

To the Graduate Council:

I am submitting herewith a dissertation written by Douglas Bruce Crawford entitled "Absorption of Four Valent Nitrogen Oxides into Aqueous Sodium Hydroxide Solutions in a Packed Tower." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

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ABSORPTION OF FOUR VALENT NITROGEN OXIDES
INTO AQUEOUS SODIUM HYDROXIDE SOLUTIONS
IN A PACKED TOWER

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Douglas Bruce Crawford
December 1990

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This dissertation is dedicated to my parents,
Margaret Anne and Lloyd W. Crawford

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ABSTRACT

The scrubbing of low partial pressures of nitrogen dioxide - nitrogen tetroxide mixtures is important to several industries. In this study a gas stream with N(IV) ($\text{NO}_2 + 2 \text{N}_2\text{O}_4$) partial pressures of 3×10^{-4} atm to 5×10^{-3} atm in air at atmospheric pressure is contacted with water and 0.3, 0.6, and 1.0 N NaOH aqueous solutions in a tower packed with high efficiency structured packing. Experimental temperatures are 23°C to 27°C. N(IV) scrubbing efficiencies range from 24% to 62%. The hydroxide concentration only slightly affects the scrubbing efficiencies. An analysis of literature data and the experimental results is used to produce an enhancement factor modifier for the concentration dependent effect of sodium hydroxide on the interfacial flux of N(IV). A review of the literature indicates that NO_2 and N_2O_4 are in equilibrium in the gas and liquid phases, that a film theory, fast reaction-regime model, referred to as a combined flux model, is available but untested for the interfacial combined flux of NO_2 and N_2O_4 and that a technique is available for comparing most previous experimental results in order to choose appropriate solubilities and rate constants for the reactive dissolution of N(IV).

A hydrolysis reaction mechanism is proposed. The mechanism is consistent with the available literature. A reaction number, the square of the Hatta number, is derived for the combined flux model and tested against a general combined flux model which does not include the fast reaction regime assumption. The N(IV) reaction number is consistent with previously

derived reaction numbers for first and second order reactions. The scrubbing experiments are conducted in the fast reaction regime. Based on the comparison of literature values and the results of the scrubbing experiments, a pseudo-second order rate constant for the hydrolysis of NO_2 , $4.5 \times 10^7 \text{ m}^3/\text{kgmol}\cdot\text{s}$, a Henry's Law constant for N_2O_4 , $0.93 \text{ kgmol}/\text{m}^3\cdot\text{atm}$, and a Henry's Law constant for NO_2 , $0.0099 \text{ kgmol}/\text{m}^3\cdot\text{atm}$ are recommended for use with the combined flux model to predict the performance of caustic N(IV) scrubbers at low N(IV) partial pressures near 25°C .

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NOMENCLATURE

The nomenclature used in this report is a combination of the standard chemical engineering nomenclature and a nomenclature introduced by Schwartz and White (1983) for expressing reaction kinetics. The reaction rate expressions used follow the physical chemists standard nomenclature. As an example, for a reaction:



the reaction rate expression for Reaction # in the aqueous phase is:

$$\begin{aligned} R_{A\#} &= - \frac{1}{a} \frac{dc_A}{dt} - \frac{1}{b} \frac{dc_B}{dt} + \frac{1}{c} \frac{dc_C}{dt} + \frac{1}{d} \frac{dc_D}{dt} \\ &= k_{A\#} c_A^a c_B^b - k_{A\#} c_C^c c_D^d \quad . \end{aligned}$$

A list of the nomenclature follows:

SYMBOL DEFINITION

a	interfacial area, m^2/m^3
c_n	concentration of species n , $kgmol/m^3$
$c_{\#}$	integration constants, units vary
D_n	aqueous phase diffusivity of species n , m^2/s
D_n^o	aqueous phase diffusivity of species n in water, m^2/s
D_n^G	gas phase diffusivity of species n in air, m^2/s
E_{OH}	enhancement factor modifier for absorption of N(IV) into sodium hydroxide solutions, unitless
G	Gas phase molar loading, $kgmol/m^2\cdot s$
h	salting coefficient for a gas, electrolytic solution mixture, $m^3/kgmol$

SYMBOL DEFINITION

h_g	salting coefficient for a gas, $m^3/kgmol$
h_+	salting coefficient for a positive ion, $m^3/kgmol(ion)$
h_-	salting coefficient for a negative ion, $m^3/kgmol(ion)$
h_t	total liquid holdup on a volume per volume basis, unitless
H_n	Henry's Law constant for species n, $kgmol/m^3\text{-atm}$
H_B°	Henry's Law constant for N_2O_4 in water, $kgmol/m^3\text{-atm}$
I	ionic strength of the electrolytes in a solution, $kgmol(ion)/m^3$
k_g	gas phase mass transfer coefficient, $kgmol/m^2\text{-atm-s}$
k_l	liquid phase mass transfer coefficient, m/s
$k_{A\#}$	aqueous phase forward reaction rate constant for Reaction #, when the # is 114 or 138 the reaction rate constant is an effective reaction rate for that reaction expression rather than a true reaction rate constant for some reaction, units vary
$k_{A\#}$	reverse aqueous phase reaction rate constant for Reaction #, units vary
k_{G1}	gas phase forward reaction rate constant for Reaction 1, $kgmol/m^3\text{-atm}^2\text{-s}$
k_{G1}	gas phase reverse reaction rate constant for Reaction 1, $kgmol/m^3\text{-atm-s}$
k_{M20}	mixed phase reaction rate constant for Reaction 20, $kgmol/m^3\text{-atm-s}$
k_{M21}	mixed phase reaction rate constant for Reaction 21, $kgmol/m^3\text{-atm}^2\text{-s}$
$K_{A\#}$	aqueous phase equilibrium constant for Reaction #, units vary
K_{G1}	gas phase equilibrium constant for Reaction 1, atm^{-1}
L	liquid molar loading, $kgmol/m^2\text{-s}$

SYMBOL DEFINITION

$M_{(n)}$	reaction number for a n^{th} order reaction, unitless
N_n	molar flux of species n , $\text{kgmol}/\text{m}^2\text{-s}$
p_n	partial pressure of species n , atm
P	total pressure, atm
Q_B	quantity of species B absorbed per unit area for a given contact time, kgmol/m^2
R	ideal gas law constant, $0.08206 \text{ m}^3\text{-atm}/\text{kgmol}\text{-K}$
Re	gas phase column Reynolds number for the gas stream, unitless
$R_{A\#}$	aqueous phase reaction rate for Reaction #, $\text{kgmol}/\text{m}^3\text{-s}$
R_{G1}	gas phase reaction rate for Reaction 1, $\text{kgmol}/\text{m}^3\text{-s}$
$R_{M\#}$	mixed phase reaction rate for Reaction #, $\text{kgmol}/\text{m}^3\text{-s}$
Sc	gas phase Schmidt number, unitless
t	time of contact, s
$t_{0.99}$	time required for a reaction to approach 99% of the equilibrium value, s
T	temperature, K
x	distance in a diffusion film, m
z	height inside the column, m
Z	height of the column, m
β	constant defined in Equation 75, m^3/kgmol
f^G	gas phase film thickness, m
f^L	liquid phase film thickness, m

SUBSCRIPT DEFINITION

ave	denotes an average value
A	denotes species A, $A = \text{NO}_2$ in and after Equation 27
b	denotes the value applies in the bulk phase
B	denotes species B, $B = \text{N}_2\text{O}_4$ in and after Equation 26
i	denotes interfacial value
in	denotes entrance stream value
I	denotes inert species
M	denotes log mean value
out	denotes exit stream value
OH	denotes hydroxide ion
t	denotes total
X	denotes species X
Y	denotes species Y
Z	denotes species Z

CHAPTER I

INTRODUCTION AND SIGNIFICANCE

The scrubbing of four valent nitrogen oxides, NO_2 and N_2O_4 , is important to nitric acid production, nuclear fuel processing, and other industries as a method of resource recovery and pollution control. The absorption of four valent nitrogen oxides, NO_2 and N_2O_4 , in water results in the formation of nitric and nitrous acid. Scrubbing NO and NO_2 mixtures with sodium hydroxide solutions is known to be very effective at removing equimolar quantities of NO and NO_2 , probably due to the acidic nature of reaction products. Since sodium hydroxide solutions are very effective for scrubbing equimolar quantities of NO and NO_2 , a packed column scrubber with an aqueous sodium hydroxide solution as the absorbent may be useful in scrubbing NO_x tail gases from some industrial processes. The mechanisms for caustic scrubbing of four valent nitrogen oxides and for caustic scrubbing of NO/NO_2 mixtures are not known sufficiently well for predicting the scrubbing efficiencies for low partial pressure gas streams. A logical first step for determining the mechanism for the caustic scrubbing of NO/NO_2 mixtures is to determine the mechanism for the caustic scrubbing of four valent nitrogen oxides.

The purposes of this study are:

1. to determine if any particular concentration of sodium hydroxide gives significantly enhanced rates of absorption of

four valent nitrogen oxides in a pilot plant scale column packed with high efficiency packing; and

2. to determine an effective model for the absorption of four valent nitrogen oxides in the NO_2 partial pressure range of 3×10^{-4} atm. to 5×10^{-3} atm.

To investigate the effect of sodium hydroxide concentrations on the rate of absorption of four valent nitrogen oxides, N(IV), solutions of distilled water, 0.3 N NaOH, 0.6 N NaOH, and 1.0 N NaOH are used as the absorbent. Experimental temperatures are maintained in the range of 23°C to 27°C. Gas phase partial pressures of N(IV) in the inlet and outlet streams are monitored with a chemiluminescent NO_x gas analyzer. A vast body of experimental results for the absorption of N(IV) into water is available for the temperature range of 20°C to 30°C; little variation in the rate of absorption of N(IV) has been noticed in that range. Data for the reactive dissolution of N(IV) into sodium hydroxide solutions (Chambers and Sherwood, 1937) and into sodium chloride solutions (Peters and Holman, 1955), and results for the reactive dissolution of N(IV) into nitric acid solutions (Hofstetzer and Kwanten, 1972) are investigated thoroughly and tested for consistency with the experimental results.

Nitrogen dioxide and dinitrogen tetroxide, also referred to as nitrogen tetroxide, establish equilibrium very rapidly in the gas phase. Results of flash photolysis and pulse radiolysis experiments have indicated that NO_2 and N_2O_4 are in equilibrium in the liquid phase as well. Karlsson (1983)

derived a model for the combined flux of NO_2 and N_2O_4 into aqueous solutions where the absorption is in the fast reaction regime. The applicability of this model is tested by deriving a reaction number, the square of the Hatta number, testing the reaction number for consistency with other reactions numbers shown by Danckwerts (1970), and comparing the reaction number to the experimental conditions. The Karlsson Combined Flux (KCF) model is compared to experimental data for the first time. Recommended kinetic and equilibrium constants presented by Schwartz and White (1983) are examined and compared to experimental results. The KCF model will be useful to chemical engineers for designing scrubbers for N(IV) . The theory used to develop and test this model will be useful in future studies of the scrubbing of equimolar or near equimolar quantities of NO and NO_2 with sodium hydroxide or other basic solutions since the techniques used in this study might be modified to include proposed mechanisms for the reactive dissolution of NO/NO_2 mixtures.

CHAPTER II

LITERATURE REVIEW

1. INTRODUCTION

Literature essential to understanding the chemical and physical phenomena related to the absorption of four valent nitrogen oxides, N(IV), in aqueous solutions is presented in this chapter. To thoroughly understand the information presented herein, one should be familiar with the theories related to the phenomena of reaction enhanced mass transfer in gas-liquid systems. Those unfamiliar with these theories are referred to Danckwerts (1970).

This review covers the following topics:

1. introduction;
2. properties of nitrogen dioxide, dinitrogen tetroxide, and nitrous acid;
3. characterization of N(IV) and related ions;
4. summary of literature regarding the rate and equilibrium of the dimerization of nitrogen dioxide;
5. summary of results of the penetration and film theories as they may be applied to the reactive dissolution of N(IV);
6. summary of literature regarding the rate of the hydrolysis of N(IV) and related solubilities;

7. determination of the best available rate of hydrolysis of N(IV) and the solubilities of NO_2 and N_2O_4 ;
8. proposed mechanisms for the hydrolysis of N(IV);
9. summary of previous models of the reactive dissolution of N(IV) which accounted for the liquid phase equilibrium between NO_2 and N_2O_4 ;
10. summary of literature indicating appropriate mass transfer parameters for towers packed with Koch Sulzer packing; and
11. literature summary.

2. PROPERTIES OF NITROGEN DIOXIDE, DINITROGEN TETROXIDE, AND NITROUS ACID

Some general properties of nitrogen dioxide, dinitrogen tetroxide, and nitrous acid are noted in most good reviews of the inorganic chemistry of nitrogen compounds such as Jolly (1964), Matasa and Tonca (1973), Stedman (1979), and Cotton and Wilkinson (1980). Nitrogen dioxide and dinitrogen tetroxide coexist when present in the gas phase, as a condensed liquid, and in aqueous solutions (Jolly and Cotton and Wilkinson). Nitrogen dioxide is a reddish-brown paramagnetic gas (Matasa and Tonca, Cotton and Wilkinson). Nitrogen tetroxide is a colorless diamagnetic gas (Cotton and Wilkinson). The equilibrium between gaseous nitrogen dioxide and gaseous nitrogen tetroxide is established very rapidly. Liquid dinitrogen tetroxide self-ionizes to form nitrosonium and nitrate ions (Jolly).

The hydrolysis of dinitrogen tetroxide (or nitrogen dioxide) produces nitric and nitrous acids. This reaction is commercially important to the production of nitric acid. Nitric acid is a strong acid; nitrous acid is a weak acid, $pK_a = 3.3$ at 25°C (Stedman, 1979), known only in dilute solutions. Nitrous acid decomposes to form water, nitrogen dioxide, and nitric oxide. Nitrous acid ionizes in solutions to form hydronium, nitrite, nitrosonium, and nitrous-acidium ions (Stedman); the proportions of each ion are controlled by the equilibrium constants of the reactions.

Daubert and Danner (1989) have compiled the values of the known physical property constants of nitrogen dioxide and nitrogen tetroxide. These values are shown in Table 1 along with the molecular weight and heat of formation of nitrous acid (CRC Handbook of Chemistry and Physics, 1962). Differences in the critical point data and the melting point data for NO_2 and N_2O_4 are due to the use of different references by Daubert and Danner; the data for these properties are actually data for equilibrium mixtures of NO_2 and N_2O_4 .

3. CHARACTERIZATION OF FOUR VALENT NITROGEN OXIDES AND RELATED IONS

There are three forms of four valent nitrogen oxides: nitrogen dioxide, dinitrogen tetroxide, and iso-dinitrogen tetroxide. All of these forms may have a significant effect on the rate of absorption of N(IV) in aqueous solutions. The results of attempts to characterize these species by electron

Table 1 Physical Properties of Nitrogen Dioxide, Dinitrogen Tetroxide, and Nitrous Acid

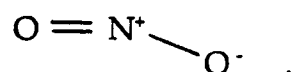
Property (units)	NO ₂ ^a	N ₂ O ₄ ^a	HNO ₂ ^b
molecular weight (kg/kgmol)	46.005	92.011	47.013
critical temperature (K)	431.35	431.15	
critical pressure (Pa)	1.01 x 10 ⁷	1.01 x 10 ⁷	
critical volume (m ³ /kgmol)	0.08249	0.08249	
melting point (K)	261.95	261.90	
boiling point (K)	294.00	302.22	
IG heat of formation (J/kgmol)	-3.31 x 10 ⁷	-9.08 x 10 ⁶	1.21 x 10 ⁸

^a Daubert, T. E., and R. P. Danner, *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*, Vol. 4, Hemisphere Publishing Corporation, New York (1989).

^b *CRC Handbook of Chemistry and Physics*, 44th ed., C. D. Hodgman, Ed., Chemical Rubber Publishing Co., Cleveland, OH, 1820 (1962).

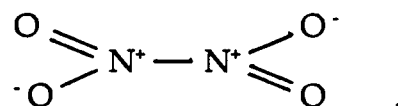
diffraction, Raman spectroscopy, and infrared spectroscopy have been summarized in several literature reviews (Laane and Ohlsen, 1980; Matasa and Tonca, 1973; and Jolly, 1964). These results may give some insight to the mechanisms important to the absorption of N(IV) in aqueous solutions.

Nitrogen dioxide and nitrogen tetroxide always exist in the presence of one another in gaseous and liquid states (Jolly, 1964). Matasa and Tonca (1973) presented the structure of nitrogen dioxide as:



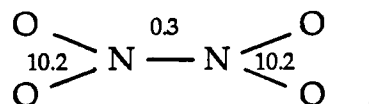
The O-N-O bond angle is 134°. The N-O bonds lengths are 1.19 Å (Laane and Ohlsen, 1980; Matasa and Tonca; and Jolly). The length of the two N-O bonds are the same due to resonance. The stretching force constants of the N-O bonds are $f_{\text{NO}} = 11.0 \text{ mdyne/Å}$ (Laane and Ohlsen).

Matasa and Tonca (1973) presented the structure of dinitrogen tetroxide as:



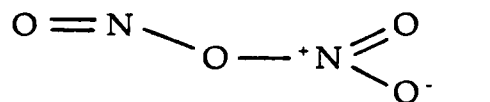
The O-N-O bond angle is 135.4°. The N-O bonds lengths are 1.19 Å (Laane and Ohlsen, 1980). The N-N bond length is 1.78 Å, significantly longer than the ordinary N-N single bond (Jolly, 1964). Interestingly, dinitrogen tetroxide has a planar structure, possibly due to a π bond between the nitrogen atoms (Matasa and Tonca). This structure is known as D_{2h} symmetry (Laane and Ohlsen). This isomer of nitrogen tetroxide may be

referred to as $D_{2h}\text{-N}_2\text{O}_4$. Laane and Ohlsen presented approximate values of the stretching force constants as shown in the diagram:

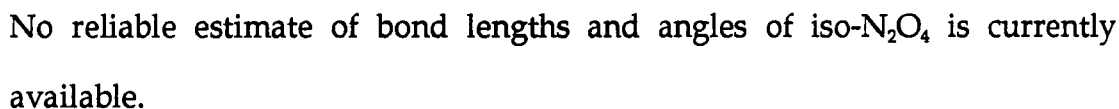


The stretching force constants are $f_{\text{NO}} = 10.2$ mdyne/Å and $f_{\text{NN}} = 0.3$ mdyne/Å. There is a great deal of evidence indicating that $D_{2h}\text{-N}_2\text{O}_4$ corresponds to two NO_2 molecules joined by a weak bond. The large bond distance and small force constant of the N-N bond indicate that the bond is very weak. The similarity of the O-N-O bond angles of $D_{2h}\text{-N}_2\text{O}_4$ and NO_2 , 135.4° and 134° respectively, and the similarity of the lengths of the N-O bonds of $D_{2h}\text{-N}_2\text{O}_4$ and NO_2 , 1.19 Å for both, support the hypothesis that $D_{2h}\text{-N}_2\text{O}_4$ corresponds to two NO_2 molecules held together by a weak N-N linkage.

Moll (1966) and Kameoka and Pigford (1977) indicated that isodinitrogen tetroxide is likely to be an important reaction intermediate for the hydrolysis of four valent nitrogen oxides. Laane and Ohlsen (1980) noted that the structure of $\text{iso-N}_2\text{O}_4$ is now known to be

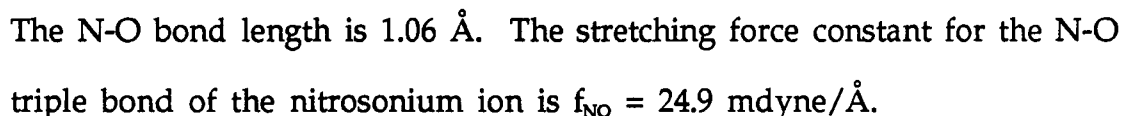


The stretching force constants are estimated to be: $f_{\text{NO}} (\text{nitroso}) = 14.7$ mdyne/Å, $f_{\text{NO}} (\text{nitro}) = 9.5$ mdyne/Å, with other stretching force constants as shown in the diagram:

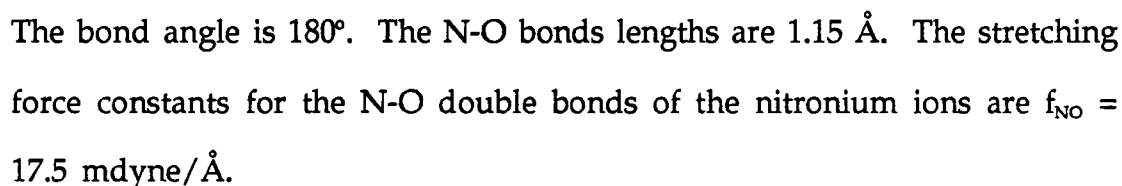


Up to four ions may be important to the absorption of four valent nitrogen oxides. These are the nitrosonium ion, the nitronium ion, the nitrite ion, and the nitrate ion. Laane and Ohlsen (1980) summarized the results available for characterizing these ions.

The nitrosonium ion, NO^+ , has a triple bond. The structure of the nitrosonium ion is



The nitronium ion, NO_2^+ , has a linear structure with two double bonds as shown:



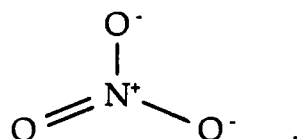
The nitrite ion, NO_2^- has a bent structure similar to nitrogen dioxide.

The bond structure is



The O-N-O bond angle is 115° . The N-O bonds lengths are $1.24 \text{ \AA}$. The stretching force constants of the N-O bonds are $f_{\text{NO}} = 7.6 \text{ mdyne/\AA}$.

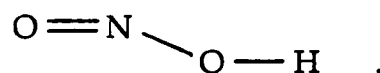
The nitrate ion, NO_3^- , is planar with bond structure as shown:



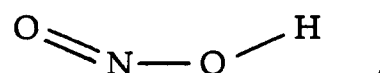
The O-N-O bond angles are 120° . The N-O bond lengths are $1.22 \text{ \AA}$. The stretching force constants of the N-O bonds are $f_{\text{NO}} = 6.0 \text{ mdyne/\AA}$.

Stedman (1979) indicated that a great deal of effort has been made to find evidence for the nitrous-acidium ion, H_2NO_2^+ , but no firm evidence has been found for the existence of sizable concentrations of this ion.

McGraw, Bernitt, and Hisatsune (1966) analyzed the infrared spectra of *cis* and *trans* isomers of nitrous acid. Either isomer exists in the presence of the other. The structure of the *trans* HNO_2 isomer is



The O-N-O bond angle is 118° . The N-O-H bond angle is 104° . The nitroso N-O double bond length is $1.20 \text{ \AA}$. The N-O single bond length is $1.46 \text{ \AA}$. The O-H bond length is $0.96 \text{ \AA}$. The stretching force constants are estimated to be: f_{NO} (nitroso) = $12.0 \text{ mdyne/\AA}$, $f_{\text{NO}} = 3.2 \text{ mdyne/\AA}$, and $f_{\text{OH}} = 7.25 \text{ mdyne/\AA}$. The structure of the *cis* HNO_2 isomer is



The O-N-O bond angle is 114° . The N-O-H bond angle is 104° . The nitroso N-O double bond length is $1.20 \text{ \AA}$. The N-O single bond length is $1.46 \text{ \AA}$.

The O-H bond length is 0.96 Å. The stretching force constants are estimated to be: f_{NO} (nitroso) = 10.7 mdyne/Å, $f_{\text{NO}} = 3.1$ mdyne/Å, and $f_{\text{OH}} = 6.6$ mdyne/Å.

4. DIMERIZATION OF NITROGEN DIOXIDE

Counce (1980) presented a review of the results of experiments conducted to determine the gas phase equilibrium of the dimerization of NO_2 :



Following is a summary of important results applicable to the absorption of N(IV). Bodenstein (1922) and Verhoek and Daniels (1931) conducted experiments to determine the gas phase equilibrium constant for Reaction 1. Hoftyzer and Kwanten (1972) correlated the data of Verhoek and Daniels with considerations of the JANAF Thermochemical Tables (1971) to give the following expression for the equilibrium constant, K_{G1} , (the subscript G1 indicates the gas phase phenomena of Reaction 1):

$$K_{\text{G1}} = 7.07 \times 10^{-10} \exp \{ 6866 / T \} . \quad (2)$$

Carrington and Davidson (1953) studied the rate of dissociation of N_2O_4 in the gas phase. The rate of this reaction is calculated for low partial pressures in Appendix A. The rate of this reaction is sufficiently rapid that equilibrium may be assumed in absorption apparatus.

Grätzel, Henglein, Little, and Beck (1969) and Treinin and Hayon (1970) studied the liquid phase dimerization of nitrogen dioxide, Reaction 1,

using pulse radiolysis experiments. Levine (1978) summarizes pulse radiolysis as an experimental technique where a very brief pulse of high energy electrons (or x-rays) is passed through a sample, ionizing some of the molecules; light absorption is used to follow the reactions of the ionized species. Grätzel et al. and Treinin and Hayon exposed oxygen free samples of nitrite ions and nitrous oxide to brief pulses of high energy electrons, 1 μ s by Grätzel et al., 30 ns by Treinin and Hayon, creating nitrogen dioxide in solution as follows:



The decay of NO_2 took place in two distinct stages: a microsecond stage attributable to the dimerization of NO_2 ; and a millisecond stage attributable to the hydrolysis of NO_2 or N_2O_4 in conjunction with Reaction 1. The measured values for the equilibrium constant for Reaction 1 are: $K_{A1} = (6.54 \pm 0.65) \times 10^4 \text{ m}^3/\text{kgmol}$ at 20°C (Grätzel et al.); and $K_{A1} = (7.7 \pm 3.4) \times 10^4 \text{ m}^3/\text{kgmol}$ at 25°C (Treinin and Hayon) (the subscript A1 indicates the aqueous phase phenomena of Reaction 1). Grätzel et al. determined the second order reaction rate constant for the dimerization of NO_2 to be $6.5 \times 10^7 \text{ m}^3/\text{kgmol}\cdot\text{s}$. Neither group of researchers attempted to distinguish between the iso- N_2O_4 and D_{2h}- N_2O_4 isomers of N_2O_4 .

Bensasson, Land, and Truscott (1983) indicate that both the pulsed sources of radiation and the detection systems employed have improved since Grätzel et al. (1969) and Treinin and Hayon (1970) used pulse

radiolysis to explore the aqueous phase equilibria of Reaction 1. Pulsed lasers are available which allow 1 picosecond (10^{-12} s) time resolutions for flash photolysis. Linear accelerators or van de Graaf generators are commonly used to deliver pulses of fast electrons over time intervals as brief as a few nanoseconds (10^{-9} s). A new series of flash photolysis and pulse radiolysis experiments using modern equipment designed to determine the aqueous phase equilibrium of Reaction 1 would be a valuable addition to the literature currently available for the $\text{NO}_x\text{-H}_2\text{O-HNO}_x$ system. Equilibrium concentrations of NO_2 and N_2O_4 in the gas and liquid phases are shown in Appendix B for low partial pressures of N(IV).

5. SUMMARY OF THE RESULTS OF THE PENETRATION AND FILM THEORIES AS THEY MAY BE APPLIED TO THE REACTIVE DISSOLUTION OF N(IV)

Danckwerts (1970) presents the results and some derivations thereof of the application of the penetration theory and the film theory to the reactions of gases and liquids. Some of these results have been used to model the experimental results of the reactive dissolution of N(IV) in aqueous solutions. One must be familiar with these results to be able to make rational conclusions regarding the validity of proposed values of parameters affecting the reactive dissolution of N(IV) in aqueous solutions.

The penetration theory has been applied to the absorption of a reactive gas into a quiescent liquid for a first order reaction. If the

absorbing species is B, and the reaction of B is first order and irreversible in the aqueous phase,



then the rate of reaction is:

$$R_{A5} = k_{A5} c_B \quad . \quad (6)$$

Assuming Henry's Law applies to the solute at the gas-liquid interface,

$$c_{B,i} = H_B p_{B,i} \quad , \quad (7)$$

then the quantity of B absorbed per unit area for contact time, t , may be approximated within 3% by:

$$Q_B = p_{B,i} H_B \sqrt{D_B k_{A5}} (t + 0.5 k_{A5}^{-1}) \quad , \quad (8)$$

if $k_{A5} t > 2$. If $k_{A5} t > 10$ Equation 8 simplifies to

$$Q_B = p_{B,i} H_B \sqrt{D_B k_{A5}} t \quad , \quad (9)$$

within 5% error bounds. Experiments conducted such that $2 < k_{A5} t < 10$ can be analyzed for $H_B \sqrt{k_{A5}}$ and $H_B / \sqrt{k_{A5}}$ separately assuming D_B can be accurately estimated. Diffusivities may be estimated by using the correlation of Wilke and Chang (1955).

The film theory has been applied to the absorption of a reactive gas into an agitated liquid for a fast first order reaction. If the absorbing species is B, and the reaction of B is first order and irreversible in the aqueous phase as shown by Reaction 5, then the absorptive flux of B is:

$$N_B = p_{B,i} H_B \sqrt{D_B k_{A5}} \quad . \quad (10)$$

The reaction qualifies as a fast first order reaction if the first order reaction number, $M_{(1)}$, defined as:

$$M_{(1)} = D_B k_{A5} k_1^{-2} \quad , \quad (11)$$

is greater than nine. These results for first order reactions also apply to pseudo-first order reactions such as



where the rate of reaction is:

$$R_{A12} = k_{A12} c_B \quad . \quad (13)$$

The applicability of these expressions for fast pseudo-first order reactions is subject to the same limitations as for the fast first order reactions.

The film theory has been applied to the absorption of a reactive gas into an agitated liquid for a fast second order reaction. If the absorbing species is A, and the reaction of A is second order and irreversible in the aqueous phase,



then the reaction rate expression is:

$$R_{A14} = k_{A14} c_A^2 \quad . \quad (15)$$

The fast second order reaction enhanced absorptive flux of A is:

$$N_A = p_{A,i}^{1.5} H_A^{1.5} \sqrt{4 D_A k_{A14} / 3} \quad . \quad (16)$$

The reaction qualifies as a fast second order reaction if the second order reaction number, $M_{(2)}$, defined as:

$$M_{(2)} = 4 D_A k_{A14} c_A k_1^{-2} / 3 \quad , \quad (17)$$

is greater than nine.

Lee and Schwartz (1981) evaluated data of the reactive dissolution of N(IV) by modeling the data as a slow second order reaction. Lee and

Schwartz show that if Reaction 14 is taken as the second order reaction, the rate of reaction can be modeled as:

$$R_{A14} = k_1 a H_A p_{A,i} / 2 + k_1^2 a^2 [1 - \sqrt{ (1 + 8 k_1 a k_{A14} H_A p_{A,i}) }] / (8 k_{A14}) . \quad (18)$$

The slow second order reaction regime is expected to apply when the rate of convective mixing is of the same order of magnitude as the rate of the chemical reaction:

$$(k_1 a)^{-1} \approx (2 k_{A14} c_{A,b})^{-1} . \quad (19)$$

6. SUMMARY OF EXPERIMENTAL DETERMINATIONS OF THE RATE OF HYDROLYSIS OF FOUR VALENT NITROGEN OXIDES AND RELATED SOLUBILITIES

Schwartz and White (1983) presented a comprehensive literature review of the literature regarding the kinetics and phase equilibria of concern to the hydrolysis of N(IV). Schwartz and White analyzed a vast array of results from different experiments for consistency of model application, validity of experimental technique, and consistency of results as compared to results of other researchers. Schwartz and White used a graphical presentation to select recommended values for parameters describing reactive dissolution of NO_2 and N_2O_4 in dilute aqueous solutions. These parameters are solubilities of NO_2 and N_2O_4 , an aqueous phase equilibrium constant for Reaction 1, and a reaction rate constant for the

hydrolysis of N(IV). These recommended values are presented after a discussion of the applicable chemistry of this system.

Counce (1980) presented a review from a historical perspective for the experimental studies giving insight to the reactive dissolution of NO_2 and N_2O_4 in dilute aqueous solutions. The literature review by Counce, in conjunction with that by Schwartz and White (1983), indicate certain aspects of the $\text{NO}_x\text{-H}_2\text{O-HNO}_x$ system which might now be considered "common knowledge" to chemical engineers and chemists with experience with this system. A summary of these aspects follows.

Reaction 1, the dimerization of NO_2 , can be expected to be at equilibrium everywhere in the gas phase at ambient temperatures. This reaction has been studied in the liquid phase by Grätzel et al. (1969) and Treinin and Hayon (1970) but the results indicating that the reaction is sufficiently rapid to be considered at equilibrium had not been incorporated in any models in the literature prior to 1983.

The hydrolysis of four valent nitrogen oxides has been considered to follow either one of two possible routes by most researchers:

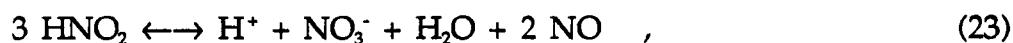


Since nitrous acid is a weak acid and nitric acid is a strong acid, if the absorbing solvent is neutral or acidic, nitrous acid exists mainly in its undissociated form. Nitrous acid decomposes in acidic solutions to form nitric oxide, nitrogen dioxide, and water:

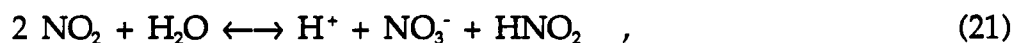


The earliest studies of the rate of hydrolysis of N(IV) are the result of studies of the decomposition of nitrous acid.

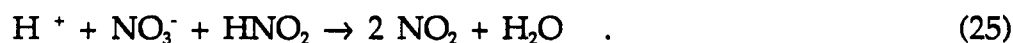
Abel and Schmid (1928) recognized the decomposition of nitrous acid in aqueous solutions,



to be the overall reaction resulting from the reaction sequence:



where the hydrolysis of N(IV) is the rate limiting step. The studies were conducted in a mixed phase reactor which maintained equilibrium between the gas and liquid phases. Counce (1980) reviewed the experiments of Abel and Schmid in detail. Abel, Schmid, Babad (1928) and Schmid and Bähr (1964) conducted phase mixed studies of the reverse of Reaction 21:



Schwartz and White (1983) used the modern value for the mixed phase equilibrium constant between aqueous nitrous acid and gaseous nitrogen dioxide and nitric oxide to determine the rate constants for hydrolysis of N(IV) resulting from the data of Abel and Schmid , the data of Abel et al., and the data of Schmid and Bähr. Since NO_2 and N_2O_4 can be assumed to have been in equilibrium in the gas phase for these experiments the rate constant can be expressed in terms of either NO_2 or N_2O_4 as

$$R_{20} = k_{M20} p_B \quad , \text{ where } B = \text{N}_2\text{O}_4 \text{ or} \quad (26)$$

$$R_{21} = k_{M21} p_A^2, \text{ where } A = \text{NO}_2 \quad (27)$$

The subscript M20 refers to the mixed phase phenomena of Reaction 20. The values of these rate constants are presented in Table 2. Either NO_2 or N_2O_4 or both NO_2 and N_2O_4 may be the reacting species.

Kramers, Blind, and Snoeck (1961), Bartholomé and Gerstacker (1961), and Hoftyzer and Kwanten (1972) studied the absorption of N_2O_4 in laminar water jets. Wendel and Pigford (1958) studied the absorption of N_2O_4 in a wetted wall column. The results of these studies were subjected to analysis by the penetration theory as the reactive dissolution of N_2O_4 by a pseudo-first order reaction, Reaction 20. Kramers et al. studied the absorption of N_2O_4 at 20°C and 30°C. Bartholomé and Gerstacker, Hoftyzer and Kwanten, and Wendel and Pigford studied the absorption of N_2O_4 at 25°C. The results of these studies are shown in Table 3. Many other researchers have used the film theory to model studies of the reactive dissolution of N_2O_4 by Reaction 20 at 25°C. These experiments were reviewed by Schwartz and White (1983). Dekker, Snoeck, and Kramers (1959), Chilton and Knell (1972), and Weisweiler and Deiss (1981) used wetted wall columns. Corriveau and Pigford (1971) and Kameoka and Pigford (1977) used wetted sphere columns. The results of these experiments are shown in Table 4. The experimental values of $H_B \sqrt{D_B k_{A20}}$ resulting from penetration theory analysis of laminar jet apparatus are compared to values resulting from film theory analysis of wetted wall and wetted sphere apparatus for experiments conducted at 25°C in Table 5.

Table 2 Mixed Phase Experimental Determinations of the Rate of Hydrolysis of N(IV) at 25°C

Source	k_{M20} (M/atm-s)	k_{M21} (M/atm ² -s)
Abel and Schmid ^a	5.92×10^2	4.06×10^3
Abel et al. ^b	6.20×10^2	4.25×10^3
Schmid and Bähr ^c	6.44×10^2 ^d	4.42×10^3 ^d

^a Abel, E., and H. Schmid, "Kinetics of Nitrous Acid. III. Kinetics of Nitrous Acid Decomposition," *Z. Phys. Chem.*, **134**, 279 (1928).

^b Abel, E., Schmid, H., and S. Babad, "Kinetics of Nitrous Acid. V. Kinetics of the Formation of Nitrous Acid from Nitric Acid and Nitric Oxide," *Z. Phys. Chem.*, **136**, 135 (1928).

^c Schmid, G., and G. Bähr, "Formation of HNO₂ from NO and HNO₃ at High Acid Strength," *Z. Physik. Chem.*, **41**, 8 (1964).

^d Data taken at 20°C. Corrected to 25°C by Schwartz and White (1983) ^e.

^e Schwartz, S. E., and W. H. White, "Kinetics of Reactive Dissolution of Nitrogen Oxides into Aqueous Solution," *Adv. Environ. Sci. Technol.*, Vol. 12, S. E. Schwartz, Ed., John Wiley & Sons, New York, 1-116 (1983).

Table 3 Penetration Theory Results of Experimental Determinations of $H_B \sqrt{k_{A20}}$ and $H_B / \sqrt{k_{A20}}$

Source	p_A (10^{-2} atm)	$H_B \sqrt{k_{A20}}$ (M/atm-s ^{0.5})	$H_B / \sqrt{k_{A20}}$ (M-s ^{0.5} /atm)
Kramers et al. ^{a,e}	4 - 14	22.0	8.8×10^{-2}
Wendel and Pigford ^{b,f}	3 - 9	16.2	5.6×10^{-2}
Bartholomé and Gerstacker ^{c,f}	10	22	9.6×10^{-2}
Hoftyzer and Kwanten ^{d,f}	4 - 40	25	3.7×10^{-2}
Kramers et al. ^{a,g}	4 - 14	24.2	6.8×10^{-2}

^a Kramers, H., M. P. P. Blind, and E. Snoeck, "Absorption of Nitrogen Tetroxide by Water Jets," *Chem. Eng. Sci.*, **14**, 115 (1961).

^b Wendel, M. M., and R. L. Pigford, "Kinetics of Nitrogen Tetroxide Absorption in Water," *Am. Inst. Chem. Eng. J.*, **4**, 249 (1958).

^c Bartholomé, E., and H. Gerstacker, "The Penetration Theory and its Application to Kinetic Investigations of Physical and Chemical Gas Absorption into Liquids," *Alta Tech. Chim., Accad. Naz. dei Lincei, Rome*, 177 (1961).

^d Hoftyzer, P. J., and F. J. G. Kwanten, "Absorption of Nitrous Gases," *Gas Purification Processes*, G. Nonhebel, Ed., Newnes-Butterworths, London, 164-167 (1972).

^e Data taken at 20°C. Diffusivity estimated at 1.23×10^{-9} m²/s.

^f Data taken at 25°C. Diffusivity estimated at 1.40×10^{-9} m²/s.

^g Data taken at 30°C. Diffusivity estimated at 1.59×10^{-9} m²/s.

Table 4 Film Theory Results of Experimental Determinations of $H_B \sqrt{D_B} k_{A20}$ at 25°C

Source	p_A (10^{-2} atm)	$H_B \sqrt{D_B} k_{A20}$ (kgmol/m ² -atm-s)
Dekker et al. (1959) ^a	1.6 - 7.0	1.1×10^{-3}
Corriveau and Pigford ^b	1.0 - 2.1	4.9×10^{-4}
Chilton and Knell ^c	1.4 - 3.6	1.4×10^{-3}
Kameoka and Pigford ^d	0.7 - 1.3	6.8×10^{-4}
Weisweiler and Deiss ^e	24	4.9×10^{-4}

^a Dekker, W. A., Snoeck, E., and H. Kramers, "The Rate of Absorption of NO₂ in Water," *Chem. Eng. Sci.*, **11**, 61 (1959).

^b Corriveau, C. E. Jr., and R. L. Pigford, "Absorption of N₂O₄ into Water," University of California, Lawrence Radiation Laboratory Report, UCRL-20479 (1971).

^c Chilton, T. H., and E. W. Knell, "The absorption of Nitrogen Oxides, Part 2: Absorption of Nitrogen Peroxide in Alkaline," *Am. Inst. Chem. Eng., Pacific Chemical Engineering Conference*, 75-81 (1972).

^d Kameoka, Y., and R. L. Pigford, "Absorption of Nitrogen Dioxide into Water, Sulfuric Acid, Sodium Hydroxide, and Alkaline Sodium Sulfite," *Ind. Eng. Chem. Fundam.*, **16**, 163 (1977).

^e Weisweiler, W., and K.-H. Deiss, "Measurement of the Absorption Rate of Nitrogen Dioxide in Water in a Falling Film Absorber," *Ger. Chem. Eng.*, **4**, 79 (1981).

Table 5 Comparison of Results of Experimental Determinations of $H_B \sqrt{D_B} k_{A20}$ at 25°C

Source	P_A (10^{-2} atm)	$H_B \sqrt{D_B} k_{A20}$ (kgmol/m ² -atm-s)
Wendel and Pigford ^a	3.0 - 9.0	6.0×10^{-4}
Dekker et al. ^b	1.6 - 7.0	1.1×10^{-3}
Bartholomé and Gerstacker ^c	10	8.2×10^{-4}
Corriveau and Pigford ^d	1.0 - 2.1	4.9×10^{-4}
Chilton and Knell ^e	1.4 - 3.6	1.4×10^{-3}
Hoftyzer and Kwanten ^f	4.0 - 40	9.4×10^{-4}
Kameoka and Pigford ^g	0.7 - 1.3	6.8×10^{-4}
Weisweiler and Deiss ^h	24	4.9×10^{-4}

^a Wendel, M. M., and R. L. Pigford, "Kinetics of Nitrogen Tetroxide Absorption in Water," *Am. Inst. Chem. Eng. J.*, 4, 249 (1958).

^b Dekker, W. A., Snoeck, E., and H. Kramers, "The Rate of Absorption of NO₂ in Water," *Chem. Eng. Sci.*, 11, 61 (1959).

^c Bartholomé, E., and H. Gerstacker, "The Penetration Theory and its Application to Kinetic Investigations of Physical and Chemical Gas Absorption into Liquids," *Alta Tech. Chim., Accad. Naz. dei Lincei, Rome*, 177 (1961).

^d Corriveau, C. E. Jr., and R. L. Pigford, "Absorption of N₂O₄ into Water," University of California, Lawrence Radiation Laboratory Report, UCRL-20479 (1971).

^e Chilton, T. H., and E. W. Knell, "The absorption of Nitrogen Oxides, Part 2: Absorption of Nitrogen Peroxide in Alkaline," *Am. Inst. Chem. Eng., Pacific Chemical Engineering Conference*, 75-81 (1972).

^f Hoftyzer, P. J., and F. J. G. Kwanten, "Absorption of Nitrous Gases," *Gas Purification Processes*, G. Nonhebel, Ed., Newnes-Butterworths, London, 164-187 (1972).

^g Kameoka, Y., and R. L. Pigford, "Absorption of Nitrogen Dioxide into Water, Sulfuric Acid, Sodium Hydroxide, and Alkaline Sodium Sulfite," *Ind. Eng. Chem. Fundam.*, 16, 163 (1977).

^h Weisweiler, W., and K.-H. Deiss, "Measurement of the Absorption Rate of Nitrogen Dioxide in Water in a Falling Film Absorber," *Ger. Chem. Eng.*, 4, 79 (1981).

Moll (1966) studied the hydrolysis of N(IV) using a rapid-mixing flow technique. Liquid N_2O_4 was injected into a turbulent water stream. The extent of reaction was determined by the changes of the temperature of the reacting stream. Moll attributed the increase in temperature as being due to Reaction 20. Schwartz and White (1983) indicate that Moll's analysis is subject to a systematic error since the work of Grätzel et al. (1969) indicates that the experiment should be analyzed as a mixed order reaction (the derivation of this result is presented in the following paragraph). Schwartz and White reexamined Moll's data using only the initial data points, giving a reaction rate of $k_{A20} = 400 \text{ s}^{-1}$ if Reaction 20 is responsible for the hydrolysis or $k_{A21} = 2.6 \times 10^7 \text{ m}^3/\text{kgmol}\cdot\text{s}$ if Reaction 21 is responsible for the hydrolysis.

Grätzel et al. (1969) studied the hydrolysis of N(IV) in aqueous solutions using pulse radiolysis. Their results concerning the dimerization of NO_2 and the experimental technique used have already been discussed in this review. Grätzel et al. assumed the dimerization of NO_2 was rapid enough compared to the hydrolysis of N(IV) to be considered at equilibrium so

$$[\text{N}_2\text{O}_4] = K_{A1} [\text{NO}_2]^2 \quad . \quad (28)$$

In the nomenclature used in this report Equation 28 is expressed as:

$$c_B = K_{A1} c_A^2 \quad . \quad (29)$$

The disappearance of N(IV) species, where

$$[\text{N(IV)}] = [\text{NO}_2] + 2 [\text{N}_2\text{O}_4] \quad , \quad (30)$$

by hydrolysis can be expressed as:

$$- dc_{N(IV)} / dt = 2 k_{A20} c_B + 2 k_{A21} c_A^2 \quad ; \text{ or} \quad (31)$$

$$- dc_{N(IV)} / dt = 2 k_{A20} K_{A1} c_A^2 + 2 k_{A21} c_A^2 \quad . \quad (32)$$

Since

$$c_{N(IV)} = c_A + 2 c_B \quad (33)$$

then

$$c_{N(IV)} = c_A + 2 K_{A1} c_A^2 \quad (34)$$

and

$$dc_{N(IV)} / dt = (1 + 4 K_{A1} c_A) dc_A / dt \quad . \quad (35)$$

Equation 32 can be rewritten as

$$- dc_A / dt = 2 (k_{A20} K_{A1} + k_{A21}) c_A^2 / (1 + 4 K_{A1} c_A) \quad . \quad (36)$$

Equation 36 exhibits either first or second order kinetics in extremes of concentration. Grätzel et al. used a mixed order kinetic equation to evaluate the results of pulse radiolysis experiments for the rate of hydrolysis of N(IV). Grätzel et al. determined the value of the rate constant $k_{A20} K_{A1} + k_{A21} = 6.5 \times 10^7 \text{ m}^3/\text{kgmol}\cdot\text{s}$ at 20°C, roughly 7 times smaller than the forward reaction rate of the dimerization of NO₂, thereby fulfilling the requirement that the use of Equation 36 was consistent with the assumption that the dimerization of NO₂ reaction was at equilibrium.

These results have important implications to engineers interested in the reactive dissolution of N(IV) in aqueous solutions. None of the experiments reviewed determined which four valent nitrogen oxide species is the reacting species for the hydrolysis. Schwartz and White (1983) point

out that if the dimerization of NO_2 , Reaction 1, is at equilibrium then the two reaction mechanisms for the hydrolysis of N(IV), Reaction 20 and Reaction 21, are indistinguishable from each other. In light of this result the hydrolysis reaction may best be represented as:



The forward reaction rate of Reaction 37 can be expressed in terms of NO_2 or N_2O_4 as:

$$R_{A37} = k_{A37} c_A^2 = k_{A37} c_B / K_{A1} \quad . \quad (38)$$

Experimental values of the rate of hydrolysis of N(IV) that have been expressed in terms of Reaction 20 or Reaction 21 can be expressed more accurately in terms of Reaction 37 where

$$k_{A37} = k_{A20} K_{A1} = k_{A21} \quad . \quad (39)$$

The aqueous phase equilibrium constant for Reaction 1 is related to the gas phase equilibrium constant for Reaction 1 by the solubilities of NO_2 and N_2O_4 as:

$$K_{A1} = K_{G1} H_B / H_A^2 \quad . \quad (40)$$

Andrew and Hanson (1961), Komiyama and Inoue (1980), and Lee and Schwartz (1981) published experimental values of the Henry's Law constant of NO_2 . Andrew and Hanson conducted their experiments before the aqueous phase equilibria of Reaction 1 was established. Andrew and Hanson modeled the reactive dissolution of N(IV) as a combination of the fast pseudo-first order hydrolysis of N_2O_4 combined with physical absorption of NO_2 . Andrew and Hanson presented the value of $H_A = 0.041 \text{ kgmol/m}^3$ -

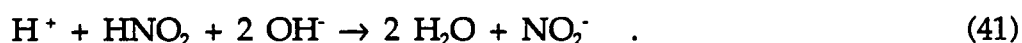
atm at 25°C. This value is not acceptable in light of the results of Grätzel et al. (1969).

Komiyama and Inoue (1980) modeled the reactive dissolution of N(IV) as being controlled by three distinct mechanisms: the fast pseudo-first order hydrolysis of N_2O_4 controlling the absorption rate at high partial pressures of NO_2 ; the fast pseudo-second order hydrolysis of NO_2 controlling the absorption rate at intermediate partial pressures of NO_2 ; and physical absorption of NO_2 controlling the absorption rate at low partial pressures of NO_2 . Komiyama and Inoue's modeling approach was relatively naive, they made no attempt to explain how one of their models might affect the accuracy of predictions of another of their models. Apparently they believed that the proposed pseudo-first order hydrolysis of N_2O_4 and the proposed pseudo-second order hydrolysis of NO_2 would not have cumulative effects on the rate of absorption of N(IV). Schwartz and White (1983) indicated that N_2O_4 accounts for a substantial proportion of the N(IV) present at the gas-liquid interface in this study in the partial pressure region where Komiyama and Inoue indicated that the fast pseudo-second order hydrolysis of NO_2 controlled the absorption rate of N(IV). Komiyama and Inoue's value for the Henry's Law constant of NO_2 was $H_A = 0.0235 \text{ kgmol/m}^3\text{-atm}$ at 15°C. This value was determined from the data in the region where the absorption was first order with respect to NO_2 , one data point each for the partial pressures of NO_2 of $1.2 \times 10^{-5} \text{ atm.}$ and $2.4 \times 10^{-5} \text{ atm.}$ Due to lack of degrees of freedom and the relative naivety of Komiyama and

Inoue's model their value for the Henry's Law constant for NO_2 should be regarded with suspicion.

Lee and Schwartz (1981) studied the reactive dissolution of N(IV) in a bubbling absorber at low to intermediate NO_2 partial pressures, $10^{-7} \text{ atm.} < p_A < 10^{-3} \text{ atm.}$ Lee and Schwartz modeled the absorption of N(IV) at partial pressures below 10^{-5} atm. as being controlled by the slow second order reaction model with NO_2 as the only absorbing species. Lee and Schwartz indicate that $H_A = 0.007 \text{ kgmol/m}^3\text{-atm}$ and $k_{A37} = 1.0 \times 10^8 \text{ m}^3/\text{kgmol-s}$ at 22°C . The justification of the use of the slow reaction model at these partial pressures should be reexamined in light of the liquid phase equilibrium between NO_2 and N_2O_4 , however this value of the Henry's Law constant of NO_2 is probably the best experimental value currently available.

If the absorbing solvent is basic, both nitrous acid and the hydronium ion are neutralized:



This prevents the reverse reaction of Reaction 37. Chambers and Sherwood (1937) studied the reactive dissolution of N(IV) in 2.7% to 34.1% sodium hydroxide solutions in both wetted wall absorbers and batch stirred absorbers. Chambers and Sherwood observed a decrease in dissolution rate with increasing sodium hydroxide concentration. Chambers and Sherwood's data for the absorption of N(IV) into water and sodium hydroxide in a wetted wall column can be analyzed to show the effect of sodium hydroxide concentration on the rate of reactive dissolution of N(IV) ; these data are

shown in Table 6; the analysis is shown in Chapter V. Chilton and Knell (1972) studied the reactive dissolution of N(IV) in 1.0 N and 5.7 N sodium hydroxide solutions in a wetted wall absorber. Chilton and Knell observed a decrease in dissolution rate with increasing sodium hydroxide. This decrease was attributed to smaller activities of water and smaller solubilities of N_2O_4 in sodium hydroxide solutions. Kameoka and Pigford (1977) observed a 7% increase in absorption rate of N(IV) in 0.2 N sodium hydroxide solution as compared to the dissolution rate in water using a string of spheres absorber. Kameoka and Pigford proposed a reaction between N_2O_4 and OH^- in addition to the hydrolysis, Reaction 37:



The rate of this reaction is

$$R_{A42} = k_{A42} C_{OH} C_B \quad , \quad (43)$$

where $k_{A42} = 147 \text{ m}^3/\text{kgmol}(\text{OH}^-)\text{-s}$. Since this reaction rate constant is based on a single hydroxide ion concentration it should be regarded only as a possibility, not as a proven fact. Kameoka and Pigford ignored the effects of electrolytes on the solubility of gases in aqueous solutions, assumed N_2O_4 reacted with water as a fast pseudo first order reaction by Reaction 20, and assumed $k_{A20} = 194 \text{ s}^{-1}$ to determine the value of k_{A42} given above.

Some electrolytes affect the solubility of gases in aqueous solutions. Danckwerts (1970) summarized the literature regarding solubility in electrolytic aqueous solutions indicating data had been correlated to the empirical formula

Table 6 Experimental Data from Chambers and Sherwood (1937)^a for the Absorption of N(IV) into Sodium Hydroxide Solutions in a Wetted Wall Column at 25°C

Run	[NaOH] ^b (kgmol/m ³)	$p_{N(IV),M}$ (atm)	Reynolds Number	$N_{N(IV),ave}$ (kgmol/m ² -s)
53	5.39	0.0522	4700	7.7×10^{-6}
54	5.39	0.0695	2900	5.5×10^{-6}
55	5.39	0.0536	3920	6.3×10^{-6}
56	0.77	0.0492	3950	11.3×10^{-6}
57	0.77	0.0486	4900	11.8×10^{-6}
58	0.77	0.0560	2550	9.7×10^{-6}
59	0.77	0.0478	3100	10.0×10^{-6}
60	0.77	0.0455	3850	12.1×10^{-6}
61	5.32	0.0332	2520	3.9×10^{-6}
62	5.32	0.0496	3460	5.5×10^{-6}
63	0.74	0.0499	4300	11.6×10^{-6}
64	0.74	0.0528	2860	11.1×10^{-6}
65	0.71	0.0569	1700	6.8×10^{-6}
66	0.71	0.0417	1450	5.0×10^{-6}
67	0.69	0.0538	1000	3.9×10^{-6}
68	5.35	0.0479	1450	3.2×10^{-6}
69	5.35	0.0588	1750	3.7×10^{-6}
70	2.86	0.0509	3000	7.4×10^{-6}

^a Chambers, F. S. Jr., and T. K. Sherwood, "Absorption of Nitrogen Dioxide by Aqueous Solutions," *Ind. Eng. Chem.*, 29, 1415 (1937).

^b Data for NaOH concentration were given as weight percent. Molarity values were interpolated using the CRC Handbook of Chemistry and Physics (1962)^c

^c *CRC Handbook of Chemistry and Physics*, 44th ed., C. D. Hodgman, Ed., Chemical Rubber Publishing Co., Cleveland, OH, 2072 (1962).

$$H_i = H_i^\circ 10^{-hI} \quad , \quad (44)$$

where I is the ionic strength of the electrolytic solution and

$$h = h_s + h_v + h_G \quad . \quad (45)$$

No literature value is available for h_G , the salting coefficient, for N_2O_4 but the values available for salting coefficients at 25°C vary from -0.103 m³/kgmol to 0.022 m³/kgmol. For sodium hydroxide solutions $h_s = 0.091$ m³/kgmol(Na⁺), $h_v = 0.066$ m³/kgmol(OH⁻). The standard error in using this expression is (2 I)%. Wilke and Chang (1955) indicated that liquid phase diffusion coefficients are inversely proportional to viscosity. The viscosity of sodium hydroxide solutions (CRC Handbook of Chemistry and Physics, 1962) at 25°C was fit to a third degree polynomial so the relationship between the diffusivity of N_2O_4 and sodium hydroxide concentration is

$$D_B = D_B^\circ / (1 + 0.264 c_{OH} - 0.0173 c_{OH}^2 + 0.0117 c_{OH}^3) \quad . \quad (46)$$

Considering the effect of electrolytes on the solubility of N_2O_4 , the effect of viscosity on diffusion coefficients, and the possibility of Reaction 42, if the reactive dissolution of N(IV) is controlled by the fast pseudo-first order hydrolysis of N_2O_4 , film theory model the flux of N(IV) into water or aqueous sodium hydroxide solutions should be modeled as:

$$N_{N(IV)} = 2 p_{B,i} \{ D_B^\circ [(k_{A37} / K_{A1}) + k_{A42} c_{OH}] / (1 + 0.264 c_{OH} - 0.0173 c_{OH}^2 + 0.0117 c_{OH}^3) \}^{0.5} H_B^\circ 10^{-hI} \quad . \quad (47)$$

Dividing Equation 47 by the film theory model for the flux of N(IV) into water controlled by the dissolution and fast pseudo-first order hydrolysis of

N_2O_4 gives an equation for the enhancement factor modifier, E_{OH} , for the reactive dissolution of N(IV) into aqueous solutions of NaOH as:

$$E_{\text{OH}} = \{ [1 + (k_{\text{A42}} K_{\text{A1}} / k_{\text{A37}}) c_{\text{OH}}] / (1 + 0.264 c_{\text{OH}} - 0.0173 c_{\text{OH}}^2 + 0.0117 c_{\text{OH}}^3) \}^{0.5} 10^{-\text{pH}} \quad (48)$$

The viscosity effects on the diffusivity result from curve fitting data reported at 25°C. Equation 48 applies at 25°C but may not be very sensitive to temperature since the reaction and viscosity effects are ratios; the change in the ratio of the rates of Reactions 37 and 42 and the change in the ratio of the viscosity of aqueous sodium hydroxide and water may be only weakly dependent on temperature.

Peters and Holman (1955) studied the reactive dissolution of N(IV) into water, 6.1 N NaOH solutions, and 4.9 N NaCl solutions in a wetted wall column at 29°C to 56°C. At 31°C the removal efficiency of N(IV) into 6.1 N NaOH was within the experimental scatter for data for the removal efficiency of N(IV) into water. At 34°C the removal efficiency of N(IV) into 4.9 N NaCl was less than half the removal efficiency of N(IV) into water. Peters and Holman's data for the removal efficiency of N(IV) into 4.9 N NaCl and water may be analyzed to estimate a value of h_c for N_2O_4 ; these data are presented in Table 7; the analysis is shown in Chapter V.

7. DETERMINATION OF THE BEST AVAILABLE VALUES FOR THE RATE OF HYDROLYSIS OF N(IV) AND THE SOLUBILITIES OF NO_2 AND N_2O_4

Table 7 Experimental Data from Peters and Holman (1955)^a for the Absorption of N(IV) into 4.9 N Sodium Chloride^b Solution and Water in a Wetted Wall Column at 34°C

Run	Solution	$P_{N(IV),M}$ (atm)	Reynolds Number	$N_{N(IV),ave}$ (kgmol/m ² -s)
1	water	0.0425	1950	7.4×10^{-6}
21	4.9 M NaCl	0.0455	1950	3.1×10^{-6}

^a Peters, M. S., and J. L. Holman, "Vapor- and Liquid-Phase Reactions between Nitrogen Dioxide and Water," *Ind. Eng. Chem.*, **47**, 2536 (1955).

^b Data for NaCl concentration were given as weight percent. Molarity values were interpolated using the CRC Handbook of Chemistry and Physics (1962)^c

^c CRC Handbook of Chemistry and Physics, 44th ed., C. D. Hodgman, Ed., Chemical Rubber Publishing Co., Cleveland, OH, 2070 (1962).

The preceding section introduced the results of mixed phase studies of the hydrolysis of N(IV), penetration theory based analyses of the reactive dissolution of N(IV), film theory based analyses of the reactive dissolution of N(IV), a pulse radiolysis study of the rate of hydrolysis of N(IV), a mixing tube study of the rate of hydrolysis of N(IV), and an analysis of data collected in the slow reaction regime for the absorption and reaction of NO₂. Schwartz and White (1983) introduced a technique by which the results of all these different studies may be compared so one could determine the best available values for: k_{A37} , the second order reaction rate constant for the hydrolysis of NO₂ in equilibrium with N₂O₄; H_B , the Henry's Law constant for N₂O₄; and H_A , the Henry's Law constant for NO₂.

As is indicated in Table 2, the results of mixed phase kinetic studies of the hydrolysis of N(IV) may be expressed by a mixed phase kinetic constant based on the partial pressure of N₂O₄, k_{M20} . These results may be expressed in terms of the homogeneous hydrolysis reaction, Reaction 37, and the Henry's Law constant for N₂O₄ by using the following relationship:

$$k_{M20} = k_{A37} H_B / K_{A1} \quad . \quad (49)$$

Table 2 presents three different values for k_{M20} reported by different researchers. These values are represented by the symbol #. Equating the right hand side of Equation 49 with any experimental result gives the following equation:

$$k_{A37} H_B / K_{A1} = \# \quad . \quad (50)$$

Taking the logarithm of both sides of Equation 50 and rearranging gives:

$$\log[H_B] = - \log[k_{A37}] + \log[\#] + \log[K_{A1}] \quad . \quad (51)$$

Clearly, plotting H_B vs. k_{A37} on a log - log graph gives a discrete straight line of slope -1 for each experimental value of k_{M20} provided a consistent value of K_{A1} is used. The equilibrium constant for Reaction 1, K_{A1} , chosen for this comparison is the value reported by Grätzel et al. (1969), $K_{A1} = 6.54 \times 10^4 \text{ m}^3/\text{kgmol}$. A comparison of the results of the three mixed phase hydrolysis experiments presented in Table 2 is shown in Figure 1.

The results of penetration theory analyses of data for the reactive dissolution of N(IV) accompanied by the fast pseudo first order hydrolysis of N_2O_4 by Reaction 20 were presented in Table 3. The listed reaction rate constant k_{A20} is equivalent to k_{A37} / K_{A1} . The penetration theory analyses resulted in experimental values of $H_B (k_{A37} / K_{A1})^{0.5}$ and $H_B (K_{A1} / k_{A37})^{0.5}$. If an experimental value of $H_B (k_{A37} / K_{A1})^{0.5}$ is represented by the symbol #, then any experimental result for $H_B (k_{A37} / K_{A1})^{0.5}$ may be expressed as:

$$H_B (k_{A37} / K_{A1})^{0.5} = \# \quad . \quad (52)$$

Taking the logarithm of both sides of Equation 52 and rearranging gives:

$$\log[H_B] = -0.5 \log[k_{A37}] + \log[\#] + 0.5 \log[K_{A1}] \quad . \quad (53)$$

Plotting H_B vs. k_{A37} on a log - log graph gives a discrete straight line of slope -0.5 for each experimental value of $H_B (k_{A37} / K_{A1})^{0.5}$. A comparison of the results of the values of $H_B (k_{A37} / K_{A1})^{0.5}$ from the four penetration theory experiments presented in Table 3 is shown in Figure 2. If an experimental value of $H_B (K_{A1} / k_{A37})^{0.5}$ is represented by the symbol #, then any experimental result for $H_B (K_{A1} / k_{A37})^{0.5}$ may be expressed as:

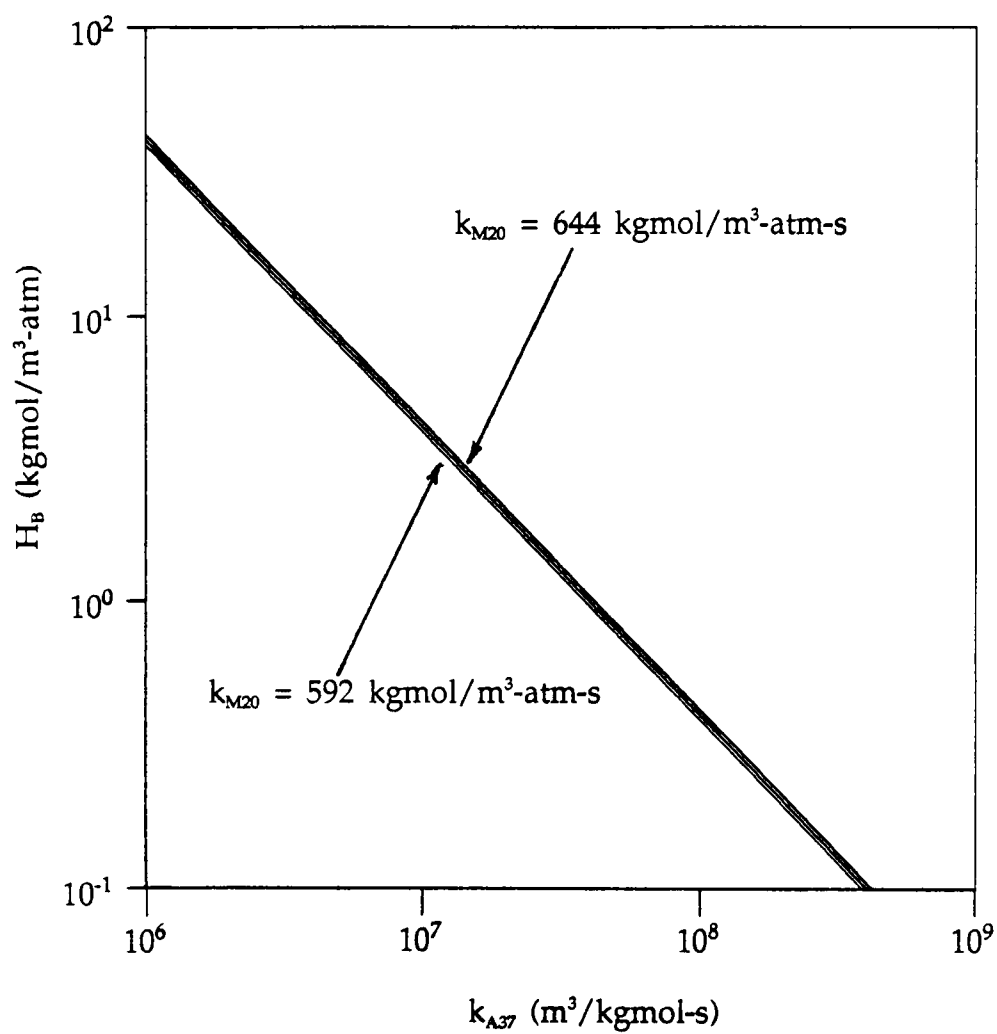


Figure 1 Graphical Presentation of the Results of the Mixed Phase Experimental Results Presented in Table 2

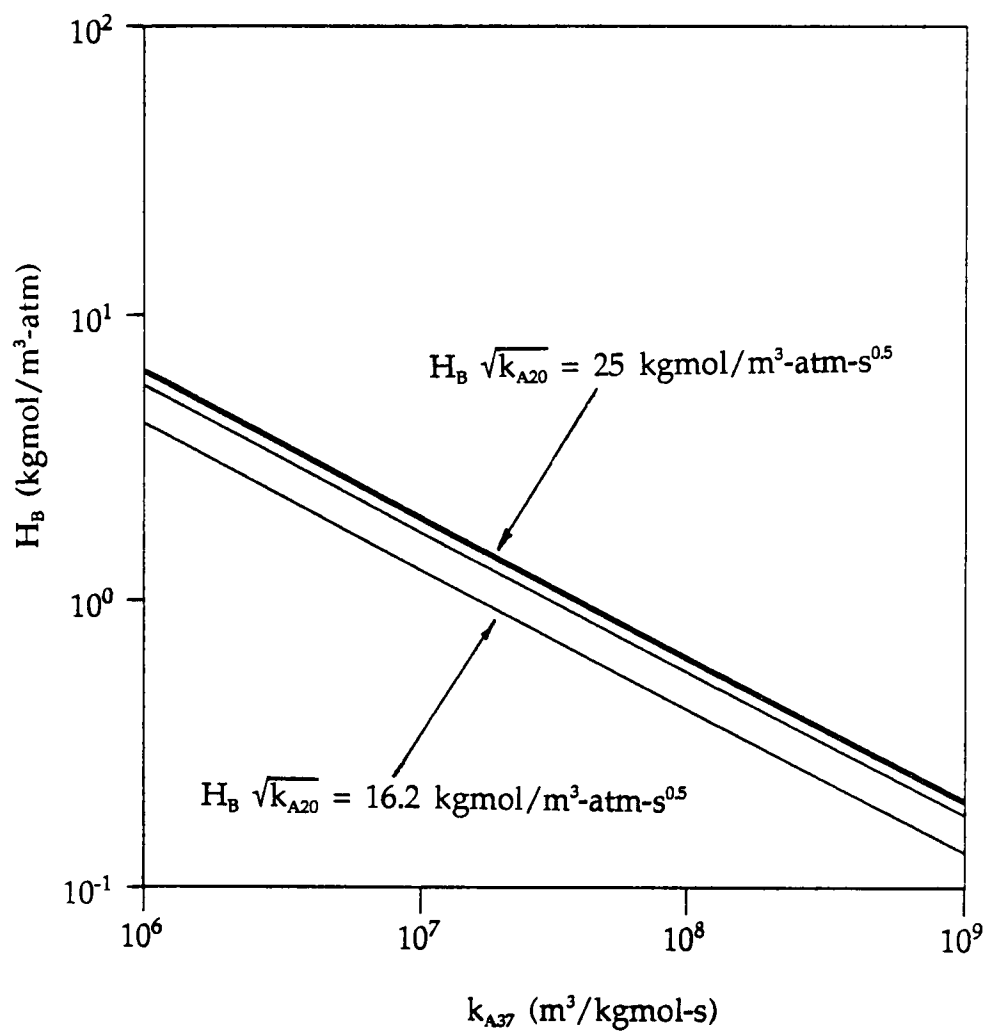


Figure 2 Graphical Presentation of the Results for the Value $H_B \sqrt{k_{A37}} / \sqrt{K_{A1}}$ Determined by the Penetration Theory as Presented in Table 3

$$H_B (K_{A1} / k_{A37})^{0.5} = \# \quad . \quad (54)$$

Taking the logarithm of both sides of Equation 54 and rearranging gives:

$$\log[H_B] = 0.5 \log[k_{A37}] + \log[\#] - 0.5 \log[K_{A1}] \quad . \quad (55)$$

Plotting H_B vs. k_{A37} on a log - log graph gives a discrete straight line of slope 0.5 for each experimental value of $H_B (K_{A1} / k_{A37})^{0.5}$. A comparison of the results of the values of $H_B (K_{A1} / k_{A37})^{0.5}$ from the four penetration theory experiments presented in Table 3 is shown in Figure 3. Figure 2 and Figure 3 both show graphical interpretations of the results of penetration theory experiments. These two sets of results are combined and shown together in Figure 4.

The results of film theory experiments for the reactive dissolution of N_2O_4 were compiled in Table 4. The results were presented in the form of a value for $H_B \sqrt{k_{A20} D_B}$ for each set of experiments. The listed reaction rate constant k_{A20} is equivalent to k_{A37} / K_{A1} . If the numerical result for the term $H_B \sqrt{k_{A20} D_B}$ obtained experimentally is represented by the symbol #, then any experimental value of $H_B \sqrt{k_{A20} D_B}$ may be expressed as:

$$H_B (k_{A37} D_B / K_{A1})^{0.5} = \# \quad . \quad (56)$$

Taking the logarithm of both sides of Equation 56 and rearranging gives:

$$\log[H_B] = -0.5 \log[k_{A37}] + \log[\#] + 0.5 \log[K_{A1} / D_B] \quad . \quad (57)$$

Plotting H_B vs. k_{A37} on a log - log graph gives a discrete straight line of slope -0.5 for each experimental value of $H_B (k_{A37} D_B / K_{A1})^{0.5}$ if a consistent value of D_B is used. Schwartz and White (1983) recommend the value $D_B = 1.4 \times 10^{-9} \text{ m}^2/\text{s}$. A comparison of the results of the values of

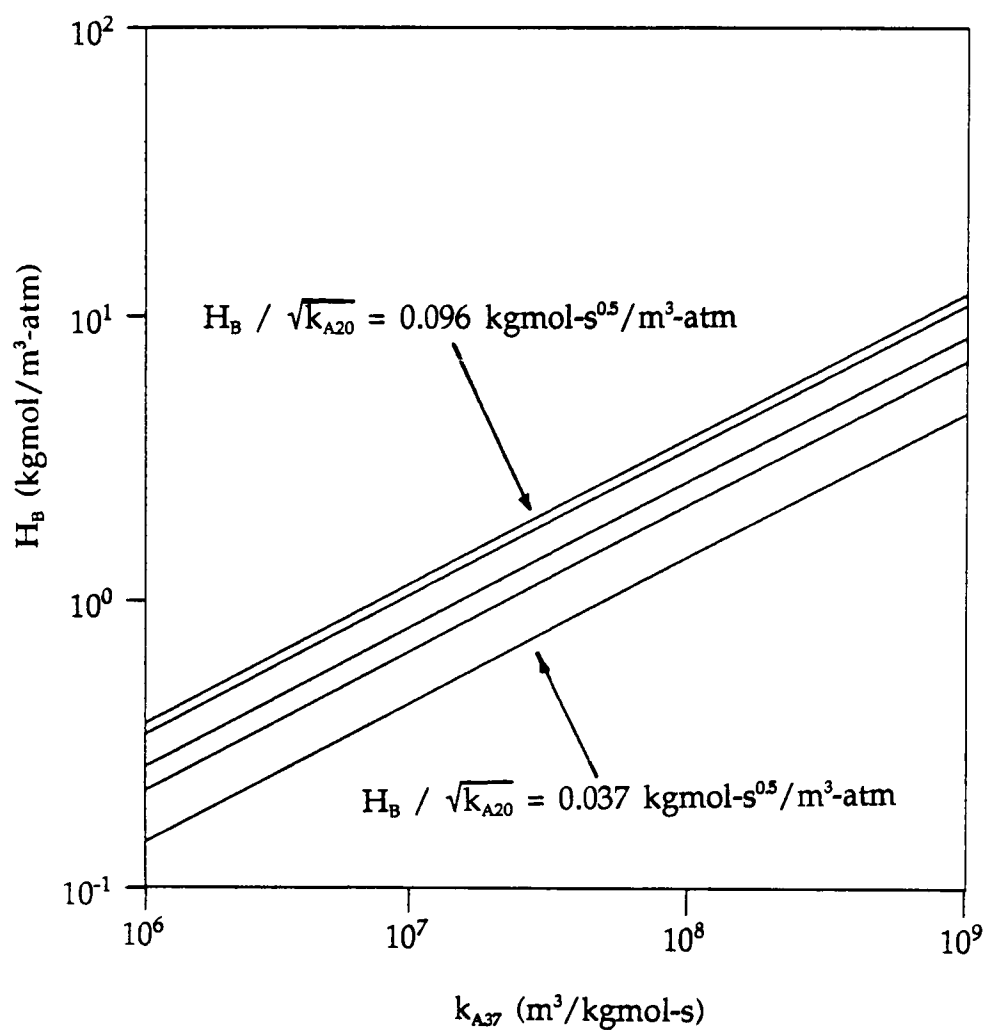


Figure 3 Graphical Presentation of the Results for the Value $H_B \sqrt{K_{A1}} / \sqrt{k_{A37}}$ Determined by the Penetration Theory as Presented in Table 3

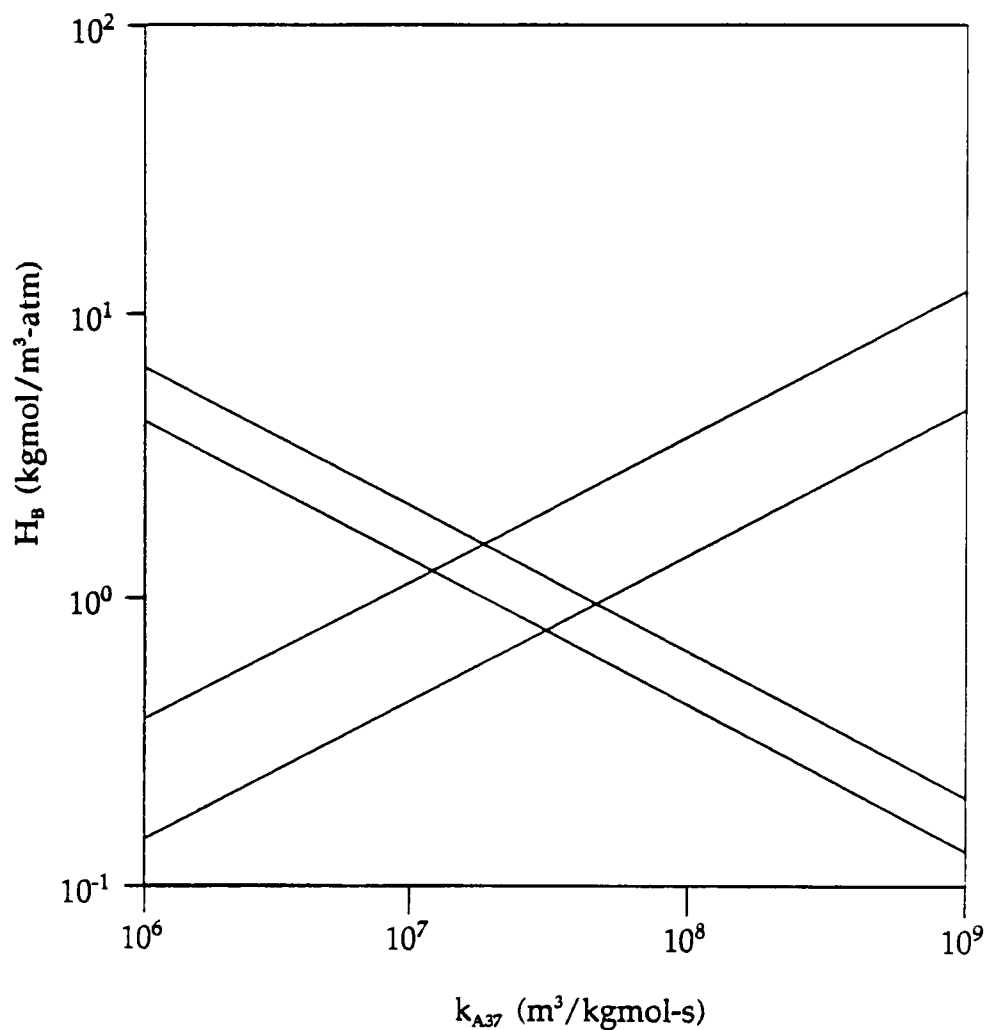


Figure 4 Graphical Presentation of the Results for the Values $H_B \sqrt{k_{A37}} / \sqrt{K_{A1}}$ and $H_B \sqrt{K_{A1}} / \sqrt{k_{A37}}$ Determined by the Penetration Theory as Presented in Table 3

$H_B (k_{A37} D_B / K_{A1})^{0.5}$ from the five film theory experiments presented in Table 4 is shown in Figure 5.

The results of the mixed phase experiments shown in Figure 1, the results of the penetration theory experiments shown in Figure 4, and the results of the film theory experiments shown in Figure 5 are all shown together in Figure 6. These experimental results are shown in Figure 7 with $k_{A37} = 2.6 \times 10^7 \text{ m}^3/\text{kgmol-s}$ determined by Moll (1966) by rapid-mixed flow tube experiments at 25°C, $k_{A37} = 6.5 \times 10^7 \text{ m}^3/\text{kgmol-s}$ determined by Grätzel et al. (1969) by pulse radiolysis experiments at 20°C, and $k_{A37} = 1.0 \times 10^8 \text{ m}^3/\text{kgmol-s}$ determined by Lee and Schwartz (1981) by using a bubbling absorber to study the absorption of NO_2 in the slow reaction regime at 22°C.

Schwartz and White (1983) used a graph similar to Figure 7 to select recommended values and uncertainties for equilibrium and rate constants describing the reactive dissolution of NO_2 and N_2O_4 in dilute aqueous solutions at 20°C to 25°C. These values are shown in Table 8. Schwartz and White's recommended values and uncertainties for k_{A37} and H_B are compared in Figure 8 to the experimental results shown in Figure 7.

Schwartz and White admitted that their choices of recommended values and uncertainties are somewhat arbitrary; their choice of recommended values for k_{A37} and H_B lies above the lines representing results for $H_B \sqrt{k_{A37}}$ from the penetration theory experiments and above the lines representing results for $H_B k_{A37}$ from the mixed phase experiments. Their choice for the recommended value for k_{A37} is the value determined by Grätzel et al. (1969)

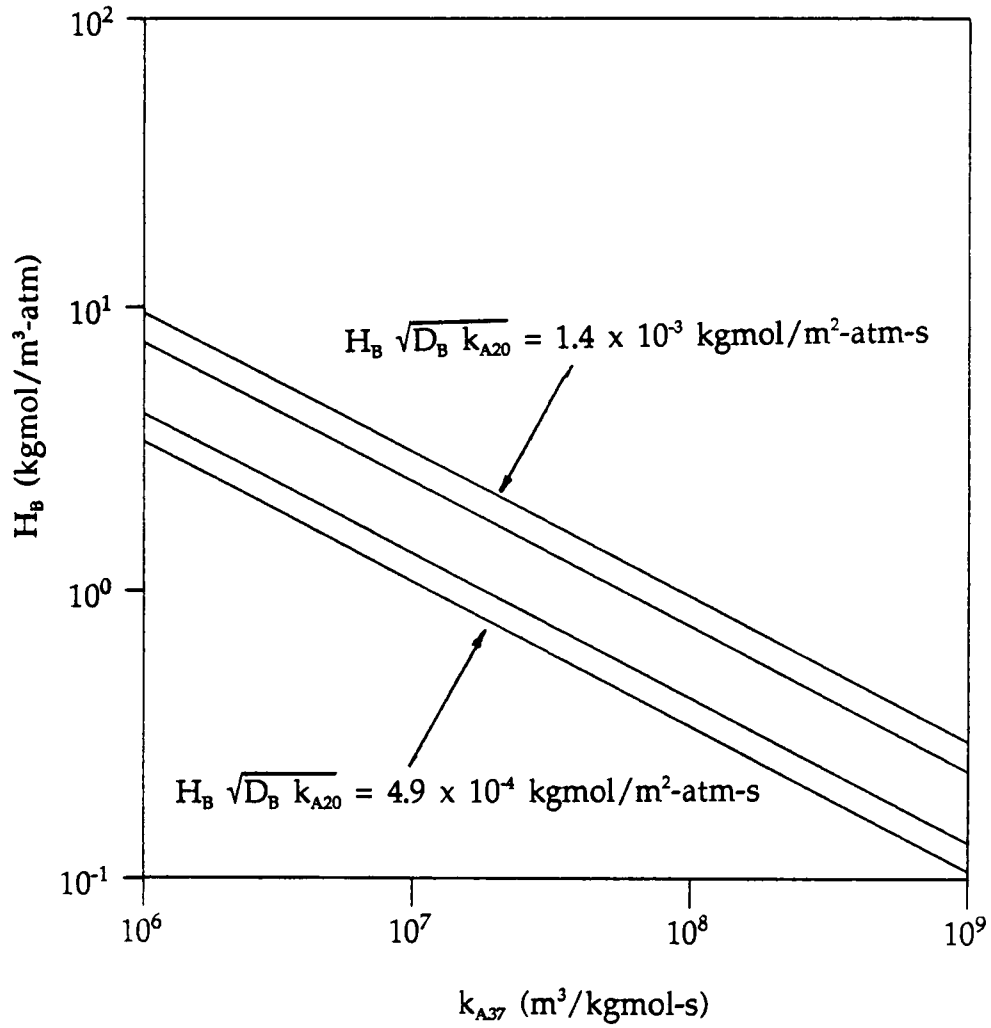


Figure 5 Graphical Presentation of the Results for the Value $H_B \sqrt{k_{A37}} / \sqrt{K_{A1}}$ Determined by the Film Theory as Presented in Table 4

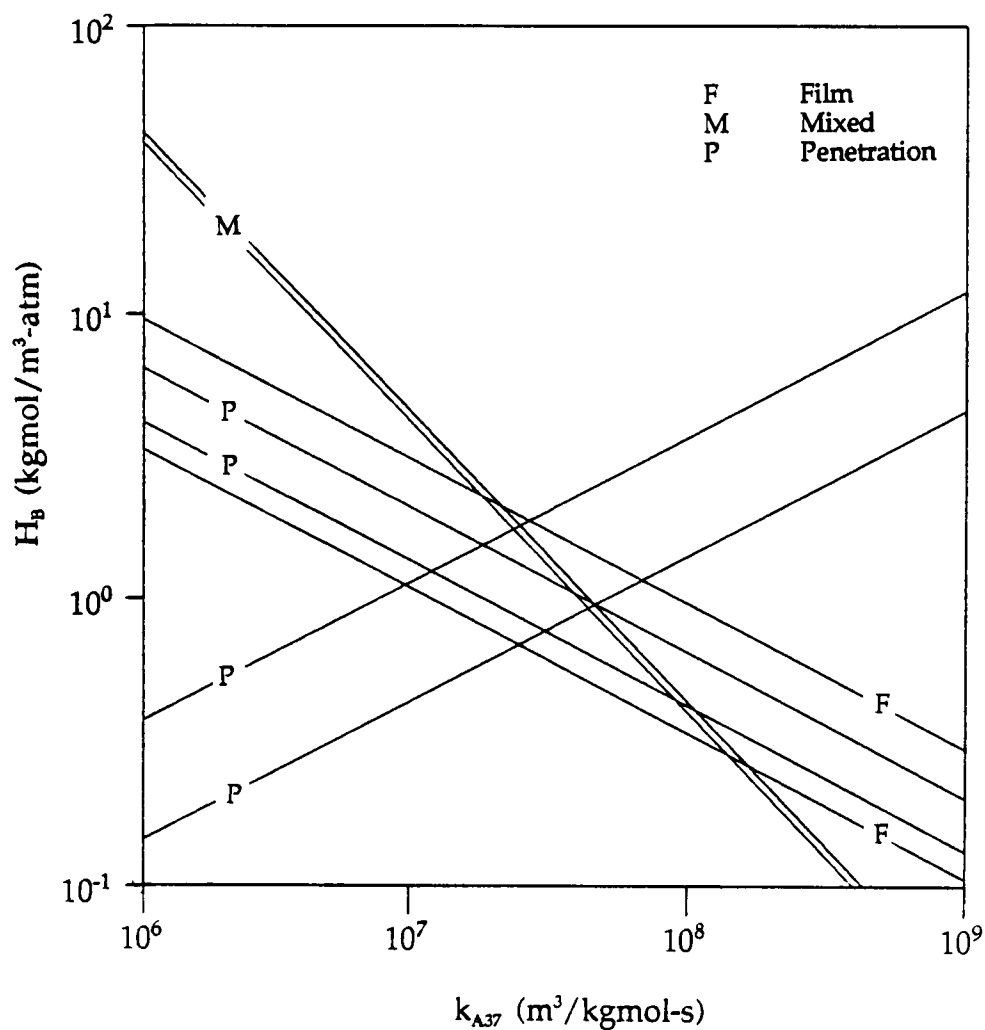


Figure 6 Graphical Presentation of the Values of H_b and k_{A37} Determined by Penetration Theory, Film Theory, and Mixed Phase Experiments

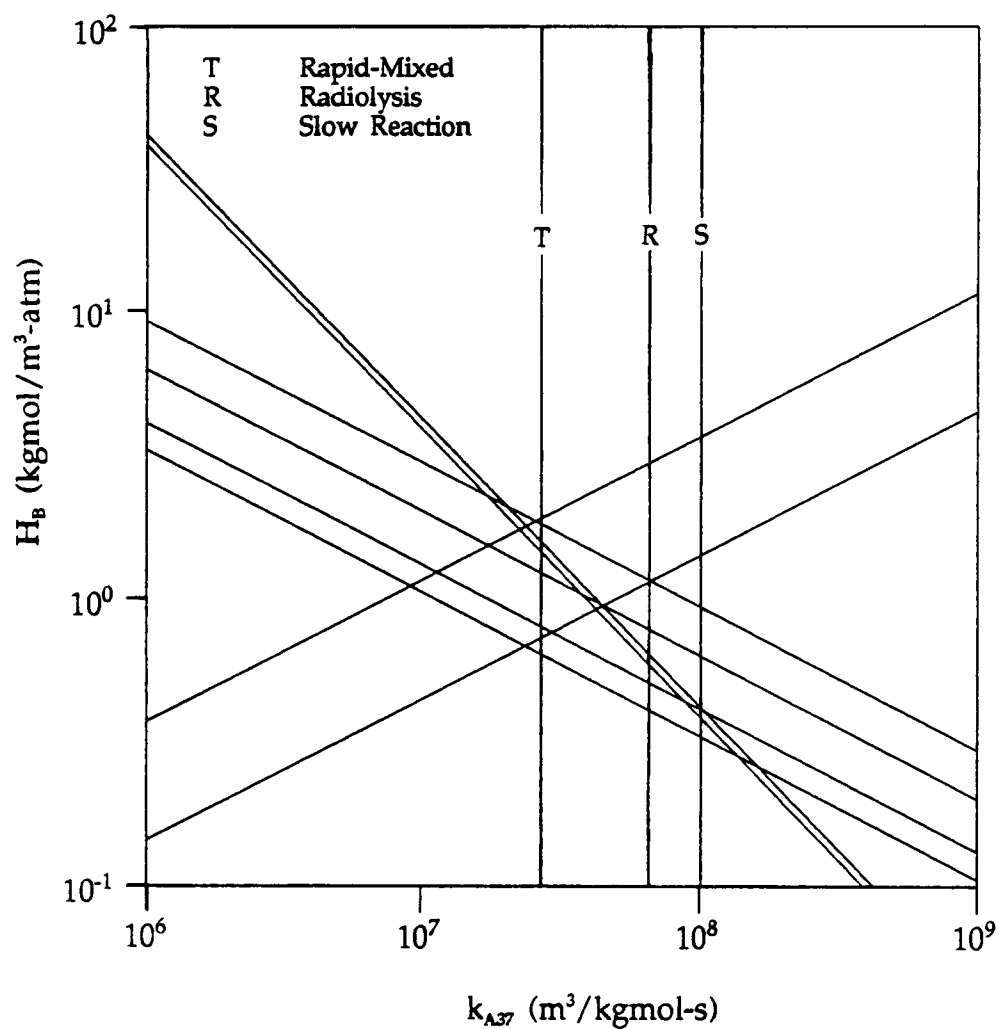


Figure 7 Graphical Presentation of the Values of H_B and k_{A37} Determined by Penetration Theory, Film Theory, Mixed Phase, Pulse Radiolysis, Rapid-Mixed Flow, and Slow Reaction Experiments

Table 8 Schwartz and White's (1983) ^a Recommended Values and Uncertainties for Equilibrium and Rate Constants Describing the Reactive Dissolution of N(IV) in Dilute Aqueous Solutions at 20°C to 25°C

Value (Units)	Minimum	Recommended	Maximum
H _A (kgmol/m ³ -atm)	0.007	0.010	0.013
H _B (kgmol/m ³ -atm)	0.45	1.00	2.00
K _{A1} (m ³ /kgmol)	6 x 10 ⁴	7 x 10 ⁴	9 x 10 ⁴
k _{A37} (m ³ /kgmol-s)	3.5 x 10 ⁷	7 x 10 ⁷	1 x 10 ⁸

^a Schwartz, S. E., and W. H. White, "Kinetics of Reactive Dissolution of Nitrogen Oxides into Aqueous Solution," *Adv. Environ. Sci. Technol.*, Vol. 12, S. E. Schwartz, Ed., John Wiley & Sons, New York, 1-116 (1983).

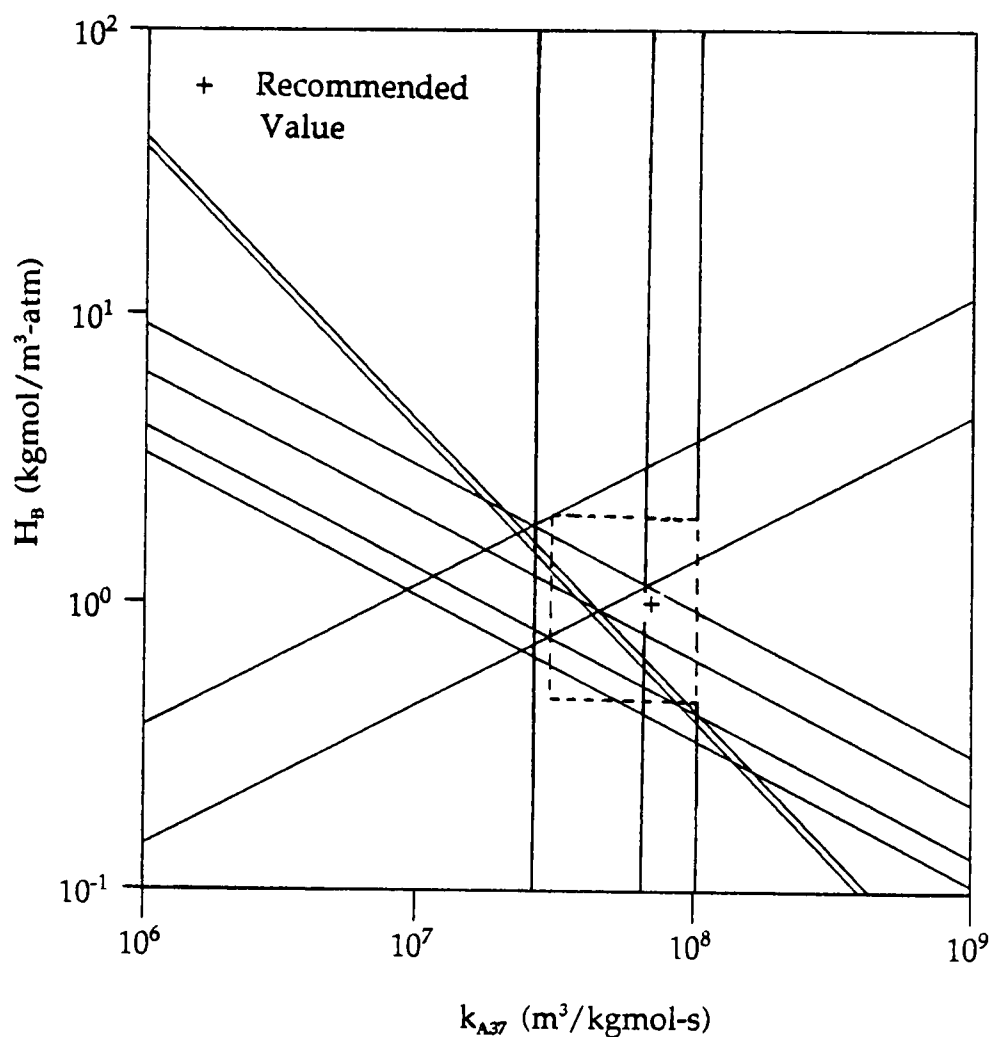


Figure 8 Graphical Presentation of Schwartz and White's (1983) ^a Recommended Values and Uncertainties of H_b and k_{A37} Compared to Experimental Values

^a Schwartz, S. E. and W. H. White, "Kinetics of Reactive Dissolution of Nitrogen Oxides into Aqueous Solution," *Adv. Environ. Sci. Technol.*, Vol. 12, S. E. Schwartz, Ed., John Wiley & Sons, New York, 1-116 (1983).

and the recommended uncertainty range includes the value determined by Lee and Schwartz (1981) but not the value determined by Moll (1966) as adjusted by Schwartz and White for mixed phase kinetics. The recommended uncertainty range includes some of the results of the penetration theory experiments as shown in Figures 2, 3 and 4 but not all of these results; the exclusion of some of the penetration theory results may be justified since the use of Equation 8 for determining the value of $H_B / \sqrt{k_{A5}}$ has not been verified for the mixed order kinetics of the hydrolysis of N(IV). While Schwartz and White's recommended values for H_B , H_A , K_{A1} , and k_{A37} can not be expected to predict the results of NO₂ scrubbing experiments perfectly, they are a fairly well chosen starting point for the analysis of the results of NO₂ scrubbing experiments.

8. PROPOSED MECHANISMS FOR THE HYDROLYSIS OF FOUR VALENT NITROGEN OXIDES

There are three forms of four valent nitrogen oxides: nitrogen dioxide, D_{2h}-dinitrogen tetroxide, and iso-dinitrogen tetroxide. All of these forms may have a significant effect on the rate of hydrolysis of N(IV) in aqueous solutions. Kameoka and Pigford (1977) presented two possible mechanisms for the hydrolysis of N(IV) involving iso-N₂O₄ as a reaction intermediate. The first mechanistic model was originally proposed by Moll (1966) (the $\rightleftharpoons$ sign represents a rapid equilibrium reaction):



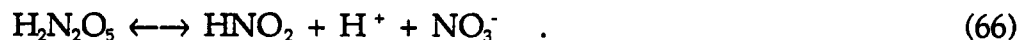
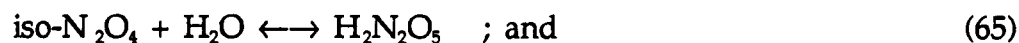


This mechanism consists of a series of known compounds and ions, excluding H_2NO_2^+ , the nitrous acidium ion whose existence has not been conclusively proven (Stedman, 1979), and reactions. Since the overall reaction, Reaction 61, is reversible, the principle of microscopic reversibility applies. Therefore Reactions 59, 60, and 61 are incorrect as written; the Reversible Moll mechanism is:

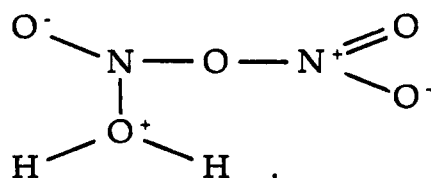


Reaction 62 is proposed as the rate limiting step. The overall reaction represented by Reactions 63 and 64 is known to occur, therefore the presence of an unknown intermediate, H_2NO_2^+ , is not a great drawback to this mechanism.

Kameoka and Pigford (1977) proposed a new mechanism for the hydrolysis of N(IV):



Kameoka and Pigford proposed the following structure for $\text{H}_2\text{N}_2\text{O}_5$:



Reaction 65 is the rate limiting step. Kameoka and Pigford claim this mechanism has several advantages over the Moll mechanism: the hydrolysis of N(IV) is shown to be first order in N_2O_4 and in H_2O , as it is expected to be and the reverse of the hydrolysis is shown to be first order in H^+ , HNO_2 , and NO_3^- as the experimental evidence indicates (Abel et al., 1928; Schmid and Bähr, 1964). The intermediate compound, $\text{H}_2\text{N}_2\text{O}_5$, has not been isolated and characterized yet so its existence is still conjecture.

Both the Reversible Moll mechanism and the Kameoka and Pigford mechanism seem plausible. It is important to notice that the reactive N_2O_4 molecule for both of the proposed mechanisms is the iso- N_2O_4 isomer, not the more common D_{2h} - N_2O_4 isomer, and that NO_2 is a reactive intermediate by Equation 58 between D_{2h} - N_2O_4 and iso- N_2O_4 . The Reversible Moll mechanism seems to be a likely reaction mechanism since iso- N_2O_4 and HNO_2 are both known to ionize to form NO^+ . The Kameoka and Pigford mechanism seems somewhat less likely since true trimolecular reactions are relatively rare; the reverse of Reaction 66 is a trimolecular reaction as written. Since HNO_3 is in rapid equilibrium with H^+ and NO_3^- , HNO_3 and HNO_2 may be the reactive species in the reverse of Reaction 66; that would make the Kameoka and Pigford mechanism seem more likely. Another weakness of the Kameoka and Pigford mechanism is that the O atom of

water, a negative dipole, is attracted to the uncharged nitroso-N atom rather than the positively charged nitro-N atom of the iso-N₂O₄ molecule.

9. ANALYSES OF THE REACTIVE DISSOLUTION OF N(IV) WHICH ACCOUNT FOR THE EQUILIBRIUM BETWEEN NO₂ AND N₂O₄

Karlsson (1983) presented a model for the reactive dissolution of N(IV) in aqueous solutions which accounts for Reaction 1, the equilibrium between NO₂ and N₂O₄. Karlsson combined Fick's Law for NO₂ and N₂O₄ with the continuity equation for N(IV):

$$N_A = - D_A dc_A / dx \quad ; \quad (67)$$

$$N_B = - D_B dc_B / dx \quad ; \text{ and} \quad (68)$$

$$dN_{N(IV)} / dx = - 2 k_{A37} c_B / K_{A1} \quad ; \text{ where} \quad (69)$$

$$N_{N(IV)} = N_A + 2 N_B \quad ; \text{ giving} \quad (70)$$

$$D_A d^2c_A / dx^2 + 2 D_B d^2c_B / dx^2 - 2 k_{A37} c_B / K_{A1} = 0 \quad . \quad (71)$$

Karlsson introduced a variable transformation for this equation:

$$U = (D_A / D_B) c_A + 2 c_B \quad ; \quad (72)$$

$$V = dU / dx \quad . \quad (73)$$

Since

$$c_B = K_{A1} c_A^2 \quad , \quad (29)$$

Equation 72 can be manipulated by the quadratic equation to express c_B as a function of U . Karlsson used this result to manipulate Equation 71 into the form

$$V dV / dU = k_{A37} [2 + \beta U - 2 (1 + \beta U)^{0.5}] / (D_B \beta) , \quad (74)$$

where:

$$\beta = 8 D_B^2 K_{A1} / D_A^2 . \quad (75)$$

Karlsson solved Equation 74 by separating the variables and integrating the equation with boundary conditions:

at the gas-liquid interface

$$U = U_i \quad \text{and} \quad (76)$$

$$V = - N_{N(OV),i} / D_B ; \quad (77)$$

at the liquid film-bulk interface

$$U = 0 \quad \text{and} \quad (78)$$

$$V = 0 . \quad (79)$$

The gas-liquid interface boundary condition is consistent with Henry's Law and Fick's Law. The liquid film-bulk interface boundary condition is consistent with the boundary condition for reactive dissolution of a gas controlled by a fast reaction. Karlsson presented his solution to Equation 72 in two forms:

$$N_{N(OV),i} = (k_{A37} D_B / \beta)^{0.5} \{ 4 U_i + \beta U_i^2 + [8 / (3 \beta)] [1 - (1 + \beta U_i)^{1.5}] \}^{0.5} , \quad \text{and} \quad (80)$$

$$N_{N(OV),i} = (N_{1,i}^2 + N_{2,i}^2)^{0.5} , \quad \text{where} \quad (81)$$

$$N_{1,i} = 2 (k_{A37} D_B / K_{A1})^{0.5} c_{B,i} , \quad \text{and} \quad (82)$$

$$N_{2,i} = (4 k_{A37} D_A / 3)^{0.5} c_{A,i}^{1.5} . \quad (83)$$

The first form, Equation 80, is easily arrived at by performing the integration of Equation 74. The second form, Equation 81, conveys a great deal more

information. Equation 82 shows the contribution of N_2O_4 to the reactive dissolution of N(IV) to be very similar to the film theory model for fast first order reaction enhanced absorption of a gas as was shown in Equation 10:

$$N_B = p_{B,i} H_B \sqrt{D_B k_{A5}} \quad . \quad (10)$$

Differences between Equation 82 and Equation 10 are all results of presentation rather than any real difference: application of Henry's Law changes $p_{B,i} H_B$ to c_B ; the first order reaction rate for N_2O_4 by Reaction 37 is k_{A37} / K_{A1} which is equivalent to k_{A5} ; and the flux of one mole of N_2O_4 is equivalent to the flux of two moles of N(IV). Equation 83 shows the contribution of NO_2 to the reactive dissolution of N(IV) to be very similar to the film theory model for fast second order reaction enhanced absorption of a gas as was shown in Equation 16:

$$N_A = p_{A,i}^{1.5} H_A^{1.5} \sqrt{4 D_A k_{A14} / 3} \quad . \quad (16)$$

Differences between Equation 83 and Equation 16 can be eliminated by substituting $c_B^{1.5}$ for $p_{A,i}^{1.5} H_A^{1.5}$ and exchanging k_{A37} for k_{A14} .

The Karlsson Combined Flux (KCF) model is represented by Equation 81. By assuming NO_2 and N_2O_4 are in equilibrium in the liquid phase by Reaction 1 and that the reactive dissolution of NO_2 and N_2O_4 can be considered to be controlled by the fast hydrolysis of the reactive species. Karlsson (1983) derived an analytical equation for the flux of N(IV) across the gas-liquid interface. At high partial pressures of N(IV), the KCF model converges to the film theory model for pseudo first order reaction enhanced absorption of N_2O_4 . At low partial pressures of N(IV), the KCF model

converges to the film theory model for pseudo second order reaction enhanced absorption of NO_2 . Unfortunately Karlsson did not test his model with experimental data.

Shadid and Handley (1989) studied the absorption of NO_2 and N_2O_4 into sodium hydroxide solutions using a baffled sieve tray. Unfortunately Shadid and Handley did not report the results of the effect of hydroxide concentration on the rate of absorption of N(IV). Shadid and Handley used the penetration theory to model their results. Model predictions were determined by using the technique of orthogonal collocation to integrate the non-linear partial differential equations applicable to this system. Shadid and Handley were apparently unaware of the KCF model, since a comparison of the results predicted by the penetration theory and the results predicted by the film theory, embodied by the KCF model, has never been attempted for this mixed order reaction system. Such a comparison would be of interest to chemical engineers, even those not involved in NO_x scrubbing.

Shadid and Handley (1989) apparently committed several errors in their analysis and presentation of their data. The most serious error was applying the gas phase equilibrium constant determined by Verhoek and Daniels (1931) for Reaction 1 to the liquid phase. Not only was the use of the gas phase equilibrium constant incorrect (by nearly four orders of magnitude), Shadid and Handley arbitrarily decreased the constant by an order of magnitude. Shadid and Handley omitted the temperature at which they conducted their experiments and they failed to mention how many

collocation points were used in their calculations. Shadid and Handley (1990) recently published a follow-up study using the same techniques to analyze the formation and decomposition of nitrous acid during the absorption of nitrogen oxides. Unfortunately they repeated their errors from the first study. While the penetration theory is another technique for analyzing the results of N(IV) absorption experiments with the assumption that NO_2 and N_2O_4 are in equilibrium, the testing of this theory conducted by Shadid and Handley can only be regarded as inconclusive.

10. SUMMARY OF LITERATURE INDICATING APPROPRIATE MASS TRANSFER PARAMETERS FOR COLUMNS PACKED WITH SULZER TYPE BX PACKING

Bomio (1977) developed correlations for height of a transfer unit for both gas and liquid phases for Sulzer Type BX packing by regressing the results of absorption experiments. Bomio (1979) indicated that the effective interfacial area of Sulzer Type BX packing is the same as the geometric area of the packing, given as $450 \text{ m}^2/\text{m}^3$, since the packing exhibits self-wetting due to capillary action. The predicted value for the liquid phase mass transfer coefficient for the absorption of NO_2 into water at 25°C and a liquid loading of $3.27 \text{ kgmol}/\text{m}^2\text{-s}$ is $k_l = 8.0 \times 10^{-5} \text{ m/s}$. The predicted value for the gas phase mass transfer coefficient for the transfer of NO_2 through air at 25°C and a gas loading of $0.0126 \text{ kgmol}/\text{m}^2\text{-s}$ is $k_g = 2.7 \times 10^{-4} \text{ kgmol}/\text{m}^2\text{-atm-s}$.

Bravo, Rocha, and Fair (1985) regressed the results of distillation experiments to develop a correlation for the gas phase Sherwood Number for Sulzer Type BX packing. Bravo et al. also indicated that the effective interfacial area is the same as the geometric area, given as $492 \text{ m}^2/\text{m}^3$. The predicted value for the gas phase mass transfer coefficient for the transfer of NO_2 through air at 25°C and a gas loading of $0.0126 \text{ kgmol}/\text{m}^2\text{-s}$ is $k_g = 3.1 \times 10^{-4} \text{ kgmol}/\text{m}^2\text{-atm-s}$. Bravo et al. show that 95% of the data regressed gave mass transfer coefficients within 25% of the predicted value. The gas phase mass transfer coefficient predicted for the same conditions by Bomio's model (Bomio, 1977) is 13% less than the value predicted by Bravo's model, within the 25% limit.

Lucero, Wilson, Counce, Singh, Ashworth, and Elliot (1989) regressed the experimental results of air stripping of VOCs to develop a correlation for the height of a transfer unit for the liquid phase for Sulzer Type BX packing. The predicted value for the liquid phase mass transfer coefficient for the absorption of NO_2 into water at 25°C and a liquid loading of $3.27 \text{ kgmol}/\text{m}^2\text{-s}$ is $k_l = 5.9 \times 10^{-5} \text{ m/s}$. This value is 27% less than the value predicted by Bomio's correlation.

Fair and Bravo (1990) recently published a survey of pressure drop and mass transfer parameter correlations for structured packing. Fair and Bravo indicate that $500 \text{ m}^2/\text{m}^3$ is the geometric area of Sulzer Type BX packing.

11. LITERATURE SUMMARY

The three four valent nitrogen oxide species, NO_2 , $\text{D}_{2h}\text{-N}_2\text{O}_4$, and $\text{iso-N}_2\text{O}_4$ have been introduced and described in some detail. NO_2 and/or $\text{D}_{2h}\text{-N}_2\text{O}_4$ are the dominant species at all temperatures at which N(IV) has been studied and in all phases in which N(IV) has been studied. NO_2 and N_2O_4 have long been known to reach equilibrium rapidly by Reaction 1 in the gas phase (Bodenstein, 1922). The gas phase isomer of N_2O_4 that has been isolated is $\text{D}_{2h}\text{-N}_2\text{O}_4$. Whether NO_2 and $\text{iso-N}_2\text{O}_4$ are in equilibrium in the gas phase has not been determined. Grätzel et al. (1969) and Treinin and Hayon (1970) showed that the liquid phase equilibrium between NO_2 and $\text{D}_{2h}\text{-N}_2\text{O}_4$ is established rapidly compared to the rate of the hydrolysis of N(IV). Moll (1966) and Kameoka and Pigford (1977) proposed that NO_2 is also in equilibrium with $\text{iso-N}_2\text{O}_4$ in the liquid phase by Reaction 58 and that the hydrolysis of $\text{iso-N}_2\text{O}_4$ is the rate limiting step of the reaction. The Moll mechanism was incorrect as presented by Moll and by Kameoka and Pigford; it was corrected and labeled the Reversible Moll mechanism. Both the Reversible Moll mechanism and the Kameoka and Pigford mechanism have several drawbacks and advantages which were discussed.

The hydrolysis of N(IV) has been studied in many different reactors and by different techniques. Those studies which were reviewed in this survey were conducted in: mixed phase reactors where the gas and liquid phases were maintained in equilibrium with each other; in short laminar jets and a wetted wall column where penetration theory analysis was used to

attempt to determine the first order rate constant for the hydrolysis of N(IV) as if N_2O_4 were the reacting species and the Henry's Law constant for N_2O_4 independently; in wetted wall columns and wetted sphere absorbers where film theory analysis was used to determine $H_B \sqrt{D_B k_{A37} / K_{A1}}$, the effective mass transfer coefficient for the absorptive flux of N(IV) if the absorption of N(IV) is controlled by the fast first order hydrolysis of N_2O_4 ; in a rapidly mixed flow tube where k_{A37} / K_{A1} was determined; in pulse radiolysis and flash photolysis experiments where K_{A1} and k_{A37} were determined independently from each other; and in other apparatus. The results of all these different experiments are compared to each other by a graphical technique in Figure 7. Schwartz and White (1983) used this approach to determine recommended values and uncertainties for these parameters; these values are presented in Table 6 and shown in Figure 8.

The only two models in the literature for the reactive dissolution of N(IV) in aqueous solutions account for the aqueous phase equilibrium between NO_2 and N_2O_4 . These models are a combined flux model derived by Karlsson (1983) but not tested with experimental data, and penetration theory analyses conducted by Shadid and Handley (1989) and (1990). The penetration theory analysis fit the experimental data well but contained several flaws as published. The derivation of the Karlsson Combined Flux (KCF) model, a fast reaction film theory model, is given in Section 9.

CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus used in this study was a 0.102 m interior diameter column packed to a height of 0.8 m with Sulzer Type BX high efficiency, gauze packing. The packing consisted of five identical elements, stacked on one another in the column; the packing fit the wall sufficiently snugly that a packing support was not needed. The liquid feed was distributed through a four prong, nine hole, X type liquid distributor.

Absorbent solutions were mixed from distilled water and sodium hydroxide pellets then diluted in a stirred, stainless steel liquid supply tank. Sodium hydroxide solutions were mixed and used in 0.02 m³ batches. The aqueous feed solution was pumped to the column with a variable speed, constant volume pump adjusted such that the liquid mass flow rate was maintained at 0.027 kg/s. The liquid feed pump needed little adjustment to maintain a constant flow rate; the influent flow rate was read from a Fisher-Porter (Model 10 A 1755) rotameter. Liquid recycle of the sodium hydroxide solutions was pumped back to the liquid supply tank by a constant speed pump throttled such that the liquid level in the column was consistently between 0.05 m and 0.15 m, well below the packing. Recycling aqueous sodium hydroxide during experimental runs was expedient. The sodium hydroxide concentration changed little during the course of a run. A slight increase in nitrate and nitrite ions in solution does not significantly

decrease the solubility of absorbing gases (Danckwerts, 1970). The liquid supply tank was filled with distilled water for the experiments which used water as the absorbent solution. The effluent water flow was throttled to maintain the same liquid level as in the sodium hydroxide solution experiments; the effluent water was not recycled. Sample taps were used to take liquid influent and effluent samples. The liquid flow portion of the experimental apparatus is shown in Figure 9.

Air was used as the diluent gas for the $\text{NO}_2\text{-N}_2\text{O}_4$ gas mixtures. Air flow rates were adjusted to $2.5 \times 10^{-3} \text{ m}^3/\text{s}$; air flow rates were read from a Brooks (Model IC 03835) air-rotameter. Liquid N_2O_4 was gasified using Sybron flexible heating tape, heated with a variac. Gas samples were analyzed with a Beckman (Model 951) NO/NO_x Gas Analyzer. The following calibration gases were used to calibrate the gas analyzer: 2200 ppm NO, 800 ppm N(IV), 2140 ppm N(IV), and 8500 ppm N(IV). The gas analyzer used a dry oxygen supply to generate ozone. The ozone/sample flow ratio was adjusted so the NO and NO_x readings were identical for the NO calibration gas. Only two calibration gas cylinders were used at a time, the operation of the gas analyzer was linear in the partial pressure range studied. The gas effluent and the gas analyzer exhaust were discharged in a fume hood. The gas flow portion of the apparatus is shown in Figure 10.

The gas analyzer was allowed to warm up at least an hour prior to use. During the warm up period the liquid and gas flows were started to allow the liquid distribution to reach steady state and to ensure complete

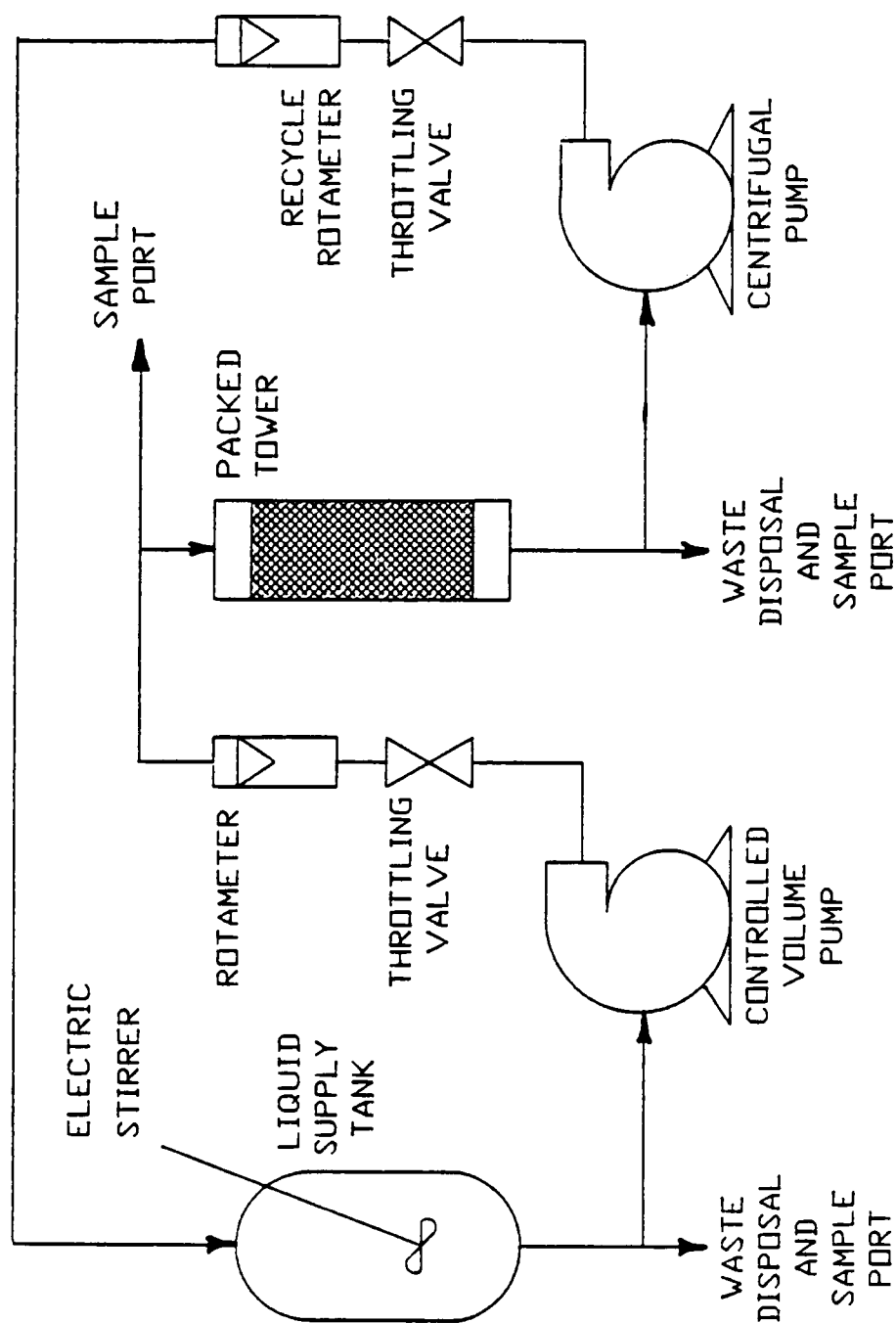


Figure 9 Liquid Flow Diagram of Experimental Apparatus

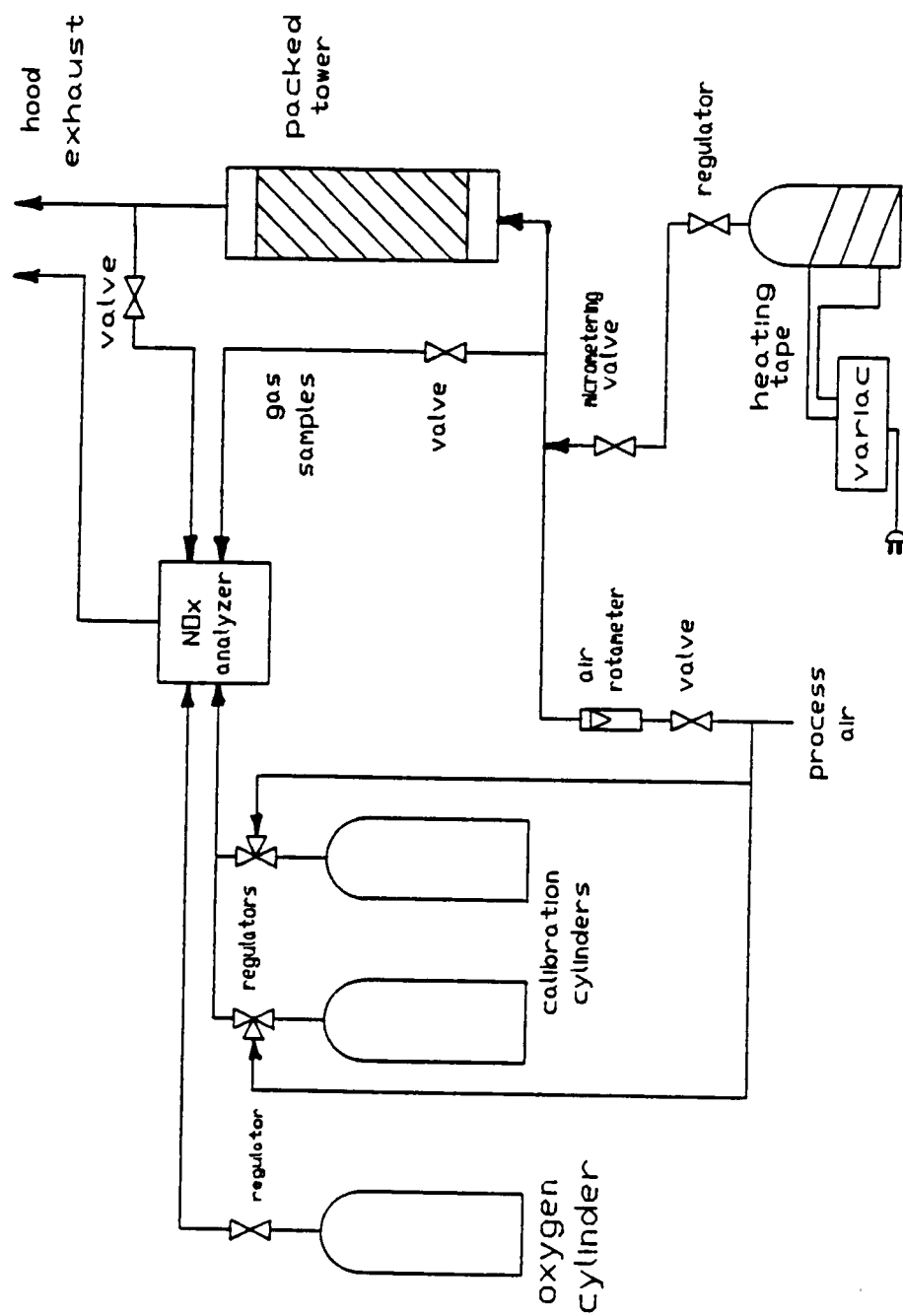


Figure 10 Gas Flow Diagram of Experimental Apparatus

wetting of the packing. Since the Sulzer Type BX packing used in the column is a gauze packing, capillary action causes self-wetting. Changes in viscosity and density of the various sodium hydroxide solutions used did not affect the interfacial area of the packing. The gas analyzer was calibrated following the warm up period; process air was used to zero the instrument. Outlet liquid temperatures were measured and recorded at the beginning and ending of each series of runs; the temperature never varied more than 1°C for a given series of runs. The experimental temperatures ranged from 23°C to 27°C. Two series of experimental runs were conducted for water, 0.3 N NaOH, 0.6 N NaOH, and 1.0 N NaOH solutions. The per pass variation in molarity was too small to be accurately measured; starting and ending values of molarity were measured by titration with a phenolphthalein indicator. After the outlet partial pressure of N(IV) reached a steady value, unchanged for one minute, the outlet NO partial pressure was checked and recorded if the reading was greater than 2% of the scale, then the inlet partial pressure of N(IV) was checked and recorded. NO partial pressure readings of no more than 2% of the scale were noticed for N(IV) calibration gases and the inlet N(IV)-air mixture; these readings were ignored as an artifact of the instrument. No significant NO readings were noticed for any of the readings of the effluent gas when NaOH scrubbing solutions were used. Gas phase partial pressure readings are estimated to be accurate within 2% of the appropriate scale used; runs with influent readings less than 1000 ppm were read on the 1000 ppm scale, runs with influent

readings less than 2300 scale were read on the 2500 ppm scale, and runs with influent readings greater than 2300 ppm were read on the 10000 ppm scale. After recording an experimental run the variac heating rate and the micrometering valve were adjusted to generate a different N(IV) influent partial pressure. A minimum of twelve minutes was allowed for the system to come to steady state before recording results.

CHAPTER IV

MODEL DEVELOPMENT

1. GAS PHASE MATERIAL BALANCE

The gas phase material balance for the reactive dissolution of N(IV) may be derived based on the following assumptions:

- (1) NO_2 and N_2O_4 are in equilibrium with each other by Reaction 1 everywhere in the gas phase;
- (2) other than Reaction 1 NO_2 and N_2O_4 do not participate in any other gas phase reactions; and
- (3) the gas phase is in plug flow.

A material balance on a differential section of packing gives the following differential equation:

$$(G / P) (dp_{\text{N(IV)}} / dz) = - a N_{\text{N(IV)}} \quad (84)$$

Since G , P , and a are assumed to be independent of position in the tower and partial pressure of N(IV), separation and integration of Equation 84 over the packed tower gives:

$$a P Z / G = \int_{P_{\text{N(IV)},\text{out}}}^{P_{\text{N(IV)},\text{in}}} (dp_{\text{N(IV)},b} / N_{\text{N(IV)}}) \quad (85)$$

Equation 85 can be integrated numerically as written for any expression for the flux of N(IV) as a function of the bulk gas phase partial pressure of N(IV), but the partial pressure of NO_2 is more useful as the dummy variable and integration limits. Since

$$p_{N(IV),b} = p_{A,b} + 2 p_{B,b} \quad (86)$$

and

$$p_{B,b} = K_{G1} p_{A,b}^2 \quad , \quad (87)$$

then

$$dp_{N(IV),b} = (1 + 4 K_{G1} p_{A,b}) dp_{A,b} \quad . \quad (88)$$

Equation 88 may be substituted into Equation 85 to give:

$$a P Z / G = \int_{p_{A,out}}^{p_{A,in}} [(1 + 4 K_{G1} p_{A,b}) dp_{A,b} / N_{N(IV),i}] \quad . \quad (89)$$

To integrate the general gas phase material balance, Equation 89, one needs an equation or combination of equations for $N_{N(IV),i}$ as a function of the bulk partial pressure of NO_2 . Assuming a technique is available for calculating $N_{N(IV),i}$ such as the fast pseudo-first order reaction film theory model or the KCF model in conjunction with an expression for the flux of $N(IV)$ through the gas phase film, Equation 89 may be integrated numerically. For a given value of $p_{N(IV),in}$ the value of $p_{N(IV),out}$ must be found by some iterative procedure such that Equation 89 is satisfied.

The Reynolds number for the gas phase under the experimental conditions is 2100 if the column diameter is used as the characteristic length, or 150 if the effective diameter of the packing is used as the characteristic length. The structured packing should induce a relatively flat gas velocity profile across the diameter of the column, but the flow can not be considered to be in the turbulent flow regime. Fair and Bravo (1990) indicated that correlations for round wetted wall columns agree well with

the correlation of Bravo et al. (1985) for the gas phase mass transfer coefficient for gauze type structured packings. Chambers and Sherwood (1937) found the wetted wall column, gas phase mass transfer coefficient correlation of Sherwood and Gilliland (1934) to apply at column Reynolds numbers as low as 1000. Due to the conclusions of Fair and Bravo and the results of Chambers and Sherwood, the fact that the gas phase flow is not in the turbulent regime should not overly affect the applicability of a gas phase mass transfer coefficient. The assumption that the gas is in plug flow can not be verified for the experimental conditions due to the low column Reynolds number, therefore the derived form of the gas phase material balance, Equation 89, may be a source of some discrepancy between model predictions and experimental results.

2. N(IV) FLUX THROUGH THE GAS PHASE FILM

The flux of NO_2 and N_2O_4 through the gas phase film may be derived based on the following assumptions:

- (1) both NO_2 and N_2O_4 obey Fick's Law of Diffusion;
- (2) mixtures of N(IV) are sufficiently dilute that binary diffusion coefficients for NO_2 and air and N_2O_4 and air may be used;
- (3) mixtures of N(IV) and air obey the ideal gas law; and
- (4) both NO_2 and N_2O_4 obey the continuity equation.

The continuity equations for NO_2 and N_2O_4 are:

$$- dN_A / dx = 2 R_{G1} = 2 k_{G1} p_A^2 - 2 k_{G1} p_B \quad (90)$$

and

$$- dN_B / dx = - R_{G1} = k_{G1} p_B - k_{G1} p_A^2 \quad . \quad (91)$$

Assuming NO_2 is dilute in air and the ideal gas law applies, Fick's Law for NO_2 is

$$N_A = - (D_A^G / R T) dp_A / dx \quad . \quad (92)$$

Assuming N_2O_4 is dilute in air and the ideal gas law applies, Fick's Law for N_2O_4 is

$$N_B = - (D_B^G / R T) dp_B / dx \quad . \quad (93)$$

Substituting Equation 92 into Equation 90 gives:

$$(D_A^G / R T) d^2 p_A / dx^2 = 2 k_{G1} p_A^2 - 2 k_{G1} p_B \quad . \quad (94)$$

Substituting Equation 93 into Equation 91 gives:

$$(D_B^G / R T) d^2 p_B / dx^2 = - k_{G1} p_A^2 + k_{G1} p_B \quad . \quad (95)$$

Adding twice Equation 95 to Equation 94 and rearranging gives:

$$(D_A^G / R T) d^2 p_A / dx^2 = - 2 (D_B^G / R T) d^2 p_B / dx^2 \quad . \quad (96)$$

This second order differential equation is satisfied by the relationship:

$$p_A = - 2 (D_B^G / D_A^G) p_B + c_1 x + c_2 \quad . \quad (97)$$

If the gas phase mass transfer coefficient, k_g , is determined for NO_2 either by measuring a value of k_g and correcting it for the molecular weight of NO_2 or by using a correlation, then using the equation

$$f^G = D_A^G / (k_g R T) \quad (98)$$

to determine the gas phase film thickness, f^G , and requiring that NO_2 and N_2O_4 be in equilibrium in the bulk gas phase and at the gas-liquid interface gives the flux of N(IV) across the gas phase film as:

$$N_{N(IV),i} = k_g (p_{A,b} - p_{A,i}) + 2 k_g (p_{B,b} - p_{B,i}) \quad . \quad (99)$$

3. KCF MODEL

The KCF model was developed in Chapter II, Equation 67 through Equation 83. Karlsson (1983) developed the KCF model to describe the reactive dissolution of N(IV) in aqueous solutions where the rate of dissolution is controlled by the hydrolysis of N(IV). This model is based on the assumptions:

- (1) the reactive dissolution of N(IV) may be modeled by the film theory;
- (2) NO₂ and N₂O₄ are in equilibrium by Reaction 1 everywhere in the liquid phase;
- (3) both NO₂ and N₂O₄ obey Fick's Law of Diffusion;
- (4) both NO₂ and N₂O₄ obey the continuity equation;
- (5) the reverse of the hydrolysis of N(IV) is sufficiently slow that it may be neglected, either due to a small liquid phase residence time or elimination of the reverse reaction by absorption into a basic solution; and
- (6) the hydrolysis of N(IV) is sufficiently fast that both N(IV) species react to completion in the liquid phase film (i.e. the absorption of N(IV) is in the fast reaction regime).

Equation 81 is a form of the KCF model; combining Equations 81, 82, 83, and 29 gives an expression for the interfacial flux of N(IV) in terms of the interfacial concentration of NO₂ as:

$$N_{N(IV),i} = [4 k_{A37} D_B K_{A1} c_{A,i}^4 + 4 k_{A37} D_A c_{A,i}^3 / 3]^{0.5} , \quad (100)$$

Equation 99, the equation for the flux across the gas-liquid interface based on the gas phase resistance, may be expressed in terms of the interfacial concentration of NO₂ as:

$$N_{N(IV),i} = k_g (p_{A,b} - c_{A,i} / H_A) + 2 k_g K_{G1} (p_{A,b}^2 - c_{A,i}^2 / H_A^2) . \quad (101)$$

Equations 100 and 101 may be solved simultaneously for the interfacial flux of N(IV) and the interfacial concentration of NO₂ for any bulk phase partial pressure of NO₂.

The KCF model may be applied to a packed tower by using the following procedure:

- (1) determine numeric values for the operating conditions of the packed tower; the conditions are the gas phase loading, the height of the tower, the interfacial area of the tower, the operating pressure of the tower, the operating temperature of the tower, and the inlet partial pressure of N(IV);
- (2) estimate the outlet partial pressure of N(IV);
- (3) integrate Equation 89 numerically, calculating a new value of the interfacial flux of N(IV) by simultaneously solving Equations 100 and 101 at each value of $p_{A,b}$ needed for the integration;

- (4) if the value of the integral of Equation 89 satisfies the equality within acceptable error limits then the estimated outlet partial pressure of N(IV) is the correct value, otherwise a new outlet partial pressure of N(IV) must be estimated and steps (3) and (4) repeated.

Since the algorithm for applying the KCF model to a packed tower indicates that Equations 100 and 101 must be solved simultaneously at any value of $p_{A,b}$ used to integrate Equation 89, an integration technique that uses few steps to achieve a given accuracy should be efficient for applying the KCF model to a packed tower.

4. GENERAL COMBINED FLUX MODEL

A general combined flux (GCF) model for the reactive dissolution of N(IV) may be derived using the following assumptions:

- (1) the reactive dissolution of N(IV) may be modeled by the film theory;
- (2) NO_2 and N_2O_4 are in equilibrium by Reaction 1 everywhere in the liquid phase;
- (3) both NO_2 and N_2O_4 obey Fick's Law of Diffusion;
- (4) both NO_2 and N_2O_4 obey the continuity equation;
- (5) the reverse of the hydrolysis reaction is sufficiently slow that it may be neglected, either due to a small liquid phase

residence time or elimination of the reverse reaction by absorption into a basic solution; and

- (6) the liquid phase material balance for N(IV) applies in the liquid bulk phase.

The GCF model avoids the fast reaction regime assumption of the KCF model. The derivation of the GCF model follows the derivation of the KCF model up to and including Equation 74:

$$V \, dV / dU = k_{A37} [2 + \beta U - 2 (1 + \beta U)^{0.5}] / (D_B \beta) \quad . \quad (74)$$

Equation 75 defines the symbol β . Karlsson solved Equation 74 by separating the variables and integrating the equation with boundary conditions:

at the gas-liquid interface

$$U = U_i \quad \text{and} \quad (76)$$

$$V = - N_{N(IV),i} / D_B \quad ; \quad (77)$$

at the liquid film-bulk interface

$$U = 0 \quad \text{and} \quad (78)$$

$$V = 0 \quad . \quad (79)$$

The boundary conditions at the gas-liquid interface are the same for the GCF model as they were for the KCF model. The boundary conditions at the liquid film-bulk interface are now controlled by the liquid phase material balance for N(IV). For a packed tower this is:

$$(L / C_t) \, dc_{N(IV),b} / dz = a \, N_{N(IV),b} - h_t \, k_{A37} \, c_{A,b}^2 \quad . \quad (102)$$

If the left hand side of Equation 102 is small compared to the terms on the right hand side of Equation 102 then the left hand side of Equation 102 may be set to zero and solved for $N_{N(V),b}$ in terms of $c_{A,b}$ as:

$$N_{N(V),b} = (h_t / a) k_{A37} c_{A,b}^2 \quad . \quad (103)$$

This assumption is shown to introduce little error in Appendix C. Equation 103 may be expressed in terms of the variables U and V as:

$$-D_B V_b = (h_t / a) k_{A37} (1 + \beta U_b / 2 - \sqrt{1 + \beta U_b}) / (\beta K_{A1}) \quad . \quad (104)$$

Equation 74 may be integrated with the boundary conditions:

at the gas-liquid interface

$$U = U_i \quad \text{and} \quad (76)$$

$$V = -N_{N(V),i} / D_B \quad ; \quad (77)$$

at the liquid film-bulk interface

$$U = U_b \quad \text{and} \quad (105)$$

$$V = V_b \quad ; \quad (106)$$

giving:

$$V_b^2 - V_i^2 = [k_{A37} / (D_B \beta)] \{ 4 (U_b - U_i) + \beta (U_b^2 - U_i^2) - [\beta / (3 \beta)] [(1 + \beta U_b)^{1.5} - (1 + \beta U_i)^{1.5}] \} \quad . \quad (107)$$

Equation 74 results from a transformation of variables of Equation 71. Equation 71 is a second order differential equation; Equation 74 is a first order differential equation, therefore another equation can be found which completes the system of equations needed to generate a general combined flux model; Equation 73 is sufficient:

$$V = dU / dx \quad . \quad (73)$$

Equation 74 may be integrated from the gas-liquid interface to any point in the liquid phase film (U,V) to give:

$$V^2 - V_i^2 = [k_{A37} / (D_B \beta)] \{ 4 (U - U_i) + \beta (U^2 - U_i^2) - [8 / (3 \beta)] [(1 + \beta U)^{1.5} - (1 + \beta U_i)^{1.5}] \} \quad (108)$$

Equation 108 may be solved for V in terms of U so Equation 73 may be separated and integrated numerically:

$$\int_0^{f^L} dx = \int_{U_i}^{U_b} (dU / V) \quad (109)$$

Since the liquid phase film thickness, f^L , is equal to D_A / k_i , Equation 109 may be expressed as:

$$D_A / k_i = \int_{U_i}^{U_b} (dU / V) \quad (110)$$

Equation 99, the equation for the flux across the gas-liquid interface based on the gas phase resistance, may be expressed in terms of U, V, and the bulk partial pressure of NO_2 as:

$$\begin{aligned} - D_B V_i &= k_g (p_{A,b} + 2 K_{G1} p_{A,b}^2) - \\ &k_g [\sqrt{(\beta^{-1} + U_i)} / (2 K_{A1}) - D_A / (4 D_B K_{A1})] / H_A - \\ &2 k_g (1 + \beta U_i / 2 - \sqrt{1 + \beta U_i}) / (\beta H_B) \quad (111) \end{aligned}$$

Equations 104, 107, 110, and 111 complete a system of four independent equations for the four unknowns U_i , U_b , V_i , and V_b ; this is the GCF model.

The GCF model may be applied to a packed tower by using the following procedure:

- (1) determine the operating conditions for the packed tower, these are the gas phase loading, the height of the tower, the interfacial area of the tower, the operating pressure of the tower, the operating temperature of the tower, and the inlet partial pressure of N(IV);
- (2) estimate the outlet partial pressure of N(IV);
- (3) integrate Equation 89 numerically, calculating a new value of the interfacial flux of N(IV) by simultaneously solving Equations 104, 107, 110, and 111 at each value of $p_{A,b}$ needed for the integration;
- (4) if the value of the integral of Equation 89 satisfies the equality within acceptable error limits then the estimated outlet partial pressure of N(IV) is the correct value, otherwise a new outlet partial pressure of N(IV) must be estimated and steps (3) and (4) repeated.

Since the algorithm for applying the GCF model to a packed tower indicates that Equations 104, 107, 110, and 111 must be solved simultaneously at any value of $p_{A,b}$ used to integrate Equation 89, an integration technique that uses few steps to achieve a given accuracy should be efficient for applying the GCF model to a packed tower.

Equation 102, the liquid phase material balance, may be expressed in terms of U_b and V_b then used as the bulk liquid boundary condition instead of Equation 104 if Equation 84 is used for the gas phase material

balance; in this case the gas and liquid material balances may be solved by a finite differences approach so the left hand side term of Equation 84 is not neglected.

CHAPTER V

RESULTS

1. EXPERIMENTAL RESULTS

As was noted in Chapter III, the experimental results are a product of eight series of experimental runs at set liquid and gas flow rates of 0.027 kg/s and $2.5 \times 10^3 \text{ m}^3/\text{s}$, respectively, and average temperatures of 23°C to 27°C where the absorbent solutions were water, 0.3 N NaOH, 0.6 N NaOH, and 1.0 N NaOH. The experimental conditions for each series of runs, series A through series H, are shown in Table 9. The partial pressure of N(IV) in the inlet gas mixture varied from $3.75 \times 10^4 \text{ atm.}$ to $4.94 \times 10^3 \text{ atm.}$ N(IV) scrubbing efficiencies ranged from 0.248 to 0.616. The scrubbing efficiencies are presented as decimal values. A scrubbing efficiency of one would indicate 100% removal of N(IV). The experimental scrubbing results are listed in Table 10 for 0.3 N NaOH, in Table 11 for water, in Table 12 for 0.6 N NaOH, and in Table 13 for 1.0 N NaOH.

All the experimental scrubbing results are combined in Figure 11. Any effect of sodium hydroxide molarity was concealed by the scatter in the experimental data. The maximum experimental temperature was 27°C during series C; the minimum experimental temperature was 23°C during series E. The high and low temperature series are shown in Figure 12. Variations in temperature had negligible effects on the experimental scrubbing efficiencies.

The following analysis of the experimental results includes an analysis of data available in the literature conducted in an effort to find an enhancement factor modifier for the flux of N(IV) into sodium hydroxide solutions. The enhancement factor modifier accounts for the reaction of N_2O_4 with OH^- and the salting out effect of electrolytes on the solubility of gases. This modifier can be multiplied by a calculated value for the flux of N(IV) into water to determine the value for the flux of N(IV) into sodium hydroxide. The values of the enhancement factor modifier are calculated for 0.3 N NaOH, 0.6 N NaOH, and 1.0 N NaOH and are compared to the experimental results.

A reaction number, the square of the Hatta number, is derived for the KCF model, then tested by comparing the predictions of the KCF model to the GCF model. Reaction numbers are calculated for the experimental runs to test the applicability of the KCF model to the experimental data. The KCF model is analyzed for sensitivity to k_{A37} , H_A , H_B , a , and k_g . The KCF model is not analyzed for sensitivity to K_{A1} since any change in K_{A1} necessitates a change in either H_A or H_B . A regression analysis of the best value of H_B for a given value of k_{A37} using the KCF model and the experimental data allows the comparison of the experimental data to the literature data presented in Figure 7. New parameters for the solubility of N_2O_4 , H_B , and the pseudo-second order hydrolysis rate constant for N(IV), k_{A37} , are recommended following this analysis. A new reaction mechanism is proposed for the hydrolysis of N(IV).

Table 9 Experimental Conditions for Each Series of Runs

Series	Beginning [OH ⁻] (kgmol/m ³)	Ending [OH ⁻] (kgmol/m ³)	Temperature (°C)	Runs
A	0.324	0.300	24.5	1 to 5
B	0.306	0.283	25.0	6 to 10
C	water	water	27.0	11 to 17
D	water	water	24.5	18 to 23
E	0.631	0.596	23.0	24 to 28
F	0.587	0.570	24.0	29 to 33
G	1.070	1.048	26.0	34 to 39
H	1.032	1.007	24.5	40 to 44

Table 10 Experimental Runs for 0.3 N NaOH Absorbents (Series A and B)

Run	$P_{N(IV),in}$ (10^{-6} atm)	$P_{N(IV),out}$ (10^{-6} atm)	N(IV) Removal Efficiency
1	4190	1610	0.616
2	3260	1440	0.558
3	1718	963	0.439
4	878	550	0.374
5	422	308	0.270
6	4280	1800	0.579
7	3060	1400	0.542
8	2460	1210	0.508
9	1363	770	0.435
10	461	341	0.260

Table 11 Experimental Runs for Distilled Water Absorbents (Series C and D)

Run	$P_{N(IV),in}$ (10^{-6} atm)	$P_{N(IV),out}$ (10^{-6} atm)	N(IV) Removal Efficiency	$P_{NO,out}$ (10^{-6} atm)
11	2980	1460	0.510	340
12	3770	1610	0.573	480
13	2820	1330	0.528	350
14	1268	748	0.410	100
15	623	443	0.289	30
16	572	404	0.294	25
17	457	343	0.249	25
18	4230	1800	0.574	530
19	4940	2030	0.589	700
20	1890	980	0.481	138
21	1953	1005	0.485	125
22	508	385	0.242	30
23	375	282	0.248	20

Table 12 Experimental Runs for 0.6 N NaOH Absorbents (Series E and F)

Run	$P_{N(IV),in}$ (10^{-6} atm)	$P_{N(IV),out}$ (10^{-6} atm)	N(IV) Removal Efficiency
24	4740	1930	0.593
25	2700	1340	0.504
26	2035	1118	0.451
27	1608	853	0.470
28	1133	673	0.403
29	4100	1760	0.571
30	2690	1340	0.502
31	2740	1340	0.511
32	1450	798	0.450
33	599	426	0.289

Table 13 Experimental Runs for 1.0 N NaOH Absorbents (Series G and H)

Run	$P_{N(IV),in}$ (10^{-6} atm)	$P_{N(IV),out}$ (10^{-6} atm)	N(IV) Removal Efficiency
34	3290	1430	0.565
35	2780	1320	0.525
36	2470	1260	0.490
37	1510	795	0.474
38	613	434	0.292
39	564	402	0.287
40	4180	1780	0.574
41	3780	1730	0.542
42	3110	1460	0.531
43	1328	758	0.429
44	921	608	0.340

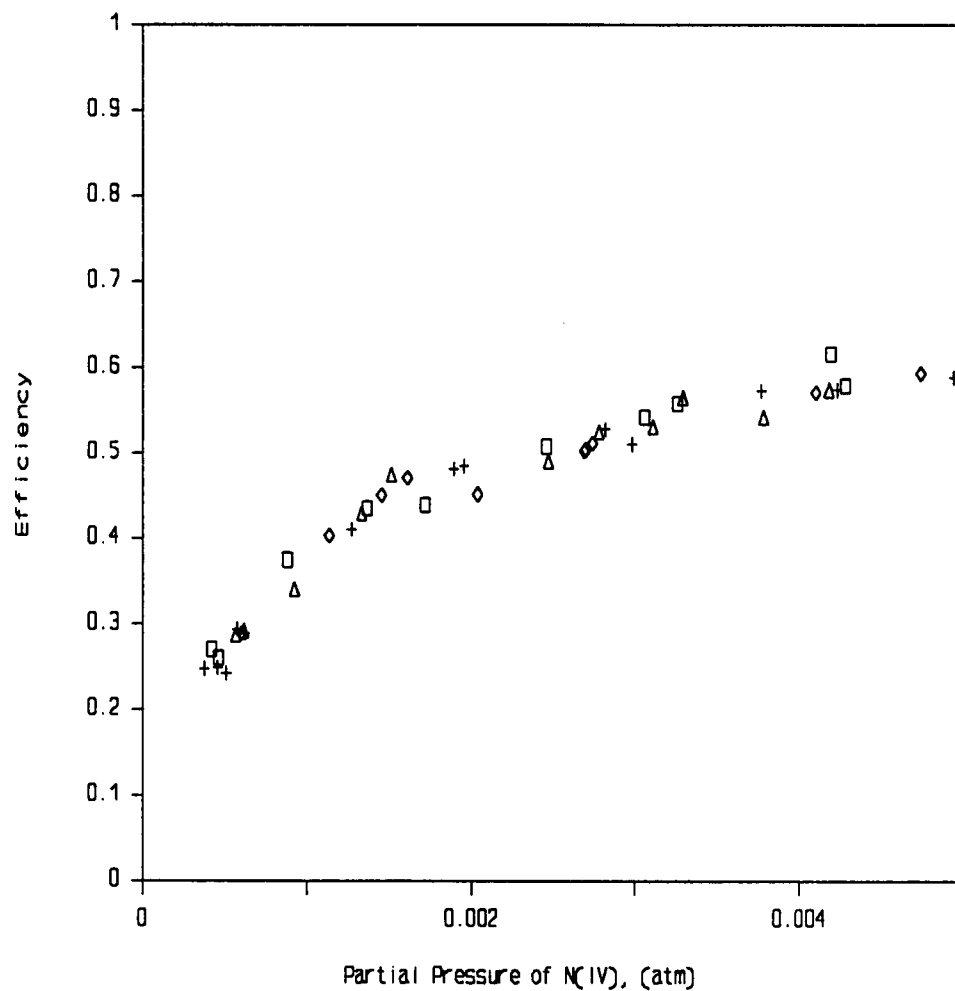


Figure 11 Experimental Scrubbing Efficiencies for N(IV) Removal in a Packed Tower for Various Sodium Hydroxide Concentrations

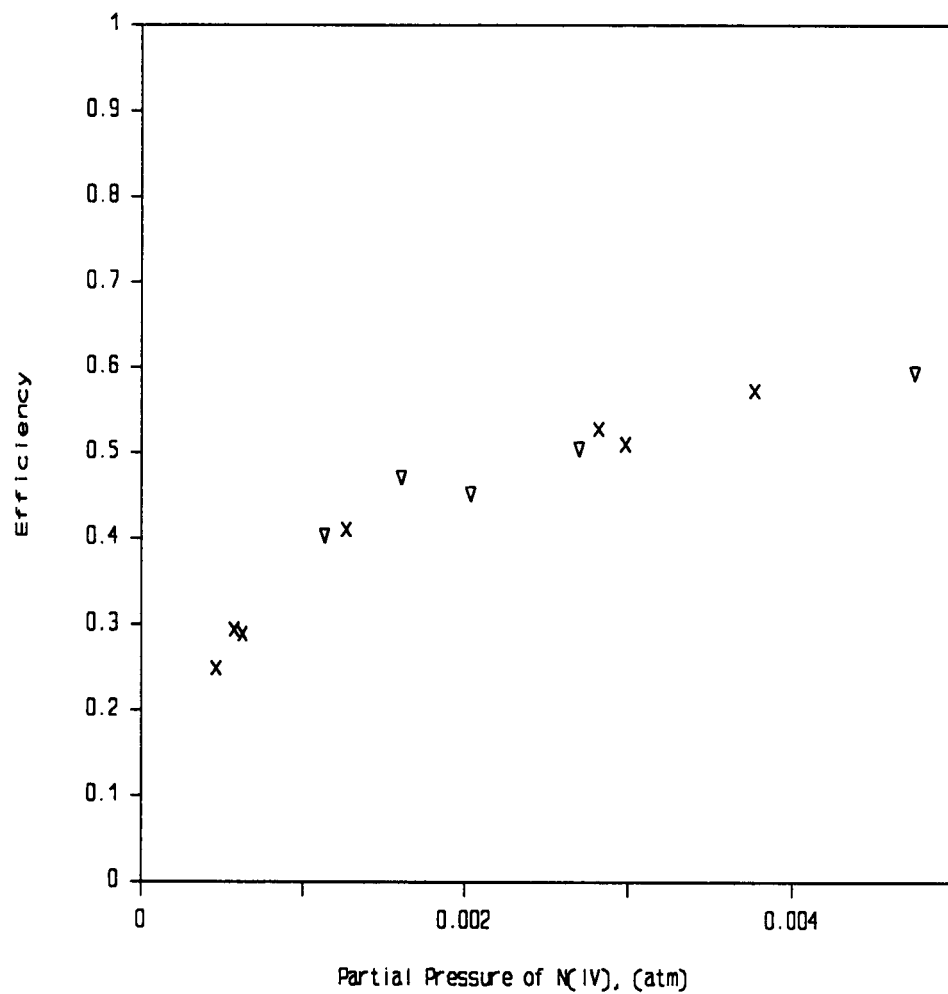


Figure 12 Experimental Scrubbing Efficiencies for N(IV) Removal in a Packed Tower at 23°C and 27°C

2. ANALYSIS OF EFFECT OF SODIUM HYDROXIDE ON EXPERIMENTAL VALUES OF

$$H_B \sqrt{D_B k_{A37} / K_{A1}}$$

The fact that the rate of absorption of N(IV) did not change appreciably with sodium hydroxide concentration is surprising in light of Equation 48:

$$E_{OH} = \{ [1 + (k_{A42} K_{A1} / k_{A37}) c_{OH}] / (1 + 0.264 c_{OH} - 0.0173 c_{OH}^2 + 0.0117 c_{OH}^3) \}^{0.5} 10^{-hI} \quad (48)$$

Equation 48 is the enhancement factor modifier for the reactive dissolution of high partial pressures of N(IV) into aqueous sodium hydroxide solutions considering the effect of electrolytes on the solubility of gases, the effect of viscosity on liquid phase diffusion coefficients, and the possibility of Reaction 42, the reaction of N_2O_4 with OH^- . If sodium hydroxide is the only electrolyte in an aqueous solution and it is completely dissociated then the ionic strength of the solution and the sodium hydroxide concentration, c_{OH} , are the same; Equation 48 may be solved for the sodium hydroxide concentration which gives the greatest enhancement of the rate of the reactive dissolution of N(IV) if the effect of viscosity on the diffusion coefficient is small enough to be neglected. Setting the partial derivative of E_{OH} (without the viscosity term) with respect to the sodium hydroxide concentration to zero and rearranging gives an equation for the sodium hydroxide concentration for which the flux of N(IV) is a maximum:

$$c_{OH} = [2 h \log_e(10)]^{-1} - k_{A37} / (K_{A1} k_{A42}) \quad (112)$$

If h_G , the salting coefficient, for N_2O_4 is assumed to be $0 \text{ m}^3/\text{kgmol}$, k_{A37} / K_{A1} is assumed to be 194 s^{-1} , and $k_{A42} = 147 \text{ m}^3/\text{kgmol}(\text{OH}^-)\text{-s}$ as indicated by Kameoka and Pigford (1977), then the Equation 48 gives $c_{\text{OH}} = 0.063 \text{ kgmol/m}^3$, the sodium hydroxide concentration for which the reactive dissolution of N(IV) should be maximized. The value of E_{OH} at $c_{\text{OH}} = 0.063 \text{ kgmol/m}^3$ is 0.9923. Neglecting the effect of viscosity on the diffusion coefficient leads to some error in Equation 112. In the case of the values given above the maximum flux of N(IV) is the flux when water is the absorbent; however, if the value of k_{A37} is higher it is reasonable to expect that the rate of reactive dissolution of N(IV) may have a maximum value with respect to the sodium hydroxide concentration of the absorbent, but that the maximum enhancement may too small to be noticed experimentally with scrubbing experiments. Since Kameoka and Pigford indicated that 0.2 N NaOH increases the rate of the reactive dissolution of N(IV) by 7% compared to the rate for the dissolution into water, it is possible that the maximum increase in the rate is significant. Fitting Equation 48 to experimental results may be the only method of determining appropriate values of h and $k_{A42} K_{A1} / k_{A37}$. These values may be used in Equation 112 to approximate the concentration of sodium hydroxide for which the rate of reactive dissolution of N(IV) is maximized.

Analysis of the experimental results of Chambers and Sherwood (1937), presented in Table 6, for values of $H_B \sqrt{D_B k_{A37} / K_{A1}}$ as a function of sodium hydroxide concentration may be used to fit Equation 48 to

determine the unknown values of h and $k_{A42} K_{A1} / k_{A37}$. Chambers and Sherwood presented results for the gas phase mass transfer film thickness determined from the vaporization of water; these results were in agreement with the correlation of Sherwood and Gilliland (1934) for gas phase mass transfer coefficients for wetted wall columns:

$$k_g = 0.023 \text{ Re}^{0.83} \text{ Sc}^{0.44} P D_i^G / (D p_{LM} R T) \quad (113)$$

Equation 113, in conjunction with data for $N_{N(IV)}$ and $p_{N(IV),M}$ from Table 6 and the Gilliland-type gaseous diffusion coefficient correlation from the Chemical Engineers' Handbook (1973), can be used in Equation 99, the equation for the flux of NO_2 and N_2O_4 through the gas phase film, to calculate the log mean interfacial partial pressures of NO_2 and N_2O_4 for the data of Chambers and Sherwood. The lowest calculated value for the interfacial partial pressure of N(IV) is 2.73×10^{-2} atm. for Run 61; using the lowest interfacial partial pressure of N(IV) and Schwartz and White's (1983) recommended values for k_{A37} , K_{A1} , and H_A to calculate the flux of N(IV) by the KCF model indicates that ignoring the second term on the right hand side of Equation 100 leads to a maximum error in the calculated value of $N_{N(IV)}$ of 1.6%. Therefore Chambers and Sherwood's data for the absorption of N(IV) may be modeled as:

$$N_{N(IV)} = 2 p_{B,M,i} H_B \sqrt{k_{A114} D_B} \quad (114)$$

where the hydrolysis of N(IV) and any reaction of N(IV) with sodium hydroxide is modeled with the effective reaction rate constant k_{A114} , the effect of sodium hydroxide concentration on the solubility of N_2O_4 is accounted for

by the Henry's Law constant for N_2O_4 , and the effect of viscosity on the diffusion coefficient of N_2O_4 is accounted for by D_B . Each of the 18 experimental runs by Chambers and Sherwood for the absorption of N(IV) into sodium hydroxide solutions in a wetted wall column can be analyzed for a value of $H_B \sqrt{k_{A114} D_B}$; these values are shown as a function of sodium hydroxide concentration in Figure 13.

The data for $H_B \sqrt{k_{A114} D_B}$ as a function of sodium hydroxide concentration may be fit to Equation 47,

$$N_{N(IV)} = 2 p_{B,i} \{ D_B^\circ [(k_{A37} / K_{A1}) + k_{A42} c_{OH}] / (1 + 0.264 c_{OH} - 0.0173 c_{OH}^2 + 0.0117 c_{OH}^3) \}^{0.5} H_B^\circ 10^{-H} \quad (47)$$

The vast majority of the data shown in Figure 13 are data at $\sim 0.7 \text{ kgmol/m}^3$ NaOH and $\sim 5.3 \text{ kgmol/m}^3$ NaOH. Equation 46 may be fit to these data more easily if a reasonable value of the salting coefficient can be found for N_2O_4 . The data of Peters and Holman for the reactive dissolution of N(IV) into water and 4.9 N sodium chloride in a wetted wall column at 34°C , presented in Table 7, may be used to estimate a value of h_c for N_2O_4 . The lowest calculated value for the interfacial partial pressure of N(IV) is $2.23 \times 10^{-2} \text{ atm.}$ for Run 61; using the lowest interfacial partial pressure of N(IV) and Schwartz and White's (1983) recommended values for k_{A37} , K_{A1} , and H_A to calculate the flux of N(IV) by the KCF model indicates that ignoring the second term on the right hand side of Equation 100 leads to a maximum error in the calculated value of $N_{N(IV)}$ of 1.7%. Therefore Peters and Holman's data for the absorption of N(IV) may be modeled with

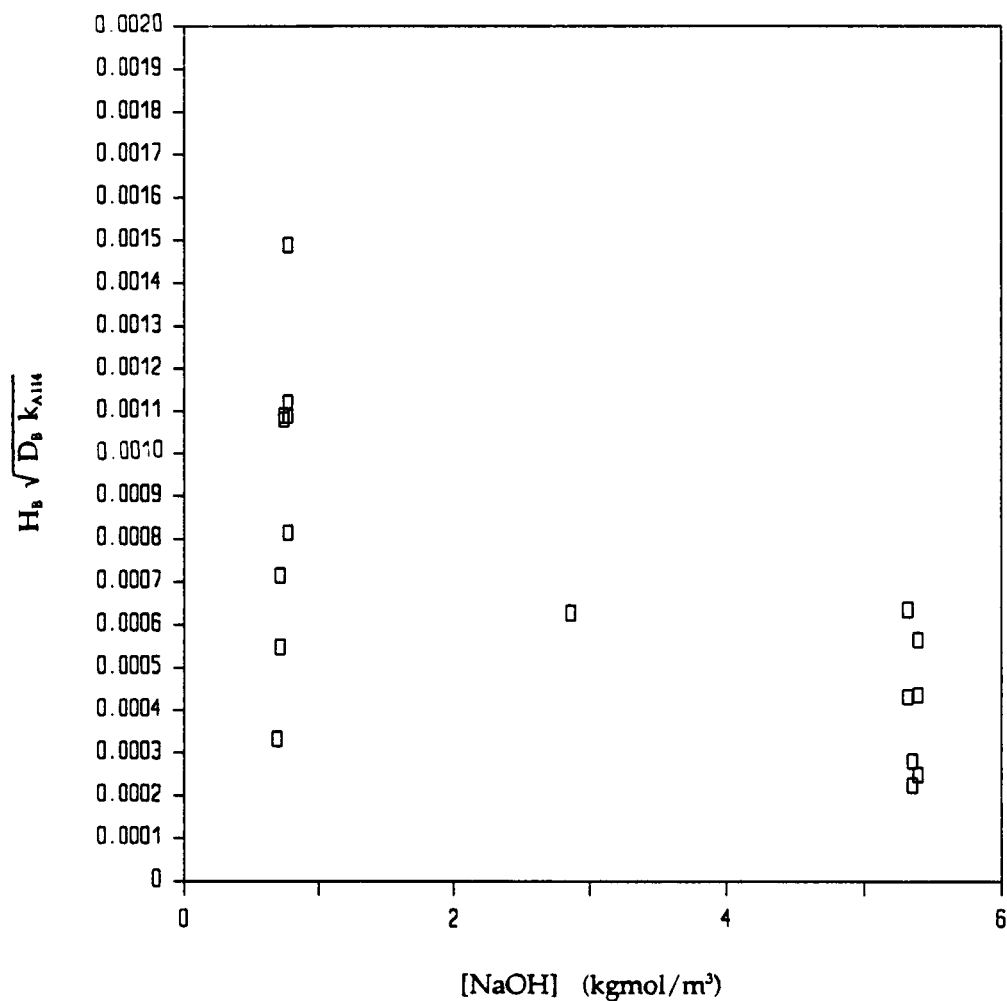


Figure 13 Experimental Values^a of $H_B \sqrt{D_B k_{A114}}$ for the Absorption of N(IV) into Sodium Hydroxide Solutions

^a Chambers, F. S. Jr., and T. K. Sherwood, "Absorption of Nitrogen Dioxide by Aqueous Solutions," *Ind. Eng. Chem.*, **29**, 1415 (1937).

Equation 114. Since NO_2 and N_2O_4 are not expected to react with sodium chloride the use of k_{A37} is appropriate if the activity of water is unaffected by the sodium chloride solution. The effect of the solution on the solubility of N_2O_4 must be considered. The effect of electrolytes on the solubility of gases was reviewed in Chapter II:

$$H_i = H_i^\circ 10^{-h_i} \quad , \text{ where} \quad (44)$$

$$h = h_+ + h_- + h_G \quad . \quad (45)$$

Using the calculated values of the flux of N(IV) shown in Table 14 and the values: $h_+ = 0.091 \text{ m}^3/\text{kgmol}(\text{Na}^+)$; and $h_- = 0.021 \text{ m}^3/\text{kgmol}(\text{Cl}^-)$; with Equations 113, 44, and 45 gives $h_G = 0.020 \text{ m}^3/\text{kgmol}$ for N_2O_4 . Since the value of h_G for N_2O_4 was calculated from two data points such that there are no degrees of freedom it is difficult to estimate the possible error in that value. Hoftyzer and Kwanten (1972) indicated that the results of N(IV) absorption at high partial pressures of NO_2 , $p_A > 0.04 \text{ atm}$, into nitric acid laminar jets of various concentrations can be modeled, as a first approximation, by Equation 44 with $e^{-0.075 I}$ replacing the term 10^{-h_i} . Since Danckwerts (1970) indicated $h_+ = 0.000 \text{ m}^3/\text{kgmol}(\text{H}^+)$ and $h_- = -0.001 \text{ m}^3/\text{kgmol}(\text{NO}_3^-)$, the value $h_G = 0.034 \text{ m}^3/\text{kgmol}$ for N_2O_4 may be deduced from the approximation shown by Hoftyzer and Kwanten, in reasonable agreement with the value derived from the data of Peters and Holman. Testing the calculated value of $h_G = 0.020 \text{ m}^3/\text{kgmol}$ for N_2O_4 against the results of Chambers and Sherwood (1937) shown in Figure 13 may be the best method of determining the usefulness of the value. Using $h_G = 0.020 \text{ m}^3/\text{kgmol}$,

Table 14 Calculated Values of $H_B \sqrt{D_B k_{A37} / K_{A1}}$ from the Experimental Data of Peters and Holman (1955)^a for the Absorption of N(IV) into 4.9 N NaCl^b Solution and Water

Run	Solution	$p_{N(IV),M,1}$ (atm)	$H_B \sqrt{D_B k_{A37} / K_{A1}}$ (kgmol/m ² -atm-s)
1	water	0.0223	2.7×10^{-3}
21	4.9 M NaCl	0.0372	4.5×10^{-4}

^a Peters, M. S., and J. L. Holman, "Vapor- and Liquid-Phase Reactions between Nitrogen Dioxide and Water," *Ind. Eng. Chem.*, **47**, 2536 (1955).

$h_+ = 0.091 \text{ m}^3/\text{kgmol}(\text{Na}^+)$, and $h_- = 0.066 \text{ m}^3/\text{kgmol}(\text{OH}^-)$ to give $h = 0.177 \text{ m}^3/\text{kgmol}$, Equation 47 is represented graphically against the results of Chambers and Sherwood in Figures 14, 15, and 16 where $k_{A42} = 0, 147$, and $357 \text{ m}^3/\text{kgmol}(\text{OH}^-)\text{-s}$, respectively, and $k_{A37} / K_{A1} = 194 \text{ s}^{-1}$; $k_{A42} = 147 \text{ m}^3/\text{kgmol}(\text{OH}^-)\text{-s}$ and $k_{A37} / K_{A1} = 194 \text{ s}^{-1}$ are the values recommended by Kameoka and Pigford (1977). The fit of Equation 47 to the results of Chambers and Sherwood is significantly better in Figure 16, where $k_{A42} = 357 \text{ m}^3/\text{kgmol}(\text{OH}^-)\text{-s}$ and $k_{A37} / K_{A1} = 194 \text{ s}^{-1}$, than in Figure 14 where Reaction 42 between the hydroxide ion and N_2O_4 was assumed not to occur. The poor fit of Equation 47 to the data in Figure 14 is compelling evidence that N_2O_4 and OH^- do react at an appreciable rate. The flux of N(IV) is 5.1% greater for $c_{\text{OH}} = 0.2 \text{ kgmol/m}^3$ than it is for water in Figure 16, where $k_{A42} K_{A1} / k_{A37} = 1.84 \text{ m}^3/\text{kgmol}$, similar to the 7% increase indicated by Kameoka and Pigford (1977). The flux of N(IV) has a maximum at $c_{\text{OH}} = 0.412 \text{ kgmol/m}^3$ and decreases for all sodium hydroxide concentrations greater than 0.412 kgmol/m^3 if $k_{A42} K_{A1} / k_{A37} = 1.84 \text{ m}^3/\text{kgmol}$ and $h = 0.177 \text{ m}^3/\text{kgmol}$ as shown in Figure 16; decreasing N(IV) fluxes for concentrations greater than 1.0 kgmol/m^3 were noticed by Chambers and Sherwood and by Chilton and Knell (1972). The values of $k_{A42} K_{A1} / k_{A37} = 1.84 \text{ m}^3/\text{kgmol}$ and $h_c = 0.020 \text{ m}^3/\text{kgmol}$ are recommended as the best available values. Since the maximum enhancement of the flux of N(IV) due to the use of sodium hydroxide is only 6.6% if the above values are correct, the choice of a sodium hydroxide concentration for the removal of NO_x

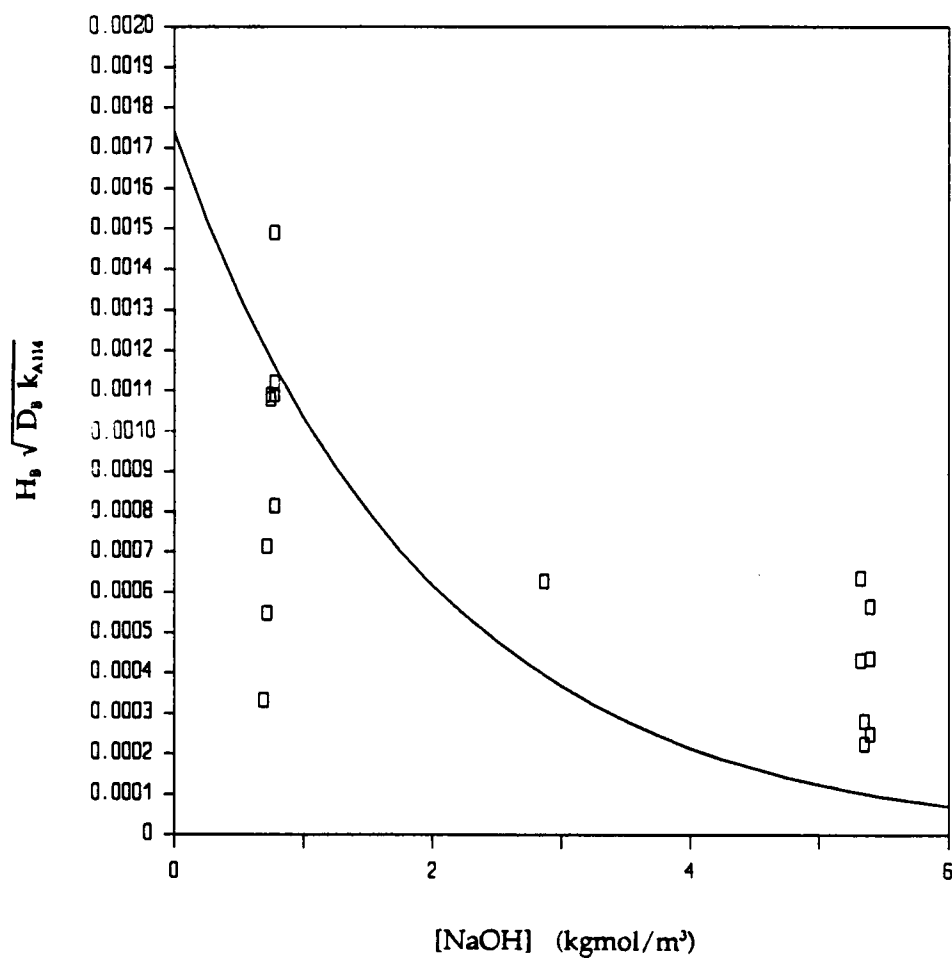


Figure 14 Comparison of Experimental Values^a of $H_B \sqrt{D_B k_{A114}}$ for the Absorption of N(IV) into Sodium Hydroxide Solutions to Calculated Values Where $h = 0.177 \text{ m}^3 / \text{kgmol}$ and $k_{A42} = 0$

^a Chambers, F. S. Jr., and T. K. Sherwood, "Absorption of Nitrogen Dioxide by Aqueous Solutions," *Ind. Eng. Chem.*, **29**, 1415 (1937).

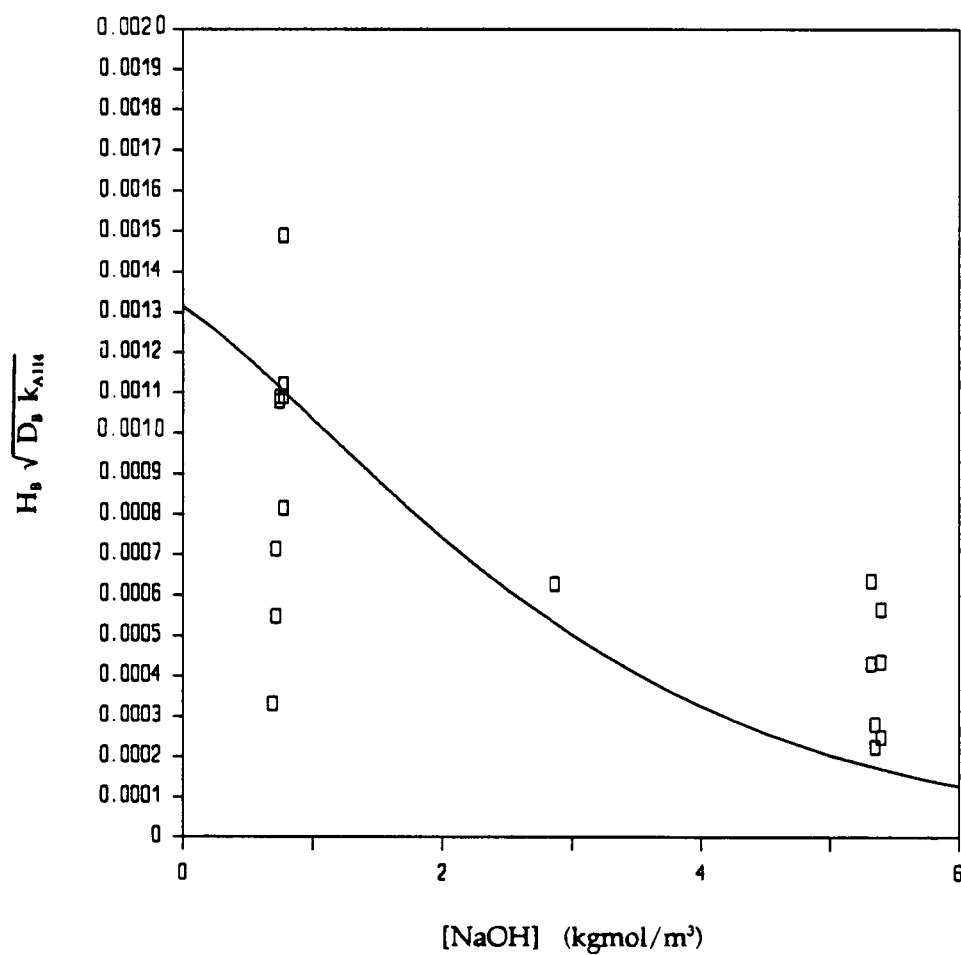


Figure 15 Comparison of Experimental Values ^a of $H_B \sqrt{D_B k_{A114}}$ to Calculated Values for $h = 0.177 \text{ m}^3 / \text{kgmol}$ and $k_{A42} K_{A1} / k_{A37} = 0.758 \text{ m}^3 / \text{kgmol}$

^a Chambers, F. S. Jr., and T. K. Sherwood, "Absorption of Nitrogen Dioxide by Aqueous Solutions," *Ind. Eng. Chem.*, **29**, 1415 (1937).

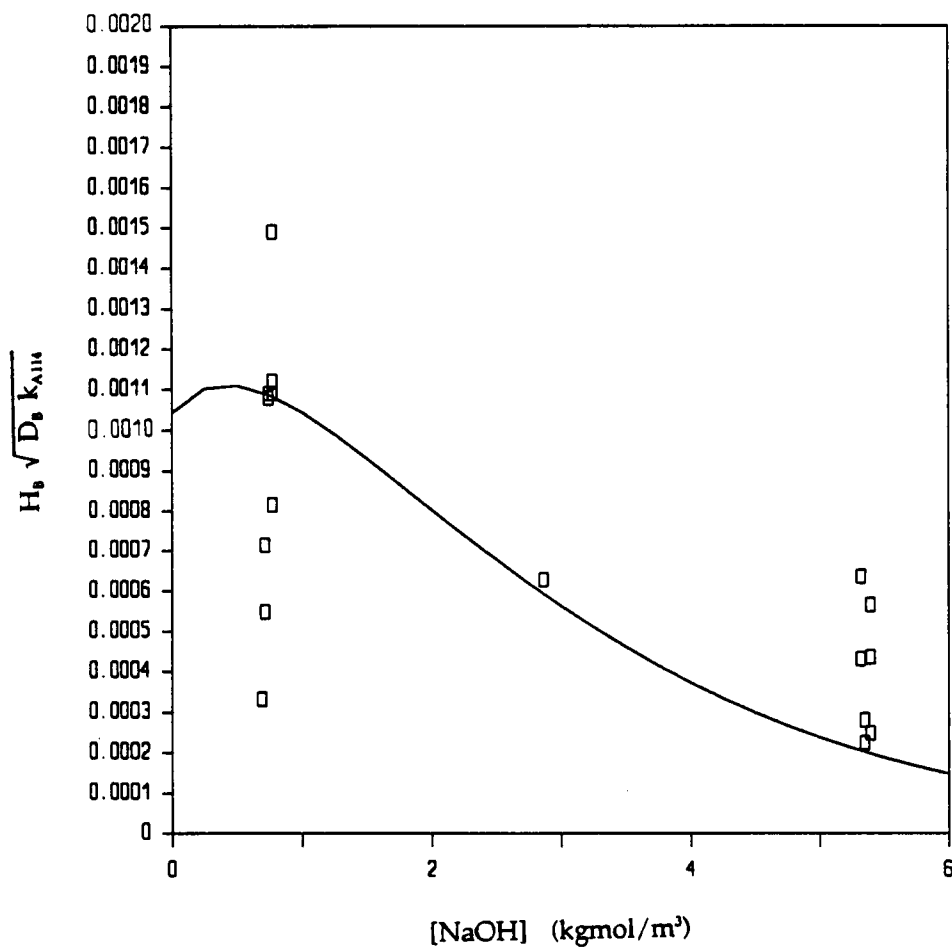


Figure 16 Comparison of Experimental Values ^a of $H_B \sqrt{D_B k_{A114}}$ to Calculated Values for $h = 0.177 \text{ m}^3 / \text{kgmol}$ and $k_{A42} K_{A1} / k_{A37} = 1.84 \text{ m}^3 / \text{kgmol}$

^a Chambers, F. S. Jr., and T. K. Sherwood, "Absorption of Nitrogen Dioxide by Aqueous Solutions," *Ind. Eng. Chem.*, **29**, 1415 (1937).

should not be very heavily influenced by the enhancing effect of sodium hydroxide concentration on the rate of absorption of N(IV), instead the economics of the disposal of the sodium contaminated waste stream would have the greatest influence on the sodium hydroxide concentration chosen. The difference in the flux of N(IV) for absorption into 0.412 N NaOH or 1.0 N NaOH using Equation 47 and the values of $k_{A42} K_{A1} / k_{A37} = 1.84 \text{ m}^3/\text{kgmol}$ and $h = 0.177 \text{ m}^3/\text{kgmol}$ is only 6.6%. This difference in the rate of flux of N(IV) would give a smaller difference in scrubbing efficiencies for a tower; the fact that no significant effect of sodium hydroxide concentration on the scrubbing efficiencies of N(IV) in a packed tower was noticed is due to variations in the data and the small range of NaOH concentrations studied rather than a lack of effect of sodium hydroxide concentrations on N(IV) absorption.

The enhancement factor modifier for the reactive dissolution of high partial pressures of N(IV) into aqueous sodium hydroxide solutions considering the effect of electrolytes on the solubility of gases, the effect of viscosity on diffusion coefficients, and the possibility of Reaction 42,

$$E_{\text{OH}} = \left\{ \left[1 + \left(k_{A42} K_{A1} / k_{A37} \right) C_{\text{OH}} \right] / \left(1 + 0.264 C_{\text{OH}} - 0.0173 C_{\text{OH}}^2 + 0.0117 C_{\text{OH}}^3 \right) \right\}^{0.5} 10^{-H} \quad (48)$$

is a simplified expression for the enhancing or reducing effects of sodium hydroxide solution on the flux of N(IV). A satisfactory fit of Equation 48 to Kameoka and Pigford's (1977) results and results calculated from Chambers and Sherwood's (1937) data is

$$E_{OH} = 10^{-0.177 \cdot I} \{ [1 + 1.84 c_{OH}] / (1 + 0.264 c_{OH} - 0.0173 c_{OH}^2 + 0.0117 c_{OH}^3) \}^{0.5} . \quad (115)$$

Equation 115 should be used to predict the enhancement or reduction in the flux of high partial pressures of N(IV) due to the use of aqueous NaOH solution absorbents. The use of the expression should be limited to N(IV) partial pressures over 0.02 atm, sodium hydroxide concentrations less than 6 kgmol/m³, and temperatures very close to 25°C since the data used to develop the expression matched these conditions. The enhancement factor modifiers for the NaOH scrubbing solutions used are: $E_{OH} = 1.062$ for 0.3 N NaOH, series A and B; $E_{OH} = 1.057$ for 0.6 N NaOH, series E and F; and $E_{OH} = 1.000$ for 1.0 N NaOH, series G and H. A regression analysis of the data from the scrubbing experiments with an appropriate model, either the KCF model or GCF model, may be used to test the applicability of the enhancement factor modifier to N(IV) partial pressures as low as 3×10^{-4} atm. The usefulness of the expression is greatly increased if the results of the regressions indicate that the enhancement factor modifier is applicable to the experimental scrubbing results.

3. DETERMINATION OF A REACTION NUMBER FOR N(IV)

Danckwerts (1970) provided a summary of mathematical techniques of modeling the reactive dissolution of gases in liquids. The fast first order reaction model and the fast second order reaction model, derived from the film theory, have already been presented in Equation 10 and Equation 16.

A first order reaction qualifies as a fast first order reaction for which Equation 10 is applicable if the first order reaction number, $M_{(1)}$, as defined in Equation 11, is greater than nine. A second order reaction qualifies as a fast second order reaction for which Equation 16 is applicable if the second order reaction number, $M_{(2)}$, as defined in Equation 17, is greater than nine. These reaction numbers, $M_{(1)}$ and $M_{(2)}$, are the squares of the Hatta numbers for first and second order reactions and can be derived from the following equation:

$$\sqrt{M_{(n)}} = \frac{\text{Flux if the gaseous component absorbs due to enhancement by a fast } n^{\text{th}} \text{ order reaction such that there is no flux into the bulk liquid phase and zero concentration of the absorbing component in the bulk liquid phase}}{\text{Flux if the gaseous component absorbs due to physical mass transfer such that there is zero concentration of the absorbing component in the bulk liquid phase}} \quad (116)$$

For a first order reaction of component B by Reaction 5, Equation 116 becomes:

$$\sqrt{M_{(1)}} = c_{B,i} \sqrt{(D_B k_{A5}) / (k_l c_{B,i})} \quad (117)$$

Simplifying Equation 117 by eliminating the concentration terms and squaring both sides of the equation gives

$$M_{(1)} = D_B k_{A5} k_l^{-2} \quad (11)$$

For a second order reaction of component A by Reaction 14, Equation 116 becomes:

$$\sqrt{M_{(2)}} = c_{A,i}^{1.5} \sqrt{(4 D_A k_{A14} / 3) / (k_l c_{A,i})} \quad (118)$$

Simplifying Equation 118 by simplifying the concentration terms and squaring both sides of the equation gives

$$M_{(2)} = 4 D_A k_{A14} c_A k_1^{-2} / 3 \quad . \quad (17)$$

Since Equation 116 may be used to derive the reaction numbers for first and second order reactions, it should be used to derive a reaction number for the reactive dissolution of four valent nitrogen oxides; this reaction number is denoted by the symbol $M_{(IV)}$. The KCF model is the numerator for the right hand side of Equation 116. An equation for physical absorption of NO_2 and N_2O_4 with zero concentration of NO_2 and N_2O_4 in the liquid phase may be written as:

$$N_{N(IV),i} = k_1 c_{A,i} + 2 k_1 c_{B,i} \quad . \quad (119)$$

Substitution of Equation 29 for the equilibrium between NO_2 and N_2O_4 by Reaction 1 in Equation 119 gives

$$N_{N(IV),i} = k_1 c_{A,i} + 2 k_1 K_{A1} c_{A,i}^2 \quad . \quad (120)$$

Equation 116 gives the square root of the reaction number, to derive $M_{(IV)}$ both the KCF model and Equation 116 should be squared. The square of the KCF model, Equation 100, is

$$N_{N(IV),i}^2 = 4 k_{A37} D_B K_{A1} c_{A,i}^4 + 4 k_{A37} D_A c_{A,i}^3 / 3 \quad . \quad (121)$$

The square of the equation for physical absorption of N(IV), Equation 118, is

$$N_{N(IV),i}^2 = k_1^2 c_{A,i}^2 (1 + 2 K_{A1} c_{A,i})^2 \quad . \quad (122)$$

Therefore the reaction number for the reactive dissolution of N(IV) in water is

$$M_{(IV)} = \frac{2 k_{A37} D_B c_{A,i} [2 D_A / (3 D_B) + 2 K_{A1} c_{A,i}]}{k_1^2 (1 + 2 K_{A1} c_{A,i}) (1 + 2 K_{A1} c_{A,i})} \quad . \quad (123)$$

Equation 123 may be rearranged into a more useful form as:

$$M_{(IV)} = \left[\frac{k_{A37} D_B}{K_{A1} k_1^2} \right] [2 K_{A1} c_{A,i}] \frac{[2 D_A / (3 D_B) + 2 K_{A1} c_{A,i}]}{(1 + 2 K_{A1} c_{A,i})^2} \quad (124)$$

The limit of Equation 124 as $c_{A,i}$ becomes large is

$$\lim_{c_{A,i} \rightarrow \text{"large"}} M_{(IV)} = \left[\frac{k_{A37} D_B}{K_{A1} k_1^2} \right] \quad (125)$$

Therefore as the interfacial concentration of NO_2 becomes large the reaction number for N(IV) approaches the reaction number for a fast first order reaction with the reaction rate constant k_{A37} / K_{A1} . The limit of Equation 124 as $c_{A,i}$ becomes small is

$$\lim_{c_{A,i} \rightarrow \text{"small"}} M_{(IV)} = \left[\frac{4 k_{A37} D_A}{3 k_1^2} \right] \quad (126)$$

Therefore as the interfacial concentration of NO_2 becomes small the reaction number for N(IV) approaches the reaction number for a fast second order reaction with the reaction rate constant k_{A37} . The reaction number for N(IV) converges to the reaction numbers for first and second order reactions at large and small NO_2 concentrations respectively, just as the KCF model converges to the film theory's fast first and second order reaction models at large and small NO_2 concentrations, respectively. The ratio of the flux of N(IV) calculated by the GCF model to that calculated by the KCF model is compared to the reaction number for N(IV) for partial pressures of NO_2 of 6.892×10^{-6} atm. to 6.892×10^{-2} atm. and mass transfer coefficients of 1×10^{-4}

m/s to 1×10^3 m/s in Figure 17 for $h_t / a = 1 \times 10^4$ m and in Figure 18 for $h_t / a = 1 \times 10^3$ m. Clearly from Figures 17 and 18 if the square root of the reaction number of N(IV), $M_{(IV)}$, is greater than three the error in using the KCF model is less than 2%. Therefore using Equation 122 as the reaction number for the mixed phase kinetics of N(IV) is consistent with previous definitions of reaction numbers for first and second order reactions.

The smallest partial pressure of N(IV) encountered in the experimental runs was 2.82×10^{-4} atm. in the exit gas stream in run 23, corresponding to a partial pressure of NO_2 of 2.81×10^{-4} atm. Using this value in conjunction with the recommended kinetic and equilibrium values from Table 8 and the calculated value for the liquid phase mass transfer coefficient of 8×10^5 m/s in Equation 122 gives the minimum experimental reaction number, neglecting the gas phase resistance at low partial pressures of N(IV), as 59.6. Since $59.6 \gg 9$ the experiments are always in the fast reaction regime or possibly the instantaneous reaction regime. Danckwerts (1970) indicated a fast reaction of z moles of component X with component Y,



can be considered instantaneous if the following inequality is true:

$$\sqrt{M_{(z)}} \gg 1 + c_{Y,b} / (z c_{X,i}) \quad . \quad (128)$$

The largest partial pressure of N(IV) encountered in the experimental runs was 4.94×10^{-3} atm. in the inlet gas stream in run 19, corresponding to a partial pressure of NO_2 of 4.64×10^{-3} atm. Neglecting the potentially significant gas phase resistance and using Equation 124 with the values

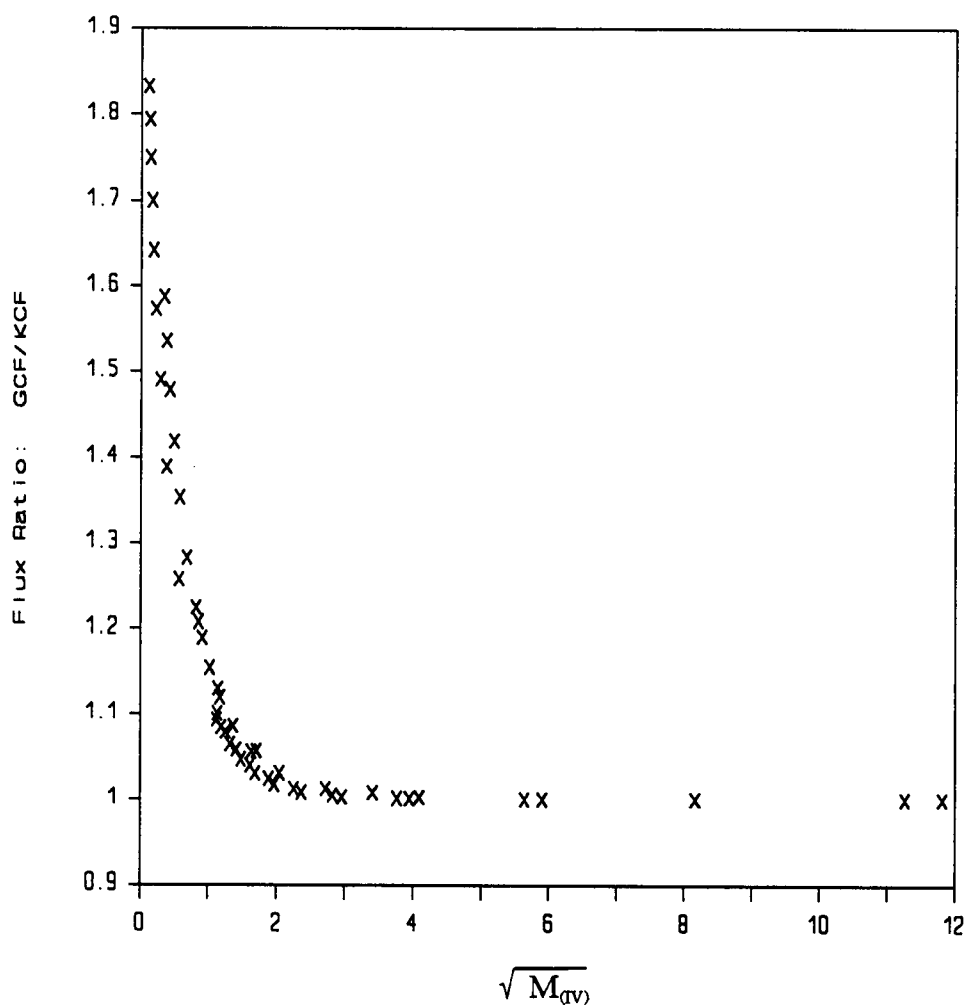


Figure 17 Comparison of Relative Flux Predictions of the KCF Model and the GCF Model for $h_t / a = 1.0 \times 10^{-4}$ m Using Recommended Values for Kinetic and Equilibrium Constants^a

^a Recommended parameters are:

k_{A37}	=	7×10^7	$\text{m}^3/\text{kgmol}\cdot\text{s}$
H_A	=	0.01	$\text{kgmol}/\text{m}^3\cdot\text{atm}$
H_B	=	1.00	$\text{kgmol}/\text{m}^3\cdot\text{atm}$

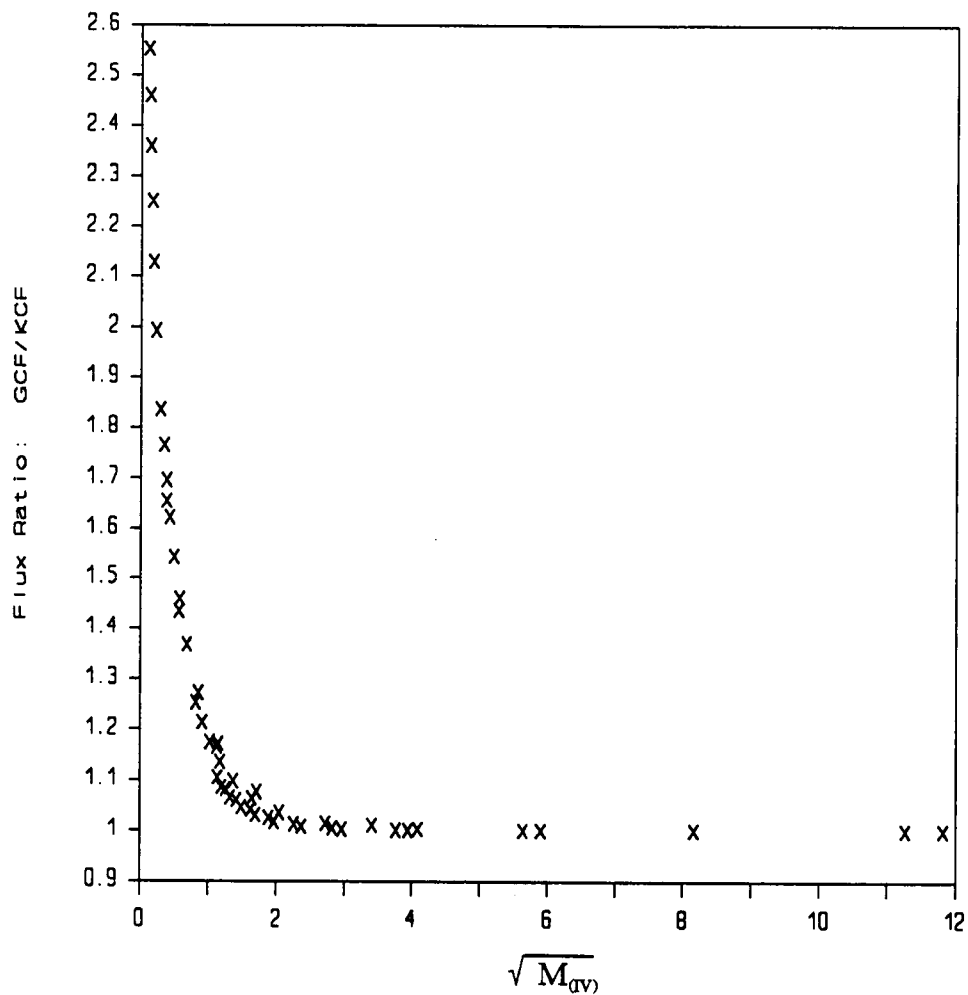


Figure 18 Comparison of Relative Flux Predictions of the KCF Model and the GCF Model for $h_t / a = 1.0 \times 10^{-3}$ m Using Recommended Values for Kinetic and Equilibrium Constants^a

^a Recommended parameters are:

k_{A37}	=	7×10^7	$\text{m}^3/\text{kgmol}\cdot\text{s}$
H_A	=	0.01	$\text{kgmol}/\text{m}^3\cdot\text{atm}$
H_B	=	1.00	$\text{kgmol}/\text{m}^3\cdot\text{atm}$

given above gives the maximum experimental reaction number as 226. Using 2 as z , NO_2 as X , and H_2O as Y in Equation 128 gives the right hand side of the inequality of Equation 128 as 5.9×10^5 . Obviously the hydrolysis of N(IV) is not an instantaneous reaction so the assumption that the reactive dissolution of N(IV) is conducted in the fast reaction regime is validated for the experimental data.

4. COMPARISON OF THE EXPERIMENTAL DATA AND THE KARLSSON COMBINED FLUX MODEL

The results of the scrubbing experiments and the predictions of the Karlsson Combined Flux model can be compared by using the best available thermodynamic and kinetic parameters with the appropriate mass transfer parameters in the KCF model. The appropriate mass transfer parameters, determined from reviewing correlations in the literature in Chapter II, are $k_g = 3.0 \times 10^{-4} \text{ kgmol/m}^2\text{-s}$ and $a = 500 \text{ m}^2/\text{m}^3$. Schwartz and White (1983) recommended Henry's Law constants for NO_2 and N_2O_4 , a liquid phase equilibrium constant for the dimerization of NO_2 , and a rate constant for the hydrolysis of N(IV) . These values are shown in Table 8. The value of K_{A1} depends on the values of K_{G1} , H_A , and H_B as shown by Equation 40:

$$K_{A1} = K_{G1} H_B / H_A^2 \quad . \quad (40)$$

Schwartz and White recommended the value $K_{G1} = 6.86 \text{ atm}^{-1}$ so the value $K_{A1} = 6.86 \times 10^4 \text{ m}^3/\text{kgmol}$ is considered to be the recommended value rather than $K_{A1} = 7 \times 10^4 \text{ m}^3/\text{kgmol}$ as shown in Table 8. A twelve point

Gaussian Quadrature formula was used to numerically integrate the integral form of the gas phase material balance using weights and quadrature points calculated by Love (1966). The predictions of the KCF model using Schwartz and White's recommended parameters and the appropriate mass transfer parameters are compared to all the experimental data for scrubbing N(IV) in a packed tower in Figure 19. The predictions of the KCF model are somewhat optimistic compared to the experimental results; the KCF model and the experimental results are in better agreement between 3.0×10^{-4} atm. and 1.5×10^{-3} atm. than at higher partial pressures. Over 1.5×10^{-3} atm. the scrubbing efficiencies predicted by the KCF model are up to 11% higher than the experimentally observed scrubbing efficiencies.

Schwartz and White's (1983) recommended values for the kinetic and equilibrium parameters for k_{A37} , H_A , and H_B included uncertainty ranges as shown in Table 8. A sensitivity analysis of the KCF model may be performed using Schwartz and White's recommended kinetic and equilibrium constants, the base values for the mass transfer parameters, and appropriate uncertainty ranges. These base values and uncertainty ranges are shown in Table 15. Figure 20 shows the predictions of the KCF model with the three values of k_{A37} : 3.5×10^7 m³/kgmol-s; 7.0×10^7 m³/kgmol-s; and 1.0×10^8 m³/kgmol-s. The value $k_{A37} = 1.0 \times 10^8$ m³/kgmol-s increases the scrubbing efficiency predictions out of the range of the experimental data; the value $k_{A37} = 3.5 \times 10^7$ m³/kgmol-s gives an adequate fit to the data at $p_{N(IV)} > 2 \times 10^{-4}$ atm. but is too conservative otherwise. Figure 21 shows

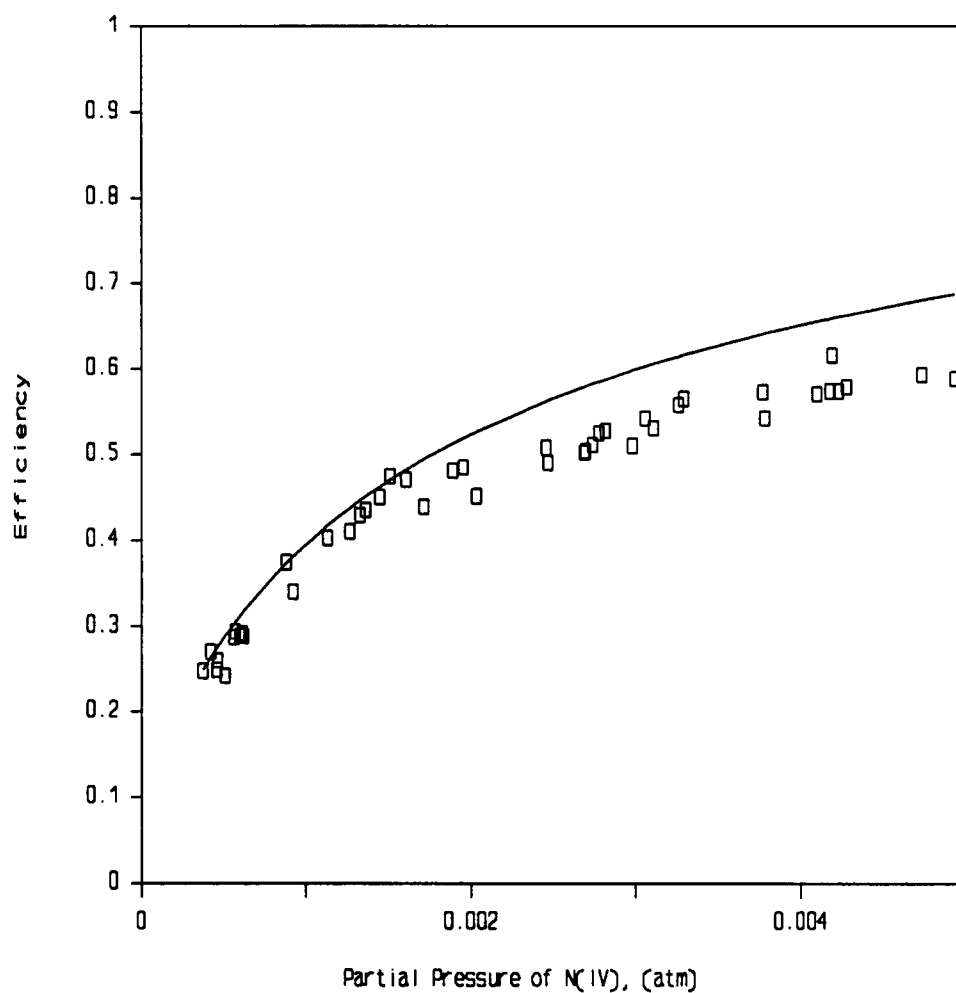


Figure 19 Experimental Results and Predictions of the KCF Model Using Recommended Parameters^a for Physical and Chemical Constants

^a Recommended parameters are:

k_{A37}	=	7×10^7	$\text{m}^3/\text{kgmol}\cdot\text{s}$
H_A	=	0.01	$\text{kgmol}/\text{m}^3\cdot\text{atm}$
H_B	=	1.00	$\text{kgmol}/\text{m}^3\cdot\text{atm}$
k_g	=	3.0×10^{-4}	$\text{kgmol}/\text{m}^2\cdot\text{atm}\cdot\text{s}$
a	=	500.0	m^2/m^3

Table 15 Base Values and Uncertainties for Equilibrium Constants, Rate Constants, and Mass Transfer Parameters for the Sensitivity Analysis of the KCF Model

Value (Units)	Minimum	Base	Maximum
H_A (kgmol/m ³ -atm)	0.007	0.010	0.013
H_B (kgmol/m ³ -atm)	0.45	1.00	2.00
k_{A37} (m ³ /kgmol-s)	3.5×10^7	7×10^7	1×10^8
k_g (kgmol/m ² -atm-s)	2.25×10^{-4}	3×10^{-4}	3.75×10^{-4}
a (m ² /m ³)	450	500	550

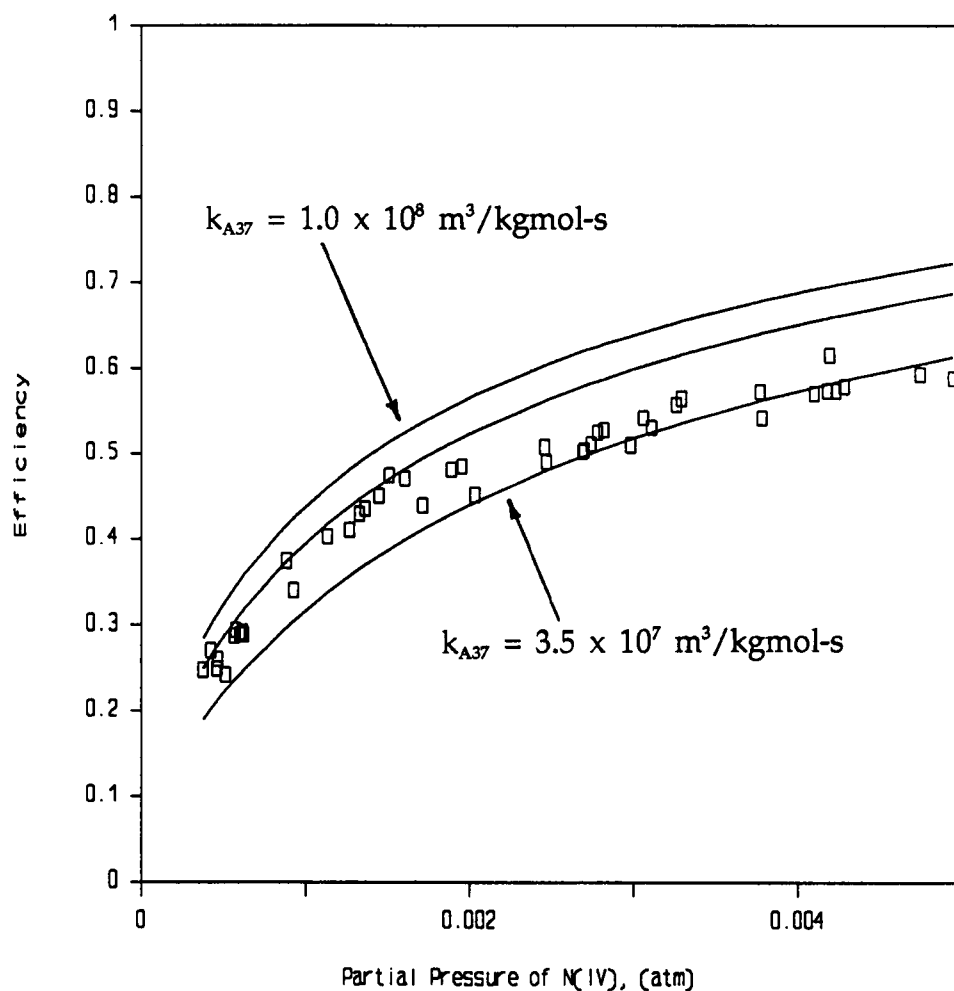


Figure 20 Effect of Uncertainties of k_{A37} on Predictions of the KCF Model Using Recommended Parameters ^a for Other Physical and Chemical Constants

^a Other Recommended parameters are:

H_A	=	0.01	kgmol/m ³ -atm
H_B	=	1.00	kgmol/m ³ -atm
k_g	=	3.0×10^{-4}	kgmol/m ² -atm-s
a	=	500.0	m ² /m ³

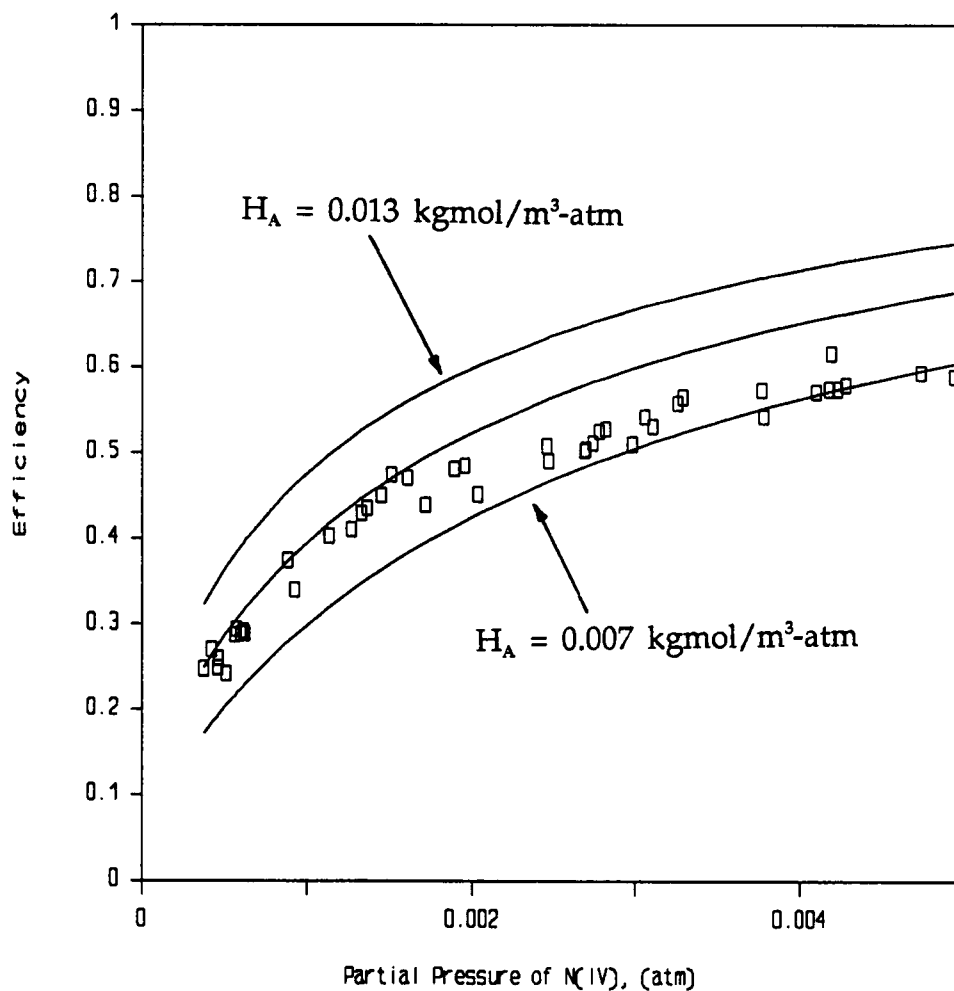


Figure 21 Effect of Uncertainties of H_A on Predictions of the KCF Model Using Recommended Parameters ^a for Other Physical and Chemical Constants

^a Other Recommended parameters are:

k_{A37}	=	7×10^7	$\text{m}^3/\text{kgmol}\cdot\text{s}$
H_B	=	1.00	$\text{kgmol}/\text{m}^3\text{-atm}$
k_g	=	3.0×10^{-4}	$\text{kgmol}/\text{m}^2\text{-atm}\cdot\text{s}$
a	=	500.0	m^2/m^3

the predictions of the KCF model with the three values of H_A : 0.007 kgmol/m³-atm; 0.010 kgmol/m³-atm; and 0.013 kgmol/m³-atm. The value $H_A = 0.013$ kgmol/m³-atm increases the scrubbing efficiency predictions out of the range of the experimental data; much of the effect of increasing H_A at the higher partial pressures is due to the resulting decrease in K_{A1} and increase in k_{A37} / K_{A1} , the first order reaction rate constant in the expression $H_B \sqrt{D_B k_{A37} / K_{A1}}$ which controls the rate of absorption of N(IV) at high partial pressures of N(IV) when the absorption is in the fast reaction regime. The effect of the increased H_A in Figure 21 is similar to the effect of the increased k_{A37} in Figure 20, however increasing H_A has a greater effect at the lower partial pressures of N(IV) than increasing k_{A37} does. The value $H_A = 0.007$ kgmol/m³-atm decreases the scrubbing efficiency predictions out of the range of the experimental data for most for the data except some at the higher partial pressures of N(IV). Figure 22 shows the predictions of the KCF model with the three values of H_B : 0.45 kgmol/m³-atm; 1.00 kgmol/m³-atm; and 2.00 kgmol/m³-atm. The value $H_B = 2.00$ kgmol/m³-atm increases the scrubbing efficiency predictions out of the range of the experimental data. The value of $H_B = 0.45$ kgmol/m³-atm gives the best fit to the experimental data thus far.

Values for the gas phase mass transfer coefficient calculated from the available correlations in the literature were shown in Chapter II. The value $k_g = 3 \times 10^{-4}$ kgmol/m²-atm-s seems to be appropriate since the correlated values are 2.7×10^{-4} kgmol/m²-atm-s and 3.1×10^{-4} kgmol/m²-atm-s. Bravo

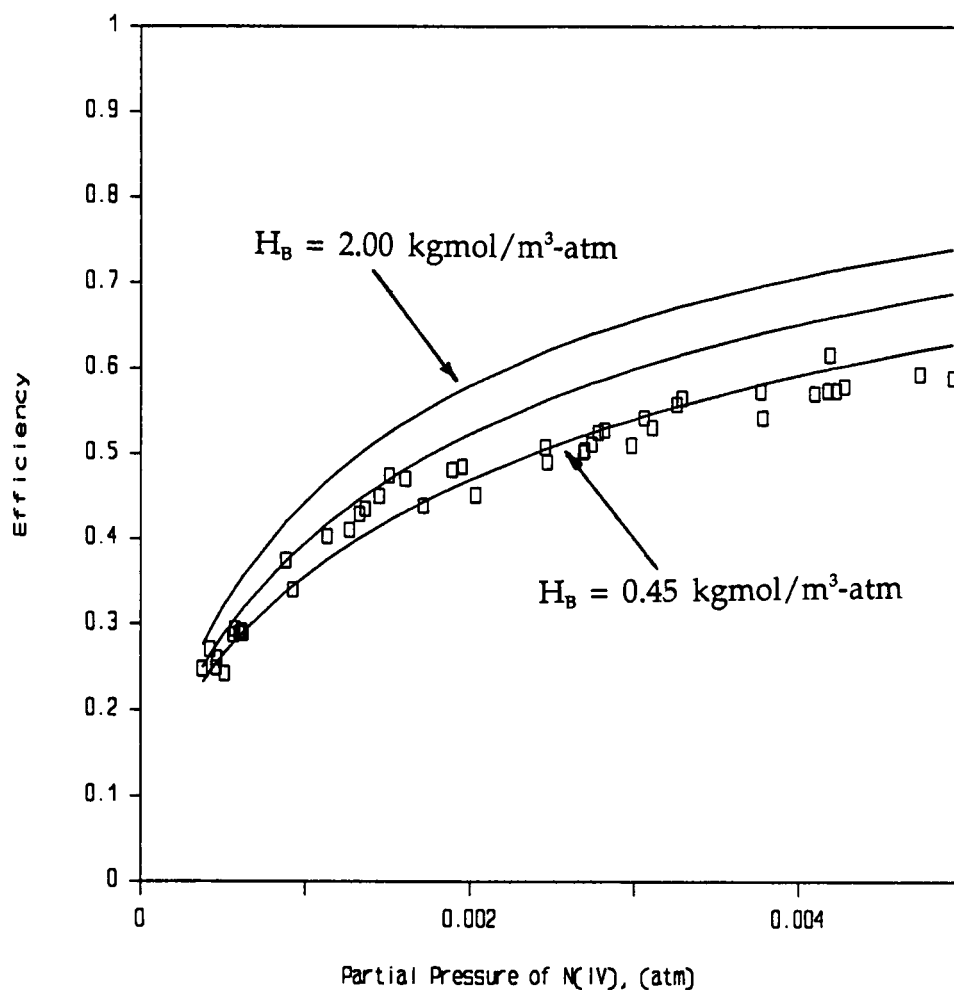


Figure 22 Effect of Uncertainties of H_B on Predictions of the KCF Model Using Recommended Parameters ^a for Other Physical and Chemical Constants

^a Other Recommended parameters are:

k_{A37}	=	7×10^7	$\text{m}^3/\text{kgmol-s}$
H_A	=	0.01	$\text{kgmol/m}^3\text{-atm}$
k_g	=	3.0×10^{-4}	$\text{kgmol/m}^2\text{-atm-s}$
a	=	500.0	m^2/m^3

et al. (1985) indicated that 95% of the data regressed gave values within 25% of their correlation. The predictions of the KCF model are compared to the experimental data in Figure 23 for $k_g = 2.25 \times 10^{-4}$ kgmol/m²-atm-s, 3.0×10^{-4} kgmol/m²-atm-s, and 3.75×10^{-4} kgmol/m²-atm-s. The effect of the gas phase mass transfer coefficient is very small at lower partial pressures of N(IV) but becomes significant at higher partial pressures of N(IV). The effective interfacial area of Sulzer Type BX packing is the same as the geometric area of the packing. Literature values for the geometric area of Sulzer Type BX packing vary from 450 m²/m³ to 500 m²/m³. The predictions of the KCF model are compared to the experimental data in Figure 24 for $a = 450$ m²/m³, 500 m²/m³, and 550 m²/m³. The value $a = 550$ m²/m³ is obviously too large as expected since it is larger than the proposed values mentioned in Chapter II. The value $a = 450$ m²/m³ fits the data better than the other values in Figure 24. The fact that Schwartz and White's recommended values for H_b and k_{A37} , in conjunction with the appropriate mass transfer parameters, lead to optimistic model predictions is not surprising since Figure 8 clearly shows Schwartz and White's choice of recommended values are liberal compared to the values $H_b \sqrt{k_{A37}}$ from the penetration theory experiments and $H_b k_{A37}$ from the mixed phase experiments.

The results of the experiments and the predictions of the Karlsson Combined Flux model can be compared by regressing the value of the Henry's Law constant for N₂O₄, H_b , for given values of the aqueous phase

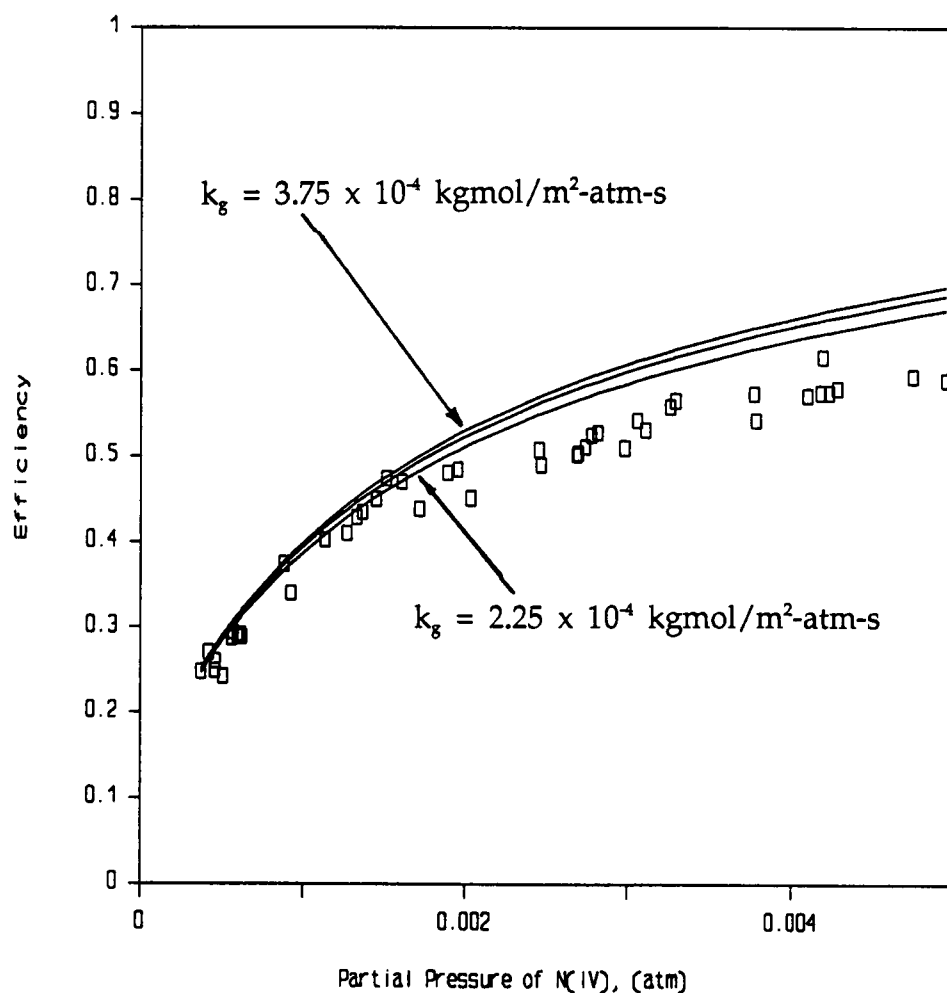


Figure 23 Effect of Uncertainties of k_g on Predictions of the KCF Model Using Recommended Parameters ^a for Other Physical and Chemical Constants

^a Other Recommended parameters are:

k_{A37}	=	7×10^7	$\text{m}^3/\text{kgmol}\cdot\text{s}$
H_A	=	0.01	$\text{kgmol}/\text{m}^3\cdot\text{atm}$
H_B	=	1.00	$\text{kgmol}/\text{m}^3\cdot\text{atm}$
a	=	500.0	m^2/m^3

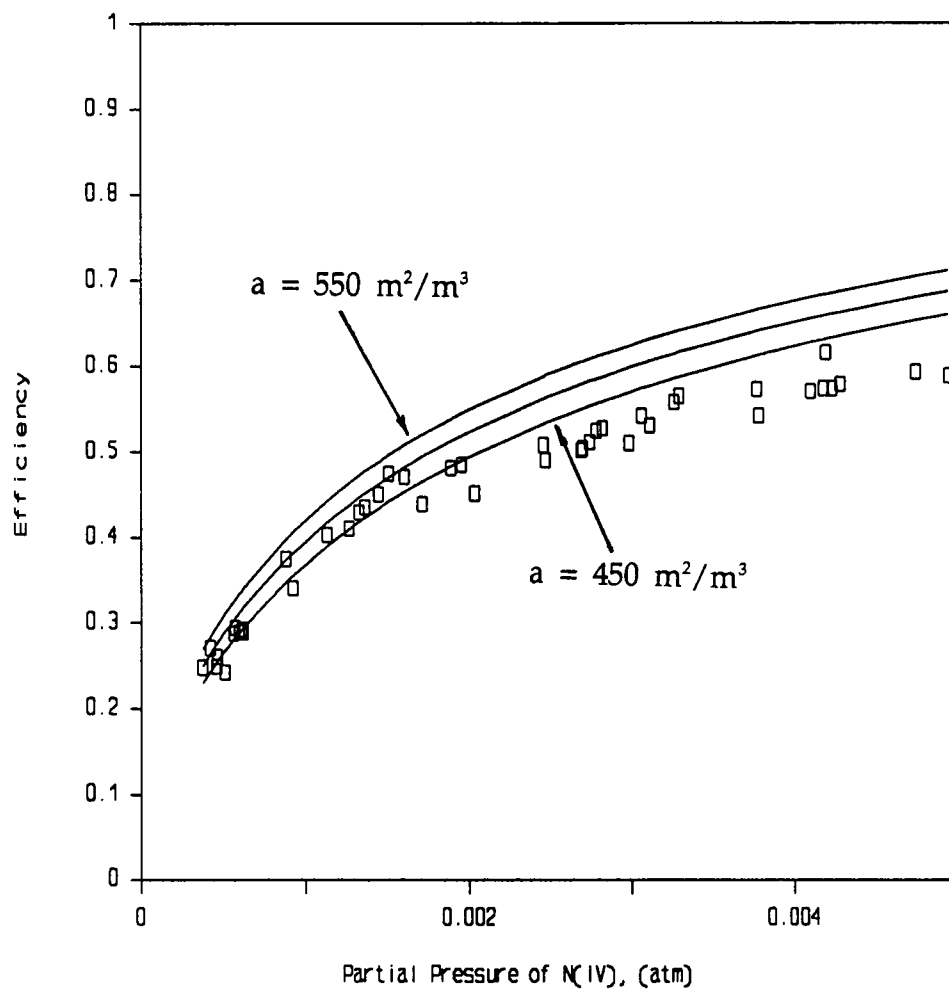


Figure 24 Effect of Uncertainties of Interfacial Area, a , on Predictions of the KCF Model Using Recommended Parameters ^a for Other Physical and Chemical Constants

^a Other Recommended parameters are:

k_{A37}	=	7×10^7	$\text{m}^3/\text{kgmol-s}$
H_A	=	0.01	$\text{kgmol}/\text{m}^3\text{-atm}$
H_B	=	1.00	$\text{kgmol}/\text{m}^3\text{-atm}$
k_g	=	3.0×10^{-4}	$\text{kgmol}/\text{m}^2\text{-atm-s}$

equilibrium constant for NO_2 and N_2O_4 , K_{A1} , the rate constant for the hydrolysis reaction, k_{A37} , and the mass transfer parameters. The value of the equilibrium constant chosen for this regression is $K_{A1} = 6.54 \times 10^4 \text{ m}^3/\text{kgmol}$, the value given by Grätzel et al. (1969), which was used to show the relationship between the values H_B and k_{A37} from the results of penetration theory, film theory, mixed phase, pulse radiolysis, rapid-mixed flow, and slow reaction experiments in Figures 7 and 8. Figure 25 is an example of the results from the regression analysis, at $k_{A37} = 7 \times 10^7 \text{ m}^3/\text{kgmol-s}$ and $K_{A1} = 6.54 \times 10^4 \text{ m}^3/\text{kgmol}$ the regressed value for H_B is $0.7940 \text{ kgmol/m}^3\text{-atm}$; the fit of the data is representative of the fit given for values satisfying the equation:

$$\log[H_B] = -0.5543 \log[k_{A37}] + 4.2487 \quad . \quad (129)$$

This line is shown in Figure 26 in comparison to the experimental results shown in Figure 7. The results for values of H_B and k_{A37} from modeling the experimental results of N(IV) absorption in a packed tower with the KCF model are very close to the intersection of the boundaries representing results for the values $H_B \sqrt{k_{A37}}$ from the penetration theory experiments and $H_B k_{A37}$ from the mixed phase experiments, the zone which probably represents the best values for H_B and k_{A37} .

Considering Figure 26, a new set of recommended values for k_{A37} and H_B is proposed as: $k_{A37} = 4.5 \times 10^7 \text{ m}^3/\text{kgmol-s}$, and $H_B = 0.93 \text{ kgmol/m}^3\text{-atm}$. These values are shown in Figure 27 with the lines from Figure 26. These values are the result of an extensive compilation and comparison of

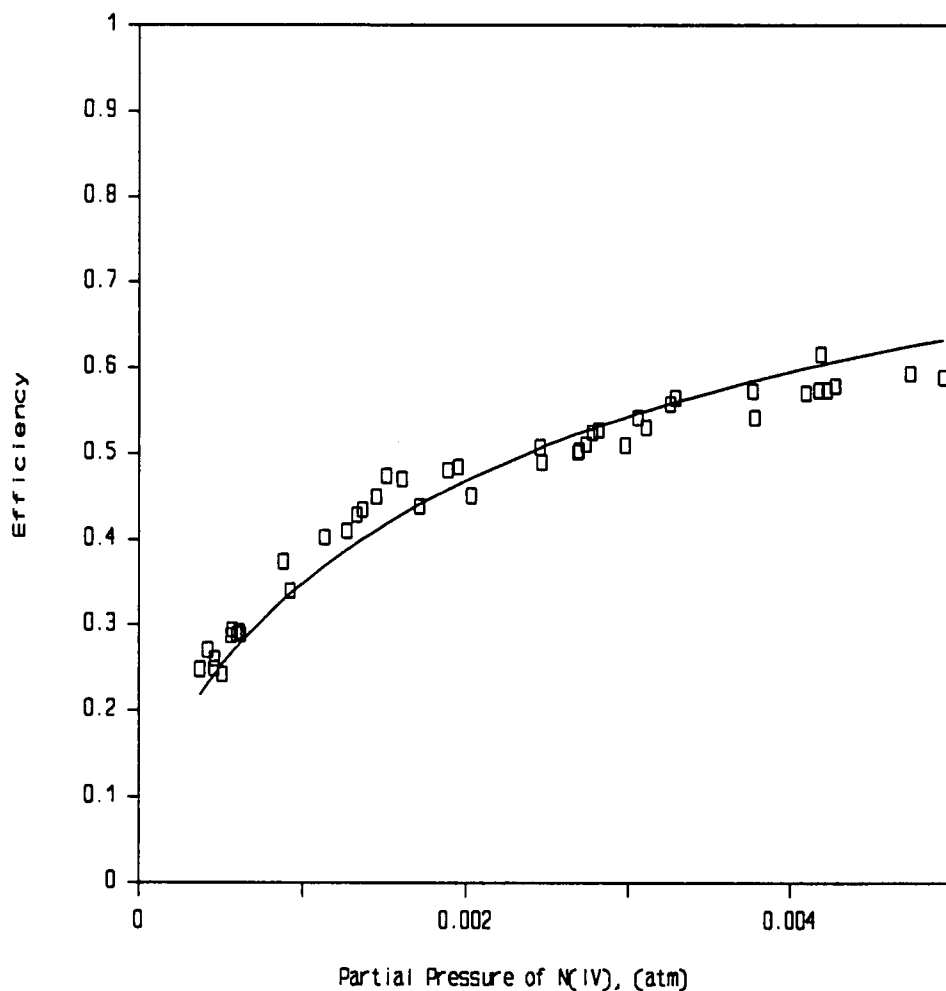


Figure 25 Example of Comparison of Experimental Results and Predictions of the KCF Model Using Regressed Values of the Henry's Law Constant for N_2O_4

^a Regressed value of Henry's Law constant for N_2O_4 ^b is:

$$H_B = 0.7940 \quad \text{kgmol/m}^3\text{-atm}$$

^b Parameters used for the regression are:

$$\begin{aligned} k_{A37} &= 7.0 \times 10^7 \quad \text{m}^3/\text{kgmol-s} \\ K_{A1} &= 6.54 \times 10^4 \quad \text{m}^3/\text{kgmol} \\ k_g &= 2.25 \times 10^{-4} \quad \text{kgmol/m}^2\text{-atm-s} \\ a &= 500 \quad \text{m}^2/\text{m}^3 \end{aligned}$$

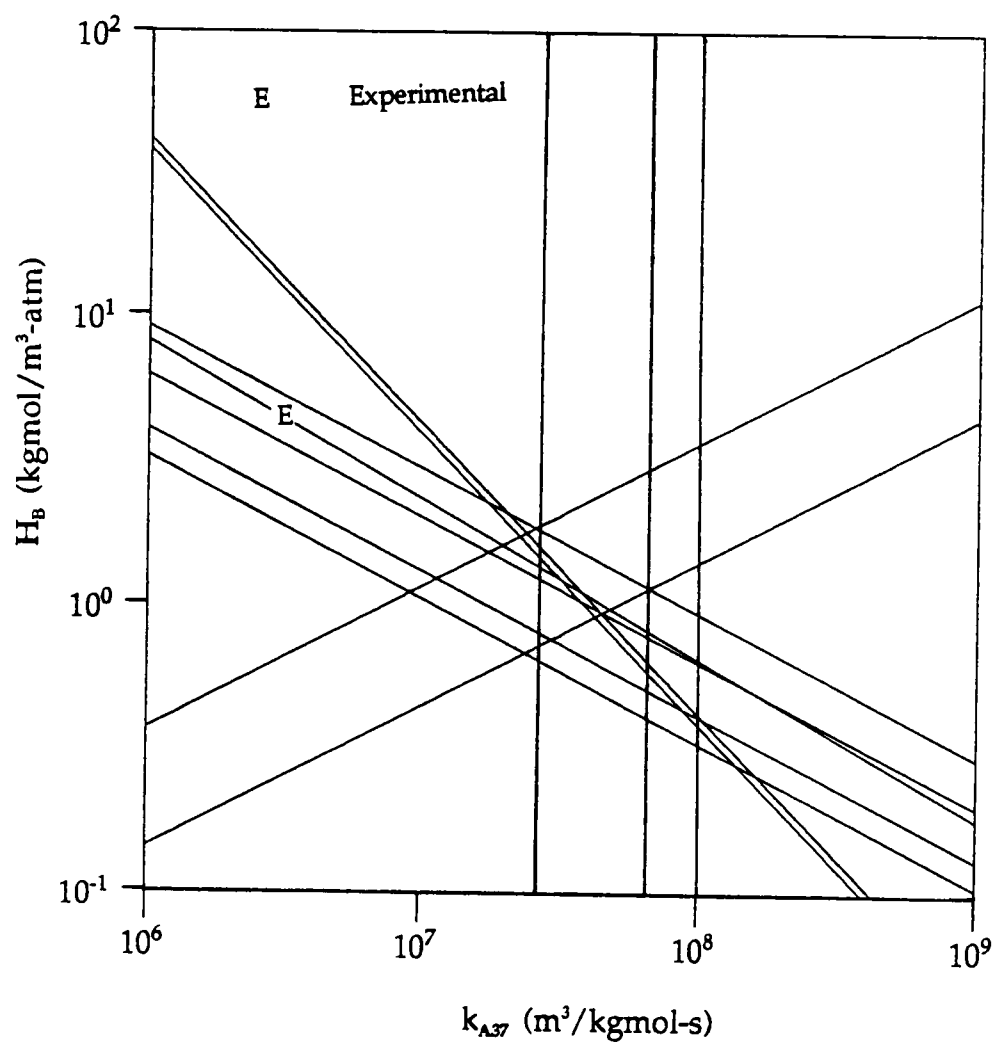


Figure 26 Regressed Relationship Between H_B and k_{A37} for Experimental Results^a Compared to Literature Values Presented in Figure 7

^a Parameters used are:

$$\begin{aligned} K_{A1} &= 6.54 \times 10^4 && \text{m}^3/\text{kgmol} \\ k_g &= 2.25 \times 10^{-4} && \text{kgmol}/\text{m}^2\text{-atm-s} \\ a &= 500.0 && \text{m}^2/\text{m}^3 \end{aligned}$$

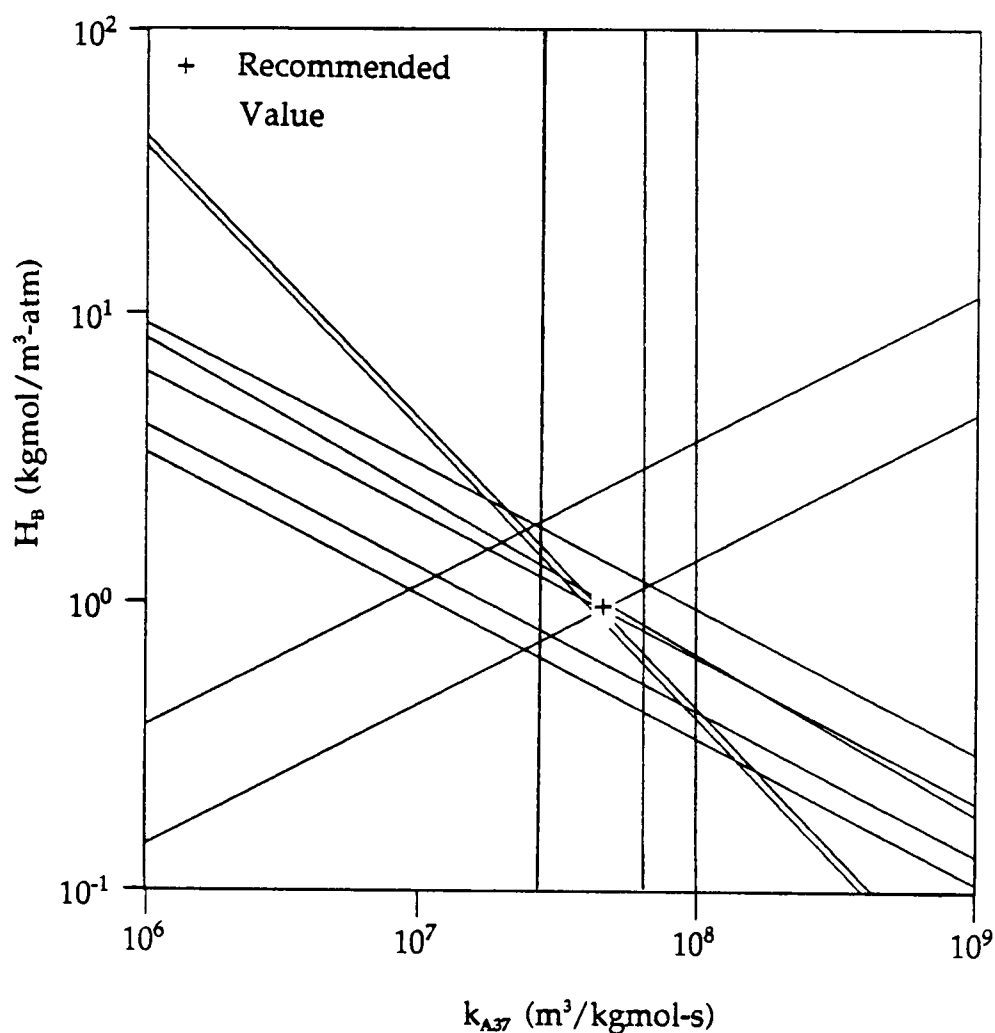


Figure 27 New Recommended Values for H_B and k_{A37} ^a Compared to Literature Values Presented in Figure 7 and Regressed Experimental Results

^aNew recommended values for the solubility of N_2O_4 and the second order rate constant for the hydrolysis of N(IV) at or near 25°C are:

$$\begin{aligned} H_B &= 0.93 \quad \text{m}^3/\text{kgmol-atm} \\ k_{A37} &= 4.5 \times 10^7 \quad \text{m}^3/\text{kgmol-s} \end{aligned}$$

literature values where the aqueous phase equilibrium constant for Reaction 1 was assumed to be $K_{A1} = 6.54 \times 10^4 \text{ m}^3/\text{kgmol}$ and comparison of these values to the experimental results. These values, in conjunction with the KCF model or GCF model, should reliably predict the results of N(IV) scrubbing experiments at temperatures near 25°C. These values are shown to give a reasonably good fit to the experimental data when used with the KCF model in Figure 28. The Henry's Law constant for NO_2 , consistent with the new recommended value for N_2O_4 , as calculated by Equation 40 is $H_A = 0.0099 \text{ kgmol}/\text{m}^3\text{-atm}$. The new recommended kinetic and equilibrium constants for the reactive dissolution of N(IV) in aqueous solutions, in conjunction with $k_1 = 8.0 \times 10^5 \text{ m/s}$ and $p_{A1} = 2.81 \times 10^4 \text{ atm}$, give a minimum reaction number for the experiments of 40. Clearly the fast reaction regime assumption of the KCF model is still valid for all the experimental data since $40 > \text{nine}$.

The scrubbing data for absorption of N(IV) into water (series C and D), 0.3 N NaOH (series A and B), 0.6 N NaOH (series E and F), and 1.0 N NaOH (series G and H) may be subjected to a regression analysis to determine the best value of H_B when $k_{A37} = 4.5 \times 10^7 \text{ m}^3/\text{kgmol-s}$ and $K_{A1} = 6.54 \times 10^4$ for each of the four sets of data. If the KCF model is used for the regression without the enhancement factor modifier, E_{OH} , then the resulting values of H_B are actually values of $E_{OH} H_B^\circ$. The results of this

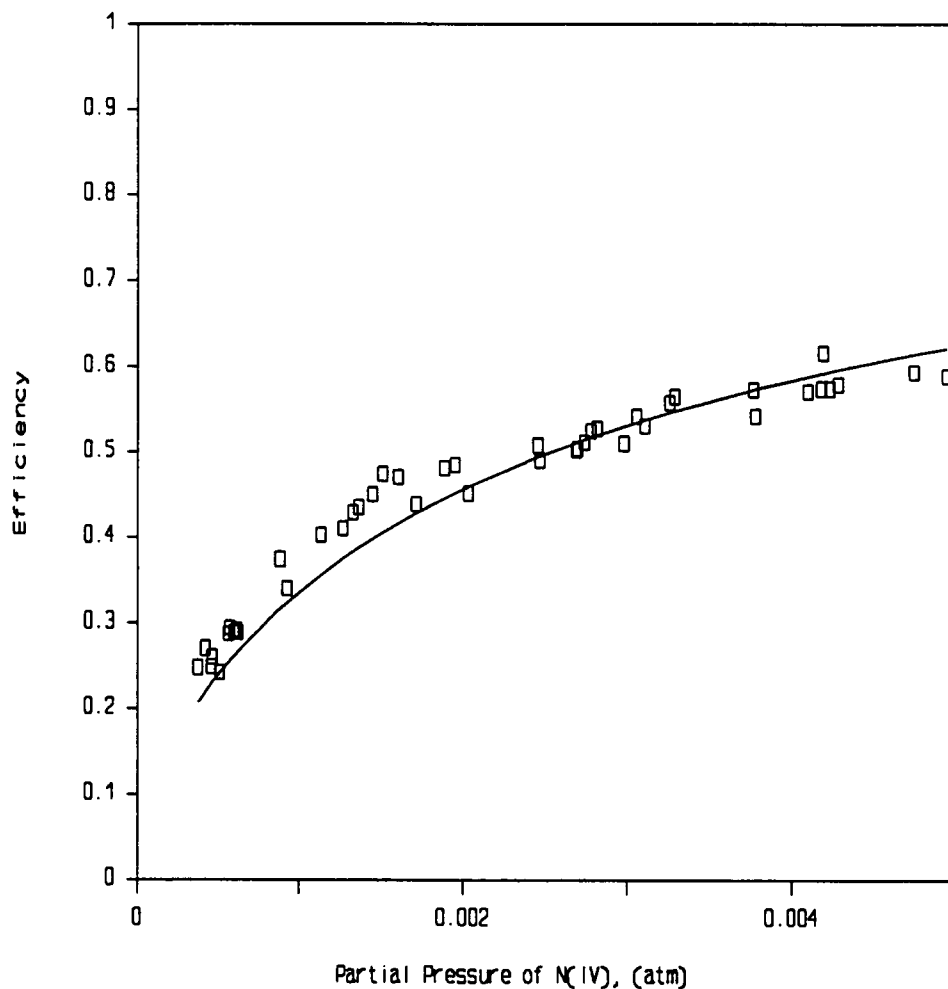


Figure 28 Predictions of the KCF Model ^a With New Recommended Values for H_b and k_{A37} ^b Compared to Experimental Results

^a Parameters used are:

$$\begin{aligned}
 K_{A1} &= 6.54 \times 10^4 & \text{m}^3/\text{kgmol} \\
 k_g &= 2.25 \times 10^{-4} & \text{kgmol}/\text{m}^2\text{-atm-s} \\
 a &= 500.0 & \text{m}^3/\text{m}^3
 \end{aligned}$$

^b New recommended values for the solubility of N_2O_4 and the second order rate constant for the hydrolysis of N(IV) at or near 25°C are:

$$\begin{aligned}
 H_b &= 0.93 & \text{m}^3/\text{kgmol-atm} \\
 k_{A37} &= 4.5 \times 10^7 & \text{m}^3/\text{kgmol-s}
 \end{aligned}$$

analysis are presented in Table 16. Except for the regressed results of the data for the 0.6 N NaOH absorbent, the predicted and experimental results are in excellent agreement. This result indicates the enhancement factor modifier for sodium hydroxide solutions may be used at partial pressures as low as 3×10^{-4} atm. The enhancement factor modifier may not be applicable to sodium hydroxide solutions with concentrations greater than 1 kgmol/m³ at N(IV) partial pressures less than 0.02 atm.

5. A NEW PROPOSAL FOR THE MECHANISM FOR THE HYDROLYSIS OF FOUR VALENT NITROGEN OXIDES

Mechanisms for the hydrolysis of four valent nitrogen oxides available in the literature were reviewed in Chapter II. The Moll (1966) mechanism was corrected for the reversibility of the reactions and renamed the Reversible Moll mechanism. The Kameoka and Pigford (1977) mechanism was also reviewed. Weak points in both of the possibly correct mechanisms were pointed out; a superior mechanism is introduced and supported below:



The overall reaction resulting from this mechanism is



Table 16 Comparison of Predicted Values for the Enhancement Factor Modifier to the Experimental Values Resulting from Least Squares Regression Analysis of the Scrubbing Data

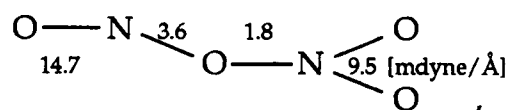
Solution	Regressed $H_B^\circ E_{OH}$ (kgmol/m ³ -atm)	Predicted $H_B^\circ E_{OH}$ (kgmol/m ³ -atm)
water	1.002	1.002 ^a
0.3 N NaOH	1.058	1.064
0.6 N NaOH	0.995	1.059
1.0 N NaOH	1.009	1.002

^a The predicted and regressed values of $H_B^\circ E_{OH}$ are the same for water because the value of E_{OH} is one.

Stedman (1979) indicated that the average lifetime of the nitrosonium ion in water is very short, the average half-life of NO^+ in water was reported as 3×10^{-10} s; such a short-lived species has a good chance of recombining with the same water molecule that it resulted from by the reverse of Reaction 64 (Stedman). Therefore Reaction 64 can not be a slow reaction; it is likely to be at equilibrium in aqueous solutions of nitric and nitrous acid. The equilibrium concentration of NO^+ is:

$$[\text{NO}^+] = [\text{H}^+] [\text{NO}_3^-] / ([\text{H}_2\text{O}] K_{A64}) \quad , \quad (132)$$

assuming the solution is an ideal solution, otherwise the equilibrium must be expressed in terms of activities rather than concentrations. Reaction 130 is also likely to be at equilibrium since Grätzel et al. (1969) and Treinin and Hayon (1970) showed NO_2 forms an equilibrium with N_2O_4 before the hydrolysis reaction proceeds to a significant degree and the force constant of the N-N bond in $\text{D}_{2h}\text{-N}_2\text{O}_4$ is very small ($f_{\text{NN}} = 0.3$ mdyne/Å, as shown in Chapter II), indicating $\text{D}_{2h}\text{-N}_2\text{O}_4$ dissociates homolytically relatively rapidly. Reaction 131 is also likely to be at equilibrium since the homolytic dissociation of $\text{iso-N}_2\text{O}_4$ is preferred to the heterolytic dissociation of $\text{iso-N}_2\text{O}_4$ assuming the force constants proposed by Laane and Ohlsen (1980) are correct:



and assuming the bond with the smaller force constant also has a smaller bond energy as indicated by Sharpe (1986). The equilibrium concentration of iso-N₂O₄ is:

$$[\text{iso-N}_2\text{O}_4] = K_{A131} [\text{NO}_2]^2 . \quad (133)$$

Reaction 62 is likely to be the rate determining step for both the forward and reverse of Reaction 37; the heterolytic dissociation of iso-N₂O₄ is slower than the homolytic dissociation of iso-N₂O₄ and the reaction of NO⁺ with water; the reaction of NO⁺ with NO₃⁻ is slower than the reaction of NO⁺ with H₂O if water is in excess (i.e. if the liquid phase is a sufficiently dilute aqueous solution that significant amounts of free water molecules are available), therefore the reaction of NO⁺ with NO₃⁻ is slower than the reaction of H⁺ with HNO₂. The rate expression for Reaction 62 is:

$$R_{A62} = k_{A62} [\text{iso-N}_2\text{O}_4] - k_{A62} [\text{NO}^+] [\text{NO}_3^-] . \quad (134)$$

Combining Equations 132, 133, and 134 gives the rate of Reaction 62 for dilute aqueous solutions and the rate of the overall reaction, Reaction 37, for dilute aqueous solutions as:

$$R_{A62} = k_{A62} K_{A131} [\text{NO}_2]^2 - \frac{k_{A62} [\text{HNO}_2] [\text{H}^+] [\text{NO}_3^-]}{([\text{H}_2\text{O}] K_{A64})} . \quad (135)$$

This reaction expression applies only for relatively dilute aqueous solutions where the concentration of NO₃⁻ is sufficiently small that Equation 64 is at equilibrium; otherwise the reaction rates of Reaction 62 and Reaction 64 might both be significant so the overall reaction expression would consist of more than one equation.

While the reaction expression for this mechanism is not a stoichiometric expression, the equilibrium constant for this mechanism is the same as the equilibrium constant for Reaction 37. No trimolecular reactions are proposed nor are any undocumented intermediates proposed, giving this mechanism a substantial advantage over both the Kameoka and Pigford mechanism and the Reversible Moll mechanism. The magnitudes of the stretching force constants for the different molecules are in agreement with the choices for fast and slow reactions for this mechanism.

If Reaction 131 is the rate limiting step of the proposed mechanism and all the other reactions are at equilibrium as was implied by Stedman (1979) in his discussion of the formation of N_2O_4 from nitric and nitrous acid, then the reaction rate expression for Reaction 131, and the overall reaction rate expression, is

$$R_{A131} = k_{A131} c_A^2 - k_{-A131} [HNO_2] [H^+] [NO_3^-] / ([H_2O] K_{A62} K_{A64}) \quad (136)$$

Although the rate and equilibrium constants differ for the reaction expressions in Equation 135 and Equation 136, the dependence of the reaction expressions on the concentrations (or activities) of the chemical components, NO_2 , H_2O , HNO_2 , H^+ , and NO_3^- , is the same for both expressions. Therefore the possibility that Reaction 131, not Reaction 62, is the rate limiting step of the hydrolysis of N(IV) does not change the overall reaction rate expression for Reaction 37 based on the reaction mechanism proposed above:

$$R_{A37} = k_{A37} c_A^2 - k_{-A37} [HNO_2] [H^+] [NO_3^-] / [H_2O] \quad (137)$$

Schmid and Bähr (1964) studied the reverse of Reaction 37 for aqueous nitric acid - nitrous acid solutions with HNO_3 concentrations ranging up to 5 kgmol/m^3 . They proposed the reaction expression:

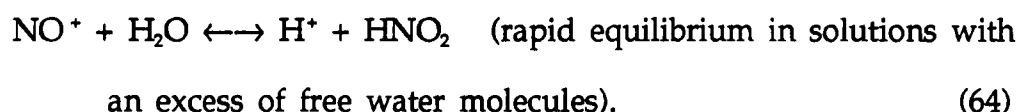
$$R_{A37} = k_{A138} [\text{HNO}_2] [\text{H}^+] [\text{NO}_3^-] \quad . \quad (138)$$

The rate constant k_{A138} was found to be relatively constant in solutions with HNO_3 concentrations up to 1 kgmol/m^3 but the value of the rate constant increased significantly at higher HNO_3 concentrations. This is evidence that Equation 137 is the correct reaction expression since the activity of water is not likely to change much in relatively dilute nitric acid but more concentrated nitric acid solutions have reduced concentrations of free water and possibly the activity of the free water is decreased in the more concentrated nitric acid solutions. If Equation 137 is the true reaction expression for Reaction 37 and the rate constant, k_{A37} , is not dependent on the concentration of HNO_3 , the decreasing concentration and activity of free water expected for increasing concentrations of nitric acid make the apparent rate constant for the reverse of Reaction 37, k_{A138} , increase with increasing nitric acid concentrations. It is interesting to note that if the proposed reaction mechanism and expression are correct, the rate constant k_{A37} is not a pseudo-second order rate constant; k_{A37} is a true second order rate constant.

CHAPTER VI

CONCLUSIONS

A thorough review of the literature regarding the structure and known reactions of the species involved indicates the aqueous phase hydrolysis of four valent nitrogen oxides, NO_2 , $\text{D}_{2h}\text{-N}_2\text{O}_4$, and $\text{iso-N}_2\text{O}_4$, is most likely to follow the mechanism:



The overall reaction resulting from this mechanism is



The reaction rate expression for Reaction 37 based on the reaction mechanism proposed above is

$$R_{A37} = k_{A37} c_A^2 - k_{-A37} [\text{HNO}_2] [\text{H}^+] [\text{NO}_3^-] / [\text{H}_2\text{O}] \quad . \quad (137)$$

This mechanism and direct chemical evidence of flash photolysis and pulse radiolysis experiments by Grätzel et al. (1969) and Treinin and Hayon (1970) indicate that mathematical models for the reactive dissolution of four valent nitrogen oxides, referred to as N(IV), must account for the dissolution, diffusion, and reaction of both NO_2 and N_2O_4 where $\text{D}_{2h}\text{-N}_2\text{O}_4$ and $\text{iso-N}_2\text{O}_4$

are treated as a single chemical species since separate equilibrium and solubility constants are not available for each N_2O_4 species.

The Karlsson Combined Flux model, referred to as the KCF model, derived by Karlsson (1983), is appropriate for the hydrolysis reaction enhanced combined flux of N(IV) into aqueous solutions where the absorption is in the fast reaction regime as set forth by Danckwerts (1970) and the reverse of the hydrolysis reaction is either eliminated chemically or occurs to a negligible extent. The flux of N(IV) predicted by the KCF model is:

$$N_{N(IV),i} = (N_{1,i}^2 + N_{2,i}^2)^{0.5}, \text{ where} \quad (81)$$

$$N_{1,i} = 2 (k_{A37} D_B / K_{A1})^{0.5} H_B p_{B,i}, \text{ and} \quad (82)$$

$$N_{2,i} = (4 k_{A37} D_A / 3)^{0.5} H_A^{1.5} p_{A,i}^{1.5}. \quad (83)$$

At high partial pressures of N(IV) the KCF model converges to the film theory model for the dissolution and pseudo-first order hydrolysis of N_2O_4 ; therefore, film theory based studies where the reactive dissolution of N(IV) was treated as the reactive dissolution of N_2O_4 were essentially correct. At low partial pressures of N(IV) the KCF model converges to the film theory model for the dissolution and pseudo-second order hydrolysis of NO_2 . Using the technique shown by Danckwerts for deriving reaction numbers for first and second order reactions, a reaction number is derived for the reactive dissolution of N(IV) by the KCF model:

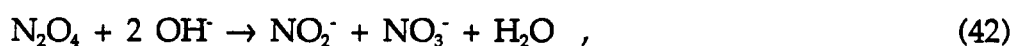
$$M_{(IV)} = \left[\frac{k_{A37} D_B}{K_{A1} k_i^2} \right] [2 K_{A1} c_{A,i}] \frac{[2 D_A / (3 D_B) + 2 K_{A1} c_{A,i}]}{(1 + 2 K_{A1} c_{A,i})^2} \quad (124)$$

This reaction number is used to prove that the KCF model is appropriate for the N(IV) scrubbing experiments.

Schwartz and White (1983) thoroughly reviewed the literature to determine the best available kinetic and equilibrium constants important to the dissolution and hydrolysis of N(IV) in dilute aqueous solutions at 20°C to 25°C. These recommended parameters are a good starting point for predicting the performance of a N(IV) scrubber; however, these parameters tend to give overly optimistic predictions compared to the actual performance of the N(IV) scrubbing experiments. A graphical presentation of these recommended parameters in comparison to the literature values for these parameters shows why the performance predictions of a model using these values might tend to be overly optimistic. Using graphical techniques similar to those used by Schwartz and White, new values are recommended for the Henry's Law constant of N_2O_4 , $H_B = 0.93 \text{ kgmol/m}^3\text{-atm}$, and the second order hydrolysis rate constant for NO_2 , $k_{A37} = 4.5 \times 10^7 \text{ m}^3/\text{kgmol-s}$, for use at or near 25°C. These values should only be used in conjunction with the aqueous phase equilibrium constant for the dimerization of NO_2 , recommended by Grätzel et al. (1969), $K_{A1} = 65400 \text{ m}^3/\text{kgmol}$, since this equilibrium constant influenced the choice of the new recommended values. The recommended values for the Henry's Law constant of N_2O_4 and the aqueous phase equilibrium constant for the dimerization of NO_2 , in

conjunction with Schwartz and White's recommended value for the gas phase equilibrium constant for the dimerization of NO_2 , 6.86 atm^{-1} , require the Henry's Law constant of NO_2 , H_A , to be $0.0099 \text{ kgmol/m}^3\text{-atm}$. The new recommended values for kinetic and equilibrium parameters important to the dissolution and hydrolysis of N(IV) in dilute aqueous solutions at or near 25°C are more consistent with the literature values than Schwartz and White's recommended values; the new recommended values combine with the KCF model to give more realistic predictions of scrubber performance than Schwartz and White's recommended values did when used with the KCF model. In addition to the chemical parameters discussed, the gas phase mass transfer coefficient and the gas-liquid interfacial area influence the model predictions of N(IV) scrubbing efficiencies. The uncertainties in the chemical parameters, however, have greater influence on the model predictions of N(IV) scrubbing efficiencies than the uncertainties in the mass transfer parameters for Sulzer Type BX packing.

A slight increase was noted in the N(IV) scrubbing efficiencies of 0.3 N NaOH absorbents in comparison to that of water, 0.6 NaOH, and 1.0 N NaOH aqueous solutions in the experimental N(IV) partial pressure range of $3 \times 10^{-4} \text{ atm}$. to $5 \times 10^{-3} \text{ atm}$. Analysis of experimental results of Peters and Holman (1955) indicates the salting coefficient of N_2O_4 is $0.020 \text{ m}^3/\text{kgmol}$. Kameoka and Pigford (1977) indicated that the reaction of the hydroxide ion with N_2O_4 :



is probably first order in both species. An analysis of the data of Chambers and Sherwood (1937) using the salting coefficient calculated from the data of Peters and Holman leads to an expression for an enhancement factor modifier for the reactive dissolution of high partial pressures of N(IV) into aqueous sodium hydroxide solutions:

$$E_{OH} = 10^{-0.177 I} \{ [1 + 1.84 c_{OH}] / (1 + 0.264 c_{OH} - 0.0173 c_{OH}^2 + 0.0117 c_{OH}^3) \}^{0.5} . \quad (115)$$

This expression fits the results of Kameoka and Pigford and the experimental scrubbing results fairly well. This expression has been tested for temperatures within a few degrees of 25°C and either of the following conditions:

1. $p_{N(IV)} > 0.02$ atm. and $c_{OH} < 6$ kgmol/m³ or
2. $p_{N(IV)} > 3 \times 10^{-4}$ atm. and $c_{OH} < 1$ kgmol/m³ .

Use of this expression out of the range of the conditions described above is inadvisable without experimental verification of the parameters involved for the considered conditions. Since the enhancement factor modifier, Equation 115, indicates sodium hydroxide has very little effect on the rate of reactive dissolution of N(IV) when the concentration of the absorbent is less than or equal to 1 kgmol/m³, this concentration range is recommended for scrubbing gaseous nitrogen oxides. Equation 115 is the only equation available for estimating the effect of sodium hydroxide concentration on the rate of the reactive dissolution of N(IV). Equation 115 might be used as a first approximation of the enhancement factor modifier out of the ranges of

operating conditions described above until further experimental determinations are made for the parameters.

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APPENDIXES

APPENDIX A

CALCULATION OF THE TIME REQUIRED FOR THE GAS PHASE DISSOCIATION OF N₂O₄ TO REACH EQUILIBRIUM

Carrington and Davidson (1953) determined the first order dissociation rate constant for Reaction 1 in the gas phase. The value $k_{G1} = 8.3 \times 10^4 \text{ s}^{-1}$ was determined at 298 K. The reaction rate expression for the gas phase dimerization of NO₂ is

$$dp_B / dt = k_{G1} p_A^2 - k_{G1} p_B \quad . \quad (139)$$

Since the four valent nitrogen oxide feed to the experimental apparatus was liquid nitrogen tetroxide diluted with air, the rate of dissociation of nitrogen tetroxide in the vapor phase must be rapid for the assumption of gas phase equilibrium between NO₂ and N₂O₄ to be accurate. If $p_{N(IV)}$ is the beginning partial pressure of N(IV) molecules, the variable substitution:

$$p_B = p_{N(IV)} - y \quad ; \quad (140)$$

$$p_A = y^2 \quad ; \quad (141)$$

into Equation 139 and integration of Equation 139 between appropriate limits gives an equation for the time required for the dissociation of N₂O₄ to approach equilibrium.

The following expression may be used to calculate the time required for N₂O₄ to dissociate to form 99% of the equilibrium partial pressure of NO₂:

$$t_{0.99} = - (K_{G1} / k_{G1}) \{ c_1 \log[(c_3 - 0.99 p_{A,eq}) / c_3] + c_2 \log[(0.99 p_{A,eq} + c_4) / c_4] \} \quad . \quad (142)$$

The constants in Equation 142 are:

$$c_3 = [(1 + 4 K_{G1} p_{N(IV)})^{0.5} - 1] / (2 K_{G1}) \quad ; \quad (143)$$

$$c_4 = p_{N(IV)} / (c_3 K_{G1}) \quad ; \quad (144)$$

$$c_1 = 1 / (c_3 + c_4) \quad ; \text{ and} \quad (145)$$

$$c_2 = -1 / (c_3 + c_4) \quad . \quad (146)$$

Use of Equation 142 for the high and low N(IV) partial pressures encountered experimentally, 4.94×10^{-3} atm. and 2.82×10^{-4} atm., indicates that the times required for the N_2O_4 to dissociate to form 99% of the equilibrium partial pressures of NO_2 are 1.75×10^{-3} s and 2.50×10^{-3} s, respectively.

APPENDIX B

CALCULATION OF EQUILIBRIUM PARTIAL PRESSURES AND CONCENTRATIONS OF NO₂ AND N₂O₄

Nitrogen tetroxide is the major absorbing N(IV) species in nitric acid production columns. At lower partial pressures of N(IV) than those usually encountered in nitric acid columns, or at the low partial pressures of N(IV) encountered in the stripping section of these columns, nitrogen dioxide may be an important absorbing species. The equilibrium partial pressures and concentrations of NO₂ and N₂O₄ are presented in Table 17 where:

$$K_{G1} = 6.86 \text{ atm}^{-1} \quad ;$$

$$H_B = 0.93 \text{ kgmol/m}^3\text{-atm} \quad ; \text{ and}$$

$$H_A = 0.0099 \text{ kgmol/m}^3\text{-atm} \quad .$$

The value of the gas phase equilibrium constant, K_{G1} , was recommended by Schwartz and White (1983). The Henry's Law constant of N₂O₄, H_B , is a new recommended value from this work. The Henry's Law constant of NO₂, H_A , is consistent with the recommended value of the liquid phase equilibrium constant for the dimerization of NO₂, 65400 m³/kgmol (Grätzel et al., 1969).

The lowest N(IV) partial pressure encountered in the scrubbing experiments was 2.82×10^{-4} atm. At this partial pressure more than 99% of the N(IV) in the gas phase is in the form of NO₂. The liquid phase

Table 17 Equilibrium Partial Pressures and Concentrations of NO_2 and N_2O_4 at 25°C

$P_{\text{N}(\text{IV})}$ (10^{-6} atm)	P_{A} (10^{-6} atm)	P_{B} (10^{-6} atm)	c_{A} (kgmol/m ³)	c_{B} (kgmol/m ³)
282	281	0.5	2.78×10^{-6}	5.03×10^{-7}
500	497	1.7	4.92×10^{-6}	1.57×10^{-6}
1000	987	6.7	9.77×10^{-6}	6.21×10^{-6}
2000	1948	26.0	1.93×10^{-5}	2.42×10^{-5}
3000	2886	57.1	2.86×10^{-5}	5.31×10^{-5}
4000	3802	99.1	3.76×10^{-5}	9.22×10^{-5}
4940	4644	148	4.60×10^{-5}	1.38×10^{-4}

concentration of NO_2 in equilibrium with the gas phase mixture is 5.5 times larger than the liquid phase concentration of N_2O_4 . The highest N(IV) partial pressure encountered in the scrubbing experiments was 4.94×10^{-3} atm. At this partial pressure 94% of the N(IV) in the gas phase is in the form of NO_2 . However the liquid phase concentration of NO_2 in equilibrium with this gas phase mixture is three times smaller than the liquid phase concentration of N_2O_4 . Nitrogen dioxide becomes increasingly important as an absorbing N(IV) species at lower N(IV) partial pressures.

APPENDIX C

CALCULATION OF ERRORS INTRODUCED BY THE ASSUMPTION THAT THE DERIVATIVE TERM OF THE LIQUID PHASE MATERIAL BALANCE IS NEGLIGIBLE

The gas phase mass balance in differential form is

$$(G / P) (dp_{N(IV),i} / dz) = - a N_{N(IV),i} \quad (84)$$

Equation 84 was manipulated to give the gas phase mass balance in integral form based on the bulk gas phase partial pressure of NO₂:

$$a P Z / G = \int_{P_{A,out}}^{P_{A,in}} [(1 + 4 K_{G1} p_{A,b}) dp_{A,b} / N_{N(IV),i}] \quad (89)$$

The liquid phase mass balance in differential form is

$$(L / C_t) dc_{N(IV),b} / dz = a N_{N(IV),b} - h_t k_{A37} c_{A,b}^2 \quad (102)$$

Equation 102 may be expressed in terms of the bulk phase concentration of NO₂ rather than N(IV) as:

$$(L / C_t) (1 + 4 K_{A1} c_{A,b}) dc_{A,b} / dz = a N_{N(IV),b} - h_t k_{A37} c_{A,b}^2 \quad (147)$$

Equation 84 may be expressed in terms of the bulk phase partial pressure of NO₂ as:

$$(G / P) (1 + 4 K_{G1} p_{A,b}) (dp_{A,b} / dz) = - a N_{N(IV),i} \quad (148)$$

Equations 147 and 148 are useful for estimating the error introduced by neglecting the left hand side (LHS) of Equation 102 when the GCF model is used.

Equation 89 may be integrated by a variety of techniques. Gaussian quadrature was used because the difficulty in determining the value of $N_{N(IV),i}$ at a given partial pressure caused the programmer to favor a technique which gives a great deal of accuracy with a minimum of integration steps. One of the disadvantages of using Gaussian quadrature, as opposed to a finite difference integration, is that the integration steps are steps in $p_{A,b}$ rather than steps in z , the axial distance in the tower. The results of the integration of the gas phase mass balance using the GCF model and the technique of Gaussian quadrature are the values of the following quantities at each quadrature point: the bulk phase partial pressure of NO_2 , the interfacial partial pressure of NO_2 , the interfacial concentration of NO_2 , the interfacial flux of $N(IV)$, the bulk liquid phase concentration of NO_2 , and the flux of $N(IV)$ into the bulk liquid phase. The interfacial concentration of NO_2 may be used to calculate the reaction number for each quadrature point. Some results of a sample integration are shown in Table 18. These integration results may be used to estimate the error in the liquid bulk phase boundary condition introduced by dropping the LHS of Equation 102.

Table 18 contains sufficient information to allow an estimate of the axial distance between quadrature points. Equation 148 may be rearranged as:

$$(dp_{A,b} / dz) = - (P a N_{N(IV),i} / G) / (1 + 4 K_{G1} p_{A,b}) \quad . \quad (149)$$

Using the approximation,

Table 18 Results of a Sample Integration^a of the Gas Phase Mass Balance in Conjunction with the GCF Model Using Gaussian Quadrature

Quadrature Point	$p_{A,b}$ (10^{-6} atm)	$c_{A,b}$ (kgmol/m ³)	$N_{N(IV),i}$ (kgmol/m ² -s)	$M_{(IV)}$
1	372	3.24×10^{-6}	3.49×10^{-9}	1.84
2	369	3.22×10^{-6}	3.44×10^{-9}	1.83
3	362	3.19×10^{-6}	3.36×10^{-9}	1.81
4	354	3.15×10^{-6}	3.25×10^{-9}	1.78
5	344	3.10×10^{-6}	3.11×10^{-9}	1.74
6	333	3.04×10^{-6}	2.97×10^{-9}	1.70
7	322	2.98×10^{-6}	2.83×10^{-9}	1.66
8	311	2.92×10^{-6}	2.69×10^{-9}	1.62
9	301	2.87×10^{-6}	2.56×10^{-9}	1.58
10	292	2.82×10^{-6}	2.46×10^{-9}	1.55
11	286	2.79×10^{-6}	2.39×10^{-9}	1.53
12	283	2.77×10^{-6}	2.35×10^{-9}	1.51

^a The operating conditions (temperature, pressure, flow rates, and column height) of the experimental scrubber are used with the new recommended values for the solubilities and the hydrolysis rate constant. The liquid phase mass transfer coefficient used causes the reaction numbers to be small enough that the KCF model is inappropriate. The mass transfer parameters are:

$$\begin{aligned} k_l &= 4.0 \times 10^{-4} \text{ m/s} \\ k_g &= 2.25 \times 10^{-4} \text{ kgmol/m}^2\text{-atm-s} \\ a &= 500 \text{ m}^2/\text{m}^3 \end{aligned}$$

The inlet and outlet partial pressures of N(IV) are 3.75×10^{-4} atm. and 2.83×10^{-4} atm. The calculated N(IV) scrubbing efficiency is 0.246.

$$(dp_{A,b}^j / dz) = (p_{A,b}^{j+1} - p_{A,b}^j) / \Delta z^j , \quad (150)$$

where the superscripts indicate the quadrature point, in Equation 149 and rearranging gives the distance between quadrature points as:

$$\Delta z^j = (p_{A,b}^j - p_{A,b}^{j+1}) (1 + 4 K_{G1} p_{A,b}^j) / (P a N_{NO_2,i}^j / G) . \quad (151)$$

The approximation,

$$(dc_{A,b}^j / dz) = (c_{A,b}^{j+1} - c_{A,b}^j) / \Delta z^j , \quad (152)$$

may be used to calculate the value of the LHS of Equation 102 at each quadrature point ($p_{A,out}$ and 0 are used for the partial pressure and concentration of NO_2 for the thirteenth quadrature point). The resulting percent absolute relative error in the bulk liquid phase mass balance is shown for each quadrature point in Table 19. The absolute relative error is below 0.06% for all the internal quadrature points. The error is significant only at the top of the column, the twelfth quadrature point. This error is caused by the rapid change in the bulk liquid phase concentration of NO_2 that occurs at the top of the absorption column. This rapid change is due to the fact that no NO_2 is in the liquid feed stream. It may be possible to eliminate, or drastically reduce this error by changing the boundary condition at the largest quadrature point to include the LHS of Equation 102. It seems unlikely that an error in the bulk liquid phase boundary condition at one of many quadrature points has a great effect on the accuracy of scrubbing efficiency predictions.

Table 19 Percent Absolute Relative Errors in the Liquid Bulk Phase Mass Balance From the Sample Integration Shown in Table 18

Quadrature Point	Percent Absolute Relative Error
1	0.05
2	0.05
3	0.05
4	0.05
5	0.05
6	0.05
7	0.05
8	0.05
9	0.05
10	0.05
11	0.05
12	23.9

VITA

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During his stay at The University of Tennessee Doug earned support with various teaching and research assistantships with the Department of Chemical Engineering, the Resources, Energy, and Environment Center, and the Department of Nuclear Engineering. With the help of Dr. R. M. (Pete) Counce, Doug gained expertise in some areas of the problems related to the manufacturing of nitric acid. This led to several publications and consulting work with Dr. Counce. Doug participated in the Civil Engineering Honors Internship program with Tennessee Eastman Company and has performed consulting work in the area of hydraulic modeling of wastewater with that company.

Doug and Melanie Crawford have moved to Mobile, Alabama. Doug is employed by CIBA-GEIGY Corporation in McIntosh, Alabama. He is a member of the Order of the Engineer, the American Institute of Chemical Engineers, and Tau Beta Pi.