

THE DETERMINATION OF DIFFUSION
COEFFICIENTS FOR CARBON DIOXIDE AND OXYGEN
IN WATER USING A QUIESCENT LIQUID
ABSORPTION APPARATUS

by

Byron John McCutchen

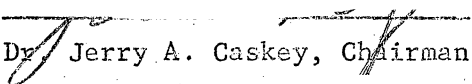
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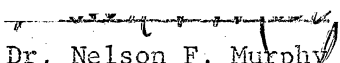
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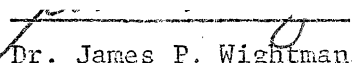
IN

CHEMICAL ENGINEERING

APPROVED:


Dr. Jerry A. Caskey, Chairman


Dr. Nelson F. Murphy


Dr. James P. Wightman

June, 1969

Blacksburg, Virginia

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I. INTRODUCTION

Molecular diffusion of gases into liquids continues to be an area rich in experimental work. The diffusivities of gases in liquids are important industrially in gas-liquid mass transfer operations. Also, diffusivities are useful in evaluating the validity of liquid state models or interfacial transfer models. The mechanisms and physical laws governing diffusion are complicated and often cannot be solved analytically. As a result, most systems used to evaluate diffusion coefficients attempt to reduce the governing form of Fick's law to the simplest possible relation.

In the early 1900's, quiescent liquid systems were used to measure diffusion coefficients. The results of these measurements were quite good but required lengthy contact times (as much as several days). Recent efforts in this area have emphasized the need for a more rapid measuring system that still fulfills industries' need for accuracy. The result of such an emphasis has been the advent of liquid laminar jets and other flow processes for measuring absorption. However, laminar jets, and flow systems in general, are not easily solved theoretically due to the difficulty in accounting for the hydrodynamic effects.

A quiescent liquid system is desirable because of its analytical simplicity. Provided the contact time could be shortened, such a system would meet industrial needs for an accurate, rapid system for

measuring diffusion coefficients. Quiescent liquid systems have been used recently in determining the retardation effects for various monolayers on gas absorption⁽⁴⁾. However, such a system has not been applied recently to determining diffusion coefficients of pure gases in water.

Water is a widely used contacting liquid in industrial applications. Recent trends in waste treatment make carbon dioxide and oxygen diffusion into water of considerable significance. As a result, most diffusion studies are evaluated on their ability to reproduce acceptable values for the diffusion coefficients of oxygen and carbon dioxide in water.

The purpose of this investigation was to evaluate a quiescent liquid absorption apparatus for measuring diffusion coefficients as to ease of measurement and reproducibility of results, using the oxygen, carbon dioxide-water systems.

II. LITERATURE REVIEW

The following section presents the literature pertinent to understanding of this thesis.

Classical Diffusion Theory

Mass transfer in the form of diffusion is distinguished by the need to deal with mixtures and their individual behavior relative to the overall motion in the system⁽⁹⁾. As a result, numerous equivalent mathematical expressions can often express the same result in different forms. However, much of the difficulty in nomenclature is eliminated in the present study because of the lack of a velocity term in the diffusion equation.

Definition of the System

In this study the system to be considered is a two-phase, two-component system of a pure gas diffusing into a pure liquid. The gas phase is identified as A and the liquid phase as B, with a binary diffusion coefficient D for the system. Unless specifically stated otherwise, the literature is assumed to utilize the above system wherein only ordinary diffusion, as a result of concentration gradients, occurs. Pressure diffusion, thermal diffusion, and forced diffusion are not considered here. Numerous diffusional processes have been used to

evaluate diffusion coefficients. In nearly every case, a form of Fick's First Law of diffusion has been used to relate the flux or motion of the fluid to the concentration of the diffusion component. It would be lengthy to derive the developments for each system in the literature, and as a result, only the significant aspects of each theoretical solution will be mentioned.

Fick's Law for a Quiescent Liquid System. The diffusion process used in this investigation is a quiescent liquid. The theoretical development of Fick's law for such a process is given in several sources^(35,9). Referring to Figure 1, the derivation by Scriven⁽³⁵⁾ will be followed.

Assume that a pure gas contacts a pure liquid at constant temperature, wherein no reaction occurs. If Fick's law applies, the flux of gas across any plane in the liquid, parallel to the interface, will be proportional to the concentration of dissolved gas in the liquid. Making a material balance over an incremental liquid elemental of thickness dY results in the following expression:

$$\frac{\partial C}{\partial t} dY = - D \frac{\partial C}{\partial Y} + \left[D \frac{\partial C}{\partial Y} + \frac{\partial}{\partial Y} \left(D \frac{\partial C}{\partial Y} \right) dY \right] \quad (1)$$

where:

- C = concentration of dissolved gas, gm/cm³
- t = time, sec
- Y = distance, cm
- D = diffusion coefficient, cm²/sec

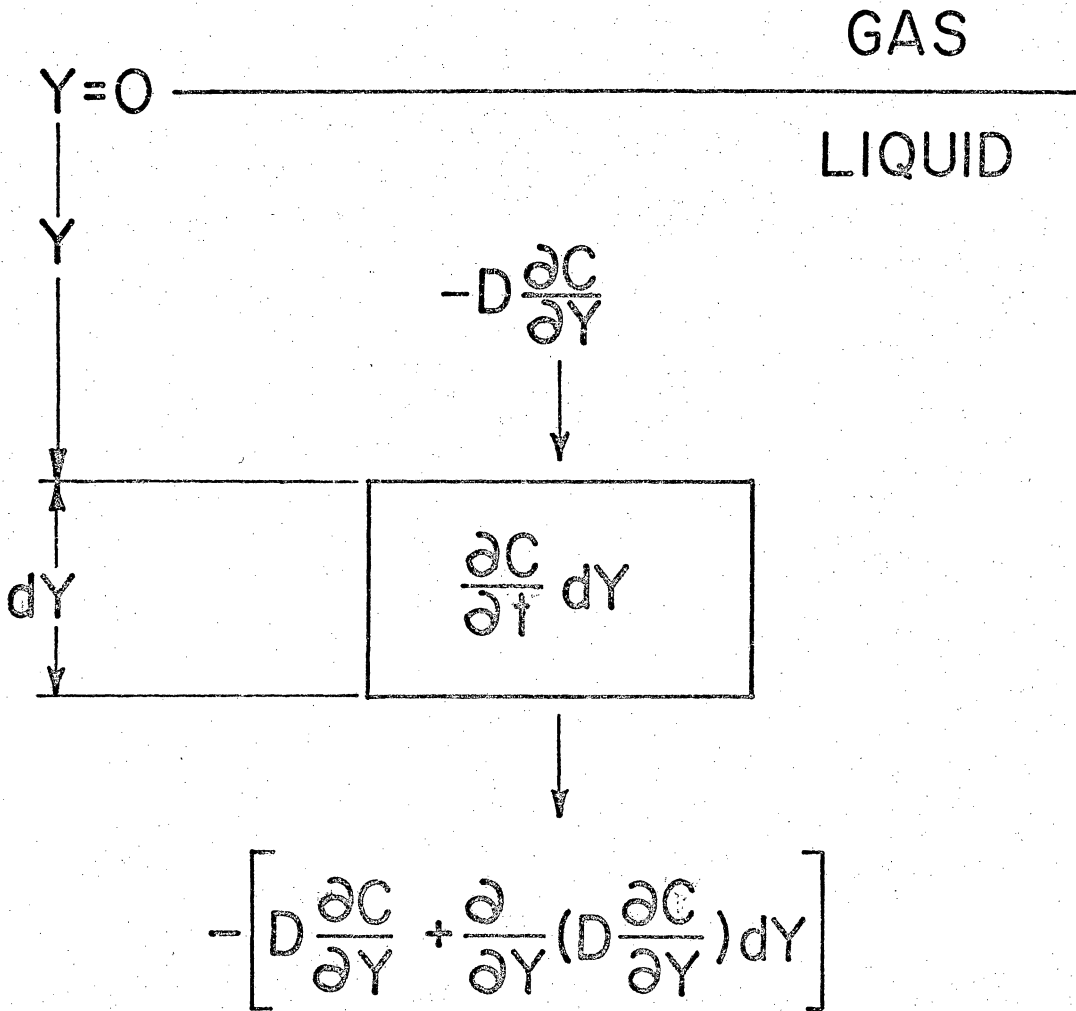


FIGURE 1. THEORETICAL QUIESCENT LIQUID ABSORPTION MODEL

If it is assumed that the diffusion coefficient is not a function of position or time, equation 1 reduces to:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial Y^2} \quad (2)$$

The solution of this equation requires three boundary conditions, one on time and two on position. If the initial concentration of gas in the liquid before contact is zero, the initial condition, $C(Y,0) = 0$, is imposed. If in addition, the liquid is assumed infinite for the contact time used, a second boundary condition becomes $C(\infty,t) = 0$. A final boundary condition is written for the physical situation at the interface wherein equilibrium is assumed. Henry's law is assumed applicable and constant if the pressure is constant. Therefore, the condition $C(0,t) = C_e$ is imposed, where $C_e = P/H$.

This is a boundary value problem which can be solved by Laplace Transforms to obtain:

$$C(Y,t) = \frac{P}{H} \left[1 - \frac{2}{\sqrt{\pi}} \operatorname{erf} \left(\frac{Y}{2\sqrt{Dt}} \right) \right] \quad (3)$$

where:

P = operating pressure, mm Hg

H = Henry's law constant, mm Hg - cm³/gm mole

The average rate of absorption of gas into the liquid between initial contact and any time t is found by the following equation:

$$\bar{N}_a = \int_0^t \left(-D \frac{\partial C(Y,t)}{\partial Y} \right)_{y=0} dt = \frac{2P}{H} \sqrt{\frac{Dt}{\pi}} \quad (4)$$

where:

\bar{N}_a = the amount of gas absorbed, gm moles/cm² - sec

This quantity can be measured experimentally in a variety of way. If the quantity $\bar{N}a$ is plotted versus \sqrt{t} the slope can be used to evaluate the diffusion coefficient for the gas-liquid system.

Interfacial Resistance. As stated by Scriven⁽³⁵⁾, the above development can be recognized as an application of Higbie's Penetration Theory (1935). The actual behavior of the gas-liquid system at the interface is still subject to interpretation, although several theoretical explanations have been presented⁽¹⁾. The existence of a resistance at the interface has recently received attention and is still being debated^(2,12). In the present study, it is assumed that no interfacial resistance exists at the gas-liquid interface.

Experimental Measurement of Diffusion Coefficients

A thorough review of both theoretical and experimental techniques for obtaining diffusion coefficients is given by Himmelblau⁽²⁰⁾. A general review of experimental techniques is given here along with a summary of the major work done using each technique.

Quiescent Liquid Systems. One of the earliest measurements of diffusion coefficients was made by Carlson⁽¹¹⁾ in 1911, using a quiescent liquid system. His apparatus utilized a pair of glass cylinders mounted on movable slabs so that the two cylinders could be brought together. One cylinder was filled with gas-free distilled water, the other with water nearly saturated with the desired gas. A one percent potassium

chloride solution was added to reduce convection currents. The experiment began when the two cylinders were contacted, thus allowing the diffusion to proceed. Very lengthy exposure times were required and elaborate precautions were undertaken to prevent vibrations during the tests. Carlson's consistency was extremely good and his results compare reasonably with more recent results.

A lengthy contact time was required for Carlson's work (several days), and the influence of convection currents was uncertain. Somewhat earlier, Hagenbach⁽¹⁸⁾ added a twenty percent gel solution to the absorbing liquid in an effort to reduce such effects. Hagenbach's data for carbon dioxide appear to be in reasonable agreement with recent values, but his values for oxygen are quite high. Himmelblau⁽²¹⁾ states that the data for oxygen may include the oxygen absorbed by the gelatin or the oxygen chemically reacted with the gelatin.

Another procedure used to reduce the possibility of convection is decreasing the size of the cylinder. Stefan⁽³⁸⁾ modified Carlson's technique by using very thin capillaries for the absorption process. However, when such fine capillaries are used, the question of sufficient mixing at the interface becomes significant. Stefan's values agree well with recent results and Carlson's work.

Some additional early measurements are referred to by Arnold⁽¹⁾ in his thorough review. Exner⁽¹⁷⁾ utilized a capillary device that used a soap film as a porous membrane through which diffusion was measured. Hüfner⁽²⁴⁾ states that earlier work yielded values of

diffusivity that were too high due to the long exposure times. However, he must have been referring to Hagenbach or Exner, since his values are in agreement with Carlson's.

No recent work in the area of gas-liquid diffusion coefficients has utilized a quiescent liquid system. However, Harvey and Smith⁽¹⁹⁾, Blank⁽³⁾, and Blank and Roughton⁽⁴⁾ have studied related phenomena using such systems. Harvey and Smith⁽¹⁹⁾ used a quiescent liquid absorption cell to measure interfacial mass transfer coefficients for carbon dioxide in pure water and with surfactants in water. They utilized an interferomic technique to evaluate the amount of gas absorbed.

The apparatus utilized in the present study has been used for gas absorption into surfactant solutions by Blank⁽³⁾ and Blank and Roughton⁽⁴⁾. The system is a modified Barcroft Differential Manometer, using a dummy cell to reduce the effects of temperature and pressure variations, and a reaction cell for the absorption process. The basic theory as presented by Dixon⁽¹⁴⁾ is presented in the Appendix on page 103. The advantages of such a system are that it is unnecessary to correct for variations in ambient pressure or temperature during a test.

Diaphragm Cells. A diaphragm cell consists of a porous disk sealed between two cylinders, one of which has a liquid with high gas concentration, and the second a liquid of low gas concentration. In this respect it is quite similar to Carlson's apparatus. Under proper mixing, concentrations can be maintained so that transfer occurs at steady state. Since the geometry of the system is usually uncertain,

the cell is calibrated with a solution of known diffusivity. Potassium-chloride solutions are widely used.

Peaceman⁽³²⁾ obtained results for carbon dioxide from diaphragm cells that were seven percent higher than best current values. Scriven⁽²⁵⁾ utilized a diaphragm cell and obtained good reproducibility for contact times of several days using carbon dioxide. Scriven's results agree well with currently accepted values.

More recent measurements with diaphragm cells have been made by Vivian and King⁽⁴²⁾ for carbon dioxide, oxygen and several other gases. They agree well with accepted values.

Steady-State Laminar Flow Systems. Recent literature on diffusion coefficients is made up largely of laminar jet studies. Himmelblau⁽²²⁾ suggests some reasons for this trend. "Jets are simple in design, have freedom from ripples, have small end effects, are stable, and have such short contact times that surface active agents do not have time to absorb on the surface. Above all, they are rapid."

However, in this apparatus, there is a velocity term in the Fick's law equation. In addition, one must consider the hydrodynamic effects on the diffusion process. The relative validity of results for such a system can be no better than the quality of fit between the theoretical model and the actual behavior.

In most flow systems, liquid exits through a nozzle into an absorption chamber filled with the desired gas. Elaborate efforts have been used to assure proper shape of the jet, based on the theoretically

assumed profile, and thereby remove the hydrodynamic considerations. Duda and Vrentas⁽¹⁶⁾ recently covered the theory of laminar jets quite thoroughly and comment as follows on the usual procedure for considering the hydrodynamics. "However, instead of theoretically incorporating the influence of the jet hydrodynamics in the analysis of the absorption data, most investigators have attempted to reduce these effects experimentally by employing special nozzles which inhibit the development of a velocity profile in the nozzle region."

Chiang and Toor⁽¹²⁾, using a laminar jet, found the absorption rate for oxygen lower than expected and indicated that an interfacial resistance was apparently involved. Baird and Davidson⁽²⁾ came to a similar conclusion by use of an annular jet. Unver and Himmelblau⁽⁴¹⁾ report good comparison between their diffusivity data for carbon dioxide, and currently accepted values, but not for some other hydrocarbons tested. Raimondi and Toor⁽³⁴⁾ report values of the diffusion coefficient one to four percent low for carbon dioxide in water, using laminar jets. Davidson and Cullen⁽¹³⁾ utilized flow around a sphere for gas absorption and report good agreement with accepted values.

Duda and Vrentas⁽¹⁶⁾ have done a rigorous analysis of jet hydrodynamics and available diffusivity data. They maintain that there is no conclusive evidence of significant interfacial resistance in jet absorption processes. In addition, they maintain that the presently accepted values of the diffusion coefficient for oxygen in water are higher than the actual value.

Dropping Mercury Electrode. The theory of the dropping mercury electrode has been reviewed by Kolthoff and Izutsu⁽²⁷⁾ and Kolthoff and Miller⁽²⁸⁾. The diffusion coefficient is related to the drop time by the Ilkovic Equation⁽²⁸⁾:

$$i_d = 0.63nFC_1 m^{2/3} t^{1/6} D_{12}^{1/2} \quad (5)$$

Where:

i_d = diffusion current, microamp

n = 2

F = Faraday

C = concentration of oxygen, moles/ml

m = weight of mercury flowing in 1 sec, gm

t = time of drop, sec

D_{12} = diffusion coefficient, cm^2/sec

According to the theory of Ilkovic, solutions of nonelectrolytes tend to a constant or "diffusion current". This current is due only to diffusion of the nondissociated molecules through the solution. When the current, i_d , is plotted against the voltage, V , the diffusion current should appear as a plateau.

Kolthoff and Miller⁽²⁸⁾ used such an apparatus. Their results for oxygen in water are higher than accepted values.

Since Kolthoff and Miller's results appeared, a modified Ilkovic equation has been used and includes an effect for both first and second diffusion currents for oxygen. The modified equation is⁽²⁶⁾

$$i_d = 607 n m^{2/3} t^{1/6} C_{D_{Ficks}}^{1/2} \left(1 + k m^{-1/3} t^{1/6} D_{Fick}^{1/2} \right) \quad (6)$$

Where:

k = frequency constant

D_{Ficks} = diffusion coefficient, cm^2/sec

and has been used by Jordan, Ackerman and Berger⁽²⁶⁾ and Kolthoff and Izutsu⁽²⁷⁾. Both of these investigations give reasonable comparison with accepted values. Jordan et al. have determined that the original Ilkovic equation gives diffusivities for oxygen approximately ten percent higher than the modified equation⁽²⁴⁾.

Interferometric Techniques. Interferometric absorption involves unsteady-state absorption in which the concentration is evaluated as a function of time. The process uses monochromatic light which passes through a fine slit and is focused through the diffusion boundary onto a photographic film or plate. The theory originates with Gouy⁽²³⁾ and more recent considerations can be found in Harvey and Smith⁽¹⁹⁾. Due to the complexity of theory and equipment required by this technique it has been used sparingly.

Summary of Diffusion Data

In order to clarify the data on diffusion coefficients for oxygen and carbon dioxide in water, data from the articles discussed above are presented in Figures 2 and 3. These data are further condensed in Tables I and II for oxygen and carbon dioxide respectively at a temperature of 25.0°C. Due to the large number of measurements made at 25°C, only a portion of the values given in Tables I and II appear in the corresponding Figures.

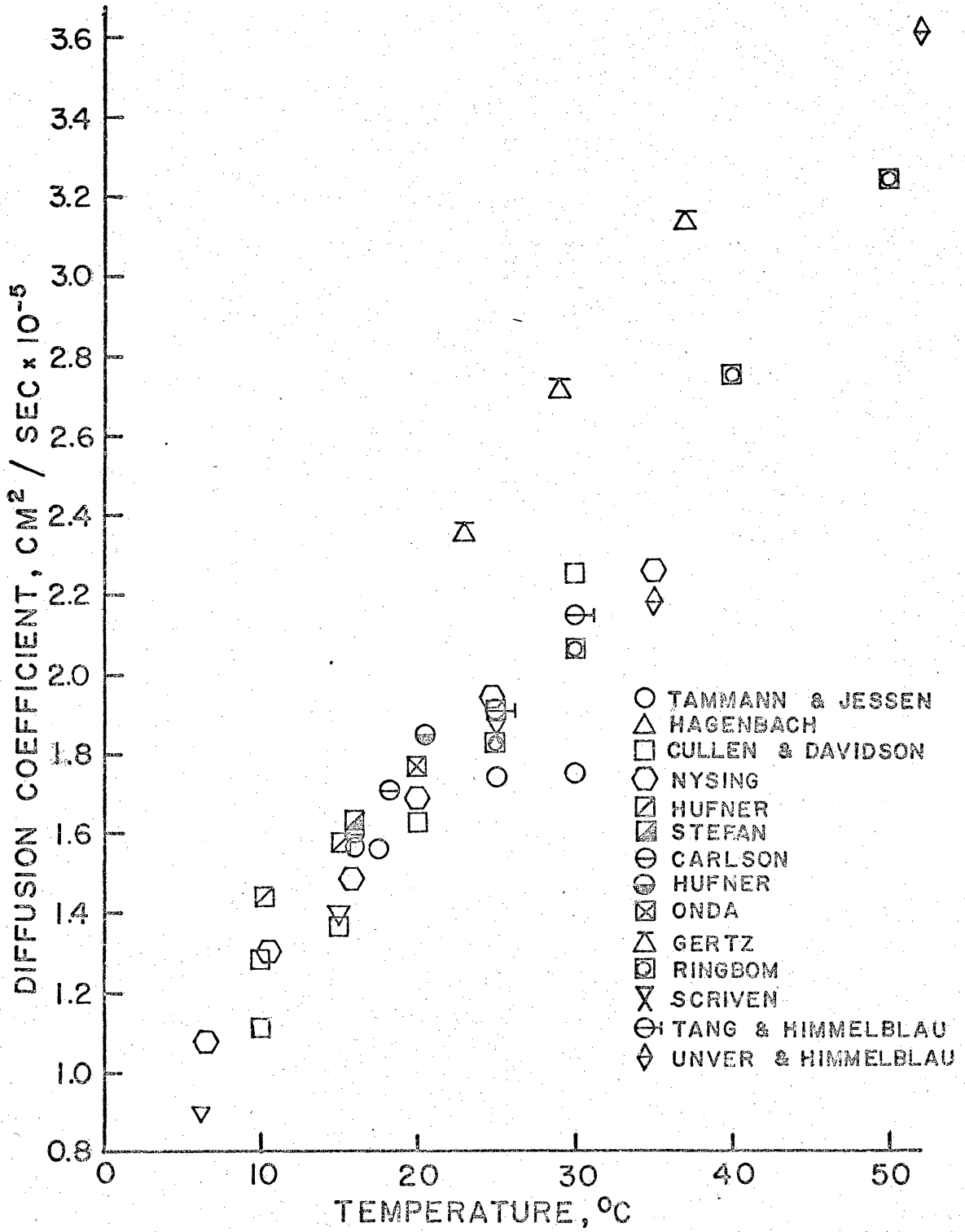


FIGURE 2. LITERATURE VALUES FOR THE DIFFUSION COEFFICIENT OF CARBON DIOXIDE IN WATER

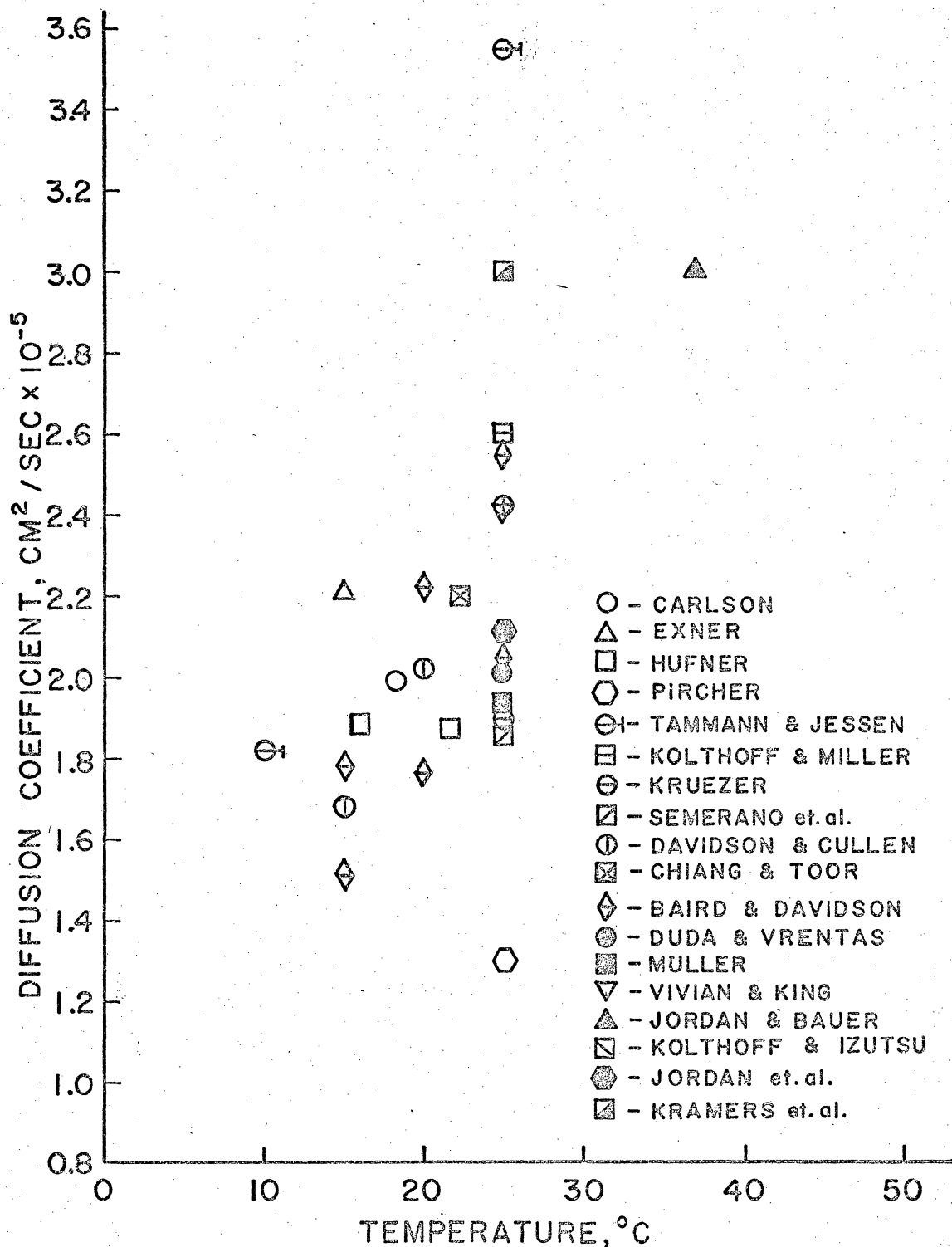


FIGURE 3. LITERATURE VALUES FOR THE DIFFUSION COEFFICIENT OF OXYGEN IN WATER

TABLE I

Diffusion Coefficients for Carbon Dioxide in Water at 25°C

Reference	Diffusion Coefficient (cm ² /sec x 10 ⁵)
Tammann and Jessen ⁽⁴²⁾	1.74
Davidson and Cullen ⁽¹³⁾	1.91
Nysing ^{(31)a}	1.94
Ringbom ⁽²⁰⁾	1.82
Scriven ⁽³⁵⁾	1.87
Tang and Himmelblau ⁽¹⁶⁾	1.90
Khem ⁽¹⁶⁾	1.92
Unver and Himmelblau ⁽⁴¹⁾	1.85
Thomas and Adams ⁽⁴²⁾	1.96
Vivian and King ⁽⁴²⁾	2.00
Duda and Vrentas ⁽¹⁶⁾	1.98
Average Value	1.90

^aActual value measured at 24.8°C

TABLE II

Diffusion Coefficients for Oxygen in Water at 25°C

Reference	Diffusion Coefficient ($\text{cm}^2/\text{sec} \times 10^5$)
Pircher ⁽¹⁶⁾	2.30
Kolthoff and Izutsu ⁽²⁷⁾	1.95
Tammann and Jessen ⁽⁴²⁾	3.54
Jordan et al. ⁽²⁶⁾	2.12
Kolthoff and Miller ⁽²⁸⁾	2.60
Hagenbach ⁽²⁰⁾	7.48
Kruezer ⁽²⁰⁾	1.90
Kramers, Douglas and Ulmann ⁽²⁰⁾	3.00
Semerano et al. ⁽³⁷⁾	1.87
Davidson and Cullen ⁽¹³⁾	2.42
Baird and Davidson ⁽²⁾	2.55 (wetted spheres) 2.03 (laminar jet)
Duda and Vrentas ⁽¹⁶⁾	2.07
Müller ⁽³⁰⁾	1.91
Vivian and King ⁽⁴²⁾	2.41

III. EXPERIMENTAL

The plan of experimentation, materials, apparatus, method of procedure, and the data and results of this investigation appear in this section.

Plan of Experimentation

The following experimental plan was pursued in the course of this investigation.

Literature Review. A survey of the literature on diffusion coefficients in the carbon dioxide, oxygen-water systems was conducted with special emphasis on quiescent liquid absorption processes. Sufficient data were found for obtaining an acceptable diffusion coefficient for both systems. A quiescent liquid system that could be applied to diffusion measurements was found.

Manometric Techniques. The diffusion system chosen for this study was an adaption of a Barcroft differential manometer. The characteristic volume for the apparatus was determined by weighing the mercury required to fill the equipment.

The amount of gas absorbed was determined by the change in liquid height on a manometer separating the absorption cell containing water and gas, and a dummy cell containing only gas.

Treatment of Data. The uptake of gas was plotted versus the square root of contact time. The shape of such a plot should be linear and the slope related to the diffusion coefficient by a multiparameter expression. The diffusion coefficient determined from each test was compared with literature values.

Materials

A detailed list of the materials used in this investigation is given in the Appendix.

Apparatus

A detailed list of apparatus used in this investigation is contained in the Appendix. The absorption apparatus was manufactured by the V.P.I. Glass Shop and required special high vacuum stopcocks to maintain a good vacuum.

Method of Procedure

This section describes the methods of procedure used in obtaining the uptake curves for carbon dioxide and oxygen in water. Because of experimental difficulties in reproducing data, more than one technique was used. Each technique is described completely under each heading.

Calibration of Apparatus. In order to evaluate the amount of gas absorbed, the volume of the reaction side, dummy side, connecting tubing, and manometer must be known.

The cross sectional area of the manometer is used in determining the volume change during absorption and must be accurately known. A bead of mercury approximately 10 centimeters in length was introduced into the manometer and moved into one leg of the manometer. The bead was then moved to several positions within the leg and the length recorded at each position. The bead was then transferred to the other manometer leg and the procedure was repeated. The mercury bead was then moved and weighed at the temperature of the measurements. From the density, weight, and average length, the cross sectional area was determined for each leg of the manometer.

Absorption Side Volume Determination. Referring to Figure 4, the total volume from stopcock 7 to stopcock 5 and down to the 15 centimeter mark on the manometer represents the reaction cell volume. Mercury was again used to measure this volume but complications occurred due to the bulk of the apparatus and the large quantity of mercury required to fill it. The determination of the volume of the reaction system was separated into two parts. First the volume of the tubing above F to the manometer was determined, then the volume of the cell and tubing up to F was determined.

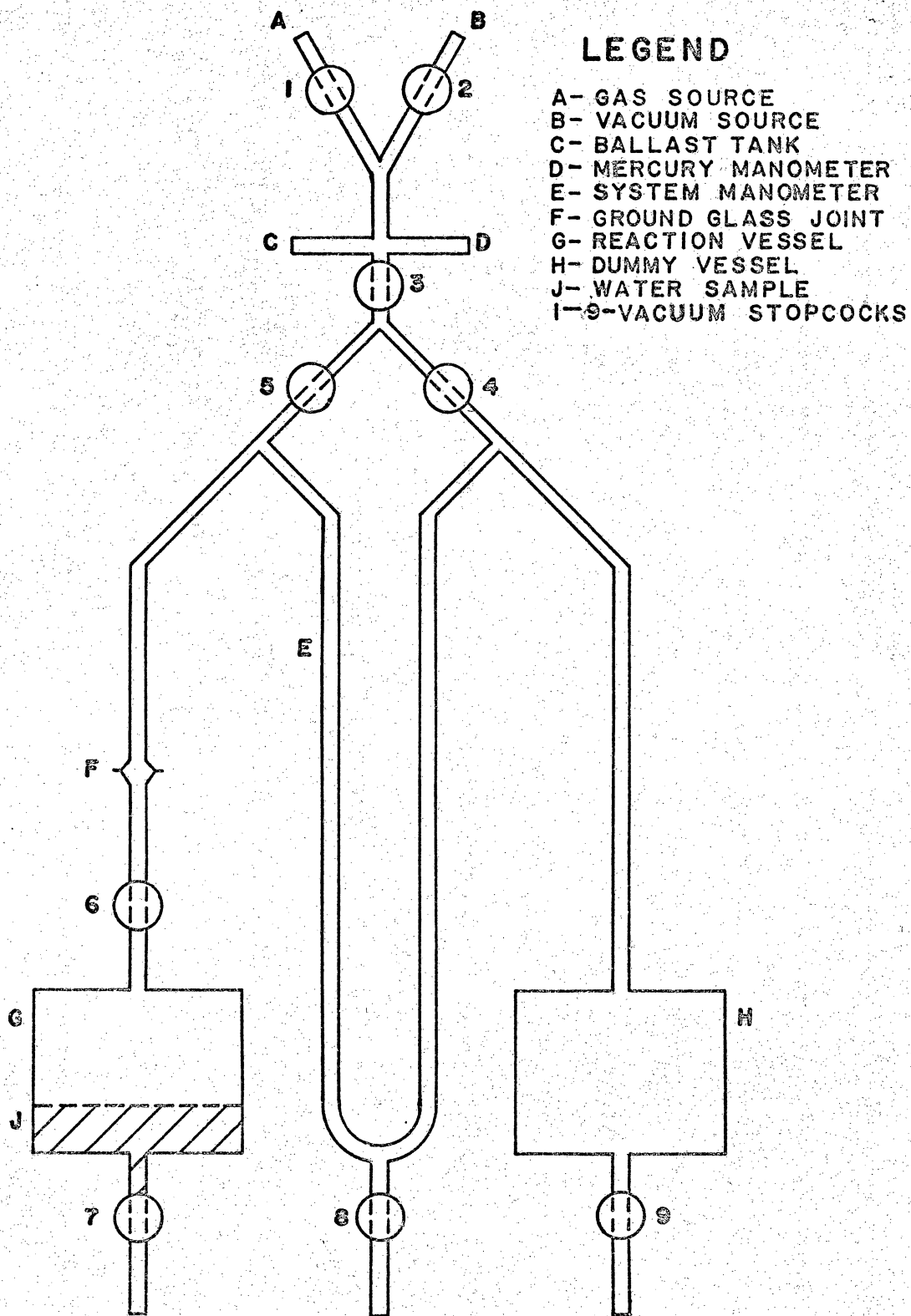


FIGURE 4. QUIESCENT LIQUID ABSORPTION APPARATUS.

The first step was to remove the reaction cell from the apparatus at the ground glass joint F. The apparatus, without the cell was then inverted and a mercury bead introduced into the tubing at F with an eyedropper. Subsequent additions of mercury were best made by rolling the bead to the opening at F and sucking it into the eyedropper until it contacted the new mercury in the eyedropper. This procedure prevented the formation of bubbles in the tubing which could not be removed, once introduced, except by dumping the mercury. The volume of mercury added was checked by tilting the apparatus to a vertical position (inverted) and noting the height in the tubing below F. When the mercury filled the tubing just to the opening at F, the level of mercury in the manometer was at 15 centimeters. The mercury was then emptied into a beaker.

The reaction cell, from F to below stopcock 7, was separated from the rest of the apparatus and filled by connecting a tube below stopcock 7 and filling with mercury from this tube. It was often difficult to remove all the air from the system when it reached the top of cell G, but by moving and shaking the cell it was removed. The cell was filled to point F, stopcock 7 closed, and the tubing removed. Then the cell was connected to the empty apparatus at F. The excess mercury caused by the union at F was

removed so that only the volume to the start of the apparatus tubing at F remained in the cell.

In order to remove the mercury, both stopcocks 6 and 7 had to be open (otherwise the mercury would not flow from the cell). In order not to include the mercury trapped in stopcock 7, the flow could not be induced by opening it. As a result, the cell was inverted into the beaker with stopcock 6 open and stopcock 7 was quickly removed beyond the edge of the beaker. This mercury plus the mercury used to fill the tubing above F was weighed and gave the volume of the absorption side of the system.

Dummy Side Volume Determination. The procedure used for measuring the volume of the dummy cell differed only slightly from that for the absorption side. Again referring to Figure 4, the dummy side consisted of the volume from stopcock 9 through cell H to stopcock 4 plus the connecting tubing to the 15 centimeter mark on the manometer.

The only change in the procedure from the reaction vessel was the method of introducing the mercury. In the dummy side procedure, the initial step was the introduction of mercury by an eyedropper into the manometer through stopcock 8 and rolling of this mercury down to stopcock 4. This procedure was repeated until the manometer was filled to the 15 centimeter mark. An etch mark was made on the

connecting tubing above cell H corresponding to the height the mercury column reached. This mercury was emptied into a beaker through stopcock 8.

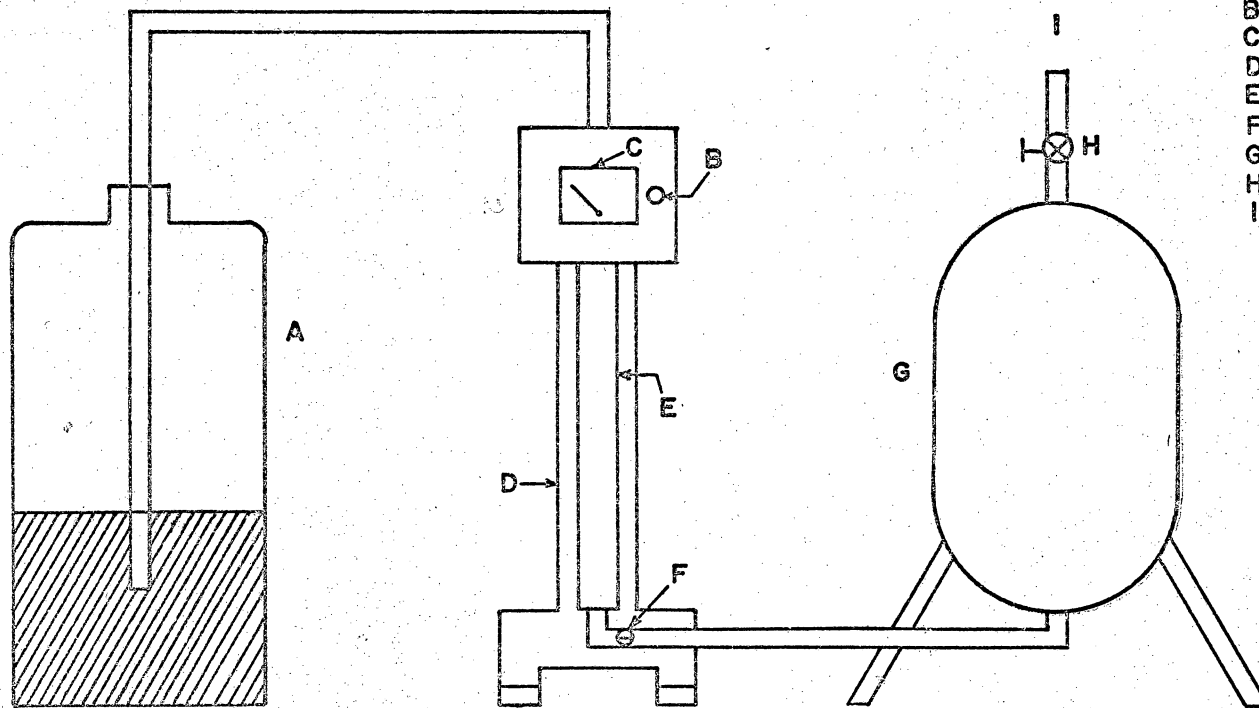
The apparatus was then fitted with tubing below stopcock 9 and the cell and tubing filled with mercury to the etch mark. This mercury plus that used in filling the tubing and the manometer was weighed to determine the volume of the dummy side of the apparatus.

Area of Cells G and H. The cross sectional area of cells G and H were determined by measuring the change in height resulting when a known volume of water was introduced into the cell. The height change upon addition of water was measured accurately with a cathatometer.

Sample Preparation. Three procedures were used in preparing water samples.

The first method utilized distilled water which was passed through a deionizer. The deionized water had a rating of less than 0.1 part per million of sodium chloride. The system used for passing water through the deionizer is shown in Figure 5. It consisted of a metal tank, G, which was filled with distilled water and pressurized with air to induce flow. The deionized water was collected and stored in a 5-gallon polyethylene bottle.

A second method for preparing water was the result of some data given in the literature that used degassed water. It was considered desirable to degas deionized water for several tests. The above



LEGEND

- A - COLLECTING TANK
- B - ON, OFF SWITCH
- C - CONDUCTIVITY METER
- D - DEIONIZER STAND
- E - MIXED RESIN COLUMN
- F - CHECK VALVE
- G - WATER SUPPLY
- H - VALVE
- I - COMPRESSED AIR

FIGURE 5. APPARATUS FOR PREPARATION OF DEIONIZED WATER SAMPLES

procedure was repeated. Water was then removed from the storage vessel, A, and placed in a flask fitted with a disperser. Argon was bubbled through the water for 20 to 30 minutes and the water placed in sample bottles for transference to the cell under argon atmosphere prior to the absorption procedure.

A third preparation was used when it was desired to have a specific initial concentration of carbon dioxide in the water sample. As indicated in Figure 6 water was placed in a flask with tubing connecting the vacuum pump, manometer, and gas source. The water was mixed by a magnetic stirrer.

In this third procedure, deionized water was placed in the flask and carbon dioxide allowed to pass through the gas space above the liquid, F. The supply valve, A, was then closed and the vacuum applied through valve B, until the desired vacuum was obtained. Gas was then allowed to enter through valve A, until the system returned to atmospheric pressure. This procedure was repeated. A third evacuation was made and the gas allowed to fill the vessel to the desired initial pressure. The system was then closed and the stirrer turned on. As absorption took place, additional gas was added to maintain the desired initial equilibrium pressure. Under rapid stirring, the system appeared to be saturated after twenty minutes as evidenced by no further change in the manometer reading.

Preparation of Apparatus. The apparatus as shown in Figure 4 was adapted to fit plastic tubing for easy connection to a manometer, vacuum pump, and gas source. The glass connections at A, B, C, and D

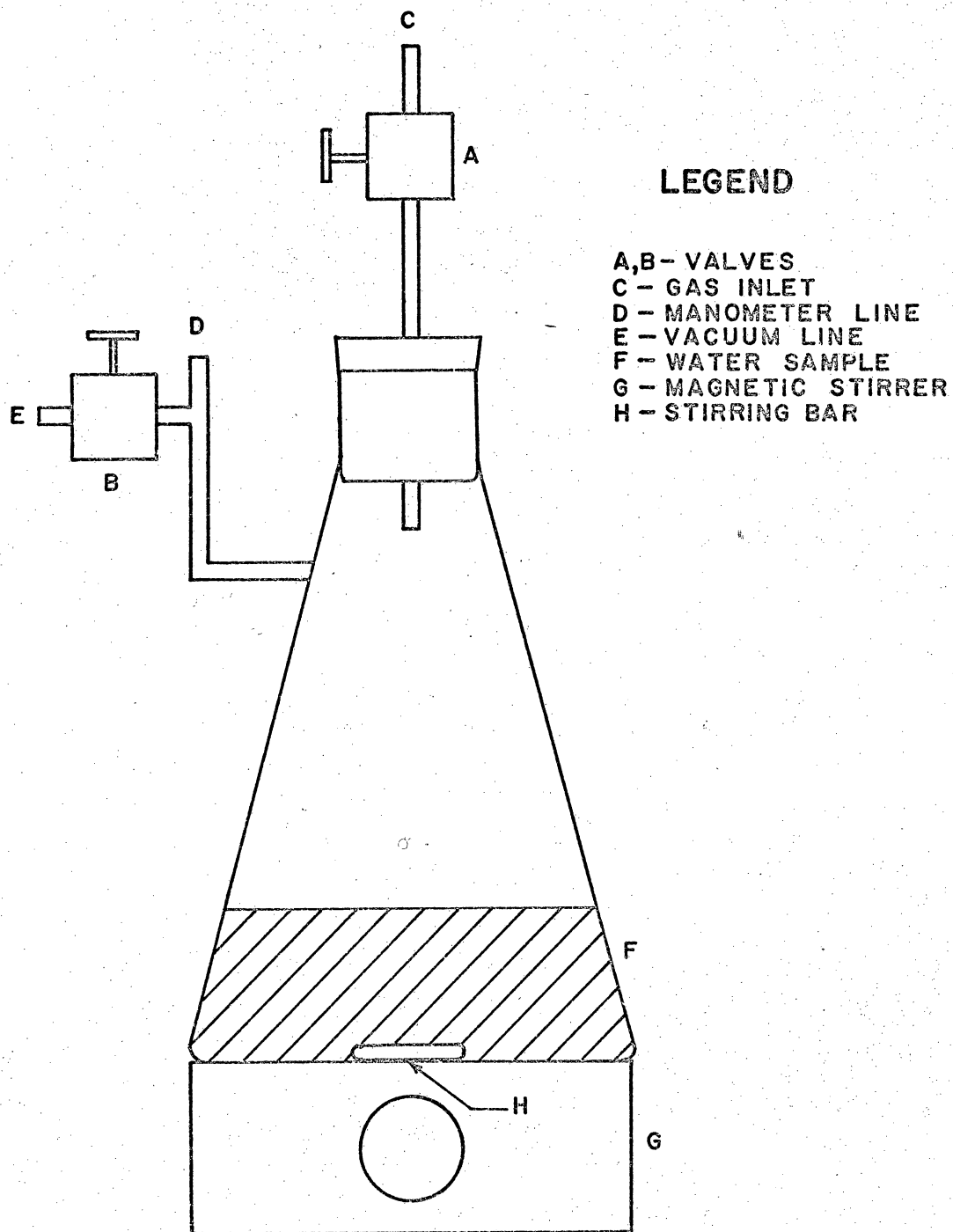


FIGURE 6. APPARATUS FOR PREPARING WATER SAMPLES WITH SPECIFIC INITIAL CONCENTRATION OF CARBON DIOXIDE

were fitted with vacuum tubing containing a metal fitting for 1/4 inch polyethylene tubing. The ballast tank was a metal cylinder, large enough to be the controlling factor in the pressure of the system (approximately three times the volume of the glass system).

Cleaning Procedure. Because of the relative scale of absorption used here, cleanliness of the glassware was of extreme importance. Prior to use, the entire system was filled with glass cleaning solution (see Materials in Appendix) and allowed to soak for 1/2 hour. The system was then flushed and filled with water and finally with acetone. The acetone was removed by passing air through the system. This procedure was repeated whenever the apparatus appeared to be unclean. The stopcocks were also cleaned with glass cleaning solution, water, and acetone.

Preparation of Stopcocks. After thorough cleaning, the apparatus was fitted with the vacuum tubing connections A, B, C, and D. Each stopcock was then placed in position. To obtain the best possible seal, the stopcock plugs were heated slightly and two thin strips of Apiezon grease applied to either side of the openings. The plug was then sealed by smooth turning motions.

After all stopcocks were in position, each was turned so that the hollow portion was open toward the top of the apparatus. The vacuum pump was connected at A, and stopcock 1 was evacuated. The procedure was repeated on stopcock 2 by attaching the vacuum to B. Connections A, C, and D were then closed. Stopcock 2 was turned to allow vacuum

into stopcock 3. When stopcock 3 had been evacuated, it was opened and vacuum opened to stopcocks 4 and 5. In a similar manner all vacuum stopcocks were secured.

Introduction of Manometer Fluid. After seating of stopcocks 1 through 8 by the above procedure, a plastic tube (Tygon) was attached to the glass tube below stopcock 8. Brodie solution was poured into the tube taking care not to form any bubbles (due to a surfactant). The plastic tube was then raised until the fluid entered both sides of the manometer E. (Some rapid up and down motion of the fluid was required to obtain the same initial level in each leg.) The height of the column of liquid was adjusted to approximately 15 centimeters on each side by raising the plastic tubing. Stopcock 8 was then closed and the excess fluid and tubing removed.

Sample Introduction. The reaction cell was separated from the system at F. A 2-inch hypodermic needle was fitted with approximately 5 inches of teflon tubing (outside diameter of 3/32 inch) and bonded to the needle with a sealant. The teflon tubing was worked through the glass tubing and stopcock 6 until it was approximately 1/4 inch above the bottom of the glass cell G. Stopcock 7 was closed. A prepared water sample was introduced into a 20 cubic centimeter syringe. The syringe was attached to the needle at the end of the teflon tubing and the cell carefully filled with 20 cubic centimeters of water. The syringe was removed and water cleared from the tubing by gentle blowing. The tube was removed and the cell reconnected to the system at F.

Constant Temperature Preparation. The apparatus was mounted on a plexiglass board using metal clips at several places on the tubing. The entire apparatus rested on foam at these points of contact and holes were cut in the plexiglass for the stopcocks and cells. This mounting board was used to steady the apparatus during the absorption procedure and allowed an easy transfer into and out of the constant temperature bath. The plexiglass sheet had two rods attached on the back by screws. These rods fit into two clamps mounted by parallel rods to the large water bath. In this way the absorption apparatus was mounted vertically in the bath and both the levelness of the liquid in the cell and the vertical attitude of the manometer assured. The bath temperature then was checked frequently and maintained to $25.0 \pm 0.05^\circ\text{C}$. Tap water circulating through a copper coil was the cooling medium. The laboratory was maintained at $77 \pm 2.0^\circ\text{F}$ also.

Evacuation Procedures. Two techniques for evacuating the system were utilized. The first procedure applied to tests where there was no initial concentration of carbon dioxide. The second procedure applied to tests made with an initial concentration of carbon dioxide present.

Initial Concentration of Carbon Dioxide Zero. In this situation the absorbing gas could not be introduced into the cell prior to the actual absorption test. Stopcocks 7, 8, and 9 remained shut throughout the test. Stopcock 6 remained open throughout the test. Stopcock 1 was closed and stopcock 2 opened.

With the ballast tank line and stopcocks 3, 4, and 5 open, the vacuum pump was started. The system was evacuated to the lowest pressure possible that did not cause degassing of the manometer fluid. The actual vacuum varied during the tests from 500 millimeters of mercury to 640 millimeters of mercury. The system was then generally purged with argon or nitrogen back to one atmosphere and the evacuation repeated. Stopcock 3 was then closed and the glassware allowed to equilibrate. With stopcock 3 closed the ballast tank was then evacuated to less than 1 millimeter of mercury absolute pressure and filled with carbon dioxide through stopcock 1. This procedure was repeated and the evacuation repeated a third time. The ballast tank was then filled with carbon dioxide to a pressure approximately 50 to 100 millimeters below atmospheric pressure. The system was now ready for an absorption test.

Specific Initial Concentration of Carbon Dioxide. In this case the water sample had been prepared as previously described. The procedure used in preparation of the water was repeated with the ballast tank closed. Three evacuations were made to 400 millimeters mercury vacuum. The system was returned to one atmosphere twice by filling with carbon dioxide. After the third evacuation the pressure was adjusted to that used for the water sample preparation. This pressure determined the initial concentration of carbon

dioxide. The system was allowed to equilibrate for one and one-half hours at this pressure (to assure equilibration) by closing stopcock 3 after setting the desired pressure. By closing stopcocks 4 and 5, equilibrium was determined when the manometer fluid height no longer changed.

The ballast tank was then opened and connected to the vacuum pump. It was evacuated to less than one millimeter of mercury absolute pressure and filled with carbon dioxide back to atmospheric pressure. A second evacuation was made to 600 millimeters mercury vacuum, and the system was filled with carbon dioxide back to atmospheric pressure. A third evacuation was made to 600 millimeters mercury vacuum, and the system was filled to a slight positive pressure (less than 2 centimeters of mercury). The system was then ready for the start of an absorption test.

Absorption Test. An absorption test began when stopcock 3 was opened allowing carbon dioxide to fill the absorption and dummy systems. After approximately five seconds stopcock 3 was closed. The test then began by closing stopcocks 4 and 5 and starting the timer simultaneously. The initial reading on the manometer E was recorded as well as the system pressure on manometer D. The change in height of the manometer fluid in E was recorded as a function of time.

Conclusion of Test. At the conclusion of the absorption test, care had to be taken in releasing the pressure to avoid blowing fluid out of manometer E. The tubing at A, B, C, and D was removed and the apparatus

removed from the bath. Stopcock 5 was then slowly opened, allowing the fluid to move toward the dummy side of the manometer. Stopcock 4 was then slowly opened allowing the fluid to return to zero. Finally stopcock 3 was opened relieving the vacuum on the system. The reaction cell was removed and cleaned.

Data and Results

The data and results obtained during this investigation are contained in this section.

Differential Manometer Constants. The data determined for the constants of the differential manometer apparatus are given in Tables III and IV. Table V summarizes the constants for the apparatus. The reaction and dummy cells were of equal volume, but the total volume of the absorption and dummy sections differ slightly. The cross sectional areas of the manometer legs differ slightly; also, the right side having a slightly smaller area.

Tests with Zero Initial Concentration of Carbon Dioxide. An initial set of 15 tests were performed using zero initial concentration of carbon dioxide. Atmospheric pressure, evacuation pressure, operating pressure and purge gas varied. The data for height of the manometer fluid as a function of time are given for Tests 1 through 15 in the Appendix in Tables X through XXIV.

Figures 7 through 21 present the gas uptake as a function of time. The general shape of each curve is similar and consists of an initial linear region followed by a jump and a second linear region. In most

TABLE III

Data for Manometer Cross Sectional Area Determination

Side	Position	High Reading cm	Low Reading cm	Bead Length cm
Left	1	28.70	19.30	9.4
Left	2	24.60	15.20	9.4
Left	3	18.10	8.70	9.4
Left	4	10.70	1.20	9.5
Right	1	28.20	18.40	9.8
Right	2	23.30	13.50	9.8
Right	3	18.10	8.40	9.7
Right	4	11.20	1.60	9.6

Average reading for left = 9.43 cm

Average reading for right = 9.73 cm

Weight of bead = 1.99 gm

TABLE IV

Data for Check on Cross Sectional
Area of Reaction Cell*

Test	Initial height cm	Final height cm	Volume change cm ³
1	21.35	21.95	20.00
2	21.95	22.55	20.00

*Measured at 77°F, one atm pressure

Height measured with cathetometer

TABLE V

Data and Calibration Constants for the Absorption Apparatus

Apparatus section	Weight of Mercury to fill section gm	Volume of Section cm ³	Area cm ²	Diameter cm
Reaction cell	--	--	33.34	6.49
Dummy cell	--	--	33.34	6.49
Reaction cell and Tubing	2142.73	158.25	--	--
Dummy cell and Tubing	2143.15	158.28	--	--
Manometer (Right side)	--	--	0.0151	0.139
Manometer (Left side)	--	--	0.0156	0.141

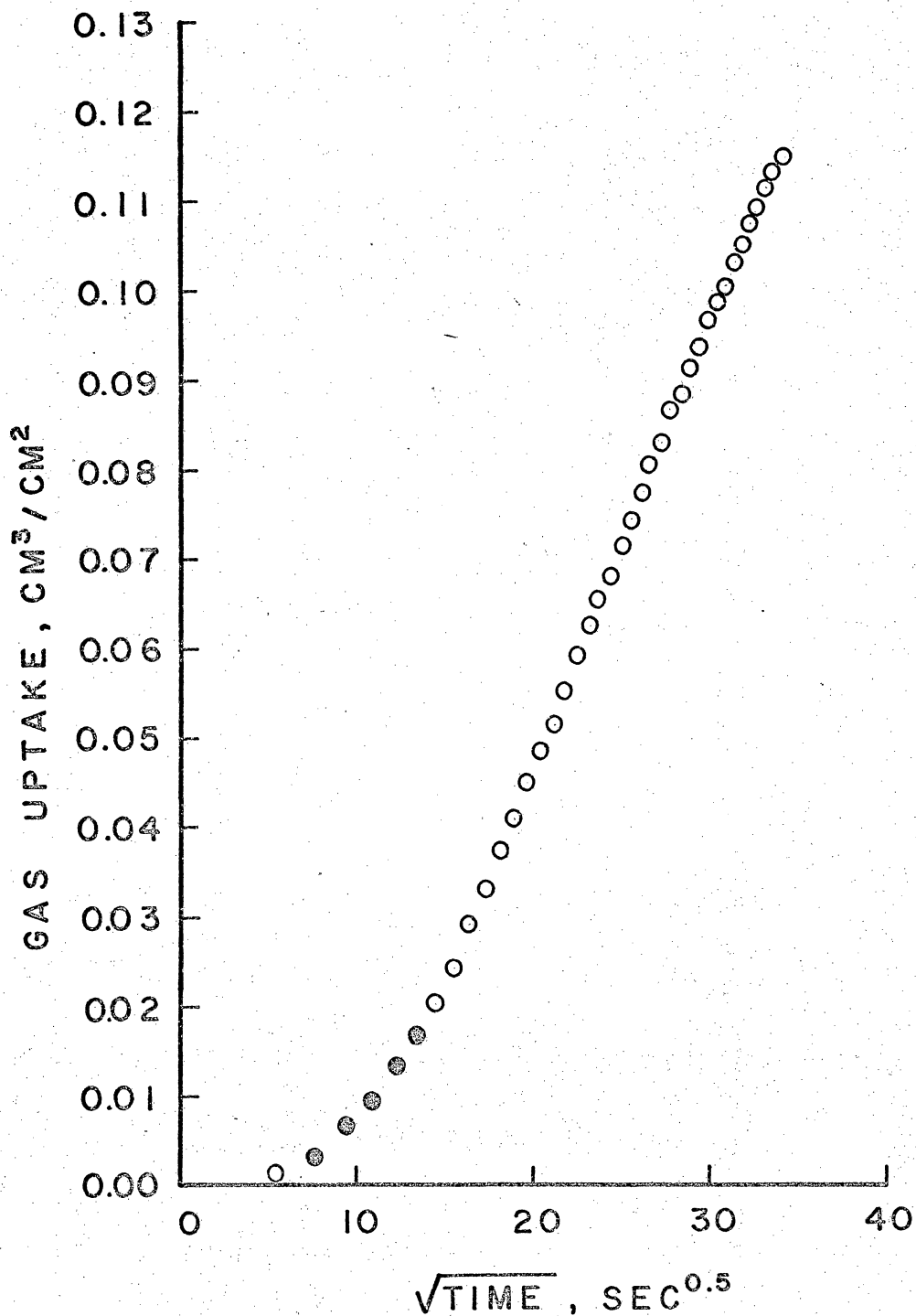


FIGURE 7. CARBON DIOXIDE UPTAKE IN WATER AT 572.40 MM HG
WITH ZERO INITIAL CONCENTRATION

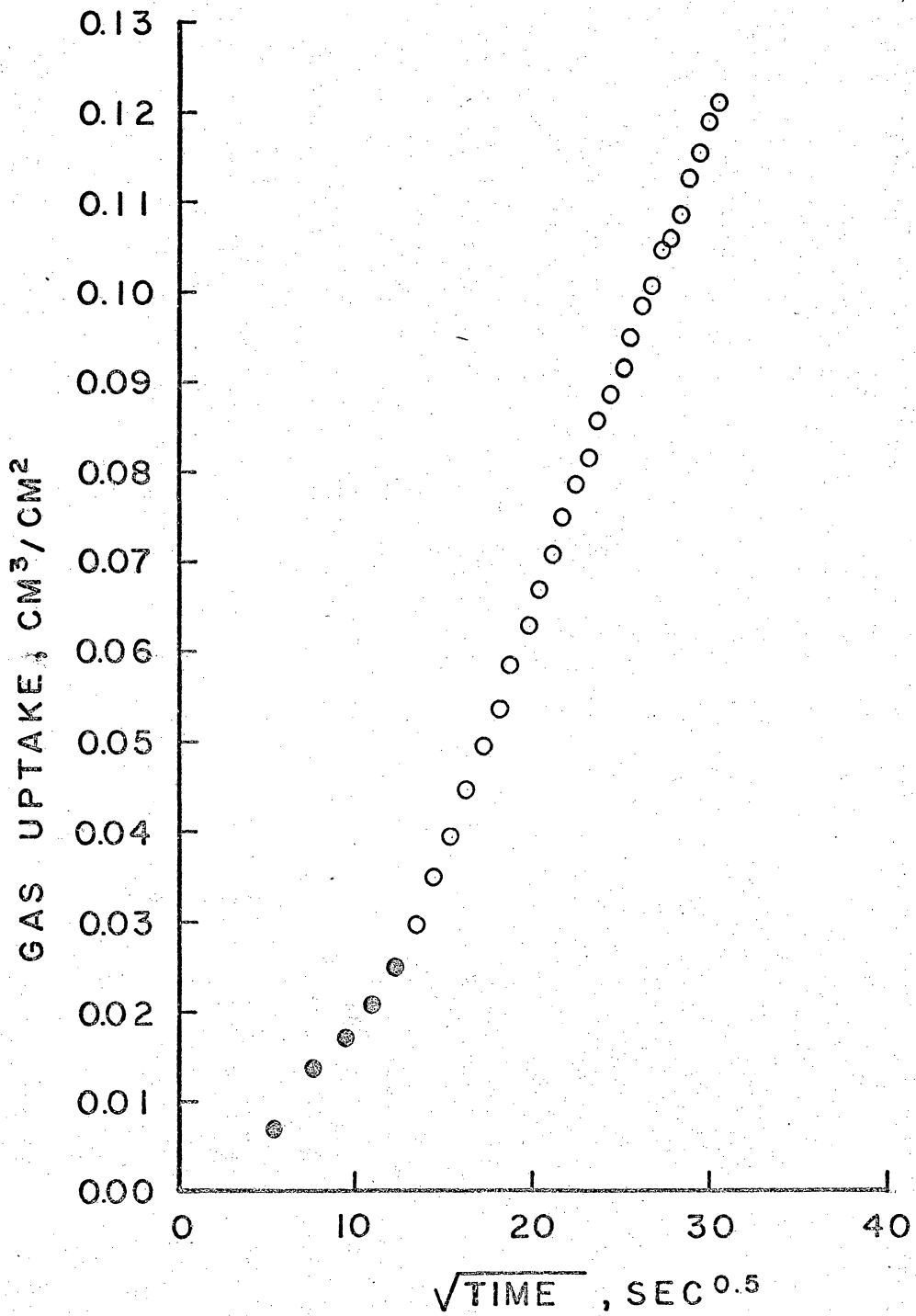


FIGURE 8. CARBON DIOXIDE UPTAKE IN WATER AT 615.70 MM HG
WITH ZERO INITIAL CONCENTRATION

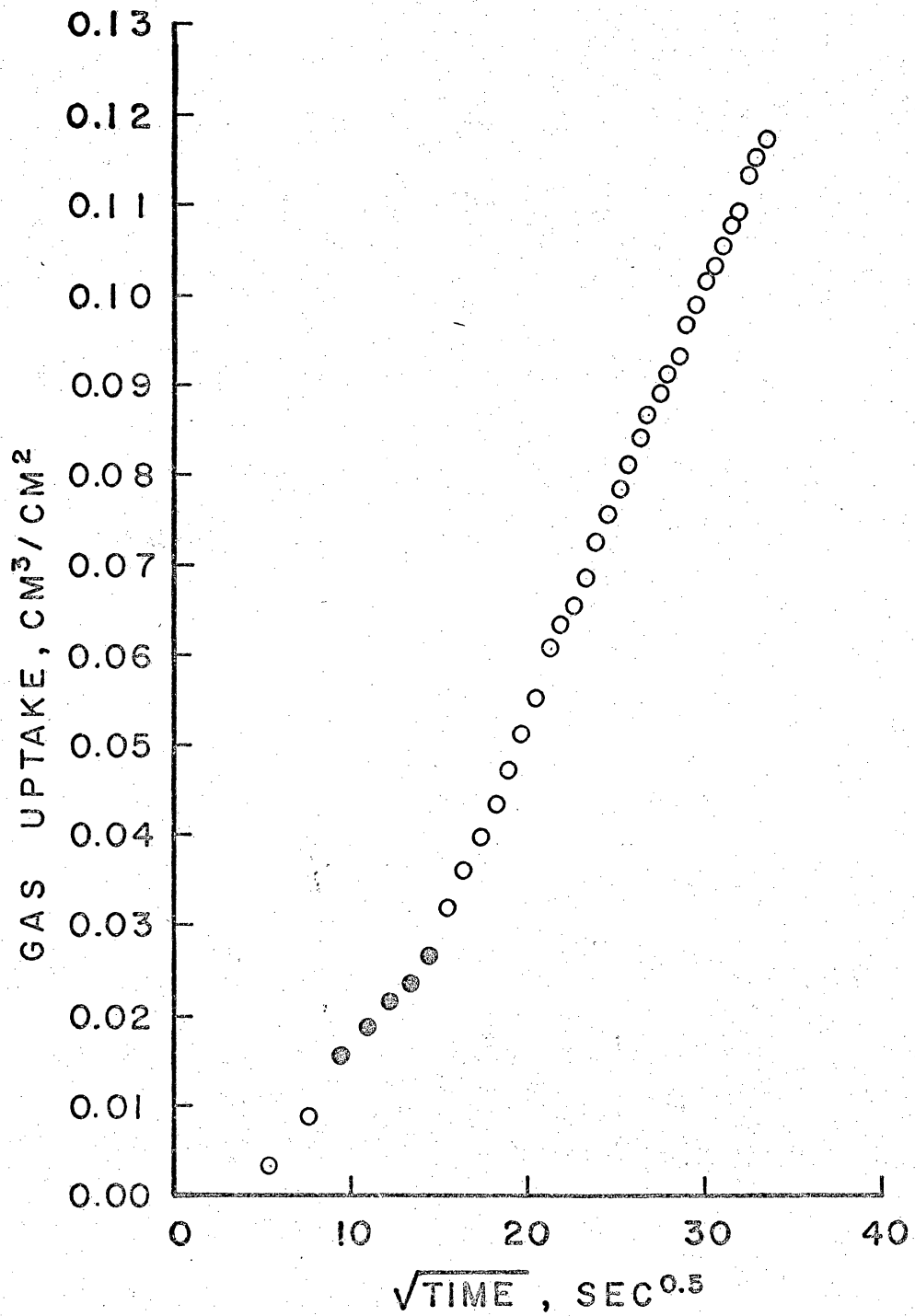


FIGURE 9. CARBON DIOXIDE UPTAKE IN WATER AT 635.30 MM HG
WITH ZERO INITIAL CONCENTRATION

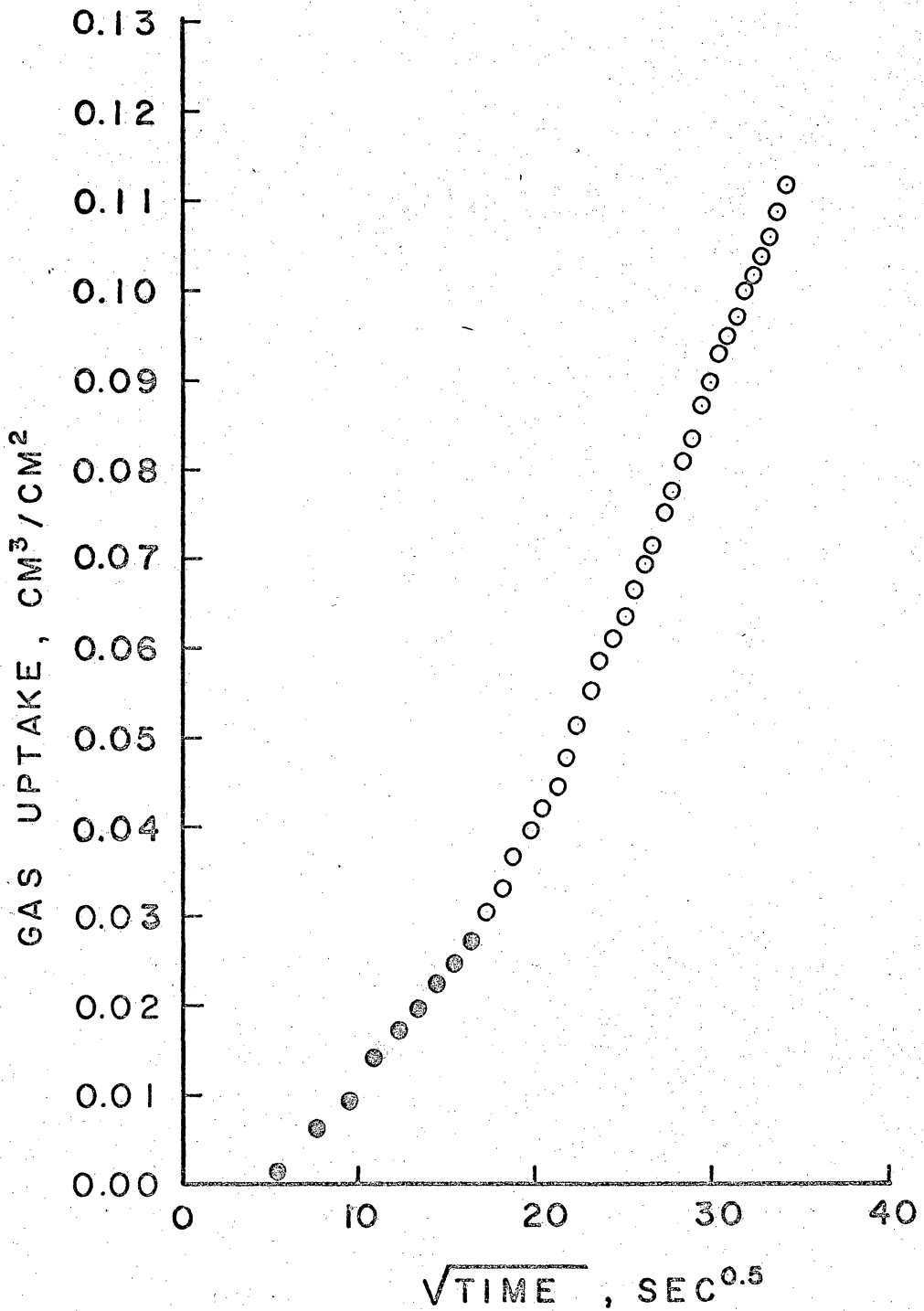


FIGURE 10. CARBON DIOXIDE UPTAKE IN WATER AT 606.30 MM HG
WITH ZERO INITIAL CONCENTRATION

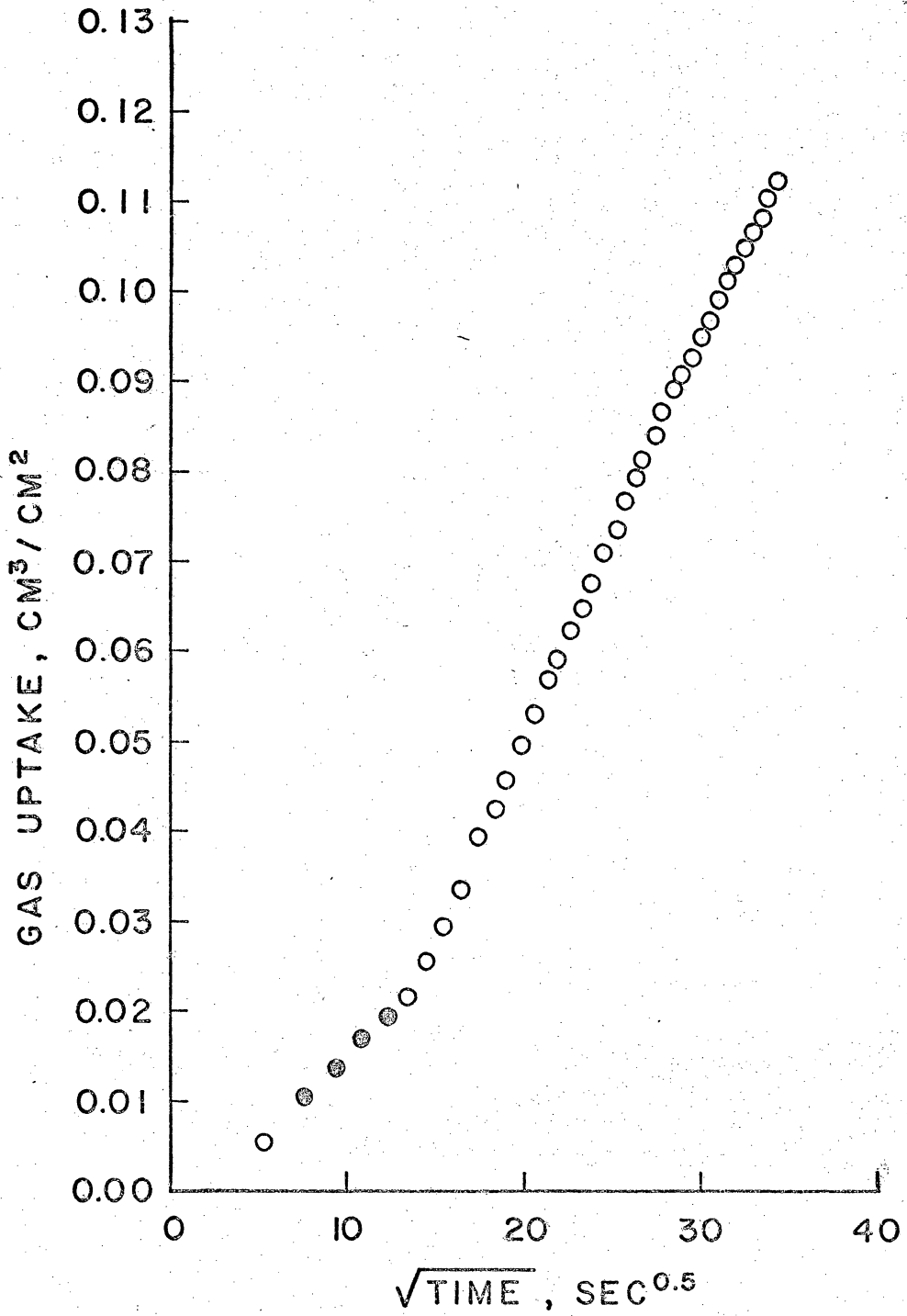


FIGURE 11. CARBON DIOXIDE UPTAKE IN WATER AT 532.00 MM HG
WITH ZERO INITIAL CONCENTRATION

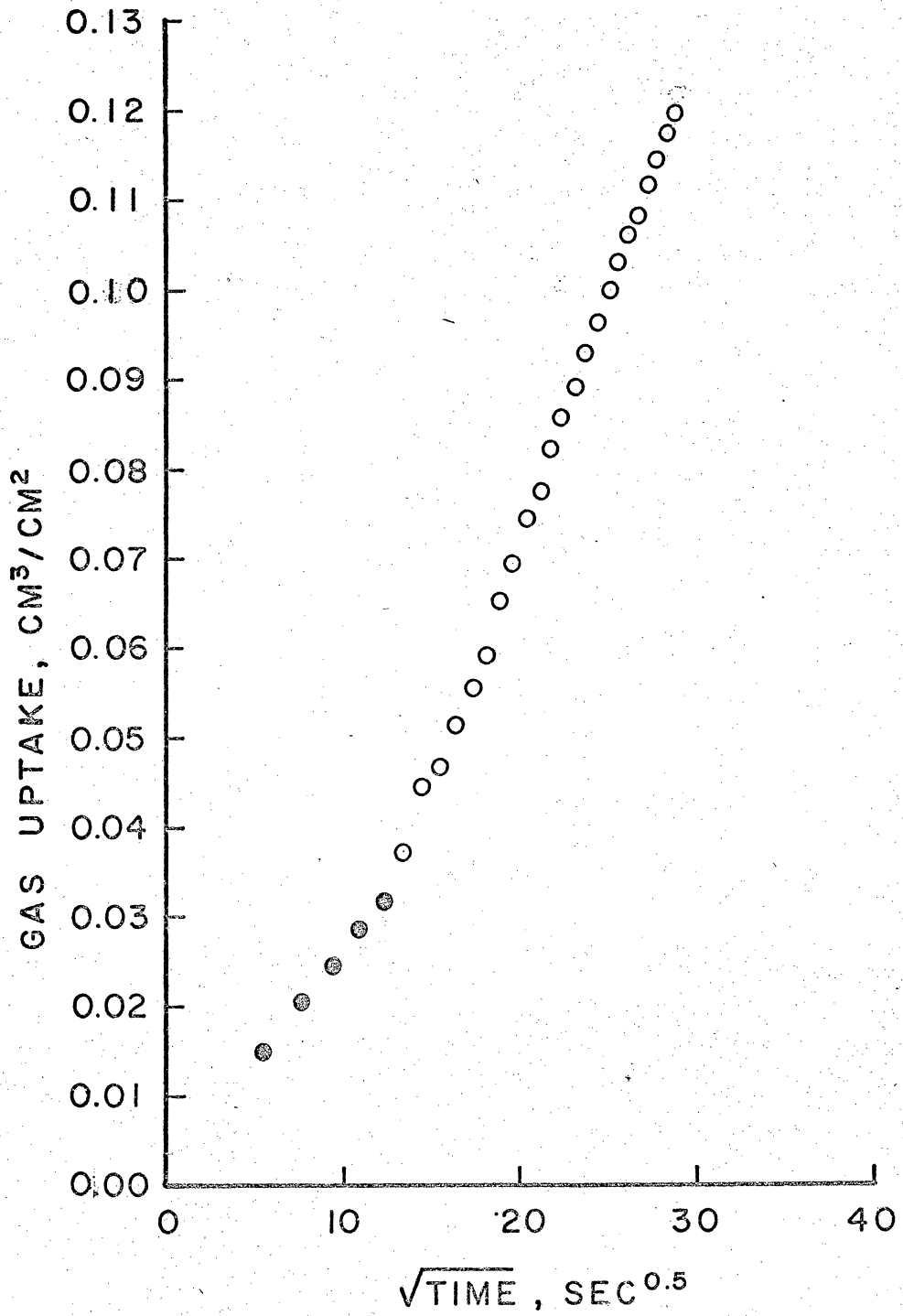


FIGURE 12. CARBON DIOXIDE UPTAKE IN WATER AT 622.00 MM HG
WITH ZERO INITIAL CONCENTRATION

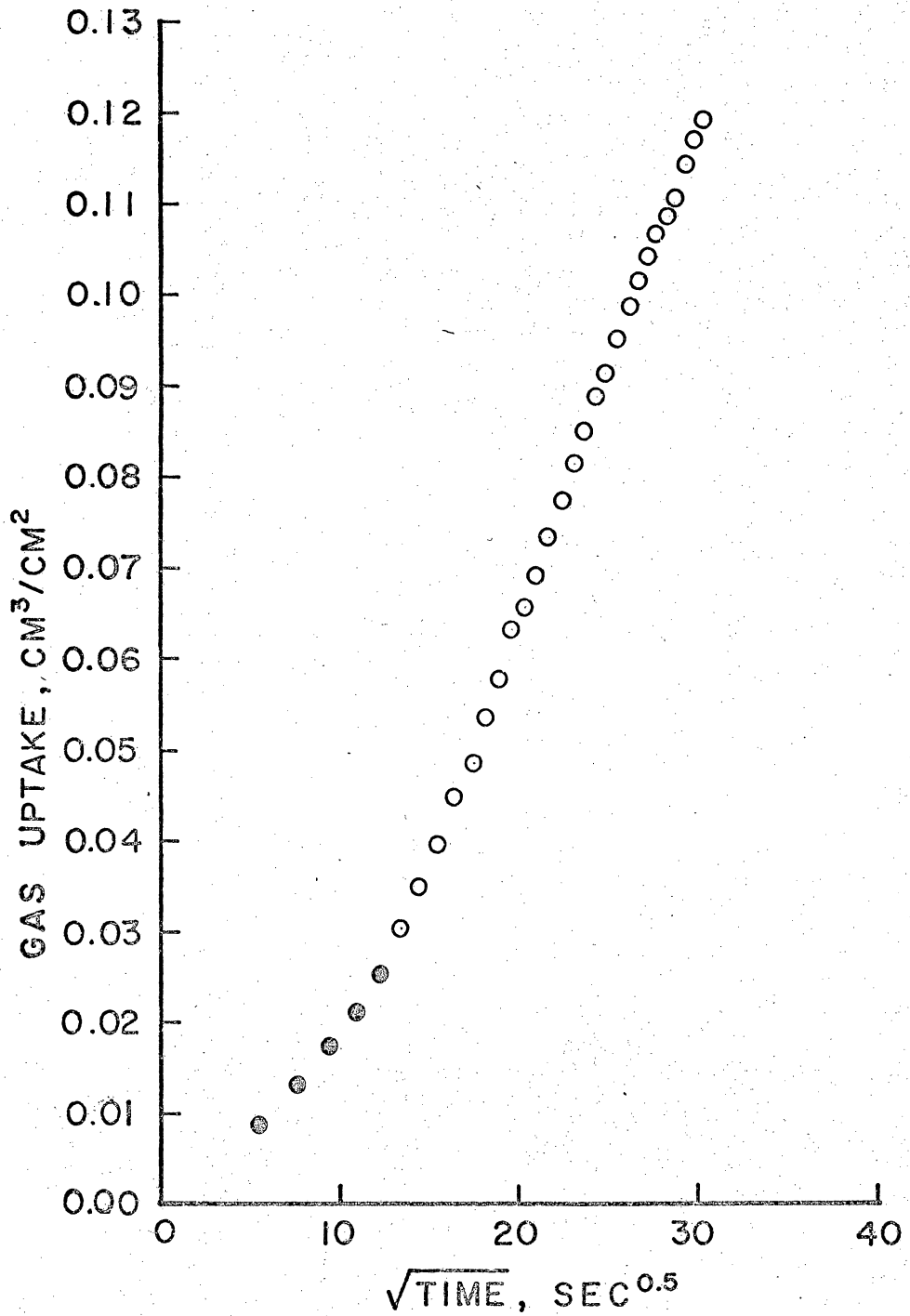


FIGURE 13. CARBON DIOXIDE UPTAKE IN WATER AT 631.40 MM HG
WITH ZERO INITIAL CONCENTRATION

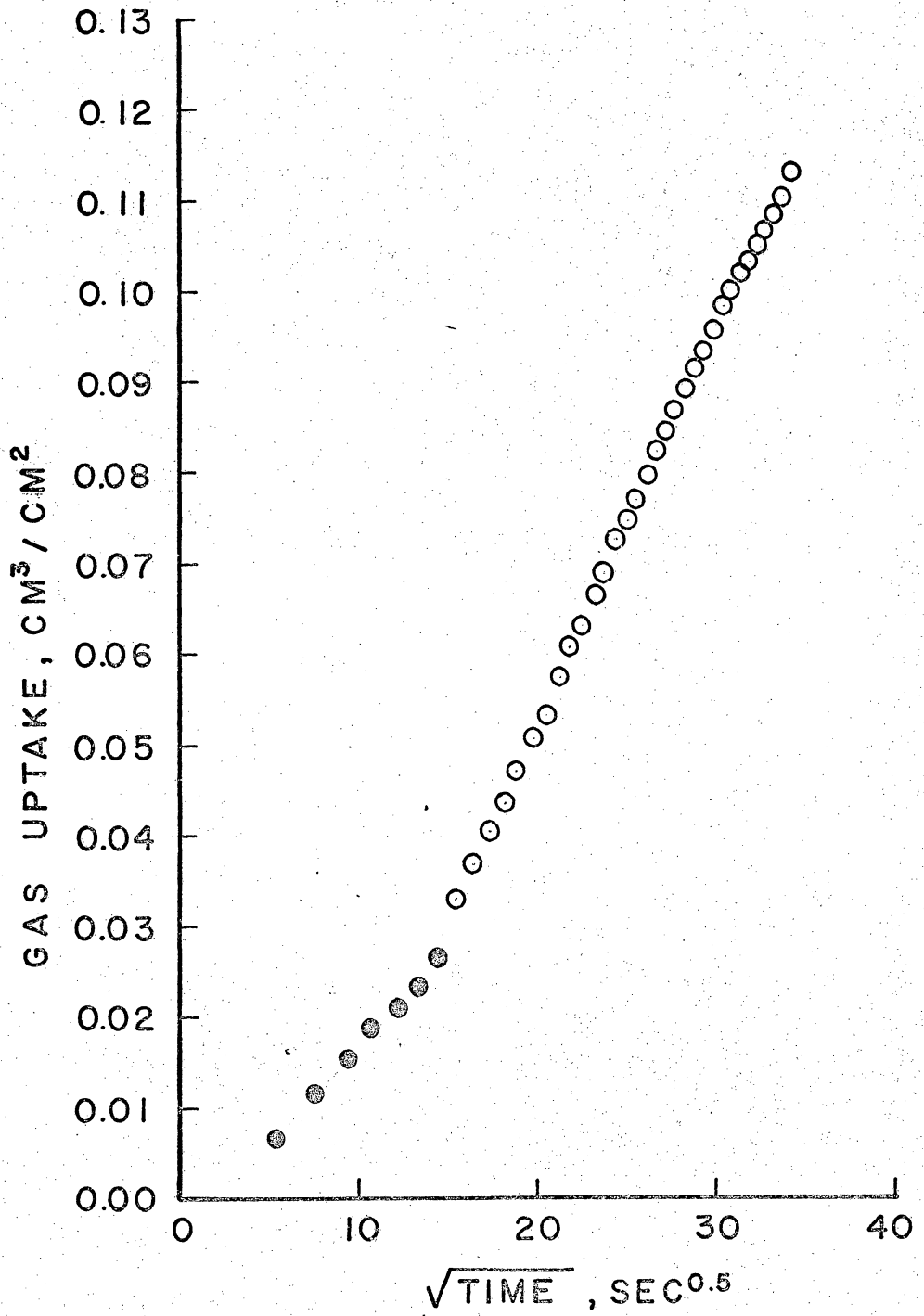


FIGURE 14. CARBON DIOXIDE UPTAKE IN WATER AT 625.30 MM HG
WITH ZERO INITIAL CONCENTRATION

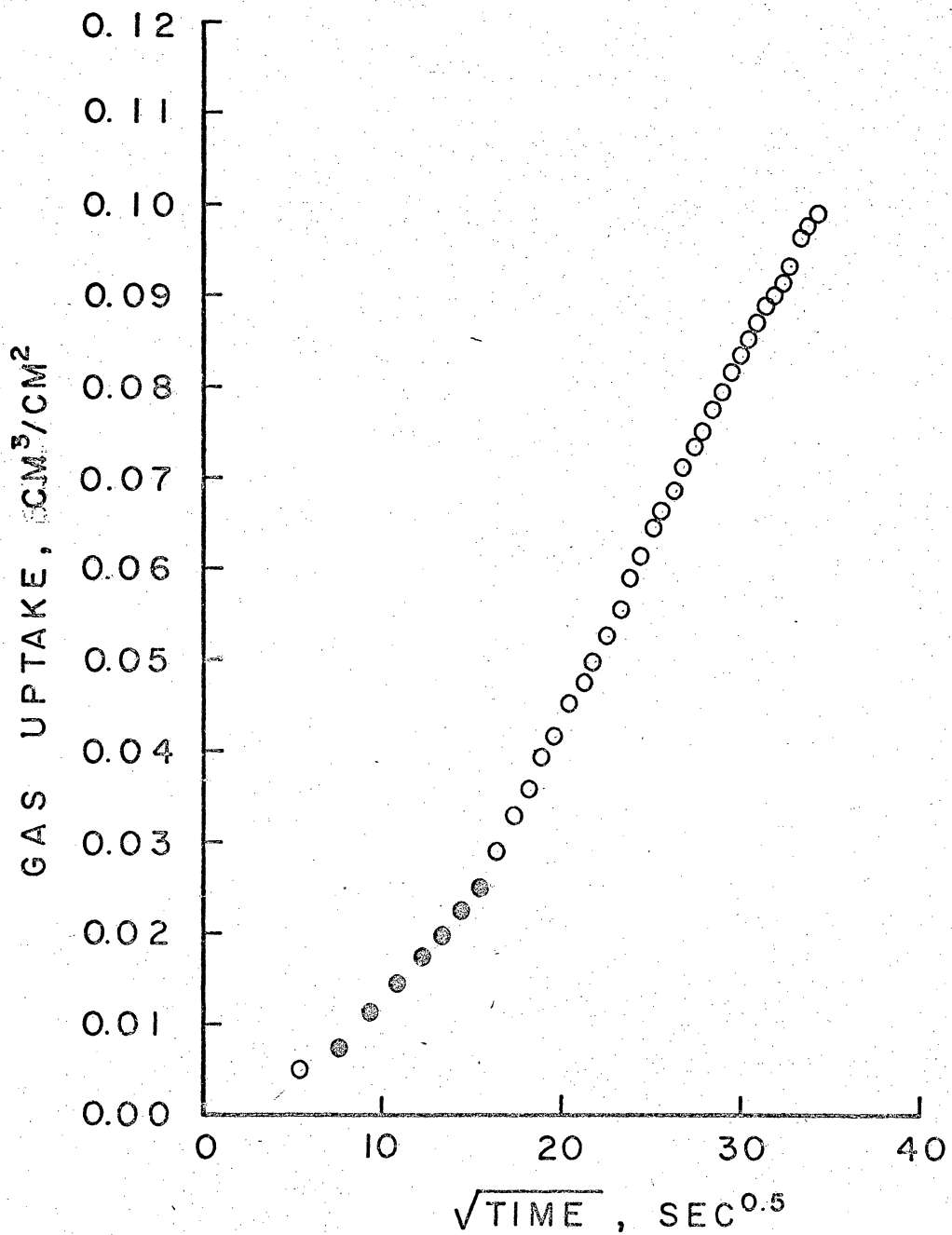


FIGURE 15. CARBON DIOXIDE UPTAKE IN WATER AT 623.30 MM HG
WITH ZERO INITIAL CONCENTRATION

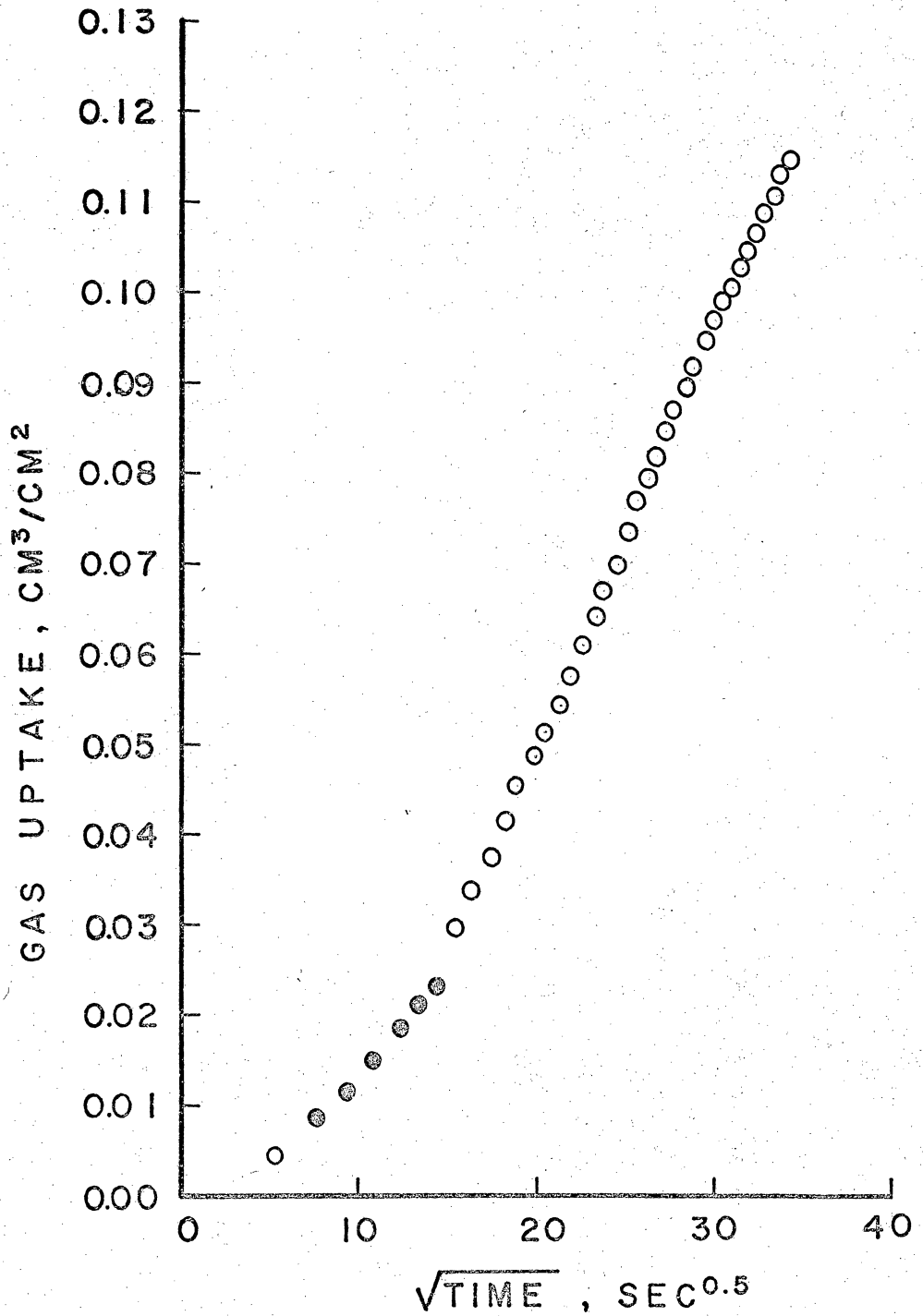


FIGURE 16. CARBON DIOXIDE UPTAKE IN WATER AT 643.30 MM HG
WITH ZERO INITIAL CONCENTRATION

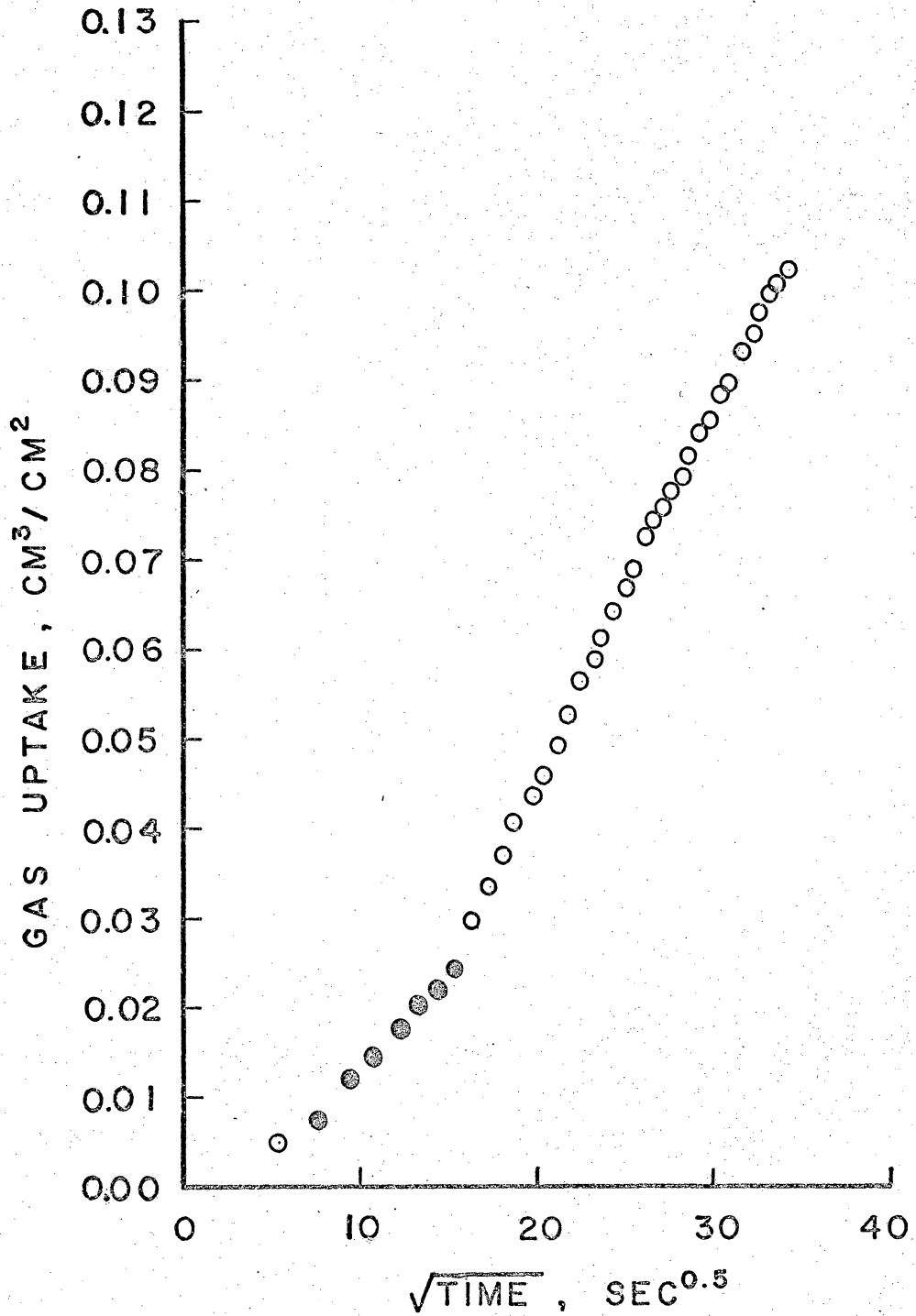


FIGURE 17. CARBON DIOXIDE UPTAKE IN WATER AT 644.20 MM HG
WITH ZERO INITIAL CONCENTRATION

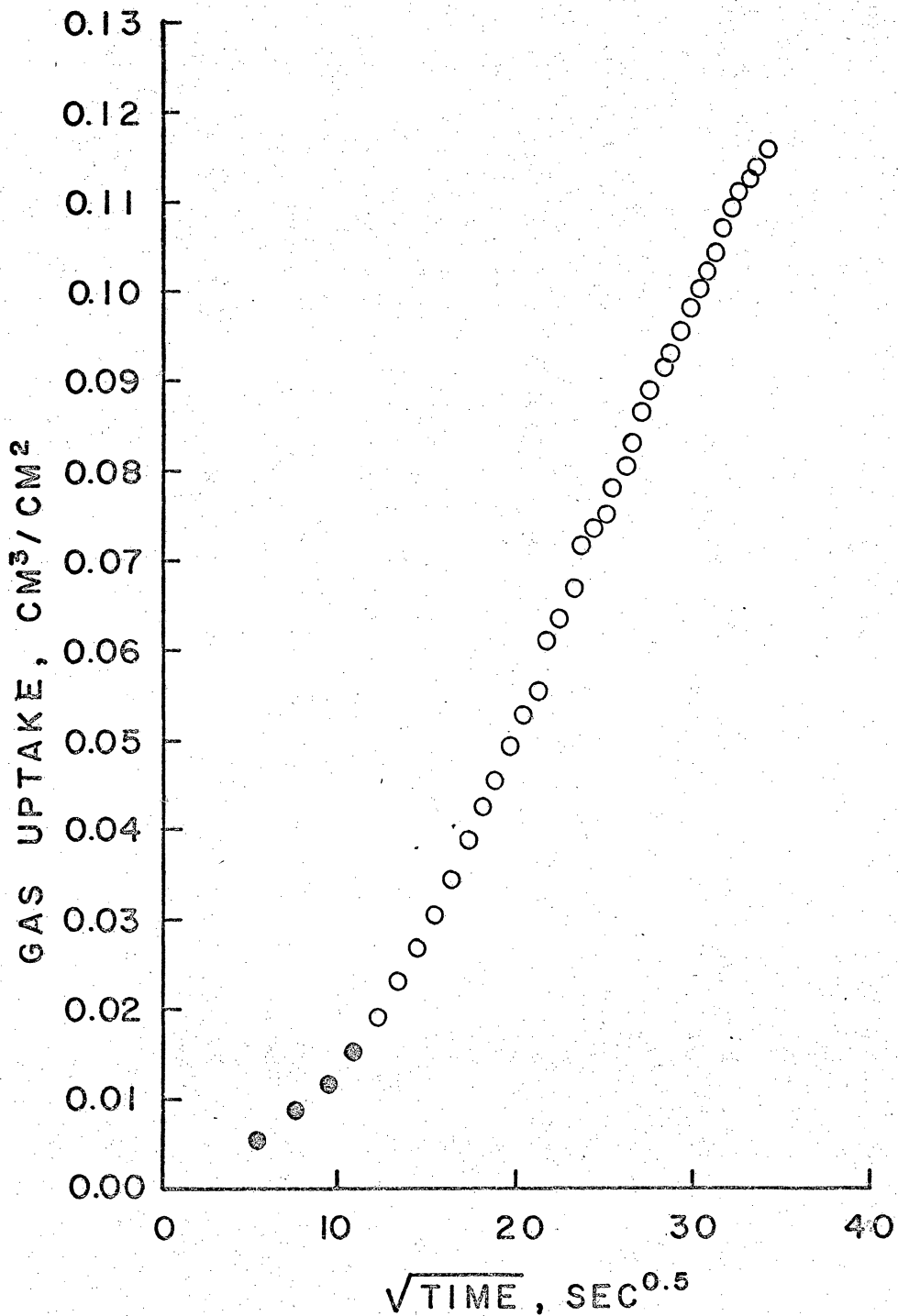


FIGURE 18. CARBON DIOXIDE UPTAKE IN WATER AT 672.00 MM HG
WITH ZERO INITIAL CONCENTRATION

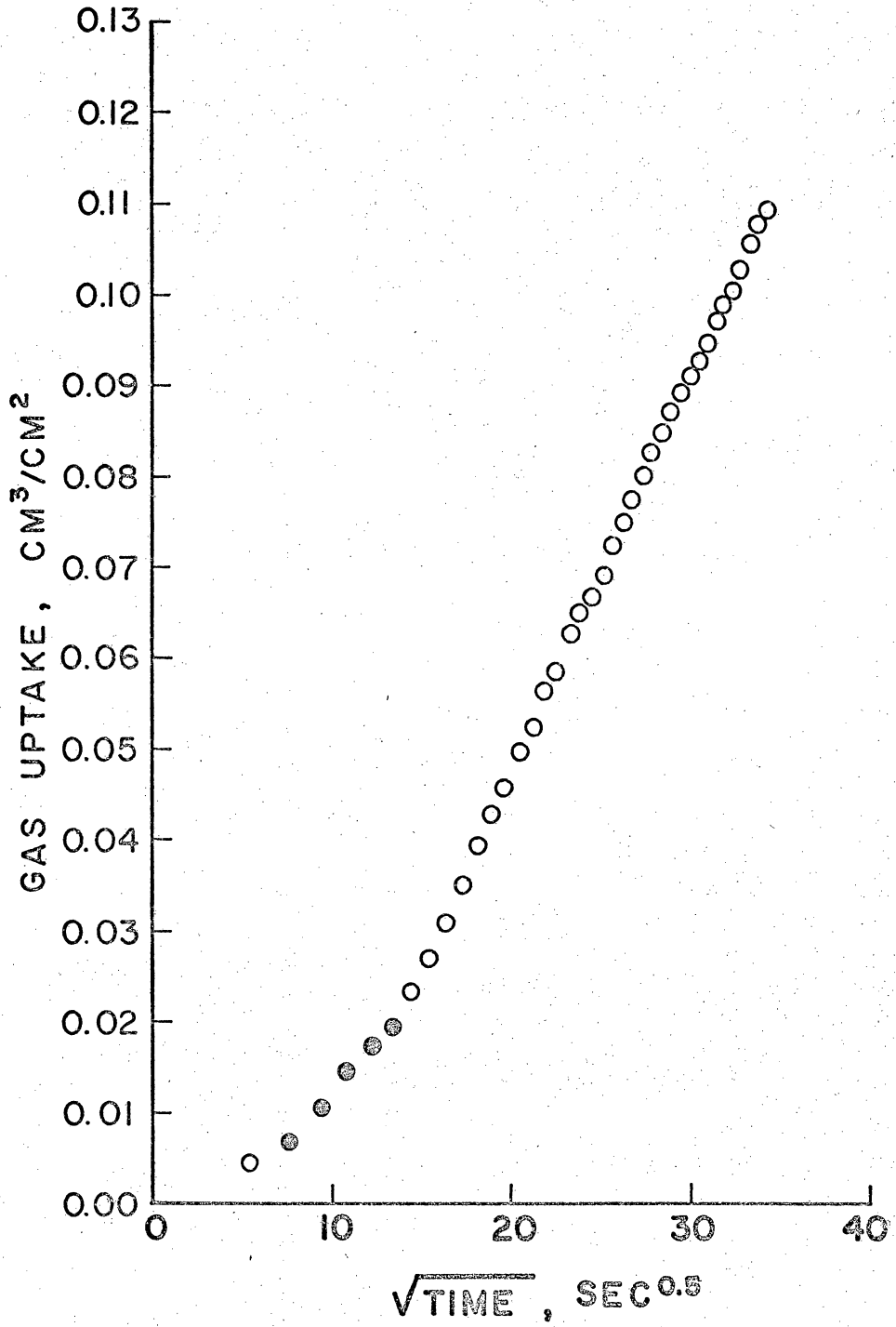


FIGURE 19. CARBON DIOXIDE UPTAKE IN WATER AT 699.40 MM HG
WITH ZERO INITIAL CONCENTRATION

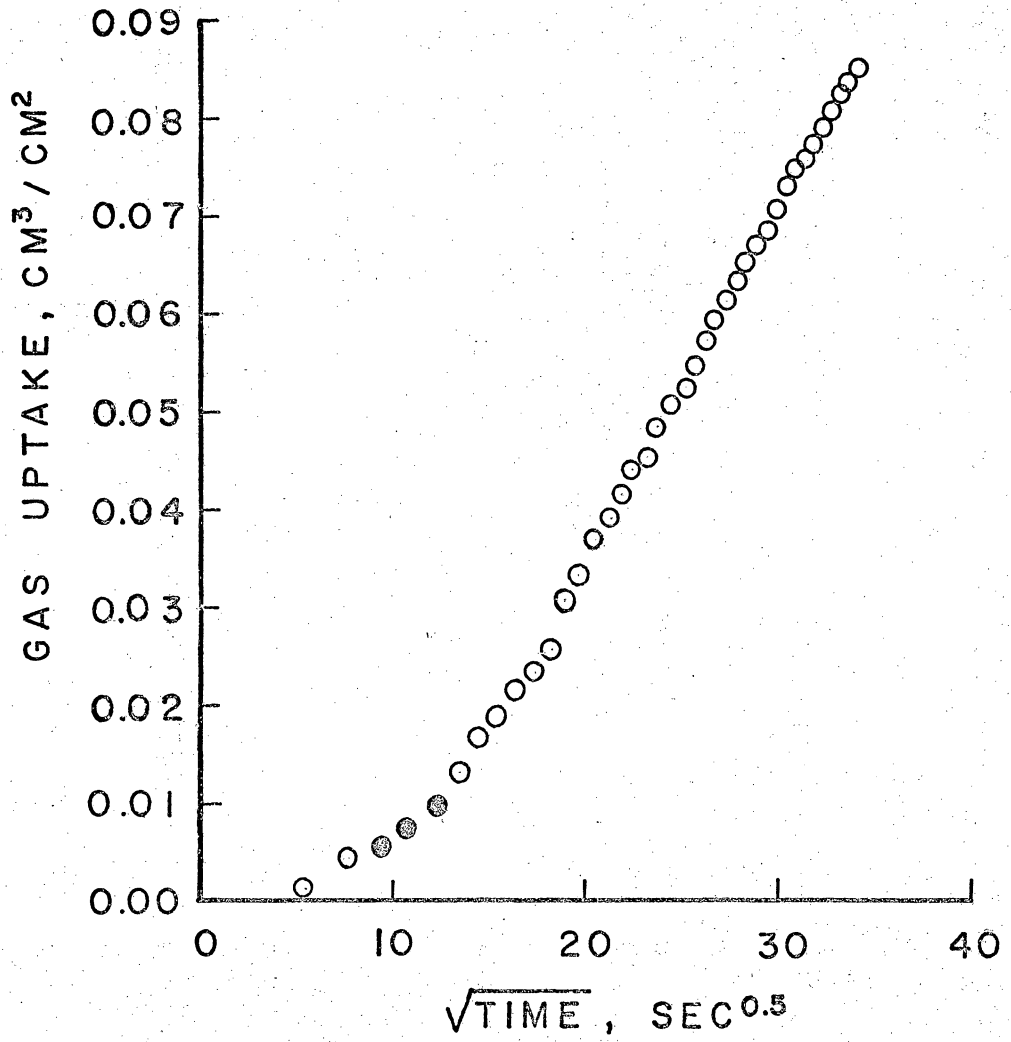


FIGURE 20. CARBON DIOXIDE UPTAKE IN WATER AT 593.30 MM HG
WITH ZERO INITIAL CONCENTRATION

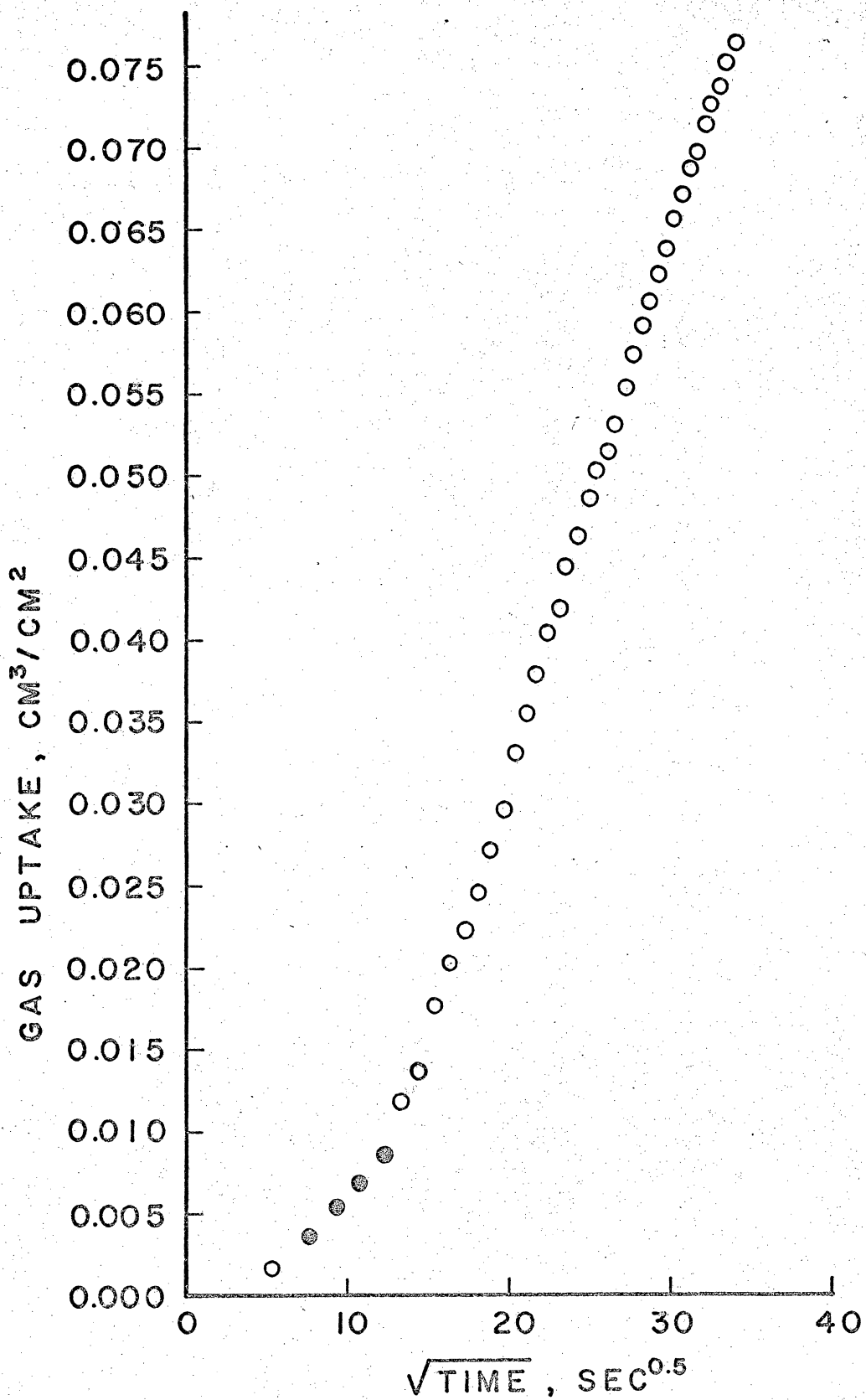


FIGURE 21. CARBON DIOXIDE UPTAKE IN WATER AT 594.20 MM HG
WITH ZERO INITIAL CONCENTRATION

cases, the first one or two points in the initial region were not linear. The solid dots represent the data points used in a least squares solution for the slope determination of the region. The second linear region is represented by more data points than the first linear section. The least squares solution for the slope of the higher linear region used all the points above the jump.

A summary of the controlling parameters and the diffusion coefficients determined for the low and high linear regions is given in Table VI. To clarify this data, the diffusion coefficients are presented in Tables VII and VIII as ascending functions of operating pressure and evacuation pressure respectively. No relationship between the chosen parameters and the diffusion coefficient is apparent.

Tests with Specific Initial Concentration of Carbon Dioxide. A total of 14 tests were made using initial carbon dioxide concentrations.

Tests 1 through 7 were performed at an approximate pressure increment of 150 millimeters of mercury. Data for these tests are given in the Appendix, Tables XXV through XXXI. The absorption curves for these tests are given in Figures 22 through 28 and have the same general shape as those with zero initial concentration. However, in these tests jumps appear at two positions. The first jump generally corresponds to the change of the slope to a higher value as in the zero initial concentration tests. The second jump appears in the higher linear region and usually follows a slight leveling of the curve. However, the curve returns to the same high slope obtained after the first jump.

TABLE VI

Diffusion Coefficients for Absorption of Carbon Dioxide in
Water at 25°C with Zero Initial Concentration

Test number	Atmospheric pressure mm Hg	Vacuum applied Δ mm Hg	Evacuation pressure mm Hg	Operating pressure mm Hg	Low Diffusion Coefficient $\text{cm}^2/\text{sec} \times 10^5$	High Diffusion Coefficient $\text{cm}^2/\text{sec} \times 10^5$	Purge Gas
14	698.40	620.00	78.40	572.40	1.52	5.80	N ₂
13	705.70	620.00	85.70	615.70	1.39	6.01	N ₂
7	710.30	540.00	170.30	635.30	1.31	4.50	Ar
15	706.30	620.00	86.30	606.30	1.21	5.60	N ₂
4	712.00	550.00	162.00	532.00	1.17	5.30	N ₂
3	702.00	660.00	42.00	622.00	1.16	6.18	N ₂
2	701.40	660.00	41.40	631.40	1.14	5.79	N ₂
8	710.30	540.00	170.30	625.30	1.08	3.73	N ₂
12	713.30	500.00	213.30	623.30	0.989	3.18	N ₂
10	713.30	560.00	153.30	643.30	0.980	4.03	N ₂
9	714.20	520.00	194.20	644.20	0.880	3.17	N ₂
5	712.00	540.00	172.00	672.00	0.862	3.72	N ₂
1	699.40	520.00	179.40	699.40	0.844	3.02	N ₂
11	713.30	500.00	213.30	593.30	0.536	2.92	N ₂
6	714.20	520.00	194.20	594.20	0.388	2.29	Ar

TABLE VII

Diffusion Coefficients as a Function of Operating Pressure

Test number	Operating pressure mm Hg	Low Diffusion Coefficient $\text{cm}^2/\text{sec} \times 10^5$
4	532.00	1.17
14	572.40	1.52
11	593.30	0.536
6	594.20	0.388
15	606.30	1.21
13	615.70	1.39
3	622.00	1.16
12	623.30	0.989
8	625.30	1.08
2	631.40	1.14
7	635.30	1.31
10	643.30	0.980
9	644.20	0.880
5	672.00	0.862
1	699.40	0.844

TABLE VIII

Diffusion Coefficients for Zero Initial
Concentration as a Function of Evacuation Pressure

Test number	Evacuation pressure mm Hg	Low Diffusion Coefficient $\text{cm}^2/\text{sec} \times 10^5$
2	41.40	1.14
3	42.00	1.16
14	78.40	1.52
13	85.70	1.39
15	86.30	1.21
10	153.30	0.980
4	162.00	1.17
7	170.30	1.31
8	170.30	1.08
5	172.00	0.862
1	179.40	0.844
9	194.20	0.880
6	194.20	0.388
11	213.30	0.536
12	213.30	0.989

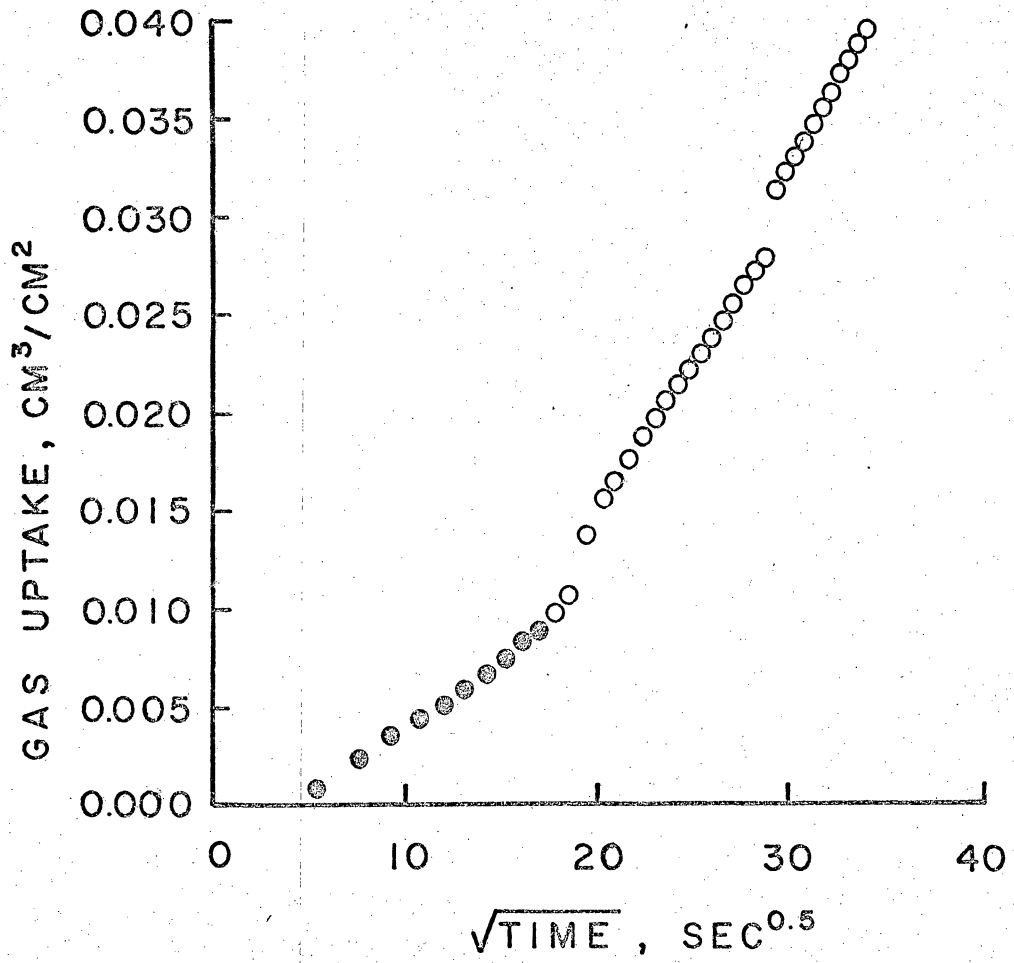


FIGURE 22. CARBON DIOXIDE UPTAKE IN WATER AT 687.80 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

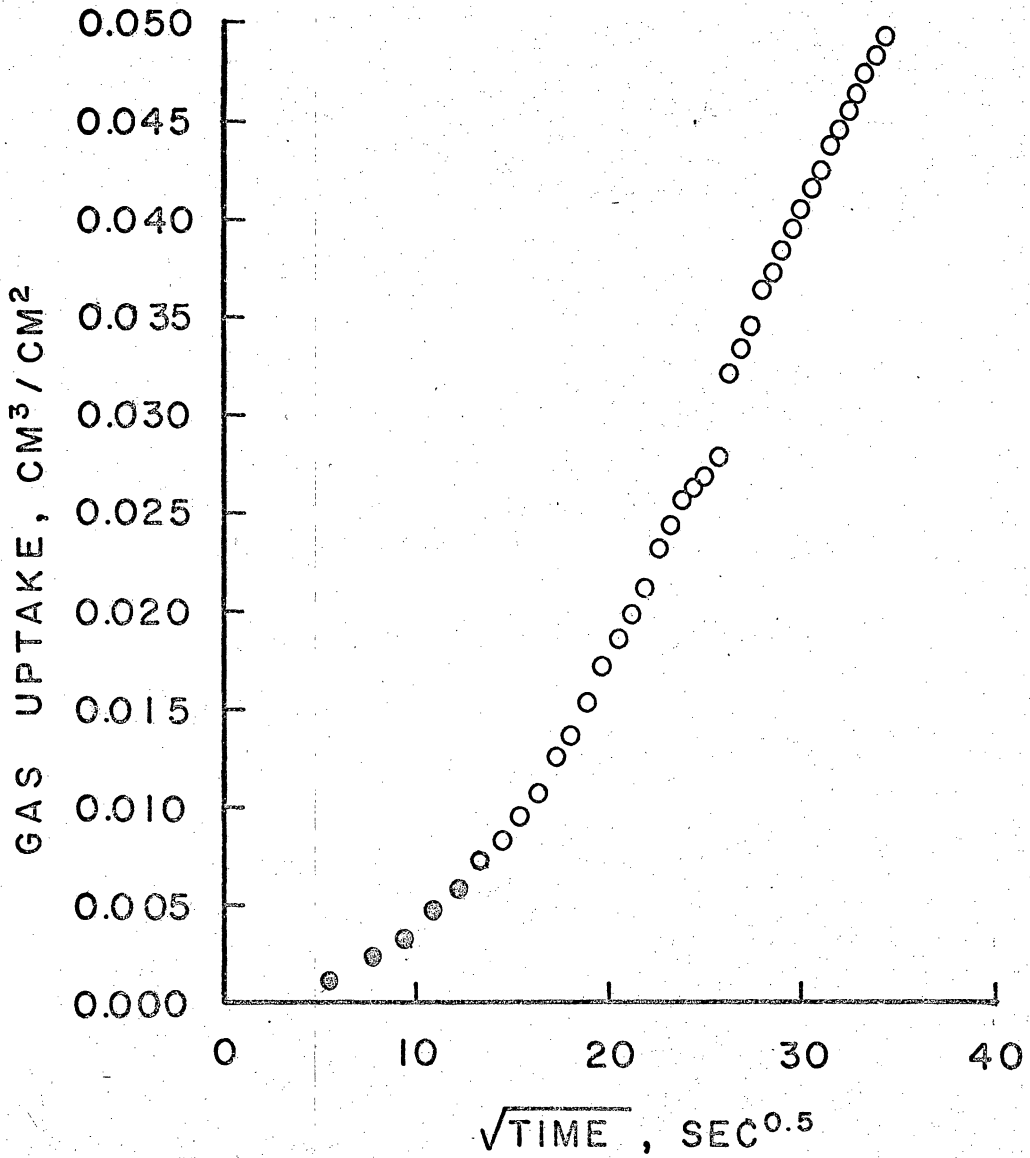


FIGURE 23. CARBON DIOXIDE UPTAKE IN WATER AT 703.90 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

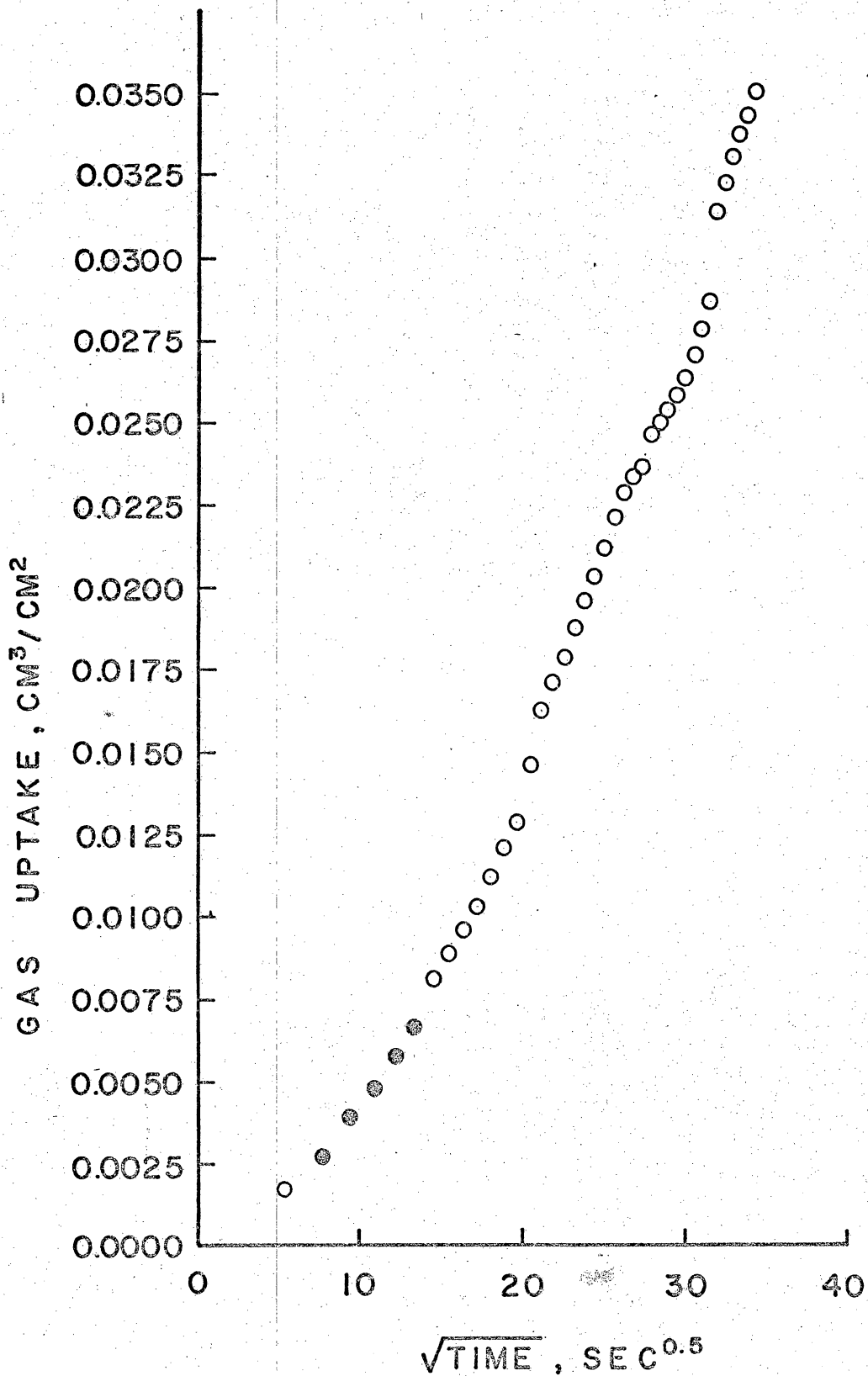


FIGURE 24. CARBON DIOXIDE UPTAKE IN WATER AT 700.00 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

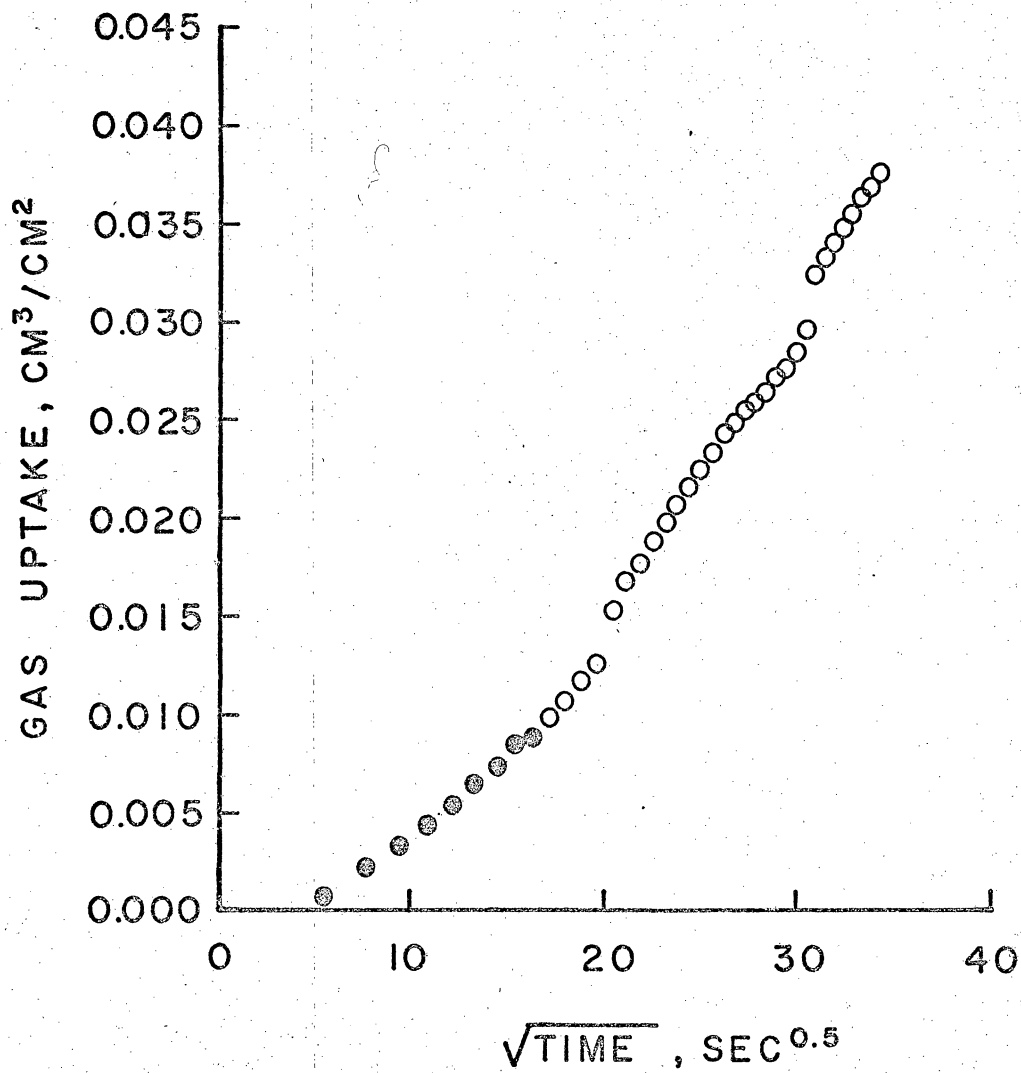


FIGURE 25. CARBON DIOXIDE UPTAKE IN WATER AT 706.90 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

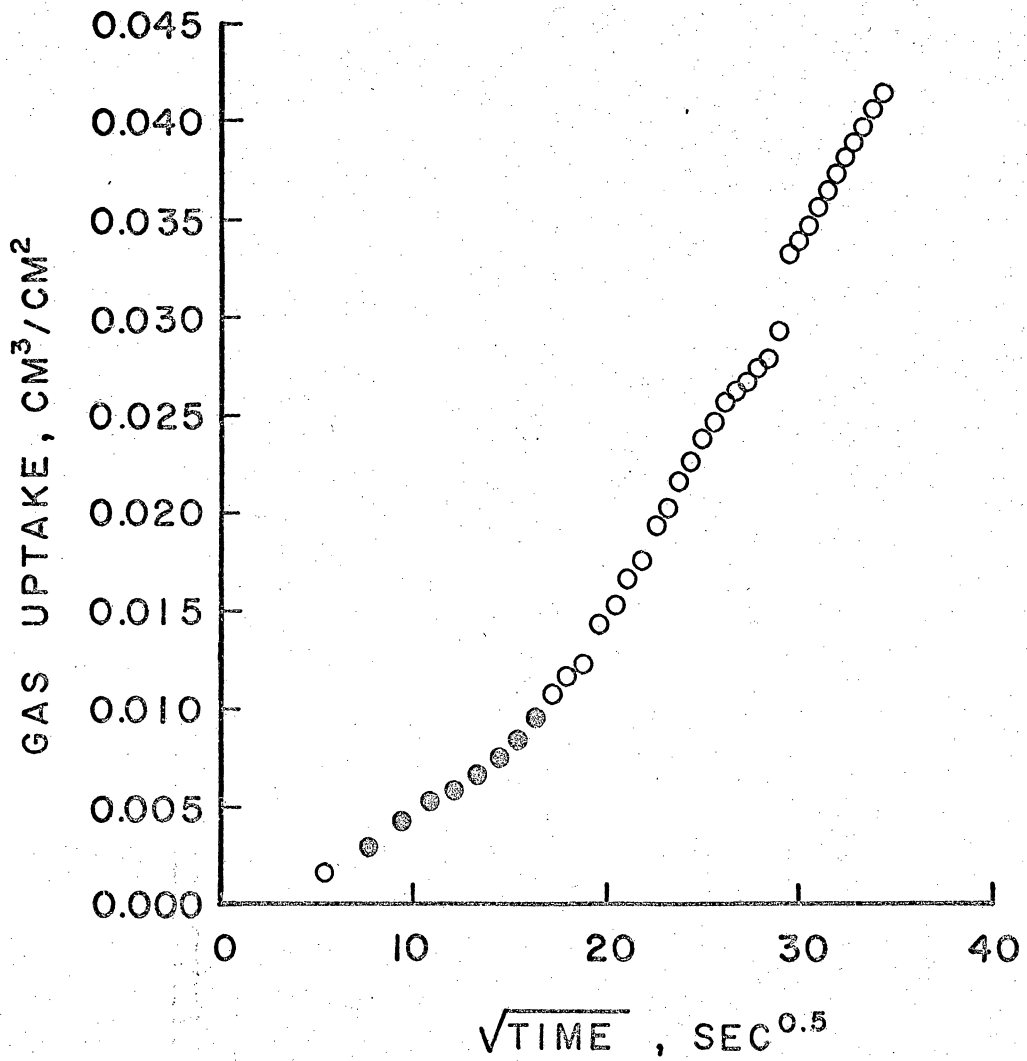


FIGURE 26. CARBON DIOXIDE UPTAKE IN WATER AT 714.60 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

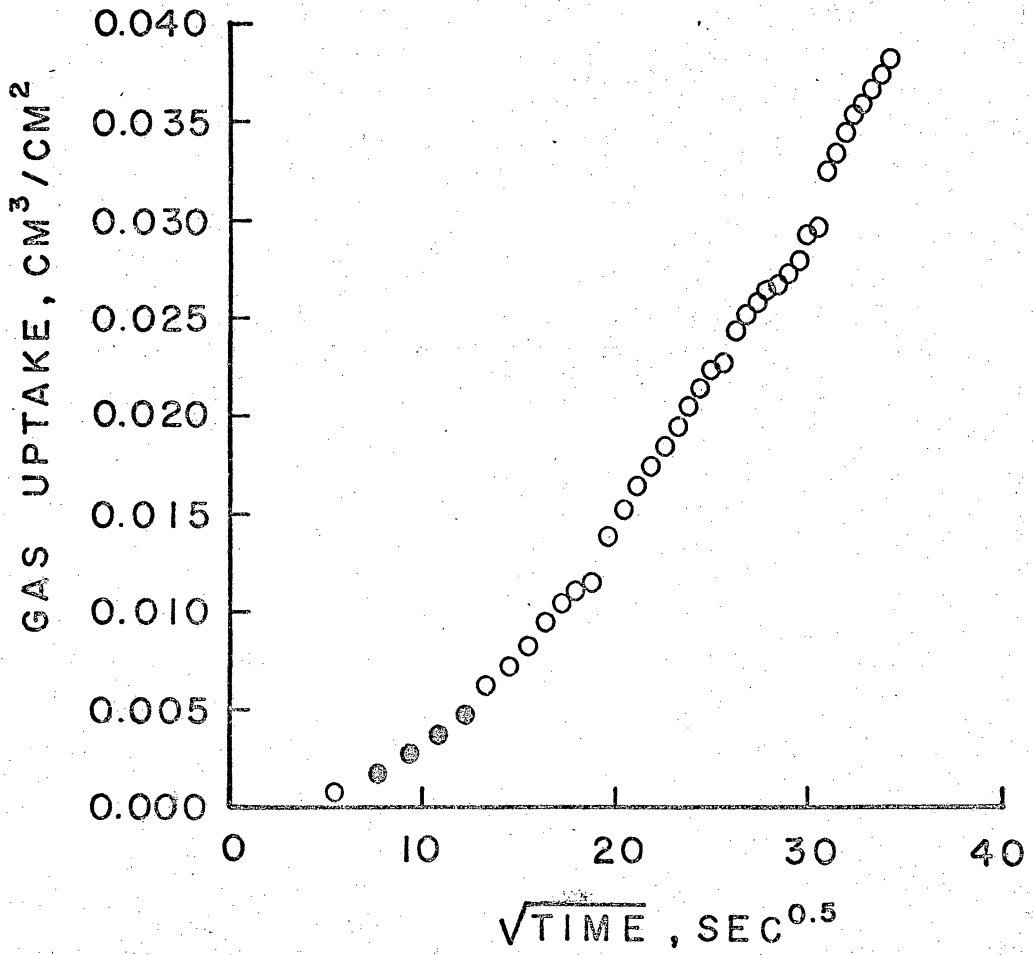


FIGURE 27. CARBON DIOXIDE UPTAKE IN WATER AT 708.80 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

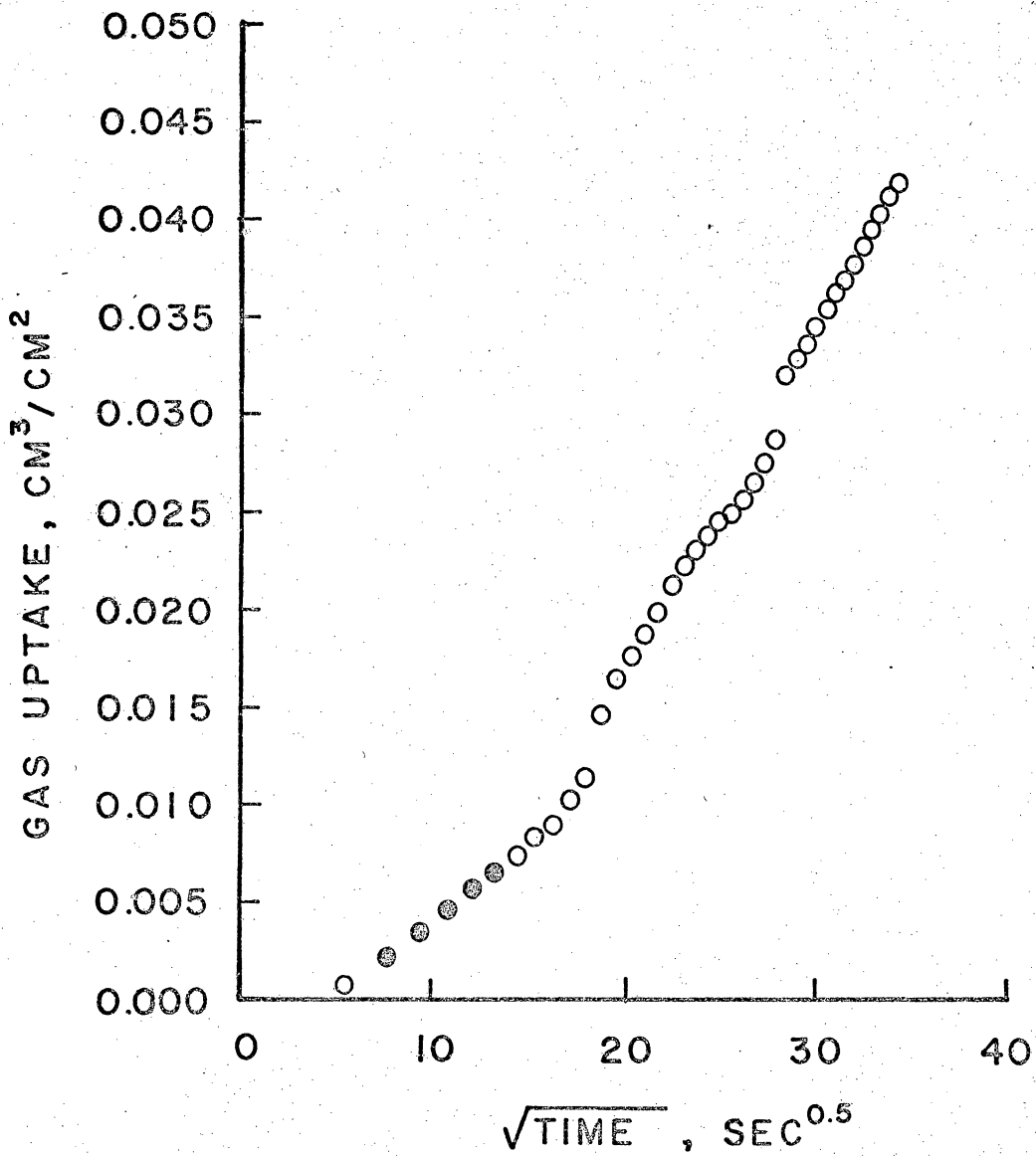


FIGURE 28. CARBON DIOXIDE UPTAKE IN WATER AT 714.80 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

The operating pressure, atmospheric pressure, and saturation pressure were varied slightly in these seven tests. The parameter values and the corresponding diffusion coefficients are presented in Table IX. The data are in good agreement including the lowest value of 1.88 for Test 3 and in excellent agreement for the remaining six tests, the values ranging from 1.94 to 2.11. Again, the solid dots represent the values used in obtaining the slopes.

Tests 8 through 14 were made at higher pressure increments. Two tests each were performed at approximately 250, 300, and 350 millimeters of mercury and one at 200 millimeters of mercury. Data for Tests 8 through 14 are given in the Appendix in Tables XXXII through XXXVIII. Figures 29 through 35 give the absorption curves for the higher pressure increment tests. The shape of these curves is identical to those for Tests 1 through 7 except for a less pronounced jump in the higher slope range for Tests 12 through 14. Again, referring to Table IX, the results are in good agreement but slightly lower than most of the values for Tests 1 through 7. The range for Tests 8 through 14 is from 1.66 to 1.95. Excluding the single low value of 1.66, the range would be 1.80 to 1.95. The solid dots represent the values used in determining the slopes. It should be noted that in some cases the initial points are used and in other cases they are ignored. The choice of what points to use was based on the behavior of the initial linear region. That is, if there appeared to be an unusual dip (such as the test at 699.55 millimeters of mercury, Figure 27) after the first several points, then the initial points were used.

TABLE IX

Diffusion Coefficients for Absorption of Carbon Dioxide in
Water at 25°C with Specific Initial Concentration

Test number	Atmospheric pressure mm Hg	Saturation pressure mm Hg	Operating pressure mm Hg	Pressure increment Δ mm Hg	Low Diffusion Coefficient $\text{cm}^2/\text{sec} \times 10^5$	High Diffusion Coefficient $\text{cm}^2/\text{sec} \times 10^5$
1	707.80	557.80	687.80	130.00	2.11	15.10
6	712.40	565.90	703.90	138.00	2.09	22.00
3	708.00	558.00	700.00	142.00	1.88	7.80
5	512.40	564.40	706.90	142.50	1.99	9.89
4	708.60	568.60	714.60	146.00	2.00	13.60
7	710.80	559.80	708.80	149.00	2.07	9.76
2	704.80	554.80	714.80	160.00	2.04	10.00
8	708.80	508.00	709.80	201.80	1.94	8.50
9	708.80	508.80	736.80	228.00	1.84	8.54
10	707.40	458.90	699.55	240.65	1.80	8.75
11	708.80	458.50	704.00	245.50	1.86	8.75
12	708.00	409.00	698.00	289.00	1.66	8.71
13	710.00	364.00	705.50	341.50	1.94	9.94
14	710.00	366.00	712.00	346.00	1.95	9.02
Average value					1.95	

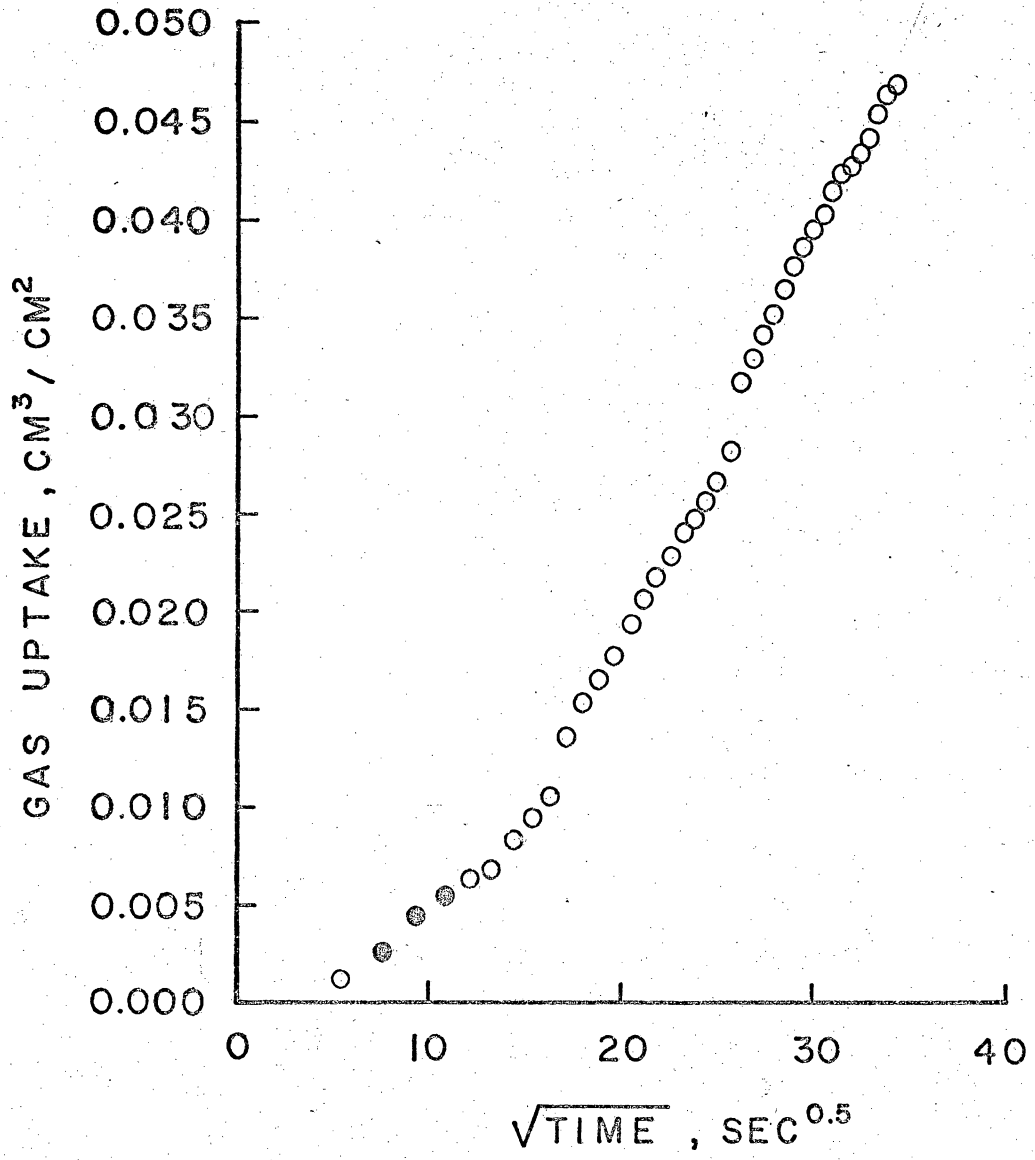


FIGURE 29. CARBON DIOXIDE UPTAKE IN WATER AT 709.80 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

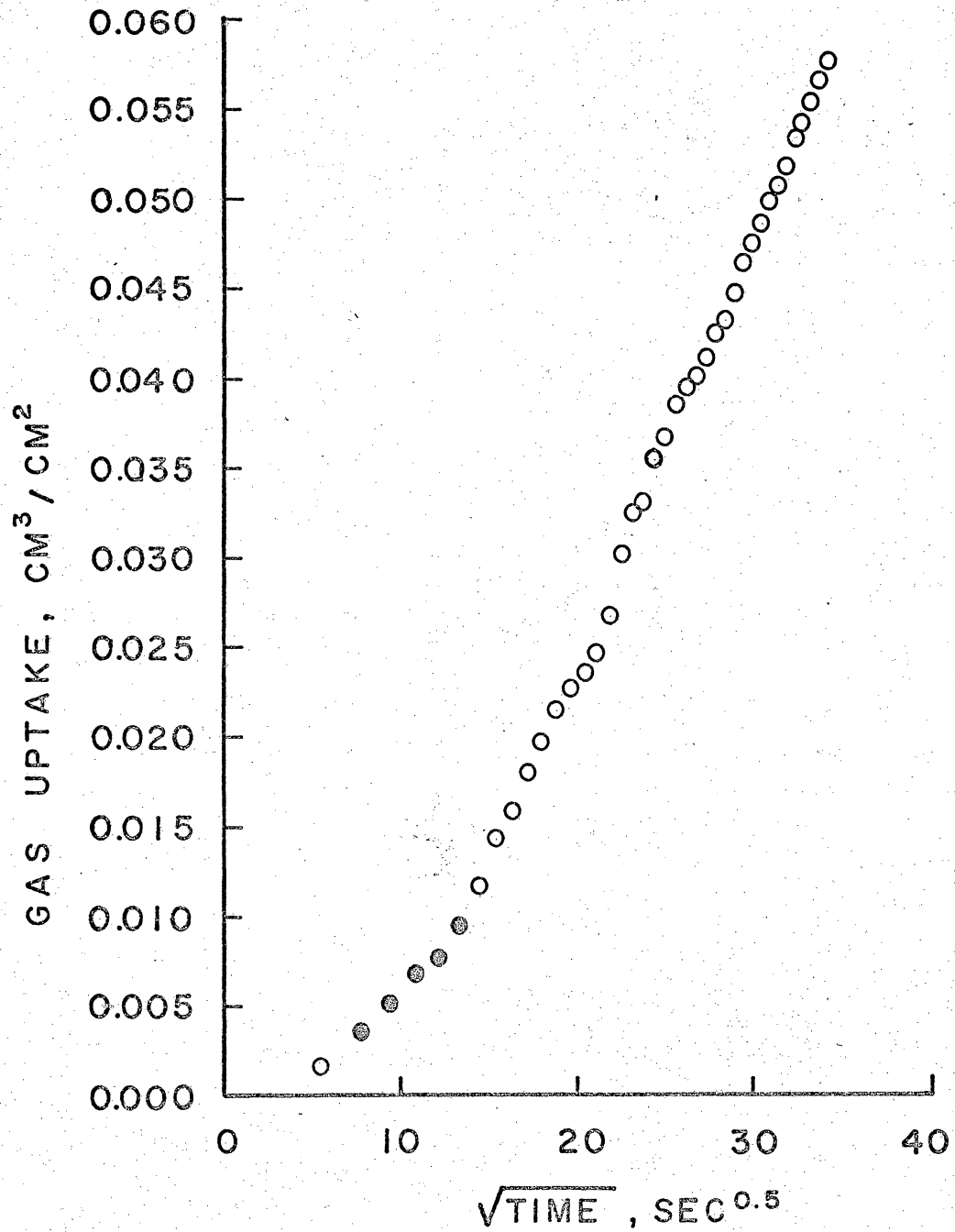


FIGURE 30. CARBON DIOXIDE UPTAKE IN WATER AT 736.80 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

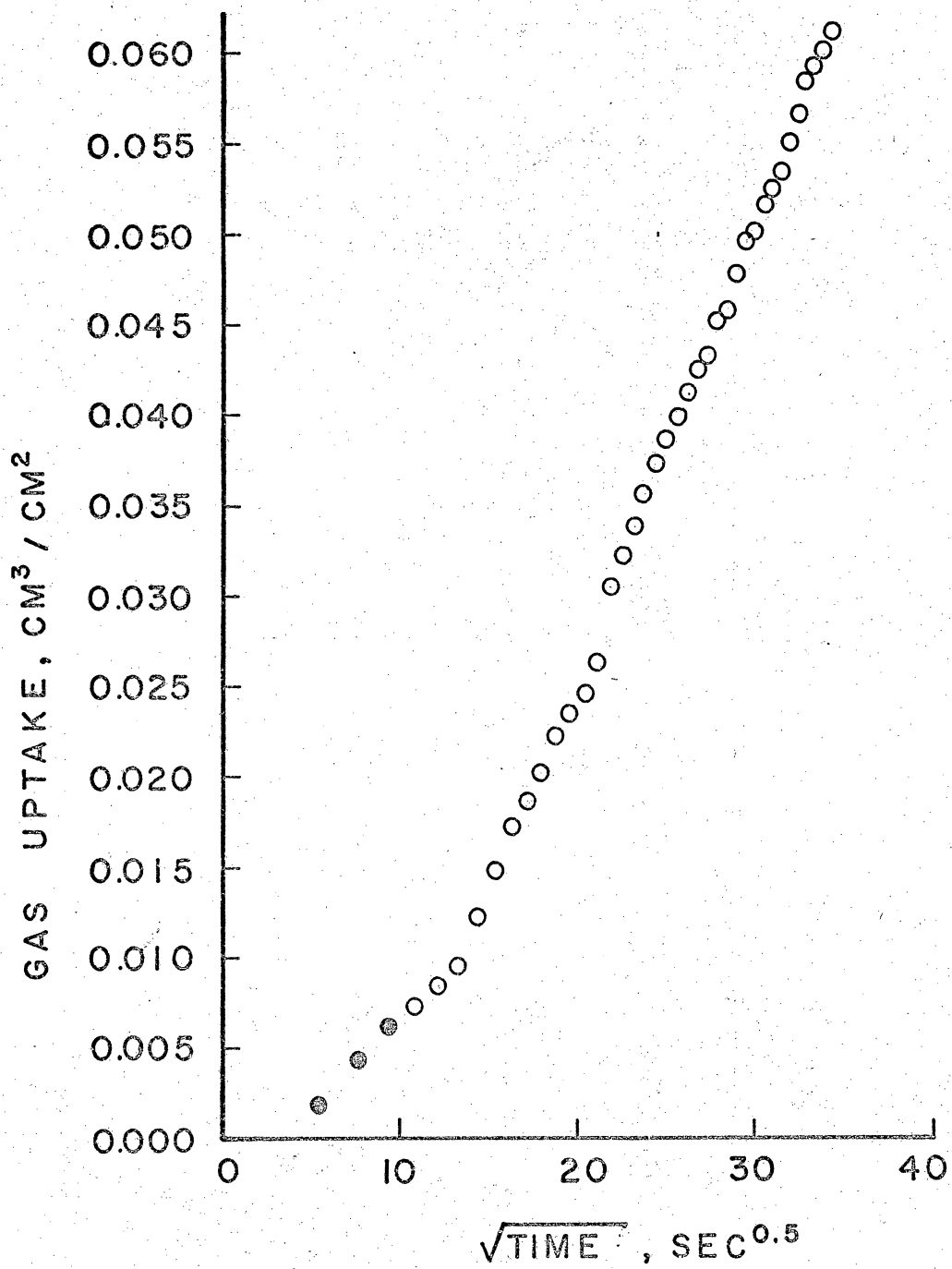


FIGURE 31. CARBON DIOXIDE UPTAKE IN WATER AT 699.55 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

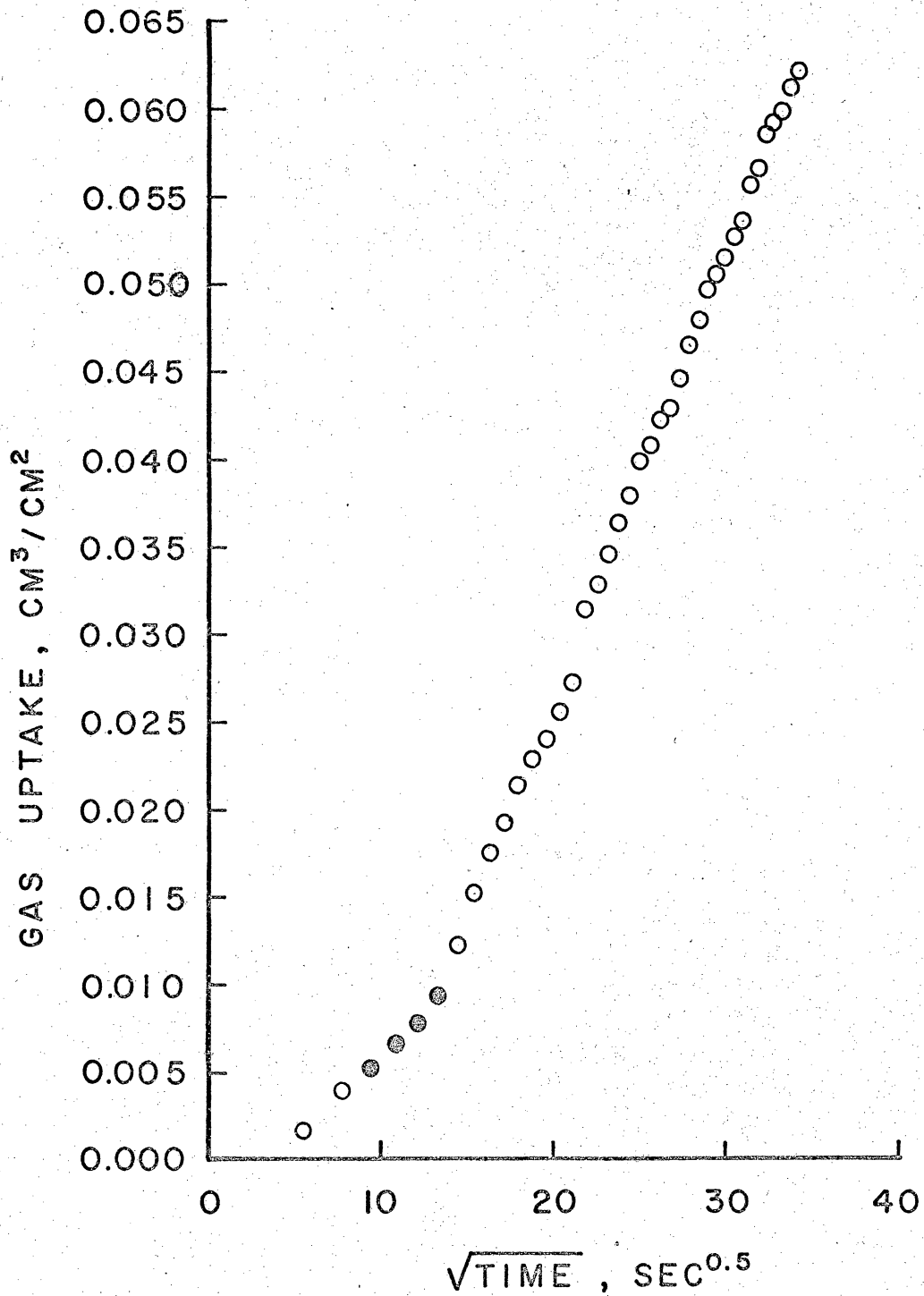


FIGURE 32. CARBON DIOXIDE UPTAKE IN WATER AT 704.00 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

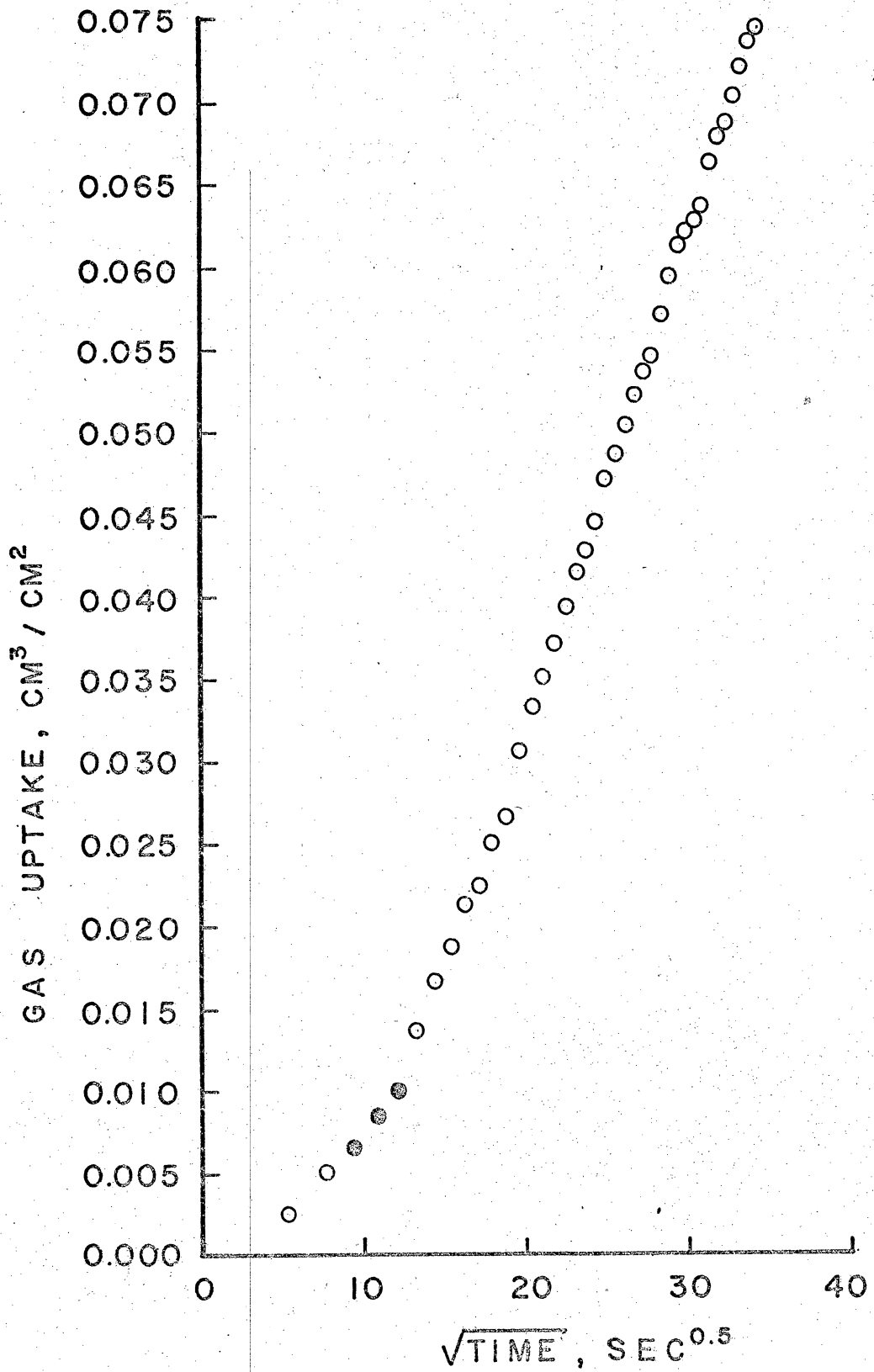


FIGURE 33. CARBON DIOXIDE UPTAKE IN WATER AT 698.00 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

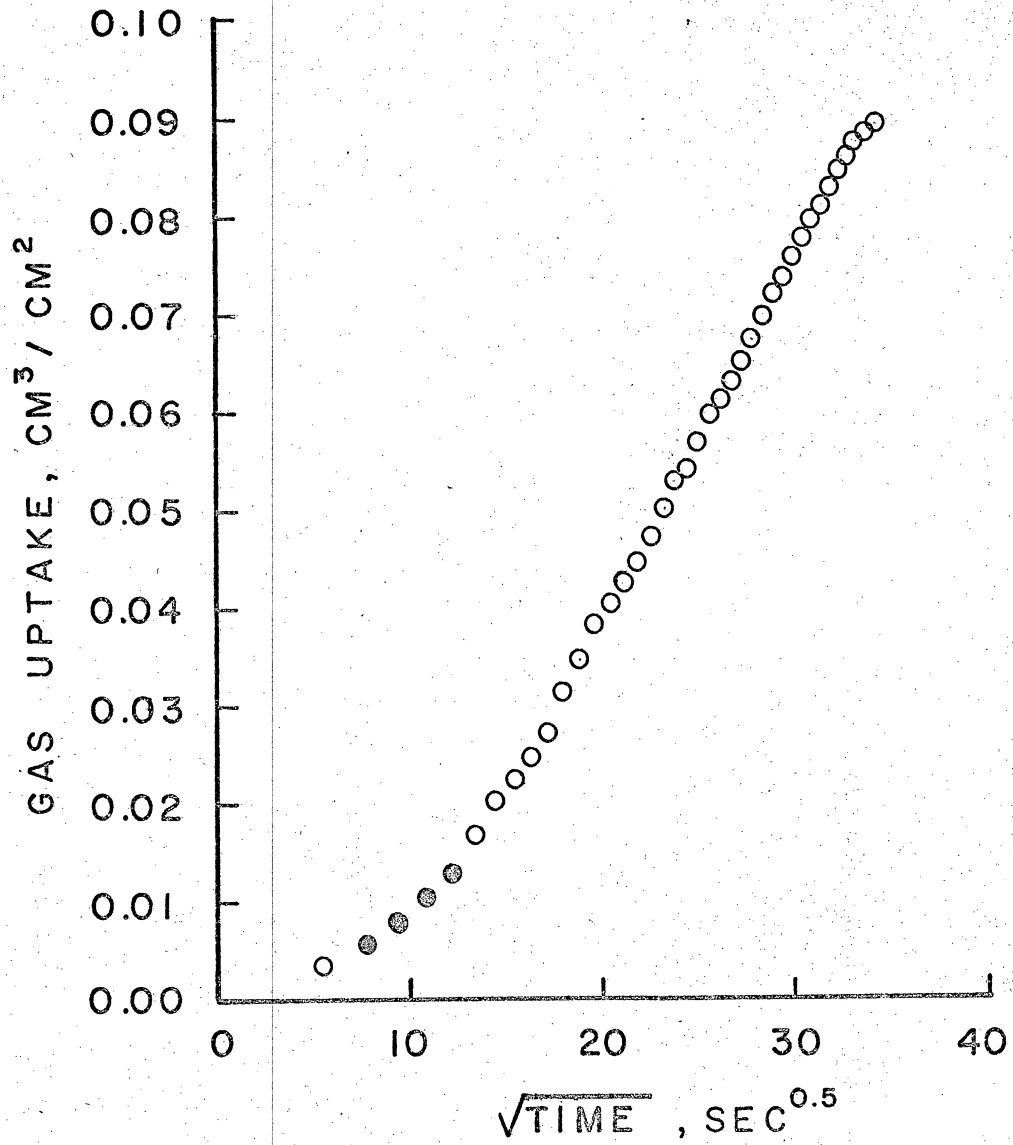


FIGURE 34. CARBON DIOXIDE UPTAKE IN WATER AT 705.50 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

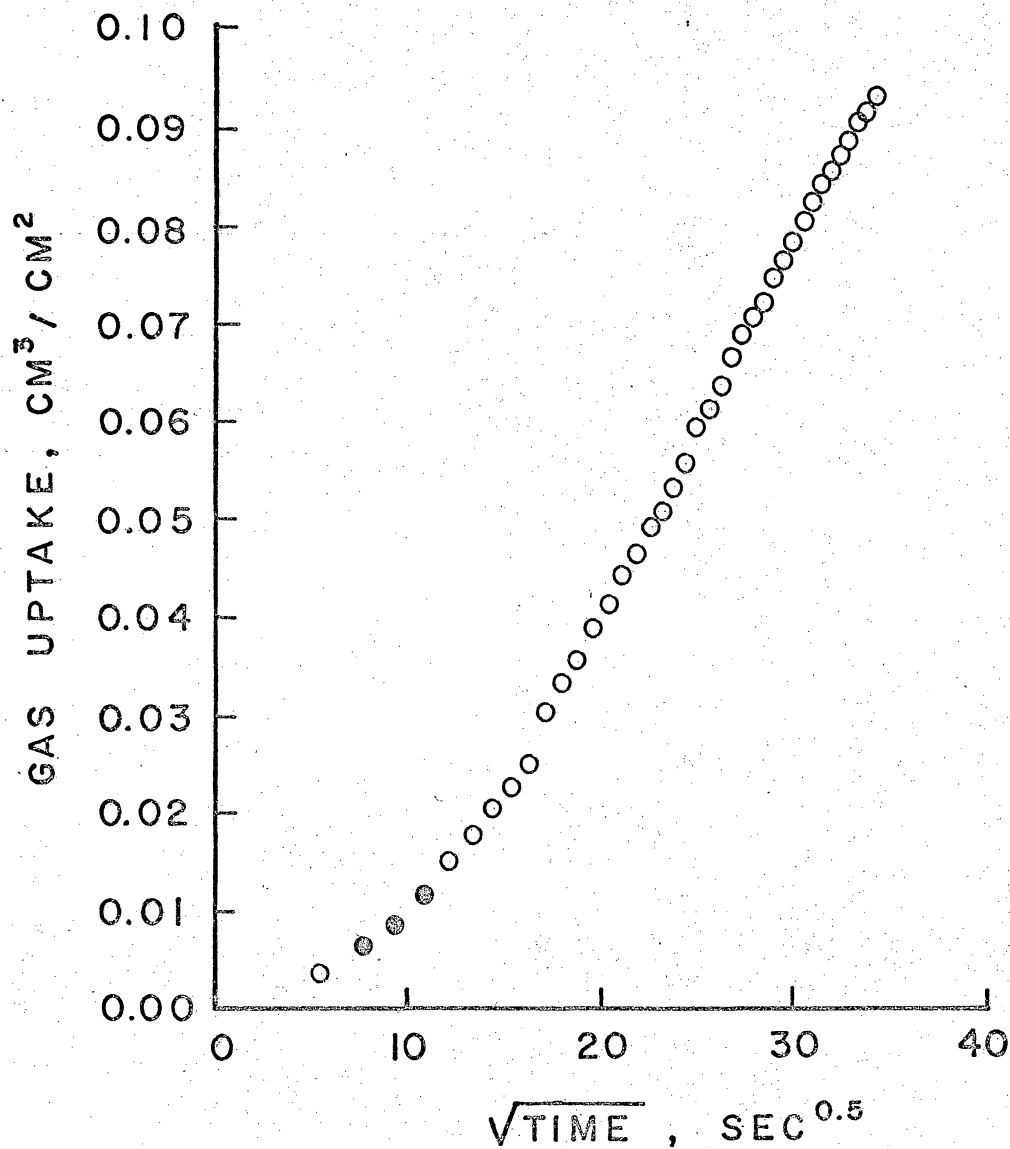


FIGURE 35. CARBON DIOXIDE UPTAKE IN WATER AT 712.00 MM HG
WITH SPECIFIC INITIAL CONCENTRATION

IV. DISCUSSION

The following discussion contains a review of the literature results, an analysis and review of the procedure used in the investigation, and a discussion of the observed results. Recommendations for future work and a summary of the limitations imposed on the investigation are also included.

Discussion of Literature

A review of previous work is presented in this section in an effort to remove discrepancies and choose a suitable standard for comparison of the results of this investigation.

Carbon Dioxide Data. As indicated in Table I, the available data for carbon dioxide is in quite close agreement. The table does not contain all available data, which is numerous, but rather summarizes the values which appear to be accepted in recent literature.

A variety of methods yield relative good agreement for the diffusion coefficient. Laminar jet studies are represented by Tang and Himmelblau⁽³⁹⁾, Thomas and Adams⁽⁴⁰⁾, Unver and Himmelblau⁽⁴¹⁾, and more recently, Duda and Vrentas⁽¹⁶⁾. Since the results are in good agreement, the relative merits of each system will be deferred to the oxygen data review.

Rather than attempt to choose a particular value that is correct, the range 1.85 to 2.00 will be used as acceptable in the carbon dioxide system.

Oxygen Data. Table II indicates that the spread for an oxygen diffusion coefficient at 25°C is much greater than for carbon dioxide. Although much of the oxygen data is taken from the same sources as for carbon dioxide, the agreement fails. This spread in the data has caused considerable concern over the possibility of an interfacial resistance for oxygen.

Referring to Figure 3 there appear to be two general ranges for the diffusion coefficient. The first set lies between 2.4 and 3.0. A second, lower set lies between 1.8 and 2.1.

The higher range is represented by Hüfner⁽²⁴⁾, Carlson⁽¹¹⁾, Baird and Davidson⁽²⁾, Vivian and King⁽⁴²⁾, and Davidson and Cullen⁽¹³⁾. Carlson and Hüfner both used quiescent liquid systems with long contact times and were subject to convection currents which would tend to increase their values. Both Baird and Davidson, and Cullen and Davidson used wetted spheres in their investigations. The form of Fick's law and the hydrodynamics of such a system are quite difficult to analyze quantitatively. However, it is not easy to determine the effect of particular variables on the value since in general it is difficult to separate the effects of individual variables.

Kolthoff and Miller used a dropping mercury electrode based on the unmodified Ilkovic equation and obtained high results. Use of the modified equation reduces the values by approximately 20 percent as seen by the value of Kolthoff and Izutsu.

This leaves only the value of Vivian and King in the high range using a diaphragm cell. No inherent difficulty can be visualized in this system that would result in high values, particularly when considering the good agreement for carbon dioxide by this technique.

The lower set of data are those of Baird and Davidson⁽²⁾, Kreuzer⁽²⁷⁾, Müller⁽³⁰⁾, Semerano et al.⁽³⁷⁾, Duda and Vrentas⁽¹⁶⁾, Jordan et al.⁽²⁶⁾, and Kolthoff and Izutsu⁽²⁷⁾.

The values obtained by Baird and Davidson, and Duda and Vrentas are from laminar jets. Both of these investigators considered hydrodynamics thoroughly, particularly Duda and Vrentas. Since both investigations are in good agreement for both carbon dioxide and oxygen, their results appear creditable.

Jordan et al. and Kolthoff and Izutsu both used a dropping mercury electrode technique with the modified Ilkovic equation. As predicted these values are indeed lower than those found by Kolthoff and Miller. In addition, the values from the modified equation agree well with the laminar jet studies.

After a careful review of the systems used to measure diffusion coefficients, Duda and Vrentas⁽¹⁶⁾ conclude that the values in the lower range are most acceptable. As a result of the above considerations and the rather doubtful aspects of many of the high range values, the lower range is chosen as the standard. As such, a diffusion coefficient in the range of 1.8 to 2.1 is considered acceptable.

Discussion of Procedure

An evaluation of the experimental equipment and procedure is given in this section.

Calibration of Apparatus. The calibration procedure for the absorption apparatus is dangerous, subject to error, and awkward. The procedure requires filling of the apparatus with mercury and determining the volume of each section by the weight of mercury required to fill it. The procedure is given in the Method of Procedure which is in the Experimental section. A discussion of the difficulties involved in this procedure follows.

The major cause of difficulty is the bulkiness of the apparatus, particularly when filled with mercury. It is very difficult even after numerous cleanings to obtain mercury free of contaminants. Any such contaminants in the form of liquid makes filling a volume such as the cells nearly impossible without trapping air or liquid in the top of the cell.

Inaccuracies can occur from trapped air, loss of small quantities of mercury during emptyings, and difficulty in exactly filling the upper and lower portions of the system so they match. However, Dixon⁽¹⁵⁾ presents a rather thorough review of procedures for calibrating such systems and considers the mercury technique the most accurate.

Another technique was attempted in the course of this investigation. This was the application of an ideal gas law to the apparatus for a temperature change. The procedure was performed as follows.

One side of the apparatus was closed off (filled with air) at a specified temperature. The other side was left open to the atmosphere. The temperature was then changed by a known amount. Since one side of the manometer was open to the atmosphere the pressure in the closed vessel was the sum (or difference) of the atmospheric pressure and the change in manometer fluid height. In addition, the change in the manometer height gives the volume change when multiplied by the cross sectional area of the manometer. Application of the ideal gas law at initial and final conditions, with the known volume change, can be used to find the volume of the system.

The difficulty with the above procedure is that the total volume change possible on the manometer is only three percent of the system volume. As such, the accuracy of the manometer readings makes the answer unreproducible.

Stopcocks. The original design of the apparatus was based on the work of Blank and Roughton⁽⁴⁾, wherein no indication was given as to the type of stopcocks used. As a result, the system originally was fitted with regular interchangeable stopcocks. Extensive trials proved these stopcocks could not be made to seal at even moderate vacuums. As a result, high vacuum stopcocks were installed. These stopcocks were more difficult to seat properly, but held at high vacuums excellently.

Sample Preparation. Three techniques were used for preparing water samples used in the tests. The first two techniques, as given in the Method of Procedure, correspond to tests at zero initial

concentration of carbon dioxide, and the third technique was used in the preparation of water samples for tests using a specific initial concentration of carbon dioxide.

The first technique used in the zero initial concentration tests utilized distilled water deionized at below 0.01 part per million of sodium chloride. In the second technique in the zero initial concentration tests, the distilled, deionized water was further treated by stripping with argon. This degassed water was used in Tests 6 and 7. The data for only two tests is insufficient to determine the effect of the degassing on absorption of carbon dioxide.

In the preparation of water for specific initial concentration tests, evacuation was carried out to 600 millimeters of mercury. Filling with carbon dioxide, and evacuation to 400 millimeters of mercury, followed by filling with carbon dioxide again, should result in primarily carbon dioxide remaining in the system. However, no quantitative test was applied to validate this effect.

Transfer of the water into the cell from the preparation flask certainly results in desorption. However, at most five minutes was required for this procedure. Checks on resaturating the water after ten minutes revealed very little desorption had occurred. The sample was treated in precisely the way described above once it was placed in the absorption cell. The evacuation and filling procedure for the cell was identical. Equilibration for from forty-five minutes to one and one-half hours revealed saturation as indicated by no further change in the manometer fluid height.

Manometer Characteristics. A definite problem, particularly for runs with no initial concentration, was the manometer behavior.

Filling the manometer with fluid always resulted in the right side being one millimeter of fluid higher than the left side. The area in each leg of the manometer was different, the right side having a value of 0.0151 square centimeters and the left side having a value of 0.0156 square centimeters. However, this should not influence the height of the fluid reached in the leg. It is still not certain what caused the differential between the two legs.

The formation of bubbles from degassing the manometer fluid occurred above 660 millimeters of mercury vacuum. The bubbles formed below the U-shaped tube and migrated up each leg causing the column of liquid to separate. Even releasing the vacuum generally would not remove these separations completely. Only by gently blowing the column back and forth in the manometer could the bubbles be removed. As a result, tests above 660 millimeters of mercury evacuation could not be made.

During the tests using an initial concentration of carbon dioxide at low pressure increments, there was a region in the high slope of the curve of the leveling off in the motion of the manometer, followed by a jump. This was thought to be caused by a resistance in the manometer since it was not apparent at higher pressure increments (Tests 12 through 14).

Mounting. One of the basic assumptions in this investigation is the quiescent nature of the liquid surface. Any disturbance of the liquid creates convection currents which render the theoretical solution

presented here invalid. In an effort to avoid this, the system was firmly attached to the bath by two rods attached to a plexiglass board on which it was mounted. The bottom of the plexiglass sheet rested on the bottom of the constant temperature bath. The surface of the fluid was observed during each test and no motion of the fluid was apparent in any of the tests.

Constant Temperature Bath. Although the constant temperature bath was quite large, frequent checks on the temperature revealed deviations of not more than one-tenth degree total.

Evacuation Procedure. In the tests with a zero initial concentration of carbon dioxide the evacuation procedure varied considerably. Again the basic approach came from Blank and Roughton⁽²⁾ wherein the vacuum was applied until the solution degassed. However, due to the problems with the manometer in this investigation, such a procedure could not be used. As a result, the tests with zero initial concentration were a trial and error procedure to determine what range of vacuums could be used. Vacuums ranged from 520 millimeters of mercury to 660 millimeters of mercury.

In the tests with specific initial concentration, the evacuation procedure was the same for each test. As a result, this parameter should not influence the results.

Discussion of Results

The following section contains a discussion of the results obtained during this investigation.

Tests with Zero Initial Concentration of Carbon Dioxide. Based on the work by Blank and Roughton⁽⁵⁾ the initial portion of the absorption curve was expected to yield the accepted values of the diffusion coefficient. The values determined from the initial linear region of the curve in the zero initial concentration tests are low in every case. Some tests approach the accepted value but at best are nearly 50 percent too low. Several of the values are extremely low. However, it must be considered that the evacuation procedure varied significantly in each test. As discussed later, this is considered to be an important factor in the zero initial concentration tests.

In the previous study by Blank and Roughton, a plot of gas absorbed versus the square root of time was nonlinear for the first 1.0 to 1.5 minutes. The same tendency appears in this investigation but to a lesser degree. Both a least squares solution and manual estimation of the slope was carried out on the points beyond this initial behavior, as indicated by the solid dots in Figures 7 through 21. Both values were in agreement. The least square values are presented in Table VI.

As indicated by Table VI, the agreement is quite poor on values for the diffusion coefficient. There appears to be no correlation between the pressure variables and the diffusion coefficient. Tables VII and VIII summarize the random relation between operating pressure and evacuation pressure, and the diffusion coefficient.

The upper range of diffusion coefficients obtained by a least squares fit of the high slope is much beyond the predicted value. As such, they are apparently a result of convection currents. The initial linear portion of the curve lasted longer in Blank and Roughton's work than in this investigation. This is quite likely due to the deeper layer of water used in this study.

Tests with Specific Initial Concentration of Carbon Dioxide.

Referring to Table IX, all but one of the diffusion coefficients (determined by manual and least square solution of the initial linear region) agree well in these initial concentration tests.

The single low value of 1.66 for Test 12 cannot be explained although the data points for the initial linear region appear to be quite irregular in Figure 33. Excluding this low test, the values range from 1.80 to 2.11. This gives an average value of 1.95 with a reproducibility of ± 0.15 . This compares favorably with the midpoint of the accepted range (1.85 to 2.00) of 1.925. Every test except 10 and 12 are within the acceptable range.

With several exceptions there appears to be a general trend to lower diffusion coefficients as the pressure increment increases. However, a definite relationship cannot be substantiated on the present data.

The value of the diffusion coefficient calculated for the higher slope adds to the probability of convection occurring beyond the slope change. The time at which the slope changes is not consistent throughout

the tests. Again the initial linear portion is somewhat shorter than in the work of Blank and Roughton⁽⁵⁾.

Convection Currents. The basic assumption in the theoretical solution to this absorption apparatus is the quiescent nature of the liquid surface.

Blank and Roughton⁽⁶⁾ offer proof that no convection occurs in their experiments by determining a theoretical mass transfer coefficient (for the quiescent system) and noting the agreement with the experimentally determined value. Based on the clear slope change seen in this study, the assumption of no convection in the initial range seems certain. In addition, the good agreement between the diffusion coefficients determined in this investigation and the accepted value, for the initial concentration tests, lends further proof to lack of convection initially.

As noted previously, the duration of non-convective absorption in this investigation was shorter than that of the previous investigation. In the original investigation, the absorbing liquid rested on a substrate of mercury. Although no specific details are given, the liquid layer appears relatively thin in the schematic of the apparatus. As a result, there would be less tendency for convection currents. In the present investigation the mercury substrate was not used, in an effort to ease filling of the cell and because its function was not explained in the previous work. There is apparently an effect, but the substrate does not appear to be an essential aspect of the apparatus.

In the early stages of this investigation, the difficulty of securing the apparatus caused some concern. Several preliminary tests made with the apparatus outside the bath indicated that the surface of the liquid was quite unstable. However, the bath apparently had a buffering effect, since no rippling or instability was apparent during tests made in the bath.

Effect of Evacuation Procedure. In tests using a zero initial concentration of carbon dioxide, the evacuation procedure apparently was an important parameter. Originally, the procedure was to have included evacuation of the system to just above the vapor pressure of water at 25°C or a vacuum of approximately 680.0 millimeters of mercury at this location (Blacksburg, Virginia). However, at vacuums of more than 660.0 millimeters of mercury, degassing of the manometer fluid became a problem for even short time periods. Gas bubbles would form in the bulk of the manometer fluid below the U-tube and rise up each leg. As these bubbles moved up the legs they would gather at certain points and separate the fluid. The legs usually could not be brought back together by simply releasing the vacuum.

In addition, gas bubbles formed in the water at the higher vacuums (greater than 620 millimeters of mercury) and then rose during the equilibration procedure. When the vacuum was released, most of the bubbles remained in solution, only to rise occasionally during the absorption tests.

Blank and Roughton⁽⁷⁾ indicate only that they degassed the solution by evacuation while connected to the system. Their apparatus used a manometer wherein the legs of the U-tube could be separated until the test began. This may be the reason they could utilize a vacuum sufficient to actively degas the solution. Again, however, preliminary tests performed on the glass cell alone indicated that degassing from the water caused significant condensation and droplet formation on the glass walls and top of the cell.

As a result of the above considerations, the evacuation pressure was in general not as high as that likely used by Blank and Roughton⁽⁵⁾. The obvious result is that gases other than carbon dioxide may have occupied the gas space. Although both nitrogen and argon were used to purge the system, air would likely have been no worse a contaminant for absorption of carbon dioxide. The low values of the diffusion coefficient observed for these tests would be expected based on the evacuation procedure. However, the random behavior can not be explained on this basis. If the evacuation pressure alone was affecting the data then some correlation should appear in the data. Such was not the case as shown by Table VII.

In the tests made with a specified initial concentration, the evacuation procedure was consistent. The only variation was the pressure at which the carbon dioxide was equilibrated. The evacuation procedure should have reduced the concentration of gases other than carbon dioxide to a minimum. Apparently this was the case.

The slight trend toward lower diffusion coefficients at higher vacuum (or lower saturation pressure) in the initial concentration tests may have been the result of less carbon dioxide being put into the system. If there were no impurities present, however, the amount of carbon dioxide should correlate to the saturation pressure only. If there were other gases in the system, then the fraction of carbon dioxide present would be a function of the saturation pressure used, provided the evacuation procedure consistently left the same quantity of impurities in the system. At any rate, the effect of evacuation on the specific initial concentration tests appears to be minimal.

Effect of Condensation. In the tests made with no initial concentration of carbon dioxide, several opportunities were present for the formation of condensation. The first opportunity occurred when the purge gas was allowed to fill the system. Some condensation was observed during this procedure. Even when the gas was allowed to enter very slowly, condensation was in evidence.

A more serious source of condensation was the very rapid pressure change resulting when the absorption test began. Condensation could be clearly observed on the sides and top of the cell during this procedure. However, much of this condensation disappeared by the end of the test. Visual inspection of the apparatus immediately after removing it from the bath evidenced a ring of condensation for every test at zero initial concentration of carbon dioxide.

The effect of condensation is to invalidate the theoretical development of the absorption process. Finely spread water droplets considerably increases the actual surface area involved in the absorption process. In addition, the assumption of a flat quiescent surface would not apply to the particles. When condensation occurs, the rate of gas uptake should be somewhat higher than expected. Since the quantity of condensation is unmeasurable, the effect of this phenomena can only be assumed. However, it seems valid to assume there would be variations in the quantity of condensation formed.

The best explanation for the large spread in the data at zero initial concentration appears to be an interaction between the evacuation procedure and the condensation phenomena. The interrelation of these two variables could reasonably explain why there is no real correlation between the pressure parameters and the diffusion coefficient.

In the tests made with a specific initial concentration, condensation was not a problem. A small quantity usually appeared during the evacuation procedure but was not present after the 90-minute equilibration. Following the equilibration procedure, the rapid pressure change at the start of the absorption also resulted in no observed condensation. Also, inspection of the apparatus after removing it from the bath following each test revealed no apparent condensation.

Temperature Effects. According to Blank and Roughton⁽⁸⁾, the temperature increased by 1°C during their absorption tests. Since the absorption in this investigation was less, a smaller temperature change should occur.

The appearance of condensation in the cell is indicative of a temperature effect. Apparently, condensation results when the pressure is increased since no condensation appeared during the actual evacuation but rather when the vacuum was released by allowing gas to fill the system. Thus, increasing the pressure in the system caused condensation and this resulted in a temperature change.

At lower evacuation pressures one would expect to see less condensation and less temperature change upon increasing the pressure to one atmosphere. As a result, the lack of condensation observed experimentally in the lower pressure increment tests (using initial specific concentration) appears reasonable.

Curvature Error. A slight error may result from the meniscus which formed between water and sides of the cell. The effect of this would be to increase the area for absorption and as a result increase the diffusion coefficient. This effect would quite likely be negligible.

Range of the Apparatus. The range of applicability for the quiescent liquid absorption apparatus is based on the size of the manometer and cells. It is desirable to utilize the total 30 centimeters available on the manometer during the non-convective portion of the absorption process.

On this basis, the absorption of carbon dioxide in water can be used in the present apparatus for determining diffusion coefficients. However, the present apparatus does not allow full utilization of the

manometer in the initial, non-convective region of absorption for the carbon dioxide-water system. More complete use of the manometer would increase the number of data points for the non-convective region of absorption.

The solubility of oxygen in water is approximately one-fifteenth that of carbon dioxide. As a result, in a 30-minute trial test, the total change in manometer fluid was only three centimeters. Since most of this change represents convective absorption, the non-convective region represents only a fraction of this height change. As a result, the oxygen-water system could not be studied with this apparatus.

A possible change in the apparatus that would make it applicable to an oxygen-water system would be increasing the area of the cells by at least 15-times. However, this would increase the diameter of the cells to four times the present size and make the apparatus awkward and even more difficult to calibrate. A more realistic approach might be to reduce the cross sectional area of the manometer. However, decreasing this area considerably might introduce capillary rise and other negative effects.

Another possible approach for both carbon dioxide and oxygen systems would be changing the manometer fluid to one that is less dense. However, the commercial measuring fluids available generally have a density of at least 0.8 grams per cubic centimeter. Since the present fluid has a density of 1.033 grams per cubic centimeters, a change to other commercial fluids would not improve the range of the apparatus appreciably.

Recommendations

The following recommendations are made for future work using quiescent liquid absorption techniques, and particularly the apparatus used in this investigation, for the determination of diffusion coefficients or interfacial resistance with surface active agents.

Use of Mercury Substrate. It is recommended that in the future a mercury substrate be used to support a thin layer of absorbing liquid. The thin layer of liquid should be less sensitive to convection currents either from external motion or from the absorption process. This would increase the amount of data applicable to non-convective absorption represented by the initial portion of the absorption curves.

Size of the Absorption Cell. Increasing the cross-sectional area of the cells would result in greater gas uptake for the oxygen-water system. It is recommended that the increase in area of the cell be correlated to any changes made in the cross-sectional area of the manometer.

Cell Design. One of the more awkward aspects of this apparatus is filling of the cell. The addition of a short tube on top of the cell with a larger bore stopcock would allow more direct injection of the water sample and reduce the danger of leaving drops of water on walls and tubing.

Manometer Arrangement. The problems of degassing the manometer fluid could probably be relieved by separating the U-tube legs with a stopcock. In addition the use of a water and dye mixture as a measuring

fluid might eliminate much of the resistance and resulting jumps of the manometer fluid observed in this investigation.

Manometer Size. A decrease in the cross-sectional area of the manometer would improve the amount of manometer length used in the non-convective absorption range. It is recommended that this be done both for carbon dioxide and oxygen systems, the new area being estimated from the results of this study.

Carbon Dioxide Absorption. It is recommended that further studies be carried out with this system using carbon dioxide to more fully evaluate its operative range at various pressures. In addition, changes suggested above should be made and the operative range compared with that for the present system. Also, several temperatures should be used in future tests to determine the accuracy of this apparatus over a range of temperatures.

Oxygen Absorption. It is recommended that changes in cross-sectional area of the cells and manometer in the measuring fluid be made to adapt the present apparatus for use with the oxygen-water system. A study similar to the present investigation should then be carried out on the oxygen-water system.

Limitations

The following are limitations imposed on this investigation.

System Studied. The applicability of the present apparatus for determining diffusion coefficients in gas-liquid systems is based on the solubility of the gas in the liquid. The solubility of carbon

dioxide in water at 25°C is 90.1 cubic centimeters per 100 cubic centimeters of water. The solubility of oxygen in water is 2.46 cubic centimeters per 100 cubic centimeters of water at 25°C. As a result the carbon dioxide-water system could be studied with the present apparatus but not the oxygen-water system.

Operating Conditions. All absorption tests were made at 25°C. Zero initial concentration tests were made using both nitrogen and argon as purge gases. Operating pressures varied from 532.00 to 736.80 millimeters of mercury and included several tests made above atmospheric pressure; most tests were conducted at pressures below atmosphere. In the specific initial concentration tests, a range of initial concentrations were used varying from 1.62×10^{-5} to 2.53×10^{-5} gram moles per cubic centimeter corresponding to saturation pressures of 364.00 to 568.60 millimeters of mercury.

V. CONCLUSIONS

Investigation of the absorption of oxygen and carbon dioxide in a quiescent liquid absorption apparatus at 25°C led to the following conclusions:

1. In tests using a zero initial concentration of carbon dioxide, the values for the diffusion coefficient varied from 0.388 to 1.52×10^{-5} square centimeters per second and were not within the acceptable range of 1.85 to 2.00×10^{-5} square centimeters per second.

2. In tests using a zero initial concentration of carbon dioxide, no correlation was apparent between the diffusion coefficient and the system parameters.

3. Using specific initial concentrations of carbon dioxide, the diffusion coefficient was found to have a value of 1.95 ± 0.15 square centimeters per second.

4. Determination of the diffusion coefficients for the carbon dioxide-water system from absorption data was possible with the present apparatus due to its solubility of 0.901 cubic centimeters per cubic centimeter of water.

5. The absorption of oxygen in water was limited due to its solubility of 0.025 cubic centimeters per cubic centimeter of water, and as a result the diffusion coefficients for this system could not be determined with the present apparatus.

VI. SUMMARY

The purpose of this investigation was to evaluate the ease of obtaining and reproducing diffusion coefficients for carbon dioxide and oxygen in water at 25°C using a quiescent liquid absorption apparatus.

Absorption curves were obtained for carbon dioxide in water using both a zero initial concentration and specific initial concentration of carbon dioxide. The evacuation pressure, operating pressure, initial concentration, and pressure increment were varied.

The zero initial concentration tests gave values for the diffusion coefficient consistently lower than expected. In addition the values were not reproducible and could not be correlated to the variation of parameters for the system. The cause of this variation was considered to be a combination of the evacuation procedure and the condensation phenomena. The interrelation of these effects was not determined.

Tests made with specific initial concentrations gave good agreement for the value of the diffusion coefficient. A value of $1.95 \pm 0.15 \times 10^{-5}$ square centimeters per second was determined to represent the diffusion coefficient for carbon dioxide at 25°C. A slight trend toward lower values of the diffusion coefficient at higher pressure gradients was observed. The effect of the evacuation pressure and condensation were considered to be minimal in these tests.

In both zero and specific initial concentration tests, convection appeared between 4 and 6 minutes after the start of the absorption test.

The absorption of oxygen in water at 25°C is nearly 15 times less than that of carbon dioxide. As a result, the absorption of oxygen was considered to be out of the applicable range for measurement of diffusion coefficients with this apparatus.

The quiescent liquid system was considered to be a rapid and reasonably accurate method for measuring the absorption of very soluble gases, such as carbon dioxide, over a limited range. The adaptability of the apparatus to less soluble gases is rather limited. However, for repeated measurements for a few chosen gases the system would be an inexpensive, competitive apparatus.

VII. BIBLIOGRAPHY

1. Arnold, J. H.: Studies in Diffusion II. A Kinetic Theory of Diffusion in Liquid Systems, J. Am. Chem. Soc., 52,3937 (1930).
2. Baird, M. H. and J. F. Davidson: Annular Jets - II, Chem. Engr. Sci., 17,473-480 (1962).
3. Blank, M.: The Permeability of Monolayers to Several Gases, The Retardation of Evaporation Monolayers Symposium, New York, N. Y., 79 (1962).
4. Blank, M. and F. J. W. Roughton: The Permeability of Monolayers to Carbon Dioxide, Trans. Faraday Soc., 56,1832 (1960).
5. *ibid*, p. 1835.
6. *ibid*, p. 1838.
7. *ibid*, p. 1834.
8. *ibid*, p. 1836.
9. Bird, R. B., W. E. Stewart, and E. N. Lightfoot: "Transport Phenomena", pp. 554-558. John Wiley and Sons, Inc., New York, N. Y., 1960.
10. *ibid*, p. 558.
11. Carlson, T.: The Diffusion of Oxygen in Water, J. Am. Chem. Soc., 33,1027 (1911).
12. Chiang, S. H. and H. L. Toor: Interfacial Resistance in Absorption of Oxygen by Water, A. I. Ch.E. Journal, 5, No. 2, pp. 165-168 (1959).

13. Davidson, J. F. and E. J. Cullen: The Determination of Diffusion Coefficients for Sparingly Soluble Gases in Liquids, Trans. Instn. Chem. Engrs., 35,51-60 (1957).
14. Dixon, M.: "Manometric Methods", pp. 24-30, Cambridge University Press, London, Eng., 1951, 3rd ed.
15. *ibid*, pp. 33-35.
16. Duda, J. L. and J. S. Vrentas: Laminar Liquid Jet Diffusion Studies, A. I. Ch.E. Journal, 14, No. 2, pp. 287-299 (1968).
17. Exner, F.: Analen der Physik und Chemie, Ser. 2, Vol. 155, pp. 321-336, 443-464; Arnold, J. H.: Studies in Diffusion II. A Kinetic Theory of Diffusion in Liquid Systems, J. Am. Chem. Soc., 52,3937 (1930).
18. Hagenback, A.: Wid. Ann., 65,673 (1898); Carlson, T.: The Diffusion of Oxygen in Water, J. Am. Chem. Soc., 33,1027 (1911).
19. Harvey, E. A. and W. Smith: The Absorption of Carbon Dioxide by a Quiescent Liquid, Chem. Eng. Sci., 10,274-280 (1959).
20. Himmelblau, D. M.: Diffusion of Dissolved Gases in Liquids, Chem. Rev., 64,527-545 (1964).
21. *ibid*, p. 542.
22. *ibid*, p. 540.
23. *ibid*, p. 543.
24. *ibid*, p. 545.
25. Hüfner, G.: Wied. Ann., 65,673 (1898); Arnold, J. H.: Studies in Diffusion II. A Kinetic Theory of Diffusion in Liquid Systems, J. Am. Chem. Soc., 52,3937 (1930).

26. Jordan, J., E. Ackerman, and R. L. Berger: Solvent Structure, Viscosity and Polarography of Oxygen, J. Am. Chem. Soc., 81,3915 (1959).
27. Kolthoff, I. M. and K. Izutsu: The Ratio of the First to the Second Diffusion Current of Oxygen at the Dropping Mercury Electrode. Diffusion Coefficient of Oxygen, J. Am. Chem. Soc., 63,1013 (1941).
28. Kolthoff, I. M. and C. S. Miller: The Reduction of Oxygen at the Dropping Mercury Electrode, J. Am. Chem. Soc., 63,1013 (1941).
29. Kruezer, F.: Helv. Physiol. Pharmacol. Acta., 8,505 (1950); Himmelblau, D. M.: Diffusion of Dissolved Gases in Liquids, Chem. Rev., 64,548 (1964).
30. Müller, A.: Helv. Physiol. Acta., 6,21 (1948); Duda, J. L. and J. S. Vrentas: Laminar Liquid Jet Diffusion Studies, A. I. Ch.E. Journal, 14, No. 2, 165-168 (1959).
31. Nysing, R. A. T. O., R. H. Hendrikz and H. Kramers: Absorption of CO₂ in Jets and Falling Films of Electrolyte Solutions, with and without Chemical Reaction, Chem. Eng. Sci., 10,88-104 (1959).
32. Peaceman, D. W.: Liquid-Side Resistance in Gas Absorption with and without Chemical Reaction, Sc. D. Thesis, M. I. T. (1951); Himmelblau, D. M.: Diffusion of Dissolved Gases in Liquids, Chem. Rev., 64,549 (1964).
33. Perry, J. H., Editor: "Chemical Engineers Handbook", p. 3-71, McGraw Hill Book Co., Inc., New York, N. Y., 1941, 4th ed.

34. Raimondi, P. and H. L. Toor: Interfacial Resistance in Gas Absorption, A. I. Ch.E. Journal, 5, No. 1, pp. 86-92 (1959).
35. Scriven, L. E.: Interfacial Resistance in Gas Absorption, pp. 1-6. Ph.D. Thesis, University of Delaware, 1956.
36. Ibid, p. 6.
37. Semerano, G., L. Riccobini, and A. Foffani: Gazz. Chim. Ital., 79, 382 (1956); Duda, J. L. and J. S. Vrentas: Laminar Liquid Jet Diffusion Studies, A. I. Ch.E. Journal, 14, No. 2, pp. 165-168 (1959).
38. Stefan, I.: Sitzbar. Akad, Wiss, Wien, Math.-naturw. Kl., Abt., 37 (1898); Himmelblau, D. M.: Diffusion of Dissolved Gases in Liquids, Chem. Rev., 64, 549 (1964).
39. Tan, Y. P. and D. M. Himmelblau: Interphase Mass Transfer for Laminar Concurrent Flow of Carbon Dioxide and Water Between Parallel Plates, A. I. Ch.E. Journal, 9, 630 (1963).
40. Thomas, W. J. and M. J. Adams: Measurement of the Diffusion Coefficient of Carbon Dioxide in Water and Aqueous Solutions of Glycerol, Trans. Faraday Soc., 61, 668 (1965).
41. Unver, A. A. and D. M. Himmelblau: Diffusion Coefficients of CO₂, C₂H₄, C₃H₆, and C₄H₈ in Water from 6° to 65°C, J. of Chem. and Engr. Data, 9, No. 3, pp. 428-431 (1964).
42. Vivian, J. E. and C. J. King: Diffusivities of Slightly Soluble Gases in Water, A. I. Ch.E. Journal, 10, No. 2, pp. 220-221 (1964).

43. Vrentas, S. J.: A Study of the Effect of Surfactants on Gas Absorption Rates, Ph.D. Thesis, University of Delaware, p. 109 (1963).

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X. APPENDIX

This section contains information required to reproduce the results of this thesis and other information of less significance than that presented in the Experimental section.

Data Tables

The following section includes all data taken on the quiescent liquid absorption apparatus. The data taken from the absorption apparatus is in the form of manometer readings as a function of time. These data are presented in Tables X through XXXVIII, and the characteristic parameters of each test are given. Tables X through XXIV are tests using zero initial concentration of carbon dioxide. Tables XXV through XXXVIII are tests made with varying initial carbon dioxide concentrations.

Derivation of Uptake Equations

This section gives details of relations between experimentally measured quantities and more useful properties of the absorption process.

Gas Uptake Equation. The relationship between pressure change on the absorption apparatus and the amount of gas absorbed is required to develop an absorption isotherm. The derivation that follows parallels that of Dixon⁽¹⁴⁾ in most respects.

TABLE X

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 572.40 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.20	14.80
60.0	15.50	14.70
90.0	15.90	14.30
120.0	16.30	13.90
150.0	16.70	13.40
180.0	17.10	13.00
210.0	17.50	12.60
240.0	18.00	12.10
270.0	18.60	11.50
300.0	19.10	11.00
330.0	19.60	10.40
360.0	20.00	10.00
390.0	20.50	9.50
420.0	20.90	9.10
450.0	21.30	8.70
480.0	21.70	8.30
510.0	22.20	7.80
540.0	22.60	7.40
570.0	23.00	7.00
600.0	23.30	6.70
630.0	23.70	6.30
660.0	24.00	5.90
690.0	24.40	5.50
720.0	24.80	5.20
750.0	25.10	4.90
780.0	25.50	4.40
810.0	25.70	4.20
840.0	26.10	3.80
870.0	26.40	3.50
900.0	26.70	3.20
930.0	26.90	2.90
960.0	27.20	2.70
990.0	27.50	2.40
1020.0	27.70	2.10
1050.0	28.00	1.80
1080.0	28.20	1.60
1110.0	28.50	1.30
1140.0	28.70	1.10
1170.0	28.90	0.90

*ATMOSPHERIC PRESSURE WAS 698.40 MM MERCURY

EVACUATION PRESSURE WAS 620.00 MM MERCURY

INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY

**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 615.70 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.50	13.90
60.0	16.40	13.10
90.0	16.80	12.70
120.0	17.30	12.30
150.0	17.80	11.80
180.0	18.40	11.20
210.0	19.00	10.60
240.0	19.60	10.00
270.0	20.20	9.40
300.0	20.80	8.80
330.0	21.30	8.30
360.0	21.90	7.70
390.0	22.40	7.20
420.0	22.90	6.70
450.0	23.40	6.20
480.0	23.90	5.70
510.0	24.30	5.30
540.0	24.70	4.90
570.0	25.20	4.40
600.0	25.50	4.10
630.0	25.80	3.70
660.0	26.30	3.30
690.0	26.70	2.90
720.0	27.00	2.60
750.0	27.40	2.10
780.0	27.60	1.90
810.0	27.90	1.60
840.0	28.40	1.10
870.0	28.70	0.70
900.0	29.10	0.30
930.0	29.40	0.10

*ATMOSPHERIC PRESSURE WAS 705.70 MM MERCURY

EVAUATION PRESSURE WAS 820.00 MM MERCURY

INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY

**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 639.30 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.60	14.60
60.0	15.90	13.80
90.0	16.70	13.00
120.0	17.10	12.80
150.0	17.40	12.20
180.0	17.70	12.00
210.0	18.00	11.60
240.0	18.70	11.00
270.0	19.20	10.50
300.0	19.60	10.00
330.0	20.10	9.50
360.0	20.50	9.10
390.0	21.00	8.60
420.0	21.50	8.20
450.0	22.00	7.60
480.0	22.40	7.10
510.0	22.70	6.80
540.0	23.00	6.50
570.0	23.50	6.00
600.0	23.90	5.60
630.0	24.20	5.30
660.0	24.60	5.00
690.0	24.90	4.60
720.0	25.20	4.30
750.0	25.50	4.00
780.0	25.80	3.70
810.0	26.00	3.50
840.0	26.40	3.10
870.0	26.70	2.80
900.0	27.00	2.50
930.0	27.20	2.30
960.0	27.50	2.00
990.0	27.70	1.80
1020.0	27.90	1.50
1050.0	28.40	1.00
1080.0	28.70	0.80
1110.0	28.90	0.50

*ATMOSPHERIC PRESSURE WAS 710.30 MM MERCURY

EVACUATION PRESSURE WAS 540.00 MM MERCURY

INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY

**BRODIE SOLUTION, DENSITY OF 1.023 GM/CC AT 20 DEG C

TABLE XIII

MANGHETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 606.30 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.20	14.80
60.0	15.70	14.20
90.0	16.00	13.80
120.0	16.60	13.20
150.0	17.00	12.80
180.0	17.30	12.50
210.0	17.60	12.20
240.0	17.90	11.90
270.0	18.20	11.60
300.0	18.60	11.20
330.0	18.90	10.90
360.0	19.30	10.50
390.0	19.70	10.10
420.0	20.00	9.80
450.0	20.30	9.50
480.0	20.70	9.10
510.0	21.10	8.60
540.0	21.50	8.20
570.0	21.90	7.80
600.0	22.20	7.40
630.0	22.50	7.10
660.0	22.90	6.80
690.0	23.20	6.40
720.0	23.50	6.10
750.0	23.90	5.70
780.0	24.20	5.40
810.0	24.60	5.00
840.0	24.90	4.60
870.0	25.30	4.20
900.0	25.70	3.90
930.0	26.00	3.60
960.0	26.20	3.30
990.0	26.50	3.00
1020.0	26.80	2.70
1050.0	27.10	2.40
1080.0	27.30	2.10
1110.0	27.60	1.90
1140.0	27.90	1.60
1170.0	28.20	1.20

*ATMOSPHERIC PRESSURE WAS 706.30 MM MERCURY
EVACUATION PRESSURE WAS 620.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XIV

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 532.00 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.70	14.40
60.0	16.30	13.80
90.0	16.70	13.40
120.0	17.10	13.00
150.0	17.40	12.70
180.0	17.70	12.40
210.0	18.10	11.80
240.0	18.60	11.40
270.0	18.90	10.60
300.0	19.70	10.10
330.0	20.20	9.80
360.0	20.60	9.40
390.0	21.10	8.90
420.0	21.50	8.50
450.0	21.90	8.10
480.0	22.20	7.80
510.0	22.60	7.40
540.0	22.90	7.10
570.0	23.30	6.70
600.0	23.70	6.30
630.0	24.00	6.00
660.0	24.40	5.60
690.0	24.70	5.30
720.0	25.00	5.00
750.0	25.30	4.70
780.0	25.60	4.40
810.0	25.90	4.10
840.0	26.10	3.90
870.0	26.30	3.60
900.0	26.60	3.30
930.0	26.80	3.10
960.0	27.10	2.80
990.0	27.40	2.60
1020.0	27.60	2.40
1050.0	27.80	2.10
1080.0	28.00	1.90
1110.0	28.20	1.70
1140.0	28.50	1.40
1170.0	28.70	1.20

*ATMOSPHERIC PRESSURE WAS 712.00 MM MERCURY
EVACUATION PRESSURE WAS 950.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XV

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 622.00 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	16.70	13.10
60.0	17.30	12.30
90.0	17.50	11.90
120.0	18.10	11.60
150.0	18.70	11.00
180.0	19.30	10.30
210.0	19.90	9.80
240.0	20.50	9.20
270.0	21.10	8.60
300.0	21.60	8.10
330.0	22.00	7.70
360.0	21.80	6.90
390.0	23.20	6.40
420.0	23.80	5.80
450.0	24.20	5.40
480.0	24.70	4.80
510.0	25.20	4.40
540.0	25.60	4.00
570.0	26.10	3.60
600.0	26.40	3.10
630.0	26.80	2.70
660.0	27.20	2.30
690.0	27.60	1.90
720.0	27.90	1.60
750.0	28.30	1.20
780.0	28.60	0.90
810.0	29.00	0.60
840.0	29.30	0.30

*ATMOSPHERIC PRESSURE WAS 702.00 MM MERCURY
EVACUATION PRESSURE WAS 660.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XVI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 631.40 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.00	15.90
60.0	16.60	15.30
90.0	17.10	12.80
120.0	17.50	12.40
150.0	18.00	11.90
180.0	18.00	11.30
210.0	19.20	10.80
240.0	19.70	10.10
270.0	20.30	9.50
300.0	20.80	8.90
330.0	21.40	8.40
360.0	21.90	7.90
390.0	22.50	7.20
410.0	22.80	6.90
440.0	23.20	6.50
470.0	23.70	6.00
500.0	24.20	5.40
530.0	24.70	5.00
560.0	25.10	4.80
590.0	25.50	4.10
620.0	25.90	3.80
650.0	26.30	3.30
680.0	26.70	2.90
710.0	27.10	2.50
740.0	27.40	2.20
770.0	27.70	1.90
800.0	27.90	1.70
830.0	28.10	1.40
860.0	28.60	1.00
890.0	28.90	0.60
920.0	29.20	0.40

*ATMOSPHERIC PRESSURE WAS 701.40 MM MERCURY
EVACUATION PRESSURE WAS 660.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XVII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 625.30 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.70	14.20
60.0	15.40	13.50
90.0	16.80	13.10
120.0	17.20	12.70
150.0	17.50	12.40
180.0	17.80	12.10
210.0	18.40	11.50
240.0	18.90	10.90
270.0	19.30	10.40
300.0	19.80	10.00
330.0	20.20	9.60
360.0	20.60	9.20
390.0	21.00	8.80
420.0	21.30	8.40
450.0	21.80	7.90
480.0	22.20	7.50
510.0	22.50	7.20
540.0	22.90	6.80
570.0	23.20	6.50
600.0	23.60	6.10
630.0	23.90	5.80
660.0	24.10	5.50
690.0	24.40	5.10
720.0	24.80	4.90
750.0	25.00	4.60
780.0	25.30	4.30
810.0	25.60	4.00
840.0	25.90	3.70
870.0	26.10	3.50
900.0	26.40	3.20
930.0	26.70	2.90
960.0	26.90	2.70
990.0	27.10	2.40
1020.0	27.30	2.30
1050.0	27.50	2.10
1080.0	27.70	1.90
1110.0	27.90	1.70
1140.0	28.10	1.40
1170.0	28.50	1.10

*ATMOSPHERIC PRESSURE WAS 710.30 MM MERCURY
EVACUATION PRESSURE WAS 540.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XVIII

HANDMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 623.30 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.60	14.40
60.0	15.90	14.10
90.0	16.40	13.60
120.0	16.80	13.30
150.0	17.10	12.90
180.0	17.40	12.60
210.0	17.70	12.30
240.0	18.00	12.00
270.0	18.50	11.50
300.0	18.90	11.00
330.0	19.30	10.60
360.0	19.70	10.20
390.0	20.00	9.90
420.0	20.40	9.50
450.0	20.70	9.20
480.0	21.00	8.90
510.0	21.30	8.60
540.0	21.60	8.20
570.0	22.10	7.80
600.0	22.40	7.50
630.0	22.70	7.10
660.0	22.90	6.90
690.0	23.20	6.60
720.0	23.50	6.30
750.0	23.80	6.00
780.0	24.00	5.80
810.0	24.30	5.50
840.0	24.50	5.30
870.0	24.80	5.00
900.0	25.00	4.80
930.0	25.20	4.60
960.0	25.40	4.40
990.0	25.60	4.20
1020.0	25.80	4.00
1050.0	25.90	3.90
1080.0	26.20	3.60
1110.0	26.60	3.30
1140.0	26.70	3.10
1170.0	26.80	2.90

*ATMOSPHERIC PRESSURE WAS 713.30 MM MERCURY
EVACUATION PRESSURE WAS 500.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XIX

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 643.30 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.50	14.50
60.0	16.00	14.00
90.0	16.40	13.60
120.0	16.80	13.20
150.0	17.20	12.80
180.0	17.55	12.45
210.0	17.80	12.20
240.0	18.60	11.40
270.0	19.10	10.90
300.0	19.50	10.50
330.0	20.00	10.00
360.0	20.50	9.50
390.0	20.60	9.10
420.0	21.20	8.70
450.0	21.50	8.40
480.0	21.90	8.00
510.0	22.50	7.50
540.0	22.70	7.20
570.0	23.00	6.80
600.0	23.40	6.50
630.0	23.80	6.00
660.0	24.20	5.60
690.0	24.50	5.30
720.0	24.80	5.00
750.0	25.10	4.70
780.0	25.40	4.40
810.0	25.70	4.10
840.0	26.00	3.80
870.0	26.30	3.50
900.0	26.60	3.20
930.0	26.80	2.90
960.0	27.00	2.70
990.0	27.30	2.50
1020.0	27.50	2.30
1050.0	27.70	2.00
1080.0	27.90	1.70
1110.0	28.20	1.50
1140.0	28.50	1.20
1170.0	28.70	1.00

*ATMOSPHERIC PRESSURE WAS 713.30 MM MERCURY

EVACUATION PRESSURE WAS 560.00 MM MERCURY

INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY

**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XX

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 644.20 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.60	14.40
60.0	15.90	14.10
90.0	16.40	13.50
120.0	16.70	13.20
150.0	17.10	12.80
180.0	17.40	12.50
210.0	17.60	12.30
240.0	17.90	12.00
270.0	18.50	11.30
300.0	19.00	10.90
330.0	19.40	10.50
360.0	19.60	10.00
390.0	20.20	9.70
420.0	20.50	9.40
450.0	20.90	8.90
480.0	21.30	8.50
510.0	21.70	8.10
540.0	22.00	7.80
570.0	22.30	7.50
600.0	22.60	7.10
630.0	22.90	6.80
660.0	23.30	6.40
690.0	23.60	6.10
720.0	23.80	5.90
750.0	24.00	5.70
780.0	24.20	5.50
810.0	24.40	5.30
840.0	24.70	5.00
870.0	25.00	4.70
900.0	25.20	4.50
930.0	25.50	4.20
960.0	25.70	4.00
990.0	25.90	3.80
1020.0	26.10	3.60
1050.0	26.30	3.30
1080.0	26.60	3.00
1110.0	26.80	2.90
1140.0	27.00	2.70
1170.0	27.20	2.50

*ATMOSPHERIC PRESSURE WAS 714.20 MM MERCURY
EVACUATION PRESSURE WAS 320.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GN/CC AT 20 DEG C

TABLE XXI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 672.00 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.60	14.30
60.0	15.90	13.90
90.0	16.30	13.50
120.0	16.80	13.00
150.0	17.20	12.60
180.0	17.70	12.20
210.0	18.10	11.70
240.0	18.50	11.20
270.0	18.90	10.80
300.0	19.60	10.20
330.0	20.00	9.80
360.0	20.40	9.40
390.0	20.80	8.90
420.0	21.20	8.50
450.0	21.60	7.90
480.0	22.20	7.50
510.0	22.50	7.20
540.0	22.90	6.80
570.0	23.30	6.40
600.0	23.70	6.00
630.0	23.90	5.80
660.0	24.20	5.40
690.0	24.50	5.10
720.0	24.80	4.80
750.0	25.20	4.40
780.0	25.50	4.10
810.0	25.80	3.80
840.0	26.00	3.60
870.0	26.30	3.30
900.0	26.60	3.00
930.0	26.80	2.70
960.0	27.10	2.30
990.0	27.30	2.20
1020.0	27.60	1.90
1050.0	27.90	1.60
1080.0	28.10	1.40
1110.0	28.30	1.20
1140.0	28.50	1.00
1170.0	28.70	0.80

*ATMOSPHERIC PRESSURE WAS 712.00 MM MERCURY
EVACUATION PRESSURE WAS 540.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXII

HANDMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 699.40 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.50	14.50
60.0	15.80	14.20
90.0	16.80	13.30
120.0	16.60	13.50
150.0	17.10	12.90
180.0	17.30	12.70
210.0	17.80	12.20
240.0	18.20	11.80
270.0	18.80	11.40
300.0	19.20	10.80
330.0	19.70	10.30
390.0	20.50	9.50
420.0	20.90	9.00
450.0	21.20	8.70
480.0	21.70	8.20
510.0	22.60	8.00
540.0	22.40	7.40
570.0	22.70	7.10
600.0	22.90	7.00
630.0	23.20	6.60
660.0	23.60	6.30
690.0	23.80	5.90
720.0	24.20	5.60
750.0	24.50	5.30
780.0	24.80	5.00
810.0	25.10	4.80
840.0	25.30	4.40
870.0	25.60	4.20
900.0	25.80	4.00
930.0	26.00	3.80
960.0	26.20	3.50
990.0	26.50	3.20
1020.0	26.70	3.00
1050.0	26.90	2.80
1080.0	27.20	2.60
1110.0	27.30	2.40
1140.0	27.60	2.20
1170.0	27.70	2.00

*ATMOSPHERIC PRESSURE WAS 699.40 MM MERCURY
EVACUATION PRESSURE WAS 520.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXIII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 593.30 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.20	14.80
60.0	15.50	14.50
90.0	15.70	14.30
120.0	15.90	14.10
150.0	16.20	13.80
180.0	16.60	13.40
210.0	17.00	13.00
240.0	17.30	12.70
270.0	17.60	12.30
300.0	17.80	12.10
330.0	18.40	11.60
360.0	18.70	11.20
390.0	19.00	10.90
420.0	19.40	10.50
450.0	19.70	10.20
480.0	20.00	9.90
510.0	20.30	9.60
540.0	20.50	9.40
570.0	20.60	9.00
600.0	21.10	8.80
630.0	21.30	8.60
660.0	21.60	8.30
690.0	21.90	8.00
720.0	22.20	7.70
750.0	22.40	7.50
780.0	22.60	7.20
810.0	22.90	7.00
840.0	23.10	6.80
870.0	23.30	6.50
900.0	23.50	6.30
930.0	23.60	6.00
960.0	24.00	5.80
990.0	24.15	5.75
1020.0	24.30	5.50
1050.0	24.50	5.30
1080.0	24.70	5.10
1110.0	24.90	4.90
1140.0	25.10	4.70
1170.0	25.20	4.50

*ATMOSPHERIC PRESSURE WAS 713.30 MM MERCURY

EVACUATION PRESSURE WAS 500.00 MM MERCURY

INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY

**BRODIE SOLUTION, DENSITY OF 1.033 GN/CC AT 20 DEG C

TABLE XXIV

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 594.20 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	14.96	14.90
30.0	15.20	14.80
60.0	15.40	14.50
90.0	15.60	14.30
120.0	15.80	14.10
150.0	16.00	13.90
180.0	16.40	13.50
210.0	16.60	13.30
240.0	17.10	12.80
270.0	17.40	12.50
300.0	17.70	12.20
330.0	17.90	11.90
360.0	18.20	11.60
390.0	18.50	11.30
420.0	18.90	10.90
450.0	19.20	10.60
480.0	19.50	10.30
510.0	19.80	10.00
540.0	20.00	9.80
570.0	20.30	9.50
600.0	20.50	9.30
630.0	20.80	9.00
660.0	21.00	8.80
690.0	21.15	8.65
720.0	21.30	8.40
750.0	21.60	8.20
780.0	21.80	7.90
810.0	22.05	7.70
840.0	22.20	7.50
870.0	22.40	7.30
900.0	22.60	7.10
930.0	22.80	6.90
960.0	23.00	6.70
990.0	23.20	6.50
1020.0	23.30	6.40
1050.0	23.50	6.20
1080.0	23.65	6.05
1110.0	23.80	5.90
1140.0	24.00	5.80
1170.0	24.10	5.60

*ATMOSPHERIC PRESSURE WAS 714.20 MM MERCURY
EVACUATION PRESSURE WAS 520.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 0.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXV

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 687.80 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	14.90	15.00
30.0	15.00	14.90
60.0	15.15	14.75
90.0	15.30	14.60
120.0	15.40	14.50
150.0	15.50	14.40
180.0	15.60	14.30
210.0	15.70	14.20
240.0	15.75	14.10
270.0	15.85	14.00
300.0	15.95	13.90
330.0	16.05	13.80
360.0	16.15	13.70
390.0	16.50	13.30
420.0	16.70	13.10
450.0	16.80	13.00
480.0	17.00	12.90
510.0	17.10	12.70
540.0	17.20	12.60
570.0	17.30	12.50
600.0	17.40	12.40
630.0	17.50	12.30
660.0	17.60	12.20
690.0	17.70	12.10
720.0	17.80	12.00
750.0	17.90	11.90
780.0	18.00	11.80
810.0	18.10	11.70
840.0	18.20	11.60
870.0	18.60	11.20
900.0	18.70	11.10
930.0	18.80	11.00
960.0	18.90	10.90
990.0	19.00	10.80
1020.0	19.10	10.70
1050.0	19.20	10.60
1080.0	19.30	10.50
1110.0	19.40	10.40
1140.0	19.50	10.30
1170.0	19.55	10.20

*ATMOSPHERIC PRESSURE WAS 707.80 MM MERCURY

EVACUATION PRESSURE WAS 150.00 MM MERCURY

INITIAL SATURATION PRESSURE WAS 557.80 MM MERCURY

**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXVI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 703.90 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	14.70	14.70
30.0	14.85	14.60
60.0	15.00	14.45
90.0	15.15	14.30
120.0	15.30	14.15
150.0	15.40	14.00
180.0	15.55	13.85
210.0	15.70	13.75
240.0	15.85	13.60
270.0	16.00	13.40
300.0	16.20	13.20
330.0	16.30	13.00
360.0	16.50	12.85
390.0	16.75	12.65
420.0	16.90	12.45
450.0	17.05	12.30
480.0	17.20	12.15
510.0	17.40	11.95
540.0	17.60	11.75
570.0	17.70	11.65
600.0	17.80	11.55
630.0	17.90	11.45
660.0	18.05	11.35
690.0	18.50	10.80
720.0	18.65	10.65
750.0	18.80	10.50
780.0	19.00	10.30
810.0	19.10	10.20
840.0	19.25	10.05
870.0	19.40	9.90
900.0	19.50	9.80
930.0	19.65	9.65
960.0	19.75	9.55
990.0	19.90	9.40
1020.0	20.00	9.30
1050.0	20.10	9.20
1080.0	20.20	9.10
1110.0	20.35	8.95
1140.0	20.45	8.85
1170.0	20.55	8.75

*ATMOSPHERIC PRESSURE WAS 712.40 MM MERCURY

EVACUATION PRESSURE WAS 146.50 MM MERCURY

INITIAL SATURATION PRESSURE WAS 565.90 MM MERCURY

**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXVII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 700.00 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	14.80	14.80
30.0	15.00	14.60
60.0	15.10	14.45
90.0	15.25	14.30
120.0	15.35	14.20
150.0	15.50	14.10
180.0	15.60	14.00
210.0	15.70	13.85
240.0	15.80	13.75
270.0	15.90	13.60
300.0	16.00	13.50
330.0	16.10	13.40
360.0	16.20	13.30
390.0	16.30	13.20
420.0	16.50	13.00
450.0	16.70	12.80
480.0	16.80	12.70
510.0	16.90	12.60
540.0	17.00	12.50
570.0	17.10	12.40
600.0	17.20	12.30
630.0	17.30	12.20
660.0	17.40	12.10
690.0	17.50	12.00
720.0	17.55	11.95
750.0	17.60	11.90
780.0	17.70	11.80
810.0	17.75	11.75
840.0	17.80	11.70
870.0	17.85	11.65
900.0	17.90	11.55
930.0	18.00	11.50
960.0	18.10	11.40
990.0	18.20	11.30
1020.0	18.55	10.90
1050.0	18.60	10.85
1080.0	18.70	10.75
1110.0	18.80	10.70
1140.0	18.85	10.60
1170.0	18.90	10.50

*ATMOSPHERIC PRESSURE WAS 706.00 MM MERCURY
EVACUATION PRESSURE WAS 149.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 550.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXVIII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 706.90 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	14.65	14.80
30.0	14.75	14.70
60.0	14.80	14.59
90.0	15.05	14.45
120.0	15.15	14.30
150.0	15.30	14.20
180.0	15.40	14.09
210.0	15.55	13.95
240.0	15.65	13.80
270.0	15.70	13.75
300.0	15.80	13.60
330.0	15.90	13.50
360.0	16.05	13.40
390.0	16.15	13.30
420.0	16.45	12.95
450.0	16.65	12.75
480.0	16.75	12.65
510.0	16.90	12.50
540.0	17.00	12.40
570.0	17.10	12.30
600.0	17.20	12.20
630.0	17.30	12.20
660.0	17.40	12.00
690.0	17.50	11.85
720.0	17.60	11.80
750.0	17.65	11.70
780.0	17.70	11.65
810.0	17.75	11.60
840.0	17.85	11.50
870.0	17.90	11.45
900.0	18.00	11.35
930.0	18.15	11.20
960.0	18.50	10.90
990.0	18.60	10.80
1020.0	18.70	10.70
1050.0	18.80	10.60
1080.0	18.85	10.50
1110.0	18.95	10.40
1140.0	19.00	10.30
1170.0	19.10	10.25

*ATMOSPHERIC PRESSURE WAS 712.40 MM MERCURY
EVACUATION PRESSURE WAS 148.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 564.40 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXIX

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 714.60 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	14.70	14.80
30.0	14.90	14.60
60.0	15.05	14.45
90.0	15.20	14.30
120.0	15.30	14.20
150.0	15.40	14.10
180.0	15.50	14.00
210.0	15.60	13.90
240.0	15.70	13.80
270.0	15.85	13.65
300.0	16.00	13.50
330.0	16.10	13.40
360.0	16.15	13.35
390.0	16.40	13.10
420.0	16.50	12.95
450.0	16.70	12.80
480.0	16.80	12.70
510.0	17.00	12.50
540.0	17.10	12.40
570.0	17.25	12.20
600.0	17.40	12.10
630.0	17.50	11.90
660.0	17.60	11.80
690.0	17.70	11.70
720.0	17.80	11.65
750.0	17.85	11.60
780.0	17.95	11.50
810.0	18.05	11.40
840.0	18.20	11.35
870.0	18.60	10.80
900.0	18.70	10.70
930.0	18.80	10.60
960.0	18.90	10.50
990.0	19.00	10.40
1020.0	19.10	10.30
1050.0	19.20	10.20
1080.0	19.30	10.10
1110.0	19.40	10.00
1140.0	19.50	9.90
1170.0	19.60	9.80

*ATMOSPHERIC PRESSURE WAS 708.60 MM MERCURY

EVACUATION PRESSURE WAS 140.00 MM MERCURY

INITIAL SATURATION PRESSURE WAS 568.60 MM MERCURY

**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXX

HANDMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 708.80 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	14.70	14.70
30.0	14.80	14.60
60.0	14.90	14.50
90.0	15.00	14.35
120.0	15.15	14.25
150.0	15.25	14.10
180.0	15.40	13.95
210.0	15.50	13.80
240.0	15.65	13.70
270.0	15.80	13.55
300.0	15.95	13.45
330.0	16.00	13.35
360.0	16.05	13.30
390.0	16.35	13.00
420.0	16.50	12.85
450.0	16.60	12.70
480.0	16.75	12.60
510.0	16.85	12.45
540.0	17.00	12.35
570.0	17.10	12.20
600.0	17.20	12.10
630.0	17.35	12.00
660.0	17.45	11.95
690.0	17.60	11.75
720.0	17.65	11.65
750.0	17.75	11.55
780.0	17.80	11.50
810.0	17.85	11.45
840.0	17.90	11.40
870.0	18.00	11.30
900.0	18.15	11.15
930.0	18.20	11.10
960.0	18.55	10.80
990.0	18.65	10.65
1020.0	18.75	10.50
1050.0	18.85	10.40
1080.0	18.95	10.35
1110.0	19.05	10.25
1140.0	19.10	10.15
1170.0	19.20	10.05

*ATMOSPHERIC PRESSURE WAS 710.80 MM MERCURY
EVACUATION PRESSURE WAS 151.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 359.80 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXXI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 714.80 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	14.80	14.90
30.0	14.90	14.80
60.0	15.05	14.65
90.0	15.20	14.50
120.0	15.35	14.35
150.0	15.45	14.20
180.0	15.55	14.10
210.0	15.65	14.00
240.0	15.75	13.90
270.0	15.85	13.80
300.0	16.00	13.65
330.0	16.10	13.50
360.0	16.50	13.10
390.0	16.70	12.90
420.0	16.85	12.75
450.0	17.00	12.60
480.0	17.15	12.50
510.0	17.25	12.30
540.0	17.40	12.20
570.0	17.50	12.10
600.0	17.60	12.00
630.0	17.65	11.90
660.0	17.70	11.85
690.0	17.80	11.80
720.0	17.90	11.65
750.0	18.00	11.55
780.0	18.20	11.40
810.0	18.55	11.00
840.0	18.65	10.95
870.0	18.75	10.80
900.0	18.85	10.70
930.0	18.95	10.60
960.0	19.05	10.50
990.0	19.15	10.40
1020.0	19.25	10.30
1050.0	19.35	10.20
1080.0	19.45	10.10
1110.0	19.55	10.00
1140.0	19.65	9.90
1170.0	19.75	9.80

*ATMOSPHERIC PRESSURE WAS 704.80 MM MERCURY
EVACUATION PRESSURE WAS 150.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 554.80 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXXII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 709.80 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	14.90	15.15
30.0	15.00	15.00
60.0	15.20	14.80
90.0	15.40	14.60
120.0	15.55	14.50
150.0	15.65	14.40
180.0	15.70	14.30
210.0	15.85	14.15
240.0	16.00	14.00
270.0	16.15	13.85
300.0	16.50	13.50
330.0	16.70	13.30
360.0	16.85	13.15
390.0	17.00	13.00
420.0	17.15	12.80
450.0	17.35	12.65
480.0	17.50	12.50
510.0	17.60	12.35
540.0	17.70	12.20
570.0	17.80	12.10
600.0	17.90	12.00
630.0	18.05	11.90
660.0	18.20	11.70
690.0	18.65	11.30
720.0	18.80	11.15
750.0	18.90	11.00
780.0	19.05	10.90
810.0	19.20	10.75
840.0	19.35	10.60
870.0	19.45	10.45
900.0	19.55	10.35
930.0	19.70	10.20
960.0	19.80	10.10
990.0	19.80	10.00
1020.0	19.95	9.95
1050.0	20.00	9.90
1080.0	20.10	9.80
1110.0	20.30	9.65
1140.0	20.40	9.55
1170.0	20.45	9.45

*ATMOSPHERIC PRESSURE WAS 708.80 MM MERCURY
EVACUATION PRESSURE WAS 200.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 508.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXXIII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 736.80 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	19.00	19.00
30.0	15.20	14.80
60.0	15.45	14.60
90.0	15.60	14.40
120.0	15.80	14.25
150.0	15.90	14.10
180.0	16.10	13.95
210.0	16.40	13.60
240.0	16.70	13.30
270.0	16.90	13.10
300.0	17.15	12.85
330.0	17.35	12.65
360.0	17.55	12.45
390.0	17.70	12.30
420.0	17.80	12.20
450.0	17.95	12.05
480.0	18.20	11.80
510.0	18.60	11.40
540.0	18.85	11.10
570.0	19.00	10.90
600.0	19.20	10.75
630.0	19.40	10.60
660.0	19.55	10.40
690.0	19.70	10.30
720.0	19.75	10.20
750.0	19.85	10.05
780.0	20.00	9.90
810.0	20.10	9.80
840.0	20.30	9.60
870.0	20.50	9.45
900.0	20.60	9.30
930.0	20.75	9.15
960.0	20.90	9.00
990.0	21.00	8.90
1020.0	21.15	8.75
1050.0	21.30	8.60
1080.0	21.40	8.50
1110.0	21.55	8.35
1140.0	21.70	8.20
1170.0	21.80	8.05

*ATMOSPHERIC PRESSURE WAS 708.80 MM MERCURY

EVACUATION PRESSURE WAS 200.00 MM MERCURY

INITIAL SATURATION PRESSURE WAS 508.80 MM MERCURY

**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXXIV

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 699.55 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	15.00
30.0	15.20	14.75
60.0	15.50	14.50
90.0	15.70	14.25
120.0	15.85	14.15
150.0	16.00	14.00
180.0	16.10	13.85
210.0	16.40	13.50
240.0	16.75	13.20
270.0	17.00	12.90
300.0	17.20	12.70
330.0	17.45	12.45
360.0	17.65	12.35
390.0	17.75	12.15
420.0	17.90	12.00
450.0	18.10	11.80
480.0	18.60	11.50
510.0	18.80	11.10
540.0	19.00	10.85
570.0	19.20	10.65
600.0	19.35	10.45
630.0	19.55	10.30
660.0	19.70	10.15
690.0	19.85	10.00
720.0	20.00	9.85
750.0	20.10	9.75
780.0	20.30	9.50
810.0	20.45	9.35
840.0	20.65	9.15
870.0	20.80	9.00
900.0	20.90	8.90
930.0	21.10	8.70
960.0	21.20	8.60
990.0	21.30	8.50
1020.0	21.50	8.30
1050.0	21.70	8.10
1080.0	21.90	7.90
1110.0	22.00	7.80
1140.0	22.10	7.70
1170.0	22.20	7.55

*ATMOSPHERIC PRESSURE WAS 707.40 MM MERCURY
EVACUATION PRESSURE WAS 248.50 MM MERCURY
INITIAL SATURATION PRESSURE WAS 558.90 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXXV

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 704.00 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.00	14.90
30.0	15.20	14.70
60.0	15.50	14.45
90.0	15.65	14.35
120.0	15.80	14.10
150.0	15.95	13.95
180.0	16.10	13.80
210.0	16.55	13.30
240.0	16.80	13.10
270.0	17.05	12.80
300.0	17.30	12.60
330.0	17.50	12.30
360.0	17.70	12.10
390.0	17.85	12.00
420.0	18.00	11.85
450.0	18.20	11.60
480.0	18.70	11.10
510.0	18.90	10.90
540.0	19.10	10.70
570.0	19.30	10.50
600.0	19.50	10.30
630.0	19.70	10.10
660.0	19.80	10.00
690.0	20.00	9.80
720.0	20.10	9.70
750.0	20.30	9.50
780.0	20.50	9.30
810.0	20.70	9.10
840.0	20.90	8.90
870.0	21.00	8.80
900.0	21.10	8.70
930.0	21.25	8.50
960.0	21.35	8.40
990.0	21.60	8.15
1020.0	21.70	8.05
1050.0	21.90	7.80
1080.0	22.05	7.70
1110.0	22.15	7.60
1140.0	22.25	7.50
1170.0	22.50	7.40

*ATMOSPHERIC PRESSURE WAS 708.00 MM MERCURY
EVACUATION PRESSURE WAS 249.50 MM MERCURY
INITIAL SATURATION PRESSURE WAS 458.50 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXXVI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 698.00 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	14.80	15.00
30.0	15.10	14.70
60.0	15.40	14.40
90.0	15.60	14.20
120.0	15.80	14.00
150.0	16.00	13.80
180.0	16.45	13.35
210.0	16.80	13.00
240.0	17.05	12.75
270.0	17.35	12.45
300.0	17.60	12.20
330.0	17.80	12.00
360.0	18.00	11.80
390.0	18.50	11.30
420.0	18.80	11.00
450.0	19.00	10.80
480.0	19.25	10.55
510.0	19.50	10.25
540.0	19.75	10.00
570.0	19.90	9.80
600.0	20.10	9.60
630.0	20.40	9.30
660.0	20.60	9.10
690.0	20.80	8.90
720.0	21.00	8.70
750.0	21.20	8.50
780.0	21.30	8.40
810.0	21.60	8.10
840.0	21.90	7.80
870.0	22.10	7.60
900.0	22.20	7.50
930.0	22.30	7.40
960.0	22.40	7.30
990.0	22.70	7.00
1020.0	22.90	6.80
1050.0	23.00	6.70
1080.0	23.20	6.50
1110.0	23.40	6.30
1140.0	23.60	6.10
1170.0	23.70	6.00

*ATMOSPHERIC PRESSURE WAS 708.00 MM MERCURY

EVACUATION PRESSURE WAS 299.00 MM MERCURY

INITIAL SATURATION PRESSURE WAS 409.00 MM MERCURY

**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXXVII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 705.50 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	15.10	14.80
30.0	15.50	14.30
60.0	15.80	14.00
90.0	16.05	13.75
120.0	16.45	13.35
150.0	16.85	12.95
180.0	17.25	12.60
210.0	17.45	12.25
240.0	17.70	12.00
270.0	18.00	11.70
300.0	18.65	11.05
330.0	19.00	10.70
360.0	19.30	10.40
390.0	19.65	10.05
420.0	19.95	9.75
450.0	20.30	9.40
480.0	20.55	9.10
510.0	20.90	8.80
540.0	21.10	8.50
570.0	21.40	8.30
600.0	21.90	7.70
630.0	22.10	7.50
660.0	22.30	7.30
690.0	22.60	7.00
720.0	22.90	6.70
750.0	22.30	6.40
780.0	23.40	6.20
810.0	23.80	6.00
840.0	23.90	5.70
840.0	24.10	5.50
900.0	24.30	5.25
930.0	24.60	5.00
960.0	24.60	4.80
990.0	25.00	4.55
1020.0	25.20	4.35
1050.0	25.40	4.20
1080.0	25.55	4.00
1110.0	25.80	3.75
1140.0	25.90	3.60
1170.0	26.10	3.40

*ATMOSPHERIC PRESSURE WAS 710.00 MM MERCURY

EVACUATION PRESSURE WAS 346.00 MM MERCURY

INITIAL SATURATION PRESSURE WAS 364.00 MM MERCURY

**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

TABLE XXXVIII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE
IN WATER AT 712.00 MM OF MERCURY*

TIME SEC	LEFT READING MM FLUID**	RIGHT READING MM FLUID**
0.0	14.80	15.00
30.0	15.20	14.60
60.0	15.50	14.30
90.0	15.75	14.05
120.0	16.10	13.80
150.0	16.40	13.50
180.0	16.80	13.00
210.0	17.20	12.60
240.0	17.50	12.30
270.0	17.75	12.00
300.0	18.00	11.70
330.0	18.60	11.25
360.0	18.90	10.80
390.0	19.30	10.40
420.0	19.55	10.05
450.0	19.80	9.85
480.0	20.10	9.65
510.0	20.40	9.30
540.0	20.70	8.90
570.0	21.05	8.60
600.0	21.20	8.45
630.0	21.55	8.10
660.0	21.90	7.80
690.0	22.10	7.60
720.0	22.30	7.40
750.0	22.50	7.10
780.0	22.80	6.80
810.0	23.10	6.60
840.0	23.35	6.30
870.0	23.50	6.10
900.0	23.80	5.80
930.0	24.00	5.60
960.0	24.20	5.40
990.0	24.40	5.20
1020.0	24.60	5.00
1050.0	24.80	4.80
1080.0	25.00	4.60
1110.0	25.15	4.45
1140.0	25.30	4.30
1170.0	25.50	4.10

*ATMOSPHERIC PRESSURE WAS 710.00 MM MERCURY
EVACUATION PRESSURE WAS 344.00 MM MERCURY
INITIAL SATURATION PRESSURE WAS 366.00 MM MERCURY
**BRODIE SOLUTION, DENSITY OF 1.033 GM/CC AT 20 DEG C

Referring to Figure 36, the quiescent liquid absorption apparatus is represented by a gas-water system, A, on the reaction side and a pure gas system, B, on the dummy side. These two sections are separated by the manometer, C. Initially the manometer level is either the same or at a known initial h . As the absorption proceeds the pressure changes in the absorption side due to the absorption of the gas. The volume on the absorption side decreases, as does the pressure. In order to make conversion to gram-moles easier in the final result, the gas uptake is expressed at standard conditions.

The initial quantity of gas present (referred to standard conditions) in the absorption side is:

$$Vg_i = Vg \times \frac{273.16}{T} \times \frac{PP-pw}{Po} \quad (7)$$

where:

- Vg_i = initial volume of gas at S.C., cm^3
- Vg = volume of gas space and tubing, cm^3
- T = temperature of test, $^{\circ}K$
- PP = initial pressure in system, mm of fluid
(Brodie solution, density of 1.033 gm/cm^3 at $20^{\circ}C$)
- pw = vapor pressure of water at temperature T ,
mm of fluid
- Po = normal pressure (760 mm Hg), mm of fluid

After a specified amount of absorption, the volume of gas remaining in the gas space is:

$$Vg_f = \left[\left(Vg - \frac{Ah}{20} \right) \times \frac{273}{T} \times \left(\frac{PP - pw + \Delta p}{Po} \right) \right] \quad (8)$$

LEGEND

- A - ABSORPTION SECTION
- B - DUMMY SECTION
- C - MANOMETER
- h - FLUID HEIGHT

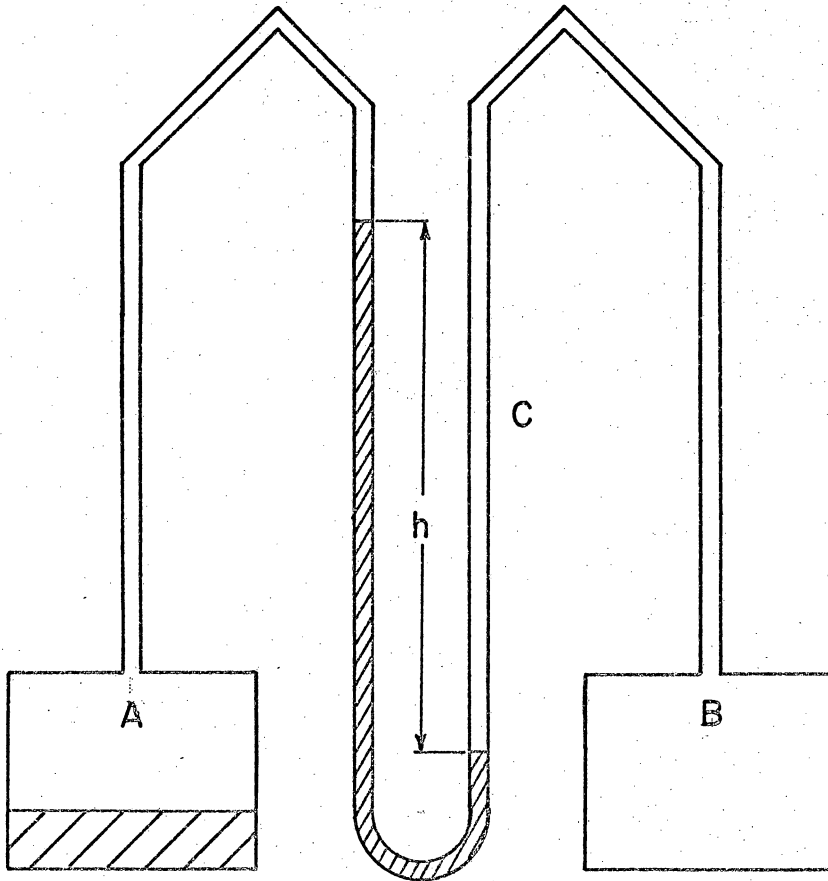


FIGURE 36. REPRESENTATION OF THE QUIESCENT LIQUID APPARATUS

where:

- V_{g_f} = final volume of gas at S.C., cm^3
- A = area of manometer bore, cm
- h = height of manometer fluid, mm of fluid
- ΔP = pressure change in reaction cell, mm fluid

Note that the pressure change in the reaction cell is not the same as the change in the manometer because the pressure has also changed in the dummy cell.

The amount of gas absorbed is the difference between the initial and final volumes of gas present. Therefore,

$$X = V_g \times \frac{273}{T} \times \frac{PP - p_w}{P_o} - V_g \times \frac{273}{T} \times \left(\frac{PP - p_w + \Delta p}{P_o} \right) + \frac{Ah}{20} \times \frac{273}{T} \times \left(\frac{PP - p_w + \Delta p}{P_o} \right) \quad (9)$$

where:

$$X = \text{gas absorbed at standard conditions, cm}^3$$

Reducing this equation to its simplest form:

$$X = \frac{273}{TP_o} \times \Delta p \times \left[\frac{Ah}{20} \times \left(\frac{PP - p_w + \Delta p}{\Delta p} \right) - V_g \right] \quad (10)$$

As a result of the absorption process, the volume in the dummy side will increase. If the gas is assumed to be ideal, this results in a decrease in pressure. However, it will be smaller than the decrease on the absorption side.

The same nomenclature used for the absorption side is used in the derivation of the volume change in the dummy side except that primes are used to refer to the dummy vessel. The initial volume of gas present in the dummy side (at standard conditions) is:

$$V_{g_i}' = V_{g'} \times \frac{273}{T} \times \frac{PP}{P_o} \quad (11)$$

where:

$$V_{g'} = \text{total gas space on dummy side, cm}^3$$

The final volume of gas present in the dummy side is:

$$V_{g_f}' = \left[\left(V_{g'} + \frac{Ah}{20} \right) \times \frac{273}{T} \times \left(\frac{PP + \Delta p'}{P_o} \right) \right] \quad (12)$$

The only change in the gas volume is the $\frac{Ah}{20}$ term. If the absorption is assumed to proceed without loss of gas, then the moles present initially and finally are the same. Therefore, the quantities are equated, realizing that a conversion factor to moles drops out.

$$V_{g_i}' = V_{g_f}' = V_{g'} \times \frac{273}{T} \times \frac{PP}{P_o} = \left[\left(V_{g'} + \frac{Ah}{20} \right) \times \frac{273}{T} \times \left(\frac{PP + \Delta p'}{P_o} \right) \right] \quad (13)$$

Cancelling terms and simplifying this equation results in the following equation:

$$-V_{g'} \Delta p' = \frac{Ah}{20} PP + \frac{Ah}{20} \Delta p' \quad (14)$$

or, solving for $\Delta p'$:

$$\Delta p' = \frac{-AhPP}{(Ah + 20 V_{g'})} \quad (15)$$

The pressure changes in the reaction and dummy vessels are related by the change in the manometer reading h as follows:

$$h = \Delta p' - \Delta p \quad (16)$$

This can be reasoned from the expected large value for Δp compared to $\Delta p'$. Solving for Δp :

$$\Delta p = \Delta p' - h \quad (17)$$

Substituting this result into the relation for the amount of gas absorbed in the reaction side gives the amount of gas absorbed in terms of known quantities.

Relation of Gas Uptake to Time. For reasons of continuity, the solution of the differential equation relating gas uptake to time for a quiescent liquid system at pressure P is repeated here. It is given by equation 4 as:

$$\bar{N}_a = \frac{2P}{H} \sqrt{\frac{Dt}{\pi}} \quad (4)$$

where:

$$\bar{N}_a = \text{gm-moles gas absorbed/cm}^2\text{-sec}$$

$$P = \text{pressure of system, mm Hg}$$

$$H = \text{Henry's Law constant, mm Hg - cm}^3\text{/gm mole}$$

$$t = \text{time, sec}$$

$$\pi = 3.1416$$

Sample Calculations

This section gives examples of the procedure followed in going from experimental quantities to other reported quantities.

Constants of the Absorption Apparatus. The procedure for determining the constants of the apparatus has been given on page 20. The calculations used in obtaining the constants are given for each part of the system.

Manometer Cross Sectional Area Determination. The cross sectional area of the manometer was determined by weighing a quantity of mercury required to fill a specific length of the manometer.

The cross sectional area of the manometer is given by:

$$A_b = W \times \frac{1}{\rho} \times \frac{1}{L} \quad (18)$$

where:

$$\begin{aligned} A_b &= \text{cross sectional area, cm}^2 \\ W &= \text{weight of mercury bead, gm} \\ \rho &= \text{density of mercury at 25°F, gm/cm}^3 \\ L &= \text{length of bead, cm} \end{aligned}$$

Substituting from Table III for the average value of the right side:

$$\begin{aligned} W &= 1.99 \\ \rho &= 13.54^{(33)} \\ L &= 9.73 \\ A_b &= 1.99 \times \frac{1}{13.54} \times 9.73 \\ &= 0.0151 \text{ cm}^2 \end{aligned}$$

Volume of Cells. The volumes of the reaction and dummy cells were determined from the weight and density of the mercury required to fill them. For a known weight of mercury, the volume it fills is given as:

$$V = \frac{W}{\rho} \quad (19)$$

where:

$$\begin{aligned} V &= \text{volume of system, cm}^3 \\ W &= \text{weight of mercury bead, gm} \\ \rho &= \text{density of mercury at 25°F, gm/cm}^3 \end{aligned}$$

Using the data from Table V for the reaction cell and tubing:

$$\begin{aligned} W &= 2,142.73 \\ V &= \frac{2,142.73}{13.54} \\ &= 158.25 \text{ cm}^3 \end{aligned}$$

Cross-Section Check on Cells. Since both cells were made from the same size glass disks, only one cell was checked for accuracy.

Upon addition of a known quantity of water to the cell, causing a specific change in height, the area of the cell is given as:

$$A_c = \frac{\Delta V}{\Delta h} \quad (20)$$

where:

$$\begin{aligned} A_c &= \text{area of the cell, cm}^2 \\ \Delta V &= \text{volume change, cm}^3 \\ \Delta h &= \text{height change, cm} \end{aligned}$$

Substituting from Table IV, for Test 1:

$$\begin{aligned} A_c &= \frac{20.00}{0.60} \\ &= 33.33 \text{ cm}^3 \end{aligned}$$

The diameter of the cell is given by the relation for the area of a circle:

$$\frac{\pi D^2}{4} = A_c \quad (21)$$

where:

$$D = \text{diameter of cell, cm}$$

Therefore,

$$\begin{aligned} D &= \frac{33.33}{0.785}^{0.5} \\ &= 6.49 \text{ cm} \end{aligned}$$

Amount of Gas Absorbed. The gas uptake is related to the change in manometer readings by the following equations derived on pages 103 through 137.

$$\Delta p' = \frac{-AhPP}{(Ah + 20 Vg)} \quad (15)$$

$$\Delta p = \Delta p' - h \quad (17)$$

$$X = \frac{273.16}{TPo} \times \Delta p \times \left[\frac{Ah}{20} \times \left(\frac{PP - pw + \Delta p}{\Delta p} \right) - Vg \right] \quad (10)$$

where:

h = change in manometer height, mm

A = area of manometer bore, cm²

PP = initial pressure in system, mm fluid

Vg = volume of gas space, cm³

Δp' = pressure change in dummy vessel, mm fluid

Δp = pressure change in reaction side, mm fluid

T = temperature of absorption run, °K

pw = vapor pressure of water, mm fluid

X = amount of gas absorbed at standard conditions, cm³

The pressures given in Tables X through XXXVIII are in mm of Hg and must be converted to mm of fluid. The densities of mercury and the measuring fluid are:

$$\rho_{Hg} = 13.54 \text{ gm/cm}^3 \text{ at } 25^\circ\text{F} \quad (33)$$

$$\rho_{\text{fluid}} = 1.033 \text{ gm/cm}^3 \text{ at } 25^\circ\text{C} \quad (14)$$

Substituting data from V and VVIX, respectively, for the first value of h:

$$\begin{aligned}h &= 16.0 \\PP &= 699.4 \times 13.54/1.033 = 9,150 \\Vg &= 158.25 \\A &= 0.0154 \\T &= 298.16 \\\Delta p' &= \frac{-0.0154 \times 16.0 \times 699.4 \times 13.54}{0.0154 \times 16.0 + 20 \times 158.25} \\&= -0.713 \text{ mm fluid}\end{aligned}$$

and substituting into equation 17:

$$\begin{aligned}\Delta p &= -0.713 - 16.0 \\&= -16.713 \text{ mm fluid}\end{aligned}$$

The vapor pressure of water and the normal pressure must be determined in mm of fluid as follows:

$$\begin{aligned}p_w' &= 23.756 \text{ mm mercury}^{(33)} \\P_o' &= 760.0 \text{ mm mercury} \\p_w &= \frac{23.756 \times 13.54}{1.033} \\&= 315.50 \text{ mm fluid} \\P_o &= \frac{760.0 \times 13.54}{1.033} \\&= 9,960 \text{ mm fluid}\end{aligned}$$

Substituting data from Table V and the calculations above into equation 10 for the gas absorption:

$$\begin{aligned}X &= \frac{273.16}{298.16 \times 9,960} \times (-16.713) \times \frac{0.0154 \times 16.0}{20.0} \times \\&\quad \frac{9,150 - 315.5 + 16.73}{(-16.713)} - 158.25 \\&= 0.223 \text{ cm}^3\end{aligned}$$

The gas absorbed per square centimeter is found by dividing the gas absorbed by the cross sectional area of the cell from Table V:

$$\begin{aligned} X' &= \frac{0.223}{33.34} \\ &= 0.0067 \text{ cm}^3/\text{cm}^2 \end{aligned}$$

Diffusion Coefficient. The relation between amounts of gas absorbed and time is given by equation 4. The units of this equation require the following value for Henry's law constant:

$$H = 2.245 \times 10^7 \text{ mm Hg--cm}^3/\text{gm mole} \quad (43)$$

The slope of a plot of gas uptake versus \sqrt{t} gives the quantity $\frac{2 P}{H} \sqrt{\frac{D}{\pi}}$ and can be used to determine the diffusion coefficient. The slope obtained from an absorption curve such as Figure 22 by a least square solution for the initial linear region has the units $\text{cm}^3/\text{cm}^2\text{-sec}^{1/2}$. Division of this quantity by the standard molar volume gives units of $\text{gm moles}/\text{cm}^2\text{-sec}^{1/2}$ as required by equation 4.

Substituting data from Table IX for Test 1:

$$P = 130.0 \text{ (}\Delta P \text{ for initial concentration tests)}$$

$$\text{Slope} = 0.846 \times 10^{-3}$$

Solving for the diffusion coefficient:

$$\begin{aligned} D &= \left[\frac{0.846 \times 10^{-3} \times 2.245 \times 10^7 \times 3.1416^{1/2}}{2 (130.0)} \right]^2 \quad (22) \\ &= 2.11 \times 10^{-5} \text{ cm}^2/\text{sec} \end{aligned}$$

Computer Programs. A computer program for calculating the amount of gas absorbed from the manometer differential h is given in Figure 37. The computer calculation used for a least squares fit of the data points is given in Figure 38.

FIGURE 37. COMPUTER PROGRAM FOR CALCULATING

GAS ABSORPTION FROM MANOMETER DATA

```

COMMON A0,A1,PP,PEQ
DIMENSION H(40),T(40),DELP(40),X(40),TSQT(40),Z(40),HCM(40),XX(40)
1 FORMAT (4F7.2)
8 FORMAT (///,55X,'ABSORPTION DATA')
13 FORMAT(///5X,15HTIME IN SECONDS,5X,15HSQUARE ROOT T ,5X,15HPRESSU
1RE CHANGE,5X,15HDELTA P VALUES ,5X,15HAMT. GAS ABSORB,5X,15HGAS AB
2SORB/SQCM)
18 FORMAT (6E20.7)
20 FORMAT (///10X,'RUN = ',I3,2X,'P = ',F9.4,2X,'PP = ',F9.4,2X,'P EV
1AC = ',F9.4,2X,'P INIT CONC = ',F9.4,2X,'PRESS. GRAD. = ',F9.4)
K=0
100 READ(5,1)P,PP,PE,PEQ
READ,N
DO 2 I=1,N,1
2 READ,T(I),H(I)
TP=298.16
VPW=315.50
VG=138.25
AM=0.0154
PC=P*13.54/1.033
PPC=PP*13.54/1.033
PA=760.0*13.54/1.033
RP=PP-PEQ
DO 4 I=1,N,1
TSQT(I)=SQRT(T(I))
HCM(I)=H(I)/10.0
DELP(I)=-((H(I)+(AM*HCM(I)*PPC/(316.56+AM*HCM(I))))
X(I)=((DELP(I)*273.16/(TP*PA))*((AM*HCM(I)/2.0)*((PPC-VPW+DELP(I))/
1DELP(I))-VG)
4 XX(I)=X(I)/33.34
WRITE (6,8)
WRITE (6,20) K,P,PP,PE,PEQ,RP
WRITE (6,13)
WRITE(6,18)(T(I),TSQT(I),H(I),DELP(I),X(I),XX(I),I=1,N)
CALL LEASQU (N,TSQT,XX,Z)
K=K+1
IF (K .GE. 31) GO TO 15
GO TO 100
15 STOP
END

```

FIGURE 37. COMPUTER PROGRAM FOR CALCULATING

GAS ABSORPTION FROM MANOMETER DATA

FIGURE 38. COMPUTER PROGRAM FOR LEAST

SQUARES FITTING OF DATA POINTS

```
SUBROUTINE LEASQU (N,X,Y,Z)
  DIMENSION X(N),Y(N),Z(N)
  COMMON A0,A1,PP,PEQ
  99 FORMAT (29X,3F20.7)
  50 FORMAT (///37X,15HSQ. ROOT T/SECS,5X,15HGAS ABSORB/SQCM,5X,15HLEAS
  1T SQ VALUES)
  75 FORMAT (///20X,'A0 = ',E15.8,'A1 = ',E15.8)
  21 FORMAT (//20X,'THE VALUE OF THE DIFFUSION COEFFICIENT IS = ',E15.7
  1)
  YSUM = 0.0
  XSUM = 0.0
  XSQSUM = 0.0
  XYSUM = 0.0
  DO 1 I = 1,N
  XYSUM = XYSUM + X(I)*Y(I)
  YSUM = YSUM + Y(I)
  XSUM = XSUM + X(I)
  1 XSQSUM = XSQSUM + X(I)**2
  C = N
  DENOM = C*XSQSUM - XSUM**2
  A0 = (YSUM*XSQSUM - XSUM*XYSUM)/DENOM
  A1 = (C*XYSUM - YSUM*XSUM)/DENOM
  PIE=SQRT(3.1417)
  SPRIM=(A1/22400.0)
  DIFSQ=(SPRIM*2.245E+07*PIE/(2.0*(PP-PEQ)))**2
  WRITE (6,50)
  DO 2 I = 1,N
  Z(I) = A0 + A1*X(I)
  2 WRITE(6,99) X(I),Y(I),Z(I)
  WRITE (6,75) A0,A1
  WRITE (6,21) DIFSQ
  RETURN
  END
```

FIGURE 38. COMPUTER PROGRAM FOR LEAST

SQUARES FITTING OF DATA POINTS

Apparatus

A listing of the apparatus and details of its operation is given in this section.

Demineralizer. Bantum model BD-1, serial number NB 689. Unit has direct reading purity meter with range from 0.0 to 10 ppm chlorine concentration and a maximum flow rate of 10 gal/hr operating at atmospheric pressure, 110 V, 60 cps. Mixed resin cartridges, part number 0809 were utilized. Manufactured by Barnstead Still and Sterilizer Company, 2 Lanesville Terrace, Boston, Massachusetts. Used in deionizing distilled water for the absorption cell.

Constant Temperature Bath. Square glass-walled bath manufactured by the V.P.I. Chemical Engineering Shop. Dimensions of 29 inches x 29 inches and 24 inches deep. Temperature controlled by Mercurial Thermoregulator, catalog number S-81835, supplied by Sargent Chemical Company, Silver Springs, Maryland, coupled to a Fischer Transitor Relay, Model 32, 115 V, 15 amp, supplied by Fischer Scientific, Pittsburg, Pennsylvania. Used to maintain system at constant temperature.

Mixers. Two "Lightnin" model "L" mixers, 110 V, 50/60 cy, serial numbers 502663 and 514807 with 12-inch shafts. Manufactured by Mixing Equipment Company, Inc., Rochester, New York. Distributed by Fischer Scientific Company, Einer and Amend, New York, New York. Used to mix constant temperature bath.

Vacuum Pump. Cenco-Megavac Pump, serial number 8730, supplied by Central Scientific Company, Chicago, Illinois. Connected to a single phase Century Motor, model CSH-81-BK4-3 AFA, 115-230 V, 60 cy, 1750 rpm. Used to evacuate the system prior to absorption.

Temperature Compensated Differential Manometer. Built by V.P.I. Glass Shop using vacuum stopcocks, 6.5 centimeter diameter glass disks, and a Barcroft manometer. Used for measuring the absorption of gases in water.

Syringe. B-D Yale 20 cc. hypodermic syringe, glass tip. Serial number 2303-20y. Manufactured by Becton, Dickinson and Company, Rutherford, New Jersey. Used to introduce liquid into absorption cell.

Timer. Graduated to 1/10 second. Catalog number 69230, 120 V, 60 cy. Obtained from Precision Scientific Company, Pittsburg, Pennsylvania. Used to measure time for absorption in system.

Thermometer. Sargent, A.S.T.M. 630, number 2375, catalog number S-80280-B. Incremented in 1/10 degrees from -8 to +32 degrees centigrade, total immersion type. Obtained from Sargent Chemical Company, Silver Springs, Maryland. Used to measure temperature of constant temperature bath.

Manometer. Model 10AA25WM, 36-inch range, U type. Manufactured by the Meriam Instrument Company, Cleveland, Ohio. Used to determine the pressure in the absorption apparatus.

Stirrer. Magnetic. Catalog number 14-511-2, 115 V, 50-60 cy, 0.2 amp. Supplied by Fischer Scientific Company, New York, New York. Used to mix water samples during initial saturation.

Flask. Side arm, 50 ml. Supplied by Sargent Chemical Company, Silver Springs, Maryland. Used to establish initial concentrations of carbon dioxide in water samples.

Materials

The following materials were used in this investigation:

Oxygen. Extra dry grade, 99.6 percent minimum. Manufactured by Air Production Company, Inc., Roanoke, Virginia. Purchased from Industrial Gas Supply, Bluefield, West Virginia. Used for gas absorption.

Nitrogen. High purity, 99.9 percent minimum. Manufactured by Air Production Company, Inc., Roanoke, Virginia. Purchased from Industrial Gas Supply, Bluefield, West Virginia. Used as purge gas.

Argon. High purity, 99.995 percent minimum. Manufactured by Air Production Company, Inc., Roanoke, Virginia. Purchased from Industrial Gas Supply, Bluefield, West Virginia. Used as purge gas.

Carbon Dioxide. Commercial grade, 99.5 percent minimum. Manufactured by Air Production Company, Inc., Roanoke, Virginia. Purchased from Industrial Gas Supply, Bluefield, West Virginia. Used for gas absorption.

Water. Distilled and deionized. Obtained from still in the Chemical Engineering Department, Virginia Polytechnic Institute. Deionized with Bantam deionizer. Used in cell for absorbing gases.

Brodie Solution. Obtained from Civil Engineering Department, Virginia Polytechnic Institute. Density of 1.033 gm/cm^3 . Used as a measuring fluid in the manometer for absorption tests.

Mercury. Purified by procedure described in Chemical Rubber Company Handbook, followed by filtration in Chemistry Department, Virginia Polytechnic Institute. Original source unknown. Obtained from Chemical Engineering Stock Room, Virginia Polytechnic Institute.

Acetone. Technical grade. Manufactured by Preiser Scientific Company, Charleston, West Virginia. Used to clean glassware and absorption apparatus.

Carbon Tetrachloride. Certified A.C.S. laboratory grade. Obtained from Fischer Scientific Company, Fair Lawn, New Jersey. Used for cleaning ground glass joints.

Stopcock Grease. Apiezon, high vacuum type. Distributed in U.S.A. by James G. Biddle Company, Plymouth Meeting, Pennsylvania, stock number N. Used to lubricate high vacuum stopcocks.

Glass Cleaning Solution. A mixture of 10 grams of sodium dichromate, 20 millimeters of water, and 175 millimeters of concentrated sulfuric acid. Used to clean glassware.

ABSTRACT

The purpose of this investigation was to evaluate the ease of obtaining and reproducing diffusion coefficients for carbon dioxide and oxygen in water at 25°C using a quiescent liquid absorption apparatus.

Absorption curves were obtained for carbon dioxide in water using both a zero initial concentration and specific initial concentration of carbon dioxide. The evacuation pressure, operating pressure, initial concentration, and pressure increment were varied.

The zero initial concentration tests gave values for the diffusion coefficient consistently lower than expected. In addition the values were not reproducible and could not be correlated to the variation of parameters for the system. The cause of this variation was considered to be a combination of the evacuation procedure and the condensation phenomena. The interrelation of these effects was not determined.

Tests made with specific initial concentrations gave good agreement for the value of the diffusion coefficient. A value of $1.95 \pm 0.15 \times 10^{-5}$ square centimeters per second was determined to represent the diffusion coefficient for carbon dioxide at 25°C. A slight trend toward lower values of the diffusion coefficient at higher pressure gradients was observed. The effect of the evacuation pressure and condensation were considered to be minimal in these tests.

In both zero and specific initial concentration tests, convection appeared between 4 and 6 minutes after the start of the absorption test.

The absorption of oxygen in water at 25°C is nearly 15 times less than that of carbon dioxide. As a result, the absorption of oxygen was considered to be out of the applicable range for measurement of diffusion coefficients with this apparatus.

The quiescent liquid system was considered to be a rapid and reasonably accurate method for measuring the absorption of very soluble gases, such as carbon dioxide, over a limited range. The adaptability of the apparatus to less soluble gases is rather limited. However, for repeated measurements for a few chosen gases the system would be an inexpensive, competitive apparatus.