1
10^{-4}	0.978	0.968	0.949	0.929
$2 \cdot 10^{-4}$	0.956	0.937	0.902	0.863
$5 \cdot 10^{-4}$	0.893	0.851	0.773	0.694
10^{-3}	0.798	0.725	0.600	0.488
$2 \cdot 10^{-3}$	0.639	0.531	0.374	0.259
$5 \cdot 10^{-3}$	0.345	0.234	0.122	0.068
10^{-2}	0.150	0.086	0.038	0.020

Table 3.4

$\frac{D_{H_3O^+}C_{H_3O^+}}{D_{HSO_3^-}C_{HSO_3^-}}$ in dilute $SO_2/Na^+/H_2O$ solutions

$T = 25°C$, $P_{tot} = 744$mm Hg

$Na^+ \frac{mole}{\ell}$	$10^6 \cdot y_{SO_2}$ 1000	500	200	100
0	6.33	6.33	6.33	6.33
10^{-4}	6.18	6.12	6.01	5.88
$2 \cdot 10^{-4}$	6.04	5.93	5.70	5.46
$5 \cdot 10^{-4}$	5.65	5.38	4.89	4.39
10^{-3}	5.04	4.59	3.80	3.09
$2 \cdot 10^{-3}$	4.04	3.36	2.36	1.64
$5 \cdot 10^{-3}$	2.18	1.48	0.769	0.431
10^{-2}	0.949	0.544	0.241	0.124
$2 \cdot 10^{-2}$	0.313	0.164	$6.73 \cdot 10^{-2}$	$3.41 \cdot 10^{-2}$
$3 \cdot 10^{-2}$	0.152	$7.77 \cdot 10^{-2}$	$3.16 \cdot 10^{-2}$	$1.59 \cdot 10^{-2}$
$5 \cdot 10^{-2}$	$5.97 \cdot 10^{-2}$	$3.01 \cdot 10^{-2}$	$1.21 \cdot 10^{-2}$	$6.11 \cdot 10^{-3}$
10^{-1}	$1.64 \cdot 10^{-2}$	$8.21 \cdot 10^{-3}$	$3.31 \cdot 10^{-3}$	$1.67 \cdot 10^{-3}$

Therefore,

$$\sum_i z_i D_i C_i = \sum_i z_i C_i (D_i - \bar{D}) \qquad (3.46)$$

The right-hand side of eq. 3.46 shows that when all diffusivities are equal to $\bar{D}$, $\bar{B}$ is identically zero. Table 3.2 shows that the D_i are approximately equal except for $D_{H_3O^+}$ and D_{OH^-}. (Note that it takes a large diffusivity difference to produce a significant effect, eq. 3.35.) Since H_3O^+ and OH^- are negligible for $Na_{tot} > 0.05M$ $(4 < pH < 9)$, the potential gradient is negligible, and equation 3.23 becomes

$$N_{SO_2} = \sum_j n_j D_j [C_j(0) - C_j(1)] \qquad (3.47)$$

Because sulfur-containing ions other than HSO_3^- are unimportant when $Na_{tot} < 0.05M$, eq. 3.47 is valid for $Na_{tot} \geq 0.03M$ (see eq. 3.43).

For $10^{-3}M < Na_{tot} < 3 \cdot 10^{-2}M$, the system is between the dilute limit (eqs. 3.33,34,35) and the concentrated limit (eq. 3.47). The enhancement of $D_{HSO_3^-}$ caused by the potential gradient in the dilute limit should decrease continuously as Na_{tot} is increased since the system gradually changes from a "binary H_3O^+/HSO_3^- salt" to a "binary Na^+/HSO_3^- salt." A linear interpolation for $D_{HSO_3^-}$ is proposed for the transition. Thus, eq. 3.23 can be simplified to

$$N_{SO_2} = \sum_j n_j D'_j [C_j(0) - C_j(1)] \tag{3.48}$$

with

$$D'_j = D_j \qquad \text{for } j \neq HSO_3^- \tag{3.49a}$$

and

$$D'_{HSO_3^-} = \begin{cases} D^*_{HSO_3^-} & Na_{tot} \leq 10^{-3}M \\ \dfrac{1}{0.029} \dfrac{\ell}{\text{mole}} [Na_{tot} - 10^{-3}M] & 10^{-3}M < Na_{tot} < 3 \cdot 10^{-2}M \\ \times (D_{HSO_3^-} - D^*_{HSO_3^-}) + D^*_{HSO_3^-} & \\ D_{HSO_3^-} & Na_{tot} \geq 3 \cdot 10^{-2} \end{cases} \tag{3.49b}$$

where $D^*_{HSO_3^-}$ is given by eq. 3.35.

The potential gradient in neutral salt solutions can be treated approximately, and eqs. 3.33,34,35 are shown to hold (section 3.2.3.2). Since $Na_{tot} \equiv 0$ in neutral salt solutions (zero alkaline sodium), eq. 3.49b summarizes completely the role of the potential gradient.

Thus, eqs. 3.22,23 can be written

$$N_{SO_2} = \frac{1}{x-x_o} \sum_j n_j D'_j [C_j(x_o) - C_j(x)] \qquad (3.50)$$

and

$$N_{SO_2} = \sum_j n_j D'_j [C_j(0) - C_j(1)] \qquad (3.51)$$

where the D'_j are given by eqs. 3.49a,b. Eqs. 3.50 and 3.51 are not explicit equations for the flux in terms of knowns. Approximations discussed in the following sections, however, allow these equations to be used to compute the flux.

3.2.3 Equilibrium Approximation

Equation 3.51 expresses the flux in terms of the boundary concentrations of the sulfur-containing species. If all chemical reactions are assumed to be instantaneous, then $C_j(0)$ are related to $C_{SO_2}(0)$ by equilibrium expressions. Similarly, $C_j(1)$ are related to $C_{SO_2}(1)$ by equilibrium expressions. Since $C_{SO_2}(0)$ and $C_{SO_2}(1)$ are known (eqs. 3.4a,b), $C_j(0)$ and $C_j(1)$ can be computed. These computations are similar to standard calculations in equilibrium solution chemistry. The calculations and computer program are described in Appendix A.

When alkaline sodium is present in solution, the equilibrium calculations assume that the total sodium concentration is equal at the boundaries to the initial concentration added to the film (see eq. 3.13). This approximation will be valid to the extent that the important sodium-containing species (Na^+, $NaHSO_3$, $NaSO_3^-$, Na_2SO_3) have equal diffusivities. Table 3.2 shows that this approximation is good.

Results of the equilibrium theory will be shown with experimental data in Chapter 5.

3.2.3.1 Equilibrium theory applied to pure water

For SO_2/H_2O solutions, eqs. 3.33-35 with the equilibrium approximation yield an analytical expression for the flux. The approximation

$$C_{H_3O+} = C_{HSO_3^-} \tag{3.52}$$

used in establishing eqs. 3.33-35, is verified in Table 3.5 which shows equilibrium compositions for water exposed to the indicated mole fraction SO_2. Therefore, the only important equilibrium is

$$SO_2(aq) + 2H_2O \rightleftharpoons H_3O^+ + HSO_3^- \tag{3.53}$$

Table 3.5

Equilibrium Compositions in SO_2/H_2O Solutions

Total Pressure = 744 mm Hg T = 25°C

$y_{SO_2} = 10^{-3}$

	CONCENTRATION	ACTIVITY COEFFICIENT
H3O-----	0.43971D-02	0.93906D+00
OH------	0.26189D-11	0.93182D+00
HSO3---	0.43930D-02	0.93283D+00
S2O5---	0.16835D-05	0.75825D+00
SO3----	0.81658D-07	0.75825D+00
SO2----	0.12081D-02	0.10008D+01

$y_{SO_2} = 10^{-4}$

	CONCENTRATION	ACTIVITY COEFFICIENT
H3O-----	0.13534D-02	0.96250D+00
OH------	0.80598D-11	0.95997D+00
HSO3---	0.13530D-02	0.96031D+00
S2O5---	0.15080D-06	0.85084D+00
SO3----	0.73144D-07	0.85084D+00
SO2----	0.12088D-03	0.10002D+01

$y_{SO_2} = 10^{-7}$

	CONCENTRATION	ACTIVITY COEFFICIENT
H3O-----	0.41514D-04	0.99264D+00
OH------	0.24645D-09	0.99255D+00
HSO3---	0.41385D-04	0.99256D+00
S2O5---	0.13212D-09	0.97059D+00
SO3----	0.64087D-07	0.97059D+00
SO2----	0.12091D-06	0.10000D+01

$y_{SO_2} = 10^{-9}$

	CONCENTRATION	ACTIVITY COEFFICIENT
H3O-----	0.41870D-05	0.99761D+00
OH------	0.24191D-08	0.99760D+00
HSO3---	0.40623D-05	0.99760D+00
S2O5---	0.12602D-11	0.99043D+00
SO3----	0.61126D-07	0.99043D+00
SO2----	0.12091D-08	0.10000D+01

Equilibrium of eq. 3.53 implies

$$K_1\gamma_{SO_2}C_{SO_2} = \gamma_{H_3O+}\gamma_{HSO_3^-}C^2_{HSO_3^-} \qquad (3.54)$$

where eq. 3.52 has been used.

Equation 3.4 states

$$C_{SO_2} = \frac{y_{SO_2}P_{tot}}{\gamma_{SO_2}H_{SO_2}} \qquad (3.55)$$

Thus,

$$C_{HSO_3^-} = \left(\frac{K_1 y_{SO_2}P_{tot}}{\gamma_{H_3O+}\gamma_{HSO_3^-}H_{SO_2}} \right)^{1/2} \qquad (3.56)$$

Substituting eqs. 3.55,56 in eq. 3.33 yields

$$N_{eq} = \frac{D_{SO_2}P_{tot}}{\gamma_{SO_2}H_{SO_2}} [y_{SO_2,o} - y_{SO_2,l}] + D^*_{HSO_3^-} \left[\frac{K_1 P_{tot}}{\gamma_{H_3O+}\gamma_{HSO_3^-}H_{SO_2}} \right]^{1/2} [y^{1/2}_{SO_2,o} - y^{1/2}_{SO_2,l}] \qquad (3.57)$$

A simple form for the facilitation factor, F, can be derived from eq. 3.57. Since

$$F_{eq} = \frac{N_{eq} - N_o}{N_o} \qquad (3.58)$$

and

$$N_o = \frac{D_{SO_2} P_{tot}}{\gamma_{SO_2} H_{SO_2}} [y_{SO_2,o} - y_{SO_2,l}] \qquad (3.59)$$

one finds

$$F_{eq} = \frac{D^*_{HSO_3^-}}{D_{SO_2}} \left(\frac{K_1 H_{SO_2}}{P_{tot}} \right)^{\frac{1}{2}} \frac{\gamma_{SO_2}}{(\gamma_{H_3O^+} \gamma_{HSO_3^-})^{\frac{1}{2}}} \left[\frac{y^{\frac{1}{2}}_{SO_2,o} - y^{\frac{1}{2}}_{SO_2,l}}{y_{SO_2,o} - y_{SO_2,l}} \right] \qquad (3.60)$$

3.2.3.2 Equilibrium theory applied to neutral salt solutions

Addition of a neutral salt $M_{\nu^+}A_{\nu^-}$ to an aqueous film puts two inert, non-volatile species into solution (the cation, M^{z+}, and the anion, A^{z-}). Equations 3.2 and 3.3 show that the flux of any inert, non-volatile species is zero everywhere in the film. Thus, eq. 3.20 can be written

$$\sum_{i \neq IN} z_i N_i = 0 \qquad (3.61)$$

where $i \neq IN$ indicates that the sum excludes inert, non-volatile species.

Substituting eq. 3.6 into eq. 3.61 yields

$$-\frac{F}{RT}\frac{d\Phi}{dx} = \frac{\frac{d}{dx}\left(\sum_{i\neq IN} z_i D_i C_i\right)}{\sum_{i\neq IN} z_i^2 D_i C_i} \tag{3.62}$$

Therefore, eq. 3.19 becomes

$$N_{SO_2} = \sum_j n_j D_j [C_j(0) - C_j(1)] \tag{3.63}$$

$$+ \int_0^1 \frac{\sum_j z_j n_j D_j C_j}{\sum_{i\neq IN} z_i^2 D_i C_i} \frac{d}{dx}\left(\sum_{i\neq IN} z_i D_i C_i\right) dx$$

Because the only important ions other than M^{z+} and A^{z-} are H_3O^+ and HSO_3^-, the expressions for the flux through an SO_2/H_2O solution and an SO_2/neutral salt solution are identical (compare eqs. 3.23, 3.63). Therefore, eq. 3.63 reduces to eqs. 3.33-35 if

$$C_{H_3O^+} = C_{HSO_3^-} \tag{3.64}$$

When eq. 3.64 holds, eqs. 3.57,60 apply under the equilibrium approximation (section 3.2.3.1). The following discussion shows that eq. 3.64 holds approximately.

In a neutral salt solution, electroneutrality requires

$$z^+ C_M + C_{H_3O^+} + z^- C_A - C_{HSO_3^-} = 0 \tag{3.65}$$

If the concentration of salt added to the film is C_o, then

$$C_o = \frac{1}{\nu^+}\int_0^1 C_M dx = \frac{1}{\nu^-}\int_0^1 C_A dx \qquad (3.66)$$

If $\bar{C}_M$ and $\bar{C}_A$ are the mean values of C_M and C_A, eq. 3.66 yields

$$\nu^+ C_o = \bar{C}_M \qquad (3.67a)$$

and

$$\nu^- C_o = \bar{C}_A \qquad (3.67b)$$

Substituting eqs. 3.67a,b into eq. 3.65 gives

$$[z^+\nu^+ + z^-\nu^-]C_o + z^+[C_M - \bar{C}_M] + z^-[C_A - \bar{C}_A] + C_{H_3O^+} = C_{HSO_3^-} \qquad (3.68)$$

The salt is electrically neutral so that

$$[z^+\nu^+ + z^-\nu^-] \equiv 0 \qquad (3.69)$$

Hence, eq. 3.64 is valid when

$$\frac{z^+[C_M - \bar{C}_M] + z^-[C_A - \bar{C}_A]}{C_{H_3O^+}} << 1 \qquad (3.70)$$

Equation 3.6 and the zero-flux condition on M^{z+} and A^{z-} show that

$$\frac{1}{z^+}\frac{d\ell nC_M}{dx} = -\frac{F}{RT}\frac{d\Phi}{dx} = \frac{1}{z^-}\frac{d\ell nC_A}{dx} \qquad (3.71)$$

Hence when the potential gradient is non-zero, the pointwise values of C_M and C_A are not equal to the mean values.

Since much complexity arises from eq. 3.71, the approximation 3.70 will be assumed to hold. With this assumption, eqs. 3.64 and 3.33-35 apply to neutral salt solutions. With the equilibrium approximation, eqs. 3.57,60 also apply. Equations 3.57,60 agree well with the data (section 5.2), justifying the simplicity of the approach.

3.2.4 Non-Equilibrium Boundary Layer Approximation

Schultz, Goddard, and Suchdeo (1974) review analyses that account for deviation from the equilibrium (instantaneous reactions) regime. These are based on a singular perturbation expansion from the equilibrium limit and are therefore valid in the limit of "fast" reactions. Similarly, a regular perturbation analysis exists from the limit of very slow chemical reactions (i.e., Fickian diffusion of SO_2(aq)). Experimental results (Chapter 5) show that most of the SO_2/alkaline solutions fall in a regime that is far from both the instantaneous and slow reaction limits where none of the perturbation analyses are valid. Hence it is necessary to develop a new non-equilibrium boundary layer analysis (NEBLA).

The principles of the NEBLA will be discussed in terms of an arbitrary facilitated transport system in which the carrier species are non-volatile. The ideas will then be applied to aqueous SO_2 solutions. Algebraic equations result which allow N_{SO_2} to be calculated.

3.2.4.1 Origin and existence of non-equilibrium boundary layers

The concept of a non-equilibrium boundary layer is not new in the facilitated transport literature (Schultz, Goddard, and Suchdeo, 1974). Previous analyses linearize the kinetics in the boundary layer; the present analysis freezes the kinetics in the boundary layer. An explanation for this difference in viewpoint follows.

When a gaseous species, A, enters a liquid film at x = 0, it diffuses some distance towards x = 1 before it reacts in solution. For diffusion-limited reactions, this distance is the distance between intermolecular collisions. For slower reactions, A will diffuse much farther before reacting. It is this distance that A diffuses before it reacts (frozen kinetics) that is the width of the boundary layer near x = 0.

The boundary layer near x = 1 can be explained by similar, but more subtle, thinking. When A enters the film at x = 0, it reacts to form carrier species that assist the transport of A. Since A is the only species that can leave the film, the entire flux must be carried by A across the boundaries x = 0,1. Between x = 0,1, the carriers assist in varying degrees.

Figure 3.2 is a sketch of the fraction of the flux that is carried by A at any point in the film. This figure shows that the faster the reactions, the larger the fraction of the flux borne by the carrier species throughout most of the film (the carrier contributions go to zero at the boundaries).

Since only A can carry the flux at the boundaries, the concentration gradient in A near each boundary is larger (magnitude) than elsewhere in the film. (Note that the gradients of the carrier species vanish at the boundaries.) Thus, with the exception of the region near x = 0, the concentration of A is decreasing more rapidly near x = 1 than elsewhere in the film.

This decrease in the concentration of A near x = 1 guarantees that reactions in this region will tend to produce A in an attempt to establish local equilibrium. Hence, the reactions that produced carrier species from A will tend to reverse, producing A from carrier species.

If these reverse reactions are slow, carrier species from the equilibrium core can diffuse toward x = 1 fast enough to maintain their concentrations in excess of

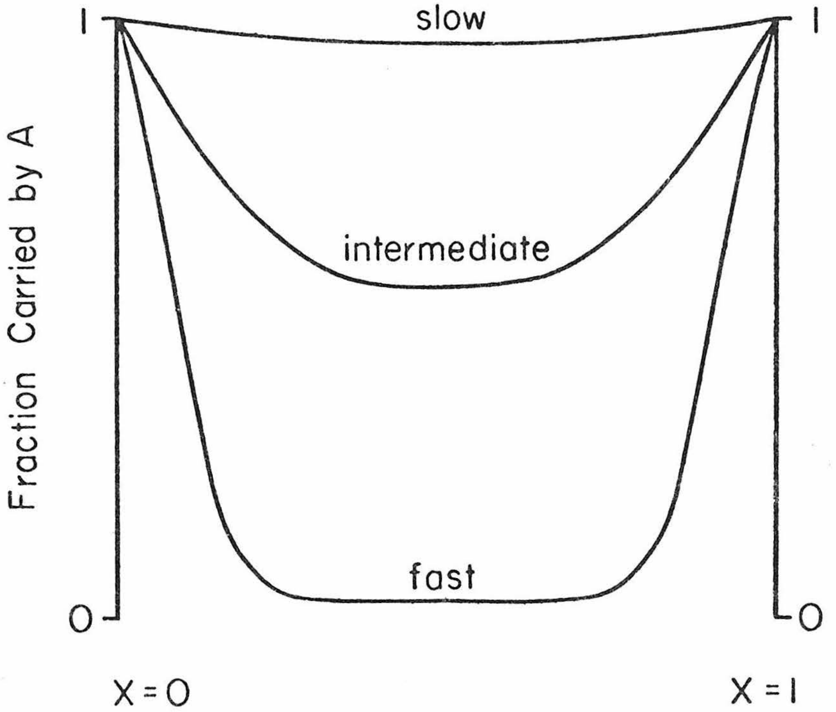


FIGURE 3.2 -- Fraction of Flux Carried by Species A - Only the volatile species A can contribute to the flux at x = 0,1. Carriers assist in the core of the film. The contribution of the carriers increases with the rate of the chemical reactions (slow, intermediate, fast).

the equilibrium amount. But, no matter how fast the reactions are, they take a non-zero time. In this time, carrier species can diffuse some distance without reacting. Thus, there must be a distance close enough to x = 1 where the carrier species diffuse to x = 1 before reacting (frozen kinetics). Over this distance, the carrier concentrations are constant and in excess of the equilibrium value because the concentration of A is decreasing (at its fastest rate) near x = 1. Thus, a non-equilibrium boundary layer exists near x = 1 with a thickness defined qualitatively by the "close enough" described above.

The foregoing discussion could be generalized to include N gaseous species undergoing transport simultaneously; N boundary layers of different widths would result.

3.2.4.2 NEBLA applied to aqueous SO_2 solutions

Figure 3.3 shows the concepts of the NEBLA applied to the transport of SO_2 in aqueous solutions. The aqueous film is divided into boundary layer and core regions. Sulfur dioxide enters the film, penetrates, and forms HSO_3^-. This ion diffuses across the film where it discharges SO_2. Other carrier species are omitted for simplicity.

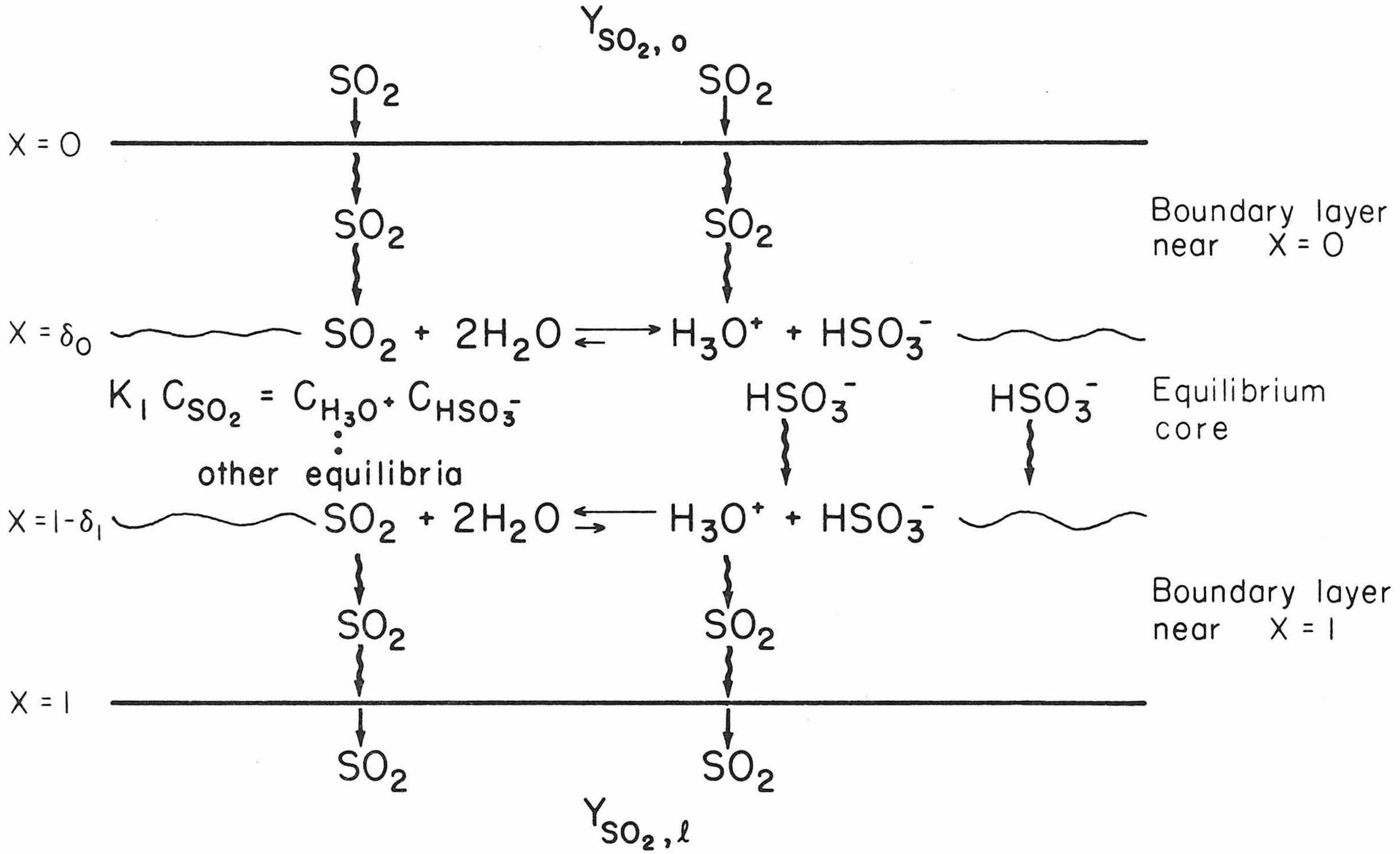


FIGURE 3.3 -- Non-Equilibrium Boundary Layers in Aqueous SO_2 Solutions - Sulfur dioxide enters film, diffuses a distance δ_o, and reacts to form HSO_3^-. Sulfur-containing ions carry most of the flux across the equilibrium core. Since the ions cannot leave the film, they must react near x = 1 to form SO_2(aq) which diffuses across the boundary layer of thickness δ_1.

Consider the boundary layer near x = 0. Sulfur dioxide molecules entering the film at x = 0 can react by

$$SO_2(aq) + 2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_3O^+ + HSO_3^- \tag{3.72}$$

or diffuse as $SO_2(aq)$ toward x = 1. To estimate the distance that an SO_2 molecule will diffuse toward x = 1 before it reacts, it is observed that the characteristic time for diffusion over a distance $\hat{\delta}_o$ is

$$\tau_D = \frac{\hat{\delta}_o^{\,2}}{\hat{D}_{SO_2}} \tag{3.73}$$

Since qualitatively it takes one reaction time

$$\tau_R = \frac{1}{k_1} \tag{3.74}$$

for an SO_2 molecule to react, the distance that a molecule diffuses before it reacts can be found by setting $\tau_D = \tau_R$. Hence

$$\hat{\delta}_o = \left(\frac{\hat{D}_{SO_2}}{k_1} \right)^{1/2} \tag{3.75}$$

In non-dimensional terms

$$\delta_o = \frac{1}{L}\left(\frac{\hat{D}_{SO_2}}{k_1}\right)^{\frac{1}{2}} \tag{3.76}$$

If reaction 3.72 is the primary mechanism of conversion of SO_2 to ionic species, then over the distance $\hat{\delta}_o$, no conversion from molecular to ionic sulfur species occurs. Other mechanisms such as

$$SO_2(aq) + {}^-OH \rightleftarrows HSO_3^- \tag{3.77}$$

and

$$SO_2(aq) + SO_3^= + H_2O \rightleftarrows 2HSO_3^- \tag{3.78}$$

are unlikely to compete with reaction 3.72 because of the low concentrations of ^-OH and $SO_3^=$ in solution.

A simple expression for the flux through the boundary layer can be deduced from the freezing of the conversion from molecular to ionic sulfur species. Under steady conditions, the flux through the boundary layer is the flux through the entire film. Hence the problem of finding the flux is solved if the flux through the boundary layer can be found. Evaluating eq. 3.50 at $x = \delta_o$ and $x_o = 0$ gives

$$N_{SO_2} = \frac{1}{\delta_o}\sum_j n_j D'_j [C_j(0) - C_j(\delta_o)] \tag{3.79}$$

The freezing of the conversion between ionic and molecular sulfur species implies that no ionic sulfur is either created or destroyed. Hence,

$$\sum_{j'} n_{j'} r_{j'} = 0 \tag{3.80}$$

where the subscript j' denotes all sulfur-containing species <u>other than</u> SO_2.

Equation 3.2 in eq. 3.80 yields

$$\sum_{j'} n_{j'} N_{j'} = \text{constant} = A' \tag{3.81}$$

Since $N_{j'} = 0$ at $x = 0$ (eq. 3.3), the constant A' is zero.

Considering the enhanced diffusivity method of accounting for the potential gradient, eq. 3.6 can be written

$$N_{j'} = -D'_{j'} \frac{dC_{j'}}{dx} \tag{3.82}$$

with $D'_{j'}$ given by eqs. 3.49a,b. Substituting eq. 3.82 into eq. 3.81 gives

$$\sum_{j'} n_{j'} N_{j'} = 0 = - \frac{d}{dx}\left(\sum_{j'} n_{j'} D'_{j'} C_{j'} \right) \tag{3.83}$$

Thus

$$\sum_{j'} n_{j'} D_{j'} C_{j'} = \text{constant} \tag{3.84}$$

or

$$\sum_{j'} n_{j'} D_{j'} [C_{j'}(0) - C_{j'}(\delta_o)] = 0 \tag{3.85}$$

Equation 3.79 therefore yields

$$N_{SO_2} = \frac{1}{\delta_o} \sum_{j'} n_{j'} D_{j'} [C_{j'}(0) - C_{j'}(\delta_o)] + \frac{1}{\delta_o} D_{SO_2} [C_{SO_2}(0) - C_{SO_2}(\delta_o)] \tag{3.86}$$

or

$$N_{SO_2} = \frac{D_{SO_2}}{\delta_o} [C_{SO_2}(0) - C_{SO_2}(\delta_o)] \tag{3.87}$$

where eq. 3.85 has been used.

Equation 3.87 shows that the flux through the boundary layer near x = 0 is Fickian diffusion of SO_2(aq). By itself, this equation does not allow the flux to be calculated since $C_{SO_2}(\delta_o)$ is unknown. It will, however, play a key role in computing the flux when the NEBLA has been fully developed.

Now consider the boundary layer near x = 1. The thickness of this layer is found by setting the diffusion time across the layer equal to the characteristic reaction time of the carrier species. Since HSO_3^- is the main carrier species in aqueous SO_2 solutions, the reaction time should be chosen from a reaction which produces $SO_2(aq)$ from HSO_3^-.

It is proposed that the reaction time be taken from the reverse of reaction 3.72. A competing route

$$HSO_3^- \underset{k_R}{\overset{k_F}{\rightleftharpoons}} SO_2(aq) + {}^-OH \tag{3.88}$$

is possible but is much slower than reaction 3.72. Although the kinetics of reaction 3.88 (k_F, k_R) have not been measured, the equilibrium coefficient is known because eq. 3.88 is the sum of eq. 3.72 and the dissociation of H_2O. Thus the equilibrium coefficient for eq. 3.88 is K_W/K_1 or $7.2\cdot10^{-13}$ l/mole at 25°C. Hence even if the reverse reaction in eq. 3.88 is diffusion limited, a practical upper limit on k_F is $\sim 1\ \mathrm{sec}^{-1}$. This characteristic time of one second is much larger than the characteristic time of the reverse reaction in eq. 3.72 ($\sim 10^{-3}$ sec).

The reaction time of HSO_3^- indicated by eq. 3.72 is

$$\tau_R = (k_{-1}C^*)^{-1} \tag{3.89}$$

where C* is a characteristic value of the H_3O^+ concentration in the boundary layer. Proper choice of C* is outlined below.

The diffusion time of HSO_3^- across a layer of thickness $\hat{\delta}_1$ is

$$\tau_D = \frac{\hat{\delta}_1^2}{\hat{D}_{HSO_3^-}} \tag{3.90}$$

Equating $\tau_D = \tau_R$,

$$\hat{\delta}_1 = \left(\frac{\hat{D}_{HSO_3^-}}{k_{-1}C^*} \right)^{\frac{1}{2}} \tag{3.91}$$

In non-dimensional terms

$$\delta_1 = \frac{1}{L} \left(\frac{\hat{D}_{HSO_3^-}}{k_{-1}C^*} \right)^{\frac{1}{2}} \tag{3.92}$$

Since the boundary layer at x = 1 is defined to be a region where carrier species fail to react, the conversion of ionic to molecular sulfur species is frozen just as for the boundary layer at x = 0. Consequently, the flux across the x = 1 boundary layer is also Fickian diffusion of SO_2(aq). Therefore,

$$N_{SO_2} = \frac{D_{SO_2}}{\delta_1} [C_{SO_2}(1-\delta_1) - C_{SO_2}(1)] \tag{3.93}$$

Here, $C_{SO_2}(1-\delta_1)$ is the concentration of $SO_2(aq)$ at the inner edge of the boundary layer, $x = 1 - \delta_1$. Equation 3.4b gives the known value of $C_{SO_2}(1)$. Since $C_{SO_2}(1-\delta_1)$ is not known, eq. 3.93 does not in itself allow the flux to be computed. It will help to compute the flux when the complete NEBLA is developed.

At this point, expressions for both boundary layer thicknesses and for the flux through each boundary layer have been derived. The last step in the NEBLA begins by evaluating eq. 3.50 at $x = 1 - \delta_1$ and $x_o = \delta_o$ yielding

$$N_{SO_2} = \frac{1}{1 - \delta_1 - \delta_o} \sum_j n_j D'_j [C_j(\delta_o) - C_j(1-\delta_1)] \qquad (3.94)$$

Because $C_j(\delta_o)$ and $C_j(1-\delta_1)$ are unknown, eq. 3.94 does not in itself allow the flux to be computed.

The NEBLA is completed by the postulate that at the boundary layer/core interfaces ($x = \delta_o$, $x = 1 - \delta_1$), all chemical reactions are at (local) equilibrium. This postulate is consistent with the existence of an equilibrium core and with the definition of the boundary layers. It proposes, however, a discontinuity in the reaction rate terms (ionic-to-molecular sulfur reactions are considered frozen in the boundary layers and instantaneous in the core).

With this postulate, $C_j(\delta_o)$ in eq. 3.94 are related to $C_{SO_2}(\delta_o)$ in eq. 3.87 by equilibrium expressions. Similarly $C_j(1-\delta_1)$ in eq. 3.94 are related to $C_{SO_2}(1-\delta_1)$ in eq. 3.93 by equilibrium expressions. These are the same expressions involved in the equilibrium theory (section 3.2.3 and Appendix A).

The freezing of the conversion from ionic to molecular sulfur in the boundary layers implies that the concentrations of all ionic species in the boundary layers are equal to the values at the core/boundary layer interfaces ($x = \delta_o$, $x = 1 - \delta_1$). Hence C* must be the H_3O^+ concentration that is in equilibrium with $C_{SO_2}(1-\delta_1)$ (i.e., when $C_{SO_2}(1-\delta_1)$ is known, C* is known). Thus, computation of N_{SO_2} by the NEBLA involves four equations (3.87, 3.92, 3.93, and 3.94) for the four unknowns δ_1, $C_{SO_2}(\delta_o)$, $C_{SO_2}(1-\delta_1)$, and N_{SO_2} (δ_o is known; eq. 3.76).

Numerical solution of these equations is necessary because of the complexity of the equilibrium equations that relate $C_j(\delta_o)$ to $C_{SO_2}(\delta_o)$ and $C_j(1-\delta_1)$ and C* to $C_{SO_2}(1-\delta_1)$. A solution algorithm is a) guess $C_{SO_2}(1-\delta_1)$, b) compute $C_j(1-\delta_1)$ and C* by the equilibrium relationships, c) compute δ_1 by eq. 3.92, d) compute N_{SO_2} by eq. 3.93, e) use this value of N_{SO_2} to find $C_{SO_2}(\delta_o)$ by eq. 3.87, f) find $C_j(\delta_o)$ from $C_{SO_2}(\delta_o)$ by the equilibrium relationships, g) use $C_j(\delta_o)$, $C_j(1-\delta_1)$, and δ_1 in eq. 3.94

to compute N_{SO_2}. If N_{SO_2} computed in step g) agrees with N_{SO_2} computed in step d), the proper guess for $C_{SO_2}(1-\delta_1)$ was made, and the equations are solved. If not, a new guess for $C_{SO_2}(1-\delta_1)$ is needed.

The NEBLA can be simplified by estimating the boundary layer thicknesses $\hat{\delta}_o$, $\hat{\delta}_1$. Using $\hat{D}_{SO_2} = 1.6 \cdot 10^{-5} cm^2 sec^{-1}$ and $k_1 = 5 \cdot 10^6$ sec^{-1} (Eigen, et al., 1961, 25°C), eq. 3.75 gives $\hat{\delta}_o = 1.79 \cdot 10^{-6}$cm. This value is much less than the 1mm film thickness generally used in the experimental portion of this study.

The boundary layer at x = 1 is more important. Note that

$$\frac{\delta_1}{\delta_o} = \left[\frac{\hat{D}_{HSO_3^-} k_1}{k_{-1} C^* \hat{D}_{SO_2}}\right]^{1/2} \simeq \left(\frac{K_1}{C^*}\right)^{\frac{1}{2}} \qquad (3.95)$$

Since $K_1 = 0.014$ mole/l and since C^* is characteristic of the high pH side of the film (pH ≃ 7-8),

$$\frac{K_1}{C^*} \simeq 10^5 \text{ to } 10^6$$

Hence $\delta_1 >> \delta_o$.

With the measured fluxes (Chapter 5), it can be shown that

$$\frac{C_{SO_2}(0) - C_{SO_2}(\delta_o)}{C_{SO_2}(0)} \leq 10^{-3} \qquad (3.96)$$

With $C_{SO_2}(\delta_o) \simeq C_{SO_2}(0)$ and $\delta_o << 1$, the boundary layer at x = 0 can be neglected, and eq. 3.94 becomes

$$N_{SO_2} = \frac{1}{1 - \delta_1} \sum_j n_j D'_j [C_j(0) - C_j(1-\delta_1)] \qquad (3.97)$$

The $C_j(0)$ are related to $C_{SO_2}(0)$ by equilibrium expressions just as $C_j(\delta_o)$ were related to $C_{SO_2}(\delta_o)$. Since eq. 3.4a gives $C_{SO_2}(0)$, $C_j(0)$ are known. (The validity of neglecting the boundary layer at x = 0 must be established in each particular case. If this approximation is invalid, both boundary layers must be retained.)

Equations 3.92,93,97 are three equations for the unknowns δ_1, N_{SO_2}, and $C_{SO_2}(1-\delta_1)$. These are solved by equating the right-hand sides of eqs. 3.93 and 3.97, and substituting eq. 3.92 in for δ_1. The result is a single implicit equation for $C_{SO_2}(1-\delta_1)$ which is solved iteratively. The technique and computer program are given in Appendix A. When $C_{SO_2}(1-\delta_1)$ is known, eq. 3.92 yields δ_1, and eq. 3.93 gives N_{SO_2}. Results of computations with these equations will be shown in sections 5.3,4 with the alkaline solution data.

CHAPTER 4: APPARATUS AND EXPERIMENTAL PROGRAM

4.1 Synopsis

Measurements of the steady-state flux of SO_2 through aqueous films of known composition are made with the apparatus shown in Figure 4.1. An aqueous film to be studied divides the cell into two halves. A cylinder of high-purity grade nitrogen (50ppm maximum impurities) provides flow to both sides of the cell. This N_2 stream is split by a tee, the flow to each side of the cell being controlled by a double-pattern needle valve (Nupro model 2MGD).

Each flow is humidified by passing through gas washing bubblers. A resistance heating tape warms the first bubbler in each line enough to cause condensation between the bubblers. Gas leaving the second bubbler is thereby saturated at room temperature.

The humidified gas on the upstream side of the cell passes through a tee where SO_2 is added through a double-pattern needle value. This SO_2 flow, adjusted to give a desired $y_{SO_2,o}$, is measured by an electronic mass flow meter (Tylan Corp. model FM 360). The output of the mass flow meter (MFM) is read in volts on a digital panel meter (DPM).

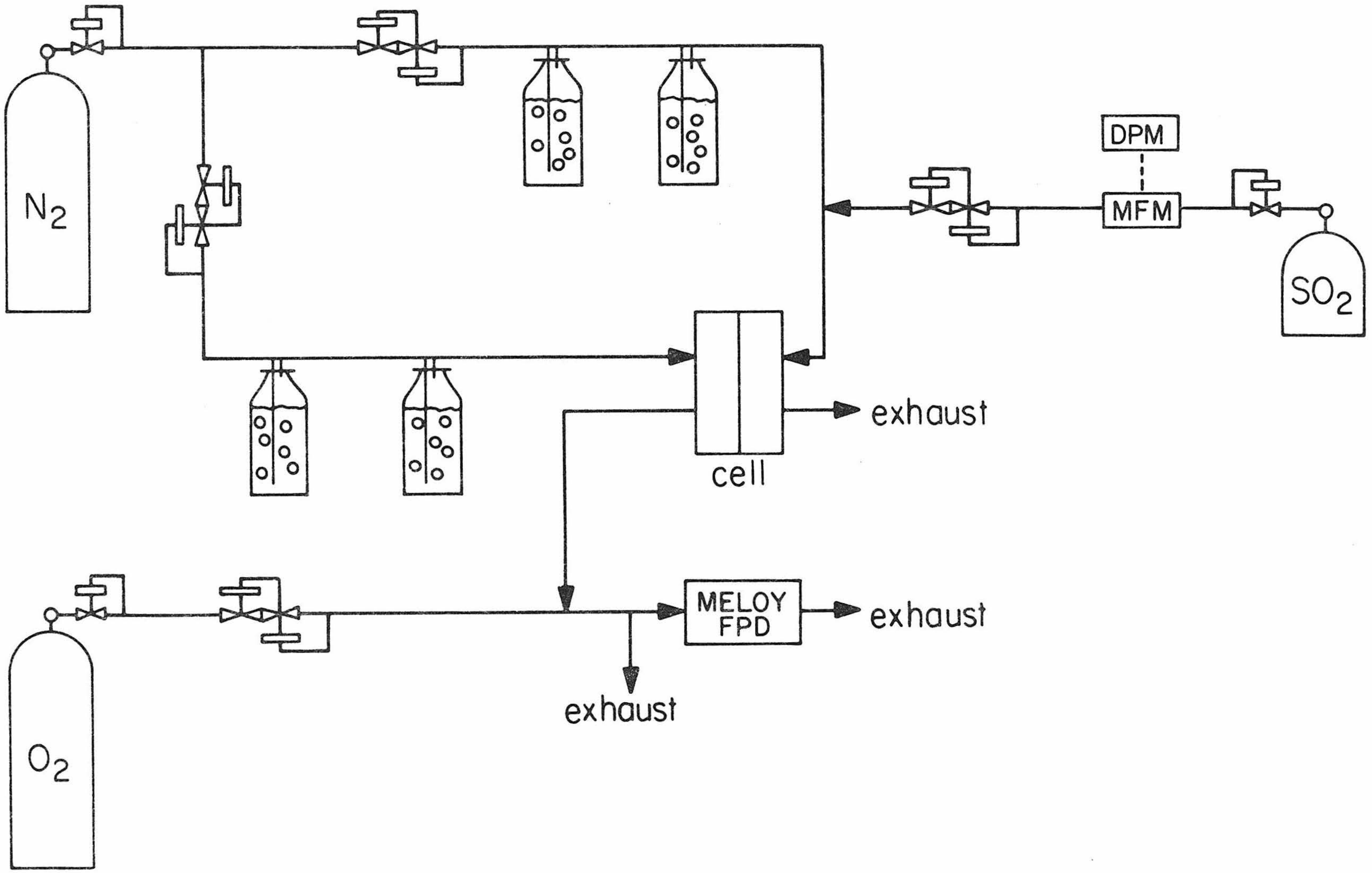


FIGURE 4.1 -- Apparatus - The aqueous film is held in the cell. Nitrogen, humidified to prevent evaporation of the film, carries SO_2 to one side of the cell. A clean N_2 stream sweeps away SO_2 that passes through the film, and the Meloy determines the concentration of SO_2 in the sweep stream.

This humidified N_2 and SO_2 stream continually flows through the upstream side of the cell, exposing the aqueous film to the desired $y_{SO_2,o}$. Less than 1% of the SO_2 entering the cell dissolves in the aqueous film, reacts, and diffuses to the other side of the film. Here, a clean, humidified N_2 stream enters the cell and carries away the SO_2 coming through the film.

A flame-photometric sulfur analyzer (Meloy model SA 120) determines the SO_2 mole fraction in the gas stream leaving the downstream side of the cell ($y_{SO_2,l}$). Oxygen, required for proper operation of the sulfur analyzer, is added downstream of the cell to avoid oxidation of SO_2 to $SO_4^=$ in the aqueous film. Teflon lines carry the downstream flow because the low ($\sim$ 0.1ppm) SO_2 concentrations in this stream are susceptible to absorption losses.

Gases from both sides of the cell exhaust to a hood through 5/16" I.D. polyethylene or teflon tubing. With this diameter, there is no pressure drop in these lines, and the cell works at room pressure (744 ± 2 mm Hg). Also, the cell operates at room temperature (24°C - 26°C) since precise temperature control is unnecessary.

4.2 Measurements and Calibrations

Data necessary for calculating the flux of SO_2 and for comparing to theory include the cross-sectional area of the aqueous film, A, the film thickness, L, the mole fraction of SO_2 in the stream sampled by the Meloy, y_m, and four flow rates: 1), 2) the wet N_2 streams going to the upstream and downstream sides of the cell, 3) the O_2 stream, and 4) the SO_2 added to the N_2 flow to the upstream side of the cell. The flows are converted to molar flow rates (moles/sec) and are given the symbols M_u, M_d, M_{O_2}, and M_{SO_2} respectively. Note that $y_m \neq y_{SO_2,1}$ because of the addition of oxygen between the cell and the Meloy. Appendix B contains a sample data reduction calculation.

Determination of the film cross-sectional area and the film thickness is explained in section 4.3.

The analog output of the Meloy sulfur analyzer indicates y_m. The analyzer is calibrated by passing a sulfur-free air stream at a known flow rate over an SO_2 permeation tube (1cm low emission; Metronics, Inc., Santa Clara, CA) and into the analyzer. This air stream is drawn from the building compressed air system. Two line regulators in series (Wilkerson model 49-038, Matheson model 70A) followed by a double-pattern needle valve (Nupro model 2MGD) provide steady flow. The stream is passed through a gas washing bottle that contains a 3% H_2O_2 solution, ensuring removal of any trace acid-gases (SO_2, H_2S) that could interfere with the calibration. Also, the stream is humidified in the washing bottle which makes the calibration gas similar to the humidified stream sampled by the Meloy during an experiment. No humidity effect was observed, however. The flow rate of this clean, humidified air stream is determined with a wet test meter (Precision Scientific Co. model 63115) before it passes over the permeation tube.

A styrofoam box, controlled to 26 ± 0.1°C by a constant temperature bath (Labline model 3052), housed the permeation tube and kept its emission rate constant. The emission rate was determined by weighing the tube once every two weeks on a Mettler model M5S/A microbalance (2μg precision). Measured SO_2 permeation rates were generally 20% higher than stated rates (Metronics Product Bulletin No. 20-70).

With a known emission rate and a known (clean) air flow rate, the calibration stream contained a known mole fraction SO_2. By adjusting the air flow rate, mole fractions in the range $0.04 \leq 10^6 \cdot y_{SO_2} \leq 0.3$ were produced. This range was ideal for the ∿0.1ppm sampled by the Meloy during experiments. Also, in this range there is a log-linear relationship between the Meloy analog output and the SO_2 concentration. With this calibration procedure, the estimated uncertainty in the measurement of y_m during an experiment is ± 5%.

The N_2 and O_2 flows (M_u, M_d, M_{O_2}) are measured with the wet test meter (WTM) before SO_2 is allowed into the system. The aqueous film is not in the cell during these measurements. Instead, a thin polystyrene disc divides the cell into its two halves, allowing determination of M_u and M_d. These two flow rates are set at 3 to 6 liters/min. The oxygen flow rate is set so that $M_{O_2}/M_d = 21/79$, simulating the atmospheric O_2/N_2 molar ratio. A 100-psi pressure drop across each double-pattern needle valve (Figure 4.1) stabilizes these flow rates. No measurable change occurred over the course of an experiment.

Flow measurements consist of timing, with a hand-held digital electronic stop watch, at least one revolution of the WTM. The volumetric flow rate is converted to a molar flow rate using room pressure, room temperature, and the ideal gas law. Three decimal place repeatability is routinely achieved.

The WTM was calibrated by displacing water out of a one-liter volumetric flask. It was found that each revolution of the WTM represented only 2916 cm^3 rather than the 3000 cm^3 indicated on the face of the WTM.

This "meter factor" of 0.972 was incorporated into all flow measurements.

A (linear) calibration curve gave the SO_2 molar flow rate, M_{SO_2}, from the DPM volt reading. Calibration was done with a bubble flow meter (a 10ml buret with 0.05 cm^3 divisions). To achieve equilibration of the SO_2 with the soap solution used in the buret, SO_2 was passed through the meter for one day before calibration data were taken. With this techinque, M_{SO_2} was determined in an experiment with an estimated uncertainty of ± 3%.

The model FM 360 mass flow meter can measure flows ranging from 0-5 to 0-10,000 cm^3/min. Different by-pass valves are inserted in the meter for different flow ranges. For the M_{SO_2} needed in the present experiments, no by-pass valve is used. In this mode, the meter measures flows from 0-5 cm^3/min.

4.3 Aqueous Film Preparation

The aqueous film is either a soaked filter or a gel and is held in a circular hole in a stainless steel disc (Fig. 4.2). The disc is type 316 stainless and is 0.64mm thick. The cross-sectional area of the aqueous film, A, is the area of this hole. Hole diameters of 3/16"-5/16" are used.

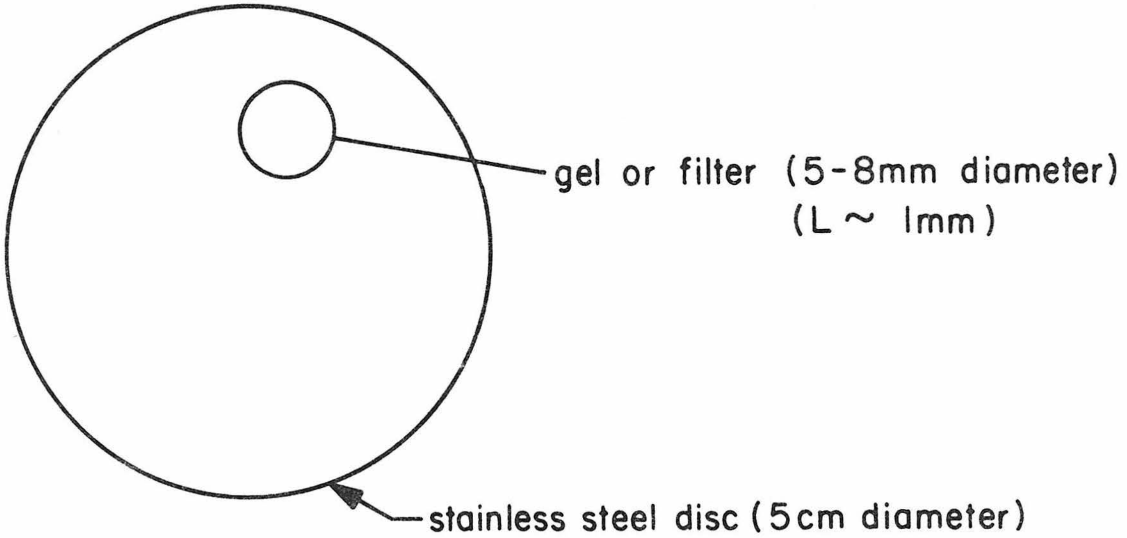


FIGURE 4.2 -- Aqueous Film Support - Gel or filter in off-centered hole in stainless steel disc. The film thickness is 1 ± 0.1mm in most experiments.

4.3.1 Soaked Filter

A soaked filter is used for studying concentrated NaOH solutions (≥ 0.5 M). The filter material is porous ultra-high molecular weight polyethylene (UHMW PE) (Porex Plastics Co., Fairburn, GA). Polyethylene is highly resistant to attack by inorganic and alkaline salt solutions (Othmer, 1962). Standard cellulosic filters manufactured by Millipore and Gelman proved unsatisfactory because of deterioration under strong alkaline conditions. The UHMW PE is sold in 1/16" thick sheets with a nominal pore size of 20μm. Discs of 1mm thickness and 3/16" diameter were cut from the sheets and inserted into the circular hole in the stainless disc.

A solution to be studied is imbibed into the filter disc. Approximately 100ml of solution is pulled through the disc with a slight aspirator suction to ensure saturation of the filter with the solution (100ml is 1000 times the void volume of the filter). Because of the aspirator suction, a small amount of RTV silicone rubber sealant (General Electric) was needed along the outer edge of the filter to hold it to the stainless steel.

With the solution imbibed in the filter, the stainless steel disc is put into the cell, and the experiment outlined in section 4.1 is performed. After the experiment, the filter is flushed with double-distilled water (∿100ml) and kept in a closed petri dish. This dish contains double-distilled water so that the filter remains submerged in distilled water until next use. Hence, the filter is never dry, so that air is not trapped in the filter interstices.

The filter is not a simple aqueous film since the filter matrix blocks some of the area exposed to SO_2 and since there is no straight diffusion path through the filter. These geometric effects (blocked surface area and tortuosity) are accounted for by calibrating the filter.

Calibration consisted of five measurements of the flux through the filter when it contained a pure water/agar gel (section 4.3.2). The ratio of the fluxes observed to the fluxes observed in the pure water/agar gel experiments (section 5.1) gave the combined effect of the area blockage and tortuosity.

If it is assumed that the fractional surface area open to transport is equal to the bulk void fraction, ε, then the tortuosity, τ, can be separated from the combined effect. Weighing a known volume of the filter material gives ε.

The following values for τ and ε were obtained

$$\varepsilon = 0.624 \pm 0.007 \tag{4.1}$$

$$\tau = 1.27 \pm 0.08 \tag{4.2}$$

Several investigators have reported values of τ for cellulosic Millipore filters that range from 1.45 to 1.63 (Donaldson and Quinn, 1975). The value obtained in this study is reasonable considering that the nominal pore size of the UHMW PE is a factor of 10 larger than that of the cellulosic Millipores.

In data analysis, the measured flux is divided by ε and multiplied by τ before comparing to theory. This adjusted flux is the flux that would have come through an aqueous film of equal thickness with no filter matrix present.

4.3.2 Agar Gels

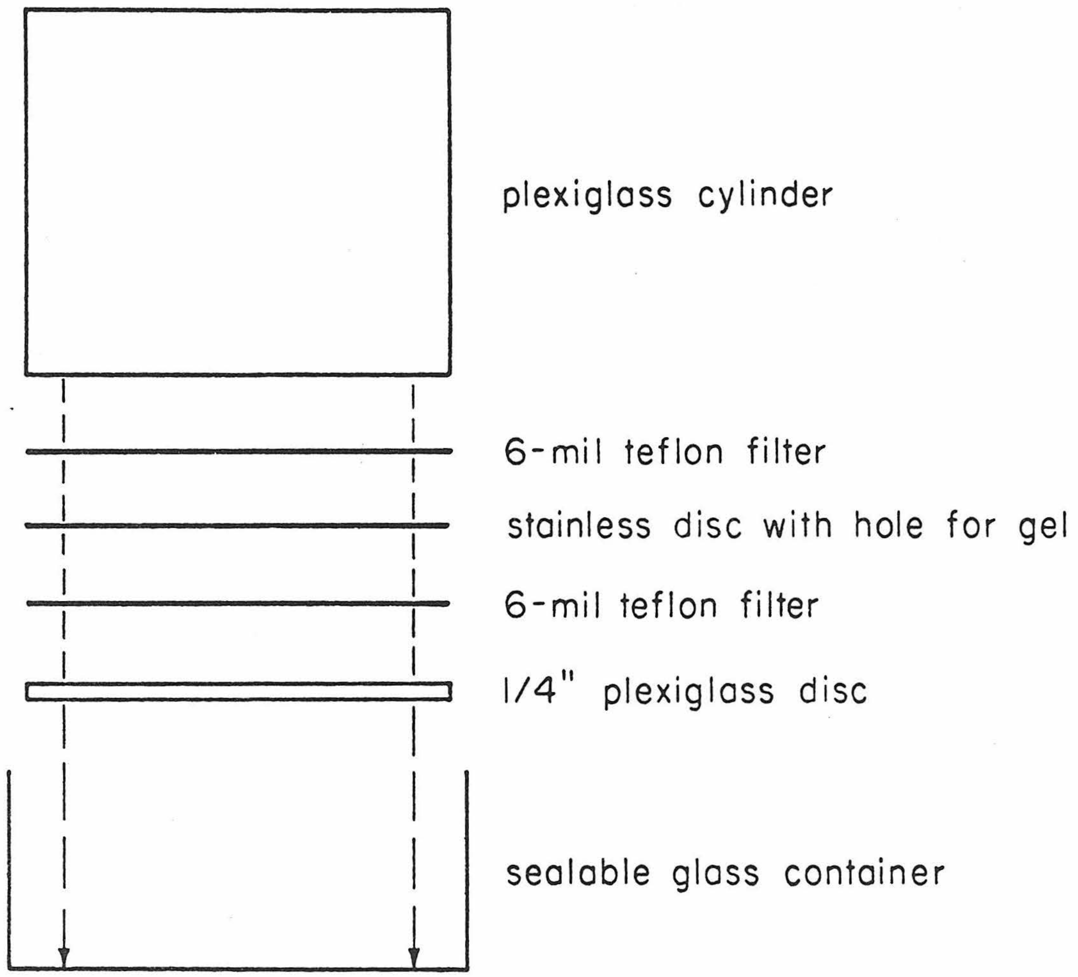
Agar gels are used for studying pure water, neutral salt solutions (0.1M - 2.0M NaCl), and alkaline salt solutions with $0.001 \leq \text{Na}_{\text{tot}} \leq 0.2\text{M}$. To prepare a gel, 1 to 1.5gms of agar (Bacto-Agar, Difco Laboratories, Detroit, MI) are placed in 75ml of double-distilled water and brought to a boil on a magnetic stirrer hot plate to dissolve the agar. When the agar is dissolved, 10ml of the hot agar solution ($\sim$80°C) is transferred by pipette into a test tube. The test tube holds the amount of 1M

NaOH that gives the desired Na_{tot} when alkaline solutions with $Na_{tot} \leq 0.05M$ are studied. When NaCl solutions are studied, the test tube contains the desired amount of dry NaCl. For $Na_{tot} = 0.2M$, a mixture of $NaHSO_3$ and Na_2SO_3 is used in the test tube. (The 0.2M Na_{tot} gels are prepared in an oxygen-free glove bag, model X-17-17, Instruments for Research and Industry Co.) The test tube holds no salts when pure water gels are being prepared.

The test tube with the hot agar and the desired salt is shaken vigorously to ensure complete dissolution and mixing of the salt. When mixing is achieved, 2cc of solution are removed by syringe for use in casting the gels.

Gel casting equipment includes a 2" diameter by 1" deep glass, sealable container, a flat plexiglas disc, two teflon filters, the stainless steel disc with the circular hole, and a plexiglas weight (Figure 4.3). The plexiglas disc is placed in the glass container followed by a teflon filter and the stainless disc. Warm agar salt solution is placed in the circular hole in the stainless disc, slightly overlapping the hole edge. The other teflon filter and the 160gm plexiglas weight are then lowered onto the stainless disc. The weight flattens the gel before it sets.

FIGURE 4.3
Gel Casting Arrangement



After two minutes, the weight is lifted, and the lid is put on the container. Four gels are cast from the same solution.

After at least 30 minutes, a gel is selected for the experiment described in section 4.1. Immediately after the experiment, the stainless disc is taken to a balance where the gel is cut out with a surgical blade and weighed. This weight and the gel density (measured by weighing a known gel volume) gives the thickness of the gel (1 ± 0.1mm).

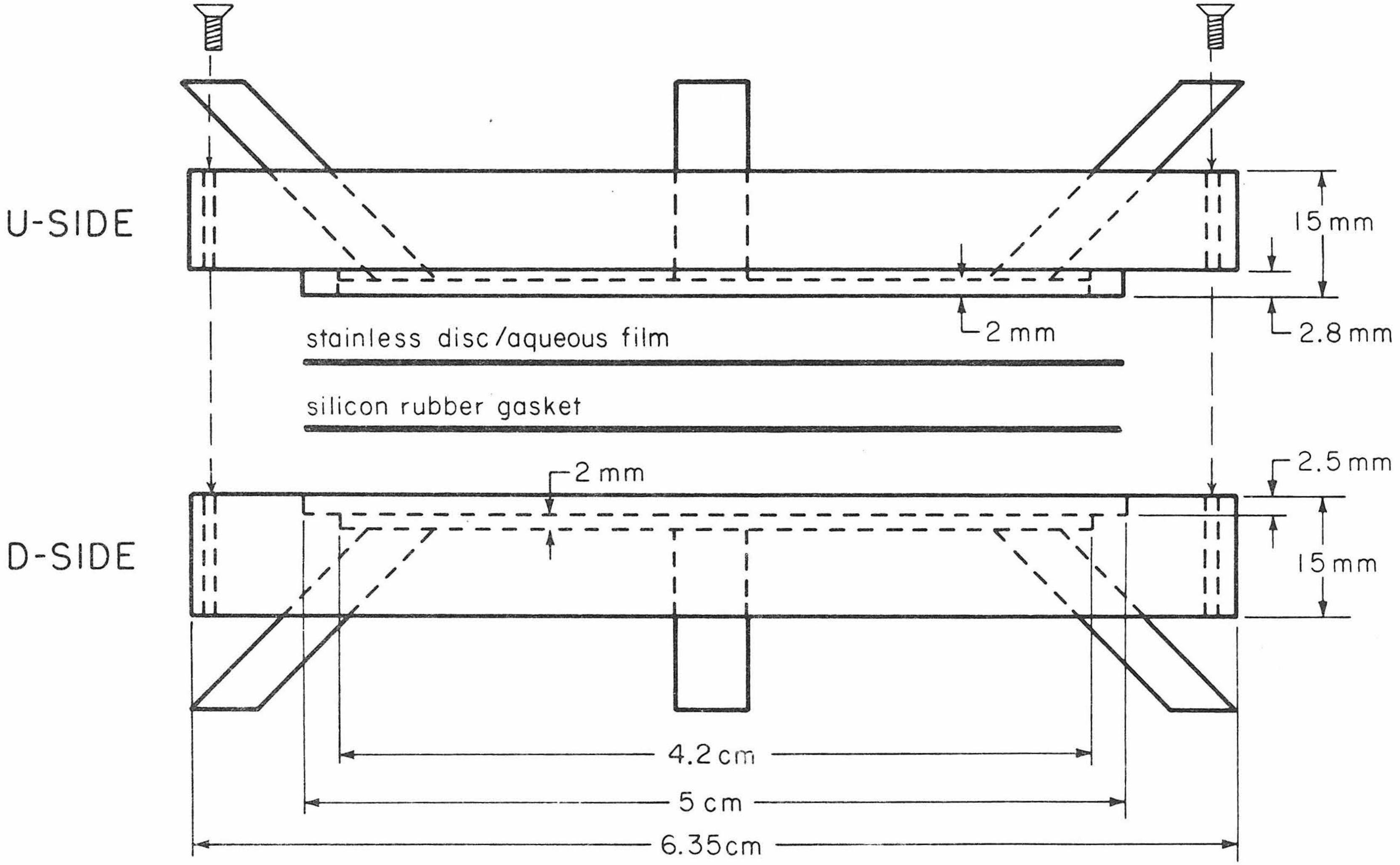
Since agar gel decreases the diffusivities of the species in the aqueous film, a 5% correction is made before data are compared to theory. This 5% correction is taken from Chilcote (1970) who measured diffusivities of Na^+ in 1% agar gels and compared them to values obtained in free aqueous solutions (e.g. diffusion cell). This 5% factor may not be precisely the proper correction for the present study, but the magnitude of the effect makes having a more precise value unimportant.

4.4 Cell Design

Figure 4.4 shows the cell configuration. The stainless disc holding the aqueous film is placed on top of a 1/32" thick rubber gasket which rests on a lip on the downstream side (D-side). The upstream side (U-side)

FIGURE 4.4

Cell Design: Arrangement for Holding Aqueous Film



is attached to the D-side by six 1" long, type 6-32 screws. Since the cell operates at room pressure, no special sealing precautions are needed.

The geometry of the gas flow to both sides of the cell is identical. Gases enter each side through two 1/4" O.D. tubes attached at 45° angles. These tubes are attached on opposite edges in such a way that a swirling motion of the gas in the cell is produced. Stagnant regions are thereby eliminated. Exhaust occurs through a centered 5/16" I.D. port.

Except for a teflon exhaust port on the D-side, the cell is 316 stainless steel. This teflon port allows the D-side stream carrying ~ 0.1ppm SO_2 to be exposed only to teflon after it leaves the cell as a precaution against absorption losses.

Figures 4.5a,b,c,d give a more complete idea of the geometry of the cell.

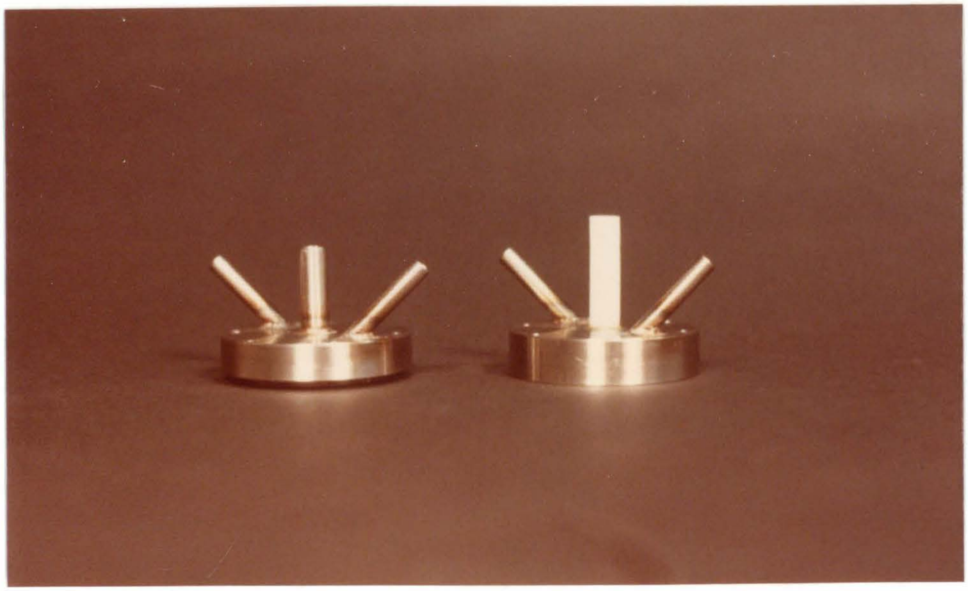
4.5 Experimental Program

Table 4.1 gives the categories and concentrations of solutions studied. Some of the questions addressed by a given category are also listed.

The pure water, neutral salt, and alkaline salt categories are the major portion of the experimental program. Flux data are taken at each concentration listed.

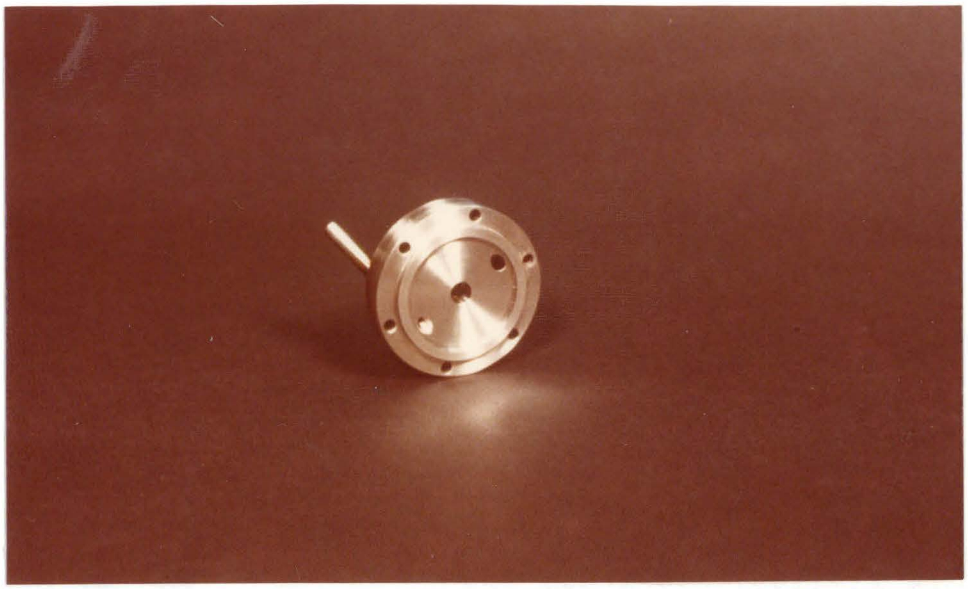
FIGURES 4.5a,b -- Cell Design

a) TOP VIEW -- Inlet ports placed to produce swirl; exhaust ports centered; six holes for screws.

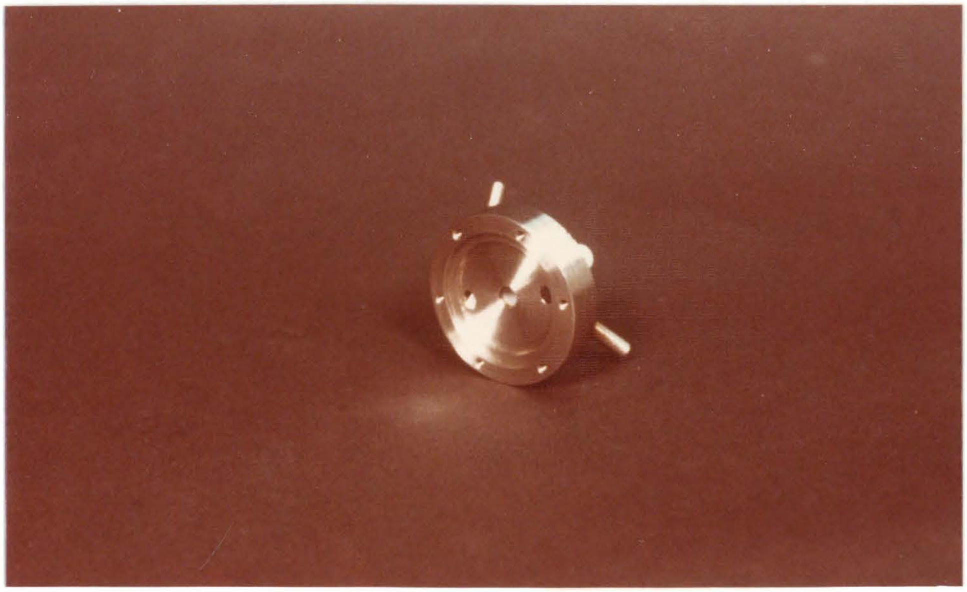


b) SIDE VIEW -- Inlet ports at 45° angle; U-side (left) rests on sealing lip.

FIGURES 4.5c,d -- Cell Design



c) PROFILE OF U-SIDE -- Raised sealing lip; 2mm deep gas chamber.



d) PROFILE OF D-SIDE -- Female sealing surface; 2mm deep gas chamber.

Table 4.1

Summary of Experimental Program

Category	Purposes/Questions Addressed
Pure Water	Equilibrium theory test ($\frac{d\Phi}{dx}$ included) Estimate k_1 for hydrolysis $SO_2(aq)+2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_3O^+ + HSO_3^-$
Neutral Salt 0.1,0.5,1.0,2.0M NaCl	Test activity coefficient model Effect of viscosity on diffusion coefficients Test effectiveness of $\frac{d\Phi}{dx}$ in a neutral salt
Alkaline Salt $NaOH/NaHSO_3/Na_2SO_3$	Look for flux increase over pure water and large facilitation factors
$Na_{tot}=10^{-3}, 10^{-2}, 0.05, 0.2, 0.5, 1.0, 2.0, 3.0M$	Test equilibrium theory and NEBLA
Variable Film Thickness $Na_{tot} = 0.05M$ $y_{SO_2,o} = 2 \cdot 10^{-4}$ $0.37mm \leq L \leq 4.8mm$	Test variation of facilitation factor with film thickness predicted by NEBLA

Gas phase SO_2 mole fractions

$10^6 \cdot y_{SO_2,o} = 100, 200, 500, 1000$

$10^6 \cdot y_{SO_2,\ell} \simeq 0.1$

Each concentration is studied with $y_{SO_2,o} = 10^{-4}$, $2 \cdot 10^{-4}$, $5 \cdot 10^{-4}$, and 10^{-3}. The mole fraction $y_{SO_2,1}$ is held constant at 0.1ppm by adjusting M_d and by changing the diameter of the hole in the stainless disc that holds the aqueous film. Three runs are made at each salt concentration and each value of $y_{SO_2,o}$. Data and error bars in Chapter 5 are based on the average and the scatter of the three runs.

In the pure water, neutral salt, and alkaline salt experiments, the film thickness is 1 ± 0.1mm. The diameter of the aqueous film held in the stainless disc is 3/16" except for Na_{tot} = 0.05M where the diameter is 5/16".

The fourth category in Table 4.1, variable film thickness, represents a small amount of data. It provides an important test of the NEBLA (section 3.2.4). Here Na_{tot} and $y_{SO_2,o}$ are held constant at 0.05M and $2 \cdot 10^{-4}$, respectively, while the film thickness is varied between 0.37mm and 4.8mm.

The following sections consider the purposes of studying each category given in Table 4.1. The goal is to provide a clear understanding of the contribution of each category to the overall goal of developing and testing the transport theory.

4.5.1 Pure Water

The equilibrium theory for pure water (eqs. 3.57,60) contains several approximations. These include the negligibility of all sulfur-containing ions other than HSO_3^-, the enhanced diffusivity implied by the potential gradient term, and the instantaneous nature of the hydrolysis of SO_2.

The approximation that only SO_2 and HSO_3^- are important in pure water can be verified two ways. One way is to examine the amount of the other sulfur species that are predicted by equilibrium calculations to exist in an SO_2/H_2O solution. This approach is taken in section 3.2.3.1. The approximation can also be verified by comparing the data to the theory that neglects all other sulfur-containing species. Thus the pure water data directly address this approximation.

Sulfur species other than SO_2 and HSO_3^- may be unimportant for pure water and neutral salts. This particular approximation, however, has no implication for the alkaline salts.

According to theory, the potential gradient causes the diffusivity of HSO_3^- to be enhanced by 73% at 25°C (eq. 3.35). Since HSO_3^- dominates the flux, the flux should also be enhanced by nearly 73%. Because the effect is so marked, the data can show whether the predicted effect is real.

This question of the effect of the potential term is relevant to pure water, neutral salt solutions, and partially, to alkaline solutions. When the effect is established in SO_2/H_2O solutions, it can be expected to exist in neutral salt solutions and in sufficiently dilute alkaline solutions. An upper limit on the magnitude of the effect is also established.

Data from SO_2/H_2O solutions can be used to test the instantaneous hydrolysis, or equilibrium, approximation. This approximation is uncertain because of the discrepancy in values of the forward rate coefficient, k_1 (section 2.3). By comparing equilibrium theory to zero-reaction theory (i.e., Fickian diffusion of $SO_2(aq)$) for the various $y_{SO_2,o}$ values (100-1000 ppm), it is seen that if Wang and Himmelblau's value for k_1 is correct, the flux should be a factor of 5 to 17 lower than if Eigen's value is correct. The magnitude of the difference between the flux in the two cases is such that a clear distinction between the rate coefficients can be made. Quantitatively, a lower limit on k_1 can be assigned based on the flux data (section 5.1.2).

None of the many sulfur-containing species present at equilibrium in alkaline SO_2 solutions would be created if the hydrolysis was slow enough. The transport problem would then reduce to Fickian diffusion of $SO_2(aq)$. Therefore, the value of k_1 is an unknown that affects the data interpretation for all solutions.

4.5.2 Neutral Salt Solutions

The NaCl solutions are studied to examine the effect of viscosity on the diffusivities and of non-idealities caused by high ionic strength. In addition, the approximate method of accounting for the potential gradient (section 3.2.3.2) is tested.

Some approximations (neglect of ions other than HSO_3^-, H_3O^+ and instantaneous kinetics) that apply to pure water apply to neutral salts also. Since these approximations are resolved in the pure water system, the neutral salt data can address the complications that arise because of the higher ionic strength.

The viscosity and non-ideality (activity coefficient) effects are difficult to separate in analyzing the flux data. Diffusion coefficients are approximately inversely proportional to solution viscosity. Some models assume an 0.8 power dependence. Under the conditions of the neutral salt experiments, the solution viscosity is a maximum of 53% higher than at infinite dilution. Since the difference between 1.53 and $(1.53)^{0.8}$ is indistinguishable within experimental error, the first power dependence of D_i on μ will be assumed (Stokes-Einstein). The neutral salt data, then, become more a test of activity coefficient models than a test of the viscosity dependence of D_i.

Solution viscosity is assumed to be the viscosity of the NaCl solution before it is exposed to SO_2. The small ($\simeq 10^{-3}$M) concentration of HSO_3^- present at steady state permits this approximation since NaCl concentrations are $\geq$ 0.1M. Viscosity data are from the Handbook of Chemistry and Physics (Weast, 1971).

The two activity coefficient models (Davies' and Bromley's) chosen for comparison are opposites in terms of complexity. Davies' model is simple in that species act the same when they have the same charge and size. Bromley's model treats all species interactions on the basis of the chemical identity and charge of each species (each species has its own interaction coefficient). The simple model deviates from the detailed model by up to a factor of two in the most concentrated solutions studied (2M NaCl). Not much difference is observed for $I \leq 0.5$M. A factor of two is large enough that a conclusion can be drawn about the reasonableness of one model as compared with the other for SO_2/NaCl solutions.

Since activity coefficients are system specific, a model that applies to one solution does not necessarily apply to another solution. The question of what activity coefficient model would be best for the alkaline solutions therefore cannot be directly answered by studying neutral salt solutions. This question is, however, addressed in section 5.2 and Appendix C.

Many investigators neglect the potential gradient in salt solutions by appealing to high ionic strengths ("supporting electrolyte" concept). The magnitude of the predicted effect (73% flux increase, eq. 3.35) is such that neutral salt data can test the approximate method (section 3.2.3.2) of accounting for the potential gradient.

The main contributions of the NaCl data to developing the theory for all aqueous solutions are in the area of non-idealities. The information gained will be used in anaylzing alkaline solution data. The potential gradient, however, is handled in a way that is specific to neutral salts.

4.5.3 Alkaline Salt Solutions

The NaOH and $NaHSO_3/Na_2SO_3$ solutions are the most complex. Because several questions are answered by the pure water and neutral salt data, the alkaline solution data can address new factors such as pH and non-equilibrium effects and complex chemical speciation.

Although non-equilibrium effects were not expected at the outset of this study, the alkaline solution data show that the equilibrium approximation fails under a wide range of conditions (Chapter 5). The NEBLA (section 3.2.4) is therefore tested by the alkaline solution data. Alkaline solution data require the complex physical chemistry in section 3.1 for proper analysis. These data thereby test the adequacy of this model and of the equilibrium and diffusion coefficients that were theoretically estimated in section 3.1.

Alkaline solution data therefore play a key role in developing the theory for SO_2 transport. The complex physical chemistry model serves as an example for other aqueous solutions since it makes clear how to include an arbitrary number of species in the transport theory. Also, the NEBLA should be applicable to other transport systems.

A practical reason that alkaline solutions are studied is that alkaline salts can greatly increase the SO_2 flux. Equilibrium theory predicts facilitation factors on the order of 10^3 to 10^4 for concentrated alkaline solutions ($\sim 3M\ Na_{tot}$) when $100 \leq 10^6 \cdot y_{SO_2,o} \leq 1000$. Data from these solutions will show whether this significant flux increase can be realized.

4.5.4 Effect of Film Thickness

According to the NEBLA, the facilitation factor should change with the film thickness (equilibrium theory predicts F independent of L). Therefore, flux data are taken with film thicknesses between 0.37mm and 4.8mm and with Na_{tot} and $y_{SO_2,o}$ held constant at 0.05M and $2 \cdot 10^{-4}$, respectively. This sodium concentration is dilute enough that ion pairs and viscosity effects are unimportant. The uncertainties in these areas, therefore, do not interfere with the film thickness effect.

These film thicknesses were achieved by casting gels in 10-mil and 3/16" thick discs. The diameter of the holes in the respective discs were 3/16" and 5/8".

The change in F with L is easy to understand. One could choose to study a film that was so thick that the boundary layers in the NEBLA would be a negligible part of the film thickness. The entire film would therefore be an equilibrium core, and the facilitation factor would closely approach the equilibrium theory value. If one were then to study a number of increasingly thinner films, the boundary layers would soon become a non-negligible part of the film. The facilitation factor would begin to decrease from the equilibrium value. Finally, a thin enough film could be chosen so that the boundary layers would comprise the entire film (i.e., no equilibrium core). At this point the flux would consist solely of Fickian diffusion of SO_2(aq), and the facilitation factor would be zero.

The NEBLA predicts F to vary by a factor of 2.47 over the range $0.37\text{mm} \leq L \leq 4.8\text{mm}$. The phenomenon is therefore not lost in experimental error. In terms of the general theory of SO_2 transport, these data test an aspect of the NEBLA not examined by the other alkaline salt data.

CHAPTER 5: RESULTS AND DISCUSSION

Results are presented in terms of three parameters:

1) Flux -- N [=] moles $cm^{-2}sec^{-1}$
2) Facilitation factor -- non-dimensional chemical reaction contribution to flux

$$F = \frac{N - N_o}{N_o} \qquad (5.1)$$

3) Enhancement over flux through pure water -- N/N_{H_2O}

The flux is the basic quantity measured by the experiment. The effect that the chemical reactions have on the flux is indicated by F. When F is large, the sulfur-containing ions are dominating the transport, and the reactions that produce these ions are very important. The enhancement factor, ϕ, used in absorption literature is equal to F+1.

The third parameter, N/N_{H_2O}, indicates whether the addition of alkaline salts to water increases the transport rate. Since a main goal of the research is to test the theories developed in Chapter 3, the values of N, F, and N/N_{H_2O} predicted by theory will be compared with the data.

5.1 Pure Water

5.1.1 Equilibrium Theory Comparison

Equations 3.57,60 summarize the equilibrium theory for SO_2/H_2O solutions. Before comparing data and theory, further approximations are possible. For the values of $y_{SO_2,o}$ and $y_{SO_2,1}$ in this study,

$$\frac{y^{1/2}_{SO_2,o} - y^{1/2}_{SO_2,1}}{y_{SO_2,o} - y_{SO_2,1}} \simeq y^{-1/2}_{SO_2,o} \qquad (5.2)$$

Hence, eq. 3.60 becomes

$$F_{eq} = \frac{D^*_{HSO_3^-}}{D_{SO_2}} \left(\frac{K_1 H_{SO_2}}{P_{tot}} \right)^{1/2} \frac{\gamma_{SO_2}}{(\gamma_{H_3O^+} \gamma_{HSO_3^-})^{1/2}} y^{-1/2}_{SO_2,o} \qquad (5.3)$$

Substituting the various coefficients (25°C) into eq. 5.3, F_{eq} becomes

$$F_{eq} = 0.171 \frac{\gamma_{SO_2}}{[\gamma_{H_3O^+} \gamma_{HSO_3^-}]^{1/2}} y^{-1/2}_{SO_2,o} \qquad (5.4)$$

Using the Davies model for activity coefficients (Appendix D), eq. 5.4 becomes

$$F_{eq} \simeq 0.18 y^{-1/2}_{SO_2,o} \qquad (5.5)$$

Figure 5.1 shows the data obtained with pure water/1% agar films of 1mm thickness. The abscissa is $y_{SO_2,o}^{-1/2}$ so that eq. 5.5 is represented by a straight line. There are four data points at each of 100, 200, 500, and 1000ppm, although some points coincide. Table 5.1 gives the average measured fluxes.

Equilibrium theory, eq. 5.5, falls close to the data verifying

a) the equilibrium approximation in this case

b) the necessity of including the potential gradient in the theory, and

c) the unimportance of sulfur-containing ions other than HSO_3^-.

As indicated by the facilitation factor, the HSO_3^- contribution to the flux is 5 to 20 times the SO_2(aq) contribution. In contrast, the HCO_3^- ion makes virtually no contribution to the flux in the CO_2/pure water system where the hydrolysis

$$CO_2 + 2H_2O \rightleftarrows H_3O^+ + HCO_3^- \qquad (5.6)$$

is much slower (Suchdeo and Schultz, 1974a).

The data for $y_{SO_2,o}$ = 100 ppm are consistently higher than the theory. Since the mass flow meter was operating at only 10% of full scale at this lowest $y_{SO_2,o}$ value, errors in calibration or imprecisions in the electronics

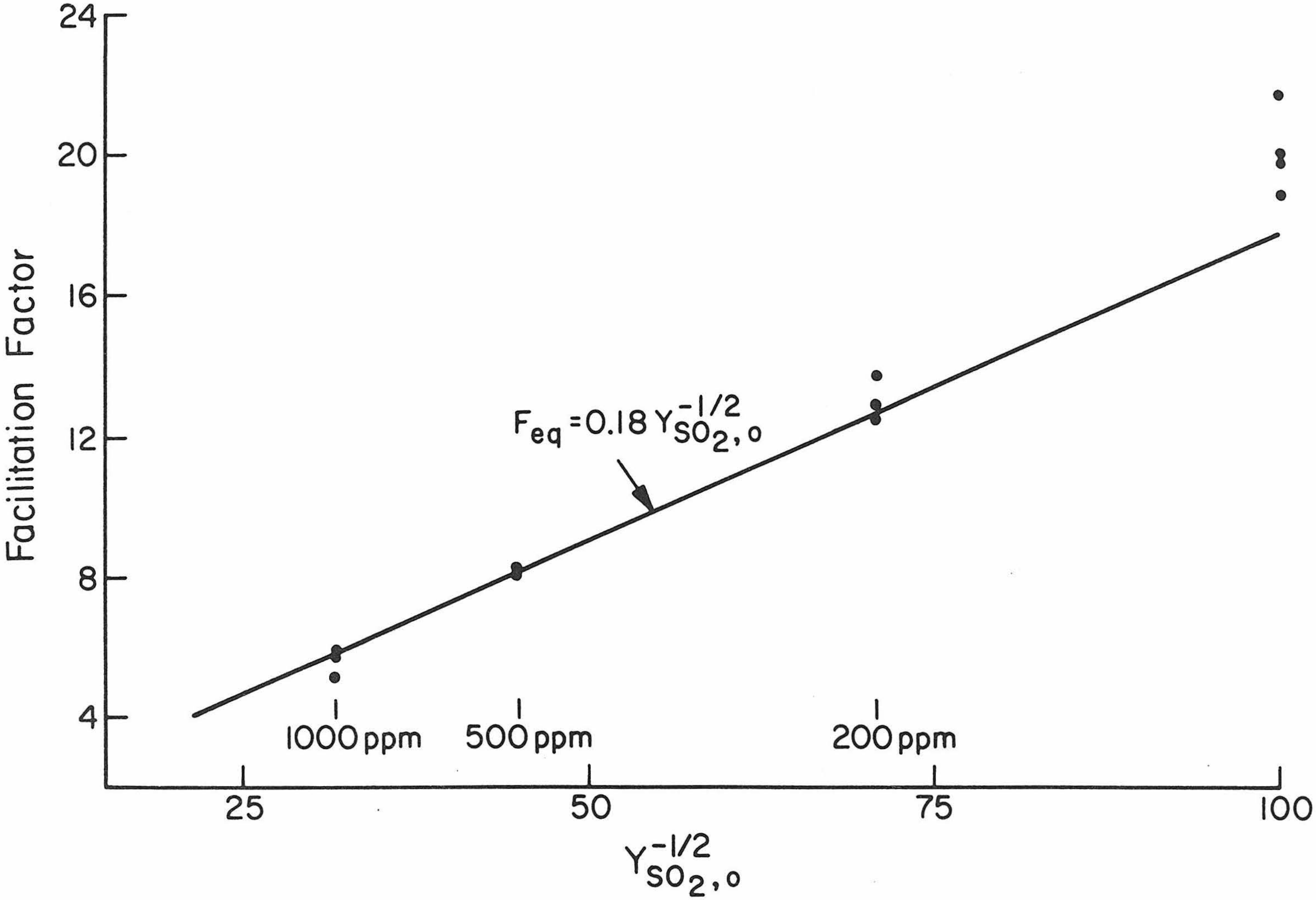


FIGURE 5.1 -- Pure Water with 1% Agar - Equilibrium theory, summarized by eqs. 3.57, 3.60, and 5.5, agrees with measurements of SO_2 transport through pure water/1% agar films. The HSO_3^- ion dominates the transport.

Table 5.1

Flux of SO_2 Through Pure Water/1% Agar Films

$10^6 \cdot y_{SO_2,o}$	$10^{10} \cdot \hat{N}$ $\frac{\text{moles}}{\text{cm}^2\text{sec}}$
100	3.81 ± 0.17
200	5.32 ± 0.37
500	8.44 ± 0.08
1000	11.9 ± 0.72

are a larger fraction of the reading. In this way, a systematic error could result.

5.1.2 Estimation of k_1

Since the data support the equilibrium approximation, reaction 3.72 must be "instantaneous." To evaluate k_1, it is necessary to define "instantaneous" quantitatively. This definition can be obtained from a perturbation analysis given by Suchdeo and Schultz (1974a) in their study of the facilitated transport of CO_2 in aqueous solutions. This analysis is a generalization of Kruezer and Hoofd's (1972) analysis. Because of the simplifications possible in the SO_2/H_2O system, the symbols used by Suchdeo and Schultz have clear analogs in the SO_2 system.

This analysis (SS-analysis) gives the facilitation factor, F_{SS}, as a function of the system parameters $y_{SO_2,o}$, $y_{SO_2,l}$, L, k_1, K_1, $\hat{D}_{SO_2}$, $\hat{D}_{HSO_3^-}$, and $\hat{P}_{tot}$. In contrast, the equilibrium theory (eq. 3.60) does not depend on k_1 or L.

The Damkohler number

$$Da = \frac{k_1 L^2}{\hat{D}_{SO_2}} \tag{5.7}$$

is the important non-dimensional parameter that arises in the SS-analysis. Qualitatively, it is the diffusion time divided by the reaction time. The facilitation factor F_{SS} is a function of the Damkohler number. When Da is large enough, F_{SS} approaches the equilibrium value, F_{eq}. A "large enough" value of Da can then be defined as the value that satisfies

$$\frac{F_{SS}(\mathrm{Da})}{F_{eq}} = \beta \tag{5.8}$$

where β has some arbitrary value close to 1. By plotting

$$\frac{F_{SS}(\mathrm{Da})}{F_{eq}} \text{ vs. Da}$$

it will be possible to see how large Da must be to approach equilibrium.

Figure 5.2 shows such a plot for $y_{SO_2,o} = 10^{-3}$ and 10^{-4}. The other $y_{SO_2,o}$ values of this study lie between these curves.

If $\beta = 0.8$ is defined as "close enough" to equilibrium, then

$$\mathrm{Da} \geq 10^5 \tag{5.9}$$

$$(y_{SO_2,o} = 10^{-4} \text{curve})$$

would give a facilitation factor that is close to the equilibrium limit. If $\beta = 0.9$ is chosen, then

$$\mathrm{Da} \geq 10^6 \tag{5.10}$$

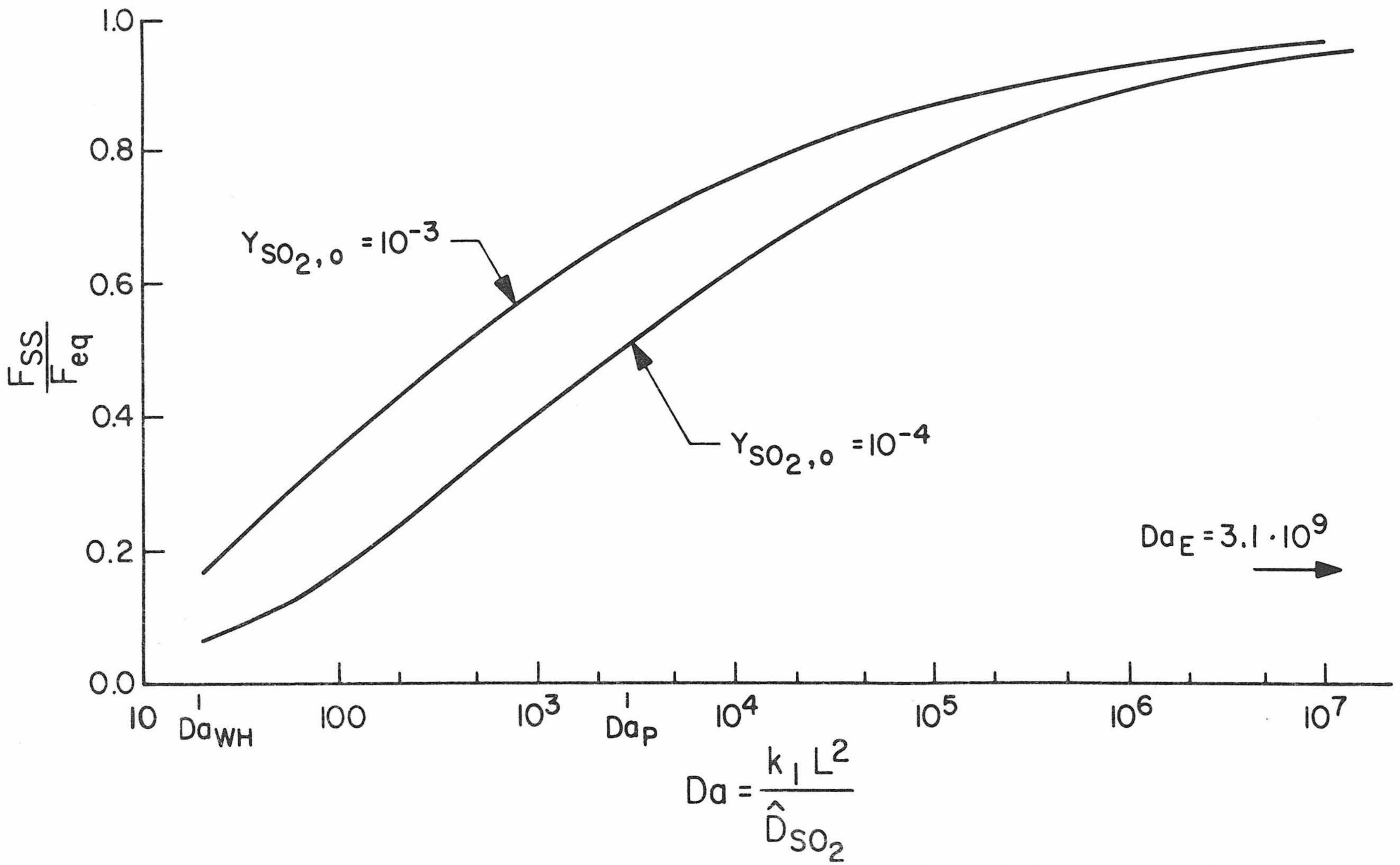


FIGURE 5.2 -- Damkohler Number Required to Reach Equilibrium Limit - Analysis of Suchdeo and Schultz (1974a) gives facilitation factor, F_{SS}, as a function of the Damkohler number. Equilibrium limit is reached when $F_{SS} = F_{eq}$. Estimate of k_1 is possible since water data are in equilibrium limit. The Damkohler numbers calculated from the rate data of Wang and Himmelblau, Phipps, and Eigen, et al., are shown.

would be required for the equilibrium limit to be achieved.

Since the SO_2/H_2O data show $F = F_{eq}$, the Damkohler number must be greater than 10^5 to 10^6. For the sake of the comparison that follows

$$Da \geq 2 \cdot 10^5 \tag{5.11}$$

is chosen.

The gel thicknesses in the pure water studies were 1mm. Given L = 1mm and $\hat{D}_{SO_2} = 1.6 \cdot 10^{-5} cm^2 sec^{-1}$, eq. 5.11 implies

$$k_1 \geq 320 \ sec^{-1} \tag{5.12}$$

Equation 5.12 gives a lower limit on k_1 that is approximately 10^4 larger than reported by Wang and Himmelblau (1964). It also comes closer to substantiating Eigen's (1961) value than the other estimates of k_1 in the literature (Table 2.4).

With a 1mm film, the Damkohler number calculated from Wang and Himmelblau's, Phipps' (1947), and Eigen's values for k_1 are

$$Da_{WH} = 19.8 \tag{5.13}$$

$$Da_P = 2550 \tag{5.14}$$

$$Da_E = 3.1 \cdot 10^9 \tag{5.15}$$

These values are marked on the x-axis in Fig. 5.2. The extent of disequilibrium implied by eqs. 5.13,14 is apparent although the perturbation analysis overestimates F_{SS} when $\beta \lesssim 0.6$. Eigen's k_1 value lies in the equilibrium limit (off the graph). This value ($k_1 = 5 \cdot 10^6 \text{sec}^{-1}$ at 25°C) will be used in the remainder of this thesis.

5.2 Neutral Salt Solutions -- NaCl

Two effects of increasing NaCl concentrations are apparent in Figure 5.3 where the complete range of NaCl data are shown with the SO_2/H_2O data (Table 5.1). First, the flux through 0.1M NaCl solutions is approximately 40% larger than through pure water films. This increase, which corresponds to an increase in the equilibrium concentration of HSO_3^-, results from the tendency of ions to stabilize each other at low enough ionic strengths ("salting in" effect). This effect is directly related to the minimum in the activity coefficient curve which exists near I = 0.1M for most species.

The second effect is the decrease in the flux that results from the increasing solution viscosity. Also, the "salting in" of HSO_3^- becomes less effective as the NaCl concentration increases. The increased solution viscosity reduces the flux at 2M to a value below the pure water data.

In Figures 5.4a,b,c,d, the NaCl data are compared with the equilibrium theory (eq. 3.57). The Davies and

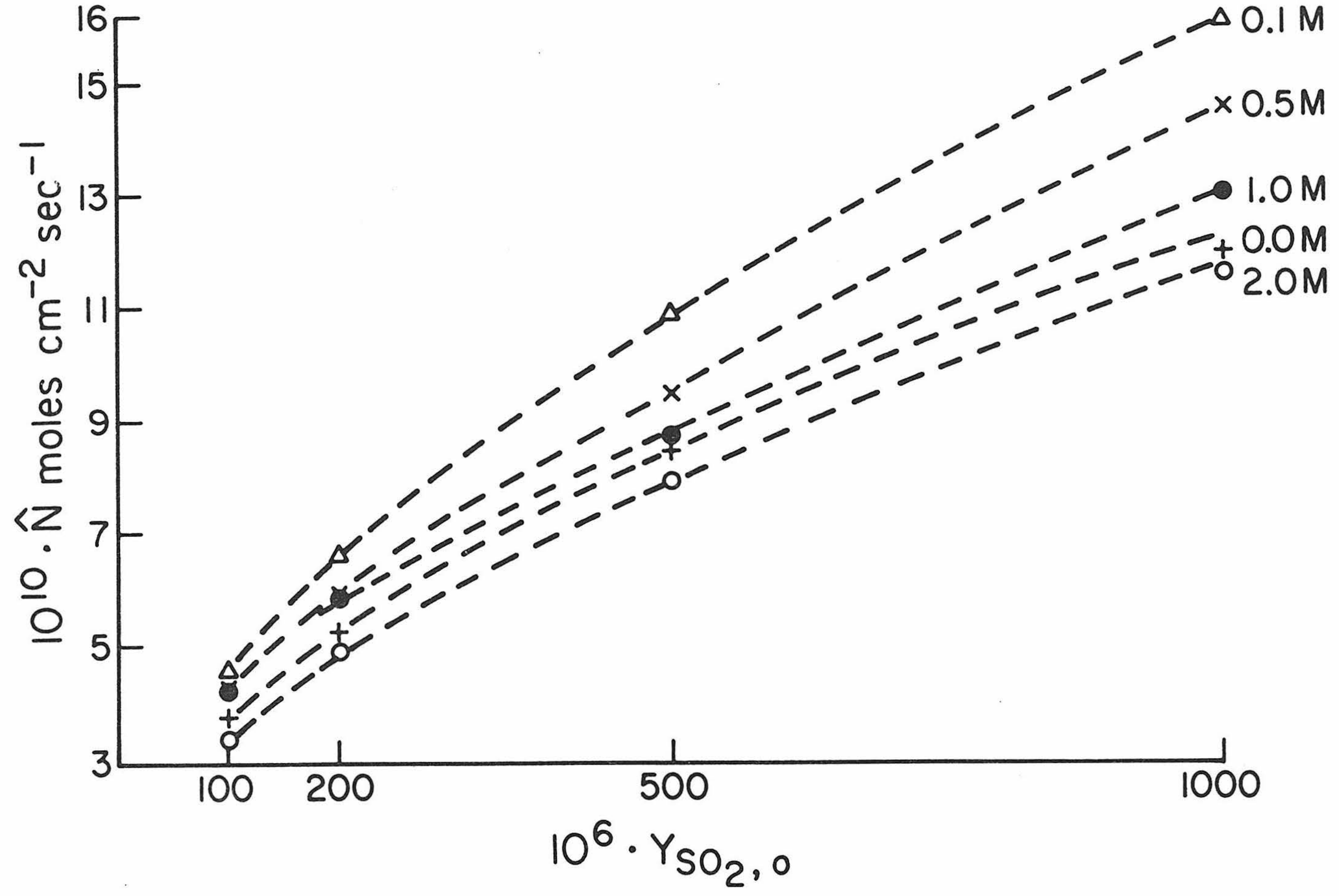
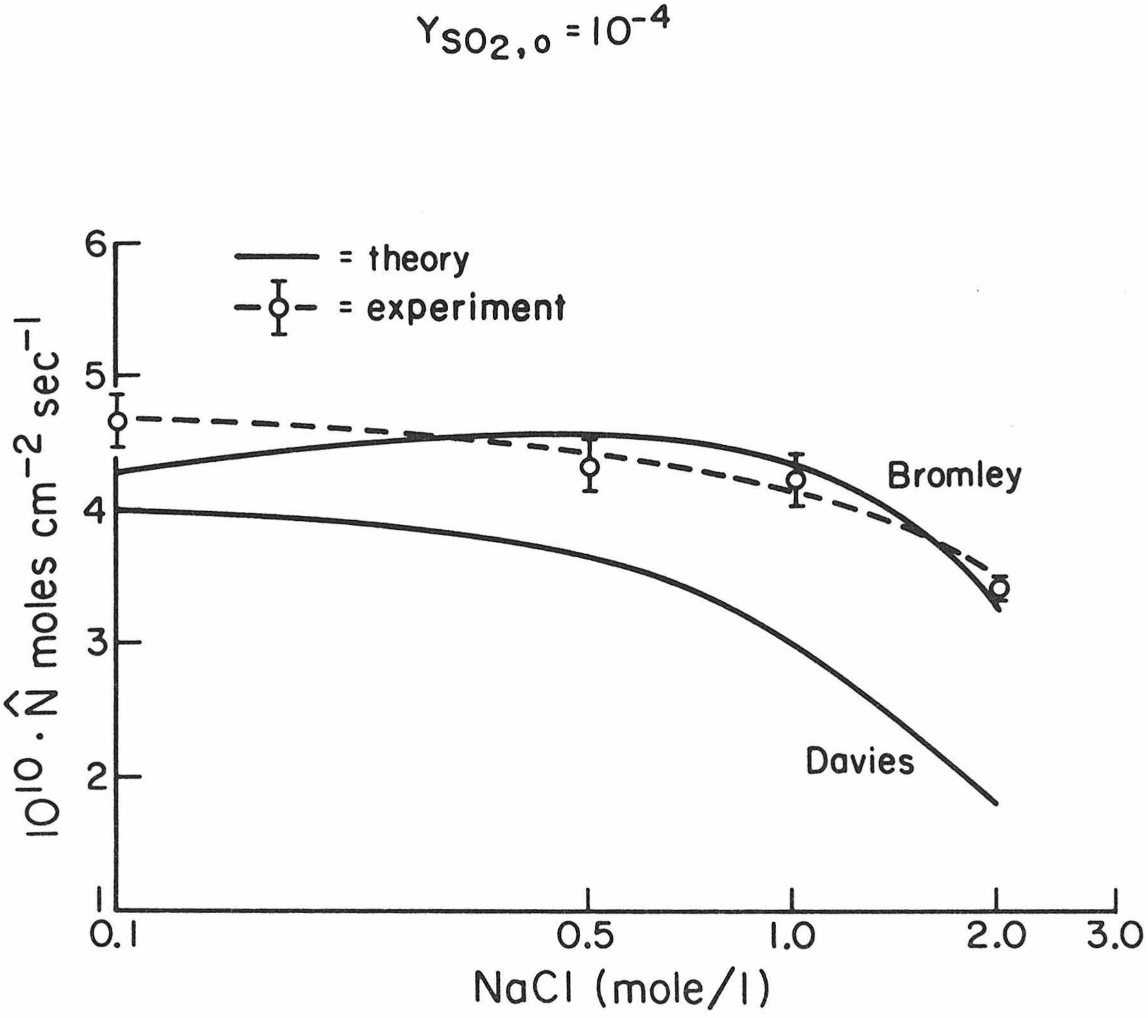
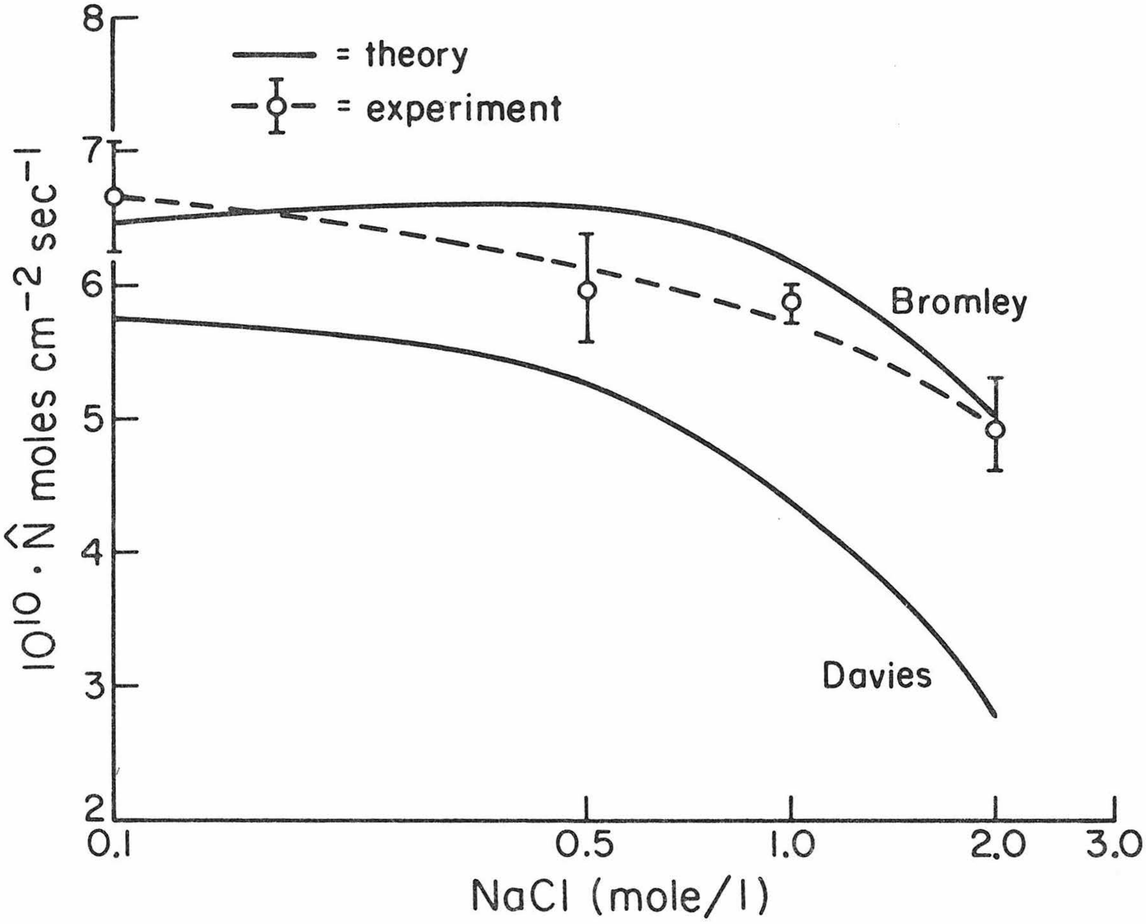


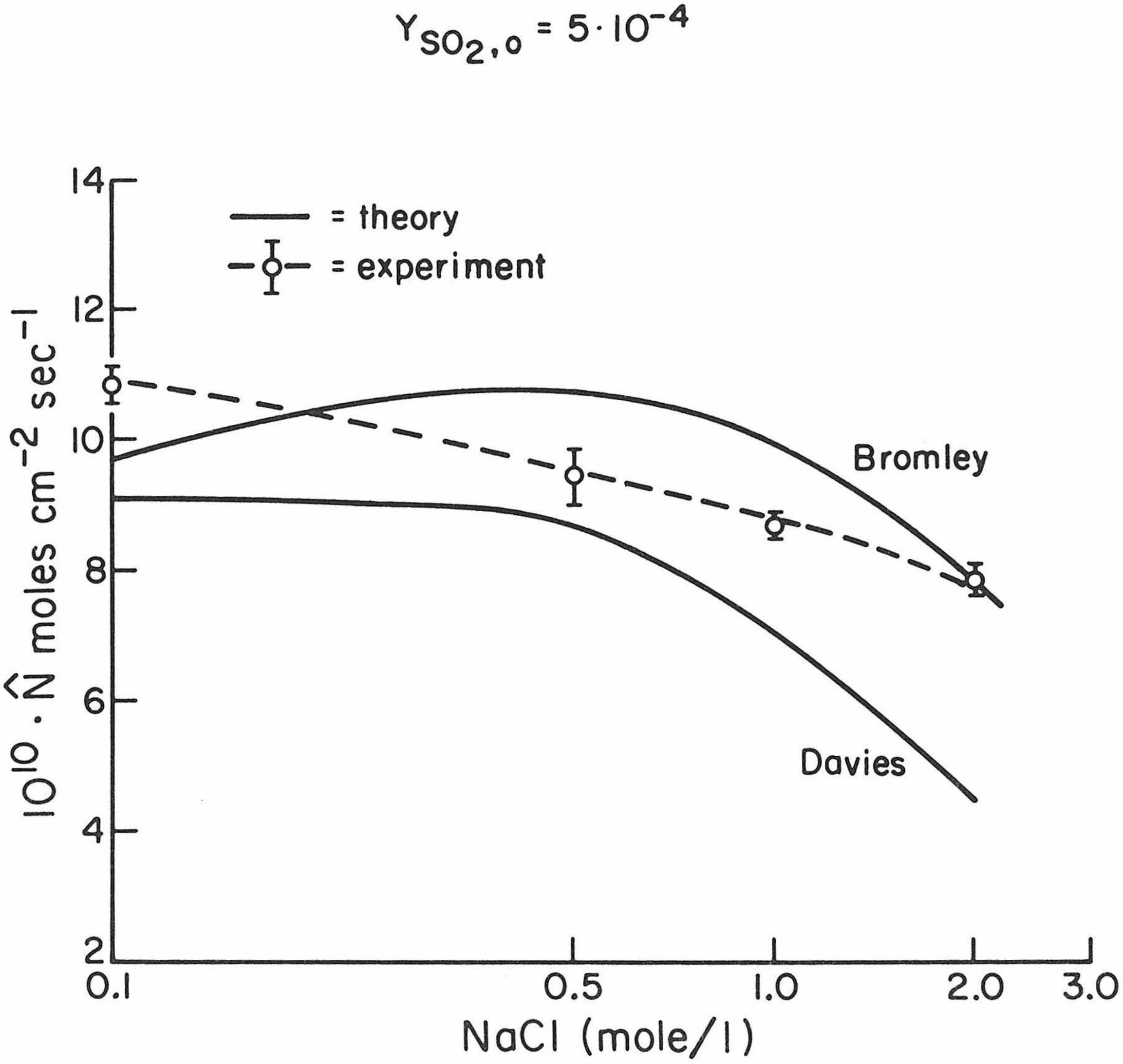
FIGURE 5.3 -- NaCl and Pure Water Data - In dilute concentrations, NaCl "salts in" the HSO_3^- ion so that the flux is higher than through water (0.0M). Continued increase in NaCl concentration increases solution viscosity and reduces "salting in" effect. Flux for 2.0M NaCl falls below water data.

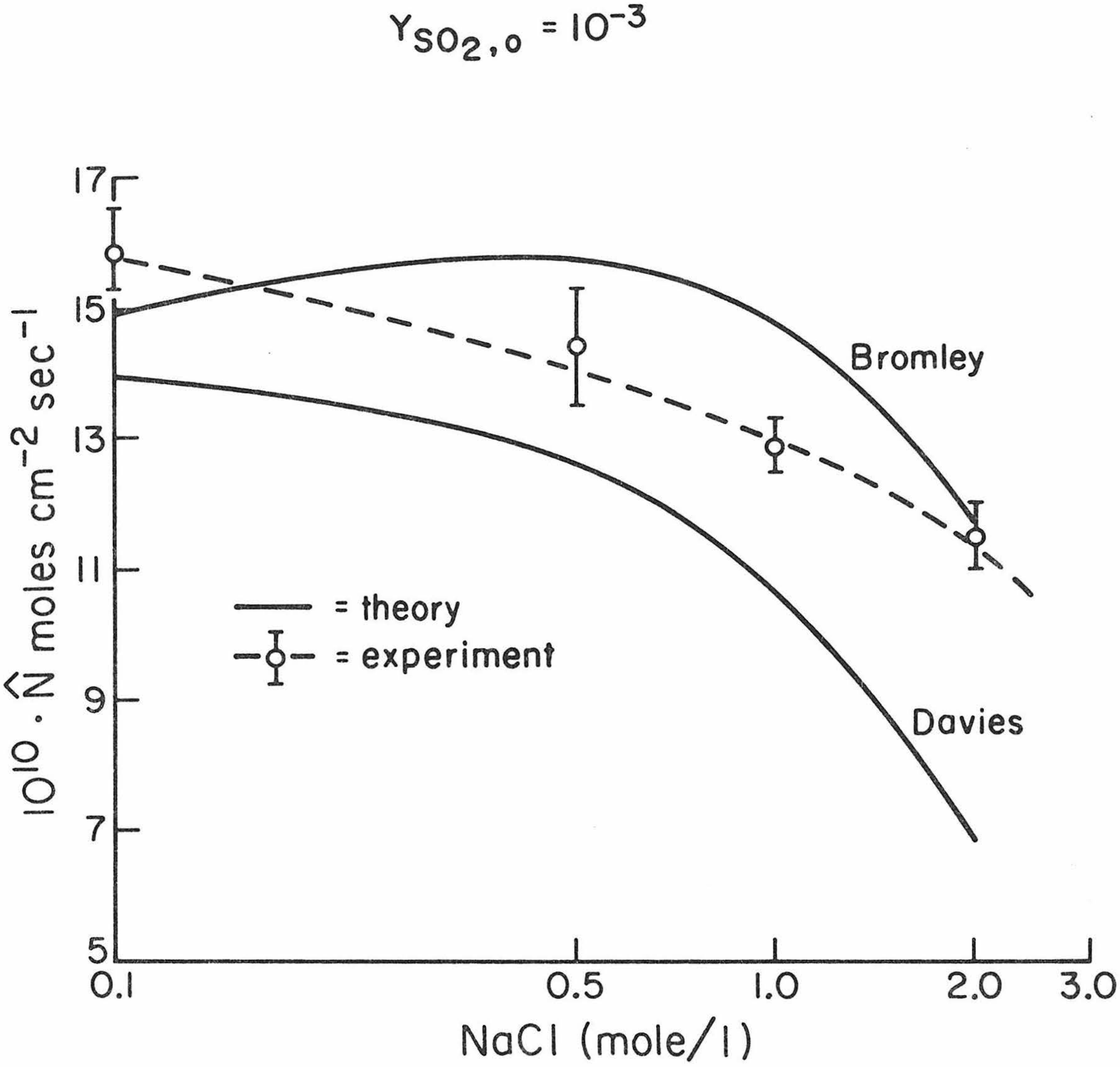
FIGURES 5.4a)-d) -- These four figures compare the NaCl data with the equilibrium theory (eq. 3.57) using both the Bromley and Davies activity coefficient models. Each figure is for a different value of $y_{SO_2,o}$ (10^{-4}, $2 \cdot 10^{-4}$ $5 \cdot 10^{-4}$, and 10^{-3}). The comparison shows that the equilibrium theory succeeds and that Bromley's model is preferable in NaCl solutions.


$Y_{SO_2,o} = 10^{-4}$
= theory
= experiment
$10^{10} \cdot \hat{N}$ moles cm^{-2} sec^{-1}
6
5
4
3
2
1
0.1
0.5
1.0
2.0
3.0
NaCl (mole/l)
Bromley
Davies

$Y_{SO_2,o} = 2 \cdot 10^{-4}$




$Y_{SO_2,o} = 5 \cdot 10^{-4}$
= theory
= experiment
$10^{10} \cdot \hat{N}$ moles cm^{-2} sec^{-1}
14
12
10
8
6
4
2
0.1
0.5
1.0
2.0
3.0
NaCl (mole/l)
Bromley
Davies


$Y_{SO_2,o} = 10^{-3}$
17
15
13
11
9
7
5
$10^{10} \cdot \hat{N}$ moles cm^{-2} sec^{-1}
0.1
0.5
1.0
2.0
3.0
NaCl (mole/l)
Bromley
Davies
= theory
= experiment

Bromley activity coefficient models (Appendix D) are used in eq. 3.57 to see which model works better for NaCl solutions. The results show that the equilibrium theory works in concentrated neutral solutions. The Stokes-Einstein dependence of D_i on μ is adequate. The potential gradient, included in the equilibrium theory, is necessary for proper modeling of the system, even in concentrated solutions. The approximate method of accounting for the potential gradient appears to be valid.

Bromley's activity coefficient model is preferable in NaCl solutions. In the most concentrated solutions, the Davies model deviates from the data by a factor of two while Bromley's model agrees well with the data. One might expect Bromley's model to be more accurate in NaCl solutions because it was developed initially for sea water. Davies' model is more generalized and is based on data for many solutions.

When the concentration is less than 0.5M, however, the Bromley model theory is not significantly closer to the data than the Davies theory. The neutral salt data therefore show that for $I \leq 0.5M$, a simple model (Davies') works as well as a complex model (Bromley's). This observation allows the Davies model to be used for other aqueous SO_2 solutions when $I \leq 0.5M$. The relative simplicity of the Davies model is an advantage in making calculations.

Often one will be faced with a chemical system for which the Bromley interaction parameters are not available.

One would like to be able to choose a universally valid activity coefficient model based on NaCl data. This desire, however, is unrealistic. Activity coefficients depend on the nature of the chemical species in a complicated manner that is the subject of current research (e.g., Cepeda, 1977). Thus, although Bromley's model works well for concentrated NaCl solutions, it may fail for other aqueous SO_2 solutions.

Some test other than the NaCl experiments must be done to obtain an activity coefficient model for the alkaline solutions when $Na_{tot} > 0.5M$. For this purpose, solubility data for SO_2 in alkaline sodium solutions taken from the literature were compared with the solubility predicted by the equilibrium computations (Appendix A). This test is shown in Appendix C where Johnstone and Blankmeyer's (1938) data are compared with computed solubility using the Davies activity coefficient model and the complex chemical speciation shown in section 3.1. Agreement is excellent (within 10%). Therefore, the Davies model is reasonable for the alkaline solutions in the present study. It is used in all theoretical calculations involving these solutions.

To establish a reasonable activity coefficient model for a given aqueous solution, one must use whatever evidence one may be able to find. Neutral salt data, however, show that whether one chooses a simple or complex γ_i model, one is not likely to be in error by more than a factor of two for $I \leq 2M$.

5.3 Alkaline Solutions -- $NaOH/NaHSO_3/Na_2SO_3$

In presenting the data, Na_{tot} is chosen as an independent variable. Alkaline solutions with the same total sodium concentration will behave the same at steady state when the alkaline salts that are used have no anions that are foreign to the SO_2/H_2O system. Therefore, the results apply to any mixture of NaOH, $NaHSO_3$, Na_2SO_3, or $Na_2S_2O_5$.

All theoretical calculations for alkaline solutions are done with a) the complex speciation and the various measured and estimated equilibrium and diffusion coefficients (section 3.1), b) the Davies γ_i model, and c) Stokes-Einstein dependence of D_i on μ. Viscosity is taken to be that of an NaOH solution with the same Na_{tot} concentration. This approximation is reasonable since viscosities of NaOH, $Na_2S_2O_3$, and Na_2SO_4 solutions with the same Na_{tot} differ by only a few per cent. Viscosity data are from the Handbook of Chemistry and Physics (Weast, 1971).

5.3.1 General Results

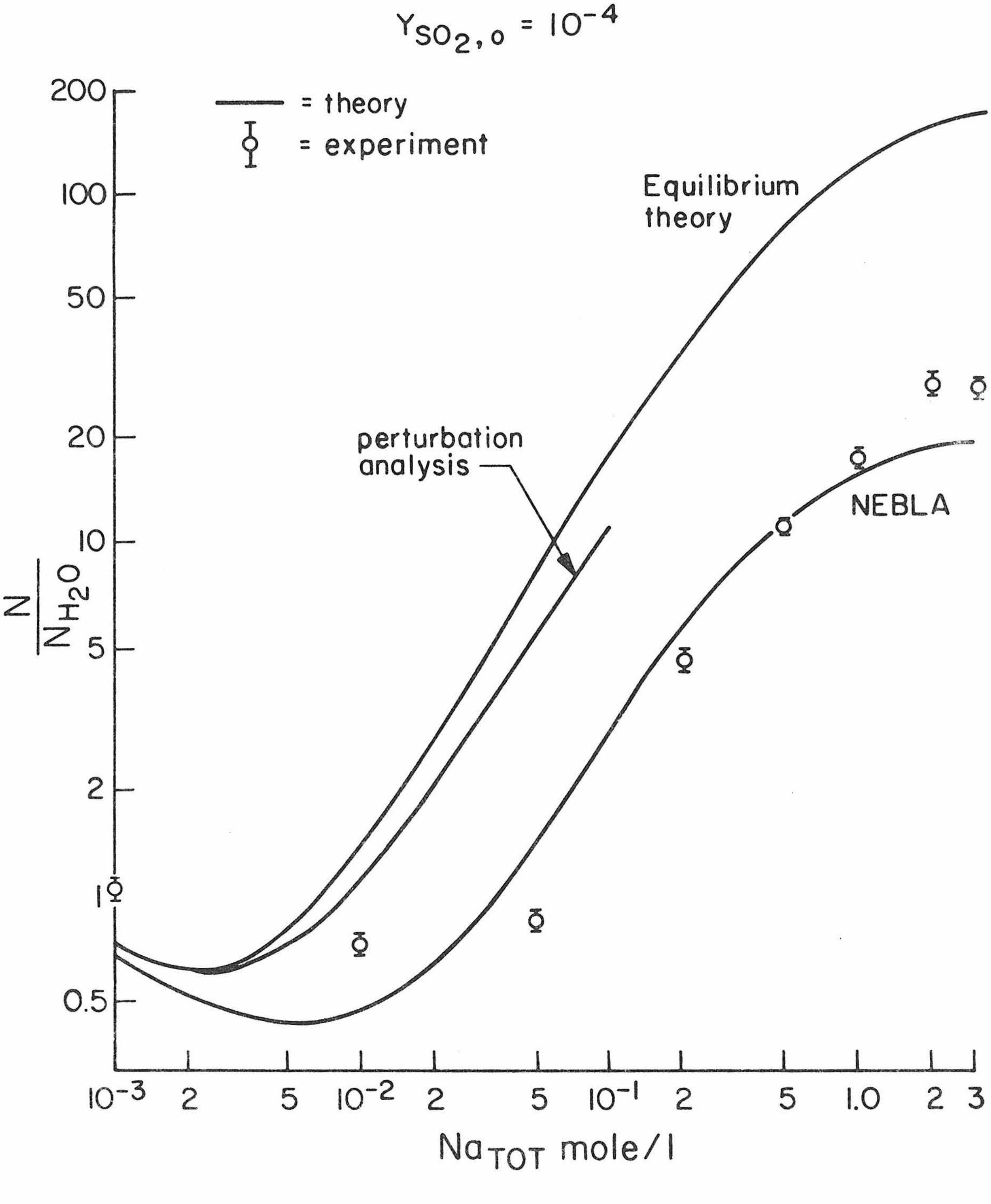
Figures 5.5a,b,c,d show the entire range of alkaline solution data for $y_{SO_2,o}$ = 100, 200, 500, and 1000ppm. The film thickness is 1mm. The y-axis on each plot is the observed flux divided by the flux through pure water (Table 5.1). Also shown are the equilibrium theory (section 3.2.3), the NEBLA (section 3.2.4), and a perturbation solution adapted from Schultz, Goddard, and Suchdeo (1974).

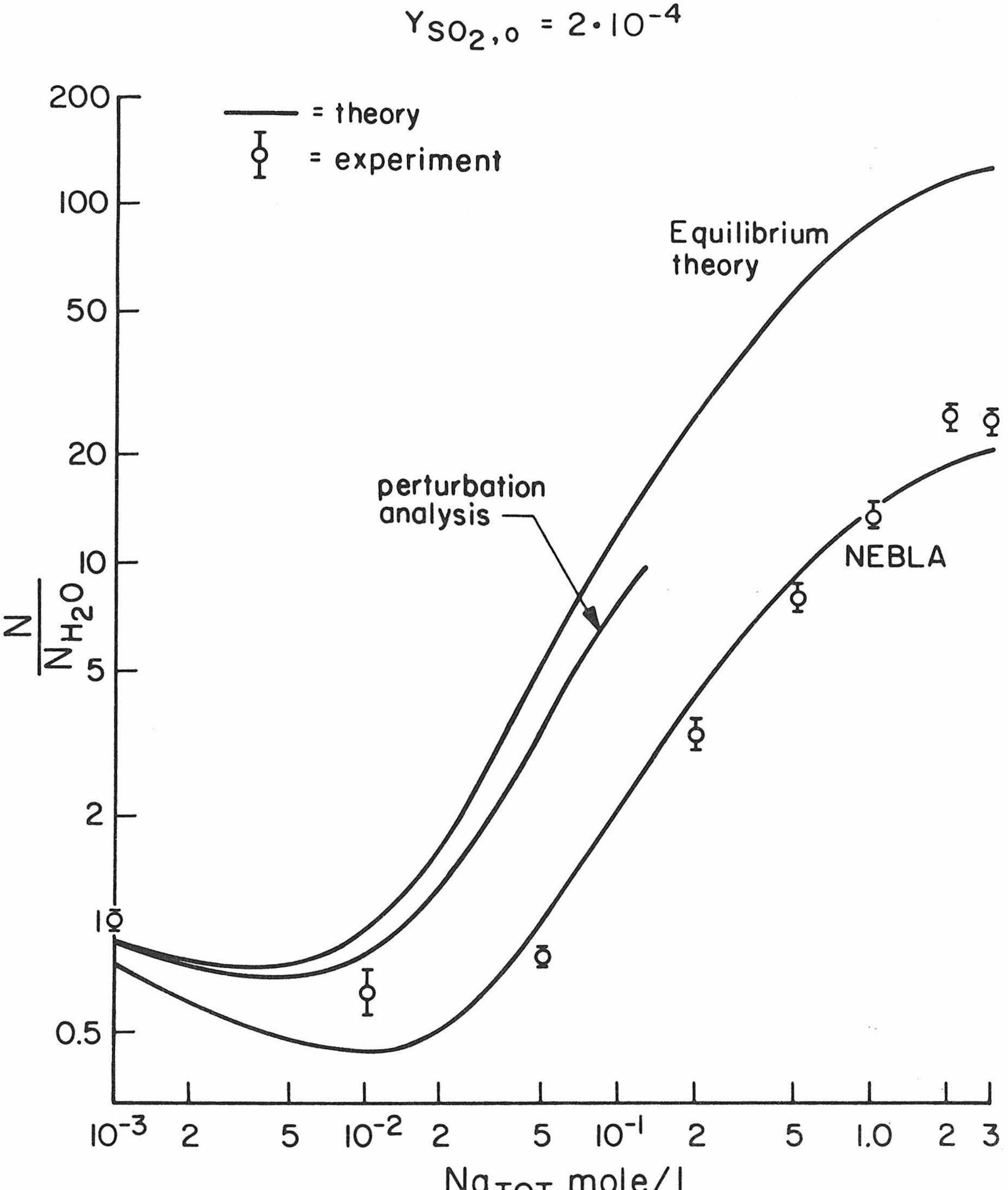
Adding alkaline salts to the solution has a significant effect since N/N_{H_2O} ranges up to 28. The intuitive notion that alkaline solutions increase the SO_2 transport rate is verified. The minimum in the curve, however, is not expected and will be discussed in section 5.3.3.

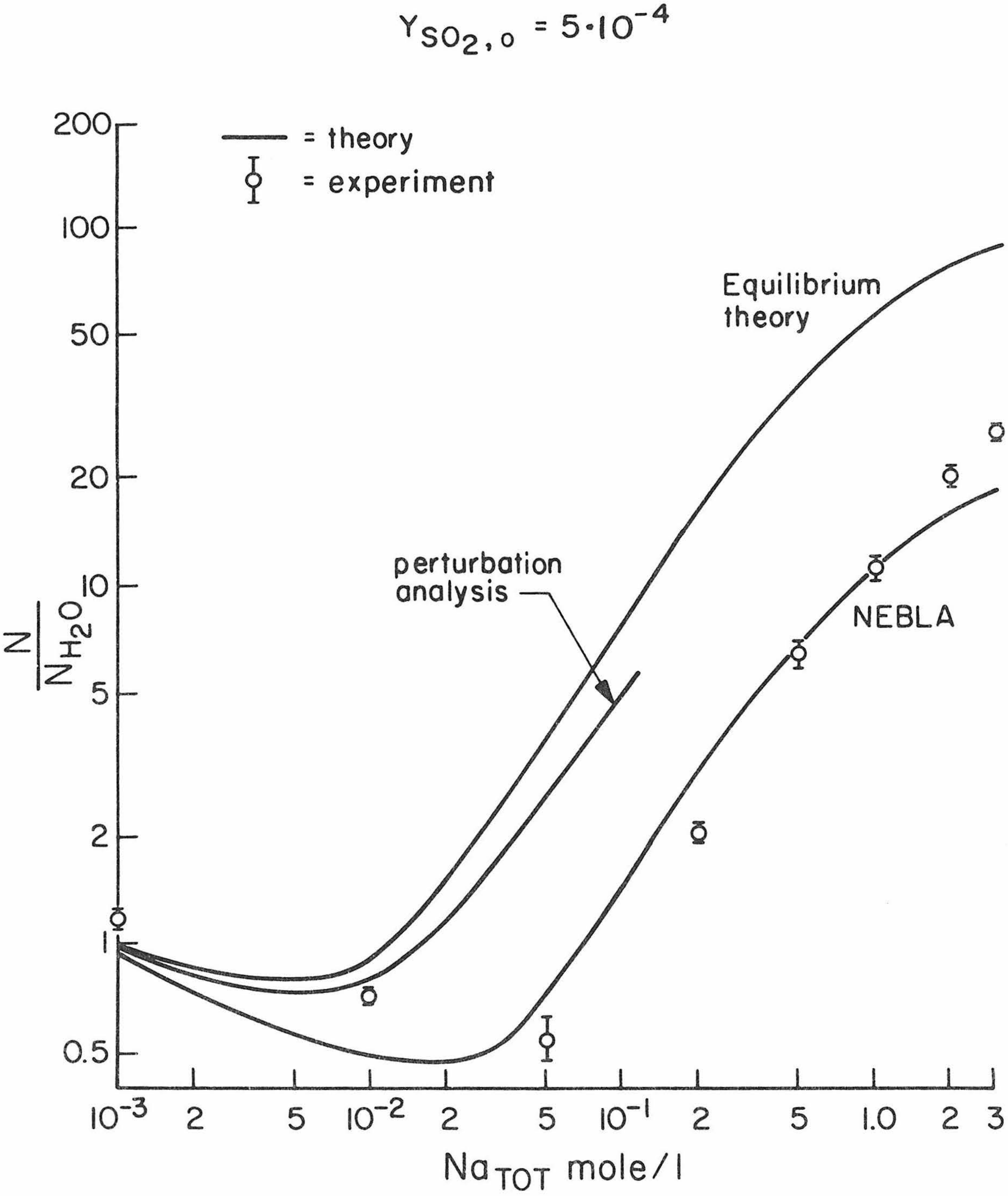
For $Na_{tot} \geq 0.03M$, the equilibrium theory overestimates the flux by about a factor of seven. The equilibrium approximation therefore can be invalid in aqueous SO_2 solutions. Quantification of what is meant by "instantaneous" is needed before the approximation can be used confidently (section 5.3.2).

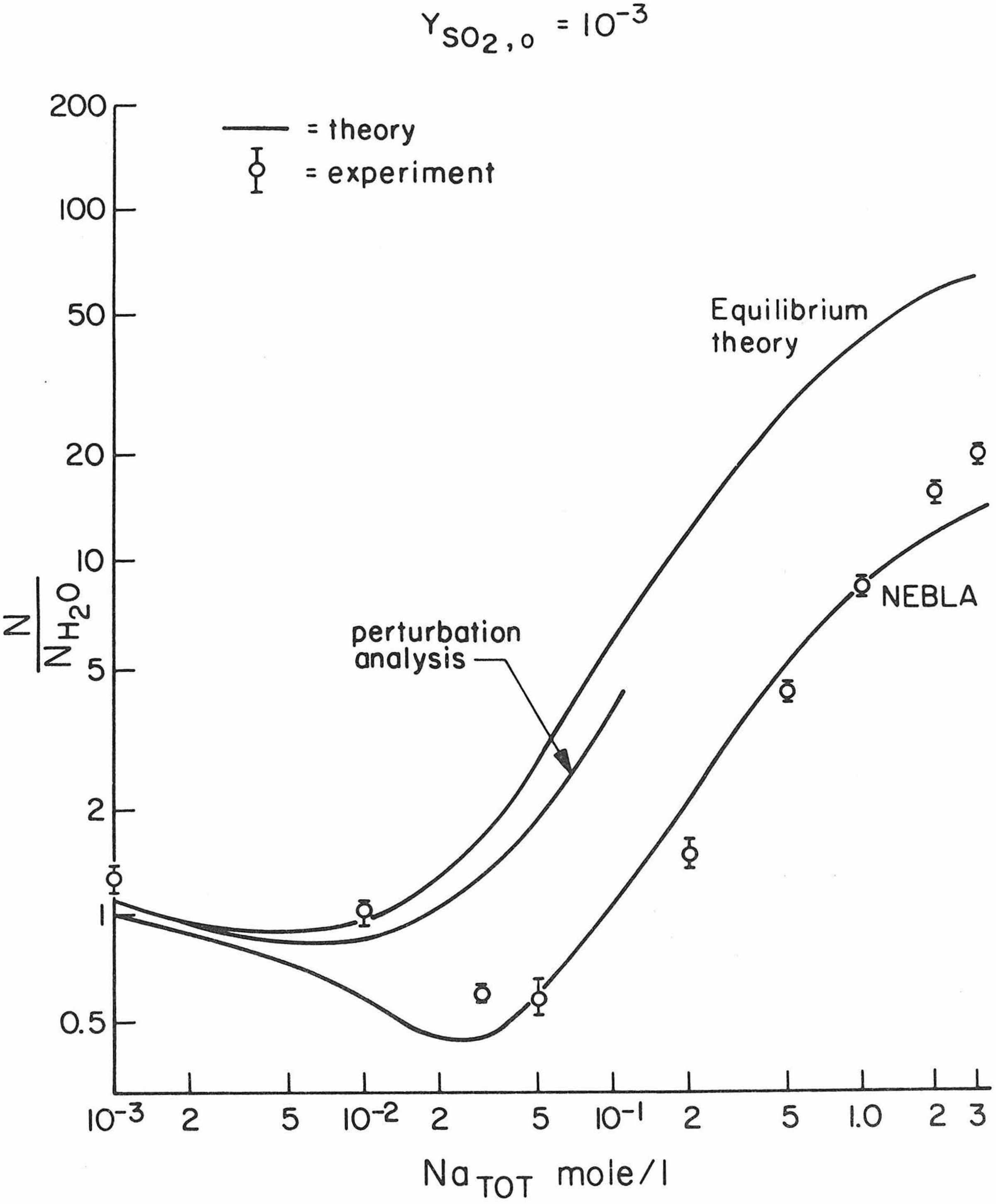
The singular perturbation analysis adapted from Schultz, Goddard, and Suchdeo overpredicts the data also. This analysis is valid in the limit of fast reactions and cannot be expected to predict a factor of seven deviation from equilibrium. It is included to show that existing perturbation analyses do not apply to the present system because it is far from equilibrium.

FIGURES 5.5a)-d) -- Alkaline solution data for $y_{SO_2,o} = 10^{-4}$, $2 \cdot 10^{-4}$, $5 \cdot 10^{-4}$, and 10^{-3} are presented in the next four figures. Alkaline sodium increases the flux by up to a factor of 28 over pure water. Equilibrium theory, a perturbation analysis adapted from Schultz, Goddard, and Suchdeo (1974), and the NEBLA are compared with the data. When $Na_{tot} > 0.03M$, the equilibrium and perturbation theories overpredict the flux by up to a factor of seven; the NEBLA is within 30%. Below 0.03M, the theory does not account for the potential gradient properly and underestimates the flux.


$Y_{SO_2,o} = 10^{-4}$
= theory
= experiment
Equilibrium theory
perturbation analysis
NEBLA
$\frac{N}{N_{H_2O}}$
200
100
50
20
10
5
2
1
0.5
10^{-3}
2
5
10^{-2}
2
5
10^{-1}
2
5
1.0
2
3
Na_{TOT} mole/l


$Y_{SO_2,o} = 2 \cdot 10^{-4}$
= theory
= experiment
Equilibrium theory
perturbation analysis
NEBLA
$\frac{N}{N_{H_2O}}$
200
100
50
20
10
5
2
1
0.5
10^{-3}
2
5
10^{-2}
2
5
10^{-1}
2
5
1.0
2
3
Na_{TOT} mole/l


$Y_{SO_2,o} = 5 \cdot 10^{-4}$
= theory
= experiment
Equilibrium theory
perturbation analysis
NEBLA
$\frac{N}{N_{H_2O}}$
200
100
50
20
10
5
2
1
0.5
10^{-3}
2
5
10^{-2}
2
5
10^{-1}
2
5
1.0
2
3
Na_{TOT} mole/l



$Y_{SO_2,o} = 10^{-3}$
= theory
= experiment
Equilibrium theory
perturbation analysis
NEBLA
$\frac{N}{N_{H_2O}}$
200
100
50
20
10
5
2
1
0.5
10^{-3}
2
5
10^{-2}
2
5
10^{-1}
2
5
1.0
2
3
Na_{TOT} mole/l

For $Na_{tot} \geq 0.05M$, the NEBLA predicts the data with a maximum deviation of 30%. When $Na_{tot} \leq 0.05M$, certain effects (section 5.3.3) make the data rise by up to 50% over the NEBLA. The deviation of a maximum of 30% must be viewed as excellent when the approximations in the NEBLA are considered. Modeling this system with N simultaneous, non-linear, second-order differential equations is probably unjustified at this point.

Table 5.2 shows the facilitation factors calculated from the data shown in Figs. 5.5a,b,c,d. These values of F are up to 450 times larger than those observed in previous SO_2 transport studies. The sulfur-containing ions dominate the flux. In the equilibrium core, $SO_2(aq)$ carries a small fraction of the flux (approximately 1/(F+1)). Because F is large, the system lies far from the zero chemical reaction limit. Therefore, the SO_2/alkaline salt system is far from both the fast and slow kinetic limits.

5.3.2 Characteristics of the NEBLA; Definition of "Instantaneous"

Reactions in the SO_2 system are considered fast by most standards, and treatments of SO_2 absorption have assumed instantaneous reactions (section 2.5.2.2). The Damkohler number is large ($3.1 \cdot 10^9$, eq. 5.15). Also,

Table 5.2

Facilitation Factors from Alkaline Solution Data

Na_{tot} mole/ℓ	$10^6 \cdot y_{SO_2,o}$ 1000	500	200	100
0.0	5.73	8.73	13.8	19.7
10^{-3}	6.86	9.60	14.7	21.2
10^{-2}	6.04	5.86	8.42	13.4
0.05	2.65	3.80	10.8	15.6
0.20	8.62	17.9	52.3	103
0.50	31.3	65.9	132	261
1.0	73.0	133	267	476
2.0	175	321	661	997
3.0	305	573	878	1370

as shown in Table 5.3, the boundary layer thickness, δ_1, is approximately 10^{-3} when $Na_{tot} \geq 0.01M$. Since the film thickness is 1mm, $\hat{\delta}_1$ is just over 1μm. Yet, this thin layer causes a factor of seven deviation from equilibrium flux. Hence, fast reactions, large Damkohler numbers or thin boundary layers must be viewed as concepts, not as proof of the validity of the equilibrium approximation.

Thus, in the context of facilitated transport, reactions can be considered "instantaneous" only when the flux predicted by a non-equilibrium theory (e.g., the NEBLA) agrees with the equilibrium theory. An example is given in Table 5.4 where the flux through pure water predicted by the NEBLA (N_{bl}) and the equilibrium theory (eq. 3.57) are shown with the measured flux (Table 5.1). The NEBLA agrees with N_{eq} to within 8%. In the absence of the data, the equilibrium theory would be confirmed by this agreement.

With the data, the NEBLA is seen to be valid for all kinetic regimes for aqueous SO_2 solutions. It would be useful to compare the NEBLA to data from other facilitated transport studies to see if the NEBLA is valid for all kinetic regimes in other systems.

Table 5.3 shows that δ_1 is $\sim 0.02\%$ for pure water ($Na_{tot} = 0$). In this case, the boundary layer is thin enough to be neglected. A statement like "thin enough"

Table 5.3

Boundary Layer Thicknesses Calculated in Analyzing Alkaline Solution Data

Entries are $10^2 \cdot \delta_1$

	$10^6 \cdot y_{SO_2,o}$			
Na_{tot} mole/ℓ	1000	500	200	100
0.0	0.0183	0.0197	0.0216	0.0231
10^{-3}	0.0380	0.0439	0.0531	0.0613
10^{-2}	0.0906	0.1074	0.1274	0.1381
0.05	0.1280	0.1338	0.1380	0.1400
0.20	0.1240	0.1256	0.1279	0.1308
0.50	0.1178	0.1194	0.1234	0.1296
1.0	0.1116	0.1138	0.1201	0.1300
2.0	0.1014	0.1043	0.1128	0.1263

Table 5.4

Boundary Layer and Equilibrium Theories Compared to Pure H_2O Results

$10^6 \cdot y_{SO_2,o}$	$10^{10} \cdot \hat{N}$ moles $cm^{-2} sec^{-1}$		
	$\hat{N}_{bl}$	$\hat{N}_{eq}$	$\hat{N}_{H_2O}$
1000	12.8	11.8	11.9
500	8.52	8.41	8.44
200	5.06	5.17	5.32
100	3.43	3.61	3.81

can be made only because N_{bl} has been compared to N_{eq}, not because δ_1 is "small."

5.3.3 The Potential Gradient and the Flux Minimum

For $Na_{tot} \lesssim 0.02M$, the data are about 50% higher than the NEBLA predicts. This deviation results from the potential gradient. In dilute alkaline solutions, the potential gradient is not identically zero, and a concentration profile in the alkali cation (Na^+) is induced (eq. 3.71).

The data analysis does not account for this profile. The potential gradient assists the motion (from $x = 0$ to $x = 1$) of negative ions (enhancement of $D_{HSO_3^-}$). Therefore it resists the diffusion of Na^+. The no-flux condition on Na^+ implies that the concentration gradient opposes the action of the potential gradient. Thus, C_{Na^+} at $x = 0$ must be greater than C_{Na^+} at $x = 1$. (A rigorous proof follows from eq. 3.71). Because the data reduction ignores this concentration difference, the SO_2 is more soluble at $x = 0$ and less soluble at $x = 1$ than is assumed in the data reduction. Therefore the concentration difference

$$C_{HSO_3^-}(0) - C_{HSO_3^-}(1)$$

which is responsible for most of the flux (see eq. 3.51) is greater than is calculated by the NEBLA. Hence, the NEBLA underestimates the flux when the potential gradient is non-zero and when Na^+ is the predominant cation ($2 \cdot 10^{-3}M \leq Na_{tot} \leq 0.03M$).

The potential gradient is also involved in producing the minimum in the flux near $Na_{tot} = 2 \cdot 10^{-2}M$. Addition of Na^+ reduces the effective diffusivity of the HSO_3^- ion as the potential gradient becomes less important (section 3.2.2 and eqs. 3.49b). Thus, although adding Na^+ increases the amount of HSO_3^- in solution, the HSO_3^- diffuses progressively slower.

The pH changes that occur as Na^+ is added also have a role in producing the minimum. In these dilute solutions, HSO_3^- is the dominant sulfur carrier. Therefore the concentration <u>difference</u>

$$C_{HSO_3^-}(0) - C_{HSO_3^-}(1)$$

is of primary importance (eq. 3.51).

To see the role of the pH in the minimum, two equations derived from the electroneutrality equation are needed:

$$C_{Na^+} + C_{H_3O^+} = C_{HSO_3^-} + 2C_{SO_3^=} \qquad (5.16)$$

and

$$C_{HSO_3^-}(0) - C_{HSO_3^-}(1) = C_{H_3O+}(0) - C_{H_3O+}(1) + 2[C_{SO_3^=}(1) - C_{SO_3^=}(0)] \qquad (5.17)$$

(OH^- and other species have been neglected (pH 3-6)). Zero Na^+ concentration gradient is assumed, rigorously true only when the potential gradient is zero.

Equation 5.17 shows that in SO_2/H_2O solutions, where $C_{SO_3^=}$ is negligible, the facilitation depends on the pH difference $C_{H_3O+}(0) - C_{H_3O+}(1)$. For T = 25°C, P_{tot} = 744mm Hg, and $100 \leq 10^6 \cdot y_{SO_2,o} \leq 1000$, the pH at x = 0 (pH(0)) in an SO_2/H_2O solution lies between 2.4 and 2.9. The pH at x = 1 (pH(1)) is 4.38 ($y_{SO_2,1} = 10^{-7}$). Therefore

$$C_{H_3O+}(0) >> C_{H_3O+}(1) \qquad (5.18)$$

so that

$$C_{H_3O+}(0) - C_{H_3O+}(1) \simeq C_{H_3O+}(0) \qquad (5.19)$$

Thus, in the dilute solution limit, the facilitation directly depends on pH(0).

Addition of Na^+ causes $C_{H_3O+}(0)$ to decrease which, according to eqs. 5.17,19, causes the facilitation factor to decrease. This $C_{H_3O+}(0)$ contribution becomes small when Na^+ approaches 0.01M. Here pH(0) ≃ 4.

The facilitation would be eliminated unless the pH becomes high enough to create some $SO_3^=$. When $SO_3^=$ is present, the term

$$2[C_{SO_3^=}(1) - C_{SO_3^=}(0)] \tag{5.20}$$

can contribute to the flux.

To see how large the pH must become before $SO_3^=$ contributes significantly to the flux, consider eq. 5.16 when the pH is high enough to make $C_{H_3O^+}$ negligible. Then

$$C_{Na^+} = C_{HSO_3^-} + 2C_{SO_3^=} = C_{HSO_3^-}\left(1 + \frac{2K_2}{C_{H_3O^+}}\right) \tag{5.21}$$

where K_2 is the equilibrium coefficent of

$$HSO_3^- + H_2O \rightleftarrows SO_3^= + H_3O^+ \tag{5.22}$$

Since $K_2 = 6.24 \cdot 10^{-8}$ mole/l at 25°C ($pK_2 = 7.2$), no significant $SO_3^=$ can be created near $x = 1$ until pH(1) approaches 7. Hence, the flux is denied the $SO_3^=$ contribution until pH(1) approaches 7.

Thus, there is a window where $pH(0) \gtrsim 4$ but $pH(1) \lesssim 7$. In this window, the facilitation mechanism switches from being based on a direct pH difference to a pH-induced $SO_3^=$ difference. The result is the minimum in the flux near $Na_{tot} = 2 \cdot 10^{-2}$ M.

5.4 Effect of Film Thickness

To test for the thickness dependence (section 4.5.4), data at fixed $y_{SO_2,o}$ ($2 \cdot 10^{-4}$) and Na_{tot} (0.05M) were taken with film thicknesses of about 0.37mm and 4.8mm. This range brackets the 1mm film thickness used in the other alkaline solution experiments. Data are shown in Fig. 5.6 with the data point from Figure 5.5b (L = 1mm). The solid line is the NEBLA, and the dashed line is a sketch of the data.

The NEBLA agrees qualitatively with the data. The observed variation in F is a factor of 2.05, and the predicted variation is a factor of 2.47. The slopes of the theory and data curves are similar. In the previous alkaline solution data, the NEBLA overpredicted the flux by $\sim$30% when Na_{tot} = 0.05M (Figs. 5.5a,b,c). The 20%-40% overprediction in Figure 5.6 is therefore part of a systematic error in the NEBLA that is unrelated to the film thickness effect.

Based on the discussion in section 4.5.4, one expects δ_1 to increase as the observed facilitation factor decreases. This notion is confirmed by Table 5.5 where the facilitation factors from Figure 5.6 are listed with L, δ_1, and $\hat{\delta}_1$. As F decreases, the boundary layer becomes a larger fraction of the film thickness. For the smallest thickness, δ_1 reaches its largest value, 0.3%. It is notable that the dimensional

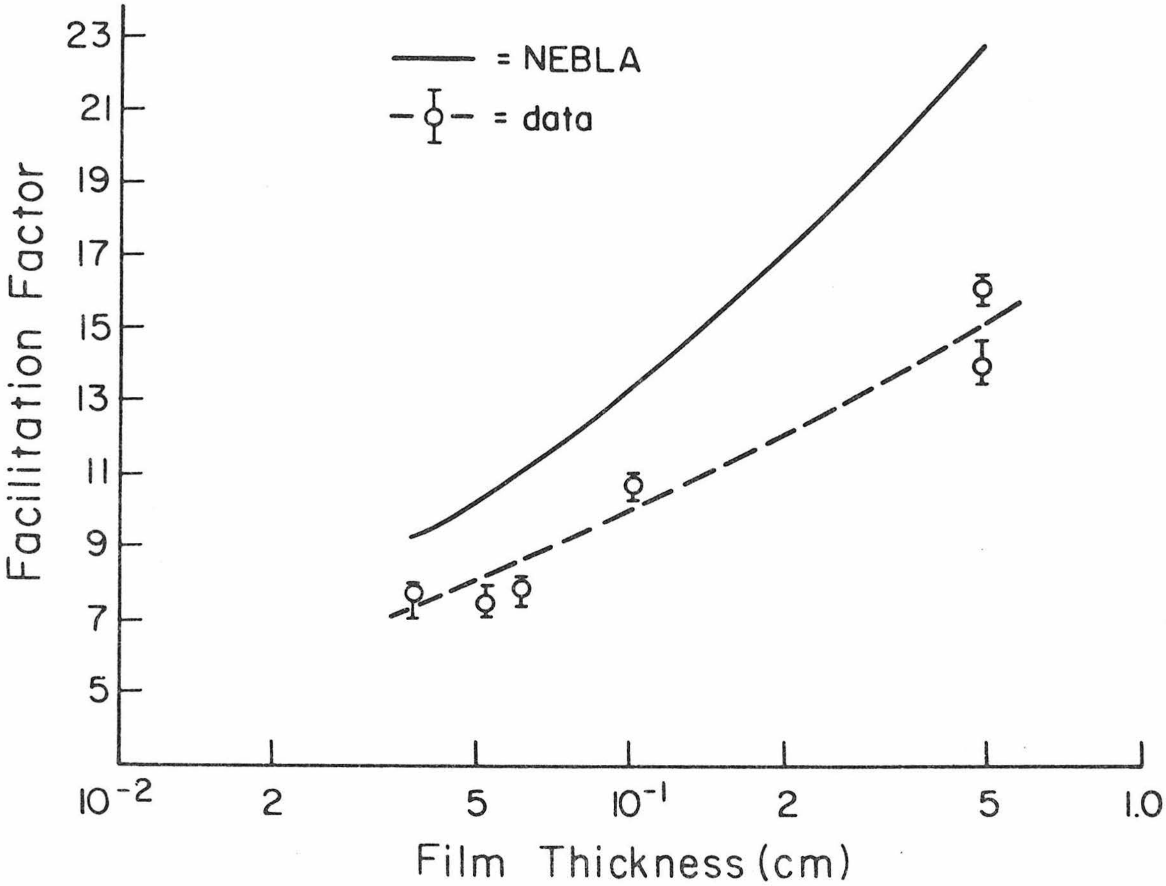


FIGURE 5.6 -- Variable Film Thicknesses - The facilitation factor changes with the film thickness. The NEBLA agrees qualitatively with the observed variation in F. Equilibrium theory predicts F independent of L.

Table 5.5

Boundary Layer Thicknesses in Variable Film Thickness Experiments

Data		Calculated by NEBLA	
L cm	F	$10^2 \cdot \delta_1$	$\hat{\delta}_1$ μm
$3.73 \cdot 10^{-2}$	7.78	0.3023	1.128
$5.11 \cdot 10^{-2}$	7.55	0.2356	1.204
$6.07 \cdot 10^{-2}$	7.93	0.2054	1.247
0.10	10.8	0.1380	1.380
0.476	14.1,16.2	0.0396	1.885

$F_{eq} = 77.6$

boundary layer thickness, $\hat{\delta}_1$, is relatively constant (1-2μm).

CHAPTER 6: SUMMARY AND RECOMMENDATIONS

A fundamental theory for the rate of SO_2 transport in water and neutral and alkaline salt solutions has been developed and tested. Most of the data have been taken under conditions typical of FGD scrubbers. The theory, summarized by eqs. 3.50 and 3.51, applies to an arbitrary aqueous SO_2 solution. Approximations allow eqs. 3.50,51 to be utilized to predict the flux through pure water and neutral and alkaline salt solutions. In principle, the problem can be treated by numerical solution of N second-order, non-linear, differential equations. There are many unknown parameters, however, and the approach adopted here avoids these difficulties.

The most important approximation is the NEBLA developed to explain the strong deviation of the alkaline solution data from the equilibrium theory. The equilibrium theory overpredicts the flux by up to a factor of seven when $Na_{tot} \geq 0.03M$. This deviation was unexpected and is the first reported observation of non-equilibrium effects in studies of SO_2 transport in aqueous solutions.

The NEBLA provides a near-quantitative prediction of the flux of SO_2 through alkaline solutions. Since the SO_2/alkaline salt system is far removed from the equilibrium and zero-reaction limits, the NEBLA represents a solution for the intermediate kinetics regime. No solution for this regime has previously been available for systems with non-linear kinetics. It may therefore provide the "missing link" in the quantitative analysis of facilitated systems.

Equations 3.92,93,97 summarize the NEBLA used in analyzing the alkaline solution data. When these equations are solved simultaneously, the equilibrium equations given in Appendix A are utilized. Equations 3.92,93,97 neglect the boundary layer near $x = 0$. Because this approximation may be invalid in other systems, the full NEBLA (eqs. 3.87,92,93,94) should be the starting point for analyzing a new system.

The boundary layer near $x = 1$ is approximately 0.1% of the film thickness ($\hat{\delta}_1 \simeq 1\mu m$). Nonetheless, this $1\mu m$ layer causes a factor of seven deviation from the equilibrium flux. For facilitated transport systems in general, appeal to fast reactions or thin boundary layers does not justify the equilibrium approximation. The equilibrium theory can be used only when the flux calculated from a non-equilibrium analysis agrees with the equilibrium flux. The NEBLA, therefore, can be used to test the validity of the equilibrium approximation (section 5.3.2).

When applied to pure water, the NEBLA predicts the boundary layer resistances to be negligible, and this is verified by experiment. Thus the NEBLA is valid for all kinetic regimes for aqueous SO_2 solutions. It would be useful to see if the NEBLA provides a valid quantitative analysis in all kinetic regimes for other facilitated transport systems.

Finally, the NEBLA agrees fairly well with the observed variation in facilitation factor in the variable thickness studies. Equilibrium theory fails to predict this variation.

The key results obtained in the alkaline salt and variable thickness studies are summarized in Table 6.1. Most of these points are discussed in sections 5.3,4.

With the equilibrium approximation, an analytical solution for the flux through SO_2/H_2O solutions (eqs. 3.57,60) is obtained from the general theory (eq. 3.51). Because pure water data agree with the equilibrium theory, a lower limit on k_1 can be set at 320 sec^{-1}. This value is well above literature values that conflict with Eigen's value for k_1. Therefore, Eigen's k_1 value should be used until more determinations of k_1 are reported in the literature.

The pure water data also show that the HSO_3^- ion dominates the transport ($5 < F < 19$). This is in contrast to the CO_2/pure water system where HCO_3^- makes little

Table 6.1

Key Points Deduced from Alkaline Solution and Variable Thickness Studies

1) NEBLA works with complex chemical speciation, various equilibrium and diffusion coefficients, Eigen's rate coefficient, Davies' γ_i model, use of NaOH viscosity for effect of μ on D_i, and by ignoring potential gradient when $Na_{tot} \geq 0.03M$.
2) Equilibrium theory overpredicts data by (up to) a factor of seven for $Na_{tot} \geq 0.03M$.
3) Existing perturbation analysis does not explain data.
4) Facilitation factors are large (up to 1370).
5) NEBLA applies (but is not restricted) to regime intermediate to fast and slow reactions.
6) NEBLA properly converges to equilibrium limit when applied to pure water.
7) Boundary layer width is approximately 0.1% of film thickness ($\hat{\delta}_1 \simeq 1\mu m$).
8) Facilitation factor depends on L, qualitatively in accord with NEBLA.
9) Addition of alkaline salt can decrease flux under some conditions (minimum in curve).
10) Significant flux increase over pure water (up to factor of 28) occurs when $Na_{tot} \geq 0.2M$.
11) Failure to account fully for effect of potential gradient causes theory to underestimate flux by $\sim$50% for $2 \cdot 10^{-3}M \leq Na_{tot} \leq 2 \cdot 10^{-2}M$.

contribution to the flux. Table 6.2 summarizes the important points deduced from the pure water data.

The general theory is applied to neutral salt solutions by the equilibrium approximation. The equilibrium theory agrees with the data when a) the potential gradient is assumed to enhance the diffusivity of HSO_3^- but not to produce Na^+ and Cl^- concentration profiles (eqs. 3.70,71), b) the diffusivities are assumed inversely proportional to the solution viscosity, and c) the Bromley model for activity coefficients is used. Since the Stokes-Einstein dependence of D_i on μ is adequate, it is carried over to the alkaline solutions.

Although the Bromley model for activity coefficients works well for NaCl solutions, the question of what model is proper for alkaline solutions is only partially answered. The simpler Davies model does not predict the data significantly worse than the Bromley model when $I \leq 0.5M$. In this way, the neutral salt data show that for $I \leq 0.5M$, the difference between a complex and simple γ_i model is small. A comparison of literature solubility data and computed equilibrium solubility (Appendix C) shows that Davies' γ_i model is satisfactory for concentrated alkaline sodium solutions.

Table 6.2

Key Points Deduced from Pure Water Data

1) Equilibrium theory works (eqs. 3.57,60).
2) Eigen's value of the rate coefficient k_1 is far preferred.
3) Only $SO_2(aq)$, HSO_3^-, and H_3O^+ must be considered in pure water solutions when $y_{SO_2} \geq 10^{-9}$ (Table 3.5).
4) Enhanced diffusivity of HSO_3^- implied by potential gradient (eq. 3.35) is needed to predict flux.
5) HSO_3^- ion dominates transport; $5 < F < 19$.

The main conclusions from the neutral salt data are summarized in Table 6.3.

Solutions containing both a neutral salt and an alkaline salt were not studied experimentally. The NEBLA applies since eqs. 3.50,51 are for an arbitrary solution. Choice of an appropriate activity coefficient model would be necessary, however, if $I > 0.5M$. Also, the net alkalinity would take the place of Na_{tot} in eq. 3.49b since it is the alkalinity that reduces the effectiveness of the potential gradient in enhancing $D_{HSO_3^-}$.

Because of the inadequacies in the physico-chemical data for aqueous SO_2 solutions, several thermodynamic, kinetic, and transport parameters have been estimated. Although the estimates are successful for the solutions studied here, it is recommended that several topics be addressed in future research. In order of importance, these topics are a) the magnitude of the rate coefficients for reactions 2.11, 2.12, 3.77, and 3.78, b) chemical speciation and thermodynamics of alkaline SO_2 solutions, c) kinetics of all other reactions, d) diffusion coefficients for $SO_3^=$ and $S_2O_5^=$, and e) diffusion coefficients for other sulfur-containing species.

Better methods for treating the potential gradient would be useful contributions to the general theory of facilitated transport. It could be fruitful to consider

Table 6.3

Key Points Deduced from Neutral Salt Data

1) Equilibrium theory works (eqs. 3.57,60); i.e., neutral salt solutions act like H_2O except for viscosity and activity coefficient effects.
2) Bromley's γ_i model is superior to Davies' model in NaCl.
3) Diffusivity inversely proportional to solution viscosity is an adequate model.
4) Potential gradient (enhancement of $D_{HSO_3^-}$) must be included in theory.
5) Choice of activity coefficient model not too important when $I \leq 0.5M$.

the diffusion coefficient difference, $D_i - \bar{D}$, in eq. 3.46 to be a perturbation parameter in an expansion from the limit of zero potential gradient.

The NEBLA would be improved by smoothing the discontinuity in the reaction rates at the boundary layer/core interfaces ($x = \delta_o$, $1 - \delta_1$). An approach to this problem could include linearizing the kinetics at $x = \delta_o$ and $x = 1 - \delta_1$ in a manner similar to the singular perturbation analysis of Schultz, Goddard, and Suchdeo. This expansion could be matched in the boundary layer by a regular perturbation expansion from the limit of frozen kinetics. A regular perturbation expansion has been applied to an entire film that has slow reaction rates (Schultz, Goddard, and Suchdeo). Combining the singular and regular perturbation analyses within the boundary later could provide a powerful tool for quantitative analysis of systems in the intermediate kinetics regime.

Finally, it is recommended that the fundamentals expressed here be applied to FGD scrubbers and other applications that involve uptake of SO_2 so that the predictions of the theory can be compared to field data.

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APPENDIX A -- Computation of Facilitation Factor by Equilibrium Theory and the NEBLA; Equilibrium Composition Calculations for $SO_2/Na^+/H_2O$ System.

This appendix gives the details of computing the facilitation factor by the equilibrium theory and the NEBLA. Each theory requires the equilibrium composition of an $SO_2/Na^+/H_2O$ solution to be known. Therefore, before the methods of computing the facilitation factor are shown, the equilibrium composition calculations are set up.

Equilibrium Composition Calculations

The following equations show how to compute the equilibrium composition of an aqueous solution that is exposed to a known partial pressure of SO_2 and contains a known concentration of sodium salts that have anions that are not foreign to the SO_2/H_2O system (i.e., NaOH, $NaHSO_3$, Na_2SO_3, $Na_2S_2O_5$ or any combination thereof). The independent variables are considered to be a) the mole fraction of SO_2 in the gas phase (fixed total pressure, P_{tot}), and b) the total concentration of sodium, Na_{tot}.

Table 3.1 gives the pertinent reaction equilibria. Equations leading from these equilibria are

$$H_{SO_2} a_{SO_2} = y_{SO_2} P_{tot} \tag{A-1}$$

$$K_1 a_{SO_2} a^2_{H_2O} = a_{H_3O^+} a_{HSO_3^-} \tag{A-2}$$

$$K_2 a_{HSO_3^-} a_{H_2O} = a_{H_3O^+} a_{SO_3^=} \tag{A-3}$$

$$K_3 a^2_{HSO_3^-} = a_{S_2O_5^=} a_{H_2O} \tag{A-4}$$

$$K_4 a^2_{H_2O} = a_{H_3O^+} a_{OH^-} \tag{A-5}$$

$$K_5 a_{NaHSO_3} = a_{Na^+} a_{HSO_3^-} \tag{A-6}$$

$$K_6 a_{NaS_2O_5^-} = a_{Na^+} a_{S_2O_5^=} \tag{A-7}$$

$$K_7 a_{Na_2S_2O_5} = a_{Na^+} a_{NaS_2O_5^-} \tag{A-8}$$

$$K_8 a_{NaSO_3^-} = a_{Na^+} a_{SO_3^=} \tag{A-9}$$

$$K_9 a_{Na_2SO_3} = a_{Na^+} a_{NaSO_3^-} \tag{A-10}$$

$$K_{10} a_{HS_2O_5^-} a_{H_2O} = a_{H_3O^+} a_{S_2O_5^=} \tag{A-11}$$

$$K_{11} a_{H_2S_2O_5} a_{H_2O} = a_{H_3O^+} a_{HS_2O_5} \tag{A-12}$$

$$K_{12}a_{NaOH} = a_{Na+}a_{OH^-} \tag{A-13}$$

For species other than H_2O and $SO_2(aq)$, the Davies activity coefficient model is used (Appendix D):

$$\ell og_{10}\gamma_i = Az_i^2 \left[b_i I - \frac{I^{\frac{1}{2}}}{1 + Ba_i I^{\frac{1}{2}}} \right] \qquad \text{(A-14)} \ \vdots \ \text{(A-27)}$$

Appendix C and section 5.2 show that Davies' model applies for all concentrations in $SO_2/Na^+/H_2O$ solutions.

The activity coefficient for SO_2 is

$$\ell og_{10}\gamma_{SO_2} = 0.076I \tag{A-28}$$

This relationship, taken from Harned and Owen (1958), is a standard form for gases dissolved in aqueous salt solutions. The coefficient 0.076 is estimated from data for other species (Randall and Failey, 1927). The magnitude of γ_{SO_2} is such that little difference arises if other reasonable values for this coefficient are chosen.

For the activity of water, Raoult's law is assumed to hold so that

$$a_{H_2O} = 1 - 0.018\frac{\ell}{\text{mole}}(\sum_i C_i) \qquad \text{(A-29)}$$

Raoult's law is valid generally in dilute solutions. It has been substantiated, however, by Johnstone and Blankmeyer (1938) for concentrated SO_2/Na^+ solutions.

Activities are related to concentrations by

$$a_i = \gamma_i C_i \qquad \text{(A-30)} \vdots \text{(A-44)}$$

The ionic strength of the solution is

$$I = \frac{1}{2} \sum_i z_i^2 C_i \qquad \text{(A-45)}$$

Electroneutrality states that

$$\sum_i z_i C_i = 0 \qquad \text{(A-46)}$$

Finally, the total amount of sodium in solution (TOTNA = Na_{tot}) is known

$$\text{TOTNA} = \sum_k n_k C_k \qquad \text{(A-47)}$$

Here n_k is the number of sodium atoms in the k<u>th</u> sodium-containing species.

Values of y_{SO_2} in eq. A-1 and of TOTNA in eq. A-47 are considered known.

Given 15 species other than H_2O ($SO_2(aq)$, HSO_3^-, $SO_3^=$, $S_2O_5^=$, H_3O^+, ^-OH, Na^+, $NaHSO_3$, $NaS_2O_5^-$, $Na_2S_2O_5$, $NaSO_3^-$, Na_2SO_3, $HS_2O_5^-$, $H_2S_2O_5$, NaOH) each with an unknown activity (a_i), concentration (C_i), and activity coefficient (γ_i), and given an unknown water activity, a_{H_2O}, and an unknown ionic strength, I, there are 47 unknowns. The 47 equations shown above can be solved numerically for these 47 unknowns. Thereby, all species concentrations can be calculated.

These calculations appear as a subroutine named COMPTH ("theoretical composition") in the computer programs that compute the facilitation factor. Before programming, algebraic manipulations reduced the 47 equations to three equations in terms of a_{H_2O}, I, and $a_{H_3O^+}$. The following discussions explain how subroutine COMPTH is employed in calculating the facilitation factor for the equilibrium theory and the NEBLA.

Equilibrium Theory Facilitation Factor Computations

Equilibrium theory is summarized by eq. 3.51

$$N_{SO_2} = \sum_j n_j D_j' [C_j(0) - C_j(1)] \qquad \text{(A-48)}$$

Therefore, the facilitation factor is

$$F = \frac{\sum_j n_j D_j' [C_j(0) - C_j(1)] - D_{SO_2}[C_{SO_2}(0) - C_{SO_2}(1)]}{D_{SO_2}[C_{SO_2}(0) - C_{SO_2}(1)]} \qquad \text{(A-49)}$$

or

$$F = \frac{\sum_{j'} n_{j'} D'_{j'} [C_{j'}(0) - C_{j'}(1)]}{D_{SO_2} [C_{SO_2}(0) - C_{SO_2}(1)]} \qquad \text{(A-50)}$$

Since TOTNA and $y_{SO_2,o}$ are known, the equilibrium equations yield $C_j(0)$. Since $y_{SO_2,1}$ is also known, the equilibrium equations allow $C_j(1)$ to be computed. These values are substituted into eq. A-50 to calculate the facilitation factor. (A total pressure P_{tot} = 744 mm Hg is assumed in all calculations.)

F_{eq} is independent of the film thickness, rate coefficients, and the solution viscosity (only diffusivity ratios appear). Thus, the computer program for calculating F_{eq} accepts Na_{tot} (TOTNA), $y_{SO_2,o}$, and $y_{SO_2,1}$, performs the equilibrium calculations for $C_j(0)$ and $C_j(1)$, calculates F_{eq} by eq. A-50, and outputs Na_{tot}, $y_{SO_2,o}$, $y_{SO_2,1}$, and F_{eq}.

<u>Equilibrium Theory Computer Program</u> -- <u>THER</u>

An ordinary session with the program THER on the Cal Tech PDP-10 time-sharing system is shown below.

```
 EXEC THER
FORTRAN: THER
MAIN.
COMPTH
SEQ2
H3O
EQUIL
NEWT
ZEROA
.BLOCK
LINK:   Loading
[LNKXCT THER Execution]

ENTER SODIUM CONCENTRATION, MOLE/LITER
2.D-01

 ENTER HIGH YSO2 VALUE
5.D-04

 SUPPRESS COMPOSITION OUTPUT?
NO

                              ACTIVITY
           CONCENTRATION     COEFFICIENT

 H3O----    0.68268D-04      0.87526D+00
 OH-----    0.21891D-09      0.76001D+00
 HSO3---    0.17962D+00      0.77771D+00
 S2O5---    0.39695D-02      0.37622D+00
 SO3----    0.38509D-03      0.37622D+00
 SO2----    0.58432D-03      0.10346D+01
 NA+ ---    0.18991D+00      0.74834D+00
 NAHSO3-    0.66177D-02      0.10000D+01
 NAS2O5     0.14927D-02      0.74834D+00
 NA2S2O5    0.83555D-03      0.10000D+01
 NASO3--    0.14481D-03      0.74834D+00
 NA2SO3-    0.81058D-04      0.10000D+01
 HS2O5-     0.11545D-04      0.74834D+00
 H2S2O5     0.51984D-10      0.10000D+01
 NAOH--     0.46915D-11      0.10000D+01
```

```
 ENTER LOW YSO2 VALUE
1.D-07

 SUPPRESS COMPOSITION OUTPUT?
NO

                                     ACTIVITY
            CONCENTRATION          COEFFICIENT

 H3O----      0.79539D-07          0.88065D+00
 OH-----      0.18845D-06          0.75598D+00
 HSO3---      0.30866D-01          0.77507D+00
 S2O5---      0.11753D-03          0.37196D+00
 SO3----      0.57009D-01          0.37196D+00
 SO2----      0.11633D-06          0.10393D+01
 NA+ ---      0.16339D+00          0.74335D+00
 NAHSO3-      0.96855D-03          0.10000D+01
 NAS2O5       0.37595D-04          0.74335D+00
 NA2S2O5      0.17864D-04          0.10000D+01
 NASO3--      0.18235D-01          0.74335D+00
 NA2SO3-      0.86651D-02          0.10000D+01
 HS2O5-       0.39810D-09          0.74335D+00
 H2S2O5       0.20833D-17          0.10000D+01
 NAOH--       0.34332D-08          0.10000D+01

 FOR YSO2 HIGH =  0.5000000000D-03 AND YSO2 LOW =  0.1000000000D-06
 THE FACILITATION FACTOR IS  0.1573698583D+03

 ENTER 0--NEW NA+; 1--NEW YSO2 HIGH; 2--NEW YSO2 LOW
0
```

```
ENTER SODIUM CONCENTRATION, MOLE/LITER
5.D-01

 ENTER HIGH YSO2 VALUE
2.D-04

 SUPPRESS COMPOSITION OUTPUT?
YES

 ENTER LOW YSO2 VALUE
1.D-07

 SUPPRESS COMPOSITION OUTPUT?
YES


 FOR YSO2 HIGH =  0.2000000000D-03 AND YSO2 LOW =  0.1000000000D-06
 THE FACILITATION FACTOR IS  0.9765879558D+03

 ENTER 0--NEW NA+; 1--NEW YSO2 HIGH; 2--NEW YSO2 LOW
^C
```

When the terminal types "Enter 0--New Na$^+$ ...", the user must decide if he wishes to make another run with different values of TOTNA, $y_{SO_2,o}$, or $y_{SO_2,1}$. If so, the appropriate number (0,1, or 2) is entered. If not, execution is terminated by ↑C.

Hard copy output of the compositions can be suppressed by entering "YES" when the terminal types "suppress composition output?".

The documentation and listing of the program THER are given below.

Program THER

Subroutines called by THER --

COMPTH (SO2P) -- computes equilibrium composition of aqueous SO_2 solution for a given partial pressure of SO_2 and a given total sodium concentration (TOTNA is available to COMPTH via common storage)

Common Storage Areas

F -- contains array ZM(15) in common with COMPTH, SEQ2, H3O, EQUIL

B -- contains TOTNA in common with COMPTH, SEQ2

CP -- contains YN in common with COMPTH

Arrays

ZM(15) -- contains concentrations of the 15 species in mole/liter units. The ordering of ZM is

I	1	2	3	4	5	6
ZM(I)	H_3O^+	OH^-	HSO_3^-	$S_2O_5^=$	$SO_3^=$	SO_2(aq)

7	8	9	10	11	12	13
Na^+	$NaHSO_3$	$NaS_2O_5^-$	$Na_2S_2O_5$	$NaSO_3^-$	Na_2SO_3	$HS_2O_5^-$

14	15
$H_2S_2O_5$	NaOH

COCL(11,2) -- contains product of n_jC_j for the 11 sulfur-containing species. COCL(J,1) corresponds to $n_jC_j(0)$ and COCL(J,2) corresponds to $n_jC_j(1)$. The ordering of COCL is

J	1	2	3	4	5	6	7	8	9	10	11
COCL(J, 1 or 2)	SO_2(aq)	HSO_3^-	$S_2O_5^=$	$SO_3^=$	$NaHSO_3$	$NaS_2O_5^-$	$Na_2S_2O_5$	$NaSO_3^-$	Na_2SO_3	$HS_2O_5^-$	$H_2S_2O_5$

D(11) -- contains diffusion coefficients at 25°C, infinite dilution, for the 11 sulfur-containing species. The ordering of D is the same as for COCL.

Scalar Variables --

FLUXTH -- intermediate result to computing F_{eq}

FTH -- equilibrium theory facilitation factor, F_{eq}

GO -- decision variable; instructs computer on whether to do another run.

SO2PH -- partial pressure of SO_2 on upstream side of film. Units of atmospheres.

SO2PL -- partial pressure of SO_2 on downstream side of film. Units of atmospheres.

TOTNA -- total sodium concentration in film, Na_{tot}. Units of moles/liter.

YN -- literal variable set to "YES" to suppress output of hard copy of compositions.

YSO2H -- mole fraction of SO_2 on upstream side of film ($y_{SO_2,o}$).

YSO2L -- mole fraction of SO_2 on downstream side of film ($y_{SO_2,l}$).

Subroutine COMPTH (SO2P)

Subroutines Called by COMPTH --

NEWT (SEQ2,X,RES2,MIT,IEQ) -- finds value of independent variable array X that satisfies the equations defined in SEQ2. SEQ2 must contain IEQ simultaneous equations. The iterative routine NEWT, which is Newton's method, will find X to a precision RES2 but will iterate a maximum of MIT times.

ZEROA (H3O,S,E,DX,HH,RES1,MXT) -- finds value of HH which satisfies the single equation H3O = 0 to a precision RES1. Iteration for HH is bisection. The root search begins at S, proceeds by increments of DX, and stops at E in the event that no root is found. A maximum of MXT iterations during the bisection is allowed.

EQUIL -- computes the equilibrium compositions given the three independent variables $a_{H_3O^+}$, a_{H_2O}, and I. All communication to and from EQUIL is through common storage areas.

Subprograms EXTERNAL to COMPTH

SEQ2(X,F,DER) -- evaluates the function values F at the values of the independent variables given in array X. The functions F represent the equilibrium equations. Also evaluates

$$\mathrm{DER(I,J)} = - \frac{\partial F_I}{\partial X_J}$$ for use in NEWT iterative scheme.

H3O(X) -- evaluates a nondimensional form of the electroneutrality equation at the point $a_{H_3O^+} = X$.

Common Storage Areas (in COMPTH)

A -- contains RES2, MXT, and IEQ in common with the BLOCK DATA program

C -- contains AC(31), ASO2, AK(13), AA, and BB in common with SEQ2, H3O, and EQUIL

F -- contains array ZM(15) in common with MAIN, SEQ2, H3O, and EQUIL

B -- contains TOTNA in common with MAIN, SEQ2, and EQUIL

AW -- contains AS, BS, W6, TION ZISQZM, DBSX1, DBSX2, in common with SEQ2 and EQUIL

CP -- contains YN in common with MAIN

Arrays (in COMPTH) --

AC(31) -- contains activities and activity coefficients of the various species
for $1 \leq K \leq 15$ AC(K) is a_K
for $16 \leq K \leq 30$ AC(K) is γ_{K-15}; AC(31) = I
The species ordering is the same as for the array ZM(15)

AK(13) -- contains the thermodynamic equilibrium coefficients at 25°C. The ordering of AK is

I	1	2	3	4	5	6	7	8	9	10	11	12	13
AK(I)	K_1	K_2	K_3	K_4	H_{SO_2}	K_5	K_6	K_7	K_8	K_9	K_{10}	K_{11}	K_{12}

X(3) -- contains the independent variables in the solution of the equilibrium equations. The ordering of X is X(1) = $a_{H_3O^+}$, X(2) = a_{H_2O}, and X(3) = I.

ZM(15) -- explained previously

Scalar Variables (in COMPTH)

AA -- corresponds to A in eq. A-14

ASO2 -- activity of SO_2(aq)

AYES -- test variable to determine whether hard copy composition output is performed

BB -- corresponds to B in eq. A-14

DX -- increment in root search for H3O = 0

E -- end point of root search for H3O = 0

HH -- root of H3O = 0

IEQ -- number of equations to be solved by NEWT

MIT -- maximum number of iterations allowed in NEWT

MXT -- maximum number of iterations allowed in NEWT

RES1,RES2 -- precision of iterative solution in ZEROA and NEWT, respectively

S -- starting point of root search for H3O = 0

TION -- $\sum_i C_i$ for use in a_{H_2O} calculation (eq. A-29)

ZISQZM -- $\sum_i z_i^2 C_i$ for use in ionic strength (I) calculation

TOTNA,YN -- previously explained

Subroutine NEWT (FF,B,TOL,MIT,IEQ)

Subroutines Called by NEWT

BNDINV(DP,IZ,ETM,EE,I) -- double precision inversion of matrix DP. Matrix is size IZ by IZ. ETM, EE, and I are error message variables. BNDINV is a canned routine on the Cal Tech IBM 370 Fortran library.

FF(B,RF,DP) -- provides function values RF when the independent variables have the values contained in B. Also provides partial derivatives

$$-\frac{\partial RF_I}{\partial B_J} = DP(I,J)$$

In this program, FF corresponds to SEQ2.

Arrays --

B(3) -- represents the independent variables $a_{H_3O^+}$, a_{H_2O}, and I.

DX(3) -- increments in variables generated by Newton method in iterating towards solution.

DP(50,3) -- contains Jacobian $-\frac{\partial RF_J}{\partial B_K}$ and its inverse. DP(J,K) = 0 for J $\geq$ 4.

RF(3) -- values of functions representing the equilibrium equations.

Scalar Variables --

AMAX -- maximum percentage change in any one independent variable computed in a given NEWT interation. Used for convergence test.

IEQ -- number of equations to be solved by NEWT

IZ -- checks proper dimensioning of NEWT arrays

IT -- counter for iterations in NEWT

MIT -- maximum possible iterations to satisfy convergence test

TOL -- maximum fractional change in any one independent variable allowed in convergence test

Subroutine ZEROA(F,A,B,DX,X,EPS,MIT)

Subprograms used by ZEROA

F(X) -- evaluates a user-defined function F at the point X; F corresponds to H3O in program THER.

Arrays --

FV(2) -- contains the values of the function F at the ponts X and X + DX.

Scalar Variables --

A -- beginning point for root search for F(X) = 0

B -- end point for root search

DX -- increments taken in going from A to B

EPS -- tolerance allowed in satisfying F(X) = 0

IT -- counter for iterations in ZEROA

MIT -- maximum iterations allowed for finding F(X) = 0 to precision EPS

X -- independent variable; root of F(X) = 0 returned to calling program

Subroutine EQUIL

Common Storage Areas --

C -- contains AC(31), ASO2, AK(13), AA, and BB in common with COMPTH, SEQ2, and H3O.

F -- contains ZM(15) in common with MAIN, COMPTH, SEQ2, and H3O.

E -- contains A(15), B(15), U(15), and ZI(15) in common with BLOCK DATA.

AW -- contains AS, BS, W6, TION, ZISQZM, DBSX1, and DBSX2 in common with COMPTH and SEQ2.

B -- contains TOTNA in common with MAIN, COMPTH, and SEQ2.

Arrays --

A(15) -- contains coefficients a_i in activity coefficient model, eq. A-14. The ordering of A is the same as for ZM(15).

B(15) -- contains coefficients b_i in activity coefficient model. Same ordering as A.

U(15) -- contains coefficients U_i in activity coefficient model. Same ordering as A and B. $U_i = 0$ for $i \neq SO_2$.

ZI(15) -- contains algebraic charge on species i ($ZI(J) = z_j$). Same ordering as A, B, and U.

AC(31), AK(13), and ZM(15) defined previously.

Scalar Variables --

G -- $\log_{10}\gamma_i$

all other important scalar variables have been defined previously

Subroutine SEQ2 (X,F,DER)

Subroutines Called by SEQ2 --

EQUIL -- defined previously

Common Storage Areas --

C -- contains AC(31), ASO2, AK(13), AA, and BB in common with COMPTH, H3O, and EQUIL.

F -- contains ZM(15) in common with MAIN, COMPTH, H3O, and EQUIL.

B -- contains TOTNA in common with MAIN, COMPTH, and EQUIL.

AW -- contains AS, BS, W6, TION ZISQZM, DBSXI, DBSX2 in common with COMPTH AND EQUIL.

Arrays --

F(3) -- the three functions derived from the equilibrium expressions whose roots are the solution.

X(3) -- contains values of the three independent variables; X(1) = $a_{H_3O^+}$, X(2) = a_{H_2O}, and X(3) = I.

DER(50,3) -- contains the partial derivatives

$$-\frac{\partial F_J}{\partial X_K} = \text{DER}(J,K)$$

In this program, DER(J,K) = 0 for J $\geq$ 4 since only three equations are being solved.

AC(31), AK(13), and ZM(15) defined previously

Scalar Variables --

AS, BS, DASX1, DASX2, DBSX1, DBSX2, DFM7X1, DFM7X2, W1, W2, W3, W4, W6, W7, W8, W9 are intermediates used to compute F(I) and DER(I,J).

Other scalar variables have been defined previously

Function H3O(X)

Subroutines Called by H3O --

EQUIL -- previously defined

Common Storage Areas --

C -- contains AC(31), ASO2, AK(13), AA, and BB in common with COMPTH, SEQ2, and EQUIL.

F -- contains ZM(15) in common with MAIN, COMPTH, SEQ2, and EQUIL.

Arrays --

AC(31), AK(13), and ZM(15) previously defined

Scalar Variables --

X -- the value of $a_{H_3O^+}$ being tried as a root of H3O = 0.

BLOCK DATA subprogram -- allows specification by DATA statements of values of variables that exist in common storage

Common Storage Areas --

A -- contains RES2, MXT, and IEQ in common with COMPTH

E -- contains A(15), B(15), U(15), and ZI(15) in common with EQUIL.

All arrays and scalars have been defined previously.

The following is a listing of program THER.

```
      IMPLICIT REAL*8 (A-H,R-Z)
      COMMON/F/ZM(15)/B/TOTNA/CP/YN
      DIMENSION COCL(11,2),D(11)
      DATA D/1.6D-05,1.47D-05,1.D-05,1.1D-05,1.4D-05,8.7D-06,
     11.1D-05,1.D-05,1.3D-05,9.D-06,1.2D-05/
C
C     WE ASSUME TOTAL PRESSURE = 744 MM HG
C
   15 TYPE 720
  720 FORMAT (' ENTER SODIUM CONCENTRATION, MOLE/LITER')
      ACCEPT 9999,TOTNA
   16 TYPE 721
  721 FORMAT (1X,' ENTER HIGH YSO2 VALUE')
        ACCEPT 9999,YSO2H
        SO2PH = 7.44D00*YSO2H/7.6D00
        TYPE 726
  726 FORMAT (1X,' SUPPRESS COMPOSITION OUTPUT?')
        ACCEPT 727,YN
  727 FORMAT (A4)
        CALL COMPTH (SO2PH)
        COCL(1,1)  = ZM(6)
        COCL(2,1)  = ZM(3)
        COCL(3,1)  = 2.D00*ZM(4)
        COCL(4,1)  = ZM(5)
        COCL(5,1)  = ZM(8)
        COCL(6,1)  = 2.D00*ZM(9)
        COCL(7,1)  = 2.D00*ZM(10)
        COCL(8,1)  = ZM(11)
        COCL(9,1)  = ZM(12)
        COCL(10,1)  = 2.D00*ZM(13)
```

```
        COCL(11,1)  =  2.D00*ZM(14)
   17 TYPE 722
  722 FORMAT (1X,' ENTER LOW YSO2 VALUE')
        ACCEPT 9999,YSO2L
        SO2PL = 7.44D00*YSO2L/7.6D00
        TYPE 726
        ACCEPT 727,YN
        CALL COMPTH (SO2PL)
        COCL(1,2)  =  ZM(6)
        COCL(2,2)  =  ZM(3)
        COCL(3,2)  =  2.D00*ZM(4)
        COCL(4,2)  =  ZM(5)
        COCL(5,2)  =  ZM(8)
        COCL(6,2)  =  2.D00*ZM(9)
        COCL(7,2)  =  2.D00*ZM(10)
        COCL(8,2)  =  ZM(11)
        COCL(9,2)  =  ZM(12)
        COCL(10,2)  =  2.D00*ZM(13)
        COCL(11,2)  =  2.D00*ZM(14)
        FLUXTH = 0.D00
        DO 100 K=2,11
  100 FLUXTH = D(K)*(COCL(K,1)-COCL(K,2)) + FLUXTH
        FTH = FLUXTH/D(1)/(COCL(1,1)-COCL(1,2))
        TYPE 701,YSO2H,YSO2L
  701 FORMAT (1H0,' FOR YSO2 HIGH = ',D17.10,' AND YSO2 LOW = ',D17.10)
        TYPE 702,FTH
  702 FORMAT (1X,' THE FACILITATION FACTOR IS ',D17.10)
        TYPE 710
  710 FORMAT (1H0,' ENTER 0--NEW NA+; 1--NEW YSO2 HIGH; 2--NEW YSO2
     1 LOW')
        ACCEPT 9999,GO
 9999 FORMAT (1G)
        IF (GO-1.D00) 15,16,17
        STOP
      END
C
      SUBROUTINE COMPTH (SO2P)
C
      IMPLICIT REAL*8 (A-H,R-Z)
      EXTERNAL SEQ2,H30
      COMMON/A/RES2,MXT,IEQ/C/AC(31),ASO2,AK(13),AA,BB
     &/F/ZM(15)/B/TOTNA/AW/AS,BS,W6,TION,ZISQZM,
     &DBSX1,DBSX2/CF/YN
      DIMENSION X(3)
      DATA AYES/'YES'/
```

```
C
C     COMPUTE TEMPERATURE DEPENDENT PARAMETERS AND ASO2
C
      AK(1) = 1.4D-02
      AK(2) =   6.24D-08
      AK(3) = 7.6D-02
      AK(4) =   1.008D-14
      AK(5) = 0.809667D00
      AK(6) = 3.D00
      AK(7) = 0.19D00
      AK(8) = 0.19D00
      AK(9) = 0.19D00
      AK(10) = 0.19D00
      AK(11) = 1.04D-02
      AK(12) = 1.D01
      AK(13) = 5.04D00
      AA = 0.5085D00
      BB =   0.3281D00
      ASO2 = SO2P/AK(5)
C
C     INITIALIZE
C
      AC(1) = (DSQRT(TOTNA*TOTNA + 4.*ASO2*AK(1))-TOTNA)/2.D00
      AC(31) = TOTNA
      AC(6) = 1.-0.018*TOTNA
      RES1 = 1.D-05
      DO 2 I = 1,3
      IF (I.EQ.3) RES1 = 1.D-07
      S = 0.01*AC(1)
      E = 1.D02*AC(1)
      DX = (E-S)/100.
      CALL ZEROA (H3O,S,E,DX,HH,RES1,MXT)
      AC(1) = HH
      AC(6) = 1.-0.018*TION
    2 AC(31) = 0.5*ZISQZM
      X(1) = AC(1)
      X(2) = AC(6)
      X(3) =AC(31)
C
C     GO INTO NONLINEAR ITERATIVE SOLUTION GIVEN THE GUESSES
C     JUST DEVELOPED
C
      MIT = 15
      CALL NEWT (SEQ2,X,RES2,MIT,IEQ)
C
      AC(1) = X(1)
      AC(6) = X(2)
      AC(31) = X(3)
```

```
      CALL EQUIL
C
C       HARD COPY COMPOSITION OUTPUT SUPPRESSED
C       IF YN = 'YES'
C
      IF (YN.EQ.AYES) RETURN
C
        TYPE 130
  130 FORMAT (1X, 29X, ' ACTIVITY')
      TYPE 131
  131 FORMAT (1X,10X, ' CONCENTRATION',4X,' COEFFICIENT')
      TYPE 132,ZM(1),AC(16)
  132 FORMAT (1H0, ' H30----',D15.5,2X,D15.5)
      TYPE 133,ZM(2),AC(17)
  133 FORMAT (1X, ' OH-----',D15.5,2X,D15.5)
      TYPE 134,ZM(3),AC(18)
  134 FORMAT (1X,' HSO3---', D15.5,2X,D15.5)
      TYPE 135,ZM(4),AC(19)
  135 FORMAT (1X, ' S205---', D15.5,2X,D15.5)
      TYPE 136, ZM(5),AC(20)
  136 FORMAT (1X, ' SO3----', D15.5,2X,D15.5)
      TYPE 137, ZM(6),AC(21)
  137 FORMAT (1X, ' SO2----',D15.5,2X,D15.5)
      TYPE 138,ZM(7),AC(22)
  138 FORMAT (1X,' NA+ ---',D15.5,2X,D15.5)
      TYPE 139,ZM(8),AC(23)
  139 FORMAT (1X,' NAHSO3-',D15.5,2X,D15.5)
      TYPE 140,ZM(9),AC(24)
  140 FORMAT (1X,' NAS205 ',D15.5,2X,D15.5)
      TYPE 141,ZM(10),AC(25)
  141 FORMAT (1X,' NA2S205',D15.5,2X,D15.5)
      TYPE 142,ZM(11),AC(26)
  142 FORMAT (1X,' NASO3--',D15.5,2X,D15.5)
      TYPE 143,ZM(12),AC(27)
  143 FORMAT (1X,' NA2SO3-',D15.5,2X,D15.5)
      TYPE 144,ZM(13),AC(28)
  144 FORMAT (1X,' HS205- ',D15.5,2X,D15.5)
      TYPE 145,ZM(14),AC(29)
  145 FORMAT (1X,' H2S205 ',D15.5,2X,D15.5)
      TYPE 146,ZM(15),AC(30)
  146 FORMAT (1X,' NAOH-- ',D15.5,2X,D15.5)
      RETURN
      END
C
      SUBROUTINE SEQ2 (X,F,DER)
C
      IMPLICIT REAL*8 (A-H,R-Z)
      COMMON/C/AC(31),ASO2,AK(13),AA,BB/F/ZM(15)/
     $B/TOTNA/AW/AS,BS,W6,TION,ZISQZM,DBSX1,DBSX2
```

```
      DIMENSION F(3),DER(50,3),X(3)
      DO 5 J = 1,50
      DO 5 K = 1,3
    5 DER(J,K) = 0.
      AC(1) = X(1)
      AC(6) = X(2)
      AC(31) = X(3)
      CALL EQUIL
      W1 = ZM(2) + ZM(3)
      W2 = 2.*(ZM(4) + ZM(5))
      W3 = ZM(9)+ZM(11)+ZM(13)
      W4 = ZM(10)+ZM(12)
      W7 = ZM(7)+ZM(1)
      W8 = W1+W2+W3
      W9 = X(3)-0.5*W7
      DASX1 = 0.-2.*AS/AC(1)
      DASX2 = 3.*AS/X(2)
      DFM7X1 = (((2.*DBSX1*BS+4.*TOTNA*DASX1)/W6/2.)-DBSX1)
     $/2./AS + (BS-W6)*DASX1/2./AS/AS
      DFM7X2 = (((2.*BS*DBSX2+4.*TOTNA*DASX2)/W6/2.)-DBSX2)
     $/2./AS + (BS-W6)*DASX2/2./AS/AS
      F(1) = DLOG(W8)-DLOG(W7)
      F(2) = DLOG(0.018*TION)-DLOG(1.-X(2))
      F(3) = DLOG(0.5*(W1+2.*W2+W3))-DLOG(W9)
      DER(1,1) = (DFM7X1+1./AC(16))/W7+(W8+W2+ZM(9)+ZM(11))/W8/X(1)
      DER(1,2) = DFM7X2/W7-(2.*W8+W2+W3)/W8/X(2)
      DER(2,1) = 0.-(ZM(1)-W8-ZM(9)-ZM(11)+X(1)*DFM7X1-ZM(8)-2.*
     $W4-ZM(15))/X(1)/TION
      DER(2,2) = 0.-1./(1.-X(2))-(2.*W8-W2/2.+W3+X(2)*DFM7X2
     $+2.*(ZM(8)+ZM(15))+3.*(W4+ZM(14)))/TION/X(2)
      DER(3,1) = 0.-0.5*(DFM7X1+1./AC(16))/W9 + (W1+4.*W2+2.*W3
     $-ZM(13))/(W8+2.*W2)/X(1)
      DER(3,2) = 0.-0.5*DFM7X2/W9-(2.*W1+6.*W2+3.*W3)/(W8
     $+2.*W2)/X(2)
      DER(3,3) = 1./W9
      RETURN
      END

        FUNCTION H30(X)

      IMPLICIT REAL*8 (A-H,R-Z)
      COMMON/C/AC(31),ASO2,AK(13),AA,BB/F/ZM(15)
      AC(1) = X
      CALL EQUIL
      H30 = (ZM(7)+ZM(1)-ZM(2)-ZM(3)-2.*(ZM(4)+ZM(5))
     $-ZM(9)-ZM(11)-ZM(13))/ZM(3)
      RETURN
      END
```

```
C
      SUBROUTINE EQUIL
C
      IMPLICIT REAL*8 (A-H,R-Z)
      COMMON/C/AC(31),ASO2,AK(13),AA,BB/F/ZM(15)/E/A(15),
     *B(15),U(15),ZI(15)/AW/AS,BS,W6,TION,ZISQZM,DBSX1,
     *DBSX2/B/TOTNA
      DO 1 J = 1,15
      G = AA*ZI(J)*ZI(J)*(B(J)*AC(31)-DSQRT(AC(31))/(1.+BB*A(J)*DSQRT(AC
     *(31)))) + U(J)*AC(31)
    1 AC(J+15) = DEXP(2.302585093D00*G)
      AC(2) = AK(4)*AC(6)*AC(6)/AC(1)
      AC(3) = AK(1)*ASO2*AC(6)*AC(6)/AC(1)
      AC(4) = AK(3)*AC(3)*AC(3)/AC(6)
      AC(5) = AK(2)*AC(3)*AC(6)/AC(1)
      DO 3 J = 1,5
    3 ZM(J) = AC(J)/AC(J+15)
      TK8 = AK(6)*AC(23)/AC(22)/AC(18)
      TK9 = AK(7)*AC(24)/AC(22)/AC(19)
      TK10 = AK(8)*AC(25)/AC(22)/AC(24)
      TK11 = AK(9)*AC(26)/AC(22)/AC(20)
      TK12 = AK(10)*AC(27)/AC(22)/AC(26)
      TK15 = AK(13)*AC(30)/AC(22)/AC(17)
      AS = 2.*(ZM(4)/TK10/TK9+ZM(5)/TK11/TK12)
      BS = 1.+ZM(3)/TK8+ZM(4)/TK9+ZM(5)/TK11+ZM(2)/TK15
      W6 = DSQRT(BS*BS+4.*TOTNA*AS)
      AC(7) = AC(22)*(W6-BS)/2./AS
      AC(8) = AC(7)*AC(3)/AK(6)
      AC(9) = AC(7)*AC(4)/AK(7)
      AC(10) = AC(7)*AC(9)/AK(8)
      AC(11) = AC(7)*AC(5)/AK(9)
      AC(12) = AC(7)*AC(11)/AK(10)
      AC(13) = AC(1)*AC(4)/AK(11)/AC(6)
      AC(14) = AC(1)*AC(13)/AK(12)/AC(6)
      AC(15) = AC(7)*AC(2)/AK(13)
      DO 4 J = 7,15
    4 ZM(J) = AC(J)/AC(J+15)
      ZM(6) = ASO2/AC(21)
      DBSX1 = (1.-BS-ZM(4)/TK9-ZM(5)/TK11)/AC(1)
      DBSX2 = (2.*(BS-1.)+ZM(4)/TK9+ZM(5)/TK11)/AC(6)
      TION = 0.
      ZISQZM = 0.
      DO 10 J = 1,15
      TION = TION + ZM(J)
   10 ZISQZM = ZISQZM + ZI(J)*ZI(J)*ZM(J)
      RETURN
      END
```

```
C
      SUBROUTINE NEWT (FF,B,TOL,MIT,IEQ)
C
C     NEWTON'S METHOD--DOUBLE PRECISION
C
      IMPLICIT REAL*8 (A-D,F-H,R-Z)
      DIMENSION B(3),DX(3),DP(50,3),RF(3)
      IZ = 3
      IF (IEQ.GT.IZ) GO TO 200
      IT = 0
  100 CALL FF(B,RF,DP)
      IT = IT + 1
      EE = 0.
      CALL BNDINV (DP,IZ,ETM,EE,I)
      DO 15 K = 1,IZ
   15 DX(K) = 0.
      DO 17 K = 1,IZ
      DO 16 J = 1,IZ
   16 DX(K) = DX(K) + DP(K,J)*RF(J)
   17 B(K) = B(K) + DX(K)
      ZA = 0.
      AMAX = 0.
      DO 18 K = 1,IZ
      IF (DABS(B(K)).GT.1.D-25) ZA = DABS(DX(K)/B(K))
   18 IF (ZA.GT.AMAX) AMAX = ZA
      IF (AMAX.LE.TOL) RETURN
      IF (IT.LT.MIT) GO TO 100
      TYPE 50,IT
   50 FORMAT (1H0, ' *** OVERRUN ON NEWT, IT = ', I7)
      TYPE 1010,RF
 1010 FORMAT (1H0, 3('    ',D20.10))
      RETURN
  200 TYPE 201
  201 FORMAT (1H0, ' YOU DUMMY,TOO MANY EQUATIONS')
      RETURN
      END
C
      SUBROUTINE ZEROA (F,A,B,DX,X,EPS,MIT)
C
C  THIS ROUTINE COMPUTES THE ROOT OF A FUNCTION
C
      IMPLICIT REAL*8 (A-H,R-Z)
      DIMENSION FV(2)
      IT = 0
      X = A
      FV(1) = F(A)
      IF (DABS(FV(1)).LT.EPS) RETURN
```

```
   10 X = A + DX
      FV(2) = F(X)
      IF (DABS(FV(2)).LT.EPS) RETURN
      IF ((FV(1)*FV(2)).LT.0.) GO TO 100
      FV(1) = FV(2)
      A = X
      IF (A.GE.B) GO TO 700
      GO TO 10
  100 TP = (X + A)/2.
      IT = IT + 1
      IF (IT.GE.MIT) GO TO 201
      Z = F(TP)
      IF (DABS(Z).LT.EPS) GO TO 507
      IF ((FV(2)*Z).GT.0.) GO TO 1010
      A = TP
      GO TO 100
 1010 X = TP
      GO TO 100
  201 TYPE 253,IT
  253 FORMAT (1H0, ' *** EXCESSIVE ITERATIONS IN ZEROA ***', I7)
      GO TO 507
  700 TYPE 50
   50 FORMAT (1H0, ' *** SORRY, NO ROOTS IN RANGE ZEROA')
  507 X = TP
      RETURN
      END
      BLOCK DATA
      IMPLICIT REAL*8 (A-H,R-Z)
      COMMON/A/RES2,MXT,IEQ/E/A(15),B(15),U(15),ZI(15)
      DATA A,B,U,ZI/9.D00,3.5D00,4.25D00,2*4.5D00,10*3.05D00,
     #0.4D00,14*3.D-01,5*0.D00,0.076D00,9*0.D00,1.D00,2*-1.D00,
     $2*-2.D00,0.D00,1.D00,0.D00,-1.D00,0.D00,-1.D00,0.D00,
     #-1.D00,2*0.D00/
      DATA RES2,MXT,IEQ/1.D-07,100,3/
      END
```

Computation of Facilitation Factor with NEBLA

The NEBLA is summarized by eqs. 3.92, 93, and 97. These three equations can be combined to give

$$\frac{\dfrac{1}{L}\left(\dfrac{\hat{D}_{HSO_3^-}}{k_{-1}C^*}\right)^{\frac{1}{2}}}{1 - \dfrac{1}{L}\left(\dfrac{\hat{D}_{HSO_3^-}}{k_{-1}C^*}\right)^{\frac{1}{2}}} \quad \frac{\sum\limits_j n_j D'_j [C_j(0) - C_j(1-\delta_1)]}{D_{SO_2}[C_{SO_2}(1-\delta_1) - C_{SO_2}(1)]} - 1 = 0 \quad \text{(A-51)}$$

Equation A-51 is an implicit equation for the single unknown $C_{SO_2}(1-\delta_1)$. The quantity $C_{SO_2}(1-\delta_1)$ is the only unknown because a) $y_{SO_2,o}$ and TOTNA are known, and hence $C_j(0)$ are known since these concentrations are in equilibrium with $y_{SO_2,o}$ and TOTNA, b) $C_{SO_2}(1)$ is known from equation 3.4b where γ_{SO_2} is calculated from eq. A-28 with I = TOTNA, and c) C* and $C_j(1-\delta_1)$ are in equilibrium with TOTNA and $C_{SO_2}(1-\delta_1)$ (the equilibrium calculations therefore fix C* and $C_j(1-\delta_1)$ when $C_{SO_2}(1-\delta_1)$ is fixed).

Thus, solving eq. A-51 for $C_{SO_2}(1-\delta_1)$ consists first of computing $C_j(0)$ and $C_{SO_2}(1)$. Then a value of $C_{SO_2}(1-\delta_1)$ is guessed, and C* and $C_j(1-\delta_1)$ are computed from the equilibrium expressions. If these results satisfy eq. A-51, then the proper value of $C_{SO_2}(1-\delta_1)$ was guessed. Iteration (bisection) achieves a proper guess for $C_{SO_2}(1-\delta_1)$.

When a proper value of $C_{SO_2}(1-\delta_1)$ is achieved, C* is known through the equilibrium computations. Therefore, eq. 3.92 yields δ_1, and eq. 3.93 yields the flux, N_{SO_2}. The facilitation factor is then computed from eqs. 3.59 and 5.1.

In the iterative guessing for $C_{SO_2}(1-\delta_1)$, the equilibrium calculations (contained in subroutine COMPTH) are slightly modified. Rather than y_{SO_2} being known, C_{SO_2} is known. Thus eq. A-1 is eliminated so that the equilibrium calculations reduce to 46 equations with 46 unknowns.

The computer program accepts the film thickness, L (cm) the total sodium concentration, TOTNA (mole/liter), and the mole fractions $y_{SO_2,o}$ and $y_{SO_2,1}$. A total pressure of 744 mm Hg and a temperature of 25°C are assumed.

The program outputs the facilitation factor, the SO_2 concentrations at $x = 0, 1 - \delta_1$, and 1, the boundary layer thickness δ_1, its dimensional form, $\hat{\delta}_1$, and C*.

NEBLA Computer Program -- BLTH2

An ordinary session on the Cal Tech PDP-10 time-sharing system is shown below.

```
 EXEC BLTH2
FORTRAN: BLTH2
MAIN.
DELBL
COMPTH
SEQ2
H3O
EQUIL
NEWT
ZEROA
.BLOCK
LINK:   Loading
[LNKXCT BLTH2 Execution]

ENTER FILM THICKNESS IN CM
1.D-01

ENTER SODIUM CONCENTRATION, MOLE/LITER
5.D-01

ENTER VISCOSITY RATIO
1.11


 ENTER DIVISIONS IN DELBL ROOT SEARCH
50.D00

 ENTER HIGH YSO2 VALUE
5.D-04

 SUPPRESS COMPOSITION OUTPUT?
YES

 ENTER LOW YSO2 VALUE
1.D-07

 SUPPRESS COMPOSITION OUTPUT?
YES


 FOR YSO2 HIGH =  0.5000000000D-03 AND YSO2 LOW =  0.1000000000D-06
 THE FACILITATION FACTOR IS  0.6584823159D+02

 CSO2-0 =  0.56001202D-03 MOLE/L AND CSO2-L =  0.11236333D-06 MOLE/L

 THE SO2 CONCENTRATION AT DEL IS  0.44810930D-04 MOLE/LITER

 THE BL THICKNESS IS  0.11942451D-03 CM. AND THE RATIO DEL/L IS  0.1
1942451D-02
```

```
 THE C-STAR VALUE IS  0.25999712D-05 MOLE/L

 ENTER 0--NEW NA+; 1--NEW PSO2 HIGH; 2--NEW PSO2 LOW
0

ENTER SODIUM CONCENTRATION, MOLE/LITER
1.D00

ENTER VISCOSITY RATIO
1.246


 ENTER DIVISIONS IN DELBL ROOT SEARCH
5.D01

 ENTER HIGH YSO2 VALUE
2.D-04

 SUPPRESS COMPOSITION OUTPUT?
YES

 ENTER LOW YSO2 VALUE
1.D-07

 SUPPRESS COMPOSITION OUTPUT?
YES


 FOR YSO2 HIGH =  0.2000000000D-03 AND YSO2 LOW =  0.1000000000D-06
 THE FACILITATION FACTOR IS  0.2587308274D+03

 CSO2-0 =  0.21442217D-03 MOLE/L AND CSO2-L =  0.10881024D-06 MOLE/L

 THE SO2 CONCENTRATION AT DEL IS  0.66938323D-04 MOLE/LITER

 THE BL THICKNESS IS  0.12005923D-03 CM. AND THE RATIO DEL/L IS  0.1
2005923D-02

 THE C-STAR VALUE IS  0.22917610D-05 MOLE/L

 ENTER 0--NEW NA+; 1--NEW PSO2 HIGH; 2--NEW PSO2 LOW
^C
```

As seen in the above example, the user is given the choice of doing another run with a different set of parameters. Execution in terminated by ↑C.

The documentation and listing of the program BLTH2 are given below. Many variables are defined in the documentation of THER since the subroutine COMPTH appears in BLTH2 and THER.

<u>Program BLTH2</u>

Subroutines Called by BLTH2 --

COMPTH(SO2P) -- computes equilibrium composition of aqueous SO_2 solution for a given partial pressure of SO_2 and a given total sodium concentration (TOTNA is available to COMPTH via common storage).

ZEROA(DELBL,S,E,DX,CDEL,RES1,MXT) -- finds value of CDEL which satisfies the single equation DELBL = 0 to a precision RES1. Iteration for CDEL is bisection. The root search begins at S, proceeds by increments of DX, and stops at E if no root is found. A maximum of MXT iterations during the bisection is allowed.

Common Storage Areas --

F, B, CP -- defined in THER documentation

AA -- contains COCL(11,2), DEL, THICK, VIS, CLL in common with DELBL

AAA -- contains D(11) in common with DELBL and BLOCK DATA

VER -- contains RPT in common with COMPTH

Arrays --

ZM(15), COCL(11,2), D(11) -- defined in THER documentation

Scalar Variables --

CDEL -- value of concentration of SO_2(aq) at $x = 1 - \delta_1$; i.e., $C_{SO_2}(1-\delta_1)$

CLL -- value of concentration of SO_2(aq) at $x = 1$; i.e., $C_{SO_2}(1)$

DEL -- nondimensional boundary layer thickness, δ_1

DELL -- dimensional boundary layer thicknesses, $\hat{\delta}_1$

DIV -- number of divisions in interval (S,E) in root search for CDEL; sometimes convergence fails and DIV must be increased (failure to converge causes DLOG or DSQRT of negative number error message). DIV = 20 is recommended

DX -- increments in root search in subroutine ZEROA

E -- end point of root search in subroutine ZEROA

MXT -- maximum number of iterations in root search in ZEROA

RES1 -- precision of root in ZEROA

RPT -- decision variable employed to tell COMPTH whether COMPTH is being called by MAIN or DELBL. When COMPTH is called by MAIN, RPT = 0. When COMPTH is called by DELBL, RPT = 1. If RPT = 0, COMPTH generates guesses for equilibrium composition from scratch. If RPT = 1, COMPTH uses output from previous call to COMPTH for guesses in current call.

S -- starting point of root search in ZEROA

THICK -- the film thickness in centimeters

VIS -- viscosity of solution divided by viscosity of water (μ/μ_o)

FTH, GO, SO2PL, TOTNA, YSO2H, YSO2L -- defined in THER documentation

Subroutines --

COMPTH(SO2P), SEQ2(X,F,DER), EQUIL, NEWT(FF,B,TOL, MIT,IEQ), ZEROA(F,AA,B,DX,X,EPS,MIT), and BLOCK DATA are explained in the documentation of THER

Function DELBL(X) -- Represents eq. A-51; the value of $C_{SO_2}(1-\delta_1)$ is assigned to X.

Common Storage Areas --

AA -- contains COCL(11,2), DEL, THICK, VIS, CLL in common with MAIN

AAA -- contains D(11) in common with MAIN and BLOCK DATA

F -- defined in THER documentation

Arrays --

COCL(11,2), D(11), ZM(15) -- defined in THER documentation

Scalar Variables --

SUM -- temporary storage for computing

$$\sum_j n_j D_j [C_j(0) - C_j(1-\delta_1)]$$

X -- concentration of SO_2(aq) at $x = 1 - \delta_1$; i.e., $C_{SO_2}(1-\delta_1)$

Y -- partial pressure of SO_2 that would be in equilibrium with the concentration of SO_2(aq) represented by X

CLL, DEL, THICK, VIS -- defined previously

<u>Function H3O(X)</u> -- defined in THER documentation

The following is a listing of program BLTH2.

```
       IMPLICIT REAL*8 (A-H,R-Z)
         EXTERNAL DELBL
       COMMON/F/ZM(15)/B/TOTNA/CP/YN/AA/COCL(11,2),DEL,THICK,VIS,CLL
      1/AAA/D(11)/VER/RPT
C
C      WE ASSUME TOTAL PRESSURE = 744 MM HG
C
         TYPE 14
    14 FORMAT (' ENTER FILM THICKNESS IN CM')
         ACCEPT 9999,THICK
    15 TYPE 720
   720 FORMAT (' ENTER SODIUM CONCENTRATION, MOLE/LITER')
       ACCEPT 9999,TOTNA
       TYPE 725
   725 FORMAT (' ENTER VISCOSITY RATIO')
       ACCEPT 9999,VIS
         TYPE 723
   723 FORMAT (1H0,' ENTER DIVISIONS IN DELBL ROOT SEARCH')
         ACCEPT 9999,DIV
    16 TYPE 721
   721 FORMAT (1X,' ENTER HIGH YSO2 VALUE')
         ACCEPT 9999,YSO2H
         RPT = 0.D00
         SO2PH = 7.44D00*YSO2H/7.6D00
         TYPE 726
   726 FORMAT (1X,' SUPPRESS COMPOSITION OUTPUT?')
         ACCEPT 727,YN
   727 FORMAT (A4)
         CALL COMPTH (SO2PH)
         E = ZM(6)/1.05D00
         COCL(1,1)  = ZM(6)
         COCL(2,1)  = ZM(3)
         COCL(3,1)  = 2.D00*ZM(4)
         COCL(4,1)  = ZM(5)
         COCL(5,1)  = ZM(8)
         COCL(6,1)  = 2.D00*ZM(9)
         COCL(7,1)  = 2.D00*ZM(10)
         COCL(8,1)  = ZM(11)
         COCL(9,1)  = ZM(12)
         COCL(10,1)  = 2.D00*ZM(13)
         COCL(11,1)  = 2.D00*ZM(14)
    17 TYPE 722
   722 FORMAT (1X,' ENTER LOW YSO2 VALUE')
         ACCEPT 9999,YSO2L
         RPT = 0.D00
         SO2PL = 7.44D00*YSO2L/7.6D00
```

```
      TYPE 726
      ACCEPT 727,YN
      CALL COMPTH (SO2PL)
      CLL = ZM(6)
      MXT = 100
      RES1  = 1.D-07
      S = (1.D00 + 1.D-09)*ZM(6)
      DX = (E-S)/DIV
      RPT = 1.D00
      CALL ZEROA (DELBL,S,E,DX,CDEL,RES1,MXT)
      FTH = (CDEL-CLL)/(COCL(1,1)-CLL)/DEL-1.D00
      DELL = DEL*THICK
      TYPE 701,YSO2H,YSO2L
  701 FORMAT (1H0,' FOR YSO2 HIGH = ',D17.10,' AND YSO2 LOW = ',D17.10)
      TYPE 702,FTH
  702 FORMAT (1X,' THE FACILITATION FACTOR IS ',D17.10)
      TYPE 703, COCL(1,1),CLL
  703 FORMAT (1H0,' CSO2-0 = ',D15.8,' MOLE/L AND CSO2-L = '
     1,D15.8,' MOLE/L')
      TYPE 704, CDEL
  704 FORMAT (1H0,' THE SO2 CONCENTRATION AT DEL IS ',D15.8,
     1 ' MOLE/LITER')
      TYPE 705,DELL,DEL
  705 FORMAT (1H0,' THE BL THICKNESS IS ',D15.8,' CM. AND THE
     1 RATIO DEL/L IS ',D15.8)
     TYPE 706,ZM(1)
  706 FORMAT (1H0,' THE C-STAR VALUE IS ',D15.8,' MOLE/L')
      TYPE 710
  710 FORMAT (1H0,' ENTER 0--NEW NA+; 1--NEW PSO2 HIGH; 2--NEW PSO2
     1 LOW')
      ACCEPT 9999,GO
 9999 FORMAT (1G)
      IF (GO-1.D00) 15,16,17
      STOP
     END
      FUNCTION DELBL(X)
      IMPLICIT REAL*8 (A-H,R-Z)
      COMMON/AA/COCL(11,2),DEL,THICK,VIS,CLL/F/ZM(15)/AAA/D(11)
      Y = 0.809667D00*X
      CALL COMPTH(Y)
      COCL(1,2) = X
      COCL(2,2) = ZM(3)
      COCL(3,2) = 2.D00*ZM(4)
      COCL(4,2) = ZM(5)
      COCL(5,2) = ZM(8)
      COCL(6,2) = 2.D00*ZM(9)
      COCL(7,2) = 2.D00*ZM(10)
      COCL(8,2) = ZM(11)
      COCL(9,2) = ZM(12)
```

```
        COCL(10,2) = 2.D00*ZM(13)
        COCL(11,2) = 2.D00*ZM(14)
      DEL = 2.0288D-07/THICK/DSQRT(ZM(1)*VIS)
        SUM = 0.D00
        DO 1 K = 1,11
    1 SUM = D(K)*(COCL(K,1)-COCL(K,2)) + SUM
        SUM = SUM*DEL/(1.D00-DEL)/D(1)
        DELBL = 1.D00-SUM/(X-CLL)
        RETURN
        END
      SUBROUTINE COMPTH (SO2P)
      IMPLICIT REAL*8 (A-H,R-Z)
      EXTERNAL SEQ2,H30
      COMMON/A/RES2,MXT,IEQ/E/A(15),B(15),U(15),ZI(15)
     &/C/AC(31),ASO2,AK(13),AA,BB/F/ZM(15)/B/TOTNA/AW/AS,BS,
     &W6,TION,ZISQZM,DBSX1,DBSX2/CP/YN/VER/RPT
      DIMENSION X(3)
      DATA AYES/'YES'/
C
C     COMPUTE TEMPERATURE DEPENDENT PARAMETERS AND ASO2
C
      AK(1) = 1.4D-02
      AK(2) =   6.24D-08
      AK(3) = 7.6D-02
      AK(4) =   1.008D-14
      AK(5) = 0.809667D00
      AK(6) = 3.D00
      AK(7) = 0.19D00
      AK(8) = 0.19D00
      AK(9) = 0.19D00
      AK(10) = 0.19D00
      AK(11) = 1.04D-02
      AK(12) = 1.D01
      AK(13) = 5.04D00
      AA = 0.5085D00
      BB =   0.3281D00
      ASO2 = SO2P/AK(5)
C
C     INITIALIZE
C
        IF (RPT.EQ.1.D00) GO TO 10
      AC(1) = (DSQRT(TOTNA*TOTNA + 4.*ASO2*AK(1))-TOTNA)/2.D00
      AC(31) = TOTNA
      AC(6) = 1.-0.018*TOTNA
      RES1 = 1.D-05
      DO 2 I = 1,3
      IF (I.EQ.3) RES1 = 1.D-07
      S = 0.01*AC(1)
      E = 1.D02*AC(1)
```

```
      DX =  (E-S)/1.D02
      CALL ZEROA (H3O,S,E,DX,HH,RES1,MXT)
      AC(1)  = HH
      AC(6)  = 1.-0.018*TION
    2 AC(31)  = 0.5*ZISQZM
      X(1)  = AC(1)
      X(2)  = AC(6)
      X(3)  =AC(31)
C
C     GO INTO NONLINEAR ITERATIVE SOLUTION GIVEN THE GUESSES
C     JUST DEVELOPED
C
   10 MIT = 15
      CALL NEWT (SEQ2,X,RES2,MIT,IEQ)
C
      AC(1)  = X(1)
      AC(6)  = X(2)
      AC(31)  = X(3)
      CALL EQUIL
      IF (YN.EQ.AYES) RETURN
        TYPE 130
  130 FORMAT (1X, 29X, ' ACTIVITY')
      TYPE 131
  131 FORMAT (1X,10X, ' CONCENTRATION',4X,' COEFFICIENT')
      TYPE 132,ZM(1),AC(16)
  132 FORMAT (1H0, ' H3O----',D15.5,2X,D15.5)
      TYPE 133,ZM(2),AC(17)
  133 FORMAT (1X, ' OH-----',D15.5,2X,D15.5)
      TYPE 134,ZM(3),AC(18)
  134 FORMAT (1X,' HSO3---', D15.5,2X,D15.5)
      TYPE 135,ZM(4),AC(19)
  135 FORMAT (1X, ' S2O5---', D15.5,2X,D15.5)
      TYPE 136, ZM(5),AC(20)
  136 FORMAT (1X, ' SO3----', D15.5,2X,D15.5)
      TYPE 137, ZM(6),AC(21)
  137 FORMAT (1X, ' SO2----',D15.5,2X,D15.5)

      TYPE 138,ZM(7),AC(22)
  138 FORMAT (1X,' NA+ ---',D15.5,2X,D15.5)
      TYPE 139,ZM(8),AC(23)
  139 FORMAT (1X,' NAHSO3-',D15.5,2X,D15.5)
      TYPE 140,ZM(9),AC(24)
  140 FORMAT (1X,' NAS2O5 ',D15.5,2X,D15.5)
      TYPE 141,ZM(10),AC(25)
  141 FORMAT (1X,' NA2S2O5',D15.5,2X,D15.5)
      TYPE 142,ZM(11),AC(26)
  142 FORMAT (1X,' NASO3--',D15.5,2X,D15.5)
      TYPE 143,ZM(12),AC(27)
  143 FORMAT (1X,' NA2SO3-',D15.5,2X,D15.5)
```

```
      TYPE 144,ZM(13),AC(28)
  144 FORMAT (1X,' HS2O5- ',D15.5,2X,D15.5)
      TYPE 145,ZM(14),AC(29)
  145 FORMAT (1X,' H2S2O5 ',D15.5,2X,D15.5)
      TYPE 146,ZM(15),AC(30)
  146 FORMAT (1X,' NAOH-- ',D15.5,2X,D15.5)
      RETURN
      END
      SUBROUTINE SEQ2 (X,F,DER)
      IMPLICIT REAL*8 (A-H,R-Z)
      COMMON/C/AC(31),ASO2,AK(13),AA,BB/F/ZM(15)/
     $B/TOTNA/AW/AS,BS,W6,TION,ZISQZM,DBSX1,DBSX2
      DIMENSION F(3),DER(50,3),X(3)
      DO 5 J = 1,50
      DO 5 K = 1,3
    5 DER(J,K) = 0.
      AC(1) = X(1)
      AC(6) = X(2)
      AC(31) = X(3)
      CALL EQUIL
      W1 = ZM(2) + ZM(3)
      W2 = 2.*(ZM(4) + ZM(5))
      W3 = ZM(9)+ZM(11)+ZM(13)
      W4 = ZM(10)+ZM(12)
      W7 = ZM(7)+ZM(1)
      W8 = W1+W2+W3
      W9 = X(3)-0.5*W7
      DASX1 = 0.-2.*AS/AC(1)
      DASX2 = 3.*AS/X(2)
      DFM7X1 = (((2.*DBSX1*BS+4.*TOTNA*DASX1)/W6/2.)-DBSX1)
     $/2./AS + (BS-W6)*DASX1/2./AS/AS
      DFM7X2 = (((2.*BS*DBSX2+4.*TOTNA*DASX2)/W6/2.)-DBSX2)
     $/2./AS + (BS-W6)*DASX2/2./AS/AS
      F(1) = DLOG(W8)-DLOG(W7)
      F(2) = DLOG(0.018*TION)-DLOG(1.-X(2))
      F(3) = DLOG(0.5*(W1+2.*W2+W3))-DLOG(W9)
      DER(1,1) = (DFM7X1+1./AC(16))/W7+(W8+W2+ZM(9)+ZM(11))/W8/X(1)
      DER(1,2) = DFM7X2/W7-(2.*W8+W2+W3)/W8/X(2)
      DER(2,1) = 0.-(ZM(1)-W8-ZM(9)-ZM(11)+X(1)*DFM7X1-ZM(8)-2.*
     $W4-ZM(15))/X(1)/TION
      DER(2,2) = 0.-1./(1.-X(2))-(2.*W8-W2/2.+W3+X(2)*DFM7X2
     $+2.*(ZM(8)+ZM(15))+3.*(W4+ZM(14)))/TION/X(2)
      DER(3,1) = 0.-0.5*(DFM7X1+1./AC(16))/W9 + (W1+4.*W2+2.*W3
     $-ZM(13))/(W8+2.*W2)/X(1)
      DER(3,2) = 0.-0.5*DFM7X2/W9-(2.*W1+6.*W2+3.*W3)/(W8
     $+2.*W2)/X(2)
      DER(3,3) = 1./W9
      RETURN
      END
```

```
      FUNCTION H3O(X)
      IMPLICIT REAL*8 (A-H,R-Z)
      COMMON/C/AC(31),ASO2,AK(13),AA,BB/F/ZM(15)
      AC(1) = X
      CALL EQUIL
      H3O = (ZM(7)+ZM(1)-ZM(2)-ZM(3)-2.*(ZM(4)+ZM(5))
     $-ZM(9)-ZM(11)-ZM(13))/ZM(3)
      RETURN
      END
      SUBROUTINE EQUIL
      IMPLICIT REAL*8 (A-H,R-Z)
      COMMON/C/AC(31),ASO2,AK(13),AA,BB/F/ZM(15)/E/A(15),
     *B(15),U(15),ZI(15)/AW/AS,BS,W6,TION,ZISQZM,DBSX1,
     *DBSX2/B/TOINA
      DO 1 J = 1,15
      G = AA*ZI(J)*ZI(J)*(B(J)*AC(31)-DSQRT(AC(31))/(1.+BB*A(J)*DSQRT(AC
     *(31)))) + U(J)*AC(31)
    1 AC(J+15) = DEXP(2.302585093D00*G)
      AC(2) = AK(4)*AC(6)*AC(6)/AC(1)
      AC(3) = AK(1)*ASO2*AC(6)*AC(6)/AC(1)
      AC(4) = AK(3)*AC(3)*AC(3)/AC(6)
      AC(5) = AK(2)*AC(3)*AC(6)/AC(1)
      DO 3 J = 1,5
    3 ZM(J) = AC(J)/AC(J+15)
      TK8 = AK(6)*AC(23)/AC(22)/AC(18)
      TK9 = AK(7)*AC(24)/AC(22)/AC(19)
      TK10 = AK(8)*AC(25)/AC(22)/AC(24)
      TK11 = AK(9)*AC(26)/AC(22)/AC(20)
      TK12 = AK(10)*AC(27)/AC(22)/AC(26)
      TK15 = AK(13)*AC(30)/AC(22)/AC(17)
      AS = 2.*(ZM(4)/TK10/TK9+ZM(5)/TK11/TK12)
      BS = 1.+ZM(3)/TK8+ZM(4)/TK9+ZM(5)/TK11+ZM(2)/TK15
      W6 = DSQRT(BS*BS+4.*TOINA*AS)
      AC(7) = AC(22)*(W6-BS)/2./AS
      AC(8) = AC(7)*AC(3)/AK(6)
      AC(9) = AC(7)*AC(4)/AK(7)
      AC(10) = AC(7)*AC(9)/AK(8)
      AC(11) = AC(7)*AC(5)/AK(9)
      AC(12) = AC(7)*AC(11)/AK(10)
      AC(13) = AC(1)*AC(4)/AK(11)/AC(6)
      AC(14) = AC(1)*AC(13)/AK(12)/AC(6)
      AC(15) = AC(7)*AC(2)/AK(13)
      DO 4 J = 7,15
    4 ZM(J) = AC(J)/AC(J+15)
      ZM(6) = ASO2/AC(21)
      DBSX1 = (1.-BS-ZM(4)/TK9-ZM(5)/TK11)/AC(1)
      DBSX2 = (2.*(BS-1.)+ZM(4)/TK9+ZM(5)/TK11)/AC(6)
      TION = 0.
      ZISQZM = 0.
```

```
      DO 10 J = 1,15
      TION = TION + ZM(J)
   10 ZISQZM = ZISQZM + ZI(J)*ZI(J)*ZM(J)
      RETURN
      END
      SUBROUTINE NEWT (FF,B,TOL,MIT,IEQ)
C
C     NEWTON'S METHOD--DOUBLE PRECISION
C
      IMPLICIT REAL*8 (A-D,F-H,R-Z)
      DIMENSION B(3),DX(3),DP(50,3),RF(3)
      IZ = 3
      IF (IEQ.GT.IZ) GO TO 200
      IT = 0
  100 CALL FF(B,RF,DP)
      IT = IT + 1
      EE = 0.
      CALL BNDINV (DP,IZ,ETM,EE,1)
      DO 15 K = 1,IZ
   15 DX(K) = 0.
      DO 17 K = 1,IZ
      DO 16 J = 1,IZ
   16 DX(K) = DX(K) + DP(K,J)*RF(J)
   17 B(K) = B(K) + DX(K)
      ZA = 0.
      AMAX = 0.
      DO 18 K = 1,IZ
      IF (DABS(B(K)).GT.1.D-25) ZA = DABS(DX(K)/B(K))
   18 IF (ZA.GT.AMAX) AMAX = ZA
      IF (AMAX.LE.TOL) RETURN
      IF (IT.LT.MIT) GO TO 100
      TYPE 50,IT
   50 FORMAT (1H0, ' *** OVERRUN ON NEWT, IT = ', I7)
      TYPE 1010,RF
 1010 FORMAT (1H0, 3('    ',D20.10))
      RETURN
  200 TYPE 201
  201 FORMAT (1H0, ' YOU DUMMY,TOO MANY EQUATIONS')
      RETURN
      END
      SUBROUTINE ZEROA (F,AA,B,DX,X,EPS,MIT)
C
C  THIS ROUTINE COMPUTES THE ROOT OF A FUNCTION
C
      IMPLICIT REAL*8 (A-H,R-Z)
      DIMENSION FV(2)
      IT = 0
        A = AA
      X = A
      FV(1) = F(A)
```

```
      IF (DABS(FV(1)).LT.EPS) RETURN
   10 X = A + DX
      FV(2) = F(X)
      IF (DABS(FV(2)).LT.EPS) RETURN
      IF ((FV(1)*FV(2)).LT.0.) GO TO 100
      FV(1) = FV(2)
      A = X
      IF (A.GE.B) GO TO 700
      GO TO 10
  100 TP = (X + A)/2.
      IT = IT + 1
      IF (IT.GE.MIT) GO TO 201
      Z = F(TP)
      IF (DABS(Z).LT.EPS) GO TO 507
      IF ((FV(2)*Z).GT.0.) GO TO 1010
      A = TP
      GO TO 100
 1010 X = TP
      GO TO 100
  201 TYPE 253,IT
  253 FORMAT (1H0, ' *** EXCESSIVE ITERATIONS IN ZEROA ***', I7)
      GO TO 507
  700 TYPE 50
   50 FORMAT (1H0, ' *** SORRY, NO ROOTS IN RANGE ZEROA')
  507 X = TP
      RETURN
      END
      BLOCK DATA
      IMPLICIT REAL*8 (A-H,R-Z)
      COMMON/A/RES2,MXT,IEQ/E/A(15),B(15),U(15),ZI(15)/AAA/D(11)
        DATA D/1.6D-05,1.47D-05,1.D-05,1.1D-05,1.4D-05,8.7D-06,
     11.1D-05,1.D-05,1.3D-05,9.D-06,1.2D-05/
      DATA A,B,U,ZI/9.D00,3.5D00,4.25D00,2*4.5D00,10*3.05D00,
     #0.4D00,14*3.D-01,5*0.D00,0.076D00,9*0.D00,1.D00,2*-1.D00,
     $2*-2.D00,0.D00,1.D00,0.D00,-1.D00,0.D00,-1.D00,0.D00,
     #-1.D00,2*0.D00/
      DATA RES2,MXT,IEQ/1.D-07,100,3/
      END
```

APPENDIX B -- Data Reduction Example

Computation of the flux and the facilitation factor from the raw data is discussed in this appendix.

Below are the data taken during an experiment with Na_{tot} = 0.2M and $y_{SO_2,o} = 5\cdot10^{-4}$. These data consist of the volumetric flow rates (Q_i, three measurements) which determine M_u, M_d, and M_{O_2}, the DPM reading which determines M_{SO_2}, and the Meloy current, I_M, which determines y_m. Also shown are the gel weight and the gel density.

The gel diameter is 3/16" so that the cross-sectional area, A, is 0.178 cm^2.

M_u	M_d	M_{O_2}	M_{SO_2}	I_M
$Q_u=73.08\frac{cm^3}{sec}$	$Q_d=68.77\frac{cm^3}{sec}$	$Q_{O_2}=18.29\frac{cm^3}{sec}$	DPM = 2.30 volts	$I_M=3.6\cdot10^{-8}$ amps
=73.08 "	=68.77 "	=18.29 "		
=73.08 "	=68.77 "	=18.28 "		

W_{gel} = 0.0193 gm $\qquad\rho_{gel}$ = 1.04 gm/cm^3

Wet test meter temperature = 25°C

Room pressure = 744 mm Hg = P_{tot}

Calculations with the raw data:

$$M_u = \frac{P_{tot}Q_u}{RT} = \frac{744\text{mmHg}\cdot 73.08\text{cm}^3\text{sec}^{-1}}{82.05\frac{\text{cm}^3\cdot\text{atm}}{\text{gmoleK}}\cdot 298\text{K}\cdot 760\frac{\text{mmHg}}{\text{atm}}} \qquad \text{(B-1a)}$$

$$= 2.924\cdot10^{-3}\text{ moles sec}^{-1}$$

$$M_d = \frac{P_{tot}Q_d}{RT} = 2.752\cdot 10^{-3} \text{ moles sec}^{-1} \qquad \text{(B-1b)}$$

$$M_{O_2} = \frac{P_{tot}}{RT}\left(\frac{18.29+18.29+18.28}{3}\right)\frac{\text{cm}^3}{\text{sec}} = 7.319\cdot 10^{-4}\frac{\text{moles}}{\text{sec}} \qquad \text{(B-1c)}$$

$$M_{SO_2} = 6.394\cdot 10^{-7}\frac{\text{moles}}{\text{sec}\cdot\text{volt}}\cdot \text{DPM} \qquad \text{(linear calibration)}$$

(B-1d)

$$= 6.394\cdot 10^{-7}\cdot 2.30\frac{\text{moles}}{\text{sec}} = 1.471\cdot 10^{-6}\ \frac{\text{moles}}{\text{sec}}$$

$$y_m = 1.651\cdot 10^{-3} I_M^{(0.571)} \qquad \text{(log-linear calibration)}$$

(B-1e)

$$= 1.651\cdot 10^{-3}\cdot (3.6\cdot 10^{-8})^{0.571}$$

$$= 9.277\cdot 10^{-8}$$

From the Handbook of Chemistry and Physics (Weast, 1971, Table 68), it is found that for an 0.2M NaOH solution

$$\frac{\mu}{\mu_o} = 1.04 \qquad \text{(B-1f)}$$

With these data, it is possible to compute $y_{SO_2,o}$, $y_{SO_2,1}$, L, N, N_o, and F for comparison to theory. The following algebraic relationships apply:

$$y_{SO_2,1} = \left(1 + \frac{M_d(1 - y_m)}{(M_d + M_{O_2})y_m}\right)^{-1} \qquad \text{(B-2)}$$

$$y_{SO_2,o} = \frac{M_{SO_2} - \frac{y_{SO_2,1}}{1 - y_{SO_2,1}} M_d}{M_u + M_{SO_2} - \frac{y_{SO_2,1}}{1 - y_{SO_2,1}} M_d} \qquad \text{(B-3)}$$

$$L = \frac{W_{gel}}{A\rho_{gel}} \qquad \text{(B-4)}$$

$$N = \frac{y_m(M_d + M_{O_2})}{(1 - y_m)\cdot A} \qquad \text{(B-5)}$$

$$\log_{10}\gamma_{SO_2} = 0.076\frac{\ell}{\text{mole}}\cdot(Na_{tot}) \qquad \text{(B-6)}$$

$$D_{SO_2} = D^o_{SO_2}\frac{\mu_o}{\mu} \qquad \text{(B-7)}$$

$$N_o = \frac{D_{SO_2}P_{tot}}{\gamma_{SO_2}H_{SO_2}L}(y_{SO_2,o} - y_{SO_2,1}) \qquad \text{(B-8)}$$

$$F = \frac{N - N_o}{N_o} \tag{B-9}$$

These relationships and eqs. B-1a-f yield

$$y_{SO_2,1} = 1.03 \cdot 10^{-7} \tag{B-10a}$$

$$y_{SO_2,o} = 5.03 \cdot 10^{-4} \tag{B-10b}$$

$$L = 0.104 \text{ cm} \tag{B-10c}$$

$$\gamma_{SO_2} = 1.04 \tag{B-10d}$$

$$D_{SO_2} = 1.54 \cdot 10^{-5} \text{ cm}^2\text{sec}^{-1} \tag{B-10e}$$

$$N = 1.67 \cdot 10^{-9} \text{ moles cm}^{-2}\text{sec}^{-1} \tag{B-10f}$$

$$N_o = 9.02 \cdot 10^{-11} \text{moles cm}^{-2}\text{sec}^{-1} \tag{B-10g}$$

$$F = 17.5 \tag{B-10h}$$

This value of F was averaged with two other experimental values with the same Na_{tot} and $y_{SO_2,o}$ to arrive at the entry in Table 5.2 (F = 17.9).

The theoretical values of F are

$$F_{eq} = 156 \tag{B-11a}$$

$$F_{bl} = 25.2 \tag{B-11b}$$

APPENDIX C -- Computed Solubility vs. Johnstone and Blankmeyer's Data; Test of Davies' γ_i Model in Concentrated Solutions

Johnstone and Blankmeyer (1938) report partial pressures of SO_2 in equilibrium with solutions that contain a known concentration of total sodium, Na_{tot} (added to the solutions as NaOH, $NaHSO_3$, or Na_2SO_3), and a measured equilibrium amount of total dissolved sulfur (i.e., $\sum_j n_j C_j$). The solutions studied range from 2M to 4.5M Na_{tot} with $0.16\text{mm Hg} \leq P_{SO_2} \leq 17.8 \text{ mm Hg}$.

As discussed in Appendix A, when Na_{tot} and the partial pressure of SO_2 are known, the concentrations of all of the species in solution are fixed. Thus, the total dissolved sulfur

$$S_T = \sum_j n_j C_j \qquad \text{(C-1)}$$

is fixed.

When Na_{tot} and P_{SO_2} are chosen from data points reported by Johnstone and Blankmeyer, an accurate equilibrium composition calculation should predict S_T to be near the values given by Johnstone and Blankmeyer. The goal here is to compare S_T predicted for SO_2/alkaline sodium solutions by the equilibrium model in Appendix A, which employs Davies' activity coefficient model, with reported

S_T values. If the agreement is good, Davies' γ_i model is shown to be adequate for concentrated ($\geq$ 0.5M Na_{tot}) SO_2/alkaline sodium solutions.

The significance of S_T is appreciated when eq. 3.51 is examined. If $D_j = D =$ constant, then eq. 3.51 becomes

$$\begin{aligned} N_{SO_2} &= D \sum_j n_j [C_j(0) - C_j(1)] \\ &= D[S_T(0) - S_T(1)] \end{aligned} \tag{C-2}$$

Table 3.2 shows that all diffusivities are approximately equal in this system when H_3O^+ and OH^- are negligible. Thus, although the following comparison will not be able to establish the validity of each individual activity coefficient, the total solubility is a more important quantity.

The data given by Johnstone and Blankmeyer is less than ideal for this comparison. One problem is that it is desired to make the comparison at 25°C because the thermodynamic equilibrium coefficients are known at this temperature (Table 3.1). Johnstone and Blankmeyer, however, report data at 90°C, 70°C, 50°C, and 35°C.

Since the data are over a range of temperatures and concentrations, Johnstone and Blankmeyer fit their data to a pseudo-theoretical curve which works well. Their findings therefore can be extrapolated with confidence some reasonably small amount outside of the range measured. Since their data ranged over 55°C, a 10°C extrapolation (from 35°C to 25°C) is not serious. This extrapolation is preferable to extrapolating theoretically the thermodynamic equilibrium coefficients from 25°C to 35°C.

It is also desired to make the comparison for $0.5M \leq Na_{tot} \leq 3M$ to establish the Davies γ_i model in the range of alkaline solutions studied in this thesis. Johnstone and Blankmeyer's data are taken, however, in the range $2M \leq Na_{tot} \leq 4.5M$. Again, the equation developed by Johnstone and Blankmeyer can easily be extrapolated into this lower (overlapping) range.

It may be argued that more appropriate data should be used for this comparison. The problem is that there are no better data. A strong point in favor of Johnstone and Blankmeyer's data is that they are taken with the solutions that are used in the alkaline solution experiments in this thesis. This is important because activity coefficients in concentrated solutions are highly dependent on the chemical nature of the solutes. Thus, although SO_2 solubility data exist for a variety of solutions, such solutions do not make sense for testing a γ_i model. It is more reasonable to extrapolate outside the immediate range of data taken than to compare to a chemically different system.

Johnstone and Blankmeyer's data are represented by the equation

$$S_T = \frac{(B^2 - D)^{\frac{1}{2}} - B}{2} \qquad \text{(C-3)}$$

where

$$B = \frac{y_{SO_2} P_{tot}}{4M} - Na_{tot} \qquad \text{(C-4)}$$

$$D = Na_{tot}^2 - \frac{y_{SO_2} P_{tot} Na_{tot}}{M} \qquad \text{(C-5)}$$

and

$$\log_{10} M = 4.519 - \frac{1987}{T} \qquad \text{(C-6)}$$

In these equations, the temperature, T is in K, P_{tot} is in mm Hg, the coefficient M has units of

$$\text{mmHg} \cdot \left(\frac{100 \text{ moles of } H_2O}{\text{mole}} \right)$$

Na_{tot} has units of

$$\frac{\text{moles of sodium}}{100 \text{ moles of } H_2O}$$

and S_T has units of

$$\frac{\text{moles of sulfur}}{\text{100 moles of } H_2O}$$

Equation C-2 is a rearrangement of eq. 1 of Johnstone and Blankmeyer (1938).

At 25°C,

$$M = 7.0993 \cdot 10^{-3}\ \text{mmHg} \cdot \left(\frac{\text{100 moles of } H_2O}{\text{mole}}\right) \qquad \text{(C-7)}$$

Given T = 25°C and a fixed P_{tot} = 744 mm Hg, if y_{SO_2} and Na_{tot} are chosen, then S_T is computed from eqs. C-3-6. Table C-1 shows the results of these calculations for $y_{SO_2} = 10^{-4}$, $2 \cdot 10^{-4}$, $5 \cdot 10^{-4}$, and 10^{-3} and Na_{tot} = 0.5, 1, 2, and 3M. The quantity S_T has been converted to mole/liter units. Also shown are the corresponding total sulfur solubilities, $\sum_j n_j C_j$, from the equilibrium equations given in Appendix A.

The maximum deviation is 10% between Johnstone and Blankmeyer's S_T values and S_T values computed from the equilibrium equations given in Appendix A.

Figure C-1 is a graph of the calculations for $y_{SO_2} = 10^{-3}$. The good agreement is reiterated.

The conclusion is that Davies' activity coefficient model is adequate for concentrated SO_2/alkaline sodium

Table C-1

Total Sulfur Solubility

Equilibrium Calculations ($S_{T,EC}$) vs.

Johnstone/Blankmeyer Equation ($S_{T,JB}$)

P_{tot} = 744 mm Hg T = 298 K

$\frac{S_{T,EC}}{S_{T,JB}}$ $\frac{\text{mole}}{\text{liter}}$	$10^6 \cdot y_{SO_2}$			
Na_{tot} mole/liter	1000	500	200	100
0.5	0.4995 - - - 0.4959	0.4962 - - - 0.4921	0.4896 - - - 0.4819	0.4796 - - - 0.4680
1.0	0.9924 - - - 0.9844	0.9830 - - - 0.9703	0.9596 - - - 0.9361	0.9286 - - - 0.8950
2.0	1.974 - - - 1.941	1.948 - - - 1.893	1.883 - - - 1.790	1.797 - - - 1.685
3.0	2.953 - - - 2.873	2.909 - - - 2.780	2.797 - - - 2.596	2.651 - - - 2.425

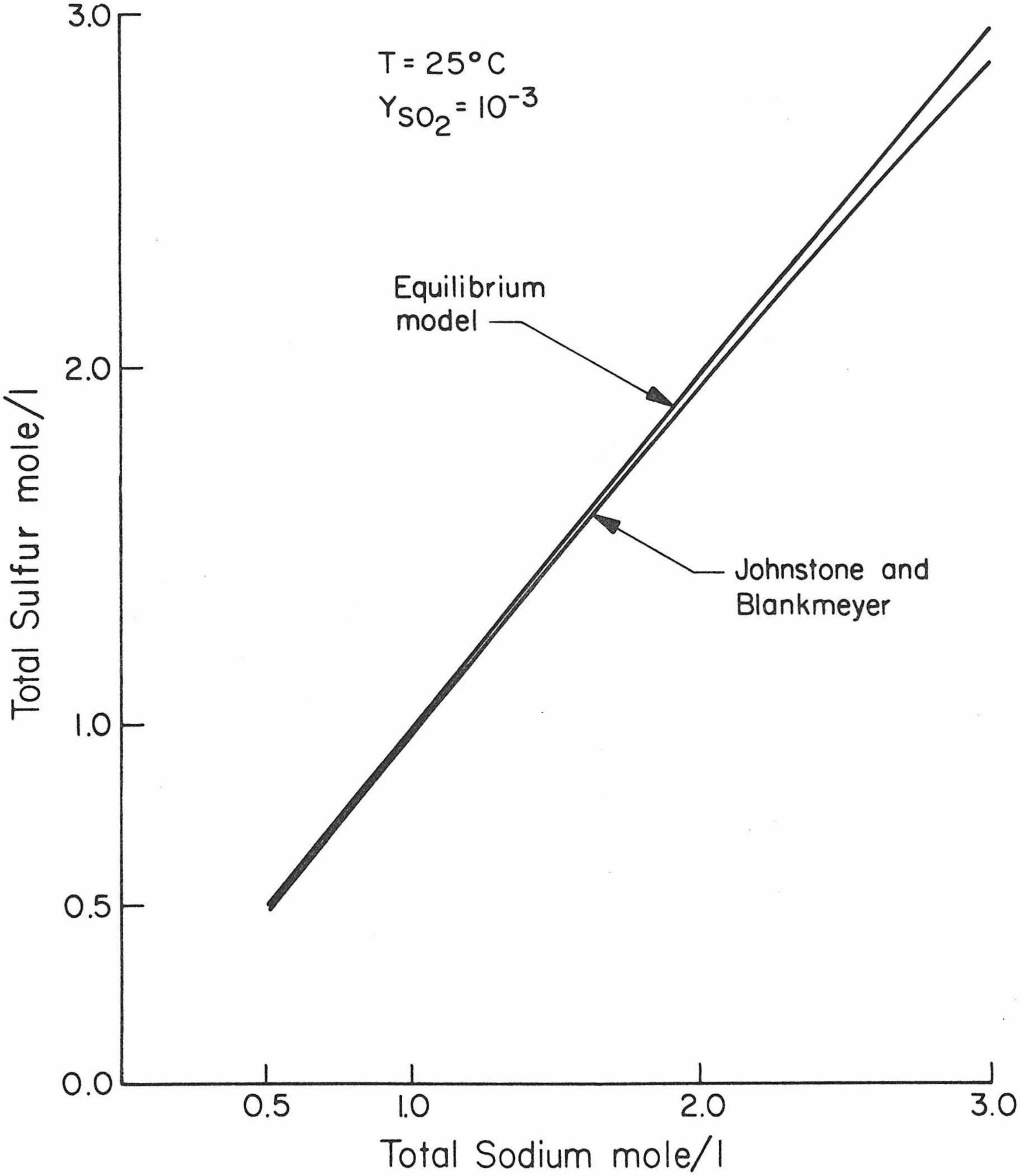

FIGURE C-1 -- Solubility of SO_2 in Alkaline Sodium Solutions - Equilibrium computations, which employ the Davies activity coefficient model, agree well with pseudo-theoretical equation from the data of Johnstone and Blankmeyer (1938).

solutions. This comparison cannot establish precision for each individual coefficient. The good agreement, however, establishes that an activity coefficient model more sophisticated than Davies' is unnecessary.

This result, combined with the observation in section 5.2 that choice of activity coefficient model is unimportant when $I < 0.5M$, establishes that Davies' activity coefficient model is adequate for the entire range of alkaline sodium solutions studied in this thesis ($10^{-3}M \leq Na_{tot} \leq 3M$).

One further observation is that S_T is approximately constant over the range $100ppm \leq y_{SO_2} \leq 1000ppm$. Thus, the effective Henry coefficient

$$\underline{m} = \frac{y_{SO_2} P_{tot}}{S_T} \tag{C-8}$$

varies by a factor of 10 as y_{SO_2} varies between 100 and 1000 ppm. This observation is the source of the comment on pg. 47 that $\underline{m}$ is likely to change by a factor of 10 in a scrubber that achieves 90% SO_2 removal, rather than a factor of two as suggested by Rochelle (1977).

APPENDIX D -- Activity Coefficient Models

This appendix presents the activity coefficient models of Davies (1962) and Bromley (1972). The Davies (or "extended" Davies) model is

$$\log_{10}\gamma_i = Az_i^2\left(b_iI - \frac{I^{\frac{1}{2}}}{1 + Ba_iI^{\frac{1}{2}}}\right) \qquad \text{(D-1)}$$

The ionic strength, I, is in units of moles/kg.

Equation D-1 is called "extended" because Davies proposed $b_i = 0.3$ for all species. It soon became apparent that letting b_i differ from species to species could improve the accuracy of eq. D-1 in fitting data. The basic form of eq. D-1 is however attributable to Davies.

The coefficients A and B arise from Debye-Huckel theory and are temperature dependent. At 25°C, A = 0.5085 and B = 0.3281Å^{-1}. Manov, et al. (1943), give values of A and B for a range of temperatures.

Values of a_i and b_i for species relevant to this thesis are listed in Table D-1. These values are obtained from Klotz and Rosenberg (1972) and Garrels and Christ (1965). For some species, the values are estimates from the known values of similar species.

Table D-1

Parameters in Davies Activity Coefficient Model

Species	a_i (Å)	b_i
H_3O^+	9.0	0.4
OH^-	3.5	0.3
HSO_3^-	4.25	0.3
$S_2O_5^=$	4.5	0.3
$SO_3^=$	4.5	0.3
Na^+	3.05	0.3
$NaS_2O_5^-$	3.05	0.3
$NaSO_3^-$	3.05	0.3
$HS_2O_5^-$	3.05	0.3

Values for neutral species (e.g., $NaHSO_3$) are irrelevant since $z_i = 0$ for neutral species.

Bromley's model is

$$\log_{10}\gamma_M = -\frac{Az_M^2 I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + B_M \sum_A m_A + \sum_A B_A m_A \qquad \text{(D-2)}$$

and

$$\log_{10}\gamma_A = -\frac{Az_A^2 I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + B_A \sum_M m_M + \sum_M B_M m_M \qquad \text{(D-3)}$$

In eqs. D-2,3, the subscript M denotes cationic species and the subscript A denotes anionic species. The coefficients B_M and B_A are the specific ion-interaction constants for a given cation or anion. The quantities m_M and m_A are the molal concentrations of a given cation or anion, and z_M and z_A are the algebraic charges. The coefficient A is the Debye-Huckel coefficient (A = 0.5085 at 25°C).

In this thesis, Bromley's model is employed only for SO_2/NaCl solutions. The relevant species therefore are H_3O^+, HSO_3^-, Na^+, and Cl^-. Values of B_i given by Abdulsattar, Sridhar, and Bromley (1977) are shown in Table D-2.

The activity coefficient for neutral ion pairs is arbitrarily set equal to one because of the uncertainties

Table D-2

Specific Ion-Interaction Coefficients in Bromley Activity Coefficient Model (25°C)

Species	B_i kg/mole
H_3O^+	0.087
HSO_3^-	-0.013
Na^+	-0.035
Cl^-	0.156

in estimating equilibrium and activity coefficients for ion pairs. Activity effects normally lie within the error bounds of the estimated equilibrium coefficients.