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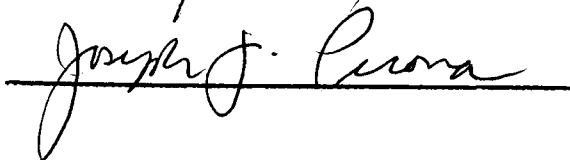
To the Graduate Council:

I am submitting herewith a thesis written by Joseph F. Birdwell entitled "Partitioning of Iodine in Offgas Generated by Dissolution of Spent Nuclear Fuel." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.



Dr. F. E. Weber, Major Professor

We have read this thesis
and recommend its acceptance:



Accepted for the Council:



The Graduate School

PARTITIONING OF IODINE IN OFFGAS GENERATED BY
DISSOLUTION OF SPENT NUCLEAR FUEL

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Joseph F. Birdwell

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ABSTRACT

A considerable amount of research has been performed regarding the scrubbing of nitrogen oxides (NO_x) from offgas streams with water and dilute nitric acid solutions. Considerably less information concerning the partitioning of iodine between the liquid and vapor phases has been accumulated. The available information has been combined to evaluate the distribution of iodine in an NO_x offgas scrubbing system. The particular system of interest removes nitrogen oxides from the iodine-containing offgas generated by the dissolution of spent nuclear fuel.

A computer simulation of the scrubbing system was developed and used to evaluate the gas/liquid iodine distribution resulting from three alternative system flowsheets. In the first, the vapor from steam stripping of the NO_x scrubber bottoms (to volatilize iodine) is recycled to the scrubber. In the second, air sparging of the scrubber bottoms tank is added. In the third, the iodine-bearing vapor from the steam stripper is not recycled to the NO_x scrubber, but the bottoms tank sparge is retained.

It has been hypothesized that recycle of the iodine-bearing stripper offgas stream results in an accumulation of iodine in the scrubber liquid. Both this hypothesis and the effect of the air sparge on NO_x removal efficiency and iodine partitioning have been evaluated.

The flowsheet simulations indicate that iodine does accumulate in the NO_x scrubber. The iodine level in the scrubber liquid was observed to be decreased by sparging the bottoms tank, thereby volatilizing iodine from solution. An additional slight decrease in system iodine retention was indicated when the iodine stripper offgas was not

recycled to the NO_x scrubber. The difference in magnitude between the effects of air sparging and steam stripping is believed to be due to the positioning of the two process in the system. In all simulations air sparging preceded steam stripping, therefore the potential for iodine removal was greatest for air sparging.

With regard to NO_x scrubbing, the removal efficiencies of the scrubber were in excess of 90% for all three flowsheets.

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SYMBOLS AND ABBREVIATIONS

a	gas-liquid interfacial area per unit volume, m^{-1}
a_i	activity coefficient of component i , $kgmol\ m^{-3}$
C_i	concentration of component i in the bulk liquid phase, $kgmol\ m^{-3}$
C_i^*	interfacial concentration of species i in the liquid phase, $kgmol\ m^{-3}$
D	diffusivity, $m^2\ s^{-1}$
D_i	diffusivity of component i in water, $m^2\ s^{-1}$
$e, \exp$	natural exponential function
E_i	enhancement factor, the factor by which the absorption of component i is increased by reaction in the liquid
G	volumetric gas flowrate, $m^3\ s^{-1}$
H	Henry's Law constant, $m^3\ atm\ kgmol^{-1}$
H_i	Henry's Law constant for the <u>ith</u> component in water, $m^3\ atm\ kgmol^{-1}$
H_v	heat of vaporization, $kcal\ kg^{-1}$
I	ionic concentration, $kg\ ion\ m^{-3}$
K_j	equilibrium constant for reaction j
K_{-j}	equilibrium constant for reaction j from the reverse (right-to- left) direction
k	a first- or pseudo-first-order reaction rate constant
k_j	forward rate constant for reaction j
k_G	gas-phase mass transfer coefficient, $kgmol\ m^{-2}\ atm^{-1}\ s^{-1}$
k_L	liquid-phase mass transfer coefficient, $m\ s^{-1}$
L	liquid flowrate $m^3\ s^{-1}$

$\ln$	base e logarithmic function
$\log$	base 10 logarithmic function
$\underline{M}$	liquid-phase molar concentration, kgmol m^{-3}
NO^*	$\text{NO} + \text{N}_2\text{O}_3$
NO_2^*	$\text{NO}_2 + 2\text{N}_2\text{O}_4 + \text{N}_2\text{O}_3$
NO_x	$\text{NO}^* + \text{NO}_2^*$
P	iodine gas-liquid partition coefficient
P_i	bulk gas partial pressure of component i, atm
P_i^*	partial pressure of specie i at the gas-liquid interface, atm
R	gas law constant, $\text{m}^3 \text{ atm kgmol}^{-1} \text{ K}^{-1}$
$\bar{R}_i$	absorption rate of <u>ith</u> specie, $\text{kgmol m}^{-2} \text{ s}^{-1}$
r_i	reaction rate for component i, $\text{kgmol m}^{-3} \text{ s}^{-1}$ or atm s^{-1}
T	temperature, K
t	time, s
V	volume, m^3
X_i	mole fraction of component i in the liquid phase
$[i]$	concentration of species i, gmol l^{-1}

1. INTRODUCTION

The objective of the thesis was to develop a computer simulation of a process system (Figure 1) to remove nitrogen oxides (NO_x) from the offgas generated by the dissolution of spent nuclear fuel. In addition to modeling the absorption/reaction mechanisms of NO_x in dilute nitric acid solutions, the simulation addresses the partitioning of iodine in the offgas between the liquid and vapor phases in the scrubbing column. The model developed was used to investigate the hypothesis that iodine accumulation occurs in the liquid phase in the NO_x scrubber and throughout the offgas scrubbing system. For comparison, iodine distribution in an alternative flowsheet where the iodine-bearing vapor generated by steam stripping of the scrubber bottoms solution bypasses the NO_x scrubber was evaluated. The effect of sparging the scrubber bottoms solution on NO_x removal efficiency and on iodine partitioning was also investigated.

The flowsheet was based on the dissolver offgas (DOG) system existing in the Integrated Equipment Test (IET) facility at Oak Ridge National Laboratory (ORNL). This pilot-scale facility was constructed under the auspices of the United States Department of Energy's Consolidated Fuel Reprocessing Program (CFRP) to provide a pilot plant for developing and testing equipment for the reprocessing of spent nuclear fuel. A block flow diagram of the chemical process portion of this facility is shown in Figure 2.

The DOG system was designed to remove nitrogen oxides from the offgas generated by the dissolution of spent nuclear fuel in nitric

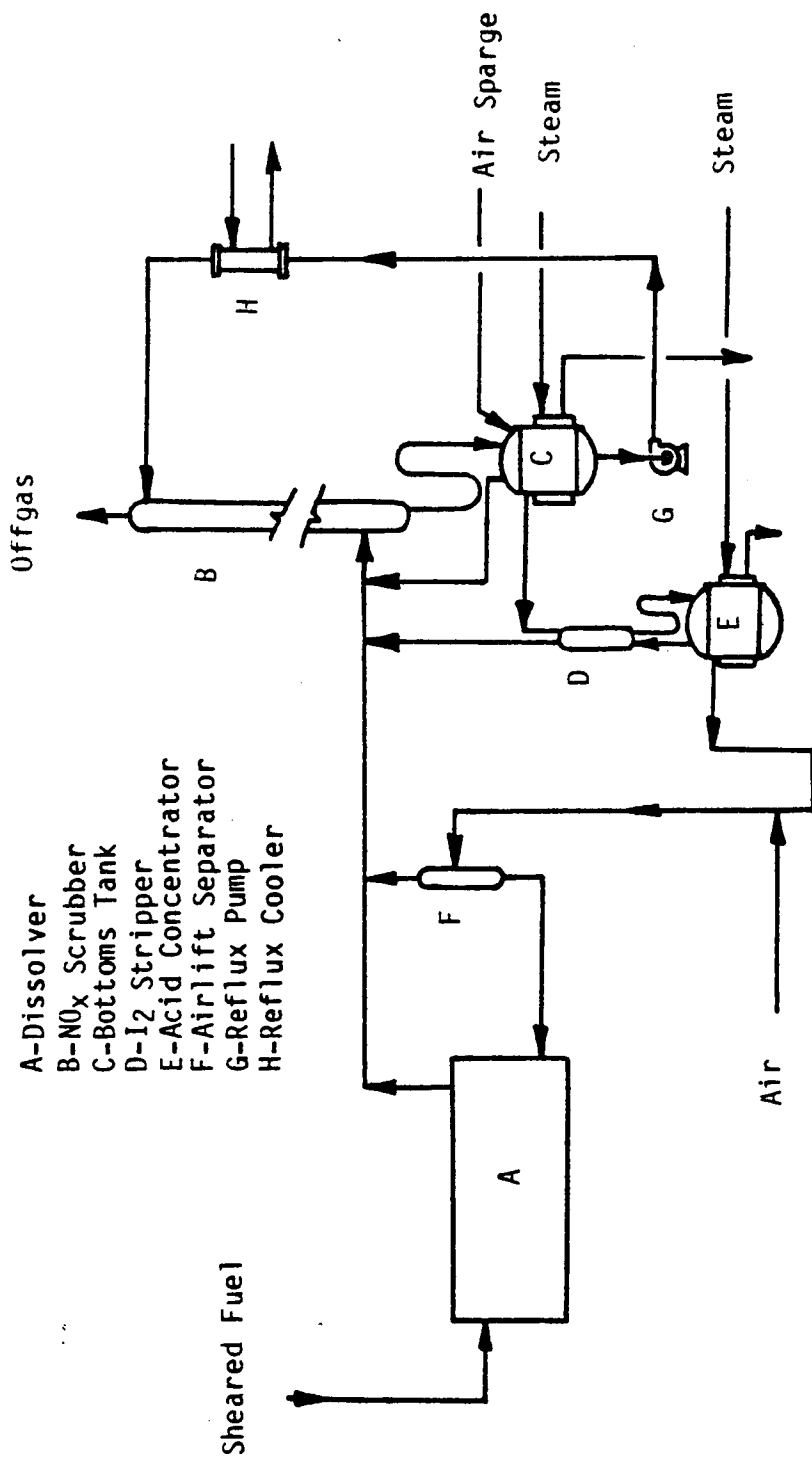


Figure 1. System for Removing Nitrogen Oxides Generated by Dissolution of Nuclear Reactor Fuel (Dissolver Offgas System).

L=LIQUID
S=SOLIDS
V=VAPOR

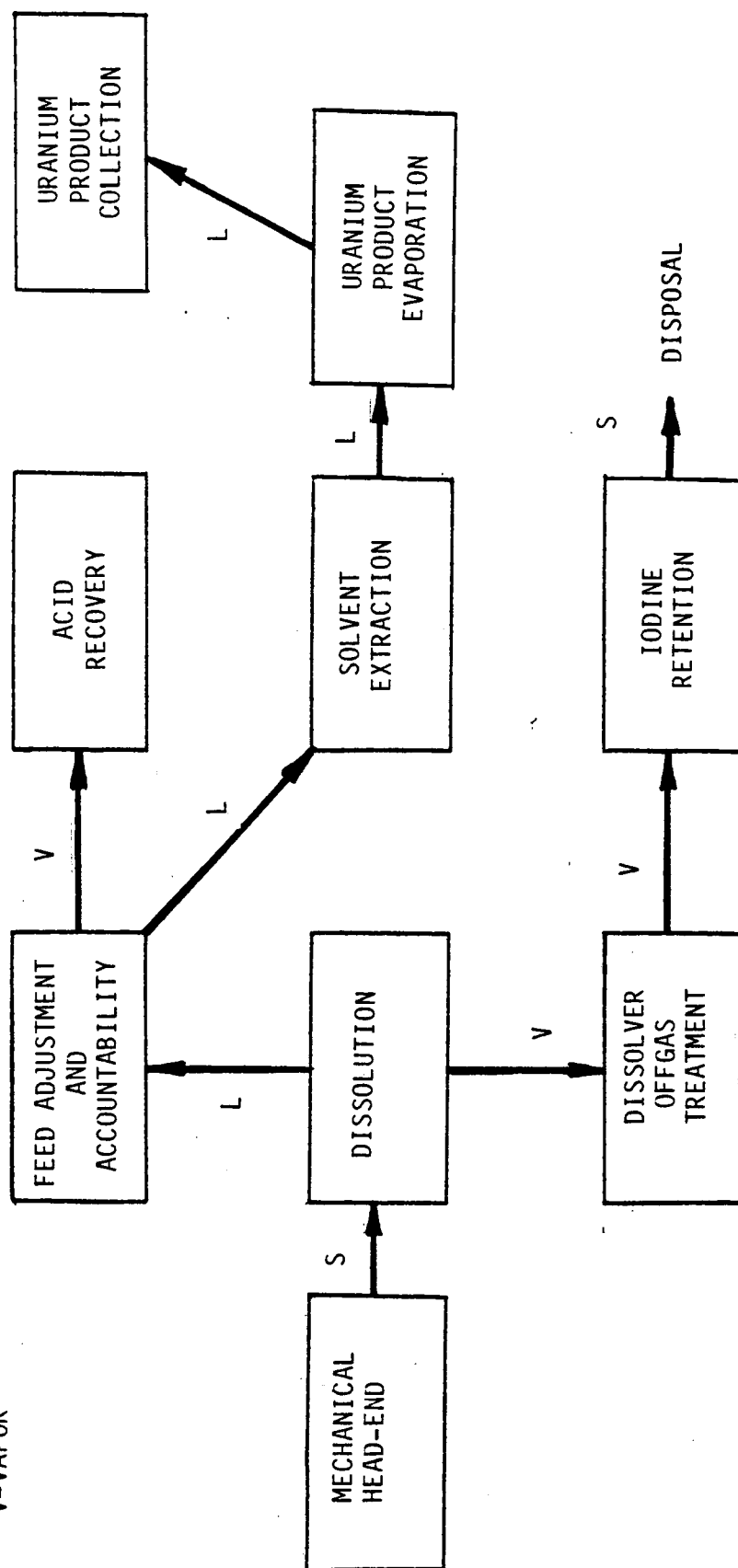


Figure 2. Block Flow Diagram of the Integrated Equipment Test Facility.

acid. Fission products, specifically iodine, pass through the system in the vapor phase for further processing downstream.

In the DOG system (Figure 1), the offgas generated in the dissolver flows to the bottom of an NO_x scrubber--a packed column consisting of two, 12-foot sections of one-inch Intalox saddles. The offgas is saturated with water due to the addition of steam to the dissolver to provide continuous offgas purging. The dissolver operates at 373 K while the scrubber is at 289 K. Therefore, most of the water and nitric acid vapors present in the dissolver offgas condense at the vapor inlet at the bottom of the scrubbing column.

The condensate from the dissolver offgas flows with the scrubber liquid into the scrubber bottoms tank. This vessel is maintained at 368 K, and is equipped with an air sparge to allow for volatilization of iodine from solution. The fraction of the scrubber bottoms acid which is produced by the scrubbing process overflows from the bottoms tank to the iodine stripper--a small column packed with 1/4-inch Intalox saddles used to volatilize iodine from the bottoms solution. The remainder of the liquid is cooled to the scrubber temperature and recycled to the top of the column. Offgas from the bottoms tank is returned to the bottom of the column with the dissolver offgas.

In the iodine stripper the liquid overflow from the bottoms tank is contacted with steam from the acid concentrator to remove iodine from the liquid. In providing steam to the stripper, the acid concentrator (which is operated at 373 K) removes water from the acid solution which was generated by NO_x scrubbing. This concentrated acid is recycled to the dissolver via airlift. The offgas from airlifting

is added to the offgas feed stream to the scrubber. In the normal operating mode, the offgas from the iodine stripper is also recycled to the scrubbing column.

Isotopes of iodine, produced from nuclear reactor fuel during the fission process, remain inside the fuel assemblies until dissolution occurs. These isotopes are volatilized when the spent fuel (contained in short segments of fuel cladding) is dissolved in hot (approximately 368 K) nitric acid. Various nitrogen oxides are also produced during dissolution by reaction of nitric acid with uranium oxides (UO_2 and U_3O_8). These components, along with nitrogen and oxygen (which enter the dissolver as air inleakage) and water and nitric acid vapors comprise the dissolver offgas. Quantitatively, the nitrogen oxides constitute less than ten mole percent and iodine less than 0.1 mole percent of the DOG.

Though present in minute amounts, control of radioactive iodine is essential because of the health hazard it poses. Since it is denser than air, iodine does not disperse readily in the atmosphere. Due to their relatively low volatilities, many iodine compounds exist primarily as liquids or solids at ambient temperatures. These two factors make ground contamination from an accidental iodine release highly probable. Iodine contamination passes into the human food chain through dairy products from animals that have ingested contaminated grasses. In humans, iodine accumulates in the thyroid gland, increasing the risk of cancer development. Understandably, control of iodine and knowledge of its whereabouts throughout the reprocessing facility is essential.

Though a large amount of information regarding NO_x scrubbing and some information on iodine partitioning is available, no attempts to combine the information to describe the processing of the DOG have been made. No calculations regarding the partitioning of iodine were included in the design of the NO_x scrubbing column in the IET facility. To simplify the design, the iodine compounds present in the DOG were assumed to stay primarily in the vapor phase.

For purposes of this thesis, the simulated process was based on an NO_x scrubbing system for processing offgas generated by spent fuel dissolution at the rate of one-half ton of heavy metal per day. Equipment sizes (i.e. packed column heights and diameters) have been determined based on the required offgas processing capacity for the typical IET flowsheet, and were not varied in this study.

2. LITERATURE REVIEW

Information on the properties and reactions involved in the $\text{NO}_x\text{-HNO}_x\text{-H}_2\text{O}$ system exists in considerable quantities. In particular, a great deal of literature concerning the absorption/reaction mechanisms in this chemical system is readily available. Though some of the information is of a theoretical nature, a greater amount of literature consists of reports on the results of experimental efforts.

The absorption of nitrogen oxides in water and dilute nitric acid has been of increasing interest in this century. Initial interest was due to its widespread commercialization in the production of the nitric acid used in the manufacture of explosives. More recently, the scrubbing process has increased in importance due to an increased interest in pollution abatement.

This literature review summarizes only that information having a direct bearing on the project. Comprehensive reviews of the literature on the $\text{NO}_x\text{-HNO}_x\text{-H}_2\text{O}$ system are presented by Hoftyzer and Kwanten (1972), Sherwood, Pigford, and Wilke (1975), and Counce (1980).

A limited amount of literature is available regarding the design of equipment for scrubbing of nitrogen oxides with water and dilute nitric acid solutions in tray and packed columns. Among the most recent data is that reported by Counce (1980), and by Counce and Perona (1980 and 1983), which has been used extensively in this thesis project.

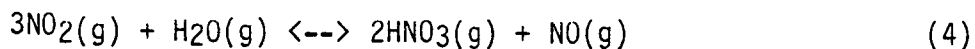
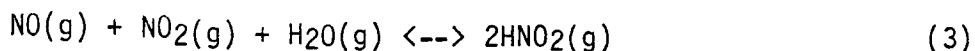
A smaller collection of information is available on the properties and reactions of iodine compounds. Most of the interest in iodine has been limited to the nuclear industry. Much of the information which

has been documented is qualitative in nature; almost all of the data is empirical. Furthermore, the lack of physical property data pertaining to iodine and its hydrolysis products makes use of property estimation techniques necessary.

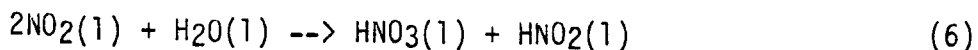
Reactions of the NO_x - HNO_x - H_2O System

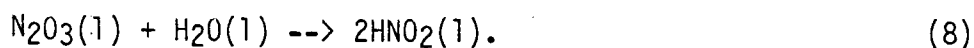
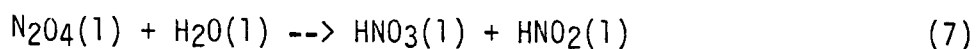
For purposes of discussion, the chemical system involved in the scrubbing of nitrogen oxides can be considered to consist of the species NO , NO_2 , N_2O_3 , N_2O_4 , HNO_2 , HNO_3 , and H_2O . For simplicity, these species will be referred to as the NO_x - HNO_x - H_2O system. The system interactions consist of gas- and liquid-phase component reactions, gas absorption into and desorption from the liquid, and vapor phase equilibrium relationships. In this literature review, related gas and liquid reactions will be grouped together for discussion.

In the gas phase, the reactions of interest are:



In the liquid phase, the reactions describing the absorptive and desorptive processes are:





These are considered irreversible due to the low concentrations of HNO_2 and HNO_3 in solution. Solubilities of the species are given in terms of Henry's Law constants in Table 1.

Reactions involving NO_2 and N_2O_4

The gas-phase equilibrium relationship between NO_2 and N_2O_4 described by equation (1) was studied by Bodenstein (1922) over the temperature range 282 to 404 K. From the data collected, Bodenstein developed the expression:

$$\log K_{-1} = -(2692/T) + 1.75 \log T + 0.00483T - 7.144 \times 10^{-6}T^2 + 3.062. \quad (9)$$

Verhoek and Daniels (1931) studied reaction (1) at low partial pressures of N_2O_4 over the range 298 to 318 K. From their data the heat of dissociation was calculated to be 14,000 kcal kmol⁻¹. From the work of Verhoek and Daniels and the JANAF Thermochemical Tables (1971), Hoftyzer and Kwanten (1972) derived the following expression for the equilibrium constant for reaction (1):

$$K_1 = (0.707 \times 10^{-9}) \exp(6866/T). \quad (10)$$

Researchers studying the liquid phase reactions involving the absorption of NO_2 have listed the primary reactions in the process as:

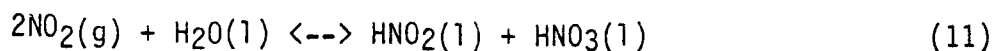


Table 1. Henry's Law Constants at 298 K

Species	H_i ($\text{m}^3 \text{ atm kg mol}^{-1}$)
NO	518.0 ^a
NO ₂	24.4 ^b
N ₂ O ₃	2.59 ^c
N ₂ O ₄	0.769 ^d
HNO ₂	0.0305 ^e
HNO ₃	8.2×10^{-13} ^f

*Table taken from Counce (1980)

^aA. G. Loomis, International Critical Tables III, 255 McGraw Hill, New York (1928).

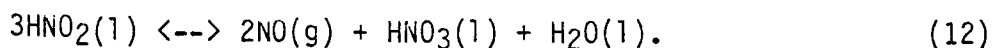
^bAndrews and Hanson, Chem. Eng. Sci. 14: 105 (1961).

^cC. E. Corriveau, Jr., Master's Thesis in Chemical Engineering, University of California, Berkeley (1971).

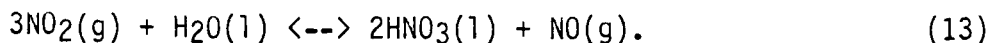
^dH. Kramer, M. P. P. Blind, and E. Snoeck, Chem. Eng. Sci. 14: 115 (1961).

^eE. Abel and E. Neusser, Monatsh. Chem. 54: 855 (1929).

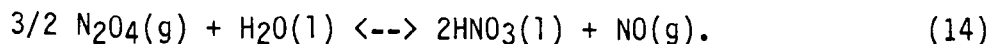
^fP. J. Hoftyzer and F. J. G. Kwanten, Processes for Air Pollution Control, 2nd ed., Chemical Rubber Co., Cleveland (1972).



The overall reaction has been expressed as:



While these early researchers expressed the reaction as the absorption of NO_2 , Carberry (1959) concluded that N_2O_4 is the reactive nitrogen oxide specie. With the inclusion of the gas-phase equilibrium relationship between NO_2 and N_2O_4 , the overall expression for the absorption reaction becomes:



The equilibrium expression for this reaction in terms of partial pressures becomes:

$$K_{14} = [\text{PNO}(\text{aHNO}_3)^2]/[\text{PN}_2\text{O}_4]^{3/2} \text{aH}_2\text{O}. \quad (15)$$

Carberry further concluded that the relationship expressed by equation (15) becomes independent of temperature over the range of HNO_3 concentrations from 10 to 55 weight percent when the expression is put in terms of PN_2O_4 , according to the relationship

$$K_c = \text{PNO}/(\text{PN}_2\text{O}_4)^{3/2}. \quad (16)$$

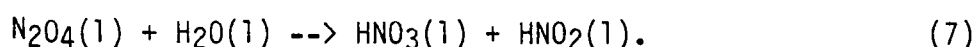
Beattie (1963), and Sherwood, Pigford, and Wilke (1975) have presented the expression

$$\log K_c = 7.412 - 20.28921w + 32.47322w^2 - 30.87w^3 \quad (17)$$

in which "w" is weight percent nitric acid. In order to utilize the

equilibrium constant " K_c ", it is required (by the equations from which the expression for the constant has been derived) that nitrous acid be present in the liquid phase.

The hydrolysis reaction of N_2O_4 during its absorption into water or dilute nitric acid is essentially irreversible due to the low concentrations of HNO_3 and HNO_2 present in the liquid phase. This reaction is described by the expression



The absorption of NO_2 - N_2O_4 into aqueous solutions of nitric acid and sodium hydroxide was studied by Sherwood and Chambers (1937). In their studies with a wetted-wall column they confirmed the finding by Bolshakoff that the rate of absorption increased proportionally to the 0.8 power of the gas velocity over the liquid. Sherwood (1937) also found that the absorption coefficient varied as the 0.8 power of the Reynolds number of the gas. These findings indicate the existence of a gas-phase resistance which controls the absorption rate. In contrast, the work of Denbigh and Prince (1947) indicated that the liquid-phase chemical reaction controls the rate of the overall absorption-reaction process. Studies by Caudle and Denbigh (1953) appear to reconcile the conflicting findings of the earlier investigations. Caudle and Denbigh explained that the gas flowrate does affect absorption due to the effect this flow has on localized mixing and eddying in the reactant liquid phase.

Wendel and Pigford (1958) performed a subsequent study of NO_2 - N_2O_4 absorption into water in a wetted-wall column. In their experiments

the gas and liquid flow rates were varied. The results indicated that neither the flowrates, nor the gas-liquid contact time influenced the reaction rate. It was therefore concluded that the hydrolysis reaction is rate-controlling. Based on penetration theory and assuming that the hydrolysis of N_2O_4 occurs in the liquid phase, the reaction rate can be described by the expression:

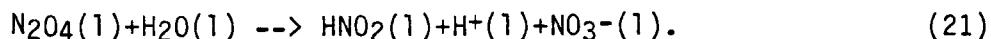
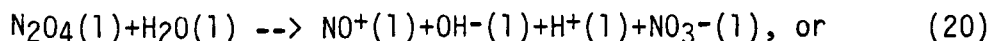
$$\bar{R}_{NO_2}^* = 2(\sqrt{Dk}/H)N_{2O_4} P_{N_{2O_4}}^* \quad (18)$$

where the asterisk indicates the partial pressure of the specie at the gas-liquid interface.

Based in part on the works of Gray and Yoffe (1953), and Miller and Watson (1957), Carberry (1959) concluded that N_2O_4 exists in solvents of high dielectric strength in the ionized form:



Based on this conclusion, the hydrolysis reaction of N_2O_4 can be expressed as:



Carberry's conclusion is supported by the kinetic and equilibrium data, and the rate expression derived from this conclusion is identical with that found by Denbigh (1947) experimentally,

$$-d(N_{2O_4})/dt = k[C_{N_{2O_4}} - (C_{N_{2O_4}})^{1/4}(C_{NO})^{1/2}]. \quad (22)$$

In addition to reconciling the conflicting findings of separate investigators, the ionization theory also corroborates the argument presented earlier by Denbigh (1947) that a hydrolysis reaction in the gas phase is highly improbable.

Due to the presence of nitrogen oxide in the offgas, Sherwood and Chambers (1937) concluded that a reaction between NO_2 and water vapor takes place in the gas film, and that the gas-phase resistance resulted from the diffusion of nitrogen dioxide through the nitric acid mist. Caudle and Denbigh (1953) concluded that the hydrolysis of N_2O_4 takes place at the gas-liquid interface, because the absorption rate was proportional to interfacial area in the reaction system, not to volume of the bulk phase, and any NO produced in the reaction system existed primarily in the liquid phase.

Peters and Holman (1955) studied the absorption of NO_2 - N_2O_4 in water and aqueous solutions of NaOH and NaCl . Both bulk phases were analyzed for the presence of NO_2^* , HNO_3 , and NaOH . The presence of nitrogen oxide in the offgas resulting from absorption of NO_2^* into a sodium hydroxide solution was interpreted to indicate a possible gas-phase NO_2^* hydrolysis reaction. However, the lack of a correlation between absorption rate and water vapor fugacity indicated the existence of a liquid-phase reaction. Therefore, Peters and Holman concluded that the N_2O_4 hydrolysis reaction may occur in both liquid and gas phases.

Dekker, Snoeck, and Kramers (1959) studied the absorption of NO_2 - N_2O_4 into water over a range of temperatures and NO_2^* gas-phase concentrations using a wetted-wall column. Their investigations led

them to conclude that N_2O_4 was more important to the absorption process than NO_2 , and that the diffusion of N_2O_4 into the liquid was accompanied by the rapid, pseudo first-order hydrolysis of N_2O_4 .

Moll (1966) evaluated the rate of the N_2O_4 hydrolysis reaction by injecting liquid N_2O_4 directly into a water stream and measuring the temperature change downstream of the N_2O_4 feed point. From his data, Moll developed the following expression for the pseudo first-order rate constant over the temperature range 300 to 318 K:

$$\ln K_7 = 16.38 - 3163/T. \quad (23)$$

Hoftyzer and Kwanten (1972) investigated the effects of NO_2^* gas concentration, temperature, and acid molarity on the absorption of NO_2 - N_2O_4 using laminar jets. Their results were correlated using equation (17), which assumed that the hydrolysis reaction took place in the liquid film, and that the reaction--not diffusion--is rate controlling. The expression developed by Hoftyzer and Kwanten covers the temperature range 276 to 348 K:

$$\log[(Dk/H)\text{N}_2\text{O}_4] = -0.52 - 760/T. \quad (24)$$

A decrease in $(\sqrt{Dk}/H)\text{N}_2\text{O}_4$ was observed with increasing acid molarity--a change attributed to the increase in the Henry's Law constant with increasing ionic strength. Hoftyzer and Kwanten proposed correcting for this change in the constant by using the factor $\exp(-0.075 I)$, where "I" represents ionic strength.

Subsequent studies of the absorption of NO_2 - N_2O_4 into water and aqueous solutions have been performed by Chilton and Knell (1972),

Kameoka and Pigford (1977), and Mahotkin and Shamsutdinov (1976).

Reactions of N₂O₃

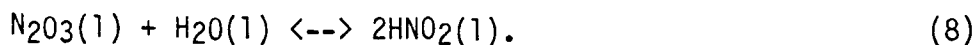
The reaction of interest in the gas phase absorption/reaction system involving N₂O₃ is:



This reaction has been studied by Abel and Proisl (1929), Verhoek and Daniels (1931), and Beattie and Bell (1957). In these investigations the heat of dissociation was determined to be 9600, 10160, and 9527+96 kcal kgmol⁻¹ respectively. Based on the results of Beattie and Bell at low N₂O₃ partial pressures over the temperature range 273 to 318 K, Hoftyzer and Kwanten (1972) developed the following expression for the equilibrium constant of reaction (2):

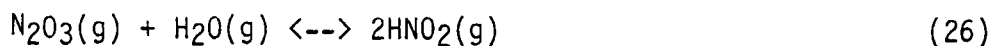
$$K_2 = (66.15 \times 10^{-9}) \exp(4740/T). \quad (25)$$

Corriveau (1971) studied the absorption of gaseous mixtures of NO* and NO₂* (including N₂O₃) into liquid-phase H₂O at atmospheric pressure and 298 K. In these studies using wetted spheres, Corriveau found N₂O₃ and N₂O₄ to be the major absorbing species over the interfacial partial pressure ranges (2.9 to 9) x 10⁻⁵ atm and (1.0 to 4.0) x 10⁻⁵ atm respectively. In these experiments the absorption of HNO₂ was found to be negligible. The liquid-phase reaction rate, ($\sqrt{Dk}/H$)N₂O₃, was found by Corriveau to be 1.59 x 10⁻³ kgmol/(m atm s). The reaction is described by the expression:

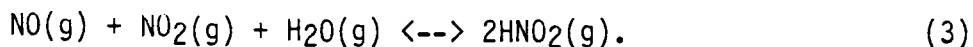


Reactions Involving HNO₂

The gas-phase equilibrium reaction



was studied by Wayne and Yost (1951) at 298 K. The equilibrium expression represents the combination of the reactions:



Both reactions (2) and (3) were found to be very fast, with a rate constant for the combined reaction (26) of $1.1 \times 10^5 \text{ atm}^{-2} \text{ s}^{-1}$. The rate constant of the reverse reaction which is apparently catalyzed by water, was found to be $6.6 \times 10^{-4} \text{ atm}^{-2} \text{ s}^{-1}$.

Ashmore and Tyler (1961), Karavaev and Skvortsov (1962), and Waldorf and Babb (1963) also studied the gas-phase equilibrium (3). The values by Ashmore (1961) and Karavaev (1962) for the reaction equilibrium constant and the heat of reaction are in close agreement.

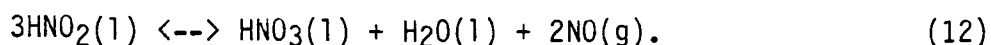
From the results of these researchers and those obtained by Wayne and Yost (1951), Hoftyzer and Kwanten (1972) developed the following expression for the equilibrium constant of reaction (3):

$$K_3 = 0.187 \times 10^{-6} \exp(4723/T). \quad (27)$$

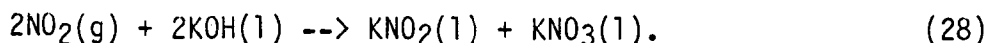
In the liquid phase, both nitric and nitrous acids are formed by the reactions of nitrogen oxides and water. While nitric acid is relatively stable in the liquid phase, nitrous acid can either decompose within the liquid to form HNO₃ and NO, or it can diffuse back

into the gas phase. In his literature review, Counce (1980) concluded that the liquid-phase disappearance of HNO_2 is the least understood element in the $\text{NO}_x\text{-HNO}_x\text{-H}_2\text{O}$ system, despite extensive investigation into this area.

Montemartini (1890) confirmed the reversible nature of the decomposition of nitrous acid in the liquid phase, according to the reaction



The depletion was observed to be first-order with respect to liquid-phase HNO_2 concentration. This investigation was conducted in both open and closed vessels containing a quiescent liquid phase at atmospheric pressure. In a later investigation, Montemartini (1892) studied the decomposition reaction in a hydrogen-sparged flask. The effluent gas was bubbled through potassium hydroxide to absorb any NO_2 while leaving NO essentially unabsorbed. The absorption of nitrogen dioxide into KOH and the subsequent reaction is described by the expression:



The decomposition of HNO_2 in HNO_3 solutions ranging from 0.8 to 5.6 M was indicated to be first order with respect to HNO_2 concentration, and was found to take place according to reaction (12). In solutions with higher HNO_3 concentrations the reaction can be expressed as



Valey (1892) studied the relationship of HNO_2 to the $\text{NO}_x\text{-HNO}_x\text{-H}_2\text{O}$ system in experiments which were conducted at atmospheric pressure and 282 to 325 K. Valey found the amount of nitrous acid formed increased with increasing acid concentration. Furthermore, in concentrated acid solutions the amount of nitrous acid produced decreased with increasing temperature, whereas in more dilute solutions the nitrous acid formation rate first increased then decreased with increasing temperature.

Valey studied the decomposition of nitrous acid in aqueous solutions with HNO_2 concentrations up to 1 M. These experiments were performed in a quiescent environment over the temperature range 284 to 304 K. Valey found reaction (12) to be reversible in solutions with HNO_3 concentrations less than 5.6 M. The decomposition of nitrous acid was found to be second order with respect to HNO_2 concentration, having a reaction rate which doubled for every 20 degree increase in temperature. Valey also observed an inverse proportionality between the rate of decomposition and the nitric acid concentration in the liquid.

Sapozhnikova (1901) investigated the equilibrium reaction (12) at 291 K and ambient pressure. Based on his results, he developed the expression:

$$K_{12} = \frac{C_{\text{H}} + C_{\text{NO}_3} - (C_{\text{NO}})^2}{(C_{\text{HNO}_2})^3}, \quad (29)$$

with which he was able to achieve an order of magnitude agreement with experimental values.

Lewis and Edgar (1911) studied the HNO_2 equilibrium reaction (12) from the HNO_3 side of the expression. They concluded that the reaction

was autocatalytic since the reaction rate, which was proportional to the nitrogen oxide feed rate, did not reach a maximum until several hours after initiation of the reaction. Lewis and Edgar developed the expression

$$K_{12r} = \frac{(C_{\text{HNO}_2})^2}{C_{\text{H}^+} C_{\text{NO}_3^-}}, \quad (30)$$

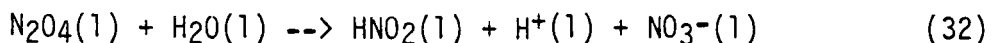
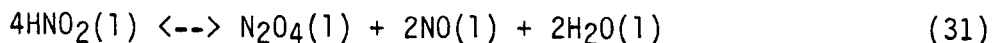
for the equilibrium constant of reaction (12) from the HNO_3 (reverse) direction.

In their study of liquid HNO_2 decomposition, Knox and Reid (1919) found that the rate of reaction (12) increased with agitation, increased surface area, and increased temperature. In their experiments over the temperature range 273 to 323 K and atmospheric pressure, the decomposition exhibited second-order behavior with respect to HNO_2 concentration in dilute HNO_3 solutions.

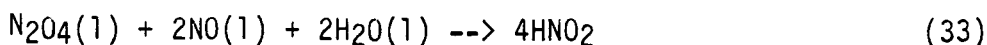
Klemenc and Pollak (1922) investigated reaction (12) in a vessel sparged with nitrogen at atmospheric pressure over the temperature range 273 to 303 K. The rate constants obtained were based on undissociated HNO_2 , and were found to increase with increased H^+ activity, undissociated HNO_2 concentration, and temperature. An approximate doubling of the rate constant for each 15 degree increase in temperature was observed.

The investigations by Abel and Schmid (1928a,b, and c); Abel, Schmid, and Babad (1928 and 1929); and Abel, Schmid, and Roemer (1930) established equilibrium constants and reaction rate constants for reaction (12) in a nitrogen oxide atmosphere.

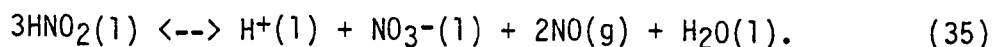
In Part I of their study, Abel and Schmid (1928a) proposed a mechanism in which the sequence of decomposition reactions was:



with the second step being rate-controlling. The formation of nitrous acid was proposed to occur according to the expressions:



with the second reaction controlling the overall reaction rate. Combining expressions (31) through (34), the overall reaction is described by the equation



From reaction (34), the rate expression was derived to be

$$+ \frac{d\text{CHNO}_2}{dt} = +K_{-35} \frac{(\text{CHNO}_2)^4}{(\text{PNO})^2} \pm K_{35}(\text{CHNO}_2 \text{ CH}^+ \text{ CNO}). \quad (36)$$

In Part II of their report the "Kinetics of Nitrous Acid", Abel and Schmid (1928b) studied the decomposition of nitrous acid in quiescent and stirred liquids in a nitrogen atmosphere. When an NO sparge was added the decomposition rate was found to decrease with increased nitrogen oxide partial pressure in the sparge gas.

In studies at ambient conditions (298 K and atmospheric pressure), Abel and Schmid (1928c) found that the rate of decomposition of HNO_2 , as described by reactions (30) and (31), increased with increasing ionic concentration. They attributed the change to a decrease in the solubility of gaseous NO .

Abel, Schmid, and Roemer (1930) studied the effects of temperature and ionic strength on the decomposition and liquid-phase formation of HNO_2 . For the decomposition reaction, they developed the following expression for the rate constant as a function of temperature and ionic concentration:

$$\log k_{35} = -6250/T + 24.43 + 0.078 I. \quad (37)$$

The heats of formation and equilibrium were found to be $21.2 \times 10^3 \text{ kcal kgmol}^{-1}$ and $11.9 \times 10^3 \text{ kcal kgmol}^{-1}$.

From investigations regarding the vapor pressure of nitrous acid in a NO atmosphere over aqueous HNO_2 solutions, Abel and Neusser (1929) determined the Henry's Law constant for the acid to be $0.0305 \text{ m}^3 \text{ kgmol}^{-1}$. This value was obtained at an ionic strength of $1.4 \text{ kg ion m}^{-3}$, and was found to increase slightly with increasing ionic strength.

Lang and Aunis (1951a,b) studied the effect of agitation, ionic strength, gas sparging, and vessel geometry on the decomposition of nitrous acid. In the earlier study, the decomposition reaction was found to be first-order in both unagitated and rapidly agitated solutions. However, the data from experiments involving no agitation were not readily reproducible, and it was recognized that a second-order analysis would probably have been as valid as the first-order

interpretation. Increased agitation and aqueous nitrous acid concentration were found to increase the depletion reaction rate. Increasing ionic strength resulted in increasing the reaction rate only at low pH levels.

In their later study, Lang and Aunis (1951b) found the rate of aqueous HNO_2 decomposition to be first-order when the system was agitated, unsparged, and was open to the atmosphere. In experiments with closed vessels, the reaction was found to approach second-order behavior, and the observed rate decreased. With regard to sparging, Lang and Aunis (1951b) found that increasing the flowrate of sparge gas had essentially the same effect as increasing the agitation of the vessel; both the rate of HNO_2 depletion, and the ratio between HNO_3 produced and HNO_2 decomposed increased. These increases were more pronounced when an oxygen sparge was utilized than when nitrogen or air sparges were used. From their studies, Lang and Aunis concluded that the degree of oxidation of nitrous acid in the liquid is significant only when nearly pure O_2 is present in the gas phase.

Komuro (1953) studied the decomposition of HNO_2 in nitric acid solutions ranging in concentration from 0 to 6 M. These experiments indicated that the rate of decomposition increased with increasing nitric acid concentration up to 1 M HNO_3 , after which no significant change in rate was observed.

An investigation into HNO_2 decomposition by Suzawa, Hondo, Manabe, and Hinokiyama (1955) confirmed the observations of Lang and Aunis (1951a,b). In experiments in which aqueous solutions of HNO_2 under hydrogen atmospheres were utilized, the decomposition of HNO_2 was found

to be first order. The rate of the reaction was observed to increase with both increasing agitation and solution acid concentration.

From experiments in a single-sieve plate NO_x absorption column, Andrews and Hanson (1961) developed rate equations which agreed closely with the measured NO_x absorption efficiency of their apparatus. For low gas-phase NO^* concentrations ($< 5 \times 10^{-4} \text{ kgmol m}^{-3}$) the kinetics of the nitrous acid decomposition were assumed to be controlling, and the rate was

$$r_{\text{HNO}_2} = -.75(k_{\text{La}})^{2/3} V^{1/3} [2k_7 \text{HNO}_2 (\text{HNO})^2 / K_1]^{1/3} (P_{\text{NO}_2})^{2/3} (P_{\text{NO}})^{2/3} \quad (38)$$

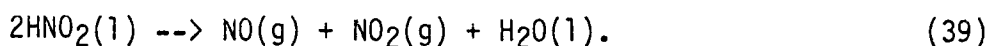
when the concentration of nitrogen oxide at the gas-liquid interface was neglected.

Schmid and Baehr (1965) investigated the formation of nitrous acid in solutions of HNO_3 up to 5 M. In their experiments with a stirred, vibrated reactor under NO atmospheres of 0.5 and 1 atm, they found no difference from the results of Abel and Schmid (1928a,b).

Safin, Mahotkin, and Galeev (1970) carried out HNO_2 decomposition experiments in both an agitated batch reactor and a film column. While the studies involving the film column produced no clear conclusions, experiments in the batch reactor were more definitive. Experiments in the unagitated batch vessel found a direct relationship between decomposition rate and surface area, and between the rate and the total liquid volume. Additional experiments in an agitated reactor found that HNO_2 continued to be depleted at increased partial pressures of NO

with no generation of HNO_3 which suggests the possibility of physical desorption of nitrous acid.

Kobayashi, Takezawa, Hara, Nikki, and Kitano (1976) studied the decomposition of nitrous acid from quiescent and agitated solutions under a nitrogen atmosphere. Though they found no correlation between the rate of decomposition and the volume of liquid present, a proportionality between the rate and the surface area was observed. The reaction was found to be first-order, and was expressed by the equation

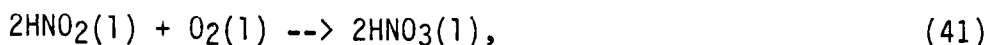


In an agitated solution the reaction rate was found to be 10 times that without agitation. Experiments with agitation also indicated that the reaction order dropped slightly (from 1.35 to 1.23) as the temperature increased from 273 to 295 K, and that the reaction rate increased slightly with increasing ionic strength. The reaction mechanism proposed as a result of the experiments agreed well with the mass transfer equation developed previously by Safkin, Mahotkin, and Galeev (1970) describing HNO_2 depletion:

$$\bar{R}_{\text{HNO}_2} = -k_L a (\text{CHNO}_2 - \text{CHNO}_2^*). \quad (40)$$

Experiments conducted by Mahotkin and Shamsutdinov (1976) found that both NO and NO_2 were generated by the depletion of HNO_2 , indicating that the desorption of HNO_2 is probable. This confirms the earlier results of Safin, Mahotkin, and Galeev (1970) obtained in unagitated batch reactor studies.

Pogrebnaya, Usov and Baranov (1976) studied the oxidation of aqueous nitrous acid in a stirred batch reactor over the pressure range 1 to 50 atm in solutions ranging in ionic strength from pH 2.9 to pH 4.0. The oxidation is expressed by the reaction



with a rate expression of the form

$$d\text{CHNO}_2/dt = -k'(\text{CHNO}_2)^2. \quad (42)$$

The effect of pH on the reaction rate is accounted for by expressing the HNO_2 concentration in terms of non-ionized nitrous acid:

$$\frac{d\text{CHNO}_2}{dt} = \frac{-K_{41}' \text{CH} + (\text{CHNO}_2)^2}{K_{44} \text{CH}}. \quad (43)$$

The equilibrium expression is



which has an equilibrium constant of $(7.31 \pm 0.1) \times 10^{-4} \text{ kgmol m}^{-3}$ at 298 K.

Komiyama and Inoue (1978) studied the depletion of HNO_2 from aqueous solutions in a bubbling contactor and a stirred, flat-surface contactor. Experiments were conducted at 288 and 298 K in a helium atmosphere at ambient pressure. Results from experiments with the bubbling contactor predicted the following rate equation:

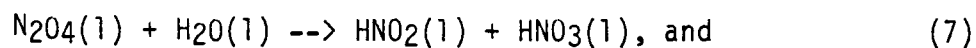
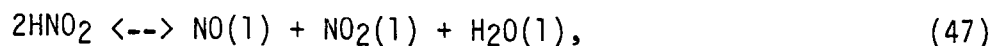
$$r_{\text{HNO}_2} = -k'(k_{\text{La}})^{2/3} (\text{CHNO}_2)^{4/3}. \quad (45)$$

In these studies the ratio between NO formed and HNO₂ depleted was found to be 2:3, agreeing with the proportions given in the overall nitrous acid equilibrium reaction (12).

Assuming the only appreciable desorption is that of nitrogen oxide, that the liquid-phase transport of NO is described by the expression

$$\bar{R}_{NO} = -k_L a(C_{NO} - C_{NO}^*), \quad (46)$$

that the equilibria

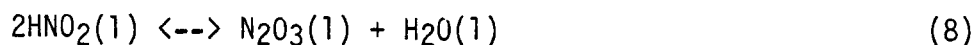


exist in the bulk liquid, and that steady state exists, the following rate expression was obtained:

$$r_{HNO_2} = (-1.5)^{2/3} [k_8 (K_{42})^2 (K_{43})^2]^{1/3} (k_L a)^{2/3} (C_{HNO_2})^{4/3}. \quad (50)$$

Ionization and Dehydration of HNO₂

The dehydration of HNO₂ as expressed by the equation



was studied by Turney and Wright (1958), and Bunton and Stedmon (1968). Turney (1958) determined the equilibrium constant at 298 K to be 9×10^{-3} , while Bunton (1968) developed the expression

$$K_{18r} = \frac{C_{N2O3}}{(C_{HNO2})^2} \quad (51)$$

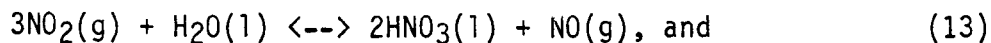
to describe the equilibrium relationship. Turney also determined the equilibrium constant of the HNO_2 ionization process



to be 7×10^{-5} at 298 K.

NO_x Scrubbing Studies

Early investigations into the scrubbing of nitrogen oxides with water and dilute nitric acid solutions were directed toward determining methods to increase the efficiency of the process. The data were most frequently used to empirically design plate columns. Theoretical design of NO_x scrubbers was based on the equilibrium reaction of NO_2 and H_2O , and on the kinetics of the oxidation of NO , given by the expressions:



According to Counce (1980) commonly used commercial NO_x scrubbers are equipped with water-cooled, bubble-cap plates, and produce nitric acid in the 58 to 70% (by weight) range. To a great extent, the design of NO_x scrubbing columns has been based on the extrapolation of empirical data from existing equipment.

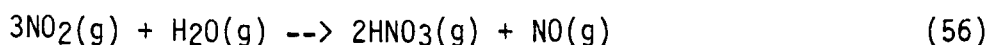
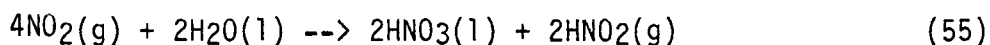
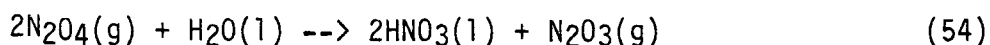
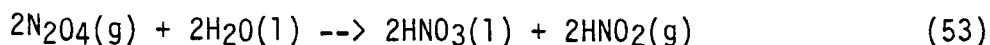
Since the mid 1950's a greater effort has been made to describe the scrubbing process theoretically. The most promising route toward development of a theoretical understanding of NO_x absorption appears to be through the use of the theory of gas absorption with chemical reaction as developed by Astarita (1967) and Danckwerts (1970).

Investigations by Fauser (1928), and by Taylor, Chilton, and Handforth (1931) studied the effects of temperature and pressure on the scrubbing process. Both studies consisted of experiments utilizing bubble-cap plate columns, and both indicated the absorption/reaction process was enhanced at lower system temperatures and higher pressures.

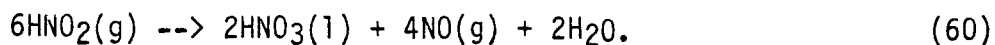
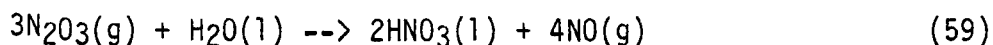
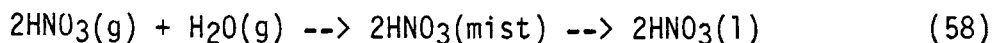
Peters, Ross, and Klein (1955) studied absorption of NO_2 in a single-plate, bubble-cap tray column. Experiments were performed with water and 2.6 M nitric acid, and with NO_2^* partial pressures up to 0.10 atmosphere. These experiments indicated that the removal of NO_2^* was proportional to the gas phase concentration of N_2O_4 . Though neither liquid flowrate nor acid concentration affected the efficiency of NO_2^* removal, increased gas-liquid contact time was found to increase the degree of NO_2^* depletion, as did increased water concentration in the vapor phase. These results led to the conclusion that the absorption reactions occurred at the gas-liquid interface.

In a three stage, bubble-cap column, Peters (1955) studied the absorption of NO_2^* into distilled water. The results of his experiments indicated an increase in NO_2^* removal efficiency as the gas moved upward in the column.

The absorption of NO_2^* from air- NO_2^* and air- NO_2^* - NO^* gas mixtures was studied by Andrews and Hanson (1961) using a column containing a single sieve tray. The predominant absorption mechanism from gases having NO_2^* partial pressures exceeding 0.01 atmosphere was found to be the absorption of N_2O_4 into the liquid phase, and its subsequent hydrolysis to HNO_3 and HNO_2 . Andrews and Hanson were also among the first to attempt to use available information on reaction and diffusion rates and equilibrium data to calculate the conversion of NO_2^* . The mechanisms proposed by Andrews and Hanson result from the combination of absorption and desorption mechanisms at steady state with the conversion of NO_x species into HNO_2 and HNO_3 . The total process described by Andrews and Hanson is given by the expressions:



followed by:



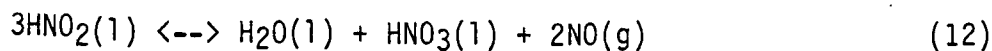
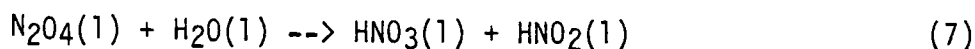
Hoftyzer and Kwanten (1972) combined the mechanism proposed by Andrews and Hanson with the stipulation that one-third mole of NO^* is desorbed for every mole of NO_2^* absorbed. The resulting model described the scrubbing process fairly accurately in a high pressure absorption system.

Bowman, Kulczak, and Shulman (1974) performed absorption studies in which an air stream containing a low level of NO_2^* was scrubbed with water in a packed column. Experiments were conducted at various superficial gas velocities, NO_2 concentration levels, and operating temperatures. The amount of NO_x absorbed and converted to acid was found to increase with decreasing temperature and gas velocity and increasing NO_2 concentration.

Karavaev and Visloguzova (1974) investigated the absorption of NO_2^* into relatively strong nitric acid solutions (15.9 to 18.6 M) in a packed, laboratory-scale column. The experiments used gas feed streams with partial pressures of NO_2^* ranging from 0.10 to 0.50 atmosphere in nitrogen, with the total system pressure assumed to be one atmosphere. Column operating temperatures were varied from 268 to 283 K. The results of this study indicated a linear decrease in NO_2^* absorption with decreasing NO_2^* concentration in the feed gas, and with increasing scrubber temperature. An increase in NO_2^* absorption with increased gas residence time and liquid load was also found. The absorption rate coefficients decreased with increasing gas-phase NO_2^* concentration and temperature, increased with liquid loading, and were essentially unaffected by changes in gas residence time. Both the rate and extent

of absorption were shown to increase with increasing acid strength in the scrub solution.

Counce and Perona (1979a,b) investigated absorption of NO_x in a three stage, sieve-plate column by recirculating aqueous HNO_3 solutions ranging in concentration from 1.1 to 3.5 M. The effects of liquid flowrate, NO_2^* concentration in the gas, noncondensable gas flowrate (NO_2^* and air), and the condensable flowrate (steam) on absorption efficiency were investigated. Evaluations of these parameters were made for the system at steady-state. The extent of NO_x absorption increased with increases in liquid and steam flow rates, and also increased with decreases in noncondensable gas flowrate and acid molarity. NO_x conversion decreased in the presence of HNO_2 in the recirculating scrubbing solution. This effect was lessened by sparging the liquid exiting the scrubber prior to recirculation, which apparently volatilized nitrous acid from the liquid. Generally, the NO_x conversions were closely predicted by a model which includes consideration of the effect of aqueous HNO_2 on the absorption process. This model, presented by Counce, Groenier, Klein, and Perona (1978), and by Counce and Perona (1980), is based on the reactions:



The model was found to most accurately describe the process when steam was not present in the feed gas.

In a study of extended NO_x scrubbing, Bolme and Horton (1979) investigated absorption of nitrogen oxides in a multi-stage sieve plate column. Primary scrubbing of the gas stream took place in a 15-plate section utilizing nitric acid solutions ranging in concentration from 4.3 to 5.6 M. These experiments indicated that the concentration of HNO_3 affects the extent of NO_2^* absorption only slightly, while adding greatly to the stability of liquid-phase HNO_2 . Furthermore, the oxidation of nitrogen oxide was found to increase somewhat with an increase in HNO_3 vapor pressure over the scrub solution.

Koegler (1979) investigated the absorption of nitrogen oxides into water and dilute HNO_3 solutions in a column containing bubble-cap plates. Experiments were conducted to determine the impact of the following variables on the absorption process: gas flow rate, NO concentration in the gas phase, NO_2 concentration in the gas phase, O_2 concentration in the gas phase, recycle acid flowrate, water flowrate, and flowrate of cooling water to the recycle stream heat exchanger. Only three of these were found to affect overall NO_2 conversion at a 95% significance level. These were NO_2 concentration in the feed gas stream, total feed gas flowrate, and flowrate of the scrub solution to the top tray in the column. Increases in the first two variables resulted in decreased NO_x absorption, while increasing the scrub solution flowrate significantly improved NO_x removal efficiency. By performing a full-factorial series on these three variables and on scrub solution recycle temperature, Koegler developed the following

expression for the performance of his eight-stage column:

$$Y = -.1067 + .2174X_1 + 5.693 \times 10^{-3}X_3 + .6219 \log X_1 \\ + .02644X_1X_2 - .5769X_1X_4, \quad (62)$$

where Y = percent NO_2 in the off gas

X_1 = percent NO_2 in the feed gas

X_2 = total gas flow (SCFM)

X_3 = average column temperature ($^{\circ}\text{F}$)

X_4 = water feed to top of column (gpm).

In addition, the scrub solution flowrate and the recycle liquid temperature were found to have negative effects on the production of HNO_2 . The percent of NO_2 in the feed gas and, to a lesser extent, the total gas flowrate affected the production of HNO_2 positively.

With regard to HNO_2 , Koegler found that the presence of this component in the liquid significantly decreased the NO_x removal efficiency. This effect was lessened by adding hydrogen peroxide or sodium hydroxide to the scrubbing solution. These agents serve to stabilize or destroy liquid-phase nitrous acid before it can decompose to form NO_x .

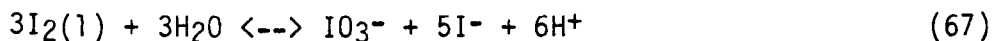
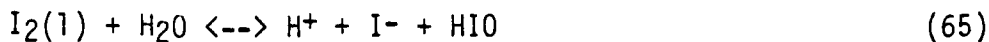
Counce and Perona (1983) investigated NO_x absorption from offgas streams with NO_x partial pressures from 0.01 to 0.10 atmosphere in experiments conducted at 298 K and atmospheric pressure. The results were compared with those predicted by the NO_x scrubbing model developed by Counce (1980). The experimental results agreed closely with the predicted values. NO_x removal efficiencies ranged from 55 to 97% for the various sets of conditions imposed in both the model and the

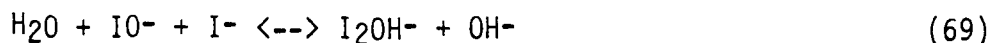
experiments. N_2O_4 was found to account to 99% of the predicted NO_x absorption from completely oxidized feed gas streams. For NO_x and NO_2 feedgas partial pressures of 0.010 and 0.002 atm respectively, Counce and Perona reported no indication of gas-phase formation or absorption of HNO_2 . This conflicts with HNO_2 gas-phase formation and absorption observed by Andrews and Hanson (1961) when a feed gas stream with a lower NO_x concentration was scrubbed with water.

Iodine Partitioning in Aqueous Solutions

Studies regarding the partitioning of iodine between the vapor phase and aqueous solutions have been performed. Additional data has been collected concerning the hydrolysis reactions of iodine. Essentially all the data available in this area has been the result of research performed under the auspices of governmental atomic energy agencies. This research was performed in order to develop an understanding of the behavior of iodine, so as to better contain fission product iodine.

Eggleton (1967) lists the following reactions and equilibria for iodine and its hydrolysis products:





According to Eggleton, reactions (67) through (70) occur appreciably only at higher pH values, and only reactions (63) through (66) rapidly reach equilibrium. This leads to use of the first four expressions and the relationship

$$[\text{HIO}] + [\text{H}_2\text{OI}^+] = [\text{I}^-] + [\text{I}_3^-] \quad (72)$$

to describe the iodine-water system.

Eggleton also addressed the volatilities of the iodine species under consideration. Bell and Gelles (1951) determined the partial pressure of gaseous I^- to be 1.6×10^{-32} atm. This partial pressure is equivalent to a partition coefficient of 1.4×10^{33} . A similarly calculated partition coefficient for H_2OI^+ is 3×10^{71} . In the absence of thermodynamic data, Eggleton assumed the partition coefficient of OI^- to lie between those of I^- and H_2OI^+ , based on molecular charge and size. Only an approximation from the work of Bell and Gelles (1951) is available for the volatility of the HIO specie. This calculation yielded a partition coefficient in the range 77 to 4300 (taking into account the range in Gibb's free energy measured by Bell and Gelles). For the purpose of developing partition coefficient calculations, Eggleton assumed the volatility of HIO to be negligible,

but limited the assumption to instances when the calculated iodine coefficient did not exceed $(10)^4$.

The partition coefficient was defined by Eggleton as

$$P = \frac{\text{mass of I}_2/\text{cm}^3 \text{ H}_2\text{O}}{\text{mass of I}_2/\text{cm}^3 \text{ gas}} = \frac{\text{moles I}_2/\text{liter H}_2\text{O}}{\text{moles I}_2/\text{liter gas}} \quad (73)$$

Under the previously stated assumptions that only reactions (63) through (66) are significant and that only the I_2 specie is volatile, the partition coefficient can be expressed by the equation

$$P = \frac{[\text{I}_2]_{\text{aq}} + .5([\text{HIO}] + [\text{H}_2\text{OI}^+] + [\text{I}^-] + 3[\text{I}_3^-])}{[\text{I}_2]_{\text{g}}} \quad (74)$$

By substitution using equations (64), (65), (66), and (72), the expression becomes:

$$P = \frac{[\text{I}_2]_{\text{aq}} + [1 + 2K_2[\text{I}_2]_{\text{aq}}[K_3/[\text{H}^+] + K_4] \cdot 5(1/[\text{I}_2]_{\text{aq}} + K_2)]^{-0.5}}{[\text{I}_2]_{\text{g}}} \quad (75)$$

Values for the equilibrium constants at 298 and 373 K are given in Table 2.

The values for the equilibrium constants at 298 K are consistent with those obtained by other experimenters, and would appear to be valid. Values given for the constants at 373 K are less reliable, as they result from the extrapolations of data at lower temperatures. The value of the equilibrium constant K_{66} at 373 K was determined by calculation from approximated thermodynamic data, as an experimentally

Table 2. Equilibrium Constants of Reactions (63) through (66)

Equilibrium Constant	Value at 298 K	Value at 373 K
K ₆₃	83 ^a	9.1 ^a
K ₆₄	768 ^b	305 ^c
K ₆₅	5.40 x 10 ^{-13d}	1.57 x 10 ^{-10e}
K ₆₆	1.2 x 10 ^{-11f}	3.9 x 10 ^{-11g}

^aCalculated by Eggleton from the data of Seidell (1940)

^bDavies and Gwynne (1952)

^cExtrapolated by Eggleton from the data of Davies and Gwynne (1952)

^dAllen and Keefer (1955)

^eExtrapolated by Eggleton from the data of Allen and Keefer (1955)

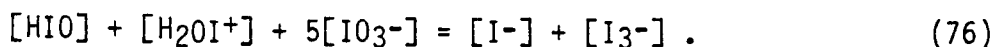
^fBell and Gelles (1951)

^gCalculated by Eggleton from thermodynamic data according to the method of Bell and Gelles (1951)

obtained value was found by Eggleton (1967) at only one temperature. The uncertainty regarding K_{66} is mitigated by the fact that it significantly affects the partition coefficient only at pH values lower than those of interest in this study. Eggleton calculated values of K_{63} from iodine vapor pressure and solubility data as an experimental value was available only at 293 K (Taylor, 1959). Eggleton reported good agreement between the experimental and calculated values at 293 K, and assumed that calculated values at 298 and 373 K were also reliable.

Eggleton noted an increase in the partition coefficient corresponding to decreasing liquid-phase iodine concentration and increasing pH. He attributed the increase in the coefficient to an increase in K_{65} with increasing temperature which more than compensated for a corresponding decrease in K_{63} at iodine concentrations less than .001 g/liter and at pH values greater than five.

In the development of a computer program for calculating the iodine partition coefficient, Parsly (1969) cited the findings of Eggleton that the formation of the iodate ion, IO_3^- , is relatively slow. A 10% conversion to iodate at 298 K requires ten years at pH 5, or 11 hours at pH 7. Parsly included consideration of iodate formation, as it occurs at a considerably faster rate (<4 seconds) at pH values of interest in his study (pH 9 to 9.5). Eggleton (1967) took iodate formation into account by including the equilibrium expression (67) in the development of the partition coefficient equation, and by also replacing equation (72) with the expression



In his calculations, Parsly relied primarily on the sources cited by Eggleton (1967) for equilibrium values. In order to perform the partition calculation over a range of temperatures, Parsly developed equations describing the equilibrium constants as functions of temperature. Values of K_{63} were calculated from iodine solubility data (Seidell, 1940) and iodine vapor pressure, according to the expression

$$K_{63} = [I_2]_{aq}/[I_2]_g, \quad (77)$$

assuming iodine behaves as an ideal gas. The equilibrium constant for reaction (64) was expressed by the relationship

$$K_{64} = \exp(-111.98 + 16.725 \ln T + 6952.3/T), \quad (78)$$

as reported by Davies and Gwynne (1952). Values of K_{65} were extrapolated by Parsly from the data of Allen and Keefer (1955) and are presented in Table 3. Parsly used the linear extrapolation

$$K_{66} = 1.2 \times 10^{-11} + 3.6 \times 10^{-13}(t - 25), \quad (79)$$

which he developed from the value of 1.2×10^{-11} reported by Eggleton (1967) at 298 K, and the value of 3.9×10^{-13} at 373 K taken from Bell and Gelles (1951). Parsly also developed the relationship

$$\log_{10} K_{67} = -48.42 + 0.17(t - 18) \quad (80)$$

for the equilibrium constant of reaction (67) from the values reported by Lundberg (1937) at 298 K (cited by Eggleton), and by Kolthoff and

Table 3. Values of K_{65} from 293 to 393 K*

Temperature (K)	K_{65}
293	3.4×10^{-13}
298	5.4×10^{-13}
303	8.4×10^{-13}
313	2.1×10^{-12}
323	4.8×10^{-12}
333	1.0×10^{-11}
343	2.2×10^{-11}
353	4.3×10^{-11}
363	8.4×10^{-11}
373	1.5×10^{-10}
378	2.1×10^{-10}
383	2.7×10^{-10}
393	4.8×10^{-10}

*Extrapolation by Parsly (1969) of data from Allen and Keefer (1955) using an Arrhenius plot.

Stenger (1947) at 291 and 333 K. In both of these expressions "t" represents temperature in degrees Celsius.

Cartan et al. (1968) have suggested that hypoiodous acid (HIO), an extremely weak acid having a dissociation constant of 4.5×10^{-13} g ion/liter at 293 K, exists as a volatile form of iodine. Experiments performed at Idaho Nuclear Corporation have confirmed the presence of HIO as a gas, however the magnitude of the liquid-vapor equilibrium constant has not been determined. Parsly assumed a value for this constant in order to examine the effect of volatile HIO on the partition coefficient. Parsly's calculations indicated a decrease in the partition coefficient resulting from the assumption that HIO exists in the vapor phase.

Morgan and Holland (1979) studied the removal of iodine from nitric acid solutions. Their studies were performed in 4 M HNO_3 with iodine concentrations ranging from 6×10^{-6} to 1×10^{-4} M. Iodine removal by steam stripping in a packed column, and by air sparging in a hold-up tank were evaluated.

In their experiments involving steam stripping, Morgan and Holland found that 96 to 98.5% of the inlet iodine was removed. Due to rapid volatilization by steam stripping, removal efficiency was independent of packing height. Changes in the iodine concentration in the feed stream and in the boil-up rate to the stripper also resulted in negligible changes to the iodine removal efficiency.

In experiments involving air sparging, 90% of the iodine in solution was volatilized within 30 minutes of sparging. Results from sparging at various temperatures indicated that the iodine removal rate

increased with increasing temperature, but that 95% iodine removal was achieved at temperatures as low as 323 K after two hours of sparging. Similarly, the rate of iodine removal was found to increase with increasing sparge air flowrate. However, the total amounts of iodine volatilized at the two different sparge rates studied (.11 and .22 scfm) were comparable.

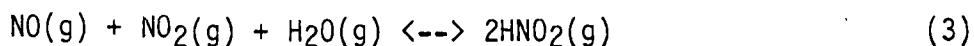
Experiments performed at different acid molarities found that iodine release rates were independent of H^+ concentration. However, the total fraction of iodine released after 3 hours of sparging was greater, and the amount of nonvolatile iodine remaining in solution was less, in lower molarity acid solutions.

Morgan and Holland (1979) noted the presence of nonvolatile iodine species in excess of the amount predicted by the model of Parsly. Nakamura et al. (1973) have identified nonvolatile organic iodine species (CH_3I , C_2H_3I , C_2H_5I , $n-C_3H_7I$, and $n-C_4H_9I$) which are formed by iodine in the presence of reagent grade nitric acid and distilled water. Kahn and Wahl (1953) hypothesized that a reactive iodine species such as HIO reacts in dilute aqueous solutions with impurities present as molecules or colloids. Two considerations were emphasized by Morgan and Holland which lessen concern over the unexplained formation of the small, nonvolatile iodine fraction in the reprocessing of nuclear fuel. First, radioactive acid solutions generated by the dissolution of the fuel pellets do not contain significant amounts of nonvolatile iodine compounds. Second, the nonvolatile iodine species in nonradioactive solutions can be almost completely volatilized by the addition of small quantities of hydrogen peroxide.

Literature Review Summary

The NO_x-H₂O-HNO₃ System

The species of interest in the scrubbing of nitrogen oxides are NO, NO₂, N₂O₃, N₂O₄, HNO₂, HNO₃, and H₂O. The reactions which describe the distribution-determining equilibria within the system are:



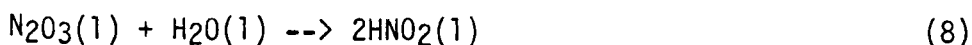
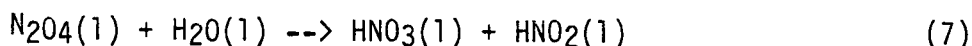
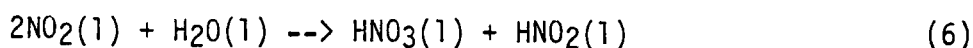
The absorption of NO_x from feed streams with larger NO_x partial pressures is enhanced by increasing the pressure or decreasing the temperature of the system, either of which favors the formation of N₂O₄. Absorption of NO_x from more dilute feed streams is improved by maximizing the partial pressure of N₂O₃. The gas phase relationship between NO₂^{*} and H₂O is not well understood. Some researchers have found that negligible gas-phase formation of HNO₂ occurs in systems having large NO_x concentrations (Counce and Perona, 1983, and Corriveau, 1971). Others have observed gas-phase HNO₂ formation in less concentrated NO_x streams (Andrews and Hanson, 1961). The gas-phase formation of nitric acid is not favored thermodynamically.

Gaseous nitrogen oxide is unstable at common scrubber temperatures and pressures when oxygen is present, and is essentially completely oxidized to NO₂ if sufficient O₂ is available. Maintaining low NO_x

scrubber temperatures is important not only to increase the solubility of the reactive species, but also because the NO oxidation reaction (which produces the more reactive NO₂ specie) has a negative temperature dependence.

The solubilities of the NO_x species, as expressed by Henry's Law constants, vary over several orders of magnitude. However, the solubilities of the species are not significant due to the rapid rate at which the hydrolysis reactions of N₂O₃ and N₂O₄ occur.

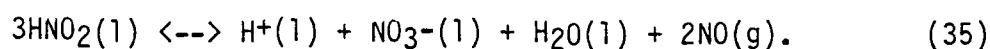
The liquid-phase reactions:



are treated as irreversible, due to the relatively low solution concentrations of nitrous and nitric acids within the scrubbing system. Furthermore, the hydrolysis of NO₂ is considered to occur in the bulk liquid due to its slow reaction rate, allowing the hydrolysis rate to be described by the rate of absorption of NO₂ into the liquid phase. Due to the rapidity of the hydrolysis reactions of N₂O₃ and N₂O₄, the behavior of these species in the scrubbing process is described by Danckwerts' (1970) film theory for absorption with chemical reaction:

$$\bar{R}_i = (\sqrt{Dk}/H_i) P_i^* \quad (81)$$

The absorption and reactions of the various NO_x species result in the liquid-phase formation of HNO_3 which is relatively stable and HNO_2 , which is unstable. Confusion concerning the depletion of nitrous acid in the liquid has hampered the efforts to understand the NO_x scrubbing process. The most definitive work on the depletion of HNO_2 was that of Abel and Schmid (1928a,b), in which they described the depletion process by the expression



With this expression, Abel and Schmid (1928b) assert that the rate of dissociation of HNO_2 is limited by the desorption of NO from the liquid phase. For this reason, the depletion of HNO_2 can be expressed as a function of NO transfer as indicated in the equation

$$r_{\text{HNO}_2} = -(3/2)k_L a [\text{CNO} - (\text{CNO})^*]. \quad (82)$$

The stoichiometry given by the expression of Abel and Schmid specifies molar ratios of HNO_3 and NO generated to HNO_2 decomposed of 1/3 and 2/3, respectively. Good agreement exists between these ratios and those reported by other researchers. However, the depletion ratios can be increased significantly as a result of sparging or agitating the HNO_2 -containing solution, perhaps because of desorption of species other than nitrous acid.

Lang and Aunis (1951b), in their investigation of the effect of oxygen on nitrous acid depletion, found that the depletion rate was unaffected by air sparging, but was greatly increased by a pure O_2 sparge. They also determined that liquid-phase oxidation of HNO_2 is

negligible in environments where the oxygen concentration is the same as in air.

NO_x Scrubbing

The earliest efforts in describing the scrubbing of nitrogen oxides were limited to the acquisition of data for the empirical design of scrubbing systems. With the advent of film theory, a more theoretical approach to understanding the problem became available. Subsequent theoretical developments and the mechanisms found as a result of experimental investigations indicate that the scrubbing of NO_x in packed columns should be quite efficient.

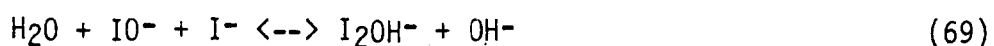
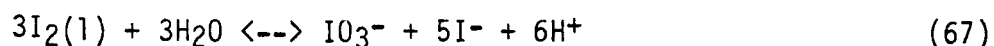
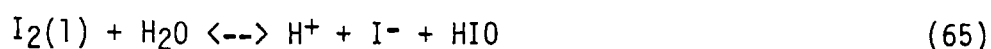
The question concerning the ability of the aqueous scrubbing solution to retain a significant concentration of HNO₂ is still unresolved. Studies by Mahotkin and Shamsutdinov (1976), Counce and Perona (1979a), and Koegler (1979) have shown that a capacity to retain nitrous acid in the scrubber solution exists. Counce and Perona (1980) have developed a model for NO_x scrubbing that describes the effect of the presence of HNO₂ on the scrubbing process. This model indicates that a loss in NO_x scrubbing efficiency results from the accumulation of HNO₂ in the scrubbing liquid.

Iodine Partitioning

Due to its lack of importance from a commercial viewpoint, the relationship of iodine and its hydrolysis products have not been as thoroughly studied, and are not as well understood as the NO_x scrubbing process. Eggleton (1967) has done the most complete work regarding the partitioning of iodine and its hydrolysis products between the liquid

and vapor phases. This work has been used by Parsly (1969) in the development of a computer program which calculates partition coefficient values as a function of temperature and solution pH.

The reactions and equilibria describing the iodine-water system are:



in which the iodine species of interest are I^- , I_3^- , I_2 , H_2OI^+ , HIO , IO^- , IO_3^- , IO_4^- , I_2OH^- , and I_2O^{2-} . Whereas reactions (67) through (70) occur appreciably only at higher pH values, the processes described by equations (63) through (67) rapidly equilibrate. Eggleton determined the volatilities of the species I^- , H_2OI^+ , and IO^- to be negligible. Defining the partition coefficient by the expression:

$$P = \frac{\text{mass of I}_2/\text{cm}^3 \text{ H}_2\text{O}}{\text{mass of I}_2/\text{cm}^3 \text{ gas}} = \frac{\text{moles of I}_2/\text{liter H}_2\text{O}}{\text{moles of I}_2/\text{liter gas}} \quad (73)$$

and assuming I_2 to be the only volatile iodine specie, Eggleton developed an expression for the partition coefficient as a function of $[\text{I}_2]_{\text{aq}}$, $[\text{H}^+]$, and the equilibrium constants of the first four expressions, K_{63} , K_{64} , K_{65} , and K_{66} , combined with the relationship

$$[\text{HIO}] + [\text{H}_2\text{OI}^+] = [\text{I}^-] + [\text{I}_3^-] . \quad (72)$$

Eggleton assumed the HIO specie to be nonvolatile. However, work by Carten et al. (1968) suggests that this specie can exist as a volatile iodine constituent. Parsly studied the effect of HIO volatility on partitioning by assuming a value for the gas/liquid equilibrium constant. The resulting calculations indicated that the partition coefficient decreases in the presence of gaseous HIO .

In general, an increase in partition coefficient with decreasing iodine concentration in the liquid and increasing solution pH was noted. This increase is due in part to a shift to the right in equilibrium relationship (65) which overcompensates for a corresponding shift to the left in equilibrium relationship (63). Eggleton found that the reaction producing the iodate ion is extremely slow in acidic solutions, requiring ten years to achieve a 10% conversion to IO_3^- in solutions having a pH value of 5. Parsly (1969) included this reaction in his model in order to calculate partition coefficients in solutions of pH 9, in which a similar conversion occurs in a matter of seconds.

Morgan and Holland (1979) have studied removal of iodine from aqueous HNO_3 solutions by sparging with air and by steam stripping. Removal by sparging was found to be enhanced at increased solution temperatures and sparge rates. However, 95% of the iodine originally in solution was removed after two hours of sparging at temperatures as low as 323 K. Similarly, though the initial rate of iodine volatilization increased with increasing sparge rate, the total quantities removed by sparging at .11 and .22 scfm were comparable after sparge periods of a few minutes or more.

Formation of a small quantity of nonvolatile iodine species has been observed by several researchers. Among these nonvolatile iodine compounds are CH_3I , $\text{C}_2\text{H}_3\text{I}$, $\text{C}_2\text{H}_5\text{I}$, $n\text{-C}_3\text{H}_7\text{I}$, and $n\text{-C}_4\text{H}_9\text{I}$. However, Morgan and Holland state that the radioactive solutions resulting from the dissolution of spent nuclear fuel do not contain significant levels of nonvolatile iodine species.

3.0 THEORETICAL DEVELOPMENT

The model for determining iodine partitioning in the NO_x scrubbing system was developed in two segments. The first segment deals only with the scrubbing of NO_x and the subsequent concentration of the nitric and nitrous acids produced. In this portion of the simulation, stream flowrates and compositions were determined for later use in iodine partitioning calculations.

The use of a recycle stream for NO_x scrubbing necessitated the use of an iterative program into which an offgas stream (from the dissolver) of known flowrate and composition, and a recycled scrubbing stream of fixed flowrate and assumed composition were input. Other known inputs to the system were the air sparge rate to the scrubber bottoms tank, the steam flowrate to the acid concentrator, the overflow rate from the scrubber tank, the acid concentrator overflow rate, and the rate of air flow to the concentrated acid airlift. Temperatures and pressures, based on those specified for the IET system, were set to the values shown in Figure 3.

Based on the assumptions of low HNO_3 and HNO_2 concentrations in the liquid, the instability of HNO_2 in the gas phase, and the low partial pressure of nitric acid over the assumed range of concentrations, the scrubber bottoms tank offgas rate and composition were determined by assuming the sparge air was saturated with water at the specified bottoms tank temperature and pressure. This assumption was justified with preliminary computer runs in which nitrogen, oxygen, and nitrogen oxides sparged from the scrubber bottoms liquid were included. By material balance calculations with the known bottoms

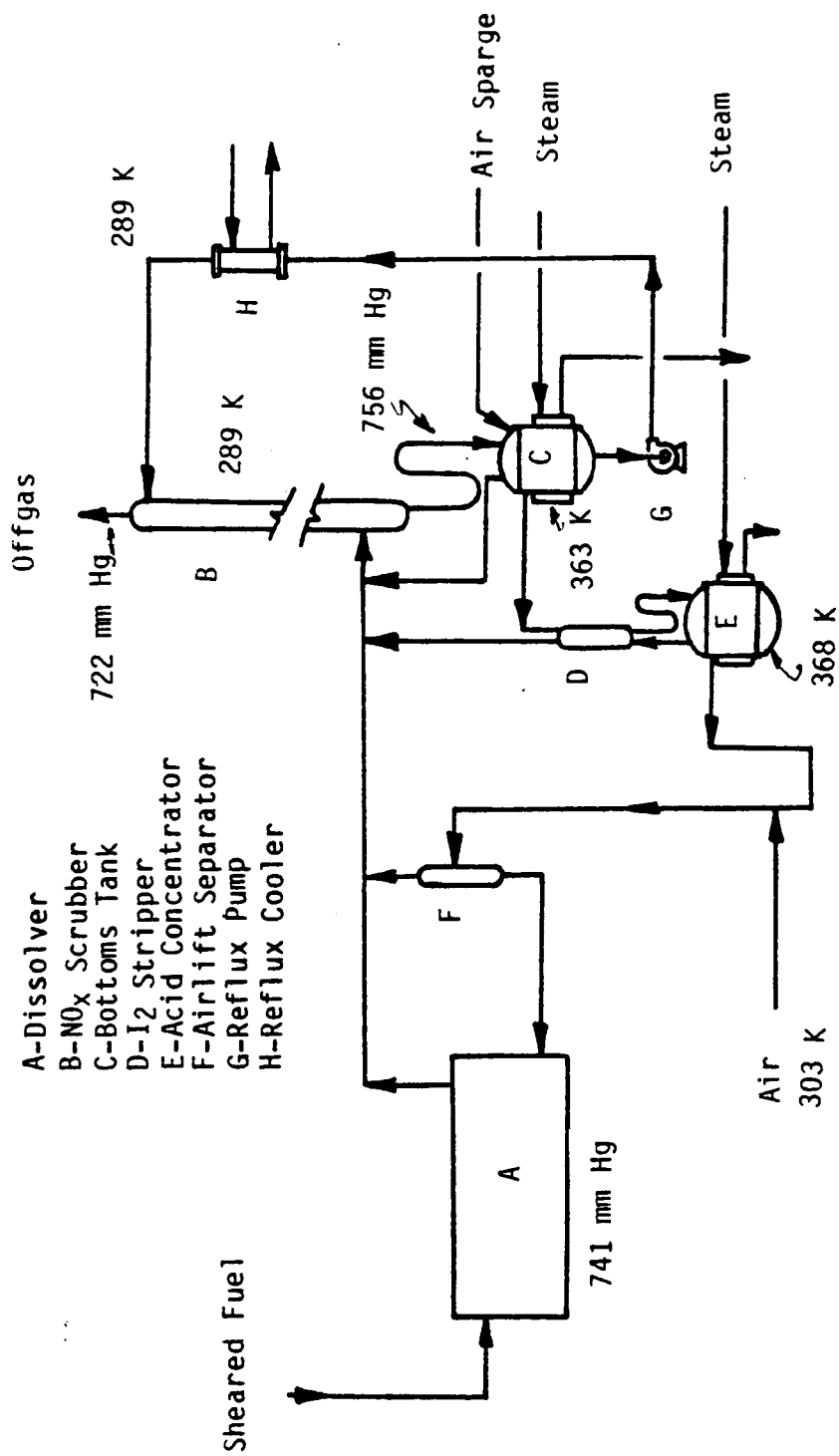


Figure 3. Dissolver Offgas System Operating Temperatures and Pressures.

tank offgas, scrubber reflux, and bottoms tank overflow rates and compositions, the liquid flowrate from the scrubber was determined.

The concentration of the acid leaving the acid concentrator was set to an assumed value. An enthalpy balance was used to determine the boil-up rate from the concentrator to the steam stripper. This calculation uses the expression:

$$H_v = 528.8026 \exp(-1.5338 X_{\text{HNO}_3}) \quad (83)$$

for determining the heat of vaporization of nitric acid solutions as a function of HNO_3 mole fraction. Due to the lack of data on the behavior of nitrous acid, its presence in the acid concentrator has been ignored. While this is a shortcoming in the NO_x portion of the simulation, the small concentration of HNO_2 likely to be present in the iodine stripper offgas should not significantly affect the iodine distribution determination. Having characterized the acid concentrator tank boil-up, the liquid stream from the iodine stripper to the acid concentrator was calculated by material balance.

Concentration of the acid solution in the iodine stripper was calculated on an incremental basis with a design procedure based on single-phase coefficients, as presented by Sherwood, Pigford, and Wilke (1975). Mass transfer coefficients and the wetted surface area value required for this calculation were determined from the models for " k_L ", " k_G ", and " a " developed by Onda, Takuchi, and Okumoto (1968). Iodine stripper calculations were performed iteratively until the calculated offgas concentration from the stripper was in agreement with the value obtained from an overall material balance using the assumed overflow

acid concentration. Preliminary runs with this calculation indicated that the vapor stream produced by the stripping of the bottoms solution was essentially pure steam. As a result, all subsequent runs were made with the HNO_3 concentration in the steam stripper offgas set at zero, and the steam stripping calculation was omitted.

The acid concentrator overflow is recycled to the rotary dissolver by an airlift which terminates in a de-entrainment vessel. Offgas separated from the airlift is recycled to the NO_x scrubber. Assuming efficient removal of entrained liquid from the vapor, the de-entrainment vessel offgas was characterized assuming that all air injected in the airlifting process remains in the vapor phase, and that water and acid at vapor pressures corresponding to the airlift temperature are also present in the offgas. The airlift temperature was calculated by an enthalpy balance involving the airlift air and the concentrator overflow stream.

Of primary interest in this study was a comparison of two flowsheets--one in which the iodine stripper offgas stream is recycled to the NO_x scrubber and one in which this stream is not recycled. In both cases the offgas streams from the scrubber bottoms tank and the airlift separator tank are added to the dissolver offgas stream to form the feed gas to the NO_x scrubber. In the case with recycle of the I_2 stripper offgas, this stream is also added to the scrubber feed gas stream. An additional case was simulated in order to study the effect of air sparging on NO_x removal efficiency and iodine partitioning. In this flowsheet, the iodine stripper offgas was recycled and the sparge

of the scrubber bottoms was deleted from the system. The three flowsheet cases simulated are shown in Figure 4.

The scrubber offgas feed stream is introduced into the NO_x scrubber which is operated isothermally at approximately 289 K. As the feed stream contains significant levels of acid and water vapors at an elevated temperature (368 K), a calculation is performed to determine the liquid/vapor split resulting from the partial condensing of the feed gas at the scrubber inlet. The assumption was made that the feed gas rapidly reaches the scrubbing column temperature at the bottom of the column due to the relatively high L-to-V ratio in the column--an assumption which was justified with operating data collected from the IET scrubbing system. The calculation of liquid and vapor constituents resulting from the partial condensing of the feed gas stream was based on equilibrium between the liquid and vapor from the feed gas. This assumption was derived from the brief residence time in the bottom of the column which prevents equilibrium from being achieved between the feed gas and the liquid exiting the column.

Having characterized the inlet vapor (the feed gas remaining in the vapor after partial condensing) and the liquid leaving the column (the liquid feed to the bottoms tank minus the liquid contribution from the condensed feed gas), an incremental calculation of mass transfer due to absorption/desorption and reaction was initiated.

The determination of NO_x conversion to nitric and nitrous acids was based on a simulation of NO_x scrubbing in packed columns developed by Counce (1980). This program performs calculations on an incremental column volume such that partial pressure and concentration gradients

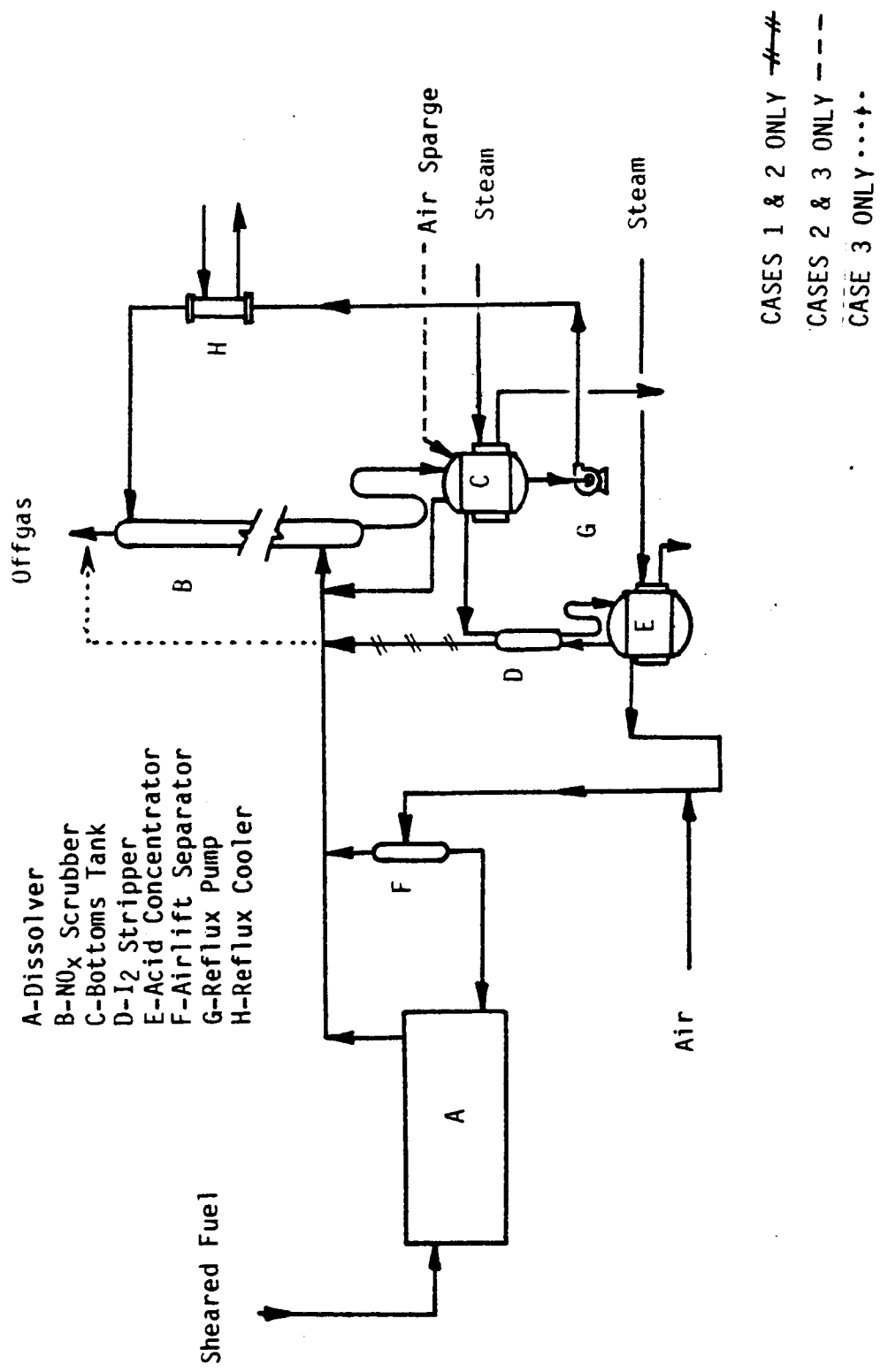


Figure 4. Dissolver Offgas System Alternative Flow Paths.

for the components within the increment can be neglected. Throughout the column the gas phase, which consists primarily of nitrogen oxides, nitrogen and oxygen, was assumed to be ideal. However, in the acid concentrator and the bottoms tank, experimentally obtained values for the partial pressures of HNO_3 and H_2O over nitric acid solutions were used (Perry 1975) due to the nonideality of this system. In the procedure utilized in this study, the column was "solved" from the bottom upward. An iterative process was used in which the scrubber recycle stream composition was adjusted until the calculated concentration was in agreement with the assumed values.

In this study, the species of interest in the gas phase were NO , NO_2 , N_2O_3 , and N_2O_4 . Consideration of HNO_2 in the gas phase was deleted from this model (a departure from the simulation by Counce, 1980) based on a study by Counce and Perona (1983) in which no evidence of gas-phase HNO_2 formation was indicated during scrubbing of nitrogen oxides at concentration levels of interest in this study. In this simulation as in the Counce (1980) model, the partial pressures of the gas-phase components were described in terms of "chemical" nitrogen oxide (NO^*) and nitrogen dioxide (NO_2^*) according to the equations:

$$P_{\text{NO}_2^*} = P_{\text{NO}_2} + 2P_{\text{N}_2\text{O}_4} + P_{\text{N}_2\text{O}_3} \quad (84)$$

$$P_{\text{NO}^*} = P_{\text{NO}} + P_{\text{N}_2\text{O}_3} \quad (85)$$

These equations can be further simplified by incorporating the equilibrium relationships:

$$P_{\text{N}_2\text{O}_4} = K_1 P_{\text{NO}_2}^2 \quad (86)$$

$$P_{N2O3} = K_2 P_{NO} P_{NO2} \quad (87)$$

which have been assumed to apply throughout the gas phase.

In the Counce model, the $HN O_2$ partial pressure term was included in the preceding expressions. Due to the assumed absence of $HN O_2$ in the gas phase this term has been omitted.

From Counce, the gas-phase performance equations for absorption/desorption of a chemical specie within a column increment are of the form

$$\text{input} = \text{output} \pm \frac{\text{disappearance or appearance due to gas-phase rxn}}{\text{disappearance or appearance due to gas-phase rxn.}} \quad (88)$$

The convention used throughout has been that disappearance terms are positive; appearance terms are negative.

On an incremental basis the molar flowrates of NO and NO_2 were corrected for the oxidation of the former to the latter by the factor $\pm G P_{NO} X_{NO}/(RT)$, where X_{NO} is the fraction of NO converted to NO_2 . The molar flowrate of oxygen was corrected for the oxygen consumed in the conversion process.

Counce (1980) described the appearance and/or disappearance of NO_2^* and NO^* by defining an absorptive flux for each component in terms of driving force (partial pressure or molar concentration gradients) and mass transfer coefficient (gas- or enhanced liquid-phase coefficient). For the i th specie,

$$\bar{R}_i = k_{G,i}(P_i - P_i^*) = (Ek_L)_i(C_i^* - C_i), \quad (89)$$

therefore, desorption is inverse absorption. Counce assumed the

enhancement factor for the desorption of NO to be equal to one. The fluxes of NO₂* and NO* are given by the expressions:

$$\bar{R}_{NO_2^*} = \bar{R}_{NO_2} + 2\bar{R}_{N_2O_4} + \bar{R}_{N_2O_3} \quad (90)$$

$$\bar{R}_{NO^*} = \bar{R}_{N_2O_3} + \bar{R}_{NO} \quad (91)$$

Insertion of the flux relationships into the gas-phase performance expressions given results in the equations:

$$\frac{G(P_{NO_2^*})_{in}}{RT} = (\bar{R}_{NO_2} + 2\bar{R}_{N_2O_4} + \bar{R}_{N_2O_3})a V + \frac{G(P_{NO_2^*})_{out}}{RT} - \frac{G P_{NO} X_{NO}}{RT} \quad (92)$$

$$\frac{G(P_{NO^*})_{out}}{RT} = (\bar{R}_{N_2O_3} + \bar{R}_{NO})a V + \frac{G(P_{NO^*})_{out}}{RT} + \frac{G(P_{NO})X_{NO}}{RT} \quad (93)$$

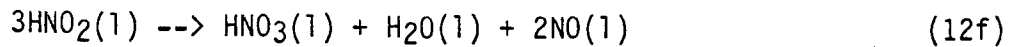
From these expressions, the partial pressures of NO* and NO₂* were determined, from which the partial pressures of the individual constituents were calculated.

The absorption reactions in the NO_x scrubber produce both nitric and nitrous acids. Counce (1980) states that while nitric acid has a relatively low vapor pressure at ambient conditions and is stable in aqueous solutions, nitrous acid has a significantly higher vapor pressure and is unstable at ambient conditions. Liquid-phase performance equations for these components in an incremental volume in which the absorption/desorption/reaction processes are occurring are:

$$\begin{aligned} \text{input HNO}_3 = \text{output HNO}_3 & - \text{production from absorption/} \\ & \text{reaction of NO}_x \text{ species} \quad (94) \\ & - \text{production from liquid-phase} \\ & \text{HNO}_2 \text{ decomposition} \end{aligned}$$

$$\begin{aligned} \text{input HNO}_2 = \text{output HNO}_2 & - \text{production from absorption/} \\ & \text{reaction of NO}_x \text{ species} \quad (95) \\ & + \text{depletion due to decomposition} \\ & \text{and desorption.} \end{aligned}$$

In this thesis and in the work by Counce (1980), the equilibrium



was assumed to apply. The concentration of NO in the liquid has been calculated using Henry's Law, $C_{\text{NO}} = P_{\text{NO}}/H_{\text{NO}}$. The absorption of NO from the bulk gas was neglected in this instance due to its low solubility. Therefore, the production of nitric acid due to the decomposition of HNO₂ is given by $1/2k_{L,\text{NO}}(C_{\text{NO}} - C_{\text{NO}}^*)$, and the depletion of nitrous acid by $3/2k_{L,\text{NO}}(C_{\text{NO}} - C_{\text{NO}}^*)$.

Combining these expressions with the flux equations for the absorbing/desorbing/reacting species yields the liquid-phase performance equations:

$$(C_{\text{HNO}_3})_{\text{in}} = (C_{\text{HNO}_3})_{\text{out}} - (.5\bar{R}_{\text{NO}_2} + \bar{R}_{\text{N}_2\text{O}_4} - .5\bar{R}_{\text{NO}})(a\Delta V/L) \quad (96)$$

$$(C_{\text{HNO}_2})_{\text{in}} = (C_{\text{HNO}_2})_{\text{out}} - (.5\bar{R}_{\text{NO}_2} + \bar{R}_{\text{N}_2\text{O}_4} + 2\bar{R}_{\text{NO}_2} + 1.5\bar{R}_{\text{NO}})(a\Delta V/L). \quad (97)$$

It should be noted that the expression for nitrous acid does not allow for the absorption of HNO₂ from the gas phase, based on the absence of HNO₂ in the gas phase as reported by Counce and Perona (1983).

After determining the flowrates and stream compositions throughout the scrubbing system, the iodine concentrations were determined. As a starting point, the amount of iodine expected to be volatilized during dissolution was input. Due to the small quantity of iodine in the offgas relative to the other constituents, the flowrates of vapor and liquid were assumed to be unaffected by the contribution of iodine.

The amount of iodine entering the scrubber in the gas phase was determined by calculating the partitioning between the portion of the feed gas condensed in the column and the fraction remaining as vapor.

Of the iodine entering the scrubber bottoms tank from the condensed feed gas, the fraction volatilized by air sparging of this vessel has been assumed to be 90%. This value was based on the work of Morgan and Holland (1979), who found that only 10% of the initial charge of iodine to an air-sparged tank remained in the liquid after 30 minutes, even when solution temperatures were as low as 323 K.

A fraction of the iodine in the scrubber bottoms is recycled to the system in the scrubber reflux stream. This stream is cooled to the column operating temperature before re-entering the scrubber. The remainder of the liquid-phase iodine from the scrubber bottoms overflows from the bottoms tank to the top of a steam stripper (consisting of a one-foot section of packing in a column). The fraction of iodine volatilized in the steam stripper and its associated bottoms vessel (the acid concentrator) has been assumed to be 95%. This assumption was also based on the experimental findings of Morgan and Holland (1979) which indicated that in excess of 95% of iodine in solution was

volatilized in a steam stripper consisting of one foot of packing, which was equipped with a reboiler.

The iodine quantities volatilized in the scrubber bottoms tank and the steam stripper were added to the amount fed from the dissolver. The liquid-vapor iodine split at the bottom of the column was then recalculated.

Calculations of iodine partitioning within the NO_x scrubbing column have been based on the assumption that each half-foot of packing represents one equilibrium stage. This assumption was taken from Perry (1950) as cited by Morgan and Holland, that this height of packing constitutes a height equivalent to a theoretical plate (HETP) for many systems. This assumption is supported by the results of Morgan and Holland that indicated volatilization of 91% of the iodine in a single equilibrium stage (the reboiler), in comparison to the expected removal of 95% as predicted by a McCabe-Thiele calculation for one stage.

The stagewise iodine partitioning calculations, performed at one-half foot intervals going upward through the column, are corrected for the change in scrubber liquid H^+ concentration resulting from the production of HNO_3 and HNO_2 in the NO_x scrubbing process. Calculations throughout the system are continued until the iodine concentration calculated for the scrubber bottoms solution is equivalent to that calculated for the reflux solution at the top of the column.

4.0 DISCUSSION OF RESULTS

NO_x Scrubbing

As previously stated, the computer simulation used in this study consists of two segments. In the first, the concentration levels of the species of interest in the NO_x-HNO_x-H₂O system were determined throughout an NO_x scrubbing system.

In order to simplify the calculations, the NO_x scrubbing simulation was separated from the iodine partitioning program, and was solved separately. This procedure was based on the assumption that no NO_x-HNO_x-iodine interactions occur. The effect of hydrogen ion concentration on the partitioning of iodine which is accounted for in the partitioning calculations. It should be noted that nitrous acid has been found to reduce the extent to which iodine hydrolysis occurs, thereby forcing the hydrolysis equilibria toward I₂(l). However, this interaction does not greatly affect the distribution of iodine as the quantities of iodine present as hydrolysis products is quite small (less than 0.1%) relative to that present as I₂(l).

The system was "solved" (i.e. steady state concentrations of the constituents were determined) for three different flowsheets (ref. Figure 4, p. 55). In the first case, the vapor effluent from the I₂ stripper was recycled to the scrubber with the feed gas. In the second case, the I₂ stripper offgas was recycled to the scrubbing system and the scrubber bottoms tank was sparged with air. In the third, the iodine stripper offgas bypassed the NO_x scrubber and the bottoms tank sparge was retained in the system.

NO_x removal efficiencies for the three simulated flowsheets are given in Tables 4, 5, and 6. Differences in NO_x removal efficiencies for the three system flowsheets were observed. In general, NO_x removal efficiencies ranged from 95 to 98%, with essentially 100% of some species removed in each case.

Removal efficiencies were greatest for the flowsheet in which the I₂ stripper offgas was recycled to the scrubber and the bottoms tank was unsparged. As shown in Table 4, the Case 1 removal efficiencies of N₂O₃ and N₂O₄ were quite high (95.28 and 99.55% respectively). The high efficiencies are due to the absence of NO_x dilution which would result from the addition of a sparge stream.

Though the scrubber solution concentrations were similar in Cases 1 and 2 (5% HNO₃, 4% HNO₂ versus 4.1% HNO₃, 3.9% HNO₂), the removal efficiencies in the sceond flowsheet were significantly lower for all constituents except N₂O₃ (ref. Table 5). The lower efficiencies are the result of NO_x dilution in the scrubber due to the addition of air to system as a sparge stream.

NO_x removal efficiencies in the Case 3 flowsheet (Table 6), were similar to those obtained for Case 2. This is despite significantly higher acid concentrations for this case (8% HNO₃, 6% HNO₂) than for the Case 2 flowsheet. As the difference between Cases 2 and 3 was the deletion of I₂ stripper offgas recycle in the latter, it is apparent that addition of the sparge stream was responsible for the drop in removal efficiencies seen from Case 1 to Case 2. This is to be expected, as the dilution of the NO_x species in the scrubber decreases

Table 4. NO_x Removal Efficiencies--Case 1 Flowsheet*

Specie	Inlet Partial Pressure (atm)	Outlet Partial Pressure (atm)	Percent Removed
NO	2.6485 x 10 ⁻²	1.8567 x 10 ⁻³	--
NO ₂	7.4425 x 10 ⁻²	5.0068 x 10 ⁻³	--
N ₂ O ₃	1.7310 x 10 ⁻³	8.1633 x 10 ⁻⁵	--
N ₂ O ₄	8.1421 x 10 ⁻²	3.6848 x 10 ⁻⁴	--
NO*	2.8216 x 10 ⁻²	1.8475 x 10 ⁻³	93.45
NO ₂ *	2.3900 x 10 ⁻¹	5.6197 x 10 ⁻³	97.65
NO _x	2.6722 x 10 ⁻¹	7.4672 x 10 ⁻³	97.21

*In the Case 1 flowsheet, the offgas from the iodine stripper is recycled to the NO_x scrubber and the scrubber bottoms tank is not sparged.

Table 5. NO_x Removal Efficiencies--Case 2 Flowsheet*

Specie	Inlet Partial Pressure (atm)	Outlet Partial Pressure (atm)	Percent Removed
NO	2.1013×10^{-2}	1.9705×10^{-3}	--
NO ₂	5.9047×10^{-2}	5.8192×10^{-3}	--
N ₂ O ₃	1.0895×10^{-3}	1.0069×10^{-5}	--
N ₂ O ₄	5.1249×10^{-2}	4.9776×10^{-4}	--
NO*	2.2102×10^{-2}	1.9639×10^{-3}	91.11
NO ₂ *	1.6263×10^{-1}	6.6754×10^{-3}	95.90
NO _x	1.8473×10^{-1}	8.6393×10^{-3}	95.32

*In the Case 2 flowsheet, the iodine stripper offgas is recycled to the NO_x scrubber, and the scrubber bottoms tank is air-sparged.

Table 6. NO_x Removal Efficiency--Case 3 Flowsheet*

Specie	Inlet Partial Pressure (atm)	Outlet Partial Pressure (atm)	Percent Removed
NO	2.1015×10^{-2}	1.9095×10^{-3}	--
NO ₂	5.9055×10^{-2}	5.6607×10^{-3}	--
N ₂ O ₃	1.0898×10^{-3}	9.4920×10^{-6}	--
N ₂ O ₄	5.1263×10^{-2}	4.7102×10^{-4}	--
NO*	2.2105×10^{-2}	1.9027×10^{-3}	91.39
NO ₂ *	1.6214×10^{-1}	6.4776×10^{-3}	96.00
NO _x	1.8425×10^{-1}	8.3803×10^{-3}	95.45

*In the Case 3 flowsheet, the iodine stripper offgas is not recycled to the NO_x scrubbing column, but the scrubber bottoms tank sparge is retained.

the driving force toward absorption and hydrolysis of these constituents.

Accumulation of HNO_2 in the scrubber liquid was indicated in all scrubbing system flowsheets. This finding is consistent with the observations of Andrews and Hanson (1961) and Koval and Peters (1960) that HNO_3 scrubbing solutions may retain significant levels of HNO_2 at steady state. Furthermore, the model developed by Counce (1980) also indicated the accumulation of HNO_2 in the scrubber liquid. The observed accumulation in this thesis is despite the assumption, based on the observations of Counce and Perona (1983), that HNO_2 is not present in significant quantities in the scrubbing column vapor. The absence of HNO_2 from the vapor results in an increased driving force favoring desorption of the acid from the liquid. Nonetheless, the rate of HNO_2 formation was found to far exceed the rate of decomposition.

Iodine Partitioning

In all three flowsheets some retention of iodine in the scrubbing liquid was found. In all cases the iodine retention level was on the order of 10^{-5} kmol/m³, and was below the liquid solubility limit. Iodine retention was greatest in the Case 1 flowsheet (I_2 stripper without bottoms tank sparging) with the iodine concentration in the scrubber reflux reaching 4.7994×10^{-5} kgmol/m³ at steady state.

Significantly lower iodine retention levels were found for Cases 2 and 3. The Case 3 flowsheet exhibited the lowest level of iodine retention, with a steady state reflux stream iodine concentration of 3.12×10^{-5} kgmol/m³. The decrease in retention between Cases 1 and

Cases 2 and 3 is due to the volatilization of iodine by sparging from the scrubber bottoms tank solution.

Though iodine retention was lower in the Case 3 simulation, the difference in liquid-phase iodine levels between this case and Case 2 was considerably less than that between Cases 1 and 2. This is most likely due to the reduced potential for iodine volatilization in the steam stripper, as it was downstream of the air sparge in simulations where both were present. The data of Morgan and Holland (1979) indicated that iodine volatilization by steam stripping was at least as effective as removal by air sparging.

Iodine concentrations throughout the three flowsheets are given in Tables 7,8, and 9.

Table 7. Iodine Partitioning Results--Case 1 Flowsheet*

Stream Description	Iodine Concentration (kgmol/m ³)
NO _x Scrubber Feedgas	9.9569 x 10 ⁻⁸
Scrubber Bottoms Tank Offgas	0
Reflux to Scrubber (Scrubber Bottoms Liquid)	4.7994 x 10 ⁻⁵
Column Liquid Effluent	4.8770 x 10 ⁻⁵
Iodine Stripper Vapor Effluent	7.2997 x 10 ⁻⁸
NO _x Scrubber Effluent Vapor	3.9996 x 10 ⁻⁷

*In the Case 1 flowsheet, the offgas from the iodine stripper is recycled to the NO_x scrubber and the scrubber bottoms tank is not sparged.

Table 8. Iodine Partitioning Results--Case 2 Flowsheet*

Stream Description	Iodine Concentration (kgmol/m ³)
NO _x Scrubber Feedgas	3.8339 x 10 ⁻⁶
Scrubber Bottoms Tank Offgas	2.0893 x 10 ⁻⁵
Reflux to Scrubber (Scrubber Bottoms Liquid)	3.6155 x 10 ⁻⁵
Column Liquid Effluent	3.0562 x 10 ⁻⁴
Iodine Stripper Vapor Effluent	5.3886 x 10 ⁻⁸
NO _x Scrubber Effluent Vapor	3.0130 x 10 ⁻⁷

*In the Case 2 flowsheet, the iodine stripper offgas is recycled to the NO_x scrubber, and the scrubber bottoms tank is air-sparged.

Table 9. Iodine Partitioning Results--Case 3 Flowsheet*

Stream Description	Iodine Concentration (kgmol/m ³)
NO _x Scrubber Feedgas	4.9811 x 10 ⁻⁶
Scrubber Bottoms Tank Offgas	1.9329 x 10 ⁻⁵
Reflux to Scrubber (Scrubber Bottoms Liquid)	3.1201 x 10 ⁻⁵
Column Liquid Effluent	2.8029 x 10 ⁻⁴
Iodine Stripper Vapor Effluent	4.9853 x 10 ⁻⁸
NO _x Scrubber Effluent Vapor	2.6001 x 10 ⁻⁷

*In the Case 3 flowsheet, the iodine stripper offgas is not recycled to the NO_x scrubbing column, but the scrubber bottoms tank sparge is retained.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The results from the NO_x simulation model are consistent with those obtained by Counce (1980), and appear to be valid. The NO_x removal efficiencies obtained were toward the high end of results reported by Counce (who observed removal efficiencies ranging from 55 to 97%). Indicated differences in acid concentrations throughout the three flowsheets investigated were consistent with the conditions established in each case.

The results of Counce suggested that retention of HNO_2 at a concentration level approaching that of HNO_3 could occur in scrubbing systems in which the scrubbing liquid was recycled. Such an accumulation was indicated in the simulations performed in this thesis. This is in spite of the assumption made in the proposed program that the amount of HNO_2 present within the column vapor is negligible. This assumption was based on observations made by Counce and Perona (1985) that HNO_2 was not present in the vapor in NO_x scrubbing systems with NO_x inlet concentrations exceeding .01 atmosphere. Nonetheless, the rate of nitrous acid formation in the liquid phase exceeded the rate of depletion due to desorption and/or decomposition.

Regarding iodine partitioning within the scrubbing system, sparging the scrubber bottoms tank reduces the iodine retained in the scrubber significantly. Iodine retention in the system is also decreased somewhat by not recycling the iodine stripper offgas to the scrubber. In the simulations performed, the effect of steam stripping was much smaller than that due to air sparging. This was due to the

arrangement of the process, in which air sparging always preceded steam stripping. This resulted in the potential for iodine volatilization in the steam stripper being much less, as the liquid-phase iodine concentration had already been lowered greatly by sparging.

Recommendations

Model Enhancement--Additional data is needed to develop a NO_x scrubbing model encompassing broader operating conditions. Specifically, Henry's Law constants and values for $(\sqrt{Dk}/H)\text{N}_2\text{O}_3$ at temperatures other than 298 K and over a range of acid concentrations are needed. Also, more studies are needed to better define the mechanisms of HNO_2 formation and depletion.

Data regarding the partitioning of iodine in packed columns needs to be obtained to verify both this study and to corroborate the results obtained by Eggleton (1967) and Parlsy (1969). In addition, further studies of iodine hydrolysis should be performed to better define the hydrolysis mechanisms.

Scrubbing System Improvements--Though detrimental to NO_x scrubbing, sparging of the scrubber bottoms solution should be retained to minimize iodine retention in the liquid phase throughout the DOG system. Recycle of the offgas from the iodine stripper to the NO_x scrubber should also be retained. Perhaps the most effective improvement to the DOG system would be the addition of hydrogen peroxide to the scrubber bottoms tank in order to volatilize iodine. Such an addition would also volatilize HNO_2 from solution, thereby increasing the NO_x removal efficiency of the scrubber.

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APPENDIXES

APPENDIX A

NO_x SCRUBBING SIMULATION

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REM  CREATE AN ARRAY FOR STORAGE OF THE HYDROGEN ION CONCENTRATION OVER
      EACH THEORETICAL STAGE
10    DIM #3,ISB(3,48)
REM  CREATE THE NECESSARY DATA ARRAYS
11    DIM XISB(8),YISOG(12),Y(12),X(12),PXISB(4),PYISOG(4),PYACBU(4)
12    DIM PXRFLX(4),XISOL(2),F(3),XEQ(3),YEQ(3),YALAF(2),YASPR(8),MW(12)
13    DIM C(12),RR(12),CIN(12),YBTBU(12),XOUT(12),YIN(12),STGC(2,24)
14    DIM VP(12),XRFLX(12),XBTF(12)
REM  COMPONENT 1 IS O2, 2 IS N2, 3 IS H2O, 4 IS HNO3, 5 IS NO2, 6 IS NO
REM  COMPONENT 7 IS N2O4, 8 IS N2O3, 9 IS NO2*, 10 IS NO*, 11 IS HNO2
REM  VARIABLES PRECEDED BY X ARE LIQUID-PHASE MOLE FRACTIONS, THOSE
REM  PRECEDED BY Y ARE VAPOR-PHASE MOLE FRACTIONS
35 - 41 DATA STEPS
65    READ TSBS,PSBS,XRFLX(3),XRFLX(4),RFLX,TACS, XACOF(3),XACOF(4)
66    READ MW(1),MW(2),MW(3),MW(4),MW(9),MW(10),MW(5),MW(6),MW(7),MW(8)
67    READ MW(11),ACSF5,HVSTS,ACOF5,FCTRF5,XRFLX(1),XRFLX(2),ALAF5,TALS
68    READ PDIS,DOGS,ASPRS,YDOG(1),YDOG(2),YDOG(3),YDOG(4),YDOG(5)
69    READ YDOG(6),MWAIR,VA(3),VAAIR,TCOL,YALAF(1),YALAF(2),YASPR(1)
70    READ YASPR(2),HTINC,H5,VA(5),VA(6),VA(7),VA(8),H6,H7,H8,H4,H11,K5
71    READ GASDENS,VCOLC,GC,VP(11),XRFLX(11),ELMNTS,TSLBS,HNO2DC
98    OPEN 'TABLE.DAT' FOR OUTPUT AS FILE #3,VIRTUAL
99    OPEN 'LP:' FOR OUTPUT AS FILE #2
100   T=TSBS//INCMT=0//P=PSBS//VDFCT=1//VSRDE=1
110   MBTBU=APSR5*MWAIR*2
115   MWBTBU=.5*MWAIR+.5*MW(3)
120   BTBU=MBTBU/MWBTBU
122   GOTO 140
123   YBTBU(3)=(.5/MW(3))*MWBTBU
125   YBTBU(1)=.79*(1-YBTBU(3))/YBTBU(2)=1-YBTBU(3)-YBTBU(1)
127   DCFCT=(HNO2DC*XRFLX(11)*RFLX/3+BTBU)/BTBU
129   BTBU=BTBU*DCFCT//SUMYBT=0
131   FOR I=1 TO 3
133     YBTBU(I)=YBTBU(I)/DCFCT
135     SUMYBT=SUMYBT+YBTBU(I)
137   NEXT I
138   YBTBU(6)=1-SUMYBT
140   SBOFS=TSBLS-RFLX//BTF=SBOFS+RFLS+BTBU-ASPRS
145   XBTF(3)=(XRFLX(3)*(RFLX+SBOFS)+YBTBU(3)*BTBU)
146   XBTF(3)=(XBTF(3)-(HNO2DC*XRFLX(11)*RFLX/3)/BTF
150   XBTF(4)=(XRFLX(4)*(RFLX+SBOFS)-(HNO2DC*XRFLX(11)*RFLX/3))/BTF
155   XBTF(11)=(XRFLX(11)*(RFLX+SBOFS)+(HNO2DC*XRFLX(11)*RFLX))/BTF
160   PRINT BTF,SBOFS,XRFLX(3),XBTF(3),XRFLX(4),XBTF(4),XRFLX(11)
161   PRINT XBTF(11)
165   T=TACS
170   GOSUB 2500
175   GOSUB 2800
176   PRINT YBTBU(4)

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REM GAP IN PROGRAM NUMBERS RESULTS FROM THE DELETION OF THE HN03-H2O
SEPARATION CALCULATION IN THE IODINE STRIPPER
REM CALCULATION OF AIRLIFT TEMPERATURE FROM ENTHALPH BALANCE
615 FOR I TO 2
620 PALAF(I)=ALAFS*YALAF(I)
625 NEXT I
630 T2=360//T1=TALS//T2=TACS
635 FOR I=3 TO 4
640 PACOF(I)=ACOFs*XACOF(I)
645 NEXT I
650 GOSUB 2710
655 CK=PALAF(1)*GCP(1)+PALAF(2)*GCP(2)-PACOF(3)*LCP(3)-PACOF(4)*LCP(4)
660 IF -.001<CK AND CK>.001 GOTO 685
665 IF CK<.001 THEN NT2=(T2+T3)/2//T1=T2
670 IF CK>.001 THEN NT2=(T1+T2)/2//T3=T2
675 T2=NT2// PRINT T2,CK
680 GOTO 650
685 T=T2
690 PRINT 'T=T2=';T
695 GOSUB 2500
700 FOR I=3 TO 4
705 YALOG(I)=XACOF(I)*VP(I)/PDIS
710 NEXT I
715 YALOG(1)=.79*(1-YALOG(3)-YALOG(4))
720 YALOG(2)=.21*(1-YALOG(3)-YALOG(4))
725 ALOGS=PALAF(1)/YALOG(1)
730 FOR I=3 TO 4
735 PALOG(I)=YALOG(I)*ALOGS
740 NEXT I
745 FGS=DOGS+ALOGS+BTBU+ISOGS
750 T=TSBS
755 GOSUB 2520
760 FOR I=1 TO 6
765 YFG(I)=YDOG(I)*DOGS+YALOG(I)*ALOGS+YBTBU(I)*BTBU+YISOG(I)*ISOGS
770 YFG(I)=YFG(I)/FGS
775 IF YFG(I)<0 THEN YFG(I)=0
780 NEXT I
785 T=TCOL//P=PSBS//PA=P/760
790 GOSUB 2500
792 VP(3)=11//VP(4)=0
795 LFG(1)=.001//LFG(3)=FGS
800 LFG(2)=(LFG(1)+LFG(3))/2
805 FOR J=1 TO 3
810 FOR I=3 TO 4
815 SXLFG(I)=(FGS*YFG(I))/(LFG(J)+(FGS-LFG(J))*VP(I)/P)
820 NEXT I
825 ADD(J)=1-SXLFG(3)-SXLFG(4)
830 IF ABS(ADD(J))<.001 THEN LFGS=LFG(J)//XLFG(3)=SXLFG(3)
//XLFG(4)=SXLFG(4)
835 NEXT J
840 IF LFGS>0 GOTO 855
845 IF ADD(1)*ADD(2)<0 THEN LFG(3)=LFG(2)// GOTO 800

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850 IF ADD(2)*ADD(3)<0 THEN LFG(1)=LFG(2)// GOTO 800
855 VINS=FGS-LFGS//LOUT=BTF-LFGS//GMOLS=VINS//LMOLS=LOUT
860 FOR I=1 TO 6
865 YIN(I)=(FGS*YFG(I)-LFGS*XLFG(I))/VINS//Y(I)=YIN(I)
870 XOUT(I)=(XBTF(I)*BTF-XLFG(I)*LFGS)/LOUT//X(I)=XOUT(I)
875 SIGYIN=YIN(I)+SIGYIN
880 NEXT I
885 XOUT(11)=(XBTF(11)*BTF)/LOUT//X(11)=XOUT(11)
890 FOR I=1 TO 6
895 YIN(I)=YIN(I)/SIGYIN//PP(I)=YIN(I)*PA//SIGPP=SIGPP+PP(I)
900 NEXT I
905 CORCT=(SIGPP+K1*PP(5)**2+K2*PP(5)*PP(6))/PA
910 FOR I=1 TO 6
915 PINA(I)=PP(I)/CORCT
920 NEXT I
925 PINA(7)=PINA(5)**2*K1//PINA(8)=K2*PINA(5)*PINA(6)
930 PARAE=78//PARDE=.0833//VSRDE=.5//GVISE=/1176E-04
935 SFTNE=.004866//SFTNS=71//DG(9)=.15091E-03//DG(10)=.19644E-03
940 DELV=VSRDE**2*3.14*HTINC//DELVS=DELV*.028317//VDFCT=.77
945 DK8=.00159//DK7=10**(-.52-760/T)
950 GOSUB 2550
955 GOSUB 2680
960 MLRDNS=(RHOLIQLMW)*1000//SIGYIN=0
965 FOR I=1 TO 11
970 C(I)=X(I)*MLRDNS
975 NEXT I
980 PINA(9)=PINA(5)+2*PINA(7)+PINA(8)//PINA(10)=PINA(6)+PINA(8)
985 FOR I=5 TO 8
990 GOSUB 2775
995 NEXT I
1000 FOR I=5 TO 10
1005 SCNOG=GVISE/(DG(I)*MW(I)*P/998.9/T)
1010 GOSUB 2600
1015 KGS(I)=KGCS
1020 NEXT I
1025 POUTA(5)=0
1027 GOSUB 2670
1030 GOSUB 2620
1035 PITT(1)=0//PITT(3)=1
1040 PITT(2)=(PITT(1)+PITT(3))/2
1045 FOR I=1 TO 3
1050 PNOIT(I)=KGS(10)*PINA(10)+KLCS*C(6)
1055 PNOIT(I)=PNOIT(I)/(KGS(10)*(1+K2*PITT(I))+DK8*K2*PITT(I)+KLCS/H6)
1060 WXMAS(I)=PITT(I)**2*(KGS(9)*2*K1+2*DK7*K1)-KLCS*C(5)
1065 WXMAS(I)=WXMAS(I)+PITT(I)*(KGS(9)+KGS(9)*K2*PNOIT(I)+KLCS/H5)
1070 WXMAS(I)=WXMAS(I)+PITT(I)*DK8*K1*PNOIT(I)-KLCS*C(5)-PINA(9)*KGS(9)
1075 IF ABS(WXMAS(I))<.1E-08 THEN PINT(5)=PITT(I)//PINT(6)=PNOIT(I)
1080 NEXT I
1085 IF ABS(WXMAS(I))<.1E-08 GOTO 1100
1090 IF WXMAS(1)*WXMAS(2)<0 THEN PITT(3)=PITT(2)//GOTO 1040
1095 IF WXMAS(2)*WXMAS(3)<0 THEN PITT(1)=PITT(2)//GOTO 1040
1100 PRINT WXMAS, PINT(5), PINT(6)

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1105 PINT(7)=K1*PINT(5)**2//PINT(8)=K2*PINT(5)*PINT(6)
1110 PINT(9)=PINT(5)+2*PINT(7)+PINT(8)//PINT(10)=PINT(6)+PINT(8)
1115 FOR I=5 TO 10
1120 IF PINT(I)<0 THEN DUMMO=1
1125 NEXT I
1130 IF DUMMO=1 THEN PRINT 'DUMMO'//END
1135 GVOLS=GMOLS/3600/GASDENS//LVOLS=LMOLS*LMW/3600/RHOLIQ/1000
1140 VV=GVOLS*3600//LV=LVOLS*3600
1150 BP=-PINT(6)/(2*PINT(2))
1155 OXNO=K5*PINA(6)*PINA(2)*DELVS*ELMNTS*VDFCT/GVOLS
1156 GOSUB 3005
1157 RCHK=-.67*.0192*((KLCS*WAREAS)**.67)*C(11)**1.33
1159 IF RR(6)>RCHK THEN RR(6)=RCHK
1160 GRR(9)=KLCS/H5*PINT(5)+2*DK7*PINT(7)+DK8*PINT(8)-.5*KLCS*C(11)
1165 GRR(10)=DK8*PINT(8)+KLCS/H6*PINT(6)-KLCS*C(6)-KLCS*.5*C(11)
1170 POUTA(9)=PINA(9)-GRR(9)*WAREAS*DELVS*ELMNTS*T*GC/GVOLS+PINA(6)
1171 POUTA(9)=POUTA(9)*OXNO
1175 POUTA(10)=PINA(10)-GRR(10)*WAREAS*DELVS*ELMNTS*T*GC/GVOLS-PINA(6)
1176 POUTA(10)=POUTA(10)*OXNO
1180 PNO2G(1)=0//PNO2G(3)+POUTA(9)
1185 PNO2G(2)=(PNO2G(1)+PNO2G(3))/2
1190 FOR I=1 TO 3
1195 ZCHK(I)=K2*POUTA(10)/(1+K2*PNO2G(I))*PNO2G(I)-POUTA(9)
1200 ZCHK(I)=ZCHK(I)+2*K1*PNO2G(I)**2+PNO2G(I)
1205 IF ABS(ZCHK(I))<.00001 THEN POUTA(5)=PNO2G(I)
1210 NEXT I
1215 IF POUTA(9)>0 GOTO 1230
1220 IF ZCHK(1)*ZCHK(3)<0 THEN PNO2G(3)=PNO2G(2)//GOTO 1185
1225 IF ZCHK(2)*ZCHK(3)<0 THEN PNO2G(1)=PNO2G(2)//GOTO 1185
1230 POUTA(6)=POUTA(10)/(1+K2*POUTA(5))
1235 POUTA(7)=K1*POUTA(5)**2
1240 POUTA(8)=K2*POUTA(5)*POUTA(6)
1270 CIN(4)=C(4)-(.5*RR(5)+RR(7)+.5*RR(6))*(WAREAS*DELVS*ELMNTS/LVOLS)
1275 CIN(11)=C(11)-(.5*RR(5)+RR(7)+2*RR(8)-1.5*RR(6))
1276 CIN(11)=CIN(11)*WAREAS*DELVS*ELMNTS/LVOLS
1280 PRINT PINA(10),POUTA(10),C(4),CIN(4),C(11),CIN(11),PINA(5),PINA(6)
1285 PRINT PINA(7),PINA(8),OXNO,PINA(9),POUTA(9)
1305 INCMT=INCMT+1
1310 PRINT INCMT,RR(6),RCHK
1315 GMOLS=GMOLS-(RR(5)+RR(6)+RR(7)+RR(8))*3600*WAREAS*DELVS*ELMNTS
1320 LMOLS=LMOLS-(RR(5)+2*RR(7)+2*RR(8)-RR(6))*3600*WAREAS*DELVS*ELMNTS
1321 ZIP1=INCMT/2//ZIP2%=INCMT/2
1322 IF ZIP1<>ZIP2% GOTO 1328
1324 ISB(1,ZIP1)=C(4)+C(11)//ISB(2,ZIP1)=VV//ISB(3,ZIP1)=LV
1328 C(4)=CIN(4)//C(11)=CIN(11)//IF C(11)<0 THEN C(11)=0
1330 X(4)=C(4)/MLRDNS//X(11)=C(11)/MLRDNS//X(3)=1-X(4)-X(11)
1335 FOR I=5 TO 10
1340 PINA(I)=POUTA(I)
1345 NEXT I
1350 C(6)=PINA(6)/H6//C(5)=PINA(5)/H5
1355 P=P-.007782//PA=P/760
1360 IF INCMT<96 GOTO 1000

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1362 CLOSE #3
1365 C(7)=PINA(7)/H7//C(8)=PINA(8)/H8//SIGX=0
1370 FOR I=5 TO 8
1375 X(I)=C(I)/MLRDNS
1380 SIGX=SIGX+X(I)
1385 NEXT I
1390 FOR I=3 TO 8
1395 X(I)=X(I)/(1+SIGX)
1400 NEXT I
1402 PRINT X(3),X(4),X(11)
1405 END
REM SPARGE EFFECT DETERMINATION
2005 SUB%=1
2010 GOTO 950
REM VAPOR PRESSURE DETERMINATION
2500 VP(1)=EXP(14.9542-588.72/(T-6.6))
2501 VP(2)=EXP(15.4075-734.55/(T-6.45))
2502 IF T=363 THEN VP(3)=489//IF T=368 THEN VP(3)=595
2503 IF T=289 THEN VP(3)=11.4
2504 IF T=363 THEN VP(4)=.5//IF T=368 THEN VP(4)=.75
2505 IF T=289 THEN VP(4)=.6
2507 VP(5)=EXP(20.5324-4141.29/(T+3.65))
2508 VP(6)=EXP(20.1314-1572.52/(T-4.88))
2509 GOSUB 2520
2510 VP(7)=(VP(5)/760)**2*K1*760
2511 VP(8)=VP(5)/760*VP(6)/760*K2*760
2514 RETURN
2520 K1=.707E-09*EXP(6866/T)
2521 K2=.6615E-07*EXP(4740/T)
2522 K3=.187E-06*EXP(4723/T)
2523 RETURN
2550 GMW=0
2553 LMW=0
2556 FOR I=1 TO 8
2559 PGMW=Y(I)*MW(I)
2562 PLMW=X(I)*MW(I)
2565 GMW=GMW+PGMW
2568 LMW=LMW+PLMW
2571 NEXT I
2574 GMSVL=(GMOLS*GMW*2.2)/((VSRDE**2)*3.14*VDFCT)/3600
2577 LMSVL=(LMOLS*LMW*2.2)/((VSRDE**2)*3.14*VDFCT)/3600
2580 RETURN
REM GAS MASS TRANSFER COEFFICIENT DETERMINATION
2601 KGC1=((PARAE*PARDE)**2)*(SCNOG**.333)*((GMSVL/PARAE/GVISE)**.7)
2602 KGC=(KGC1*5.23)/(.7302*T*1.8/PARAE/DG(I))
2603 KGCS=KGC/2.2/.0929
2604 RETURN
REM LIQUID MASS TRANSFER COEFFICIENT
2621 GOSUB 2680
2622 RNOL=LMSVL/(PARAE*LIQVIS)
2623 FRNOL=(PARAE*LMSVL**2)/(32.172*RHOLI*62.4)
2624 WNOL=(LMSVL*2)/(PARAE*SFTNE*RHOLI*62.4)

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2625 WAREA1=(-1.45*RNOL**.1)*(FRNOL**-.05)*(WNOL**.2)*((SFTNS/61)
    **-.75)
2626 WAREA=PARAE*(1-EXP(WAREA1))*WAREAS=WAREA*.3048
2627 SCNOL=LIQVIS/(RHOE*.11397E-09*T)
2628 KLC1=((PARAE*PARDE)**.4)*(SCNOL**-.5)*((LMSVL/WAREA/LIQVIS)**.667)
2629 KCL=(KLC*.0051)/(RHOE/32.172/LIQVIS)**.333
2630 KLCS=KLC*.3048
2631 RETURN
REM LIQUID VISCOSITY DETERMINATION
2671 LIQVIS=.2367E-03*EXP(3.3567*X(4))
2672 RETURN
REM LIQUID DENSITY SUBROUTINE
2681 WTFCT(4)=(X(4)*MW(4))/LMW
2682 RHOLIQ25=.97935/((1-.0065409*WTFCT(4))+(.31194E-04*WTFCT(4)**2))
2683 RHOLIQ=1.0789*RHOLIQ25+.0029366*T-.0031548*T*RHOLIQ25-.073416
2684 RHOE=RHOLIQ*62.43
2685 RETURN
REM AIRLIFT ENTHALPY BALANCE
2711 GOSUB 2725
2712 GCP(1)=7.44*EL-.00162*FL+.2133E-05*GL-.6975E-09*HL
2713 GCP(2)=6.713*EL-.44E-06*FL+.139E-05*GL-.636E-09*HL
2714 LCP(3)=18*AL
2715 LCP(4)=1.125*(28.414*AL-.003577*BL)
2716 RETURN
REM AIRLIFT ENTHALPY BALANCE TEMPERATURE TERMS
2726 EL=T2-TALS
2727 FL=T2**2-TALS**2
2728 GL=T2**3-TALS**3
2729 HL=T2**4-TALS**4
2730 AL=TACS-T2
2731 BL=TACS**2-T2**2
2732 RETURN
REM GAS DIFFUSION COEFFICIENT DETERMINATION
2776 DG(I)=.0043*T**1.5*(1/MW(I)+1/MWAIR)**.5
2777 DG(I)=DG(I)/(P/760*(VA(I)**.333+VAAIR**.333)**2)
2778 DG(I)=DG(I)/929.03
2779 RETURN
2800 ISOGS=ACSGS*HVSTS/550/MW(3)//PRINT ISOGS
2805 ACOFS=SBOFS-ISOGS
2810 YISOG(3)=1//YISOG(4)=0
2815 XACOF(3)=(XRFLX(3)*SBOFS-ISOGS)/ACOF5
2820 XACOF(4)=1-XACOF(3)
2850 ACOFMW=0
2855 FOR I=3 TO 4
2860 P1MW=XACOF(I)*MW(I)
2865 ACOFMW=P1MW+ACOFMW
2870 NEXT I
2875 HVNAS=528.8026*EXP(-1.5338*XACOF(4))
2880 ACBUS=(ACSFS*HVSTS)/HVNAS/ACOFMW
2885 YACBU(3)=LOG(XACOF(3))*32+1.0237//YACBU(4)=1-YACBU(3)
2890 IF YACBU(3)>1 THEN YACBU(3)=1//YACBU(4)=0
2895 FOR I=3 TO 4

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2900 XISB(I)=(ACBUS*YACBU(I)+ACOFs*XACOF(I))/(ACBUS+ACOFs)
2905 NEXT I
2910 ISBS=ACBUS+ACOFs
2915 ISOGS=SBOFS-ACOFs//PRINT ISOGS
2920 RETURN
3005 RR(5)=KLCS/H5*PINT(5)-KLCS*C(5)
3010 RR(6)=KLCS/H6*PINT(6)-KLCS*C(6)
3015 RR(7)=DK7*PINT(7)
3020 RR(8)=DK8*PINT(8)
3025 RR(11)=KLCS*C(11)
3030 RETURN
```

APPENDIX B

IODINE PARTITIONING DETERMINATION

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5  DIM C(48),VV(48),LV(48),I2V(48),I2L(48)
7  DIM #3, ISB(3,48)
10 - 11 DATA STATEMENTS
95  OPEN 'TABLE.DAT' FOR INPUT AS FILE #3, VIRTUAL
100 READ RFLXV,BTBUV,SBOFV,DOGV,BTFV,FGV,LFGV,VFGV,LOUTV,ISOGV,I2SCFT
105 READ SPGFCT,I2MOLS,I2RFLX
150 OPEN 'LP:' FOR OUTPUT AS FILE #2
175 FOR I=1 TO 48
176 C(I)=ISB(1,I)
178 VV(I)=ISB(2,I)
180 LV(I)=ISB(3,I)
182 PRINT C(I),VV(I),LV(I)
185 NEXT I
187 T=289
188 CLOSE #3
190 I2ISOG=I2RFLX*SBOFV*I2SCFT/ISOGV
195 IF BTBUV>0 GOTO 500
200 I2BTF=I2RFLX
205 I2FG=(I2MOLS+ISOGV*I2ISOG)/FGV
210 GOSUB 1000
220 I2VFG=(I2FG*FGV)/(VFGV+AK1*LFGV)
225 I2LFG=I2VFG*AK1
230 I2LOUT=(I2BTF*BTFV-LFGV*I2LFG)/LOUTV
235 I2V(1)=I2LOUT/AK1
245 I2L(1)=(I2V(1)*VV(1)+I2LOUT*LOUTV-I2VFG*VFGV)/LV(1)
250 I=1/I2L(J)=I2LOUT//GOSUB 3000
255 PRINT I2V(1),I2L(1),I,TI2AQ
260 IF I2L(1)>I2SOL THEN I2L(1)=I2SOL//PRINT 'SOL LIMIT'
265 FOR I=2 TO 48
270 J=I-1
275 I2V(I)=I2L(J)/AK1
280 I2L(I)=(I2V(I)*VV(I)+I2L(J)*LV(J)-I2V(J)*VV(J))/LV(I)
285 IF I2L(I)>I2SOL THEN I2L(I)=I2SOL//PRINT 'SOL LIMIT REACHED'
290 GOSUB 3000
295 PRINT I2V(I),I2L(I),I,TI2AQ
300 NEXT I
350 END
500 I2BTF=((SBOFV+RFLXV)*I2RFLX)/(1-SPGFCT)/BTFV
505 I2BTBU=SPGFCT*I2BTF*BTFV/BTBUV
510 I2FG=(I2MOLS+I2BTBU*BTBUV+I2ISOG*ISOGV)/FGV
515 GOTO 210
REM IODINE EQUILIBRIUM CONSTANTS
1005 AK1=120//AK3=.25E-12//I2SOL=.9653E-03
1010 AK2=EXP(-111.98+16.725*LOG(T)+6952.3/T)
1015 AK4=.12E-10+.36E-12*(T-298)
1050 RETURN
REM HYDROLYSIS EQUILIBRIUM RELATIONSHIPS

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```
3005 PH=LOG10(1/C(I))
3010 HIONC=EXP(-2.303*PH)
3015 XX=((AK3*I2L(J))/HIONC+AK4*I2L(J))/(1+AK2*I2L(J))
3020 IMIN=SQR(XX)//I2=AK2*IMIN*I2L(J)
3025 HIO=(AK3*I2L(J))/(IMIN*HIONC)
3030 H2OI=AK4*I2L(J)/IMIN
3035 TI2AQ=I2L(J)+.5*(HIO+H2OI+IMIN+3*I3)
3050 RETURN
```

VITA

Joseph Franklin Birdwell, Jr. was born in Kingsport, Tennessee on October 10, 1957, where he attended school until the age of 15. At that time he moved with his family to Knoxville, Tennessee and attended Farragut High School from which he graduated in 1975. He entered the University of Tennessee in September of that year, and received a Bachelor of Science degree in Chemical Engineering in June 1979.

Immediately after graduation, the author accepted employment with E. I. DuPont de Nemours at a Photo Products Department plant in Brevard, North Carolina. In 1980 (after ten months employment with DuPont) he accepted a position at Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee, in part to have access to the University of Tennessee in order to further his education. The author will continue to be employed at ORNL after graduation.