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STUDY OF THE EFFECTS OF
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PIONEER VENUS PROBE WINDOWS

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The purpose of this investigation was to determine the change of transmittance to be expected as several contaminates, possibly found in the Venusian atmosphere, condense upon candidate Pioneer Venus Probe window materials. Transmittance loss was to be studied as a function of the mass concentration of liquid droplets deposited upon one surface of the various window materials. The possible contaminates were water vapor, hydrochloric acid, sulfuric acid, and mercury vapor. Sapphire and fused quartz were studied over the wavelength range of 0.3 to 3.5 microns, and Irtran 4 and Irtran 6 were investigated in the infrared region from 3.0 to 15.5 microns.

Present estimates of the particles which make up the Venusian cloud indicate that the particles are most likely spherical in shape with diameters of approximately 2 to 3 microns. The experimental determination of transmittance as the test windows were coated with \( \text{H}_2\text{O} \) and \( \text{HCl} \) droplets having diameters of 2 to 3 microns was rather difficult, because of the short lifetime of the aerosols. For example, water droplets with diameters of 2 microns completely evaporate within a few seconds, even in an atmosphere of 100 percent relative humidity. Since the condensation of \( \text{H}_2\text{O} \) and \( \text{HCl} \) upon window materials and the measurement of the loss of transmittance accompanying their deposition presented special problems, this investigation was divided into two separate parts.

In Part I, the theoretical transmittance loss that may be caused by the deposition of aerosols upon the Pioneer Venus Probe windows was calculated, and the validity of these computations was checked by experimental studies.
The aerosols used in the experimental studies were monodisperse polystyrene latex particles, DOP (dioctylphthalate) droplets, \( \text{H}_2\text{SO}_4 \) droplets, and polydisperse Hg droplets. The polystyrene and DOP aerosols were used primarily to establish the validity of the theoretical calculation of transmittance. \( \text{H}_2\text{SO}_4 \) and Hg were two of the contaminates of specific interest. It was found that the physical parameters of condensates of \( \text{H}_2\text{SO}_4 \) and Hg remained essentially unchanged with time, making it possible to study these contaminates in some detail. The transmittance of the aerosol contaminated windows was measured over the wavelengths of interest, and the condensates were photographed to determine the size and shape of individual droplets. For low mass concentrations of aerosols deposited upon the window surface, photomicrographs were used to determine the amount of condensate present. When the total mass of condensate deposited upon the windows was greater than 10 micrograms a microbalance was used to weigh the contaminant. Theoretical and experimental data were in close agreement.

Part II of this report deals with the loss of window transmittance experimentally observed as \( \text{H}_2\text{O} \) and \( \text{HCl} \) condense upon one of the window surfaces. To study this loss of transmittance it was necessary for the condensation to take place in a carefully controlled environment. A condensation chamber was constructed, into which measured volumes of \( \text{H}_2\text{O} \) and \( \text{HCl} \) were injected. The chamber was maintained at a temperature sufficient to vaporize these contaminates. The surface of the test window was maintained at a cool temperature so that any condensation taking place within the chamber occurred upon the test window. With this apparatus it was possible to determine the amount of condensate that had formed and to measure the resulting window transmittance.

In depositing \( \text{H}_2\text{SO}_4 \) and \( \text{HCl} \) upon the surface of Irtran 4 and Irtran 6
there was the possibility of the Irtran surface being attacked by the acid. No degradation of the window material was observed in any of the experiments in which the $\text{H}_2\text{SO}_4$ aerosol was deposited upon the surface of an Irtran window, or where the HCl condensed upon the surface of an Irtran window. To supplement these results, a number of experiments were performed specifically to determine the effect of $\text{H}_2\text{SO}_4$ and HCl upon Irtran 4 and Irtran 6 under various conditions, and these investigations are described in Part II of this report.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. RADIATION TRANSMISSION THROUGH TRANSPARENT WINDOWS WITH LIQUID DROPLETS DEPOSITED ON ONE SIDE</td>
<td>2</td>
</tr>
<tr>
<td>III. EXTINCTION COEFFICIENT ( (K_s) )</td>
<td>5</td>
</tr>
<tr>
<td>IV. EFFECT OF POLYDISPERSITY</td>
<td>8</td>
</tr>
<tr>
<td>V. VARIATION OF REFRACTIVE INDEX WITH WAVELENGTH</td>
<td>9</td>
</tr>
<tr>
<td>VI. EFFECT OF SURFACE CONTAMINATION AND CORROSION</td>
<td>9</td>
</tr>
<tr>
<td>VII. OPTICAL GEOMETRY</td>
<td>11</td>
</tr>
<tr>
<td>VIII. CALCULATION OF TRANSMISSION LOSS</td>
<td>12</td>
</tr>
<tr>
<td>IX. EXPERIMENTAL RESULTS</td>
<td>13</td>
</tr>
<tr>
<td>X. CONCLUSIONS</td>
<td>17</td>
</tr>
<tr>
<td>XI. REFERENCES</td>
<td>19</td>
</tr>
</tbody>
</table>
LIST OF TABLES

TABLE

I. RELATIVE TRANSMITTANCE OF RADIATION THROUGH A TRANSPARENT WINDOW COATED WITH 2 MICRONS DIAMETER LIQUID DROPLETS, m = 1.45
  (REF: VENUS CLOUD MODEL$^6$)

II. RELATIVE TRANSMITTANCE OF LIGHT BY SULFURIC ACID DROPLETS ON IR-4

III. RELATIVE TRANSMITTANCE OF LIGHT BY SULFURIC ACID DROPLETS ON IR-6

IV. ATTENUATION OF LASER LIGHT BY MERCURY* DROPLETS ON GLASS

V. ATTENUATION OF LIGHT BY MERCURY* DROPLETS ON GLASS

VI. ATTENUATION OF LIGHT BY MERCURY* DROPLETS ON IR-4

VII. SIZE DISTRIBUTION AND MASS CONCENTRATION OF MERCURY DROPLETS DEPOSITED ON IR-4 WINDOW SURFACE
LIST OF FIGURES

FIGURE

1. OPTICAL ARRANGEMENT FOR THE TRANSMITTANCE MEASUREMENT

2. THE CALCULATED VARIATION OF THE EXTINCTION COEFFICIENT ($K_s$) FOR WATER DROPLETS AS A FUNCTION OF PARTICLE

3. CALCULATED TRANSMITTANCE OF LIGHT ($\lambda = 0.5$ MICRONS) PLOTTED AS A FUNCTION OF PARTICLE RADIUS WHEN AN OPTICAL WINDOW SURFACE IS COATED WITH WATER DROPLETS AT A CONCENTRATION OF 50 MICROGRAMS/CM$^2$

4. OPTICAL ARRANGEMENT FOR TRANSMITTANCE MEASUREMENT IN WHICH THE DETECTOR ACCEPTS SOME OF THE SCATTERED LIGHT

5. CALCULATED RELATIVE TRANSMITTANCE PLOTTED AS A FUNCTION OF WAVELENGTH OF RADIATION FOR DIFFERENT NUMBER CONCENTRATION OF PARTICLES (2 microns diameter, $m = 1.45$) DEPOSITED ON THE WINDOW SURFACE

6. EXPERIMENTAL RELATIONSHIP OBSERVED BETWEEN MASS CONCENTRATION OF H$_2$SO$_4$ DROPLETS ON WINDOW SURFACE AS A FUNCTION OF TIME OF DEPOSITION IN ELECTROSTATIC PRECIPITATOR

7. CALCULATED AND EXPERIMENTAL TRANSMITTANCE PLOTTED AS A FUNCTION OF SURFACE CONCENTRATION OF AEROSOLS ($d_p = 2.0$ MICRONS) ON OPTICAL WINDOWS

8. RELATIVE TRANSMITTANCE PLOTTED AS A FUNCTION OF WAVELENGTH OF RADIATION OF A SAPPHIRE WINDOW WITH ONE SURFACE COATED WITH 20 $\mu$g/cm$^2$ OF 2 MICRON-DIAMETER H$_2$SO$_4$ DROPLETS

9. RELATIVE TRANSMITTANCE THROUGH DIFFERENT WINDOWS AS A FUNCTION OF MASS CONCENTRATION OF H$_2$SO$_4$ DROPLETS DEPOSITED ON THE WINDOW SURFACE. (DROplet DIAMETER BEFORE DEPOSITION APPROXimates 2 MICRON,
10. RELATIVE TRANSMITTANCE OF IR RADIATION OF DIFFERENT WAVELENGTHS THROUGH A 2 mm THICK IRTRAN 4 WINDOW AS A FUNCTION OF MASS CONCENTRATION OF H₂SO₄ DROPLETS DEPOSITED ON THE WINDOW SURFACE

11. RELATIVE TRANSMITTANCE OF IR RADIATION OF DIFFERENT WAVELENGTHS THROUGH A 2 mm THICK IRTRAN 6 WINDOW AS A FUNCTION OF Mass CONCENTRATION OF H₂SO₄ DROPLETS DEPOSITED ON THE WINDOW SURFACE

12. RELATIVE TRANSMITTANCE PLOTTED AS A FUNCTION OF MASS CONCENTRATION OF H₂SO₄ DROPLETS DEPOSITED ON AN IR-6 WINDOW SURFACE FOR DIFFERENT WAVELENGTHS. (THE CURVES SHOW THE DETAILS OF VARIATION OF TRANSMITTANCE WITH THE WAVELENGTH OF RADIATION THAT ARE NOT SHOWN IN FIGURE VII)

13. OBSERVED RATE OF INCREASE OF AVERAGE DIAMETER OF H₂SO₄ DROPLETS AGGLOMERATED ON IR-4 WINDOW SURFACE WITH INCREASING CONCENTRATION AS 2 MICRON-DIAMETER DROPLETS ARE DEPOSITED

14. OBSERVED RATE OF INCREASE OF AVERAGE DIAMETER OF H₂SO₄ DROPLETS AGGLOMERATED ON IR-6 WINDOW SURFACE WITH INCREASING MASS CONCENTRATION AS 2 MICRON-DIAMETER H₂SO₄ DROPLETS ARE DEPOSITED

15. RELATIVE TRANSMITTANCE OF IR RADIATION THROUGH A 2 mm THICK IRTRAN 4 WINDOW COATED WITH Hg DROPLETS (MASS CONCENTRATION: 1.4 x 10⁻² g/cm²) PLOTTED AS A FUNCTION OF WAVELENGTH

16. 2 MICRON DIAMETER POLYSTYRENE LATEX PARTICLES (THESE PARTICLES USED AS A STANDARD TO DETERMINE MAGNIFICATION: 2750X)

17. DOP ON SURFACE-DEACTIVATED GLASS SLIDE: CONCENTRATION - 3.5 x 10⁶ PARTICLES/cm²; d_p = 2 MICRONS; CALCULATED TRANSMITTANCE - 81%; RELATIVE EXPERIMENTAL TRANSMITTANCE - 85%; λ = 0.6328 MICRON LASER

18. SULFURIC ACID ON SURFACE-DEACTIVATED FUSED SILICA: CONCENTRATION -
8 \times 10^6 \text{ PARTICLES/cm}^2 (10 \mu\text{g/cm}^2); \text{ CALCULATED TRANSMITTANCE - 59%} \\
\text{RELATIVE EXPERIMENTAL TRANSMITTANCE - 46%}; \lambda = 0.6328 \text{ MICRON LASER} \\
19. \text{ SULFURIC ACID ON SURFACE-DEACTIVATED FUSED SILICA: CONCENTRATION - 120 \mu\text{g/cm}^2; CALCULATED TRANSMITTANCE - 16.3%; RELATIVE EXPERIMENTAL TRANSMITTANCE - 14.8%; }\lambda = 0.6328 \text{ MICRON LASER} \\
20. \text{ SULFURIC ACID ON SAPPHIRE; CONCENTRATION - 30 \mu\text{g/cm}^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 41%; }\lambda = 0.6328 \text{ MICRON LASER} \\
21. \text{ SULFURIC ACID ON QUARTZ: CONCENTRATION - 10 \mu\text{g/cm}^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 70%; }\lambda = 0.6328 \text{ MICRON LASER} \\
22. \text{ SULFURIC ACID ON QUARTZ: CONCENTRATION - 15 \mu\text{g/cm}^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 58%; }\lambda = 0.6328 \text{ MICRON LASER} \\
23. \text{ SULFURIC ACID ON IR-4: CONCENTRATION - 10 \mu\text{g/cm}^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 97%; }\lambda = 8.5 \text{ MICRONS} \\
24. \text{ SULFURIC ACID ON IR-4: CONCENTRATION - 20 \mu\text{g/cm}^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 89%; }\lambda = 8.5 \text{ MICRONS} \\
25. \text{ SULFURIC ACID ON IR-4: CONCENTRATION - 40 \mu\text{g/cm}^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 75%; }\lambda = 8.5 \text{ MICRONS} \\
26. \text{ SULFURIC ACID ON IR-4: CONCENTRATION - 80 \mu\text{g/cm}^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 63.5%; }\lambda = 8.5 \text{ MICRONS} \\
27. \text{ SULFURIC ACID ON IR-4: CONCENTRATION - 200 \mu\text{g/cm}^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 38.6%; }\lambda = 8.5 \text{ MICRONS} \\
28. \text{ SULFURIC ACID ON IR-6: CONCENTRATION - 10 \mu\text{g/cm}^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 98%; }\lambda = 8.5 \text{ MICRONS} \\
29. \text{ SULFURIC ACID ON IR-6: CONCENTRATION - 60 \mu\text{g/cm}^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 67%; }\lambda = 8.5 \text{ MICRONS} \\
30. \text{ SULFURIC ACID ON IR-6: CONCENTRATION - 140 \mu\text{g/cm}^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 31%; }\lambda = 8.5 \text{ MICRONS}
31. SULFURIC ACID ON IR-6: CONCENTRATION - 1,300 µg/cm²; RELATIVE 
EXPERIMENTAL TRANSMITTANCE - 18% MAGNIFICATION: 275X;
\[ \lambda = 8.5 \text{ MICRONS} \]

32. MERCURY DROPLETS ON GLASS: CONCENTRATION - 6,120 µg/cm²; RELATIVE
EXPERIMENTAL TRANSMITTANCE - 62%; CALCULATED TRANSMITTANCE - 59%;
MAGNIFICATION: 687X; \[ \lambda = .450 \text{ MICRONS} \]

33. MERCURY ON IR-4: CONCENTRATION - 13,400 µg/cm²; RELATIVE
EXPERIMENTAL TRANSMITTANCE - 60%; CALCULATED TRANSMITTANCE - 62%;
MAGNIFICATION: 687X; \[ \lambda = 2.0 \text{ MICRONS} \]
I. INTRODUCTION

Transmission of UV, visible and IR radiation through a transparent window may suffer a considerable loss if these surfaces become coated with aerosol particles. Deposits of solid particles and liquid droplets on transparent substrates scatter and/or absorb radiation. An estimation of the transmission loss, as a beam of radiation passes through these windows, can be made if the size parameter of the deposited aerosol and the refractive index of the aerosol are known. The purpose of this work is to investigate the transmission loss of Pioneer Venus Probe radiation windows if their exposed surfaces become contaminated with droplets of water, hydrochloric acid, sulfuric acid, and mercury which may be found in the Venusian atmosphere. Transmission loss is to be studied as a function of mass concentration of liquid droplets deposited on one surface of test window materials while the wavelength of the transmitting radiation is in the range of 0.3 to 30 microns. The parameters that affect the transmittance of radiation through a window are: (1) particle size, (2) surface concentration of particles, (3) wavelength of the radiation, (4) angle of acceptance of the radiation by the detector, and (5) the refractive index of the aerosol. From the existing theories on the optical properties of aerosols, an estimation of the transmission loss can be...
made as the above parameters are varied. One of the existing models of Venusian clouds has been considered, and the transmission loss that may be caused by the deposition of aerosols upon the Pioneer Venus Probe windows has been calculated. The validity of these computations was checked by experimental studies. This approach is believed to be less tedious and time consuming compared to a purely experimental study. This is particularly true since the generation and deposition of liquid droplets of H$_2$O, HCl, H$_2$SO$_4$ and Hg in controlled quantities on test windows made of sapphire, fused quartz, IR-4, and IR-6 and the subsequent measurement of transmission at wavelengths varying from 0.3 to 30 microns present many practical problems.

Experimental data on the transmittance of test windows made of sapphire, quartz, IR-4, and IR-6 as a function of the surface contamination with liquid droplets of H$_2$SO$_4$ and Hg are presented in this report. The observed transmittance is in close agreement with the theoretically expected results. All calculations and measurements have been performed assuming normal ambient atmospheric conditions.

II. RADIATION TRANSMISSION THROUGH TRANSPARENT WINDOWS WITH LIQUID DROPLETS DEPOSITED ON ONE SIDE

A solid particle or a liquid droplet deposited on a transparent window will scatter and/or absorb radiation. Attenuation of radiation through the window will depend on angles of illumination and collected cones of radiation received by the detector placed behind the window. If an arrangement as shown in Figure 1 is considered, it is possible to write

\[ P_0 = P_T + P_{abs} + P_{sca} + P_r \] (1)
where $P_0$ is the power of the incident beam, $P_T$ is the power of the transmitted beam, $P_{\text{abs}}$ represents the power of radiation absorbed by the deposited aerosol, $P_{\text{sca}}$ represents the power of radiation scattered by the deposited aerosol, and $P_r$ is the power of the light reflected from the window surfaces. The window is considered to be scatter-free and lossless. If $P_r$ is small, the amount of radiation scattered and absorbed by the particles can be written from the Bouguer-Beer law

$$ T = I_T/I_0 = \exp (-K_s \pi r_p^2 n) \quad (2) $$

where $I_T$ is the intensity of the transmitted beam, $I_0$ is the intensity of the incident beam ($I_0 = P_0$/surface area illuminated), $r_p$ is the radius of the droplets, $n$ is the number of particles deposited per square centimeter, and $K_s$ is the particle extinction coefficient. $K_s$ is denoted by

$$ K_s = \frac{\text{total flux scattered and absorbed by the particle}}{\text{flux geometrically incident on the particle}} = Q_{\text{sca}} + Q_{\text{abs}} $$

where $Q_{\text{sca}}$ and $Q_{\text{abs}}$ are often referred to as particle scattering and particle absorption coefficients, respectively.

If the window is not a lossless one, the transmittance $T$ should be replaced by the relative transmittance ($T_c$), and Equation (2) can be expressed as

$$ T_c = I_T/I_{0T} = \exp (-K_s \pi r_p^2 n) \quad (3) $$
where \( I_{OT} \) is the transmitted light through the window when there are no surface deposits. Since the candidate Pioneer Venus Probe window materials have finite absorption in their transmission spectrum of radiation, Equation (3) is used in the present work to indicate the effect of aerosol deposition. The absolute transmittance of the window can be determined from the following equation

\[
T_a = (I_T/I_{OT})(I_{OT}/I_o) = I_T/I_o. \tag{4}
\]

Equation (3) is based on the following assumptions: (1) the detector measures radiation that is undeviated from the direction of propagation of \( I_o \), (2) the droplets are spherical and do not "wet" the window surface, (3) the effect of the proximity of the droplets with the window surface supporting them is neglected, (4) droplet deposition on the window surface is random, and (5) scattering phenomena involving a change of the emitted wavelength such as fluorescence and Raman scattering are not considered.

Equation (3) indicates that if particle size \( r_p \), droplet concentration \( n \), and extinction coefficient \( K_s \) are known, the intensity of the transmitted light can be determined. However, the extinction coefficient, \( K_s \), is a complex function of aerosol size parameter, \( \alpha \), and the aerosol refractive index, \( m \), that is,

\[
K_s = f(\alpha, m) \tag{5}
\]

where

\[
\alpha = 2\pi r_p/\lambda, \tag{6}
\]

\[
m = m_o(1 - ik), \tag{7}
\]
\( \lambda \) is the wavelength of radiation, \( m \) is the complex refractive index which is a function of \( \lambda \), and \( k \) is the absorption coefficient.

In general, the value of \( K_s \) will depend on the scattering and absorption properties of the aerosol. Depending on the value of \( \alpha \), aerosol scattering can be analyzed in three regions: (1) \( \alpha < 0.3 \) or \( r_p \ll \lambda \), (2) \( 0.3 < \alpha \leq 50 \), and (3) \( \alpha > 50 \). The first region is known as the Rayleigh scattering region, the second region is referred to as the Mie scattering region, and in the third case Fraunhofer diffraction theory can be applied. It should be noted here that the above correspondences are not precise and the above values are considered primarily for the purpose of computation of \( K_s \).

III. EXTINCTION COEFFICIENT \( (K_s) \)

Values of \( K_s \) for droplets of \( H_2O, HCl, H_2SO_4 \) and \( Hg \) having \( r_p \) in the range of 0.1 to 5 microns and \( \lambda \) in the range of 0.3 to 30 microns (or \( \alpha \) varying from 0.02 to 100 approximately) can be determined experimentally.\(^1\)

An outline of the method of theoretical computation is indicated below.

(1) Rayleigh Region:

(a) non-absorbing particle, \( m \) real, \( k = 0 \)

\[
K_s = \frac{(8\alpha^4/3)(m^2 - 1)^2}{(m^2 + 2)}.
\] (8)

(b) for \( m = m_0(1 - ik) \)

\[
Q_{sca} = \frac{(8\alpha^4/3)((m^2 - 1)/(m^2 + 2))^2,}{
\] (9)

\[
Q_{abs} = -4\alpha Im((m^2 - 1)/(m^2 + 2)),
\] (10)
and \[ K_s = Q_{sca} + Q_{abs} \] (11)

where the term \( \text{Im} \) stands for "imaginary part of."

(c) electrically conducting material (when \( m_0 \) is large)

\[ K_s = 8a^{4/3}. \] (12)

(2) Mie Region:

No simple formula would be valid for this region. \( K_s \) should be calculated from exact Mie Theory. In the Mie region, the value of \( K_s \) generally varies from a small fraction to a maximum value as \( a \) increases from an initial value of 0.3. As \( a \) increases further, \( K_s \) displays a number of maxima with decreasing values until a constant value of 2 is attained. Mie scattering tables can be used for computing \( K_s \).

For a totally reflecting sphere (\( m \rightarrow \infty \), large real or complex values of \( m \)), an empirical formula,\(^2\)

\[ K_s = 2 + 0.07a^{-2/3} + 0.49a^{-1} \] (13)

can be applied for \( m \) in the range \( 6 \leq m \leq 90 \). This formula applies to metals exposed to IR radiation.

(3) Scattering Based on Geometrical and Physical Optics:

The Rayleigh Gans equation may be applied in this case.

\[ K_s = 2 - 4(sin \rho)/\rho + 4(1 - cos\rho)/\rho^2 \] (14)

where \( \rho = 2a(m - 1) \).
The above formula is applicable only for values of m close to 1. In general, for a large value of \( \alpha \), \( K_s \) approaches the value of 2. It may be noted here that as \( \alpha \) approaches a very large value, the measured value of \( K_s \) will be near unity, since most of the scattered light will be in the forward direction and it becomes difficult to separate the scattered light from the transmitted light beam.

To illustrate the variation of \( K_s \) as a function of \( \alpha \), the calculated value of \( K_s \) is plotted for water droplets as a function of \( \alpha \) in Figure 2. Minor deviations in the curve are not shown. \( K_s \) has a small value in the Rayleigh region. In the Mie region, \( K_s \) approaches a maximum value somewhere in the region of \( \alpha \) varying from 0.3 to 10, and then shows a number of maxima as \( \alpha \) increases. The exact value of \( \alpha \) where the first maximum occurs depends on the value of \( m \), that is, the larger the value of \( m \) the lower the value of \( \alpha \) at the first maximum. If the aerosol is monodisperse, \( K_s \) shows a number of oscillations as well as some ripple structure in the Mie region. In the Fraunhofer region \( K_s \) approaches the limiting value of 2.

The extinction coefficient, \( K_s \), can be considered as the ratio of the apparent scattering cross-sectional area of a particle to its geometrical cross-sectional area projected in the direction of the incoming beam. If we consider a gram of liquid atomized to \( n \) number of droplets of equal size, the specific surface area (or the geometrical cross-sectional area) increases by a factor of \( 1/r_p \), where \( r_p \) is the radius of the droplet. Since the exponential term in Equation (3) is \( (-K_s \pi r_p^2 n) \), it is evident that for a given mass of material, there is an optimum sized particle which will cause maximum scattering of light, or minimum transmission of light for a given wavelength of radiation. Figure 3 shows transmission of light (\( \lambda = 0.5 \) microns) plotted as a function of particle radius when one of the surfaces of a transparent window is coated with 50 micrograms of water droplets per
square centimeter.

The above discussion is applicable for a monodisperse aerosol with a known refractive index. Since aerosols are inherently unstable in nature, the effect of polydispersity must be considered. A finite size range of droplets must be considered since the droplets will be in dynamic equilibrium involving many physical processes such as generation, evaporation, condensation, coagulation, etc.

IV. EFFECT OF POLYDISPERSITY

In general, when the aerosol deposits contain a wide spectrum of droplet diameters, a theoretical analysis of the extinction coefficient is extremely difficult. However, experiments made with transparent polydisperse spheres show that \( K_s \) rises monotonically with increasing particle size parameter to the value of 2 when \( 2a(m - 1) \) exceeds 6. In general, when the scattering aerosol is polydisperse, the amplitudes of oscillations and ripples of \( K_s \) are highly damped and \( K_s \) approaches the limiting value of 2. If the droplets' size distribution is known, Equation (3) can be expressed as

\[
T_c = \exp \left( - \sum_{i=1}^{m} n_i K_{s_i} r_i^2 n_i \right) \tag{15}
\]

where

\[
\sum_i n_i = n
\]

and the subscript \( i \) designates the size interval of the droplet radius. If the count median radius \( r_{\text{CMD}} \) of the droplets' size distribution is known and if \( (2\pi r_{\text{CMD}}/\lambda) > 10 \), then \( K_s \) can be assumed to have the value of 2, and Equation (15) can be approximated by

\[
T_c = \exp(-2\pi r_{\text{CMD}}^2 n) \tag{16}
\]
for a polydisperse aerosol.\textsuperscript{6}

V. VARIATION OF REFRACTIVE INDEX WITH WAVELENGTH

Since $K_s$ is a function of $\lambda$ and $m$, the variation of $m$ with $\lambda$ must be considered. Although the refractive indices of $H_2O$, $HCl$, $H_2SO_4$ and Hg at certain wavelengths are available in the literature, a comprehensive dispersion curve ($m$ vs $\lambda$) for $\lambda$ varying from 0.3 to 30 microns, and for all of the above chemicals may not be readily available. Further, the refractive indices data for any one of the above droplets must be evaluated relative to the surrounding medium which, in this study, will be the atmosphere of Venus and, thus, somewhat ambiguous.

The refractive index is, in general, a complex quantity and both $m_0$ and $k$ in Equation (7) must be determined. The wavelength region where a strong absorption occurs is, probably, of no practical interest, since such radiations would be absent due to absorption of such radiation by the surrounding ambient vapors.

VI. EFFECT OF SURFACE CONTAMINATION AND CORROSION

Evaporated droplets from a window surface may leave some solid residue on the surface. Further, if chemical reactions take place between the aerosol and the window material, additional scattering centers will be generated because of the surface irregularities. Further, if the window surface is "wetted" by the droplets, the transmission characteristics would differ widely. For example, a thin film of transparent liquid having a refractive index between that of the medium and that of the window material, will actually improve transmission by reducing the surface reflection. In practice, the "wetting" of the window surface by the deposited liquid droplets will depend on the properties of the liquid, the surface structure, and
the previous history of the surface contamination. Even in a "non-wetting" condition the liquid droplets sag and a spherical liquid drop deposited on the surface approaches a disc shape with the droplet increasing in diameter. Thus, if a monodisperse aerosol containing liquid droplets 2 microns in diameter is deposited on a window surface having a finite area, the initial deposits will be fairly monodisperse. However, with the increasing deposition the deposits become polydisperse in size as two or more droplets begin to occupy the same site. The shape and size distribution may have irregular spectra with the final deposits. A theoretical estimation of transmittance becomes difficult due to the irregular size and shape of the deposits. If an estimation of mass concentration on the surface is to be made by counting the particles on a photomicrograph, a considerable error may result since the relationship between the measured diameter and the equivalent diameter of a sphere having the same mass is a function of the droplet size and of the surface condition.

VII. OPTICAL GEOMETRY

The intensity of the transmitted light $I_T$ in Equation (3) is the intensity of the undeviated light transmitted through the window. Figure 1 shows an optical arrangement in which a collimated beam of light is incident on the test window and a pin-hole spatial filter is placed in front of the detector so that the detector reads the intensity of the transmitted light $I_T$. In the optical arrangement of the Pioneer Venus Probe window, the value of the semi-angles ($\theta_s$ and $\theta_d$) subtended by the source of radiation and the detecting device on the window surface is greater than zero. The optical setup that allows some of the scattered light to be received by the detector is shown in Figure 4. The measured value of transmittance increases as $\theta_s$ and $\theta_d$ increase. Thus the effective value of $K_s$ decreases as $\theta_d$ and $\theta_s$ increase.
In the Rayleigh scattering region, the percentage deviation is small (less than 2 percent for \( \theta_s = \theta_d = 10^0 \)) since only a small portion of the incident beam is scattered within an angle of \( 10^0 \) from the incident beam.

In the Mie scattering region, the effective value of \( K_s \) depends on \( \alpha \), the particle size parameter. As \( \alpha \) increases, the intensity distribution of the forward scattered radiation changes in a complex manner, but in general, most of the scattered light falls into a small solid angle around the forward direction. Previous experimental studies\(^1\) show that for \( \alpha < 12 \) and \( \theta_d < 5^0 \), the change in \( K_s \) is less than 5 percent. However, if the values of \( \alpha \) and \( \theta_d \) are larger than 12 and 5 degrees, respectively, a significant change in the effective value of \( K_s \) occurs. For example, if \( \alpha = 50 \), and \( \theta_d = 20^0 \), the effective value of \( K_s \) is approximately 1, regardless of the composition of the droplets.\(^6\)

VIII. CALCULATION OF TRANSMISSION LOSS

Flux and polarization calculations\(^5\) of the radiation reflected from the clouds of Venus suggest that the clouds are composed of transparent liquid droplets with a mean diameter of 2 microns and a refractive index in the vicinity of 1.45. This is the top haze layer of clouds where probable temperature and pressure are approximately 200 \( ^0 \)K and 50 millibar, respectively. Below this layer, there is an optically dense cloud of highly reflecting particles in an environment with a temperature of 235 \( ^0 \)K and with a pressure of 150 millibars.

During the descent of the Pioneer Venus Probe through the cloud, the droplets may deposit on the exposed side of the window. The deposition will probably be caused by (1) impaction, (2) thermal forces, and (3) electrostatic forces. The rate of deposition of droplets on the window surface can
be estimated from the anticipated mechanisms of deposition. If \( n \) is the number of droplets deposited per square centimeter of window surface, the transmission loss can be calculated for any given wavelength from Equation (3). Table I lists some estimated values of transmittance for \( n = 10^5, 10^6, \) and \( 10^7 \) droplets per square centimeter and for wavelength varying from 0.3 to 30.0 microns. Figure 5 is a curve of the calculated transmittance as a function of wavelength of radiation.

IX. EXPERIMENTAL RESULTS

The aerosols used in the experimental studies are (1) monodisperse polystyrene latex particles (2 microns diameter, \( \rho_p = 1.05, m = 1.6 \) at \( \lambda = 0.5 \) microns); (2) DOP (dioctylphthalate) droplets (average diameter of 2 microns, \( \rho_p = 0.98, m = 1.48 \) at \( \lambda = 0.5 \) microns); (3) \( \text{H}_2\text{SO}_4 \) (96%) droplets (average diameter of 2 microns, \( \rho_p = 1.83, m = 1.43 \) at \( \lambda = 0.5 \) microns); and (4) polydisperse Hg droplets \( \rho_p = 13.55, m = (1.3 - i2.9) \) at \( \lambda = 0.5 \) microns). The radiation window materials used were (1) quartz, (2) sapphire, (3) IR-4, and (4) IR-6.

An experimental determination of transmission of radiation through the test window materials coated with \( \text{H}_2\text{O} \) and HCl droplets is rather difficult because of the short lifetime of the aerosol. For example, water droplets with diameters of 2 microns will evaporate completely within a few seconds even in an atmosphere of 100 percent relative humidity. Lifetime of the droplets are considerably extended if soluble nuclei are present in the droplets thus lowering their vapor pressure. On the otherhand, \( \text{H}_2\text{SO}_4 \) droplets are highly hygroscopic and the droplets may grow in size if moisture is present in their environment. Thus the approach to the problem was to obtain experimental data on some representative aerosols for different values of \( \alpha \) to support the validity of the theoretical estimation.
DOP and \( \text{H}_2\text{SO}_4 \) droplets were generated by using a Rapaport-Weinstock aerosol generator.\(^1\) Hg droplets were generated by boiling mercury in a partial vacuum and condensing the vapor on the test windows. DOP and \( \text{H}_2\text{SO}_4 \) droplets were deposited on the window surface by employing an electrostatic precipitator. The electrostatic precipitator-sampling unit was built for the purpose of depositing an aerosol on an electrically nonconducting surface. Figure 6 shows an approximate relationship between the time of deposition and the mass of \( \text{H}_2\text{SO}_4 \) deposited per square centimeter with the high voltage set at +10 kV.

Polystyrene and DOP aerosols were used primarily to establish the validity of the theoretical calculation on transmittance. These aerosols are generally considered to be non-toxic and can be generated in controlled size ranges. For polydisperse droplets, the transmittance varies much less with the refractive index \( m \) or with the droplet-compositions than it does with the particle size parameter \( 2\pi r/\lambda \). Thus, experiments performed with any suitable test aerosol will yield results that can be used for estimating the transmittance values for other aerosols having the same concentration.

Transmittance of the aerosol-contaminated windows was measured by using (1) the optical arrangement shown in Figure 1 using a He-Ne laser at a wavelength of 6328 \( \text{A} \), (2) a Bausch and Lomb Spectronic 600 Spectrophotometer where the wavelength of the incident radiation was varied from 2200 \( \text{A} \) to 7000 \( \text{A} \) and (3) a Perkin Elmer Model 21 Infrared Spectrophotometer where the wavelength of incident radiation was varied from 1.5 to 15.5 microns. In the first method the semi-angles subtended by the source of illumination and the detection device are nearly zero, i.e., \( \theta_s = \theta_d = 0 \) and a true value of transmittance is measured at a known wavelength. In the second and third methods of transmittance measurements, both \( \theta_s \) and \( \theta_d \) have finite values. In the two double-beam spectrophotometers used for transmittance measurements,
the slit width varied with wavelength thus resulting in a deviation from the Bouguer-Beer law given in Equation (1).

When the mass concentration (mass deposition/cm$^2$) of aerosols deposited on the window surface was low the concentration was measured by using photomicrographs, and when the total mass deposited on the windows was greater than 10 micrograms, a microbalance was used to determine the amount of contaminants deposited per square centimeter of the window surface.

The curve in Figure 7 shows the percent transmittance as a function of the number of particles per square centimeter of window surface and the mass concentration in micrograms per square centimeter. The curve is for droplets with diameters of 2 microns and shows calculated values of transmittance for $K_s = 2, 3, \text{and } 4$. Experimental data obtained for different concentrations of polystyrene latex particles, DOP droplets, and H$_2$SO$_4$ droplets with diameters of 2 microns are in close agreement with the expected results. Higher values of mass concentration of liquid droplets on the surface of windows could not be obtained without coalescence of two or more droplets at the same site resulting in an increase in droplet diameter.

Figure 8 shows the variation of transmittance as a function of wavelength of radiation. The substrate used was a 2mm-thick sapphire window having H$_2$SO$_4$ droplets with a mass concentration of 20 μg/cm$^2$ and droplet size in the range of 1 to 2 microns in diameter deposited on one of its surfaces. The curve shows the relative transmittance values observed with the Bausch and Lomb Spectronic 600 and the Perkin Elmer Model 21 Spectrophotometer. The data are corrected for transmission loss through the window material due to absorption in the material and reflection loss at the two surfaces.

Figure 9 shows the variation of relative transmittance as a function of mass concentration in μg/cm$^2$. The transmittance was measured at $\lambda = 6328$ Å.
using the laser beam method. The measured value of transmittance in this method is generally lower than the corresponding value measured with the Bausch and Lomb Spectronic 600 Spectrophotometer at \( \lambda = 6300 \) A. This difference in the measured value of transmittance is partly a result of the finite values of \( \theta_s \) and \( \theta_d \) in the spectrophotometer.

Figures 10 and 11 show the variation of transmittance as a function of mass concentration plotted for different wavelengths in the IR region. Figure 10 shows the attenuation caused by \( \text{H}_2\text{SO}_4 \) droplets deposited on IR-4 windows whereas Figure 11 is for IR-6 windows. In general, as the wavelength increases, transmittance increases because of the decreasing value of \( K_s \) with increasing \( \alpha \). In Figure 12 the detailed variations of the observed values of transmittance for different values of \( \lambda \) are shown for the IR-6 window. Tables II and III show the attenuation of IR radiation by \( \text{H}_2\text{SO}_4 \) droplets deposited on IR-4 and IR-6 windows as a function of mass concentration in \( \mu g/cm^2 \).

A detailed calculation of the expected value of transmittance is complicated by the fact that both mean droplet diameter and standard deviation of the droplet size distribution \( (\sigma_d) \) increase with increasing mass deposition. Figures 13 and 14 show the nature of variation of count mean diameters \( (d_{\text{CMD}}) \) of \( \text{H}_2\text{SO}_4 \) droplets as a function of mass concentration per unit area deposited on IR-4 and IR-6 windows, respectively.

Tables IV, V and VI show the observed and calculated values of transmittance for Hg droplets. All attempts to generate monodisperse Hg droplets with a diameter of 2 microns were unsuccessful. Experiments carried out here and elsewhere\(^6\) indicated that mercury vapor does not condense on nuclei to form a monodisperse aerosol. Experimental data are presented here for a polydisperse aerosol of Hg droplets with a size variation of 2 to 100 microns in diameter. Because of the large droplet size and the polydispersity the
value 2 was used for $K_s$ in calculating the expected transmittance using Equation (2). Table VII shows a typical size distribution of Hg droplets deposited on an IR-4 window surface. The experimental data were in close agreement with the calculated results. The curve in Figure 15 shows the transmittance as a function of wavelength for an IR-4 window with mercury deposits of $1.4 \times 10^{-2}$ g/cm$^2$. Experiments with Hg droplets in the visible range were performed using glass as a substrate for experimental expediency. Similar results may be expected for the quartz and sapphire window materials.

In the above experiments with $\text{H}_2\text{SO}_4$ and Hg droplets deposited on the windows no significant deterioration of the surface condition of the windows was observed. Since $\text{H}_2\text{O}$ and HCl droplets with diameters of 2 microns have a very short lifetime, experiments on transmittance measurements were performed using a condensation chamber.

Photomicrographs of some of the deposits are presented in Figures 16 through 33. These figures show the size and shape distribution of the DOP, mercury, and sulfuric acid contaminant particles on the various substrates. Concentration and transmittance data are included with each photomicrograph. The magnification for all photomicrographs is 2750X unless otherwise stated.

X. CONCLUSIONS

Theoretical calculations and experimental observations were made on the transmittance of radiation through sapphire, quartz, IR-4, and IR-6 windows with surface deposits of droplets of $\text{H}_2\text{SO}_4$ and Hg. The experimental data were in close agreement with the expected results. The following conclusions can be made for droplets with diameters of 2 microns deposited on candidate radiation window materials:

(1) Loss of transmission through the radiation windows is generally less
than 10 percent for a surface deposition of less than 5 $\mu g/cm^2$.

(2) For Irtran 4 and 6 windows a surface concentration of 30 $\mu g/cm^2$ did not attenuate IR transmission appreciably.

(3) $H_2SO_4$ droplet concentration of 1300 $\mu g/cm^2$ did not cause the IR transmission to fall below 18 percent of the original transmission of the window.

(4) If the degree of contamination of the windows in the Pioneer Venus Probe can be estimated, the resulting loss of transmission can be calculated with a fair degree of accuracy.

In summary, transmittance of radiation through a transparent window coated with liquid droplets will depend on the aerosol refractive index, the surface concentration of the droplets, as well as the ratio of the droplet diameter to the wavelength of the radiation. The aerosol refractive index and the ratio of the droplet diameter to the wavelength of the radiation determine the value of the extinction coefficient $K_s$. In the Rayleigh region, $K_s$ is small thus resulting in an insignificant transmission loss. In the Mie region, $K_s$ varies from a small fraction to a maximum value of 5 or higher and displays a number of maxima and minima around the value of 2. Transmittance in this region can be calculated from Equation (3) if $K_s$ is known or if an estimation of transmittance can be made from a family of curves having probable $K_s$ values. In the Fraunhofer region, a value of 2 for $K_s$ will yield a conservative as well as a close estimate of transmittance.
XI. REFERENCES


TABLE I
RELATIVE TRANSMITTANCE OF RADIATION THROUGH A TRANSPARENT WINDOW COATED WITH 2 MICRONS DIAMETER LIQUID DROPLETS, $m = 1.45$ (REF: VENUS CLOUD MODEL\textsuperscript{6})

<table>
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<tr>
<th>Wavelength $\lambda$ (micron)</th>
<th>Size Parameter $2\pi r/\lambda$</th>
<th>$K_s$ Ref: 5</th>
<th>Tr = $\exp(-k_s n r^2 n)$</th>
</tr>
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<td>n = $1 \times 10^7$</td>
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<td>$\lambda$ in micron</td>
<td>Particle/sq cm</td>
<td>Particle/sq cm</td>
<td>Particle/sq cm</td>
</tr>
<tr>
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<td>----------------</td>
<td>----------------</td>
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<td>Wavelength $\lambda$ (microns)</td>
<td>Relative Transmittance</td>
<td>MASS CONCENTRATION (µg/cm²)</td>
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<td>-------------------------------</td>
<td>------------------------</td>
<td>-----------------------------</td>
<td></td>
</tr>
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### TABLE III
RELATIVE TRANSMITTANCE OF LIGHT BY SULFURIC ACID DROPLETS ON IR-6

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<tr>
<th>Wavelength ($\lambda$, microns)</th>
<th>Relative Transmittance Mass Concentration (µg/cm²)</th>
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TABLE IV
ATTENUATION OF LASER LIGHT BY MERCURY* DROPLETS ON GLASS

<table>
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<tr>
<th>λ (microns)</th>
<th>Measured Transmittance (percent)</th>
<th>Calculated Transmittance (percent)</th>
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<tr>
<td>0.6328</td>
<td>76%</td>
<td>77.2%</td>
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</table>

*Mercuroy concentration was 6.6 X 10^{-3} (g/cm²)
**TABLE V**
ATTENUATION OF LIGHT BY MERCURY* DROPLETS ON GLASS

<table>
<thead>
<tr>
<th>$\lambda$ (microns)</th>
<th>Measured Transmittance (percent)</th>
<th>Calculated Transmittance (percent)</th>
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<td>0.702</td>
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*Mercury concentration was $6.1 \times 10^{-3}$ (g/cm$^2$)
**TABLE VI**

ATTENUATION OF LIGHT BY MERCURY* DROPLETS ON IR-4

<table>
<thead>
<tr>
<th>( \lambda ) (microns)</th>
<th>( I_0 ) (percent)</th>
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*The concentration of mercury was approximately 1.4 \( \times 10^{-2} \) grams/cm\(^2\) yielding an expected (calculated) value of corrected transmittance of 61.5%.
TABLE VII
SIZE DISTRIBUTION AND MASS CONCENTRATION OF MERCURY DROPLETS DEPOSITED ON IR-4 WINDOW SURFACE

<table>
<thead>
<tr>
<th>Radius $r_i$ cm</th>
<th>No. of Particles $n_i$ per cm$^2$</th>
<th>Mass Concentration $\frac{4}{3}\pi \rho r_i^3 n_i$</th>
<th>Transmittance $\exp(-2\pi r_i^2 n_i)$</th>
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<tr>
<td>$2 \times 10^{-4}$</td>
<td>$8.5 \times 10^4$</td>
<td>$1.4 \times 10^{-2}$</td>
<td>0.616</td>
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<tr>
<td>$12 \times 10^{-4}$</td>
<td>$8.9 \times 10^4$</td>
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<td>$20 \times 10^{-4}$</td>
<td>$1.6 \times 10^3$</td>
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<td>$28 \times 10^{-4}$</td>
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<tr>
<td>$36 \times 10^{-4}$</td>
<td>$9.2 \times 10^2$</td>
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<tr>
<td>$61 \times 10^{-4}$</td>
<td>$4.1 \times 10^2$</td>
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gram/cm$^2$
FIGURE 1

OPTICAL ARRANGEMENT FOR THE TRANSMITTANCE MEASUREMENT
THE CALCULATED VARIATION OF THE EXTINCTION COEFFICIENT ($k_s$) FOR WATER DROPLETS AS A FUNCTION OF PARTICLE
CALCULATED TRANSMITTANCE OF LIGHT (λ = 0.5 MICRONS) PLOTTED AS A FUNCTION OF PARTICLE RADIUS WHEN AN OPTICAL WINDOW SURFACE IS COATED WITH WATER DROPLETS AT A CONCENTRATION OF 50 MICROGRAMS/CM².
FIGURE 4

OPTICAL ARRANGEMENT FOR TRANSMITTANCE MEASUREMENT IN WHICH THE DETECTOR ACCEPTS SOME OF THE SCATTERED LIGHT
Figure 5

Calculated relative transmittance plotted as a function of wavelength of radiation for different number concentration of particles (2 microns diameter, m = 1.45) deposited on the window surface.
Figure 6

Experimental relationship observed between mass concentration of $\text{H}_2\text{SO}_4$ droplets on window surface as a function of time of deposition in electrostatic precipitator.
FIGURE 7

CALCULATED AND EXPERIMENTAL TRANSMITTANCE PLOTTED AS A FUNCTION OF SURFACE CONCENTRATION OF AEROSOLS ($d_p = 2.0$ MICRONS) ON OPTICAL WINDOWS
FIGURE 8

RELATIVE TRANSMITTANCE PLOTTED AS A FUNCTION OF WAVELENGTH OF RADIATION OF A SAPPHIRE WINDOW WITH ONE SURFACE COATED WITH 20 μg/cm² OF 2 MICRON-DIAMETER H₂SO₄ DROPLETS
RELATIVE TRANSMITTANCE THROUGH DIFFERENT WINDOWS AS A FUNCTION OF MASS CONCENTRATION OF H$_2$SO$_4$ DROPLETS DEPOSITED ON THE WINDOW SURFACE. (DROplet DIAMETER BEFORE DEPOSITION APPROXIMATES 2 MICRON, WAVELENGTH = 6328 A)
Figure 10

Relative transmittance of IR radiation of different wavelengths through a 2 mm thick IRTRAN 4 window as a function of mass concentration of \( \text{H}_2\text{SO}_4 \) droplets deposited on the window surface.

- \( \lambda = 3.5 \, \mu \text{m} \)
- \( \lambda = 8.5 \, \mu \text{m} \)
- \( \lambda = 7.5 \, \mu \text{m} \)
- \( \lambda = 13.5 \, \mu \text{m} \)
FIGURE 11

RELATIVE TRANSMITTANCE OF IR RADIATION OF DIFFERENT WAVELENGTHS THROUGH A 2 mm THICK IRTRAN 6 WINDOW AS A FUNCTION OF MASS CONCENTRATION OF H₂SO₄ DROPLETS DEPOSITED ON THE WINDOW SURFACE
FIGURE 12

RELATIVE TRANSMITTANCE PLOTTED AS A FUNCTION OF MASS CONCENTRATION OF $H_2SO_4$ DROPLETS DEPOSITED ON AN IR-6 WINDOW SURFACE FOR DIFFERENT WAVELENGTHS. (THE CURVES SHOW THE DETAILS OF VARIATION OF TRANSMITTANCE WITH THE WAVELENGTH OF RADIATION THAT ARE NOT SHOWN IN FIGURE VII.)
FIGURE 13

OBSERVED RATE OF INCREASE OF AVERAGE DIAMETER OF H₂SO₄ DROPLETS AGGLOMERATED ON IR-4 WINDOW SURFACE WITH INCREASING CONCENTRATION AS 2 MICRON-DIAMETER DROPLETS ARE DEPOSITED
FIGURE 14

OBSERVED RATE OF INCREASE OF AVERAGE DIAMETER OF $\text{H}_2\text{SO}_4$ DROPLETS
AGGLOMERATED IN IR-6 WINDOW SURFACE WITH INCREASING MASS CONCENTRATION AS
2 MICRON-DIAMETER $\text{H}_2\text{SO}_4$ DROPLETS ARE DEPOSITED
FIGURE 15
RELATIVE TRANSMITTANCE OF IR RADIATION THROUGH A 2 mm THICK IRTRAN 4 WINDOW COATED WITH Hg DROPLETS (MASS CONCENTRATION: 1.4 X 10^{-2} g/cm^2) PLOTTED AS A FUNCTION OF WAVELENGTH
FIGURE 16

2 MICRON DIAMETER POLYSTYRENE LATEX PARTICLES (THESE PARTICLES USED AS A STANDARD TO DETERMINE MAGNIFICATION: 2750X)
FIGURE 17

DOP ON SURFACE-DEACTIVATED GLASS SLIDE: CONCENTRATION - 3.5 x 10^6 PARTICLES/cm²; d_p = 2 MICRONS; CALCULATED TRANSMITTANCE - 81%; RELATIVE EXPERIMENTAL TRANSMITTANCE - 85%; \( \lambda = 0.6328 \) MICRON LASER
FIGURE 18
SULFURIC ACID ON SURFACE-DEACTIVATED FUSED SILICA: CONCENTRATION - 8 $\times$ 10$^6$ PARTICLES/cm$^2$ (10 $\mu$g/cm$^2$); CALCULATED TRANSMITTANCE - 59%; RELATIVE EXPERIMENTAL TRANSMITTANCE - 46%; $\lambda$ = 0.6328 MICRON LASER
FIGURE 19

SULFURIC ACID ON SURFACE-DEACTIVATED FUSED SILICA: CONCENTRATION - 120 μg/cm²; CALCULATED TRANSMITTANCE - 16.3%; RELATIVE EXPERIMENTAL TRANSMITTANCE - 14.8%; λ = 0.6328 MICRON LASER
FIGURE 20

SULFURIC ACID ON SAPPHIRE; CONCENTRATION - 30 µg/cm²; RELATIVE EXPERIMENTAL TRANSMITTANCE - 41%; λ = 0.6328 MICRON LASER
FIGURE 21

SULFURIC ACID ON QUARTZ: CONCENTRATION - 10 µg/cm$^2$; RELATIVE EXPERIMENTAL TRANSMITTANCE - 70%; $\lambda = 0.632$ MICRON LASER
SULFURIC ACID ON QUARTZ: CONCENTRATION - 15 μg/cm²; RELATIVE EXPERIMENTAL TRANSMITTANCE - 58%; λ = 0.6328 MICRON LASER
FIGURE 23

SULFURIC ACID ON IR-4: CONCENTRATION - 10 \( \mu g/cm^2 \); RELATIVE EXPERIMENTAL TRANSMITTANCE - 97%; \( \lambda = 8.5 \) MICRONS
FIGURE 24

SULFURIC ACID ON IR-4: CONCENTRATION - 20 \mu g/cm^2; RELATIVE EXPERIMENTAL TRANSMITTANCE - 89%; \lambda = 8.5 MICRONS
FIGURE 25

SULFURIC ACID ON IR-4: CONCENTRATION - 40 $\mu$g/cm$^2$; RELATIVE EXPERIMENTAL TRANSMITTANCE - 75%; $\lambda$ = 8.5 MICRONS
FIGURE 26

SULFURIC ACID ON IR-4: CONCENTRATION - 90 µg/cm²; RELATIVE
EXPERIMENTAL TRANSMITTANCE - 63.5%; λ = 0.5 MICRONS
FIGURE 27

SULFURIC ACID ON IR-4: CONCENTRATION - 200 µg/cm²; RELATIVE EXPERIMENTAL TRANSMITTANCE - 38.6%; \( \lambda = 8.5 \) MICRONS
FIGURE 28

SULFURIC ACID ON IR-6: CONCENTRATION - 10 μg/cm²; RELATIVE EXPERIMENTAL TRANSMITTANCE - 98%; λ = 8.5 MICRONS
FIGURE 29

SULFURIC ACID ON IR-6: CONCENTRATION - 60 \( \mu g/cm^2 \); RELATIVE EXPERIMENTAL TRANSMITTANCE - 67%; \( \lambda = 8.5 \) MICRONS
FIGURE 30

SULFURIC ACID ON IR-6: CONCENTRATION - 140 μg/cm²; RELATIVE EXPERIMENTAL TRANSMITTANCE - 31%; λ = 8.5 MICRONS
FIGURE 31

SULFURIC ACID ON IR-6: CONCENTRATION - 1,300 μg/cm²;
RELATIVE EXPERIMENTAL TRANSMITTANCE - 18% MAGNIFICATION: 275X
λ = 8.5 MICRONS
FIGURE 32

MERCURY DROPLETS ON GLASS: CONCENTRATION = 6,120 μg/cm²; RELATIVE EXPERIMENTAL TRANSMITTANCE = 62%; CALCULATED TRANSMITTANCE = 59%; MAGNIFICATION: 687X; \[ \lambda = 0.450 \text{ MICRONS} \]
FIGURE 33

MERCURY ON IR-4: CONCENTRATION - 13,400 µg/cm²; RELATIVE EXPERIMENTAL TRANSMITTANCE - 60%; CALCULATED TRANSMITTANCE - 62% MAGNIFICATION: 687X
\[ \lambda = 2.0 \text{ MICRONS} \]
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>1</td>
</tr>
<tr>
<td>II.</td>
<td>4</td>
</tr>
<tr>
<td>III.</td>
<td>5</td>
</tr>
<tr>
<td>IV.</td>
<td>10</td>
</tr>
<tr>
<td>V.</td>
<td>12</td>
</tr>
<tr>
<td>VI.</td>
<td>15</td>
</tr>
</tbody>
</table>

I. INTRODUCTION

II. WORK PERFORMED

III. CONDENSATION OF WATER ON CANDIDATE WINDOW MATERIALS

IV. CONDENSATION OF HYDROCHLORIC ACID ON CANDIDATE WINDOW MATERIALS

V. THE CHEMICAL EFFECT OF HCl AND H₂SO₄ UPON IRTRAN WINDOW MATERIALS

VI. REFERENCE
LIST OF FIGURES

FIGURE
1. CONDENSATION CHAMBER
2. CONDENSATION CHAMBER
3. CONDENSATION CHAMBER IN SAMPLE BEAM OF INFRARED SPECTROPHOTOMETER
4. RELATIVE TRANSMITTANCE OF A QUARTZ WINDOW AS WATER CONDENSES
5. RELATIVE TRANSMITTANCE OF A SAPPHIRE WINDOW AS WATER CONDENSES
6. RELATIVE TRANSMITTANCE OF A QUARTZ WINDOW AS WATER CONDENSES
7. RELATIVE TRANSMITTANCE OF A SAPPHIRE WINDOW AS WATER CONDENSES
8. VARIATION OF RELATIVE TRANSMITTANCE WITH WAVELENGTH FOR DIFFERENT AMOUNTS OF WATER CONDENSED ON A SAPPHIRE WINDOW
9. RELATIVE TRANSMITTANCE OF AN IRTRAN 4 WINDOW AS WATER CONDENSES
10. RELATIVE TRANSMITTANCE OF AN IRTRAN 6 WINDOW AS WATER CONDENSES
11. VARIATION OF RELATIVE TRANSMITTANCE WITH WAVELENGTH FOR DIFFERENT AMOUNTS OF WATER CONDENSED ON AN IRTRAN 4 WINDOW
12. VARIATION OF RELATIVE TRANSMITTANCE WITH WAVELENGTH FOR DIFFERENT AMOUNTS OF WATER CONDENSED ON AN IRTRAN 6 WINDOW
13. RELATIVE TRANSMITTANCE OF A QUARTZ WINDOW AS HCl CONDENSES
14. RELATIVE TRANSMITTANCE OF A SAPPHIRE WINDOW AS HCl CONDENSES
15. RELATIVE TRANSMITTANCE OF AN IRTRAN 4 WINDOW AS HCl CONDENSES
16. RELATIVE TRANSMITTANCE OF AN IRTRAN 6 WINDOW AS HCl CONDENSES
17. TRANSMITTANCE OF IRTRAN 4 (2mm THICK)
18. TRANSMITTANCE OF IRTRAN 6 (1mm THICK)
19. RELATIVE TRANSMITTANCE OF AN IRTRAN 4 WINDOW AFTER ONE POLISHED SURFACE HAD BEEN EXPOSED TO 50%(VOL.) H2SO4 AT 50 °C FOR VARIOUS TIMES

70<
I. INTRODUCTION

The transmittance of an optical window can be determined from the formula

\[ T = \frac{I}{I_0} \]  

where \( I_0 \) is the intensity of the radiation incident upon the window and \( I \) is the intensity of the radiation transmitted by the window. The transmittance is almost always less than unity, since some of the incident radiation is lost by reflection, scattering, and absorption as it passes through the window. A number of factors affect the observed transmittance of a window, among them the index of refraction, homogeneity, thickness, surface finish, and cleanliness of the window material, as well as the wavelength at which the measurements are made.

The formation of a condensate upon a window can cause a marked change
in the measured transmittance. If, in Equation 1, the radiation transmitted by the window upon which the condensate has formed is measured as 40 units and the incident radiation is 100 units, then the transmittance would be 40 percent. This value alone is of little use, as it is not known whether the low transmittance is due to the window itself or to the condensation that has formed. If it is also known that the window had a transmittance of 50 percent before the condensation has formed, then it can be seen that the condensation did not substantially reduce the window transmittance. If, however, the transmittance of the window alone had been 95 percent, then the presence of the condensate would have been of great consequence.

A more useful means of determining the loss of transmittance of a window due to the presence of condensation is to rewrite Equation 1 in the form

\[ T_c = \frac{I_{w+c}}{I_w} \]  

where \( T_c \) is the transmittance of the condensate alone, \( I_w \) is the intensity of the radiation transmitted by the clean window, and \( I_{w+c} \) is the intensity of the radiation transmitted by the window and condensate. In the first example above, \( T_c \) would be 40/50 or 80 percent, meaning that 20 percent of the light normally transmitted by the window was lost because of the presence of the condensate. In the second example, \( T_c \) would be 40/95 or only 42 percent. In this case 58 percent of the radiation transmitted by the clean window was lost due to the presence of the condensate. These transmittances show the true effect of the condensate, and are not influenced by variations in structure from one specific window to another.

In order to avoid confusion in this report, the ratio of transmitted radiation to incident radiation (\( T \)) will be referred to as "transmittance."
The ratio of radiation transmitted by window and condensate to that transmitted by the window alone \((T_c)\) will be termed "relative transmittance."

It is necessary to consider a number of factors in designing an experiment for measuring the loss of relative transmittance of various window materials as known amounts of condensate are deposited upon the surface of a window. One of these factors is the condition necessary for condensation to take place. If a condensate, such as water, is to be present upon a window for the time necessary to take measurements, then the liquid condensate and the water vapor in the atmosphere around the window must be in equilibrium. The vapor pressure of the liquid at window temperature must equal the partial pressure of the vapor in the atmosphere. If the partial pressure of the vapor is not great enough, then no condensation will take place. When the partial pressure of the vapor in the atmosphere reaches a value equal to the vapor pressure of the liquid (which will be at window temperature) condensation begins. In a closed system, any additional vapor added to the atmosphere will be removed by condensation until equilibrium is restored. Once a condensate has formed, the removal of vapor from the atmosphere will result in enough of the condensate evaporating until the removed vapor is replaced. From this observation it can be concluded that the chamber must be air tight, so that the partial pressure of the vapor in the atmosphere can be controlled, but provision must be made for varying the amount of vapor present in order to control the amount of condensate deposited. The chamber should be heated, preferably to a temperature above the boiling point of the condensing substance. In this manner the substance can be injected into the chamber as a liquid, but it will immediately become entirely vaporized. The window upon which the condensation is to form must be cooled, and should be by far the coolest surface within the chamber. Under these conditions it can be safely assumed
that all of the excess liquid injected into the chamber will condense, and that all of the condensation occurs only upon the window surface and not anywhere else within the chamber.

The necessity of an air-tight chamber dictates that the window be cooled from the outside. The temperature of the window must be carefully maintained, as fluctuations will directly affect the amount of liquid condensate present on the surface.

Also, some means must be used to prevent water vapor, present in the room air, from condensing on the outside of the cool window. This can be precluded by cooling the window with a stream of refrigerated dry air, thus simultaneously cooling the surface and flushing it of unwanted water vapor.

Finally, the chamber must be constructed of materials that will resist corrosive compounds such as hydrochloric acid, which is one of the possible condensates to be tested. The over-all dimensions of the chamber are dictated by the requirement of compatibility with the instruments to be used for transmittance measurements.

II. WORK PERFORMED

A diagram of the condensation chamber is shown in Figure 1. The chamber is constructed of stainless steel, which has been passivated so as not to react with acids. The chamber is constructed as a double cylinder. Heater tape is wrapped around the walls of the inner cylinder for the purpose of heating the chamber. Chamber temperature is monitored with a thermocouple and maintained within one degree centigrade.

Provision is made for mounting an optical window at each end of the chamber. One of these windows is necessary only as a means of introducing a beam of light into the chamber. Since condensation upon this window would
be most undesirable the window is allowed to reach thermal equilibrium with
the chamber walls as the chamber is heated.

The second window is the test window, and it is cooled by the flow of
dry, refrigerated air. A circular nozzle arrangement causes air to flow
uniformly on the surface of the test window. Any "cold spots" on this
surface will result in uneven condensation. This window is thermally
insulated from the walls of the condensation chamber by a teflon disc.

The test window temperature was monitored on the outside of the chamber
since hydrochloric acid would probably have an adverse effect upon a
temperature sensing device.

Two stainless steel valves were used to vent the condensation chamber
and to flush it with dry nitrogen. The liquid to be condensed was injected
through a self-healing septum. It was found unnecessary to provide additional
heating for the injection system, as the chamber heat was sufficient to
completely vaporize the liquids used.

A photograph of the condensation chamber is shown in Figure 2. The
rectangular plate shown in this figure fits into the sample holder of the
spectrophotometers used to measure window transmittance. Figure 3 shows the
condensation chamber positioned in the sample beam of the Perkin Elmer
Model 21 Spectrophotometer.

III. CONDENSATION OF WATER ON CANDIDATE WINDOW MATERIALS

Initial experiments were carried out in the visible region of the
spectrum using water as the condensate and fused quartz test windows. In
this manner the condensation could be observed as it formed, and some under-
standing could be gained of the processes occurring within the chamber. The
chamber was mounted on a Heath Monochromator which allowed the light passing
through the test chamber to be scanned over the range of 4000 to 9500 angstroms.
For the first experiment the monochrometer was set at 5000 angstroms and the chamber temperature was maintained at 130°C and the temperature of the test window was 21.5°C. The vapor pressure of water at 21.5°C is 19.2 mm Hg. Considering the temperature of the chamber and the volume of the chamber which was 0.8 liters, it would be necessary to inject 12.3 microliters of water before the partial pressure of water within the chamber would reach 19.2 mm Hg at which time condensation could begin. In the actual experiment it was found to be necessary to inject 14 microliters of water before condensation began to form. Mathematically, this quantity of water would be required to initiate condensation if the window temperature inside the chamber were 23.5°C indicating an approximate two degree temperature rise across the quartz window.

As additional small quantities of water were added to the chamber, it was observed that the intensity of light transmitted by the window began to drop sharply. After the total amount of water injected reached 18 microliters, the rate of decrease in intensity lessened and eventually leveled off. A typical plot of relative transmittance as a function of the amount of condensate formed in milligrams per square centimeter is shown in Figure 4 for the quartz window.

A number of figures in this report illustrate the change of relative transmittance for various window materials as water or hydrochloric acid condenses upon one surface of the window. It is convenient to show several curves in most of these figures for visual comparison. A linear scale for the condensate mass concentration upon the window (mg/cm²) readily illustrates the manner in which relative transmittance decreases rapidly as the condensate begins to form, but if several different curves are superimposed their individual characteristics become difficult to distinguish. Utilizing a logarithmic scale for the condensate mass concentration emphasizes the
variations in similar curves but visually minimizes the initial decrease of relative transmittance and compresses those portions of the curve corresponding to large amounts of condensation. In all of the figures in which relative transmittance is shown as a function of condensate mass concentration a logarithmic scale has been chosen for the horizontal axis. One representative curve from each figure is also plotted using a linear scale and inserted in the figure so that the true transmittance characteristics can be readily ascertained.

During these experiments a number of visual observations were made. Referring to Figure 4, it was noted that for a quantity of water condensate of 0.1 mg/cm² a faint haze could be seen upon the test window. As more water was injected, this haze became more obvious until at about 0.6 mg/cm² the haze appeared to be quite dense. At approximately 0.8 mg/cm² of water the condensate began to appear slightly "grainy," similar to the appearance of etched glass, and with the addition of more water the "grains" could be distinguished as tiny water droplets. As more water was added the droplets grew in size and the intensity of light transmitted by the window and condensate leveled off. A point was reached (around 18 mg/cm² of water) beyond which the relative transmittance no longer decreased as more condensate formed upon the window. At this point the condensate was in the form of very large water drops. The relative transmittance would then change with time, fluctuating at random over several percent as the condensate continually rearranged itself on the window surface.

Figure 5 is also a plot of relative transmittance as a function of the amount of condensate formed in milligrams per square centimeter except that the window material is sapphire rather than quartz. In Figure 5 the results of two consecutive experiments made under identical conditions are presented. A clean sapphire window was mounted on the condensation chamber, which was
then flushed with dry nitrogen and heated to 130 °C. The sapphire test window was then cooled, and when equilibrium conditions were attained known volumes of water were injected into the chamber. After the loss of transmittance had leveled off, the chamber was again flushed with dry nitrogen to evaporate the condensate from the window and remove this moisture from the chamber. Upon again attaining equilibrium Experiment Number 1 was repeated. In each experiment 19.0 microliters of water were required before condensation could begin. This volume of water indicates that the window temperature inside the chamber was approximately 28.5 °C for both experiments. The data for relative transmittance as a function of mass density of condensate obtained during these two runs result in curves similar in shape but differing greatly in relative transmittance for a given quantity of condensate formed (Figure 5). The two curves are almost identical over the range of 1.4 to 2.2 mg/cm² of window surface, after which they level off at different values.

The explanation for this lack of repeatability is that the actual loss of relative transmittance is determined more by the nature of the condensate formed than by the quantity of condensate present. Experiment Number 1 was performed with a clean window. When the condensation which had been formed was evaporated it probably left behind some deposits which did not alter the transmittance of the window, but which could act as centers around which condensation could readily occur during the second experiment. A difference in the size, shape, and distribution of the water droplets formed would affect the relative transmittance.

Figures 6 and 7 are similar to Figures 4 and 5 except that they represent the relative transmittance at several different wavelengths. The curves in Figure 6 were obtained by condensing water upon a quartz window. They represent the relative transmittances measured at 1.5, 2.5, and 3.5 microns in the near infrared region, using the Perkin-Elmer Model 2
Spectrophotometer. A small linear plot of the 3.5 micron curve is inserted in Figure 6.

It can be seen from Figure 6 that the addition of condensate above 1.2 mg/cm² resulted in an improvement in the relative transmittance. This is the result of a change in the size, shape, and distribution of the water droplets as more and more condensate formed. Figure 7 presents similar data for the condensation of water upon a sapphire window.

The variation in relative window transmittance with wavelength for certain specific mass densities of water condensate on a sapphire window is shown in Figure 8. The relative transmittances from 0.45 to 0.9 microns were obtained with the Heath Monochromator, while those from 1.5 to 4.5 microns were measured using the Perkin Elmer Model 21. It should not be expected that the points obtained from two separate experiments on two different instruments could be joined to form one continuous curve, but the two sets of data are presented together so that the general trend of the data can be observed. In general, it is seen that the relative transmittance is less at the shorter wavelengths for a given set of condensation conditions. The consistently low relative transmittances at 3.5 microns are attributed to a strong water absorption band which influenced these readings downward.

Figure 9 illustrates the change in relative window transmittance when water condensed upon Irtran 4 infrared window material. The four curves illustrate measurements at 3.5, 7.5, 11.5, and 15.5 microns. Similar information is shown in Figure 10 for the condensation of water upon Irtran 6. The variation of relative transmittance as a function of wavelength for certain specific quantities of condensed water is shown for Irtran 4 in Figure 11 and for Irtran 6 in Figure 12. The low values which are seen for wavelengths of 3.5, 6.45, and 14.0 microns are due to the infrared absorption bands of water.
IV. CONDENSATION OF HYDROCHLORIC ACID ON CANDIDATE WINDOW MATERIALS

A series of experiments similar to those previously described were conducted, substituting hydrochloric acid as the condensate. The initial experiments were performed in the visible region of the spectrum using quartz and sapphire window materials. The first observation made with HCl as the condensate was that for a given window temperature the relative transmittance began to decrease much sooner than would be expected if water had been the condensate. In these and all subsequent experiments it was found that the quantity of hydrochloric acid injected into the chamber before condensation began was approximately one-half that necessary had water been the condensate. In addition, once condensation had begun the intensity of the radiation transmitted by the window dropped at a much more rapid rate than had been the case with water. Only one or two additional microliters (0.2 to 0.4 mg/cm$^2$) of hydrochloric acid were sufficient to cause the relative transmittance to drop from the 100 percent value to 10 or 20 percent, measurements being made at a wavelength of 0.5 microns.

Figure 13 shows the loss of relative transmittance of a quartz window with hydrochloric acid as the condensate at wavelengths of 1.5, 2.5, and 3.5 microns. The mass density of the condensate upon the window is approximate for all curves dealing with hydrochloric acid. The specific gravity of hydrochloric acid varies from 1.0 for very dilute concentrations to 1.19 for the 37 percent HCl used in these experiments. It is believed that as the HCl was injected into the condensation chamber the acid was vaporized forming water vapor and HCl gas. As the water vapor began to condense upon the window it again absorbed some of the HCl gas, but the exact quantity has not been determined. Therefore, the actual weight of condensate resulting from the injection of one microliter of acid depends upon the concentration of the condensate. For convenience, a specific gravity of
1.0 was assumed for the condensate in determining its mass density. Figure 14 shows similar data obtained for a sapphire window.

Figure 15 shows the loss of relative transmittance of an Irtran 4 window as hydrochloric acid condensed upon its surface. The relative transmittance is shown for specific amounts of condensate at wavelengths of 3.5, 7.5, 11.5, and 15.5 microns. Figure 16 illustrates the relative transmittance loss as hydrochloric acid condenses upon a window made of Irtran 6 material.

In conclusion, a certain minimum quantity of a potential condensate must be present in an atmosphere before condensation can take place. The specific amount of the substance necessary for condensation is determined by the temperature of the surface upon which the condensation is to form. For example, it may be of interest to determine whether or not water will condense upon a window which has a temperature of 20 °C. Since the vapor pressure of water at this temperature is 17.5 mm Hg, it is necessary for the partial pressure of water vapor in the atmosphere around the window to be at least this value before condensation can occur. Once condensation has begun, the relative transmittance of an optical window decreases rapidly. It is impossible to accurately predict the actual loss of relative transmittance for a given amount of condensate because the loss will vary over a wide range, depending upon the window material, surface finish, and cleanliness. As more and more condensation takes place, the rate at which the relative window transmittance drops will decrease and eventually level off. Further condensation may not lower the relative window transmittance, and in fact, may actually improve it, depending upon how the condensate arranges itself upon the window surface.

The condensation of hydrochloric acid upon the optical windows tested produced the same general results as were obtained when water was the
condensate, except that only about one-half the volume of hydrochloric acid was required to initiate the formation of condensation, and the drop in relative transmittance accompanying condensation was at a more rapid rate.

V. THE CHEMICAL EFFECT OF HCl AND H₂SO₄ UPON IRTRAN WINDOW MATERIALS

In the Technical Progress Report for work performed under NASA Research Grant NGL 04-001-007 dated November 15, 1973, the results of several tests were reported in which hydrochloric and sulfuric acids were placed in contact with Irtran 4 and Irtran 6 materials. The information contained in that part of the above report pertaining to these tests is included here, together with some additional data which has been obtained.

The manufacturer of Irtran materials reports that concentrated acids "attack" Irtran 4 and 6, the initial results being a "blush on the surface only, sufficient to attenuate the transmittance of the material," and with the "eventual complete disintegration or dissolving of the piece." A series of simple tests was run to determine the extent of damage which could be expected if either sulfuric acid or hydrochloric acid condensed upon the surface of windows made from Irtran 4 and Irtran 6.

Some scraps of Irtran material were obtained from the manufacturer for the purpose of destructive testing. The scraps appeared to be pieces of window material which had been broken and were not suitable for sale. The surfaces of the materials were polished smooth, but the granular structure of the pieces could be ascertained by examining the unpolished edges. Irtran 4 is made up of extremely coarse grains, while those of Irtran 6 are appreciably smaller. A Perkin-Elmer 21 IR Spectrophotometer was employed to measure the infrared transmittance of these samples over the range of 2 to 15 microns, and the transmittance was found to compare quite closely with the information published by the manufacturer. The transmittance for
an Irtran 4 sample, 2 millimeters thick, is shown in Figure 17. A similar curve for Irtran 6, 1 millimeter thick, is shown in Figure 18.

A 50 percent by volume aqueous solution of sulfuric acid was prepared and placed on the surface of an Irtran 4 sample. The acid did not contact the edges of the material, but only one of the polished surfaces. After 30 minutes of contact the acid solution was washed off, the material dried, and the transmittance remeasured. No measurable change was observed in the transmittance of the sample after being exposed to the sulfuric acid solution for 30 minutes at room temperature. The acid solution was applied to the sample surface for two additional 30 minute periods, giving a total exposure of 1.5 hours. After each application the transmittance was rechecked, and there was still no measurable change in the transmittance of the material. The test piece was then completely immersed in the sulfuric acid solution for two hours, after which the transmittance was again measured. After a total of 3.5 hours exposure to the sulfuric acid solution, 1.5 hours with only one surface in contact with the solution and 2 hours with the entire piece immersed, the transmittance had not changed by a measurable amount from the original values.

The same tests were made using the 50 percent by volume aqueous solution of sulfuric acid on Irtran 6 material. As with Irtran 4, there was no measurable change in transmittance from the original values after 1.5 hours of contact between the acid solution and one polished surface and an additional two hours of contact with the piece totally immersed in the acid solution.

A similar set of tests was run using concentrated hydrochloric acid (37 percent HCl) on the Irtran 4 and 6 materials. After three 30 minute periods during which the concentrated HCl was in contact with one of the polished surfaces of Irtran 4 there was no measurable decrease in the
transmittance of the sample. The Irtran 4 was then totally immersed in the acid for 1.5 hours, during which time it was seriously attacked. The polished surfaces of the material became rough and the granular structure was apparent. The transmittance of the sample had decreased to zero over the range of 2 to 15 microns. In a subsequent test a sample of Irtran 4 material was totally immersed in the 37 percent HCl for a period of one hour. This sample was severely attacked, but the transmittance was surprisingly good, considering the general appearance of the material. The transmittance of this sample is shown in Figure 17.

When the concentrated hydrochloric acid was placed in contact with one polished surface of an Irtran 6 sample for three 30 minute periods there was no measurable change in the transmittance of the sample. Total immersion in the acid for 1.5 hours also had no obvious ill effects upon the transmittance. As a result of this apparent immunity to HCl it was decided to leave the Irtran 6 sample immersed in the concentrated hydrochloric acid over the entire weekend. After 66 hours of immersion it was found that the Irtran 6 had been attacked by the acid. The surface was no longer smooth, but appeared grainy. Fine grains of the material could be observed floating in the acid and lying on the bottom of the container. The transmittance of this piece of Irtran 6 was measured, and the results are shown in Figure 18. Since the grain size of the material is small the transmittance of the sample was not affected greatly at the longer wavelengths, but the shorter wavelengths do show the marked deterioration of the sample.

All of the tests described were carried out at room temperature. A similar series of experiments was made inside an oven where the temperature was maintained at 50 °C. When 50 percent by volume sulfuric acid was placed upon the polished surface of Irtran 6 material for three thirty minute periods no measurable loss of transmittance was recorded. An identical
test conducted on Irtran 4 material did result in a loss of transmittance by the material. The relative transmittance of the Irtran 4 material after each of the three thirty minute exposures to the sulfuric acid is shown in Figure 19.

Experiments carried out with 37 percent HCl at 50 °C were inconclusive. At elevated temperatures the hydrochloric acid evaporated and did not stay in contact with the Irtran surfaces long enough to have a detrimental effect.

It has been concluded that applying 50 percent sulfuric acid or concentrated hydrochloric acid to the polished surfaces of Irtran 4 and Irtran 6 for periods up to 1.5 hours at room temperature will not have an adverse effect upon the transmittance of the material. Total immersion in hydrochloric acid is very harmful to the Irtran 4 material, and over a long period also affects the Irtran 6, especially for the shorter wavelengths of radiation.

Sulfuric acid at 50 °C had no adverse effect upon Irtran 6, but did degrade the transmittance of Irtran 4. Tests made with hydrochloric acid at 50 °C were inconclusive.

VI. REFERENCE

FIGURE 2
CONDENSATION CHAMBER
FIGURE 3

CONDENSATION CHAMBER IN SAMPLE BEAM OF INFRARED SPECTROPHOTOMETER
FIGURE 4

RELATIVE TRANSMITTANCE OF A QUARTZ WINDOW AS WATER CONDENSES
FIGURE 5

RELATIVE TRANSMITTANCE OF A SAPPHIRE WINDOW AS WATER CONDENSES
FIGURE 6

RELATIVE TRANSMITTANCE OF A QUARTZ WINDOW AS WATER CONDENSES
Figure 7

Relative transmittance of a sapphire window as water condenses.
Variation of relative transmittance with wavelength for different amounts of water condensed on a sapphire window.

- 0.2 mg/cm²
- 0.4 mg/cm²
- 0.6 mg/cm²
- 1.0 mg/cm²
- 1.2 mg/cm²
- 1.6 mg/cm²
- 2.4 mg/cm²
- 2.6 mg/cm²
- 8.0 mg/cm²

FIGURE 8

VARIATION OF RELATIVE TRANSMITTANCE WITH WAVELENGTH FOR DIFFERENT AMOUNTS OF WATER CONDENSED ON A SAPPHIRE WINDOW
Figure 9

Relative Transmittance of an IRTRAN 4 Window as Water Condenses
FIGURE 10

RELATIVE TRANSMITTANCE OF AN IRTRAN 6 WINDOW AS WATER CONDENSES
FIGURE 11

VARIATION OF RELATIVE TRANSMITTANCE WITH WAVELENGTH FOR DIFFERENT AMOUNTS OF WATER CONDENSED ON AN IRTRAN 4 WINDOW
FIGURE 12
VARIATION OF RELATIVE TRANSMITTANCE WITH WAVELENGTH FOR DIFFERENT AMOUNTS OF WATER CONDENSED ON AN IRTRAN 6 WINDOW
FIGURE 13

RELATIVE TRANSMITTANCE OF A QUARTZ WINDOW AS HCl CONDENSES
FIGURE 14

RELATIVE TRANSMITTANCE OF A SAPPHIRE WINDOW AS HCl CONDENSES
Figure 15

Relative transmittance of an IRTRAN 4 window as HCl condenses.
FIGURE 16

RELATIVE TRANSMITTANCE OF AN IRTRAN 6 WINDOW AS HCl CONDENSES

- 3.5 microns
- 7.5 microns
- 11.5 microns
- 15.5 microns
THIS CURVE APPLIES TO:
(1) BEFORE TREATMENT WITH ACIDS
(2) POLISHED SURFACE EXPOSURE TO 50% H$_2$SO$_4$ FOR 90 MINUTES
(3) POLISHED SURFACE EXPOSURE TO CONCENTRATED HCl FOR 90 MINUTES

AFTER 1 HOUR IN CONCENTRATED HCl

FIGURE 17
TRANSMITTANCE OF IRTRAN 4 (2mm THICK)
THIS CURVE APPLIES TO:
(1) BEFORE TREATMENT WITH ACIDS
(2) POLISHED SURFACE EXPOSURE TO 50% $\text{H}_2\text{SO}_4$ FOR 90 MINUTES
(3) POLISHED SURFACE EXPOSURE TO CONCENTRATED $\text{HCl}$ FOR 90 MINUTES

AFTER 66 HOURS IN CONCENTRATED $\text{HCl}$

FIGURE 18
TRANSMITTANCE OF IRTRAN 6 (1mm THICK)
FIGURE 19

RELATIVE TRANSMITTANCE OF AN IRTRAN 4 WINDOW AFTER ONE POLISHED SURFACE HAD BEEN EXPOSED TO 50%(VOL.) H₂SO₄ AT 50 °C FOR VARIOUS TIMES.

- ○ 30 MINUTE EXPOSURE
- □ 1 HOUR EXPOSURE
- × 1.5 HOUR EXPOSURE