GAS ABSORPTION WITH CHEMICAL REACTION

by

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td></td>
</tr>
<tr>
<td>Equipment</td>
<td>2</td>
</tr>
<tr>
<td>Procedure</td>
<td>4</td>
</tr>
<tr>
<td>Chemical Analysis</td>
<td>9</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>11</td>
</tr>
<tr>
<td>The Absorption of Chlorine in Water</td>
<td>11</td>
</tr>
<tr>
<td>The Absorption of Ammonia in Phosphate Solutions</td>
<td>29</td>
</tr>
<tr>
<td>CONCLUSIONS</td>
<td>63</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>67</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>68</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>70</td>
</tr>
</tbody>
</table>
INTRODUCTION

Gas absorption is a unit operation in which the transfer of a soluble gas from a gas mixture into a liquid takes place. In most industrial applications of this operation, one of the most important considerations is the selection of a proper absorbent. The usual objective in the selection of an absorbent for scrubbing a gas is to find a liquid, or possible a solution, which has a very large capacity for absorbing the solute gas without building up an appreciable equilibrium back pressure. This can be accomplished readily by choosing a chemical with which the solute gas will react irreversibly. The mechanism of such mass transfer is one of physical absorption combined with the chemical reaction in the liquid phase.

Theories governing the absorption rate in the presence of a chemical reaction have been proposed by Hatta (5), Davis and Grandall (3) and Weber and Nilson (15). A theory based on the unsteady-state diffusion concept proposed by Higbie (6) has been developed for slow first-order reactions and for rapid second-order reactions taking place in the liquid-film. Some advances in the theory in this field have been made in recent years. However, the picture is still far from complete. It is not yet possible to make a general correlation between gas absorption with chemical reaction and gas absorption without chemical reaction. Each case must still be studied experimentally.

The purpose of this investigation was to study gas absorption with chemical reaction in a specially designed disc column.
It is a continuation of the previous work by Hwu (7). Two working equations from which individual film coefficients may be evaluated were developed by Hwu. The present work was confined to the study of the absorption of ammonia into mono-ammonium orthophosphate solutions and di-ammonium orthophosphate solutions in order to further ascertain the gas-film characteristics of this column. The absorption of chlorine into water was also studied because of the unusual behavior of this system resulting from the pronounced ionization of chlorine in water. By continuing the present work, absorption data for different systems can be collected. It is hoped that this material will help in amassing sufficient data to gain an understanding of the mechanism by which transfer between gas and liquid phases occurs when absorption is accompanied by irreversible chemical reaction in the liquid phase, and thus to contribute to the development and extension of the theory of gas absorption.

**EXPERIMENTAL**

**Equipment**

The main experimental equipment used in this experiment was a disc column. This type of equipment was first reported by Stephen and Morris (13). It possesses the advantages of both packed and wetted wall columns and is particularly suitable for the determination of liquid film coefficients for systems involving chemical reactions. The construction and assembly of the disc column at Kansas State College was reported by Hwu (7).
It consisted mainly of a Pyrex glass column with an inside diameter of 1/8 inch and a height of 34 inches. A series of 35 unglazed ceramic discs with a diameter of 1.5 cm. and a thickness of 0.48 cm. were mounted vertically and centrally in the column. They were threaded edgewise upon a Fiberglas cord and successive discs were maintained at right angles with each other. The principal constants of this disc column are listed in the Appendix.

Two fifty-gallon stainless-steel tanks were used as storage tanks. The phosphate solutions were prepared in batches. A certain amount of the chemicals was added to a definite quantity of distilled water and agitated for more than thirty minutes to make sure of complete solution.

The details of the column and the schematic arrangement of the experimental equipment are shown on Plates I and II respectively. The inlet liquid was pumped from the storage tanks into the liquid feeder at the top of the column. The liquid rate was controlled by a Fisher-Porter C-clamp Flowrater. The liquid flowed downward over the surface of the discs while the gas stream passed upward counter-currently. In the absorption of ammonia in ammonium phosphate solution, air-ammonia mixtures were used, while in the absorption of chlorine in water, both pure chlorine and air-chlorine mixtures were used. Air from the compressed air supply and ammonia (or chlorine) from a cylinder were metered by flowmeters and the combined gas streams were mixed by passing thoroughly before entering the column. Manometers were installed on the gas line to measure the pressure
of the gas and the pressure difference inside and outside the column.

The effluent liquid flowed down through the effluent passage and then went through a sampler. The sampler, as shown on Plate II, consisted of an overflow arrangement with two Pyrex tubes placed concentrically. The liquid sample was siphoned off with a rubber tube which was connected through a glass tee to a buret for measuring the volume of sample. The liquid was kept flowing continuously through the sampling system during operation.

Procedure

In starting, the air was first expelled from the effluent liquid passage by raising and lowering the sampler. Liquid was then introduced into the top of the column, and the gas was turned on slowly. A sudden increase in the gas rate would cause the gas to rush out of the column before the water head was built up in the liquid feeder to balance the gas pressure inside the column. Meanwhile, the sampler was placed at the proper position so that the liquid level was kept up to the neck of the long funnel inside the column. This was done in order to minimize the end effect of absorption.

In the absorption of chlorine in water, the first sample was taken thirty minutes after starting. The samples were then taken successively at a time interval of ten minutes until the analysis of the samples showed the chlorine absorbed was constant. In the ammonia-phosphate system, a total of four samples were taken. The first one was taken one hour after starting and the
EXPLANATION OF PLATE I

Close-up View of Disc Column

A. Pyrex tube  
B. Ceramic discs  
C. Supporting Fiberglas cord  
D. Liquid feed jet  
E. Long stem funnel  
F. Gas inlet  
G. Gas outlet  
H. Liquid feed cylinder  
I. Effluent to liquid sampler  
J. Drain for liquid lost by splash
EXPLANATION OF PLATE II

Schematic Diagram of Experiment Layout

A. Disc column
B. Liquid feed cylinder
C. Drain for liquid lost by splash
D. Liquid sampler
E. Air inlet
F. Solute gas cylinder
G. Air surge tank
H. Air filter
I₁, I₂. Pressure reducers
J₁, J₂. Needle valves
K₁, K₂, K₃. Rotameters
L. Gas mixer
M₁, M₂, M₃, M₄. Manometers
N₁, N₂. Gas sampling points
O. Liquid inlet
P. Centrifugal pump
Q₁, Q₂, Q₃. Thermometers
remaining were taken every ten minutes. The longer time for this case is to make sure the system reached a steady state because the analysis required a longer time and the results were not immediately available.

Chemical Analysis

Chlorine in Water. The chlorine absorbed in the water was determined by the following method Perry (11). The determination depends primarily upon the reaction:

$$\text{Cl}_2 + 2\text{KI} \rightarrow 2\text{KCl} + \text{I}_2$$

The iodine liberated by the chlorine is titrated with Na$_2$S$_2$O$_3$ solution and the equivalent chlorine calculated.

The following procedures were used throughout the whole experiment:

(A) Twenty ml of a tenth normal solution of KI were added to a 250 ml Erlenmeyer flask.

(b) Ten to twenty ml of sample (depending on the experimental conditions) were added to the flask. The delivery tip of the buret was just above the surface of the iodine solution. The flask was then closed and the contents were vigorously shaken.

(C) The sample was titrated with a standardized tenth normal solution of sodium thiosulfate. When the color of the solution became faint, a few drops of starch solution were added, and titration was continued until the solution became colorless.
Ammonia in Phosphate Solution. The amount of ammonia absorbed was determined in the following way. The inlet liquid was analyzed so that the content of phosphate and ammonia (expressed in terms of $P_2O_5$ and $N_2$ respectively) were known. The analysis of the exit liquid gave the ammonia content after absorption. The difference between these two is the amount of ammonia absorbed. All of the analyses were done by the Analytical and Service Laboratory of the Chemistry Department of Kansas State College.

The analysis of the ammonia content was done by the Kjeldahl method described by Scott (11). Following is the procedure:

(A) Five ml of sample were placed in a Kjeldahl flask. A few pieces of granulated zinc and 25 ml of $K_2S$ and $Na_2S_2O_3$ solution were added, and the flask shaked.

(B) A sufficient amount of NaOH solution to make the solution strongly alkaline was added.

(C) The flask was connected to a condenser by means of a Kjeldahl connecting bulb, taking care that the tip of the condenser extended below the surface of a standard acid solution in a receiver. The contents were mixed by shaking, and the liberated $NH_3$ distilled into standard acid. This was then titrated with standard alkaline solution, using methyl red as the indicator.

The analysis of the phosphate content was based on the conventional method used for the analysis of fertilizer (9). The procedures were as follows:
(A) Ten to thirty-five ml of sample were placed in a flask and neutralized with NH₄OH (using litmus paper), then made slightly acid with nitric acid.

(B) Fifteen to twenty ml of a 50 per cent solution of NH₄NO₃ were added.

(C) Thirty-five to fifty ml of ammonium molybdate solution were added, and the sample shaken for 30 minutes.

(D) The precipitate was filtered and washed.

(E) The precipitate was transferred back to the flask. An excess of standard alkaline solution was added and the excess was back titrated with standard HCl solution.

RESULTS AND DISCUSSION

The Absorption of Chlorine in Water

Summary of Experimental Results. A total of 21 runs were made for the absorption of chlorine in water. The effect of water rate and the effect of gas rate were studied. In the study of the effect of liquid rate, pure chlorine was used, while in the other cases, air-chlorine mixtures were used. The liquid rate was measured as the rate in pounds per hour per foot of perimeter of a tube with the same surface area per foot of length as the surface area of the ceramic discs per foot of length in the column. The liquid rate varied from 100 lbs per hour per foot of perimeter to 450 lbs per hour per foot of perimeter; and the temperature was within the range of 25° C. to 30° C. The data obtained are presented in Tables 1 and 2 in the appendix.
The overall coefficient was calculated from the equation:

\[
K = \frac{W (C_2 - C_1)}{A \Delta C_{lm}} \quad (1)
\]

\[
\Delta C_{lm} = \frac{(C_{e1} - C_2) - (C_{e2} - C_1)}{\ln \frac{C_{e1} - C_2}{C_{e2} - C_1}} \quad (2)
\]

Where \( W \) is the liquid rate in lbs. per hr. \( C_1 \) and \( C_2 \) are the concentrations of the inlet and outlet liquid respectively expressed in pounds of chlorine per pound of water. \( C_{e1} \) and \( C_{e2} \) are the interfacial equilibrium concentrations corresponding to the inlet and outlet gas stream respectively. The solubility data for chlorine in water was taken from Perry's Handbook (10). \( A \) is the absorption surface area, its numerical value was 0.22 square feet, based on dry packing. The units of \( K_L \) used are pounds of chlorine transferred per hour per square foot of absorption surface per unit concentration (expressed in pounds of chlorine per pound of water).

Because of the low solubility of chlorine in water, the resistance to the transfer of chlorine can be considered to be offered entirely by the liquid film. Therefore the observed overall coefficient, \( K_L \) can be regarded as the liquid film transfer coefficient \( k_L \). These observed values were further corrected to a common temperature level of 20° C. by the following equation:

\[
k_L \propto e^{nt} \quad (3)
\]

Where \( e \) is the base of the natural system of logarithms

\( n \) is a constant
t is temperature, °C.

With \( t \) expressed in °C, Whitney and Vivian reported a value of 0.021 for the constant \( n \), which is the value used in this work. This is fairly close to the value of 0.023 proposed by Sherwood and Holloway (12) for the general case.

**Discussion of Experimental Results.** The effects of gas rate and liquid rate upon the liquid film transfer coefficient, \( k_L \), were studied. The results may be summarized as follows:

**Gas Rate:** Runs 1 to 5 were carried out under conditions of constant liquid rate and constant gas composition, but with gas velocity varying from 1.96 to 4.21 ft./sec. (The free area for gas flow in the column was equivalent to the area of a tube with a diameter of 0.059 ft. This equivalent diameter was used for calculating gas velocities throughout this work.) The coefficients for these runs are given in Table 2. The results show as was expected, that gas rate has no appreciable effect on the value of the liquid film coefficient. Plate III is a plot of \( k_L \) versus various gas rate.

**Liquid rate:** The variation of liquid film transfer coefficient, \( k_L \), with different liquid rates is shown on Plate IV. The values of \( k_L \) have been corrected to 20°C. Values of \( k_L \) at various liquid rates are shown in Table 2. They are correlated in the following form.

\[
k_L = 0.0163 \cdot \sqrt{0.81}
\]  

(4)

where \( \sqrt{\cdot} \) is the liquid rate in pounds per hour per foot of perimeter.

Previous work on the absorption of chlorine in water was
done by Adams and Edmonds (1), by Vivian and Whitney (14) and by Whitney and Vivian (17) (13). Their data indicated that the liquid film coefficient varied as the 0.8 and 0.6 power of the liquid rate respectively. The value of 0.81 obtained in this work is close to that obtained by Adams and Edmonds, but much higher than that of Whitney and Vivian. However, in view of the unusually high sensitivity of this disc column to liquid rate as shown by Hwu (7), this result is more comparable to that of Vivian and Whitney (14).

Table 1. Effect of gas rate on \( k_\text{L} \) for the absorption of chlorine in water. Liquid rate 31.4 lbs/hr. Temperature corrected to 20° C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Gas Rate (ft./sec.)</th>
<th>Liquid film transfer coefficient ( k_\text{L} ) (lbs./(hr.) (sq.ft.) (lbs.)/cu.ft.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.84</td>
<td>0.58</td>
</tr>
<tr>
<td>2</td>
<td>3.02</td>
<td>0.59</td>
</tr>
<tr>
<td>3</td>
<td>2.26</td>
<td>0.565</td>
</tr>
<tr>
<td>4</td>
<td>1.26</td>
<td>0.706</td>
</tr>
<tr>
<td>5</td>
<td>4.21</td>
<td>0.684</td>
</tr>
</tbody>
</table>

The numerical value of \( k_\text{L} \) is only 70 per cent of the calculated value based on the equation proposed by Hwu (7), which was obtained from the absorption date of \( \text{CO}_2 \) in water. The departure of the experimental values from the predicted values is shown on Plate IV.

Vivian and Whitney (14) also found that the experimental value of \( k_\text{L} \) is only 1/3 to 2/3 of that predicted from an equation based on the data for the absorption of oxygen in water. An
Table 2. Effect of liquid rate on \( k_L \) for the absorption of chlorine in water. Temperature corrected to 200 C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Liquid Rate (lbs./hr.)</th>
<th>Liquid Film Transfer Coefficient ( k_L ) (1)</th>
<th>( k_L ) (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>244</td>
<td>1.2978</td>
<td>1.7889</td>
</tr>
<tr>
<td>2</td>
<td>195.3</td>
<td>0.9886</td>
<td>1.3694</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>1.0367</td>
<td>1.3598</td>
</tr>
<tr>
<td>4</td>
<td>163</td>
<td>0.6997</td>
<td>0.9345</td>
</tr>
<tr>
<td>5</td>
<td>285</td>
<td>1.0787</td>
<td>1.3739</td>
</tr>
<tr>
<td>6</td>
<td>180.3</td>
<td>0.9144</td>
<td>0.7963</td>
</tr>
<tr>
<td>7</td>
<td>133</td>
<td>0.6188</td>
<td>0.7656</td>
</tr>
<tr>
<td>8</td>
<td>103.9</td>
<td>0.7444</td>
<td>0.6007</td>
</tr>
<tr>
<td>9</td>
<td>346.6</td>
<td>1.1554</td>
<td>1.7934</td>
</tr>
<tr>
<td>10</td>
<td>423.6</td>
<td>1.0398</td>
<td>2.0162</td>
</tr>
<tr>
<td>11</td>
<td>434.6</td>
<td>1.7578</td>
<td>2.2937</td>
</tr>
<tr>
<td>12</td>
<td>344.1</td>
<td>1.5818</td>
<td>2.0867</td>
</tr>
<tr>
<td>13</td>
<td>368.7</td>
<td>1.75</td>
<td>2.2603</td>
</tr>
<tr>
<td>14</td>
<td>118.9</td>
<td>0.6498</td>
<td>0.8186</td>
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<td>15</td>
<td>118</td>
<td>0.7704</td>
<td>0.958</td>
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<tr>
<td>16</td>
<td>103.9</td>
<td>0.5314</td>
<td>0.6878</td>
</tr>
</tbody>
</table>

(1) \( k_L \) calculated by using total chlorine concentration as driving force
(2) \( k_L \) calculated by using molecular chlorine concentration as driving force

Explanation of the failure of the chlorine-water system to correlate with the other systems was offered by Whitney and Vivian as follows:

The main difference between the absorption of chlorine by water and other physical gas absorptions is the hydrolyzing effect when chlorine dissolves in water. The following chemical reactions take place:

\[
\begin{align*}
\text{Cl}_2 \text{gas} & \rightleftharpoons \text{Cl}_2\text{aq} & \text{(a)} \\
\text{Cl}_2\text{aq} + \text{H}_2\text{O} & \rightleftharpoons \text{HOC}1 + \text{H}^+ \text{+ Cl}^- & \text{(b)}
\end{align*}
\]
EXPLANATION OF PLATE III

Effect on Gas Rate on $k_L$ for the absorption of Chlorine in water

Ordinate: Liquid film transfer coefficient, $k_L$, lbs./ (hr.) (sq.ft.) (lbs.) / cu.ft.

Abscissa: Gas rate, $G$, ft./sec.

Experimental conditions

Liquid rate----------31.4 lbs./hr.
Chlorine composition----10% Cl$_2$ in air
Temperature corrected to 200 C.
EXPLANATION OF PLATE IV

Effect of Liquid Rate on $k_L$ for the Absorption of Chlorine in Water

Ordinate: Liquid film transfer coefficient, $k_L$, lbs./ (hr.) (sq. ft.) (lbs.) cu.ft.

Abscissa: Liquid rate, $f'$, lbs./ (hr.) (ft.)

Curve I: Predicted value of $k_L$ from the data for the absorption of CO₂ in H₂O

Curve II: Experimental values

Experimental conditions

Chlorine composition-----pure chlorine
Temperature corrected to 20°C.
PLATE IV

[Graph showing two lines labeled I and II with data points]
When reaction (b) reaches equilibrium, the dissolved chlorine is present in the water in three forms: unreacted molecular chlorine, \( \text{Cl}_2 \), hypochlorous acid, \( \text{HOCI} \), and chloride ion. When physical equilibrium exists between the gas and liquid, and when, in addition, the second chemical reaction is at equilibrium, the following conditions apply according to the law of mass action.

For reaction (a)

\[
\frac{C_{\text{Cl}_2}}{C_{\text{HOCI}} C_{\text{Cl}}} = \frac{p}{H}
\]

where \( H \) is the Henry's law constant and \( p \) is the partial pressure of chlorine in the gas phase.

For reaction (b)

\[
\frac{C_{\text{HOCI}} C_{\text{Cl}} C_H}{C_{\text{Cl}_2}} = K_e
\]

If \( C \) represents the concentration of total dissolved chlorine, from the above expression, we have:

\[
C = \frac{p}{H} + \frac{K_e p}{H}^{1/3}
\]

The validity of this equation was proved by Whitney and Vivian (16).

It was pointed out by Whitney and Vivian that the rate of the physical reaction (a) at the interface is almost certain to be very large, though the chemical reaction (b) may be relatively slow. Thus, chlorine molecules may dissolve in the liquid and begin to diffuse through the liquid film before reaction (b) has an opportunity to occur. If this is true, the concentration of chlorine in the liquid at the interface will be that of dissolved but unreacted chlorine which is less than \( C \), as shown before. If the reaction is so slow that the chlorine molecules penetrate a considerable distance into the liquid without reaction, the
true driving force available to produce diffusion is $\Delta C_{Cl_2}$ (molecular chlorine) rather than $\Delta C$ (total chlorine). It is apparent that this driving force is smaller when the concentration is that of unreacted chlorine than when it is total chlorine. As a result the transfer coefficient based on the concentration of molecular chlorine is larger. This is called the pseudo transfer coefficient.

The driving force based on the molecular concentration was calculated through equation (2) using the molecular chlorine concentration instead of the total chlorine concentration. The interfacial equilibrium concentration was calculated by using equation (5), and the numerical value of H given in Perry's Handbook (10). The molecular chlorine concentration in the liquor was computed by subtracting the concentration of hydrolyzed chlorine, from the total chlorine concentration, which was determined by direct analysis. The chemical equilibrium constant, $K_e$, was obtained from Perry's Handbook (10). However, it was found that the hydrolyzed chlorine concentration is too small to be significant and the total chlorine concentration of the liquor was used as that of the molecular concentration. The only difference in the calculation of the two driving forces, then lies in the values of $C_{e1}$ and $C_{e2}$ used. For the calculation of the actual coefficients, these concentrations were taken from solubility data for total chlorine concentration at the existing chlorine partial pressure in the gas phases. For the calculation at the pseudo coefficients, these concentrations were calculated from equation (5) using values of H corresponding to molecular
chlorine only.

The effect of liquid rate on the pseudo coefficient is shown on Plate V. The following correlation was obtained for the pseudo coefficients:

\[ k_L = 0.01173 \sqrt{0.855} \]  

(3)

As shown on Plates V and VI, the pseudo transfer coefficients are much closer to the values of the liquid film transfer coefficient calculated from the equation for the absorption of carbon dioxide in water.

From the foregoing discussion, it was concluded that in designing for the absorption of chlorine, if the values of \( k_L \) are to be predicted from equations based on other systems, such as CO₂, the molecular chlorine concentration should be used in the driving force term instead of total chlorine concentration.

The points on the plot concentration of chlorine in the outlet liquor versus water rate are scattered, but show a trend of decreasing with an increase of water rate. (Plate VII) When compared with results obtained from the same column previously, there is some inconsistency. So far, three different gases have been used for the study of gas absorption: ammonia, chlorine, and carbon dioxide.

(a) For the NH₃ - H₂O system, the exit liquor concentration decreases as the water rate increases.

(b) For the Cl₂ - H₂O system, the exit liquor concentration (total chlorine content) decreases as the water rate increases.

(c) For the CO₂ - H₂O system, the exit liquor concentration increases as the water rate increases as reported by Hwu.
EXPLANATION OF PLATE V

Effect of Liquid Rate on the Pseudo Transfer Coefficient of the Absorption of Chlorine in Water

Ordinate: Pseudo transfer coefficient, $k_L$, lbs./ (hr.) (sq.ft.) (lbs.) cu.ft.

Abscissa: Liquid rate, $F$, lbs./ (hr.) (ft.)

Curve I: Predicted value of $k_L$ from the date of the absorption of CO$_2$ in H$_2$O

Curve II: Pseudo transfer coefficient from the experimental data.

Experimental conditions

Chlorine composition---------pure chlorine

Temperature corrected to 20°C C.
PLATE V
EXPLANATION OF PLATE VI

Comparison of Predicted, Experimental and Pseudo Liquid Film Transfer Coefficients for the Absorption of Chlorine in Water

Ordinate: Liquid Film Transfer coefficient, $k_L$, 
1 lb./hr. (sq. ft.) (lbs.) (lbs.) 
cu. ft.

Abscissa: Liquid rate, $P$, lbs./hr.-ft.

Curve I: Predicted value of $k_L$

Curve II: Value of pseudo transfer coefficient

Curve III: Experimental value of $k_L$
It was pointed out by Hwu that there are two opposing factors influencing the outlet liquor concentration, first the time of contact with the gas stream and second the degree of turbulence which affords the "mixing" effect below the liquid surface and provides fresh surfaces for absorption. In the case of the absorption of carbon dioxide in water, the latter factor plays a dominant role. It was also pointed out that the high smoothness and the poor wettability of the disc itself made some contribution to this situation.

Since both CO₂ and Cl₂ experiments were carried out in the same equipment and under the same operating conditions, and since in both systems the liquid-film controls, similar results were expected for the two systems. The explanations made by Hwu apparently fail in the case of chlorine.

Furthermore, the resistance to molecular diffusion is inversely proportional to the diffusion coefficient. These values are given in Perry's Handbook as follows:

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
<th>Diffusion Coefficient at 200 C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>water</td>
<td>1.5</td>
</tr>
<tr>
<td>NH₃</td>
<td>water</td>
<td>1.76</td>
</tr>
<tr>
<td>Cl₂</td>
<td>water</td>
<td>1.22</td>
</tr>
</tbody>
</table>

Increasing the time of contact has the effect of increasing the amount of gas dissolved. However, if the contact time is short as compared with that required for reaching equilibrium, then the contact time has a greater influence on those gases with large diffusion coefficients. In other words, for gases with large diffusion coefficients, the exit liquor concentration
should increase to a greater extent with a given increment of contact time than for gases with small diffusion coefficient. Conversely for a given increment in water exit concentration would be conversely reduced to the greatest extent in the case of ammonia, among the three gases above, with carbon dioxide and chlorine following in order.

It is recognized that the degree of turbulence is proportional to the water rate. It was proposed by Danckwerts (2) that the rate of absorption is proportional to the number of fresh surfaces exposed to the gas. The rate of creation of fresh surface is, in turn, a function of turbulence and therefore of the rate of liquid flow from one disc to the next. Therefore, the exit liquor concentration should increase with the water rate.

Since the conditions for the absorption of chlorine in water in this work were the same as those for the absorption of carbon dioxide in water in the work of Hwu, and since both systems have the same characteristics, the effect of turbulence should be the same. However, the time of contact has a greater influence on the carbon dioxide-water system, than on the chlorine water system. If Hwu's explanation holds true, in the case of the absorption of chlorine in water, the outlet liquor concentration should decrease, not increase with the decrease of water rate, and this tendency should be more pronounced than that found in the carbon dioxide-water system.

Unfortunately, insufficient data are available to resolve this inconsistency. However, it may be pointed out that the exit
liquor concentrations in Hwu's work on both ammonia and carbon dioxide absorbed in water are widely scattered, and that while the latter shows a tendency to increase with the liquid rate, the slope can not be accurately determined. Hwu's data on ammonia and carbon dioxide in water, and the data for the chlorine water system are shown in Plates VII and VIII.

The Absorption of Ammonia in Phosphate Solutions

**Summary of Experimental Results.** Forty-four runs on the absorption of ammonia in phosphate solutions were made. (The data are presented in Tables 3 and 4 in the Appendix). Mono-ammonium orthophosphate and di-ammonium orthophosphate were used in concentrations up to 0.25M. Again the effects of gas rate and liquid rate were studied. The gas and liquid rates were in the same range as those used in the study on the absorption of ammonia in water. The liquid rate varied from 100 to 350 lbs./(hr.) (ft. of perimeter), and the rate varied from 2 to 6 ft./sec. The ammonia concentration in the air stream was between 5% and 10%.

The overall transfer coefficient were calculated through the following equation:

\[
K_G = \frac{\text{NH}_3 \text{ Absorbed}}{A \Delta P_{lm}}
\]  

(9)

The amount of ammonia absorbed was determined by the difference of ammonia content in the liquid stream before and after going through the column. "A" is the absorption surface area,
EXPLANATION OF PLATE VII

Plot of Exit Liquor Concentration vs. Liquid Rate

Ordinate: Exit liquor concentration, C, lbs./100 lbs. H₂O

Abscissa: Liquid rate, r', lbs./(hr.) (ft.)

Legend:

- Cl₂ - H₂O data
- NH₃ - H₂O data
EXPLANATION OF PLATE VIII

Plot of Exit Carbon Dioxide Conc. vs. Liquid Rate

Ordinate: Exit concentration, $C$, lbs. CO$_2$/100 lbs. H$_2$O

Abscissa: Liquid rate, $R$, lbs./hr.-ft.
and for this column had a value of 0.22 sq. ft. on the dry basis. $F_{lm}$ is the logarithmic mean driving force.

Since the solubility of ammonia in phosphate solution was not available, the evaluation of the exact mean driving force was impossible. However, it could be found for the two limiting cases: (a) assuming that there was no back pressure of ammonia such as would be the case in a strong acid solution, (b) assuming that the same relationship existed in the ammonia-phosphate system as in the ammonia-water system and that the same Henry's law constant applied.

Values of $K_G$ based on these two assumptions were calculated and subsequently corrected to a standard temperature of 20° C. using the equation proposed by Molstad (8).

$$K_G \propto 24.3 - 0.175 t$$

(10)

where $t$ is temperature, °C.

**Discussion of Experimental Results.** The primary usefulness of this specially designed column is in the study of the liquid film coefficients for various systems, both with and without chemical reaction. This should make it possible to find a general correlation for $k_L$ and $k'_L$ where $k_L$ is the liquid film coefficient with chemical reaction and $k'_L$ is that without chemical reaction. The ammonia-phosphate system was first studied to further ascertain the column characteristics with respect to the gas film resistance. This system has the advantage that the desired ratios of ammonium ion and the phosphate ion can be readily obtained. The overall gas film coefficient, $K_G$ is related to the individual gas and liquid film
coefficients by the equation:

\[
\frac{1}{K_G} = \frac{1}{k_G} \frac{H}{k_L} \tag{11}
\]

\[
\frac{H}{k_L} = \frac{1}{K_G} - \frac{1}{k_G} \tag{11a}
\]

Where \( K_G \) is the overall transfer coefficient, \( k_L \) and \( k_G \) are the individual coefficients of the liquid film and the gas film, respectively, and \( H \) is the Henry's law constant, defined by the equation:

\[
p = HC \tag{12}
\]

Since \( k_G \) can be determined from the equations developed by Hwu (7) using ammonia and water and carbon dioxide and water and if \( K_G \) is determined experimentally, then the liquid film coefficient, \( k_L \) can be evaluated. However, in cases where \( K_G \) is close to the value of \( k_G \), so that the gas film comprises the controlling resistance, the difference between these two reciprocals is very small. Therefore, a slight experimental error in the determination of \( K_G \) would result in a large error in \( k_L \) and make the correlation unreliable.

Another approach then is to compare the total transfer coefficient \( K_G \) instead of the film coefficients, \( k_G \). Using the data for the absorption of ammonia into water reported by Hwu (7), the following correlation was obtained:

\[
K_G \propto g^{0.391} \sim 0.377 \tag{13}
\]

**Effect of Gas Rate:** The numerical values of \( K_G \) were calculated by equation (9) for each of the two extremes for which the driving force could be evaluated. These values are given in
Tables 3 and 4 and are shown graphically in Plates IX to XII. For the di-ammonium phosphate system the numerical values of $K_G$ based on the assumption of no ammonia back pressure lie below the corresponding values of $K_g$ for ammonia absorbed in water. On the other hand, the values based on the assumption that the Henry's law constant for ammonia in water applies, lie above those of the ammonia-water system. In the mono-ammonium phosphate system the values of $K_G$ based on both of these assumptions are greater than the corresponding values for the ammonia-water system. However, the slope of the lines appear to be nearly the same in all cases as that in the ammonia-water system. This is consistent with the absorption of ammonia in sulfuric acid as reported by Doherty and Johnson (4). In the absorption of ammonia in 3.5N sulfuric acid, their numerical values of $K_g$ were 1.45-1.65 times those for the absorption of ammonia in water, but the slopes of the straight lines were the same.

The near constancy of the effect of gas velocity on the different systems can also be explained by Hatta's theory for absorption followed by a rapid, irreversible reaction in the liquid phase. Hatta (5) visualized a double film on the liquid side with the chemical reaction occurring at the boundary between them. Hatta further postulated that, the double liquid film disappears gradually as the concentration of the reacting solute in the liquid phase increases. In other words, the function of the reacting solute is only to reduce the resistance offered by the liquid side. The absorption of ammonia is recognized as one in which the gas film controls and the main
Table 3. Effect of gas velocity on \( K_G \) for the absorption of ammonia in mono-ammonium phosphate solution. Temperature corrected to 200°C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Gas Rate (Pt./sec.)</th>
<th>Liquid Concentration (M./Liter)</th>
<th>lbs./(lit.) (sq.ft.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.006</td>
<td>0.154</td>
<td>7.93</td>
</tr>
<tr>
<td>2</td>
<td>6.07</td>
<td>0.154</td>
<td>12.03</td>
</tr>
<tr>
<td>3</td>
<td>4.578</td>
<td>0.154</td>
<td>10.09</td>
</tr>
<tr>
<td>4</td>
<td>3.31</td>
<td>0.154</td>
<td>9.26</td>
</tr>
<tr>
<td>5</td>
<td>4.573</td>
<td>0.06</td>
<td>9.94</td>
</tr>
<tr>
<td>6</td>
<td>6.04</td>
<td>0.06</td>
<td>12.68</td>
</tr>
<tr>
<td>7</td>
<td>2.336</td>
<td>0.06</td>
<td>7.46</td>
</tr>
<tr>
<td>8</td>
<td>3.16</td>
<td>0.058</td>
<td>8.85</td>
</tr>
<tr>
<td>9</td>
<td>2.11</td>
<td>0.1</td>
<td>7.53</td>
</tr>
<tr>
<td>10</td>
<td>3.17</td>
<td>0.1</td>
<td>8.746</td>
</tr>
<tr>
<td>11</td>
<td>4.29</td>
<td>0.1</td>
<td>9.9</td>
</tr>
</tbody>
</table>

(1) \( K_G \) calculated by assuming that no back pressure of \( \text{NH}_3 \) existed over the solution.

(2) \( K_G \) calculated by assuming the Henry's law constant for \( \text{NH}_3-\text{H}_2\text{O} \) applies.

Resistance to the transfer of solute gas is offered by the gas film; hence, the values of \( K_G \) do not vary much even with the presence of chemical reaction. The relationship between \( K_G \) and gas velocity, should, therefore, be almost the same in all cases.

Values of \( K_G \) for this system, (where the concentration of di-ammonium phosphate is high), calculated by using the same value of Henry's law constant as that in water, were unusually high. (Fig. 3) This indicates the inadequacy of the assumption. Since, according to this assumption, the mean driving force can be expressed by the following equation:
Table 4. Effect of gas velocity on \( K_G \) for the absorption of ammonia in di-ammonium phosphate solution. Liquid rate approximately 30 lbs./hr. Temperature corrected to 20\(^\circ\) C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Gas Velocity (ft./sec)</th>
<th>Liquid Concentration (lbs./hr.)</th>
<th>Overall transfer coefficient ( K_G ) (sq.ft.)</th>
<th>Concentration (atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( K_G(1) )</td>
<td>( K_G(2) )</td>
</tr>
<tr>
<td>5</td>
<td>1.21</td>
<td>0.1</td>
<td>7.14</td>
<td>8.99</td>
</tr>
<tr>
<td>6</td>
<td>6.057</td>
<td>0.1</td>
<td>9.57</td>
<td>12.34</td>
</tr>
<tr>
<td>7</td>
<td>4.926</td>
<td>0.1</td>
<td>8.54</td>
<td>11.24</td>
</tr>
<tr>
<td>8</td>
<td>2.171</td>
<td>0.1</td>
<td>6.51</td>
<td>8.19</td>
</tr>
<tr>
<td>9</td>
<td>2.171</td>
<td>0.0262</td>
<td>6.25</td>
<td>12.93</td>
</tr>
<tr>
<td>10</td>
<td>3.296</td>
<td>0.0262</td>
<td>7.77</td>
<td>13.94</td>
</tr>
<tr>
<td>11</td>
<td>6.06</td>
<td>0.0267</td>
<td>11.95</td>
<td>25.28</td>
</tr>
<tr>
<td>12</td>
<td>4.93</td>
<td>0.0267</td>
<td>9.71</td>
<td>16.01</td>
</tr>
<tr>
<td>13</td>
<td>2.546</td>
<td>0.09</td>
<td>5.67</td>
<td>8.04</td>
</tr>
<tr>
<td>14</td>
<td>2.171</td>
<td>0.09</td>
<td>8.61</td>
<td>10.11</td>
</tr>
<tr>
<td>15</td>
<td>3.171</td>
<td>0.09</td>
<td>11.13</td>
<td>11.01</td>
</tr>
<tr>
<td>16</td>
<td>4.3</td>
<td>0.09</td>
<td>10.01</td>
<td>11.89</td>
</tr>
<tr>
<td>17</td>
<td>5.27</td>
<td>0.09</td>
<td>9.96</td>
<td>11.71</td>
</tr>
<tr>
<td>18</td>
<td>2.171</td>
<td>0.069</td>
<td>6.27</td>
<td>7.2</td>
</tr>
<tr>
<td>19</td>
<td>6.07</td>
<td>0.069</td>
<td>11.05</td>
<td>12.7</td>
</tr>
<tr>
<td>20</td>
<td>3.31</td>
<td>0.069</td>
<td>7.75</td>
<td>8.77</td>
</tr>
<tr>
<td>21</td>
<td>4.564</td>
<td>0.069</td>
<td>8.86</td>
<td>10.29</td>
</tr>
<tr>
<td>22</td>
<td>2.17</td>
<td>0.024</td>
<td>6.79</td>
<td>7.06</td>
</tr>
<tr>
<td>23</td>
<td>2.85</td>
<td>0.024</td>
<td>7.87</td>
<td>8.35</td>
</tr>
<tr>
<td>24</td>
<td>4.3</td>
<td>0.024</td>
<td>9.94</td>
<td>10.63</td>
</tr>
<tr>
<td>25</td>
<td>5.27</td>
<td>0.024</td>
<td>10.4</td>
<td>11.08</td>
</tr>
</tbody>
</table>

(1) \( K_G \) calculated by assuming no back pressure of ammonia over the phosphate solution.
(2) \( K_G \) calculated by assuming the Henry's law constant for \( \text{NH}_3 \)-\( \text{H}_2\text{O} \) applied.
(3) \( K_G \) calculated by assuming no concentration effect existed.

\[
\Delta P_{lm} = \frac{(P_1-P_{e1}) - (P_2-P_{e2})}{\ln \frac{P_1-P_{e1}}{P_2-P_{e2}}} \tag{14}
\]

where \( p \) = partial pressure of the solute gas in the entering gas stream.
EXPLANATION OF PLATE IX

Effect of Gas velocity on the Overall Transfer Coefficient, $K_G$, for the Absorption of $\text{NH}_3$ in ($\text{NH}_4\text{H}_2\text{PO}_4$) solution.

Ordinate: Overall transfer coefficient, $K_G$, lbs./(hr.) (sq.ft.) (atm.)

Abscissa: Gas velocity, $V$, ft./sec.

Fig. 1. Solution concentration 0.069 M.
Liquid rate 3/lbs. hr.

Fig. 2. Solution concentration 0.024 M.
Liquid rate 30 lbs./hr.

Legend:

☐: Assuming no back pressure of $\text{NH}_3$ over the solution.

○: Assuming the Henry's law constant for $\text{NH}_3\cdot\text{H}_2\text{O}$ applies.

△: Assuming no concentration effect.

Solid line: Data on the absorption of $\text{NH}_3$ in $\text{H}_2\text{O}$. 
Figure 1.

Figure 2.
EXPLANATION OF PLATE X

Effect of Gas velocity on the Overall Transfer Coefficient, $K_g$, for the Absorption of $\text{NH}_3$ in $\text{(NH}_4\text{)}_2\text{HPO}_4$ solution

**Ordinate:** Overall transfer coefficient, $K_g$, lbs./(hr.)(sq. ft.)(atm.)

**Abscissa:** Gas velocity, $V$, ft./sec.

**Fig. 3.** Solution concentration 0.262 M.
Liquid rate 30 lbs./hr.

**Fig. 4.** Solution concentration 0.09 M.
Liquid rate 31.4 lbs./hr.

**Legend:**

- $\square$: Assuming there is no back pressure of $\text{NH}_3$ over the solution.
- $\bullet$: Assuming the Henry's law constant for $\text{NH}_3-\text{H}_2\text{O}$ applies.
- $\triangle$: Assume no concentration effect.

**Solid line:** Data of the absorption of $\text{NH}_3$ in $\text{H}_2\text{O}$.
Figure 3.

Figure 4
EXPLANATION OF PLATE XI

Effect of Gas velocity on the Overall Transfer Coefficient, \( K_G \), for the Absorption of \( \text{NH}_3 \) in \( (\text{NH}_4)_2\text{PO}_4 \) Solution.

Ordinate: Overall transfer coefficient, \( K_G \), lbs./(hr.) (sq.ft.) (atm.)

Abscissa: Gas velocity, \( V \), ft./sec.

Fig. 5. Solution concentration 0.1 M
Liquid rate 30.4 lbs./hr.

Fig. 6. Solution concentration 0.06 M.
Liquid rate 30.4 lbs./hr.

Legend:

\( \Delta \): Assuming no \( \text{NH}_3 \) back pressure over the solution.

\( \circ \): Assuming the Henry's law constant for \( \text{NH}_3-\text{H}_2\text{O} \) applies.

Solid line: Data of the absorption of \( \text{NH}_3 \) in \( \text{H}_2\text{O} \).
Figure 5.

Figure 6.
EXPLANATION OF PLATE XII

Effect of Gas Rate on the Overall Transfer Coefficient, $K_G$, for the Absorption of $NH_3$ in
\((NH_4)_2PO_4\).

Ordinate: Overall transfer coefficient, $K_G$, lbs./ (hr.) (sq.ft.) (atm.)

Abscissa: Gas velocity, $V$, ft./sec.

Solution concentration 0.154 M.

Liquid rate 30 lbs./hr.

Legend:

△: Assuming no back pressure of $NH_3$ over the solution.

○: Assuming the Henry's law constant for $NH_3$-$H_2O$ applies.

Solid line: Data of the absorption of $NH_3$ in $H_2O$. 
\[ p_2 = \text{partial pressure of the solute gas in the leaving gas stream.} \]

\[ p_{e1} = \text{equilibrium partial pressure of the solute gas over the liquid stream, leaving.} \]

\[ p_{e2} = \text{equilibrium partial pressure of the solute gas over the entering liquid stream.} \]

\[ p_{e1} \text{ and } p_{e2} \text{ are expressed by the following equations (15) and (16):} \]

\[ p_{e1} = HC_2 \quad (15) \]

\[ p_{e2} = HC_1 \quad (16) \]

\[ C_1 \text{ and } C_2 \text{ are the entering liquid concentration and outlet liquid concentration respectively. } H \text{ is the Henry's law constant.} \]

When the initial concentration of the liquid is high, \( p_{e2} \) is relatively large as compared with \( p_2 \). This makes the value of \( \ln \frac{p_1-p_{e1}}{p_2-p_{e2}} \) large and the mean driving force \( \Delta p_{1m} \) small. Since \( K_G \) is inversely proportional to the mean driving force, values of \( K_G \) calculated on this basis become unusually high.

**Effect of Liquid Rate:** Values of \( K_G \) calculated on both assumptions are given in Tables 5 and 6 and plotted versus liquid rate in Plates XIII and XIV. The slope of these straight lines appear to be nearly the same.

As may be expected from Hatta's theory, the numerical value of the ratio \( K_G/K_{G(H_2O)} \) (where \( K_G \) is the overall transfer
coefficient for the absorption of ammonia in phosphate solution and \( K_{G(H_2O)} \) is that for water) depends on the concentration of the liquid, the gas rate and the liquid rate. The liquid film resistance becomes small as the liquid rate increases. Since the only effect of the presence of chemical compounds is to reduce the resistance offered by the liquid film, the effect of concentration on the value of \( K_G/K_{G(H_2O)} \) is less pronounced at the high liquid rate than that at low liquid rate. This observation was also made by Doherty and Johnson. The absence of this tendency in this experiment may be attributed to the fact that the liquid rate was not high enough.

**Effect of Concentration:** The data shown in Plates IX, X, XIV indicate that all values of \( K_G \) for the absorption of ammonia by di-ammonium phosphate solutions calculated on the assumption of no back pressure of ammonia are less than those for the absorption of ammonia in water, while those calculated using the Henry's law constant for the ammonia-water system are well above those for water. Since these represent the two extremes the true values of \( K_G \) should lie between these two limits. An assumption was made that the presence of di-ammonium phosphate has no effect at all. The absorption mechanism itself in this case is essentially the same as in the absorption of ammonia by water and the solubility of ammonia in the phosphate solution is the same as that in water. The values of \( K_G \) s calculated on this basis were in most cases, nearly the same as those for water. The values of \( K_G \) calculated this way are also given in Tables 5 and 6 and plotted against the gas velocity in Plates XV and XVI.
Table 5. Effect of Liquid rate on $K_g$ for the absorption of ammonia in di-ammonium phosphate solution. Gas rate, 2.171 ft./sec. Temperature corrected to 20° C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Liquid Rate (lbs./hr.)</th>
<th>Concentration (Moles/liter)</th>
<th>Overall transfer coefficient $K_g$ (lbs./(hr.) (ft.))</th>
<th>$K_g$ (lbs./(hr.) (sq.ft.)) (atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>233</td>
<td>0.1</td>
<td>6.51</td>
<td>8.19</td>
</tr>
<tr>
<td>2</td>
<td>322</td>
<td>0.1</td>
<td>7.98</td>
<td>11.18</td>
</tr>
<tr>
<td>3</td>
<td>169</td>
<td>0.1</td>
<td>5.7</td>
<td>7.14</td>
</tr>
<tr>
<td>4</td>
<td>109</td>
<td>0.1</td>
<td>4.27</td>
<td>5.26</td>
</tr>
</tbody>
</table>

(1) $K_g$ calculated by assuming no back pressure of ammonia over the phosphate solution.
(2) $K_g$ calculated by assuming the Henry's law constant for $NH_3-H_2O$ applies.
(3) $K_g$ calculated by assuming no concentration effect existed.

Table 6. Effect of liquid rate on $K_g$ for the absorption of ammonia in Monoammonium phosphate solution. Constant gas rate 3.34 ft./sec. Temperature corrected to 20° C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Liquid Rate (lbs./hr.)</th>
<th>Concentration (Moles/liter)</th>
<th>Overall transfer coefficient $K_g$ (lbs./(hr.) (sq.ft.))</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>236</td>
<td>0.0563</td>
<td>8.03</td>
</tr>
<tr>
<td>13</td>
<td>331</td>
<td>0.0563</td>
<td>10.05</td>
</tr>
<tr>
<td>14</td>
<td>175</td>
<td>0.0563</td>
<td>7.76</td>
</tr>
<tr>
<td>15</td>
<td>111</td>
<td>0.0563</td>
<td>5.46</td>
</tr>
<tr>
<td>16</td>
<td>236</td>
<td>0.093</td>
<td>9.52</td>
</tr>
<tr>
<td>17</td>
<td>299</td>
<td>0.093</td>
<td>9.92</td>
</tr>
<tr>
<td>18</td>
<td>164.5</td>
<td>0.093</td>
<td>7.74</td>
</tr>
<tr>
<td>19</td>
<td>109.3</td>
<td>0.093</td>
<td>5.95</td>
</tr>
</tbody>
</table>

(1) $K_g$ calculated by assuming no back pressure of ammonia over the phosphate solution.
(2) $K_g$ calculated by assuming the Henry's law constant for $NH_3-H_2O$ applies.
Effect of Liquid Rate on the Overall Transfer Coefficient for the absorption of NH\textsubscript{3} in (NH\textsubscript{4})\textsubscript{2}PO\textsubscript{4} Solution.

Ordinate: Overall transfer coefficient, \( K \), lbs./(hr.) (sq.ft.) (atm.)

Abscissa: Liquid rate, \( \dot{F} \) lbs./(hr.) (ft.)

Fig. 7. Solution concentration 0.093 M.
Gas velocity 3.32 ft./sec.

Fig. 6. Solution concentration 0.0563 M.
Gas velocity 3.32 ft./sec.

Legend:

\( \Delta \) : Assuming no back pressure of NH\textsubscript{3} over the solution.

\( \circ \) : Assuming the Henry's law constant for NH\textsubscript{3}-H\textsubscript{2}O applies.

Solid Line: Data on the absorption of NH\textsubscript{3} in H\textsubscript{2}O.
Figure 7.

Figure 8.
EXPLANATION OF PLATE XIV

Effect of Liquid Rate on the Overall Transfer Coefficient for the Absorption of NH₃ in (NH₄)₂HPO₄ Solution.

Ordinate: Overall transfer coefficient, K, lbs./ (hr.) (sq.ft.) (atm.)

Abscissa: Liquid rate, √r’, lbs./ (hr.) (ft.)

Solution concentration 0.1 M.
Gas velocity 3.32 ft./sec.

Legend:

□: Assuming there is no back pressure of NH₃ over the solution.
△: Assuming the Henry's law constant for NH₃-H₂O applies.
○: Assuming no concentration effect.

Solid Line: Data of the absorption of NH₃ in H₂O.
EXPLANATION OF PLATE XV

Plot of $K_G$ versus gas velocity, $V$, at various Concentration Levels for the Absorption of Ammonia in $(\text{NH}_4)_2\text{HPO}_4$ Solution.

Ordinate: Overall transfer coefficient, $K_G$, lbs./hr. (sq.ft.) (atm.)

Abscisca: Gas velocity, $V$, ft./sec.

Experimental conditions

Liquid rate: 30 lbs/hr.

Temperature corrected to 20°C.

Legend:

- $0.262$ M.
- $0.09$ M.
- $0.069$ M.
- $0.024$ M.

Remark: $K_G$ calculated on the basis that there is no concentration effect.
EXPLANATION OF PLATE XVI

Effect on Concentration on the Overall Transfer Coefficient, $K_o$, for the absorption of Ammonia in $(NH_4)H_2PO_4$ Solution.

Ordinate: Overall transfer coefficient, $K_o$, lbs./(hr.)(sq.ft.)(atm.)

Abscissa: Concentration $C$, M./liter

Liquid rate: 30 lbs./hr.

Gas velocity:

Curve I 6.07 ft./sec.
Curve II 4.3 ft./sec.
Curve III 2.17 ft./sec.

Remark: $K_o$ calculated on the assumption that there was no concentration effect.
Apparently liquid concentration has no effect on the film coefficients determined in this way.

For the absorption of ammonia in mono-ammonium phosphate solutions, values of $K_G$ calculated on both limiting conditions (a) and (b) as stated before, are greater than those for water in most cases. The effect of concentration on $K_G$ and $K_G$ is shown in Plates XVII and XVIII.

According to Hatta's theory, when the concentration is below a certain value, the relation between concentration and $K_G$ is linear. Values of $K_G$ calculated by using the solubility data of ammonia in water do show this tendency. However, $K_G$ calculated on the assumption that there is no back pressure, does not show this characteristic.

The difference in behavior of these two similar compounds can be explained by the fact that the pH of the di-ammonium salt solution was about 7.5, which is similar to water, while the mono-ammonium salt solution was slightly acidic. The absorption of ammonia in water can be expressed as:

$$\text{NH}_3 \rightarrow \text{NH}_3^{aq}$$

$$\text{NH}_3^{aq} + \text{H}_2\text{O} \rightarrow \text{NH}_4^{+} + \text{OH}^{-}$$

The first step is simply physical equilibrium, while the second one involves chemical reaction. When the liquid used for absorption is acidic, the equilibrium will tend to shift from left to right. This results from the neutralization between hydrogen ion and hydroxyl ion. The result is that more ammonia is absorbed.
EXPLANATION OF PLATE XVII

Effect of Concentration on the Overall Transfer Coefficient, $K_g$, for the absorption of Ammonia in (NH$_4$)$_2$PO$_4$ Solution.

Ordinate: Overall transfer coefficient, $K_g$, lbs./ (hr.) (sq.ft.) (atm.)

Abscissa: Concentration, $C$, moles/liter

Liquid rate: 30 lbs./hr.

Gas velocity:

Curve I  4.5 ft./sec.
Curve II  3 ft./sec.
Curve III 2.5 ft./sec.

Remark: $K_g$ calculated using Henry's law constant for NH$_3$-H$_2$O.
EXPLANATION OF PLATE XVIII

Effect of Concentration on the Overall Transfer Coefficient, $K_G$, for the Absorption of Ammonia in $(NH_4)_2PO_4$ Solution.

Ordinate: Overall transfer coefficient, $K_G$, lbs./ (hr.) (sq.ft.) (atm.)

Abscissa: Concentration, $C$, moles/liter

Liquid rate: 30 lbs./hr.

Gas velocity:

Curve I  4.5 ft./sec.
Curve II  3 ft./sec.
Curve III 2 ft./sec.

Remark: $K_G$ calculated on the assumption of not back pressure of NH$_3$ over the solution.
The actual mechanism is by no means so simple, because it involves a series of equilibrium systems. However, this kind of reaction can be considered as a neutralization reaction between an acid and a base. As far as neutralization is concerned, the most important factors are the hydrogen ion concentration and the hydroxyl ion concentration. The higher values of $K_G$ for the absorption of ammonia is mono-ammonium phosphate solution compared with those for water can be explained by the fact that the mono-ammonium salt solution is slightly acidic. Along this line of reasoning, it is expected that if some other substances like $\text{Na} (\text{NH}_4)^+\text{HPO}_4$ or $\text{Na} (\text{NH}_4)^2\text{PO}_4$ are used for the absorption of ammonia, the corresponding values of $K_G$ should be less than these for water. This prediction is shown in Plate XIX.

CONCLUSIONS

The results of the present work and the conclusions derived therefrom are summarized as follows:

1. The liquid film coefficient for the absorption of chlorine in water was determined. It was shown that $k_L$ varies with 0.81 power of the liquid rate. This exponent is lower than that for the absorption of carbon dioxide in water. This is consistent with the previous work of Vivian and Whitney (14). The following empirical equation was obtained:

$$k_L = 0.01163 \phi^{0.81}$$

2. It was found that the numerical value of $K_G$ for the
EXPLANATION OF PLATE XIX

Prediction of the Overall Transfer Coefficient, $K_G$, for the absorption of $NH_3$ in different solutions

Ordinate: Overall transfer coefficient, $K_G$, lbs./ (hr.) (sq.ft.) (atm.)

Abscissa: Gas velocity, G ft./sec.

Curve I  \((NH_4)_2HPO_4\)
Curve II \((NH_4)_2HP0_4\)
Curve III \(Na(NH_4)HP0_4\)
Curve I \(Na_2HP0_4\)
absorption of ammonia in di-ammonium orthophosphate solution is essentially the same as that in water. No concentration effect was observed.

3. The absorption of ammonia in mono-ammonium phosphate solution was also studied. The liquid rate effect and the gas rate effect seem to be nearly the same as that for water. It was also shown that $K_g$ does increase with an increase in concentration.
ACKNOWLEDGMENTS

The author wishes to express his gratitude to the Kansas State College Engineering Experiment Station for the financial assistance which made this research possible, and to:

Dr. S. L. Wang and Henry T. Ward for their advice and encouragement during the course of this work,

Professor William H. Honstead for his guidance during the writing of the thesis,

The Chemical Engineering Department as a whole for the use of material and equipment.
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Paper trade J. No. 10, 31 1941. Reported by Vivian, J. E.
and R. P. Whitney (14).
Table 1. Absorption of Chlorine into water at varied gas rate.

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Table 2. Liquid-film coefficient for the absorption of chlorine into water at varied liquid rate.

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<td>ŵ₁̂ (lbs./(sq. ft.) (hr.))</td>
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<td>1.7974</td>
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**Table 3. Overall coefficient for the absorption of ammonia into diammonium hydrogen phosphate solution.**

*Assuming no back pressure of NH3 over the solution.*

**Assuming the Henry's law constant for NH3-NH4 applies.**

**Assuming no concentration effect.**
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<td>20.4</td>
<td>30.4</td>
<td>50</td>
<td>30.4</td>
<td>20.4</td>
<td>50</td>
<td>20.4</td>
<td>30.4</td>
<td>20.4</td>
<td>50</td>
<td>20.4</td>
<td>50</td>
<td>30.4</td>
<td></td>
</tr>
<tr>
<td>(lbs./hr.ft.)</td>
<td>253</td>
<td>253</td>
<td>253</td>
<td>253</td>
<td>253</td>
<td>253</td>
<td>253</td>
<td>253</td>
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<td>253</td>
<td>253</td>
<td>253</td>
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<td></td>
</tr>
<tr>
<td>Gas rate Q (cfm/hr)</td>
<td>10.74</td>
<td>9.78</td>
<td>40.05</td>
<td>28.93</td>
<td>44.99</td>
<td>29.45</td>
<td>28.93</td>
<td>40.05</td>
<td>31.28</td>
<td>20.78</td>
<td>31.28</td>
<td>43.11</td>
<td>32.90</td>
<td>32.90</td>
<td>43.11</td>
<td>32.90</td>
<td>32.90</td>
<td>43.11</td>
<td></td>
</tr>
<tr>
<td>(ft./sec)</td>
<td>2.008</td>
<td>1.07</td>
<td>4.678</td>
<td>2.33</td>
<td>6.045</td>
<td>3.566</td>
<td>2.16</td>
<td>11.1</td>
<td>11.17</td>
<td>4.49</td>
<td>5.24</td>
<td>5.24</td>
<td>5.24</td>
<td>5.24</td>
<td>5.24</td>
<td>5.24</td>
<td>5.24</td>
<td>5.24</td>
<td></td>
</tr>
<tr>
<td>Lit. comp. (Hg)</td>
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<td>0.154</td>
<td>0.154</td>
<td>0.154</td>
<td>0.154</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
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<td>0.0663</td>
<td>0.0663</td>
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<tr>
<td>(kg grams/100 grams soln)</td>
<td>0.84</td>
<td>0.84</td>
<td>0.84</td>
<td>0.84</td>
<td>0.84</td>
<td>1.04</td>
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<td>1.04</td>
<td>0.76</td>
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</tr>
<tr>
<td>Outlet</td>
<td>0.368</td>
<td>0.4</td>
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<td>0.368</td>
<td>0.368</td>
<td>0.19</td>
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</tr>
<tr>
<td>Gas composition (Hg lb./ft. of air)</td>
<td>0.0619</td>
<td>0.0619</td>
<td>0.0619</td>
<td>0.0619</td>
<td>0.0619</td>
<td>0.188</td>
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<tr>
<td>Inlet</td>
<td>0.0048</td>
<td>0.0048</td>
<td>0.0048</td>
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</tr>
<tr>
<td>Outlet</td>
<td>720.1</td>
<td>725.8</td>
<td>725.1</td>
<td>721.4</td>
<td>720.8</td>
<td>720.3</td>
<td>720.8</td>
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<tr>
<td>Gas pressure (psig)</td>
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<td>721.7</td>
<td>721.7</td>
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<td>721.7</td>
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</tr>
<tr>
<td>Inlet</td>
<td>10.3</td>
<td>10.3</td>
<td>10.3</td>
<td>10.3</td>
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<td></td>
</tr>
<tr>
<td>Kg. (lbs/hr)(sq.ft.)(atm)</td>
<td>10.03</td>
<td>10.05</td>
<td>10.05</td>
<td>10.05</td>
<td>10.05</td>
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</tr>
</tbody>
</table>
Sample Calculation

A. Absorption of Chlorine in Water

Run No. 3

Observed data:

Liquid Rate
\[ W = 38.1 \text{ lb./hr. or } 16.86 \text{ l./hr.} \]
\[ = 300 \text{ lbs./hr. ft.} \]

Liquid Concentration
Inlet \( X_1 = 0 \)
Outlet \( X_2 = 2.224 \) gram Cl\(_2\) per liter

Liquid Temperature
Inlet 23.5° C.
Outlet 24° C.

Atmospheric Pressure = 740.1 mm Hg
Room Temperature = 27° C.

Manometer Reading
Column Inlet 2.2 mm Hg
Column Outlet 1.6 mm Hg

Absorption Surface = 0.22 sq. ft.

Calculation:

Corrected Pressure = 740.1 - 27 (0.128) = 736.6 mm Hg

Partial Pressure of Chlorine
Inlet = 736.6 - 2.2 = 734.8 mm Hg = 0.972 atm
Outlet = 736.6 - 1.6 = 735.0 mm Hg = 0.971 atm

Interfacial Equilibrium Pressure
Inlet = 6.64 grams of Cl\(_2\) per liter
Outlet = 6.55 grams of Cl\(_2\) per liter

Mean Driving Force is calculated from the following equation:

\[ \Delta C_{im} = \frac{(6.64 - 2.224) - 6.55}{6.55} = 5.4014 \text{ g/l} \]

\[ h_L = \frac{W (X_2 - X_1)}{A \Delta C_{im}} = \frac{22.44 \times 16.86}{0.22 \times 5.4014} = 31.8 \text{ g/ft.}^2 \]

Since

\[ \lambda_L \propto e^{a2.17} \]

\[ \lambda_L \text{[corrected to } 20^\circ] = 1.125 \times 1.523^{1.65} = 1.036 \text{ ft} \]

In the calculation of pseudo transfer coefficient, only the difference of molecule chlorine concentration can be counted as
driving force and molecule concentration of chlorine was calculated by the following equation:

\[ C = Hf \]

Values of \( C \) are given by Whitmey and Vivian.

The interfacial equilibrium concentrations were found as follows:

<table>
<thead>
<tr>
<th></th>
<th>Inlet</th>
<th>Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_1 )</td>
<td>5.342 grams of ( Cl_2 ) per liter</td>
<td>5.336 grams of ( Cl_2 ) per liter</td>
</tr>
</tbody>
</table>

Mean driving force

\[ \Delta C_m = \frac{(5.342 - 2.244) - 5.336}{1.18} = 4.18 \]

\[ \bar{q}_L = \frac{2.244 \times 16.86}{4.18 \times 0.22} = 40.9 \text{ grams/}(\text{hr.} \times \text{sq. ft.}) \frac{7}{4} \]

\[ = 145 \text{ lbs/}(\text{hr.} \times \text{sq. ft.}) \frac{18}{60} \text{ ft} \]

\[ \bar{q}_L \text{(Corrected to 20\text{C})} = 1.3598 \]

B. Absorption of Ammonia in Phosphate Solution

Run No. 9 in Table 3

Observed data:

Absorption Surface = 0.22 sq.ft.
Liquid rate = 29.6 lbs./hr. = 235 lbs./hr. ft.
Gas rate
   Air rate 0.34 cu.ft./min. of \( G = 1.53 \) lbs./hr.
   \( NH_3 \) rate 0.0161 cu.ft./min.
Liquid concentration
   \( (NH_4)_2 \) \( HPO_4 \) = 0.262 M./liter
   \( NH_3 \) (reported as grams N per 100 grams of solution)
   Inlet 0.712
   Outlet 0.802
Mean liquid temperature = 24.5\text{C}.
Barometric pressure = 737 mm Hg
Room temperature = 23\text{C}.
Manometer reading
   Column Inlet = 0.58 mm Hg
   Column Outlet = 0.3 mm Hg
Calculation:

Corrected pressure = 737 mm Hg - 23(0.1197) = 734.2 mm Hg

Inlet gas concentration \( \gamma_1 = \frac{0.0161 \times 0.0442}{0.34 \times 0.075} = 0.0279 \text{ lb. of} \quad \text{NH}_3 \text{ per lb. of air} \)

By material balance

\[ W (x_2 - x_1) = G (\gamma_1 - \gamma_2) \]
\[ x_2 - x_1 = (0.802 - 0.712) \times \frac{17}{14} \times \frac{1}{1000} = 0.001093 \text{ lb. of} \quad \text{NH}_3 \text{ per lb. of water} \]

\[ 29.6 \times 0.001093 = 1.53 (0.0279 - \gamma_2) \]
\[ \gamma_2 = 0.0067 \text{ lb. of} \quad \text{NH}_3 \text{ per lb. of air} \]

Partial pressure of \text{NH}_3 at inlet

\[ (734.2 + 0.5) \times \frac{0.0161}{0.34 + 0.0161} = 35.22 \text{ mm Hg} \]

Partial pressure of \text{NH}_3 at outlet

\[ (734.2 + 0.33) \times \frac{0.0067/17}{1/29 + 0.0067/17} = 8.3 \text{ mm Hg} \]

Mean driving force

(1) Assume there is no back pressure

\[ p_{1m} = \frac{35.22 - 8.3}{\ln \frac{35.22}{8.3}} = 16.83 \text{ mm Hg} \]

(II) Assume the solubility of ammonia in phosphate solution is the same as that in water

\[ \log \frac{p'}{c} = 4.699 - \frac{3460}{T,^\circ \text{R}} \]

where \( p' = \text{equilibrium partial pressure of ammonia in atm} \)

\( c = \text{concentration of ammonia in molality} \)

now \( T = 24.5^\circ \text{C.} \), or \( 536.1^\circ \text{R} \)

\[ \log \frac{p'}{c} = 4.699 - \frac{3460}{536.1} = 2.244 \]
\( p' = 0.01754 \text{ C} \)

**Interfacial equilibrium pressure**

- **Inlet**
  \[ P_{\text{in}} = 0.01754 \times 760 \times 0.802 \times \frac{1}{14} \times \frac{1}{100} \times 1000 \]
  \[ = 7.64 \text{ mm Hg} \]

- **Outlet**
  \[ P_{\text{out}} = 0.01754 \times 760 \times 0.702 \times \frac{1}{14} \times \frac{1}{100} \times 1000 \]
  \[ = 6.78 \text{ mm Hg} \]

\[ P_{\text{lm}} = \left( \frac{35.22 - 7.64}{8.3 - 6.78} \right) \times 760 \]

\[ = 0.01183 \text{ atm} \]

(III) Assume the presence of \((NH_4)_2\)HPO_4 has no effect

\[ P = 0.01754 \times 0 \text{ C} \]

**Interfacial equilibrium pressure**

- **Inlet**
  \[ P_{\text{in}} = 0.01754 \times 760 \times (0.802 - 0.712) \times \frac{1}{14} \times \frac{1}{100} \times 1000 \]
  \[ = 0.86 \text{ mm Hg} \]

- **Outlet**
  \[ P_{\text{out}} = 0 \]

\[ \Delta P_{\text{lm}} = \left( \frac{35.22 - 0.86}{8.3} \right) = 18.34 \text{ mm Hg} = 0.0241 \]

**Overall transfer coefficient** \( K_G \) were calculated by the following equation:

\[ K_G = \frac{W(X_2 - X_1)}{A \Delta P_{\text{lm}}} \]

For case I

\[ K_G = \frac{29.6 \times 0.001093}{0.0245 \times 0.22} = 6.01 \text{ lbs./}(\text{hr.})(\text{sq.ft.})(\text{atm}) \]

For case II

\[ K_G = \frac{29.6 \times 0.001093}{0.01183 \times 0.22} = 12.44 \text{ lbs./}(\text{hr.})(\text{sq.ft.})(\text{atm}) \]
For case III

\[ K_G = \frac{29.6 \times 0.00109}{0.0241 \times 0.22} = 6.11 \text{ lbs.} / (\text{hr.})(\text{sq. ft.})(\text{atm}) \]

Since

\[ K_G = 24.3 - 0.175t \]

\[ t = 24.5^\circ \text{ C} \]

Take 20^\circ \text{ C.} as reference, the temperature correction factor equals

For case I \[ K_G = 6.25 \text{ lbs.} / (\text{hr.})(\text{sq. ft.})(\text{atm}) \]

For case II \[ K_G = 12.44 \text{ lbs.} / (\text{hr.})(\text{sq. ft.})(\text{atm}) \]

For case III \[ K_G = 6.35 \text{ lbs.} / (\text{hr.})(\text{sq. ft.})(\text{atm}) \]

### Principal Constants of the Disc Column

<table>
<thead>
<tr>
<th>Number of discs</th>
<th>32</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter of the disc</td>
<td>1.5 cm (0.594 inch)</td>
</tr>
<tr>
<td>Thickness of the disc</td>
<td>0.48 cm (0.188 inch)</td>
</tr>
<tr>
<td>Diameter of the Pyrex column</td>
<td>1 1/8 inches</td>
</tr>
<tr>
<td>Mean perimeter for liquid flow</td>
<td>0.127 ft.</td>
</tr>
<tr>
<td>Equivalent diameter for gas flow</td>
<td>0.059 ft.</td>
</tr>
<tr>
<td>Absorption surface*</td>
<td>0.22 sq. ft.</td>
</tr>
</tbody>
</table>

* Dry basis.

### Nomenclature

- **A** = absorption surface area, sq. ft.
- **C** = contraction of solute gas in liquor
- **C_e** = interfacial equilibrium concentration of solute gas in liquid
- \( \Delta C_{\text{lm}} \) = logarithmic driving force expressed in concentration term
- **G** = mass rate of air, lbs./hr.
- **H** = Henry's law constant, defined by \( \phi = HC \)
$K_G$ = overall transfer coefficient $\text{lbs.} / (\text{hr.})(\text{sq. ft.})(\text{atm})$

$k_G$ = gas film transfer coefficient $\text{lbs.} / (\text{hr.})(\text{sq. ft.})(\text{atm})$

$K_L$ = overall transfer coefficient $\text{lbs.} / (\text{hr.})(\text{sq. ft.})(\text{lbs. / cu. ft.})$

$k_L$ = liquid film transfer coefficient $\text{lbs.} / (\text{hr.})(\text{sq. ft.})(\text{lbs. / cu. ft.})$

$p$ = partial pressure of solute gas in the gas stream

$P_{12}$ = logarithmic driving force expressed in atm

$V$ = gas velocity $\text{ft. / sec.}$

$X_1$ = concentration of solute in inlet liquid $\text{lb. / lb.}$

$X_2$ = concentration of solute in effluent $\text{lb. / lb.}$

$Y_1$ = inlet gas concentration of $\text{lb. / lb.}$

$Y_2$ = outlet gas concentration $\text{lb. / lb.}$

$W$ = liquid rate, $\text{lbs. / hr.}$
GAS ABSORPTION WITH CHEMICAL REACTION

by

CHI TIEN

B. S., National Taiwan University, China, 1952

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1954
The purpose of this thesis was to study the absorption of ammonia into mono-ammonium orthophosphate solution as well as di-ammonium orthophosphate solution to further ascertain the gas-film characteristics of the disc column, a specially designed new type of laboratory column, which can be used as a versatile research tool for the study of gas absorption with chemical reactions.

The absorption of chlorine in water was also studied because of the pronounced hydrolyzing effect of dissolved chlorine in water. For this reason, attempts to correlate the chlorine-water system with other similar systems in which the liquid film also is the controlling resistance such as carbon dioxide and water, have resulted in failure.

The absorption of chlorine in water was carried out at liquid rates varying from 100 to 450 lbs./(hr.)(ft.) and gas rates varying from 1.5 to 5 ft./sec. The temperature ranged from 25° C. to 30° C. The liquid film coefficients determined from the experimental data did not vary with the gas rate, and were correlated with the water rate by the following equations:

\[ k_L = 0.01163 \sqrt{r^{0.81}} \]

by using the total chlorine concentration as driving force.

\[ k_{L2} = 0.01173 \sqrt{r^{0.855}} \]

by using the molecular chlorine concentration as driving force.

The absorption of ammonia in phosphate solutions was carried out at liquid rates varying from 100 to 350 lbs./(hr.)(ft.) and
gas rates varying from 2 to 6 ft./sec. The concentration of the entering phosphate solution varied from 0.024 to 0.26 moles/liter. Since the solubility of ammonia in phosphate solutions is not available, two assumptions were made: (a) That no back pressure of ammonia over the phosphate solution existed. (b) That the same solubility relationship existed between the ammonia-water system and the ammonia-phosphate system. Values of the overall transfer coefficients, $K_g$, were calculated on both assumptions.

It was shown that there is no concentration effect for the absorption of ammonia in diammonium phosphate solutions. There is some increase of the numerical value of $K_g$ with an increase of the solution concentration, but not to any great extent. This was expected because this system is one in which the gas film controls. This is also a verification of Hatta's theory for the absorption of gas in a liquid followed by a rapid irreversible reaction.