7/25/68

ABSORPTION OF SULFUR DIOXIDE BY CHARGED AQUEOUS DROPLETS

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

by

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Physics

Georgia Institute of Technology

March, 1972

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Approved:

Chairm

Date approved by Chairman: 2-21-72

ACKNOWLEDGMENTS

I would like to express my gratitude to my thesis advisor, Dr. Michael J. Matteson, for his direction and encouragement. I would also like to thank the Department of Health, Education, and Welfare for financial support during this research.

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SUMMARY

The rate of absorption of sulfur dioxide by electrically charged water droplets was studied. The droplets were charged by passing distilled water through a No. 24 gage hypodermic needle attached to a constant voltage source. The droplets fell through a chamber containing 2000 ppm sulfur dioxide in air, and were collected in a grounded metal cup. The collected solution was withdrawn, oxidized with hydrogen peroxide, and analyzed for sulfuric acid. By measuring droplet residence time, surface area, and charge, the specific absorption rate was correlated with the surface charge density. It was found that the specific absorption rate increased approximately parabolically with change in the surface charge density. The results of an investigation of the effects of humidity were not conclusive.

CHAPTER I

INTRODUCTION

Background

Air pollution is a serious and growing problem in the United States. Each year greater amounts of pollutants such as carbon monoxide, sulfur dioxide, and nitrogen oxides are dumped into our atmosphere. Although much effort and money are being expended to solve this problem, it continues to become worse. One of the reasons for this is that an economical means of removing sulfur dioxide from stack gas has not been found.

Most methods of sulfur dioxide removal consist of some type of wet scrubbing (1). In such a system, a liquid is brought into contact with the stack gas and the sulfur dioxide is absorbed by the liquid. In order to improve sulfur dioxide removal systems, it is important to know as much as possible about the phenomenon of sulfur dioxide absorption by a liquid. This phenomenon is interesting from other aspects also, as can easily be seen from this quotation from Transport Phenomena (2).

> Two-fluid mass-transfer systems offer many challenging problems: the flow behavior is complicated, the moving interface is virtually inaccessible to sampling, the interfacial area is usually unknown, and many of the practically important systems involve liquid-phase chemical reactions. A better basic understanding of these systems is needed.

The effects of various physical parameters on the absorption of a gas by a liquid have been studied. Some of these parameters are:

composition of the gas, composition of the liquid, time of contact, temperature of the gas, and temperature of the liquid. However, little work has been done to examine the effect of surface electric charge on the absorption of a gas by a liquid. This charge is present in most systems since there is a contact potential between most liquids and gases. There has been some research on the effect of electric fields on condensation (3). Indeed, the Wilson cloud chamber is based upon the fact that ions aid the nucleation of a super-saturated vapor. This phenomenon has not been suitably accounted for theoretically. Most explanations assume that the electric field which arises in the drop due to the presence of an ion causes approaching gaseous molecules to be preferentially aligned in such a way that interaction with the liquid crystal surface of the drop is strengthened (4).

At the 1971 National Meeting of the American Institute of Chemical Engineers, A. M. Marks, of the Marks Polarized Corporation, presented a paper entitled "Charged Aerosols for Air Purification and Other Uses" (5). In the paper he presented data showing that his company had a device which would absorb noxious gases efficiently if it could be operated at temperatures below 100 °C. The device was a venturi scrubber with the aqueous solution introduced by a metal capillary at a high electric potential. This high field resulted in a very fine aerosol in the venturi throat. The large surface area of the aerosol permitted excellent absorption efficiencies. There was not, however, any measurement of the aerosol size or the amount of aerosol entrained by the gas flow. Thus, there was no method for analyzing, even qualitatively, the effect the field had upon gas absorption.

Purpose and Objectives

An aerosol of charged liquid droplets may serve as an efficient medium for scrubbing noxious components from discharged stack gases. In order to design a system to do this most efficiently, knowledge of the effect of the presence of charges upon the absorption rate is required. Consequently, this study has examined the effect that the surface charge density of the drop (coul/cm^2) has upon the specific absorption rate ($\text{moles/cm}^2\text{-sec}$) of 2000 ppm sulfur dioxide in air. These two fluids have been chosen since absorption rates of sulfur dioxide by water are well known and therefore can be compared with results obtained when the water surface is charged. Also, sulfur dioxide is the noxious gas released in the largest quantities by coal burning. Sulfur dioxide is also a polar molecule with a structure much like that of water, which makes comparison of the chosen system with that of condensation of water vapor not unreasonable. The experimental approach was to expose charged water drops to an atmosphere containing a known concentration of sulfur dioxide for a measured length of time. The surface charge density and surface area of the drop were measured, and finally, the amount of sulfur dioxide absorbed was determined. The drops were formed one at a time and spent most of their lifetime attached to the needle.

Theory

One of the most popular models for gas absorption by a liquid is the two-film one. Two films are postulated as existing at the phase boundary between two fluids. It is assumed that mass transfer through these films takes place only by diffusion. These two films may be considered as two diffusional resistances in series with an equilibrium condition existing at the interface. The difference in concentration across the films represents a chemical potential that causes mass transfer. From diffusional principles and the law of continuity for steady state mass transfer, which states that a concentration build up cannot occur in either film, the rate of diffusion may be expressed as

$$N_A = k_L (c_i - c) = k_G (p - p_i) \tag{1}$$

Where N_A is the rate of mass transfer in mass per unit area per unit time. The symbol k_L is the liquid film coefficient and k_G is the gas film coefficient. The symbols c and p represent, respectively, concentration in the liquid and partial pressure in the gas of the substance of interest. The subscript i denotes the interfacial value. The coefficients k_L and k_G are usually very difficult to measure and so the equations are developed employing overall coefficients, K_G and K_L where

$$N_A = K_L (c_e - c) = K_G (p - p_e) \tag{2}$$

where e denotes equilibrium values. That is, p_e is the partial pressure of the diffusing substance in equilibrium with a solution having a concentration c of the diffusing substance. On the other hand, c_e is the concentration of the diffusing substance in a solution in equilibrium with a partial pressure, p, of the diffusing substance.

With a sulfur dioxide-water system there is a special situation. Sulfur dioxide is not very soluble in water and this results in a high liquid film resistance (6). In a case such as this

$$K_L \approx k_L \tag{3}$$

and at low transfer rates

$$k_L \approx \frac{cD}{d} \tag{4}$$

where c is the molar concentration, D is the diffusivity of sulfur dioxide in water, and d is the film thickness. This results in the equation

$$N_A = \frac{cD}{d} (c_e - c) \tag{5}$$

Thus, a change in absorption rate can only be explained by assuming that either the diffusivity of the sulfur dioxide changes or that the film thickness changes.

According to the theories of ordinary diffusion in liquids, the diffusivity, D_{AB}, of a single particle or solute molecule of A through a stationary liquid medium, B, is

$$D_{AB} = kT \frac{U_A}{F_A} \tag{6}$$

in which k is Boltzmann's constant, T is the liquid temperature, U_A is the particle velocity, U_A/F_A is the mobility, M, of the particle of A. The mobility is also the steady state velocity attained by A under the action of a unit force. From Stoke's Law, for zero slip

$$F_A = 6\pi \mu_B U_A R_A \qquad (7)$$

where μ_B is the viscosity of the pure solvent and R_A is the radius of the diffusing particle.

By applying an electric field to the droplet, an increase might be expected in the mobility of species A from M to M+dM and thereby an increase in the diffusivity and rate of mass transfer of A in the solvent. An alternative explanation would be that this is an inappropriate model. The partial pressure at the surface of the liquid could be increased to a value higher than that of the bulk gas by interaction of the molecular dipoles with the electric field. This would result in a higher equilibrium concentration at the surface than would otherwise be observed. This experiment is not designed to determine the cause of an increase in the absorption rate but merely to determine if such an increase exists.

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

The experimental apparatus (Figure 1) was designed to permit the measurement of specific parameters. Drops of water must be generated and charged; then these drops must be brought into contact with a mixture of sulfur dioxide and air; and, finally, they must be captured. The size of the drop, its surface charge density, the concentration of the sulfur dioxide-air mixture, and the amount of time the drop is in contact with the mixture must all be measured. Also, the amount of sulfur dioxide absorbed by the drop must be measured. Other quantities of interest are: the water temperature, the sulfur dioxide-air mixture temperature, the relative humidity of the mixture, and the applied voltage. Knowledge of these quantities allows calculating the rate of absorption per unit area. This rate may then be considered as a function of the surface charge density of the drop. The absorption takes place in a reaction chamber (Figure 2) in which the charged drops move downwards while the sulfur dioxide-air mixture moves upwards.

The various components of the apparatus will be described according to their function. The first may be called the drop producer. It was composed of a polyethylene reservoir, a water pressure regulator, a stopcock, a high voltage source, and a hypodermic needle. The water pressure regulator was a plexiglass reservoir which maintained a constant head of water

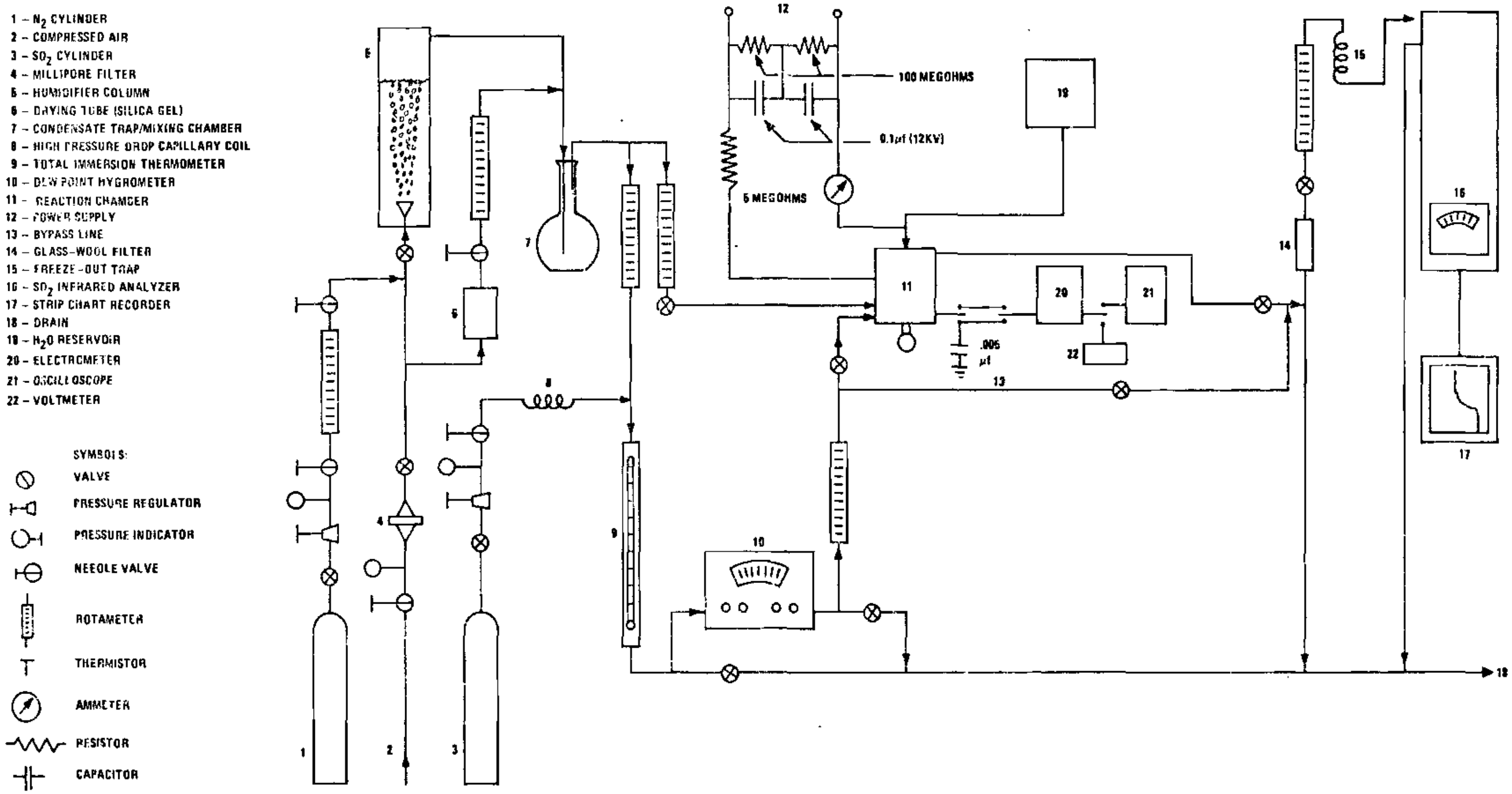

Figure 1. Experimental Apparatus

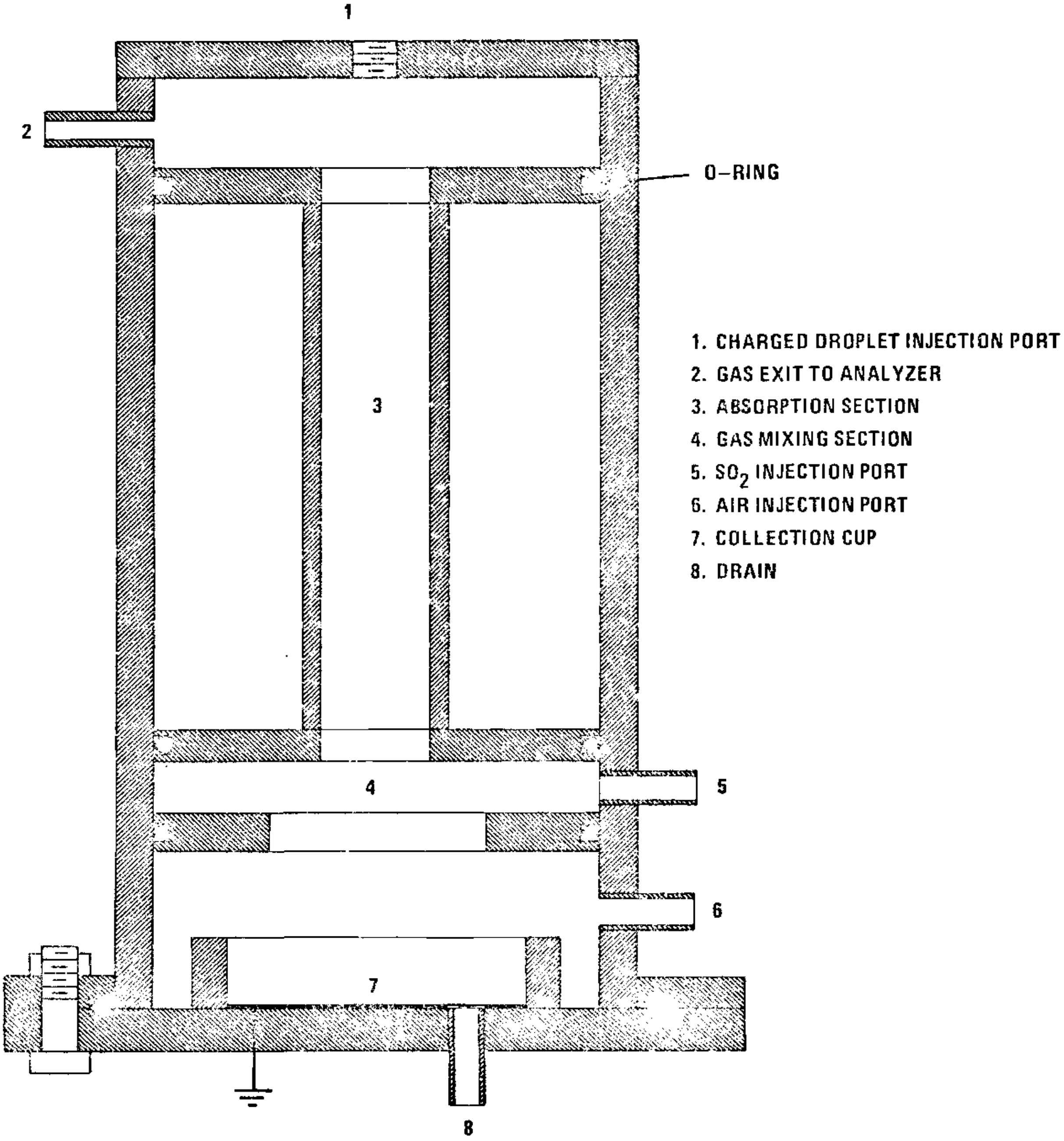

Figure 2. Reaction Chamber(Drawn Full Scale)

by means of a drain outlet at a fixed height. Most of the water flowed into the reservoir and then out at the drain in the center. A small quantity of water, which flowed into the reaction chamber, exited by way of an outlet in the bottom of the reservoir. The water used in this experiment was distilled and deionized; it had a total conductivity equivalent to 0.1 parts per million of NaCl. The water which flowed down the pressure regulator drain was captured in another polyethylene container and recycled. This recycling had its effects in the results as will be seen.

In an experiment, water flowed from the main reservoir; through the pressure regulator; through a Matheson, Model 601, rotometer; through the stopcock; and through the needle to form drops. The needle was a No. 24 hypodermic needle that had been ground square and polished at the end. The drops were charged by means of a Beckman high voltage source electrically connected to the hypodermic needle. The high voltage supply was stabilized somewhat and protected against undue current drain by a low pass filter of high resistance (Figure 3).

The next group of components will be called the sulfur dioxide producer. It consisted of a metered supply of air of variable humidity; a metering system for the introduction of sulfur dioxide into the airstream; an EG & G, Model 880, dew point hygrometer; and a Beckman, Model 215A, nondispersive infrared analyzer. Shop air was passed through a diaphragm-type pressure regulator and then through a Millipore filter. Next, the air stream was split into two streams. One stream was bubbled upward through a water column and the other passed through a column of silica gel. This gave a low humidity stream and a high humidity stream. The two

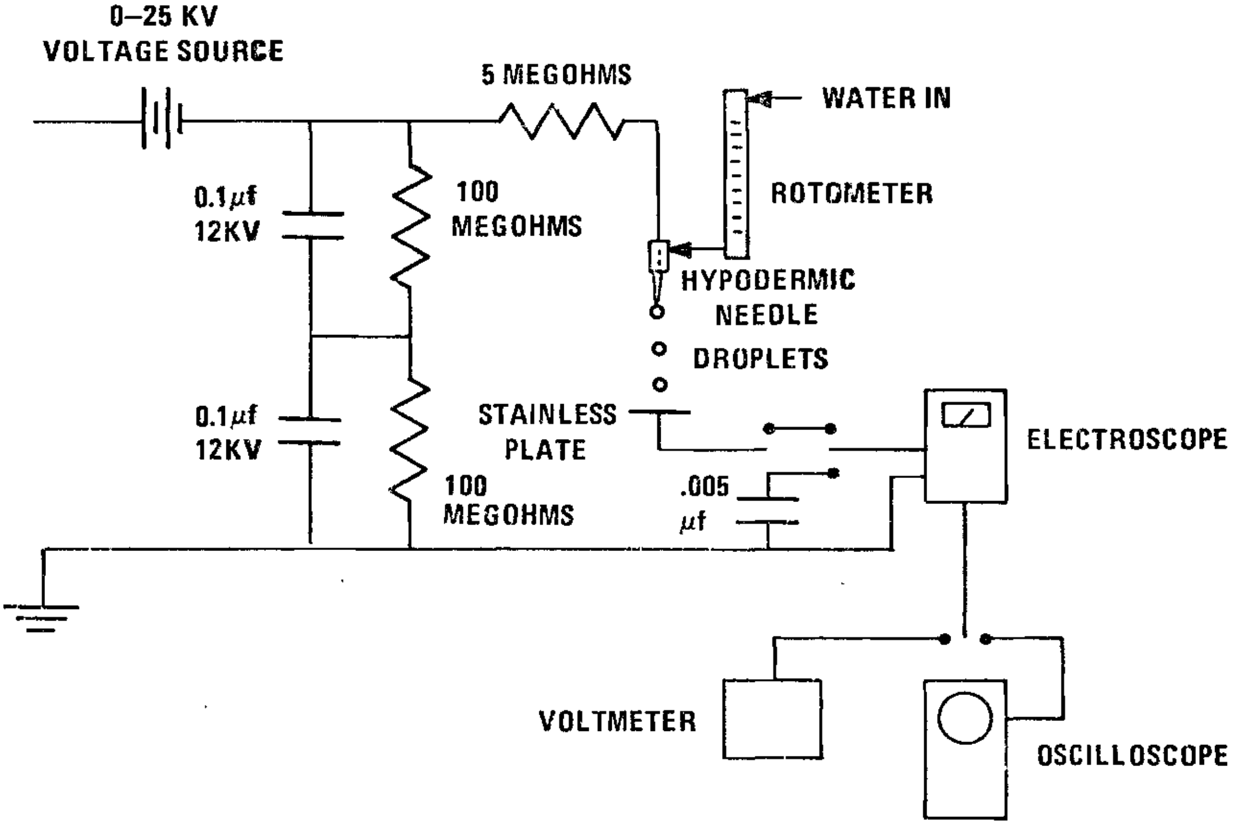

Figure 3. Drop Parameter Measuring System

streams were then recombined in the desired proportions. The humidity of the mixture was established by needle valves on each of the separate streams. The mixture was then again divided into two streams. The first stream flowed through a Matheson, Model 603, rotometer and provided "flushing" air for the lower part of the reaction chamber. The purpose of this flushing air is given later. The second stream passed through a Matheson, Model 604, rotometer and then sulfur dioxide was added to it by means of a metering system. This metering system consisted of a bottle of high pressure sulfur dioxide, a diaphragm-type pressure regulator, and a metal capillary immersed in a heat reservoir. For a constant pressure of several pounds at the bottle end of the capillary, a constant flow of sulfur dioxide emerged from the air-stream end of the capillary. The heat reservoir maintained a constant capillary temperature so that the capillary diameter did not change due to thermal expansion.

This sulfur dioxide and air mixture then entered the reaction chamber, mixed with the flushing air, contacted the drops, and, finally left the reaction chamber. The mixture then flowed around a thermometer and then into the dew point hygrometer. The mixture next flowed through an ice-and-acetone cold trap and into the infrared analyzer which monitored the sulfur dioxide concentration. High humidity has an effect on the infrared analysis, and water drops condensing inside the analyzer affect it very adversely. The cold trap reduced the relative humidity to less than fifteen percent.

The third group of apparatus components was the previously mentioned reaction chamber. This chamber was a plexiglass cylinder three inches in inside diameter and six and a half inches long. The drops fell down the axis of the cylinder and the gas mixture flowed upward along the axis. The hypodermic needle was mounted inside a Teflon plug for electrical isolation; this plug screwed into the top of the chamber. The drops fell onto a stainless steel plate at the bottom of a cup, collected there, and then ran out a pipe to a collection reservoir. The gas flow pattern within the interior of the reaction chamber was controlled by a number of baffles. The flushing air, mentioned earlier, entered at the bottom of the reaction chamber and flowed upward through a hole in an otherwise solid disk directly over the drop collection cup. This effectively prevented any contact of sulfur dioxide with the water resting on the stainless steel plate. This does, however, introduce the problem of desorption at this point and this problem will be examined later.

The sulfur dioxide-air mixture entered above this disk and mixed with the flushing air. The mixture then flowed into a pipe with an inside diameter of 0.75 inch and up to the top of the chamber where it exited. The mixture then was directed to the hygrometer and Beckman analyzer.

The fourth apparatus grouping measured the drop parameters (Figure 3). It consisted of the rotometer; a Condensor Products glass capacitor; a Keithley, Model 610A, electrometer; a Keithley, Model 6103A, voltage divider; a Hewlett Packard oscilloscope; and a Honeywell digital voltmeter. The drops fell on the stainless steel plate. In order to measure the number of drops per unit time, the plate was attached to the electrometer which functioned as a high-gain amplifier with outputs into the oscilloscope. Thus, a pulse on the oscilloscope was seen for each drop. In order for the pulse to be sharp and in order for pulses of drops, which were not highly charged, to be observed, the reaction chamber was enclosed in grounded aluminum foil to shield sixty cycle noise. When it was desired to observe the charge delivered by the drops, the stainless steel plate was connected to the capacitor and the charge was stored. The voltage of the capacitor was monitored by the electrometer and the signal was sent to the digital voltmeter. The RC time constant for the capacitive circuit was 3410 ± 25 seconds. The water flow rate was determined by the Matheson, Model 601, rotometer. The voltage divider was used with the electrometer to determine the applied voltage. The voltage divider was a resistor chain across which the entire voltage was imposed. The electrometer measured the voltage across one one-thousandth part of the resistance and thus measured only 0.001 part of the whole voltage. The drop size can be calculated from the flow rate and the drop rate. From the drop rate and the charge delivered per unit time, the charge per drop can also be calculated. The surface charge density can be calculated from these quantities.

The fifth group, the drop collection components, consisted of a stopcock, a volumetric flask, a pipette, some reagent H_2O_2, and polyethylene bottles. Five milliliters of three percent hydrogen peroxide was pipetted into a polyethylene bottle. When sufficient water collected in the reservoir below the mixing chamber, the stopcock was opened and 25 ml was delivered into the volumetric flask. This was then poured into the polyethylene bottle where the H_2O_2 reacted with the acid according to

$$H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O \qquad (8)$$

The bottles were weighed before and after the sample was deposited so that the sample mass was accurately known.

The final apparatus group was related to the solution concentration measurement. It consisted of an ac conductance meter and a thermometer. The solution temperature and conductance were measured and the concentration determined from these parameters.

CHAPTER III

PROCEDURE AND DATA ANALYSIS

Prior to making experimental tests, the infrared analyzer was allowed to equilibriate for a minimum of four hours and all other instruments were allowed to warm for at least one hour. Next the infrared analyzer was calibrated. Dry nitrogen was passed through the analyzer and the output was set to zero. Next, sulfur dioxide of known concentration was passed through the instrument and the gain adjusted to obtain the reading which corresponded to factory calibration. At this point, the air flow was turned on and the flows were stabilized. Sulfur dioxide was added until the infrared analyzer indicated a reading which corresponds to 1950 parts per million.

Now the water flow was turned on. The quantities of water and air flowing were such that only a very small percentage of the sulfur dioxide was absorbed and thus the sulfur dioxide concentration within the reaction chamber was essentially constant. For each set of data which determined a specific absorption rate and a surface charge density, the applied voltage was measured by means of the voltage divider and the electrometer. The water temperature was measured by means of a mercury thermometer.

Five milliliters of three percent hydrogen peroxide was pipetted into a polyethylene sample bottle. The mass of the bottle and the hydrogen peroxide were measured. Next, the reading of the rotometer which measured water flow was taken. The readings of the rotometers which measure air flow was taken. The air temperature and dew point were noted. The reading of the infrared analyzer was taken. The water flow rate was checked to see if it had remained constant and any change noted. The stainless steel plate was connected electrically to the capacitor and the capacitor voltage was monitored by the electrometer. Voltage readings were recorded at 30, 60, 90, and 120 seconds. The stainless steel plate was then connected directly to the electrometer which was set to indicate current. The electrometer output was connected to the oscilloscope. The number of milliseconds between drops was recorded. During all of these measurements of electrical parameters, the water flow out of the collection cup was stopped so that this was not a source of charge leakage.

Now the sample, which had been collecting in the reservoir, was allowed to run into a volumetric flask of 25 milliliters capacity. The contents of the flask were added to the sample bottle and mixed so that the hydrogen peroxide oxidized the sulfurous acid to sulfuric acid. This was done because sulfuric acid has a much lower vapor pressure than dissolved sulfur dioxide. The sample bottle was again weighed to determine the size of the sample.

The next step was the analysis of the contents of the sample. This was done conductimetrically. The specific conductance of a sulfuric acid solution is a function only of its concentration and temperature (7). The conductance meter was first calibrated by measuring the conductance of a 0.1 normal solution of potassium chloride of known temperature. The sample was placed in a clean container and a clean conductance cell was lowered into it. The resistance was measured and then the temperature of the sample was measured.

Next, the manner in which the data were reduced to the desired quantities was examined. The notation used for both measured and calculated quantities may be found in Table 1. The two most important parameters which were calculated were the surface charge density and the specific absorption rate. The surface charge density S, is given by

$$S = (I \cdot W \cdot 0.001)/4\pi R^2 \tag{9}$$

and I, the current, is calculated from the capacitor charging curve by means of

$$E = Q/c = I_1 R_1$$

where R_1 is the system resistance and I_1 is the leakage current.

Taking the derivative of voltage with respect to time:

$$\frac{dE}{dt} = \frac{\frac{dQ}{dt}}{c} \tag{10}$$

where

$$\frac{dQ}{dt} = I - I_1 = I - \frac{E}{R_1} \tag{11}$$

therefore, combining (10) with (11) shows that E can be determined from

$$\frac{dE}{dt} = \frac{IR_1 - E}{R_1 c} \tag{12}$$

integrating (12)

$$-\frac{t_2 - t_1}{R_1 c} = \ln(IR_1 - E_2) - \ln(IR_1 - E_1)$$

Table 1. Notation

Measured Quantities

W = milliseconds between drops
V = applied voltage
F_1 = flow rate of water in cm^3 per min
F_2 = rotometer #603 reading
F_3 = rotometer #604 reading
T_w = water temperature, °C
T_a = air temperature, °F
T_d = dew point temperature, °F
IR = reading of infrared analyzer
$E(30)$ = capacitor voltage after 30 seconds
$E(60)$ = capacitor voltage after 60 seconds
$E(90)$ = capacitor voltage after 90 seconds
$E(120)$ = capacitor voltage after 120 seconds
M = sample mass in grams
Re = sample resistance
T_R = sample temperature (°C) during resistance measurement

Calculated Quantities

N_A = specific absorption rate in units of 10^{-7} moles per (cm^2-sec)
S = surface charge density in units of 10^{-9} coulombs per cm^2
R = drop radius in cm
t_R = drop residence time in milliseconds
RH = percent relative humidity
I = charge delivery rate in coul/sec

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and letting $t_1 = E_1 = 0$

$$\exp(-\frac{t_2}{R_1 c}) = 1 - \frac{E_2}{IR_1}$$

there is obtained

$$I = \frac{E_2}{R_1} [1 - \exp(-\frac{t_2}{R_1 c})]^{-1} \tag{13}$$

This leaves the radius of the drop to be calculated. The volume of each drop is $\pi D^3/6$, where D is the diameter. Thus,

$$R = \frac{1}{2} (\frac{6}{\pi} \cdot F_1 \cdot \frac{1}{60} \cdot W \cdot 0.001)^{1/3} \tag{14}$$

The other major quantity which must be calculated is the specific absorption rate. It is given by

$$N_A = \frac{T}{A \cdot W \cdot 0.001 + 4\pi R^2 t_f} \tag{15}$$

where T is the number of moles transferred per drop, A is the time average area of the drop during drop formation, and t_f is the time of drop fall through the reaction chamber. The number of moles per drop is

$$T = c \cdot F_1 \cdot \frac{1}{60} \cdot W \cdot 0.001$$

where c is the concentration of the sample in moles per cm^3. The value of c is found from the conductance measurement. Conductance values are found in the International Critical Tables as follows (9).

$$\Lambda = 1000\ k/c \tag{16}$$

where Λ = the equivalent conductance

k = the specific conductivity, and

c = the concentration of $\frac{1}{2}\ H_2SO_4$

Table 2. Conductance Data

$c = 1.0 \times 10^{-6}$ moles/ml	$\Lambda = 399.5$
$c = 2.0 \times 10^{-6}$	$\Lambda = 390.3$
$c = 5.0 \times 10^{-6}$	$\Lambda = 364.9$

Using a linear approximation to the relations between Λ and concentration and temperature leads to the equation

$$c = \frac{-\ Y + \ Y^2 - 4XZ}{4X} \quad \text{in units of } 10^{-6} \text{ moles/cm}^3 \tag{17}$$

$X = -\ 5.408 - 0.128(T_R)$

$Y = 256.234 + 6.0648(T_R)$

$Z = -$ cell constant $\times\ 10^6$/Re

The coefficients in the above equations were obtained by means of a least squares fit, the curves matching the tabulated constants to within one percent. The concentration was then adjusted to account for the dilution by the hydrogen peroxide.

A, the time average area during drop formation, equals

$$A = \frac{1000}{W} \int_{t=0}^{t=W} 4\pi R^2(t)\ dt \tag{18}$$

where $R(t) = \frac{1}{2}\left(\frac{6}{\pi} \cdot F_1 \cdot \frac{1}{60}\ t\right)^{1/3}$

$$A \cdot \frac{W}{1000} = 12\pi R^2 \cdot \frac{W}{5000}$$

The final quantity needed for this calculation is the time for the drop to fall, t_f. Solving Laplace's equation

$$\nabla^2 \phi = 0$$

for the electrostatic potential inside the cylinder, it is found that the potential along the axis of the cylinder is proportional to the distance along the axis from the needle. This means that the electric field in the vertical direction, along the axis, is constant. Then the acceleration, a, of the drop due to the electric field and gravity is

$$a = 980 + \frac{I \cdot W \cdot V \cdot 6 \times 10^8}{L_1 \cdot F_1 \cdot W} \tag{19}$$

where L_1 is the distance the drop falls. But there is a drag proportional to the square of the veolcity, so that

$$\frac{d^2Z}{dt^2} = a - \frac{7.458 \times 10^{-4}}{R}\left(\frac{dZ}{dt}\right)^2 \tag{20}$$

The differential equation leads to a solution in terms of a hyperbolic tangent function. For small arguments, this function may be approximated quite well by the first two terms of its Taylor expansion. This leads to a solution of the form

$$t_f = \sqrt{\frac{3R}{a \cdot 7.458 \times 10^{-4}} \left(- 1 + \sqrt{\frac{1 + 4L_2 \cdot 7.458 \times 10^{-4}}{3R}} \right)} \qquad (21)$$

where L_2 is the distance the drop falls while in contact with sulfur dioxide. This completes the calculation of N_A.

The relative humidity is found from the empirical relation

$$RH = 100 \exp \left[\frac{Q_1}{T_a + Q_2} - \frac{Q_1}{T_d + Q_2}\right] \qquad (22)$$

where $Q_1 = 7470.074004$

$Q_2 = 398.0358958$

The residence time is found from

$$t_R = W + 1000t_f \qquad (23)$$

in units of milliseconds.

One step in the analysis of these data was the determination of possible sources of error. The errors made were either reading errors or they were systematic in nature. The systematic errors included those which arose due to instruments which were out of calibration and those which arose due to an instrument which did not really measure the quantity intended. The first type can be corrected and the second can be minimized. In order to correct the instrument readings, they were checked against more accurate standards. The infrared analyzer and conductance meter were calibrated before each use. The rotometers in the air flow were calibrated by Mr. Hugh Stringer and Mr. Walter Busbee by measuring the volume of gas, which passed at a constant rate, by water displacement (8). They found that the factory calibration curves were accurate. They also found that the dew point hygrometer consistently indicated 0.5°F low. Comparison of flow rates of water measured by the Model 601 rotometer with the volume of water which was delivered in a given time showed that the factory curves for this rotometer were also accurate. The capacitor was measured on a bridge and found to have a value of 4.88×10^{-9} farads at 1000 Hz. Observation of the discharge curve of this capacitor gave an RC time constant of 3410 ± 25 seconds. This implied a system electrical resistance of 6.98×10^{11} ohms, which was good isolation. The Keithley electrometer was calibrated against the fixed voltage standard furnished by Honeywell for the calibration of the digital voltmeter. It was found that a corrective factor of 1.014 was needed. Comparison of the sweep time of the oscilloscope with 60 Hz line voltage gave a correction factor of 1.031.

In this experiment several assumptions were made about the validity of measurements. Most of these were that fluid parameters were the same inside the reaction chamber and in the lines leading to and from the chamber. For example, the air temperature was measured in a line about three feet from the chamber and it was assumed that the temperature in the chamber was the same. These assumptions were all justified in a simple way. In this case the shop air temperature never differed from the temperature of the room air by more than 1°F. Since the apparatus was in thermal equilibrium with the room air, there should have been very little heat transfer between the air used in the experiment and the experimental apparatus.

One of the assumptions was that no sulfur dioxide was absorbed by the water while it was on the stainless steel plate. To confirm the validity of this assumption water was placed in the bottom of the reaction chamber and tests made with the flushing air both on and off. The result was that much sulfur dioxide was absorbed when the flushing was not used but none was absorbed, within the limits of measurement, when it was employed. It is possible that some sulfur dioxide was desorbed at this point. This effect would lead to an unknown bias in the experimental data. It would not, however, affect the relationship of the samples since all were about the same concentration and were in contact with the flushing air for the same length of time.

The next area requiring consideration was the error produced in calculated results by random errors associated with reading instrument scales. In the calculation of S, this quantity was obtained as a function of c, E_2, R_1, t_2, W, and F_1. To a fair approximation, the standard deviation in S is equal to the square root of the sum of the squares of the standard deviations of the parameters (10). In this section, observed standard deviations will be denoted:

$d(c) = .2\%$ $\qquad d(E_2) < 1\%$

$d(R_1) = .8\%$ $\qquad d(t_2) < 1\%$

$d(W) < 1\ \%$ $\qquad d(F_1) \approx 2\%$

From these values the value of d(S) can be calculated: $d(S) < 2.7\%$.

Similarly, N_A is a function of F_1, W, R_R, Re, t_f, and the cell constant. The variations due to F_1 and W will cancel to a large degree, because they both appear in the numerator and denominator of the expression for N_A. Therefore, their contributions to the variation will be arbitrarily multiplied by 1/2. This leads to:

$$\frac{1}{2}d(F_1) = 1\% \qquad \frac{1}{2}d(W) < .5\%$$

$$d(T_R) = .5\% \qquad d(Re) = 2\%$$

$$d(t_f) = 2\% \qquad d(\text{cell constant}) = 1\%$$

From these values one can calculate

$$d(N_A) = 3.2\%$$

It is interesting to note that the standard deviation of 3.2 percent for N_A correlates well with the two percent standard deviation experimentally observed at "zero" charge density and 36 percent relative humidity. This might lead to the belief that larger deviations, elsewhere, are due to actual disturbances in the system. These disturbances are evidently associated with the presence of the high electric fields since they are not exhibited by the data at zero field strength.

CHAPTER IV

DISCUSSION OF RESULTS

The calculated quantities are listed in Table 3, Appendix I. The experimentally measured parameters are listed in Table 4, Appendix II. The relationship between surface charge density and specific absorption rate is summarized in Figures 4, 5, and 6. Surface charge density is related to applied voltage in Figure 7 and to drop radius in Figure 8. It is noted that the results in Figures 4 and 5 proved to be reproducible at later times. The results in Figure 6, however, are unconfirmed due to an inability to produce humidities that were in this range again. It is significant that all of the absorption rate curves have a somewhat parabolic appearance.

There are some observed effects which are attributed to contamination of the water. At the start of the experimentation, the water had a resistance of 100,000 ohms as measured by the conductance cell. At the end of the experimentation, the water had a measured 30,000 ohms resistance. This change would have little effect on the analysis of H_2SO_4 concentration but it could be important in surface phenomena. Thus, the smaller drops which formed at zero applied voltage during the latter part of the experimentation might be explained. Also, very small quantities of surface agents may cause a reduction in the rate of sulfur dioxide absorption (11).

From the figures in this chapter, it is seen that the absorption rate of sulfur dioxide is appreciably enhanced by high surface charge densities. At extremely high surface charge densities, the drop spontaneously breaks up into many small droplets. Measurements in this region would be very difficult because the drops are not all of the same size and they do not arrive at the bottom of the chamber in a periodic manner. Indications from extrapolation of the data show that the increase in absorption rate could even be termed dramatic under high surface charge conditions.

A scrubber which used a charged aerosol would be most efficient if it combined the production of the smallest aerosol with the highest obtainable surface charge densities. This could be done by charging the drop in a region where the gradient of the electric field was as low as possible. Next the charged drop would be broken into an aerosol by passing it through a region of high field gradient. During formation of the drop the only forces trying to break the drop up would be the mutual repulsion of the charges. When the drop entered the region of high gradient field, however, the field would interact with the different charges with different strengths as a function of location. This effect added to the mutual repulsion would break the drop into smaller drops.

Although it was not among the research objectives, it can be seen that, during any one day, the surface charge density is proportional to the applied voltage. The proportionality constant and the intercept seem to vary somewhat from day to day and with humidity change.

Data points 25, 26, 27, and 28 have been eliminated from the graphs as erroneous. Charged drops were observed to be deposited on the sides of the reaction chamber during these experiments and later comparison showed that points 26 and 27 were far from the others on the graphs.

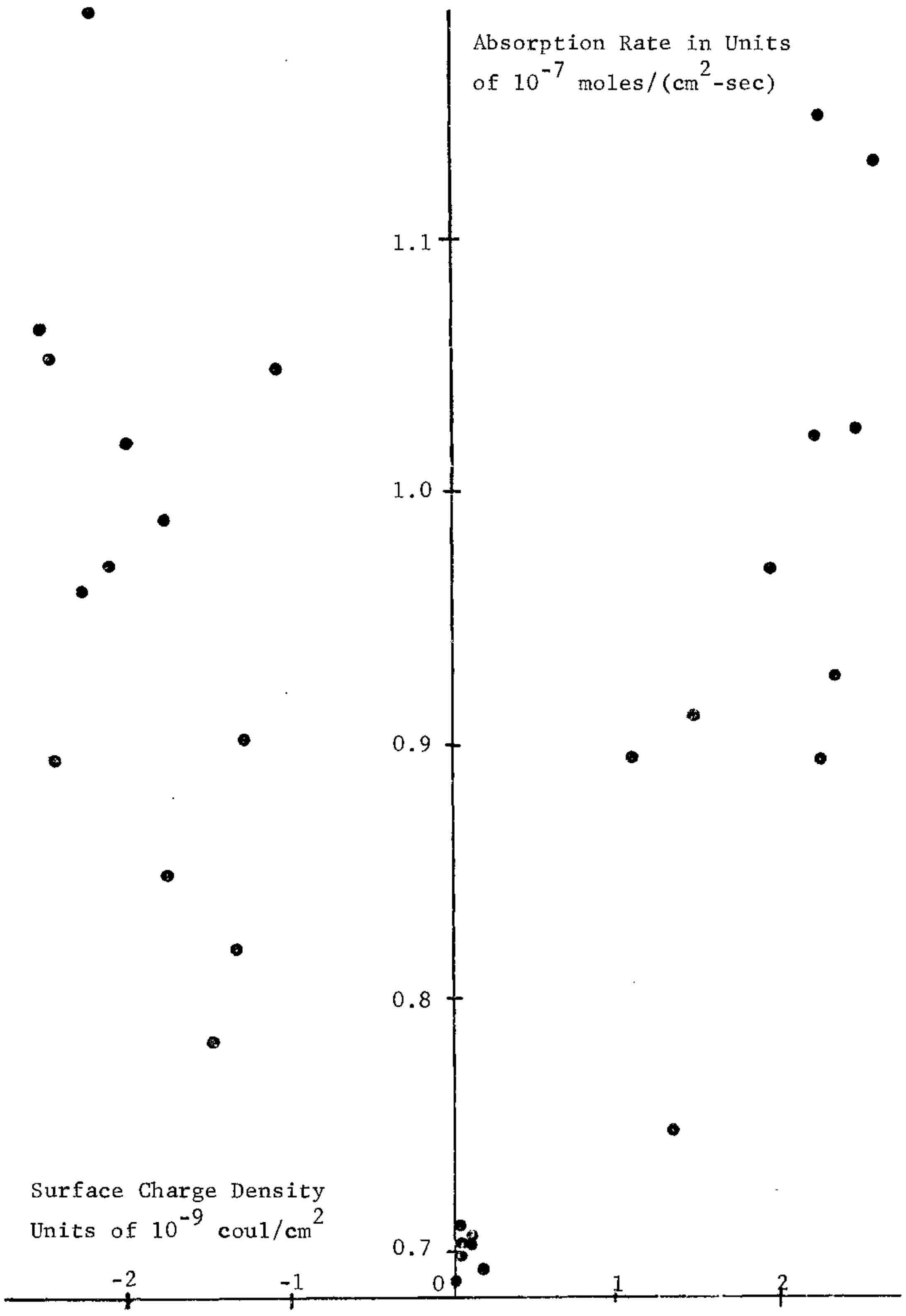

Figure 4. Specific Absorption Rate *versus* Surface Charge Density
The values were found at 36% relative humidity.

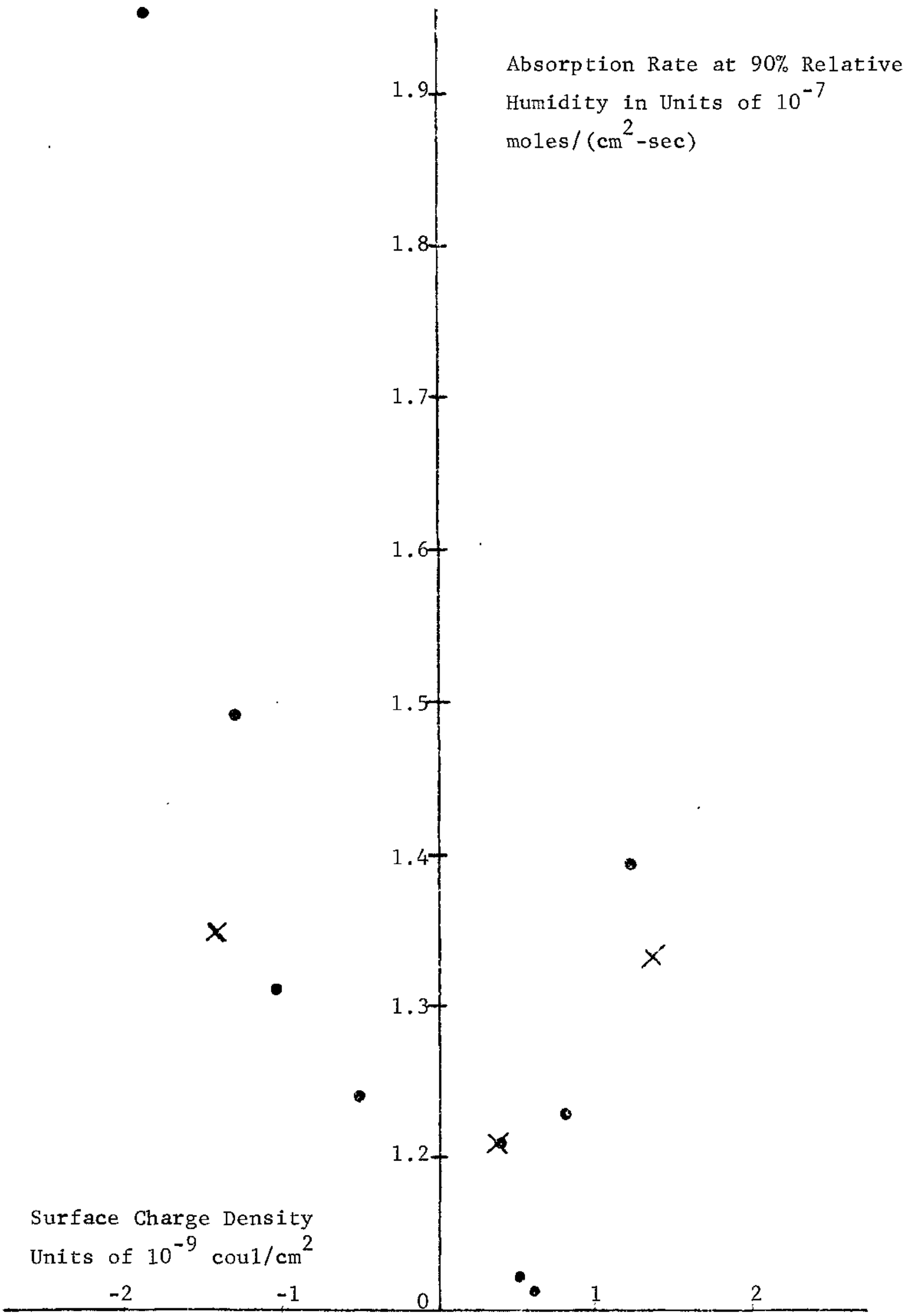

Figure 5. Specific Absorption Rate versus Surface Charge Density

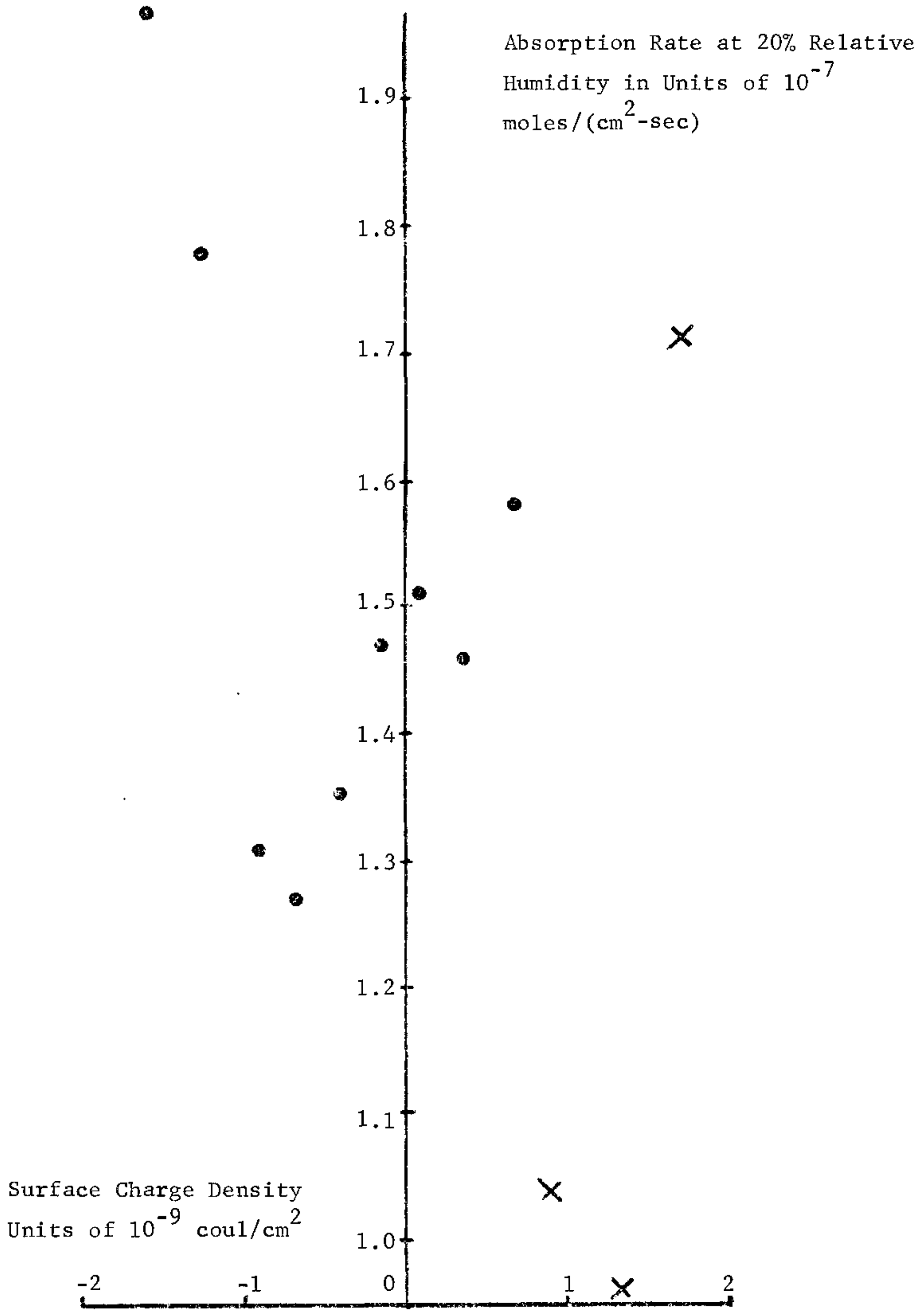

Figure 6. Specific Absorption Rate *versus* Surface Charge Density

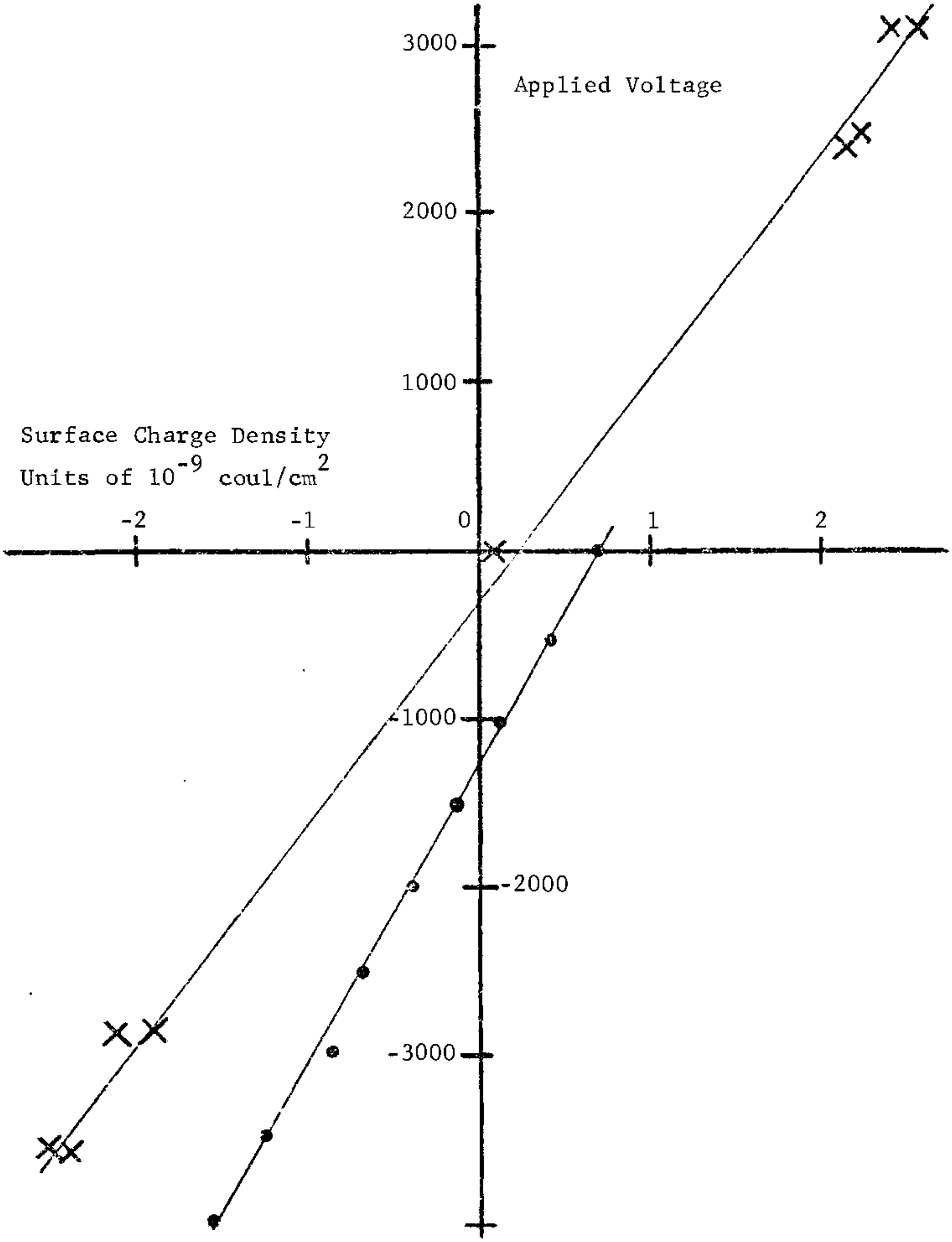

Figure 7. Surface Charge Density <u>versus</u> Applied Voltage

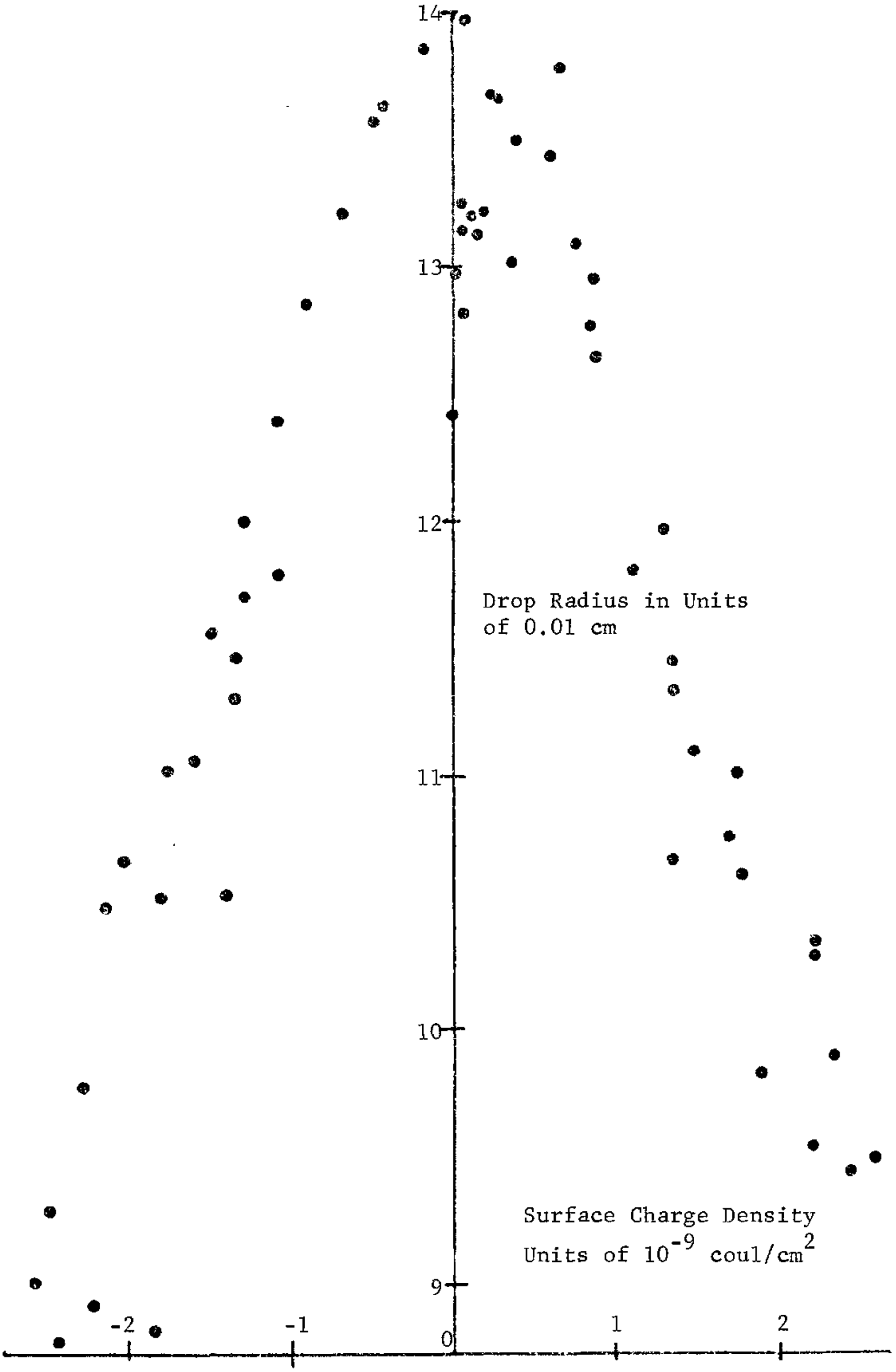

Figure 8. Drop Radius *versus* Surface Charge Density

CHAPTER V

CONCLUSIONS

1. Within the range of surface charge densities from -3×10^{-9} to 3×10^{-9} coul/cm^2, the specific absorption rate of sulfur dioxide by water drops increases with increasing magnitude of surface charge density.

2. Within the range of surface charge densities from -3×10^{-9} to 3×10^{-9} coul/cm^2, the surface charge density is proportional to the applied voltage.

3. The interaction of the needle, the water, and the air results in a positive electric charge on the drops which is influenced by other unknown quantities.

4. Humidity influences the specific absorption rate of sulfur dioxide by water drops, but the exact relationship was not established in this experiment.

CHAPTER VI

RECOMMENDATIONS

The effects observed in this research might be explained by either an increased diffusivity of the sulfur dioxide in the water or by an increased equilibrium concentration at the surface of the drop. If the latter hypothesis is true, then the equilibrium concentration in water will change with surface charge density. Much higher surface charge densities could be obtained by using a plane of water at very high potential.

The specific absorption rate could be studied using various chemicals and surface active agents in the water and using combinations of gases. It is the author's opinion that little could be discovered by examining the absorption of nonpolar gases by a charged liquid. This is purely his opinion unsupported by any experimentation.

APPENDIX I

This section contains a table of the parameters of interest in comparing the absorption rates which arise at various charge densities and relative humidities.

Table 3. Calculated Quantities

Run No.	N_A 10^{-7}	S 10^{-9}	R	t_R	V	RH (%)	T_w (°C)
1	Void						
2	Void						
3	1.58	0.681	.138	858	0	29.5	22.9
4	1.46	0.388	.135	801	- 500	23.6	23.5
5	1.51	0.0945	.140	853	-1000	20.9	23.7
6	1.47	-0.162	.139	847	-1500	19.8	23.7
7	1.35	-0.409	.137	792	-2020	20.6	23.9
8	1.27	-0.686	.132	730	-2525	19.7	24.0
9	1.31	-0.916	.129	672	-2995	19.9	23.5
10	1.73	-1.28	.120	570	-3500	20.1	23.5
11	1.97	-1.60	.111	470	-4010	19.7	23.5
12	1.04	0.903	.129	690	500	18.8	23.7
13	0.960	1.30	.120	556	1000	18.9	23.7
14	1.71	1.74	.108	467	1495	21.8	23.8
15	1.21	0.433	.137	827	0	82.5	23.8
16	1.12	0.620	.134	812	496	88.6	23.9
17	1.11	0.751	.131	753	1000	89.3	24.0
18	1.23	0.899	.126	701	1520	89.5	24.0
19	1.39	1.37	.113	544	2670	91.7	24.0
20	1.43	1.80	.106	512	3540	91.4	24.0
21	1.24	-0.508	.136	913	-1200	92.0	24.0
22	1.31	-1.04	.122	667	-2840	92.0	24.0
23	1.49	-1.36	.113	561	-3640	92.3	24.0
24	1.95	-1.96	.088	316	-5110	92.6	24.0
25	1.11	0.0101	.130	677	0	36.3	24.9
26	0.969	-2.24	.134	714	-2500	36.1	25.0
27	1.58	-3.27	.056	167	-3450	36.4	25.1

Table 3. Continued

Run No.	N_A 10^{-7}	S 10^{-9}	R	t_R	V	RH (%)	T_w (°C)
28	1.22	0.836	.128	650	1000	35.7	25.2
29	Void						
30	.706	0.0139	.130	806	0	35.7	24.6
31	.989	-1.81	.105	494	-2500	35.4	24.3
32	.846	-1.77	.110	465	-3830	37.7	24.8
33	.894	1.14	.118	542	860	35.3	25.0
34	.911	1.50	.111	472	1400	35.3	25.0
35	.971	1.95	.098	371	1880	35.2	24.9
36	1.19	-2.25	.090	333	-5085	36.7	25.0
37	1.21	.401	.130	744	0	82.9	25.0
38	1.35	-1.42	.105	442	-4580	82.9	25.0
39	1.33	1.38	.107	449	2140	82.9	25.0
40	.922	.316	.137	786	0	37.1	24.6
41	Void						
42	.694	.194	.132	682	0	39.5	25.5
43	.707	.163	.131	729	0	38.5	25.5
44	.733	.142	.132	729	0	37.9	25.6
45	.818	-1.35	.115	528	-2225	35.4	25.6
46	.903	-1.30	.117	544	-2220	36.6	25.5
47	1.05	-1.09	.117	544	-2220	36.1	25.5
48	.735	.0691	.132	713	0	36.7	25.0
49	.710	.0710	.133	724	0	35.1	25.0
50	.970	-2.14	.105	425	-2900	34.1	25.0
51	1.02	-2.03	.107	441	-2885	35.0	24.9
52	1.02	2.24	.103	407	2480	35.0	24.9
53	1.15	2.27	.103	407	2520	35.2	24.7
54	1.06	-2.55	.090	345	-3610	36.6	24.3
55	1.05	-2.49	.093	326	-3610	37.2	24.3

Table 3. Concluded

Run No.	N_A 10^{-7}	S 10^{-9}	R	t_R	V	RH (%)	T_w (°C)
56	1.03	2.47	.094	343	3160	37.2	24.6
57	1.13	2.64	.094	340	3175	36.4	24.7
58	.687	.024	.124	682	0	38.1	23.6
59	.748	1.38	.115	564	1990	38.2	23.8
60	.783	-1.51	.115	574	-2060	38.0	23.8
61	.926	2.38	.099	408	2800	37.0	23.8
62	.960	-2.31	.098	403	-2760	37.6	23.9
63	.698	.062	.128	734	0	37.0	23.9
64	.894	-2.45	.087	322	-3170	38.0	23.8
65	.891	2.27	.095	381	2890	37.0	23.8

APPENDIX II

This section contains a table of experimental data in which the symbols have the following meanings:

F_2 = the reading of the 603 rotometer

F_3 = the reading of the 604 rotometer

T_a = the air temperature

T_d = the dew point temperature

IR = the reading of the infrared analyzer

E_x = the capacitor voltage after x seconds

M = the mass of the sample

Table 4. Experimental Data

Run No.	W msec	F_1 ml/min	F_2	F_3	T_a °F	T_d °F	IR	E_{30}	E_{60}	E_{90}	E_{120}	M gm	Re	T_R °C
1	Void													
2	Void													
3	680	.946	1.99	3.30	76.1	42.0	60.5	1.4	2.8	4.2	5.6	24.767	75.2	25.0
4	625	.958	1.99	3.30	75.8	36.0	60.2	.8	1.7	2.5	3.3	24.665	82.1	25.0
5	675	.984	1.99	3.30	75.8	33.0	60.5	.2	.4	.6	.8	24.614	78.6	25.0
6	670	.975	1.99	3.30	76.2	32.0	60.3	- .3	- .7	- 1.1	- 1.4	24.672	80.5	25.0
7	617	1.006	1.99	3.30	76.3	33.0	59.1	- .9	- 1.9	- 2.7	- 3.5	24.662	90.7	25.0
8	559	1.009	1.99	3.30	76.7	32.3	60.2	- 1.62	- 3.19	- 4.67	- 6.09	24.648	99.7	25.0
9	504	1.031	1.99	3.30	76.3	32.2	60.2	- 2.3	- 4.5	- 6.5	- 8.4	24.709	101.4	25.0
10	408	1.034	1.99	3.30	74.6	31.0	60.5	- 3.4	- 6.7	- 9.8	-12.8	24.728	84.1	25.0
11	315	1.047	1.99	3.30	74.6	30.5	60.2	- 4.8	- 9.2	-13.4	-17.4	25.395	81.2	23.8
12	518	1.021	1.99	3.30	75.4	30.0	58.7	2.2	4.3	6.4	8.3	24.726	121.1	23.8
13	390	1.074	1.99	3.30	75.6	30.3	58.7	3.6	7.15	10.3	13.5	24.675	145.6	23.8
14	306	.994	1.99	3.30	75.8	34.0	58.1	5.0	9.8	14.4	18.5	24.724	86.1	23.8
15	650	.961	2.00	3.20	75.9	70.2	60.7	.92	1.79	2.58	3.29	24.656	100.0	23.8
16	636	.932	2.00	3.28	76.0	72.4	60.3	1.30	2.43	3.46	4.39	24.642	107.8	22.8
17	580	.947	2.00	3.29	76.4	73.0	59.9	1.64	2.95	4.04	4.91	24.687	112.0	22.9
18	530	.930	2.00	3.28	76.2	72.9	59.8	2.0	3.9	5.6	7.1	24.637	104.3	22.8
19	382	.930	2.00	3.28	76.6	74.0	60.0	3.4	6.3	9.1	11.8	24.633	104.6	22.5
20	355	.819	2.00	3.29	76.2	73.5	60.5	4.2	8.0	11.6	15.0	24.667	101.6	22.4
21	735	.831	2.00	3.20	76.0	73.5	61.7	- .94	- 1.88	- 2.70	- 3.53	24.582	93.4	22.5

Table 4. Continued

Run No.	W msec	F_1 ml/min	F_2	F_3	T_a °F	T_d °F	IR	E_{30}	E_{60}	E_{90}	E_{120}	M gm	Re	T_R °C
22	500	.876	2.00	3.25	76.1	73.6	61.0	- 2.4	- 4.1	- 6.9	- 8.9	24.633	101.8	22.5
23	400	.883	1.97	3.23	75.9	73.5	61.2	- 3.2	- 6.2	- 8.8	-11.5	24.629	97.3	22.8
24	173	.964	1.96	3.21	75.8	73.5	61.1	- 6.5	-12.5	-18.3	-23.4	24.659	94.0	22.7
25	505	1.064	2.13	3.23	77.9	49	59.8	.025	.048	.072	.094	24.853	118.7	24.4
26	548	1.064	2.13	3.23	78.4	49.3	59.4	- 5.4	-10.6	-15.6	-20.5	24.738	132.4	24.2
27	40	1.063	2.21	3.30	78.6	49.7	58.4	-18.8	-37.2	-56.6	-74.1	24.928	108.5	24.0
28	480	1.063	2.21	3.30	78.7	49.3	58.7	2.16	4.22	6.20	8.07	24.513	108.2	23.8
29	510	1.135	2.20	3.15	74.4	45.5	62.7	- .114	- 0.226	- 0.322			128	23.7
30	630	.847	2.16	3.14	74.2	45.3	61.2	.027	.054	.082	.109	24.917	167	22.7
31	335	.848	2.16	3.15	73.5	44.5	63.3	- 4.4	- 8.8	-13.2	-17.5	24.285	157	22.7
32	310	1.052	2.16	3.15	76.7	49	59.2	- 4.97	-10.0	-15.5	-20.8	24.816	182	22.7
33	375	1.073	3.16	3.14	77.6	48	59.8	3.10	6.22	9.34	12.6	24.940	164	22.7
34	310	1.073	2.16	3.15	77.6	48	59.6	4.51	8.78	12.9	17.1	24.602	169	22.7
35	215	1.073	2.25	3.17	76.5	47	60.5	6.46	12.8	19.1	25.4	24.572	175	22.7
36	191	.930	2.25	3.17	76.4	48	59.9	- 6.9	-14.0	-21.0	-28.0	25.093	143.9	22.5
37	570	.947	2.06	3.10	76.6	71	70	.91	1.84	2.47	3.40	24.495	143.3	22.3
38	288	.988	2.06	3.10	76.6	71	70	- 4	- 8	-12	-16	24.715	161	22.6
39	289	1.025	2.06	3.10	76.6	71	71.8	4	8	11.9	15.8	24.932	168	22.6
40	610	1.023	1.88	3.17	75.5	47.5	60	.70	1.4	2.13	2.91	20.935	146.5	24.0
41	Void													
42	510	1.105	1.89	2.99	76.2	49.8	59.9	.489	.997	1.45	1.92	24.638	204.5	23.8

Table 4. Concluded

Run No.	W msec	F_1 ml/min	F_2	F_3	T_a °F	T_d °F	IR	E_{30}	E_{60}	E_{90}	E_{120}	M gm	Re	T_R °C
43	555	.996	1.85	2.99	76.1	49.0	59.9	.375	.742	1.11	1.49	24.380	189	23.8
44	555	1.017	1.85	2.99	78.8	51.0	59.9	.323	.674	.982	1.30	24.481	184.5	23.5
45	365	1.007	1.89	2.95	78.4	48.8	58.5	- 3.56	- 7.15	-10.8	-14.2	24.441	184	23.3
46	380	1.026	1.89	2.96	78.4	49.7	59.3	- 3.42	- 6.89	-10.3	-13.6	24.832	168	23.7
47	380	1.030	1.89	2.96	78.4	49.3	59	- 2.84	- 5.84	- 8.71	-11.5	24.241	144.5	23.9
48	540	1.030	1.90	2.99	77.5	49	59	.168	.322	.482	.641	24.437	184	23.0
49	550	1.036	1.90	2.99	77.2	47.5	58.7	.169	.333	.497	.661	24.325	188	23.0
50	270	1.038	1.90	2.99	76.3	46	58.9	- 6.10	-13.0	-19.4	-25.7	24.580	173	23.2
51	285	1.04	1.90	2.99	75.2	45.7	58.9	- 5.49	-12.3	-18.2	-24.1	24.488	162.5	23.3
52	252	1.054	1.90	2.99	75.8	46.4	61.4	6.53	14.3	21.4	27.2	24.707	177	23.3
53	252	1.067	1.90	2.99	75.8	46.4	60.9	6.61	14.4	21.7	28.6	24.965	157	23.0
54	200	.894	1.90	2.99	76.0	47.6	60.8	- 7.8	-15.5	-22.3	-29.4	24.376	170.5	23.0
55	180	1.083	1.90	2.99	75.8	47.8	61.1	- 8.35	-18.5	-27.7	-32.4	24.786	185.5	23.0
56	194	1.056	1.90	2.99	75.8	47.8	60.8	7.92	17.6	26.3	30.9	24.838	184.5	22.9
57	193	1.064	1.90	2.99	75.5	47	60.8	8.81	19.1	27.8	32.7	24.653	166	24.0
58	510	.916	1.89	2.99	74.8	47.6	59.4	.055	.105	.160	.218	24.187	196	22.6
59	400	.917	1.89	2.99	75.0	47.8	59.2	3.29	6.45	9.66	14.3	23.852	196	22.6
60	410	.916	1.89	2.99	75.2	47.9	59.1	- 3.47	- 6.77	-11.3	-14.9	24.897	184.5	22.6
61	255	.918	1.89	2.99	75	47	59	6.22	13.6	20.4	27.1	24.697	178	22.7
62	250	.919	1.89	2.99	75.3	47.7	58.9	- 6.00	-13.5	-19.9	-26.6	24.178	172.5	22.7
63	560	.920	1.89	2.99	75	47	58.8	.136	.268	.398	.532	24.635	184	22.6
64	176	.916	1.89	2.99	75	47.7	58.7	- 7.77	-15.7	-23.2	-30.6	24.117	196.5	22.6
65	230	.920	1.89	2.99	75	47	58.8	6.72	13.1	19.6	25.9	24.288	189	22.5

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