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PARAMETERS AFFECTING HYDROGEN CHLORIDE MEASUREMENTS

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13. ABSTRACT (Maximum 200 words)

The launching of solid rocket boosters releases numerous gases, including hydrogen chloride. Monitoring the concentrations of these gases and predicting their atmospheric transport is required for safety reasons and for compliance with environmental laws. Monitoring of these gases is difficult because they are hydrophilic and tend to condense on atmospheric aerosols. Once such gases are condensed in the atmospheric aerosols, they will not appear on gas-phase sensors unless provision is made to evaporate the aerosols. Transport of the gases will also be governed by the chemistry in the aerosols and movement of the aerosols in the atmosphere, as opposed to the gas-phase chemistry alone. The objective of this project is to investigate the behavior of hydrogen chloride in the presence of atmospheric aerosols. The thermodynamics of HCl in the gas and liquid phase will be reviewed, and kinetics of mass transfer, diffusivity, and sticking coefficients on water of HCl will be measured. The evaporation of atmospheric aerosols will also be discussed.

14. SUBJECT TERMS

Hydrogen chloride, aerosol, diffusivity, sticking, condensation, atmospheric chemistry, laser fluorescence, hyrdophilic, humid air, water, salt water

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EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of this report was to characterize the physical state of hydrogen chloride (HCl) in air as a function of pressure and relative humidity, because a reliable estimate of the distribution of HCl between the gas phase and aqueous aerosols is needed to allow accurate modeling of the dispersion of this pollutant from successful launches and to direct emergency responses in the event of a catastrophic abort.

B. BACKGROUND

An ever-increasing number of atmospheric dispersion models are available to permit modeling of environmental impacts of atmospheric releases of toxic or pollutant materials. All but the most complex generally assume that the material dispersing is a passive component of the air mixture, whereas many of the emissions from rocket launches or aborts are capable of reacting with atmospheric constituents. Computational modules can be incorporated into codes to accommodate dense gases, terrain features, and transformations of the constituents, provided an experimental base adequate to permit generation of an analytical description of the phenomenon is available. This project was undertaken to address the question of the capture of HCl from the gas phase by condensed and uncondensed atmospheric water.

C. SCOPE

Behavior of HCl in the presence of water was predicted for three conditions: a stable fog, uncontaminated air, and above the dew point. Subsequent determinations at a range of relative humidities and pressures provided estimates of the efficiency of HCl--water collisions (sticking coefficient). These were compared with other known properties and found to be reasonable values. Infrared spectroscopic properties of HCl in air were found to be unchanged as a function of humidity (up to the dew point). Finally, estimates of rates of evaporation were calculated and shown to be unimportant under the conditions of the determinations, but potentially quite rapid under conditions of efficient heat transfer.

D. METHODOLOGY

Sticking coefficients were estimated by measuring the uptake of HCl by uniform-sized water droplets generated by delivery of water through a vibrating orifice. Contact times are calculated from the dimension across the gas path and the velocity of the droplets. A double-reciprocal plot of results from a series of determinations at different pressures was extrapolated to zero to determine the reciprocal of the "true" sticking coefficient.

Hydration of HCl was tested for by measuring the Fourier-transform infrared spectrum of HCl at different relative humidities. Related properties were calculated from known values as a check of reasonability of the values determined.

E. TEST DESCRIPTION

Two experiments were conducted to measure sticking coefficients, both involving rapid passage of HCl in air. In one, 0.005M quinine was added as a fluorescent probe, and the fluorescence spectrum of the falling drops was measured at a fixed point below their introduction into the HCl stream. In the second, the drops escaped against a slight pressure gradient of clean He into a collection chamber, whence the collected liquid was removed and titrated with aqueous alkali. Fourier-transform infrared spectra of HCl at graduated relative humidities from 0 to 40 percent were measured with a commercial instrument.

F. RESULTS

The sticking coefficient of HCl in air below 40 percent relative humidity is 0.3 ± 0.1. At higher humidities, water--HCl aerosols form, and the fraction of free HCl decreases at decreasing pressure. Henry's law provides an accurate estimate of the distribution in the presence of aerosols.

G. CONCLUSIONS

Below the threshold for aerosol formation, a dispersion model may ignore processes removing HCl onto water without compromising the accuracy of the calculation. At higher humidities, Henry's law provides a satisfactory description of the distribution of HCl between the two phases.

H. RECOMMENDATIONS

Modelers may wish to incorporate a module, activated at relative humidities exceeding 40 percent, to account for aerosol entrapment of HCl at high humidity conditions. However, as the transport properties of aerosols differ from those of buoyant gases, additional modifications will be required to accommodate the altered transport properties of aerosol-bound HCl.
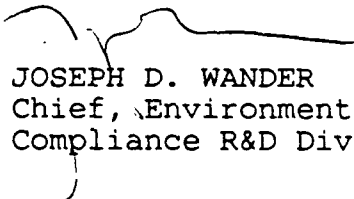
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PREFACE

This project is titled "Parameters Affecting Hydrogen Chloride Measurements," and the original principal investigator was Dr. Douglas M. Brenner. When Dr. Brenner left The Aerospace Corporation in November of 1987, Dr. L. Robbin Martin became the principal investigator. The laboratory work on mass transfer was conducted by Dr. N. Alan Abul-Haj, a National Research Council Postdoctoral Fellow. The laboratory work on spectroscopy was done by Dr. Karl Westberg. Questions should be addressed to Dr. L. R. Martin M5-754, The Aerospace Corporation, P. O. Box 92957, Los Angeles, CA 90009, telephone (213) 336-6920.

This technical report has been reviewed by the Public Affairs office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.

JOSEPH D. WANDER
Chief, Environmental
Compliance R&D Division

Neil J. Lamb, Col, USAF, BSC
Chief, Environics Division

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INTRODUCTION

A. PROJECT OBJECTIVES

Significant quantities of gases, including hydrogen chloride, are released at launch sites during firing of solid rocket boosters. The objective of this project is to investigate the behavior of hydrogen chloride in the presence of atmospheric aerosols. This is necessary for accurate monitoring of concentration levels and prediction of atmospheric transport of the hydrogen chlorides.

B. BACKGROUND

A number of gases that may be released at launch sites are toxic and may cause significant environmental impacts under unfavorable meteorological conditions. As examples, solid rocket boosters release hydrogen chloride as a combustion product, and hydrazines or nitric acid can be spilled from liquid fuel motors. Monitoring the concentrations of such gases and predicting their atmospheric transport is required for safety reasons and for compliance with environmental laws. Monitoring is complicated by the fact that the gases mentioned are hydrophilic and might condense on atmospheric aerosols. Should such gases be incorporated into the aerosols, they will not appear on gas-phase sensors unless provision is made to evaporate the aerosols during the analysis scheme. Furthermore, the environmental fate of such gases will be governed by chemistry in the aerosol and the transport of the aerosol in the atmosphere, rather than by gas-phase chemistry alone.

C. SCOPE

The amount of gas dissolved in the aerosol droplets will depend on both thermodynamic and kinetic factors. The main text of this report will be organized into four parts--one is thermodynamic, and three are kinetic.

The first part presents calculations of the atmospheric partitioning of HCl between gas and liquid phases for different, assumed environmental conditions. The second part discusses kinetic measurements of the rate of mass transfer of HCl from the gas to the liquid phase. This part was the main focus of the experimental work, and involves both diffusion and the sticking coefficient. The third part presents the results of some spectroscopic studies on HCl in humid atmospheres. This work is related to the diffusivity of HCl, and therefore is also related to kinetics and mass transfer. Last is a discussion of some work on the rate of evaporation of aqueous aerosols, and how this might influence the design of atmospheric sampling devices.

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SECTION II

THERMODYNAMICS: HCl--WATER EQUILIBRIA IN THE ATMOSPHERE

In any kind of kinetic work, it is very important to determine at the outset if the chemical reactions to be studied will go to completion. This basic requirement is sometimes overlooked in atmospheric chemistry. Such an omission can lead to serious error, because reactions that essentially go to completion in laboratory experiments may not do so at atmospheric concentrations. Gases of chemical interest in the troposphere may typically fall in the ppm to ppb regime, and at such low concentrations, the kinetic and thermodynamic behavior may be significantly different from the behavior at high concentrations.

This section will deal with the thermodynamic properties of HCl in aqueous solutions and will present some calculations of the fraction in the aqueous phase for various atmospheric conditions. These calculations will show that HCl concentrates in the condensed phase and that the kinetics of this process will be an important concern. Also, HCl concentrates more in the condensed phase of fogs and clouds at lower pressures than it does at higher pressures. This counter-intuitive property is caused by the extensive dissociation of HCl in water.

The dissolution of HCl in water may be described as a two-step process:

$$HCl(g) \rightleftharpoons HCl(aq) \qquad\qquad K_h$$

$$HCl(aq) \rightleftharpoons H^+ + Cl^- \qquad\qquad K_a$$
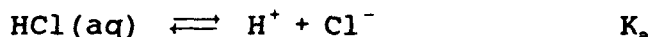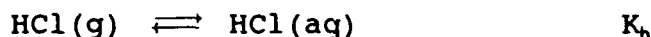
The first equilibrium constant is the Henry's law solubility constant, and the second is the acid ionization constant. From experimental work, the product of the two constants is well established (Reference 1):

$$K_h K_a = 2.0 \times 10^6 \ (moles/liter)^2 atm^{-1} = K$$

Solving the equilibrium relationship gives

$$P_{HCl} = \frac{\gamma_{\pm}^2 [H^+][Cl^-]}{K}$$

where $\gamma_{\pm}$ is the mean activity coefficient. The values for the individual equilibrium constants are not well established; the Henry's law constant is thought to be on the order of 2 moles/liter-atm, and the acidity is on the order of 10^6 moles/liter. The separate constants are not required for further calculations here, and we will just use the product of the two, which we will call K. In our atmospheric calculations,

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we will use actual experimental data for K, but first, we will look at an idealized treatment of the equilibria to gain a better physical picture of the behavior of HCl in water. In this simplified picture,

let

$$[H^+] = [Cl^-]$$

$$\gamma_\pm = 1$$

$$a_{H_2O} = 1$$

then,

$$[HCl] = \sqrt{KP_{HCl}}$$

For sea water, which is a common aerosol,

let

$$[Cl^-] = 0.5M + [H^+]$$

Then,

$$[HCl] = \frac{-0.5 + \sqrt{0.25 + 4KP_{HCl}}}{2}$$

These simplified equilibria are plotted in Figure 1, which gives total HCl concentration (mostly ionized) in the aqueous phase as a function of measured equilibrium partial pressure in the gas phase. Note that the aqueous concentration rises as the square root of the partial pressure. This idealized system may be contrasted with some experimental data from the literature in Figure 2 (Reference 2). The square root behavior is still followed for highly dilute systems. At high concentrations, the aqueous concentration rises still more slowly than the square root of the pressure because of changes in the activity coefficients.

The equilibrium data must be applied to three hypothetical atmospheric situations to show how HCl will partition between the gas and liquid phases. The three cases will be (1) preexisting fog, (2) "pure" air, and (3) natural aerosol. The calculation

SIMPLIFIED THEORY

EQUILIBRIUM PRESSURE OF HCl IN WATER AT 20^0 C.

PURE WATER

SALT WATER

[HCl], moles/liter

10

1

0.1

0.01

10^{-9} (1 ppb)

10^{-8}

10^{-7}

10^{-6} (1 ppm)

10^{-5}

10^{-4}
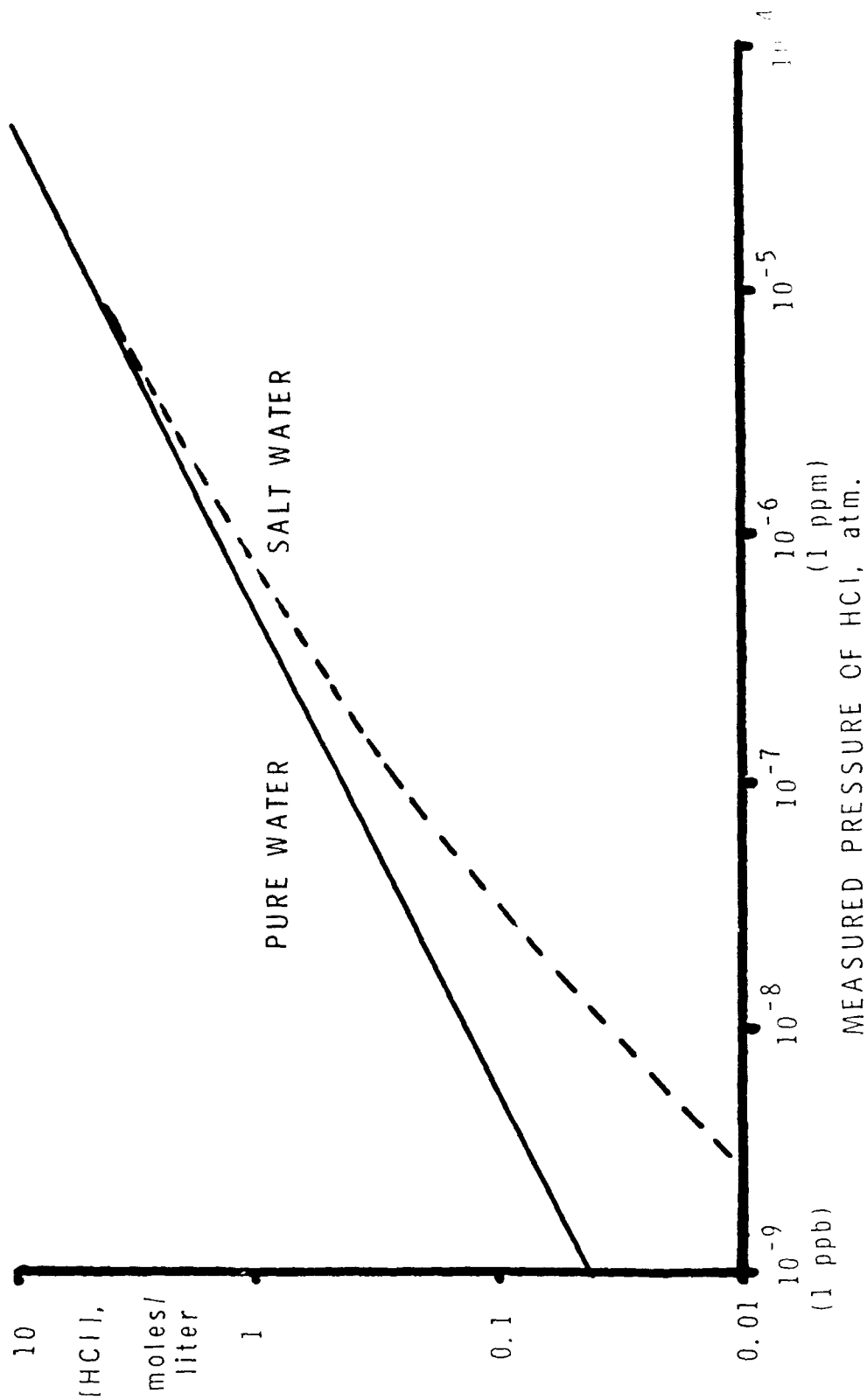
MEASURED PRESSURE OF HCl, atm.

Figure 1. Partial Pressure of HCl Over Water: Simplified Theory

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EXPERIMENTAL DATA OF FRITZ AND FUGET,
EQUILIBRIUM PRESSURE OF HCl AT 20°C.
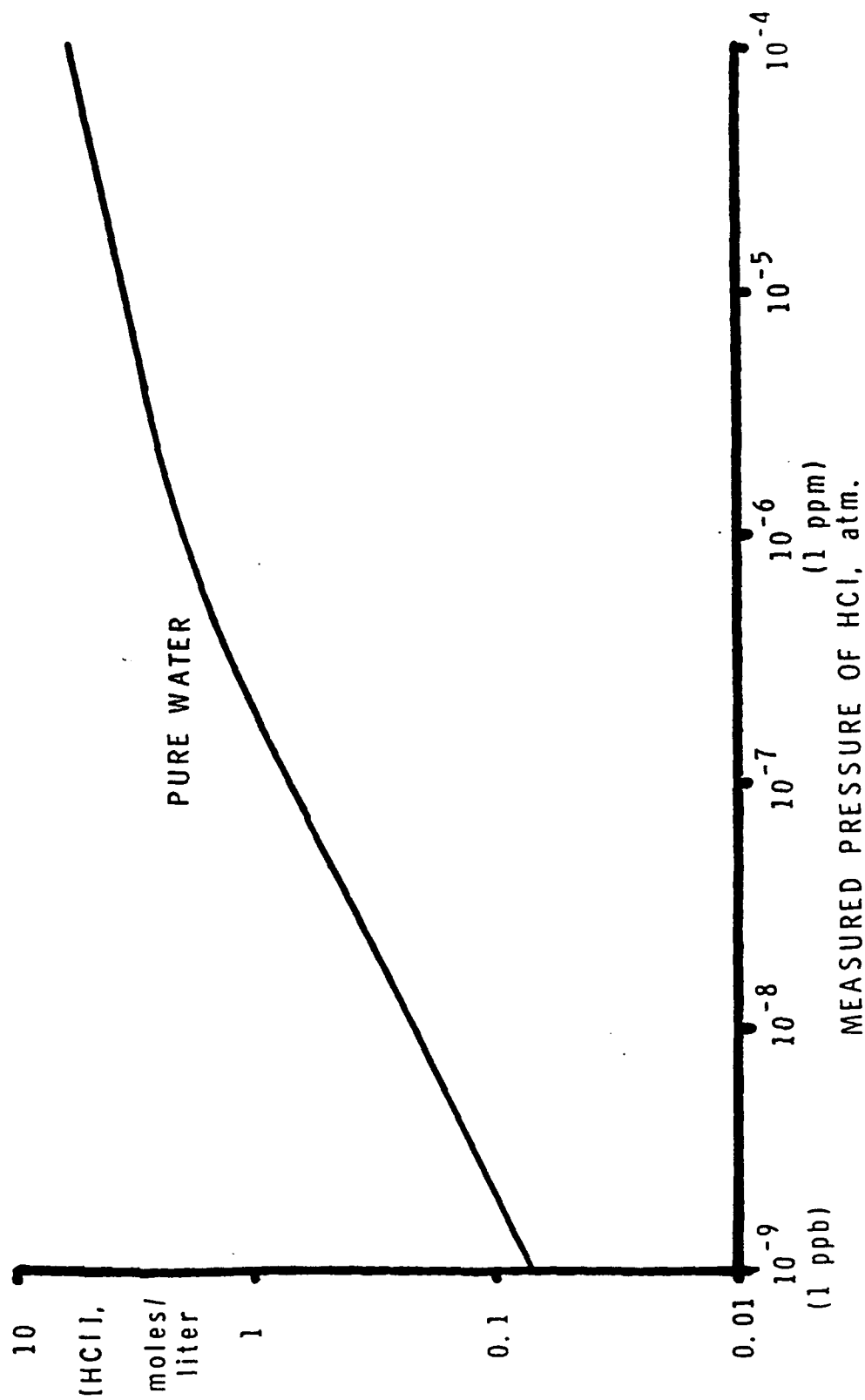
Figure 2. Partial Pressure of HCl Over Water: Literature Data

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begins by writing an expression for the percent of HCl in the *gas* phase:

$$\% = 100 \times \frac{m_{HCl}(g)}{m_{HCl}(g) + ([HCl] \times L)}$$

in which m_{HCl} is the total mass of HCl in the gas phase, [HCl] is the aqueous concentration of HCl and L is the liquid water content of the atmosphere.

A.   CASE 1:   PREEXISTING FOG

Fog is frequently found at coastal launch sites; this case is easiest to treat theoretically since it may be assumed that the amount of liquid water is a constant; *i.e.*, it is not affected by the amount of HCl. In this example, we will choose a nominal 1 mL of liquid water per cubic meter (10^{-3} liter/m^3). For this case, the formula gives

$$\% = \frac{100 \times \dfrac{1000P}{RT}}{\left[\dfrac{1000P}{RT} + \dfrac{[HCl]}{1000}\right]}$$

Simplifying,

$$\% = \frac{100}{\left[1 + \dfrac{RT[HCl]}{10^6 P}\right]}$$

This function is shown in a log-log plot in Figure 3. Note that the fraction of HCl in the gas phase *declines* as the partial pressure is lowered, and is less than 2 percent below 1 ppm measured HCl pressure. This behavior follows from the square root dependence of the total solubility of HCl in water. This behavior appears at first glance to violate Le Chatelier's principle. However, the apparent conflict with intuition about the Second Law of Thermodynamics is resolved because HCl ionizes nearly completely in the liquid phase; therefore the system gains entropy when the HCl dissolves in the aerosol. This entropy gain outweighs the entropy loss from concentration of the HCl in a small fraction of the total volume.

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CASE 1, PRE-EXISTING FOG.

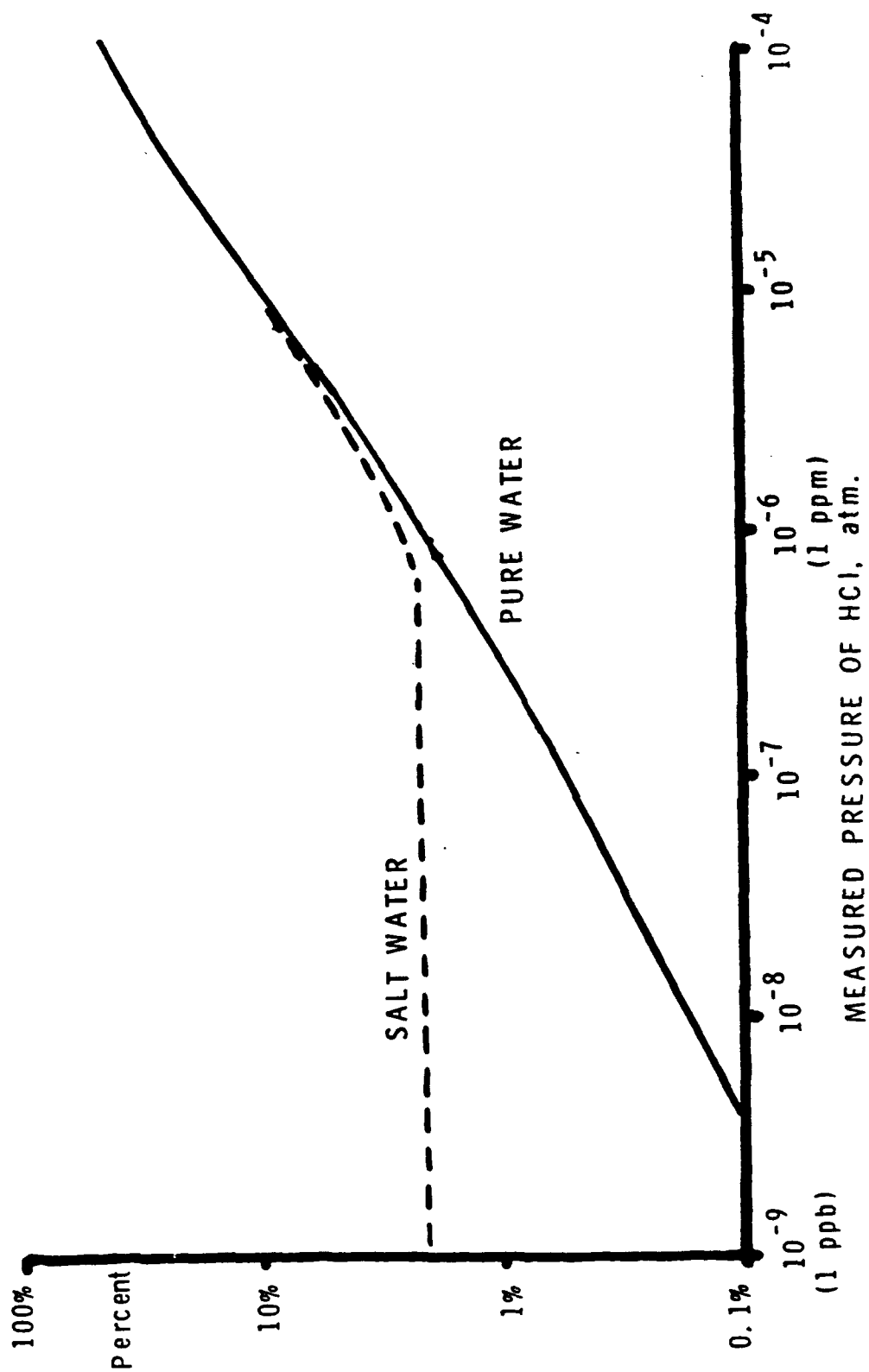PERCENT HCl IN GAS PHASE ($1 ml/m^3$, $20^o C.$)

Figure 3. Fraction of HCl in Gas Phase for Preexisting Fog

B.   CASE   2:   "PURE"   AIR

A second example will examine perfectly pure air, *i.e.*, air without preexisting aerosol particles. The title is in quotation marks because air without particles is found only in the laboratory; tropospheric air always contains some aerosol particles. Pure air is able to form aerosols when HCl is added, because concentrated HCl solutions have a reduced vapor pressure of water (this effect was neglected in Case 1). Thermodynamic data of the kind needed to make these calculations have been given by R. A. Rhein (Reference 3). We will quote two figures from Reference 3. The first (Figure 4) presents data on the temperature, humidity, and HCl concentration dependence of the existence ͼ an aerosol phase. The region to the right of each temperature ابeled curve is where the aerosol exists in equilibrium with gas. The existence of aerosol in pure air is favored by low temperatures, high relative humidity, and high partial pressure of HCl. Figure 5, from Rhein's paper, shows additional information for a single temperature curve at 20 Celsius. This figure has information on both the amount of aerosol and its composition as a function of HCl partial pressure and relative humidity at this temperature.

Using this information to generate a plot of percent HCl in the gas phase as in Figure 3, derives Figure 6. This kind of plot is of less use for pure air than it is for fogs. What it does say is that, for truly "pure" air, all of the HCl will be in the gas phase up to some critical concentration, then most of it will be in the aerosol phase above this HCl pressure. The point at which aerosol forms is very sensitive to the HCl pressure, as was shown in Figure 4. The dashed line showing the percent of HCl in the gas phase when aerosol is formed is only approximate. It differs from the corresponding part of the curve in Figure 3 because the amount of liquid water is not fixed. In calculations of this kind at extreme conditions it should be kept in mind that boundary conditions are important. This means that it is important to specify if additional water vapor is needed in the system to maintain the relative humidity at the specified values. The calculations shown are for fixed relative humidity, and would require the addition of water to sustain the large amounts of aerosol condensation predicted at these high loadings of HCl.

C.   CASE   3:   NATURAL   AEROSOL

Since the real troposphere always contains some aerosol, it would be useful to include the effect of this on the calculations. Doing this introduces many additional complications. For example, the natural aerosol will vary in composition and amount, depending on the site and the weather. In addition, the new substances introduced by the aerosol will greatly complicate the thermodynamics. Thus, this third case must be taken only as a qualitative indication of the effects

CASE II.   "PURE" AIR
(FIGURE FROM R.A. RHEIN)
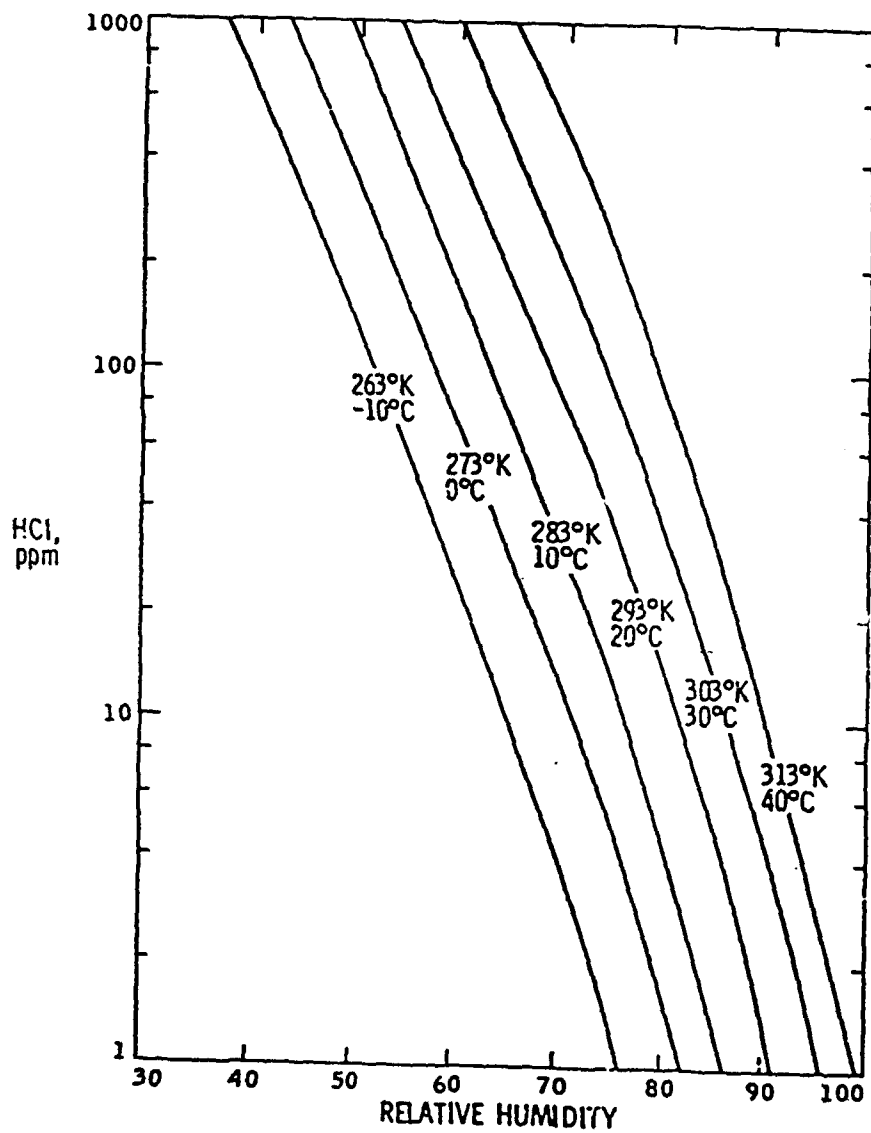
Figure 4.   Formation of HCl Aerosol in "Pure" Air
(from JPL Technical Memorandum 33-658)

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CASE II. "PURE" AIR
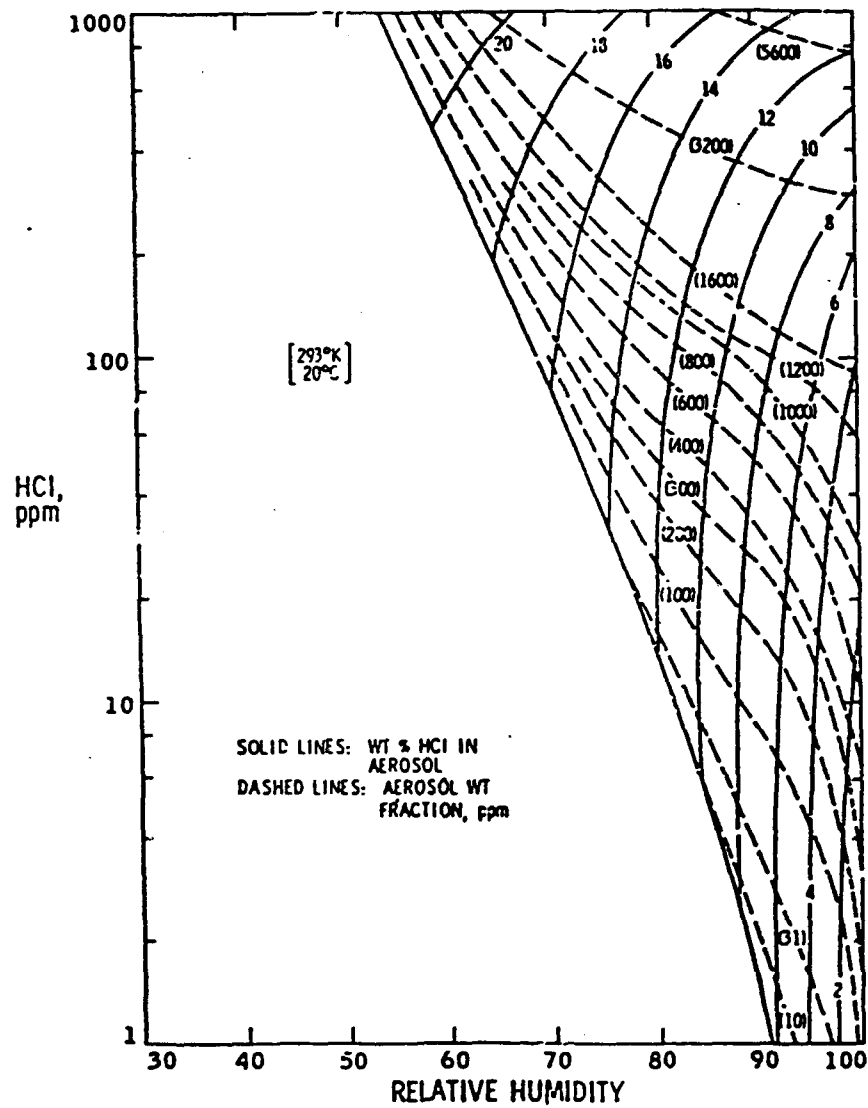## (FIGURE FROM R.A. RHEIN)

Figure 5.   Composition of HCl Aerosol in 'Pure" Air
(from JPL Technical Memorandum 33-658)

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CASE II, "PURE" AIR, 75% RELATIVE HUMIDITY, 20°C.

%HCl IN GAS PHASE

AEROSOL FORMATION
AT 30 PPM HCl

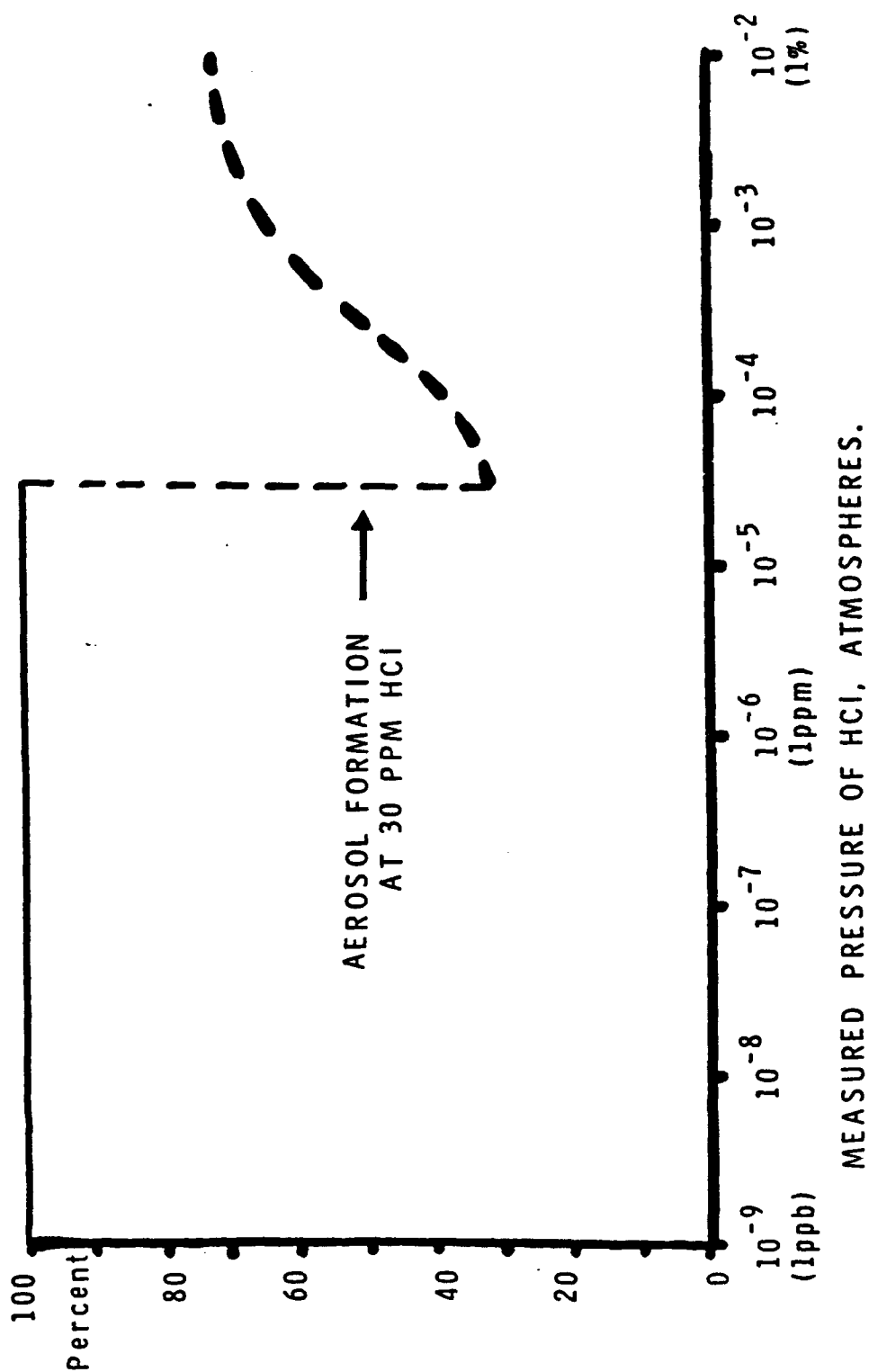MEASURED PRESSURE OF HCl, ATMOSPHERES.

Figure 6. Fraction of HCl in Gas Phase for "Pure" Air

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that may be expected, and the numbers are not very meaningful unless a full study with a comprehensive computer model is carried out. Attempts at developing full models have been made by Seinfeld, *et al.* (Reference 4).

Figure 7 quotes some data from Reference 5 on the hygroscopicity of the natural aerosols. Such aerosols typically contain sea salt, which is hygroscopic because of the magnesium chloride present, or ammonium bisulfate, which mostly comes from sulfur pollution and is also hygroscopic. The highly simplified picture used for the calculations for Case 3 assumes that at low HCl concentrations, the preexisting aerosol simply provides an amount of pure liquid water given by Figure 7. This liquid will allow some of the HCl to leave the gas phase at low concentrations of HCl. At high levels of HCl, the effect of the natural aerosol will be negligible, relative to the HCl itself. The final result is shown in Figure 8, which gives the estimated percent of HCl in the gas phase as a function of HCl partial pressure in natural air. Because the amount of liquid present in the natural, *i.e.*, unpolluted and not foggy troposphere, is small, the HCl should be mostly observable in the gas phase at low partial pressures. This conclusion must be taken with caution, however, because a relatively small amount of pollution or water vapor from a launch could greatly increase the amount of liquid available. If large amounts of steam are present as a result of a launch, then large amounts of aerosol would be expected, with an expected large percentage of the HCl in the liquid phase.

CASE III, NATURAL AEROSOL.

ASSUME 200 MICROGRAMS (DRY WEIGHT) PER m^3.

(TYPICALLY NaCl, NH_4HSO_4, $MgCl_2 \cdot XH_2O$)

(FIGURE FROM RASOOL)
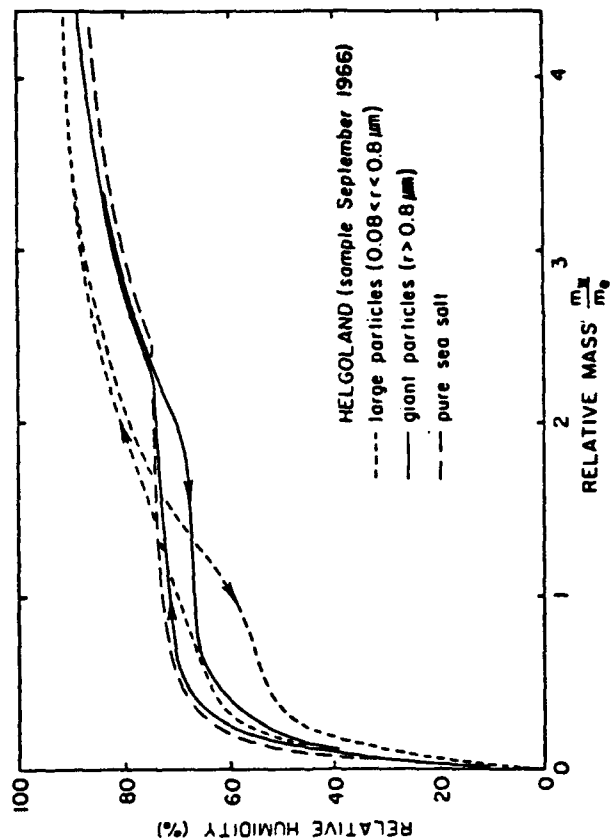
Variation of the relative mass of a maritime aerosol deposit with relative humidity

(By courtesy of *Ann. der Meteorologie* and Junge.)

THUS, AT 75% R.H., ABOUT 400 MICROGRAMS H_2O PER m^3
WILL BE PRESENT.

Figure 7.   Composition of Natural Aerosol

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CASE III. NATURAL AEROSOL, 75% R.H., 20°C.

% HCl IN THE GAS PHASE

Percent

100

80

60

40

20

0

10^{-9} (1ppb) 10^{-8} 10^{-7} 10^{-6} (1ppm) 10^{-5} 10^{-4} 10^{-3} 10^{-2} (1%)
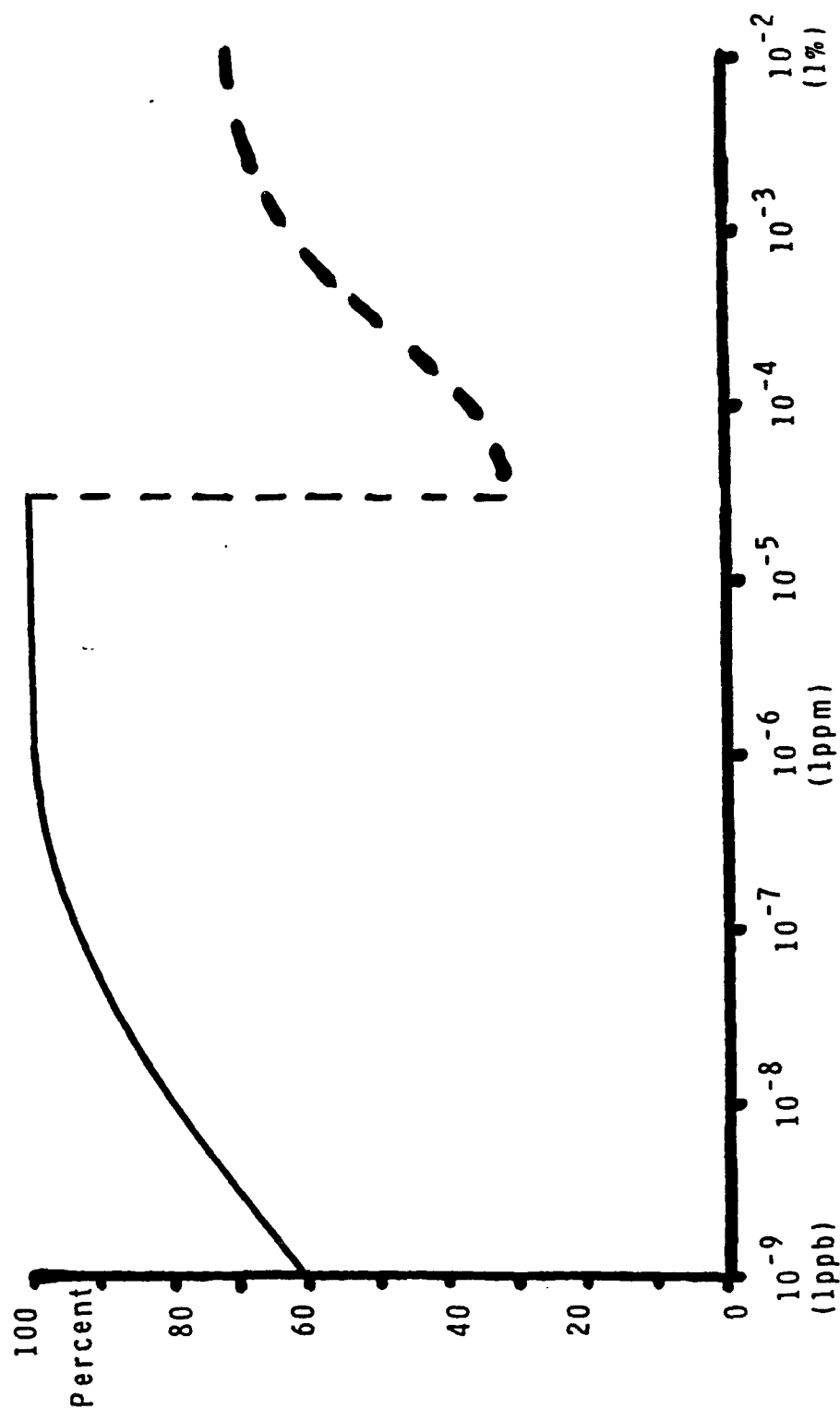
MEASURED PRESSURE OF HCl, ATMOSPHERES.

Figure 8. Fraction of HCl in Gas Phase for Natural Aerosol

SECTION III

KINETICS: STICKING COEFFICIENT MEASUREMENT

A sticking coefficient is the probability that a gas molecule striking a surface will adhere to that surface. Thus, a sticking coefficient of unity means that 100 percent of the gas molecules striking a surface will stick to it, and a coefficient of zero means that all of the gas molecules are reflected upon collision with the surface. Sticking coefficients are of interest in gas--liquid or gas--solid reactions whenever mass transfer between phases is rapid. Rapid transfer is typically encountered when dealing with small systems such as aerosol droplets or capillaries at atmospheric pressure, or in any system at low pressure. In these cases, gas-phase diffusion is rapid, and the sticking coefficient becomes a significant factor in the rate of mass transfer. Such systems are encountered in fogs and clouds in the troposphere, and at high altitudes, where the pressure is low and release of liquids may produce an aerosol.

Measurement of sticking coefficients is difficult, because an experiment must be designed in which mass transfer across a phase boundary (sticking) is the rate-limiting step. This, in turn, means that diffusive resistance to mass transfer must be kept to a minimum by operating at low pressure or with small particles or both. In addition, the time scale must be short (on the order of milliseconds) because mass transfer is rapid on aerosols and saturation will set in at longer times, invalidating the measurements.

The requirement for small particles and short times also means that it is difficult to set up boundary conditions for kinetic measurements of this kind. In cloud chambers, for example, it is impossible to change the chemical environment of the cloud in a short time. Thus, such experiments do not lend themselves to this kind of study. For these reasons, it was not until quite recently that meaningful measurements of sticking coefficients of any kind were available. It is still true that only about six reports have been made of sticking coefficients for gases on water.

Our laboratory apparatus meets difficult boundary conditions by passing a stream of microdroplets moving at high speed through an atmosphere of gas containing small amounts of HCl. The amount of HCl entering the droplets may be measured by a laser fluorescence technique, or by a collection/bulk analysis technique. The droplets are small enough that diffusion is rapid compared to the sticking process, and the time scale is kept short by the high speed of the droplets and a short interaction zone with the HCl. These measurements have produced a value for the sticking coefficient, and also have shown how the effect of diffusion and sticking may be combined quantitatively to give net rates of mass transport over a wide range of pressures and particle sizes. The latter information is based on our data being consistent with a theory of mass transport developed by S.

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E. Schwartz (Reference 6).

A. LASER FLUORESCENCE METHOD

The experimental setup for the laser fluorescence studies is shown schematically in Figure 9. The output of a Spectra Physics Nd:YAG laser, Model DCR 2A, is doubled to pump a Spectra Physics tunable dye laser, Model PDL-2. The dye laser operates on DCM dye from Exciton Corporation, and the output is frequency doubled to give 320-nm wavelength radiation delivering approximately 2 millijoules/pulse at 10 pulses/second. The fluorescence from the microdroplets is collected and imaged on the entrance slit of a SPEX Model 1870, 0.5-meter monochromator. The output of the monochromator, in turn, is collected on a vidicon-type optical multichannel analyzer controlled by a computer, EG&G Model 1460-V OMA III. The droplet generator is a Berglund--Liu type (Reference 7) vibrating orifice device (TSI Model 3054) driven by a Hewlett--Packard frequency synthesizer, Model HP3325A with high-voltage output. The droplet generator is fed from a pressurized liquid reservoir, and the liquid is high-purity water containing quinine hydrochloride indicator, 5×10^{-3} moles/liter. There were typically 33,000 droplets/second, with a radius of 25 micrometers.

Calibration of the laser fluorescence system was done in two ways. First, spectra were obtained for a series of HCl concentrations in the indicator using a standard liquid cell spectrometer. Second, spectra were obtained for the same solutions in the droplet system. These two methods gave identical spectra for the same amounts of HCl. From these spectra, a calibration curve was constructed which is shown in Figure 10. Figure 11 shows a series of droplet spectra at different partial pressures of HCl in the carrier gas.

Examination of the series of spectra in Figure 11 will show that the system displays an isosbestic point near 4200 angstroms. This is because the two peaks correspond to a singly- and doubly-protonated quinine species. It is not necessary to determine the ratio of the two species in order to obtain data, however. The calibration curve is empirically correct and is all that is required to establish the amount of HCl in the droplets.

A schematic of the gas-handling and mixing system is shown in Figure 12. This system is able to prepare mixtures of HCl and helium at specified relative humidities.

B. COLLECTED DROPLET METHOD

Laser light entering the microdroplets may not uniformly sample the droplet volume, because of internal reflections. If there is a radial concentration gradient of HCl in the droplet

pressurized
liquid
reservoir

HP
function
generator

TSI
vibrating orifice
droplet generator

collection optics

Spex 0.5-m
monochromator

cylindrical
lens

WEX
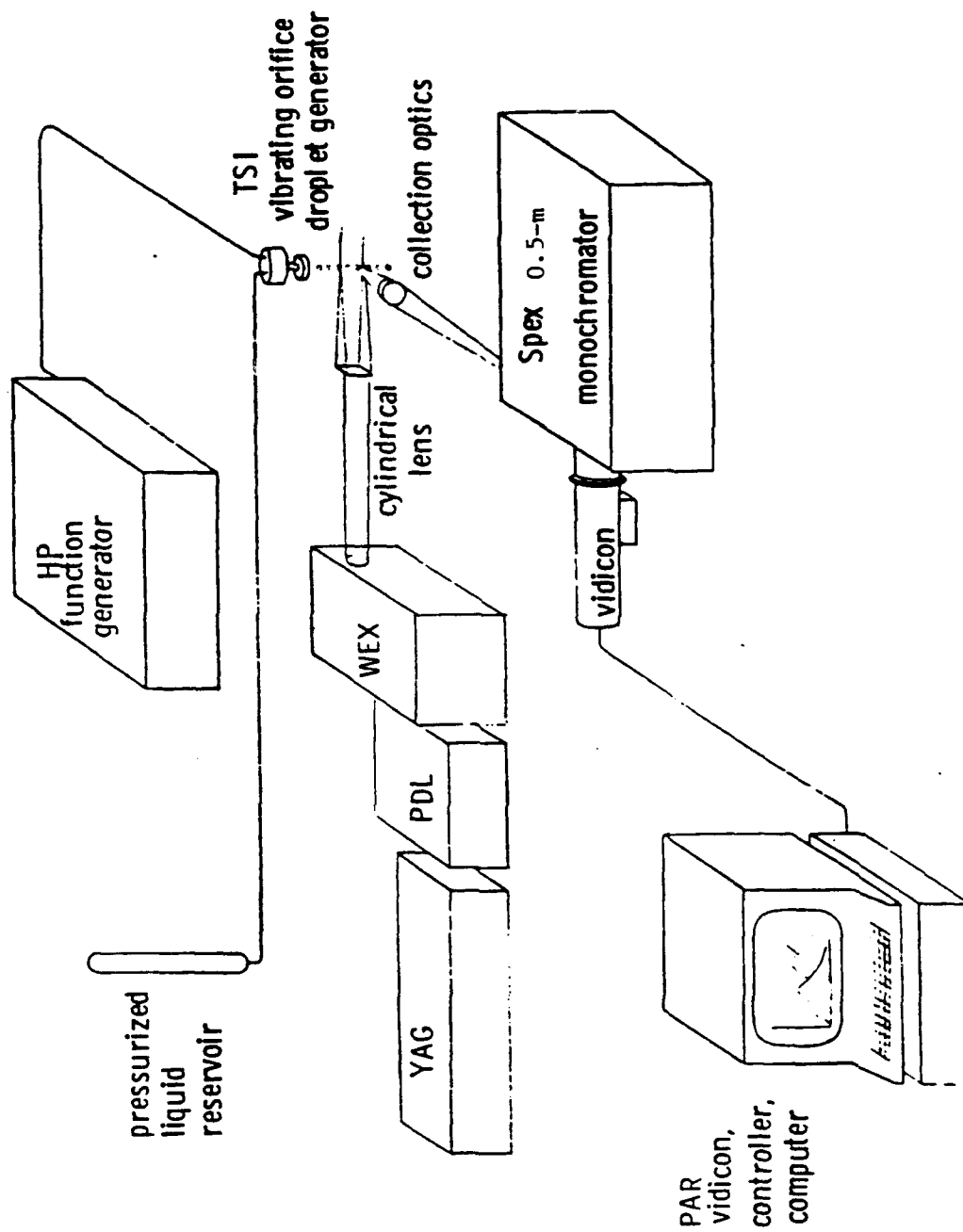
PDL

vidicon

YAG

PAR
vidicon,
controller,
computer
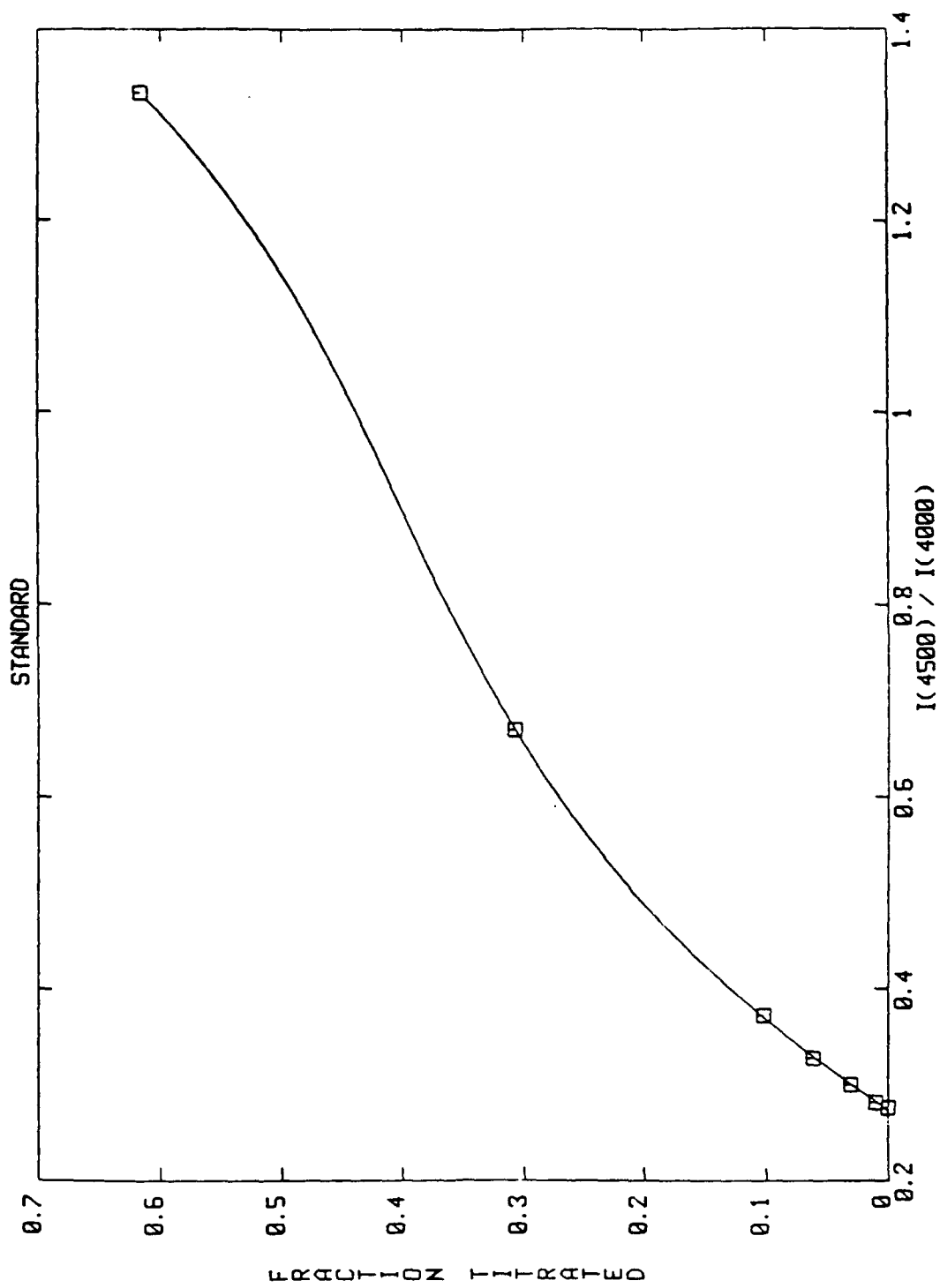
Figure 9. Schematic of Laser System

Figure 10. Fluorescence Calibration Curve

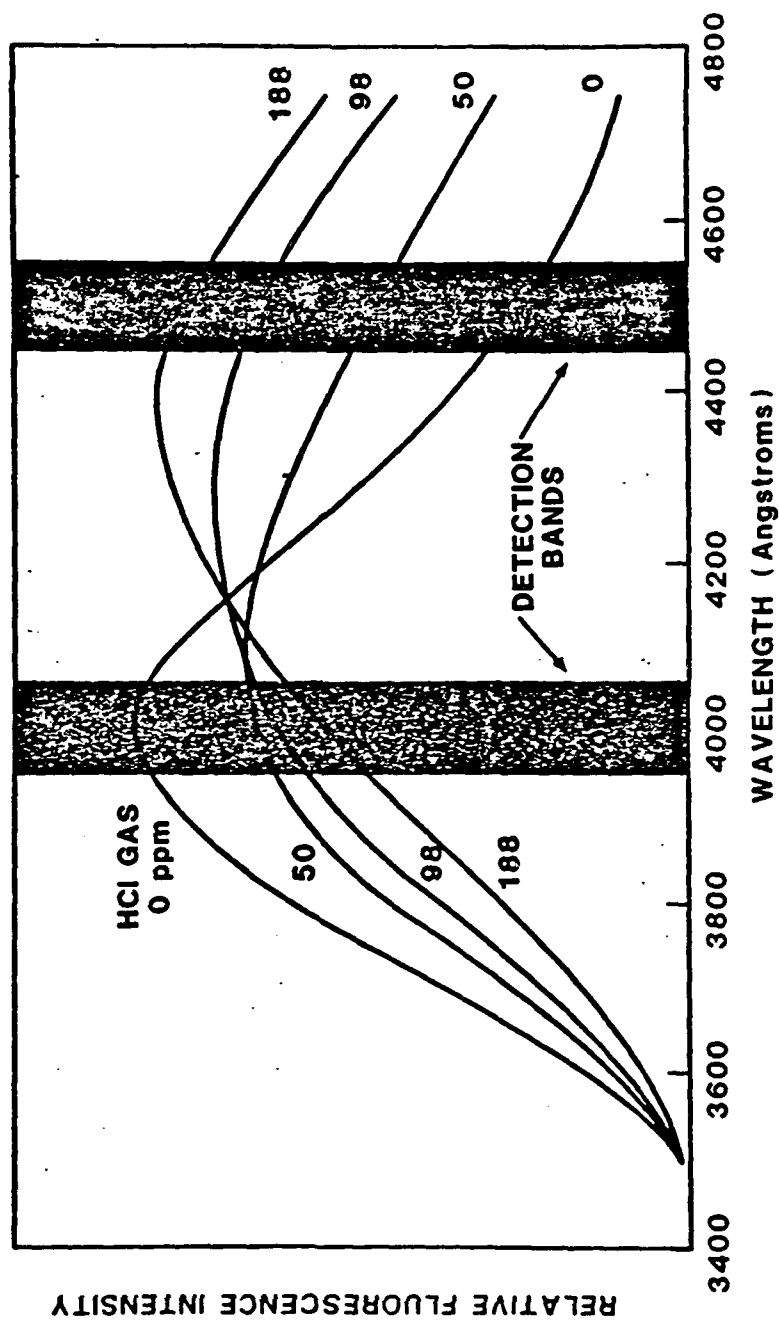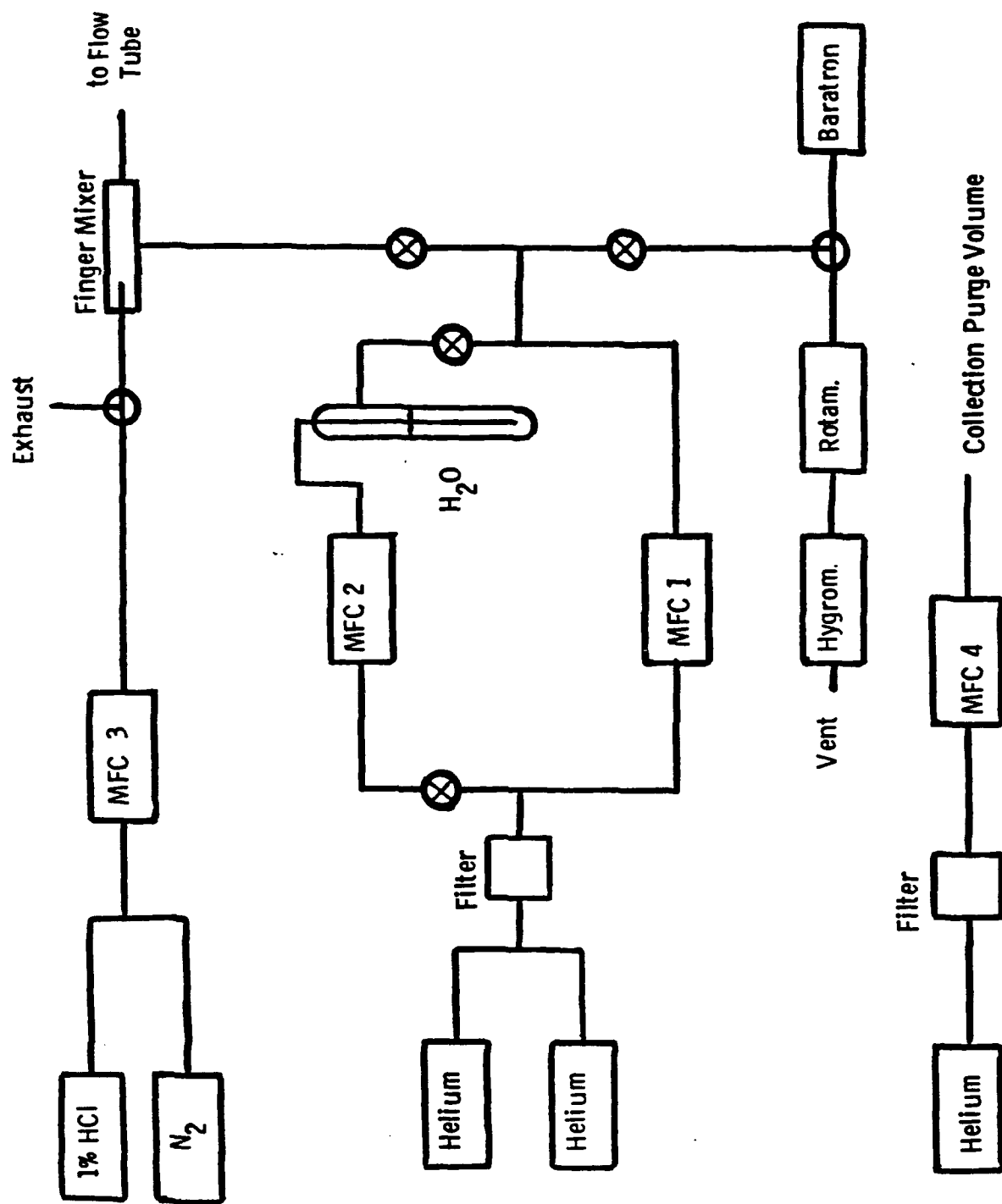# Quinine Fluorescence from Isolated Droplets

Figure 11. Microdroplet Spectra

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Figure 12. Schematic of Gas Handling System

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because of diffusion rate limitations, there may be errors in the sampling. Because of these concerns, a series of experiments was based on collection and bulk analysis of the droplets.

Figure 13 shows the collected-drop experimental apparatus. The droplets are fired across a 1-cm-diameter flow tube, while the HCl/carrier gas is flowing down the tube. The droplets then enter a collector filled with inert gas to stop the exposure. A small purge flow keeps the HCl out of this region. Since the dissolution of HCl in water is essentially irreversible, there is no loss of HCl from the liquid after it enters the collection chamber. Thus, time resolution of the order of a millisecond is achieved by the high droplet speed and short path lengtn. The entire system may be operated at reduced pressure to vary the diffusivity of the carrier gas. After the system has run for about 15 minutes, liquid is removed through the "air lock" for analysis. An aliquot of the liquid is titrated with standardized sodium hydroxide solution, and the end point is measured with a pH electrode. This method eliminates the need for quinine indicator in the microdroplets.

C. EXPERIMENTAL DATA

Determination of the sticking coefficient is a two-step process, because of the complex interaction between diffusion and sticking. The first step is to prepare plots of the amount of HCl entering the droplets as a function of partial pressure of HCl in the carrier gas at constant total pressure. The carrier gas in all of these experiments was helium, in which HCl has a high diffusivity. Examples of these plots are given in Figure 14 for the laser experiments and in Figure 15 for the collected droplet experiments. Both types of data are linear, but there is a difference of about a factor of three in the HCl concentration, which we believe is due to the sampling error in the laser method. Therefore, the laser data are corrected for this calibration error in the plots.

Achieving linearity in these plots was difficult, because the sticking coefficient is so large that there is a tendency for the surface of the droplet/and or the indicator near the surface to saturate with HCl. This effect was overcome by using rather high concentrations of quinine: 5×10^{-3} moles/liter. Another problem was depletion of the HCl in the carrier gas. This was overcome by use of a "delivery" tube of waxed glass to ensure rapid and uniform flow of the gas across the droplets. In the collected droplet experiments, the flow tube achieves this inherently.

These plots are obtained at constant total pressure, and therefore at constant diffusivity. The slope of the plots gives an "observed" sticking coefficient, which is the apparent sticking coefficient at this diffusivity. The observed sticking

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DROPLET GENERATOR

HCl FLOW

COLLECTION
VOLUME PURGE

AIR/VACUUM

"AIR LOCK"

LIQUID REMOVAL
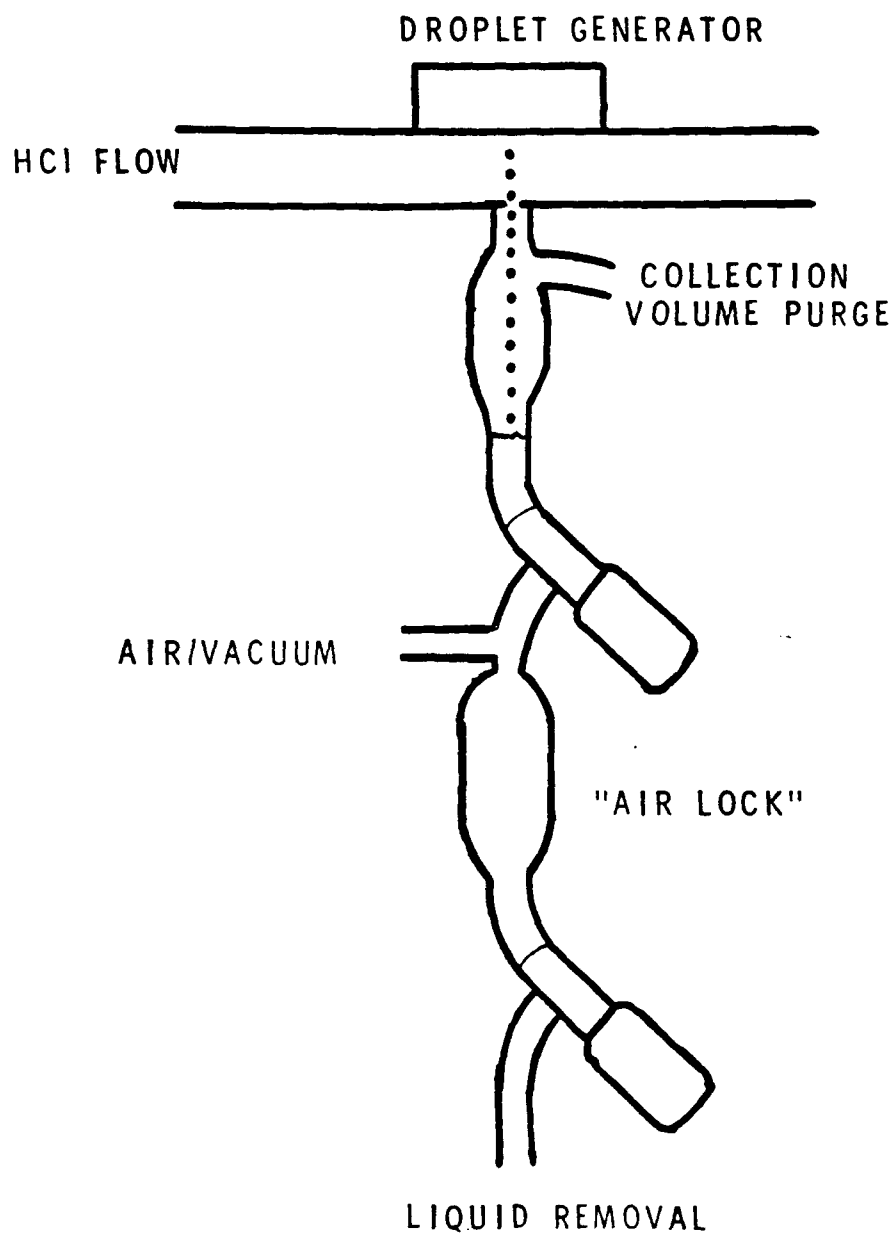
Figure 13.   Schematic of Collected Drop Apparatus

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LASER DATA 50% R.H.

P71.8263 [HCl] = 27.031   * PHCl + 5.74294E-06

α_{obs} = 0.17
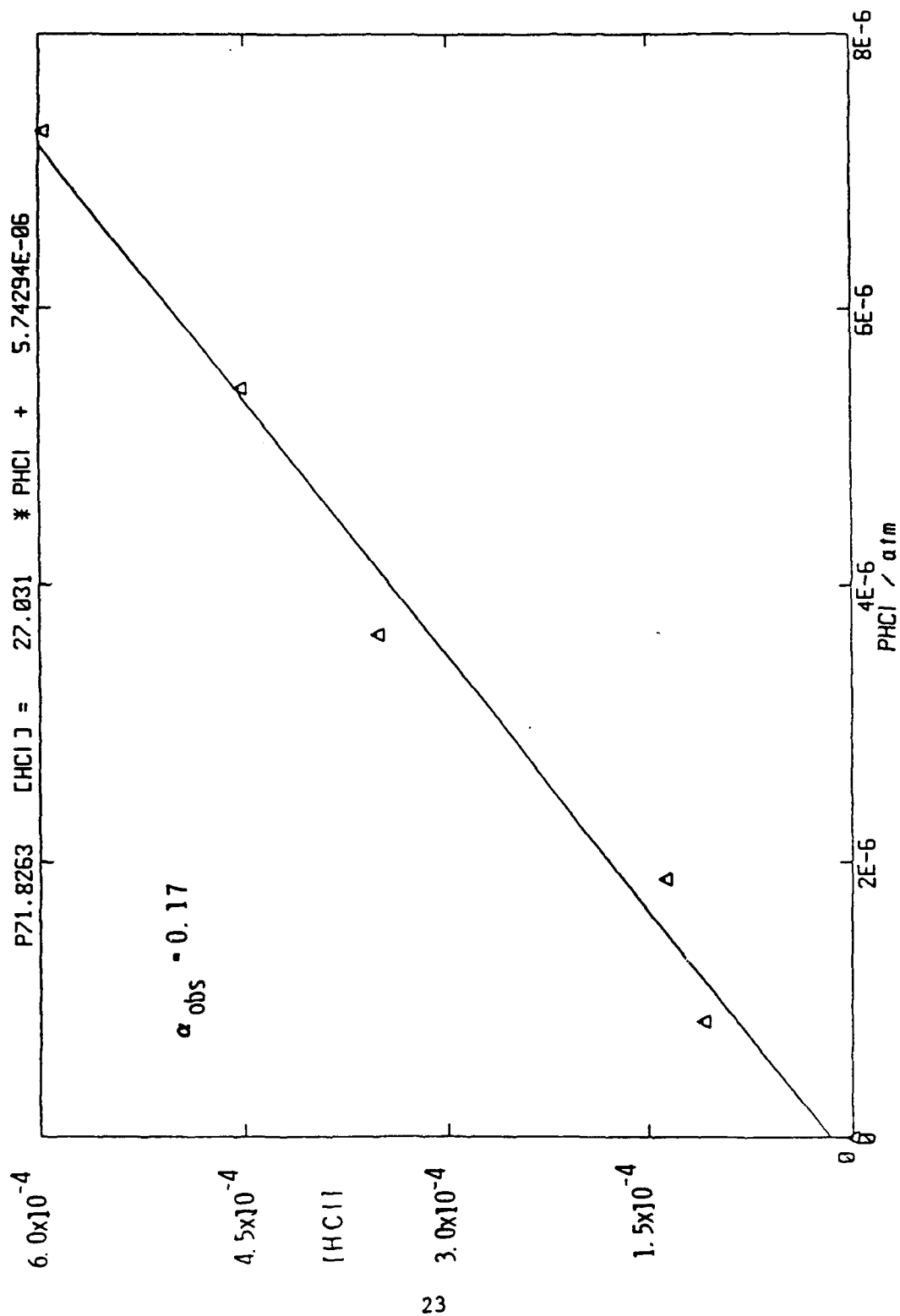
Figure 14. Laser Data. [HCl] vs HCl Pressure

COLLECTED DROP DATA, DRY

P200.F7   [HCl] =   52.191   * PHCl   + -7.88835E-06

α_{obs} = 0.061

[HCl]

PHCl / atm

Figure 15. Collected Drop Data. [HCl] vs HCl Pressure

coefficient is computed from the following formulas:

$$\alpha_{obs} = \frac{observed\ rate\ of\ mass\ transfer\ to\ drop}{maximum\ collision\ rate\ of\ HCl\ with\ drop}$$

$$= \frac{R}{\left[\dfrac{P_{HCl}v}{4RT}\right]\left[\dfrac{4\pi r^2}{(4/3)\pi r^3}\right]}$$

$$= \frac{[HCl]}{t} \cdot \frac{4rRT}{3P_{HCl}v}$$

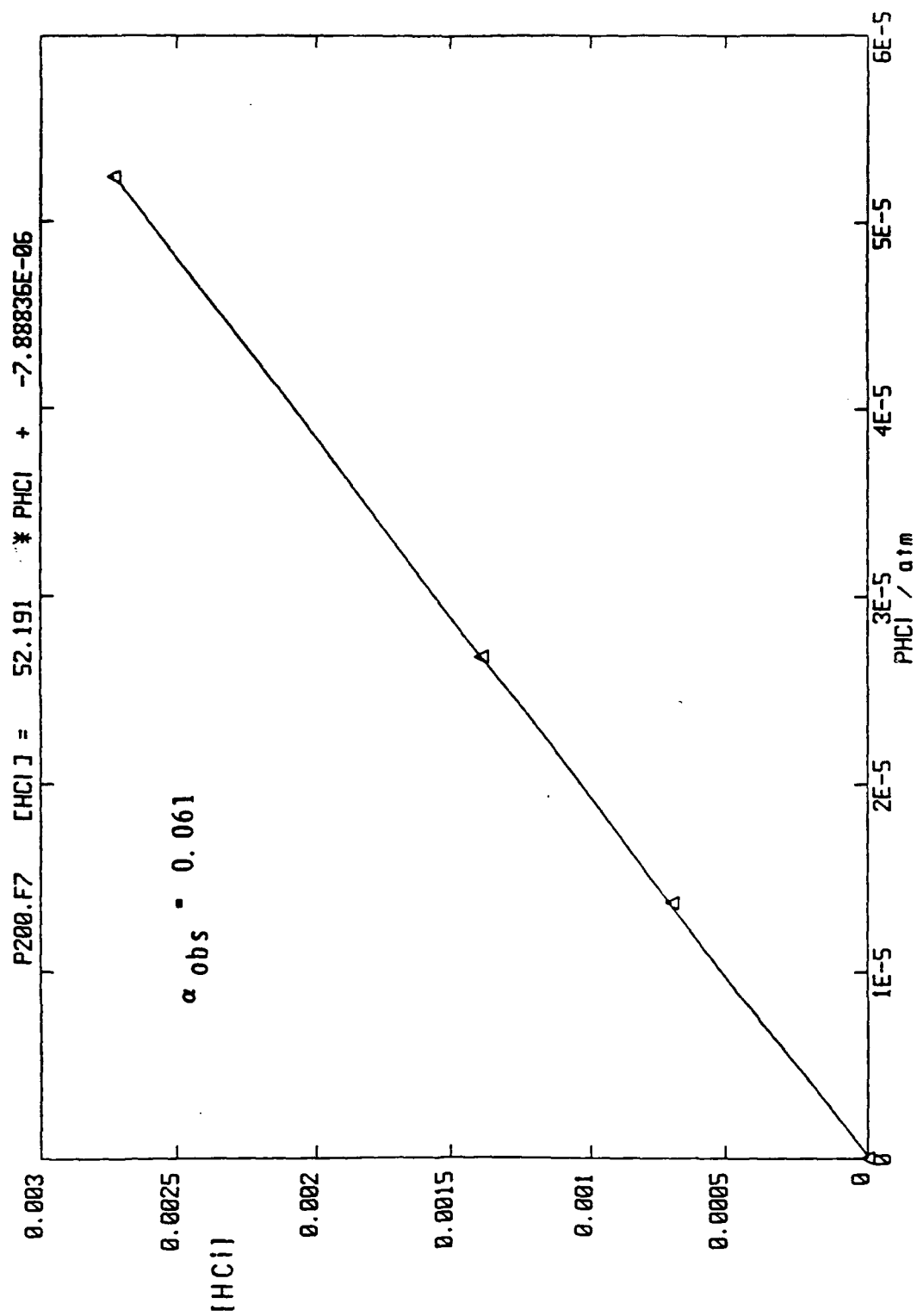In these formulas, P_{HCl} is the partial pressure of hydrogen chloride, r is the droplet radius, R is the gas constant, T is the absolute temperature in kelvins, and v is the average molecular speed.

The second step in the data analysis is to extrapolate these observed sticking coefficients to zero pressure (*i.e.*, to a situation of no diffusive limitation to mass transfer) to obtain the true sticking coefficient. This extrapolation is aided by a theory of combined diffusive and sticking mass transfer developed by S. E. Schwartz (Reference 6). His theory is based on a steady-state solution to the problem of radial diffusion to a drop. The solution is analogous to a "resistor" model in that the reciprocal transfer rates, *i.e.*, the "resistances" to mass transfer, are additive. The final solution may be expressed very simply by using the "observed" sticking coefficient as a shorthand way of describing the rate of mass transfer:

$$\frac{1}{\alpha_{obs}} = \frac{1}{\alpha} + \frac{rv}{4D}$$

In this equation, r is the droplet radius, v is the average molecular speed, and D is the diffusivity of HCl in the carrier at the pressure of the experiment. This equation suggests that a plot of the reciprocal of our observed sticking coefficients *versus* the reciprocal diffusivity (or, equivalently the pressure) should give a straight line, with a slope given by constants and with intercept equal to the reciprocal of the true (zero pressure) sticking coefficient. The calculations used diffusivities for HCl in helium of 0.471 cm^2/s, and for HCl in water vapor of 0.147 cm^2/s. These are based on empirical formulas checked against the HCl/N_2 system (References 8 and 9).

Figures 16 and 17 show plots of this kind for the laser and the collected drop experiments, respectively. The theoretical slope for all the data is about 25.0. Observation of straight lines with approximately the theoretical slope provides a

convincing source of support for this theory, and a convenient means of extrapolation to the true sticking coefficient. In plotting our data, we have included only points taken at 200 torr of helium and below. The reason for this is that the higher pressures involve a significant correction for droplet velocity, *i.e.*, "sweeping out" of HCl in the droplet's path; we do not have an accurate method for making this correction.

This agreement also implies that the theory may be used as an essential part of atmospheric or laboratory computer models of the mass transport in aerosol systems.

Since experiments here were done initially at zero relative humidity, there was some concern that evaporation of the droplets might lead to an underestimation of the sticking coefficient. This is because, at low humidities, there is a net flow of water vapor radially outward from the droplets. To find out the effect of humidity, some experiments were done with both techniques at 50 percent relative humidity. Experiments of this kind are difficult because of the increased tendency of HCl to stick on walls, and because the diffusivity of the helium--water vapor system is not well known and must be calculated. Nevertheless, the waxing and rapid flow techniques described previously made it possible to work at least up to 50 percent relative humidity. An example of the second kind of plot for the collected droplet experiments at 50 percent relative humidity is shown in Figure 18. Since the limiting sticking coefficient is similar to that at zero relative humidity, we believe that evaporation of the droplets does not measurably affect the determination of α under our experimental conditions.

The conclusion from this section is that the sticking coefficient of HCl on water is 0.3 ± 0.1. This means that the rate of mass transfer in the troposphere will be governed primarily by diffusion, with the quantitative behavior described by the Schwartz formulas. Furthermore, the fact that the formulas work at 50 percent relative humidity means that the diffusivity of HCl is not changed by this humidity, other than as defined by the correction for the mole fraction of water vapor. This implies that gas-phase HCl is effectively not hydrated under these conditions. This conclusion is consistent with the spectroscopic results discussed in the next section.
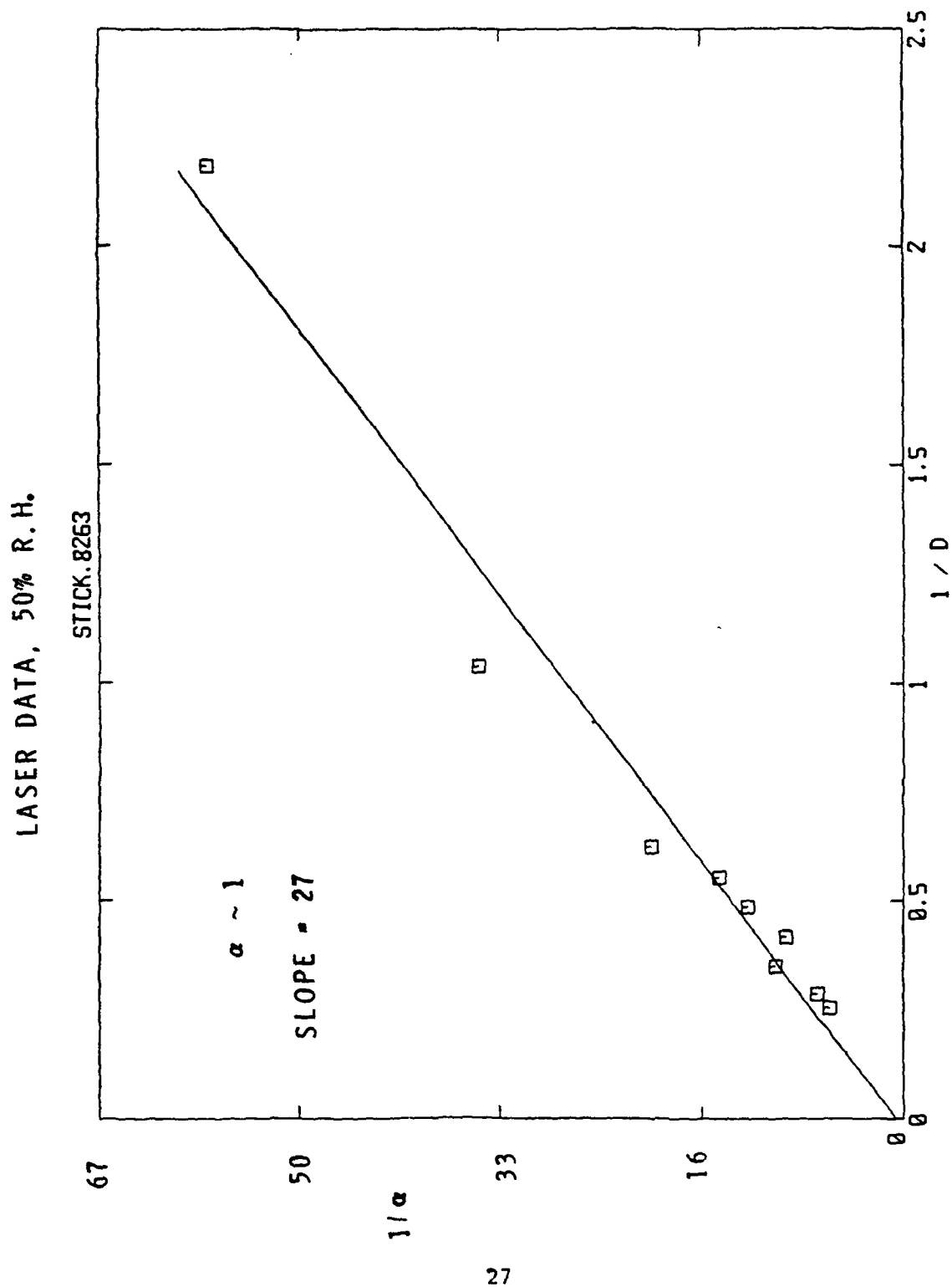
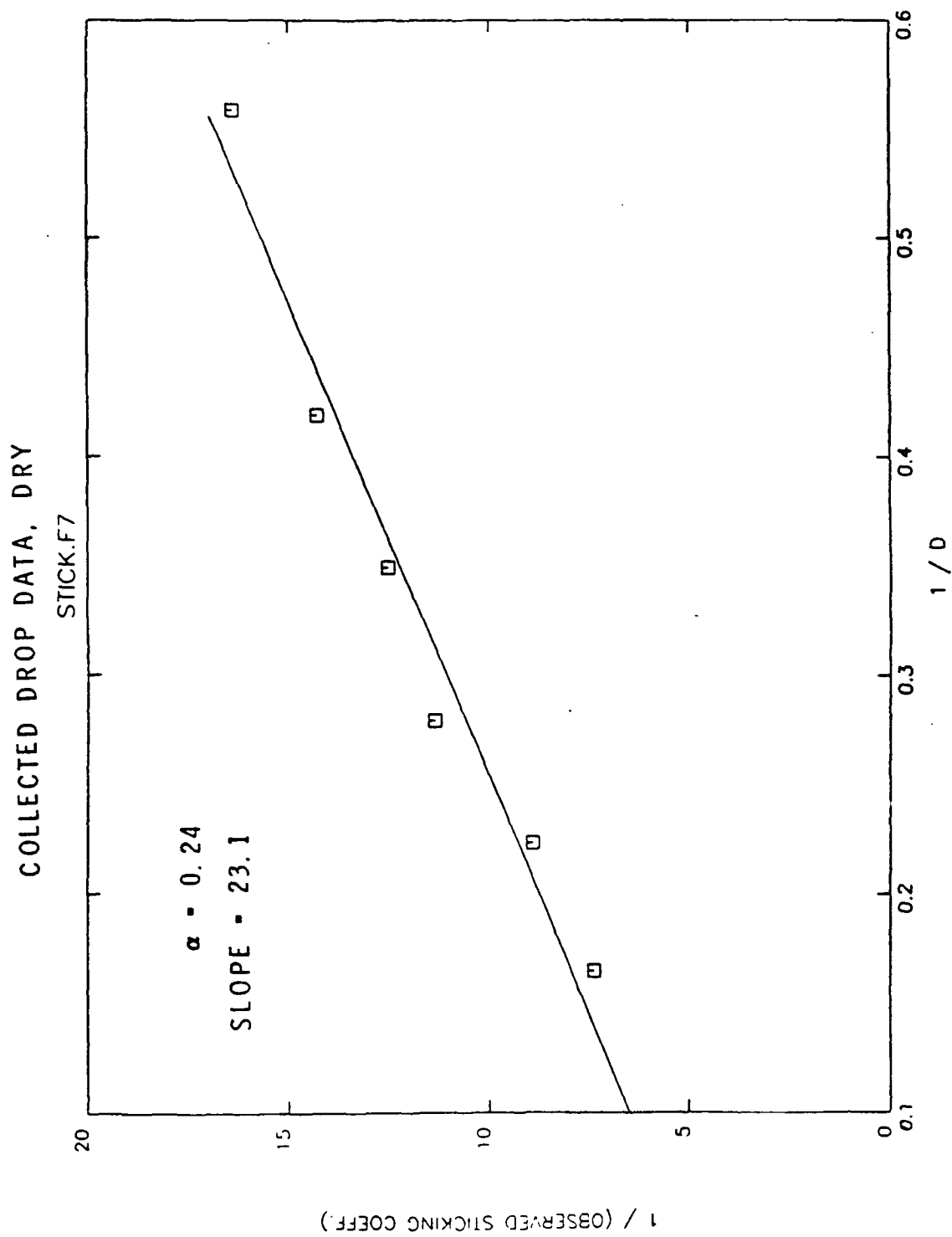Figure 16. Laser Data. Total Pressure Dependence

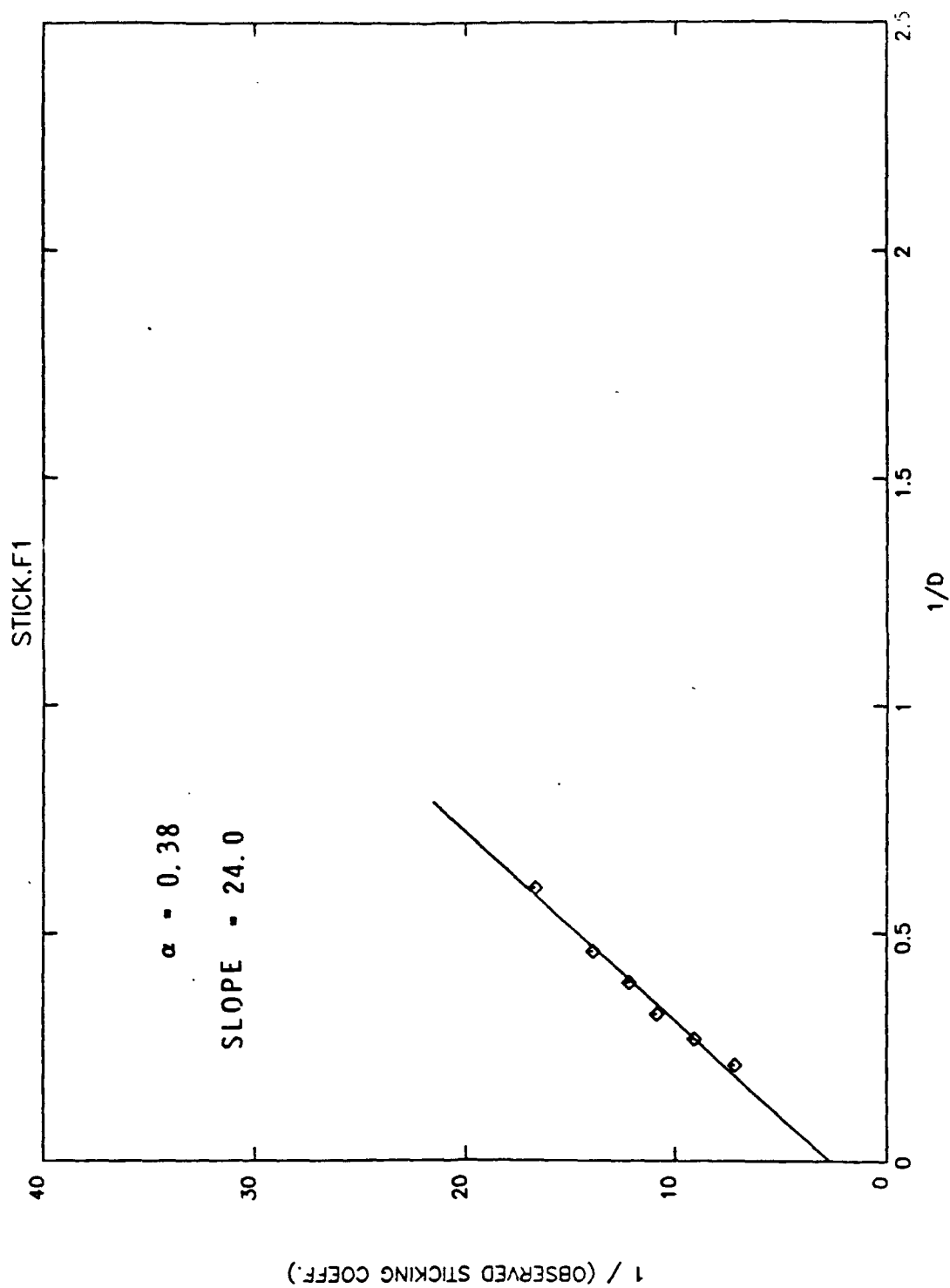Figure 17. Collected Drop Data. Total Pressure Dependence

Figure 18. Collected Drop Data. 50 Percent Relative Humidity Data

SECTION IV

KINETICS: SPECTROSCOPIC STUDY OF HCl

Because hydrogen chloride is highly soluble in water, there has been speculation that the gas phase molecule might readily form hydrates such as $HCl \cdot H_2O$ or higher hydrates, $HCl \cdot nH_2O$. Such hydrates would be much less diffusive than HCl itself, and would have different spectroscopic properties as well. For this reason, a high-resolution spectroscopic study was done to search for hydrated HCl molecules in the gas phase.

These experiments were conducted by Dr. Karl Westberg. The spectrometer was a Beckman Model FT 2200 Fourier Transform Infrared Spectrometer. This is a multiple-path instrument with a 20 meter effective pathlength. The infrared absorption spectrum of HCl was measured between 3200 and 2600 cm^{-1} at 0, 20, 30, and 40 percent relative humidity. This was done at both high resolution (0.25 cm^{-1}) and medium resolution (2 and 4 cm^{-1}). Attempts to take spectra at relative humidities greater than 40 percent failed because of very rapid HCl/H_2O aerosol formation.

The positions of the HCl absorption lines did not change with relative humidity, and there was no evidence for adduct ($HCl \cdot H_2O$) formation. In fact, no evidence of any sort was uncovered that would suggest that gas--filter correlation spectroscopy cannot accurately measure gas-phase HCl concentrations in humid air if aerosol does not form. However, the measurements show that the concentration of gas-phase HCl is often a poor indication of the total amount of HCl present, because in humid air, HCl/H_2O aerosols form on ever-present particles and on walls.

As we mentioned in the previous section, these results are consistent with the sticking coefficient results because a hydrated HCl molecule would have reduced diffusivity, and therefore a very different theoretical slope in the type 2 plots. Since this is not observed, both the spectroscopic and the mass transfer experiments tend to rule out the existence of such hydrates. With the wisdom of hindsight, this is not surprising. The high solubility of HCl in water results from the high ionization constant, not from a high Henry's law constant. Thus, the affinity of molecular HCl for water is not extremely high.

SECTION V

KINETICS: EVAPORATION RATE OF WATER DROPLETS

Time and resources did not permit measurement of the rate of evaporation of water droplets in our apparatus. However, recent papers in the literature have measured the sticking coefficient of water on water, with particular reference to work by I. N. Tang's group at Brookhaven (Reference 10). His work, based on shape resonances, shows that the condensation of water on water may be accounted for only by a sticking coefficient of unity. If this is the case, thermodynamic arguments may be used to calculate the evaporation coefficient.

The argument is as follows. In the absence of diffusion limitations, the rate at which water molecules may condense on the surface is given by the collision rate times the sticking coefficient:

$$\text{rate per unit area} = \frac{\alpha n v}{4}$$

where n is the number density of molecules in the gas phase, v is the average molecular speed, and α is the sticking coefficient. As in any rate process, reversibility requires that, at equilibrium, the rate of molecules entering and leaving the surface be the same:

$$\frac{\alpha n v}{4} = \frac{\alpha' n' v}{4}$$

where n' is the number density of gas molecules in the liquid phase and α' is the "escape coefficient." Cancellation of terms gives

$$\alpha = \alpha' K_h$$

where K_h is the dimensionless Henry's law coefficient for the undissociated gas in the liquid (liquid/gas), or, in the case of water on water, it is the liquid density divided by the vapor density, which is about 4.36×10^4 at $25°C$. Thus, the escape coefficient is the reciprocal of this, or 2.30×10^{-5} at $25°C$.

The escape coefficient may be used to calculate the maximum possible rate of evaporation at a given temperature. This problem is completely analogous to the condensation problem, but with the sign reversed. The only way a droplet could be forced to evaporate faster than this would be to break the surface by exploding the droplet with a high-energy laser. We begin by considering the rate law for droplet evaporation:

The number of molecules in the droplet is

$$N = \frac{4}{3}\pi n r^3$$

where n is the molecular number density in the drop and r is the radius of the drop.

The rate of evaporation is

$$\frac{dN}{dt} = -\alpha' n v \pi r^2$$

where v is the average molecular speed. If we differentiate the first expression we get

$$\frac{dN}{dt} = 4\pi n r^2 \frac{dr}{dt}$$

Equating the two derivatives,

$$\frac{dr}{dt} = \frac{-\alpha' v}{4}$$

Integration of this gives

$$r = r_0 - \alpha' v t / 4$$

Thus, the rate law for evaporation of the drop is zero order in the droplet radius, with a time for complete evaporation given by

$$t = \frac{4r_0}{\alpha' v}$$

Substitution of the appropriate values for water molecules at room temperature and a 10-micrometer radius droplet gives

$$t = 3.0 \text{ milliseconds}$$

This would be the evaporation rate in the absence of diffusive and heat transfer limitations. We may use the theoretical formula from the previous section to calculate the effect of the diffusion resistance of air on this rate. As

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before, the rate is most conveniently expressed as an effective sticking--in this case, evaporation--coefficient:

$$\frac{1}{\alpha_{obs}} = \frac{1}{\alpha'} + \frac{rv}{4D}$$

where D is the diffusivity. In our case, the diffusivity of water vapor in air at one atmosphere is about 0.24 cm^2/s. Substitution of values into the second term shows that it is negligible in relation to the first term. Thus, there will be no significant diffusive limitation to the rate of evaporation of water. More likely, it will be difficult to supply the necessary enthalpy of evaporation to the drop on such a short time scale. If a sufficient source of infrared radiation or heated air is available, these calculations indicate that evaporation of the droplets on a millisecond time scale should be possible.

SECTION VI

CONCLUSIONS

As a result of the experimental work and calculations done in this study, the following conclusions about HCl released into the environment are presented.

1. For preexisting fog or a very humid environment, most of the HCl (98 percent) would be expected to condense on aerosols. If the air is very clean and dry, most will remain in the gas phase. There may be substantial error in gas-phase only measurements if natural aerosol or pollutants are present at greater than background levels.

2. The sticking coefficient of HCl on water is on the order of 0.3. This means that the transfer of gas-phase HCl to aerosols will be quite rapid, and governed by formulas combining diffusive and phase boundary mass transfer. The diffusivity and sticking coefficient of HCl do not appear to be sensitive to relative humidity, at least up to 50 percent relative humidity.

3. High-resolution infrared spectroscopy does not indicate any hydrates of HCl forming in the gas phase, at least up to 40 percent relative humidity. This is consistent with the mass transfer experiments.

4. The rate of evaporation of aqueous droplets may be calculated from thermodynamics and some recent literature measurements for the sticking coefficient of water on water. The evaporation coefficient is 2.3×10^{-5}. This value means that the rate of evaporation of 10-micrometer radius droplets will not be diffusion-limited, but may take place in about 3 milliseconds if sufficient heat can be delivered to the droplets.

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