THE EFFECT OF SMALL SURFACE WAVES ON
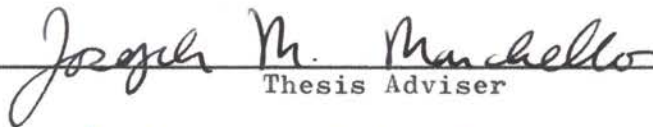
MASS TRANSFER RATE

By

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1957

Submitted to the faculty of the Graduate School of the
Oklahoma State University in partial fulfillment
of the requirements for the degree of
MASTER OF SCIENCE
May, 1962

THE EFFECT OF SMALL SURFACE WAVES ON

MASS TRANSFER RATE

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PREFACE

Almost every unit operation utilized by the chemical and petroleum industries makes use of mass transfer equipment. As would be expected, there has been considerable work done to improve the design of this type equipment. Several recent investigators have noted that small surface waves enhanced interfacial mass transfer. The purpose of this thesis is to determine a correlation between some characteristic of the surface waves, say wave length, and the rate of interfacial mass transfer. Experimental data were taken which verified the theoretical correlations.

iii

TABLE OF CONTENTS

# LIST OF ILLUSTRATIONS

# LIST OF TABLES

# LIST OF PLATES

CHAPTER I

INTRODUCTION

Mass transfer rate is the controlling or limiting parameter
in many industrial processes. In most unit operations, mass
transfer is effected between drops or liquid films. Effective-
ness of the mass transfer process is dependent on the surface
area exposed or available for molecular migration to take place.
To enjoy the benefits of high contact area, the liquids used
are usually in the form of drops or films.

A salient feature of absorption and extraction is the
dispersion of one of the phases in order to improve the rate
of mass transfer. Very little attention has been given to the
combined hydrodynamic and diffusional effect. One of the
objectives of this investigation was to study these effects
in order to improve the basic design criteria for mass transfer
operations. Among the major factors effecting the rate of mass
transfer is interfacial disturbances in the form of small
surface waves.

Relatively little is known about the role of surface waves
in mass transfer operations. An examination of the influence
of small surface waves on the rate of mass transfer to and
from liquids has been made in this work. Both theoretical
and experimantal aspects of the problem were considered
in a coordinated investigation of interfacial phenomena. The

1

primary objective of this phase of the work was to verify and extend the recently proposed theory of interfacial turbulence.

The work of this thesis was directed toward a combined theoretical and experimental investigation of the influence of small surface waves on interfacial mass transfer. The objectives were:

1. Investigate the hydrodynamics of small surface waves. The main portion of this work was an experimental study of ripples generated on a horizontal liquid surface.

2. Measure the mass transfer rate of carbon dioxide absorbing into water. Data were taken on the system with and without surface ripples on the horizontal water surface. This work was to be carried out in conjunction with item 1 of above.

3. Develop the theory of mass transfer for small surface waves. Use this information to explain the experimental results obtained in items 1 and 2 of above.

CHAPTER II

LITERATURE SURVEY

An aim of fundamental mass transfer studies is to provide
a basis for correlating and predicting coefficients for the
design of commercial equipment. A quantitative explanation
of mass transfer in absorption and extraction apparatus is
inherently based upon a knowledge of flow conditions and
diffusion mechanisms existing in the system.

Many mass transfer operations spread the liquid in a thin
film to increase the mass transfer rate by increasing the
interfacial area. Several models have been proposed for mass
transfer mechanisms of liquid films; however, relatively
little is known about the effects of surface waves, flow
patterns and mixing which takes place at the various surface
irregularities.

A number of workers (1, 2, 3, 4) have investigated the
characteristics of liquid films in gravity flow down the
surface of a vertical pipe (wetted wall column). Other
techniques employed include liquid running over a sphere
(2) and liquid jets (7). For the most part, these studies
have been limited to overall hydrodynamics, mass transfer,
and heat transfer studies of the film with the results being
expressed in terms of diminsionless groups of the pertinent

3

variables. King, Boyle, and Ogle (5) have given a theo-
retical explanation for the oscillations observed in water
flowing down a slotted trough. Their analysis is similar
to the earlier investigations of oscillating jets (6).

Interfacial effects in absorption have been studied by
Bond and Donald (8). A wetted wall column was used for the
absorption of ammonia from a gas stream. The minimum water
rate which would just maintain a continuous film was determined.
Below this minimum flow rate, the film breaks down and there
is a considerable reduction in the liquid area. The results
are interpreted as being due to a difference in surface tension
between the point where the film breaks and the main bulk of
the liquid. The basis for this explanation lies in the
Marangoni effect, wherein movement in an interface is caused
by longitudinal variations of the interfacial tension.

Localized stirring at the interface in certain liquid
extraction experiments have been reported by several investi-
gators (9, 10). The intensity of the surface activity, inter-
facial turbulence, varies considerably from system to system,
and rates of mass transfer tend to be abnormally high in those
extraction experiments in which interfacial turbulence occurs
(10).

Sternling and Scriven (11) have used a simplified mathe-
matical model to analyze the mechanism which supplies the mechan-
ical energy of interfacial turbulence. They have posed the
problem as one of hydrodynamic stability with diffusion and
interfacial movement acting as "coupled" processes. The

methods of conventional linear stability theory have been applied to determine the conditions for the onset of instability and the nature of the dominant disturbance. Their results relate interfacial tension (dynamic) and concentration profile near the surface to the interfacial turbulence level.

Russian investigators (12, 13) have done some work on mass transfer of a gas to an agitated liquid. Kishinevskii and Serebryanskii (12) have found that the absorption (q) of $N_2$, $O_2$ and $H_2$ into rapidly stirred water could be represented by:

$$q = k(C^* - C) \tag{1}$$

where $C^*$ is gas concentration at the interface, $C$ is the bulk gas concentration and k is the coefficient of absorption. k for all the gases was approximately equal (1.15 - 1.21) despite the wide range of molecular diffusion coefficients, D(0.63 to 2.17) (14). At slower rates of stirring, k decreased approximately 4.5 times and D became the controlling factor.

Japanese investigators are actively pursuing the phenomena of ripples and pulses causing increased mass transfer rate (13, 15, 16). Hikita, Nakaniski and Kataoka (16) have investigated mass transfer rates of several gases into several liquids using the wetted wall column technique. For high values of Reynolds Number, the empirical equation is:

$$H_L \ (\rho^2 g/\mu^2)^{1/3} = 2.36 Re (Sc)^{1/2} \tag{2}$$

but for low values of Reynolds Number (120) a small surface tension effect was noted:

$$H_L(\rho^2 g/\mu^2)^{1/3} = 22.8(Re)^{1/2}(Sc)^{0.38}(\rho^2 Z^3/\mu^2)^{0.4}$$

$$(\sigma/72)^{0/15} \tag{3}$$

This correlation also includes the length of the column while
Krasheninnikov and Durasova (17) state that absorption rate
coefficient depends only on column diameter, not length.
Shirotsuka and Honda (13) have investigated the effect of
pulsing the flow on the solution of 2-naphthol into water
flowing through a pipe formed from solid 2-naphthol.

Recently a number of investigators (16, 18) have made
note of the fact that ripples on the surface of a liquid
increase the rate of mass transfer. Striba and Hurt (1)
in a paper entitled "Turbulence in Falling Liquid Films"
have based the criterion for turbulence on whether or not
experimental results check mass transfer theory based solely
on molecular diffusion. It has been noted that rippling -
and therefore increased rate of mass transfer - occurs at
values of Reynolds Number as low as 25 for wetted wall columns.
Striba and Hurt attributed the increased rate of mass tranfer
to turbulence near the interface which was confirmed with
dye studies. Dye injected into the liquid film was dissipated
within 12 to 14 inches when ripples were present, but defined
a fine straight line when no ripples were present.

A majority of the investigators, whether they used wetted
wall columns, film flow over spheres or pulsed liquid flow
in pipes, have noted the fact that ripples on the surface,
even at very low values of Reynolds Number, cause abnormally

high mass transfer. Striba and Hurt (1) have noted that the increase in surface area due to the surface tension waves (ripples) was not enough to cause the increased mass transfer and have suggested some degree of turbulence as an answer to this phenomena.

# CHAPTER III

## EXPERIMENTAL APPARATUS

After determining which variables were important and pertinent to this study, a search of the literature was made to determine if an apparatus to study these variables had already been constructed by previous investigators. The search was fruitless, so an original unit was designed.

The apparatus was designed so that the rate of transfer of a light phase (either gas or liquid) into a heavy phase (liquid) could be studied. After this study it would then be necessary to impose ripples or waves of various characteristics on the interface. The pressure of the gas on the liquid and its temperature and rate of flow into the transfer section must be known. Accordingly, the apparatus pictured in Plate 1 and shown schematically in Figure 1 was designed. The apparatus was constructed of Plexiglass so that the properties of the surface waves could be studied with photographic equipment. Waves were generated by a flat plate extending over the entire liquid depth. This generating surface was motivated by a motor-driven cam mechanism, Figure 2.

Coulson (19) derived the following equation for surface wave velocity, C (Appendix A).

$$c^2 = \left[ \frac{g\lambda}{2\pi} + \frac{2\pi\sigma}{\lambda\rho} \right] \left[ \tanh \left( \frac{2\pi h}{\lambda} \right) \right] \qquad (4)$$
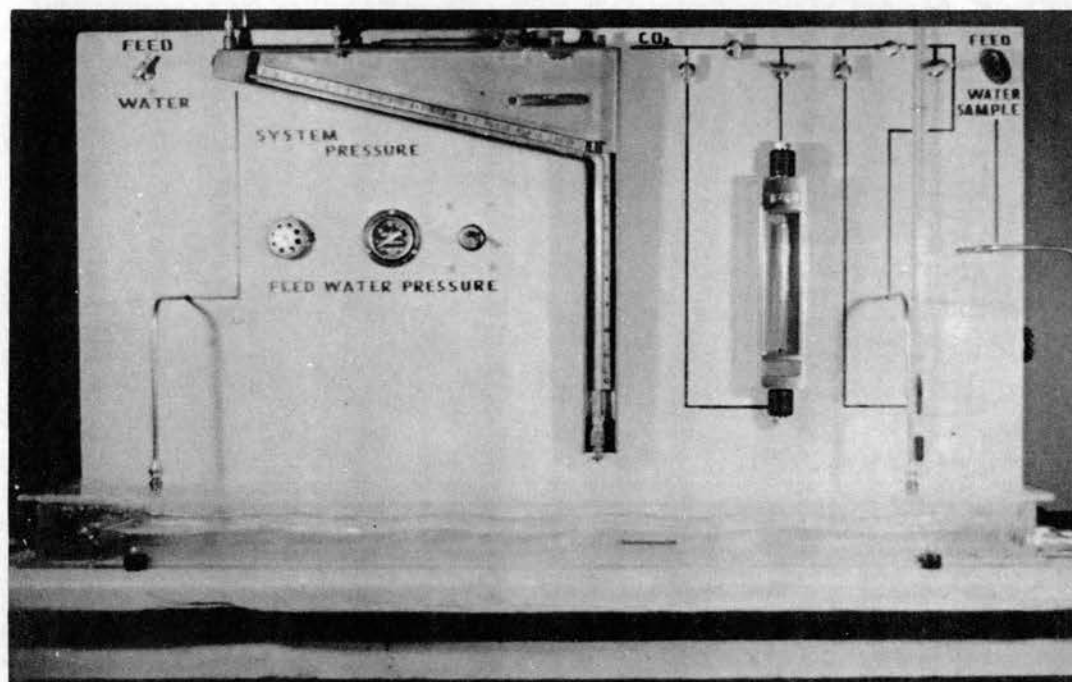
PLATE I

Overall View of the Apparatus

Head
Tank

Camera

Wave Generator

Weir

Gas
Cylinder
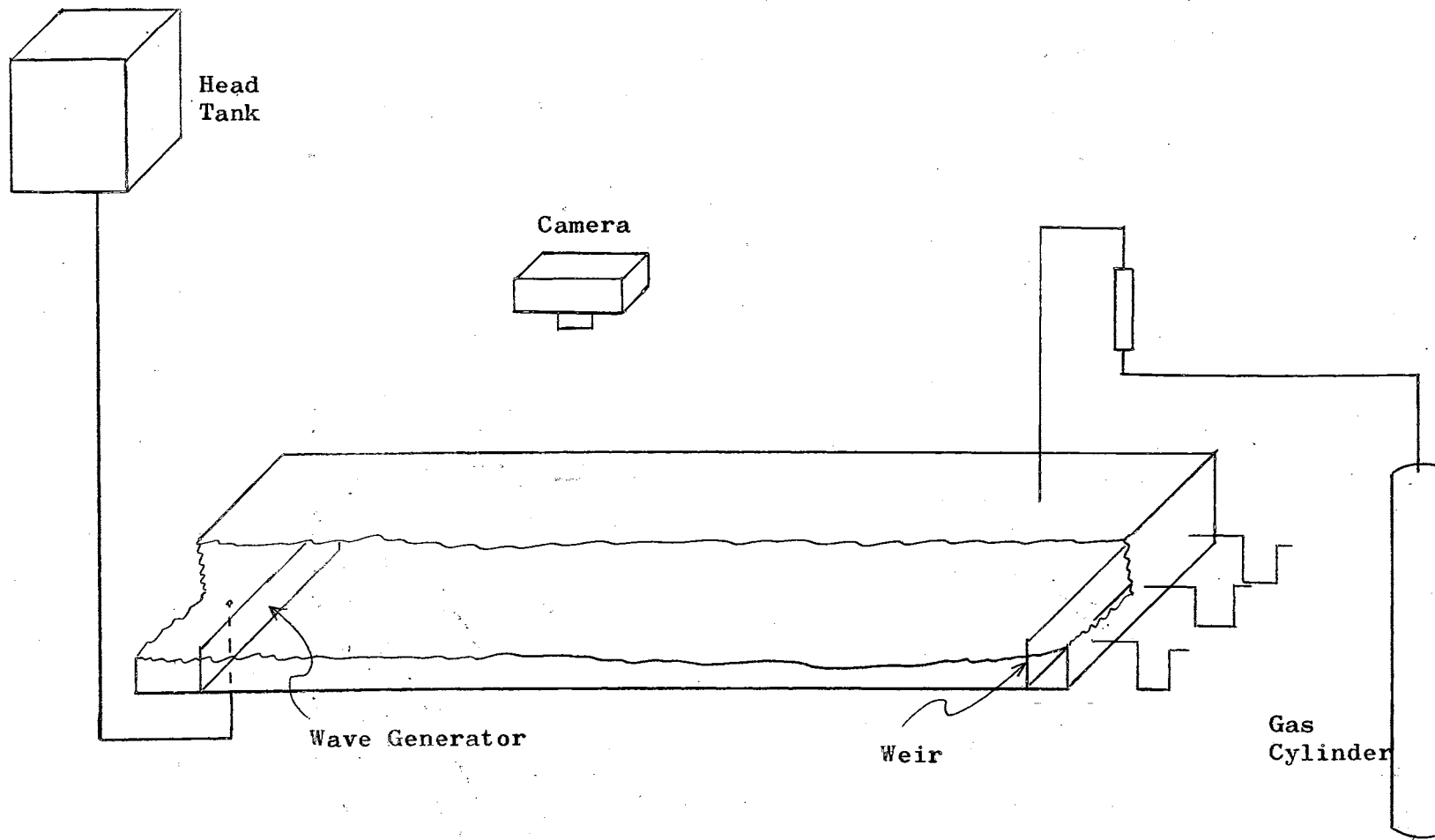
Figure 1.  Schematic of Surface Wave Equipment

Generating Surface

Springs (3)

Offset Cams (2)
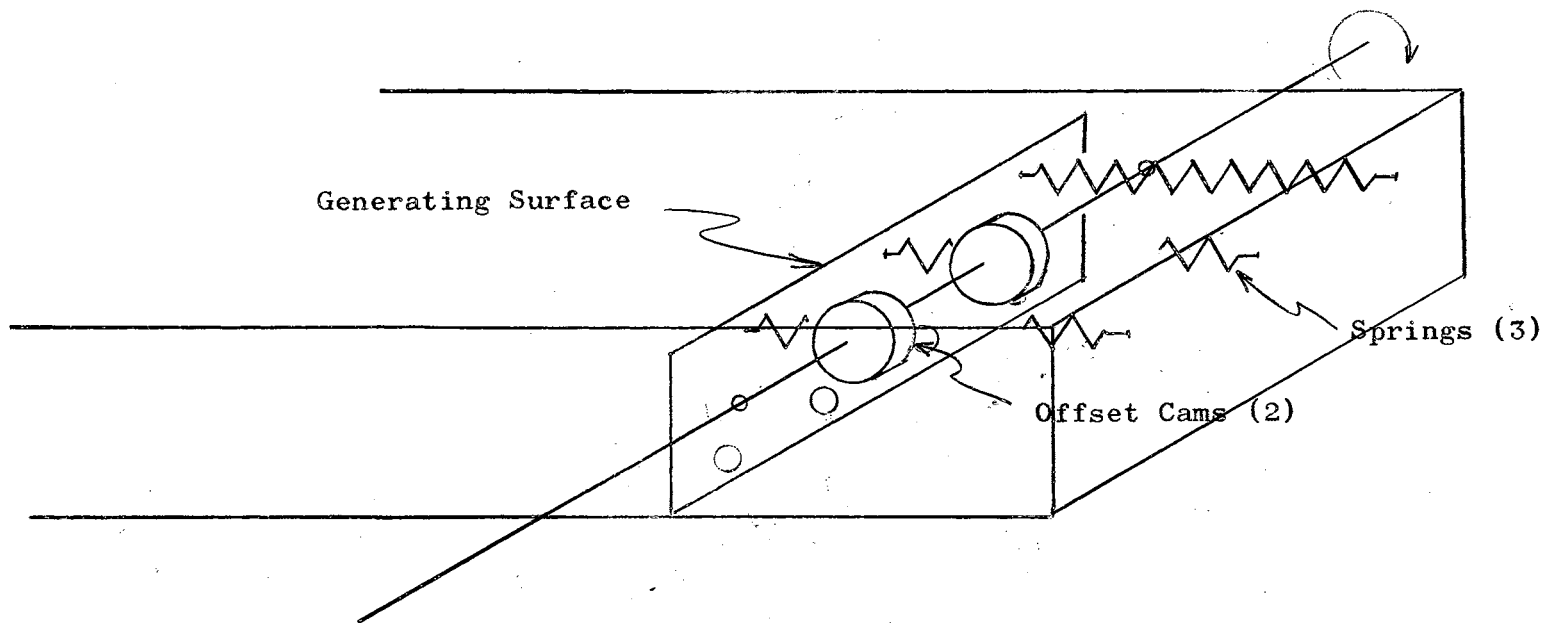
Figure 2. Detail of Wave Generator

It can be noted that if the depth of the liquid is equal to or greater than the wave length, the equation reduces to:

$$c^2 = \frac{g\lambda}{2\pi} + \frac{2\pi\sigma}{\lambda}\frac{}{\rho} \tag{5}$$

Accordingly, the liquid depth was designed to be three centimeters. To minimize the effect of side drag on the waves, the unit was designed as wide as was considered practicable, i.e., twenty centimeters. Again, from a practical viewpoint and to minimize end effects, the length was chosen to be 100 centimeters.

Wave generation was accomplished by a flat stainless steel plate which was hinged to the bottom of the mass transfer section and free to describe an arc at the top. The wave generator was driven by off-set circular cams acting against tension supplied by three coil springs. The cams were driven by a variable speed, a. c. motor.

Gas pressure was measured by a slant leg manometer using $CCl_4$. Gas flow rate was measured using the gas bubble technique as described by Raimondi and Toor (7). Frequency of rotation of the cam shaft (and therefore wave frequency) was determined using a tachometer. This tachometer was calibrated within an accuracy of one per cent by Oklahoma State University's Research and Development Laboratory.

CHAPTER IV

EXPERIMENTAL PROCEDURES

The system selected for study was water and $CO_2$. The water

and $CO_2$ system has been studied by many investigators and there is

considerable data available concerning solubilities and diffusion

coefficients. The $CO_2$, commercial grade, was used as received.

The water used was once-distilled city tap water.

Wave Studies

Before any mass transfer work was done, wave characteristics

were studied with the aid of photographic equipment. A plot of

wave length vs frequency was made from equation (5) and is shown

in Figure (3). A camera was placed on a tripod above and look-

ing directly down upon the test section. The wave generator was

then turned on and pictures taken at several different wave fre-

quencies. A typical picture is shown in Plate 2.

The frequency obtained from the tachometer was then plotted

as a function of wave lengths obtained from the picture. The

wave lengths were measured by obtaining the overall length of

several waves and dividing by the number of waves. The overall

length was read from a meter stick which was in the picture at

the same distance from the camera as the waves. Using this

procedure, the shorter wave lengths were measured as the average
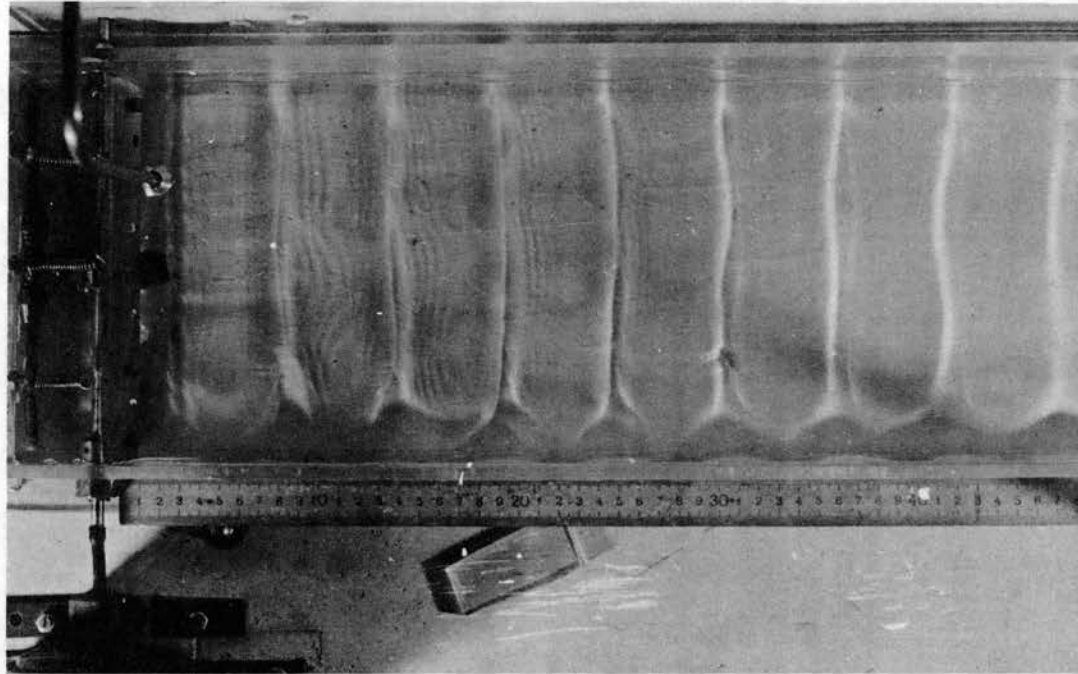
PLATE II

Typical Wave Length Picture

length of up to ten waves. The longer lengths were the average of two and three waves. There is therefore a greater possibility of error in measurement of the longer waves. A plot showing the calculated curve and experimental data points are shown in Figure (3).

Amplitude studies were attempted with the camera placed in such a manner as to take pictures in the vertical plane. This method was not successful because the amplitudes were small and the waves were damped at the wall due to the wetting effect of the water on the walls of the Plexiglass box.

Start Up - Mass Transfer Runs

The mass transfer section was filled completely with water to expel all the air. All the exits were then sealed off except the water exit. Water could be drained out through three one-half inch copper tubing stand pipes. Water was then displaced down to weir height with $CO_2$. The flow rate of $CO_2$ into the system was adjusted to be exactly equal to the rate of absorption by the water. This was accomplished by adjusting the $CO_2$ inlet valve until the system pressure remained within $\pm$ 0.01 inches $CCl_4$ which required frequent adjusting.

Each run required approximately four to six minutes of $CO_2$-water contact time before a steady state wave train could be attained and the first reading taken. The rate of flow was calculated from the length of time required for a soap bubble to sweep out fifty cubic centimeters as measured by the "bubble meter". Flow rate readings were taken every five to ten minutes during each run.

The curve represents equation (4).

The O's represent experimental data

Frequency, Cycles Per Minute
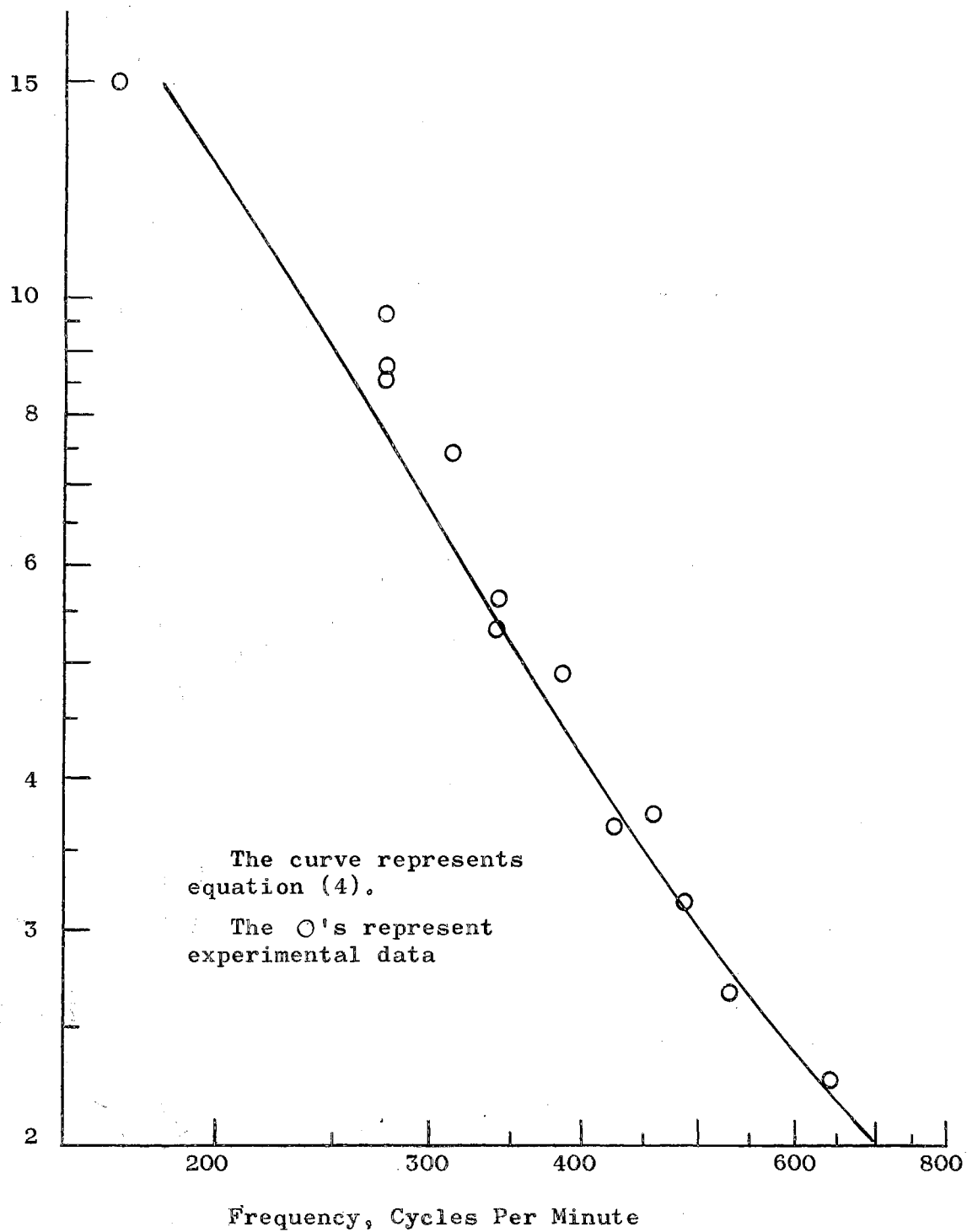
Figure 3.  Frequency - Wave Length Relationship for Water Waves

CHAPTER V

RESULTS AND DISCUSSION

The experimental investigations were carried out in two steps. The first step dealt with the verification of the theory of small surface waves. The second step was the measurement of the rate of mass transfer into a liquid which had small waves on its surface.

## Wave Studies

The properties of small surface waves were studied with the aid of photographic equipment as discussed in the previous chapter. The frequencies and wave lengths obtained are presented in Table I and Figure 3.

As shown in Figure 3 the experimental results are in fair agreement with equation (5). The data appear to lie slightly above the theoretical curve. This is explained in part by the influence of the bottom and sides of the Plexiglass box on the waves having wave lengths of the order of the liquid depth. The experimental accuracy is greater for the shorter waves because of the larger number of waves observed in any one photograph.

Efforts to determine the amplitude of the surface waves experimentally were unsuccessful. This was due to an inability to accurately photograph the waves from the side. The difficulty

TABLE I

FREQUENCIES AND WAVE LENGTHS OF

SMALL WATER WAVES

| Frequency, cps | Wave Length, cm. |
|---|---|
| 265 | 9.66, 8.72, 8.56 |
| 313 | 7.44 |
| 340 | 5.37, 5.65 |
| 387 | 4.9 |
| 422 | 3.67 |
| 459 | 3.76 |
| 485 | 3.18 |
| 530 | 2.66 |
| 648 | 2.27 |
| 724 | 1.87 |

was primarily due to the surface effects between the water and the

Plexiglass walls.

In place of direct experimental measurements a method was

developed by which the amplitudes and the mass transfer area

could be estimated. The expression for the surface area is:

$$A = \frac{4LW}{\lambda} \sqrt{\left(\frac{\lambda}{4}\right)^2 + \left(\frac{2}{\lambda}\right)^2 \left[bh_1 - \frac{8A_o bh_2}{W h_1}\right]^2} \qquad (6)$$

This equation is derived in Appendix C and plotted in Figure 4.
The derivation was done in conjunction with Dr. J. M. Marchello.

## Mass Transfer

The rate of mass transfer was determined for carbon dioxide
dissolving in water. As described in the previous section runs
were made with and without surface waves. Pure carbon dioxide
was used so that the only resistance to transfer was in the
liquid phase.

An equation which describes mass transfer in the presence
of surface waves has been developed. The rate of mass transfer
is given by the expression

$$N = C_i \sqrt{\frac{\epsilon + D}{\pi \theta}} \qquad (7)$$

The derivation of this equation was done in conjunction with
Dr. J. M. Marchello and is shown in Appendix B. Equation (7)
applies to unsteady state mass transfer into a liquid which has
small waves on its surface. Equation (7) also applies to steady
state situations in which the velocity is constant.

Experimentally the rate of diffusion was determined as a
function of time. The volume of gaseous carbon dioxide absorbed
per minute was determined by measuring the input to the Plexiglass
box at a constant pressure. This volumetric rate, R, is related
to the mass transfer rate, N, by the expression:

$$R = \frac{NA}{\rho} \qquad (8)$$

where A is the mass transfer area and $\rho$ is the molar density of the
gas.

Combining equations (7) and (8) yields:

$$R = \left(\frac{AC_i}{\rho}\right)\sqrt{\frac{(D+\epsilon)}{\pi\theta}} \tag{9}$$

Equation (6) indicates that a plot of $R^2$ versus $1/\theta$ should yield a straight line with a slope of

$$\left(\frac{AC_i}{\rho}\right)^2\left(\frac{D+\epsilon}{\pi}\right)$$

and which passes through the origin.

The start up procedure for the mass transfer runs is described in the previous section. In recording the data the time at which the absorption rate was measured was taken to be the time from which the $CO_2$ was first introduced into the Plexiglass box up to the time at the middle of the flow rate measurement.

Since it was difficult to determine exactly when the situation described by equation (7) actually started, it was decided to back calculate the starting time. If the time measurements are in error by a constant amount $\theta_o$ then the actual time is given by the expression

$$\theta = \theta_{exp} + \theta_o \tag{10}$$

Substituting equation (10) into (9) gives

$$R = \left(\frac{AC_i}{\rho}\right)\sqrt{\frac{(D+\epsilon)}{\pi(\theta_{exp}+\theta_o)}} \tag{11}$$
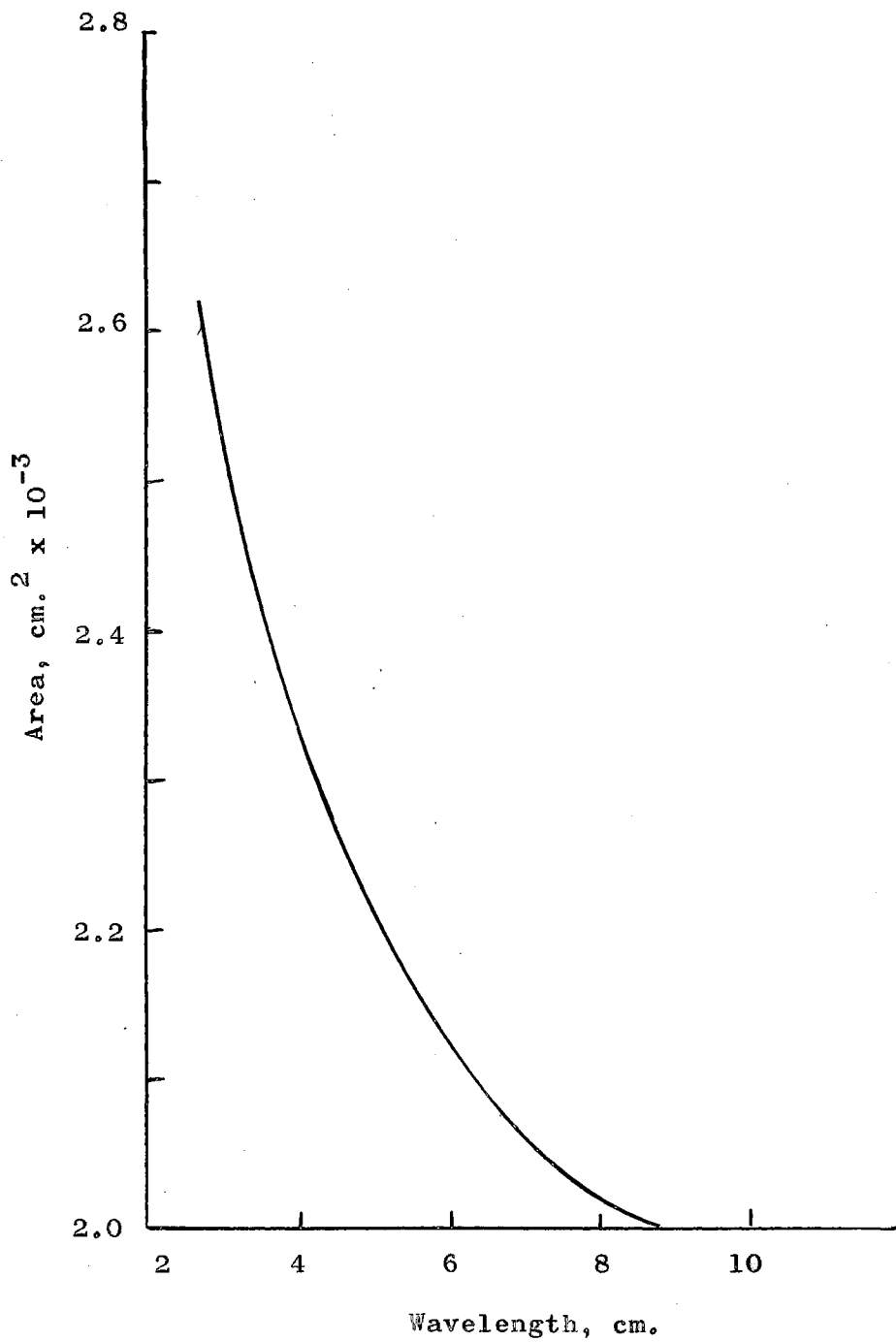
Squaring and rearranging equation (11) gives

Figure 4. Variation of Surface Area with
Wave Length

$$\Theta_{exp} = \left[ \frac{A^2 c_i^2}{\rho^2 \pi} \ (D + \epsilon) \right] \ (\frac{1}{R^2}) - \Theta_o \qquad (12)$$

The equation indicates that a plot of the reciprocal of the absorption rate squared versus time will be a straight line with $\Theta_o$ being the intercept.

Nine mass transfer runs were made. In three of these the oscillating plate was stationary and there were no waves on the surface. In the remaining six runs the plate was operated at four different frequencies. The results of these runs are given in Table II and plotted in Figures 5, 6, 7, 8, and 9.

In equation (12) if mass transfer occurred by molecular diffusion alone into the water, $\epsilon = 0$ and assuming $\Theta_o = 0$,

$$\Theta = \left[ \frac{A^2 c_i^2 D}{\rho^2 \pi} \right] \ \frac{1}{R^2} \qquad (13)$$

To see whether this situation actually occurred the value of the slope was calculated. The values for the various physical constants (22), (24) and properties are:

$C_i = 3.25 \times 10^{-5}$ gmoles/cm$^3$

$D = 1.062 \times 10^{-3}$ cm$^2$/min

$\rho = 4.08 \times 10^{-5}$ gmoles/cm$^3$

$A = 2000$ cm$^2$ (without waves)

$\pi = 3.1416$

Using these quantities the value of $\left[ \frac{A^2 c_i^2 D}{\rho^2 \pi} \right]$ was $0.0854 \times 10^{+4}$.

As can be seen from Figure 5 this slope is approximately thirty times too small indicating that a fair amount of natural convection

was present even in the runs without waves.

The slopes and intercepts of $\theta_{exp}$ versus $\dfrac{1}{R^2}$ for the first forty minutes of each run are given in Table III. These values were obtained by fitting the data to a least-squares straight line. The average absolute deviation for all runs was 2.3 minutes. For times greater than about forty minutes, equation (12) no longer applies as pointed out in Appendix B.

## Eddy Diffusivity

The eddy diffusivity can be calculated from the slope by use of the relationship

$$\epsilon = \left( \frac{\rho^2}{A^2 c_i^2} \right) \left( slope \right) - D \qquad (14)$$

Values of the eddy diffusivity calculated from equation (14) are given in Table IV and plotted in Figure 10.

The eddy diffusivity was calculated in two ways. First, using the area correction shown in Figure 4 and second making no area correction. The reasons for not using the area correction are that it is open to question and for many wave forms the percentage increase in the area would be constant. As an example, consider triangular waves for which the amplitude is always one fourth the wave length. In this case, as shown by equation (C-5), the surface area with waves is always 1.414 times greater than the smooth area. A similar situation would apply in the case of sine waves.

As shown in Figure 10 the eddy diffusivity for frequencies less than 500 cpm does not vary greatly with the frequency of the waves. Due to the waves the average increase in the eddy diffusivity, above that for natural convection, is 28 per cent as calculated with the area correction and 52 per cent as calculated without the area correction. This result is in agreement with the situation in which the area increase is a constant factor as mentioned above. These results are consistent with wetted wall column data (23) in which the surface waves tend to decrease the height of a liquid mass transfer unit by as much as 100 per cent.

## TABLE II

## MASS TRANSFER DATA

| Run No. and Frequency, CPM | Time, Min. | Rate, cc/min | $\frac{1}{R^2} \times 10^4$ $(cc/min)^{-2}$ | Run No. and Frequency, CPM | Time, Min. | Rate cc/min | $\frac{1}{R^2}$ $(cc/min)^{-2}$ |
|---|---|---|---|---|---|---|---|
| | 7.58 | 43.35 | 5.32 | | 14.31 | 30.9 | 10.46 |
| 18, | 10.60 | 41.5 | 5.81 | 19, | 22.36 | 29.2 | 11.73 |
| | 15.73 | 34.0 | 8.65 | | 30.37 | 28.8 | 12.05 |
| 0 | 23.37 | 28.4 | 12.40 | 265 | 38.06 | 23.7 | 17.80 |
| | 1.00 | 24.8 | 16.27 | | 45.58 | 23.25 | 18.48 |
| | | | | | | | |
| | 13.82 | 30.67 | 10.74 | | 4.77 | 74.3 | 1.81 |
| 24, | 19.78 | 31.91 | 9.95 | 26, | 8.38 | 65.6 | 2.33 |
| | 22.91 | 27.55 | 13.42 | | 11.19 | 56.39 | 3.15 |
| 0 | 29.95 | 26.27 | 14.68 | 260 | 16.53 | 47.47 | 4.42 |
| | 51.18 | 21.33 | 22.47 | | 22.05 | 45.18 | 4.90 |
| | | | | | 27.64 | 38.86 | 6.62 |
| | 13.32 | 30.1 | 11.04 | | 39.72 | 34.64 | 8.33 |
| 25, | 16.85 | 29.1 | 11.81 | | | | |
| | 28.42 | 26.9 | 13.82 | | | | |
| 0 | 28.95 | 26.2 | 14.56 | | | | |
| | 35.51 | 24.5 | 16.66 | | | | |
| | 44.12 | 22.2 | 20.30 | | | | |

(Cont'd.)

TABLE II (Cont'd.)

| Run No. and Frequency, CPM | Time, Min. | Rate, cc/min | $\frac{1}{R^2} \times 10^4$ (cc/min)$^{-2}$ | Run No. and Frequency, CPM | Time, Min. | Rate cc/min | $\frac{1}{R^2}$ (cc/min)$^{-2}$ |
|---|---|---|---|---|---|---|---|
| | 8.42 | 59.5 | 2.82 | | 4.19 | 27.5 | 0.61 |
| | 10.42 | 59.4 | 2.84 | | 11.34 | 72.7 | 1.89 |
| 20, | 16.59 | 42.5 | 5.54 | 21, | 19.45 | 55.2 | 3.28 |
| | 22.71 | 35.2 | 8.08 | | 28.59 | 42.0 | 5.67 |
| 340 | 29.79 | 32.3 | 9.58 | 485 | 32.66 | 37.9 | 6.96 |
| | 64.1 | 22.5 | 19.74 | | 39.72 | 34.4 | 8.45 |
| | | | | | 62.12 | 22.0 | 20.62 |
| | 10.02 | 47.6 | 4.41 | | 8.55 | 82.7 | 1.46 |
| 23, | 13.00 | 49.0 | 4.16 | 22, | 13.67 | 59.9 | 2.79 |
| | 19.62 | 39.8 | 6.31 | | 19.49 | 50.2 | 3.97 |
| 340 | 36.79 | 31.4 | 10.14 | 530 | 25.58 | 42.6 | 5.50 |
| | 48.93 | 26.8 | 13.9 | | 56.11 | 22.3 | 20.1 |

## TABLE III

### SLOPES AND INTERCEPTS FOR EQUATION (9)

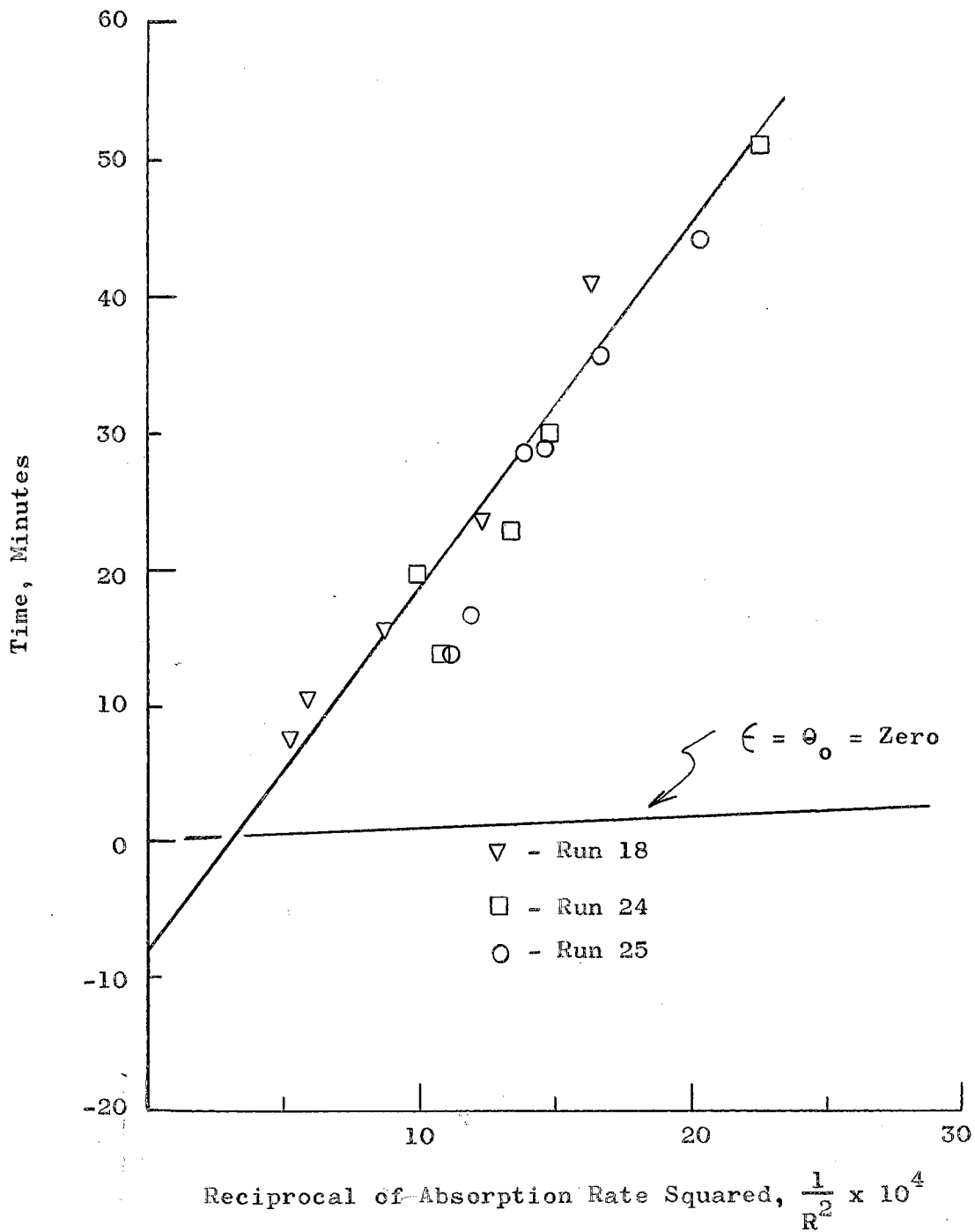| Frequency CPM | Slope $\dfrac{A^2 c_i^2 (\epsilon + D)}{\rho^2 \pi}$ | Intercept $\Theta_0$, Min |
|---|---|---|
| 0 | $2.58 \times 10^4$ | -8.37 |
| 260 | $5.16 \times 10^4$ | -4.68 |
| 265 | $3.00 \times 10^4$ | -12.70 |
| 340 | $3.62 \times 10^4$ | -2.91 |
| 485 | $4.39 \times 10^4$ | +2.99 |
| 530 | $4.27 \times 10^4$ | +2.17 |

Figure 5. Mass Transfer Rate as a Function of Time

Frequency = 0 CPM
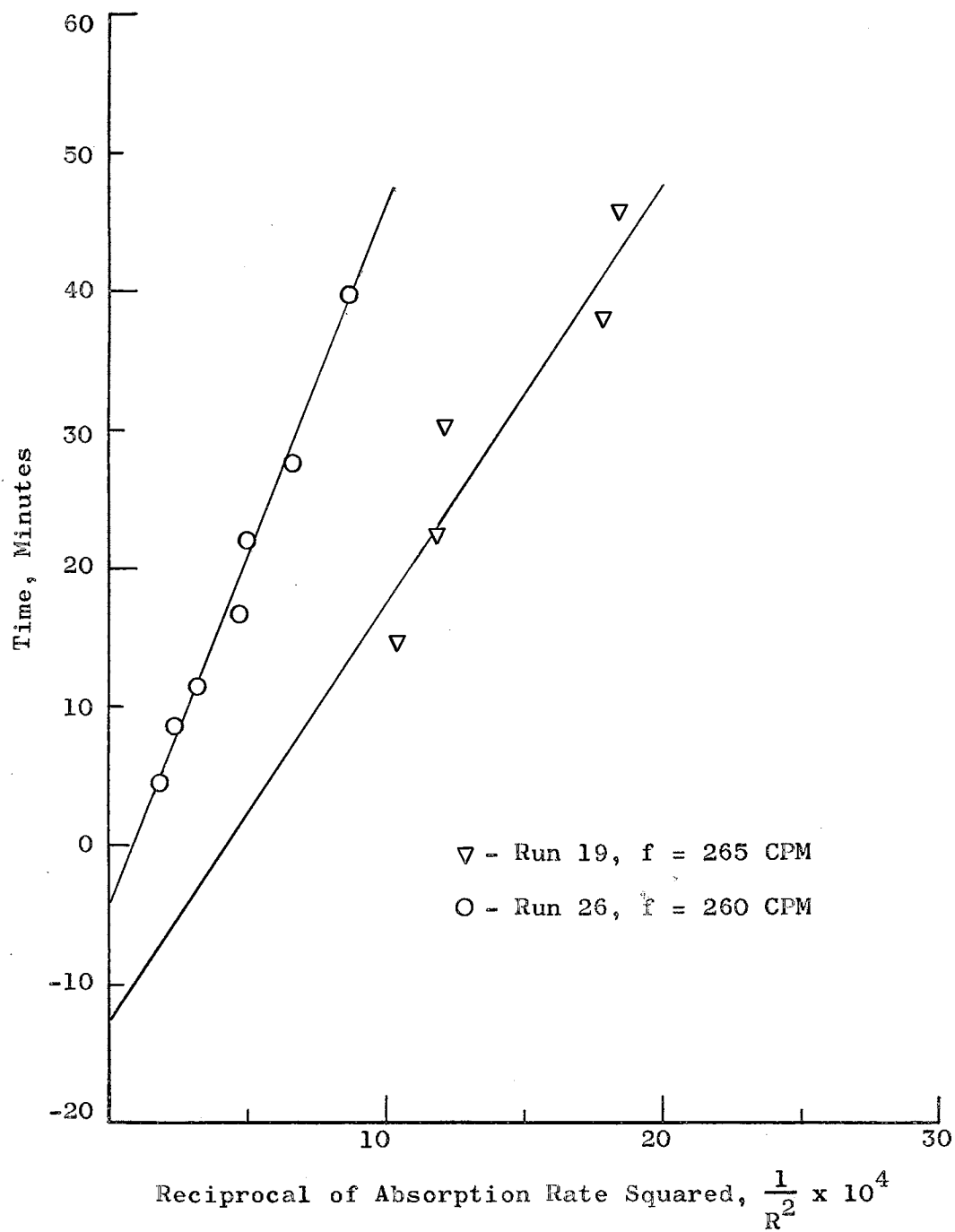
Figure 6. Mass Transfer Rate as a Function of Time
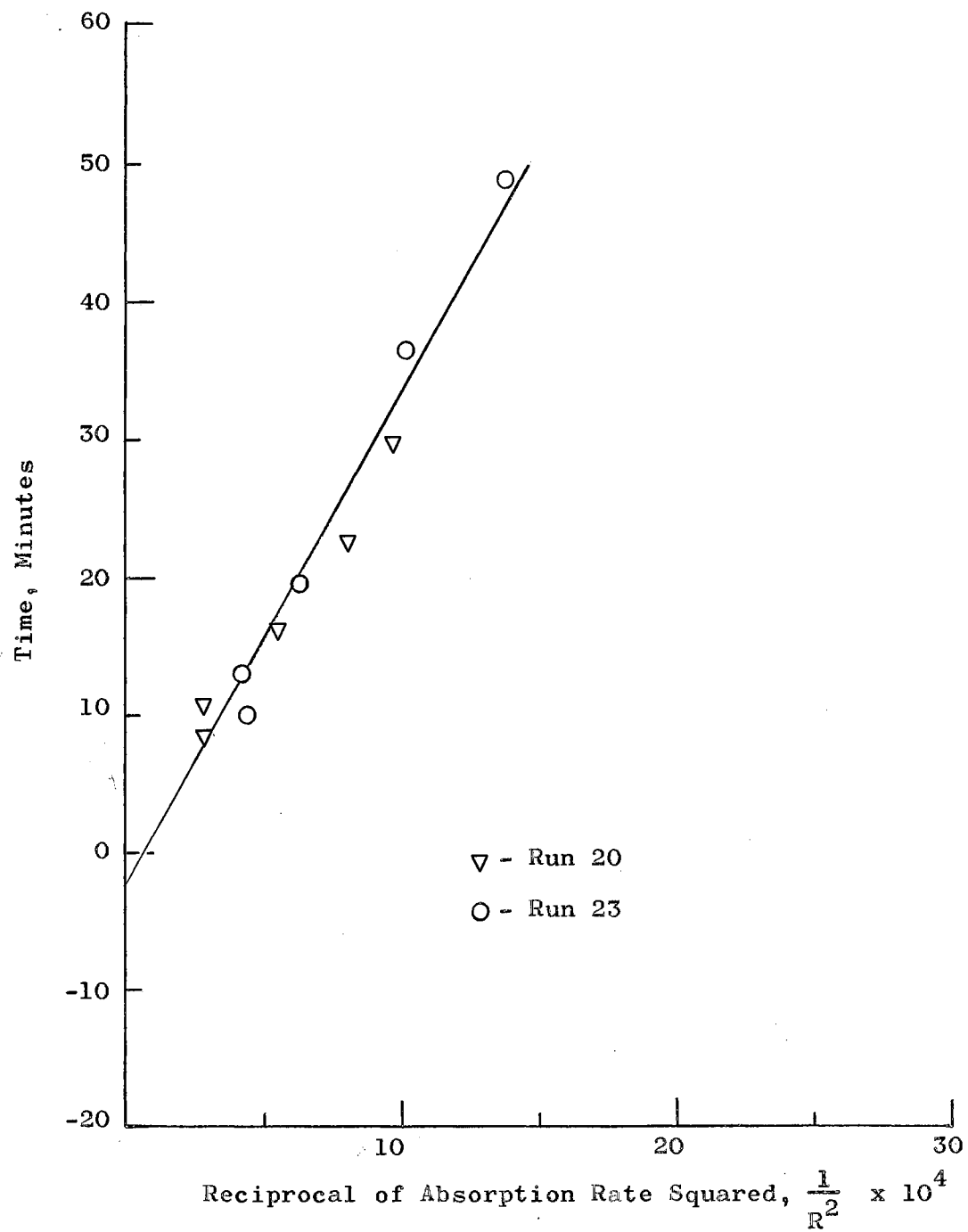
Figure 7. Mass Transfer Rate as a Function of Time

Frequency = 340 CPM
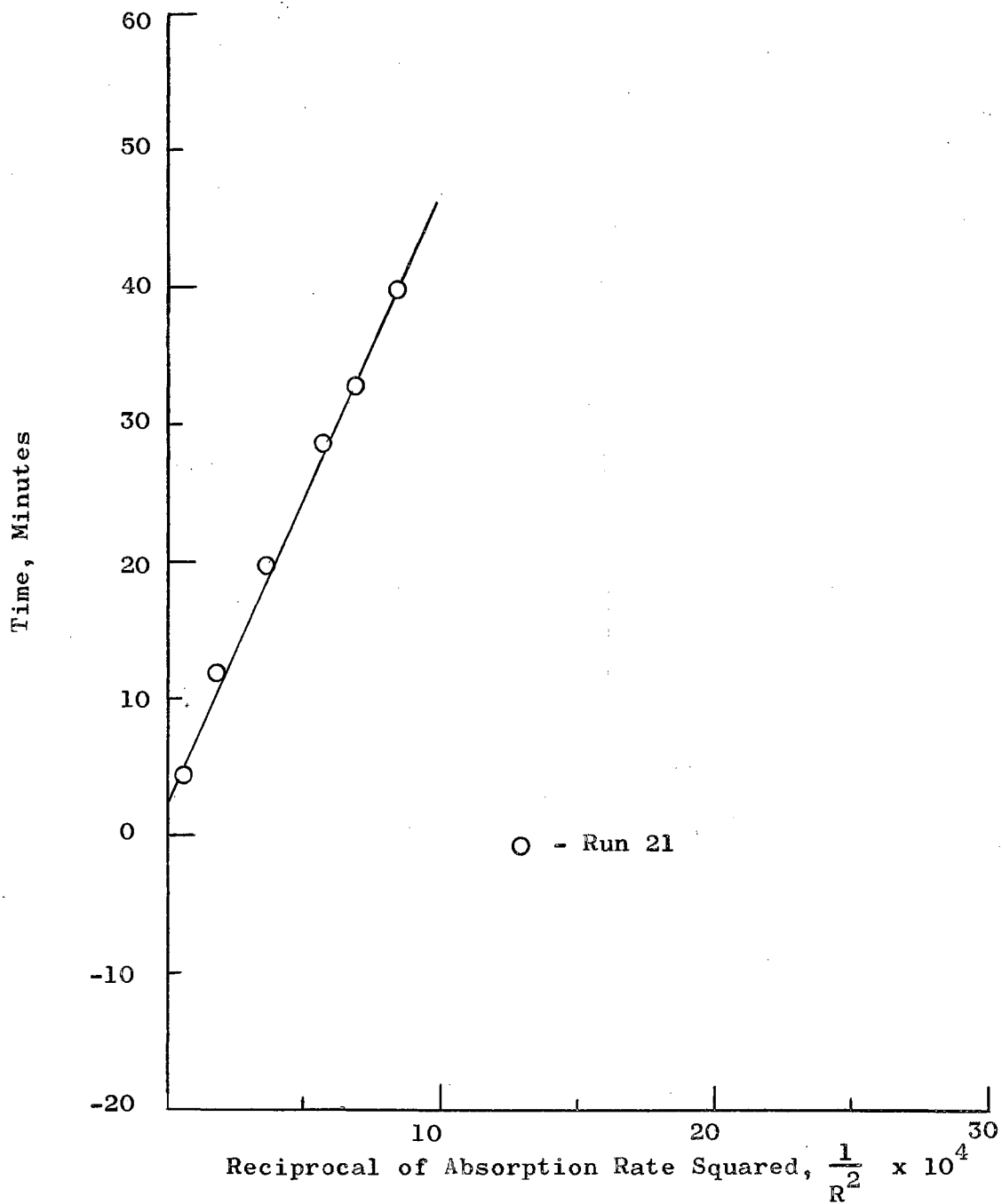
Figure 8. Mass Transfer Rate as a Function of Time

Frequency = 485 CPM
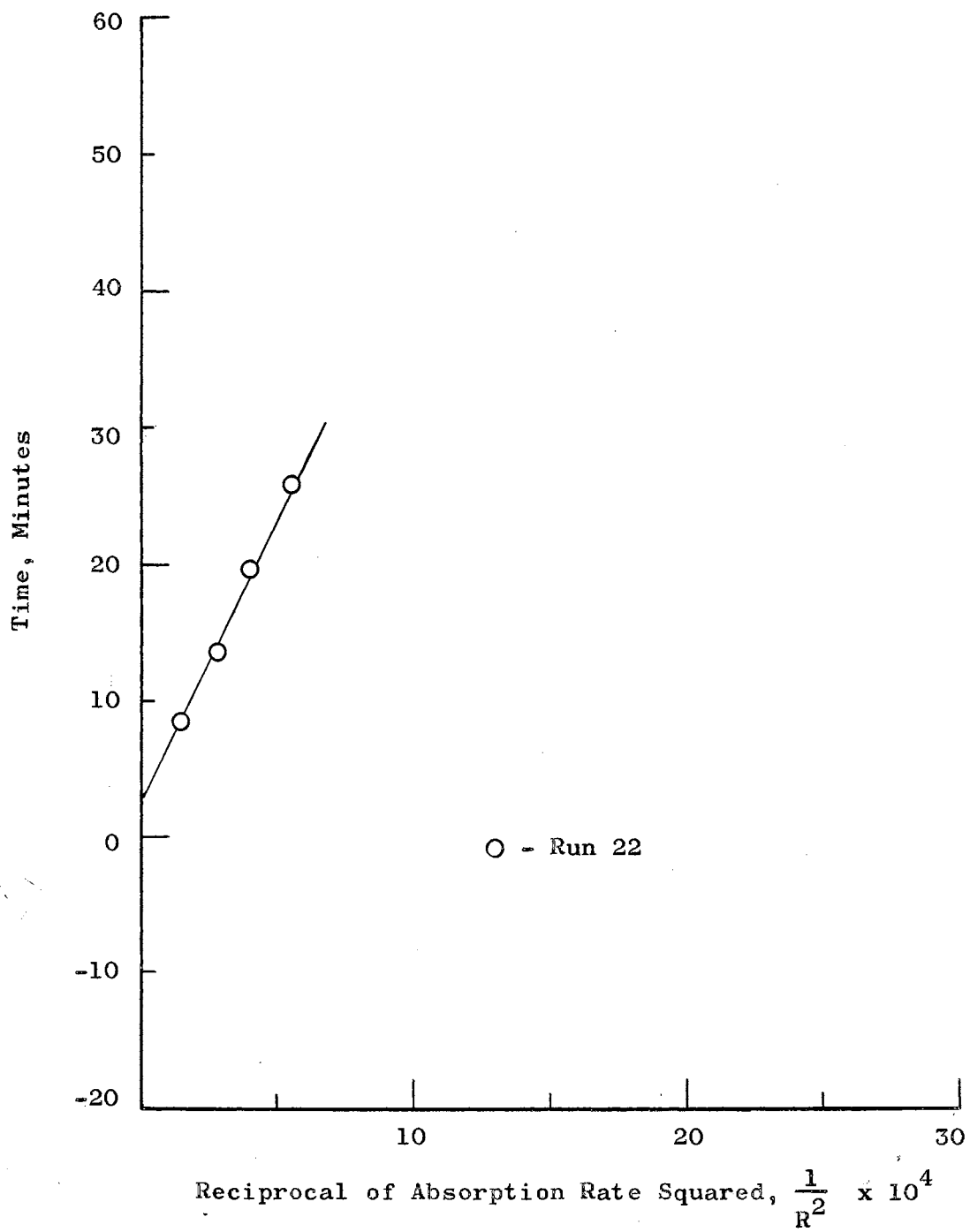
Figure 9.  Mass Transfer Rate as a Function to Time
Frequency = 530 CPM

TABLE IV

CALCULATED VALUES OF
EDDY DIFFUSIVITY

| | | $\epsilon$ x $10^3$, $Cm^3$/min | |
|---|---|---|---|
| Frequency CMP | Run No. | With Area Correction | Without Area Correction |
| 0 | 18, 24, 25 | 30.87 | 30.87 |
| 260 | 26 | 62.16 | 62.82 |
| 265 | 19 | 35.53 | 36.08 |
| 340 | 20, 23 | 40.43 | 43.75 |
| 485 | 21 | 33.45 | 53.29 |
| 530 | 22 | 26.79 | 51.80 |
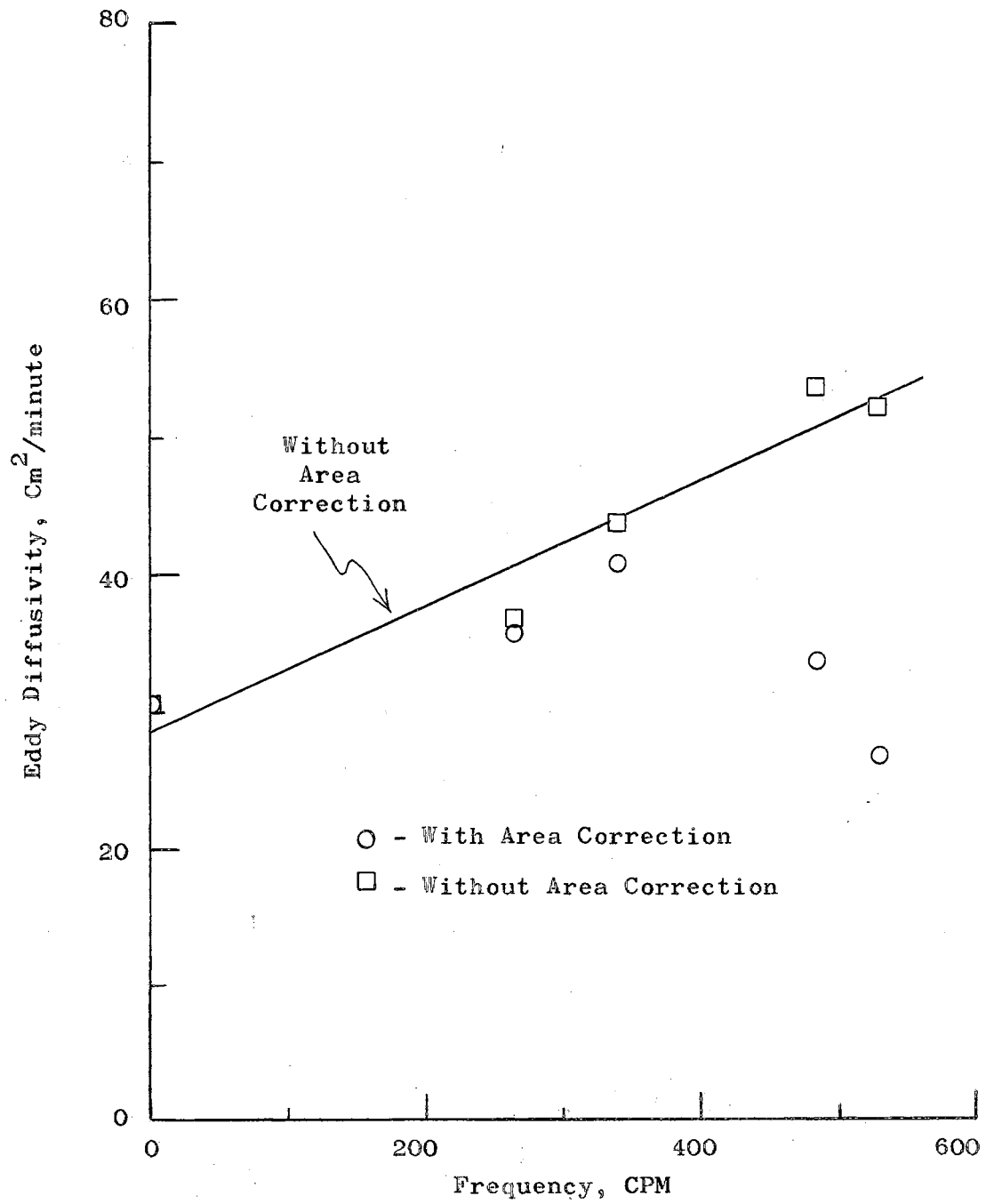
Figure 10. Variation of Eddy Diffusivity With Frequency

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Restatement of Thesis Goals

The work of this thesis was directed toward an investigation
of the effect of small surface waves on the rate of interfacial
mass transfer. The objectives were:

1. Investigate the hydrodynamics of small surface
   waves. The main portion of this work was an
   experimental study of ripples generated on a
   horizontal surface.

2. Measure the mass transfer rate of carbon dioxide
   absorbing into water. Data were taken on the
   system with and without surface waves on the
   horizontal water surface.

3. Develop the theory of mass transfer for small
   surface waves and use the theory to explain
   the experimental results obtained in items 1
   and 2 of above.

Conclusions

Small Surface Waves

The photographic investigation of small water waves
agreed well with theoretical analysis found in the literature (19).

## Mass Transfer Rate

The mass transfer rates for carbon dioxide absorbing into water were measured with and without surface waves. The results obtained during the first forty minutes of each run were in good agreement with the theory developed under objective 3.

## Mass Transfer Theory

A theoretical analysis of unsteady-state mass transfer into a liquid with small surface waves was carried out. The eddy diffusivity was assumed to be constant and equilibrium was assumed to exist at the interface. The resulting equations were used to calculate the interfacial eddy diffusivity from the experimental data. For frequencies less than 500 cpm the eddy diffusivity does not appear to vary greatly with the frequency of the waves.

## Recommendations

The present equipment is limited to frequencies below 550 cpm because of spray generated by the plate at the higher speeds. It appears that it will be necessary to use sonic or ultrasonic techniques in order to obtain higher frequencies.

A method should be developed by which the amplitudes and surface areas of the waves can be measured.

Other gas-liquid and liquid-liquid systems should be studied and situations in which there is resistance in both phases should be investigated.

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## NOMENCLATURE

$A$      - Surface area, $cm^2$

$A_o$      - Open area for flow through the oscillating plate, $cm^2$

$a$      - Amplitude of the waves, cm

$b$      - Travel of oscillating plate at the water level, cm

$C$      - Concentration, gram mols/$cm^3$

$C*$      - Equilibrium concentration, gram mols/$cm^3$

$C_i$      - Same as $C*$

$c$      - Wave velocity, cm/min

$CPM$      - Cycles per minute

$D$      - Molecular diffusivity, $cm^2$/min

$f$      - Frequency, 1/min

$g$      - Gravitational constant, 980 $cm/sec^2$

$H_L$      - Height of liquid transfer unit, cm

$h_1$      - Height of water level, cm

$h_2$      - Height of the holes in the oscillation plate, cm

$k$      - Mass transfer coefficient, cm/min

$L$      - Length of channel, cm

$N$      - Mass transfer rate, gram moles/$cm^2$min

$P$      - Pressure, atm

$q$      - Same as $N$

$R$      - Volumetric rate of absorption, $cm^3$/min

Re      - Reynolds Number

RPM     - Revolutions per minute

Sc      - Schmidt Number

t       - Time, min

$\vec{U}$      - Velocity vector, cm/min

V       - Potential Energy, ergs

$V_a$     - Average velocity of the plate, cm/sec

$\vec{v}$      - Velocity vector, cm/min

W       - Width of the channel, cm

Z       - Column length, cm

z       - Depth of liquid, cm

$\epsilon$      - Eddy diffusivity, $cm^2/min$

$\Theta$      - Time, min

$\lambda$      - Wave length, cm

$\mu$      - Viscosity, centipoise

$\rho$      - Density, gram mols/$cm^3$

$\sigma$      - Surface tension, dynes/cm

$\emptyset$      - Velocity potential, 1/min

$\mathcal{L}$      - Elevation of the surface, cm

## APPENDIX A

## DEVELOPMENT OF THE WAVE EQUATION

The surface wave equation is based upon two assumptions that are never strictly obeyed by any fluid under any set of conditions, but can be closely approached by a number of fluids including water.  These assumptions are:

      i)   the fluid is incompressible

     ii)   the motion is irrotational

The second assumption is equivalent to neglecting viscosity and permits the introduction of a velocity potential $\emptyset$.

Combining the expression for irrotational flow and the incompressible continuity equation,

$$\vec{U} = -\nabla\emptyset = -\text{ grad } \emptyset \tag{A-1}$$

$$\nabla\vec{U} = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \tag{A-2}$$

we obtain Laplace's equation

$$\nabla^2 \emptyset = \frac{\partial^2\emptyset}{\partial x^2} + \frac{\partial^2\emptyset}{\partial y^2} + \frac{\partial^2\emptyset}{\partial z^2} = 0 \tag{A-3}$$

Since there is no normal component of velocity on a fixed boundary

$$\frac{\partial\emptyset}{\partial n} = 0 \tag{A-4}$$

where differentiation normal to a fixed boundary is denoted by $\partial/\partial n$.

41

Coulson (19) has shown that Bernoulli's equation (developed from the equations of motion) can be written as:

$$\frac{P}{\rho} + \frac{1}{2} \vec{U}^2 + V - \frac{\partial \emptyset}{\partial t} = \text{constant} \qquad (A\text{-}5)$$

which, at the free surface reduces to:

$$\frac{1}{2} \vec{U}^2 + V - \frac{\partial \emptyset}{\partial t} = \text{constant} \qquad (A\text{-}5a)$$

where $V$ is the potential of external force. Assuming that the velocity $\vec{U}$ is so small that $\vec{U}^2$ can be neglected and that the external forces are the external pressure and gravity we may put $\vec{U}^2 = 0$ and $V = g\mathcal{L}$. $\mathcal{L}$ is the elevation of the surface of fluid above the undisturbed free surface. Bernoulli's equation becomes:

$$\mathcal{L} = \frac{1}{g} \left[ \frac{\partial \emptyset}{\partial t} \right] \qquad \text{free surface} \qquad (A\text{-}6)$$

Letting $H(x, y, z, t)$ be any property of a particle of the fluid, $\frac{DH}{Dt}$ is the variation of that property when we keep to the same particle of fluid.

$$\frac{DH}{Dt} = \frac{\partial H}{\partial t} + u \frac{\partial H}{\partial x} + v \frac{\partial H}{\partial y} + w \frac{\partial H}{\partial z} \qquad (A\text{-}7)$$

Keeping to the same particle on the surface of a liquid on which surface waves are occuring, we have:

$$\mathcal{L}(x, y, t) - z = 0 = f(x, y, z, t) \qquad (A\text{-}8)$$

where $z$ is measured from the free surface, figure (11). Therefore $f$ is a function that is always zero for a particle on the free surface. Now putting $H$ equal to $f$ we have:

$$\frac{Df}{Dt} = 0 = \frac{\partial \mathcal{L}}{\partial t} + U\frac{\partial \mathcal{L}}{\partial x} + v\frac{\partial \mathcal{L}}{\partial y} - w \qquad (A\text{-}9)$$

From equation (6) we have:

$$\frac{\partial \mathcal{L}}{\partial x} = \frac{1}{g} - \frac{\partial}{\partial t}\left(\frac{\partial \emptyset}{\partial x}\right) = -\frac{1}{g}\frac{\partial u}{\partial t} \qquad (A\text{-}10)$$

and

$$\frac{\partial \mathcal{L}}{\partial x} = -\frac{1}{g}\frac{\partial v}{\partial t} \qquad (A\text{-}11)$$

Equation (9) then becomes:

$$\frac{\partial \mathcal{L}}{\partial t} + \frac{u}{g}\frac{\partial u}{\partial t} - \frac{v}{g}\frac{\partial v}{\partial t} - w = 0 \qquad (A\text{-}9a)$$

or

$$\frac{\partial \mathcal{L}}{\partial t} - \frac{1}{2g}\frac{\partial(u^2)}{\partial t} - \frac{1}{2g}\frac{\partial(v^2)}{\partial t} - w = 0 \qquad (A\text{-}9b)$$

Since the velocity is assumed to be so small that $\vec{U}^2$ can be neglected equation (9) reduces to:

$$\frac{\partial \mathcal{L}}{\partial t} = w = -\frac{\partial \emptyset}{\partial z} \qquad (A\text{-}12)$$

Combining equations (6) and (12) yields:

$$\frac{\partial^2 \emptyset}{\partial t^2} + g\frac{\partial \emptyset}{\partial z} = 0 \qquad (A\text{-}12a)$$

Summarizing the important relations in the above development we have:

    i) Laplace's equation, $\nabla^2 \emptyset = 0$, in the liquid.

    ii) $\frac{\partial \emptyset}{\partial n} = 0$ on a fixed boundary.

    iii) $\mathcal{L} = \frac{1}{g}\frac{\partial \emptyset}{\partial t}$ on the free surface.

    iv) $\frac{\partial \mathcal{L}}{\partial t} = -\frac{\partial \emptyset}{\partial z}$ on the free surface.

v) $\dfrac{\partial^2 \phi}{\partial t^2} + g \dfrac{\partial \phi}{\partial z} = 0$ on the free surface.

The above five conditions depend on the surface tension being negligible. It can be seen that conditions (i), (ii), and (iv) are true regardless of the surface tension but that (iii) and (v) are affected by surface tension.

Surface tension acts as a stretch membrane placed on the surface of the liquid. The pressure just under the surface, P, is therefore not equal to atmospheric, $P_o$, but rather can be shown to be

$$P = P_o - \sigma \left[ \dfrac{\partial^2 \mathscr{L}}{\partial x^2} + \dfrac{\partial^2 \mathscr{L}}{\partial y^2} \right] \qquad (A\text{-}13)$$

Combining equation (13) with equation (5) yields the new condition (iiia)

(iiia) $\dfrac{\partial \phi}{\partial t} - g\mathscr{L} + \dfrac{\sigma}{\rho} \left[ \dfrac{\partial^2 \mathscr{L}}{dx^2} + \dfrac{\partial^2 \mathscr{L}}{dy^2} \right] = \left( \dfrac{\partial \phi}{\partial t} \right)_o - gz = 0$

Combining (iiia) with (iv) yields:

(Va) $\dfrac{\partial^2 \phi}{\partial t^2} + g \dfrac{\partial \phi}{\partial z} - \dfrac{\sigma}{\rho} \left[ \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} \right] \left( \dfrac{\partial \phi}{\partial z} \right) = 0$

on the free surface.

Capillary or surface tension waves should fit conditions (i), (ii), (iiia), (iv), and (Va). Condition (i) can be solved as:

$$\phi = (Ae^{mz} + Be^{mz}) \cos m (x - \gamma t) \qquad (A\text{-}14)$$

where A, B, m, and $\gamma$ are to be determined from the other conditions. (ii) gives, at the bottom of the tank, $\dfrac{\partial \phi}{\partial z} = 0$,

that is at z = -h

$$Ae^{-mh} - Be^{+mh} = 0$$

So that

$$Ae^{-mh} = Be^{mh} = \frac{1}{2} c$$

Therefore

$$\emptyset = c \cosh m(z + h) \cos m (x - \gamma t) \qquad (A-15)$$

which satisfies (i) and (ii). Substitution into condition (iv) and integrating in t gives the form of $\emptyset$ which is

$$\emptyset = \frac{c}{\gamma} \sinh m h \sin m(x - \gamma t) \qquad (A-16)$$

Choosing (Va) as the remaining condition to satisfy we obtain:

$$-m^2 \gamma^2 c \cosh m h \cos m(x - \gamma t)$$

$$+mcg \sinh m \cos m(x - \gamma t)$$

$$+\frac{m^3 c}{\rho} \sinh m h \cos m(x - \gamma t) = 0$$

rearranging we obtain the equation for the wave velocity:

$$c^2 = \frac{g}{m} + \frac{m}{\rho} \tanh m h \qquad (A-17)$$

when h is large, tanh m h = 1, and using the condition $m = 2\pi/\lambda$, we have:

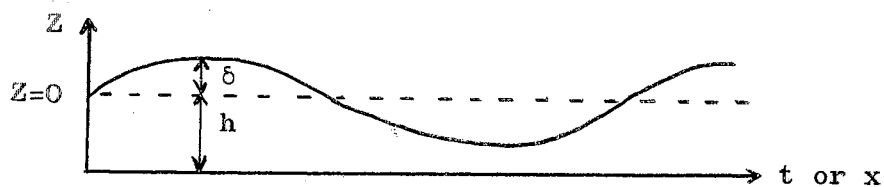$$c^2 = \frac{g\lambda}{2\pi} + \frac{2\pi\sigma}{\lambda\rho} \qquad (A-18)$$



Figure 11. Surface Wave Relation

## APPENDIX B

## DEVELOPMENT OF THE MASS TRANSFER EQUATION

For unsteady-state diffusion of a gas into a stagnant liquid the differential equation which applies is known as Fick's Second Law:

$$\frac{\partial C}{\partial \Theta} = D \nabla^2 C \qquad (B-1)$$

When there is fluid motion present the equation which applies is the mass transfer equation analogous to the Fourier-Poison equation (20):

$$\frac{\partial C}{\partial \Theta} + \vec{\nabla}\cdot (\vec{v}C) = D \nabla^2 C \qquad (B-2)$$

In cases where there are fluctuations in velocity the usual approach has been to divide the variables into fluctuating and nonfluctuating components. This was first done by Prandtl (21) in his analysis of turbulent flow. For equation (B-2) the velocity and concentration become:

$$v = v + v'$$

$$C = C + C'$$

Substituting these relations into equation (B-2) yields:

$$\frac{\partial (C + C')}{\partial \Theta} + \nabla(v + v')(C + C') = D \nabla^2 (C + C') \qquad (B-3)$$

In order to get useful information from an expression like equation (B-3) it is necessary to time-average each term. The

rules of averaging are as follows (21):

$$\bar{f} = f, \qquad \overline{f'} = 0$$

$$\overline{ff'} = 0, \qquad \overline{f'g'} = 0$$

Applying these rules to equation (B-3) gives:

$$\overline{\frac{\partial(C + C')}{\partial \Theta}} + \nabla\overline{(vC + vC' + v'C = v'C')} = D \overline{\nabla^2(C+C')} \qquad (B-4)$$

Assuming that all of the variables are step-wise continuous allows one to carry out the averaging inside the differentiation. Doing this, equation (B-4) becomes:

$$\frac{\partial \bar{C}}{\partial \Theta} + \nabla(\bar{v}C) + \nabla(\overline{v'C'}) = D \nabla^2\bar{C} \qquad (B-5)$$

For the experimental conditions $\bar{v} = 0$ so that equation (B-5) becomes:

$$\frac{\partial \bar{C}}{\partial \Theta} + \nabla(\overline{v'C'}) = D \nabla^2\bar{C} \qquad (B-6)$$

The usual practice is to define an eddy diffusivity by the relationship:

$$\nabla(\overline{v'C'}) = - \epsilon \nabla^2\bar{C} \qquad (B-7)$$

The original development of equation (B-7) comes from Prandtl's (21) mixing length theory. A similar result was obtained by G. I. Taylor (21) using his theory of diffusion by continuous motion.

Combining equations (B-6) and (B-7) gives a relationship which describes the present experimental conditions:

$$\frac{\partial \bar{C}}{\partial \Theta} = (\epsilon + D) \nabla^2\bar{C} \qquad (B-8)$$

This equation applies when there are velocity fluctuations but no net velocity or fluid motion.

Assuming that the eddy diffusivity, $\epsilon$, does not vary with time or position the solution to equation (B-8) is similar to standard solutions to unsteady state conduction problems. For the experimental conditions it is reasonable to assume that $\epsilon$ is constant with time. During the early part of any given run while the $CO_2$ has not penetrated too deeply into the water it is also reasonable to assume that $\epsilon$ is independent of depth.

For the experimental apparatus there will be only one distance dimension for diffusion. That is, equation (B-8) becomes:

$$\frac{\partial C}{\partial \Theta} = (\epsilon + D) \frac{\partial^2 C}{\partial Z^2} \qquad (B-9)$$

The boundry conditions are:

$$\Theta = 0, \qquad C = 0$$

$$Z = 0, \qquad C = C_i$$

$$Z = \infty, \qquad C = 0$$

For these conditions the solution to equation (B-9) becomes (20):

$$C = C_i \left[ 1 - erf\left( \frac{Z}{\sqrt{4 (\epsilon + D)\Theta}} \right) \right] \qquad (B-10)$$

For small values of $\left[ Z/4(\epsilon + D)\Theta \right]$ equation (B-10) becomes:

$$C = C_i \left\{ 1 - \frac{Z}{\sqrt{\pi(\epsilon + D)\Theta}} + \frac{Z^3}{12(\epsilon + D)\Theta} - \ldots \right. \qquad (B-11)$$

The rate of mass transfer across the gas-liquid interface is given by:

$$N = - (\epsilon + D) \left. \frac{\partial C}{\partial Z} \right|_{Z = 0} \qquad (B-12)$$

Then from equation (B-11) :

$$\frac{\partial C}{\partial Z}\bigg|_{Z = 0} = -C_i / \sqrt{\pi(\epsilon + D)\theta} \qquad (B-13)$$

and the rate becomes:

$$N = C_i \sqrt{(\epsilon + D)/\pi\theta} \qquad (B-14)$$

Equation (B-14) gives the rate of mass transfer across the interface as a function of; equilibrium concentration, $C_i$, molecular diffusivity, $D$, eddy diffusivity, $\epsilon$, and time, $\theta$.

APPENDIX C

DEVELOPMENT OF AMPLITUDE RELATIONSHIP

One of the major difficulties in analyzing mass transfer data in the presence of surface waves or ripples arises in trying to determine the increase in the mass transfer area due to the ripples. Since efforts to experimentally determine this area failed due to an inability to accurately photograph the wave amplitudes, an indirect approach has been developed.

During a cycle of the oscillating plate, water is lifted up in front of the plate to form the wave crest. Figure (12) shows this process schematically.
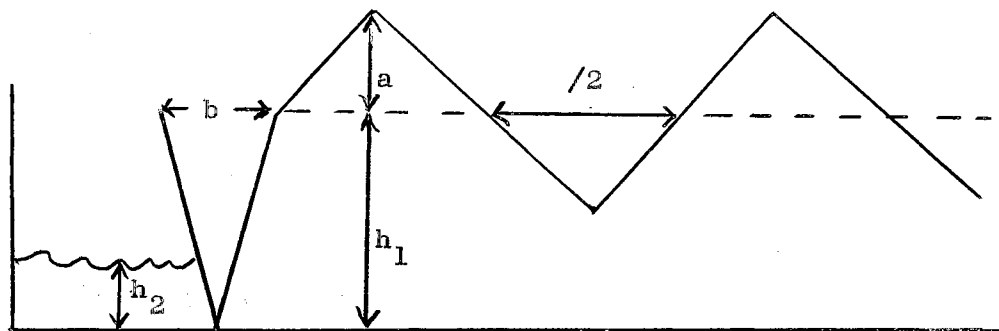


Figure 12. Schematic of Idealized Waves

Figure (12) shows the general behavior of the oscillating plate. The amount of water inside the triangle covered by the plate motion is swept out to form the crest of the new wave. The actual crest is reduced in size by the amount of water which flows back through the holes in the plate and around the plate edges. That is:

$$1/2 \ b \ h_1 \ W = 1/2a \ (\lambda/2) \ W + 2Q/f \qquad (C-1)$$

The average velocity of the plate at the point where the holes are is:

$$V_a = f(2b)(h_2/h_1) \qquad (C-2)$$

The volume flow rate of water through the holes in the oscillating plate is:

$$Q = V_a A_o = 2fb(h_2/h_1)A_o \qquad (C-3)$$

Substituting equation (C-3) into (C-1) gives an expression for the amplitudes of the waves:

$$a = (2/\lambda) \left[ bh_1 - 8\frac{A_o}{W}b \ \frac{h_2}{h_1} \right] \qquad (C-4)$$

The surface area for mass transfer without waves is LW where L is the length of the box and W is the width. Assuming triangular waves, the fractional increase in area due to the waves is:

$$\left( \sqrt{(\lambda/4)^2 + a^2} \right) \Big/ (\lambda/4)$$

Note that if there are no waves, a = 0, this term becomes unity. Then the area for mass transfer with surface waves is:

$$A = LW \ \sqrt{(\lambda/4)^2 + a^2} \Big/ (\lambda/4) \qquad (C-5)$$

Using equation (C-4) in (C-5) yields the relationship:

$$A = \frac{4LW}{\lambda} \sqrt{\left(\frac{\Delta}{4}\right)^2 + \left(\frac{2}{\lambda}\right)^2 \left[bh_1 - \frac{8A_o}{W} b \frac{h_2}{h_1}\right]^2} \qquad (C-6)$$

Equation (C-6) represents an approximate expression for the surface area with waves. All of the terms in equation (C-6) were measured experimentally. Use of this equation may induce errors of as much as 10%.

VITA

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