

THE EFFECT OF THE POSITIONS AND MOLECULAR  
WEIGHT OF HYDROPHILIC FUNCTIONAL GROUPS OF SURFACTANTS  
ON GAS ABSORPTION RATES

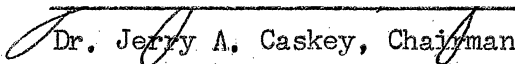
by

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## I. INTRODUCTION

Within the past two decades the effect of surfactants on mass transfer rates has received increasing attention in the chemical and chemical engineering literature. In the early 1920's, evaporation control by monolayers of insoluble surfactants was studied to conserve water supplies in lakes and reservoirs. It was found that monolayers do fulfill the requirement as an effective barrier to evaporation, but they also should not be harmful to aquatic life or subsequent users of the water. It was then that many investigations were conducted to study the effect of surfactants on absorption using gases essential to aquatic life.

Of these experiments, most results have been inconclusive. There have been two main reasons for this. One is that the techniques were not reliable enough to measure the transport of small quantities of gas. The other is that the surfactants used were a mixture of several compounds. Therefore, it was not possible to determine whether the observed effect was due to a single compound or several compounds present at the interface.

During the past few years, there has been an increasing awareness of ecology by the general public. Chemical and sanitary engineers have been especially aware of the problems presented to water pollution by various detergents which contain many surfactants. As the concern for

the effect of the surfactants becomes important, engineers want to know the contribution of the sizes and interfacial orientation of the surfactant molecules to the interfacial resistance. Also a suitable model is necessary to describe the mass transfer. Much has been learned, but much remains unknown.

The purpose of this investigation was to determine the effects of the hydrophilic functional group on interfacial resistance.

## II. LITERATURE REVIEW

The following is brief survey of the literature relevant to this thesis.

### Theory for Gas Absorption

In order to determine quantitatively the effect of surfactants on gas absorption rates, a mathematical model which can describe the system is needed. Several models have been developed with the assumption that the gas concentration at the liquid surface is in equilibrium with gas phase due to a lack of knowledge about the interface. Another assumption is that a form of Fick's Second Law of Diffusion is used.

Description of the System. Davis and Rideal<sup>(12)</sup> present a simple description of mass transfer across an interface. If a molecule of gas passes across the gas-liquid interface, it encounters a total resistance which is the sum of three separate resistances, resistance through the gas phase, resistance across the monomolecular region constituting the interface, and resistance through liquid below the interface. For a pure liquid(Figure 1),  $R_L$  is necessary zero, and  $R_I$  is low for a clean liquid surface.

Development of Model for Interfacial Resistance for Quiescent State Systems. Since it would be lengthy to present the development for the models in the literature, only one will be reviewed here.

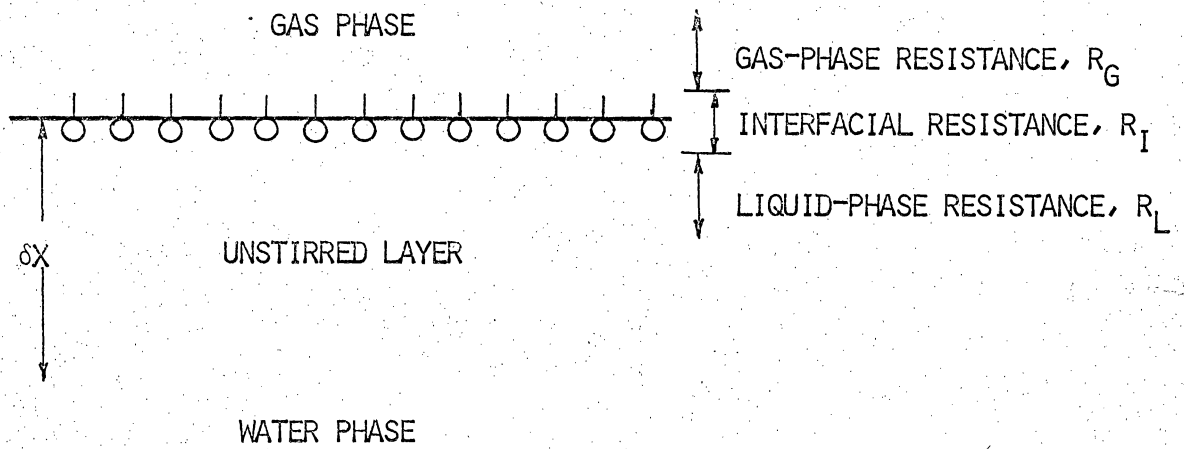


FIGURE 1. TOTAL RESISTANCE AT GAS-WATER INTERFACE

Davis, J. T. and E. K. Rideal: "Interfacial Phenomena", p. 301,  
Academic Press, New York, 1963, 2 ed.



If a gas such as carbon dioxide is being absorbed into solution, the resulting unsteady state is described by

$$\partial C / \partial t = D \partial^2 C / \partial x^2 \quad (1)$$

where  $C$  = concentration of the solute gas, gm mole/cm<sup>3</sup>

$D$  = diffusion coefficient, cm<sup>2</sup>/sec

$t$  = time, sec

$x$  = distance normal to phase boundary, cm

According to the model described by Bussey<sup>(5)</sup>, the boundary conditions come from three assumptions: (1) the liquid is effectively infinite in depth, (2) the absorption process is isothermal, and (3) the absolute pressure in the absorption vessel does not change significantly during the absorption period of interest.

$$C(x, 0) = C_0 \quad (2)$$

$$C(\infty, t) = C_0 \quad (3)$$

$$C(0, t) = C_1(t) \quad (4)$$

The functional form of  $C_1(t)$  indicates that Bussey<sup>(5)</sup> does not assume equilibrium at the interface. Also he assumed that the rate of gas absorption for surfactant solutions has the same model for pure water system. Through deviation in terms of change in pressure, a time dependent interfacial resistance was derived. Herbert<sup>(21)</sup> gives a similar development in term of change in volume, thus adapting the development to the apparatus used in this investigation. The interfacial resistance is given by

$$R_i / \sqrt{t} = 1/k_i \sqrt{t} = \left( \frac{\sigma_E - \sigma_R}{\sigma_E} \right) \sqrt{\frac{\pi}{D}} \quad (5)$$

where  $R_i$  = interfacial resistance, sec/cm  
 $k_i$  = interfacial mass transfer coefficient, cm/sec  
 $\sigma_E$  = slope of gas uptake versus  $\sqrt{t}$  plot for pure carbon dioxide-water system,  $\text{cm}^3/\text{cm}^2 \text{ sec}^{\frac{1}{2}}$   
 $\sigma_R$  = slope of gas uptake versus  $\sqrt{t}$  plot for aqueous surfactant solution system,  $\text{cm}^3/\text{cm}^2 \text{ sec}^{\frac{1}{2}}$

#### Experimental Measurement of Interfacial Resistance

The interfacial resistance can be found by measuring the rate of gas absorption. Many experimental techniques have been devised. Himmelblau<sup>(22)</sup> has reviewed some of the methods used. Actually most of the common techniques fall into two categories, unsteady-state and steady-state systems. The unsteady-state quiescent systems will be reviewed with emphasis here. The gases commonly used have been carbon dioxide, oxygen, sulphur dioxide and ammonia.

Unsteady-State Quiescent Systems. This category has been used in many forms. Common to all of them, the major problems have been eliminating convection currents caused by density differences, and keeping the system from vibrations which would upset the quiescent nature of the liquid.

One of the earlier workers to use this method was Carlson<sup>(9)</sup> in 1911. To reduce convection, he added 1% potassium chloride to increase the

density of the solution and assumed that the electrolyte has little effect on the diffusion coefficient. Very lengthy contact time was required. The whole apparatus was set on a firm base to prevent vibration.

Some workers attempted to eliminate convection by adding colloids to the liquid. Hagenbach<sup>(16)</sup> used a 20% gelatin solution. He stated that the gelatin used offered greater resistance to the diffusing gas. Similarly, Tamman and Jessen<sup>(35)</sup> added agar to water with the assumption that agar has little effect on the rate of diffusion. Davidson and Cullen<sup>(11)</sup> suggested there is some evidence this assumption is true in specific cases, but it is unlikely that it is generally true.

Another way of eliminating convection is to enclose the liquid in a capillary thereby decreasing the size of the cylinder. The apparatus used by Ringbom<sup>(33)</sup> consisted of a gas-saturated and a gas-free water column (introduced from either end into a capillary tube) separated by a pure gas phase. The rate at which gas-saturated water column was moving into the displaced gas phase gave a measure of diffusion coefficient of the gas in water.

Blank<sup>(1)</sup> noticed when the gas uptake was plotted versus the square root of time, the curve was a straight line up to a certain time, about a few minutes, and then the slope began to change. He suggested that it was due to the onset of convection. Bussey<sup>(7)</sup> noticed the same thing, and the same reason was given. Only this initial linear portion of the curve was used in their calculations. Blank<sup>(1)</sup> put a mercury substrate

in the cell; no specific reason was given. McCutchen<sup>(30)</sup> recommended that the layer of mercury 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.

Many techniques of measuring the amount of gas absorption have been used. Carlson<sup>(9)</sup> in 1911 analyzed the liquid. Gouy<sup>(22)</sup> first considered the use of interferometric techniques in which the progress of diffusion of the gas into the liquid is followed and recorded by the change of the refractive index of the liquid is a function of distance and time. Flank<sup>(1)</sup> used a Barcroft temperature-compensated differential manometer by recording the height of column as a function of time.

Later on, more sophisticated techniques were devised. Flevan and Quinn<sup>(32)</sup> used a pressure transducer to measure the pressure difference. Bussey<sup>(6)</sup> used a Decker differential pressure sensor and the output signal was amplified and then recorded continuously on a strip chart. However, he noticed the inability to measure short contact times and that the frequency response technique developed by Lamb<sup>(24)</sup> can overcome this problem.

Steady-State Laminar Flow System. This category includes the use of liquid jets and flow apparatus of different geometry<sup>(22)</sup> such as wetted spheres, wetted wall columns, stirred flasks, flow in rectangular ducts and rotating drums. However, only laminar jets will be reviewed here, since they have been the mostly widely used.

Himmelblau<sup>(22)</sup> gives a summary of the advantages of jets. "Jets are simple in design, have freedom from ripples, have small end effects, are stable and have such short time that surface active agents do not have time to adsorb to the surface. Above all they are rapid." Also, jets are very suitable for obtaining values for industrial work ( $\pm 5\%$ ), and with more care, data of  $\pm 1\%$  precision can be obtained.

Duda and Vrentas<sup>(13)</sup> have done a rigorous analysis of jet hydrodynamics. They noted that laminar liquid jets possess several advantages over other methods. Yet there are still two uncertainties associated with jet absorption studies which must be resolved before this experimental technique can gain wide acceptance as an accurate method of measuring diffusion coefficients. The first is the possible existence of a significant resistance to mass transfer at the phase interface. If this is large, then short contact time equipment can be of little use. The second uncertainty is the influence of the jet hydrodynamics on the rate of mass transfer.

#### The Effect of Surfactants on Mass Transfer Rates

This section deals mainly with gas absorption, but other types of mass transfer will be mentioned if gas absorption literature is not available.

There have been many experiments reported on this topic. Most of them agree that surfactants do cause interfacial resistance and decrease the rate of gas absorption. However, there are a few workers<sup>(4,8,36)</sup>

that have reported that some or all soluble surfactant monolayers do not produce an interfacial resistance. The retardation of water evaporation by surfactant monolayers has been much studied but the permeability of monolayers to gases other than water vapor has not been examined as much.

Variables Investigated. The variables investigated in the existing literature are bulk concentration, surface concentration, temperature, structure of the surfactant molecules and rate of agitation.

Most of the literature agrees that the rate of absorption decreases with increasing surface concentration of surfactant if they do cause interfacial resistance. However, some investigators reported bulk concentration instead of surface concentration. Boyadzhiev<sup>(3)</sup> and O'Connor<sup>(31)</sup> noticed that for some surfactants the rate of absorption decreased with increasing surface concentration up to a limiting value.

Burnett<sup>(4)</sup> who studied straight-chained surfactants with four to twenty-four carbon atoms, observed that most insoluble surfactants decreased the rate of gas absorption while most soluble surfactants increased the absorption rates. He also concluded that the interfacial movements during gas absorption with soluble surfactants were caused by the Marangoni effect which is the generation of movement in an interface by longitudinal variations of interfacial tension.

Goodridge and Robb<sup>(15)</sup> reported that the resistance due to surfactants decreased with rising temperature. However, nothing was found for the effect of pressure.

Increasing chain length of surfactant molecules increase interfacial resistance has been reported by many investigators, (1,2,10,20) In addition to that, Caskey<sup>(10)</sup> observed that the surface orientation of surfactant molecules changes the magnitude of gas absorption rates. Blank and Rougton<sup>(2)</sup> found that for the same hydrocarbon chain length the interfacial resistance varies with polar groups, hydroxyl group being a more effective retarder than carboxyl group, and that other factors besides molecular diameter are involved in the passage of small molecules through condensated monolayers. Herbert<sup>(20)</sup> observed that different surfactant hydrophilic functional groups cause different magnitudes on interfacial resistance, but no reason was found for the variation.

As for the effect of agitation of the liquid phase, Goodridge and Robb<sup>(16)</sup> found that the conductance of gas increases with higher rate of agitation.

On the whole, with the exception of chain length and concentration, not much has been done to determine the contribution of each of these variables to the interfacial resistance.

Causes of Interfacial Resistance. Goodridge and Robb<sup>(15)</sup> suggest that the presence of surfactants in the interfacial region could have four effects which, working either singly or in conjunction, would account for the considerable reduction in absorption rates. They are the energy barrier effect, sieve effect, hydrodynamic effect and interfacial turbulence effect. The energy barrier effect is caused by

the potential energy barrier gas molecule have to overcome in order to penetrate the surfactant film and enter the liquid. The film may act as a sieve, reflecting a fraction of the incoming gas molecules by collision. The hydrodynamic effect is due to the creating of a boundary layer or increase the depth of an existing one by the film. They mentioned that carbon dioxide-water system does not exhibit any interfacial turbulence. They concluded that interfacial phenomena can be explained, in both a quantitative and qualitative manner by postulating an energy barrier and hydrodynamic effect operating at the same time.



### III. EXPERIMENTAL

This section includes the plan of experimentation, procedure, and results.

#### Plan of Experimentation

The following is the experimental plan pursued in this investigation.

Literature Review. A survey of the literature shows that many studies have been made to determine the gross effect of surfactants on gas absorption. In spite of a number of studies concerning the hydrophobic chain length, very few investigations have been made to study the effect of the orientation of surfactant molecules. The property selected for study in this investigation was the effect of the position of the hydrophilic functional group on gas absorption which has not been previously studied.

Selection of Apparatus. The unsteady-state quiescent absorption apparatus constructed by McCutchen<sup>(26)</sup> was used in this investigation. The apparatus is similar to the one used by Elank and Roughton<sup>(2)</sup> with a Barcroft differential manometer. It has a dummy cell to reduce the effect of temperature variation and a reaction cell on the other side of the manometer. (see Figure 2) The amount of gas absorbed is

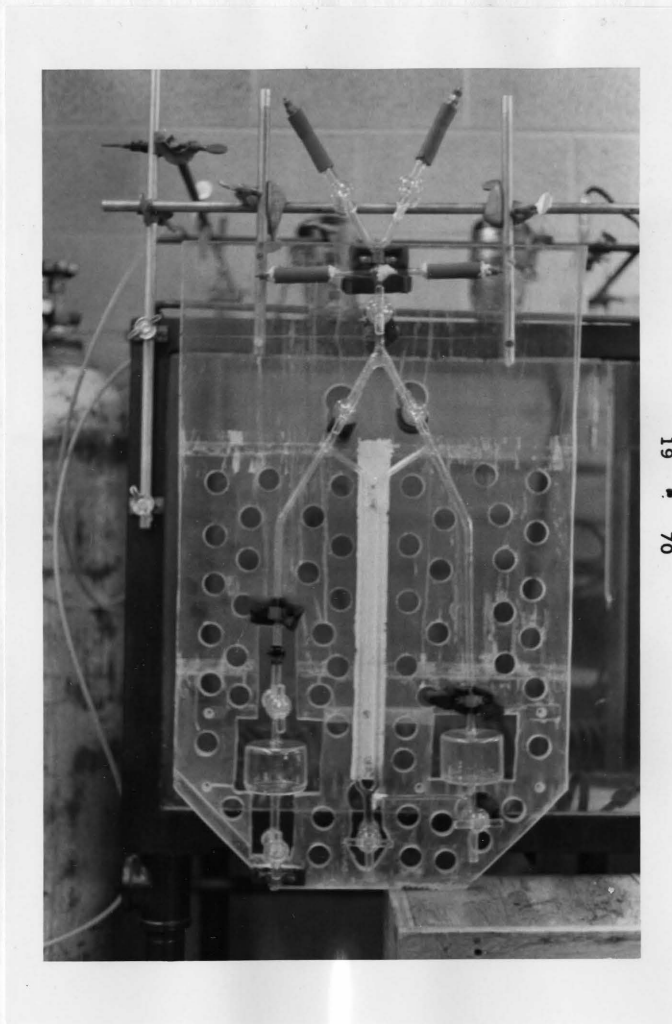


FIGURE 2. UNSTEADY-STATE ABSORPTION APPARATUS

determined by the change in the height of the manometer fluid. Meriam D-3166 was chosen as the manometer fluid because of its low vapor pressure and low density.

Selection of System. Carbon dioxide was used as the absorbing gas throughout the investigation. N-octanol, 4-octanol and lauryl diglycol amide solutions were used to study the effect of the position of the hydrophilic functional groups. Octanols were used instead of decanols because the solubility of the decanols was too low.

Treatment of Data. The gas absorbed for deionized water was calculated and plotted versus the square root of time. The slope of the initial linear portion of the plot was used to calculate the diffusion coefficient. The average value of the diffusion coefficients was taken as the standard for this investigation. This provided a standard slope whereby the interfacial resistance for surfactant tests were calculated. A range could be seen from the tests made with pure deionized water, and a similar range was expected for the runs with surfactants.

The surface tension of the surfactant solutions at different concentrations was measured at 25°C. The surface tension data were plotted on semi-log paper from which the surface concentration was calculated using Gibbs' adsorption isotherm. The surface concentration was required in order to correlate the interfacial resistances. Gas absorption tests were repeated for each surfactant at different bulk concentrations. The slope from a plot of gas absorbed versus the square

root of time used in the calculation of interfacial resistance (see equation 40). The results for each surfactant were plotted as the interfacial resistance versus surface concentration.

Improvement of the Model. Originally, the uptake of carbon dioxide in surfactant solutions was considered to be a function of the square root of time, the same as for pure water. This assumption led to an interfacial resistance which was a function of time. In order to develop an interfacial resistance independent of time, another model was developed.

#### Method of Procedure

The following is a description of the procedure used.

Preparation of Surfactant Solutions. The deionized water both for testing and making surfactant solutions was prepared by passing distilled water through a Bantam demineralizer. A flow rate of about ten gallons per hour was induced by pressuring with a metal tank containing the distilled water.

Surfactant solutions with specific concentrations were prepared by adding the correct amount of surfactant to the corresponding amount of deionized water in a volumetric flask. A double-pan analytical balance was used to weigh the surfactant. If the surfactant was a sparingly soluble liquid, a glass petri dish was used to weigh the surfactant as this was easier to wash the liquid into the volumetric flask. Lower concentrations were prepared by the diluting of the initial solution with deionized water using a pipette.

Constant Temperature Preparation. The laboratory temperature was controlled with an electronic relay which operated in conjunction with a thermometer type thermoregulator. The electronic relay controlled a warm air fan. An air conditioning unit provide the cooling medium. The laboratory was maintained at  $77.0^{\circ} \pm 0.5^{\circ}$  F.

A large water bath was used to control the apparatus temperature. Heating coils were connected to a transistor relay and a thermostat. Tap water, circulating through a copper coil, served as the cooling medium. The temperature of water bath was maintained at  $25.0 \pm 0.05^{\circ}$ C.

Equilibrium Surface Tension Measurement. Three separate samples were drawn from each surfactant solution of a specified concentration and were placed in Petri dishes with covers to retard evaporation. The samples were allowed to sit for at least an hour to insure that equilibrium conditions were reached. An apparent surface tension for each sample was measured with a Fisher interfacial tensiometer. The average value of the three samples gave the apparent surface tension of the surfactant solution at a particular concentration. The actual equilibrium surface tension was obtained by applying a correction factor<sup>(14)</sup> to the apparent surface tension.

Presaturation of a Solution for Absorption. The solution was placed in a side-arm flask which was connected to a vacuum pump, mercury manometer and carbon dioxide gas source. The arrangement is shown in Figure 3. The supply valve A was closed and a vacuum was applied through valve B until the desired evacuation pressure was

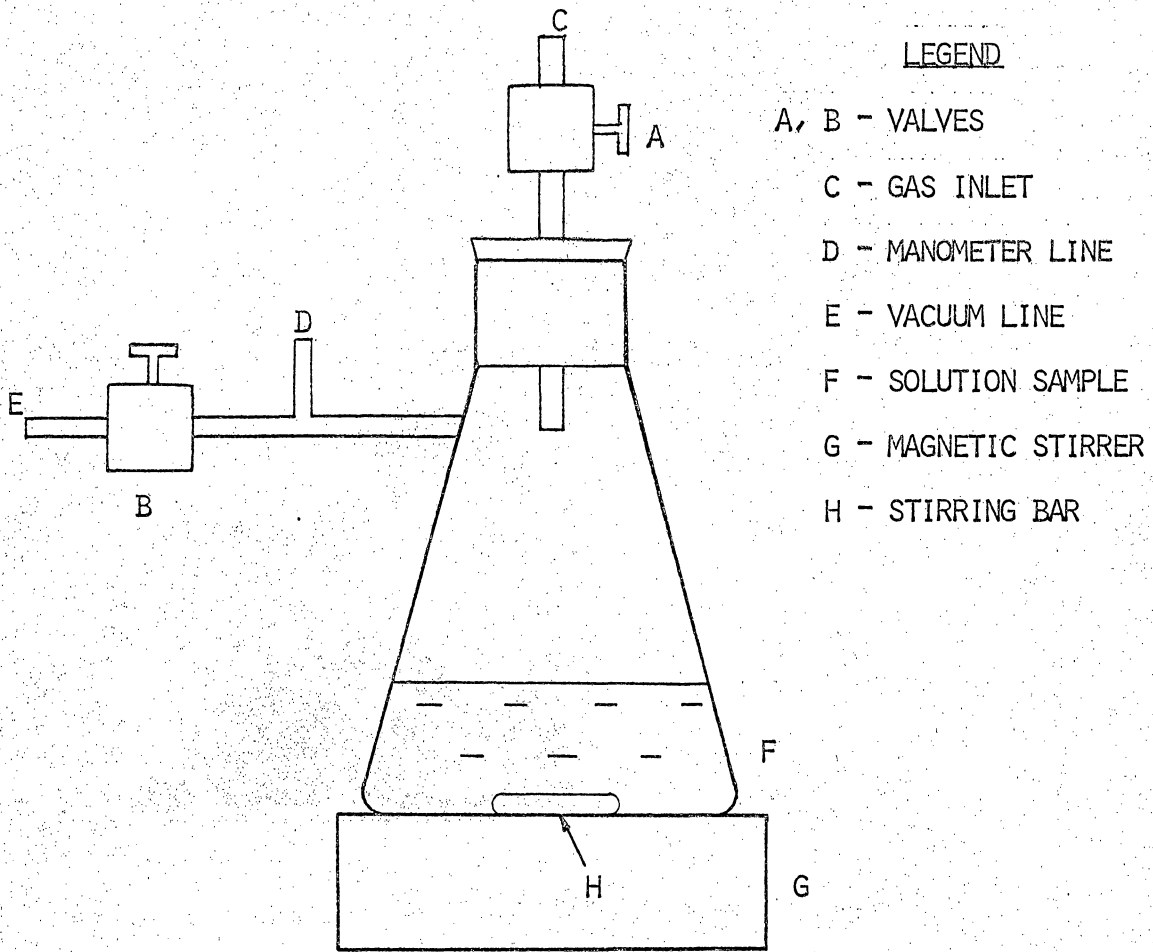


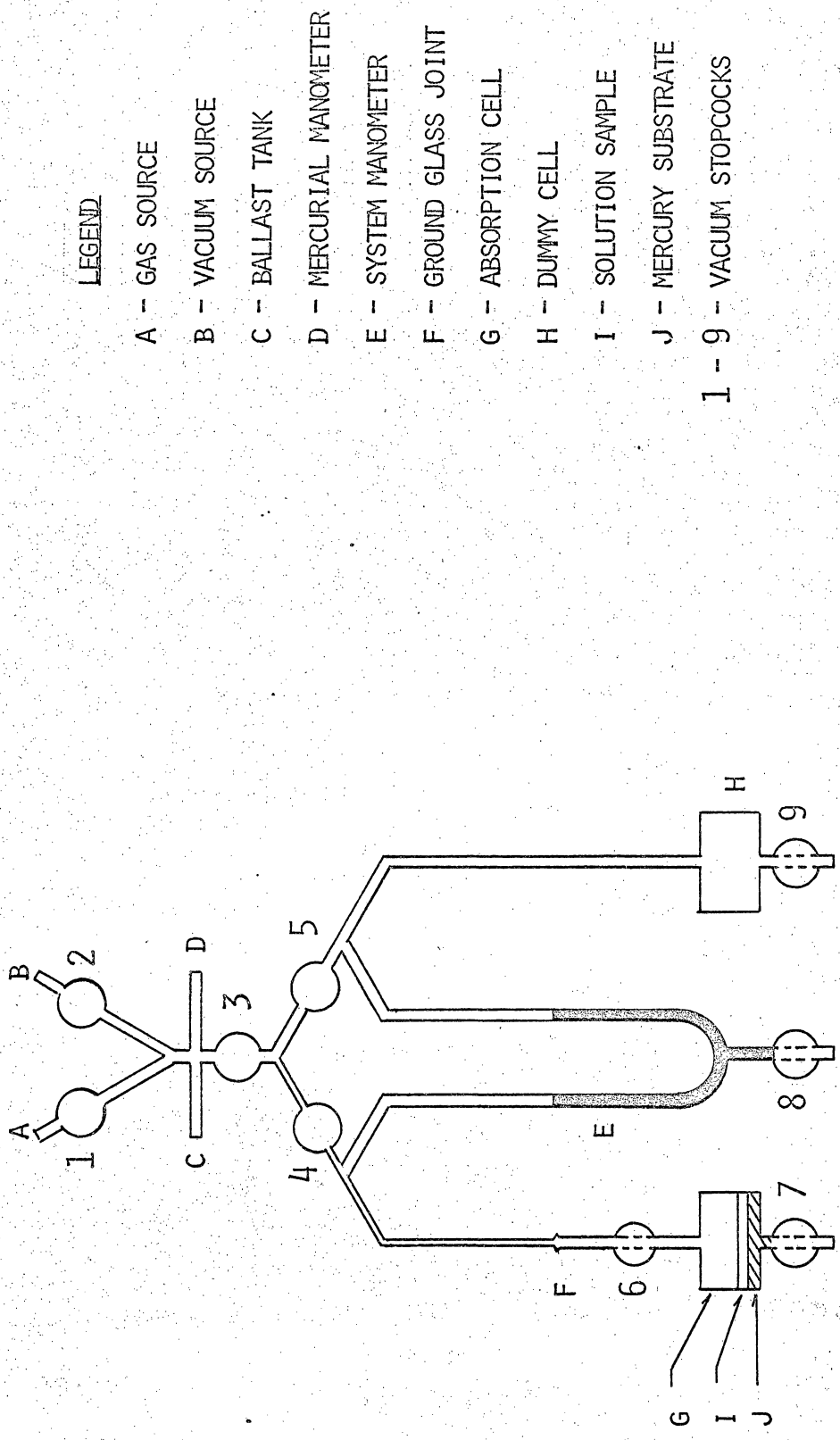
FIGURE 3. APPARATUS USED TO PREPARE SURFACTANT SOLUTIONS FOR ABSORPTION

attained. Usually this evacuation pressure was at the bubble point and the solution was allowed to degas for a short time. Valve B was then closed and carbon dioxide was allowed to enter through valve A until the system returned to atmospheric pressure. The procedure was repeated two times. The system was then closed and the magnetic stirrer turned on. As absorption took place, carbon dioxide was added to maintain a pressure near the atmospheric pressure. The solution became saturated in about twenty minutes when no further changes in the manometer height were seen. This pressure was the presaturation pressure of the solution.

Preliminary Preparation of the Absorption Apparatus. In this and the subsequent subsections, all the capital letters and numbers refer to Figure 4.

The gas absorption cell had to be clean before reliable absorption tests could be made. The cell was cleaned by filling with glass cleaning solution. After about half an hour, the cell was flushed and filled with deionized water. Then the water was removed and the cell was rinsed with acetone. The acetone was removed by passing air through the apparatus. Care was taken to ensure that the air used was free from impure substances such as grease, etc.

Occasionally the vacuum stopcocks had to be cleaned. The vacuum grease was removed with chlorinated hydrocarbon such as carbon tetrachloride. Then, just sufficient amount of clean vacuum grease was applied around the plug. The plugs were fitted with their own matched counter-part and sealed by smooth turning motions.



LEGEND

- A - GAS SOURCE
- B - VACUUM SOURCE
- C - BALLAST TANK
- D - MERCURIAL MANOMETER
- E - SYSTEM MANOMETER
- F - GROUND GLASS JOINT
- G - ABSORPTION CELL
- H - DUMMY CELL
- I - SOLUTION SAMPLE
- J - MERCURY SUBSTRATE
- 1 - 9 - VACUUM STOPCOCKS

FIGURE 4. SCHEMATIC DIAGRAM OF UNSTEADY-STATE ABSORPTION SYSTEM



After each stopcock was placed in its correct position, it was turned so that the hollow portion of the plug was opened to the top of the apparatus. The vacuum pump was connected at A, and stopcock 1 was evacuated. The procedure was repeated for stopcock 2 by attaching the vacuum pump to B. Connections at A, C and D were then closed and stopcock 2 was turned to allow the evacuation of stopcock 3. Stopcock 3 was turned to allow the evacuation of stopcocks 4 and 5. The remaining stopcock were evacuated in similar manner.

Introduction of Manometer Fluid. Meriam D-3166, the manometer fluid was introduced into the Barcroft manometer through stopcock 8. A soft plastic tubing was fitted with a funnel at one end and attached to the glass tube below stopcock 8 at the other end. The meriam D-3166 fluid was allowed to flow into both arms of the manometer. The plastic tubing was raised until the desired height of fluid was obtained. Stopcock 8 was then closed and excess fluid and tubing removed.

Introduction of Mercury Substrate and Solution. The absorption cell was detached from the system at the ground glass joint, and mounted vertically on a ring stand with clamps. A hypodermic needle was fitted onto five inches of Teflon tubing. With stopcock 6 opened, Teflon tubing was worked through the glass tube until it touched the bottom of the cell. Stopcock 7 was closed. Twelve cubic centimeters of clean purified mercury was introduced into the cell with a syringe attached to the needle at the end of the Teflon tubing. Ten cubic centimeters

of solution presaturated with carbon dioxide was introduced in the same manner with another clean syringe. Gentle blowing through the tubing was necessary to remove the last drop of solution. The Teflon tubing was removed and the cell reconnected to the system at the ground glass joint. Extreme precautions were taken to avoid any splashing of solution on the cell wall.

Preparation Absorption Apparatus for an Absorption Test. The plexiglass board to which the absorption apparatus was attached was mounted in the water bath. The board should be vertical and resting on the bottom of the bath to insure stability. Connections were made to the vacuum pump, mercury manometer and ballast tank. Stopcock 1 and ballast tank were closed and stopcock 2 was opened to allow the evacuation of the entire absorption apparatus. The apparatus was evacuated to approximately 450 mm of mercury vacuum. Stopcock 2 was then closed and carbon dioxide was allowed to enter through stopcock 1 until the system returned to atmospheric pressure. This procedure was repeated. A third evacuation was made and carbon dioxide was allowed to fill the system until the desired initial pressure was attained. This pressure would be the initial concentration of carbon dioxide in the surfactant solution. Stopcock 3, 4, and 5 were closed and the system to equilibrate at this pressure. Usually it took about one and a half to two hours to equilibrate as shown by no further change in the height of the manometer fluid. The pressure in the system after equilibration is called the saturation pressure.

With stopcock 3 closed, the ballast tank was evacuated to almost the highest vacuum that could be obtained with the vacuum pump by opening stopcock 3. Then, stopcock 2 was closed and carbon dioxide was allowed to enter through stopcock 1 until the ballast tank returned to atmospheric pressure. This procedure was repeated and the ballast tank was filled to a slight positive pressure.

Absorption Test. After equilibration, the system was ready for an absorption test. The cooling water and agitators were turned off to avoid upsetting the quiescent system. Stopcocks 4 and 5 were opened to allow the manometer fluid to flow back to its original level. Then stopcock 3 was opened for about six seconds to allow carbon dioxide to fill the absorption and dummy cell. The increase in pressure was referred to as the step increase in pressure in this thesis. The resultant pressure after the step increase was called the operating pressure. After closing stopcocks 4 and 5 simultaneously, the timer was started immediately and the reading on the mercury manometer was recorded. Then, the change in height of the fluid in the Barcroft manometer was recorded as a function of time.

The change in height of the manometer fluid was measured with a cathetometer for some runs. The meniscus of the manometer fluid was brought into focus and aligned with respect to a cross hair in the eyepiece. The position of the telescope on the scale was then read to the nearest 0.1 millimeter using the vernier scale. The telescope was made to travel downward with the meniscus of the manometer fluid.

Conclusion of Absorption Test. At the conclusion of the test, the tubing at A, B, C and D was disconnected and the apparatus was removed from the water bath. Stopcock 3 was opened. Stopcocks 4 and 5 were opened simultaneously to avoid the loss of fluid from the Barcroft manometer. The absorption cell was then removed and cleaned.

### Results

The results obtained in this investigation are presented in this section.

Preliminary Gas Absorption Results. The manometer readings for the absorption of carbon dioxide in deionized water are given in the Appendix, Tables VI to XVI. The results of these tests were calculated to give the uptake values. The uptake values are shown in Figures 5 to 15. Tests 1 to 6 were measured at intervals of 15 seconds. All the other tests were measured at intervals of 30 seconds. Tests 7 to 11 were measured with a cathetometer.

In order to show the initial portion in detail, not all the available data points from the latter portion were plotted. The upper limit of the initial linear portion was found by determining the break point which was the location of the jump in slope. The slope of this initial linear region was used in the calculation of the diffusion coefficient.

The diffusion coefficients for each test are given in Table I, along with the corresponding parameter values: saturation pressure,

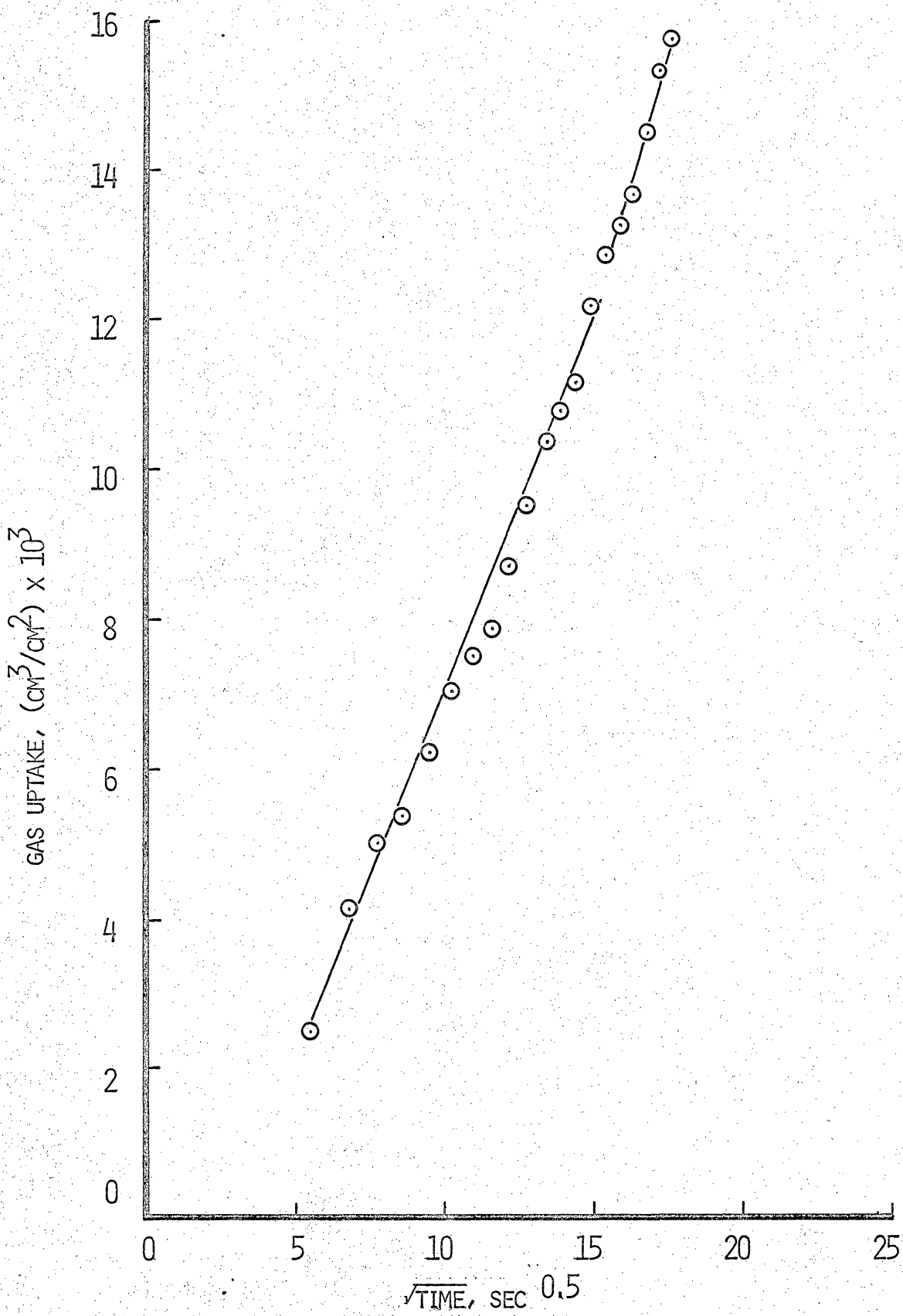


FIGURE 5. CARBON DIOXIDE UPTAKE IN DEIONIZED WATER  
AT 25°C AND 690.0 MM Hg (TEST NUMBER 1)

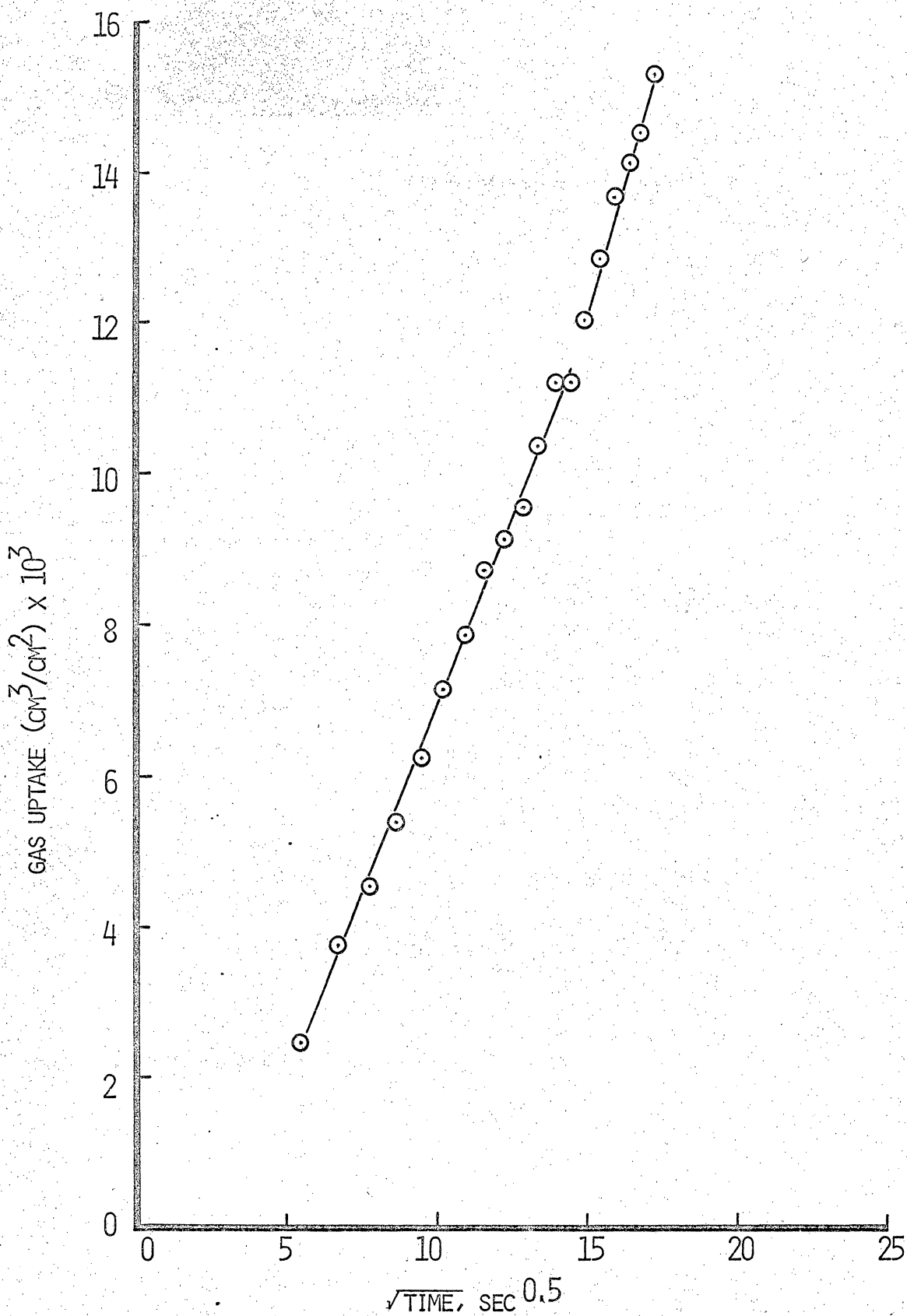


FIGURE 6. CARBON DIOXIDE UPTAKE IN DEIONIZED WATER  
AT 25° C AND 700.0 MM Hg (TEST NUMBER 2)

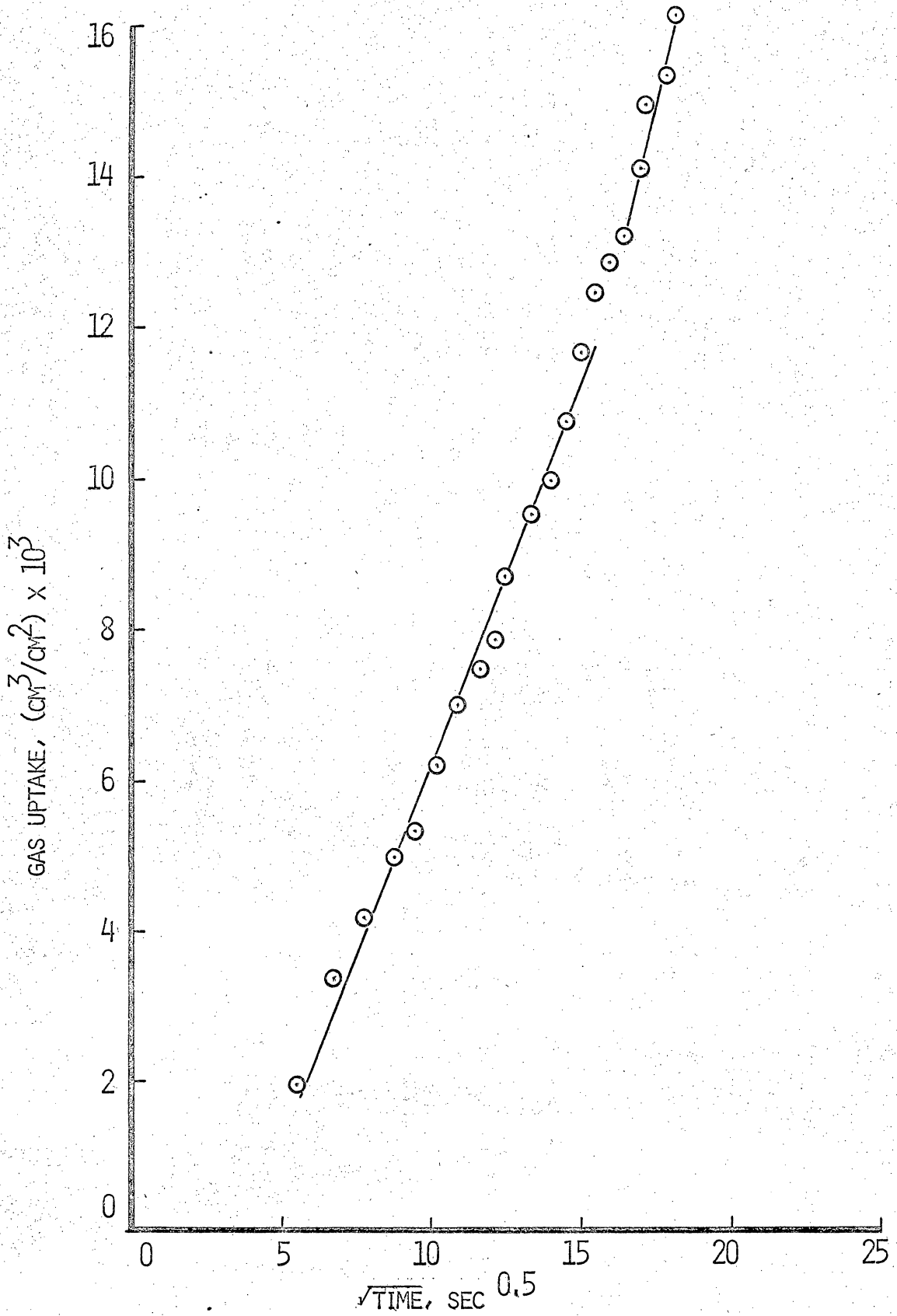


FIGURE 7. CARBON DIOXIDE UPTAKE IN DEIONIZED WATER AT 25°C AND 699.0 MM Hg (TEST NUMBER 3)

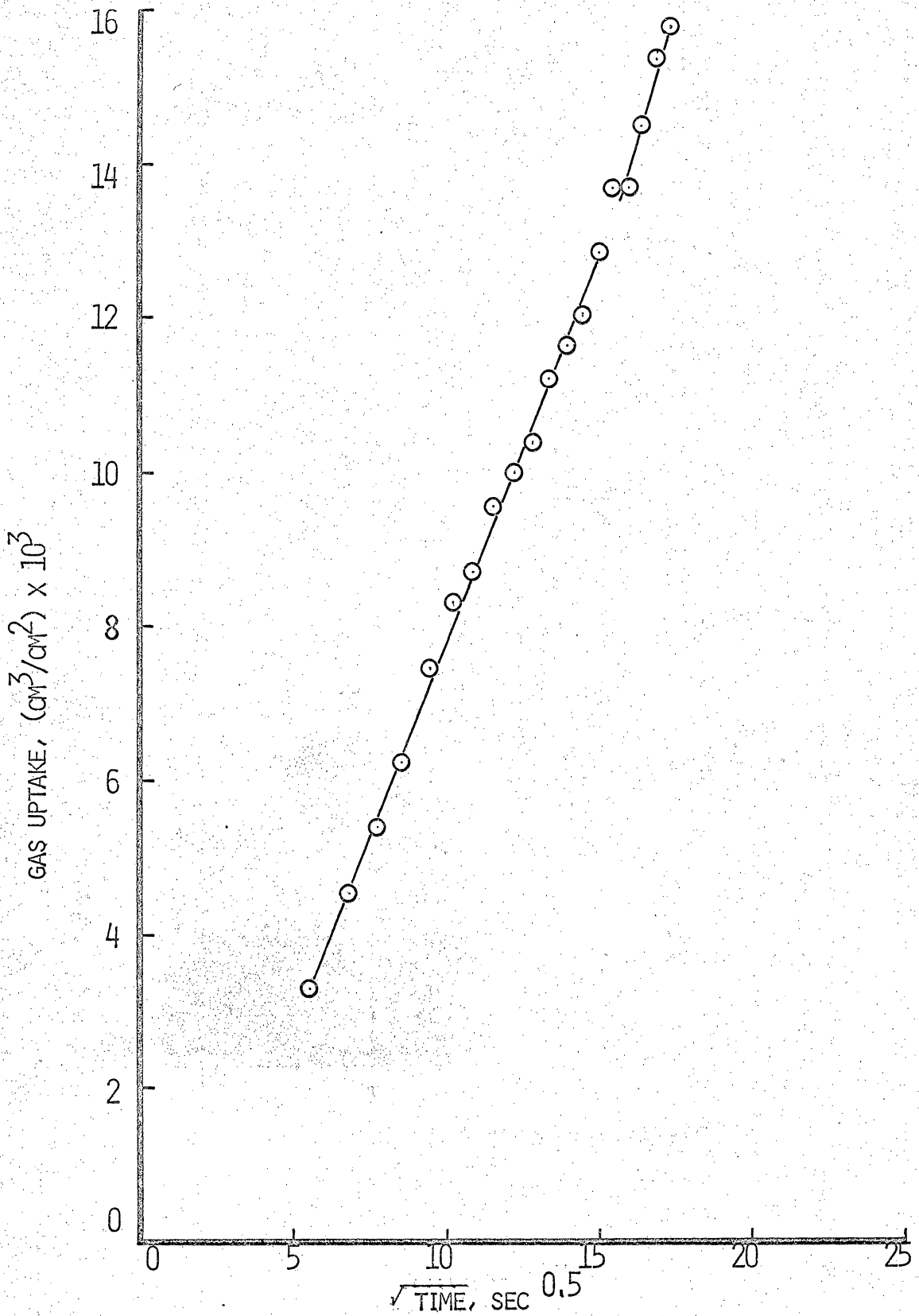


FIGURE 8. CARBON DIOXIDE UPTAKE IN DEIONIZED WATER AT 25°C AND 700.0 MM Hg (TEST NUMBER 4)



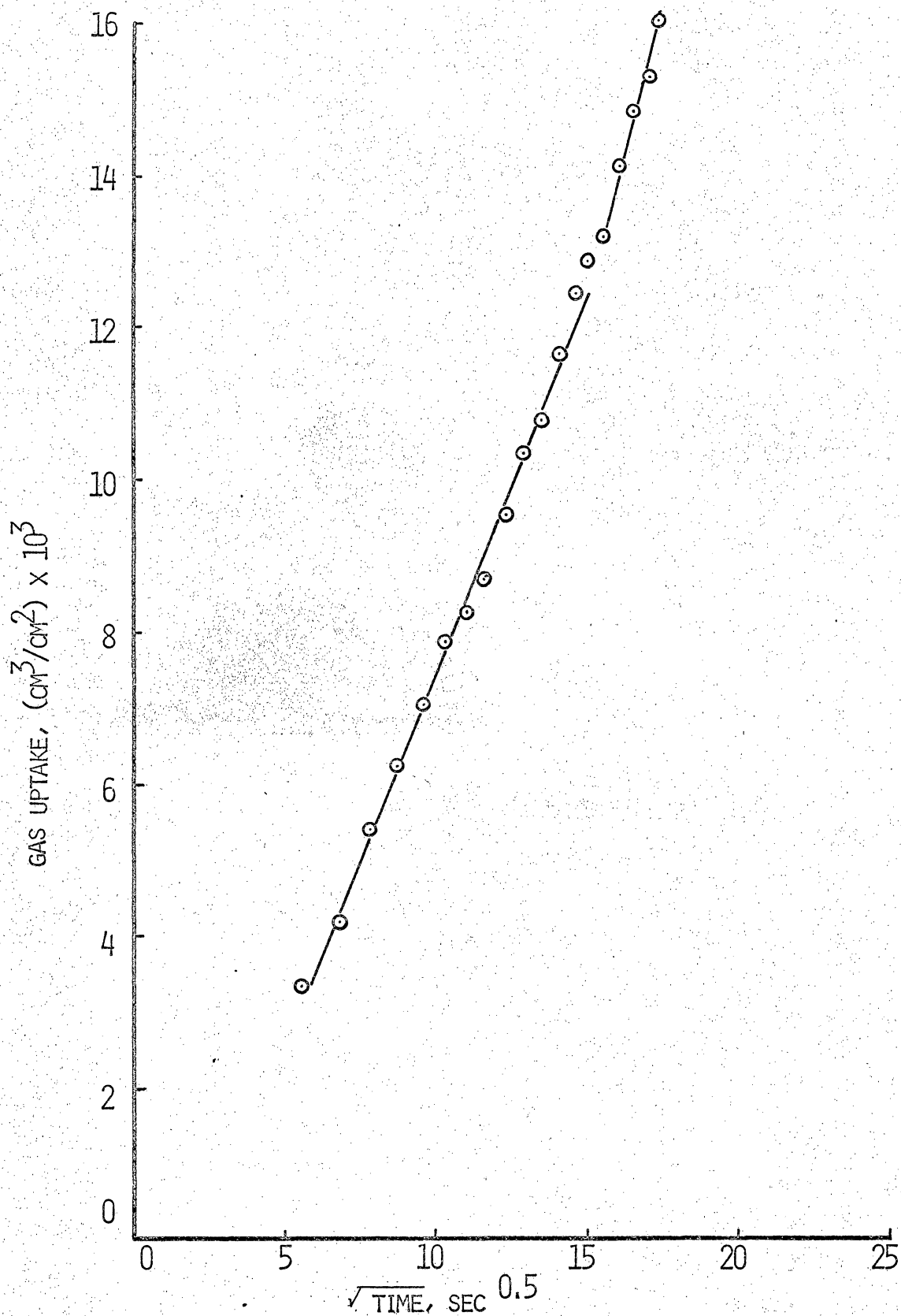


FIGURE 9. CARBON DIOXIDE UPTAKE IN DEIONIZED WATER AT 25°C AND 702.0 MM Hg (TEST NUMBER 5)

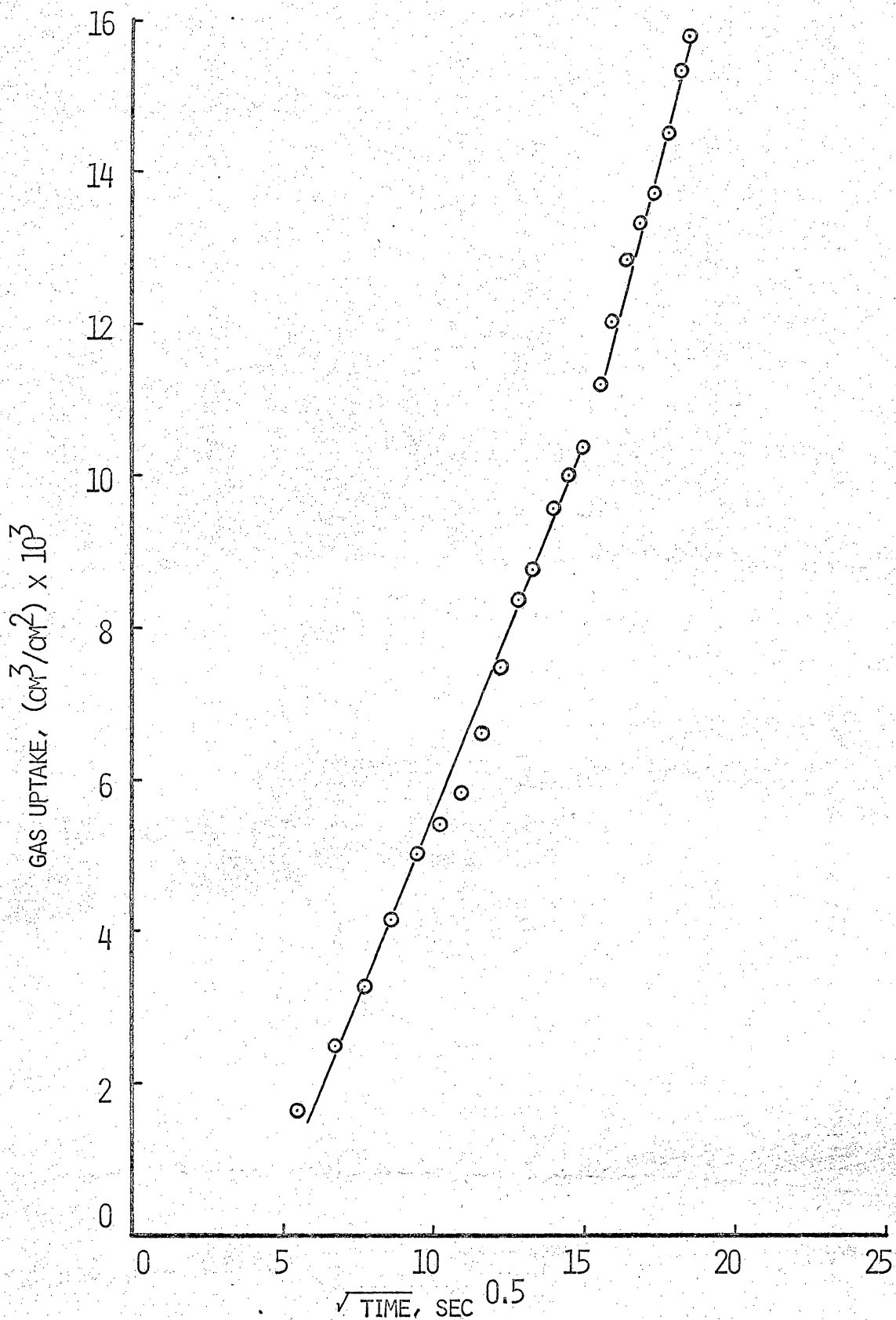


FIGURE 10. CARBON DIOXIDE UPTAKE IN DEIONIZED WATER  
AT 25°C AND 704.0 MM Hg (TEST NUMBER 6)

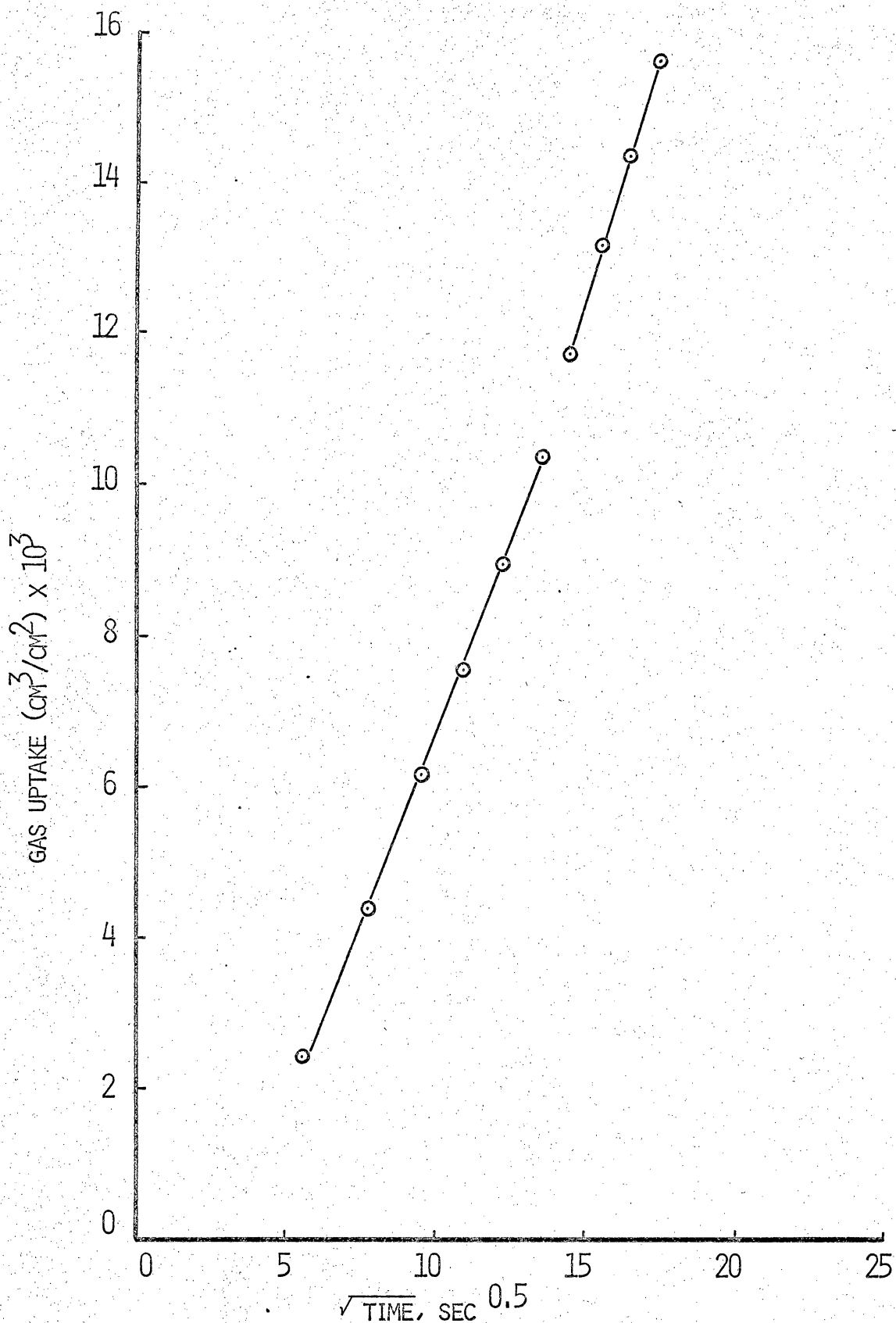


FIGURE 11. CARBON DIOXIDE UPTAKE IN DEIONIZED WATER AT 25°C AND 703.0 MM Hg (TEST NUMBER 7)

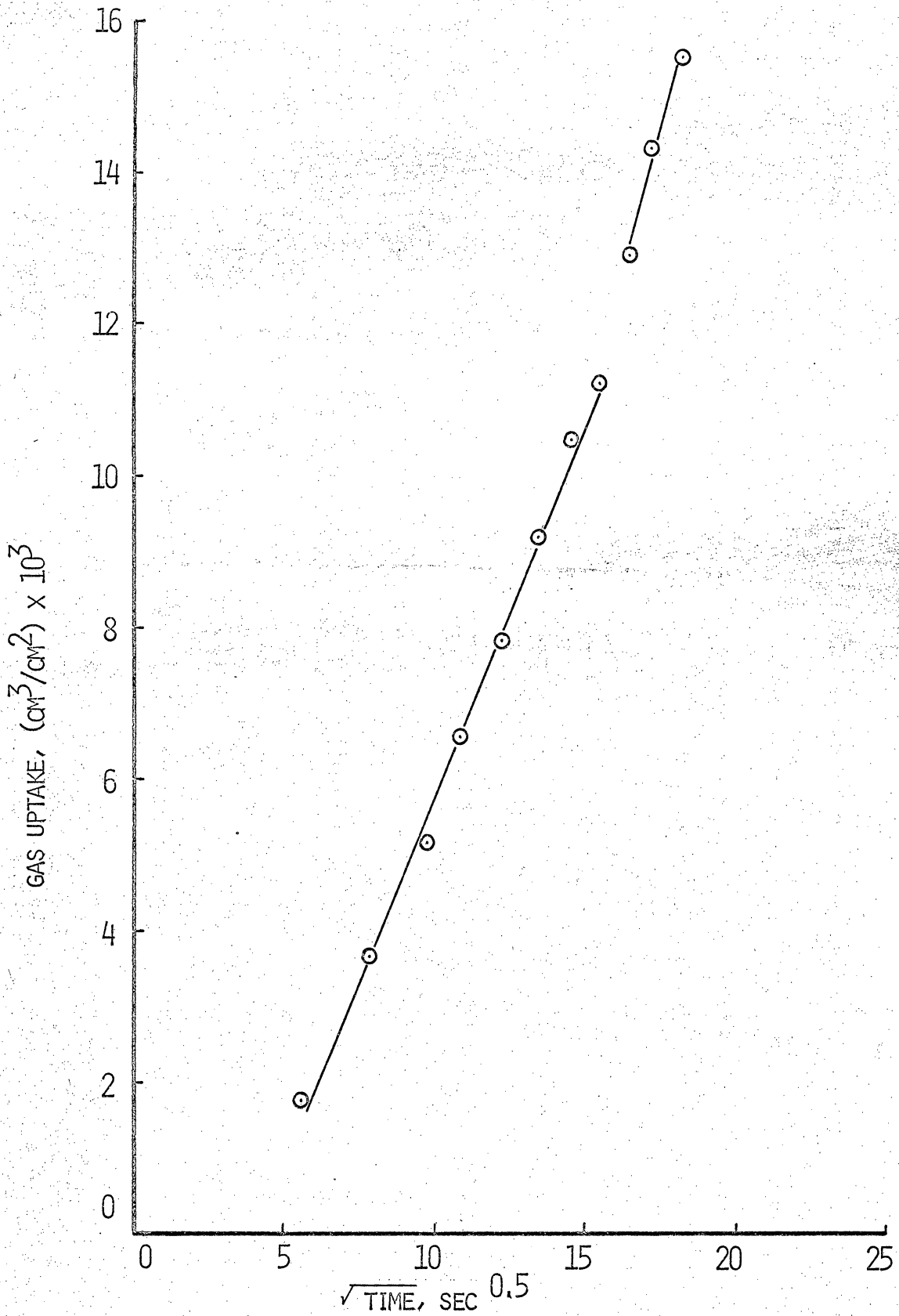


FIGURE 12. CARBON DIOXIDE UPTAKE IN DEIONIZED WATER AT 25°C AND 700.0 MM Hg (TEST NUMBER 8)

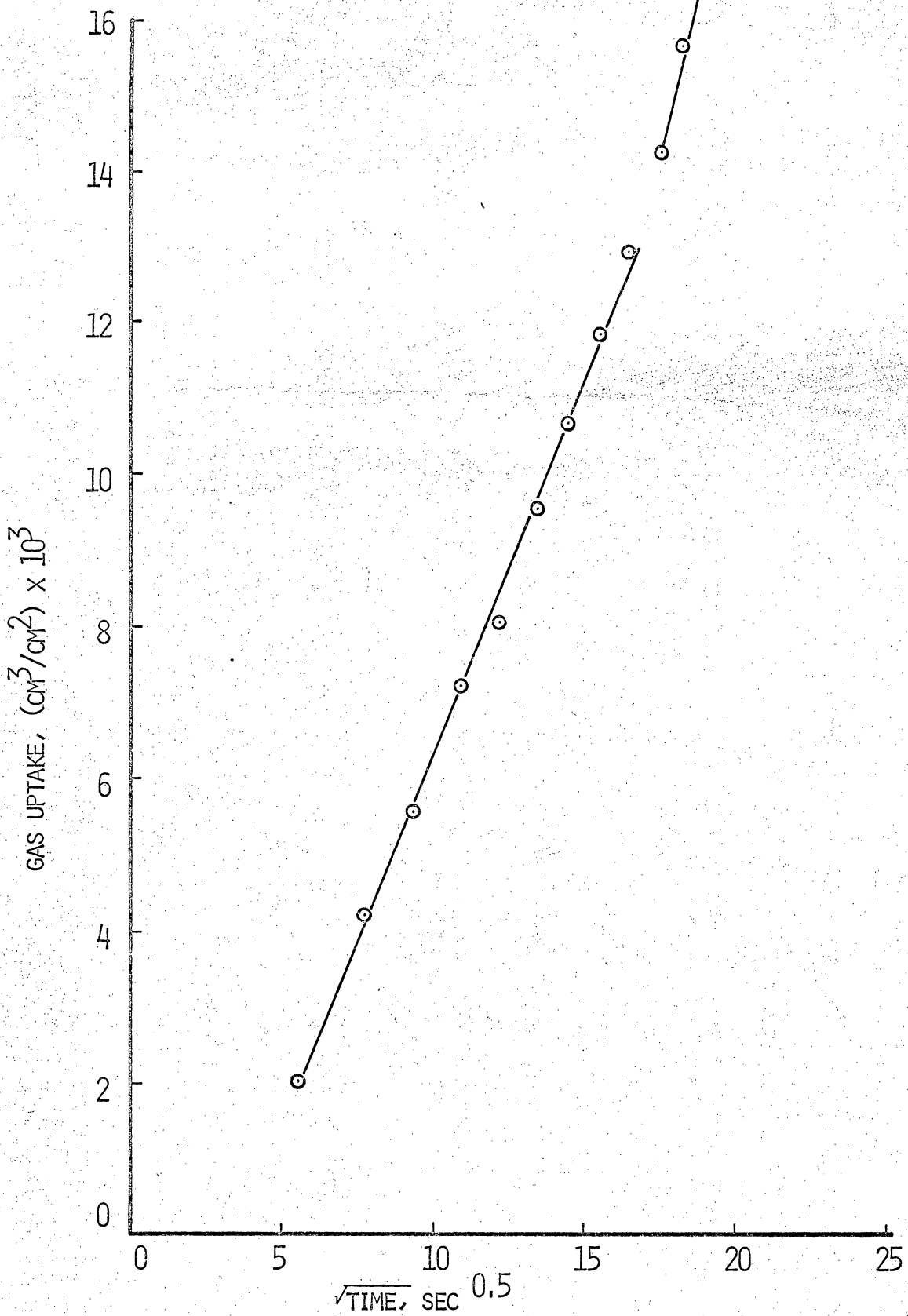


FIGURE 13. CARBON DIOXIDE UPTAKE IN DEIONIZED WATER AT 25°C AND 702.0 MM Hg (TEST NUMBER 9)

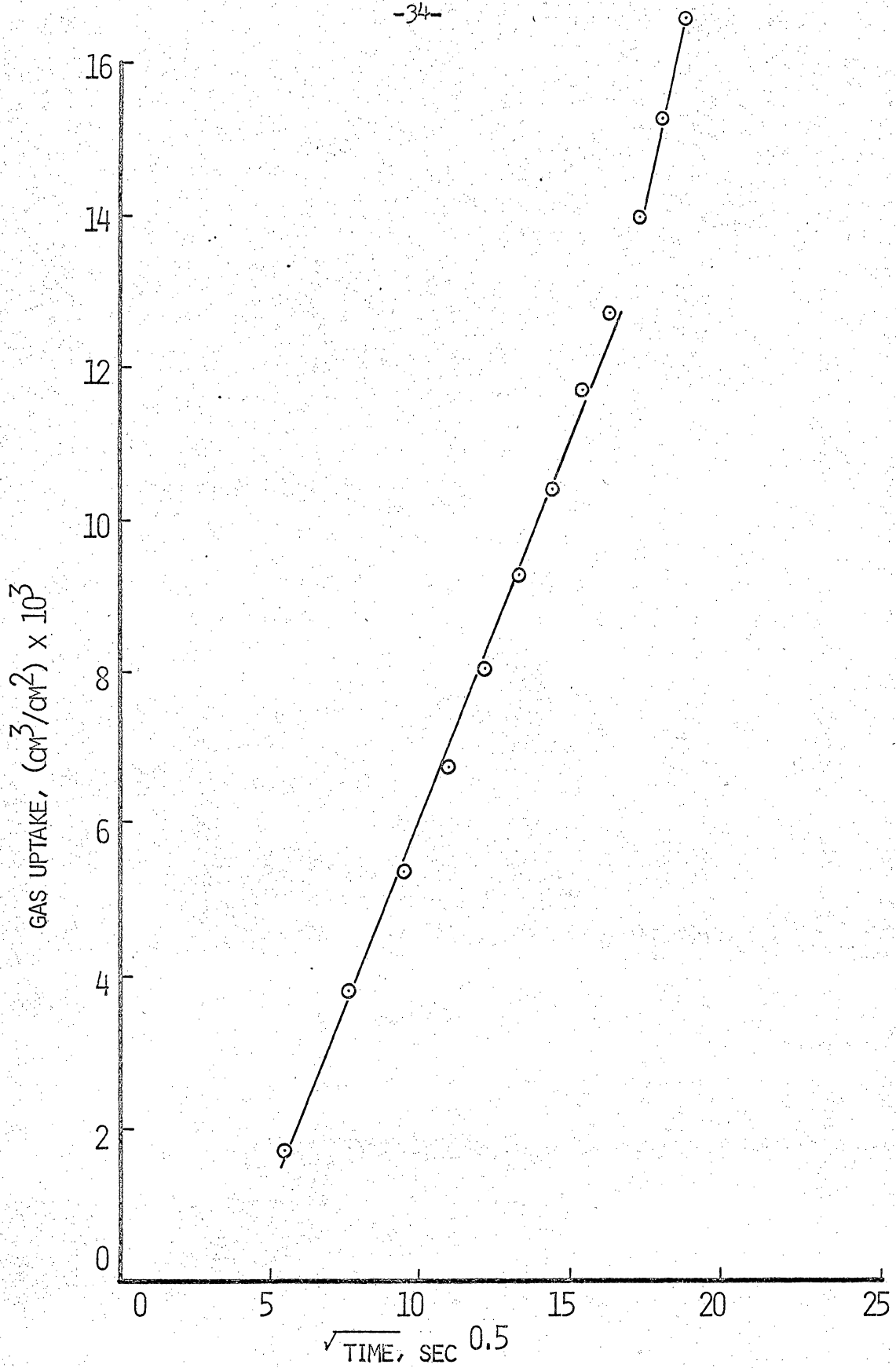


FIGURE 14. CARBON DIOXIDE UPTAKE IN DEIONIZED WATER AT 25°C AND 701.0 MM HG (TEST NUMBER 10)

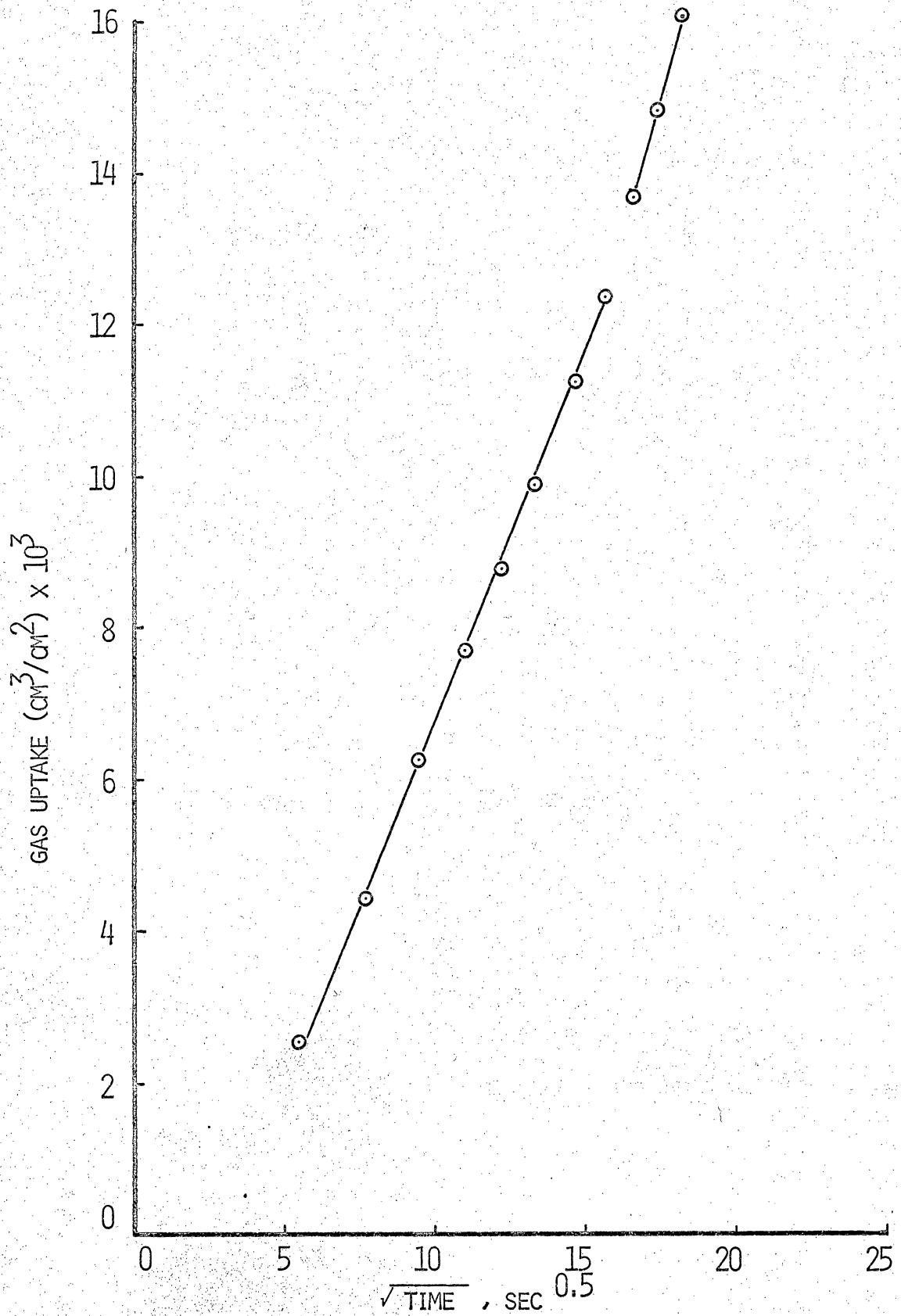


FIGURE 15. CARBON DIOXIDE UPTAKE IN DEIONIZED WATER AT 25°C AND 700 MM Hg (TEST NUMBER 11)

TABLE I

Diffusion Coefficients for Absorption of Carbon Dioxide  
into Deionized Water at 25°C

Test Number	Saturation Pressure mm Hg	Operating Pressure mm Hg	Pressure Increment mm Hg	Diffusion Coefficient cm <sup>2</sup> /sec x 10 <sup>5</sup>
1	498.5	690.0	191.5	1.98
2	500.0	700.0	200.0	1.97
3	498.0	699.0	201.0	1.95
4	500.0	700.0	200.0	1.97
5	500.0	702.0	202.0	1.93
6	500.0	704.0	204.0	1.89
7	500.0	703.0	203.0	1.91
8	500.0	700.0	200.0	1.92
9	500.0	702.0	202.0	1.91
10	500.0	701.0	201.0	1.94
11	500.0	700.0	200.0	1.91



operating pressure and the pressure increment. Saturation pressure is the pressure at which a deionized water sample was given a specific initial concentration of carbon dioxide. Operating pressure is the pressure at which the absorption process took place. The pressure increment is the difference between the operating pressure and the saturation pressure.

Equilibrium Surface Tension Results. The average apparent surface tensions, correction factors and actual equilibrium surface tensions for the aqueous solutions of n-octanol, 4-octanol and lauryl diglycol amide are given in Tables II to IV. The average apparent surface tension for each surfactant solution was found by averaging the values obtained from three separate samples of the solution. The correction factor for each solution was calculated using equation (26) in the Appendix.

Figures 16 to 18 show the surface tension-surface concentration relationships of the three surfactant solution. These relationships were determined by a computer program using equation (29).

Gas Absorption Results with Surfactant Solutions. The manometer readings for the absorption of carbon dioxide in aqueous surfactant solutions are given in the Appendix, Tables XVI to XXX. The results of these tests were calculated to give the uptake values which are shown in Figures 19 to 33. The tests with lauryl diglycol amide solutions were measured with a cathetometer.

TABLE II

Equilibrium Surface Tensions of Aqueous N-Octanol Solutions at 25°C

Bulk Concentration	Average Apparent Surface Tension	Correction Factor	Actual Surface Tension
ppm	dyne/cm		dyne/cm
400	38.3	0.897	34.5
300	42.5	0.902	38.3
200	48.6	0.908	44.1
150	53.7	0.914	49.1
100	60.0	0.920	55.2
50	65.2	0.926	60.4
25	68.6	0.929	63.8
10	72.6	0.933	67.8
5	74.7	0.935	69.8
0	76.8	0.936	71.9

TABLE III

Equilibrium Surface Tensions of Aqueous 4-Octanol Solutions at 25°C

Bulk Concentration ppm	Average Apparent Surface Tension dyne/cm	Correction Factor	Actual Surface Tension dyne/cm
400	55.4	0.915	50.7
300	57.7	0.917	52.9
200	60.5	0.920	55.7
150	63.6	0.924	58.7
100	66.8	0.927	62.0
50	68.5	0.929	63.7
25	69.1	0.930	64.2
10	73.4	0.933	68.5
5	74.0	0.934	69.1
0	76.8	0.936	71.9

TABLE IV

Equilibrium Surface Tensions of Aqueous Lauryl  
Diglycol Amide Solutions at 25°C

Bulk Concentration	Average Apparent Surface Tension	Correction Factor	Actual Surface Tension
ppm	dyne/cm		dyne/cm
40	36.2	0.895	32.4
30	42.0	0.902	37.8
20	43.9	0.905	39.8
10	52.5	0.914	48.0
5	60.3	0.920	55.5
1	70.4	0.931	65.5
0.5	75.0	0.935	70.2
0	76.8	0.936	71.9

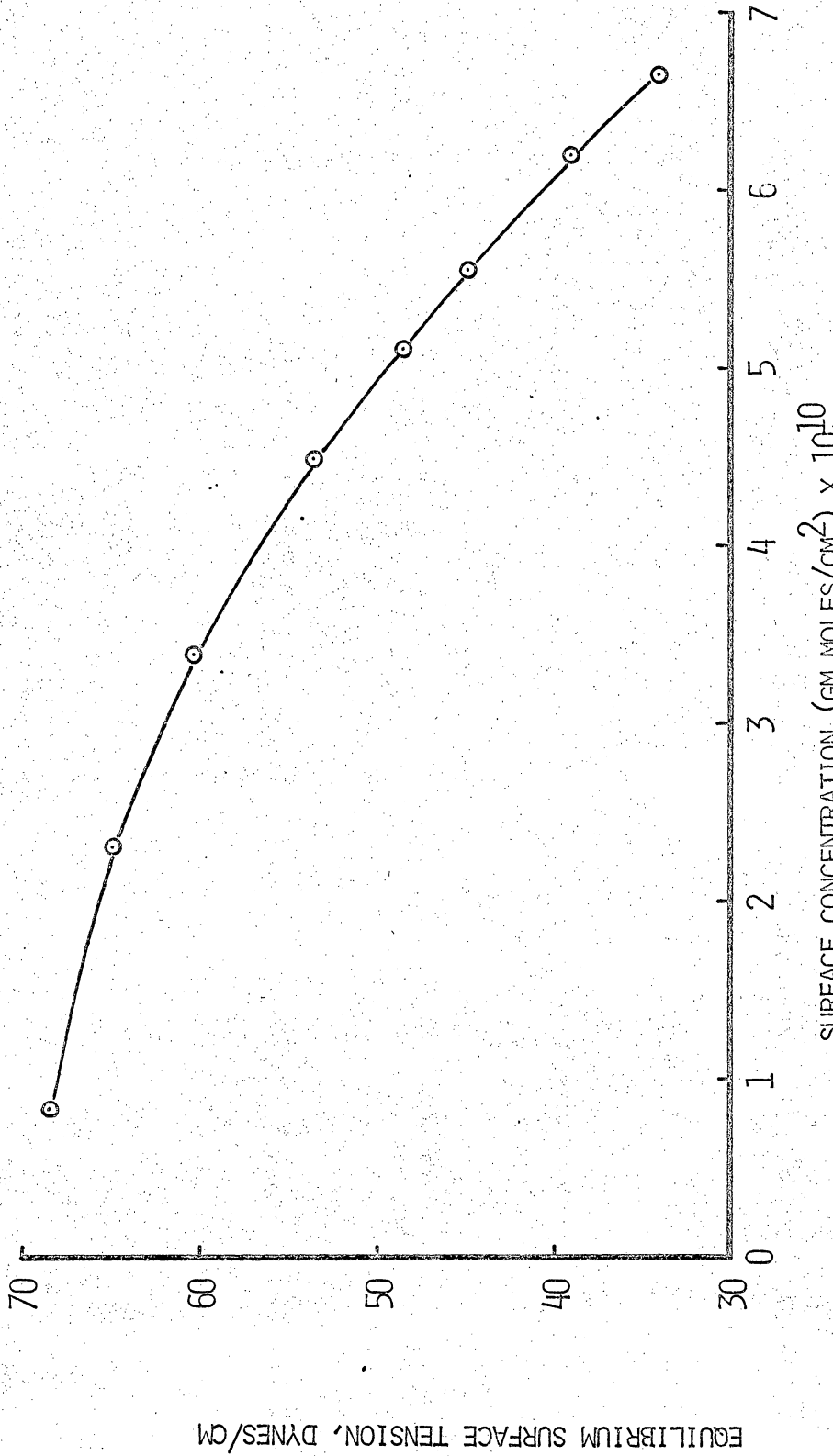


FIGURE 16. EQUILIBRIUM SURFACE TENSION VERSUS SURFACE CONCENTRATION: N-OCTANOL

EQUILIBRIUM SURFACE TENSION, DYNES/CM

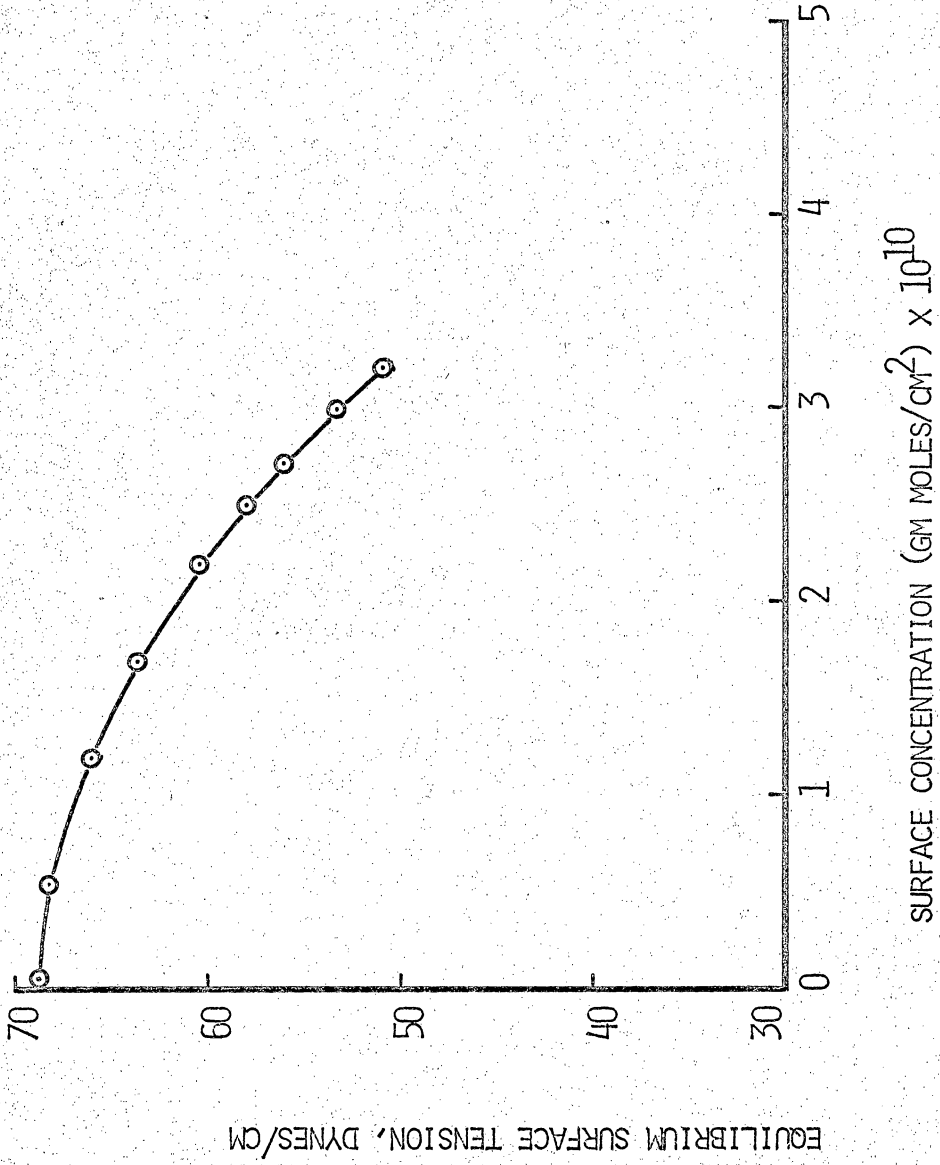


FIGURE 17. EQUILIBRIUM SURFACE TENSION VERSUS SURFACE CONCENTRATION: 4-OCTANOL

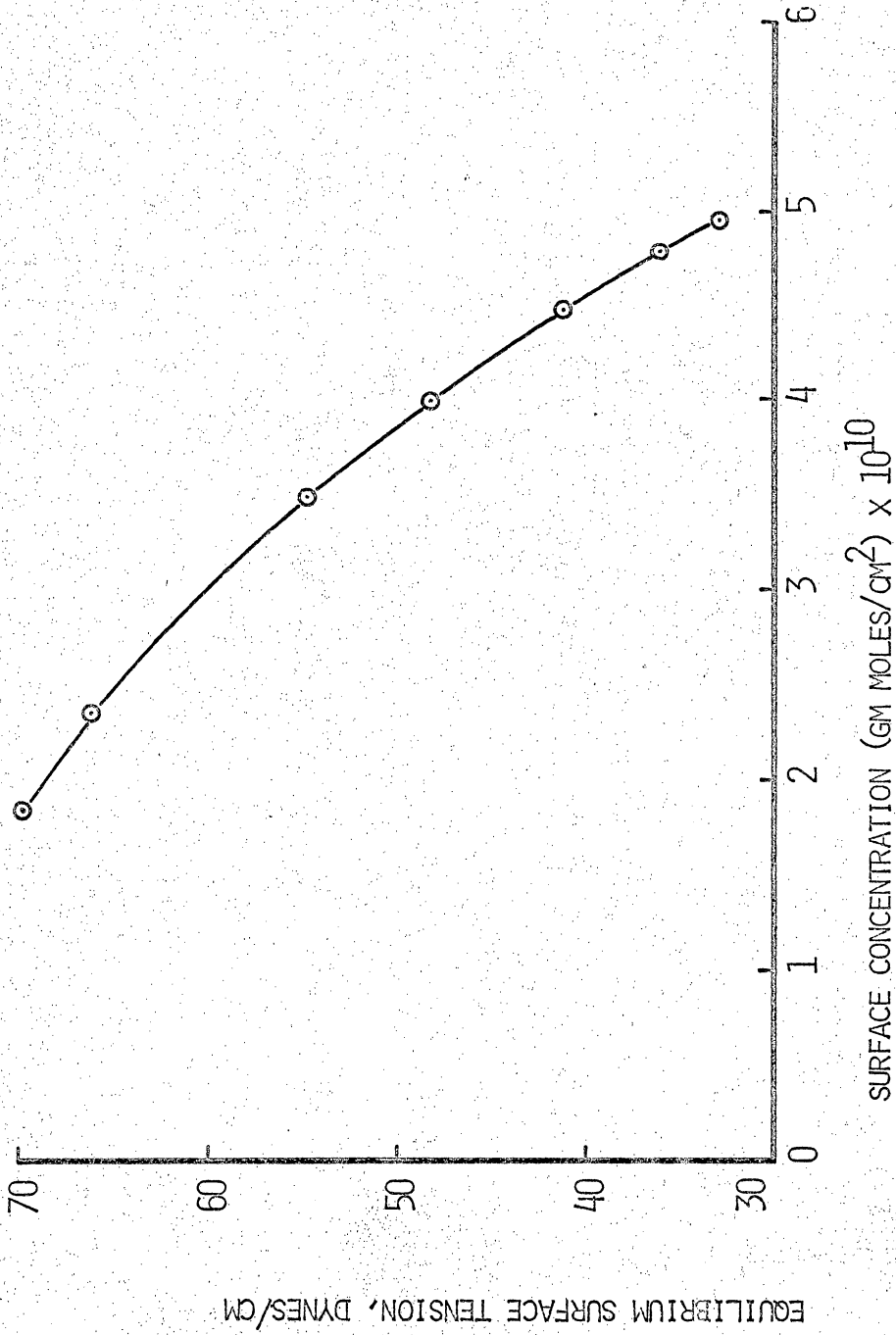


FIGURE 18. EQUILIBRIUM SURFACE TENSION VERSUS SURFACE CONCENTRATION: LAURYL DIGLYCOL AMIDE

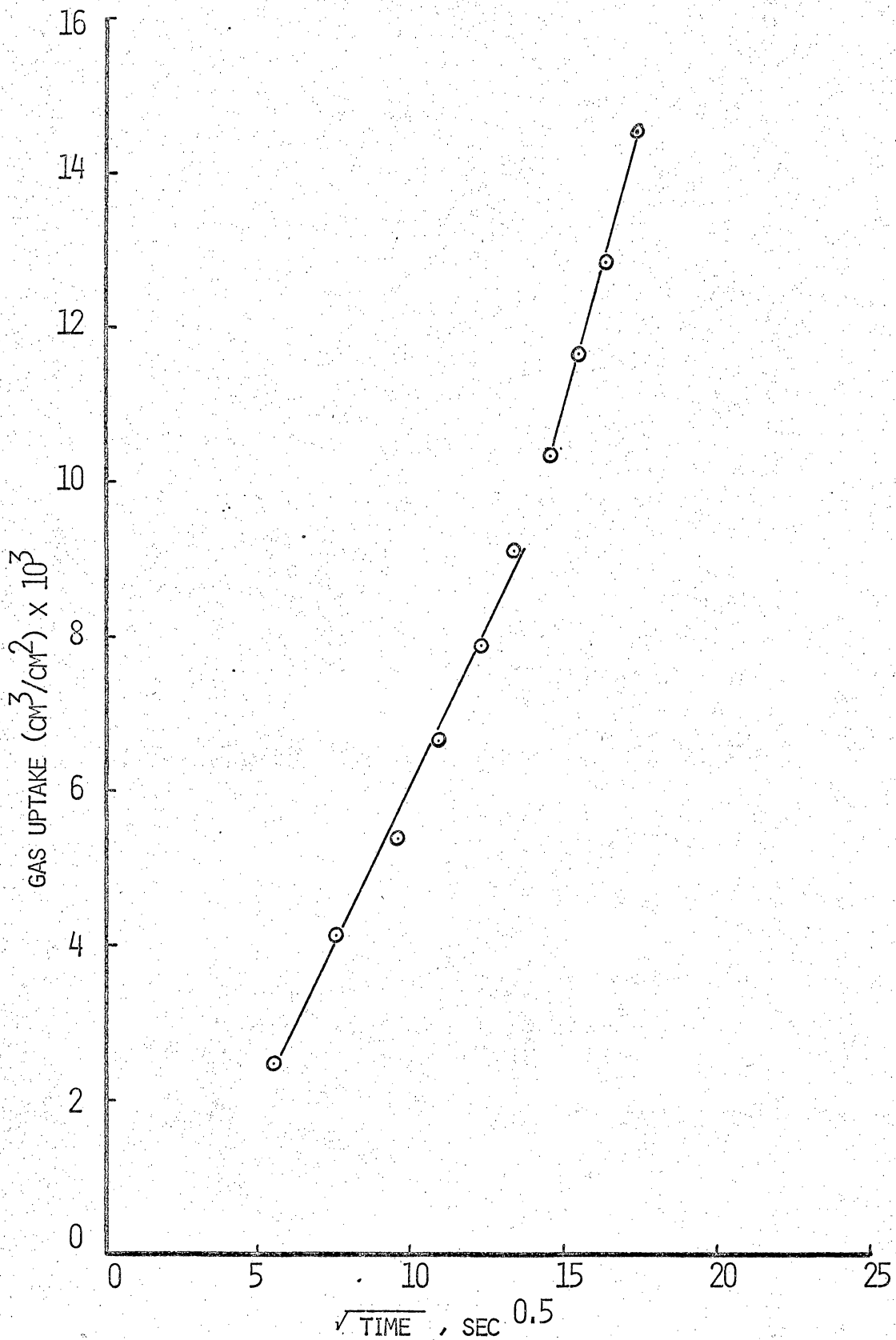


FIGURE 19. CARBON DIOXIDE UPTAKE IN N-OCTANOL SOLUTION (300 PPM) AT 25°C AND 700 MM Hg



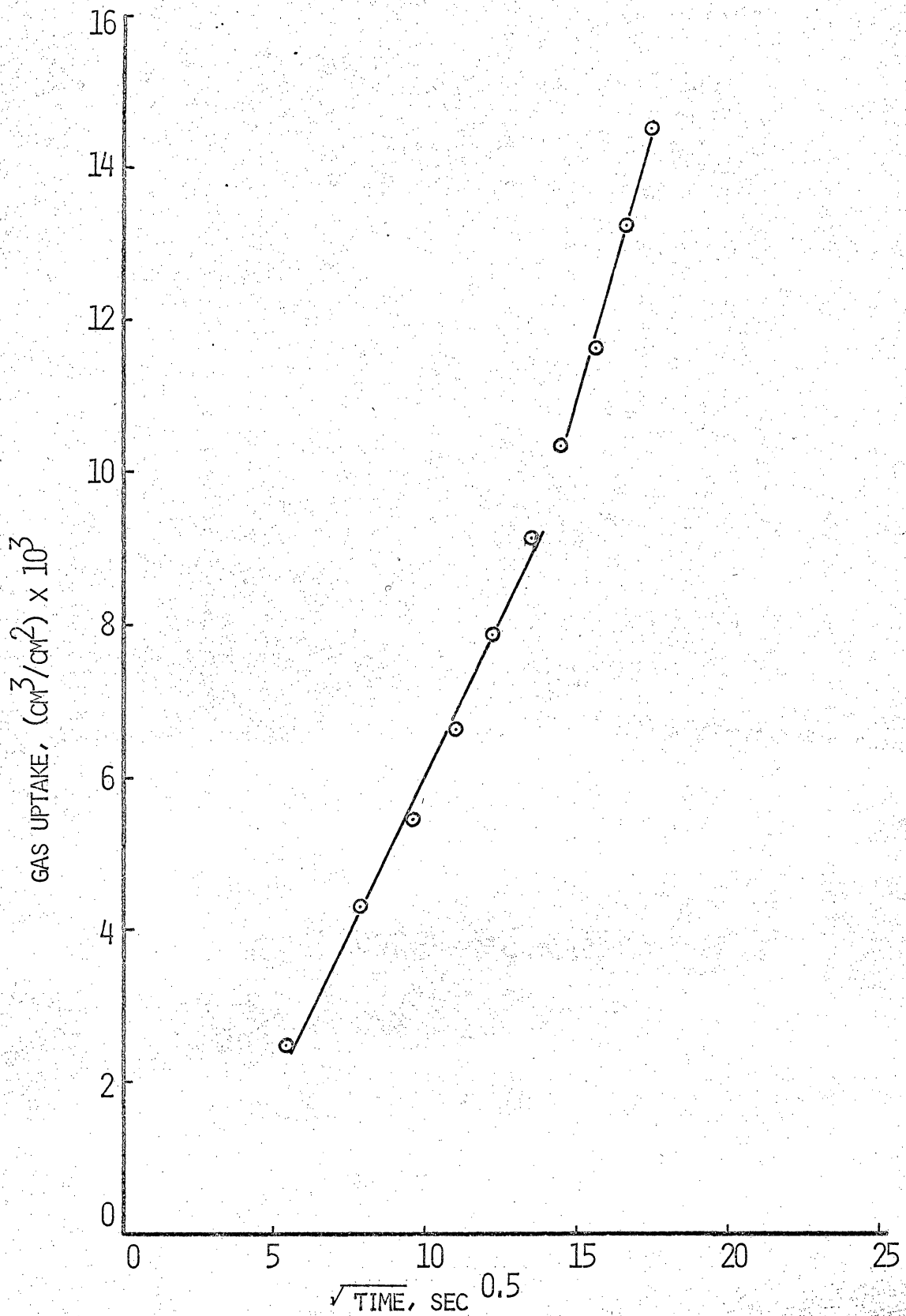


FIGURE 20. CARBON DIOXIDE UPTAKE IN N-OCTANOL SOLUTION  
(200 PPM) AT 25°C AND 700.0 MM Hg

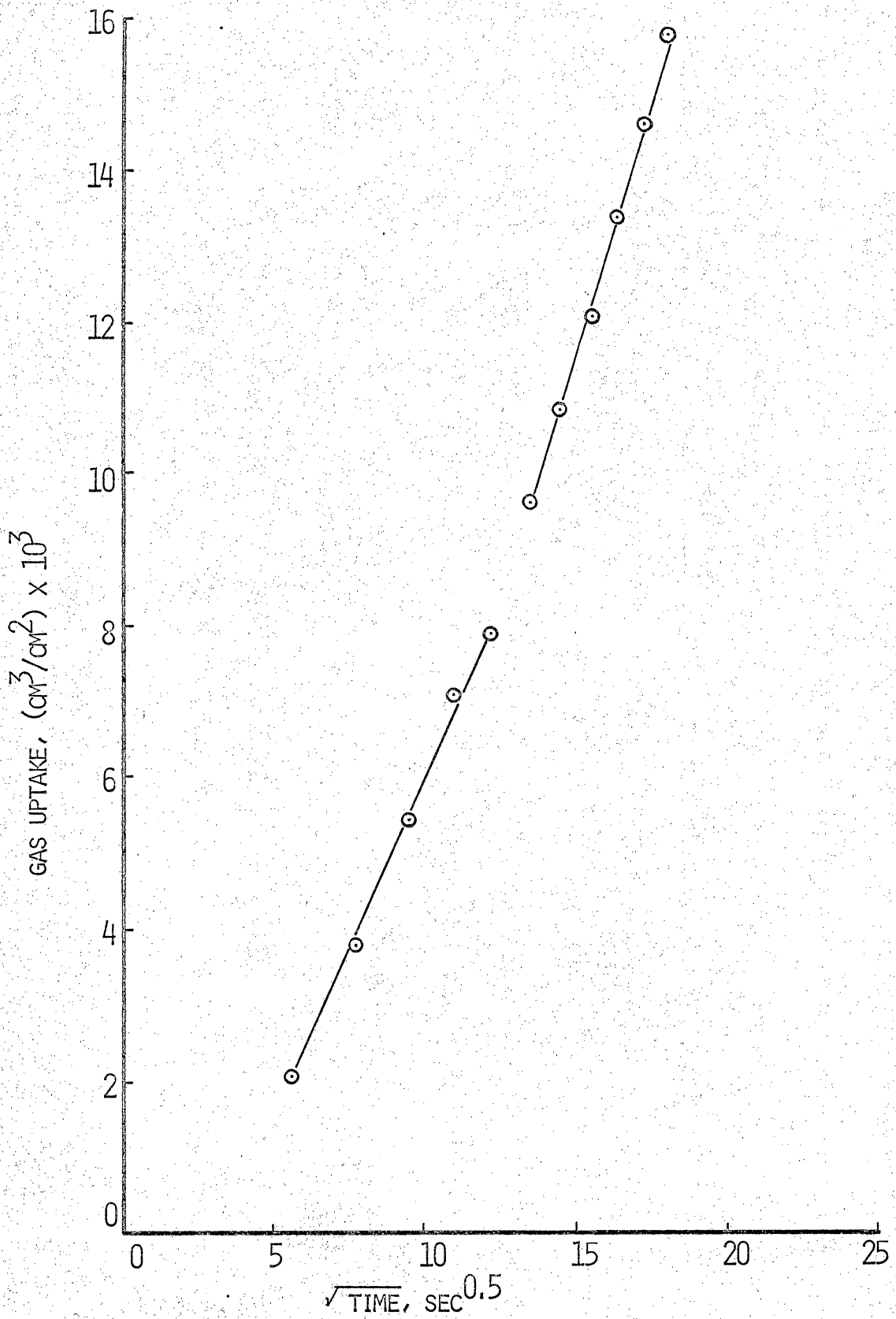


FIGURE 21. CARBON DIOXIDE UPTAKE IN N-OCTANOL SOLUTION  
(100 PPM) AT 25°C AND 700.0 MM Hg

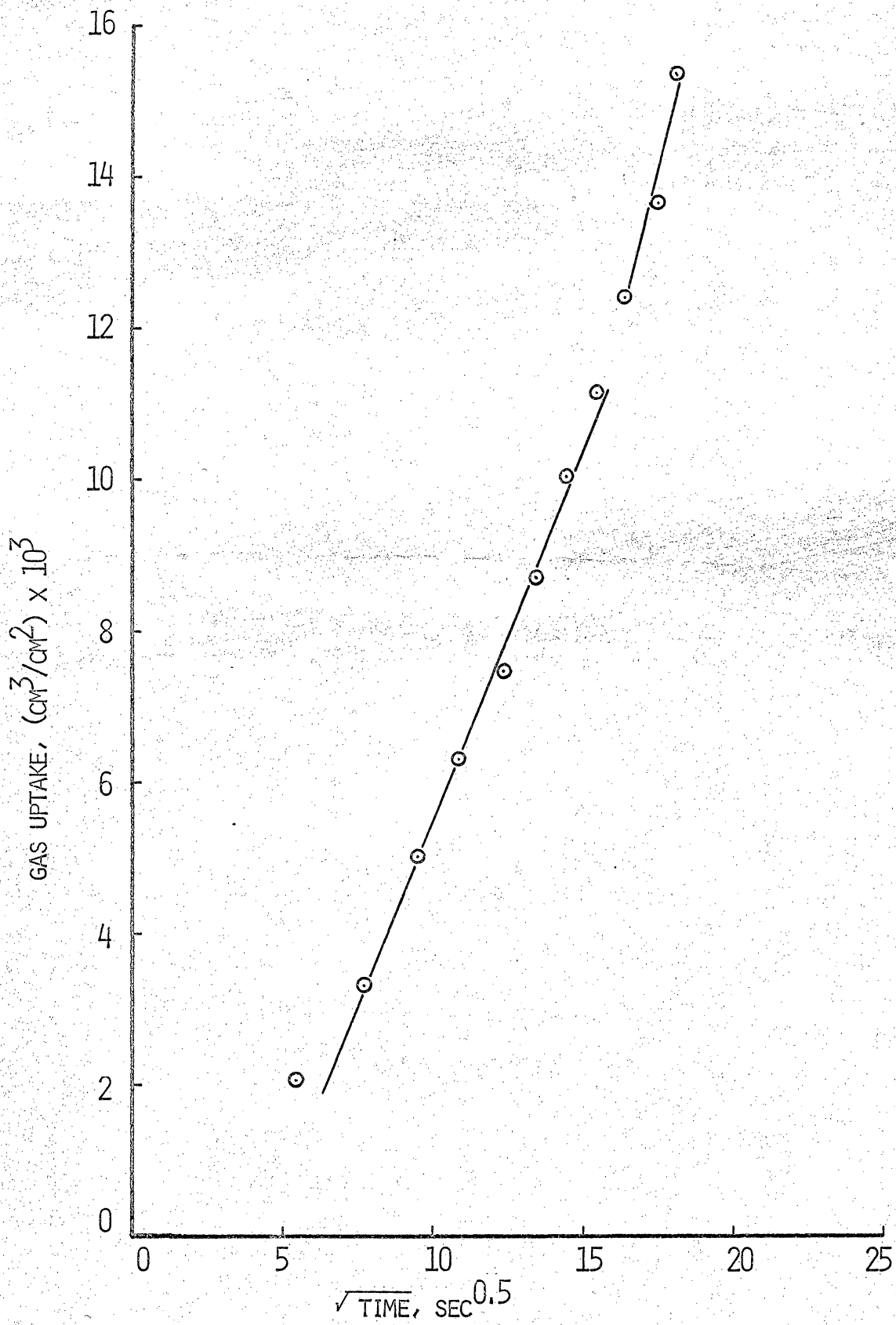


FIGURE 22. CARBON DIOXIDE UPTAKE IN N-OCTANOL SOLUTION  
(50 PPM) AT 25°C AND 700.0 MM Hg

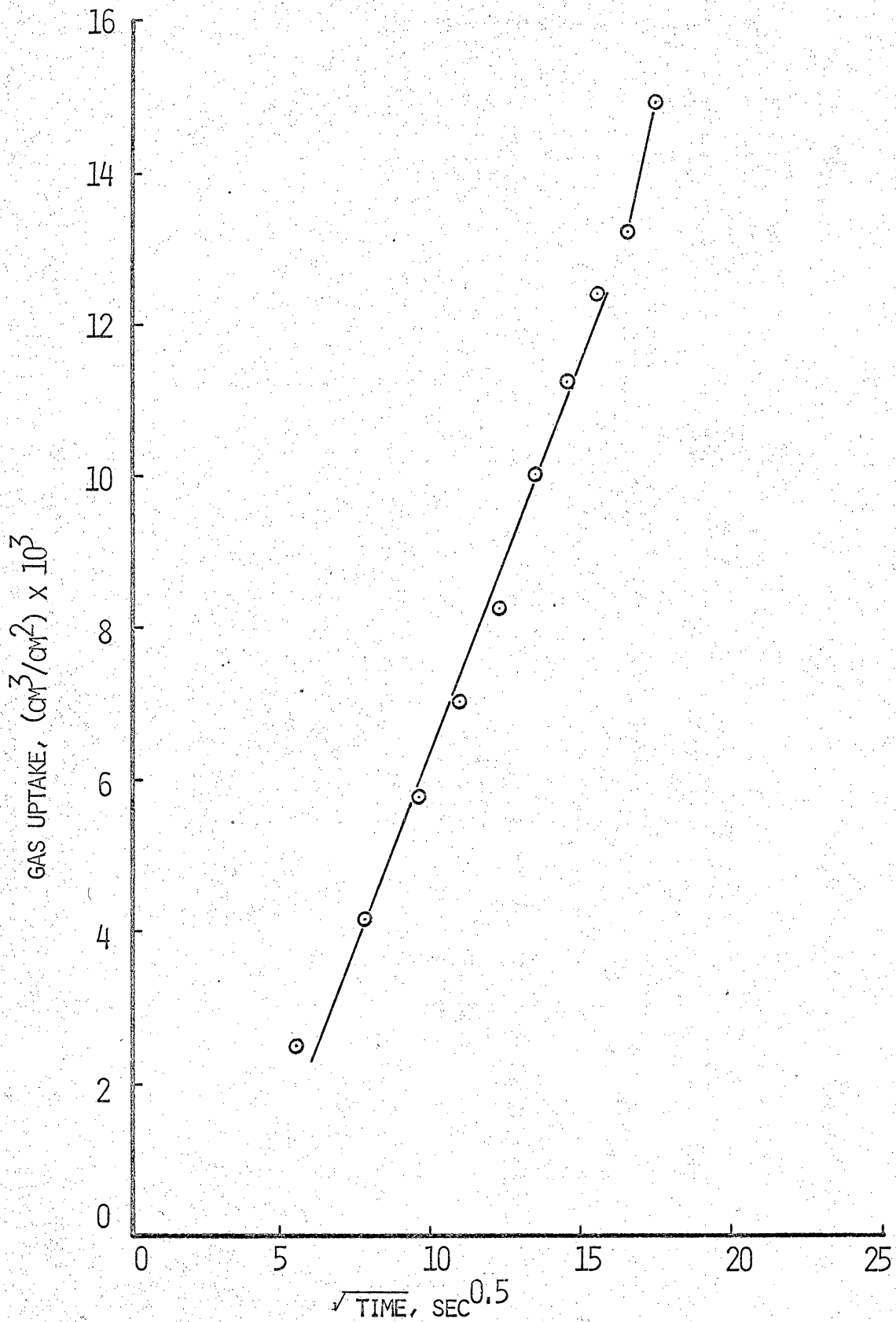


FIGURE 23. CARBON DIOXIDE UPTAKE IN N-OCTANOL SOLUTION  
(10 PPM) AT 25°C AND 700.0 MM Hg

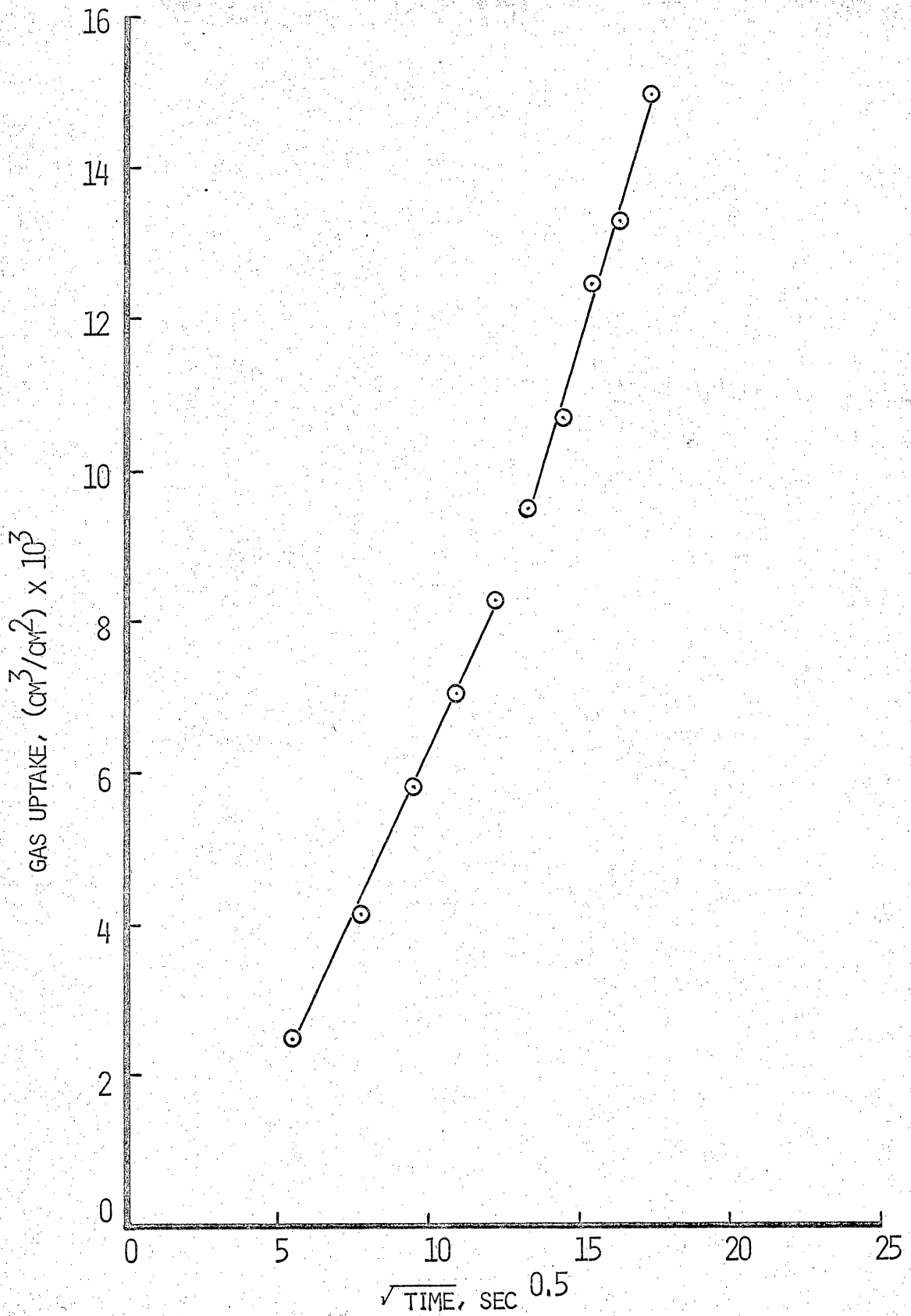


FIGURE 24. CARBON DIOXIDE UPTAKE IN 4-OCTANOL SOLUTION (300 PPM) AT 25°C AND 700.0 MM Hg

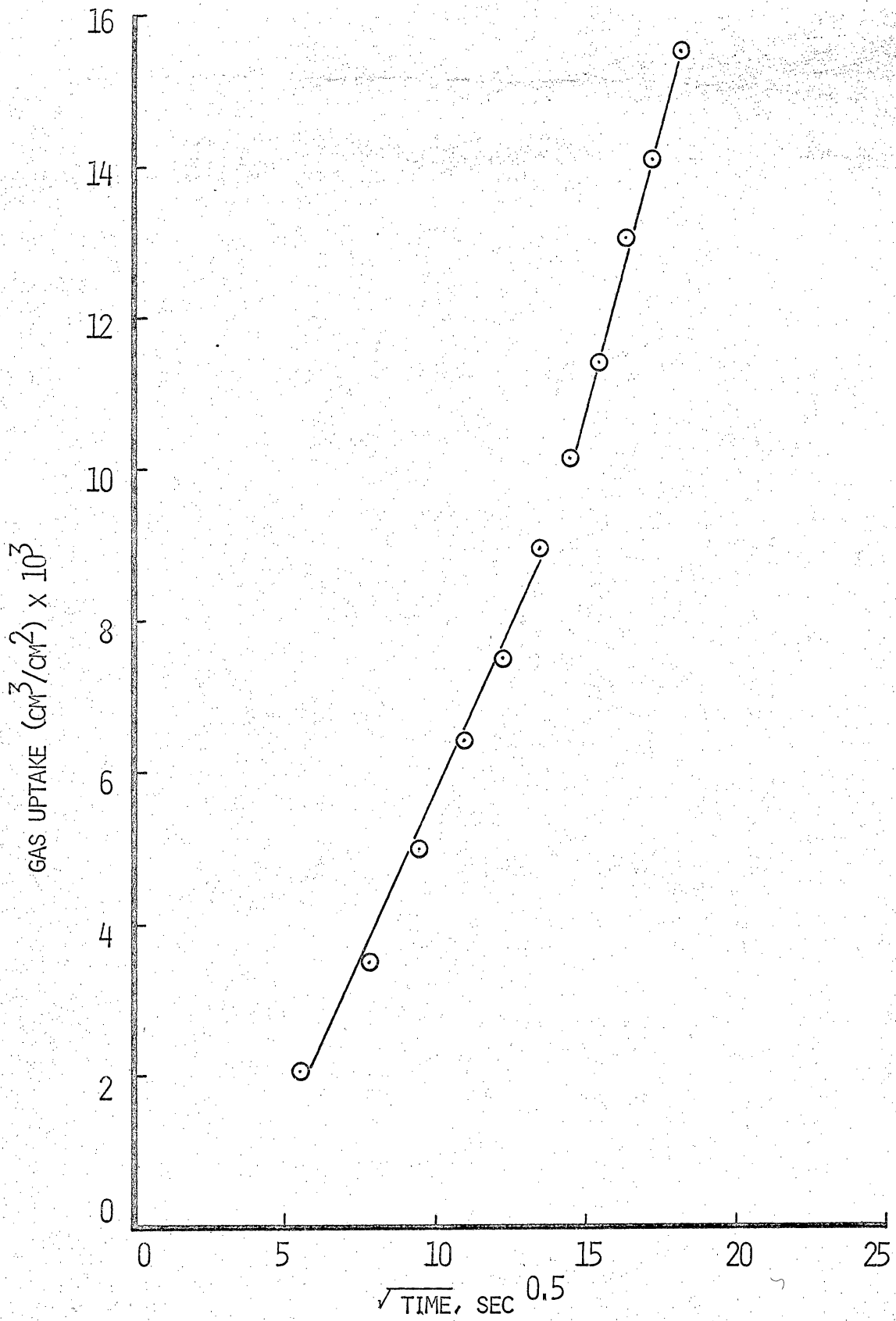


FIGURE 25. CARBON DIOXIDE UPTAKE IN 4-OCTANOL SOLUTION (200 PPM) AT 25°C AND 700.0 MM Hg

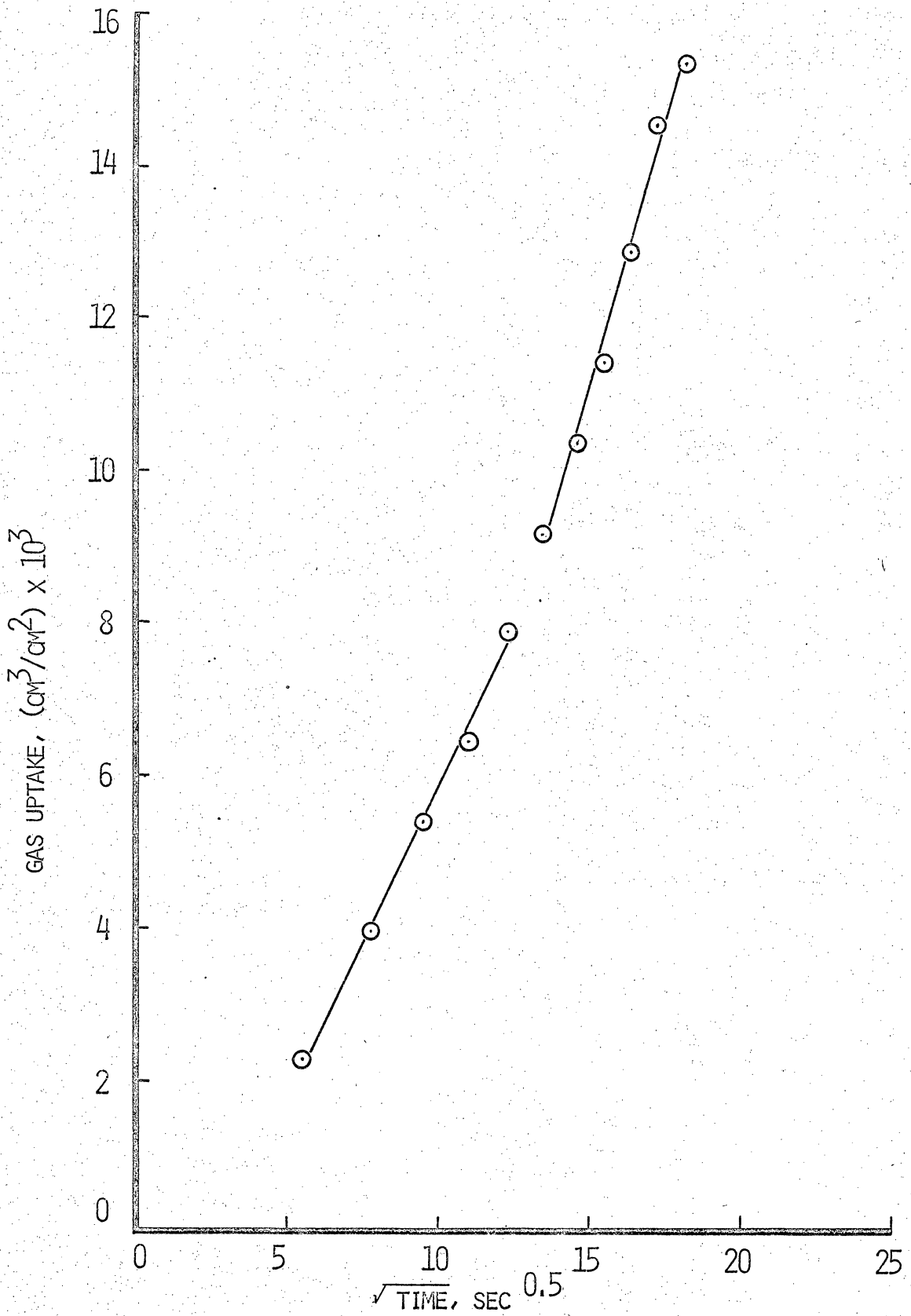


FIGURE 26. CARBON DIOXIDE UPTAKE IN 4-OCTANOL SOLUTION (100 PPM) AT 25°C AND 700.0 MM Hg

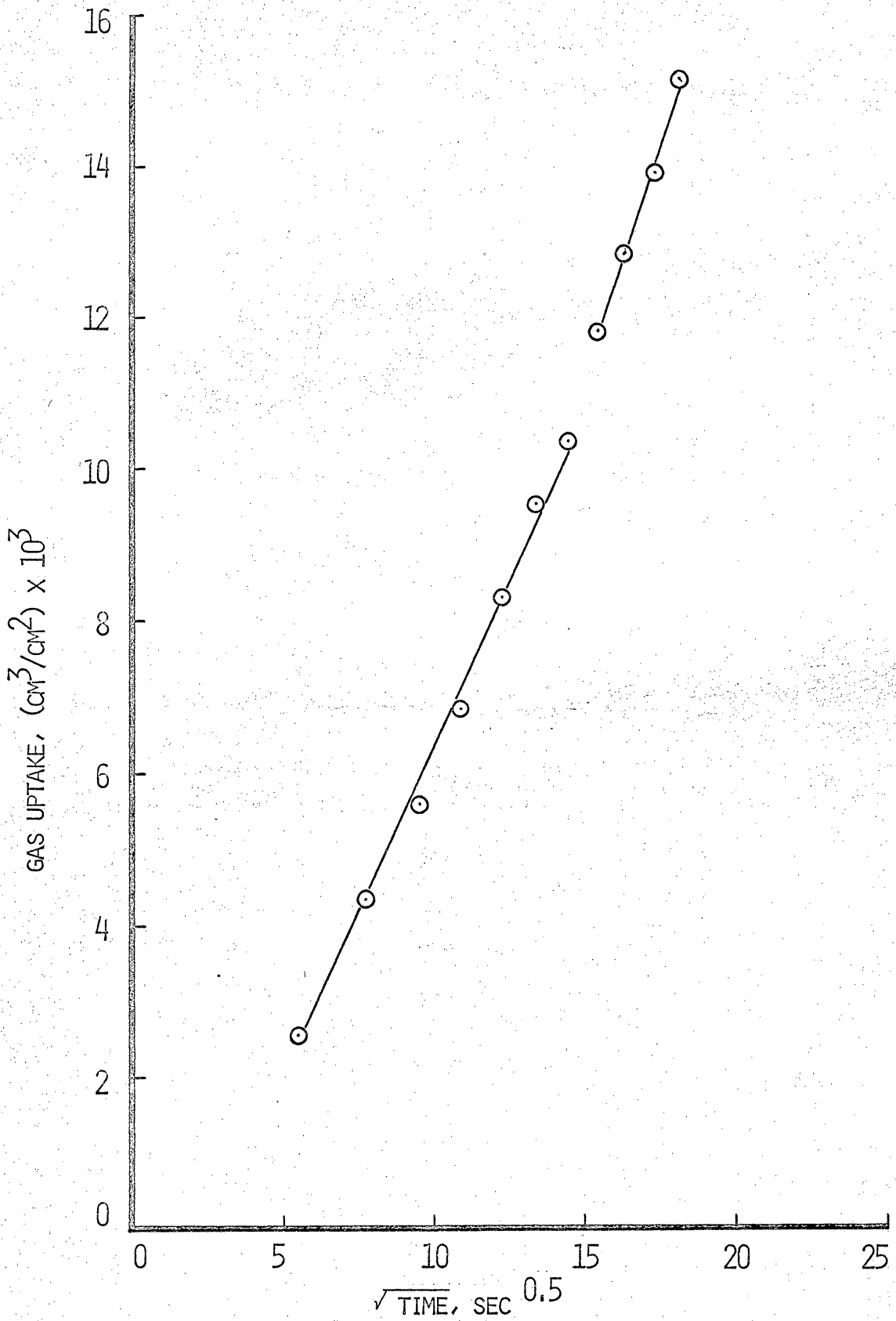


FIGURE 27. CARBON DIOXIDE UPTAKE IN 4-OCTANOL SOLUTION (50 PPM) AT 25°C AND 700.0 MM Hg



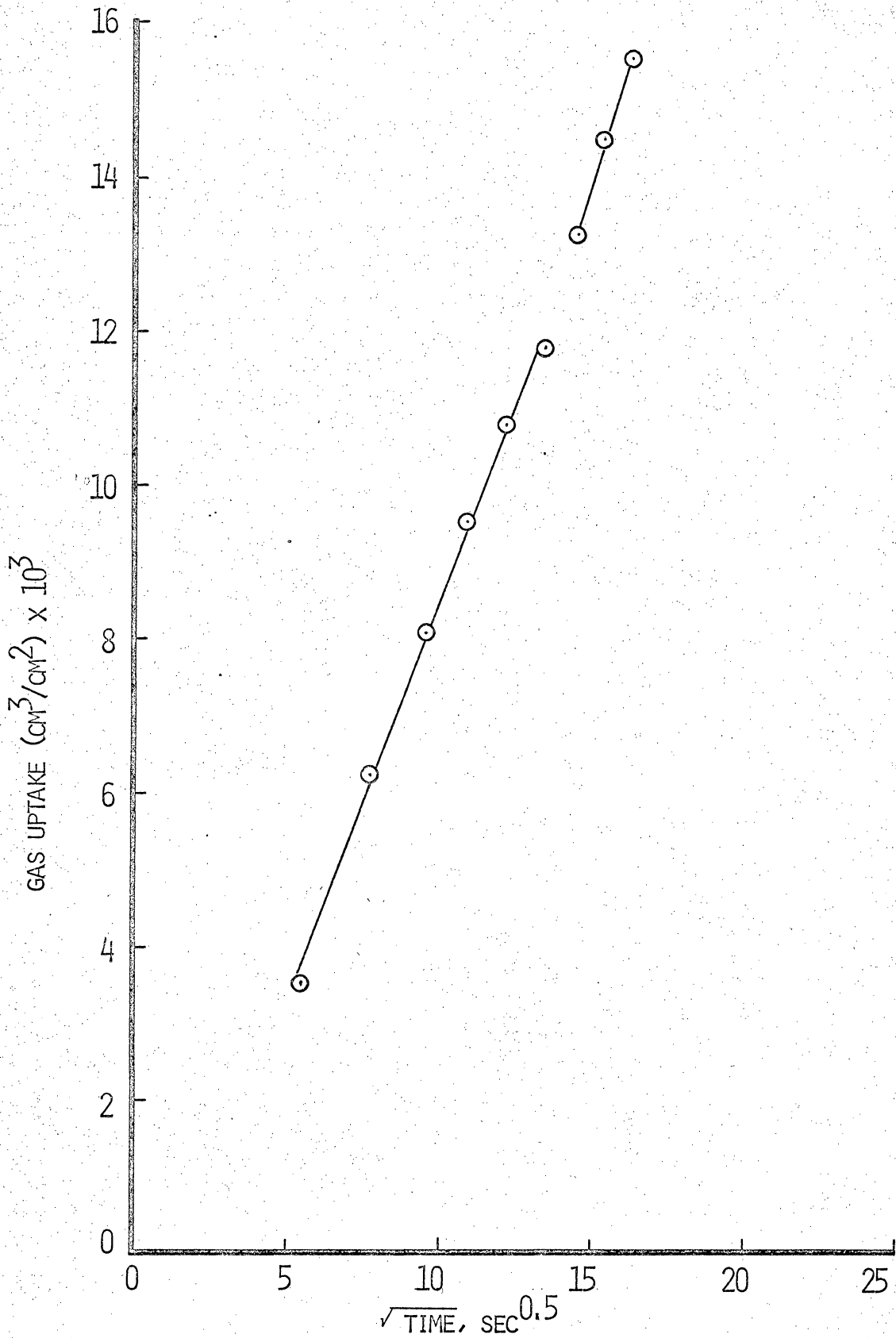


FIGURE 28. CARBON DIOXIDE UPTAKE IN 4-OCTANOL SOLUTION  
(10 PPM) AT 25°C AND 700.0 MM Hg

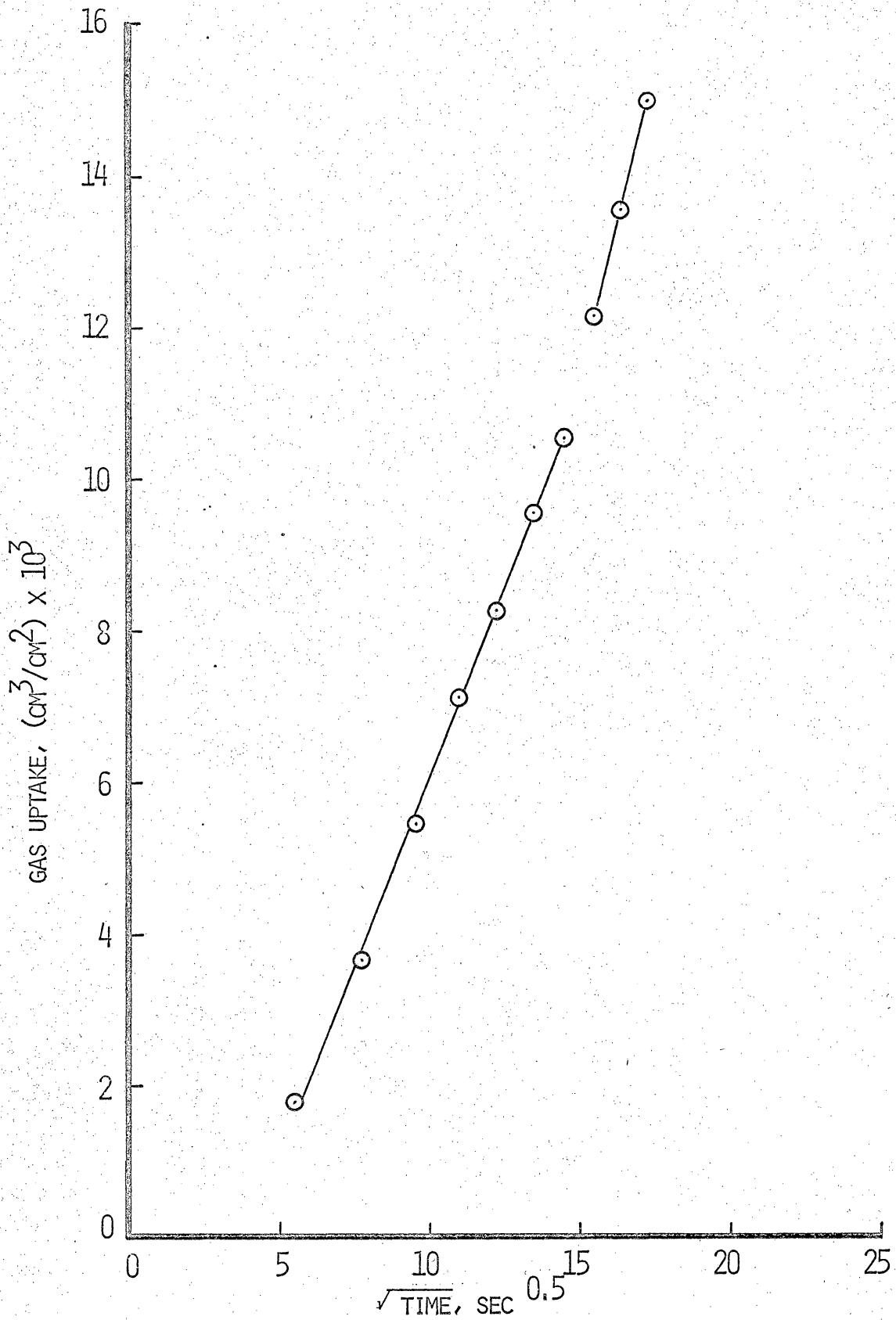


FIGURE 29. CARBON DIOXIDE UPTAKE IN LAURYL DIGLYCOL AMIDE SOLUTION (30 PPM) AT 25°C AND 701.5 MM Hg

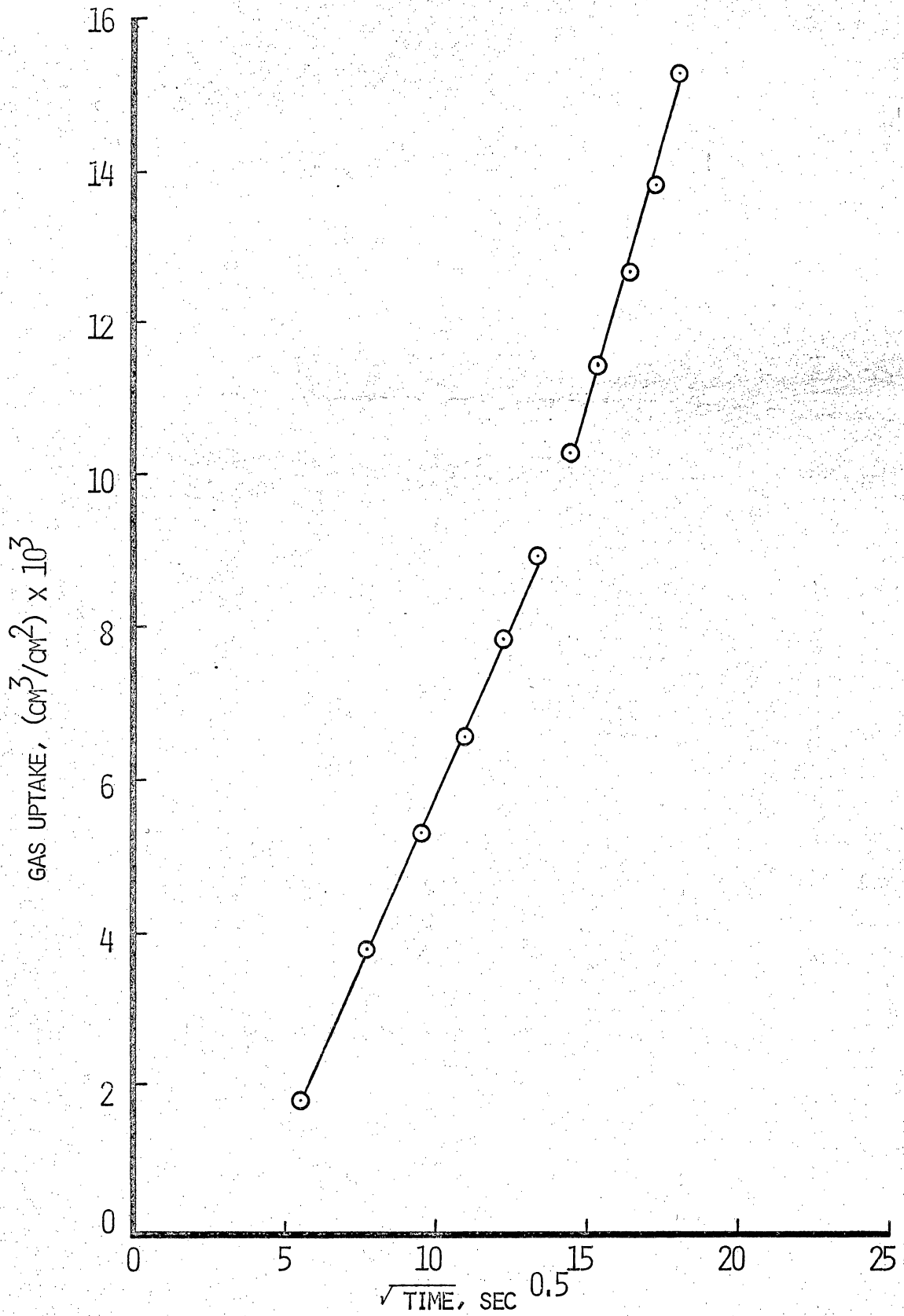


FIGURE 30. CARBON DIOXIDE UPTAKE IN LAURYL DIGLYCOL AMIDE SOLUTION (20 PPM) AT 25°C AND 700.0 MM Hg

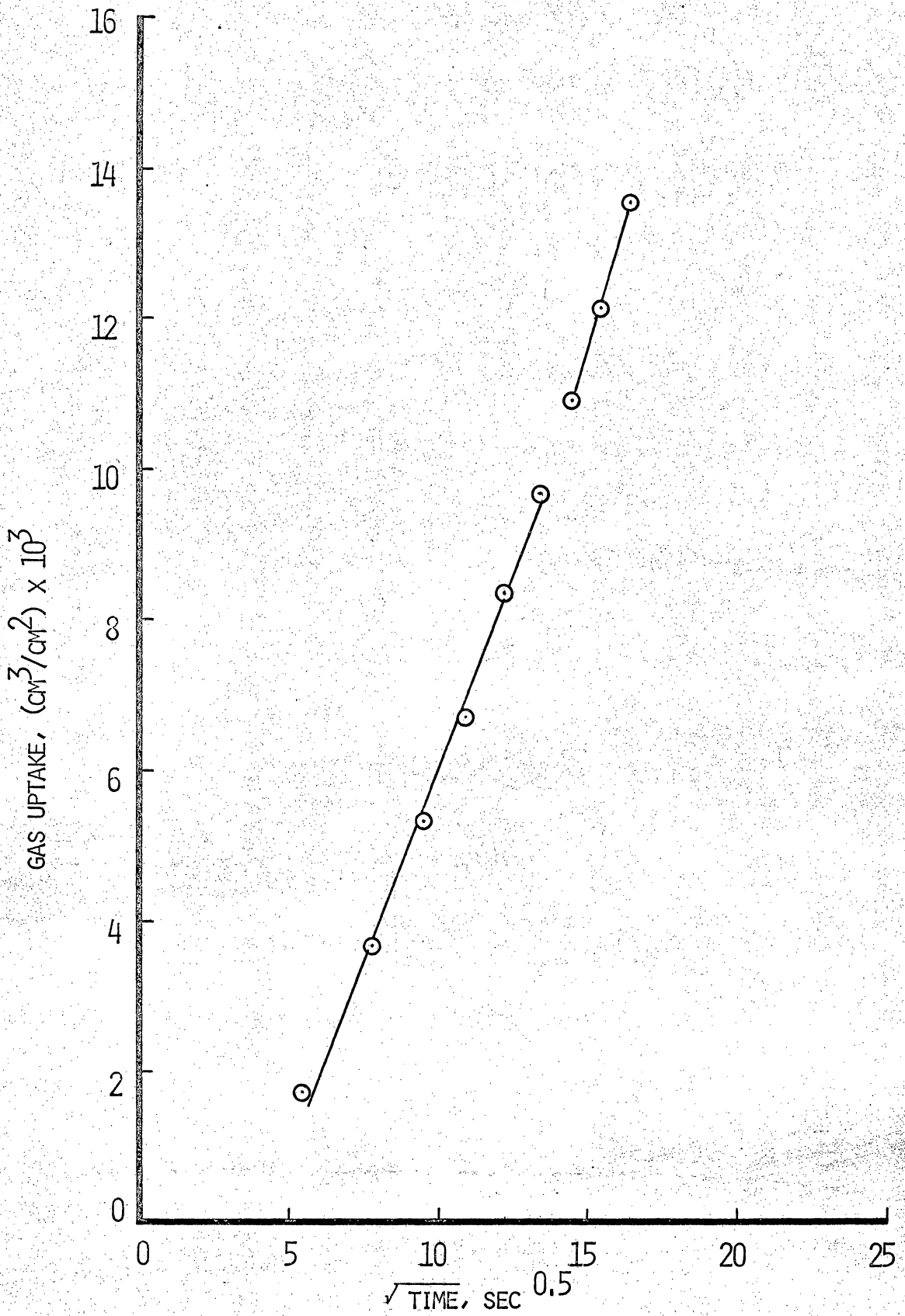


FIGURE 31. CARBON DIOXIDE UPTAKE IN LAURYL DIGLYCOL AMIDE SOLUTION (10 PPM) AT 25°C AND 715 MM Hg

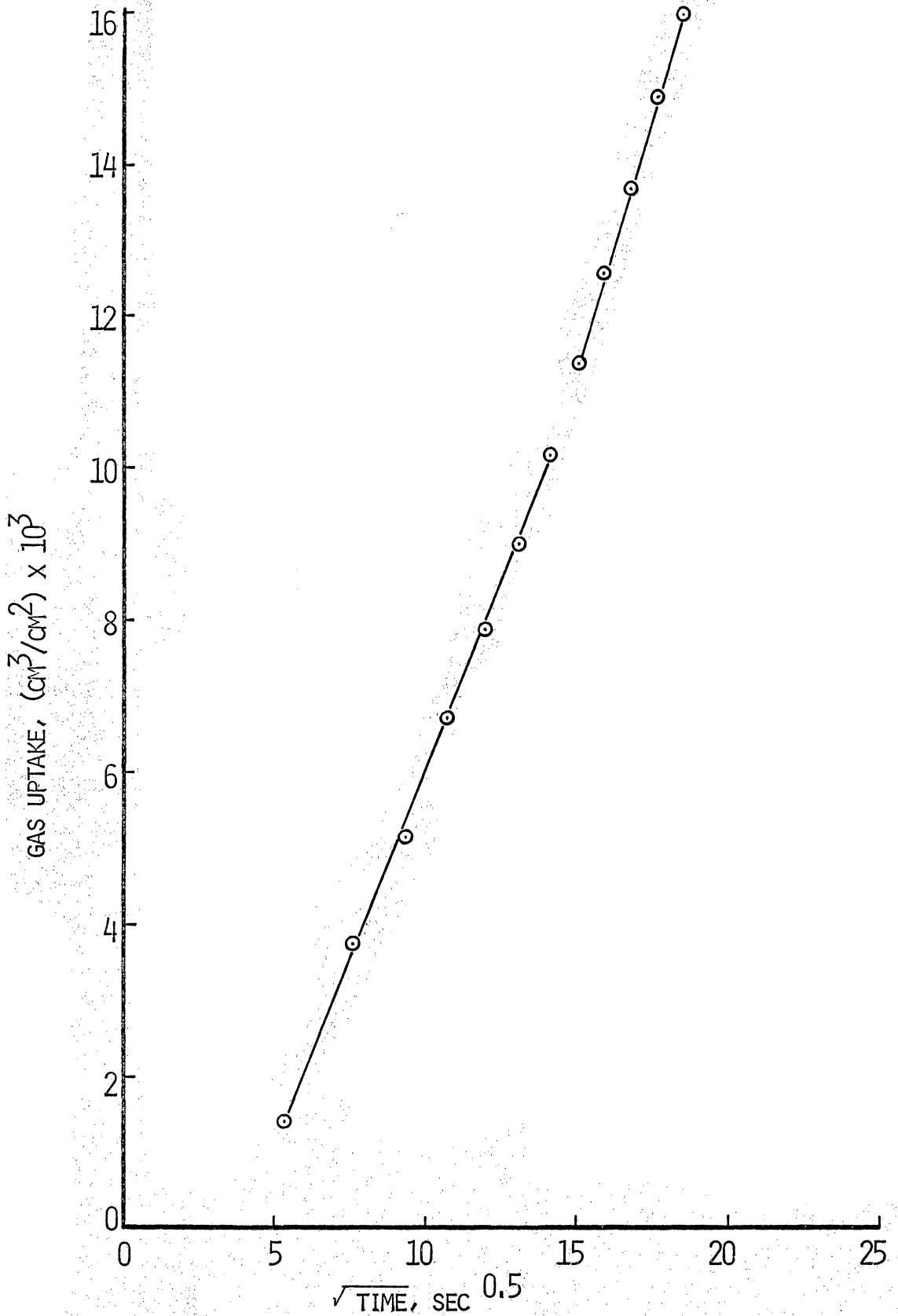


FIGURE 32. CARBON DIOXIDE UPTAKE IN LAURYL DIGLYCOL AMIDE SOLUTION (5 PPM) AT 25°C AND 697.0 MM Hg

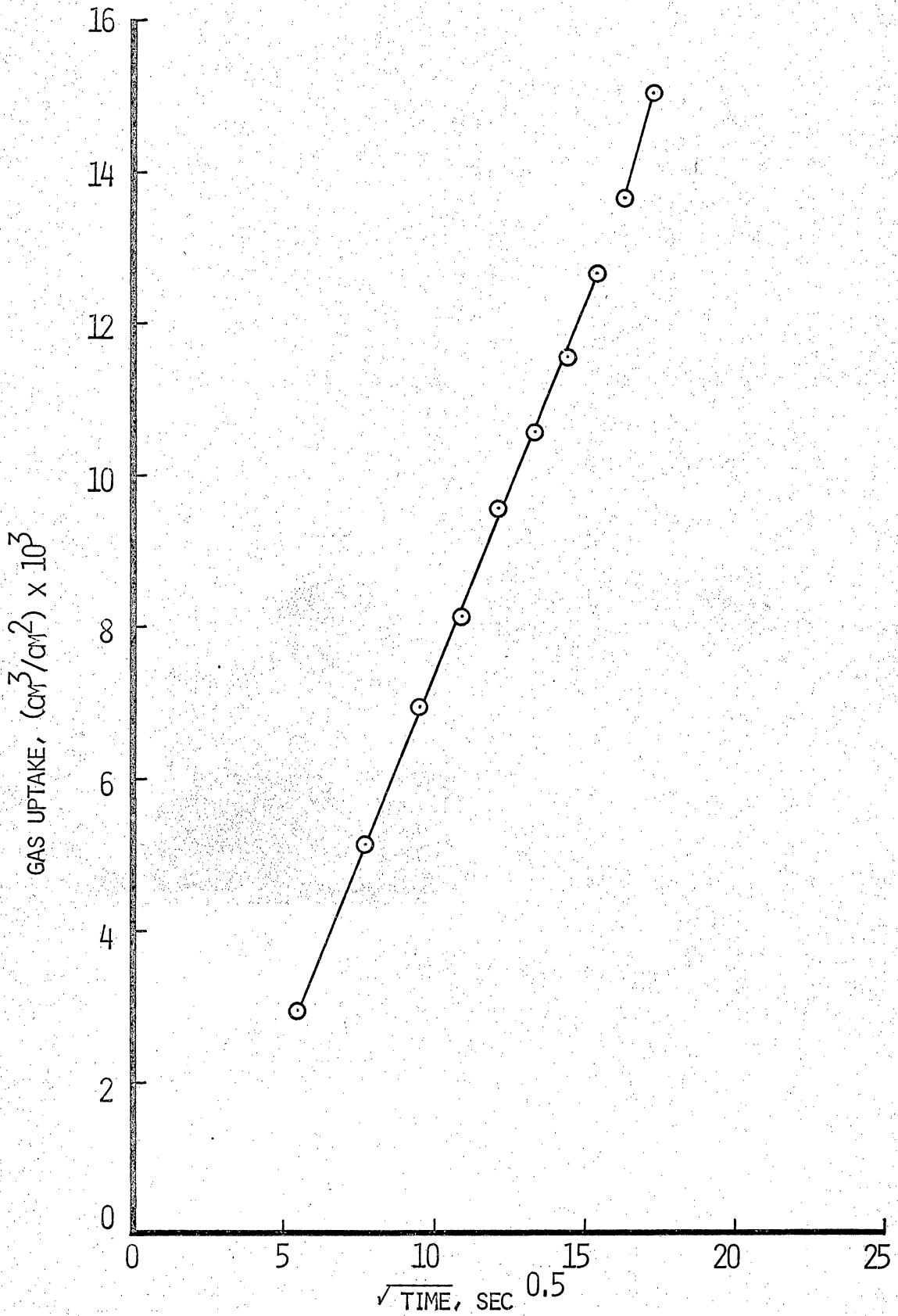


FIGURE 33. CARBON DIOXIDE UPTAKE IN LAURYL DIGLYCOL AMIDE SOLUTION (1 PPM) AT 25°C AND 700.0 MM Hg

Similar to the preliminary gas absorption tests with deionized water, not all the data available were plotted and the slope was determined from the initial linear region. The slope was used to calculate the interfacial resistance using equation (40).

Interfacial Resistance Results. The interfacial resistance for each surfactant solution was plotted with the corresponding surface concentration. The surface concentration of a surfactant solution was found by referring the corresponding surface tension to the curve of that surfactant in Figure 15 through 17. The results were given in Figure 33. The results for lauryl diglycol amide was again plotted with the results of Herbert<sup>(18)</sup> for lauryl diethanol amide.

A new time independent model for interfacial resistance was developed in the Appendix. The results calculated by a computer program using this model were plotted in Figure 35.



FIGURE 34. INTERFACIAL RESISTANCE VERSUS SURFACE CONCENTRATION



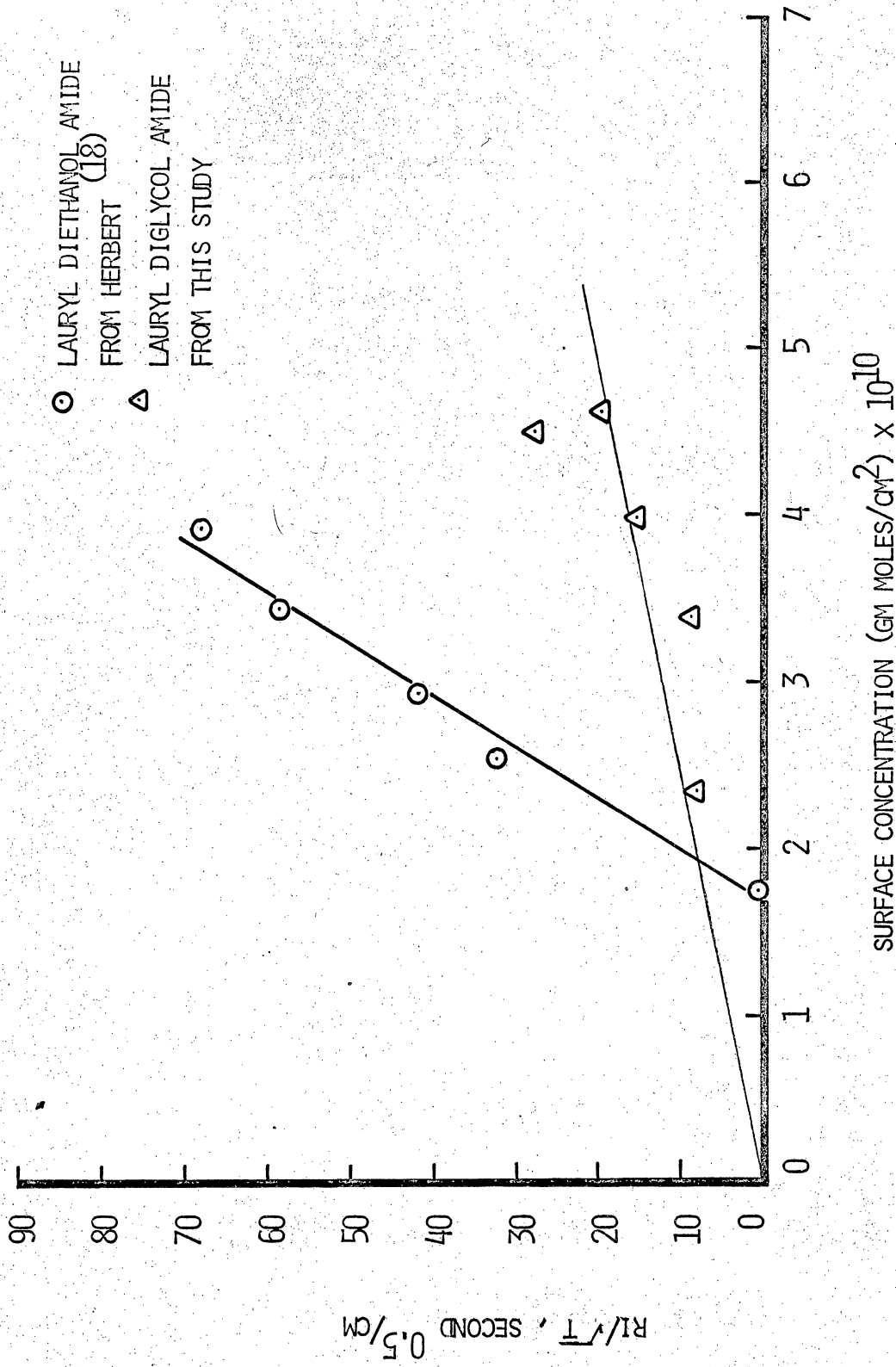


FIGURE 35. INTERFACIAL RESISTANCE VERSUS SURFACE CONCENTRATION:  
COMPARISON OF TWO AMIDES

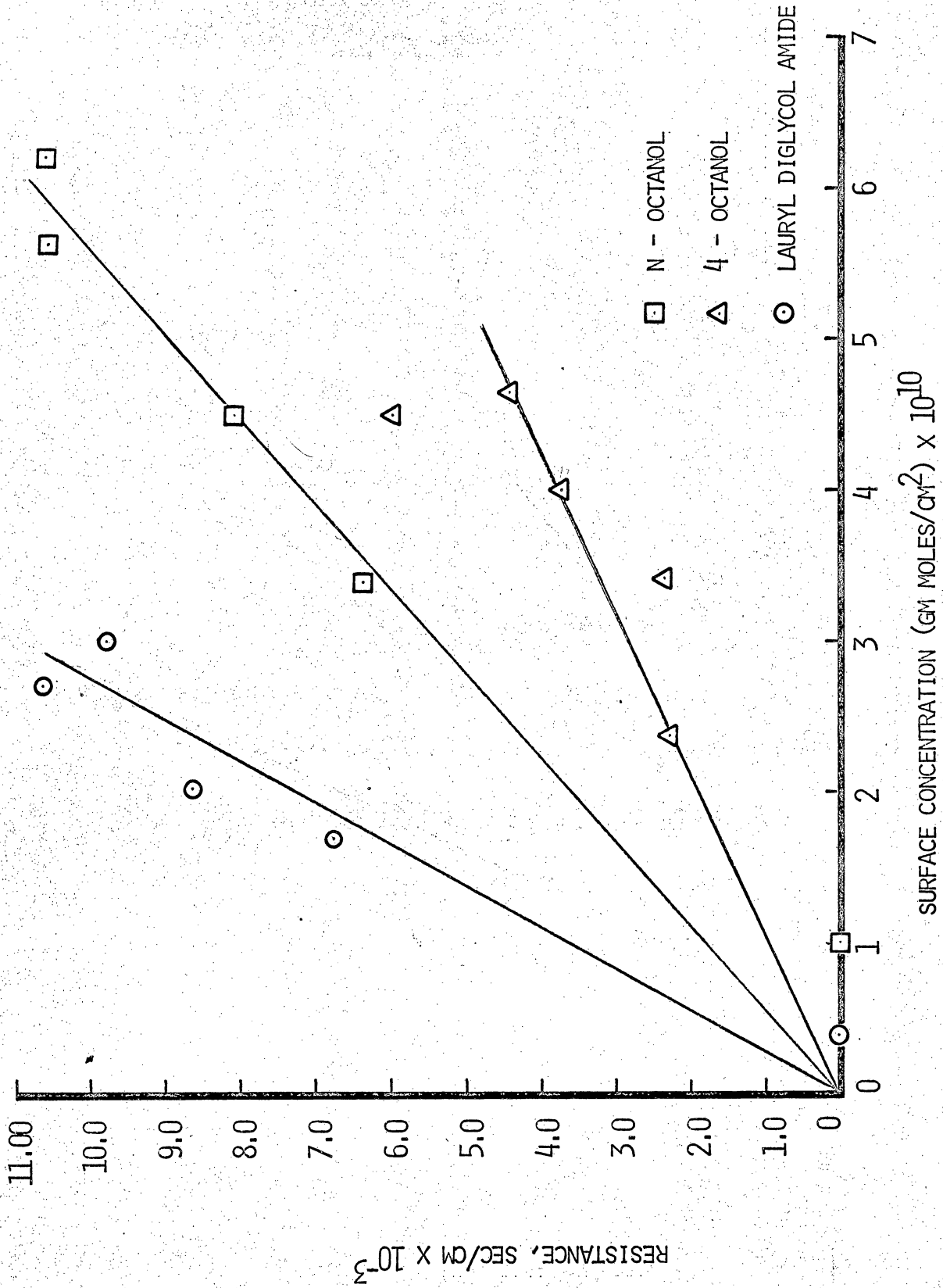


FIGURE 36. INTERFACIAL RESISTANCE VERSUS SURFACE CONCENTRATION USING THE TIME INDEPENDENT MODEL

#### IV. DISCUSSION

In this section, the literature, apparatus, procedure and the results obtained during this investigation are analyzed and criticized. Recommendations for future work are also included.

##### Discussion of Previous Work

The results of previous investigations are compared and evaluated in this section.

Diffusion Coefficient of Carbon Dioxide. Himmelblau<sup>(23)</sup> and McCutchen<sup>(25)</sup> have summarized the experimental diffusivities of carbon dioxide in water. The range was from  $1.74$  to  $2.00 \times 10^{-5}$  square centimeters per second. With the exception of two earlier reported values,  $1.74 \times 10^{-5}$  by Tamman and Jessen in 1929, and  $1.82 \times 10^{-5}$  by Ringbom in 1938, they were all within the range of  $1.85$  to  $2.00 \times 10^{-5}$  square centimeters per second. The difference in the earlier values was probably due to the less reliable experimental techniques available to the earlier workers. Therefore, the latter range was regarded as the acceptable range in this investigation.

From examining the published values, two characteristics were seen. One was that a variety of techniques were used; laminar jets were used by a large number of recent workers, but only a few investigators have used quiescent systems. The other was that nothing was

said about the range of values obtained and whether the reported value was an average or not.

Previous Work Done with the Same Equipment. McCutchen<sup>(29)</sup>

determined the diffusion coefficient of carbon dioxide in water at 25°C with the carbon dioxide at a specific initial concentration using the same equipment as this investigation. He found a range of 1.66 to  $2.11 \times 10^{-5}$  square centimeters per second. With the same equipment, Herbert<sup>(19)</sup> found a range of 1.92 to  $2.07 \times 10^{-5}$  square centimeters per second. From the results of these two reports, a range can be expected with this equipment for all runs.

From examining the gas uptake graphs of McCutchen<sup>(29)</sup>, sudden jumps of discontinuities in absorption rate curves can usually be seen. Also, the initial points scatter about a straight line while the second half of the data stay quite linear. Herbert<sup>(18)</sup> only plotted the initial linear portion. However, the critical factor in the work of McCutchen and Herbert was determining the point in which the latter half of the data broke from the initial linear portion. The number of points used affects the value of the diffusion coefficient.

Herbert<sup>(18)</sup> studied the interfacial resistance of sodium lauryl sulfate, sodium dodecylbenzene sulfonate and lauryl diethanol amide. Lauryl diethanol amide is similar in structure to lauryl diglycol amide used in this investigation, except for two hydroxyl groups. Therefore the interfacial resistance results of lauryl diethanol amide can be compared with the lauryl diglycol amide results of this investigation.

### Discussion of Procedure

The following section is an evaluation of the experimental equipment and technique.

Stability of the System. Any disturbance of the solution in the absorption cell upsets the quiescent nature of the system which was the basic assumption in this investigation. In order to avoid this, the apparatus was firmly mounted on aluminum rods and the agitators were turned off during the gas absorption data taking period. Resting the plexiglass board on the bottom also helped to prevent the apparatus from vibrating. However, the occasional vibration of the building affecting the system raised some questions.

Manometer Characteristics. In calibrating the absorption apparatus, McCutchen<sup>(28)</sup> found that the cross sectional area of manometer E (Figure 4) was different for the two arms; the right arm had a value of 0.0151 square centimeters, and the left had a value of 0.0156 square centimeters. The fluid in the right arm was observed to be about one millimeter higher than the left side as read by markings on the glass. It was suspected to be due solely to capillary action. Upon later examination using a cathetometer, the marking of the scale on the two legs were not level, causing the right side to appear higher than the left.

Meriam D-3166 was used as the manometer fluid. It was found to be a suitable fluid because it can withstand high vacuum and no degassing

was observed throughout the investigation. However, the fluid was found to be quite temperature sensitive. The density of meriam D-3166 was found to be 1.043 at 25°C and 1.047 at 20°C. As the fluid was quite viscous, it was found that some of the fluid stuck to the wall and it took a few minutes for all of it to flow down. Therefore, it was necessary to wait a few minutes before it was used again for the absorption test.

Vacuum Stopcocks. The absorption apparatus was fitted with high vacuum stopcocks which were matched. Numbers were marked on both parts of the stopcock. Occasionally when the stopcock became stiff, it was necessary to clean the stopcocks and regrease so they would be easier to turn.

Cleanliness of Absorption Cell. The cleanliness of the absorption cell was very important. If the cell were dirty, water droplets would stick to the cell wall and the meniscus of water with the wall was not regular. These effects would increase the interfacial area used in the calculation.

Many precautions were taken to avoid any impurities from entering the cell. The cell was cleaned with glass cleaning solution, rinsed with water and then acetone. Compressed air in laboratory was used to evaporate the acetone. The compressed air used to remove acetone vapor was suspected to be a major cause of impurities in the cell. Therefore, other means of drying or using air filter should be considered. The mercury used was cleaned by a physical chemistry

technique<sup>(34)</sup>, filtering through a filter paper with a pin hole. The scum left behind was collected for later purification. This technique was sufficient for this study as there was no opportunity for the mercury to amalgamate with metals.

Constant Temperature Arrangement. The temperature of the room did not stay at 25°C constantly. During hot summer days, the temperature was usually about  $25.5 \pm 0.5^\circ\text{C}$ .

The temperature of the water bath was relatively constant with a deviation of not more than  $\pm 0.1^\circ\text{C}$ . However, on hot days, the temperature of the cooling water went as high as  $24.6^\circ\text{C}$ . The cooling water was turned off during an absorption test. Otherwise the cooling water could cause an unequal distribution of temperature after the agitators were turned off.

Surface Tension Measurement. To insure accuracy of the surface tension measurements using the Fisher interfacial tensiometer, the platinum ring was cleaned by rinsing in benzene and again in acetone in place of methyl ethyl ketone which was not available. The ring was then heated in the oxidizing portion of a gas flame.

The Fisher tensiometer was calibrated with deionized water at 25°C to a surface tension of 71.9 dynes per centimeter (apparent surface tension was 76.9).

Presaturation of Samples with Carbon Dioxide. The water of surfactant solutions were placed in a side-arm flask. The flask was evacuated and refilled with carbon dioxide three times. Evacuations

were carried out to 700 millimeters of mercury to insure sufficient removal of air in the flask, and the sample was allowed to degas so that any previously dissolved gas would be desorbed.

McCutchen<sup>(27)</sup> and Herbert<sup>(17)</sup> presaturated the samples with carbon dioxide to the saturation pressure of the absorption test. They suggested that very little desorption occurred while transferring the solutions to the absorption cell. This conclusion was based on tests of exposing the presaturated solutions to the atmosphere for ten minutes. However, it was found that carbon dioxide desorbed while evacuating the air from the absorption apparatus. Based on five tests, the extent to which the samples were presaturated had little bearing on the final results. Yet, it was preferable to presaturate the samples to a pressure higher than the saturation pressure so that a larger amount of carbon dioxide would be retained in the solution after evacuation in the absorption cell had taken place. The samples were then resaturated to establish an initial concentration in the sample solution.

#### Preparation of the Absorption Apparatus for an Absorption Tests.

In evacuating the absorption apparatus, the vacuum pressure should not be drawn over 500 millimeters of mercury to avoid excessive desorbing of carbon dioxide from the solution, making the pre-saturation step useless.

The value for the operating pressure was not important in the experimental determination of the diffusion coefficient for the pure carbon dioxide-water system. As for the tests with surfactant solutions,



the slope of gas uptake plot versus the square root of time would have to be corrected for different step pressure increase before interfacial resistance could be calculated. Therefore, the operating pressure was left at pressure around 700 millimeters of mercury.

After allowing carbon dioxide to refill the system to be operating pressure, the time taken to turn the valves 4 and 5 off was quite critical. The reason is that if the timer was not started immediately, the concentration of the sample at time zero would not correspond to the recorded initial concentration which is the saturation pressure. According to Blank and Rougton<sup>(2)</sup>, six seconds was necessary for the pressure to settle down to a steady level. Yet if the valves were not closed and timer turned on fast enough, the readings obtained would be undesirable, i. e. absorption had taken place before the timer was started.

### Discussion of Results

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

Diffusion Coefficient Results. Referring to Table I, the values obtained for the diffusion coefficient of the pure carbon dioxide-water system ranged from 1.89 to  $1.98 \times 10^{-5}$  square centimeters per second. All of these values fell between 1.85 to  $2.00 \times 10^{-5}$ , the acceptable range for this investigation. The average of the values determined from Tests 1 to 11 was  $1.93 \times 10^{-5}$  square centimeters per second with a reproducibility of  $\pm 0.05 \times 10^{-5}$ .

All tests were taken under almost the same saturation pressure and operating pressure, around 500 millimeters and 700 millimeters of mercury respectively. Tests 1 to 4 were taken under the same conditions except the difference in presaturation pressure. The results showed that the presaturation pressure had little bearing on the diffusion coefficient.

Attempts were made to improve the precision of the measurements in the tests. The manometer change for tests 1 to 6 was recorded in intervals of 15 seconds while the others were recorded in intervals of 30 seconds. No significant difference was observed. From Tests 7 to 11, the change was recorded with a cathetometer. The advantages will be discussed in a later subsection. Even though the tests all gave diffusion coefficients within the acceptable range, the improvement in precision using the cathetometer did narrow down the range. However, no conclusion can be drawn unless more tests were taken using the cathetometer or other recording instrument with high precision.

About ten gas absorption tests were taken without turning off the agitators in the water bath, not being aware that they would disturb the quiescent nature of the system. The diffusion coefficient value of these results were found to be much higher than the acceptable range. Also there was no range to which they were distributed, showing that the results obtained were useless and were not recorded in this thesis.

Equilibrium Surface Tension Results. The surface tension for each surfactant at each concentration was the average of three samples. Many troubles were encountered in getting satisfactory surface tension

data, especially with the octanols. It was found the surface tension data obtained for samples from the same solution could differ as much as three dynes per centimeter. Even the surface tension for the same sample could be different at different time. Any set of samples having values close to each other was considered as acceptable, i.e. within one dyne per centimeter of each other. Any set of samples that had wider distribution of values was discarded and the surface tension was measured again with new samples.

There were many factors that could have contributed to the deviation. First was the time taken to achieve the equilibrium state. It was not known how long was required and also whether the equilibrium state was disturbed when the sample was transferred and the ring dropped into the sample solution. Second was the effect of evaporation. Condensation was sometimes observed on the petri dish cover. The amount evaporated might either reduce or increase the concentration of the surfactant solution. Third was the effect of temperature variation in the room. The temperature variation could cause condensation on the petri dish cover and could also change the surface tension as a function of temperature.

No critical micelle concentration was observed for the aqueous solution of the three surfactants. Probably, the surfactants were not soluble enough to get to the critical micelle concentration and they were all non-ionic. It should be noted that some non-ionic surfactants have critical micelle concentration and others do not.

Examining Figures 16 and 17, the surface tension of 4-octanol was lower than n-octanol at the same surface concentration, suggesting that the branched structure reduces surface tension more than a linear structure.

A program was used to fit the surface tension data to a polynomial equation. The program was modified to punch the values of surface tension and natural logarithm of the bulk concentration in gm moles/cm<sup>3</sup> on computer cards besides on the printed output. Using the previous polynomial equation, another program was developed to calculate the surface concentration from Gibbs' adsorption equation. These results are shown in Figures 16 to 18.

Structure of the Surfactants. The molecular formula of n-octanol is  $\text{CH}_3(\text{CH}_2)_7\text{OH}$  and that of 4-octanol is  $\text{CH}_3(\text{CH}_2)_2\text{CHOH}(\text{CH}_2)_3\text{CH}_3$ . The molecular weights used in this investigation for both isomers were 130 grams per mole. The molecular formula of lauryl diglycol amide was considered to be  $\text{CH}_3(\text{CH}_2)_{11}\text{CON}(\text{CHOHCH}_2\text{OH})_2$ . The molecular weight used was 333 grams per mole.

Effect of Condensation. When the apparatus was filled with carbon dioxide after evacuating the air, condensation of water vapor on the cell wall was observed on the side and top of the cell. The condensation increased the actual surface area involved in gas absorption. This would probably be one of the contributions to the deviation in results taken at the same operating conditions. The amount of vapor condensed was observed to decrease with small step changes in pressure. However, it was noted that most of the condensation disappeared after the equilibrium period before the absorption test.

Temperature Effects. According to Blank and Rougton<sup>(2)</sup>, the temperature increased by 1°C during their absorption tests. The appearance of condensation in the cell would be an indication of temperature change as a result of pressure increase in the system. There was some concern over the unequal increase in temperature on the two sides of the apparatus due to the difference in diameter in the glass tubes leading to the dummy cell and the absorption cell.

Convection Currents. It has been assumed by many workers that no convection occurs in the initial range. On examining the gas uptake curve, the initial portion was quite linear, thus suggesting that the assumption of no convection in this range is valid. However, the initial portion was not exactly linear even for tests using the cathetometer. It can be seen from the computer output (Figure 38) that an extra point usually cause a slight increase in slope. This may be caused by some minute convection currents or some other effects that were not accounted for.

Gas Absorption Results. The gas uptake curves for the absorption of carbon dioxide in the aqueous surfactant solutions are shown in Figures 19 to 33. As in the case with pure water, the upper boundary of the initial linear region was determined by the location of the point from which the slope changed. It was found that the second part of the curve stayed quite linear with very little scatter in the data points. Therefore it was easier to locate lower boundary of this line. The points below this point were used to calculate the slope of the initial linear region by a least squares fit.

It was found that the slope of the initial linear portion increased moderately as an extra point was taken into consideration. The number of points considered was crucial to the value of the slope. The interpretation of the plot depends on the method used to find the break point. This is especially true when the data points scatter.

In some of the plots, such as Figure 23, the first point scattered quite badly from the line. To avoid misleading results, the first point was used in the least square fit. The reason might be the delay in turning valves 4 and 5 off and starting the timer when the absorption test started.

The original computer program was developed with a gas volume space of 136.25 cubic centimeters and a manometer fluid density of 1.043 grams per cubic centimeter. These values should be adjusted if the volume of mercury substrate and solute changes, and if the manometer fluid is changed.

Use of the Cathetometer. In an effort to increase precision of the measurements, a cathetometer was used to measure the height changes in the manometer. Tests 7 to 11 for water and tests for lauryl diglycol amide were measured with a cathetometer. The tests with lauryl diglycol amide without using the cathetometer were not used in this investigation. However, the data were recorded in the laboratory notebook.

By comparing the gas absorption plots, many advantages could be seen with the increased precision. All the points fit quite well to two straight lines, the initial linear portion and the latter portion.

Therefore, there was no trouble in locating the break point which was the intersection of the two straight lines. Also, the first point was always on the line and so would not affect the slope to a misleading value.

Interfacial Resistance. The slope of the initial linear portion of the uptake versus square root of time curves for each test with surfactants was used to calculate interfacial resistances using equation (40). Negative values for interfacial resistance was impossible so a zero resistance was used which was the lowest possible interfacial resistance. The values tabulated should be considered as a point in a range rather than an exact value. As discussed earlier, the tests with pure water system showed a range in the diffusion coefficient which is equivalent to a difference of  $0.02 \times 10^{-3} \text{ sec}^{\frac{1}{2}}/\text{cm}$  in the slope. This difference in the slope could cause a difference to as much as  $15 \text{ sec}^{\frac{1}{2}}/\text{cm}$  in the interfacial resistance.

The interfacial resistances were plotted as a function of surface concentration in Figure 34. From this figure, the three surfactants are seen to have different interfacial resistance. At high surface concentrations, 4-octanol has the highest interfacial resistance. However, at lower surface concentrations, they are almost the same. N-octanol and 4-octanol are isomers, similar in having an eight carbon chain and the same molecular weight, but the position of the hydroxyl group is different. Therefore the position of the hydrophilic group affects the interfacial resistance. The branched chain in 4-octanol may be the cause for the greater resistance than the straight chain in n-octanol, as explained by the sieve effect.

Lauryl diglycol amide has the lowest interfacial resistance in comparison with the two octanols, even though it has the highest molecular weight and a longer carbon chain. The reason may be due to the space orientation of the molecule and the size of hydrophilic group. The whole portion of amide other than the hydrophobic chain could be considered as the hydrophilic group containing four hydroxyl groups.

The results for lauryl diglycol amide were also compared the results of Herbert<sup>(18)</sup> for lauryl diethanol amide, in Figure 35. Lauryl diethanol amide caused a higher interfacial resistance with increasing surface concentration. The structure of the two compounds are similar in that the hydrophobic portions are the same. Yet lauryl diglycol amide has two extra hydroxyl groups and a higher molecular weight for the hydrophilic portion. It suggest that larger hydrophilic groups and a higher molecular weight for the hydrophilic portion. It suggest that larger hydrophilic groups cause less interfacial resistance, but more research is needed to drawn definite conclusions. Also, the lower interfacial resistance may be caused by the extra hydroxyl groups. It may also suggest that the higher the number of hydroxyl groups in the hydrophilic portion of surfactant, the lower the interfacial resistance. The same deduction may also be applied to other hydrophilic function groups, such as carboxyl groups.

Interfacial Resistance Using A New Model. According to the original model, the interfacial resistance for surfactant solution was a function of the square root of time, the same as for pure water system.



It was suspected that an interfacial resistance not as a function of time may better describe the gas absorption into surfactant solutions. Under the assumption that gas absorption rate was a function of time, a new model was developed.

A computer program was used to calculate the interfacial resistance and the gas absorption rates and then fitted to a first order algebraic equation. The average values of the interfacial resistance at different concentrations were plotted as a function of surface concentration as shown in Figure 36. Comparing with Figure 34, the two graphs showed the same correlation except in the magnitude of the interfacial resistance which is in a different unit. Therefore the new model serves the same purpose in finding correlation of the interfacial resistance with surface concentration.

#### Recommendations

The following recommendations are made for future study of the effects of surfactants on gas absorption with special concern for the quiescent absorption apparatus used in this investigation.

Operating Conditions. Further gas absorption tests using this apparatus should be made at a smaller step increase in pressure. This would lower the effect of condensation on the cell wall. Also, it would be advantageous to conduct research on the effect of temperature and pressure changes on the performance of this apparatus.

Design of Apparatus. The two sides of the apparatus should be identical geometrically, including the cell, glass pipings and places of valves. This would avoid the complication of unfavorable effects arising from different flow conditions and other unexpected factors.

A cell which can be opened and sealed like that of a desiccator should be constructed. This special form would allow the cell to be cleaned and dried easier and simpler. In addition to that, the sample solution could be introduced faster with better accuracy using a pipette.

Transfer of System. The manual transfer of the apparatus into the water bath usually would move the meniscus of the cell and may even leave solution droplets on the cell wall. Using a mechanical device to transfer the apparatus would maintain the system vertical.

Short Contact Time. Nothing is known about the characteristics of gas absorption in the initial 30 second region. After successful development of high precision data taking technique, a study in the gas absorption in short time would be rewarding.

Data Taking. An examination of the data for surfactant solutions of different concentration are very close together. Sometimes, it was hard to see any difference. Higher precision in measurement is necessary to improve it. It is recommended that an electronic sensor technique with a plotter be used to measure the pressure changes.

Plotting Gas Uptake Graphs. It was noted that the gas uptake versus square root of time plots do not intersect at the origin. It is recommended that the point at which the gas uptake line intersects the square root of time axis be taken as the origin. This would enable more uniform correlations.

Surface Tension. The values of equilibrium surface tension changes the value of surface concentration. Therefore, investigation should be carried out to measure the equilibrium surface tension accurately.

Surfactant Hydrophilic Functional Groups. 2-Octanol and 3-octanol should be studied to see the way other positions of hydrophilic group affect interfacial resistance. Then, other hydrophilic functional groups may be studied to confirm the conclusion.

Also of interest is the density of packing and composition of the hydrophilic head group. More investigation in this area would show whether they lower the interfacial resistance or not.

## V. CONCLUSIONS

The investigation of the effect of the position of surfactant hydrophilic function group on the rate of absorption of carbon dioxide in water led to the following conclusions:

1. Using the unsteady-state absorption apparatus, the diffusion coefficient for the carbon dioxide-water system at 25°C was found to be  $1.93 \pm 0.05 \times 10^{-5}$  square centimeters per second.
2. The higher the surface concentration of octanols, the higher the interfacial resistance to gas absorption.
3. The location of hydroxyl group at different positions on the hydrophobic chain cause different magnitude of interfacial resistance, with location of hydroxyl group at branched position causing a higher resistance than at end of hydrophobic chain.
4. The molecular weight of hydrophilic functional group cause different magnitude of interfacial resistance, with higher molecular weight causing a lower resistance.

## VI. SUMMARY

The purpose of this investigation was to determine the effect of the position and the molecular weight of hydrophilic group on the rate of gas absorption.

A quiescent-state absorption apparatus was used with carbon dioxide and water as the absorption system. Three surfactants with hydroxyl groups were selected for study, namely, n-octanol, 4-octanol and lauryl diglycol amide.

Preliminary absorption tests were made using pure deionized water to determine the diffusion coefficient for the system. A value of  $1.93 \pm 0.05 \times 10^{-5}$  square centimeters per second was obtained. The absorption tests were repeated with the three surfactant solutions at different concentrations. Then the interfacial resistance for each solution was calculated.

The results of the surfactants were compared with each other and were also compared with the results of lauryl diethanol amide previously investigated. The octanol with hydroxyl group at a branched position was found to cause a higher interfacial resistance than those with hydroxyl groups at the end of the hydrophobic chain. It was also concluded that increasing the molecular weight of the hydrophilic group decreased the interfacial resistance.

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## IX. APPENDIX

The following sections contain the data tables, derivation of equations, sample calculations and other information less important than that presented in the Experimental section.

### Data Tables

The following section includes all the data used in this investigation.

Calibration Data. The data obtained by McCutchen<sup>(28)</sup> for the physical constants of the quiescent apparatus are given in Table IV.

Manometer Readings. The manometer readings for the absorption tests are given as a function of time. For the tests that were measured with a cathetometer, only the cathetometer readings for the right arm are tabulated. Tables VI to XVI give the manometer readings for the absorption of carbon dioxide in deionized water (Tests 1 to 11). Tables XVII to XXXI give the manometer readings for the absorption of carbon dioxide in the aqueous surfactant solutions. In each tests, meriam D-3166 was used as the manometer fluid.

It should be noted that the tables given do not include all the tests taken. These include duplicated tests for deionized water, N-octanol solution and lauryl diglycol amide solutions. They were recorded in the laboratory notebook.

TABLE V

Data and Calibration Constants for the Absorption Apparatus

Apparatus Section	Weight of Mercury to fill Section gm	Volume of Section cm <sup>3</sup>	Area cm <sup>2</sup>	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

McCutchen, B. J.: The Determination of Diffusion Coefficients for Carbon Dioxide and Oxygen in Water Using a Quiescent Liquid Absorption Apparatus, p. 36, M.S. Thesis, Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia (1969).

TABLE VI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN WATER AT 690.00 MM MERCURY\*  
TEST NUMBER 1

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	14.70	14.70
15	15.00	14.60
30	15.10	14.50
45	15.30	14.30
60	15.40	14.20
75	15.50	14.20
90	15.60	14.10
105	15.70	14.00
120	15.70	13.90
135	15.80	13.90
150	15.90	13.80
165	16.00	13.70
180	16.10	13.60
195	16.10	13.50
210	16.20	13.50
225	16.30	13.40
240	16.40	13.30
255	16.50	13.30
270	16.50	13.20
285	16.60	13.10
300	16.70	13.00
315	16.80	13.00
330	16.90	12.90
345	16.90	12.80
360	17.00	12.70
375	17.10	12.70
390	17.20	12.60
405	17.30	12.50
420	17.30	12.50
435	17.40	12.40
450	17.50	12.30
465	17.50	12.30
480	17.60	12.20
495	17.70	12.20
510	17.70	12.10
525	17.80	12.10
540	17.85	12.00

\*ATMOSPHERIC PRESSURE 711.50 MM MERCURY

SATURATION PRESSURE 498.50 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE VII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN WATER AT 700.00 MM MERCURY\*  
TEST NUMBER 2

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	15.00	15.00
15	15.10	14.80
30	15.20	14.60
45	15.40	14.50
60	15.50	14.40
75	15.60	14.30
90	15.70	14.20
105	15.80	14.10
120	15.90	14.00
135	16.00	13.90
150	16.00	13.80
165	16.10	13.80
180	16.20	13.70
195	16.30	13.60
210	16.30	13.60
225	16.40	13.50
240	16.50	13.40
255	16.60	13.30
270	16.70	13.30
285	16.70	13.20
300	16.80	13.10
315	16.90	13.00
330	16.90	12.90
345	17.00	12.90
360	17.00	12.80
375	17.10	12.70
390	17.20	12.60
405	17.30	12.60
420	17.40	12.50
435	17.40	12.40
450	17.50	12.40
465	17.50	12.30
480	17.60	12.30
495	17.70	12.20
510	17.70	12.10
525	17.80	12.10
540	17.80	12.00

\*ATMOSPHERIC PRESSURE 714.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE VIII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN WATER AT 699.00 MM MERCURY\*  
TEST NUMBER 3

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	14.90	14.90
15	15.00	14.80
30	15.20	14.70
45	15.30	14.50
60	15.40	14.40
75	15.50	14.30
90	15.60	14.30
105	15.70	14.20
120	15.80	14.10
135	15.80	14.00
150	15.90	14.00
165	16.00	13.90
180	16.10	13.80
195	16.10	13.70
210	16.20	13.60
225	16.40	13.60
240	16.50	13.50
255	16.50	13.40
270	16.60	13.40
285	16.70	13.30
300	16.80	13.20
315	16.80	13.10
330	16.90	13.00
345	17.00	12.90
360	17.10	12.90
375	17.20	12.80
390	17.30	12.70
405	17.30	12.60
420	17.40	12.50
435	17.50	12.50
450	17.50	12.40
465	17.60	12.40
480	17.70	12.30
495	17.70	12.20
510	17.80	12.20
525	17.80	12.10
540	17.90	12.00

\*ATMOSPHERIC PRESSURE 714.00 MM MERCURY

SATURATION PRESSURE 498.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE IX

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN WATER AT 700.00 MM MERCURY\*  
TEST NUMBER 4

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	14.90	14.90
15	15.10	14.70
30	15.30	14.50
45	15.50	14.40
60	15.60	14.30
75	15.70	14.20
90	15.80	14.00
105	15.90	13.90
120	16.00	13.90
135	16.10	13.80
150	16.10	13.70
165	16.20	13.70
180	16.30	13.60
195	16.30	13.50
210	16.40	13.50
225	16.50	13.40
240	16.60	13.30
255	16.60	13.30
270	16.70	13.20
285	16.80	13.10
300	16.80	13.00
315	16.90	13.00
330	17.00	12.90
345	17.00	12.80
360	17.10	12.80
375	17.20	12.70
390	17.30	12.60
405	17.30	12.60
420	17.40	12.50
435	17.40	12.40
450	17.50	12.40
465	17.60	12.30
480	17.70	12.30
495	17.70	12.20
510	17.80	12.20
525	17.80	12.10
540	17.90	12.10

\*ATMOSPHERIC PRESSURE 712.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE X

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN WATER AT 702.00 MM MERCURY\*  
TEST NUMBER 5

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	14.70	14.80
15	15.10	14.50
30	15.20	14.40
45	15.30	14.30
60	15.50	14.20
75	15.60	14.10
90	15.70	14.00
105	15.80	13.90
120	15.80	13.80
135	15.90	13.80
150	16.00	13.70
165	16.10	13.60
180	16.10	13.50
195	16.30	13.50
210	16.40	13.40
225	16.40	13.10
240	16.50	13.30
255	16.60	13.20
270	16.70	13.10
285	16.70	13.00
300	16.80	12.90
315	16.90	12.80
330	17.00	12.80
345	17.10	12.70
360	17.10	12.60
375	17.20	12.50
390	17.30	12.50
405	17.30	12.40
420	17.40	12.30
435	17.50	12.30
450	17.60	12.20
465	17.60	12.10
480	17.70	12.10
495	17.80	12.00
510	17.80	11.90
525	17.00	11.90
540	17.90	11.80

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C



TABLE XI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN WATER AT 704.00 MM MERCURY\*  
TEST NUMBER 6

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	15.00	15.00
15	15.00	14.90
30	15.20	14.80
45	15.30	14.70
60	15.40	14.60
75	15.50	14.50
90	15.60	14.40
105	15.60	14.30
120	15.70	14.20
135	15.80	14.20
150	15.90	14.10
165	16.00	14.00
180	16.00	13.90
195	16.10	13.80
210	16.20	13.80
225	16.20	13.70
240	16.30	13.60
255	16.40	13.50
270	16.50	13.40
285	16.60	13.40
300	16.60	13.30
315	16.70	13.20
330	16.80	13.10
345	16.90	13.10
360	17.00	13.00
375	17.00	12.90
390	17.10	12.80
405	17.20	12.70
420	17.30	12.70
435	17.30	12.60
450	17.40	12.50
465	17.50	12.50
480	17.50	12.40
495	17.60	12.40
510	17.70	12.30
525	17.80	12.30
540	17.80	12.20

\*ATMOSPHERIC PRESSURE 707.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
 IN WATER AT 703.00 MM MERCURY\*  
 TEST NUMBER 7

TIME SEC	CATHETOMETER READING CM FLUID**
0	13.88
30	13.69
60	13.35
90	13.14
120	12.97
150	12.80
180	12.63
210	12.47
240	12.30
270	12.15
300	12.00
330	11.85
360	11.68
390	11.53

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XIII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN WATER AT 700.00 MM MERCURY\*  
TEST NUMBER 8

TIME SEC	CATHETOMETER READING CM FLUID**
0	13.69
30	13.47
60	13.25
90	13.07
120	12.90
150	12.75
180	12.58
210	12.43
240	12.28
270	12.13
300	11.97
330	11.82
360	11.69
390	11.51

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY  
SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XIV

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN WATER AT 700.00 MM MERCURY\*  
TEST NUMBER 9

TIME SEC	CATHETOMETER READING CM FLUID**
0	13.70
30	13.46
60	13.19
90	13.01
120	12.83
150	12.72
180	12.54
210	12.40
240	12.26
270	12.12
300	11.96
330	11.79
360	11.64
390	11.49

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY  
SATURATION PRESSURE 500.00 MM MERCURY  
\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XV

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN WATER AT 701.00 MM MERCURY\*  
TEST NUMBER 10

TIME SEC	CATHETERMETER READING CM FLUID**
0	13.71
30	13.50
60	13.24
90	13.06
120	12.89
150	12.73
180	12.58
210	12.44
240	12.28
270	12.16
300	12.00
330	11.84
360	11.68
390	11.51
420	11.39

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XVI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
 IN WATER AT 700.00 MM MERCURY\*  
 TEST NUMBER 11

TIME SEC	CATHETOMETER READING CM FLUID**
0	13.75
30	13.44
60	13.21
90	12.99
120	12.82
150	12.68
180	12.54
210	12.37
240	12.23
270	12.07
300	11.93
330	11.78
360	11.63
390	11.47
420	11.33

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XVII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN A 300 PPM N-OCTANOL SOLUTION  
AT 700.0 MM MERCURY\*

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	15.00	15.00
30	15.30	14.70
60	15.50	14.50
90	15.70	14.40
120	15.90	14.30
150	16.00	14.10
180	16.20	14.00
210	16.30	13.80
240	16.50	13.70
270	16.60	13.50
300	16.80	13.30
330	17.00	13.20
360	17.10	13.00

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM O-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XVIII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN A 200 PPM N-OCTANOL SOLUTION  
AT 700.0 MM MERCURY\*

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	14.90	15.00
30	15.30	14.70
60	15.50	14.50
90	15.70	14.40
120	15.80	14.20
150	16.00	14.10
180	16.10	13.90
210	16.30	14.80
240	16.40	13.60
270	16.60	13.40
300	16.80	13.30
330	17.00	13.10
360	17.10	12.90

\*ATMOSPHERIC PRESSURE 713.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C



TABLE XIX

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN A 100 PPM N-OCTANOL SOLUTION  
AT 700.0 MM MERCURY\*

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	14.90	15.00
30	15.20	14.70
60	15.40	14.50
90	15.60	14.30
120	15.80	14.10
150	15.90	14.00
180	16.10	13.80
210	16.30	13.70
240	16.40	13.50
270	16.60	13.40
300	16.70	13.20
330	16.90	13.10
360	17.00	12.90

\*ATMOSPHERIC PRESSURE 713.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XX

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN A 50 PPM N-OCTANOL SOLUTION  
AT 700.0 MM MERCURY\*

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	14.90	15.00
30	15.20	14.70
60	15.40	14.60
90	15.60	14.40
120	15.80	14.30
150	15.90	14.10
180	16.10	14.00
210	16.20	13.80
240	16.40	13.70
270	16.50	13.50
300	16.70	13.40
330	16.90	13.20
360	17.00	13.00

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XXI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
 IN A 10 PPM N-OCTANOL SOLUTION  
 AT 700.0 MM MERCURY\*

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	14.90	15.00
30	15.20	14.60
60	15.50	14.50
90	15.70	14.30
120	15.80	14.10
150	16.00	14.00
180	16.20	13.80
210	16.40	13.70
240	16.50	13.50
270	16.60	13.40
300	16.80	13.20
330	17.00	13.00
360	17.20	12.90

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XXII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN A 300 PPM 4-OCTANOL SOLUTION  
AT 700.0 MM MERCURY\*

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	14.90	15.00
30	15.30	14.70
60	15.50	14.50
90	15.70	14.30
120	15.80	14.10
150	16.00	14.00
180	16.10	13.80
210	16.30	13.70
240	16.50	13.50
270	16.60	13.40
300	16.80	13.20
330	17.00	13.00
360	17.10	12.90

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY  
SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XXIII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
 IN A 200 PPM 4-OCTANOL SOLUTION  
 AT 700.0 MM MERCURY\*

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	14.90	14.90
30	15.20	14.70
60	15.40	14.55
90	15.60	14.40
120	15.75	14.20
150	15.90	14.10
180	16.10	13.95
210	16.25	13.80
240	16.40	13.65
270	16.60	13.45
300	16.70	13.30
330	16.90	13.15
360	17.10	13.00

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XXIV

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN A 100 PPM 4-OCTANOL SOLUTION  
AT 700.0 MM MERCURY\*

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	15.00	15.00
30	15.25	14.70
60	15.50	14.55
90	15.70	14.40
120	15.80	14.25
150	16.00	14.10
180	16.15	13.95
210	16.30	13.80
240	16.45	13.70
270	16.60	13.50
300	16.75	13.25
330	16.90	13.20
360	17.10	13.05

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY  
SATURATION PRESSURE 500.00 MM MERCURY  
\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XXV

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
 IN A 50 PPM 4-OCTANOL SOLUTION  
 AT 700.0 MM MERCURY\*

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	15.00	15.10
30	15.35	14.75
60	15.60	14.55
90	15.75	14.40
120	15.90	14.25
150	16.10	14.10
180	16.20	13.90
210	16.30	13.80
240	16.50	13.65
270	16.60	13.50
300	16.75	13.40
330	16.90	13.25
360	17.05	13.05

\*ATMOSPHERIC PRESSURE 711.00 MM MERCURY  
 SATURATION PRESSURE 500.00 MM MERCURY  
 \*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XXVI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN A 10 PPM 4-OCTANOL SOLUTION  
AT 700.0 MM MERCURY\*

TIME SEC	LEFT READING CM FLUID**	RIGHT READING CM FLUID**
0	14.95	15.00
30	15.40	14.55
60	15.75	14.25
90	16.00	14.05
120	16.20	13.90
150	16.30	13.70
180	16.45	13.60
210	16.65	13.45
240	16.80	13.30
270	16.90	13.15
300	17.10	13.00
330	17.25	12.85
360	17.40	12.70

\*ATMOSPHERIC PRESSURE 710.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C



TABLE XXVII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
 IN A 30 PPM LAURYL DIGLYCOL AMIDE SOLUTION  
 AT 709.5 MM MERCURY\*

TIME SEC	CATHETOMETER READING CM FLUID**
0	13.70
30	13.48
60	13.25
90	13.03
120	12.83
150	12.69
180	12.53
210	12.41
240	12.21
270	12.04
300	11.87
330	11.69
360	11.52
390	11.33
420	11.18

\*ATMOSPHERIC PRESSURE 711.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XXVIII

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN A 20 PPM LAURYL DIGLYCOL AMIDE SOLUTION  
AT 700.0 MM MERCURY\*

TIME SEC	CATHETOMETER READING CM FLUID**
0	13.55
30	13.33
60	13.09
90	12.90
120	12.75
150	12.59
180	12.46
210	12.29
240	12.15
270	12.00
300	11.86
330	11.68
360	11.51
390	11.35
420	11.18

\*ATMOSPHERIC PRESSURE 711.00 MM MERCURY  
SATURATION PRESSURE 500.00 MM MERCURY  
\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XXIX

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
 IN A 10 PPM LAURYL DIGLYCOL AMIDE SOLUTION  
 AT 715.0 MM MERCURY\*

TIME SEC	CATHETERMETER READING CM FLUID**
0	13.71
30	13.50
60	13.25
90	13.06
120	12.89
150	12.69
180	12.53
210	12.38
240	12.23
270	12.06
300	11.88
330	11.74
360	11.58
390	11.41
420	11.27

\*ATMOSPHERIC PRESSURE 711.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XXX

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
 IN A 5 PPM LAURYL DIGLYCOL AMIDE SOLUTION  
 AT 697.0 MM MERCURY\*

TIME SEC	CATHETOMETER READING CM FLUID**
0	13.69
30	13.52
60	13.23
90	13.06
120	12.87
150	12.74
180	12.59
210	12.45
240	12.30
270	12.15
300	12.02
330	11.87
360	11.74
390	11.60
420	11.45

\*ATMOSPHERIC PRESSURE 711.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

TABLE XXXI

MANOMETER READINGS FOR THE ABSORPTION OF CARBON DIOXIDE  
IN A 1 PPM LAURYL DIGLYCOL AMIDE SOLUTION  
AT 700.0 MM MERCURY\*

TIME SEC	CATHETOMETER READING CM FLUID**
0	13.63
30	13.27
60	13.00
90	12.78
120	12.63
150	12.46
180	12.33
210	12.21
240	12.08
270	11.96
300	11.79
330	11.65
360	11.50
390	11.39
420	11.24

\*ATMOSPHERIC PRESSURE 711.00 MM MERCURY

SATURATION PRESSURE 500.00 MM MERCURY

\*\*MERIAM D-3166, DENSITY 1.043 GM/CC AT 25 DEG C

Derivation of Interfacial Resistance Model.

The time dependent model for interfacial resistance is described in detail by Bussey<sup>(5)</sup> and Herbert<sup>(21)</sup>. Presented here is a development of the time independent interfacial resistance. Although it is similar to the former model, it is in a more generalized form.

Starting with a form of the Fick's Second Law as in equation (1),

$$\partial\phi/\partial t = D \partial^2\phi/\partial x^2 \quad (6)$$

where  $\phi = C - C_0$  (7)

The boundary conditions are:

$$\phi(x, 0) = C(x, 0) - C_0 = 0 \quad (8)$$

$$\phi(\infty, t) = C(\infty, 0) - C_0 = 0 \quad (9)$$

$$\phi(0, t) = \phi_i \quad (10)$$

$$N(0, t) = -D\partial\phi(0, t)/\partial x \quad (11)$$

where  $N$  = gas absorption rate, gm mole/(sec)(cm<sup>2</sup>)

A Laplace transform solution yields

$$C(x, t) = \frac{1}{\sqrt{\pi D}} \int_0^t \frac{1}{\sqrt{t-\tau}} \exp\left[-\frac{x^2}{4D(t-\tau)}\right] N(0, \tau) d\tau \quad (12)$$

at  $t = 0$ ,

$$C(x, 0) = \frac{1}{\sqrt{\pi D}} \int_0^t \frac{1}{\sqrt{t-\tau}} N(0, \tau) d\tau \quad (13)$$

Up to this point, the development is the same as Bussey<sup>(5)</sup>. After this, the following assumption is made:

$$\phi = K + At^B \quad (14)$$

where  $K, A, B$  are parameters.

It should be noted that this is a more generalized form than Bussey<sup>(5)</sup> where  $B = \frac{1}{2}$  and  $K = 0$ . From (14)

$$N(0, t) = \partial \phi / \partial t = ABt^{B-1} \quad (15)$$

Substituting (15) into (13)

$$\phi(0, t) = \frac{AB}{\sqrt{\pi D}} \int_0^t (t - \tau)^{\frac{1}{2}-1} \tau^{B-1} d\tau \quad (16)$$

From MacLaurin series,

$$(t - \tau)^{-\frac{1}{2}} = \frac{1}{t^{0.5}} + \sum_1^{\infty} \frac{(2n-1)(2n-3)(2n-5)\dots(1)}{(2^n)(n!)} (-1)^n \frac{\tau^n}{t^{n+0.5}} \quad (17)$$

Substituting (17) into (16), and integrating yields,

$$\phi(0, t) = \frac{AB}{\sqrt{\pi D}} t^{B-\frac{1}{2}} \left[ \frac{1}{B} + \sum_1^{\infty} \frac{(2n-1)(2n-3)\dots(1)}{2^n(n!)(B+n)} (-1)^n \right] \quad (18)$$

Substituting gamma function for the series and simplifying yields

$$\phi(0, t) = \frac{AB}{\sqrt{\pi D}} t^{B-\frac{1}{2}} \frac{\Gamma(B) \Gamma(\frac{1}{2})}{\Gamma(B + \frac{1}{2})} \quad (19)$$

Equating (19) with (7)

$$C(0, t) = C_o + \frac{AB}{\sqrt{D}} t^{B-\frac{1}{2}} \frac{\Gamma(B)}{\Gamma(B + \frac{1}{2})} \quad (20)$$

The driving force in concentration is

$$\Delta C = C_e - C_i = C_e - C(0, t) \quad (21)$$

where  $C_e$  = equilibrium concentration, gm mole/cm<sup>3</sup>  
 $C_i$  = concentration at interface, gm mole/cm<sup>3</sup>

Substituting (20) into (21),

$$\Delta C = C_e - C_o - \frac{AB}{\sqrt{D}} t^{B-\frac{1}{2}} \frac{\Gamma(B)}{(B + \frac{1}{2})} \quad (22)$$

Expressing the concentration in terms of pressure using Henry's law

$$\Delta C = (PP - Ps) \frac{V_g}{H} - \frac{AB}{\sqrt{D}} t^{B-\frac{1}{2}} \frac{\Gamma(B)}{\Gamma(B + \frac{1}{2})} \quad (23)$$

where  $V_g$  = volume of gas space,  $\text{cm}^3$

PP = operating pressure in system, mm mercury

Ps = saturation pressure in system, mm mercury

H = Henrys' law constant,  $2.245 \times 10^7$  (mm Hg)( $\text{cm}^3$ )/gm mole

The time independent infacial resistance is given by

$$R_i = \frac{\Delta C}{N} \quad (24)$$

where  $R_i$  = interfacial resistance, sec/cm

### Sample Calculations

The following section gives examples of the procedure used to obtain the results from the experimental data.

Calculation of Equilibrium Surface Tension. Readings of the surface tensiometer give apparent surface tension. In order to obtain the true surface tension the following relationship is used

$$S_t = S_a \times F \quad (25)$$

where  $S_t$  = true surface tension, dyne/cm

$S_a$  = apparent surface tension, dyne/cm

F = correction factor



The correction factor <sup>(14)</sup> can be read off from a chart, and is defined in the following form

$$F = 0.7250 + \left( \frac{0.0145S_a}{C_r^2(D-d)} + 0.04534 - \frac{1.679r}{R} \right)^{\frac{1}{2}} \quad (26)$$

where  $C_r$  = circumference of the ring, 6.015 cm

$D$  = density of the lower liquid phase, gm moles/cm<sup>3</sup>

$d$  = density of the upper air phase, gm moles/cm<sup>3</sup>

$r$  = radius of the wire of the ring, 0.01778 cm

$R$  = radius of the ring, 0.9578 cm

From Table II, the average apparent surface tension  $S_a$ , of a 400 ppm aqueous n-octanol solution is 38.3 dynes/cm. Using equation (26) the correction factor is

$$F = 0.725 + \left( \frac{0.0145(38.3)}{6.015^2(1)} + 0.04534 - \frac{1.679 \times 0.01778}{0.9578} \right)^{\frac{1}{2}}$$

$$= 0.8968 \quad (27)$$

$$S_t = 34.5 \text{ dynes/cm} \quad (28)$$

#### Calculation of Equilibrium Surface Concentration. Equilibrium

surface concentration for non-ionic surfactants is calculated from Gibbs' adsorption equation

$$\eta = - \frac{1}{RT} \left( \partial S_t / \partial \ln C_b \right)_T \quad (29)$$

where  $\eta$  = surface concentration, gm moles/cm<sup>2</sup>

$C_b$  = bulk liquid concentration, gm moles/liter

$R$  = gas constant,  $8.314 \times 10^7$  ergs/(gm moles)(°K)

The derivative in this equation is calculated from a polynomial regression equation of the form

$$S_t = A_1 + A_2 \ln C_b + A_3 (\ln C_b)^2 \quad (30)$$

where  $A_1$ ,  $A_2$  and  $A_3$  are constants

Equation (30) is differentiated with respect to  $\ln C$  to obtain

$$\frac{\partial S_t}{\partial \ln C_b} = A_2 + 2 A_3 \ln C_b \quad (31)$$

Using the computer program in Figure 39, the regression coefficients were calculated by fitting the experimental data points to equation (30).

For n-octanol, the polynomial regression obtained is

$$S_t = -126.2336 - 39.00351 \ln C_b - 1.946333(\ln C_b)^2 \quad (32)$$

Equation (31) becomes

$$\frac{\partial S_t}{\partial \ln C_b} = -39.00351 - 2 (1.946333)(\ln C_b) \quad (33)$$

The surface concentration was calculated by substituting the above equation into Gibbs' equation using the computer program in Figure 40.

For a surface tension of 34.27 dynes/cm and  $\ln C_b = -5.7855$

$$\begin{aligned} \eta &= - \frac{- 2(1.946333)(-5.7855) - 39.00351}{(8.314 \times 10^7)(298.16)} \\ &= 3.190208 \times 10^{-10} \text{ gm moles/cm}^2 \end{aligned} \quad (34)$$

Calculation of Diffusion Coefficient. A computer program (Figure 37) was used. The following equations are used in the calculation of gas uptake.

$$\Delta p' = \frac{-A h PP}{(A h + 20 V_g)} \quad (35)$$

$$\Delta p = \Delta p' - h \quad (36)$$

$$X = \frac{273.16}{T p_o} \times \Delta p \times \frac{Ah}{20} \times \frac{PP - p_w + \Delta p}{\Delta p} - V_g \quad (37)$$

where  $h$  = difference in height of the fluid in the manometer arms, mm

$A$  = area of manometer bore,  $\text{cm}^2$

$PP$  = operating pressure in system, mm fluid(meriam D-3166)

$V_g$  = volume of gas space,  $\text{cm}^3$

$\Delta p'$  = pressure change in dummy vessel, mm fluid(meriam D-3166)

$\Delta p$  = pressure change in reaction cell, mm fluid(meriam D-3166)

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

$T$  = temperature of absorption test,  $^{\circ}\text{K}$

$p_w$  = vapor pressure of water, mm fluid(meriam D-3166)

$p_o$  = standard pressure, mm fluid(meriam D-3166)

The operating pressure for all the absorption tests originally expressed in mm mercury must be converted to mm of meriam D-3166 fluid in the calculation in this section. The density of mercury was taken as  $13.534 \text{ gm/cm}^3$  and that of meriam D-3166 was taken as  $1.043 \text{ gm/cm}^3$  at  $25^{\circ}\text{C}$ .

Test number 11 in Table XVI is taken to show the sample calculation. The results are shown in the computer output in Figure 38, listed under appropriate headings. The results are analyzed to locate the break point of the data from the initial linear region. The intercept, slope,

predicted values of gas uptake and the deviation from actual value of uptake are listed for each additional points used. The maximum deviation allowed is  $0.0004 \text{ cm}^3/\text{cm}^2$ . The number of points used in the initial linear region are listed again as the square root of time versus the gas uptake as well as the least square predicted value. The values are plotted in Figure 15 with a few extra points to show the break point.

The diffusion coefficient is calculated from the following equation

$$D = \left[ \frac{(dQ/Ad\sqrt{t}) \times \sqrt{\pi}}{2 (C_e - C_o)} \right]^2 \quad (38)$$

where  $Q$  = amount of gas absorbed, gm moles  
 $A$  = interfacial area,  $\text{cm}^2$   
 $C_e$  = equilibrium concentration of dissolved gas in the bulk liquid phase,  $\text{gm moles}/\text{cm}^3$   
 $C_o$  = initial concentration of dissolved gas in the bulk liquid phase,  $\text{gm moles}/\text{cm}^3$   
 $D$  = diffusion coefficient,  $\text{cm}^2/\text{sec}$   
 $t$  = contact time, sec

In calculating  $C_e$  and  $C_o$ , Henry's law was assumed to be valid over the range of the concentration of carbon dioxide concerned. Expressing in terms of operating pressure and saturation pressure,

$$D = \left[ \frac{(dQ/Ad\sqrt{t}) \times \sqrt{\pi}}{2 (PP - Ps)/H} \right]^2 \quad (39)$$

where  $dQ/Ad\sqrt{t}$  = slope of the gas uptake curve,  $\text{cm}^3/(\text{cm}^2)(\text{sec}^{\frac{1}{2}})$   
 $PP$  = operating pressure, mm Hg  
 $Ps$  = saturation pressure, mm Hg  
 $H$  = Henry's law constant,  $2.245 \times 10^7 \text{ (mm Hg)(cm}^3\text{)}/\text{gm mole}$

From Figure 15,

$$\begin{aligned} PP - P_s &= 700.0 - 500.0 = 200 \text{ mm Hg} \\ \text{slope} &= 0.9827 \times 10^{-3} \text{ cm}^3/(\text{cm}^2)(\text{sec}^{\frac{1}{2}}) \end{aligned}$$

From the computer program output in Figure 38

$$D = 1.905 \times 10^{-5} \text{ cm}^2/\text{sec}$$

Calculation of Interfacial Resistance. The interfacial resistance

to gas uptake caused by a surfactant solution is given by

$$\frac{R_i}{\sqrt{t}} = \frac{1}{k_i \sqrt{t}} = \frac{\sigma_E - \sigma_R}{\sigma_R} \sqrt{\frac{\eta}{D}} \quad (40)$$

where

$R_i$  = interfacial resistance, sec/cm

$k_i$  = interfacial mass transfer coefficient, cm/sec

$\sigma_E$  = slope of gas uptake versus  $\sqrt{t}$  plot for pure carbon dioxide-water system,  $\text{cm}^3/(\text{cm}^2)(\text{sec}^{\frac{1}{2}})$

$\sigma_R$  = slope of gas uptake versus  $\sqrt{t}$  plot for carbon dioxide-surfactant solution system,  $\text{cm}^3/(\text{cm}^2)(\text{sec}^{\frac{1}{2}})$

From all the tests with pure water systems, the average for diffusion coefficient is  $1.934 \times 10^{-5} \text{ cm}^2/\text{sec}$ , with  $\sigma_E = 0.99 \times 10^{-3} \text{ cm}^3/(\text{cm}^2)(\text{sec}^{\frac{1}{2}})$ . From Figure 19,  $\sigma_R = 0.867 \times 10^{-3} \text{ cm}^3/(\text{cm}^2)(\text{sec}^{\frac{1}{2}})$  for the absorption of carbon dioxide into a 300 ppm aqueous n-octanol solution

$$R_i/\sqrt{t} = \left( \frac{0.99 - 0.867}{0.867} \right) \sqrt{\frac{3.1416}{1.934 \times 10^{-5}}} = 57.14 (\text{sec}^{\frac{1}{2}})/\text{cm} \quad (41)$$

Calculation of Time Independent Interfacial Resistance Model.

The gas absorption is a function of time as expressed in equation (15).

At different times, the absorption rate is different, but the parameters

A, B and K are almost the same for a surfactant solution. A computer program (Figure 41) was used to fit the parameters to equation (14), and equations (23) and (24) were used to calculate the interfacial resistance. For 300 ppm n-octanol solutions,

$$N = (0.9144 \times 10^{-3})(0.512)t^{-0.003578 -1} \quad (42)$$

At  $t = 30$  sec

$$N = 0.6861 \times 10^{-4} \text{ gm moles}/(\text{sec})(\text{cm}^2)$$

$$R_i = 1007 \text{ sec/cm}$$

And since seven points were used according to Figure 19,

$$R_i = 1007, 1086, 1103, 1096, 1076, 1048, 1016$$

at  $t = 30, 60, 90, 120, 150, 180, 210$  respectively

The average of these seven points is

$$R_i = 1061.7 \text{ cm/sec}$$

This value is taken as the interfacial resistance for 300 ppm n-octanol solution.

FIGURE 37. COMPUTER PROGRAM FOR CALCULATING  
GAS UPTAKE FROM MANOMETER DATA

```

C   T---TIME IN SECONDS,   N---NUMBER OF EXPERIMENTAL OBSERVATIONS
C   P--ATMOSPHERIC PRESSURE IN MM HG, PC--ATMOSPHERIC PRESSURE IN MM FLUID
C   H IS DIFFERENCE IN THE HEIGHT OF THE MANOMETER LEGS IN MM FLUID
C   PP IS THE SYSTEM OPERATING PRESSURE IN MM HG
C   PE IS THE EVACUATION PRESSURE IN MM HG
C   PEQ IS THE SATURATION PRESSURE IN MM HG
C   TP IS THE SYSTEM OPERATING TEMPERATURE IN DEG. KELVIN
C   VG IS THE VOLUME OF GAS SPACE IN SYSTEM IN CUBIC CM
C   AM IS THE CROSS SECTIONAL AREA OF THE MANOMETER LEGS IN SQUARE CM
C   PPC IS THE OPERATING PRESSURE IN MM FLUID
C   PA IS NORMAL ATMOSPHERIC PRESSURE IN MM FLUID
C   DELP ARE THE DELTA PRESSURE VALUES
C   X IS THE AMOUNT OF GAS ABSORBED IN CUBIC CM
C   XX IS THE AMOUNT OF GAS ABSORBED PER UNIT AREA IN CC PER SQ CM
C   DMAN---DENSITY OF MANOMETER FLUID
COMMON PP,PEQ
DIMENSION H(40),T(40),DELP(40),X(40),TSQT(40),Z(40),HCM(40),XX(40)
K=1
100 READ,P,PP,PE,PEQ
    READ,N
    READ(5,10) (T(I),H(I),I = 1,N)
10  FORMAT (2F10.0,60X)
    TP=298.16
    VPW= 23.756*13.534/1.043
    VG = 136.25
    AM = 0.01535
    DMAN=1.043
    PPC=PP*13.534/DMAN
    PA=760.0*13.534/DMAN
    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)
8  FORMAT (1H1////,58X,'ABSORPTION DATA')
    WRITE (6,20) K,P,PP,PE,PEQ,RP
20  FORMAT(//14X,'TEST NO ',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)
    WRITE (6,13)
13  FORMAT(//13X,15HTIME IN SECONDS,6X,15HSQUARE ROOT T ,4X,15HPRESSU
1RE CHANGE,5X,15HDELTA P VALUES ,5X,15HMT. GAS ABSORB,5X,15HGAS AB
2SORB/SQCM)
    WRITE(6,18)(T(I),TSQT(I),H(I),DELP(I),X(I),XX(I),I=1,N)
18  FORMAT (7X,6E20.7)
    CALL LEASQU (N,TSQT,XX,Z)
    K=K+1
    IF (K .GE. 31) GO TO 15
    GO TO 100
15  STOP
    END

```

308.395



FIGURE 37. (CONTINUED)

```

SUBROUTINE LEASQU (N,X,Y,Z)
DIMENSION X(N),Y(N),Z(N)
DIMENSION AO(30),A1(30)
COMMON PP,PEQ
C AO IS THE INTERCEPT OF THE LEAST SQUARES LINE
C A1 IS THE SLOPE OF THE LEAST SQUARES LINE
C DIFSQ IS THE DIFFUSION COEFFICIENT IN SQ CM PER SEC
WRITE (6,1)
1 FORMAT(////14X,1HK,10X,5HA0(K),15X,5HA1(K),16X,4HYCAL,18X,2HYD)
YSUM = 0.0
XSUM = 0.0
XSQSUM = 0.0
XYSUM = 0.0
DO 100 K=1,N
XSUM = XSUM + X(K)
H(I)=H(I)*(1.0+.151/.156)
YSUM = YSUM + Y(K)
XYSUM = XYSUM + X(K)*Y(K)
XSQSUM = XSQSUM + X(K)**2
C K-- THE NO. OF POINTS USED TO CALCULATE THE SLOPE
C IF THE INTERVAL IS 30 SEC. PUT K-5 INSTEAD OF K-10
IF (K-5) 100,101,101
101 C = K
DENOM = C*XSQSUM - XSUM**2
AO(K) = (YSUM*XSQSUM - XSUM*XYSUM)/DENOM
A1(K) = (C*XYSUM - YSUM*XSUM)/DENOM
YCAL = AO(K)+A1(K)*X(K)
YD= Y(K)-YCAL
WRITE (6,201) K,AO(K),A1(K),YCAL,YD
201 FORMAT (9X,16,4E20.8)
C ALLOWED DEVIATION FROM PREDICTED POINT -- 0.0005
IF (YD-0.0005) 100,100,112
100 CONTINUE
112 K = K-1
WRITE (6,50)
50 FORMAT (///37X,15HSQ. ROOT T/SECS,5X,15HGAS ABSORB/SQCM,5X,15HLEAS
1T SQ VALUES)
DO 300 I =1,K
Z(I) = AO(K)+A1(K)*X(I)
WRITE (6,99) X(I),Y(I),Z(I)
99 FORMAT (29X,3F20.7)
300 CONTINUE
212 PIE = SQRT(3.1416)
SPRIM = (A1(K)/22400.0)
DIFSQ = (SPRIM*2.245E+07*PIE/(2.0*(PP-PEQ)))**2
WRITE (6,75) AO(K),A1(K)
75 FORMAT (///20X,'AO = ',E15.8,'A1 = ',E15.8)
WRITE (6,21) DIFSQ
21 FORMAT (///20X,'THE VALUE OF THE DIFFUSION COEFFICIENT IS = ',E15.7
1)
RETURN
END

```

FIGURE 38. COMPUTER PROGRAM OUTPUT FOR THE  
CALCULATION OF DIFFUSION COEFFICIENT

ABSORPTION DATA

TEST NO 11 P = 710.0000 PP = 700.0000 P EVAC = 210.0000 P INIT CONC =

TIME IN SECONDS	SQUARE ROOT T	PRESSURE CHANGE	DELTA P VALUES	AMT. GAS ABSORB	GAS ABSORB/SQCM
0.300000E 02	0.5477225E 01	0.6100639E 01	-0.6369330E 01	0.8443409E-01	0.2532516E-02
0.600000E 02	0.7745966E 01	0.1062692E 02	-0.1109495E 02	0.1470751E 00	0.4411370E-02
0.900000E 02	0.9486833E 01	0.1495640E 02	-0.1561510E 02	0.2069894E 00	0.6208438E-02
0.120000E 03	0.1095445E 02	0.1830191E 02	-0.1910793E 02	0.2532848E 00	0.7597022E-02
0.150000E 03	0.1224745E 02	0.2105704E 02	-0.2198438E 02	0.2914092E 00	0.8740526E-02
0.180000E 03	0.1341641E 02	0.2381216E 02	-0.2486082E 02	0.3295327E 00	0.9884004E-02
0.210000E 03	0.1449138E 02	0.2715767E 02	-0.2835365E 02	0.3758236E 00	0.1127245E-01
0.240000E 03	0.1549193E 02	0.2991280E 02	-0.3123009E 02	0.4139442E 00	0.1241584E-01
0.270000E 03	0.1643167E 02	0.3306152E 02	-0.3451746E 02	0.4575096E 00	0.1372254E-01
0.300000E 03	0.1732050E 02	0.3581664E 02	-0.3739388E 02	0.4956275E 00	0.1486585E-01
0.330000E 03	0.1816589E 02	0.3876855E 02	-0.4047577E 02	0.5364672E 00	0.1609080E-01
0.360000E 03	0.1897366E 02	0.4172049E 02	-0.4355766E 02	0.5773056E 00	0.1731570E-01
0.390000E 03	0.1974841E 02	0.4486922E 02	-0.4684502E 02	0.6208649E 00	0.1862222E-01
0.420000E 03	0.2049390E 02	0.4762433E 02	-0.4972142E 02	0.6589777E 00	0.1976538E-01

K	A0(K)	A1(K)	YCAL	YD
5	-0.26394530E-02	0.92976470E-03	0.87477900E-02	-0.72643160E-05
6	-0.26709830E-02	0.93378170E-03	0.98570100E-02	0.26993450E-04
7	-0.28905610E-02	0.96018190E-03	0.11023780E-01	0.24866310E-03
8	-0.30880750E-02	0.98270340E-03	0.12135890E-01	0.27995180E-03
9	-0.33534450E-02	0.10115590E-02	0.13268160E-01	0.45437360E-03

SQ. ROOT T/SECS	GAS ABSORB/SQCM	LEAST SQ VALUES
5.4772250	0.0025325	0.0022944
7.7459650	0.0044114	0.0045239
9.4868320	0.0062084	0.0062347
10.9544500	0.0075970	0.0076769
12.2474400	0.0087405	0.0089475
13.4164000	0.0098840	0.0100963
14.4913700	0.0112725	0.0111526
15.4919300	0.0124158	0.0121359

INTERCEPT = -0.30880750E-02 SLOPE = 0.98270340E-03

THE VALUE OF THE DIFFUSION COEFFICIENT IS = 0.1904633E-04 SQCM/SEC

FIGURE 39. COMPUTER PROGRAM FOR CALCULATING  
REGRESSION COEFFICIENTS TO EQUILIBRIUM  
SURFACE TENSION VALUES

```

    DIMENSION X(1100),DI(100),D(66),B(10),E(10),SB(10),T(10),XBAR(11),
    1STD(11),COE(11),SUMSQ(11),ISAVE(11),ANS(10),P(300)
    1 FORMAT(A4,A2,I5,I2,I2,F10.1)
    6 FORMAT(12H0 INTERCEPT,E20.7)
    7 FORMAT(26H0 REGRESSION COEFFICIENTS/(6E20.7))
    8 FORMAT(1H0/24X,24HANALYSIS OF VARIANCE FOR,I4,19H DEGREE POLYNOMI
    1AL/)
    11 FORMAT(32H DEVIATION ABOUT REGRESSION ,I6,F17.5,F14.5)
    13 FORMAT(17H0 NO IMPROVEMENT)
    14 FORMAT(1H0//27X,18HTABLE OF RESIDUALS//16H OBSERVATION NO.,5X,7HX
    1VALUE,7X,7HY VALUE,7X,10HY ESTIMATE,7X,8HRESIDUAL/)
    100 READ(5,1) PR,PR1,N,M,NPLOT,WGT
        WRITE (6,3) PR,PR1
C     PR--IDENTIFICATION
    3 FORMAT(27H1POLYNOMIAL REGRESSION.....,A4,A2/)
C     M--HIGHEST ORDER TO BE TESTED
C     NPLOT--NON ZERO NUMBER      WGT--MW X 10**3
C     N--NO OF OBSERVATIONS,
        WRITE (6,4) N
    4 FORMAT(23H0NUMBER OF OBSERVATIONS,I6//)
        L = N * M
        DO 110 I = 1,N
            J = L + I
            READ (5,2) X(I),X(J)
    2 FORMAT(2F10.1)
    110 X(I) = ALOG(X(I)/WGT)
        CALL GDATA (N,M,X,XBAR,STD,D,SUMSQ)
        MM = M + 1
        SUM = 0.0
        NT = N - 1
        DO 200 I = 1,M
            ISAVE(I) = I
            CALL ORDER (MM,D,MM,I,ISAVE,DI,E)
            CALL MINV (DI,I,DET,B,T)
            CALL MULTR (N,I,XBAR,STD,SUMSQ,DI,E,ISAVE,B,SB,T,ANS)
            WRITE (6,5) I
            IF(ANS(7)) 140,130,130
    130 SUMIP = ANS(4) - SUM
            IF(SUMIP) 140,140,150
    140 WRITE (6,13)
            GO TO 210
    150 WRITE (6,6) ANS(1)
            WRITE (6,7) (B(J),J = 1,I)
C     COEFFICIENT OF POLYNOMIAL REGRESSION SAVED FOR PUNCH
            CA = ANS(1)
            CB = B(1)
            CC = B(2)
            WRITE (6,8) I
            WRITE (6,9)
    9 FORMAT(1H0,5X,19HSOURCE OF VARIATION,7X,9HDEGREE OF,7X,6HSUM OF,9X
    1,4HMEAN,10X,1HF,9X,20HIMPROVEMENT IN TERMS/33X,7HFREEDOM,8X,7HSQUA
    2RES,7X,6HSQUARE,7X,5HVALUE,8X,17HOF SUM OF SQUARES)
            SUM = ANS(4)
            WRITE (6,10) I,ANS(4),ANS(6),ANS(10),SUMIP

```

FIGURE 39. (CONTINUED)

```

10 FORMAT(20H0 DUE TO REGRESSION,12X,I6,F17.5,F14.5,F.3 5,F20.5)
   NI = ANS(8)
   WRITE (6,11) NI,ANS(7),ANS(9)
   WRITE (6,12) NT,SUMSQ(MM)
12 FORMAT(8X,5HTOTAL,19X,I6,F17.5///)
   COE(1) = ANS(1)
   DO 160 J = 1,I
160 COE(J + 1) = B(J)
   LA = I
200 CONTINUE
210 IF(NPLOT) 100, 100, 220
220 NP3 = N + N
   DO 230 I = 1,N
   NP3 = NP3 + 1
   P(NP3) = COE(1)
   L = I
   DO 230 J = 1,LA
   P(NP3) = P(NP3) + X(L) * COE(J + 1)
230 L = L + N
   N2 = N
   L = N * M
   DO 240 I = 1,N
   P(I) = X(I)
   N2 = N2 + 1
   L = L + 1
240 P(N2) = X(L)
   WRITE (6,3) PR,PR1
   5 FORMAT(32HOPOLYNOMIAL REGRESSION OF DEGREE,I3)
   WRITE (6,5) LA
   PUNCH 20,PR,PR1,N
20  FORMAT (2A4,I2)
   PUNCH 21,CA,CB,CC
21  FORMAT (3E16.8)
   WRITE (6,14)
   NP2 = N
   NP3 = N + N
   DO 250 I = 1,N
   NP2 = NP2 + 1
   NP3 = NP3 + 1
   RESID = P(NP2) - P(NP3)
   PUNCH 22,P(I),P(NP3)
22  FORMAT (2E16.8)
250 WRITE (6,15) I,P(I),P(NP2),P(NP3),RESID
15  FORMAT(1H0,3X,I6,F18.5,F14.5,F17.5,F15.5)
   GO TO 100
   END

```



FIGURE 40. COMPUTER PROGRAM FOR CALCULATING  
SURFACE CONCENTRATION

```

C   COMP--NAME OF COMPOUND           N--NO. OF OBSERVATIONS
C   CONL--NATURAL LOG. OF BULK CONC.
C   A,B,C---CONSTANTS OF LEAST SQUARE EQUATION
      R= 8.314E7
      T = 298.0
1000 READ (5,1) COMP,COMP1,N
      1  FORMAT (2A4,I2)
      READ,A,B,C
      WRITE (6,2) COMP,COMP1,N
      2  FORMAT (1H1,2A4,20X,'NO. OF OBSERVATIONS',16//)
      WRITE (6,4) A,B,C
      4  FORMAT (1H0,3F15.7///)
      WRITE (6,10)
      10 FORMAT (1H0,10X,'NO.',10X,'CONL',12X,'ST',12X,'SLOPE',5X,'SURFACE
1CONC.'//)
      DO 100 I=1,N
      READ,CONL,ST
C   ST--SURFACE TENSION
      SLOPE= B+ 2.0*C*CONL
      SCONC=-SLOPE/(R*T)
C   SCONC--SURFACE CONC.
      WRITE (6,3) I,CONL,ST,SLOPE,SCONC
      3  FORMAT (10X,I3,3F16.5,E16.8/)
100  CONTINUE
      GO TO 1000
      END

```

FIGURE 41. COMPUTER PROGRAM FOR CALCULATING  
TIME INDEPENDENT INTERFACIAL RESISTANCE

```

C   PROGRAM FOR FINDING TIME-INDEPENDENT RESISTANCE
C   N--NO. OF POINTS USED   OPPR--OPERATING PRESSURE,   SATPR--SAT PRESSURE
C   TIME IN SECONDS
C   UP -- GAS UPTAKE
C   REAL NA(12),NUM
C   DIMENSION TIME(12),UP(12),RSAA(12),DELICI(12),B(220),X(12),A(220),R
C   2(220),Y(12),C(220),DEV2(220),VAR(220)
C   R-THE NO. SHOW HOW WELL THE EQUATION IS FIT
C   DEV2--STANDARD DEVIATION
1   FORMAT (16F5.2)
   READ(5,1)(TIME(I),I=1,12)
70  READ,N,OPPR,SATPR
2   FORMAT (8F10.3)
   READ(5,2)(UP(I),I=1,N)
   J=1
   B(J)=0.4000
50  BI=B(J)
   DO4I=1,N,1
   X(I)=(TIME(I)**BI)
4   Y(I)=UP(I)
   SUM1=0.0
   DO5I=1,N,1
5   SUM1=SUM1+X(I)
   SUM2=0.0
   DO6I=1,N,1
6   SUM2=SUM2+Y(I)
   SUM3=0.0
   DO7I=1,N,1
7   SUM3=SUM3+(X(I)*Y(I))
   SUM4=0.0
   DO8I=1,N,1
8   SUM4=SUM4+(X(I)**2.0)
   SUM5=0.0
   DO9I=1,N,1
9   SUM5=SUM5+(ABS(Y(I))**2.0)
   NUM=N
   U=SUM3-SUM1*SUM2/NUM
   V=SUM4-((SUM1**2.0)/NUM)
   W=SUM5-((SUM2*SUM2)/NUM)
   A(J)=U/V
   C(J)=(SUM4*SUM2-SUM3*SUM1)/(NUM*SUM4-SUM1**2.0)
   R(J)=U/(SQRT(V*W))
13  BF=B(J)
   AF=A(J)
   CF=C(J)
   SUM6=0.0
   DO12I=1,N,1
   T=UP(I)-(CF+AF*(TIME(I)**BF))
12  SUM6=SUM6+(T*T)
   DEV2(J)=SUM6
C
CALL GMMMA(BF,GBF,IER)
BF1 = BF +0.50000
CALL GMMMA(BF1,GBF1,IER)

```

FIGURE 41. (CONTINUED)

```

DO 14 I =1,N,1
NA(I)=AF*BF*(TIME(I)**(BF-1.0))
C STANDARD DIFFUSION COEFFICIENT--1.93E-05
DELCI(I)=((OPPR-SATPR)*(2.24E04/2.245E07))-(AF*BF*GBF*TIME(I)**(BF
1-0.50))/(SQRT(1.93E-05)*GBF1)
14 RSAA(I)=DELCI(I)/NA(I)
SUM7=0.0
DO 30 I=1,N
30 SUM7=SUM7+RSAA(I)
SUM8=0.0
DO 31 I=1,N
31 SUM8=SUM8+(RSAA(I)*RSAA(I))
VAR(J)=(SUM8-((SUM7*SUM7)/NUM))/(NUM-1.0)
J=J+1
IF(J-2) 10,10,11
10 B(J)=B(J-1)+0.004
GO TO 50
11 IF(VAR(J-1)-VAR(J-2)) 18,18,23
18 B(J)=B(J-1)+0.004
GO TO 50
15 FORMAT(/10X,'TIME',20X,'ABSORPTION RATE',20X,'INTERFACIAL RESISTA
3NCE')
23 WRITE(6,15)
WRITE(6,16)(TIME(I),NA(I),RSAA(I),I=1,N)
16 FORMAT(/(10X,F6.1,23X,E10.4,23X,E13.4))
19 WRITE(6,17) A(J-2),B(J-2),C(J-2)
17 FORMAT(/10X,'A=',E11.4,10X,'B=',E11.4,10X,'C=',E11.4)
WRITE(6,21) R(J-2),DEV2(J-2)
21 FORMAT(10X,'R(J)=' ,E13.6,10X,'DEV2=' ,E13.6)
GO TO 70
END

```

### Materials

A listing of the materials used in this investigation is presented in the following section.

Acetone. Technical grade. Supplied by Preiser Scientific Company, Charleston, West Virginia. Used to clean glass ware, absorption apparatus and platinum ring of interfacial tensiometer in place of methyl ethyl ketone.

Benzene. Purified, 99 to 100%. Supplied by J. T. Baker Company, Phillipsburg, New Jersey. Used to clean platinum ring of interfacial tensiometer.

Carbon Dioxide. Commercial grade, 99.5 per cent minimum. Manufactured by Air Production Company, Inc., Roanoke, Virginia. Purchased from Industrial Gas Supply Company, Bluefield, West Virginia. Used as the absorbing gas.

Carbon Tetrachloride. Certified A.C.S. laboratory grade. Supplied by Fisher Scientific Company, Fair Lawn, New Jersey. Used for cleaning grease from stopcocks.

Grease, Stopcock. Apiezon, high vacuum stopcock grease. Distributed in the U.S.A. by James G. Biddle Company, Plymouth Meeting, Pennsylvania. Used to lubricate high vacuum stopcocks.

Lauryl Diglycol Amide. Lauryl diglycol amide flakes obtained from K & K Laboratories, Inc., Plainview, New York. No analysis available. Used as a surface active additive to water.

Mercury. Original source of mercury unknown. Used as measuring fluid in the U-type manometer and as substrate in the absorption cell.

Meriam D-3166. Density  $1.043 \text{ gm/cm}^3$  at  $25^\circ\text{C}$ . Obtained from the Meriam Instrument Company, Cleveland, Ohio. Used as a measuring fluid in the Barcroft manometer.

N-octanol. Liquid n-octanol obtained from K & K Laboratories, Inc., Plainview, New York. No analysis available. Used as a surface active additive to water.

4-octanol. Liquid 4-octanol obtained from K & K Laboratories, Inc., Plainview, New York. No analysis available. Used as a surface active additive to water.

Sodium Dichromate. Crystal sodium dichromate. Original source unknown. No analysis available. Used for making glass cleaning solution.

Sulfuric Acid, Concentrated. Purity 95 to 98 per cent. Lot 792005. Obtained from Fisher Scientific Company, Chemical Manufacturing Division, Fair Lawn, New Jersey. Used for making glass cleaning solution.

Water. Distilled water deionized with a Bantam demineralizer. Conductivity of  $2.0 \times 10^{-6}$  ohms. Used for gas absorption tests and making surfactant solutions.



### Apparatus

A listing of the apparatus used in this investigation is given in the following section.

Balance, Analytical. Fisher double pan balance, model number 220-D, serial number M-13360, capacity 200 gm, accurate to 0.0001gram. Manufactured by Volland & Sons, Inc., New Rochell, New York. Used to weigh surfactants.

Barometer, Mercurial. Barometer calibrated from 656 to 770 mm and accurate to 0.1 mm with vernier. Manufactured by Fisher Scientific Company, Silver Springs, Maryland. Used to determine barometric pressure.

Bath, Constant Temperature Water. Square glass-walled bath constructed by the Chemical Engineering Shop. Dimensions of 29 inches x 29 inches and 24 inches deep. Used to control the system temperature.

Cathetometer. 40 cm range accurate to 0.01 cm with vernier. Manufactured by Eberbach, Ann Arbor, Mich. Used to measure the height of meniscus in the Barcroft manometer.

Deionizer. Bantam model BD-1, flow rate 10 gal/hr, 110 volts, 60 cycles, Manufactured by Barnstead Still and Sterilizer Company, Boston, Mass. Used to deionize distilled water.

Dishes, Petri. Covered, made of pyrex brand glass. Manufactured by Fisher Scientific Company, Pittsburgh, Pennsylvania. Used as containers for surfactant solutions while measuring surface tensions.

Flask, Side Arm. 50 ml. Supplied by Sargent Chemical Company, Silver Springs, Maryland. Used to establish initial concentrations of carbon dioxide in surfactant solutions.

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

Manometer, Temperature Compensated Differential. Made by attaching Barcroft manometer to two 6.5 cm diameter glass cell with soft glass tubing. Built by Virginia Polytechnic Institute Glass Shop. Used to measure the absorption of carbon dioxide in surfactant solutions.

Mixers. Two "Lightnin" model "L" mixers, serial number 502663 and 514807, 110 volts, 60 cycles. Manufactured by Mixing Equipment Company, Einer and Amend, New York. Used to mix constant temperature bath.

Pump, Vacuum. Cenco-Magavac vacuum pump, serial number 8730. Manufactured by Central Scientific Company, Chicago, Illinois. Used to evacuate the system.

Relay, Electronic. Fisher-Serfass electronic relay, 115 volts, 60 cycles. Manufactured by Fisher Scientific Company, Pittsburgh, Pennsylvania. Used in conjunction with room temperature thermoregulator.

Relay, Transistor. Fisher transistor relay, model 32, 115 volts, 15 amp. Manufactured by Fisher Scientific Company, Pittsburgh, Pennsylvania. Used in conjunction with constant temperature bath thermoregulator.

Stirrer, Magnetic. Catalog number 14-511-2, 115 volts, 50/60 cycles, 0.2 amp. Manufactured by Fisher Scientific Company, New York. Used to mix water samples during initial saturation.

Syringe, Hypodermic. B-D Yale 20 cc syringe, serial number 2303-20Y. Manufactured by Becton, Dickinson and Company, Rutherford, New Jersey. Used to introduce surfactant solutions and mercury into absorption cell.

Tensiometer, Interfacial. Model 20, 6.015 cm platinum ring, range 0-90 dynes/cm, readings  $\pm 0.1$  dynes/cm. Manufactured by Fisher Scientific Company, Pittsburgh, Pennsylvania. Used to determine surface tensions of surfactant solutions.

Thermometer. Sargent, A.S.TM. 630, number 2375, catalog number S-80280-B. Incremented in 0.1 degrees from -8 to +32 degrees Centigrade, total immersion type. Manufactured by Sargent Chemical Company, Silver Springs, Maryland. Used to measure temperature of water bath.

Thermoregulator. Catalog number S-81835, contact thermometer type, tungsten wire electrode,  $\pm 0.05^{\circ}\text{C}$  sensitivity. Manufactured by Sargent Chemical Company, Silver Springs, Maryland. Used to regulate water bath temperature.

Thermoregulator. Serial number 2421292, contact thermometer type, tungsten wire electrode,  $\pm 0.05^{\circ}\text{C}$  sensitivity. Manufactured by Fisher Scientific Company, Pittsburgh, Pennsylvania. Used to regulate room temperature.

Timer. 115 volts, 60 cycles, 5 watts, graduated to 0.1 second. Manufactured by Fisher Scientific Company. Pittsburgh, Pennsylvania. Used to measure time during absorption tests.

THE EFFECT OF THE POSITIONS AND MOLECULAR WEIGHT OF HYDROPHILIC  
FUNCTIONAL GROUPS OF SURFACTANTS ON GAS ABSORPTION RATES

Yan Pui Samuel To

Abstract

The purpose of this investigation was to determine the effect of the positions and the molecular weight of surfactant hydrophilic functional groups on the rate of gas absorption.

A quiescent unsteady-state absorption apparatus was used with carbon dioxide and water as the absorption system. Three surfactants with hydroxyl groups were selected for study, namely, n-octanol, 4-octanol and lauryl diglycol amide.

Preliminary absorption tests were made using pure deionized water to determine the diffusion coefficient for the system. A value of  $1.93 \pm 0.05 \times 10^{-5}$  square centimeters per second was obtained. The absorption tests were repeated with the three surfactant solutions at different concentrations. Then the interfacial resistance for each solution was calculated.

The results of the surfactants were compared with each other and were also compared with the results of lauryl diethanol amide previous investigated. The octanol with hydroxyl group at a branched position was found to cause a higher interfacial resistance than those with hydroxyl groups at the end of the hydrophobic chain. It was also concluded that increasing the molecular weight of the hydrophilic group decreased the interfacial resistance.