12-1957

An Investigation of Techniques for the Separation of Hydrogen and Deuterium: Part I: Zone Refining of Mixtures of Ordinary and Heavy Water; Part II: The Reaction of Iron with Mixtures of Ordinary and Heavy Water; Part III: Gas Chromatography with Hydrogen and Deuterium Samples

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Hilton A. Smith, Major Professor

We have read this dissertation and recommend its acceptance:

William H. Fletcher & John A. Dean

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
To the Graduate Council:

I am submitting herewith a dissertation written by Carl Owens Thomas entitled "An Investigation of Techniques for the Separation of Hydrogen and Deuterium: Part I: Zone Refining of Mixtures of Ordinary and Heavy Water; Part II: The Reaction of Iron With Mixtures of Ordinary and Heavy Water; Part III: Gas Chromatography With Hydrogen and Deuterium Samples." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

[Signature]
Major Professor

We have read this dissertation and recommend its acceptance:

[Signatures]

Accepted for the Council:

[Signature]
Dean of the Graduate School
AN INVESTIGATION OF TECHNIQUES FOR THE SEPARATION OF
HYDROGEN AND DEUTERIUM

PART I: ZONE REFINING OF MIXTURES OF ORDINARY
AND HEAVY WATER

PART II: THE REACTION OF IRON WITH MIXTURES OF
ORDINARY AND HEAVY WATER

PART III: GAS CHROMATOGRAPHY WITH HYDROGEN AND
DEUTERIUM SAMPLES

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

by
Carl Owens Thomas

December, 1957
ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. Hilton A. Smith for his generous and thoughtful guidance in the course of this work. He wishes to thank his wife for her patience, understanding, and encouragement, without which this work could not have been completed. In addition, Mr. Charles E. Bailey was very helpful with the matrix algebra manipulations.

This work was made possible through a research grant from the U. S. Atomic Energy Commission for the period from September, 1955 to September, 1957.
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PART I

ZONE REFINING OF MIXTURES OF ORDINARY AND HEAVY WATER
CHAPTER I

INTRODUCTION

A. Previous Work

1. Equilibrium Separation Factor

The freezing point of pure heavy water (D₂O) is 3.80° higher than that of ordinary water.¹,² This difference in the freezing points has been the basis for a number of attempts to separate the two isotopic forms by fractional crystallization. Although many of the early measurements were inconclusive, Eucken and Schafer¹ were able to confirm experimentally the theoretically predicted temperature difference between the solid and the liquid phases in a mixture of the two forms of water. Weston³ rechecked the theoretical calculations which indicate that the heavy water should concentrate in the solid phase. Romaniów⁴ was granted a patent on a method for the concentration of heavy water by a fractional freezing process.

Smith and Posey⁵-⁸ determined experimentally the equilibrium separation factor. They found that vigorous agitation is necessary in order to maintain concentration equilibrium between the body of the liquid and the thin film in which freezing occurs at the surface of the ice. Their value of 1.0211 ± 0.0007 for the equilibrium separation factor, α, is in fair agreement with the calculated value of 1.023 reported by Eucken and Schafer. Since the liquid phase becomes progressively depleted in deuterium as freezing proceeds, the process is analogous to a Rayleigh distillation. Therefore Smith and Posey calculated the value of the
separation factor from the equation,
\[ \Delta \log \left[ 1 + \frac{m(l-y)}{M(l-x)} \right] = \log \left[ 1 + \frac{dy}{Mx} \right] \] (1)

where \( M \) is the total number of moles in the liquid phase, \( m \) is the total number of moles in the solid phase, \( x \) is the mole fraction of deuterium in the liquid phase, and \( y \) is the mole fraction of deuterium in the solid phase. Their work appears to show conclusively that fractional crystallization of a mixture of ordinary and of heavy water produces isotopic separation with the heavy water concentrating in the solid phase.

2. **Zone Refining**

Many processes for the separation of the components of a mixture depend upon "multiple equilibrations," either in a continuous manner or in a discontinuous manner. The ordinary distillation column is an example of continuous multiple equilibration. The theoretical plate concept is used to define the region of the column in which separation, equivalent to that in a single batch equilibration, occurs. The counter-current extraction apparatus of Craig and Post\(^9\) is an example of discontinuous multiple equilibration. Each of the above methods produces separation which is much larger than that available in one equilibration.

The analogous multiple equilibration process for fractional crystallization is the zone-refining technique which was developed by Pfann\(^{10-13}\) from earlier work done by Schwab and Wichers\(^{14}\). Schwab and Wichers were interested in the purification of benzoic acid and acetonilide. Pfann was working on the purification of germanium for electri-
cal applications. The zone-refining technique has been successful, and its many applications have been discussed in a recent review.  

3. **Theoretical Background**

Pfann's original article on zone refining presents a mathematical analysis of the system. The treatment neglects the change in density produced by melting or by freezing and does not apply to the boundary conditions at the end of the sample where normal freezing occurs. Normal freezing begins when the leading edge of the liquid zone reaches the end of the sample and there is no further feed into the liquid zone. The analytical treatment developed by Lord does not account for normal freezing at the end of the sample and becomes complicated for a large number of passes. Reiss developed an analytical approach in which the complete concentration profile could be calculated for values of the segregation coefficient close to unity. Burris, Stockman, and Dillon developed a method for calculating the concentration profile taking into account normal freezing at the end of the sample. They could not develop an analytical solution to their equations and were forced to use a card-programmed electronic computer for their numerical calculations. Hulme developed an analysis of the concentration gradient existing at the solid-liquid interface. The gradient is present in the liquid because of slow diffusion. Birman developed a mathematical treatment which includes the boundary conditions at the ends of the sample. The method allows direct numerical calculation of the solute distribution after any number of passes with any initial distribution.
B. Purpose

The separation factor for a single fractional crystallization in the $\text{H}_2\text{O-}\text{D}_2\text{O}$ system is much too small, and the required freezing rate is too slow for a batch process to give a useful separation of the isotopic forms of water. The purpose of this work was to continue some preliminary experiments\textsuperscript{7,8} on zone refining in the $\text{H}_2\text{O-}\text{D}_2\text{O}$ system and to attempt to determine whether or not the technique would be useful for the separation of heavy water from ordinary water.
CHAPTER II

THEORETICAL

A. The Process

Birman's method\textsuperscript{20} was used for the development of a mathematical analysis to describe zone refining in the H$_2$O-D$_2$O system, since it includes the boundary conditions and since it allows numerical solution of the equations by algebraic methods. Hulme's refinement,\textsuperscript{19} which covers the concentration gradient at the freezing interface, was not included, since the data of Posey and Smith\textsuperscript{5-8} include a value for an effective separation factor in an unstirred solution.

The sample, in the shape of a slender rod or cylinder, may be considered to be a series of segments of identical, but arbitrary length. The refining process is conducted at an ambient temperature low enough so that the sample is a solid, and segments are melted in sequence by passing a heat source along the sample. The length of the melted zone is less than that of the sample, so that after a time the sample solidifies behind the zone. One "pass" is completed when the liquid zone has traversed the entire length of the sample. The boundary condition referred to as "normal freezing" begins when the leading edge of the liquid zone reaches the end of the sample and when there is no additional solid material to be melted.

Three basic assumptions regarding the process are made in order to simplify the calculations:
(1) The rate of diffusion in the solid is negligible. The concentration of solute supplied to the liquid phase by the melting solid is identical with the solute concentration in the solid immediately ahead of the liquid zone.

(2) Diffusion in the liquid is complete. There is no concentration gradient in the liquid, and material solidifies behind the liquid zone in concentration equilibrium with the material in the liquid.

(3) The segregation coefficient, \( k \), is constant and is defined by equation 2,

\[
\frac{c_s}{c_l} = k
\]

where \( c_s \) is the solute concentration in the solid freezing in equilibrium with the liquid and where \( c_l \) is the solute concentration in the liquid. The units of concentration are taken as moles per unit of volume.

These assumptions are valid only for the idealized system upon which this mathematical treatment is based.

If \( k > 1 \), the solute concentrates in the solid phase, which produces a net movement of solute along the sample in a direction opposite to the motion of the liquid zone.

B. The Difference Equations

Consider the sample divided into \( N \) equal segments, of arbitrary length. Let \( D_{n,p} \) be the number of moles of deuterium, as heavy water, in the \( n \)-th segment after the \( p \)-th pass. A pass, previously defined,
can be divided into a series of basic progressions. At the beginning of the first progression of the p-th pass the melted zone consists of segments 1 through M, inclusive, which are mixed completely. The zone width is M segments, and T, the total number of moles of deuterium in the liquid zone is given by equation 3,

\[ T = \sum_{n=1}^{M} D_{n,p-1} \]  

which defines the initial boundary condition.

Segment 1 freezes in equilibrium with the liquid in segments 2 through M inclusive. By definition, the number of moles of deuterium in the segment which freezes is \( D_{1,p} \). The number of moles of deuterium in the remaining \( M-1 \) liquid segments is \( \frac{M-1}{k} D_{1,p} \). This follows from equation 2 if the volume of a segment is defined as the unit of volume in the system. A material balance gives equation 4, which is applicable to the first progression.

\[ \sum_{n=1}^{M} D_{n,p-1} = \left[ 1 + \frac{M-1}{k} \right] D_{1,p} \]  

The second progression begins as the zone advances by melting segment \( M+1 \). The melting adds \( D_{M+1,p-1} \) moles of deuterium to the liquid phase. The total amount of deuterium in the liquid phase is then

\[ \left[ \frac{M-1}{k} \right] D_{1,p} + D_{M+1,p-1} \]  

The amount of deuterium in segment 2, which next freezes, is \( D_{2,p} \), and in the remaining liquid is \( \frac{M-1}{k} D_{2,p} \). A material balance gives equation 5, which can be rearranged to give equation 6.
Equation 6 applies to the second progression, which is begun when segment $M + 1$ melts and which is completed when segment 2 freezes. Thus, equation 6 may be generalized to apply to $N - M$ progressions. If $\lambda$ is the index number of the progression, equation 4 applies when $\lambda = 1$, and equation 7, the generalized form of equation 6, applies when $\lambda = 2 \ldots (N - M + 1)$.

Normal freezing begins when segment $N - M + 2$ freezes in equilibrium with the remaining liquid. By definition, the amount of deuterium in segment $N - M + 2$ is $D_{N-M+2,p}$, and the amount remaining in the liquid is $\frac{M-2}{k} D_{N-M+2,p}$. The sum of these two terms is equal to the amount of deuterium remaining in the liquid phase at the completion of the preceding progression. A material balance gives equation 8, which can be rearranged to give equation 9.

$$\left[ \frac{M-1}{k} \right] D_{N-M+1,p} + \frac{M-2}{k} D_{N-M+2,p} + D_{N-M+2,p} = 0$$

Equation 9 can be generalized to give equation 10, which applies to progressions $\lambda = (N - M + 2 + m)$, where $m = 0 \ldots (M - 2)$.

$$0 = - \left[ \frac{M-1}{k} \right] D_{\lambda-1,p} + \frac{M-2-m}{k} D_{\lambda,p}$$
The three difference equations are summarized below.

\[ \sum_{n=1}^{M} D_{n,p-1} = \left[ 1 + \frac{M-1}{k} \right] D_{1,p} \quad \text{for} \quad \lambda = 1 \quad (4) \]

\[ D_{\lambda+M-1,p-1} = - \left[ \frac{M-1}{k} \right] D_{\lambda-1,p} + \left[ 1 + \frac{M-1}{k} \right] D_{\lambda,p} \quad \text{for} \quad \lambda = 2 \ldots (N-M+1) \quad (7) \]

\[ 0 = - \left[ \frac{M-1-m}{k} \right] D_{\lambda-1,p} + \left[ 1 + \frac{M-2-m}{k} \right] D_{\lambda,p} \quad \text{for} \quad \lambda = (N-M+2+m) \quad (10) \]

\[ m = (M-2) \]

C. The Separation Factor and the Segregation Coefficient

Equation 1, from which Smith and Posey calculated the value of the separation factor, \( \lambda \), is too unwieldy to be used in a detailed analysis of the zone refining process. Equation 1 can be simplified by the following sequence of approximations to give an expression of the same form as that of equation 2.

Let \( H_i' \) = the mole fraction of \( H \), as \( H_2O \), in the ice phase,

\[ H_i = \text{the total number of moles of } H, \text{ as } H_2O, \text{ in the ice phase,} \]

and \( H_i = \text{the total number of moles of } H, \text{ as } H_2O, \text{ per unit volume} \)

in the ice phase.

The unit volume is taken as that of a segment. It follows that the volume of the liquid phase is equal to the number of segments in the liquid phase. A parallel notation, \( D_i', \overline{D}_i, \) and \( D_i \) will refer to the deuterium, and a subscript \( w \) will refer to the liquid phase. Equation 1
now can be rewritten as:

\[ \log \left[ 1 + \frac{H_1}{H_w} \right] = \log \left[ 1 + \frac{D_1}{D_w} \right] \]  

(11)

or

\[ \log \left[ \frac{H_w + H_1}{H_w} \right] = \log \left[ \frac{D_w + D_1}{D_w} \right] \]  

(12)

The observed separation factor is often defined by equation 13.

\[ \lambda = \left( \frac{D_1}{D_w} \right) \left( \frac{H_w}{H_1} \right) \]  

(13)

Equations 14-a, 14-b, and 14-c apply to the condition where the amount of solid which forms is so small that the concentrations in the bulk of the liquid do not change.

\[ \lim_{H_i \to 0} \log \left( \frac{H_w + H_1}{H_w} \right) = 0 \]  

(14-a)

\[ \lim_{H_1 \to 0} \log \left( \frac{H_w + H_1}{H_w} \right) = 0 \]  

(14-b)

\[ \lim_{H_1' \to 0} \left( \frac{H_1'}{H_w' H_1} \right) = 0 \]  

(14-c)

A similar set of equations exists for the deuterium fractions. Therefore, under the condition specified for equations 14, equation 12 and equation 13 are identical.

An alternate separation factor, \( \lambda^* \), is defined by equation 15.

\[ \lambda^* = \left( \frac{D_1}{D_w} \right) \left( \frac{H_w}{H_1} \right) \]  

(15)
It can be shown that \( \lambda^* = \lambda \). If \( N_i \) and \( N_w \) are the number of segments in the ice and in the liquid phases respectively, then

\[
\left( \frac{D_i}{D_w} \right) \left( \frac{H_w}{H_i} \right) = \left( \frac{N_i D_i}{N_w D_w} \right) \left( \frac{N_w H_w}{N_i H_i} \right) = \left( \frac{D_i'}{D_w'} \right) \left( \frac{H_w'}{H_i'} \right) = \left( \frac{D_i}{D_w} \right) \left( \frac{H_w}{H_i} \right)
\]

(16)

since

\[
D_i' = \frac{\overline{D_i}}{\overline{D_i} + \overline{H_i}} \quad H_i' = \frac{\overline{H_i}}{\overline{D_i} + \overline{H_i}} \quad D_w' = \frac{\overline{D_w}}{\overline{D_w} + \overline{H_w}} \quad H_w' = \frac{\overline{H_w}}{\overline{D_w} + \overline{H_w}}
\]

(17)

Therefore

\[
\lambda^* = \left( \frac{D_i}{D_w} \right) \left( \frac{H_w}{H_i} \right) = \lambda = \left( \frac{D_i}{D_w} \right) \left( \frac{H_w}{H_i} \right).
\]

(18)

The ratio of the molecular weights for \( D_2O \) and \( H_2O \) is, to a very good approximation, identical with the density ratio for the two liquid and for the two solids\(^a\) in the vicinity of the freezing point.\(^{21-23}\)

Therefore the number of moles of \( D_2O \) or of \( H_2O \) is equal to a constant, \( C_i \), per unit volume of ice, and is equal to another constant, \( C_w \), per unit volume of liquid in the vicinity of the freezing point.\(^b\)

\(\text{MW}(D_2O)\quad\text{MW}(H_2O)\)

\[
\frac{\text{MW}(D_2O)}{\text{MW}(H_2O)} = 1.112, \quad \frac{d(D_2O)}{d(H_2O)} = 1.107 \text{ for ice at } 0^\circ, \text{ and } \frac{d(D_2O)}{d(H_2O)} = 1.106 \text{ for liquid water at } 4.3^\circ.
\]

\(\text{density} = \text{mass/vol.}\)

\(\text{moles/vol.} = (\text{mass/MW})/\text{vol.}\)

\(\text{mass/vol.} = \text{density} = (\text{MW})(\text{moles/vol.})\)

Therefore

\[
\frac{d(D_2O)}{d(H_2O)} = \frac{\text{MW}(D_2O)}{\text{MW}(H_2O)} \cdot \frac{\text{moles/vol.} (D_2O)}{\text{moles/vol.} (H_2O)}
\]

But the density ratio is essentially equal to the MW ratio. Therefore the number of moles of \( D_2O \) per unit volume is equal to the number of moles of \( H_2O \) per unit volume, to a good approximation.
In addition, solutions of D$_2$O in H$_2$O are very nearly ideal in a thermodynamic sense.\textsuperscript{24,25} The heats of mixing\textsuperscript{26} are very small and the maximum temperature difference between the solidus and the liquidus curves in the melting diagram is only 0.02°C.\textsuperscript{1} Therefore the constants, C$_i$ and C$_w$, may be applied to solutions of D$_2$O in H$_2$O. Equation 18 can be rewritten as follows:

\[
\lambda = \left( \frac{D_i}{D_w} \right) \left( \frac{H_w}{H_i} \right) = \left( \frac{D_i}{C_i - D_i} \right) \left( \frac{C_w - D_w}{D_w} \right)
\] (19)

since

\[
H_i = C_i - D_i \quad \text{and} \quad H_w = C_w - D_w.
\] (20)

Thus

\[
\lambda \left( \frac{C_i}{D_i} \right) - 1 = \left( \frac{C_w}{D_w} \right)
\] (21)

In the experimental work to which this analysis applies, C$_i$/D$_i$ and C$_w$/D$_w$ have values of about 2, and $\lambda$ is very nearly equal to 1. Therefore equation 22 is a good approximation to equation 21.

\[
\lambda \left( \frac{C_i}{D_i} \right) = \left( \frac{C_w}{D_w} \right)
\] (22)

Equation 22 can be rearranged to give an expression for $\lambda$ which has the same form as the expression for the segregation coefficient.

\[
\lambda \left( \frac{C_i}{C_w} \right) = \frac{\lambda}{1.090} = \frac{D_i}{D_w}
\] (23)

\[k = C_s/C_i\] (2)

The ratio, C$_w$/C$_i$ = 1.090, can be calculated from the water-ice density ratio for either D$_2$O or H$_2$O. The expression $\lambda$/1.090 is equivalent to the segregation coefficient, k, as defined by Birman.
Two points are implied by the form of equation 23. They are:

1. If $\lambda < 1.090$, the heavy water will move in the same direction as the zone movement. A previous statement restricted this direction of movement to situations where $\lambda < 1$.
2. Separation will occur for $\lambda = 1$.

These two points force a closer examination of the significance of $C_i/C_w$ in equations 22 and 23. Let us assume that the frozen water sample is contained in a tube which is not closed at either end. When ice melts at the leading edge of the zone, there is a decrease in volume. When water freezes at the trailing edge of the zone, there is an increase in volume. The net effect is to move the entire sample through the tube in the same direction as the zone movement. This constitutes a change in deuterium concentration relative to fixed segments of the tube, but it does not contribute to isotopic separation. If the $D_i$ and $D_w$ terms instead of the $H_i$ and $H_w$ terms are eliminated from equation 18, equation 24 may be derived.

$$\frac{1}{1.090 \lambda} = \frac{H_i}{H_w}$$

(24)

Thus, the density-ratio term in the denominator affects both isotopic forms of water in the same manner.

If the sample tube is closed at the ends so that no net movement of sample is possible, the density ratio may be dropped. For all of the experimental work discussed in this report, the sample tube was closed at the ends. A high pressure zone developed in the end of the tube toward which the zone moved. The effect is predicted by the above interpretation.
In many zone-refining processes, the sample is not contained, but is self-supporting. The density ratio for liquid and solid water is much larger than the density ratio for the liquid and solid phases in most other systems. Thus the effect which is produced by the density ratio would be more noticeable in the H\textsubscript{2}O-D\textsubscript{2}O system.

Equation 25 may be used to define the segregation coefficient for the purpose of calculating the concentration profile in an H\textsubscript{2}O-D\textsubscript{2}O system which is subjected to zone refining in a closed container.

\[ \chi = \frac{D_1}{D_W} \]  

(25)

D. Numerical Solution of Difference Equations

Equations 4, 7, and 10 may be written in matrix form

\[ AC_p = BC_{p-1} \]  

(26)

where A and B are N x N matrices of the coefficients of D\textsubscript{n,p} and D\textsubscript{n,p-1} respectively, and where \( n = 1 \ldots N \). \( C_p \) and \( C_{p-1} \) are N x 1 column matrices formed from the numerical values of D\textsubscript{n,p} and D\textsubscript{n,p-1} respectively. Since A is not singular, equation 26 may be written as

\[ C_p = (A^{-1}B)C_{p-1} \]  

(27)

where \((A^{-1}B)\) is another N x N matrix. The general form of the matrix \((A^{-1}B)\) is given in Table I. The manipulative procedures for arriving at the matrix are discussed in several standard text books.\textsuperscript{27,28}

Equation 28 relates the initial concentrations \( C_0 \) to the concentrations \( C_1 \) after the first pass.

\[ C_1 = (A^{-1}B)C_0 \]  

(28)
**TABLE I**

THE (A⁻¹B) MATRIX OF THE DIFFERENCE EQUATION COEFFICIENTS***

<table>
<thead>
<tr>
<th>λ*</th>
<th>Matrix Elements**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \frac{1}{y} )</td>
</tr>
<tr>
<td>2</td>
<td>( \frac{x}{y^2} )</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{x^2}{y^3} )</td>
</tr>
<tr>
<td>4</td>
<td>( \frac{x^3}{y^4} )</td>
</tr>
<tr>
<td>5</td>
<td>( \frac{x^4}{y^5} )</td>
</tr>
<tr>
<td>6</td>
<td>( \frac{x^5}{y^6} )</td>
</tr>
<tr>
<td>7</td>
<td>( \frac{x^6}{y^7} )</td>
</tr>
<tr>
<td>8</td>
<td>( \frac{x^7}{y^8} )</td>
</tr>
<tr>
<td>9</td>
<td>( \frac{x^8}{y^9} )</td>
</tr>
<tr>
<td>10</td>
<td>( \frac{x^9}{y^{10}} )</td>
</tr>
</tbody>
</table>

*The definition of \( \lambda \) has been given in the text.

**\( x = \frac{1}{\alpha} \).

\( y^{-1} = \alpha / (1 + \alpha) \).

***The accuracy of the \( A^{-1} \) matrix was verified by taking the product \( A^{-1}A \), which gave the proper unit matrix.
Therefore, after $p$ passes,

$$C_p = (A^{-1}B)^p C_0.$$  \hfill (29)

A simple zone-refining process in an $\text{H}_2\text{O}-\text{D}_2\text{O}$ system was evaluated numerically by the use of equation 29. The following conditions were assumed:

- $N = 10$, the number of segments in the sample,
- $M = 2$, the number of segments in the liquid zone,
- $\alpha = 1.02$, the value of the equilibrium separation factor found by Posey and Smith.

The equilibrium value for the separation factor was used in the calculations in order to evaluate the maximum isotopic separation which might be expected. The calculated concentration profiles are shown in Figure 1, and the numerical values of the column matrices, $C_p$, are given in Table II. An initial uniformly distributed unit concentration was assumed. The figure and the table may be converted to other concentration units by multiplication by the proper conversion factor.
Figure 1

Theoretical Concentration Profiles
### TABLE II

**NUMERICAL VALUES OF COLUMN MATRICES**

<table>
<thead>
<tr>
<th>Segment Number</th>
<th>0</th>
<th>1</th>
<th>Pass Number</th>
<th>4</th>
<th>8</th>
<th>16</th>
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<tr>
<td>1</td>
<td>1.010</td>
<td>1.0176</td>
<td>1.0298</td>
<td>1.0478</td>
<td>1.0697</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.005</td>
<td>1.0103</td>
<td>1.0194</td>
<td>1.0377</td>
<td>1.0547</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.003</td>
<td>1.0060</td>
<td>1.0123</td>
<td>1.0234</td>
<td>1.0337</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.001</td>
<td>1.0024</td>
<td>1.0064</td>
<td>1.0106</td>
<td>1.0130</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>1.0008</td>
<td>1.1126</td>
<td>1.1139</td>
<td>0.9983</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.000</td>
<td>0.9999</td>
<td>0.9999</td>
<td>0.9937</td>
<td>0.9807</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.999</td>
<td>0.9978</td>
<td>0.9942</td>
<td>0.9806</td>
<td>0.9614</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.998</td>
<td>0.9969</td>
<td>0.9847</td>
<td>0.9645</td>
<td>0.9415</td>
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</tr>
<tr>
<td>9</td>
<td>0.998</td>
<td>0.9873</td>
<td>0.9712</td>
<td>0.9498</td>
<td>0.9253</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.978</td>
<td>0.9667</td>
<td>0.9510</td>
<td>0.9303</td>
<td>0.9062</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER III

EXPERIMENTAL

A. Apparatus

1. Linear Apparatus

The apparatus and the method were similar to those described by Posey and Smith. The water sample, which was contained in a length of plastic tubing, was immersed in a low-temperature bath and was frozen. Narrow zones, spaced at equal intervals, were melted by small electrically heated coils. The arrangement of the apparatus is shown in Figure 2. The tubing was pulled at a rate of 5 inches per hour through the annular heaters. When the tubing had moved a distance equal to the spacing between two adjacent heaters, the drive mechanism quickly moved the tubing an equal distance in the opposite direction. The cyclic motion transferred the liquid zones from one heater to the next. In this manner, the zones traversed the entire length of the sample while the sample container made short strokes equal to the distance between the heaters.

The temperature of the liquid zones could not be determined, but the fact that alternate solid and liquid zones formed was verified by the presence of alternate hard and soft regions in the sample tube.

2. Spiral Apparatus

A spiral arrangement of the sample tube was used for most of the experiments. The spiral geometry, illustrated in Figure 3, allowed
Thread to Drive Mechanism

Annular Electrical Heaters

Tygon Tube Containing Mixed Water Sample

Retracting Spring

Figure 2

Linear Zone Refining Apparatus
Figure 3
Spiral Zone Refining Apparatus
approximately 40 zones to be located in the space occupied by 3 or 4 zones in the linear apparatus.

The Tygon plastic tube, containing the sample, was wound onto a 1 1/2-inch diameter cylinder of 1/2-inch mesh hardware cloth. The cylinder was mounted in the thermostat with the axis horizontal and with about 50 per cent of each turn submerged in the bath liquid. The entire coil was frozen by packing Dry Ice around it. The bath was covered with a sheet of plywood in which was cut a 1-inch wide slot. The slot was located immediately above and ran the length of the spiral. A heater, placed above the slot, maintained a temperature of 35° to 40° at the exposed surface of the spiral. The heating element was Nichrome wire, and was supported on an arched backing by Sauereisen cement. Under these operating conditions, each ice zone moved almost to the top of a turn before it was completely melted. Freezing occurred within the first 1/2 inch after the tubing reentered the bath. The melted zone occupied a length of about 1 1/2 inches, or about 25 per cent of each circumference.

The cylinder was rotated by a geared-down Telechron motor, which gave an operating speed of 0.75 revolutions per hour, or a linear speed of 4.1 inches per hour.

3. Thermostat

The frozen zones in the spiral apparatus were maintained in a refrigerated brine bath. The bath was operated at -10° which was the minimum temperature obtainable. An alcohol-water bath was used with the linear apparatus. The presence of the annular heaters in the bath limited its minimum temperature to about -3°.
4. **Plastic Tubing**

The water samples were contained in sections of Tygon plastic tubing, manufactured by the U. S. Stoneware Company. The tubing had an inside diameter of 1/8 inch and a wall thickness of 1/16 inch. Smith and Posey found that there is no detectable isotopic exchange between Tygon and mixtures of ordinary and heavy water.

5. **Preparation of Samples**

Since the density ratio for heavy water and for ordinary water is, to a very close approximation, equal to the molecular weight ratio, water mixtures of the desired mole fractions were made up by direct volumetric methods. All of the water samples contained approximately 45 mole per cent of heavy water. The values were determined more precisely after the sample was prepared. The heavy water, which was reported to be 99.8 per cent pure, was supplied by the Stuart Oxygen Company. The ordinary water was obtained from the general laboratory supply and was redistilled before use.

6. **Analytical Method**

The compositions of the water samples were determined by the falling drop method of Combs, Googin, and Smith.29 At the completion of each run, the entire water sample was frozen in the Tygon tubing by the addition of Dry Ice to the thermostat bath. The tubing was cut into sections, wiped dry with tissue, and the water was allowed to melt and to run into numbered flasks. Each numbered sample was distilled, collected in a Pyrex ampoule, sealed, and stored until the analyses were performed.
After each distillation a barely visible residue usually remained. The residue gave a strong qualitative test for chloride. It appears probable that the residue was a salt contamination which was picked up from the brine bath.

The samples taken from the linear apparatus were not distilled before analysis.

B. Results

Several runs were made with the linear apparatus in order to check the results of Smith and Posey, and to obtain practice with the technique. Figure 4 is a plot of the concentration profile after 62 passes with the linear apparatus. The concentration profile obtained by Smith and Posey after 50 passes with a similar apparatus is included for comparison.

Concentration profiles for several runs which were made with the spiral apparatus are shown in Figure 5. The horizontal lines indicate the initial concentration profiles. The straight lines were fitted to the data points by the least-squares method, in which the squares of the ordinate differences were minimized.
Figure 4

Concentration Profiles From Linear Zone Refining Apparatus
Figure 5
Concentration Profiles From Spiral Zone Refining Apparatus
CHAPTER IV

DISCUSSION

A. Theoretical

The hypothetical zone-refining process upon which the theoretical development was based was one in which a single liquid zone moved along the sample. A pass was completed each time that the liquid zone completely traversed the length of the sample. In a spiral apparatus which simultaneously contains L liquid zones, the spiral must rotate L times about its axis before a zone traverses the entire length of the sample. Each succeeding rotation about the axis completes an additional pass. If the apparatus is rotated R times there will be $R - L$ complete passes. The number of complete passes in a linear, multiple-zone apparatus may be determined in an analogous manner.

At the completion of the experiment there will remain $L - 1$ liquid zones which have traversed only a portion of the total length of the sample. The exact treatment of the concentration distribution in a multiple-zone apparatus for zone refining is complicated by these initial and final conditions which are superimposed upon the distribution produced by the completed passes.

The numerical calculations upon which Figure 1 is based were performed for a sample length of 10 segments and a zone width of 2 segments. These values were selected in order to reduce the quantity of the arithmetical manipulations. A more accurate treatment would require a larger number of segments for the sample and for the liquid zone.
B. Experimental

The concentration profiles shown in Figures 1, 4, and 5 show that the zone-refining process does concentrate D$_2$O in the direction which is predicted by the theory. However, the maximum concentration difference obtained with 373 complete passes was less than the theoretical difference for 4 passes. In addition, the restrictions which were applied in order to reduce the quantity of the calculations also lowered the theoretical value of the separation.

The apparatus in which Posey and Smith determined the equilibrium separation factor, χ, was vigorously shaken in order to maintain concentration equilibrium between the bulk of the liquid and that at the solid-liquid interface. In addition the freezing occurred at a very slow rate. Under these conditions they found that χ = 1.0211. The value of χ determined with rapid freezing and without agitation was from 1.0007 to 1.002. The absence of agitation probably accounts for the great quantitative difference between the theoretical and the experimental concentration profiles.

In the spiral apparatus the freezing interface was in a vertical portion of the tubing. Because of the temperature gradient immediately above the freezing interface, there was the possibility that a density inversion in the liquid would contribute a mixing effect and thus improve the separation factor. However, no significant mixing appears to have resulted from this geometrical arrangement.
C. Future Work

Zone refining with the apparatus discussed in this report is a batch process. However, several arrangements have been reported whereby the process may be made continuous.\textsuperscript{12,30} It is possible that such an arrangement might be adapted to the separation of D\textsubscript{2}O and H\textsubscript{2}O in a continuous operation.

The zone-refining process for the separation of D\textsubscript{2}O from H\textsubscript{2}O is so slow at present that its application may not be practical. The slowness is caused primarily by incomplete diffusion within the liquid which limits the rate of zone movement and reduces the effective separation factor. Adequate stirring of the liquid zones might increase the effective separation factor to a value near that obtained by Smith and Posey for the equilibrium separation factor. Figure 2 shows that with an effective separation factor of 1.02 a reasonably large concentration gradient will be established after a small number of passes. Efficient stirring might also allow a more rapid zone movement.

Such stirring might be accomplished by ultrasonic techniques.\textsuperscript{31} High-frequency vibrations could be introduced by mechanical or by magnetostrictive methods into the shaft of the spiral, or a piezoelectric transducer might be immersed directly in the thermostat bath.
CHAPTER V

SUMMARY

A theoretical analysis was developed for the separation of the isotopic forms of water by a zone-refining process. The separation was experimentally confirmed but was found to be much less than that predicted by the theory. The quantitative discrepancy was attributed to the very slow rate of diffusion in the water.

Several methods were suggested by which the magnitude of the isotopic separation might be increased, and by which the batch process might be converted into a continuous process.
BIBLIOGRAPHY


PART II

THE REACTION OF IRON WITH MIXTURES OF ORDINARY AND HEAVY WATER
CHAPTER I

INTRODUCTION

A. The Problem

An important part of the development of nuclear power is the procurement of heavy water which is used as a moderator in certain types of nuclear reactors. A moderator slows down the neutrons, which are produced in fission, to speeds at which they are more efficient in producing further fission. It can be seen from Table I\(^1\) that heavy water has a decided advantage as a moderator. The current high cost of heavy water is a serious disadvantage, however. Although the heavy water represents a capital investment, since it is not consumed in the operation of the reactor, the interest charges on the investment may contribute significantly to the cost of nuclear power production.

Since the natural concentration of deuterium in water is approximately 1 part in 7000, and since separation factors are relatively small for all available processes, it is necessary in the initial concentration stages to handle very large quantities of materials. The initial hundred-fold enrichment is responsible for the major portion of the production cost.\(^2\) As concentration proceeds smaller and smaller amounts of material remain to be processed.

Separation processes may be classified according to energy requirements as shown in Table II.\(^2\) The highest separation factor is obtained in the electrolytic process. However, the energy cost is high
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<thead>
<tr>
<th>Material</th>
<th>Scattering Cross Section (barns) $\sigma_s$</th>
<th>Capture Cross Section (barns) $\sigma_c$</th>
<th>Moderating Power* $M = (\sigma_s / \sigma_c)E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Water</td>
<td>46</td>
<td>0.66</td>
<td>67</td>
</tr>
<tr>
<td>Heavy Water</td>
<td>10.5</td>
<td>0.0009</td>
<td>5820</td>
</tr>
<tr>
<td>Beryllium</td>
<td>6</td>
<td>0.009</td>
<td>160</td>
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<tr>
<td>Graphite</td>
<td>4.8</td>
<td>0.0045</td>
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*E is the mean log energy loss per collision.
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<tr>
<th>Method</th>
<th>Approximate Energy Cost Per Pound of Heavy Water</th>
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<tr>
<td>A. High Energy Requirements</td>
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<tr>
<td>1. Diffusional Processes</td>
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<tr>
<td>2. Electrolysis of Water</td>
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<td>3. Centrifugation</td>
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<td>B. Moderate Energy Requirements</td>
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<td>1. Chemical Exchange Reactions</td>
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<td>3. Ammonia Distillation</td>
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<td>C. Low Energy Requirements</td>
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</tbody>
</table>
and the method is economically practical only when a market exists for electrolytic hydrogen or when the method is used for the final concentration of water which has been enriched by a more economical process. The Consolidated Mining and Smelting Company of Canada, Ltd., at Trail, British Columbia produces large quantities of electrolytic hydrogen for the synthesis of ammonia. Prior to the ammonia synthesis the electrolytic hydrogen is processed for the recovery of deuterium. Initial enrichment is obtained by several stages of catalytic exchange with water. Final enrichment is obtained in several electrolysis stages.

The commercial production of hydrogen by the reaction between iron and steam is economically competitive with the electrolytic process. The process is conducted at temperatures of 1500° to 1800° F. The reaction is rapid at this elevated temperature, but the separation factor is much smaller than that which may be obtained at lower temperatures.

Smith and Posey studied the reaction between iron and water in the temperature range 80° to 130° and between iron and steam in the temperature range 110° to 340°. They observed separation factors of 4.42 to 5.22 for the reaction with water and of 1.4 to 3.2 for the reaction with steam. The reaction rate at these temperatures is much lower than that in the commercial process. Some increase in the reaction rate was obtained by using finely divided iron powder which had a large specific surface area. The reaction was found to be stifled by its products before the iron powder was consumed.

The production of hydrogen by the reaction of iron with water is a corrosion process which is generally assumed to proceed by a galvanic
mechanism, with hydrogen gas being liberated at cathodic positions on the metal surface, and with iron being oxidized at anodic positions on the surface. In order for the reaction to take place a complete electrochemical cell must be formed. The electrodes may be formed by chemically dissimilar areas of the metal surface or by concentration gradients within the electrolyte. Part of the electrical path is between the cathode and the anode within the metal, and the remainder of the path is through the solution which is in contact with the metal.

In the decomposition of water by the reaction with iron, as in the electrolysis of water, the residual water is enriched in the heavy isotope, and the hydrogen which is produced is enriched in the lighter isotope. Isotope enrichment has also been observed in the reaction between water and other metals.

The reverse reaction, the reduction of iron oxide by hydrogen gas, gives isotope enrichment. In this case, the water which is produced by the reaction is enriched in the heavier isotope, and the residual hydrogen is enriched in the lighter isotope. Therefore, the forward and the reverse reactions combine to concentrate the heavy isotope, deuterium, in the liquid phase and to concentrate the lighter isotope in the gas phase.

The work discussed in this report was a continuation of the investigation which was begun by Smith and Posey. The following factors, which affect the reaction rate and the isotope separation in the production of hydrogen by the reaction of iron with aqueous salt solutions, were investigated:
(1) The chemical and the physical condition of the metal;
(2) The nature of the salt solution;
(3) The temperature;
(4) The effect of various cathodic surfaces which were introduced by plating other metals onto the iron;
(5) Methods of stirring the solutions.

Corrosion processes are usually investigated with the purpose of reducing or eliminating the corrosion. However, the reverse was true for the work discussed in this report. An attempt was made to increase the reaction rate in order to take advantage of the increased isotope separation factor which may be obtained by lowering the temperature.

B. The Separation Factor

1. Equilibrium Separation Factor

The equilibrium separation factor may be defined by equation 1,

$$\lambda = \frac{(D/H)_a}{(D/H)_b}$$  \hspace{1cm} (1)

where D and H may be expressed as the concentration, the mole fraction, or the mole per cent of deuterium and of hydrogen in forms a and b. The relationships were discussed in detail in Section I of this report.

2. Kinetic Separation Factor

A process for separating hydrogen and deuterium may depend upon the relative reaction rates of the two isotopic forms. If the reaction is first order with respect to the hydrogen and the deuterium concentrations, the kinetic separation factor may be expressed by equation 2,
where \( \frac{dD}{dt} \) and \( \frac{dH}{dt} \) are the rates of reaction of deuterium and of hydrogen and where \( D \) and \( H \) are the concentrations of deuterium and hydrogen in the reacting material. In the present case the reacting material may be either liquid water or steam.

Equation 2 may be rearranged and integrated between limits to give equation 3,

\[
\alpha \ln \frac{H_0}{H} = \ln \frac{D_0}{D}
\]

where \( H_0 \) and \( D_0 \) are the initial concentrations and \( H \) and \( D \) are the final concentrations of hydrogen and deuterium in the reacting material.

The conditions upon which the above derivation of the kinetic separation factor is based are analogous to a Rayleigh distillation in which the parent material becomes progressively depleted in one of the isotopic forms as the reaction proceeds.

The extent of the reaction may be made small enough so that the concentrations in the reacting material are essentially constant throughout the reaction. When this condition exists it is possible to use the expression for the equilibrium separation factor as a good approximation of the expression for the kinetic separation factor.

Eyring and Cagle\(^ {15} \) calculated the theoretical kinetic separation factor for the production of hydrogen by the metal-water reaction. Their calculations were based on the mechanism\(^ {16} \)

\[
\text{HOOH} + Me \rightarrow \text{HO} - - \text{H} - - \text{Me} \rightarrow \text{HO} + \text{HMe}
\]
drogen and the deuterium concentrations. They arrived at equation 5,

\[ \alpha = \frac{\sinh \left( \frac{h\gamma_{OH}}{2kT} \right)}{\sinh \left( \frac{h\gamma_{OD}}{2kT} \right)} \]  \hspace{1cm} (5)

which at ordinary temperatures may be simplified to give equation 6.

\[ \alpha = e \frac{1410}{RT} \]  \hspace{1cm} (6)

Although experimentally determined separation factors\textsuperscript{11-14,17-19} have generally been lower than those predicted by equations 5 and 6, the temperature dependence has been verified. The theoretical treatment of Eyring and Cagle does not account for the variation in the separation factor which is produced by changes in the chemical and the physical nature of the cathode. This variation has been observed in many investigations.\textsuperscript{11,17,18}
CHAPTER II

EXPERIMENTAL

A. Apparatus

1. Reaction Rates

   a. Method A. The apparatus illustrated in Figure 1 was used in collecting most of the data on the rate of the iron-water reaction. The reaction flask was made from a Pyrex tube with an inside diameter of about 1 cm. Eight flasks and 8 manometers were provided so that a large amount of data could be collected quickly.

   The volume of the salt solution used in each flask was approximately 10 ml. The gas-phase volume of a flask and manometer combination was approximately 12 ml. The flasks and the manometers were paired in a random manner in order to reduce the effect of inaccuracies in their volume calibrations.

   The flasks were connected to the manometers through ball joints which were sealed with Apiezon-T grease. Test runs indicated that the ball joints, when clamped, could hold hydrogen gas at an internal pressure of 50 cm. of mercury for a week without a noticeable loss in pressure. Occasionally a leak developed during a run. However, leaks could be detected easily when the data were plotted. They were indicated by an abrupt decrease in the apparent reaction rate.

   The general procedure for a run was as follows:

   (1) Several glass beads were placed in the flask to support the iron sample at a distance of about 1 cm. above the bottom
Figure 1

Apparatus for Measuring Rate of Hydrogen Evolution

(Method A)
of the flask;

(2) A freshly prepared iron sample was placed in the flask;

(3) A freshly prepared salt solution was filtered directly into the flask until the liquid surface reached the lower calibration mark;

(4) The flask was closed and was lowered into the thermostat;

(5) After temperature equilibrium was reached, which usually required about thirty minutes, the pressure in the flask was read periodically from the attached manometer.

b. Method B. The apparatus illustrated in Figure 2 was used to check the data obtained by Method A. It was necessary to show conclusively that the ball joints did not leak, since leaks would cause the apparent reaction rate to be lower than the correct value.

The volume of the flask was about the same as that of the flasks used in Method A. However, the manometer was sealed onto a side arm which contained a mercury reservoir. Two marks were made on the flask. The lower mark was at the surface of the salt solution. The volume of the flask up to the lower mark and the volume between the two marks were determined by adding water to the flask.

After the flask was loaded with the reactants, the neck was cut off with a torch as near as possible to the upper mark. A capillary vent was left, which was sealed when the reactants had been brought to temperature equilibrium with the thermostat. Otherwise, the procedure was the same as that described for Method A.
Figure 2

Apparatus for Measuring Rate of Hydrogen Evolution

(Method B)
c. **Method C.** The apparatus illustrated in Figure 3 was designed for runs on a larger scale than was possible with methods A and B. A 1200-ml. receiving flask was separated from the reaction flask by a mercury check valve. The valve was described by Posey. Before each run the receiving flask was evacuated. The use of the mercury check valve with the evacuated receiving flask allowed the reaction to be run at constant pressure, thereby providing a comparison with the reaction-rate data obtained under varying pressures by methods A and B. Since each run required from three to five days, several units were assembled to expedite the measurements.

Method C was also used to collect hydrogen-deuterium mixtures for the evaluation of separation factors.

d. **Thermostat.** An oil-bath thermostat, containing approximately 5 gallons of oil, was used in each of the methods described above. The temperature was maintained constant within approximately 0.5°.

An aluminum-block thermostat, illustrated in Figure 4, was used in addition to the oil-bath thermostat with Method C. The aluminum block was heated by a 90-watt cartridge heater which was inserted into a hole drilled in the block. Temperature regulation of approximately 0.25° was obtained by a Fenwal control inserted into a second hole drilled in the block. The block was covered with magnesia pipe insulation.

With methods A and B a reference flask containing an aqueous solution of sodium chloride was used. Pressure readings on the reaction
Figure 3

Apparatus for Measuring Rate of Hydrogen Evolution and Collecting Hydrogen for Separation Factor Measurements

(Method C)
Figure 4

Aluminum Block Thermostat

(Approximately 1/3 True Size)
flasks were made during the portion of the thermostat heating cycle in which the reference-flask pressure was at a predetermined value. Therefore, the water vapor pressure was constant for all readings which were made during a run.

In method C a water-cooled reflux condenser was placed directly above the reaction flask. The cooling-water temperature was usually about 15°. Since the mercury check valve was set to operate at a pressure of approximately 850 mm. of mercury the partial pressure of the water vapor was less than 2 per cent of the total pressure in the apparatus and it was disregarded.

2. **Separation Factors**

   a. **By Method C.** The hydrogen-deuterium mixture, which was collected in the receiving flask shown in Figure 3, was oxidized by copper oxide at approximately 300° in a Pyrex tube furnace. The water which was produced by this reaction was collected in a cold trap. The method has been described in detail by Posey. 7

   A small sample of the salt solution was taken before and after each run. The samples were vacuum distilled, and the water was collected in a cold trap. About 130 ml. of salt solution was used in each of the runs. The amount of water which was consumed in the reaction was small in comparison to the total amount of water present. However, the change in the composition of the residual water during a run was large enough to affect the calculation of the separation factor. Therefore the arithmetical average of the compositions at the beginning and at the end of the run was used in calculating the separation factor.
The isotopic composition of the water samples was determined by the falling-drop method of Combs, Googin, and Smith.20

b. By Electrolysis. Separation factors were determined in a series of electrolysis experiments with an external E. M. F. of about 4 volts and a current density of 0.06 to 4 amperes per cm.² The direct current was obtained from a combination of a selenium rectifier and a variable transformer.

All electrolysis experiments were conducted with 1 M. ferrous chloride solutions at temperatures of 30° to 45°. The heating was a result of the current carried by the solution.

A much larger fraction of the water was decomposed in the electrolysis runs than in the runs by method C. No hydrogen was collected in the electrolysis runs. Instead, the separation factor was determined from the initial and the final concentrations of the reacting water.

Most of the electrolysis experiments were conducted in a simple apparatus which consisted of a 180-ml. tall-form beaker, a cathode and an anode, and a source of direct current.

Experiments with this simple apparatus were further classified with respect to the manner of stirring the solution. In the first type, the only stirring was that which was provided at the surface of the cathode by the evolution of hydrogen gas. In the second type, the beaker was placed in the oil bath of an ultrasonic generator, directly above the barium titanate crystal transducer. The ultrasonic generator, which was manufactured by the Crystal Research Laboratories of Hartford, Connecticut, produced sufficient energy to create an oil-water emulsion in a test tube in less than one minute.
A third type of stirring was obtained with the apparatus shown in Figure 5. The center rod, which was rotated at various speeds by a cone-drive stirring motor, was the cathode. The rotation of the cathode provided some stirring at its surface. For additional stirring an off-balance weight was attached to the upper portion of the rod. In this manner the cathode was caused to vibrate vigorously as it rotated.

B. Materials

1. Salt Solutions

Most of the reaction-rate experiments and all of the separation-factor experiments were conducted with 1 M. ferrous chloride solutions. For runs in which no measurement of the separation factor was made, ordinary distilled water was used for the preparation of the salt solution. A standardized hydrochloric acid solution was prepared. The acid was added through a reflux condenser to an excess of iron powder in a 500-ml. Florence flask. The mixture was digested on a steam bath for two hours or more. Apparently with shorter digestion periods small amounts of unreacted acid sometimes remained and produced erroneously high reaction rates during the early part of some of the runs.

Immediately before a run the freshly prepared salt solution was filtered through Whatman No. 1 filter paper directly into a reaction flask which contained an iron sample. The filtrate was a clear blue-green color.

For runs in which separation-factor measurements were made, the above procedure for preparing the salt solutions was modified. A salt
Figure 5
Electrolysis Cell With Rotating Cathode
solution of approximately twice the desired strength was prepared as
described above. A calculated amount of heavy water was added slowly
to the hot salt solution through the reflux condenser. In this manner
a salt solution which contained approximately 45 mole per cent of heavy
water was prepared. The heavy water was obtained from the Stuart Oxygen
Company and was reported to be 99.8 per cent pure.

Additional runs for the evaluation of reaction rates were con-
ducted with 0.1 M., with 2 M., and with 3 M. ferrous chloride solutions.
A few runs were made with 1 M. ferrous iodide and with 1 M. ferrous sul-
fate solutions, which were prepared by the technique described above.

2. **Iron Samples**

   a. **Sources.** Iron samples in several chemical and physical forms
   were used in studying the effects of physical geometry, surface treat-
   ment, fabrication method, chemical composition, etc., on the reaction
   rates and on the separation factors. The materials are described below:

   (1) Iron powder (reduced by hydrogen) was obtained from Merck
   and Company. Several runs were made with this material in
   order to check the results which were reported by Smith and
   Posey and to obtain practice with the measurement technique.

   (2) Iron wire, a reagent grade for standardization purposes, was
   obtained from the J. T. Baker Chemical Company and from the
   Baker and Adamson Chemical Company. The wire size was AWG-36.

   (3) Small slugs of extremely pure bulk iron were obtained from
   the Bell Telephone Laboratories and from the Batelle Institute.
   A discussion of the preparation of very pure iron samples has
been given by Moore. 21

(4) Ordinary low-carbon steel plate, rod, and tubing samples were also used.

b. Fabrication. The iron and steel samples were fabricated as follows:

(1) Wire samples of a known length were wound onto a glass spindle of 3 mm. diameter. The spiral length was about 3 cm. for 1 meter of wire. When the glass spindle was removed, the spiral diameter expanded to about 5 mm.

(2) Small cylindrical slugs of very pure iron were machined on a lathe. In some cases additional surface smoothing was obtained by filing or by polishing with emery cloth.

(3) Small rectangular slugs of steel plate were cut with a hacksaw and were smoothed with a file and with emery cloth.

(4) Steel tube and rod sections were cut with a hacksaw and the ends were smoothed with a file.

c. Cleaning. In most cases the metal samples were cleaned by washing with hot C. P. toluene and then by pickling in various acids. It has been found that traces of hydrophobic contaminants on the surface of metals are often not removed by treatment with organic solvents or with non-oxidizing acids. The presence of hydrophobic contaminants may have a significant effect on the rate of chemical reactions at the surface of the metal. 22 Such contaminants may be removed by treatment with an oxidizing acid or by air oxidation at elevated temperatures. However, reaction rate data obtained from several samples which were cleaned by each of these two methods were essentially the same as the data obtained
from samples cleaned in the ordinary manner described above. An additional test of the cleanliness of the metal surfaces was based on the fact that a water drop exhibits a measurable contact angle when hydrophobic contaminants are present on the surface of the metal. \(^{22}\) In the absence of such contaminants the water drop spreads and wets the surface, producing a contact angle which is too small to be detected. The apparatus required for this test are an ordinary nebulizer for applying small drops of distilled water to the metal surface and a low-power magnifying glass for observing the contact angle of the drops on the metal surface. A piece of freshly split mica provides a clean surface for reference purposes.

d. **Plating.** Cathodic surfaces can be applied to iron powder only by generalized chemical means which provide no control over the fraction of the surface which is covered. However, with bulk samples predetermined fractions of the surface may be plated with a variety of metals.

Several methods were used for the application of metal surfaces to the iron samples. In the simplest of these the iron sample was partially immersed in the appropriate salt solution, and the plating was accomplished by ordinary chemical displacement. The method was used to apply mossy coatings of platinum, of palladium, and of copper, which were easily dislodged from the sample surface.

Some of the iron samples were plated with bright platinum by thermal decomposition. A solution of chloroplatinic acid was evaporated to dryness and was dissolved in a small amount of ethyl alcohol. Ten volumes of synthetic oil of wintergreen were added per volume of
alcohol. The oily solution was applied to the surface of the iron and was burned off at a low heat in a gas flame. Approximately a dozen successive applications gave a heavy coating of bright platinum which was attached quite firmly to the foundation metal. The platinum could be removed by undercutting with strong hydrochloric acid.

The major portion of the plating was applied electrically by a brush-plating technique. Kits for this purpose were obtained from the Rapid Electroplating Company of Chicago, Illinois. Surfaces of gold, silver, copper, brass, nickel, and cadmium were applied in this manner. In these kits the metal salt was blended with a starch-base paste, which was applied with a brush. In the electrical circuit the iron sample was one electrode and the brush was the other electrode. The metal salts were present as the chlorides, except for the gold and the silver which were present as chloride-cyanide mixtures. The cathodic coating applied in this manner was thin, and flaws in the foundation metal could not be covered. In addition, under the conditions of the reaction the coatings did not adhere firmly to the foundation metal.

e. Surface Area. The surface area of the iron powder was measured by the BET-nitrogen-adsorption method and by the krypton-adsorption method. The values found by these two methods were 3.5 meter$^2$ gm.$^{-1}$ and 3.4 meter$^2$ gm.$^{-1}$ respectively. The iron powder used in this work was believed to be from the same stock as that used by Posey,$^7$ which was reported to have a surface area of 1.6 meter$^2$ gm.$^{-1}$. Posey's value was obtained by the BET-nitrogen-adsorption method and by the rapid-nitrogen adsorption method.
The surface area of a sample of the J. T. Baker iron wire was measured by the krypton-adsorption method and was found to be 24.3 cm\(^2\) meter\(^{-1}\). A roughness factor of 3.67 was calculated from the surface area and the wire dimensions.

The bulk-iron samples, other than the wire, were too small for surface-area measurements to be made on them. In order to provide some basis for comparison of surfaces, photomicrographs were made of several of these samples. The photographs are shown in Figures 6-a through 6-i. The wire in Figure 6-a is a sample of the J. T. Baker material. All of the photographs were made with 50X magnification.

C. Calculations

1. Reaction Rates

In order to obtain a comparison between the reaction rates observed with powder and with bulk samples, the rate of hydrogen evolution was calculated in ml. cm\(^{-2}\) min\(^{-1}\). The hydrogen volume was corrected to 30\(^\circ\) and a pressure of 760 mm. of mercury. At constant temperature

\[ P_1 V_1 = P_2 V_2 \]  
\[ P_1 \Delta V_1 = V_2 \Delta P_2 \]  
\[ \Delta V_1 = (V_2/P_1) \Delta P_2 \]  
\[ \Delta V_1/cm^2 = (V_2/A_{P_1}) \Delta P_2 \]

where \( V_2 \) = the gas-phase volume of the flask and the manometer;
\[ P_1 = 760 \text{ mm.} \];
\[ \Delta P_2 \] = the observed pressure change in mm. of mercury;
Figure 6-a.
J. T. Baker Iron Wire
A - Fresh Sample
B - After 100 Hours in 1 M. Ferrous Chloride at 98°

Figure 6-b.
Low Carbon Steel Plate
After Pickling With Sulfuric Acid to Remove Scale

Figure 6-c.
Low Carbon Steel Plate
After 100 Hours in 1 M. Ferrous Chloride at 98°
Figure 6-d.
Battelle Iron Sample
Before Run. Surface
Finished With Fine File.

Figure 6-e.
Battelle Iron Sample
After 200 Hours in 1 M.
Ferrous Chloride at 98°.

Figure 6-f.
Same Sample as in Figure 6-e.
Surface Refinished With Fine
File and Emery Cloth.
Figure 6-g.  
Battelle Iron Sample  
After 300 Hours in 1 M.  
Ferrous Chloride at 98°.

Figure 6-h.  
Bell Telephone Iron Sample  
After 200 Hours in 1 M.  
Ferrous Chloride at 98°.

Figure 6-i.  
Low Carbon Steel Tubing  
After Pickling With  
Sulfuric Acid to Remove  
Scale.
A = the sample surface area in cm.$^2$; and

$\Delta V_1$ = the total volume of hydrogen evolved, corrected to $30^\circ$.

The values of $\Delta V_1$/cm.$^2$, as the ordinate, were plotted versus time, as the abscissa, and the reaction rates were determined from the slopes of the lines. In almost every case a straight line appeared to fit the data for the entire run. The slopes of the straight lines were determined by the method of least squares, in which the squares of the ordinate differences were minimized. For reasons already discussed no correction for the vapor pressure of water was included.

2. **Separation Factors**

Since the change in the isotopic composition of the solutions was small during a run by method C, equation 11 was used in calculating the separation factors.

$$\lambda = \frac{(D/H)_{\text{average values for the residual water}}}{(D/H)_{\text{gas produced by the reaction}}}$$

(11)

where D and H are the mole fractions of deuterium and of hydrogen as indicated. Equation 11 has the same form as equation 1, which defines the equilibrium separation factor. However, for the condition stated above the expression for the equilibrium separation factor is a good approximation of the expression for the kinetic separation factor.

The separation of the hydrogen isotopes by the chemical or the electrical decomposition of water is a kinetic process. In the electrolysis runs enough water was decomposed so that there was a significant change in the composition of the reacting water. Therefore, for the electrolysis runs it was necessary to calculate the separation factors from equation 3, which defines the kinetic separation factor.
CHAPTER III

RESULTS

A. Reaction Rates

1. Iron Powder

Method C was used to make several runs with iron powder in 1 M. ferrous chloride solutions at 98°. The rates of hydrogen evolution were calculated in ml. cm.\(^{-2}\) min.\(^{-1}\). The volume term was corrected to 30° and a pressure of 760 mm. of mercury.

Table III summarizes the reaction rates which were obtained in this manner. The data provide a comparison between the present work and that of Smith and Posey\(^7,8\) and confirm the quenching effect which they reported for the reaction with iron powder. The data also allow a comparison to be made between the reaction rates observed with iron powder and with bulk-iron samples.

2. Bulk Iron

   a. Unplated samples. Reaction-rate measurements were made with bulk iron and steel in several physical and chemical forms in order to evaluate the effect of physical geometry, of surface preparation, and of physical and chemical composition on the reaction rates. The samples were supported by glass beads at a distance of approximately 1 cm. above the bottom of the flask, as shown in Figures 1-3. A black, magnetic-oxide product settled to the bottom of the flask, and other oxide products collected at the surface of the salt solution as the run progressed.
### TABLE III

RATE OF HYDROGEN EVOLUTION IN THE REACTION OF IRON POWDER WITH 1 M. FERROUS CHLORIDE SOLUTION AT 98°C

<table>
<thead>
<tr>
<th>Data Source</th>
<th>Extent of Reaction ( \text{ml. cm}^{-2} \times 10^4 )</th>
<th>Reaction Rate ( \text{ml. cm}^{-2} \text{ min}^{-1} \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Smith and Posey⁷,⁸</td>
<td>32</td>
<td>15</td>
</tr>
<tr>
<td>Present Work</td>
<td>32</td>
<td>15</td>
</tr>
<tr>
<td>Smith and Posey⁷,⁸</td>
<td>100</td>
<td>46</td>
</tr>
<tr>
<td>Present Work</td>
<td>100</td>
<td>46</td>
</tr>
</tbody>
</table>

\( \text{A} \) - Calculated on the assumption of a specific surface area of \( 1.6 \times 10^4 \text{ cm}^2 \text{ gm}^{-1} \).

\( \text{B} \) - Calculated on the assumption of a specific surface area of \( 3.45 \times 10^4 \text{ cm}^2 \text{ gm}^{-1} \).

\( ^a \) Values arbitrarily selected. Does not indicate completion of reaction.
No oxide product was visible on the surface of the samples. Although the total quantity of hydrogen evolved per cm.$^2$ of surface area was many times larger than that produced in the reaction with iron powder, no quenching was observed.

Variations in the nature of the sample had very little effect on the rate of the reaction. The surfaces were prepared in a variety of ways. Different degrees of roughness were introduced by machining, by filing, and by polishing with emery cloth. Some of the samples were pickled extensively in hydrochloric acid or in sulfuric acid before starting the runs. In addition, the corrosion which occurred during a run increased the surface roughness. Typical surface conditions are illustrated in Figures 6-a through 6-i.

The results of measurements made with 1 M. ferrous chloride solutions at 98° are summarized in Table IV. The reaction rates, which were essentially constant throughout each run, were averaged arithmetically, and no distinction was made regarding the surface preparation of the sample. Since for the bulk-iron samples true surface area measurements could not be made, except on the wire samples, a unit roughness factor was arbitrarily assumed for all of the bulk-iron samples in calculating the rates.

In any heterogeneous reaction the surface area should be a factor in the reaction rate. This conclusion was confirmed by the fact that reaction rates, calculated per unit of surface area, were in reasonable agreement for runs with iron powder and with bulk iron, although the specific surface areas of the two forms differed by orders of magnitude. The significant surface area appears to be determined
TABLE IV

RATE OF HYDROGEN EVOLUTION IN THE REACTION OF BULK IRON SAMPLES WITH 1 M.
FERROUS CHLORIDE SOLUTIONS AT 98°

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extent of Reaction ml. cm.⁻² x 10⁴</th>
<th>Reaction Rate ml. cm.⁻² min.⁻¹ x 10⁴</th>
<th>n*</th>
<th>Precision*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire (J. T. Baker)</td>
<td>7000</td>
<td>1.54</td>
<td>2</td>
<td>0.01</td>
</tr>
<tr>
<td>Wire (Baker and Adamson)</td>
<td>10000</td>
<td>1.55</td>
<td>13</td>
<td>0.05</td>
</tr>
<tr>
<td>Low Carbon Steel Plate</td>
<td>7000</td>
<td>0.90</td>
<td>3</td>
<td>0.04</td>
</tr>
<tr>
<td>Low Carbon Steel Tubing</td>
<td>11000</td>
<td>1.07</td>
<td>2</td>
<td>0.05</td>
</tr>
<tr>
<td>Pure Iron (Battelle)</td>
<td>14000</td>
<td>1.17</td>
<td>5</td>
<td>0.07</td>
</tr>
<tr>
<td>Pure Iron (Bell Telephone)</td>
<td>10000</td>
<td>1.04</td>
<td>3</td>
<td>0.07</td>
</tr>
</tbody>
</table>

*Precision is defined throughout this report as

\[ P = \pm \frac{\sum d}{n \sqrt{n}} \]

where d is the deviation of a single measurement from the arithmetical average, and where n is the number of measurements considered in the calculation.
by the gross dimensions of the metal rather than by the condition of
the surface. This observation has been reported elsewhere.\textsuperscript{10} Reaction
rates with iron powder agreed very well with those obtained by Smith
and Posey,\textsuperscript{7,8} although the specific surface area reported by them was
\(1.6 \times 10^4 \text{ cm.}^2 \text{ gm.}^{-1}\) as compared with \(3.4 \times 10^4 \text{ cm.}^2 \text{ gm.}^{-1}\) found in the
current investigation. With bulk-iron samples the condition of the
metallic surface, as illustrated in Figures 6-a through 6-i, appeared
to have little or no effect upon the reaction rate. The reaction rates
per unit of surface area were in fair agreement when an arbitrary
roughness factor of unity was assumed, although a roughness factor of
3.67 was actually found for the iron wire, and visual examination of
the iron slugs indicated that their roughness factor was probably
greater than unity.

The effects of temperature, salt type, and salt concentration
were investigated. For temperatures somewhat above 100° it was neces-
sary to operate the system at a pressure greater than atmospheric. The
increase in the reaction rate did not appear to justify the increased
manipulative problems associated with pressurized operation. Therefore
the majority of the investigation was conducted at a temperature of
approximately 100°.

Several salt types were investigated. Ferrous chloride was
chosen for most of the work since it appeared to produce a slightly
greater reaction rate than any of the other salt types which were
studied and since it was desirable to have a direct comparison with
the earlier work of Smith and Posey. An increase in the salt concen-
tration to a value greater than 1 M. produced only a slight increase in
the reaction rate.

The effects of temperature, salt type, and salt concentration are summarized in Tables V, VI, and VII.

b. Partially plated samples. The tendency of metals to corrode by displacing hydrogen ions from solution is indicated in a general way by their position in the electrochemical series\textsuperscript{23} which is shown in Table VIII. It should be noted that the potentials given in the table apply only to the condition where the metal is in contact with a solution of the indicated ion at unit activity. In addition the potential is for a zero current condition. In a corrosion cell the electrical path within the metal between the cathode and the anode has a very low ohmic resistance which affects the measured potential difference between the two electrodes. In addition the phenomenon of hydrogen overvoltage is not included in the table. The relationship between potential and corrosion rate has been discussed in detail by Hayes.\textsuperscript{24}

Some measurements of the reaction rate were made with samples of wire, of Bell Telephone iron, of Battelle iron, and of steel plate which were partially plated with mossy deposits of platinum, of palladium, and of copper. In general, the initial rates were several times larger than those which were obtained with unplated iron samples. However, the hydrogen evolution rates dropped off and approached the values which were obtained with unplated iron. The mossy deposits had a tendency to become detached from the iron, and they collected a layer of red-brown iron oxide very quickly. This oxide layer eventually turned black. The reproducibility of the rate measurements with this type of plating was very poor.
TABLE V

RATE OF HYDROGEN EVOLUTION IN THE REACTION OF BULK IRON WITH VARIOUS CONCENTRATIONS OF FERROUS CHLORIDE SOLUTION AT 98°

<table>
<thead>
<tr>
<th>Salt Concentration</th>
<th>Wire (Baker and Adamson) Reaction Rate</th>
<th>Low Carbon Steel Tubing Reaction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ml. cm.(^{-2}) min.(^{-1}) x 10^4</td>
<td>n</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>0.1 M.</td>
<td>0.32</td>
<td>3</td>
</tr>
<tr>
<td>1.0 M.</td>
<td>1.55</td>
<td>13</td>
</tr>
<tr>
<td>2.0 M.</td>
<td>2.06</td>
<td>6</td>
</tr>
<tr>
<td>3.0 M.</td>
<td>2.10</td>
<td>3</td>
</tr>
</tbody>
</table>
## TABLE VI

RATE OF HYDROGEN EVOLUTION IN THE REACTION OF IRON WIRE WITH 1 M. FERROUS CHLORIDE SOLUTIONS AT VARIOUS TEMPERATURES

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Reaction Rate $\text{ml. cm.}^{-2} \text{min.}^{-1} \times 10^4$</th>
<th>n</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>80°</td>
<td>0.72</td>
<td>2</td>
<td>0.04</td>
</tr>
<tr>
<td>98°</td>
<td>1.55</td>
<td>13</td>
<td>0.05</td>
</tr>
<tr>
<td>115°</td>
<td>3.05</td>
<td>2</td>
<td>0.07</td>
</tr>
</tbody>
</table>
TABLE VII

RATE OF HYDROGEN EVOLUTIONS IN THE REACTION OF IRON WIRE WITH VARIOUS 1 M. SALT SOLUTIONS AT 98°

<table>
<thead>
<tr>
<th>Salt Solution</th>
<th>Reaction Rate</th>
<th>n</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous Chloride</td>
<td>1.55</td>
<td>13</td>
<td>0.05</td>
</tr>
<tr>
<td>Ferrous Iodide</td>
<td>0.51</td>
<td>3</td>
<td>0.06</td>
</tr>
<tr>
<td>Ferrous Sulfate</td>
<td>1.12</td>
<td>3</td>
<td>0.02</td>
</tr>
<tr>
<td>Metal</td>
<td>Reaction</td>
<td>Potential</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------------------------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg → Mg(^{++}) + 2e</td>
<td>+2.37</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al → Al(^{+++}) + 3e</td>
<td>+1.66</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn → Zn(^{++}) + 2e</td>
<td>+0.76</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr → Cr(^{+++}) + 3e</td>
<td>+0.74</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>Fe → Fe(^{+++}) + 2e</td>
<td>+0.44</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd → Cd(^{++}) + 2e</td>
<td>+0.40</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni → Ni(^{++}) + 2e</td>
<td>+0.25</td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td>Sn → Sn(^{++}) + 2e</td>
<td>+0.14</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>Pb → Pb(^{++}) + 2e</td>
<td>+0.13</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H → H(^{+}) + 1e</td>
<td>+0.00</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>Cu → Cu(^{++}) + 2e</td>
<td>−0.34</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>2Hg → Hg(^{2+}) + 2e</td>
<td>−0.79</td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>Ag → Ag(^{+}) + 1e</td>
<td>−0.80</td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
<td>Pt + 2H(_2)O → Pt(OH)(_2) + 2H(^{+}) + 2e</td>
<td>−0.98</td>
<td></td>
</tr>
<tr>
<td>Palladium</td>
<td>Pd → Pd(^{++}) + 2e</td>
<td>−0.99</td>
<td></td>
</tr>
<tr>
<td>Gold</td>
<td>Au → Au(^{+++}) + 3e</td>
<td>−1.50</td>
<td></td>
</tr>
</tbody>
</table>
Some runs were made with iron samples which were partially plated with bright platinum which was applied by thermal decomposition. The rate of hydrogen evolution was 3 to 5 times as great as that obtained with unplated iron. The rate did not fall off with time, and there was no visible accumulation of iron oxide on the platinum surface. At the end of a run of this type, the platinum plate was stripped by undercutting the platinum with strong hydrochloric acid, and a second run was made on the stripped iron sample. The rate with the stripped sample was much lower than the original rate on an unplated sample.

Plating was applied electrically by the brush-plating technique to sections of steel tubing. The entire outside surface of the tube was plated by this method. Since the tube wall was thin, the plated surface was approximately 50 per cent of the total surface. The effect of relative cathode and anode areas was investigated by Whitman and Russell. Figure 7 illustrates the relationship between the corrosion rate and the relative electrode areas. For a fixed anode area an increase in the cathode area by a factor of 20 increased the corrosion rate only by a factor of 10 above the normal corrosion rate. It should be noted that the corrosion rate in Figure 7 is specified per unit area of the anode. The current density at the cathode actually dropped by a factor of 2. It therefore appeared that for a fixed total sample area no significant increase in the rate of production of hydrogen would be obtained for moderate changes in the relative areas of the electrodes. A cathode-to-anode area ratio of approximately unity was chosen as a convenient and easily reproducible value.
Effect of Area of Copper Cathode on Galvanic Corrosion of Iron Anode in Aerated 3 Per Cent Sodium Chloride Solution at 30° 10
The increase which was produced in the reaction rate by the artificial introduction of galvanic couples is shown in Table IX. Cathodic polarization by hydrogen probably prevented the reaction rate from being much larger. Oxidizing agents are powerful corrosion accelerators because of their ability to depolarize the cathode by the oxidation of hydrogen to form water. Dissolved oxygen is a common depolarizing agent and its effect on the corrosion rate is shown in Table IX.\textsuperscript{10,25,26} It can be seen that cathodic depolarization may further increase the reaction rate by an order of magnitude or more. Since hydrogen was the desired product in the current work, it was not possible to take advantage of oxidative depolarization of the cathode. Instead, the preparation and the handling of the salt solutions was done in such a manner as to minimize the amount of dissolved air. The ferrous solutions were continually in contact with excess metallic iron and were always a blue-green color.

Most of the hydrogen was evolved at the cathodic surface, which did not appear to collect an oxide layer. However, some bubble formation was still observed at the unplated surface. The most vigorous evolution of hydrogen occurred on the cathodic surface near its edge, and a portion of the plating usually flaked off during a run, as if it were undercut by the chemical reaction. There was some tendency for the rate to fall off as the runs with brush-plated samples progressed.

In calculating the rate per unit area, a unit roughness factor was arbitrarily assumed for the plated samples, as was previously done for the unplated samples. In addition, the area used was that of the entire sample.
TABLE IX

RATE OF HYDROGEN EVOLUTION IN THE REACTION OF CATHODICALLY COATED STEEL TUBING WITH 1 M. FERROUS CHLORIDE SOLUTIONS AT 98°C

<table>
<thead>
<tr>
<th>Cathodic Surface</th>
<th>Reaction Rate (ml. cm.⁻² min.⁻¹ x 10⁴)</th>
<th>n</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel Tubing (Uncoated)</td>
<td>1.07</td>
<td>2</td>
<td>0.05</td>
</tr>
<tr>
<td>Gold</td>
<td>4.3</td>
<td>2</td>
<td>0.7</td>
</tr>
<tr>
<td>Silver</td>
<td>2.8</td>
<td>2</td>
<td>0.4</td>
</tr>
<tr>
<td>Copper</td>
<td>3.1</td>
<td>2</td>
<td>0.4</td>
</tr>
<tr>
<td>Brass</td>
<td>3.3</td>
<td>2</td>
<td>0.4</td>
</tr>
<tr>
<td>Nickel</td>
<td>3.9</td>
<td>2</td>
<td>0.4</td>
</tr>
<tr>
<td>Cadmium</td>
<td>2.5</td>
<td>2</td>
<td>0.4</td>
</tr>
</tbody>
</table>
### TABLE X

**EFFECT OF OXIDIZING AGENTS ON THE CORROSION RATE OF METALS**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Solution</th>
<th>Corrosion Rate mg. dm.² day⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>Air-saturated 5 per cent sulfuric acid at 30°</td>
<td>530</td>
</tr>
<tr>
<td>Nickel</td>
<td>Air-free 5 per cent sulfuric acid at 30°</td>
<td>20</td>
</tr>
<tr>
<td>Monel</td>
<td>Air-saturated 5 per cent sulfuric acid at 30°</td>
<td>240</td>
</tr>
<tr>
<td>Monel</td>
<td>Air-free 5 per cent sulfuric acid at 30°</td>
<td>40</td>
</tr>
<tr>
<td>Monel</td>
<td>Air-free 1.6 per cent sulfuric acid at 30°</td>
<td>140</td>
</tr>
<tr>
<td>Monel</td>
<td>Air-free 1.6 per cent sulfuric acid plus 0.18 per cent ferric sulfate at 30°</td>
<td>1215</td>
</tr>
</tbody>
</table>
B. Separation Factors

1. **By Method C**

Both plated and unplated samples of steel tubing were used in the measurement of the separation factor by method C. With an unplated sample about 400 cm$^2$ of surface area was required in order to generate a liter of hydrogen in five days. With cathodically plated samples the required time was shorter.

Steel tubing was used for these runs since it provided the most convenient form for plating, for obtaining a large surface area, and for physically supporting the sample in the reaction flask. Eight pieces of the tubing were placed on end in the reaction vessel which contained approximately 130 ml. of 1 M. ferrous chloride solution. Water mixtures containing approximately 45 mole per cent of heavy water were used.

For runs with cathodically plated samples the outside surface of each tube section was plated. Table XI lists the separation factors obtained in the reaction of 1 M. ferrous chloride solution, at 100$^\circ$, with unplated and with plated samples of steel tubing. No measurements were made with bright platinum or palladium plate, since the heat treatment used in applying these metals caused a reduction in the activity of the foundation metal.

2. **By Electrolysis**

A series of electrolyses was performed by the methods described in the preceding chapter. The purpose of these runs was to determine the effect of vigorous stirring upon the separation factor. The results are given in Table XII.
### TABLE XI

SEPARATION FACTORS OBSERVED IN THE REACTION OF CATHODICALLY COATED STEEL TUBING WITH 1 M. FERROUS CHLORIDE SOLUTIONS AT 100°

<table>
<thead>
<tr>
<th>Cathodic Surface</th>
<th>Separation Factor</th>
<th>n</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel Tubing (Uncoated)</td>
<td>6.1</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>Gold</td>
<td>5.7</td>
<td>4</td>
<td>0.4</td>
</tr>
<tr>
<td>Silver</td>
<td>5.6</td>
<td>2</td>
<td>0.7</td>
</tr>
<tr>
<td>Copper</td>
<td>6.0</td>
<td>2</td>
<td>1.0</td>
</tr>
<tr>
<td>Brass</td>
<td>6.0</td>
<td>2</td>
<td>0.7</td>
</tr>
<tr>
<td>Nickel</td>
<td>4.8</td>
<td>2</td>
<td>0.9</td>
</tr>
<tr>
<td>Cadmium</td>
<td>5.3</td>
<td>2</td>
<td>0.7</td>
</tr>
</tbody>
</table>
### TABLE XII

EFFECT OF STIRRING ON SEPARATION FACTORS OBSERVED IN THE ELECTROLYSIS OF 1 M. FERROUS CHLORIDE SOLUTIONS WITH STEEL ELECTRODES AT 30° TO 45°

<table>
<thead>
<tr>
<th>Method of Stirring</th>
<th>Separation Factor</th>
<th>n</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen evolution at cathode</td>
<td>7.23</td>
<td>3</td>
<td>0.09</td>
</tr>
<tr>
<td>Rotating cathode with off-balance weight attached</td>
<td>7.61</td>
<td>3</td>
<td>0.08</td>
</tr>
<tr>
<td>Ultrasonic agitation</td>
<td>8.32</td>
<td>5</td>
<td>0.07</td>
</tr>
</tbody>
</table>
In all of the electrolysis experiments with an iron anode, a black deposit adhered loosely to the cathode and reacted vigorously with hydrochloric acid to produce hydrogen gas. However, after several hours of electrolysis the deposit became firmly attached to the cathode and reacted more slowly with hydrochloric acid. After six hours of electrolysis with the rotating cathode the deposit was so firmly attached to the cathode that it could not be removed from the cell through the hole in the Teflon bushing. The cathode did not become coated when a platinum anode was used in the ferrous chloride solutions. A finely divided green precipitate formed in the vicinity of the iron anode, but did not adhere to it. No coating was visible on the anode in any of the electrolyses which were performed.
CHAPTER IV

DISCUSSION

A. Reaction Rates

1. Experiments With Iron Powder

Posey\textsuperscript{7,8} investigated the reaction between water and iron powder, for which he reported a specific surface area of $1.6 \times 10^4 \text{ cm.}^2 \text{ gm.}^{-1}$. As part of the investigation discussed in this report some additional runs were made with water and iron powder. Although the iron powder was believed to be from the same stock as that used by Posey, a specific surface area of $3.45 \times 10^4 \text{ cm.}^2 \text{ gm.}^{-1}$ was found. The disagreement in the specific surface areas may have been the result of partial oxidation of the iron surface, or it is possible that the two powders were not from the same stock. It is improbable that the difference in the surface areas could be the result of analytical errors. All of the measurements were made by the same laboratory. In addition, each value given above was obtained by two independent methods as discussed earlier in this report.

Because of the uncertainty regarding the specific surface areas the values of the reaction rates for both powders, which are shown in Table III, were calculated for both surface areas. The calculated reaction rates for the two powders agree very well, if the two powders are arbitrarily assumed to have the same specific surface area. There are two possible explanations for this fact. The first is that the mass of the iron, rather than the surface area, is the significant factor in
the reaction rates. The second is that sub-macro variations in the specific surface areas, which might account for the disagreement noted above, do not significantly affect the reaction rates. The second explanation appears to be more reasonable, especially in view of additional data obtained with bulk-iron samples.

The quenching effect, although somewhat smaller than that observed by Posey, was confirmed.

2. Experiments With Unplated Bulk Iron Samples

a. Effect of temperature, salt type, and salt concentration. Posey discussed in detail the effects of these variables upon the rate of the reaction between iron powder and water. For the work discussed in this report it was desirable to obtain a large reaction rate with simple apparatus and procedures. The data presented in Tables V, VI, and VII were obtained for the purpose of determining the most desirable operating conditions. On the basis of these data it was decided to perform the remainder of the experiments in 1 M. ferrous chloride solutions at 98-100°.

b. Effect of surfaces. With the bulk-iron samples, variations in the surface roughness factor, which were purposely introduced by mechanical and by chemical methods, had no observable effect on the reaction rate. This observation further supports the statements in the preceding section which dealt with the surface area of the iron powder.

The agreement between the reaction rates calculated for iron powder and for bulk iron is good, when the relative magnitudes of the specific surface areas and the absence of information on the roughness
factor of the iron powder are considered.

c. **Quenching.** No quenching was observed in any of the runs with bulk-iron samples, although the extent of the reaction per unit of surface area was several orders of magnitude greater than that per unit of surface area with the powders. Posey concluded that the quenching effect which he observed in the reaction of iron powder with water was caused by the deposition of an oxide coating on the anodic portion of the surface. The bulk-iron samples were supported above the bottom of the reaction flask, and the magnetic oxide product was observed to settle to the bottom of the flask. In discussing the formation of oxide coatings at the anode, Evans\(^2\) states that in a solution which is free of dissolved oxidizing agents the oxide product will be precipitated at some distance from the anode. In a solution containing dissolved oxidizing agents the oxide product will be precipitated at the surface of the anode. In the current work the salt solutions were prepared and handled in such a manner that the amount of dissolved oxygen and other oxidizing agents was minimized. The geometry used in the experiments allowed the oxide product to settle away from the sample, while with the powder experiments the oxide product settled to the bottom of the flask together with the sample.

3. **Experiments With Partially Plated Bulk Iron Samples**

The acceleration of corrosion by the introduction of galvanic couples is a well-known engineering fact. A common technique for preventing corrosion is based upon the preferential oxidation of an expendable metal which is included in the system. In the present work
the application of cathodic surfaces by plating portions of the iron surface increased the rate of hydrogen production by a factor of from 2 to 4.

The data shown in Table X indicate that a reduction of the cathodic polarization might further increase the reaction rate by a significant amount. Oxidative depolarization would not be practical since the purpose of the reaction is to produce hydrogen gas. A large increase in the surface area, such as that which is accomplished by platinizing, reduces the polarization. Abrasion of the cathode, by a technique similar to sand-blasting, will also increase the surface area. Further reduction of polarization may be accomplished by stirring. Ultrasonic techniques would allow the thin film at the surface of the cathode to be stirred vigorously.

B. Separation Factors

1. Calculations

   a. The equations used. The separation of hydrogen and deuterium by chemical or by electrical decomposition of water depends upon the difference in the reaction rates of the two species. Therefore, the separation is a kinetic process and a kinetic separation factor should be calculated. Equation 3 defines the kinetic separation factor insofar as the mechanism which was assumed in deriving it is valid.

   For the integration of equation 2 to give equation 3 it was not necessary to limit the extent of the reaction. Since the extent of the reaction in the electrolysis experiments was large enough to signifi-
cantly affect the concentration in the reacting water, equation 3 was used to calculate the kinetic separation factor.

A very small fraction of the water was decomposed in the chemical reaction between iron and water, and the composition of the reacting water remained nearly constant. Therefore equation 11, which has the same form as equation 1, was used in calculating the separation factor. Equation 1 defines the equilibrium separation factor. However, for a very small extent of reaction it is a good approximation for the expression of the kinetic separation factor.

b. Precision. The precision, which was defined in Table IV, was much better for the electrolysis of water than for the chemical decomposition of water by the reaction with iron. The analytical technique was the same for both types of runs. Variations in the nature of the plated surface applied to the iron samples may account for the poorer precision of the data in Table XI. Similar difficulties have been reported elsewhere.

2. Effect of Cathode Material

The average values of the separation factors in the chemical reaction of iron with water vary from 4.8 for a brass cathode to 6.1 for uncoated steel. The values of the separation factors are not sufficiently precise to show conclusively any variation due to the nature of the cathode. From the data in Table XI a composite separation factor of 5.7 may be calculated with a precision of 0.2.
3. **Effect of Stirring**

Topley and Eyring\(^{19}\) discussed in detail the effect upon the observed separation factor of a concentration gradient in the thin film of liquid at the cathode surface. They concluded that the effect should be small. The data in Table XII show that efficient stirring can increase the separation factor. In the case of ultrasonic agitation the increase may be due to other factors in addition to stirring. It has been shown that the nature of a chemical process may be affected by ultrasonic energy.\(^{28,29}\)

4. **Effect of Current Density**

The current density was varied from 0.06 to 4 amperes cm.\(^{-2}\) of cathode surface without any noticeable effect upon the separation factor.

5. **Comparison of Electrolysis and Chemical Decomposition Experiments**

These experiments were run at different temperatures and cannot be directly compared. In Figure 8 the separation factors obtained in this investigation are compared with selected values taken from the literature. Figure 8 also includes the theoretical curve of separation factor versus temperature which was calculated by Eyring and Cagle.\(^{15}\)
Comparison of Separation Factors Observed in Present Work With Values Reported Elsewhere
CHAPTER V

SUMMARY

The production of hydrogen by the reaction of iron with various salt solutions was studied. A preliminary investigation of the effects of temperature, salt type, and salt concentration led to the selection of 1 M. ferrous chloride as the electrolyte and 98-100° as the operating temperature. Under these conditions it was possible to increase the rate of hydrogen production by plating various metals onto portions of the iron surface. These metals served as cathodic surfaces for the evolution of hydrogen. The increase in the reaction rate appeared to be limited by polarization of the cathode.

The reaction rate per unit area of the iron samples was approximately the same for uncoated iron powder and for uncoated bulk iron. Therefore, a much larger amount of bulk iron was required in order to obtain a given total reaction rate. However, the geometrical arrangements which are possible with bulk iron were capable of eliminating the quenching effect observed with iron powder.

The introduction of various cathodic surfaces to increase the reaction rate did not appear to affect significantly the separation factor. Some electrolysis experiments were performed with steel electrodes in order to investigate the effects upon the separation factor of various methods of stirring the solution. Vigorous agitation of the solution with an ultrasonic generator increased the separation factor by approximately 15 per cent. The separation factors calculated for the reaction
between iron and water and for the electrolysis of water are consistent with other values reported in the literature.
BIBLIOGRAPHY
BIBLIOGRAPHY


PART III

GAS CHROMATOGRAPHY WITH HYDROGEN AND DEUTERIUM SAMPLES
CHAPTER I

INTRODUCTION

A. The Problem

This problem was undertaken in an attempt to evaluate the application of the gas-chromatographic method to the separation of hydrogen from deuterium. Because of the current requirements for heavy water in the field of nuclear energy, methods for separating the two isotopes are potentially of practical value. In addition, since the gas-chromatographic method can be applied to gas samples of only a few milliliters, a successful separation would provide a useful and simple analytical tool.

In attempting the separation of the isotopes, the elution technique was employed. Of the three general chromatographic techniques, elution, displacement, and frontal analysis, elution is the only one which normally may be expected to separate completely the components of a sample.

B. Background

1. Gas Chromatography

The first use of the chromatographic technique is frequently credited to Tswett. However, there are many publications which show that the method was employed and that general principles were appreciated long before Tswett's first paper on the subject.
Gas chromatography was proposed initially by Martin and Synge in 1941. Since that date the method has developed rapidly. At present a large body of literature on the subject is available. Bibliographies, reviews, and books have been published in which a great amount of information on the applied aspects of gas chromatography and detailed discussions of the present state of chromatographic theory can be found.

There is one major difference between liquid chromatography and gas chromatography. The difference is in the nature of the mobile phase. In liquid chromatography the mobile phase is an incompressible liquid, but in gas chromatography the mobile phase is a compressible gas. With this one exception the theory, the manipulative procedures, and the subdivisions based on variations in technique are similar.

At the same time that Martin and Synge proposed the gas chromatographic method, they suggested that the chromatographic technique might be applicable to the separation of isotopes. However, there have been only a few attempts to apply the method to isotope separations. Glueckauf, Barker, and Kitt reported the enrichment of lithium isotopes by ion-exchange chromatography and of neon isotopes by adsorption chromatography at low temperatures. Complete separation was not accomplished. Spedding, Powell, and Svec described a method for separating nitrogen isotopes by ion exchange. Glueckauf and Kitt reported the separation of hydrogen and deuterium by displacement chromatography at room temperature in a column containing palladium black on asbestos. The column was charged initially with a mixture of hydrogen and deuterium containing 47 per cent of the latter. Hydrogen was used as the displacing agent. Pure
deuterium was displaced ahead of the hydrogen and was separated from the hydrogen by a diffuse region containing a mixture of the two gases.

2. **Hydrogen-Palladium System**

   Hydrogen is a diatomic gas; therefore, a mixture of hydrogen and deuterium contains three molecular species, $\text{H}_2$, $\text{HD}$, and $\text{D}_2$ in equilibrium with each other. The conversion of $\text{HD}$ to $\text{H}_2$ and $\text{D}_2$ is catalyzed by palladium since the metal dissolves the hydrogen and the deuterium in atomic form. As $\text{H}_2$ and $\text{D}_2$ are separated from each other in a chromatographic column, the $\text{HD}$ concentration is continually reduced and may eventually reach zero if the $\text{H}_2$ and the $\text{D}_2$ can be completely separated.

   A chromatographic column containing palladium as the fixed phase functions as a partition column toward hydrogen and deuterium samples since they are soluble in the metal. Typical absorption isotherms$^{18,19}$ are shown in Figures 1 and 2. In the region from zero pressure to the inflection points of the curves the hydrogen is present in the $\alpha$-phase. The face-centered-cubic lattice of palladium expands from a lattice dimension of 3.883 Å to approximately 3.894 Å during the formation of the $\alpha$-phase. At this degree of expansion the lattice becomes unstable and expands to a new lattice dimension of approximately 4.018 Å with an abrupt increase in the solubility of hydrogen. The expanded condition is referred to as the $\beta$-phase. The absorption and the desorption isotherms are not identical, but exhibit hysteresis during the transition between the $\alpha$-phase and the $\beta$-phase. In Figures 1 and 2, the region in which the $\alpha$-phase and $\beta$-phase coexist is represented by the area under the dotted lines. The critical mixing point, at which
Figure 1

Hydrogen-Palladium Evolution Isotherms"
Figure 2
Deuterium-Palladium Evolution Isotherms$^{19}$
the two phases become one, is at approximately \(310^\circ\) and 20 atm. for hydrogen-palladium and at approximately \(276^\circ\) and 35 atm. for deuterium-palladium.

The hydrogen-palladium system has been more thoroughly studied than has any other hydrogen alloy, and additional information is available on the deuterium-palladium system. The general subject of hydrogen in metals has been treated by Smith\(^2\) in a monograph which includes several chapters on the hydrogen-palladium and the deuterium-palladium systems. The data upon which the preceding discussion was based were taken from this monograph.

The form of the absorption isotherms, shown in Figures 1 and 2, led Glueckauf and Kitt\(^1\) to believe that elution peaks would exhibit extreme "tailing" properties which would make them unsuitable for resolution into isolated bands. For this reason, they did not attempt any experimental work on the separation of the two isotopes by the elution technique.
CHAPTER II

APPARATUS AND MATERIALS

A. General

Figure 3 is a photograph of the apparatus which was used to investigate the separation of hydrogen and deuterium by gas chromatography. Figure 4 is a functional diagram of the system. The apparatus can be divided into four main sections. These are:

1. Equipment for providing a controlled and measured flow of carrier gas;
2. Equipment for introducing a measured amount of sample gas into the system;
3. The column, the column packing, and the heating unit;
4. The detector, the associated electrical circuitry, and the recorder.

B. Carrier Gas System

1. Carrier Gas

The carrier gas must be chemically inert in the system under investigation. Since the thermal conductivity of a gas is related to its molecular weight, the carrier gas must have a molecular weight different from that of the sample if a thermal conductivity device is used for the detector.
Figure 3

Photograph of Gas Chromatography Apparatus
Figure 4

Functional Diagram of Gas Chromatography Apparatus
Longitudinal diffusion of the carrier gas in the column causes broadening of the peaks and increases the H.E.T.P. This effect is reduced by using a carrier gas of high molecular weight. With hydrogen and deuterium samples the use of a carrier gas having a high molecular weight not only reduces diffusion, but also increases the katharometer sensitivity.

These factors led to the selection of argon as the carrier gas. Cylinders of argon were obtained from The Matheson Company and from the Welding Gas Products Company. No difference in operation was observed as a result of changing the source of the argon.

2. Flow Rate Control

The diaphragm pressure regulator at the argon cylinder provided adequate flow rate control.

3. Flow Rate Measurement

A set of capillary orifices, cut from thermometer stems, was calibrated for use as an indicating flow-rate meter. The calibration was performed with the apparatus illustrated in Figure 5. The leveling bulb was raised until the burette was filled with liquid. The burette was then filled through the stopcock with argon, and the stopcock was closed. The capillary orifice was connected to the burette stopcock with a short piece of Tygon tubing. The stopcock was opened, and the volume of gas remaining in the burette was recorded at specified times. The pressure in the burette at these times was determined from the difference in height between the liquid surface in the leveling bulb and in the burette. The total change in the gas volume in the burette
Figure 5

Apparatus for Calibration of Orifice Flow Meters
was plotted versus time. The flow rate was determined from the slope of this curve and was plotted versus the pressure drop across the capillary orifice to give the flow-rate calibration curve.

Concentrated sulfuric acid was used as the liquid in the calibration apparatus. Several calibrations were checked with n-butyl phthalate and with Nujol as the liquid. In this way, it was possible to show that the viscosity of the liquid did not cause significant errors in the readings. No vapor pressure corrections were necessary, since at room temperature the vapor pressures for all three liquids are very low.

The manometer used for measuring the pressure drop across the capillary orifice, when installed in the gas-chromatography apparatus, contained n-butyl phthalate. For a specified pressure differential the manometer reading was approximately 13 times as large as that which would have been obtained with a mercury manometer. Both the capillary orifice and the manometer were vented to the atmosphere.

The capillary orifice calibration process was subject to several cumulative errors. The calibration was valid for only one gas and at only one temperature. Therefore, the orifice flow-rate meter was used only as an approximate indicating device.

For more accurate measurements a soap-film meter was used. The soap-film meter is simple and accurate, it requires no calibration, its reading is independent of the nature of the gas being measured, and it offers essentially no back pressure. All calculations in this report were based on readings obtained with this type of meter and corrected to 0° and a pressure of 760 mm. of mercury. A dilute solution
of a commercial liquid detergent was used in the meter, and all readings were corrected for the vapor pressure of water.

The maximum difference in the flow rate indicated by the capillary orifice and the soap-film flow-rate meters was approximately 10 per cent.

C. Sample System

The sample system was used to prepare hydrogen and deuterium mixtures of known composition and to inject known amounts of the mixtures into the column. The functional diagram of the sample system is included in Figure 4.

The volume of the by-pass cell was determined by weighing the amount of mercury it would hold. The by-pass cell was evacuated and filled with a sample of hydrogen, of deuterium, or of a mixture of the two gases at a measured pressure. The carrier gas stream was then rerouted to sweep the sample into the column. It was possible to inject the hydrogen or deuterium continuously at known pressures into the column.

Ordinary commercial tank hydrogen was obtained from the National Cylinder Gas Company, and was used without further purification. Deuterium, reported to be 99.5 per cent pure, was obtained from the Stuart Oxygen Company. Nitrogen, which was sometimes used as an internal marker for the hydrogen and deuterium samples, was obtained from the National Cylinder Gas Company.
D. Column Assembly

1. Column

The column was a single piece of copper tubing 43 feet long. It had an outside diameter of $\frac{5}{16}$ inch and an inside diameter of $\frac{7}{32}$ inch. The column was folded once before it was filled with the packing material, which was poured slowly into both sides of the folded column and was compacted by vibration. The packed column was folded several more times until its overall length was approximately 5 feet, and it was then installed in the apparatus.

2. Packing

The column packing was palladium metal deposited on a granular material. After some preliminary experiments a sample of flint quartz, supplied by Whittaker, Clark, and Daniels, Inc., was selected as a support for the palladium metal. By weight, the quartz grain size distribution was 24 per cent on 40 mesh, 50 per cent on 60 mesh, and 26 per cent through 60 mesh. The quartz was washed several times with hot 20 per cent nitric acid and rinsed with hot distilled water. The treatment cleaned the surface of the grains and removed most of the very fine particles.

A solution of palladium chloride in concentrated hydrochloric acid was added to the granular quartz, and the mixture was evaporated to dryness on a steam bath. The mixture of quartz and palladium chloride was poured into the column in the manner described above. The short entrance section of the column, which was not enclosed in the heater, was packed with uncoated quartz.
After the column was installed in the apparatus, it was heated to approximately 150° and was swept with hydrogen gas to reduce the palladium chloride to the metal. Acid fumes could be detected with litmus paper at the exit end of the column until the reduction was complete. In addition, the completion of the reduction was detected with the katharometer. Hydrogen was used as the reference gas. Prior to completion of the reduction hydrogen chloride gas in the sensing side of the katharometer produced a large output signal. When the reduction was complete, both sides of the katharometer contained hydrogen, and the output signal was zero except for a residual component caused by bridge unbalance. The completion of the reduction was further verified by withdrawing a small portion of the column packing and conducting a qualitative chemical analysis for chloride, but none was detected. The reduction with a hydrogen flow rate of approximately 10 ml. min.⁻¹ required approximately seventy-two hours.

The column contained 7 grams of palladium metal. The interstitial volume of the uncoated quartz was measured by water displacement and was found to be approximately 100 ml. for the 43-ft. column. Since the volume of the palladium metal was less than 1 ml., no correction was made for it.

3. Column Heater

Two pieces of Pyrex tubing, 3 inches in diameter, were joined to give a section 6 feet in length. The tube was mounted in a vertical position.
Two heating elements of Nichrome ribbon were wound onto the tube. Each element extended the full length of the tube. The ribbon had a resistance of $1.04$ ohms per foot, and each element had a total resistance of $27$ ohms. The heating elements were operated independently of each other by two Powerstats (autotransformers). The combined maximum power dissipation was approximately $1$ kilowatt.

The tube furnace was insulated with prefabricated lagging sections, which were $1$-inch thick. The ends of the tube were closed with Pyrex wool.

The maximum operating temperature of the tube furnace was approximately $300^\circ$. No regulating device was necessary. Intermittent manual adjustment of the Powerstats provided temperature regulation of approximately $1^\circ$.

E. Detection System

1. Requirements

Detector requirements for gas chromatography and the characteristics of a variety of detectors have been discussed in detail in two recent publications.\textsuperscript{13,14} Detectors may be classified as differential or as integral instruments. The differential type of instrument provides a signal which is a function of the sample concentration in the detector at a specified time. The katharometer\textsuperscript{23} (thermal conductivity cell) is a differential detector. The integral type of instrument provides a signal which is a function of the total amount of sample which has passed through the detector. An automatic titration device\textsuperscript{24}
is an integral detector.

A satisfactory detector for gas chromatography should exhibit as many of the following characteristics as possible:

1. Sensitivity to small amounts of sample;
2. Insensitivity to variations in gas-flow rate;
3. Rapid response;
4. Small internal volume, which is related to the ability to resolve two closely spaced peaks;
5. Stability and reproducibility;
6. Simplicity;
7. Adaptability to automatic recording.

In addition, since the various molecular species in the sample are separated from each other in the gas chromatography column, the detector should provide a signal which is independent of the chemical properties of the sample and which depends only on the amount of sample present.

2. Katharometer

The katharometer was chosen for this work. All of the characteristics listed above are exhibited by the katharometer to some extent, and it is one of the simplest of the available detectors. The design theory for hot-wire katharometers has been thoroughly discussed.\textsuperscript{13,14}

A thermistor is a more sensitive detection element for a katharometer than is a hot-wire element, since a thermistor has a larger temperature coefficient of resistance. Figure 6 illustrates the difference in the temperature coefficients for a typical thermistor and for a platinum wire.
A = Thermistor mixture of manganese and nickel oxides

B = Thermistor mixture of manganese, nickel, and cobalt oxides

C = Platinum

Figure 6

Resistance-Temperature Characteristics for Platinum and For Two Types of Thermistor Material
In many gas-chromatographic applications it is necessary to operate the entire katharometer at an ambient temperature of 150° or higher in order to avoid condensation in the katharometer of samples having high boiling points. Since thermistors generally have short life and poor stability, when operated at high ambient temperatures, they have not been used as frequently in gas chromatography work as have the hot-wire elements. However, there was no possibility of condensation of any materials used in this work, and it was possible to use thermistors in constructing the katharometer. A matched pair of mounted thermistors was obtained from the Victory Engineering Corporation. The characteristic performance curves of the thermistors are shown in Figure 7. The thermistors were heated by a constant direct current of 0.015 ampere obtained from a 32-volt battery. At this current the thermistors operated with a negative temperature coefficient of resistance in the region to the right of the various maxima in Figure 7. The ambient temperature of the katharometer was approximately 30° for all of this work.

A cross-sectional view of the symmetrical, double-cell katharometer is shown in Figure 8. The scale of the drawing is approximately 2/3 of full size. The katharometer block was machined from solid brass. The thermistors were held in place with Sauereisen cement. The volume of each thermistor cavity was about 0.6 ml. Several turns of copper tubing were soldered to the surface of the cylindrical block. An adjustable stream of tap water flowing through the copper tubing kept the katharometer ambient temperature at about 30°. No additional temperature regulation was required.
Thermistor suspended in still air by its own leads. Ambient temperature; A = 0°, B = 25°, C = 60°.

Figure 7
Thermistor Performance Curves
W - Direction of Gas Flow
X - Sauereisen Cement Plug
Y - Approximate Position of Thermistor Bead
Z - Silver Soldered Seams

Approximately 2/3 Full Size

Figure 8
Katharometer Block
The gas-flow path in the katharometer was a compromise between the requirements for rapid response and for insensitivity to variations in gas flow rate. The most rapid response and the greatest sensitivity to flow-rate fluctuations would be obtained by placing the thermistor directly in the gas stream. In this instrument the thermistors were placed slightly to the side of the gas stream so that the sample reached the thermistor partly by diffusion and partly by turbulent flow. Insensitivity to such flow-rate fluctuations as were present was exhibited by the smoothness of the base line on the recorder.

A small amount of the argon-carrier gas flowed through a needle valve and a length of thermometer-capillary tubing into the reference side of the katharometer, which was vented directly to the atmosphere. The sensing side was vented to the atmosphere through the flow-rate meter.

3. Measuring and Recording Circuit

The complete circuit for the detection system is shown in Figure 9. The Wheatstone bridge consisted of the two matched thermistors and two 1500-ohm precision resistors, which had low temperature coefficients of resistance. Each thermistor had a resistance of approximately 75 ohms when suspended by its own leads in still air at an ambient temperature of 25° and when carrying a direct current of 0.015 ampere.

Since the value of the fixed resistance in each arm was much larger than the resistance of the thermistor, the current through each arm of the bridge was nearly constant, irrespective of variations in thermistor resistance. Therefore, the voltage signal from the bridge
t-1, t-2: A-33 Matched thermistors
(Victory Engineering Corp.)

R-1, R-2: 1500 ohms
R-3: 125 ohms, wire-wound
R-4: 10 ohms
R-5: 75 ohms, wire-wound
R-6: 5 ohms
R-7: 25,000 ohms
R-8: 50,000 ohms
R-9: 4700 ohms
R-10: 1500 ohms
R-11: 100 ohms
R-12: 47 ohms
R-13: 10 ohms
R-14: 5 ohms
R-15: 7500 ohms
S-1: Galvanometer shorting switch
S-2: Coarse sensitivity selector switch
S-3: Bridge current ON-OFF switch
S-4: Fine sensitivity selector switch
S-5: Polarity reversing switch
M-1: Lamp-and-scale galvanometer
M-2: Bridge current milliammeter

Figure 9

Complete Circuit for Detection System
was almost a linear function of the resistance change in the sensing thermistor.

The sensitivity of the recording system could be varied without changing the load across the bridge. A Brown potentiometer recorder, obtained from the Minneapolis-Honeywell Company, was used to record the output signal from the katharometer bridge circuit. The recorder had a full-scale sensitivity of 5 m.v., a full-scale pen speed of 4.5 seconds, and a chart speed of 6 inches per hour.
CHAPTER III

THE DISTRIBUTION ISOTHERM AND COLUMN DESORPTION EXPERIMENTS

A. Distribution Isotherms

The distribution coefficient, \( k \), is defined by equation 1.

\[
k = \frac{\text{concentration of solute in the fixed phase}}{\text{concentration of solute in the mobile phase}}
\]  

(1)

For a linear distribution isotherm \( k \) is a constant equal to the slope of the isotherm. Ideal elution chromatography based on linear isotherms produces symmetrical peaks. The requirements for ideal chromatography are:

1. the rate of solute transfer between the fixed and the mobile phases is infinitely high;
2. the exchange between the two phases is thermodynamically reversible;
3. longitudinal diffusion is infinitely slow.

These conditions are simultaneously obtainable neither in theory nor in practice. For example, requirements (1) and (2) as well as (1) and (3) are mutually contradictory. However, for the mathematical analysis of chromatographic systems these conditions are often arbitrarily assumed to exist.

If the distribution coefficient is not a constant, the isotherms may be concave toward either axis. Ideal elution chromatography under these conditions produces an asymmetrical peak. The three types of distribution isotherms and the corresponding typical elution peaks are shown
in Figure 10. The theory and the mathematical analysis of these peaks has been thoroughly discussed in the literature of gas chromatography.\textsuperscript{6,15,26-36}

A linear distribution isotherm is usually more desirable than either type of non-linear isotherm for elution chromatography, since the mathematical analysis is simpler and better separations generally can be obtained. The linear type of isotherm is most frequently encountered in partition chromatography where the solute dissolves in the fixed phase. The non-linear type of isotherm is frequently encountered when the solute is adsorbed at the surface of the fixed phase.

Typical distribution isotherms for the hydrogen-palladium and the deuterium-palladium systems are shown in Figures 1 and 2. In these two figures the coordinates are reversed relative to the form in which distribution isotherms are normally shown. It can be seen that these isotherms exhibit the characteristics of both types of non-linear isotherm. The data points for these isotherms were obtained by allowing the gas-metal system to come to equilibrium, which is normally a very slow process. Gillespie and Hall\textsuperscript{37} were able to accelerate the attainment of equilibrium by the use of a 360\degree heat treatment prior to each measurement. Nace and Aston\textsuperscript{38} used an extremely finely divided palladium black, but still found that at room temperature two to six hours were required to reach pressure equilibrium after the addition of an increment of hydrogen to the system. At higher temperatures equilibrium is reached more quickly.
Figure 10

Distribution Isotherms and Corresponding Typical Elution Peaks
In an ideal chromatographic column the equivalent of hundreds of
equilibrations may occur in less than one hour. It is evident, there­
fore, that the evolution isotherms shown in Figures 1 and 2 may be quite
different from the effective distribution isotherms which are applicable
to a chromatographic column containing palladium as the fixed phase.
For this reason, the following experiments were performed in an effort
to obtain information regarding the nature of the distribution isotherms
which would be applicable to an operating column. It was especially
important to determine whether the column operated as an adsorption
column or as a partition column with the hydrogen gas actually dissolved
in the palladium metal.

B. Experimental Procedure

Hydrogen was injected continuously at a constant pressure into
the column. Argon was used as the reference gas. After a time the thermal­
conductivity-bridge recorder indicated the break through of hydrogen. At
this point the mobile phase in the column was hydrogen. The column was
then swept with the argon carrier until the recorder trace showed that
the gas leaving the column was essentially pure argon. The curve traced
by the thermal-conductivity-bridge recorder during this type of experi­
ment is referred to as the column-desorption curve. Similar experiments
were performed with deuterium.

The hydrogen and the deuterium samples were injected at a constant
input pressure of 10 psig. The flow rate during the desorption portion
of the run was fixed by the argon input pressure.
C. Experimental Results

A typical set of column desorption curves for hydrogen and for deuterium are shown in Figures 11, 12, and 13. These curves were obtained with the coarse sensitivity control of the recorder at the 25,000 ohm tap and with the fine sensitivity control at position 3 (see Figure 9). A number of runs were made at a higher sensitivity in order to examine the base of the step at the right side of the curves. Tailing was found to occur at the base of this step.

There are two distinct portions of these curves which are separated by the breaks at points X. On either side of X the tailing is characteristic of a distribution isotherm which is concave toward the axis of the mobile phase. The equilibrium distribution isotherms for the hydrogen-palladium and for the deuterium-palladium systems have two regions of concavity toward the pressure axis. It, therefore, appears possible that the steps which are present in the column desorption curves may correspond to the transition between the \( \lambda \)-phase and the \( \beta \)-phase. The upper portion of the curves would correspond to desorption from the \( \beta \)-phase, and the lower portion would correspond to desorption from the \( \lambda \)-phase.

If the above interpretation is correct, it follows that in the column the rate of diffusion of hydrogen and deuterium within the metal is sufficiently rapid for the \( \lambda \) and the \( \beta \)-phase solutions to form. Hence the metal acts as a solvent for the gas, and the column may be considered as a partition column. If the rate of diffusion within the palladium metal were too slow for H-Pd and D-Pd solutions to form the
A - H₂, Argon input pressure 53 psig
B - H₂, Argon input pressure 30 psig (break at 155 minutes)
C - D₂, Argon input pressure 53 psig
D - D₂, Argon input pressure 30 psig

Column Desorption Curves for Hydrogen and Deuterium at 75–80°
Figure 12

Column Desorption Curves for Hydrogen and Deuterium at 100-105°
Figure 13

Column Desorption Curves for Hydrogen at 175-180° and at 245°
desorption curves should not show the breaks at points X. The rapidity of the solution process is probably a result of the very finely divided state of the palladium metal in the column. If the metal were assumed to have formed a smooth coating of uniform thickness on the quartz particles, it can be shown that this coating would be only approximately 20 molecules thick. It appears more probable that the reduction process at a temperature of only 150° may have formed a very finely divided powder which would also have a large surface development.
CHAPTER IV

SEPARATION OF THE HYDROGEN ISOTOPEs BY DISPLACEMENT
AND BY FRONTAL ANALYSIS TECHNIQUES

A. Purpose

Glueckauf and Kitt\textsuperscript{17} reported the separation of hydrogen and deuterium by displacement chromatography in a column containing palladium supported on asbestos as the fixed phase. In addition, they performed some experiments using the break-through technique, which is analogous to classical chromatographic frontal analysis. For the work discussed in this report, some separations were performed by both methods in order to check the results of Glueckauf and Kitt and to obtain additional information on the characteristics of the column used.

B. Experimental Procedures

In displacement chromatography the sample is first carried onto the column in a stream of the carrier or is injected in an undiluted form. It is then displaced along the column by a component which is held more strongly by the fixed phase. The displacer may also be carried onto the column in a stream of the carrier or injected in an undiluted form. Figure 14 illustrates the relationship between the distribution isotherms and the gas concentration for the case where the displacer, D, is carried onto the column at a constant concentra-
Figure 14
Relationship Between Distribution Isotherms and Displacement Analysis
tion, $C_d$. In this figure the effect of the pressure gradient along the column is neglected. Component B is displaced at a gas-phase concentration $C_b$ by the displacer D. The control line does not cut the isotherm for component A, and A is moved along by an elution process. The theory of displacement chromatography has been discussed in detail by Tiselius.\textsuperscript{39}

For the displacement experiments discussed in this report the sample by-pass cell was filled with a 1:1 mixture of hydrogen and deuterium at a total pressure of 10 psig. The sample size was determined by the volume of the by-pass cell. The sample was swept through the column by a stream of hydrogen which was also used as the reference gas. Therefore, the recorder deflection was a function of the deuterium concentration in the gas emerging from the column.

Prior to each run the column was swept with argon until essentially no hydrogen remained in the column.

For the break-through experiments hydrogen and deuterium were fed simultaneously to the column until the feed composition appeared in the effluent. The feed composition, an approximately equimolar mixture of hydrogen and deuterium, was determined by the relative flow rates of the two gas streams through calibrated capillary orifices. The orifices, after installation, were calibrated by comparison with the soap-film flow-rate meter.
C. Results

Figure 15 illustrates the results of a typical displacement run with a constant sample size and gas flow rate at several different temperatures. The recorder reading for 100 per cent deuterium concentration was determined by passing hydrogen through the reference side of the cell and deuterium through the sensing side of the cell.

The sample size could be varied with no effect other than a corresponding variation in the width of the deuterium peak.

The recorder trace for a typical break-through experiment is shown in Figure 16. Curves were obtained at temperatures of $60^\circ - 65^\circ$ and $100^\circ - 105^\circ$.

The data shown in Figures 15 and 16 are in agreement with the results reported by Glueckauf and Kitt.\(^7\)
Temperature 80-85°
Sample composition approximately 50 mole per cent deuterium

Figure 15
Displacement Curve For Separation of Deuterium From Hydrogen
Temperature 100-105°
Feed composition approximately
50 mole per cent deuterium

Argon (Present in the column at the beginning of the run)

Recorder Deflection in Millivolts

Time in Minutes

Figure 16

Break-Through Curve for Separation of Deuterium From Hydrogen
CHAPTER V

THE RETENTION VOLUME

A. Theoretical

Qualitative identification of a compound in a particular chromatographic system is often accomplished by measurement of the $R_f$ factor, which is defined by equation 2.

$$R_f = \frac{\text{rate of movement of the solute}}{\text{rate of movement of the carrier liquid}}$$

The residence time of a solute molecule in a chromatographic column is $1/R_f$ times the residence time of the average carrier molecule, where the carrier is the major component of the mobile phase. The retention volume may then be defined by equation 3.

$$V_R = \frac{a l}{R_f} = t F$$

where $a$ = the cross-sectional area of the mobile phase in the column;

$l$ = the length of the column;

t = the retention time, which is the time required for the center of the solute zone to emerge from the column, measured from the time the sample was injected;

$F$ = the volume rate of flow of the carrier, measured at the exit of the column.

Equation 3 is applicable to a system in which the mobile phase is incompressible, in which case the value of $F$ measured at the exit of the column is the same as the volume rate of flow at any point in
the column. For a compressible carrier, as with gas chromatography, the flow rate is no longer constant throughout the column, and a correction factor must be evaluated. Various aspects of the correction have been discussed in the literature of gas chromatography. The following elements of the derivation are based on material from Littlewood, Phillips, and Price,\textsuperscript{40} James and Martin,\textsuperscript{41} and Keulemans.\textsuperscript{42}

Let

\[ t_c = \int_0^1 \frac{dx}{v} \]

(4)

and

\[ t_s = \int_0^1 \frac{dx}{vR_x} \]

(5)

where \( t_c \) and \( t_s \) = the retention times of a carrier and of a solute molecule;

\( x \) = a distance measured along the axis of the column;

\( l \) = the length of the column;

\( v \) = the linear velocity of the gas at point \( x \).

In addition,

\[ av = F \frac{P_0}{P_x} = K \frac{dP_x}{dx} \]

(6)

where \( P_x \) and \( P_0 \) are the gas pressures at point \( x \) and at the exit of the column, and \( K \) is a column constant, the permeability, which is a function of the viscosity of the mobile phase and the nature of the column packing.
Equation 5 may then be rewritten as

$$t_s = \int_0^1 \frac{aP_x}{R_f P P_0} \, dx,$$

or

$$t_s = \int_{P_0}^P \frac{K a P_x^2}{R_f F^2 P_0^2} \, dP_x,$$

which upon integration gives

$$t_s = \frac{K a (P^3 - P_0^3)}{3 R_f F^2 P_0^2},$$

where $P$ is the inlet pressure.

Since $V_R = t_F$,

$$V_R = \frac{K a P_0}{3 R_f F} \left[ \frac{(P/P_0)^3}{3 - 1} \right].$$

Equation 6 may be rearranged to give

$$F dx = K \frac{P_x}{P_0} \, dP_x.$$

Equation 11 may be integrated over the length of the column and then rearranged to give

$$F = \frac{K P_0}{2} \left[ \frac{(P/P_0)^2}{3 - 1} \right].$$

Equations 10 and 12 may be combined to give

$$V_R = \frac{2 a P_0}{3 R_f F} \left[ \frac{(P/P_0)^3}{(P/P_0)^2 - 1} - 1 \right].$$

If $P = P_0$, there will be no compression along the column and the situation will be analogous to that for chromatography with an incompressible mobile phase. For this limiting case
\[ V_R^0 = \frac{3}{2} V_R \left[ \frac{(P/P_0)^2}{(P/P_0)^3 - 1} \right] \]  

where \( V_R = t_F \) and \( F \) is measured at the column exit. If \( F \) is measured at a temperature different from that at which the column is operated, \( V_R^0 \) may be further corrected to the column temperature.

Littlewood, Phillips, and Price introduced an additional correction. They determined the retention time, \( t_i \), for a gas which was not retarded by the column packing. Then

\[ V_R^0 = \frac{3}{2} (t_S - t_i) F \left[ \frac{(P/P_0)^2}{(P/P_0)^3 - 1} \right], \]  

and \( V_R^0 \), for the ideal case, is dependent only upon the nature and the amount of the column packing and upon the nature of the solute.

B. Procedure

The retention volumes of hydrogen and of deuterium were investigated with the 43-ft. column which was described in Chapter II of this section. The column contained 7 grams of palladium metal supported on granular flint quartz. Argon was the carrier gas. Column temperature, gas-flow rate, and sample size were varied during the experiments. The volume of the sample-by-pass cell was 1.32 ml. and the sample size was varied by controlling the sample pressure at which the by-pass cell was filled.

The exit pressure was assumed to be equal to the barometric pressure in the laboratory, since the pressure drop through the soap-film flow-rate meter was found to be negligible. The input pressure,
which had a maximum value of approximately 3 atmospheres, was measured with a mercury manometer. The ground-glass stopcocks, which were held down by ball-joint clamps, began to leak at a pressure of approximately 50 psig.

Most of the samples contained nitrogen at a partial pressure of approximately 3 cm. of mercury. The nitrogen provided a marker so that the retention volume could be fully corrected by the method of Littlewood, Phillips, and Price. A typical recorder trace is reproduced in Figure 17. The corrected retention time was measured from the center of the nitrogen peak to the leading edge of the hydrogen or the deuterium peak.

The flow rate was corrected to 0° and 760 mm. of mercury, after correcting for the vapor pressure of water in the flow meter. The vapor pressure was checked gravimetrically by collecting the vapor in a drying tube filled with magnesium perchlorate. The observed vapor pressure was 95 per cent of that of pure water at the same temperature. Small errors in the measurement of the temperature and the rate of movement of the soap film could account for a 5 per cent error in the gravimetric determination of the vapor pressure. Therefore it was assumed that the liquid detergent caused no significant lowering of the vapor pressure of the water in the meter.
Figure 17

Typical Recorder Trace for Retention Volume Experiments
C. Results

Figure 18 illustrates the effect of temperature and of flow rate upon the corrected retention volume. For correction to the column temperature the values of $V^0_R$ must be multiplied by $T/273$, where $T$ is the column temperature indicated in the figure. A sample of 1.32 ml. at a pressure of 80 cm. of mercury was used.

The retention volume for a given set of conditions is dependent upon the previous history of the column. The numbered data points, in Figure 19, for the retention volume of deuterium at 75-80° indicate the sequence of the experiments which followed a series of experiments with hydrogen. The elapsed time for each experiment was approximately forty-five minutes. In order to obtain reasonably reproducible values of the retention volume it was necessary to "condition" the column by sweeping several hydrogen or deuterium samples through it and to maintain a fixed time interval between runs.

Figure 20 illustrates the effect of sample size upon the retention volume. The sample size was 1.32 ml. at the pressures and temperatures indicated in the figure. These values could not be fully corrected since the data were obtained early in the investigation before the input-pressure manometer was installed and before arrangements were made for introducing nitrogen markers. Thus the retention volumes given in Figure 20 are simply the product of the retention time, measured from the start of the runs to the leading edge of the elution peaks, and the corrected flow rate.
Horizontal lines indicate range of flow-rate values. Vertical lines indicate precision as defined in Part II of this report.

Figure 18

Fully Corrected Retention Volumes for Hydrogen
Numbers indicate sequence of experiments with $D_2$, immediately following a series of runs with $H_2$.

Figure 19

Fully Corrected Retention Volumes for Deuterium at 75-80°
Horizontal lines indicate range of flow-rate values. Vertical lines indicate precision as defined in Part II of this report.

\[ P = 25 \text{ cm.}, T = 63-68^\circ \]
\[ P = 50 \text{ cm.}, T = 63-68^\circ \]
\[ P = 80 \text{ cm.}, T = 63-68^\circ \]

\[ P = 25 \text{ cm.}, T = 100-105^\circ \]
\[ P = 50 \text{ cm.}, T = 100-105^\circ \]
\[ P = 80 \text{ cm.}, T = 100-105^\circ \]

Flow Rate, ml. min.\(^{-1}\), corrected to 0\(^\circ\) and 760 mm.

Figure 20

Relationship of Uncorrected Retention Volume to Sample Size for Hydrogen
CHAPTER VI

SEPARATION OF HYDROGEN ISOTOPES BY ELUTION CHROMATOGRAPHY

A. Column Efficiency

1. The Separation Factor

The distribution coefficient, $k$, was defined by equation 1.

$$k = \frac{\text{concentration of solute in the fixed phase}}{\text{concentration of solute in the mobile phase}}$$ (1)

The separation factor, $\lambda$, for two components of a sample is defined by equation 16,

$$\lambda = \frac{k_1}{k_2}$$ (16)

where $k_1$ and $k_2$ are the distribution coefficients for components 1 and 2. Equation 16 defines an equilibrium separation factor analogous to that defined in Parts I and II of this report. The previously discussed conditions which are assumed to exist in ideal chromatography also imply the establishment of an equilibrium distribution of sample components between the fixed and the mobile phases. An additional condition for ideal chromatography may be introduced at this point. It is that the value of the distribution coefficient must be unaffected by the presence of other sample components. In an ideal elution chromatographic process, two components will be separated if the value of $\lambda$ is different from unity, and if the column contains a sufficient number of theoretical plates.

The separation of hydrogen and deuterium by frontal analysis and by displacement techniques, which was reported by Glueckauf and Kitt.
and confirmed in the present work, is conclusive evidence that $\hat{\alpha}$ is different from unity in a column containing palladium as the fixed phase.

2. Theoretical Plate Concept

The performance of a chromatographic column in an elution process is somewhat analogous to the performance of the Craig countercurrent distribution apparatus. The Craig apparatus operates with intermittent flow, and equilibrium is essentially complete in each stage before solute is transferred to the next stage. Let the ordinal numbers of the stages begin with zero. The distribution curve showing the amount of sample in each stage after $n$ transfers may be obtained by plotting the terms of the expansion of

$$\left[ \frac{1}{1 + E} + \frac{E}{1 + E} \right]^n$$

where $E = k(V_L/V_U)$,

$V_L$ = the volume of liquid in the lower phase of each stage of the apparatus,
$V_U$ = the volume of liquid in the upper phase of each stage of the apparatus,

$1/(1 + E) = \text{the normalized probability of finding a molecule in the upper phase, which is transferred after each equilibration, and}$

$E/(1 + E) = \text{the normalized probability of finding a molecule in the lower phase, which remains in the flask after each equilibration.}$
If $k$ is constant and is independent of the presence of other sample components, the distribution will approach a Gaussian one for large values of $n$ (i.e., $n > 100$).

In an analogous manner, we can consider the chromatographic column to consist of a series of theoretical plates, such that in each plate equilibrium is established between the mobile and the fixed phase. The distribution curve showing the amount of sample in each plate, after $n$ volumes of carrier gas, each equal to the volume of carrier gas in one plate, have entered the column then may be calculated from the terms of the expansion of equation 17 by letting $E = k(A_f/A_m)$. $A_f$ and $A_m$ are the cross-sectional areas of the fixed and the mobile phases in the column, exclusive of the cross-sectional area of the inert supporting material.

The sample concentration detected at the exit of an ideal elution column is that present in the mobile phase of the last theoretical plate after equilibration. The probability, $P_n^r$, of a molecule being in the last plate of a column containing $r$ plates, after $n$ volumes of carrier gas as defined above have entered the column, is

$$P_n^r = \frac{n!}{r!(n-r)!} p^r (1 - p)^{n-r}$$

(18)

where

$$p = \frac{1}{1 + E}.$$  

(19)

Equation 18 defines the general term of a binomial expansion. The distribution of probabilities about the maximum will approach a Gaussian one when $n$, $r$, and $n - r$ are large, as is generally true in gas chromatography.
Martin and Synge\(^6\) and James and Martin\(^24\) have discussed the mathematical treatment of the distribution in detail. It should be noted that the treatment is further complicated by the compressibility of the mobile phase in gas chromatography, and also by the fact that \(k\) is generally not a constant.

In systems operating with linear distribution isotherms, the treatment provides a useful method for calculating a value for the number of theoretical plates in a column, which in turn provides a measure of the separating efficiency of the column. At a constant flow rate \(n\) is directly proportional to the time. It can be shown that the distribution curve of \(P^n\), plotted as a function of time, has two points of inflection at values of \(t\) corresponding to

\[
p \sqrt{r} \ (t - t_m)/t_o = \frac{1}{2}
\]

where \(t_m\) is the retention time to the peak maximum and \(t_o\) is the retention time for a molecule of the carrier gas. Between these two points lies 68.3 per cent of the area under the curve.\(^45\) This fraction of the sample will emerge from the column in a period of time, \(\tau\), defined by equation 21.

\[
\tau = 2 \ t-o/p \sqrt{r}
\]

It follows that the number of theoretical plates may be calculated from

\[
r = l(t_m^2/\tau^2),
\]

since

\[
t_m = t_o/p
\]

and

\[
\tau/t_m = 2/\sqrt{r}.
\]
It may be difficult in practice to locate accurately the inflection points, especially since the actual peaks only approximate the theoretical curves, and a further simplification has been recommended.\textsuperscript{46} Tangents are drawn to the peak at the approximate points of inflection. The length of the base line, $y$, cut by these two tangents is then measured. The length of the base line, $x$, corresponding to the uncorrected retention time, is measured. Then
\[ r = 16(x/y)^{2}. \] (25)

The intermittent flow theory has been shown to lead to a binomial type distribution. Glueckau\textsuperscript{26} and Klinkenberg and Sjénitzer\textsuperscript{47} have shown that the distribution curve for a continuous flow theory is of the Poisson type. After the peak maximum has passed through a large number of plates the Poisson distribution may be approximated by a Gaussian type of curve. However, the peak widths predicted by the binomial and by the Poisson distribution for an equal number of plates are not the same.

Several useful conclusions may be drawn from the above considerations. For a column of a given physical length, the sharpness of the elution peaks may be increased by increasing the number of plates in the column. In addition, the number of plates required to accomplish a chromatographic separation is larger than the number required for a distillation separation. Because of reflux in a distillation process, all the plates participate simultaneously in the separation. In a chromatographic column only a fraction of the plates are in use at any specified time.
3. Miscellaneous Variables

a. Sample injection technique. The theoretical treatment of the chromatographic elution process included the assumption that the entire sample was injected into the first plate of the column. In practice this is generally not possible and the elution peak consists of a number of overlapping peaks of the type discussed above. It is advantageous, however, to inject the sample as compactly as possible.

b. Equipment design. A number of design variables, such as the internal volume of the detector, also affect the observable separation. These factors have been discussed elsewhere in this report.

B. Peak Shapes

The peaks obtained in elution chromatography with hydrogen and deuterium samples in a column containing palladium as the fixed phase are usually of the type characteristic of an isotherm which is concave toward the pressure axis. A series of preliminary experiments indicated that the effect of variables such as temperature and flow rate was qualitatively the same for both hydrogen and deuterium. Therefore, as an economy measure, hydrogen was used for most of the experiments in which the effect of various parameters upon the peak shape was investigated.

Figure 21 illustrates the effect of temperature upon the peak shape for a sample size of 1.32 ml. at 155 cm. of mercury. It can be seen that although the peak becomes sharper as the temperature is increased, the retention time decreases. The decrease in the retention
Effect of Temperature Upon Peak Shapes in the Elution Chromatography of Hydrogen Samples
time can be predicted from the fact that the occlusion of hydrogen in palladium is an exothermic process. Therefore, the hydrogen is less soluble in the metal at elevated temperatures. These two effects tend to cancel each other with respect to improvement of the separating efficiency of the column. Since the distribution isotherms for this system are not linear, equation 22 is not applicable to the calculation of the number of theoretical plates in the column. However, a large value of $t_m/\gamma$ is desirable. Figure 22 is a plot of $t_m/\gamma$ versus temperature for a sample size of 1.32 ml. at 155 cm. of mercury. The peak width at the half-height was arbitrarily taken as the value of $\gamma$.

When the uncorrected value of $t_m$, which was measured from the time of injection of the sample, was used in calculating the ratio, it appeared that a more favorable value of the ratio could be obtained at high temperatures. When the corrected value of $t_m$, which was measured from the nitrogen marker, was used the ratio $t_m/\gamma$ was more nearly constant.

The variations shown in Figure 22 cannot be attributed to temperature alone, since it is impossible to keep both the gas-flow rate and the pressure gradient along the column simultaneously constant as the temperature is varied. Both the flow rate and the pressure gradient affect the ratio $t_m/\gamma$ as shown in Figure 23. The maximum in the curves in Figure 23 is also shown by the curves for data obtained at 75-80° and at 245-250°.

Several runs were made with hydrogen samples which had a volume of 4.37 ml. and a pressure of 85 cm. of mercury. This was approximately twice the amount of hydrogen used in the runs previously discussed. At
Vertical lines indicate the precision of the measurement as defined in part II of this report. Horizontal lines indicate the temperature spread during the measurement. Flow rates and input pressures are indicated in Figure 21.

Figure 22

Effect of Temperature Upon the Ratio $t_m/\gamma$
Vertical lines indicate the precision of the measurement as defined in part II of this report. Horizontal lines indicate the flow-rate spread during the measurement.

Temperature 175-180°

Sample size, 1.32 ml. at 155 cm. of mercury

Figure 23

Effect of Flow Rate Upon the Ratio $t_m/\tau$
a temperature of 175-180° an uncorrected value of 12.2 ± 0.2 and a corrected value of 2.15 ± 0.05 were found for the ratio $t_m/\gamma$. It can be seen, by reference to Figure 22, that the ratio was markedly increased by increasing the size of the sample. This is the reverse of the condition generally observed in chromatography and is apparently related to the effect of the $\alpha, \beta$-phase transition upon the shape of the elution peaks. With the larger sample, the position of the maximum, for the type curve shown in Figure 23, was shifted from a flow rate of approximately 15 ml. min.$^{-1}$ to approximately 45 ml. min.$^{-1}$.

The calculation of the number of theoretical plates in a column requires the use of the uncorrected value of $t_m$. Thus, it appears from the data shown in Figure 22 that better separation should be obtained at higher temperatures. The conclusion is misleading, since the separation factor defined by equation 16 approaches unity as the temperature is increased. Peak sharpness is not a sufficient criterion of separation efficiency, since sharp peaks may be obtained under conditions such that the value of the separation factor is very small.

C. Separation of Deuterium From Hydrogen by Elution Chromatography

A number of runs were performed with samples containing approximately 50 volume per cent each of hydrogen and of deuterium. Figure 24 illustrates the type of curve obtained for the maximum separation of hydrogen and deuterium with the apparatus described in this report. The conditions under which this run were performed were as follows:
Figure 24

The Partial Separation of Deuterium From Hydrogen by Elution Chromatography
Column length: 43 ft.
Palladium content: 7 gm.
Sample size: 4.37 ml. at 100 cm. of mercury
Temperature: 175-180°
Input pressure: 50 psig
Gas flow rate: 60 ml. min.-1

The dotted lines in the figure indicate the average location of H₂ and D₂ peaks for pure samples run under the same conditions. It can be seen that the distribution isotherms for hydrogen and for deuterium are not independent of each other, and that the separation is not as large as would be expected from the properties of the peaks for the pure samples. Additional evidence for this conclusion was presented in the chapter on the retention volume.

The temperature could be varied between approximately 150° and 190° before the peaks merged. At lower temperatures the peaks were too broad to distinguish any resolution which might have occurred. At higher temperatures the peaks were sharp, but no resolution was distinguishable, probably because, as has already been noted, the separation factor decreases with increasing temperature.
CHAPTER VII

DISCUSSION

A. Apparatus

1. Thermal Conductivity of Gases

   a. General considerations. A consideration of the mechanism of energy transfer in a monatomic or a diatomic gas such as those used in the current work, leads to the following relationship for thermal conductivity,

\[ \lambda = \frac{\varepsilon \eta \left( \frac{C_p}{C_v} \right)}{4} \]

where \( \lambda \) = the thermal conductivity in cal. cm.\(^{-1}\) sec.\(^{-1}\) deg.\(^{-1}\),
\[ \varepsilon = \frac{9 \left( \frac{C_p}{C_v} \right) - 5}{4}, \] and \( 1 \leq \varepsilon \leq 2.5, \)
\( \eta \) = coefficient of viscosity in dyne sec. cm.\(^{-2}\),
\( C_p \) and \( C_v \) = the specific heats at constant pressure and at constant volume.

Since the viscosity of a gas is independent of pressure, as long as the pressure is higher than the range in which molecular flow occurs and lower than the range where non-ideality becomes significant, it follows that the thermal conductivity of a gas is independent of pressure under the same circumstances. The thermal conductivities of hydrogen, of argon, and of nitrogen decrease by only 10 per cent as the gas pressure is decreased from 80 cm. to approximately 10 cm. of mercury. Below a pressure of approximately 10 cm. of mercury the thermal conductivities of the three gases decrease very rapidly as the pressure de-
creases. Thus in the pressure range above approximately 10 cm. of mercury thermal conductivity is a useful tool for determining the composition of simple gas mixtures. At low pressures composition may also be determined by thermal conductivity, but the experimental difficulties are increased by the necessity for careful control of the pressure. For this reason thermal conductivity is used at low pressures usually to measure pressure, rather than composition. The Pirani gage is a pressure sensitive device of this sort.

At normal temperatures large molecules generally have lower thermal conductivities than small molecules. For the four gases used in this investigation the values of $\lambda x 10^5$ at $0^\circ$ are as follows:

- argon 3.91,
- nitrogen 5.77,
- deuterium 34.00,
- hydrogen 40.21.

The thermal conductivity of a mixture of two gases is usually not a linear function of the composition. However, at low sample concentrations such as exist in gas chromatography the relationship between the thermal conductivity of the mixture and the amount of a sample component is almost linear.

b. Considerations in present apparatus. Argon is readily available and is relatively inexpensive. Although specially purified argon can be obtained, the material used in this work was an ordinary commercial grade which is often used for shielded-arc welding. Over a six-month period in which this grade of argon was used no changes were ob-
served in the operating characteristics of the column. Hence, it was concluded that any impurities present in the argon had no cumulative effect upon the palladium metal in the column.

Since the katharometer is a differential device, the maximum sensitivity in gas chromatographic work is obtained by using a gas for the carrier and the reference which has a thermal conductivity as different as possible from that of the sample. For hydrogen and deuterium samples, argon is obviously a better choice than nitrogen.

A second consideration is that the difference in the bridge response toward two different gases such as hydrogen and deuterium becomes smaller as the difference in the thermal conductivity of the carrier and the sample components becomes larger. With an argon carrier the responses toward hydrogen and deuterium differed by approximately 8 per cent.

In the displacement and the break-through experiments, hydrogen was used as the reference gas. This reduced the absolute sensitivity of the bridge, but allowed the detection and measurement of deuterium in the presence of hydrogen with greater sensitivity.

Both sides of the katharometer were operated at approximately atmospheric pressure, and the instrument was insensitive to the small pressure variations which occurred in normal operation.

2. The Katharometer

a. The katharometer block. The gases, after leaving the column, flowed up through an inverted U-shaped passage in the block, and the reference gas flowed through an identical passage. The thermistors were located in the down leg of each inverted U. The path was designed to
allow the gases to come to temperature equilibrium with the block before reaching the thermistors.

The brass block provided a high-capacity heat sink of high thermal conductivity. Thus, it prevented rapid fluctuations in the ambient temperature at which the thermistors operated.

b. Temperature control. The brass catharometer block was wrapped with several turns of copper tubing which carried cooling water. A large quantity of heat was conducted through the metal connections from the column to the block. Without cooling and with a column temperature of 180° the block temperature rose to 60-70°. Reduction of the temperature differential between the thermistor beads and the heat sink reduced the sensitivity of the bridge. With cooling water flowing through the coil, the block temperature could be held to 30° even when the column temperature was as high as 275°. An ambient temperature of 30° provided adequate sensitivity, although the sensitivity could be further increased by operating at a still lower ambient temperature. This was not done since on many summer days the dew point was above 20°, and it was desirable to avoid condensation of moisture on the block.

No temperature control beyond that discussed above was required. A seventy-two hour run to check the noise level and drift at maximum sensitivity and maximum signal output showed a long-term drift of less than 1 per cent of full-scale on the recorder and essentially no short-term fluctuations. Since other factors than temperature control also affect the stability and the noise level, it was apparent that the block temperature was sufficiently steady.
d. **Analytical accuracy.** Slow changes in sensitivity should not affect the accuracy of the katharometer for analytical applications. The area under an elution peak is proportional to the amount of the sample component. Therefore, if the relative sensitivities toward the various sample components are known, it is possible to correct for slow sensitivity changes by normalizing the areas under the peaks.

e. **Flow rate sensitivity.** The location of the thermistors was a compromise between the requirements for maximum concentration sensitivity and minimum flow-rate sensitivity. Flow-rate sensitivity was checked by passing argon through the reference side of the cell and hydrogen through the sensing side of the cell. The hydrogen flow rate was varied from almost zero to approximately 100 ml. min$^{-1}$. The flow-rate variations produced a signal shift at the recorder of less than 1 per cent of the total signal. The flow-rate range checked was large enough to cover most of the flow rates used in the present work.

f. **Effect of thermistor cavity size.** The volume of the sensing-thermistor cavity affects the resolution in gas chromatography in a manner analogous to the effect of slit width upon spectrographic resolution. However, in gas chromatography there is no loss of sensitivity as a result of decreasing the volume of the cavity. Rather, the sensitivity may be increased as the spacing between the thermistor and the walls of the katharometer is decreased. Therefore, it is advantageous to make the volume of the cavity as small as is physically possible.

In the katharometer described in this report the volume of each thermistor cavity was approximately 0.6 ml. Samples as small as 1.32 ml. were used. However, by the time the sample had passed through the column and had reached the katharometer, the peak width at its half
height was 10 to 20 ml. for the sharpest peaks. Thus it appears that, relative to other factors, the volume of the thermistor cavities did not affect the resolution. This conclusion implies that diffusion of the sample into and out of the cavity was rapid, but the assumption has not been experimentally verified. However, a comparison of the geometry of this instrument with that of other katharometers indicates that the assumption is justified.

3. Effect of Sample Injection Technique

In order to take full advantage of the separation ability of the column, it is necessary to introduce the sample quickly and with a minimum of interruption of the gas flow through the column. Liquid samples usually are introduced by means of a micrometer syringe through a rubber stopper. Gases generally are introduced through a by-pass system similar to the one used in this work, although Tenny and Harris have described a pipette for the introduction of gas samples.

It is probable that the present sample-introduction system could be improved with a corresponding increase in resolution of sample components. Approximately thirty seconds are required to manipulate the stopcocks in the sample system. The time could be shortened by the use of metal snap valves. Also, the dead volume between the sample by-pass cell and the column packing could be reduced.

4. Effect of Supporting Material in Column

A large specific surface area in the fixed phase is desirable for rapid exchange of sample between the fixed and the mobile phases. For this reason, some of the early work was done with Celite 545 as the
support for the palladium metal. The Celite 545 particles are very small and the surface area of the individual particles is further increased by their skeletal structure. The pressure drop required in order to establish the desired flow rates through the column was excessive. A 25-lb. inlet pressure produced a flow rate at 100° of approximately 10 ml. min.⁻¹ of argon through an 8-ft. column. The same inlet pressure produced a flow rate of approximately 16 ml. min.⁻¹ through the 43-ft. column which was packed with the flint quartz material. The effect of particle size upon resolution has been reported by Dimbat, Porter, and Stross.⁵

5. Electrical Circuit

a. General properties of the Wheatstone bridge. The following discussion refers to Figure 9 of this section. The output signal, ΔE, of the bridge is defined by equation 27,

\[ \Delta E = \left[ \frac{t_1 + \Delta t_1}{t_1 + \Delta t_1 + R_2} - \frac{t_1}{t_1 + R_2} \right] E \]  

(27)

where \( t_1 \) is the initial resistance of the sensing thermistor, \( R_2 \) is the value of the fixed resistance in the same arm of the bridge, and \( E \) is the total voltage applied across the bridge. It can be seen that a constant current condition may be approached by making the value of \( R_2 \) much larger than that of \( t_1 \). In this manner bridge sensitivity is also increased to a maximum value defined by equation 28.

\[ \Delta E = I \Delta t_1 \]  

(28)

If the power input to the thermistors is constant and if heat is transferred from the thermistors only by conduction through the gas, then
the difference, $\triangle T$, in the temperature of the reference and the sensing thermistors is

$$\triangle T = \left[ \frac{\lambda_r - \lambda_m}{\lambda_m} \right] (T_1 - T_s) \quad (29)$$

where $T_1$ is the temperature of the reference thermistor, $T_s$ is the temperature of the heat sink, $\lambda_r$ is the thermal conductivity of the reference gas, and $\lambda_m$ is the thermal conductivity of the sample mixture.

If the thermistors have a linear resistance-versus-temperature relationship, which is approximately true only for very small changes in resistance,

$$\frac{\triangle t_1}{t_1} = \frac{\triangle T_1}{T_1} \quad (30)$$

Then from equation 28,

$$\triangle E = I t_1 \left( \frac{\lambda_r - \lambda_m}{\lambda_m} \right) \left( \frac{T_1 - T_s}{T_1} \right) \quad (31)$$

The above conditions are obviously only approximations of those extant in the present instrument. The impedance of the measuring circuit, although high, still contributes to non-linearity. The temperature coefficients of resistance are not constant, and the thermal conductivities of the gas mixtures are not linear functions of the concentration. Heat is transferred from the thermistors to the heat sink by radiation and by conduction through the leads, in addition to the transfer by conduction through the gas.

In spite of the approximations to ideal behaviour the non-linearity which may be attributed to the circuit design is only 0.3 per cent as calculated from equation 32.
Per cent non-linearity = \( \frac{10 \left( S_1 - S_2 \right)}{S_2} \times 100 \)  

where \( S_1 \) is the voltage signal for a 1-ohm increase and \( S_2 \) is the voltage signal for a 10-ohm increase in the resistance of the sensing thermistor. The calculation is for a thermistor resistance of 75 ohms and a current of 15 mA through each arm of the bridge at balance.

The bridge sensitivity may be further increased by shunting the thermistors with an ohmic resistance. 61 Theoretically there is no upper limit to the sensitivity that may be achieved in this manner. The technique is used in practice only for relatively small increases in sensitivity, since it increases the bridge time constant, decreases the stability, and causes large deviations from linearity.

b. Zero controls. It was rarely necessary to obtain a true balance of the bridge. Instead, the zero controls were used to place the recorder trace at a convenient position on the chart.

c. Effects of chart and pen speeds. A chart speed of 6 inches per hour and a pen speed of 4.5 seconds for full-scale deflection were used. By means of the zero controls the pen could be made to traverse the entire chart width and return while the chart advanced approximately the width of the line drawn by the pen. The spike produced in this manner was much narrower than any peak obtained in elution chromatography. Hence, it was concluded that the chart and pen speeds did not significantly limit the resolution.

6. Temperature Profile in the Column Heater

The vertical temperature profile in the column heater was investigated by lowering a thermocouple into the heater. In the vicinity of
200° the bottom of the heater was approximately 10° cooler than the top. Since the temperature affects the operation of the column, it is possible that elimination of this temperature gradient might improve the resolution.

B. Distribution Isotherms

1. Nature of the Distribution Isotherms

In a chromatographic column the sample may be held at the surface of the fixed phase by chemical or physical forces, or it may dissolve in the fixed phase. In the former case the column is referred to as an adsorption column and in the latter case it is referred to as a partition column. In most chromatographic applications there is no difficulty in determining by which method the sample is held.

When hydrogen or deuterium is equilibrated with palladium metal some gas is adsorbed at the surface. A much larger amount may be dissolved but the solution process is a slow one. Nace and Aston found that at room temperature two to six hours were required to reach equilibrium. Since a chromatographic elution experiment with the 43-ft. column containing palladium as the fixed phase usually required less than two hours at room temperature, there was some question as to whether the rate of solution would be sufficiently rapid for the column to function as a partition column.

The column desorption curves found in Figures 11, 12, and 13 provide evidence that a \( \beta \)-phase solution formed in the column. Figure 1 indicates that an equilibrium pressure of 1.8 atmospheres, or 12 psig,
should be sufficient to form the \( \beta \)-phase solution of hydrogen up to a temperature of approximately 170°. At 245° an equilibrium pressure of approximately 10 atmospheres should be necessary to establish the \( \beta \)-phase solution. Since this pressure was not reached in the column, the break at point \( x \) in curve C of Figure 13 must be attributed to some other factor. The distribution isotherms exhibit an inflection point, which is more apparent for the high-temperature curves in Figure 1, at a pressure lower than that at which the \( \alpha - \beta \) transition occurs. Also, the change of slope in the vicinity of this inflection point is greater for the high temperature curves. This inflection may account for the slight break in curve C of Figure 13.

A comparison of Figures 1 and 2 indicates that, at a given temperature, a much higher pressure is required to maintain a \( \beta \)-phase solution of deuterium in palladium than is required for hydrogen. The curves in Figure 11 exhibit this fact in that the transition from the \( \beta \)-phase occurs sooner for deuterium than for hydrogen.

2. Factors Affecting the Rate of Attainment of Equilibrium

a. Temperature. It is logical to expect that equilibrium would be more rapidly approached as the temperature is increased. Quantitative results have been reported to support this conclusion. Sieverts\textsuperscript{62} reported that for fully annealed palladium metal equilibrium of the metal with hydrogen gas was seemingly unattainable at temperatures below 140°. Tammann and Schneider,\textsuperscript{63} and Smith and Derge\textsuperscript{64} have also shown that equilibrium is reached more rapidly at elevated temperatures. Similar results have been reported by Lambert and Gates.\textsuperscript{65}
b. **Condition of the metal.** Since solution must occur through the surface of the metal, a large surface development should increase the rate at which equilibrium is attained. Holt\(^{66}\) reported that at room temperature the rate of absorption of hydrogen by palladium black was several times more rapid than the rate with palladium foil.

Both the rate and the magnitude of the occlusion of hydrogen by palladium are significantly dependent upon the previous history of the metal. Krause and Kahlenberg\(^{67}\) showed that the rate of occlusion of hydrogen by palladium metal progressively increased as the metal structure was gradually opened up by successive occlusions, with intervening expulsions of hydrogen by heating. The effect of the previous history of the metal is also exhibited by the gradual change in the retention volume of deuterium in a series of experiments following treatment of the metal with hydrogen as shown in Figure 19.

3. **Determination of Distribution Isotherms and Partition Coefficients**

   a. **By displacement techniques.** James and Phillips\(^{68}\) have shown how the distribution isotherms, and consequently the partition coefficients, may be determined by a chromatographic displacement technique. The sample to be investigated is injected into the column and is then swept through the column by a displacing agent which is more strongly held by the fixed phase. The composition of the effluent from the column is given by a curve such as that shown in Figure 15. The region of mixed components becomes narrower as the relative absorption strength of the displacing agent is increased. For calculation purposes the boundary between the deuterium and hydrogen in Figure 15
may be set by drawing a vertical line such that two triangles of equal area are formed by the line, the sloping portion of the step, and the extensions of the horizontal lines for 100 per cent deuterium and for 100 per cent hydrogen.

The area under the curve is proportional to the total amount of sample and is also the product of the recorder deflection and the length of the step in time units. The recorder deflection is proportional to the concentration of the sample at the exit of the column and the time is proportional to the total quantity of gas which has flowed through the column. These statements are expressed by equations 33 and 34, which are equivalent to each other.

\begin{align*}
\text{Area} &= \text{recorder deflection} \times \text{time} \\
\text{Amount of sample} &= \text{concentration} \times \text{flow rate} \times \text{time}
\end{align*}

Therefore,

\begin{equation}
C_m = \frac{A}{Rt}
\end{equation}

where

- \(C_m\) = the concentration of the sample in the mobile phase,
- \(A\) = the amount of the sample,
- \(R\) = the flow rate measured at the exit of the column, and
- \(t\) = the step width of the sample in time units.

The three terms on the right side of equation 35 may all be measured. Then the concentration, \(C_m\), equivalent to the concentration \(C_B\) in Figure 14, of the sample in the mobile phase at the exit of the column may be determined. It should be noted that the sensitivity of the katharometer was not involved in the calculation of the concentration. The detector merely provides a method for locating events as a function of time.
At the time when the deuterium first emerges from the column it is absorbed on a fractional length of the column packing equal to the length of the deuterium step divided by the break-through time of the displacing agent, hydrogen. Since the mobile phase is compressible, the linear velocity is not constant along the column and the preceding statement is strictly true only in the limiting case when the ratio of the input to the exit pressures approaches unity. The amount of deuterium absorbed in this fraction of the column may be determined from the total amount of deuterium used, the concentration in the mobile phase, the fractional length of the column, and the cross-sectional area of the mobile phase by means of equation 36.

\[ A_f = A - C_m aL \]  
\( (36) \)

where \( A_f \) = the amount of deuterium absorbed by the fixed phase,
\[ a = \text{the cross-sectional area of the column mobile phase, and} \]
\[ L = \text{the length of the column upon which deuterium is absorbed.} \]

In addition,

\[ aL = V_R^N f_L \]  
\( (37) \)

where
\[ V_R^N = \text{the retention volume for nitrogen, and} \]
\[ f_L = \text{the fraction of the column length upon which deuterium is absorbed.} \]

Therefore,

\[ C_f = \frac{A_f}{f_L W} \]  
\( (38) \)

\[ C_f = \frac{A - C_m V_R^N f_L}{W f_L} \]  
\( (39) \)
where

\( C_f \) = the concentration of the sample in the fixed phase,

\( W \) = the weight of the fixed phase, exclusive of the inert

supporting material.

Then,

\[
k = \frac{C_f}{C_m} = \frac{Rt - \frac{W_{fL}}{W_{fL}}}{W_{fL}}.
\]  

(40)

If the dimensions of \( C_f \) are moles \( \text{gm.}^{-1} \) and the dimensions of \( C_m \) are moles \( \text{ml.}^{-1} \) then equation (40) gives the dimensions of \( k \) as \( \text{ml.} \) \( \text{gm.}^{-1} \).

An alternative method may be described by reference to Figure 14. If the absorption isotherm and the concentration, \( C_B \), of the displacing agent are known the control line can be drawn. The concentration, \( C_B \), is equivalent to the \( C_m \) of equation 35. The intersection of the dotted line for \( C_B \) with the control line gives one point on the absorption isotherm.

If the amount of the sample is sufficiently reduced, the pressure differential across the portion of the column containing the sample will be small and the errors resulting from compression will be reduced. By altering the concentration of the displacer, other points on the isotherm may be determined.

The method is applicable only for systems which exhibit isotherms concave toward the pressure axis. For this type of isotherm, the partition coefficient varies along the length of the column as a function of pressure. This is a second reason for restricting the calculations to the limiting case where the ratio of the input to the exit pressure
approaches unity.

The number of theoretical plates in the column is not involved in the calculation of the partition coefficient by equation 40. Thus, the only advantage to increasing the length of the column beyond that required to establish the zones is to increase the size of the sample which may be handled. In addition, it is necessary to compare the partition coefficients obtained by the displacement technique with those obtained by normal equilibrium distribution techniques in order to ascertain how closely the equilibrium distribution is approached in the column. Therefore, the displacement chromatographic technique appears to have no advantage over the normal equilibrium technique for the determination of partition coefficients, except in that the equipment and the procedures are simpler in the chromatographic method.

b. By frontal analysis. The equilibrium separation factor for hydrogen and deuterium is defined by equation 41.

\[
\lambda = \frac{k_H}{k_D} \tag{41}
\]

where \(k_H\) and \(k_D\) are the partition coefficients for hydrogen and for deuterium in the column.

Glueckauf and Kitt\(^{17}\) calculated the separation factor from a series of break-through experiments. Their calculation was based on the following equations of mass conservation, which apply at the moment the feed composition appears at the exit of the column.

\[
\text{Total feed of hydrogen} = \text{amount of hydrogen absorbed} + \text{amount of hydrogen in mobile phase} + \text{amount of hydrogen which has emerged from the column at the moment the feed composition emerges from the column.} \tag{42}
\]
In an ideal column the last term on the right side of equation 42 is zero.

Equation 42 may be written as
\[ v_0c_H = Xf_H + Yc_H \]  
(43)

where
\[ v_0 = \text{the total volume of hydrogen and deuterium fed to the column}, \]
\[ c_H = \text{the concentration of hydrogen in moles liter}^{-1}, \text{of the inflowing gas}, \]
\[ X = \text{the volume of the column, exclusive of the inert supporting material}, \]
\[ Y = \text{the volume of the mobile phase, which may be determined from the retention volume of an inert gas, and} \]
\[ f_H = \text{the amount of hydrogen absorbed, in equilibrium with the feed gas, per volume unit in the column}. \]

A similar equation may be written for deuterium,
\[ v_0c_D = Xf_D + Yc_D + (v_b - v_a)c'_D \]  
(44)

where \( v_b = \text{the product of gas flow rate, measured at the column exit, and the break-through time of the feed composition}, \)
\[ v_a = \text{the product of gas flow rate, measured at the column, exit, and the break-through time for the leading edge of the deuterium, and} \]
\[ c'_D = \text{the concentration of deuterium in the outflowing gas}. \]

Then,
\[ v_b - v_a = \text{the product of the gas flow rate, at the column exit, and the deuterium step width in time units}. \]
Also,

\[ Y = v_a . \]  \hspace{1cm} (45)

Equations 42 through 45 are valid only when the input and the exit pressures are identical. Equations 43 and 44 may be rearranged to give

\[ (v_o - v_a) c_H / f_H = X, \]  \hspace{1cm} (46)

\[ (v_o - v_a) c_D / f_D - (v_b - v_a) c_D' / f_D = X . \]  \hspace{1cm} (47)

Now,

\[ f_H = R c_H t_H^0 \]  \hspace{1cm} (48)

where

\[ R = \text{the volume flow rate at the entrance to the column, and} \]

\[ t_H^0 = \text{the corrected break-through time for hydrogen, when zero time is taken as the break-through time for a material which is not absorbed by the column.} \]

In like manner,

\[ f_D = R c_D t_D^0 . \]  \hspace{1cm} (49)

The partition coefficients for hydrogen and for deuterium may be evaluated by the use of equations 46 through 49, for the limiting case where there is no pressure gradient along the column.

Glueckauf and Kitt\(^1\) defined the separation factor by equation 50.

\[ 1/\lambda = k_D / k_H = (c_H / c_D) \left( f_D / f_H \right) \]  \hspace{1cm} (50)

Upon elimination of \( X \) from equations 46 and 47, we have

\[ 1/\lambda = 1 - \frac{(v_b - v_a) c_D'}{(v_o - v_a) c_D} , \text{ or} \]  \hspace{1cm} (51)

\[ 1/\lambda = 1 - \frac{(v_b - v_a) P'}{(v_o - v_a) P} \]  \hspace{1cm} (52)
where

\[ P' = \text{the exit pressure, and} \]

\[ P = \text{the partial pressure of deuterium at the entrance of the column.} \]

Figure 25 is a plot of the separation factor as a function of temperature. Glueckauf and Kitt were not specific as to their feed composition or pressure gradient. They state that input pressures up to 24 cm. of mercury above atmospheric were used, and they imply that the feed composition was approximately 55 mole per cent deuterium. For the present work, an input pressure of 80 cm of mercury above atmospheric was used, and the feed composition was approximately 50 mole per cent deuterium. The fact that the distribution isotherms are concave toward the pressure axis, except in the vicinity of the \( \alpha, \beta \)-phase transition, may account for the lower values of the separation factor obtained in the present work.

Glueckauf and Kitt obtained an expression for the temperature dependence of the separation factor.

\[ \log \alpha = \frac{215}{T} - 0.47 \quad (53) \]

where \( T \) is the temperature in degrees Kelvin. The data obtained in the present work give an expression,

\[ \log \alpha = \frac{222}{T} - 0.51 \quad (54) \]

The temperature coefficients in both cases are similar to that observed by Gillespie and Downs, but the absolute values are different.

The break-through technique is suitable only for the study of systems involving distribution isotherms which are concave toward the pressure axis. With the displacement technique, once the step is formed,
Temperature Dependence of Deuterium-Hydrogen Separation Factor in a Chromatographic Column With Palladium as the Fixed Phase
its width should not change except as a result of pressure changes. With the break-through technique the corrected retention time, \( t^0 \), becomes larger as the column length is increased. Thus, the break-through technique offers an advantage over the normal equilibration technique for the determination of partition coefficients.

The detector sensitivity is not involved in the calculation of \( k \) from break-through data. In addition, it should be noted that there is no necessity for direct analysis of the composition of the fixed phase.

c. **By elution analysis.** Anderson\(^70\) and Porter, Deal, and Stross\(^71\) have discussed methods for the determination of the partition coefficient from elution chromatographic data. Several simplifying assumptions are necessary. They are:

1. No change in volume occurs as the gas passes through the column. Therefore the input and exit pressures must be identical.
2. The partition coefficient for the sample component must be constant throughout the column.
3. The entire sample must be charged initially into the first plate of the column.
4. All rate effects can be accounted for by means of the theoretical plate concept, and
5. The H.E.T.P. must be small relative to the column length and must be constant throughout the column.

The partition coefficient, \( k \), is defined by equation 55.

\[
k = \frac{C_f}{C_m}
\] (55)
If \( C_f \) and \( C_m \) are both expressed in \( \text{gm. ml}^{-1} \), \( k \) is dimensionless and may be expressed by equation 55,

\[
k = \left[ \frac{V_R^o}{v_mX} - 1 \right] (v_m/v_f) \tag{56}
\]

where

\( V_R^o \) = the corrected retention volume as defined by James and Martin,

\( v_m \) = the gas-space volume fraction in the column,

\( v_f \) = the fixed-phase volume fraction in the column, and

\( X \) = the total volume of the column.

The volume of the inert supporting material is not included in the calculation of \( v_m \), \( v_f \), and \( X \).

Equation 56 is based on the following considerations. 26

\( c \) = the amount of sample in 1 ml. of the mobile phase,

\( a_1 \) = the amount of sample in 1 ml. of the column, exclusive of the volume of the inert supporting material, at equilibrium with mobile phase of concentration \( c \), and

\( a_2 \) = the amount of sample in 1 ml. of the absorbent.

Then,

\[
a_1/c = (a_2/c)v_f + v_m \tag{57}
\]

\[
a_2/c = k \tag{58}
\]

\[
a_1/c = V_R^o/X \tag{59}
\]

Equation 56 follows from the substitution of equations 58 and 59 into equation 57. Equation 56 is equivalent to the expression used by Porter, Deal, and Stross\textsuperscript{71} for gas-liquid partition chromatography, and by Simpson and Wheaton\textsuperscript{72} for ion-exchange work.
The use of $V^0_R$ corrects for the change in volume resulting from the pressure gradient along the column. In elution chromatography, even with a zero pressure gradient, the partition coefficient for a sample component can be constant along the column only if the distribution isotherm is linear.

Although the calculation is strictly valid only for a system involving linear isotherms, equation 56 was used for the approximate calculation of the partition coefficients and the separation factors at one temperature. The point is included in Figure 25. Considering the assumptions which were made in the calculation, the agreement with the single stage equilibrium measurement at approximately the same temperature is good.

It should be pointed out that the break-through experiments were carried out with mixed hydrogen and deuterium samples, while the separation factor calculated from elution data was based on separate runs with hydrogen and with deuterium, and that a number of runs were made with each before a reproducible value of $V^0_R$ was obtained. This fact probably accounts for the higher value of the separation obtained from elution data as compared with that obtained from the break-through data, and also for the better agreement between the values obtained from the break-through experiment and the single stage equilibration.
C. Chromatographic Separation of Hydrogen and Deuterium

1. Relative Merits of the Various Methods

Neither the displacement nor the frontal-analysis (break-through) technique is capable of completely separating the components of the sample. However, a fraction of the deuterium may be separated in a very pure state. Both methods are simple, and are capable of providing information on the distribution isotherm, the partition coefficients, and the separation factor, for systems involving isotherms which are concave toward the pressure axis.

The elution technique is capable of separating completely the components of a sample under proper operating conditions. The apparatus and the manipulations are somewhat more complex than those for the two methods mentioned above. In addition, the elution technique functions best for systems involving linear isotherms. It may be used with non-linear isotherms but the separations are more difficult.

The elution technique is particularly useful for analytical purposes, since the amount of each component is proportional to the area under the corresponding elution peak. The area may be recorded directly by means of an electronic integrator or a mechanical ball-and-disc integrator.

All three methods involve batch operation and are therefore not particularly well suited for preparative processes without further modification. A number of methods for continuous chromatography have been reported. 73-75
2. Factors Affecting Separation by the Elution Process

a. The separation factor and the number of theoretical plates. The requirements for an analytical separation of an equimolar mixture of two components have been discussed by van Deemter, Zuiderweg, and Klinkenberg. Glueckauf has discussed the separation in a more general manner, and has prepared a family of curves showing the number of theoretical plates required to reduce the fractional impurity between two elution peaks to a specified value for a given separation factor. The plot applies to a system involving linear isotherms.

Figure 25 shows that an equilibrium separation factor of approximately 1.42 should be obtained if the partition coefficient for hydrogen is unaffected by the presence of deuterium, and vice versa. The separation factor determined from frontal-analysis and from single-stage equilibration data with mixed samples is approximately 1.3. In order to reduce the fractional impurity to 0.1 per cent, approximately 350 theoretical plates are required for a separation factor of 1.42 and approximately 550 theoretical plates are required for a separation factor of 1.3. This is equivalent to an H.E.T.P. of 3.7 cm. in the former case, and 2.4 cm. in the latter case in the 43-ft. column. Much lower values for the H.E.T.P. have been reported for gas-liquid partition columns in which the rate of attainment of equilibrium is rapid. A slower approach to equilibrium, such as has been reported for the hydrogen-palladium system, will increase the value of the H.E.T.P. In addition, the non-linearity of the isotherms increases the number of theoretical plates required to reduce the fractional impurity to a given value.

b. Temperature. Figure 25 illustrates the fact that the separation factor is reduced by an increase in temperature. However, at an
elevated temperature the rate of equilibration is larger and consequently the H.E.T.P. may be lower. The inter-relations of these two factors is shown by the fact that better resolution was obtained at 175-180° than at lower temperatures.

c. Factors resulting from non-ideality in the column. The effect of various physical parameters in linear non-ideal chromatography has been discussed by van Deemter, et. al. Linear chromatography is that in which the distribution between the fixed and the mobile phases follows a linear isotherm. Non-ideal chromatography is that in which the shape of the band moving through the column changes as a result of irreversible processes, such as diffusion and eddy motions. In order to increase peak sharpness and to improve resolution it is necessary to approach ideal chromatography as closely as possible.

When the sample size influences the peak width, it is convenient to use the standard deviation, or the variance, as a measure of peak width. The variance is the sum of five contributions:

(1) Sample size,

(2) Axial eddy diffusion caused by the packing,

(3) Axial diffusion, which is inversely related to the linear velocity of the gas in the mobile phase,

(4) Diffusion into the interphase between the mobile and the fixed phases, and

(5) Diffusion into the fixed phase.

The effect of linear velocity upon the H.E.T.P. has been shown experimentally by van Deemter, et. al. There exists an optimum linear velocity in the column, for which the H.E.T.P. is a minimum, as
is shown by Figure 26. Below this optimum velocity, axial diffusion along the column spreads the peak. Above this optimum velocity the rate of mass transfer between the fixed and the mobile phases spreads the peak. The effect is also illustrated in Figure 23, in which the ratio $t_m/\gamma$ has a maximum value when plotted versus flow rate.

Since the linear velocity is not a constant along the column length, it is not possible to maintain the optimum flow rate throughout the column. The velocity profiles shown in Figure 27 may be calculated from the pressure drop across the column. It can be seen that operating conditions may be chosen so that the optimum flow rate occurs in the major portion of the column.

Dimbat, Porter, and Stross have investigated the effect of particle size in the packing of the column upon the resolution obtained in gas-liquid partition chromatography. Under ideal conditions it would appear that a decrease in the particle size would increase the specific surface area, if the fixed phase were distributed uniformly on the packing, and thus increase the rate of mass transfer between the fixed and the mobile phases. However, the column is not ideal and also the pressure drop across the column which is necessary to establish a given volume flow rate may be prohibitively high for a packing composed of fine particles. Dimbat, Porter, and Stross found that optimum resolution with a minimum pressure drop was obtained when the column was packed with 35 to 60-mesh material. In the present work, Celite-545 was initially investigated. Its use was discontinued because of the high pressure required to operate the column. However, the effect of particle
Figure 26

Effect of Linear Velocity Upon the H.E.T.P. and the Contribution of Various Factors to the H.E.T.P.
Figure 27

The Velocity Gradient Along the Column as a Function of the Input to Exit Pressure Ratio

\[ \frac{p_i}{p_o} = 1.5 \]
size upon the resolution in the column was not investigated and it is possible that the particle size used was not the optimum one.

d. Method of evaluating optimum conditions in present work. The separation of hydrogen from deuterium by elution chromatography in a column containing palladium as the fixed phase was studied as a function of temperature, flow rate (and hence the pressure drop), and sample size. Since it was difficult to perform experiments to evaluate the effect of each factor independently, and since the performance of the column with mixed gas samples could not be predicted reliably from the performance with pure samples of hydrogen and deuterium, a factorially designed set of experiments were performed. The approximate values of the variables were selected from information obtained in runs with hydrogen and with deuterium samples. The elution curve shown in Figure 24 was the best curve obtained from this set of experiments.

D. Suggestions for Further Work

1. Elution Chromatography

The separation of hydrogen from deuterium by elution chromatography appears to be possible. Because of the non-linearity of the distribution isotherms, a larger number of theoretical plates is required for the separation than would be the case for a system of linear isotherms. A decrease in the H.E.T.P. in the present column might be obtained by further work. The effect of particle size upon the resolution has not yet been studied. In addition, the effects of variations in the method of preparing the palladium metal have not been investigated. A number of
other metals also dissolve hydrogen and deuterium in large quantities and might prove suitable for use as a fixed phase. For example, a Pd-Ag alloy containing 40 per cent silver will dissolve a much larger amount of hydrogen than will the pure palladium metal. Also, the rate and the magnitude of the solution process are dependent on the previous history of the metal and consequently the separation might be improved by various methods of pretreatment of the column.

The method of injecting the sample can be improved, so that the sample is injected quickly and compactly into the column. The effect of sample size should be investigated in more detail. Also, the length of the column might be increased.

The chromatographic elution technique is capable of providing information from which thermodynamic data may be calculated. The work might be extended to obtain information of this type.

The principal application of the chromatographic elution technique is an analytical one. The sensitivity of the katharometer detector is such that the sample size used in the present work might be considerably reduced. For example, the nitrogen marker peaks were generated by quantities of nitrogen as small as 1.32 ml. at a pressure of 2 cm. of mercury, and with the detector system operating below its maximum sensitivity. Since the sensitivity toward nitrogen with an argon carrier is much less than the sensitivity toward hydrogen, it is evident that very small samples of hydrogen could be measured by the detector. Hydrogen-deuterium mixtures are frequently analyzed either by mass-spectral or by diffusion methods. The mass-spectral method requires very complex and expensive equipment and its accuracy is somewhat limited. The pin-
hole diffusion method requires a larger sample than is required for the gas-chromatographic method. Static thermal conductivity measurements may also be used to analyze hydrogen-deuterium mixtures, but there are a number of experimental difficulties such as the requirement for an accurate calibration curve and rigid temperature control.

If satisfactory separation of hydrogen from deuterium could be obtained by the elution process, the method might be extended to include samples containing tritium.

2. Other Methods

The normal chromatographic technique is not well suited to preparative processes, since it is a batch operation. A similar technique which is capable of continuous operation is the hypersorption process. Hypersorption was originally a light hydrocarbon recovery process designed to permit processing and recovery of hydrocarbons from streams which could not be handled economically by the conventional recovery processes. The elements of the operation of hypersorption involve contacting the feed stream with a moving bed of adsorbent which has been previously stripped and cooled to the desired temperature. The adsorbent flows downward through a column. The feed gas is injected at the center of the column, and passes upward countercurrent to the moving bed of adsorbent. The less strongly adsorbed component is liberated at the top of the column. The more strongly adsorbed component is carried downward in the column and is stripped from the adsorbent at the bottom of the column by a heater. Thus a reflux condition is established at the bottom of the column which displaces any of the less strongly ad-
sorbed component which may be present in the lower section of the column. Thus, a concentration gradient is established along the column with pure components at either end of the column and a mixture of the components in the region between. The stripped adsorbent is lifted from the bottom of the column to the top and is reused. The pure components are taken from the column at suitable points near the bottom and the top.

The hypersorption process has been successfully used for a number of years, and has become well established as a commercially practical tool. Since the rate of mass transfer in a chromatographic column has been shown to be sufficiently rapid to obtain partial separation of hydrogen from deuterium, it appears that hydrogen and deuterium might be successfully separated in a continuous operation by a technique similar to the hypersorption process.
CHAPTER VIII

SUMMARY

The separation of hydrogen and deuterium by gas chromatography was investigated using a column in which the fixed phase was palladium metal supported on granular flint quartz. Displacement, frontal-analysis, and elution techniques were used. Hydrogen was the displacing agent in the displacement experiments.

The experimental results reported earlier by Glueckauf and Kitt, in which a sample of very pure deuterium was prepared by the displacement and by the frontal-analysis techniques, were verified.

The equilibrium separation factor, \( \alpha \), was calculated from data obtained by the frontal-analysis and by the elution techniques. The values obtained were in fair agreement with those reported by Glueckauf and Kitt for measurements made by the frontal-analysis technique and by single-stage equilibration measurements. The temperature dependence of the separation factor was found to be represented by the expression,

\[
\log \alpha = \frac{222}{T} - 0.51
\]

The slope of the line was in agreement with that found by Glueckauf and Kitt, and by Gillespie and Downs.

Partial resolution of the components of a hydrogen-deuterium mixture was obtained by elution chromatography, using argon as the carrier and as the reference gas. The separation of the two components was less than that which might be expected from a comparison of the elution peaks for pure hydrogen and for pure deuterium. Thus, the partition coefficient for either component of the mixture is not independent of the presence
of the other component. This conclusion was further verified by the fact that following a series of runs with hydrogen it was necessary to "condition" the column by several runs with deuterium before a reproducible value for the retention volume of deuterium could be obtained.

The results appear to justify further investigation of the elution process for the separation of hydrogen from deuterium, with possible extension to mixtures containing tritium.

Since the elution process is a batch method, its primary applications should be the procurement of data regarding the characteristics of the column and the analysis of mixtures of the isotopes of hydrogen. The hypersorption process might be suitable for a continuous separation of the isotopes.
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VITA

Carl Owens Thomas was born in Birmingham, Alabama, on October 7, 1926, the son of Oscar Burton and Susie Mae Thomas. He attended the public schools of Birmingham, Alabama, and was graduated from Phillips High School in May, 1943.

He entered Howard College in June, 1943. From January, 1944 to October, 1945 he served on active duty with the U. S. Naval Air Force. Upon release from the U. S. Navy he returned to Howard College and graduated with a Bachelor of Arts degree in Mathematics in June, 1947. During the summer of 1947 he was employed by the American Cast Iron Pipe Company of Birmingham, Alabama as an analytical chemist.

He entered Johns Hopkins University in September, 1947 and received a Master of Arts degree in Chemistry in June, 1949. He remained in the Graduate School of Johns Hopkins University until the summer of 1950. He was an instructor in analytical chemistry in the McCoy College of Johns Hopkins University from September, 1947 until June, 1950, and was employed on a temporary basis by the Applied Physics Laboratory of Johns Hopkins University during the summer of 1950.

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He was married to the former Martha Skinner of Birmingham, Alabama, in March, 1955.