ABSTRACT<br>SOLUTE DISPERSION AND ADSORPTION IN LIQUID-SOLID CHROMATOGRAPHIC COLUMNS<br>by Yale S. Finkle

This research project was a continuation of previous work which had the overall objective of developing a reliable scale-up procedure for liquid-solid chromatographic columns. The purpose of this study was to evaluate and analyze values for equilibrium constants and mass transfer coefficients at various flow rates of a solute passing through a bed packed with an adsorbing material. It was assumed that the axial dispersed, plug flow model, with adsorption occurring, described the unsteady state chromatography process.

The pulse injection and response technique was used to calculate equilibrium constants and mass transfer coefficients. The axial dispersion coefficients were estimated from data of previous research in this area. Actual calculations were made from analyses of solute concentration versus time curves at two positions in the bed which was packed with irregularly shaped particles of a synthetic molecular sieve. A dilute aqueous solution of sodium chloride was used as the solute so that concentrations could be measured by electrolytic conductance.

The results of the work indicated that an equilibrium condition existed between the solute in the fluid phase and

Yale S. Finkle the solute on the packing surface. It was also found that the controlling factor in the adsorption process was mass transfer through the liquid-film resistance.

# SOLUTE DISPERSION AND ADSORPTION IN LIQUID-SOLID CHROMATOGRAPHIC 

 COLUMNS
## By

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## A THESIS

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TABLE OF CONTENTS
Page
ACKNOWLEDGMENTS ..... ii
LIST OF TABLES ..... v
LIST OF FIGURES ..... vi
INTRODUCTION ..... 1
PREVIOUS WORK ..... 2
THEORY ..... 6
Model of Dispersion in Adsorbing Bed ..... 6
Experimental Method ..... 10
APPARATUS AND PROCEDURE ..... 14
The Flow System ..... 14
Conductivity Cells ..... 16
Tracer Injection System ..... 16
Tracer Solution ..... 18
Packing Material ..... 18
Measuring and Recording Apparatus ..... 18
Liquid Level Control ..... 21
Determination of Void fraction ..... 23
Packing Procedure ..... 27
End Effects ..... 28
Run Procedure ..... 30
Analysis of Concentration-Time Distributions ..... 31

TABLE OF CONTENTS (Cont.)
Page
RESULTS AND DISCUSSION ..... 34
Calculation of Void Fraction ..... 34
Calculation of Dispersion Coefficients ..... 34
Calculation of Equilibrium Constants ..... 39
Calculation of Mass Transfer Coefficients ..... 44
Correlation of Mass Transfer Data ..... 46
Discussion of Mass Transfer Data ..... 49
Discussion of Errors in Experimental Pro- cedure and Data Analysis ..... 55
CONCLUSIONS ..... 58
RECOMMENDATIONS FOR FUTURE WORK ..... 59
APPENDIX A ..... 60
APPENDIX B ..... 65
NOMENCLATURE ..... 67
BIBLIOGRAPHY ..... 69

## LIST OF TABLES

Table Page
I. Void fraction data (Runs 3-14) ..... 35
II. Void fraction data (Runs 15-38) ..... 36
III. Data for runs 3-14 ( $\epsilon=0.4470$ ) ..... 40
IV. Data for runs $15-38 \quad(\epsilon=0.4454)$ ..... 41
V. Data from this work used for mass transfer correlation ..... 48
VI. Data of Al-Khudayri ..... 51
VII. Data of Resnick and White ..... 52
VIII. Data of Hurt ..... 54

## LIST OF FIGURES

Figure Page

1. Diagram of adsorbing bed ..... 6
2. Incremental length of bed ..... 7
3. The arrangement of $\mathrm{AlO}_{4}$ and $\mathrm{SiO}_{4}$ tetrahedra which yield open cavities in some zeolites ..... 11
4. Tetrahedral arrangement of truncated octa- hedra in zeolite type $X$ ..... 13
5. Model of the structure of zeolite type X based on packed oxygen atoms ..... 13
6. Schematic diagram of flow system ..... 15
7. Conductivity cell ..... 17
8. Specific conductance of sodium chloride at $25^{\circ} \mathrm{C}$ ..... 19
9. Schematic of electrical circuit for conductivity measurements ..... 20
10. Schematic of rectifying amplifying circuit ..... 22
11. Diagram of fritted glass joint ..... 26
12. Diagram of method employed for packing main section of column ..... 29
13. Typical concentration-time curves for cells 1 and 2 ..... 32
14. Hawley's and Gentile's data correlated by a plot of $4 \mathrm{MU} / \mathrm{D}_{\mathrm{v}}$ vs. $\mathrm{D} / \mathrm{D}_{\mathrm{V}}$ ..... 38
15. Equilibrium constants at various flow rates ..... 43
16. Mass transfer coefficients at various flow rates ..... 45
17. Correlated mass transfer data ..... 47

## INTRODUCTION

Liquid-solid chromatography has long been used as an analytical tool in the laboratory, and it is this use that we naturally associate with it. However, there has been an ever increasing use of liquid-solid chromatography as a separational technique and this has presented the problem of scaling-up an optimized laboratory column for industrial purposes.

At present, the general scale-up procedure for chromatographic columns is to first optimize a small laboratory column with respect to the pressure drop and time required to effect the separation and then to increase the cross sectional area of the column in proportion to the amount of material to be separated. This method of scale-up is not always precise and it would be highly desirable to determine exactly what factors in the chromatographic process actually influence the scale-up procedure. In an effort to reach this goal, a detailed study of the liquid-solid chromatography process has been undertaken.

The liquid-solid chromatography process can be visualized in the following manner. Consider a packed bed with a solvent running continuously through it. At some initial time zero a "pulse" containing the two components to be separated is injected uniformly into the bed. As the solvent carries the pulse through the bed, the components will separate from each other due to the difference in adsorptivities of the components upon the packing material. The length of the packed column needed to produce a particular separation depends upon the amount and relative difference in the adsorptivities of the components involved.

The chromatography process can be considered as a fluid flow process superimposed upon an adsorption-desorption process.

Hawley ${ }^{1}$ began the study of chromatographic separations by theoretically showing how the fluid flow and adsorption processes could be separated. Once this was accomplished, the fluid flow process was studied separately by employing inert, spherical, glass beads as the column packing. For this study the axial, dispersed, plug flow model was used to describe flow through the column packed with beads of uniform size. ${ }^{1}$

Since the scale-up procedure of taking the optimized laboratory column for a particular separation and increasing
its diameter in proportion to the amount of material to be passed through the column was frequently unsuccessful, it was decided ${ }^{1}$ to study the fluid flow process by determining which variables could cause the axial diffusivity to be a function of column diameter.

The pulse injection technique for determining the axial dispersion coefficients was used since it is the same injection technique used in liquid-solid chromatography. Aris ${ }^{2}$ has shown that when the aforementioned technique is employed, the axial dispersion coefficient can be determined from the following equation.

$$
\begin{equation*}
\frac{2 D}{U L}=\frac{\sigma_{2}^{2}-\sigma_{1}^{1}}{\mu_{2}-\mu_{1}} \tag{1}
\end{equation*}
$$

where
$\begin{aligned} \sigma_{n} & = \\ & \text { variance of concentration-time distribution at point } n(n=1 \text { or } 2) .\end{aligned}$
$\mu_{n}=\frac{\text { mean time of concentration-time distribution at }}{\text { measuring point } n(n=1 \text { or } 2) \text {. }}$
D = dispersion coefficient
$\mathrm{U}=$ interstitial velocity
L = length of column between measuring points.
The results of Hawley's study showed that in the absence of adsorption, the axial dispersion coefficient is independent of the column diameter and length, that viscous fingering ${ }^{1}$ is not an important consideration in chromatographic columns up to six inches in diameter even when the mobility ratio is as high as 100 , and that the axial dispersion coefficient is proportional to particle diameter.

Since the shape of the packing material is very irregular in chromatography, it was of interest to determine the effect of packing irregularity upon the dispersion coefficient. Gentile ${ }^{4}$ studied the fluid flow process in the same manner as Hawley. However, where as Hawley used uniform, spherical, glass beads as packing, Gentile used irregular glass particles obtained from crushing glass raschig rings. Gentile's results ${ }^{4}$ showed that for flow between one and one-hundred feet per hour and particle diameters of order of magnitude of $10^{-3}$ inches, the diffusivity increases as the shape of packing material becomes more random.

Up until Hawley began his study of dispersion in liquidsolid chromatographic columns, little effort had been funneled toward producing a suitable method for scaling-up chromatographic columns for industrial purposes. However, there was an extensive study, by many people, of axial dispersion of fluids flowing through porous media. Many theoretical models ${ }^{\mathbf{1}}$ were developed to describe flow of fluids through packed beds. Correlations dealing with the prominent variables have been developed and are useful in the scale-up of chromatographic separations.

The purpose of this research project is to study the entire chromatography process. That is, the fluid flow process occurring simultaneously with the adsorption process. Specificly, it is hoped that measurement and analyses of an equilibrium constant (if one exists for the system considered) and mass transfer coefficients obtained at
various flow rates will enable the determination of the best conditions under which the column should be operated. Ultimately, it is hoped that a scaled-up separation can be predicted by simply knowing the mass transfer chracteristics and values of the equilibrium constants associated with the components to be separated and the packing employed for the separation.

## THEORY

Basically, this research is simply a continuation of the work of Hawley and Gentile. The major difference being that the adsorption process was introduced into the experimental system by use of a packing which would hopefully simulate the adsorption-desorption phenomena.

The first part of this section will deal with the mathematical model of the chromatography process. The theory and reasoning behind the experimental method will also be examined.

Model of Dispersion in an Adsorbing Bed

Consider a bed packed with an adsorptive material and having two concentration measuring devices located at $\mathbf{X}_{\mathbf{1}}$ and $X_{2}$ (Figure 1).


> Figure 1. Diagram of adsorbing bed.

Solvent is continually flowing through the bed with a volumetric flow rate $W$. A pulse of tracer is injected into the bed at some point prior to $\mathbf{X}_{1}$ and is allowed to flow through the bed past $X_{2}$. Unsteady state adsorption is occurring in the bed along with solute dispersion.

The following assumptions are necessary:

1. The tracer is injected uniformaly across the bed.
2. The flow is uniform over the cross section of the bed.
3. The adsorption isotherm is linear.

Let $C_{A}$ be the average concentration of component $A$ of the tracer across a section of the column. Assume that the mass transfer by dispersion is proportional to the axial concentration gradient $\frac{\partial C_{A}}{\partial X}$. The proportionality constant is termed the axial dispersion coefficient $D$, and is the sum of the molecular diffusivity and the eddy diffusivity.

The equations describing the dispersion and adsorption in the packed bed are obtained by making a material balance on an incremental length of the packed bed as shown in Figure 2.


Figure 2. Incremental length of bed.

There are terms similar to the above which describe the input and output for components of the tracer other than $A$. A major assumption at this point, is that there are no interactions between the components of the tracer. For a two
component tracer, this would mean that component $B$ would not effect the isotherm of $A$ or vice versa.

The equations resulting from the material balance on component $A$ over the incremental length of the bed are as follows.

## Liquid Phase

$$
\begin{equation*}
\frac{\partial^{2} c_{A}}{\partial x^{2}}-\frac{W}{D \in A} \frac{\partial c_{A}}{\partial x}-\frac{K_{x} a}{D \epsilon}\left(c_{A}-c_{A i}\right)=\frac{1}{D} \frac{\partial c_{A}}{\partial t} \tag{2}
\end{equation*}
$$

Solid Phase

$$
\begin{align*}
\frac{K_{x} a}{1-\epsilon}\left(c_{A}-c_{A i}\right) & =\frac{\partial c_{A S}}{\partial t}  \tag{3}\\
C_{A S} & =m C_{A i} \tag{4}
\end{align*}
$$

where:

$$
\begin{aligned}
\mathrm{X} & =\text { axial distance } \\
\mathrm{t} & =\text { time } \\
\mathrm{W} & =\text { volumetric flow rate } \\
\mathrm{D} & =\text { axial dispersion coefficient } \\
\epsilon & =\text { void fraction of bed } \\
\mathrm{A} & =\text { cross sectional area of column } \\
\mathbf{K}_{\mathrm{X}} & =\text { mass transfer coefficient } \\
\mathrm{a} & =\text { solids transfer area per volume } \\
C_{A} & =\text { concentration of component } A \text { in the tracer } \\
C_{A i} & =\text { concentration of component } A \text { at the solid- } \\
C_{A S} & =\text { concentration of component } A \text { on the solid } \\
m & =\text { equilibrium constant defined by Equation }(4) .
\end{aligned}
$$

Equation (4) represents assumption (3) on page 7 .
The boundary conditions for the above problem are:

$$
\begin{array}{lll}
C_{A}=0 & \text { when } t=0 & \text { for } x>x_{1} \\
\text { at } x=x_{1} & C_{A}=C_{A O}(t) & \text { for } t>0 \\
\text { at } x=\infty & C(t)=\text { finite } & \text { for } t>0 . \tag{7}
\end{array}
$$

A restriction on $C_{A O}(t)$ is that it must be a "hump" function of time to represent a pulse input. ${ }^{1}$

The complete solution of Equations (2) through (7) for $C_{A}, C_{A S}$, and $C_{A i}$ is not obtainable in closed form. However, Hawley ${ }^{1}$ has shown, by employing some formal mathematical properties of the LaPlace Transform, that the complete solution is not necessary. Essentially, what happens is that the parameters of interest, $K_{x}, m$, and $D$, are related to the differences in variances and mean times of concentrationtime distributions at two positions in the bed. Hawley's results ${ }^{1}$ yield the following equations for an infinitely long bed in which both axial dispersion and adsorption are occurring.

$$
\begin{align*}
\mu_{2}-\mu_{1}=\frac{\epsilon A L}{W} & +\frac{1-\epsilon}{m W} A L  \tag{8}\\
\sigma_{2}^{2}-\sigma_{1}^{2}= & \frac{2 A L}{m^{2} K_{x} a} \frac{(1-\epsilon)^{2}}{W}+\frac{2 L}{W^{3}}(D \in A)^{3} \times  \tag{9}\\
& {\left[\frac{(1-\epsilon)}{\epsilon m D}+\frac{1}{D}\right] }
\end{align*}
$$

where:

$$
\begin{aligned}
L= & \text { distance between measuring points } \\
\mu_{1}= & \text { mean time of concentration-time distribution } \\
& \text { at measuring point } 1
\end{aligned}
$$

```
\mu
    at measuring point 2
\mp@subsup{\sigma}{1}{\prime}}\mp@subsup{}{}{2}=\mathrm{ variance of concentration-time distribution
    at measuring point 1
\mp@subsup{\sigma}{2}{2}}=\mathrm{ variance of concentration-time distribution
    at measuring point 2.
```


## Experimental Method

Since this project was a continuation of work started at Michigan State University, it was decided that the most efficient method of attacking the problem would be to employ the same general experimental apparatus and procedure as was used by Hawley ${ }^{1}$ and Gentile ${ }^{4}$. Thus the pulse tracer input method utilizing two measuring points in the column was employed. As was done previously, a dilute solution of sodium chloride was used as the tracer along with distilled water as the solvent.

It was desirable to find a type of packing which would introduce or simulate the adsorption phenomena in the experimental system. A synthetic zeolite (type "13-X") made by Linde Division of Union Carbide appeared to fit the necessary requirements. Type " $13-\mathrm{X}$ " is a member of a group of zeolites which are complex alumino-silicate compounds having the important characteristic of openness of the [(Al, Si) $\left.0_{2}\right]_{n}$ framework ${ }^{5}$ (Figure 3). This is the characteristic which makes possible their use as ion exchangers and selective adsorbants or "molecular sieves".


Pigure 3. The arrangement of $\mathrm{AlO}_{4}$ and $\mathrm{8iO}_{4}$ tetrahedra which yield open cavatien in some zeolites

The framework of the $x$ type zeolite consists of octahedra joined at the octahedral faces by hexagonal prisms (Figure 4). The corresponding structure of oxygen atoms is shown in Figure 5. The cations in type $X$ zeolite can occupy three types of positions. ${ }^{6}$

Type 1. in the center of the hexagonal prism, 16 sites per unit cell

Type 2. on the six membered rings, the unjoined hexagonal faces, 32 sites per unit cell

Type 3. on the walls of the channels, 48 sites per unit cell.

Type "13-X" is the sodium form of type $X$ zeolite and contains 86 cations per unit cell distributed in the three different sites.

The void spaces in the zeolite structure consist of elliptical cavities $13 \AA$ in length, entered by apertures of distorted, chair-shaped, 12 -membered rings which have a free diameter of $8 \AA^{6}$. The overall structure, as shown in Figure 5, is that of a densely packed structure of oxygen atoms which surrounds relatively large interstitial voids.

Zeolite type "13-x" was chosen for use in this research project in hopes that its structure and properties would simulate an adsorption process. Due to the relatively large cavities along with the ion exchange property of the zeolite, it was thought that the soidum ions would diffuse on and into the packing particles and exchange with the zeolite cations. This process would simulate the adsorptiondesorption phenomena by slowing the flow of sodium ions through the column.


Figure 4. Tetrahedral arrangement of truncated octahedra in zeolite type $X$.


Figure 5 Model of the structure of zeolite type $X$ based on packed oxygen atoms. The three types of cation sites are shown.

## APPARATUS AND PROCEDURE

The principle equipment required for this experimentation consisted of one-half inch diameter glass pipe for the column, conductivity cells and automatic recorder for measuring tracer concentration-time curves at two points in the column, a manometer for measuring pressure drops through the packed bed, and a photoelectric amplifier system for maintaining a constant liquid level above the packing.

## The Flow System (Figure 6)

The column was composed of various lengths of glass, pyrex pipe with flanged ends. In all cases, the inside diameter of the pipe was one-half inch. The main section of the column, which was placed between the two conductivity cells, was 18 inches long and had two extending side arms located three inches from each end. The side arms were 8 mm . in diameter and two inches long. A three-inch length of pipe was placed below the bottom conductivity cell and a 12 -inch length of pipe was located above the first cell. The tracer injection mechanism (see below) was located above the 12 -inch length and below the sixinch uppermost section of the column.

The solvent feed line and the outlet line were made of 1/4-inch diameter copper tubing. The outlet line began at the bottom of the column and was extended upward so that


Figure 6. Schematic diagram of flow system.
its end was near the level of the packing. Both a globe valve and a micrometer valve were located in the outlet line. The globe valve served to facilitate rapid on-off control of flow, while the micrometer valve was used to help set a desired flow rate. The solvent (water) feed line was connected directly into the tracer injection mounting.

The distilled water was stored in a 12 gallon, resincoated, steel tank. It was fed to the column by subjecting the storage tank to nitrogen pressure. Nitrogen was also used to pressurize the column when fast flow rates were desired.

Conductivity Cells (Figure 7)

The two conductivity cells were identical to those designed and used by Hawley ${ }^{1}$. The cells were machined from plexiglass to specifications indicated in Figure 7. The wire was No. 25 platinum wire.

Tracer Injection System (Figure 6)

The tracer was injected into the column via a 10 ml . Luer-Lok Syringe. The syringe receptacle extended from a four-inch long brass fitting located between the 18 -inch and 12 -inch long glass sections.

The mounting which received the syringe was stainless steel and extended two inches outward from the column. A small (between two and five mm. in diameter) stainless steel



Figure 7. Conductivity cell
tube joined the syringe mounting (Figure 6) from the inside of the brass section and extended approximately eight inches down the center of the 12 -inch glass pipe section. Thus, the tracer could be introduced into the column four inches above the first conductivity cell.

## Tracer Solution

The tracer was a 2 gram/liter aqueous solution of sodium chloride. Sodium chloride was used because its concentrations can be readily determined by electrolytic conductance. However, it must be remembered that a dilute solution of sodium chloride is necessary to insure that conductance is proportional to the concentration. Figure 8 shows that the specific conductance of sodium chloride is proportional to its concentration over the range 0 to 2,000 parts per million ( $2 \mathrm{~g} / 1$ ).

The value of the molecular diffusivity $D_{v}$ for a 0.5 molar solution of sodium chloride at $30^{\circ} \mathrm{C}$ is $1.84 \times 10^{-5}$ $\mathrm{cm}^{2} / \mathrm{sec} .7$.

## Packing Material

As mentioned previously, zeolite type "13-X" was used as packing. The zeolite was crushed in a mortar and pestle and screened to obtain the particles between 60 and 80 mesh.

## Measuring and Recording Appartus

Figure 9 shows a diagram of the circuit designed by Hawley ${ }^{1}$ to measure and record tracer concentrations as a function of time at the two conductivity cells. Actually the circuit is measuring conductance, but as shown in
$19$



Figure 8 for the tracer involved, the concentration is proportional to the conductivity.

The circuit was designed so that the voltage across resistor $R$ would be proportional to the reciprocal of the cell resistance $R_{c}$, and is given by

$$
\begin{equation*}
E=I R \tag{10}
\end{equation*}
$$

where

$$
\begin{equation*}
I=V /\left(R_{c}+R\right) \tag{11}
\end{equation*}
$$

If $R_{C}$ is much larger than $R$, then

$$
\begin{equation*}
E=V R / R_{C} \tag{12}
\end{equation*}
$$

However, since both $V$ and $R$ are constant, $E$ is proportional to $1 / R_{c}$.

The voltage source was a variable frequency audio oscillator. The A.C. voltage across $R$ was amplified, rectified, and measured with a Sargent Multi-Range Recorder.

A diagram of the rectifying-amplifying circuit is shown in Figure 10.

## Liquid Level Control

To make the operation of the experimental system as automatic as possible, a liquid level control device was desirable. In previous work ${ }^{1,4}$, the liquid level above the packing was controlled by the manual manipulation of valves.

A photoelectric-amplifier system connected to a solenoid valve located in the solvent feed line was used as the liquid level control. The system was purchased from Worner Electronic Devices Inc. and consisted of a Model 66-T Amplifier,

Figure 10. Schematic of rectifying amplifying circuit.
a Model 36 Exciter Lamp, and a Model 26 Photocell. The solenoid was a Hoke two way normally closed valve. This solenoid valve permitted flow only when energized.

The control system functioned in the following manner. The photoelectric cell (see Figure 6) was activated by the falling meniscus of the water (i.e. it interrupted the light beam through the column) and in turn opened the solenoid valve allowing solvent to enter the column and raise the level of the meniscus only slightly to above the photoelectric cell. Once the level of the meniscus passed above the photo cell, the light from the exciter lamp was transmitted through the water and activated the photo cell which closed the solenoid valve. This process was constantly repeated and thus kept the liquid level at the photo cell position.

## Determination of Void Fraction

The void fraction of the packed bed was calculated using the Blake-Kosney relationship ${ }^{8}$ :

$$
\begin{equation*}
\frac{\epsilon^{3}}{(1 \rightarrow \epsilon)^{2}}=\frac{150 V_{0} L \mu}{\Delta \operatorname{Pg}_{C} d^{2}(e f f)} \tag{13}
\end{equation*}
$$

where

$$
\begin{aligned}
d_{(e f f)}= & \text { effective diameter of packing particles, } \\
& \text { feet } \\
V_{0} \quad= & \text { superficial velocity of liquid through } \\
& \text { bed, ft/hr }
\end{aligned} \quad \begin{aligned}
\mu \quad= & \text { viscosity of flowing liquid, } \mathrm{lb} / f t-h r
\end{aligned}
$$

$$
\begin{aligned}
\Delta \mathrm{P}= & \text { pressure drop across packed bed, } \mathrm{lb} / \mathrm{ft}^{2} \\
\mathrm{~L}= & \text { length of packed bed across which } \Delta \mathrm{p} \text { is measured, } \\
& \text { feet } \\
\epsilon= & \text { void fraction of bed } \\
g_{C}= & \text { gravitational constant, (lb mass } \left.\sec ^{2}\right) /
\end{aligned}
$$

To determine the void fraction using Equation 13 it was necessary to measure the pressure drop through the bed and its corresponding superficial velocity. Once this was known, $\epsilon$ could be found by trial and error.

Since the packing was composed of irregular particles, it was necessary to define an effective particle diameter as the diameter a sphere would need to possess the same surface area as the irregular particle. ${ }^{4}$ Therefore, a bed of spheres having diameters equal to the effective diameter would have the same total surface area as the bed of irregular particles. The value for the effective diameter used in this work was the same value that Gentile used. ${ }^{4}$ This value was 0.00497 inch. Although Gentile used a different packing material, the effective diameters of the two packings were assumed to be nearly equal since both materials had been screened into the same size range ( $60-80$ mesh).

The pressure drop versus flow rate measurements had to be made in the same bed as the experimental runs since the void fraction of the bed depended upon the manner in which the irregular particles arranged themselves. Each time the column was packed, it would possess a different void fraction because the particles would pack differently.

In order to accomplish the above, two side arms (see Figure 6) were extended from the column section between the two conductivity cells. A fritted glass joint was attached to each extended arm and then the glass joints were connected to a manometer using $1 / 4$-inch Tygon tubing. Mercury was the measuring fluid used in the manometer. The rest of the pressure measuring system (Tygon tubing and manometer) contained water only. The fritted glass joints (see Figure 11) enabled the extended arms and one chamber of the glass joints to be filled with packing. The fritted glass permitted flow of liquid through the pressure measuring system, while preventing any movement of the packing material.

Before any pressure drop measurements were taken, water was allowed to flow through the column for several hours. It was hoped that this would completely set the particles in the bed so that there would be no further rearrangement. Measurements were made by simply setting a certain flow rate, waiting for the manometer to come to equilibrium and then reading the corresponding pressure drop. Runs were made on two separate days to insure the void fraction remained constant. Once the pressure drop studies were completed, the manometer was taken out of the system by clamping the Tygon tubing leads. Experimental adsorption runs could now be made.


Figure 11. Diagram of fritted glass joint.

## Packing Procedure

It was extremely important for the correct operation of the experimental system, that there was absolutely no air entrapped in the packed column. Therefore, much care was taken in packing the column.

The best general approach to the packing problem was to start with the bottom brass section (see Figure 6) by filling it with water and then to add the packing and let it settle. Before the packing was introduced into the column, it was slurried with water to remove air from the surface of the particles. A small piece of cotton cloth was placed in the bottom of the brass section to restrict the packing while allowing the flow of solvent. The three inch section was now added and packed in the same manner. A conductivity cell was then placed on top of the three inch section and the main (18-inch) section was fastened into place. A small amount of water was added to the main section and a packing support was allowed to settle into place on top of the conductivity cell. The packing supports were pieces of cotton cloth glued to a stainless steel rim which was just under $1 / 2$ inch in diameter and one-sixteenth of an inch thick. The conductivity cells should contain only water. Care must be taken to keep the cells free of air bubbles and packing particles.

In order to obtain a uniformly packed bed in the main section of the column, the packing was dropped down the
column while water was slowly flowing upward. This method enabled the small, light particles to be carried out of the column with the rising water. A diagram of the set-up used for the above procedure is shown in Figure 12. To fill the extended arm and glass joint with packing, the end of the glass joint was disconnected from the tubing leads to the manometer. Packing was then carried into the arm and left chamber of the joint by the flowing water.

After the main section was packed, the column was continually tapped in an effort to settle the packing in a permanent arrangement. If this was not done now, the packing would settle once the column was in operation and would leave a space under the top conductivity cell.

Once the tapping was completed, the top cell was added and the 12 -inch section was fastened into place. Another packing support was allowed to settle in place and enough packing was added to bring the top of the bed three inches above the first cell. The remaining sections of the column were added and the photo cell and light source were clamped into place about one inch above the top of the packed bed.

## End Effects

End effects is a term used to denote the results of conditions at the end of column which tend to disrupt the flow pattern. Obviously, it is desirable to minimize end effects whenever possible. For this work, it was assumed that end effects did not exist since there were at least

Overflow for water and light packing particles


Figure 12. Diagram of method employed for packing main section of column.
three inches of packing above and below the first and second conductivity cells respectively.

## Run Procedure

To begin a run, the desired flow rate was set by using the micrometer valve and nitrogen pressure. To obtain low flow rates ( 0.00 to $2.00 \mathrm{ft} / \mathrm{hr}$ ), the column was opened to the atmosphere and the flow rate was controlled by the positioning of the outlet tubing*. The outlet could be located anywhere between the top of the packing and the liquid level in the column. At low flow rates the micrometer valve was found to be insensitive to controlling the flow rate. The flow rate was measured by collecting liquid from the outlet tubing in a burette (calibrated in twentieths of a milliliter) over a known period of time.

Once the desired flow rate was obtained, the liquid level was allowed to drop to the top of the packing and then a measured amount (pulse) of sodium chloride solution was injected, via syringe, into the column. The pulse was then allowed to enter the bed, the flow was stopped, solvent was carefully introduced to bring the liquid level back to photo cell height, and the flow was started again.

As the tracer passed through the column, the conductance versus time curves were recorded on a Sargeant Multi Range Recorder (catalog number S-72150). The two cells were

* piece of three-eights inch diameter Tygon tubing was attached to the copper tubing outlet line so that the outlet fluid could be easily collected for flow rate measurements.
hooked into the measuring circuit by means of a two-way switch enabling transfer from one to the other.

Before the pulse reached the conductivity cell, the recorder speed, range, and zero point were set. The zero point reading could be set by preference while pure solvent was passing through the cell. The range was set to give the maximum pen deflection without going off the chart. A resistance box was placed in the measuring circuit in place of the cells to determine what recorder ranges yielded scale readings proportional to conductance. It was found over the extimated resistance span of the cells (one to 100,000 ohms), that only the ranges of 5,25 , and 50 mv . could be used. Thus, it was necessary to vary the concentration of the tracer solution to find the one which would yield the optimum output curves using only the aforementioned recorder ranges.

## Analysis of Concentration-Time Distributions

Typical recorder output for both cells is shown in
Figure 13. Referring back to Equations 8 and 9, it is seen that values are needed for $\mu_{2}, \mu_{1}, \sigma_{2}^{2}$, and $\sigma_{1}^{2}$.

$$
\begin{equation*}
\mu_{N}=\int_{0}^{\infty} c t d t / \int_{0}^{\infty} c d t \tag{14}
\end{equation*}
$$

and

$$
\begin{equation*}
\sigma_{N}^{2}=\int_{0}^{\infty} c(t-\mu)^{2} d t / \int_{0}^{\infty} c d t \quad N=1,2 \tag{15}
\end{equation*}
$$

where the subscripts 1 and 2 refer to the upper and lower conductivity cells respectively.

Equations 14 and 15 were solved numerically using Simpson's Rule and the IBM 1800 Digital Computer. A copy of the Fortran program used to analyze the output curves can be found in Appendix A.

The input data for the computer consisted of scale readings obtained from the recorder chart at equally spaced time increments. The actual input values were equal to the scale readings minus the zero point. These corrected scale readings could be used as values of $C$ in Equations 14 and 15 because they were proportional to concentration.

## RESULTS AND DISCUSSION

## Calculation of Void Fraction

The void fraction of the packed bed was determined as discussed in the previous section. Runs 3 through 14 were made in the same bed, while runs 15 through 38 were made after the column had been repacked. Tables I and II present the data used in the Blake-Kosney Relationship to calculate void fraction. The void fraction for runs 3 through 14 was found to be equal to 0.4770 and its value for runs 15 through 38 was 0.4544 . To be certain that the void fraction of each bed remained constant, two sets of data were taken a day apart. Flow was maintained through the column during the one day interval.

## Calculation of Dispersion Coefficients

To evaluate an equilibrium constant and a mass transfer coefficient at a given flow rate using Equations 8 and 9, it is necessary to know the value of the dispersion coefficient at the flow rate in question. Since Hawley showed that an adsorption process occurring simultaneously with axial dispersion in a packed bed has no effect on the dispersion coeffient, it was assumed that dispersion coefficients evaluated in the inert beds of Hawley and Gentile could be used for this work.

Hawley ${ }^{1}$ has reported that for flow in a pipe a log-log plot of $D / D_{V}$ versus $d_{t} U / D_{v}$ where

Table I. Void fraction data (runs 3-14).

| Run | $\begin{gathered} \text { Pressure } \\ \text { Drop, } \Delta \mathrm{p} \\ \text { in. Hg. } \end{gathered}$ | Flow Rate $\mathrm{ml} / \mathrm{min}$ | $\begin{aligned} & \mathrm{V}_{0} / \Delta \mathrm{P} \\ & (\mathrm{ml} / \mathrm{min}) \\ & \text { in. } \mathrm{Hg} . \end{aligned}$ |
| :---: | :---: | :---: | :---: |

Set 1

| 1 | 0.90 | 2.35 | 2.61 |
| :--- | :--- | :---: | :---: |
| 2 | 2.05 | 5.45 | 2.66 |
| 3 | 3.10 | 8.44 | 2.72 |
| 4 | 4.05 | 10.90 | 2.69 |
| 5 | 5.15 | 13.85 | 2.69 |
| 6 | 6.20 | 16.75 | 2.70 |

Set 2

| 1 | 1.05 | 2.68 | 2.54 |
| :--- | ---: | :---: | :---: |
| 2 | 2.02 | 5.20 | 2.58 |
| 3 | 3.05 | 8.26 | 2.68 |
| 4 | 4.10 | 11.25 | 2.75 |
| 5 | 5.06 | 13.70 | 2.71 |
| 6 | 6.28 | 17.60 | 2.80 |

Table II. Void fraction data (runs 15-38).

| Run | Pressure <br> Drop, $\Delta \mathrm{P}$ <br> in. Hg. | Flow Rate <br> $\mathrm{ml} / \mathrm{min}$ | $\mathrm{V}_{0} / \Delta \mathrm{P}$ <br> (ml/min $)$ <br> in. Hg. |
| :---: | :---: | :---: | :---: |

Set 1

| 1 | 0.70 | 2.08 | 2.98 |
| :--- | ---: | ---: | ---: |
| 2 | 1.86 | 5.45 | 2.93 |
| 3 | 2.95 | 8.64 | 2.94 |
| 4 | 3.65 | 10.90 | 2.99 |
|  | $\left(V_{0} / \Delta P\right)_{\text {ave }}=2.96(\mathrm{ml} / \mathrm{min})$ in. Hg. |  |  |

Set 2

| 1 | 1.50 | 4.34 | 2.90 |
| :--- | ---: | ---: | ---: |
| 2 | 2.55 | 7.50 | 2.94 |
| 3 | 3.32 | 9.75 | 2.94 |
| 4 | 4.07 | 11.95 | 2.94 |
|  | $\left(V_{0} / \Delta P\right)_{\text {ave }}=2.94(\mathrm{ml} / \mathrm{min})$ in. Hg. |  |  |

$D-$ dispersion coefficient
$D_{v}-$ molecular diffusivity
$d_{t}-$ tube diameter
$U-$ interstitial velocity
should yield a straight line. It is logical to assume that a similar plot would correlate data for packed beds. Both Hawley and Gentile used the aforementioned plot to correlate their data. They replaced $d_{t}$ in the above relationships with four times the hydraulic radius, 4 M . For a packed bed of spheres

$$
4 M=\frac{2}{3} \frac{\epsilon}{1-\epsilon} d_{(e f f)}
$$

A plot of $\log D / D_{v}$ versus $\log 4 M U / D_{v}$ based upon both Hawley's and Gentile's data is seen in Figure 14. The value of the dispersion coefficient used in Equations 8 and 9 was determined from the equation describing the line best fitting Hawley's data (see Figure 14). The equation of this line was $D=9.0 D_{V}\left(4 M U / D_{V}\right)^{1.043}$.

Gentile's data was taken in beds of irregular glass particles and as Figure 14 shows, the dispersion coefficient was larger compared with the data taken in beds of glass spheres. Since this work involved packed beds of irregularly shaped (Appendix B) particles (60-80 mesh), it would seem logical that Gentile's dispersion data should be used for evaluations in this work. However, this was found not to be the case, and Hawley's data for spheres was used instead.


Figure 14. Hawley's and Gentile's data correlated by a plot of $4 \mathrm{MU} / \mathrm{D}_{\mathrm{v}}$ vs. $\mathrm{D} / \mathrm{D}_{\mathrm{v}}$.

A possible explanation for the fact that Gentile's data did not give good results in analyses concerned with this thesis is the difference in the type of packing used in this work compared to Gentile's work or that mass transfer may affect axial dispersion. It is quite possible that inherent characteristics of the packing such as surface roughness or surface porosity are the primary contributors to the dispersion for some substances while packing shape is the primary contributor for other substances. Figure 14 shows definitely that for glass particles, packing shape affects dispersion. However, this might not be true for substances other than glass (i.e. molecular sieve).

## Calculation of Equilibrium Constants

The equilibrium constant for the adsorption process occurring in the experimental work of this thesis is calculated using Equation 8 and the tabulated values are found in Tables III and IV.

A plot of flow rate versus equilibrium constant is shown in Figure 15. The plot seems to confirm the idea that an equilibrium process is occurring. There is some scatter, but the error between the lowest and highest value for the equilibrium constant is approximately $15 \%$ and is considered as good results for the type of experimental measurements employed in this study.

The actual magnitude of the equilibrium constant was compared to the results of batch studies ${ }^{9}$, made by Barrer,
Table III. Data for runs 3-14 ( $\epsilon=0.4470$ ).

| Run | $\sigma_{2}^{2} \mathrm{sec}^{2}$ | $\sigma_{1}^{2} \mathrm{sec}^{2}$ | $\mu_{2} \mathrm{sec}$ | $\mu_{1} \sec$ | $\mathrm{U} \mathrm{ft} / \mathrm{hr}$ | m | $\mathrm{K}_{\mathrm{x}} \mathrm{ft} / \mathrm{hr}$ | $\mathrm{D} \mathrm{ft} \mathrm{ft}^{2} / \mathrm{hr}$ |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| 3 | 96,753 | 5,926 | 942.12 | 256.50 | 1.9571 | 2.0590 | 0.01178 | 0.00424 |
| 4 | 121,108 | 16,389 | 983.50 | 330.19 | 1.6551 | 2.1880 | 0.01432 | 0.00356 |
| 5 | 264,434 | 11,718 | $1,687.9$ | 328.06 | 1.5195 | 1.6415 | 0.00576 | 0.00326 |
| 9 | 171,910 | 9,918 | $1,312.9$ | 321.58 | 1.2707 | 2.0990 | 0.01876 | 0.00270 |
| 10 | 148,365 | 9,526 | $1,226.8$ | 284.82 | 1.2668 | 2.1468 | 0.05797 | 0.00269 |
| 11 | 240,038 | 17,214 | $1,712.5$ | 432.72 | 0.8257 | 2.4408 | -0.01363 | 0.00172 |
| 12 | 265,899 | 21,742 | $1,598.1$ | 456.04 | 0.8141 | 2.1278 | -0.01403 | 0.00170 |
| 13 | 189,667 | 27,146 | $1,249.3$ | 502.57 | 0.8824 | 2.1699 | -0.00823 | 0.00185 |
| 14 | 300,135 | 64,781 | $1,934.1$ | 585.92 | 0.8430 | 2.2794 | -0.01953 | 0.00176 |

Table IV. Data for runs $15-38(\epsilon=0.4454)$.

| Run | $\sigma_{2}^{2} \sec ^{2}$ | $\sigma_{1}^{2} \sec ^{2}$ | $\mu_{2} \sec$ | $\mu_{1} \sec$ | U ft/hr | m | $\mathrm{K}_{\mathrm{x}} \mathrm{ft} / \mathrm{hr}$ | $\mathrm{D} \mathrm{ft}^{2} / \mathrm{hr}$ |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| 15 | 19,884 | $1,490.0$ | 381.89 | 104.77 | 4.2108 | 2.1891 | 0.02587 | 0.00974 |
| 16 | 22,966 | $2,383.2$ | 390.17 | 126.11 | 4.2108 | 2.2081 | 0.01861 | 0.00974 |
| 17 | 19,982 | $1,691.8$ | 391.99 | 118.85 | 4.1519 | 2.2723 | 0.02483 | 0.00960 |
| 18 | 38,202 | $3,205.3$ | 594.11 | 169.30 | 2.9240 | 2.2314 | 0.02131 | 0.00666 |
| 19 | 41,843 | $4,367.3$ | 600.93 | 195.36 | 2.9240 | 2.1645 | 0.01908 | 0.00666 |
| 20 | 608,149 | 87,698 | $2,498.7$ | 817.96 | 0.5508 | 2.3818 | -0.01068 | 0.00116 |
| 21 | 693,730 | 124,501 | $2,650.9$ | 914.18 | 0.5525 | 2.2071 | -0.01556 | 0.00117 |
| 22 | $2,147,246$ | 553,728 | $4,936.1$ | $2,253.6$ | 0.2570 | 2.2360 | -0.00198 | 0.00052 |
| 24 | $1,994,133$ | 420,288 | $4,424.2$ | $1,862.4$ | 0.2509 | 2.2751 | -0.00158 | 0.00050 |
| 26 | 630,080 | 160,004 | $2,410.7$ | 811.76 | 0.5027 | 2.1505 | -0.00431 | 0.00106 |
| 27 | 40,243 | $2,269.6$ | 622.24 | 175.88 | 2.4943 | 2.2379 | 0.06517 | 0.00564 |
| 28 | 41,456 | $2,877.6$ | 633.29 | 179.97 | 2.4365 | 2.2361 | 0.07621 | 0.00550 |
| 29 | 43,342 | $3,991.0$ | 645.54 | 204.17 | 2.4493 | 2.3703 | 0.03928 | 0.00553 |

.

| Run | $\sigma_{2}^{2} \sec ^{2}$ | $\sigma_{1}^{2} \sec ^{2}$ | $\mu_{2} \sec$ | $\mu_{1} \sec$ | $U \mathrm{ft} / \mathrm{hr}$ | m | $\mathrm{K}_{\mathrm{x}} \mathrm{ft} / \mathrm{hr}$ | $\mathrm{D} \mathrm{ft} \mathrm{ft}^{2} / \mathrm{hr}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 32 | 20,071 | $2,394.1$ | 419.13 | 137.73 | 3.9021 | 2.2790 | 0.04088 | 0.00900 |
| 33 | 20,184 | $2,343.0$ | 408.98 | 133.79 | 3.8914 | 2.2791 | 0.04005 | 0.00897 |
| 34 | 20,966 | $3,349.2$ | 402.75 | 142.74 | 3.8658 | 2.2892 | 0.04395 | 0.00891 |
| 35 | 29,544 | $5,185.6$ | 522.06 | 177.45 | 3.4600 | 2.2440 | 0.02751 | 0.00794 |
| 36 | 25,493 | $3,726.8$ | 453.99 | 179.70 | 3.4600 | 2.2858 | 0.04091 | 0.00794 |
| 37 | 40,277 | $3,029.7$ | 543.80 | 172.76 | 3.0067 | 2.1699 | 0.01689 | 0.00686 |
| 38 | 41,011 | 6.084 .9 | 566.75 | 203.54 | 2.9572 | 2.1477 | 0.02318 | 0.00674 |

$\odot \quad \odot$
$\infty$
$\odot$
$\odot \quad \odot$

employing molecular sieve (13-X) and a NaCl solution. Barrer, exhibited his results by plotting the nonlinear isotherm for the above mentioned system. A value for $m$ was calculated from Barrer's data by finding the slope of a line drawn tangent to the isotherm curve at the concentration of the tracer solution used in this study ( $2 \mathrm{~g} / 1$ ). The slope of the line was found to be about 0.05 . However, Barrer's measurements were made with packing in the shape of pellets $1 / 16$ of an inch in diameter and $1 / 4$ of an inch long. Since the packing of this study was of different shape and much smaller than the pellets, it would have more surface area. It was calculated that the irregularly shaped particles used in this study had approximately 8.40 times as much surface area as the pellets used by Barrer. This means that Barrer's value of $m$ corrected for the packing shape of this work would be about (8.40)(0.05) $=0.420 \mathrm{com}-$ pared to the experimental value of between 2.10 and 2.30 . At this time the deviations in the above values for the equilibrium constant cannot be explained.

Calculation of Mass Transfer Coefficients

The values of the mass transfer coefficients for this study were calculated using both Equations 8 and 9 and axial dispersion coefficients from Figure 14. The results are tabulated in Tables III and IV.

A plot of mass transfer coefficient versus flow rate is shown in Figure 16. The plot indicates a general trend
$45$

of the mass transfer coefficient to increase with increasing flow rate. The tabulated data reveals that flow rates less than one foot per hour yielded negative mass transfer coefficients. This is physically impossible and may pos sibly be explained by the fact that the values used for the dispersion coefficient in this flow range were taken from extrapolating the data shown in Figure 14. As can be seen in Figure 14, there is very little dispersion data in the low flow range and thus no firm justification for the extrapolation.

The scatter of the data observed in Figure 16 can reasonably be blamed upon errors compiled during the actual run and the analysis of the data. These errors will be discussed in further detail later in this thesis.

## Correlation of Mass Transfer Data

The mass transfer data of this study were compared to data collected by several other investigators using completely different experimental systems. The data of this work, of Resnick and White ${ }^{\mathbf{1 0}}$, of Al-Khudayri ${ }^{11}$, and of Hurt ${ }^{12}$ is correlated on a plot of $\mathrm{Re} / 1-\epsilon$ versus $\mathrm{Sh} /(\mathrm{Sc})^{1 / 3}$.

The results of the correlation are shown in Figure 17 , and the data used for the plot are tabulated in Table $V$. As can be seen, the data of Resnick and White ${ }^{10}$, Hurt ${ }^{12}$, and Al-Khudayri ${ }^{11}$ tend to fit a straight line in the higher flow range. The data of this work, although taken at much slower flow rates, appears to fall on the extrapolated


Table V. Data from this work used for mass transfer correlation.

| Run | $\operatorname{Re} /(1-\epsilon)$ | Sc | Sh | $\mathrm{Sh} /(\mathrm{Sc})^{1 / 3}$ |
| :---: | :---: | :---: | :---: | :---: |
| 3 | 0.03961 | 518.9 | 0.06843 | 0.00853 |
| 4 | 0.03349 |  | 0.08316 | 0.01037 |
| 9 | 0.02572 |  | 0.10894 | 0.01358 |
| 15 | 0.08638 |  | 0.15022 | 0.01873 |
| 16 | 0.08638 |  | 0.10806 | 0.01347 |
| 17 | 0.08517 |  | 0.38706 | 0.01798 |
| 18 | 0.05998 |  | 0.12377 | 0.01543 |
| 19 | 0.05998 |  | 0.11081 | 0.01381 |
| 27 | 0.05116 |  | 0.37850 | 0.04720 |
| 28 | 0.04998 |  | 0.44262 | 0.05519 |
| 29 | 0.05024 |  | 0.22814 | 0.02845 |
| 30 | 0.05088 |  | 0.10151 | 0.01265 |
| 31 | 0.07571 |  | 0.17893 | 0.02231 |
| 32 | 0.08005 |  | 0.23740 | 0.02960 |
| 33 | 0.07983 |  | 0.23261 | 0.02900 |
| 34 | 0.07930 |  | 0.25530 | 0.03183 |
| 35 | 0.07098 |  | 0.15980 | 0.01992 |
| 36 | 0.07098 |  | 0.23761 | 0.02963 |
| 37 | 0.06168 |  | 0.09811 | 0.01223 |
| 38 | 0.06066 |  | 0.13461 | 0.01678 |

straight line fit of the higher flow rate data. Figure 17 indicates that the mass transfer coefficients evaluated in this study compare favorably to values calculated from completely different experimental methods.

## Discussion of Mass Transfer Data

A closer look into the methods used in obtaining the data in Figure 17 might help in determining the controlling mechanisms involved in the work of this thesis.

Before the works of Al-Khudayri ${ }^{11}$, Resnick and White ${ }^{\mathbf{1 0}}$, and Hurt ${ }^{12}$ are discussed in more detail and conclusions made, it will be helpful to keep in mind a few facts concerning available mass transfer data. First of all, there are wide discrepancies between mass transfer correlations for low velocity flow of gases through packed beds ${ }^{\mathbf{1 1}}$. Also, Resnick and White ${ }^{11}$ found that discrepancies in correlations occurred between data taken with large particle sizes and data taken with small particle sizes, and the smaller the size the greater the deviations. This work involves evaluating mass transfer coefficients employing both slow flow rates and small particle sizes. The flow rates used in this work were, in fact, much slower than those used in any other work the author could locate. It would be fairly safe to say that little if any experimental work has been conducted in an attempt to evaluate mass transfer coefficients at flow rates as slow as those used in this work. It was also noted that
the particle size employed in this work was considerably smaller than sizes employed in other experimental work. Considering the above discussion, it could be expected that the mass transfer data of this work would be in disagreement with the majority of the other experimental work. Basically this is true ${ }^{11}$. However, Figure 17 indicates experimental work which tends to agree with the work of this thesis.

Al-Khudari ${ }^{11}$ was primarily interested in gathering mass transfer data for gas-solid systems with the gas film resistance controlling. He took precautions in his experimental work to minimize other resistances and to eliminate other effects which might be detrimental to the results. His packing consisted of aluminum balls coated with a metallic halide. The fluid passed through the packing was a mixture of ammonia and an inert gas. The ammonia formed a complex with the coating on the packing to insure adsorption was occurring. Data used in Figure 17 from Al-Khudayri's work are listed in Table VI.

Resnick and white ${ }^{\mathbf{1 0}}$ also measured mass transfer coefficients with the gas film resistance controlling by evaporating fixed and fluidized beds of naphthalene into air, hydrogen, and carbon dioxide. The data they accumulated for fixed beds are shown in Table VII.

Hurt ${ }^{12}$ decided to undertake a study of transfer rates to packed beds since at the time only a sparse amount of data was available in this area. He was primarily interested in

Table VI. Data of Al-Khudayri (11).

| System | Sc | $\mathrm{Re} /(1-\epsilon)$ | $\mathrm{Sh} /(\mathrm{Sc})^{1 / 3}$ |
| :--- | :---: | :---: | :---: |
| Halide- <br> ammonia | 1.31 | 5.57 | 0.488 |
|  | 2.22 | 0.340 |  |
|  | 7.85 | 0.613 |  |
|  | 4.09 | 0.375 |  |
|  | 7.10 | 0.278 |  |
|  | 13.25 | 0.716 |  |
|  | 17.33 | 0.795 |  |
|  | 25.45 | 1.374 |  |

Table VII. Data of Resnick and White (10,11).

| System | $\begin{gathered} d_{p} \\ c m \end{gathered}$ | $\epsilon$ | $\begin{gathered} a \\ \mathrm{~cm}^{2} / \mathrm{cc} \end{gathered}$ | $\begin{gathered} \mathrm{D}_{\mathrm{m}} \\ \mathrm{~cm}^{2} / \mathrm{sec} \end{gathered}$ | Sc | $\operatorname{Re} / 1-\epsilon$ | $\mathrm{Sh} /(\mathrm{Sc})^{1 / 3}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Naphthaleneair | 0.0833 | 0.391 | 53.74 | 0.064 | 2.39 | 19.70 | 0.770 |
|  |  |  |  |  |  | 18.05 | 0.775 |
|  |  |  |  |  |  | 12.96 | 0.481 |
|  |  |  |  |  |  | 7.88 | 0.401 |
| Naphthalene$\mathrm{CO}_{2}$ |  |  |  | 0.0562 | 1.471 | 41.00 | 1.361 |
|  |  |  |  |  |  | 28.75 | 0.843 |
| Naphthalene$\mathrm{H}_{2}$ |  |  |  | 0.270 | 4.023 | 2.96 | 0.174 |
|  |  |  |  |  |  | 2.30 | 0.153 |

accurate experimental measurement of gas film H.T.U. and thus was careful to insure that the gas film resistance was controlling. He investigated three different systems one of which was the evaporation of naphthalene into air from naphthalene particles. The data is tabulated in Table VIII. Considering the preceding discussion along with Figure 17 it would seem entirely logical to conclude that the controlling mechanism in the work of this thesis is the liquid film resistance. The overall mass transfer process can be visualized as sodium ions from the dilute tracer slowly diffusing through the stagnant liquid film at the interface between the liquid and the packing and then instantaneously reacting (ion exchange) at the surface of the packing. This explanation would also give further credence to the conclusion, supported by the horizontal line fitting the data of Figure 15, that an equilibrium process was occurring. It must be remembered that these conclusions were made by assuming that a straight line extrapolation was correct for the correlated data of this work. Since there is no available data in the area between $\operatorname{Re} /(1-\epsilon)=0.10$ to 2.0 , the straight line extrapolation was assumed to be correct. Results exhibited by Figure 16 also add validity to the above conclusions. If the liquid film resistance is the controlling factor in mass transfer, the mass transfer coefficient would certainly increase with a larger flow rate since the liquid film thickness decreases as flow rate increases. This phenomena was observed and is illustrated in Figure 16.

54

| System | $\begin{gathered} d_{p} \\ c m \end{gathered}$ | $\epsilon$ | $\begin{gathered} \mathrm{a} \\ \mathrm{~cm}^{2} / \mathrm{cc} \end{gathered}$ | $\begin{gathered} \mathrm{D}_{\mathrm{m}} \\ \mathrm{~cm}^{2} / \mathrm{sec} \end{gathered}$ | Sc | Re | Re/1- | $\mathrm{Sh} /(\mathrm{Sc})^{1 / 3}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Naphthaleneair | 0.965 | 0.375 | 3.89 | 0.064 | 2.50 | 670 | 1072 | 20.37 |
|  |  |  |  |  |  | 324 | 518 | 12.02 |
| (cylinders) |  |  |  |  |  | 160 | 256 | 7.31 |
|  |  |  |  |  |  | 57.2 | 91.5 | 7.00 |
|  |  |  |  |  |  | 28.5 | 45.6 | 2.41 |
|  |  |  |  |  |  | 15.3 | 24.5 | 1.79 |
| (cylinders) | 0.432 |  | 8.68 |  |  | 300 | 480 | 9.84 |
|  |  |  |  |  |  | 145 | 232 | 5.98 |
|  |  |  |  |  |  | 72.0 | 115.2 | 3.38 |
|  |  |  |  |  |  | 26.8 | 42.9 | 1.78 |
|  |  |  |  |  |  | 12.8 | 20.5 | 1.10 |
|  |  |  |  |  |  | 6.9 | 11.0 | 0.77 |
| $\begin{gathered} (3-4 \text { mesh } \\ \text { flakes }) \end{gathered}$ | 0.559 | 0.40 | 6.44 |  |  | 395 | 658 | 20.12 |
|  |  |  |  |  |  | 190 | 317 | 12.68 |
|  |  |  |  |  |  | 94 | 157 | 7.50 |

Discussion of Errors in Experimental Procedure and Data Analysis

Much theoretical work has been done in the area of pulse injection and response techniques. However, experimental work in this field is lacking tremendously and this is due, most likely, to the many experimental problems which can arise in work such as this. Rao and Hoelscher ${ }^{3}$ used this technique to study dispersion and adsorption in gas-solid systems, but other than this, the author could locate no other work applying the pulse injection technique to systems where dispersion and adsorption were occurring simultaneously.

The most frequent problems arising in the actual experimental procedure of this work were those of injecting a pulse so that tailing on the output curves would be minimal, keeping a constant flow rate through the column during the span of an entire run, and trying to prevent the output curves from being deflected off the width of the chart paper. Many completed runs were discarded for one or more of the above listed reasons.

For the vast majority of runs, the tails of both the first and second curves did not return to the base line at which the curves were started. This meant that before the runs could be analyzed a base line somewhere between these two points had to be chosen. It was later realized that the actual positioning of the base line could result in as much as a $50 \%$ change in value of the mass transfer coefficient.

The author found that the best results in analyzing the curves were obtained when the base line was chosen closer to its beginning value than to the value indicated by the tail of the curve. This meant that the tail of the curve had to be extrapolated downward to the chosen base line. To eliminate errors incurred by guessing at a correct base line value and then extrapolating, it is suggested that refinements be made in the measuring system which might possibly result in stronger input signals to the recorder. Possibly, all that is needed is a more sensitive recorder. Actually there were several other problems that suggested the replacement of the recorder with a more sophisticated model. First of all the chart speeds could be varied only by manually changing gears. Also, the lowest chart speed available made runs under $1 / 2$ a foot per hour unreliable because the output curves had such wide spreads on the chart paper. Secondly, the range settings were extremely hard to duplicate and this often resulted in output curves exceeding the width of the chart paper. As a matter of fact, several of the runs analyzed in this work were so done only after the top portions of the curves had been estimated and drawn in by hand.

The most difficulty encountered in this experimentation was adjusting the flow rate and then keeping it constant. Many runs had to be discarded because of changes in the flow rate. This problem became predominant below flow rates of $1 / 2$ foot per hour and both tabulated runs at $1 / 4$
foot per hour were analyzed even though the flow rate varied over the duration of the run.

Considering all the problems involved in the actual gathering and analyses of the data of the unsteady state experiments of this work, it would seem entirely reasonable to blame the scatter in the data (Figures 15 and 16) on a combination of many experimental factors.

## CONCLUSIONS

An axial dispersed, plug flow model, with adsorption occurring, was used to describe the unsteady state chromatography process. Equilibrium constants and mass transfer coefficients were evaluated at various flow rates using the pulse injection and response technique.

The variance between the highest and lowest values of the equilibrium constants evaluated at flow rates between 0.00 and $4.25 \mathrm{ft} / \mathrm{hr}$ was only $15 \%$. The fact that these values were relatively constant indicates that the chromatography process, as simulated in this study, was occurring under equilibrium conditions. That is, the sodium ions in the fluid were in equilibrium with sodium ions on the packing surface.

The mass transfer coefficients were evaluated over the same flow range as were the equilibrium constants and showed a strong tendency to increase with increasing flow rate. When correlated, the mass transfer coefficients of this study compare favorably with data taken with the gas film resistance controlling (gas-solid system). This led to the conclusion that the adsorption occurring in this study was controlled by the liquid film resistance (liquid-solid system). Therefore, the adsorption phenomena can be visualized as the diffusion of tracer ions through a liquid film resistance with subsequent instantaneous adsorption at the packing surface.

## RECOMMENDATIONS FOR FUTURE WORK

The following are recommendations for further work that will be helpful in attaining an accurate and complete method of scaling-up chromatographic separations.

1. The third moment of the output curves, which can be mathematically related to the dispersion coefficient ${ }^{3}$, should be calculated and used to evaluate dispersion coefficients. This would eliminate the approximation method used in this work and certainly eliminate a possible cause of error.
2. A complete investigation should be made into end effects and their relation and importance to the chromatographic separation.
3. A system in which interparticle diffusion is a major factor should be investigated. Porous glass beads could possibly be used as a packing in this system.
4. Finally, an actual separation of two components should be predicted and then tested.

APPENDIX A
FORTRAN PROGRAM USED FOR ANALYZING CONCENTRATION-TIME DISTRIBUTIONS ON THE IBM 1800 COMPUTER


### 0.00212



$$
\infty^{-1} \sigma^{-1}
$$



$$
1 \begin{aligned}
& \text { DO } 1 \mathrm{I}=2, \mathrm{M} \\
& \text { AREA }=\text { AREA }+(\mathrm{H} / 3.0) *(2.0 * Y(2 * I-1)+4.0 * Y(2 * I)) \\
& \text { RETURN } \\
& \text { END }
\end{aligned}
$$

APPENDIX B


## NOMENCLATURE



Greek Letters:
є - void fraction
$\mu \quad-\quad v i s c o s i t y ~ o f ~ s o l v e n t, ~ l b / f t-h r$
$\mu_{1}$ - mean-time of concentration-time distribution at cell \#1, hr
$\mu_{2}$ - mean-time of concentration-time distribution at cell \#2, hr
$\sigma_{1}^{2}$ - variance of concentration-time distribution at cell \#1, $\mathrm{hr}^{2}$
$\sigma_{2}^{2}$ - variance of concentration-time distribution at cell \#2, hr ${ }^{2}$

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