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ALUMINUM VAPOR RELEASE IN THE UPPER ATMOSPHERE

General Electric Company/RESD

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Project Engineer

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ALUMINUM VAPOR RELEASE IN THE UPPER ATMOSPHERE

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Based on the exothermic nature of intermetallic reactions techniques have been developed which are capable of generating high temperatures in the condensed phase. By proper selection, based on the relative vapor pressures of all the components, it is possible to selectively vaporize metals for atmospheric release applications.

Laboratory experiments and ground tests conducted on a chemical system consisting of Ti/B/Al resulted in the development and flight test of an aluminum vapor

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release payload. A successful atmospheric experiment was conducted at Wallops Is., VA, in January 1975, involving the oxidation of atomic aluminum by molecular oxygen.

Atomic aluminum was observed in resonance line fluorescence, while the product AlO was monitored from band radiation measurements. The observed kinetics of the oxidation process was in good agreement with estimates based on available laboratory chemical rate constants and on standard atmospheric properties.

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I. INTRODUCTION

Atmospheric release experiments may provide a suitable means for the study of the oxidation of metal atoms. The appeal of this approach to the problem is significant for a variety of reasons which include: a) the ability to produce large quantities of unstable species, b) the absence of confining walls, and c) the availability of atomic oxygen. However, the feasibility of performing useful atmospheric experiments using pure metal vapors must be established. The present program was undertaken to demonstrate that aluminum can be released in the atmosphere without the production of large quantities of gaseous side products which can effect the chemical behavior of the gaseous metal vapor.

II. THERMOCHEMICAL CONSIDERATIONS

The high exothermicity associated with some condensed phase intermetallic reactions was identified (Reference 1) as a convenient and potentially effective means of generating metal vapors for atmospheric releases. The metal of interest in this investigation was aluminum.

In order for the above schemes to be of practical interest the following criteria must be satisfied: 1) Reaction can be easily initiated; 2) once initiated the reaction must be self-sustained at a fast rate; 3) the realized temperatures must be high enough to vaporize aluminum; 4) production of high aluminum yields at a reasonable cost; 5) the system must be scalable to large quantities and 6) the reaction should not be explosive.

Specifically one of the most promising reactions which was identified was the reaction between titanium and boron (in the condensed phase) to form titanium diboride according to the following stoichrometry:

$$\mathrm{Ti(s)} + 2\mathrm{B(s)} \longrightarrow \mathrm{Ti\ B_2(c)} + \text{heat.}$$

Due to favorable thermochemical properties this is a "gasless" reaction i.e. the only product in addition to heat is the condensed phase of TiB_2. The calculated adiabatic temperature resulting from the above reaction is 4043°K.

In view of the fact that the boiling point of aluminum (2736°K) is considerably less than the calculated adiabatic temperature it is safe to assume that the system can be used as an "aluminum vaporizer" by simply adding aluminum to the mixture. The vapor pressure of aluminum in comparison to the other two components of the system (Ti and B) is shown in Figure 1. Since the vapor pressure of aluminum is two and three orders of magnitude higher than that of Ti and B respectively it is expected that extremely small amounts of gaseous titanium and boron would be generated during an aluminum release. Using the thermochemical properties (Table I) which govern the yield of aluminum vapor, the Ti/B/Al system was balanced near the boiling point of aluminum:

$$\underset{(298^{\circ}K)}{Ti(s) + 2\,B(s) + 0.22\,Al(s)} \longrightarrow \underset{(2700^{\circ}K)}{TiB_2(s) + 0.21\,Al(g)}$$

This suggests that as much as 0.22 gram-atoms (or 5.93 g) of Al could be vaporized by 1 - mole (69.52 g) of TiB_2 which corresponds to a predicted efficiency of 7.8% based on the total chemical weight.

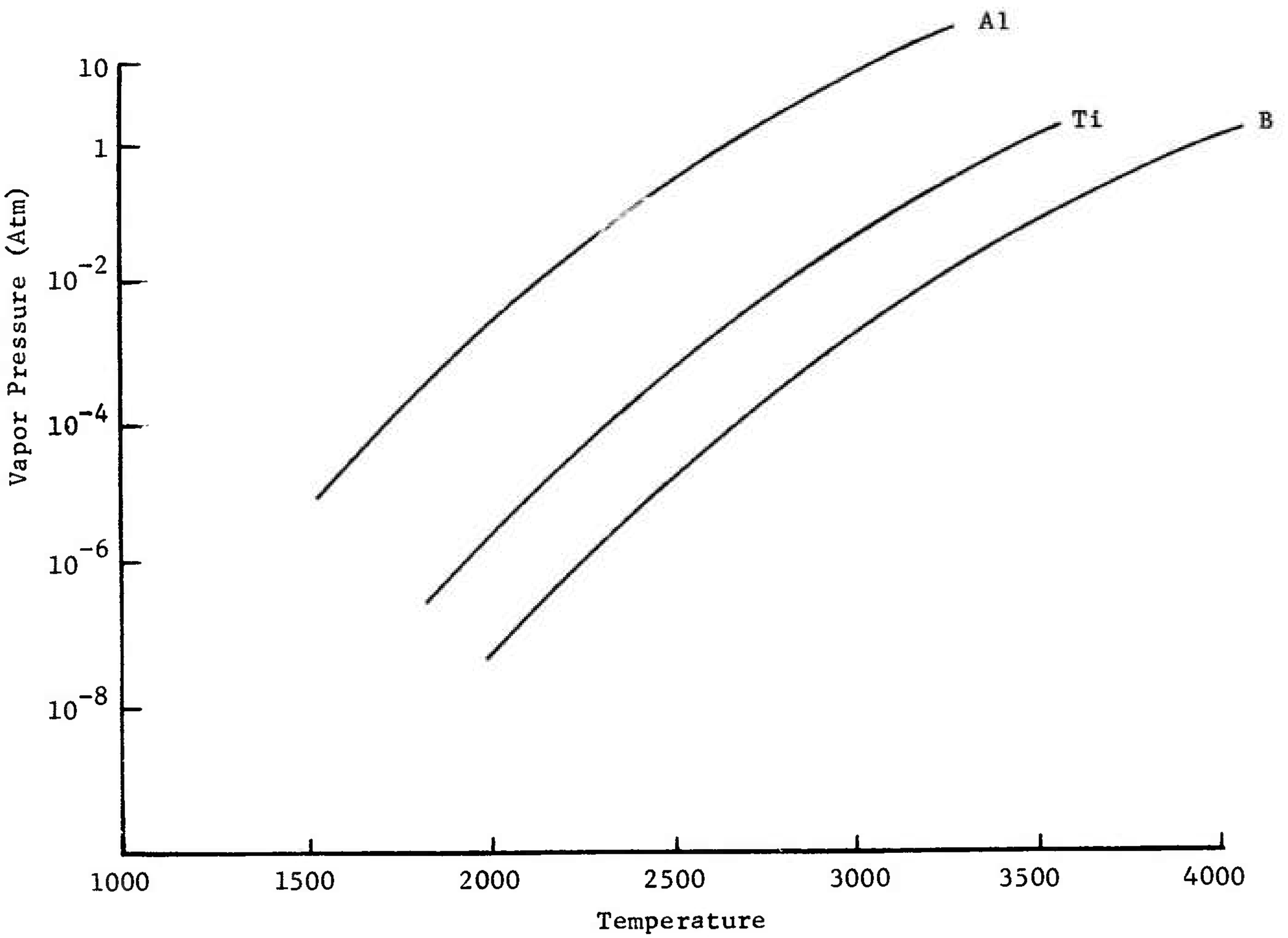


FIGURE 1. VAPORIZATION PROPERTIES

TABLE I. THERMOCHEMICAL PROPERTIES OF METALS AND COMPOUNDS(2)

Material	Melting		Enthalpy Change	Heat of Formation	Vaporization	
	M.P. ^oK	ΔH (k cal/mole)	$H_{2700} - H_{298}$ (k cal/mole)	$\Delta H_{f(2700)}$ (k cal/mole)	B.P. ^oK	ΔH (298) (k cal/mole)
Al	932	2.55	16.8		2736	76.5
Ti	1940	4.0	19.1		3575	112.7
B	2300	5.1	15.3		3950	129.2-137.9
TiB_2	3193	12 ± 3	50.4	-84.7	>4000	

III. LABORATORY RESULTS AND PAYLOAD DEVELOPMENT

Samples containing Ti/B/Al at a weight ratio 2/1/0.7 were formulated using adhesive binders or by sintering under pressure at 100°C-150°C. Studies on these samples included initiation techniques, observation on the duration of the reaction, identification of aluminum atoms by mass spectrometry and emission spectroscopy, X-ray diffraction of reactants and products as well as yield determination of released aluminum.

Items of interest which became immediately apparent are that this system can be initiated simply, is self-sustaining at a fast rate, and looks promising in terms of producing aluminum vapor at a low cost. Heating locally a very small fraction of the mixture to 650°C either by hot wire or conventional initiators starts the reaction which lasts several milliseconds in the case of small (gram - like) samples or 200-300 milliseconds when the sample size is increased to 2.6 kg.

Additional measurements relating to yield of aluminum are shown in Table II. The range for recovered aluminum is 4.8 - 11%. In addition to aluminum it appears that titanium is also generated in the vapor; its quantity is about a factor of ten less than aluminum. A typical X-ray diffraction pattern of the Ti/B/Al formulation (containing 20% Al by weight) shown in Figure 2 depicts the presence of crystalling titanium and aluminum and amorphous boron. Figure 2 is the diffraction pattern of the metallic film which coats the walls of the vacuum chamber; it is apparent that this material is relatively pure aluminum . The diffraction pattern of the residue product is shown in Figure 4 which matches the ASTM data on TiB_2. The lack of any Ti or Al peaks suggests that the reaction went to completion and that most of the available aluminum was removed from the mixture to a large extent via vaporization.

TABLE II. ALUMINUM RELEASE FROM THE Ti/B SYSTEM

Reaction	Quantity(g)	Analytical Method	Wt. % Released
$\mathrm{Ti(s) + 2B(s) + Al(s) - 20\% \text{ by weight)}} \longrightarrow \mathrm{Ti\ B_2\ (c) + Al\ (g)}$	1	Atomic Absorption Spectrophotometry (collected coating)	6.4 Al 0.6 Ti
"	2	" "	4.8 Al 0.45 Ti
"	100	Weight (Al deposited on walls of vacuum chamber)	11 Al
		X-ray Diffraction of Reactants and Products	>10 Al
"	2,600	Emission Spectroscopy Identification of Al-lines and AlO-bands (1 atm, air)	

FIGURE 2. X-RAY DIFFRACTION STARTING MATERIAL

TITANIUM + BORON + ALUMINUM

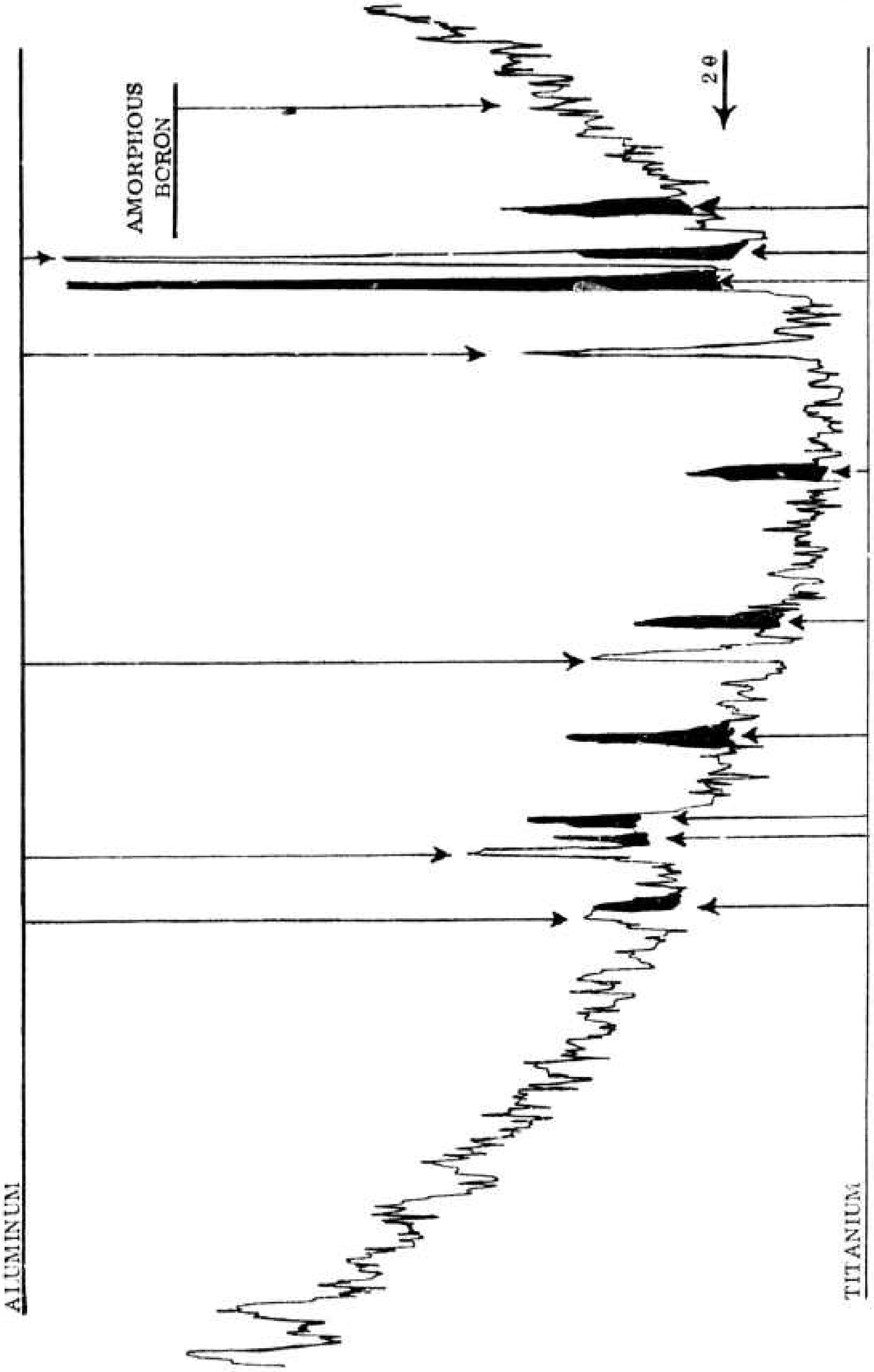
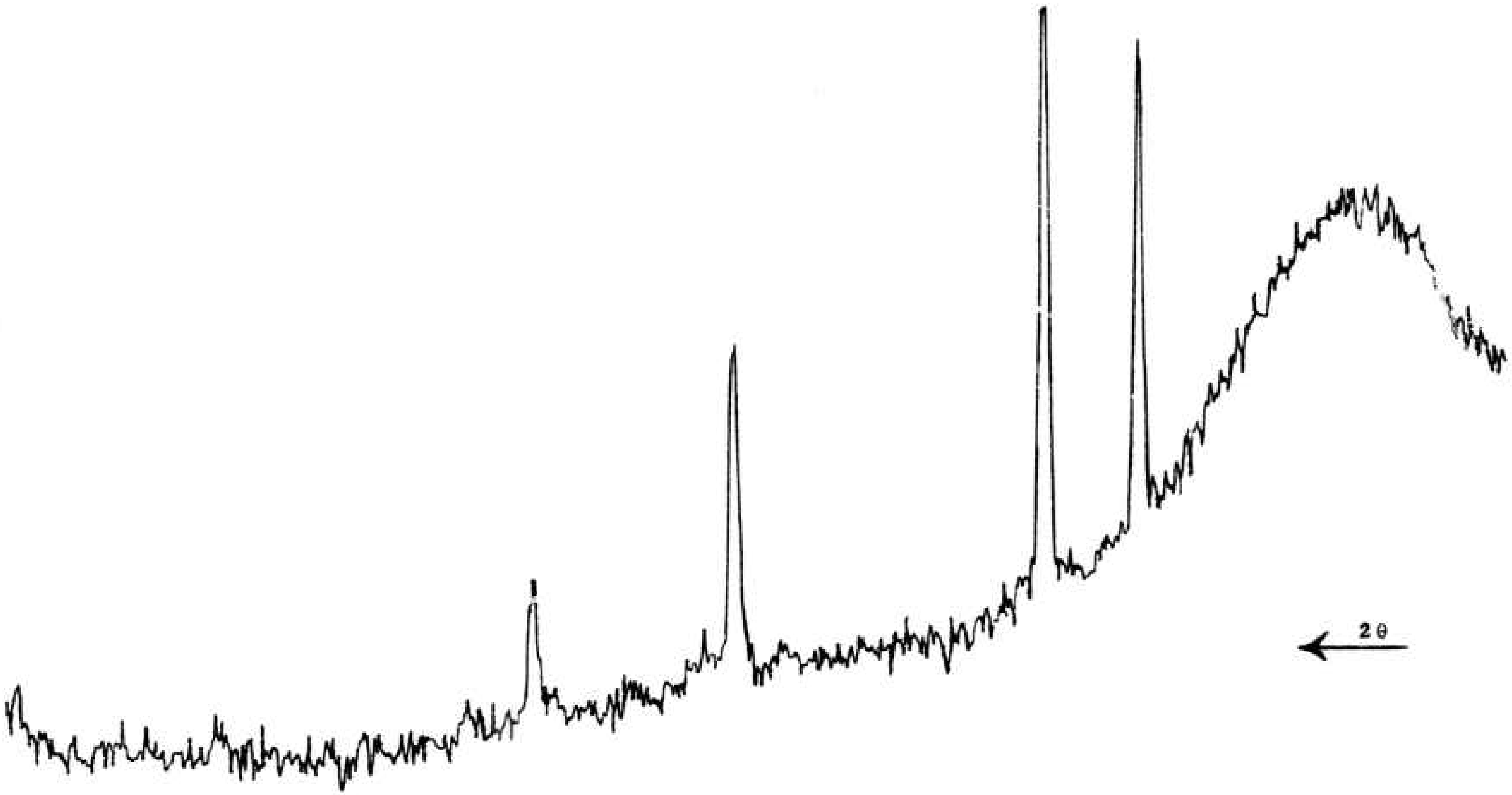


FIGURE 3. X-RAY DIFFRACTION VAPORIZED PRODUCT

ALUMINUM



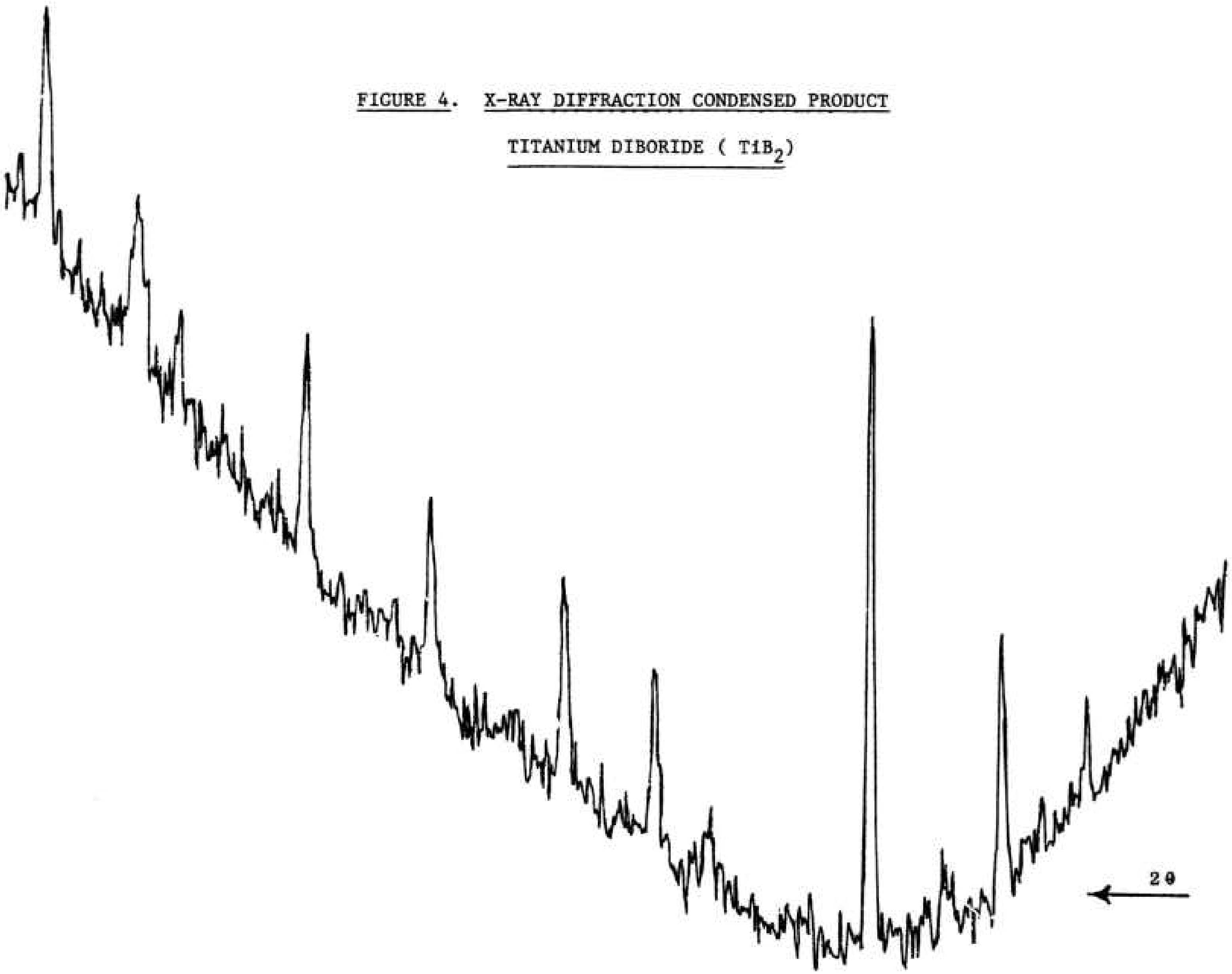


FIGURE 4. X-RAY DIFFRACTION CONDENSED PRODUCT

TITANIUM DIBORIDE (TiB_2)

The observed yield of 4.8 - 11% is in good agreement with the value of 7.8% predicted in the previous section.

The largest sample quantity involved in a ground test was the 2.6 kg canister referred to in Table II and shown in Figure 5. The cloud shown in photo-B is due to aluminum oxide formed as soon as the aluminum vapor interacts with the surrounding air. Photo-C exhibits the remains of the canister and $Ti\ B_2$ particles (on the ground).

The payload prepared for flight contained 6 kg - Ti, 3 kg-B and 2 kg-Al (a total of 12.7 kg chemical mixture*) enclosed in a canister 15 cm in diameter, 56 cm long, as shown in Figure 6. The release canister housed inside the rocket skin, is initiated by hot tungsten wire which is attached to the lid and is heated by a 20 V, 20A battery. Release was scheduled to occur at an altitude of 150 Km on the down-leg by removing the rocket-nose and firing through the lid which is designed to burst.

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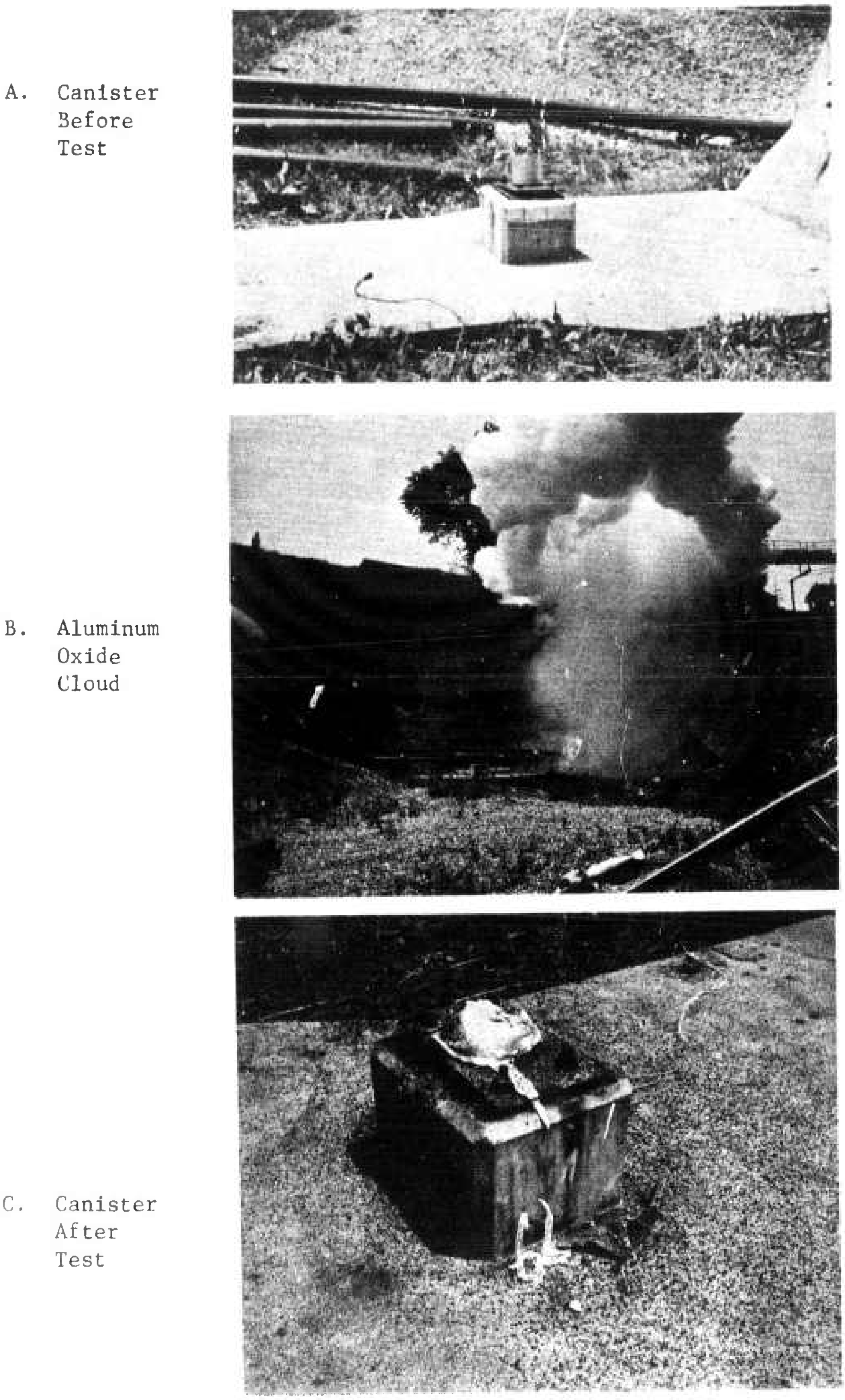
* This mixture, due to its large size, was not sintered as previously described.

FIGURE 5. ALUMINUM VAPOR RELEASE IN GROUND TEST

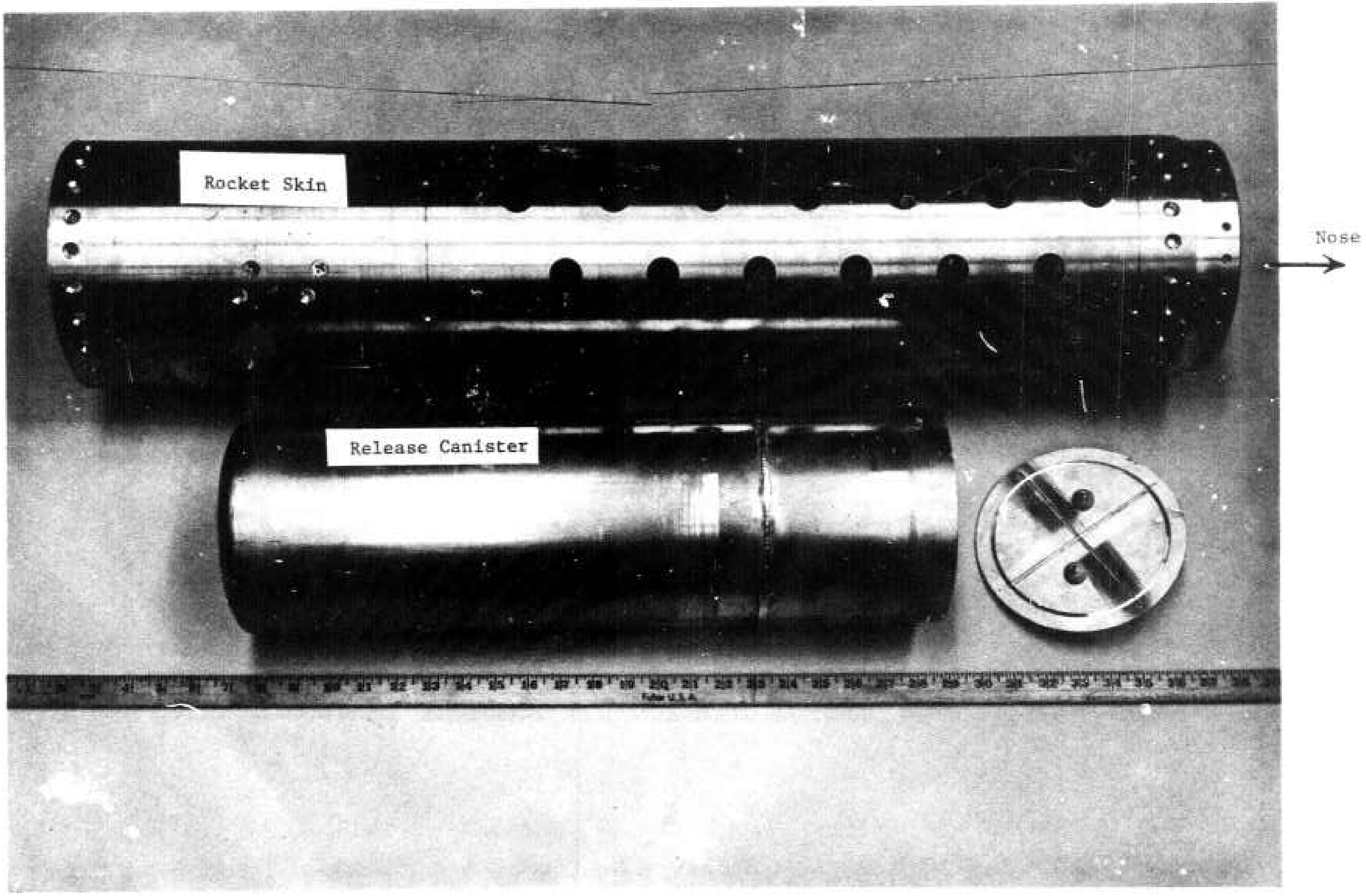


A. Canister Before Test

B. Aluminum Oxide Cloud

C. Canister After Test

FIGURE 6. ALUMINUM PAYLOAD FOR FLIGHT



IV. ATMOSPHERIC RELEASE OF ALUMINUM

A. Preflight Prediction of Resonance Fluorescence Produced By Atmospheric Aluminum Releases

The present analysis was undertaken in support of the experimental atmospheric release program. The intent of the calculations was to predict the altitude behavior of the intensity of resonance fluorescence produced by atomic aluminum released in the atmosphere. This enabled the optimization of the release altitude and provided estimated signal levels.

The release package as discussed in the previous section contains a mixture of 6 kg of titanium, 3 kg of boron and 2 kg of aluminum. Upon initiation, the titanium and boron react producing large quantities of heat.

$$\mathrm{Ti(s)} + 2\mathrm{B(s)} \longrightarrow \mathrm{Ti\ B_2(s)} + \text{heat}$$

The aluminum is vaporized and released in atomic form.

The geometry of the release cloud has been estimated using the semi-empirical method of Reference 3. The cloud is assumed Gaussian with an initial radius given by:

$$r_o = f \left(\frac{m_T}{\rho} \right)^{1/3} \tag{1}$$

where:

r_o = initial Gaussian radius

m_T = mass released

ρ = atmospheric density

f = empirical constant

Comparison between Equation (1) and measurements of the size of atmospheric releases allows the evaluation of the proportionality constant, f, as a function of altitude (see Figure 7). At low altitudes, f approaches the theoret-

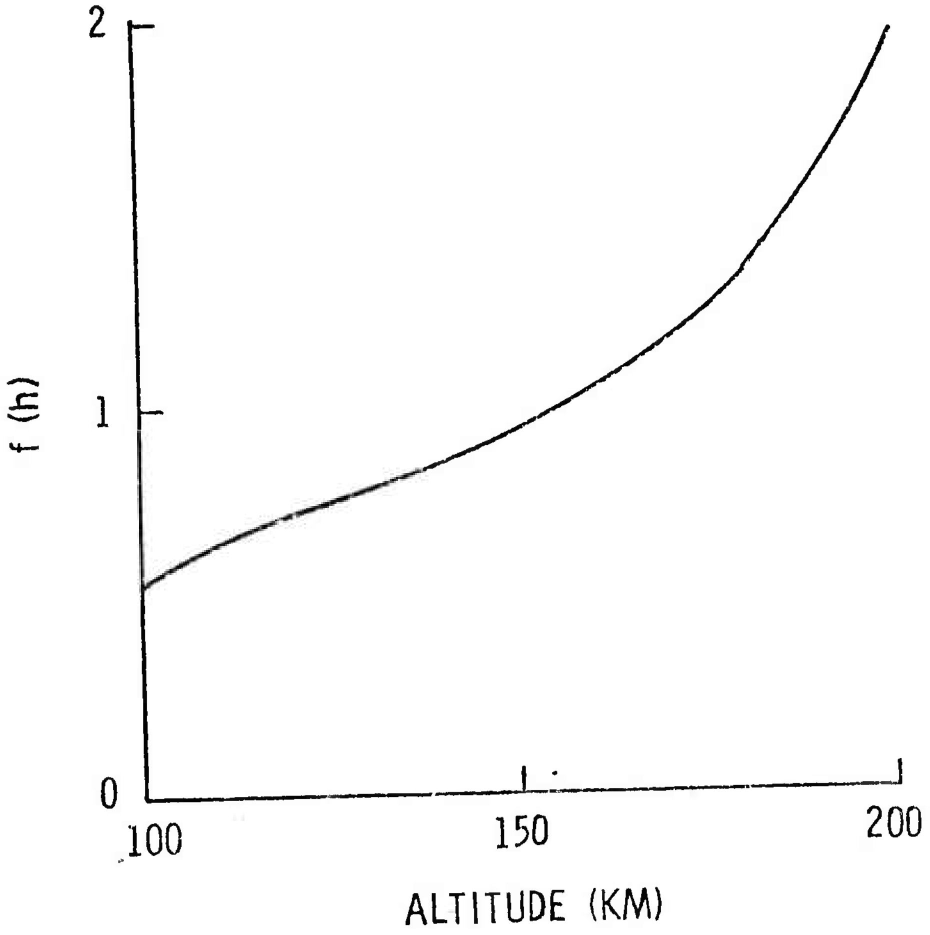


FIGURE 7. PROPORTIONALITY BETWEEN GAUSSIAN CLOUD RADIUS AND $(m_T/\rho)^{1/3}$

ical limit predicted by a point energy release. However, as altitude increases, transport phenomena become significant and the measured Gaussian radius after pressure equilibration is larger than that of the simplified theory.

The center point number density of a Gaussian cloud is related to the total amount of material released by (Reference 3):

$$n_o = \frac{n_T}{r_o^3 \pi^{3/2}} \qquad (2)$$

where

n_o = center point number density

n_T = total atoms released

However, atomic aluminum reacts rapidly with oxygen (Reference 4).

$$Al + O_2 \longrightarrow AlO + O \qquad (3)$$

In fact, calculations (Reference 5) show that reaction 3 reaches steady state in about four seconds at 160 km altitude. For this reason, it is assumed that reaction 3 is equilibrated, i.e.,

$$\frac{[Al]}{[AlO]} = k_p \frac{[O]}{[O_2]} \qquad (4)$$

Thus, the center point aluminum atom concentration is given by

$$[Al]_o = \frac{n_o}{1 + k_p \frac{[O]}{[O_2]}} \; k_p \frac{[O]}{[O_2]} \qquad (5)$$

Table III summarizes the properties of the release cloud of interest as calculated using the methodology outlined above. Also shown is the assumed atmospheric structure (Reference 6) and the value of the equilibrium constant computed using the JANAF tables as corrected for the most recent dissociation energy of AlO, 5.15 ev (Reference 7). These properties will be used to estimate the intensity of resonance fluorescence as a function of altitude.

TABLE III
ATMOSPHERIC AND RELEASE PROPERTIES

	ALTITUDE			
	100	120	140	160
T(^{o}K)	210	349	714	1022
ρ(p/cc)	1.04 (13)	5.23 (11)	7.52 (10)	2.62 (10)
$0/0_2$	.108	1.21	2.26	4.79
r_o (cm)	8.22 (3)	2.77 (4)	6.25 (4)	1.08 (5)
n_o (p/cc)	1.40 (13)	3.67 (11)	3.19 (10)	6.12 (9)
k_p	5.71 (-2)	9.42 (-2)	1.62 (-1)	1.79 (-1)
Al/AlO	6.17 (-3)	1.14 (-1)	3.66 (-1)	8.57 (-1)
n_{Al} (p/cc)	8.59 (10)	3.26 (10)	8.55 (9)	2.82 (9)

The relationship between the intensity of resonance fluorescence and the cloud properties is derived in (Reference 8) for a doppler broadened line viewed perpendicular to the solar flux. The derivation assumes that each solar photon which is absorbed is re-radiated into 4π steradians. The resulting resonance fluorescence is integrated over wave number to give the total intensity in the line. A second integration over the line-of-sight through the Gaussian cloud then gives the intensity as viewed by an observer. The final equations are summarized below:

$$N = \frac{H_{\nu}(\infty)\ \Delta\nu D}{\pi^{1/2}\ 2\ \mathrm{ERFC}\ (\eta/r_o)}\ \mathrm{EXP} - (\eta^2/r_o^2)\ (1\ -\mathrm{EXP}\ -\tau) \qquad (6)$$

where:

$$\tau = \frac{\pi}{2}^{1/2}\ \tau_o\ \mathrm{ERFC}\ (\eta/r_o)\ \ \mathrm{EXP} - (\rho\ \cos\ \alpha)^{2/}r_o^2 \qquad (7)$$

$$\tau_o = n_o\ k_o\ r_o \qquad (8)$$

$$k_o = \frac{g_u\ A_{ul}}{\Delta\nu_D\ Q\ 8\pi^{3/2}\ c\nu^2} \left(e^{-hcE_1\ k_T} - e^{-hcE_u/k_T} \right) \qquad (9)$$

and where:

N = radiance observed normal to solar flux (w/cm^2-ster)

$H\nu(\infty)$ = solar spectral intensity (w/cm^2-cm^{-1})

$\Delta\nu D$ = doppler width = $\frac{\nu o}{C}\sqrt{2kT/M}$ (cm^{-1})

g_u = statistical weight of upper level

A_{ul} = Einstein coefficient of spontaneous emission (sec^{-1})

ν = wave number (cm^{-1})

E_1, E_u = energy levels of transition (cm^{-1})

Q = partition function

η = coordinate parallel to solar flux

TABLE IV

OPTICAL PROPERTIES OF RELEASE CLOUD

	ALTITUDE			
	100	120	140	160
Temperature (^{o}K)	216	349	714	1022
Partition Function	3.86	4.52	5.19	5.42
Doppler Width (cm^{-1})	3.03 (-2)	3.91 (-2)	5.59 (-2)	6.69 (-2)
k_o (3961) (cm^{2})	9.11 (-13)	8.21 (-13)	6.33 (-13)	5.41 (-13)
k_o (3944) (cm^{2})	9.80 (-13)	6.59 (-13)	3.95 (-13)	3.17 (-13)
T_o (3961)	643	855	338	165
T_o (3944)	692	677	211	96.5

TABLE V.

PREDICTED RESONANT FLUORESCENT INTENSITY OF RELEASE CLOUDS

	ALTITUDE			
	100	120	140	160
Doppler Width (cm^{-1})	3.03 (-2)	3.91 (-2)	5.59 (-2)	6.69 (-2)
F_{peak} (n/r_o, T) (3961)	3.65	3.76	3.41	3.15
F_{peak} (n/r_o, T) (3944)	3.69	3.68	3.24	2.94
N (3961) (w/cm^2-ster)	6.15 (-9)	8.17 (-9)	1.06 (-8)	1.17 (-8)
N (3944) (w/cm^2-ster)	6.21 (-9)	8.00 (-9)	1.00 (-8)	1.09 (-8)
N (TOTAL) (w/cm^2-ster)	1.24 (-8)	1.62 (-8)	2.06 (-8)	2.26 (-8)

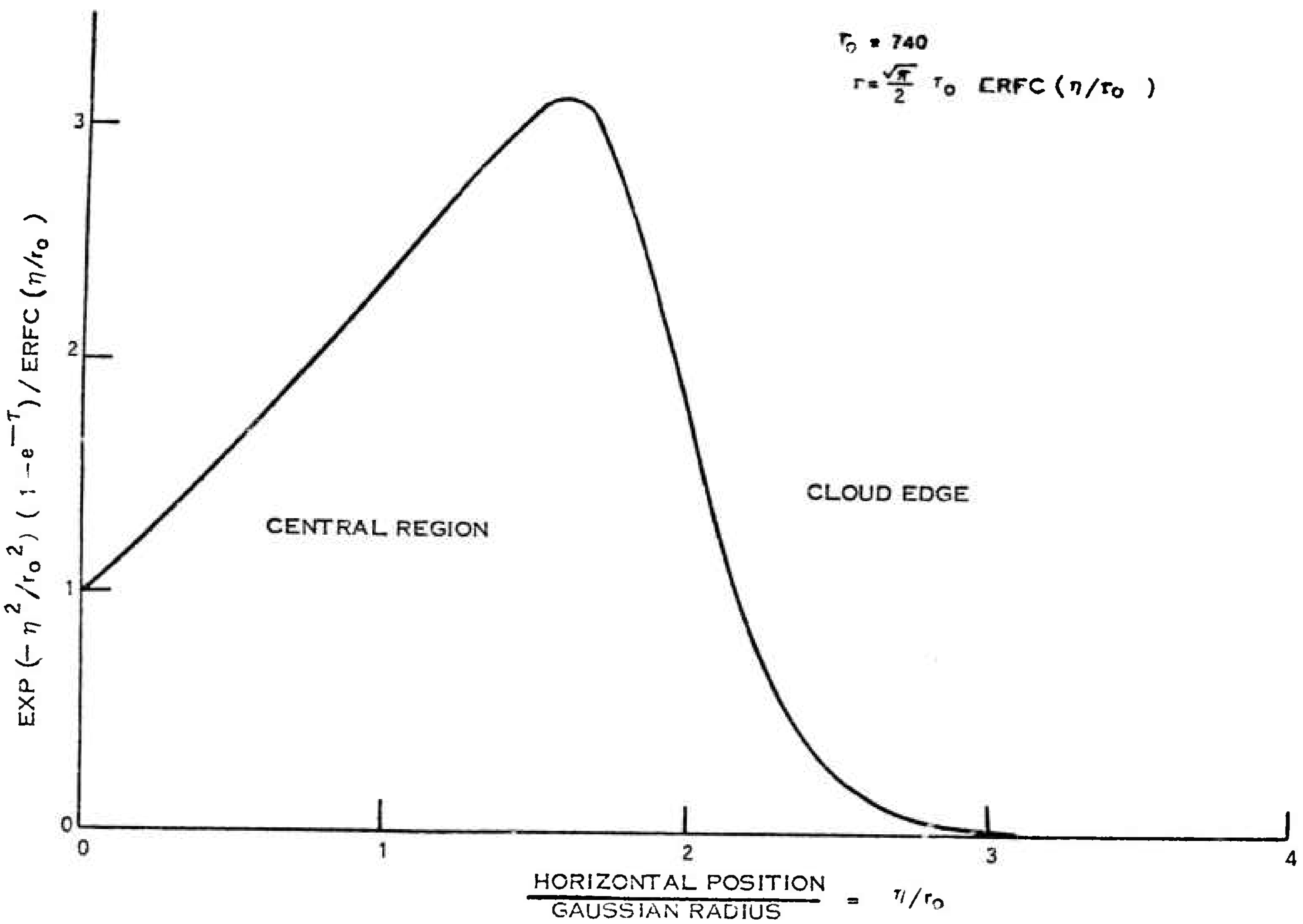


FIGURE 8. RADIAL VARIATION OF CLOUD INTENSITY VIEWED NORMAL TO SOLAR FLUX.

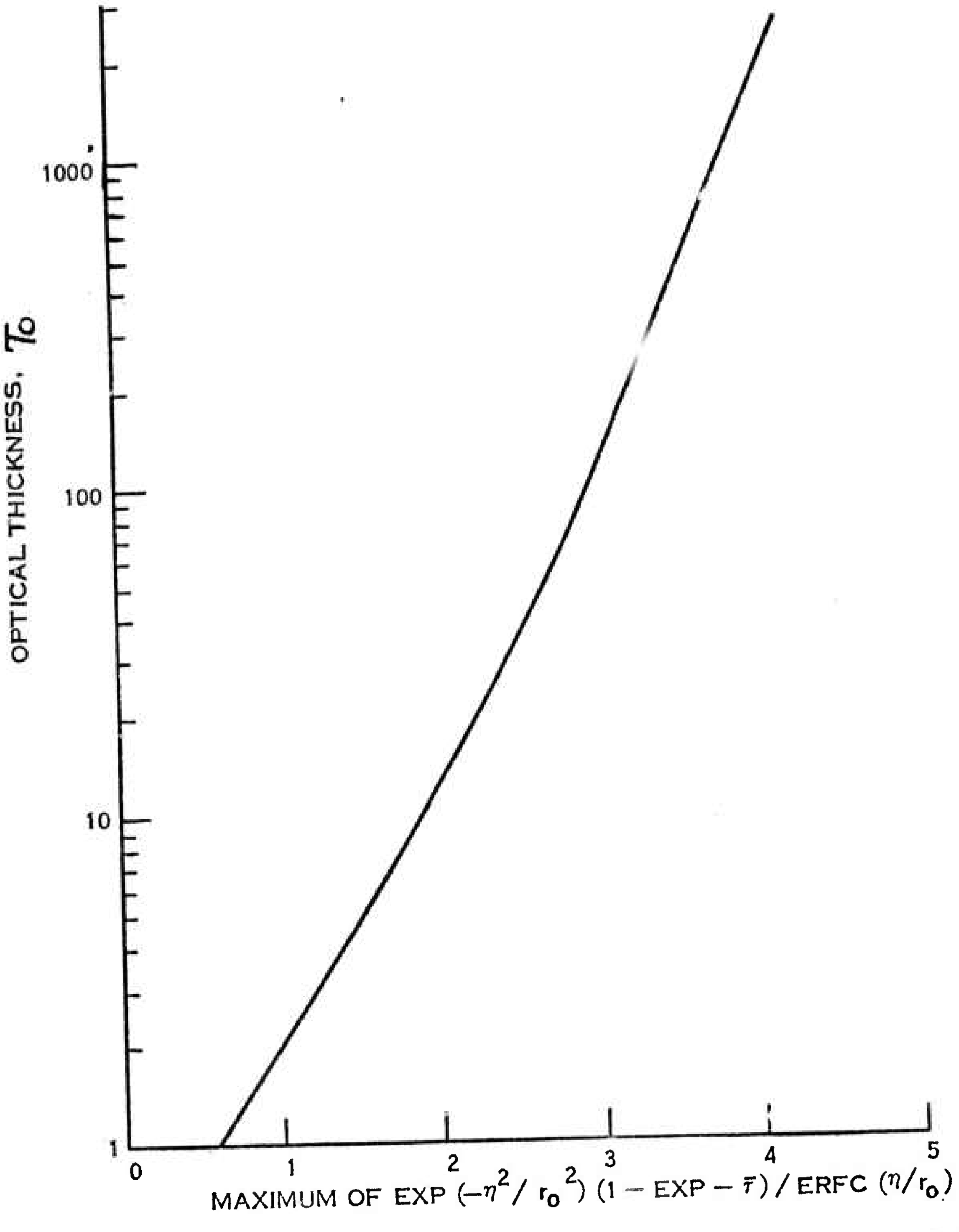


FIGURE 9. VARIATION OF MAXIMUM RESONANT FLUORESCENT INTENSITY WITH OPTICAL THICKNESS.

ρ = vertical coordinate

α = elevation angle of cloud

Table IV presents the optical properties of the release cloud as a function of altitude for the two aluminum resonance lines. Of most significance, are the large values computed for the optical thickness, τ_o. This implies that multiple scattering and photon diffusion effects become important in the central region and on the shady side of the cloud. In fact, the cloud is sufficiently thick such that very few photons reach the shady side and the release resembles a half-moon when viewed perpendicular to the solar flux. This point is illustrated by Figure 8 which shows the function:

$$F(\eta/r_o, \tau) = \mathrm{EXP}\ (-\eta^2/r_o^2)\ (1 - \mathrm{EXP} - \tau)/\mathrm{ERFC}\ (\eta/r_o) \tag{10}$$

plotted vs. η/r_o. The sharp rise to a maximum and subsequent decay toward the central region are quite apparent in the figure. It is pointed out that the single scattering theory does not describe the core of the release accurately. However, in the vicinity of the maximum, the optical thickness is sufficiently small ($\tau \sim 3$) such that single scattering applies. For the above reasons, the peak intensity in the cloud will be represented by the maxima of curves similar to Figure 8. These have been computed as a function of τ_o and are shown in Figure 9. In turn, the peak resonant fluorescent intensity of the cloud is given by:

$$N_{peak} = \frac{H_\nu(\infty)\ \Delta_\nu D}{2\pi^{1/2}}\ F_{peak}\ (\eta/r_o, \tau) \tag{11}$$

Application of Equation (11), requires a knowledge of the solar flux incident upon the release cloud. Unfortunately, the aluminum resonance lines appear as Fraunhofer lines in the sol spectrum. Additional complications result when it is recognized that the aluminum lines also fall in the tail region of the very strong Fraunhofer lines caused by calcium ions. Consequently, exact line profiles could not be used. Rather, as suggested by Armstrong (Reference 9), the solar flux was assumed constant and reduced by an order of magnitude from the level of the adjoining continuum (Reference 9), a factor which is in good agreement with measurements by the Utrecht group (Reference 10). The resulting intensity was taken as 1.97×10^{-7} watts/cm^2-cm^{-1}.

Table V presents the resonant fluorescent intensity as a function of altitude conputed using Equation (11). The dominant variable in the calculations is the Doppler width which varies by about a factor of two in the altitude range of interest. The peak resonant fluorescent intensity also varies by this factor. Consequently, from the point of view of observation, a release at 160 km will provide the maximum signal. However, because of the small altitude variation of intensity, this specific altitude is not critical.

A second consideration in selecting the optimum release altitude is the decay of intensity with time. As the released aluminum diffuses into the ambient atmosphere the optical thickness, τ_o decreases. From Equations 2 and 8

$$\tau_o = \frac{k_o\, n_T}{\pi^{3/2}\, r_o^2} \tag{12}$$

Further, the Gaussian radius of a release cloud grows as (Reference 5)

$$r^2\,(t) = r_o^{\,2} + 4Dt \tag{13}$$

where D = atmospheric diffusion coefficient

thus,

$$\tau_o = \frac{k_o\, n_T}{\pi^{3/2}\,(r_o^{\,2} + 4Dt)} \tag{14}$$

Referring to Figure 9 and Equation (11), the intensity of resonance fluorescence decreases by a factor of two as τ_o decreases by factors of 40 and 25 for 140 and 160 km, respectively. Using these values to estimate the time at which the cloud intensity reaches half its maximum value, and the diffusion coefficients of Reference 11, ($D_{140} = 7 \times 10^7$, $D_{160} = 2 \times 10^8$ cm^2/sec) in Equation 14 gives times of 558 and 365 sec at 140 and 160 km altitude. Thus, the duration of resonance fluorescence is reasonable for observation at either altitude.

It is now necessary to consider the instrumentation proposed for the experiment. The camera has an f/1.4 (focal length 150 mm) lens, uses Kodak 2475 film, and is blocked with a narrow bandpass filter centered at 3953 A. The transmission is 40% at the wavelength of the aluminum resonance lines. Applying the photographic equation to the filtered camera:

$$E = It = N \frac{\pi T_o T_a}{4f^2} \tag{15}$$

where:

E = exposure

I = intensity at focal plane

t = exposure time

T_o = transmission of optics = .9 x .4

T_a = transmission of atmosphere = .417 (assumed 45° elevation)

f = f-number of lens = 1.4

Results in:

$$E = 6 \times 10^{-2} N \tag{16}$$

To estimate the threshold for clear observation of the release, a film density of 0.3 above fog is assumed. Thus, $E = 6.31 \times 10^{-10}$ (Eastman Kodak 2475 film specification) and:

$$N_{THRESHOLD} = \frac{6.31 \times 10^{-10}}{6 \times 10^{-2}} \sim 10^{-8} \text{ (w/cm}^2\text{-ster)} \qquad (17)$$

or

$$N_{THRESHOLD} = 10^{-8}\ I_{THRESHOLD}^{t} \qquad (18)$$

Comparison between Equation (18) and the predictions of Table V shows that the intensity of resonance fluorescence from aluminum is about a factor of two larger than the threshold intensity of the camera for an exposure time of one second. As the exposure time is increased, a further factor of safety will be introduced. It is thus recommended that the aluminum be released between 140 and 160 km and that the camera be shuttered to provide a 5 second exposure time. This latter recommendation will result in an exposure one order of magnitude above threshold.

B. Flight Results and Analysis

A titanium/boron/aluminum release experiment was successfully conducted by AFCRL following the Aladdin Program. The canister which was launched from Wallops Island, Va., on January 15, 1975, was fired at an altitude of 150 km. Data from the event were gathered using a spectrometer and filtered TV camera to observe the aluminum resonance lines and photography to record the intensity of the 0,0 band of AlO. The observations discussed below were kindly provided prior to publication by Dr. D. F. Kitrosser of AFCRL who also reduced the AlO 0,0 band photographic intensities to total AlO concentrations.

The release cloud was acquired by the optical instrumentation at about t_o + 9 sec. As is shown in Figure 10, the Al resonance lines are initially obscured in absorption and then fluoresce. The relative intensity of the two resonance lines is presented in Figure 11. The development of the AlO cloud is shown in Figure 12. Figure 13 shows the total number of AlO molecules in the cloud as a function of time.

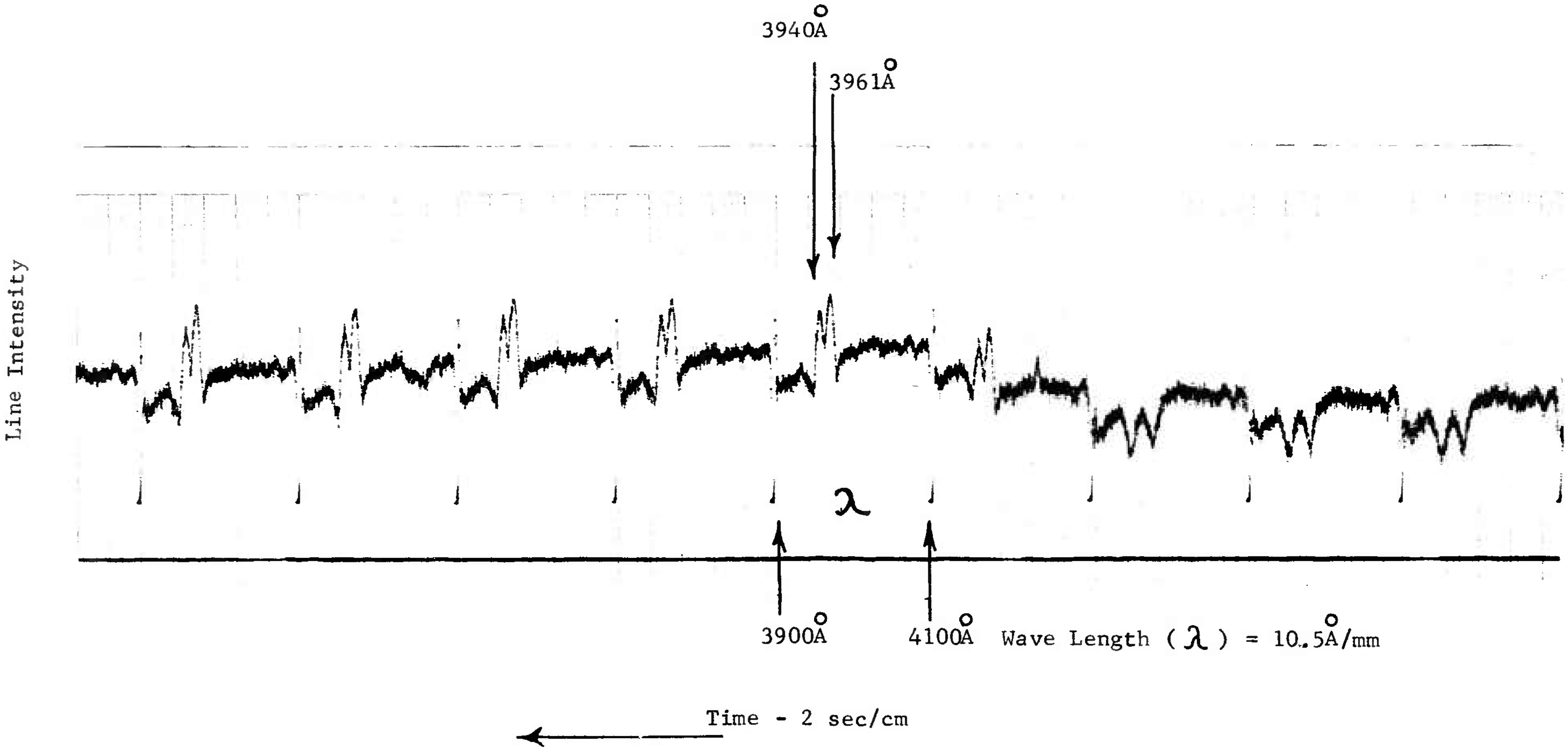


FIGURE 10 . ALUMINUM RESONANCE LINES

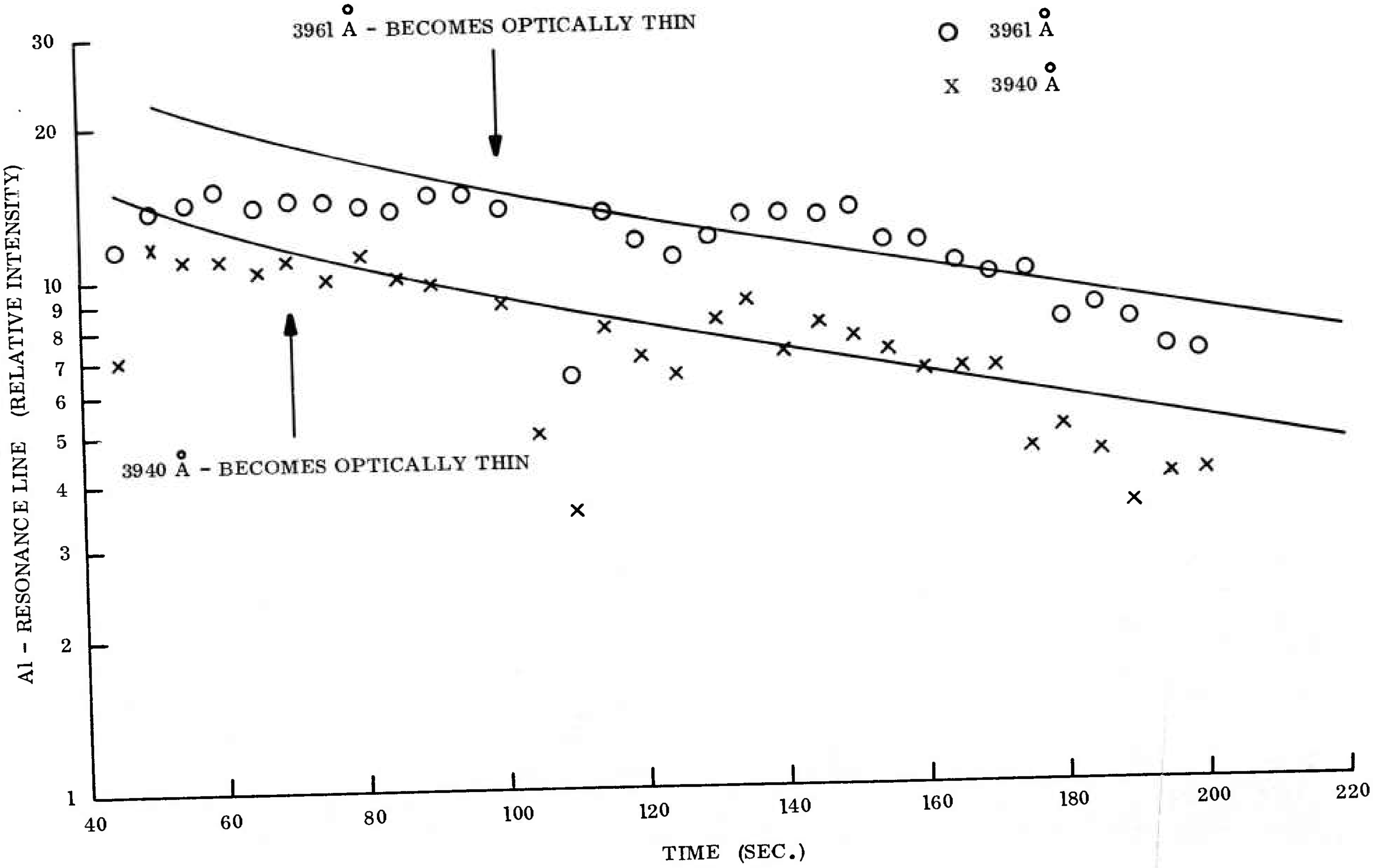
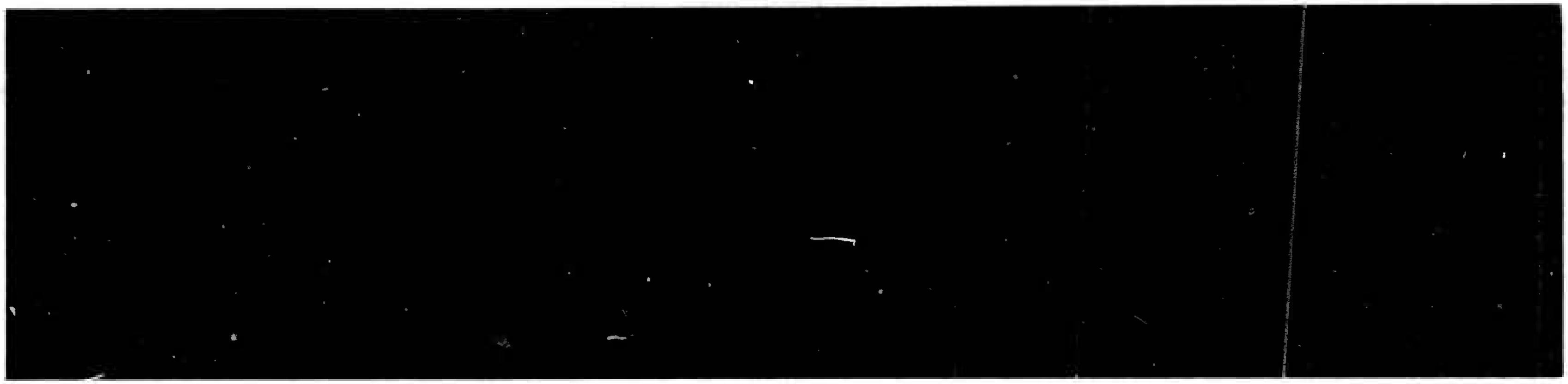


FIGURE 11. ALUMINUM RESONANCE LINE INTENSITY FROM CLOUD AT LATE TIMES



TIME AFTER RELEASE (SEC)	52	112	338	398
EXPOSURE DURATION (SEC)	1.0	1.0	2.8	2.8

GE Al VAPORIZER RELEASE
WALLOPS, VA 15 JAN 75 17:46:00 LT
SOLAR DEPRESSION 8°, ALTITUDE 150 km

COLOR DUE TO PHOTO-EXCITED AlO
SCALE - 1 cm 2.2 km

FIGURE 12. DEVELOPMENT OF ALUMINUM OXIDE CLOUD

]

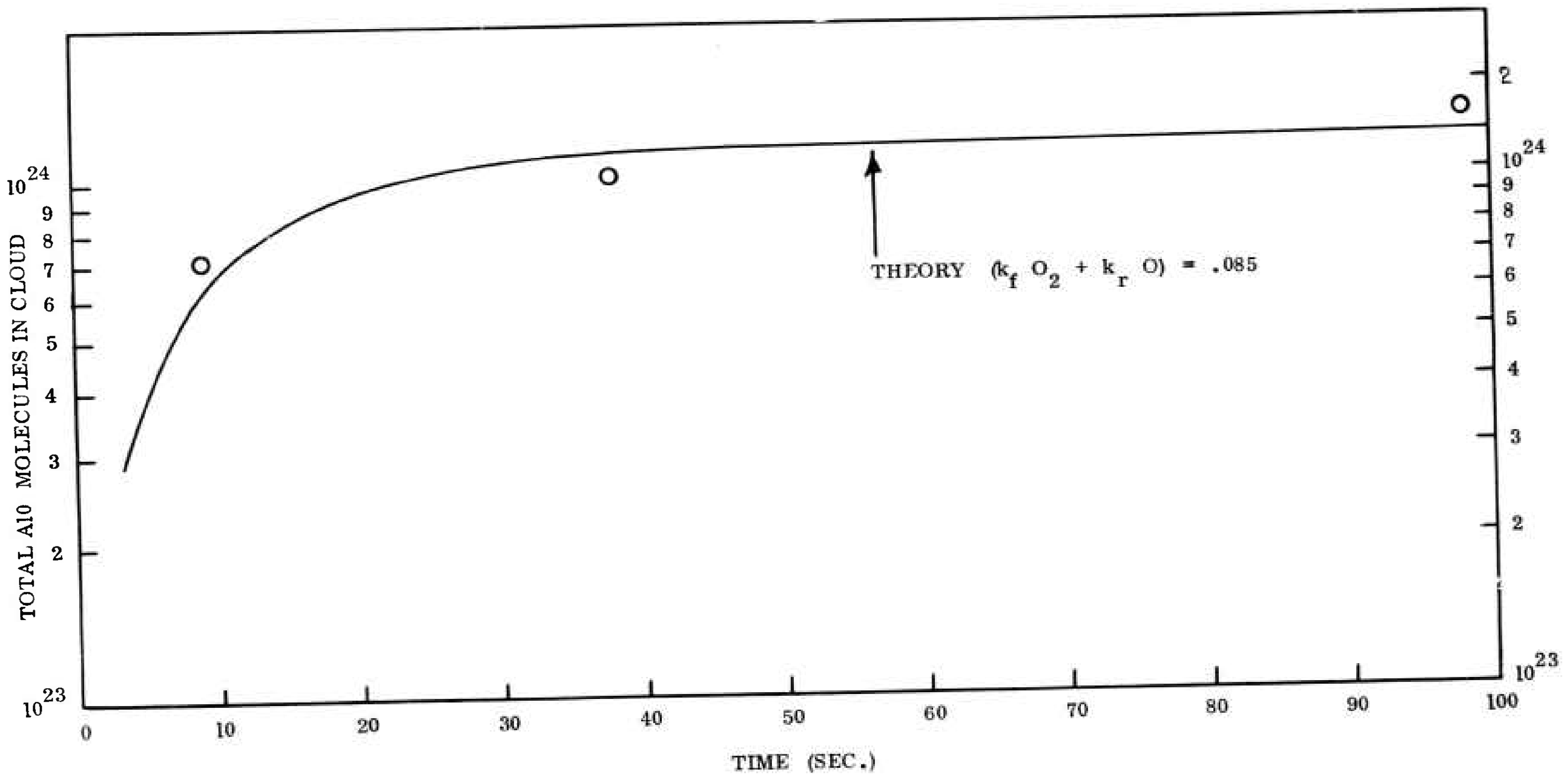


FIGURE 13. OXIDATION OF ALUMINUM VAPOR

Analysis of the results requires an investigation of the chemistry of Al atoms as they diffuse into and become oxidized by the ambient atmosphere. At early times the chemistry should be dominated by the fast reaction:

$$\mathrm{Al} + \mathrm{O_2} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{AlO} + \mathrm{O}$$

The time behavior of AlO under these conditions is described by a spherical diffusion equation:

$$\frac{\partial \mathrm{AlO}}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial \mathrm{AlO}}{\partial r} + k_f \cdot \mathrm{O_2} \cdot \mathrm{Al} - k_r \cdot \mathrm{O} \cdot \mathrm{AlO} \qquad (19)$$

where:

$\mathrm{AlO}, \mathrm{O_2}, \mathrm{O}$ = number density

D = diffusion coefficient

r = radius of cloud

t = time

If it is assumed that all species diffuse at the same rate, the ambient atmosphere is uniform in the vertical direction, Al and AlO are the only aluminum species present in the cloud, and that aluminum element has a Gaussian distribution, Equation (19) can be written:

$$\frac{\partial \mathrm{AlO}}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial \mathrm{AlO}}{\partial r} + k_f\, \mathrm{O}\, (a_T - \mathrm{AlO}) + k_r \cdot \mathrm{O} \cdot \mathrm{AlO} \qquad (20)$$

where the aluminum element distribution, $a_T = a_T\,(r,\ t)$, is given by:

$$a_T(r,\ t) = \frac{A_T}{\pi^{3/2}\,(r_o^{\,2} + 4Dt)^{3/2}} \exp\left(\frac{-r^2}{r_o^{\,2} + 4Dt}\right) \qquad (21)$$

where:

A_T = total amount of aluminum released

The solution of Equation 21 assuming that Al atoms are the released species can be written:

$$A10(r, t) = \frac{k_f\, 0_2\, A_T \exp\left(\frac{-r^2}{r_o^2 + 4Dt}\right)}{(k_f\, 0_2 + k_r\, 0)\pi^{3/2}\,(r_o^2 + 4Dt)^{3/2}} \left[1 - \exp -(k_f\, 0_2 + k_r\, 0)t\right] \quad (22)$$

Integration of Equation (22) over the cloud results in:

$$(A10)_T = \frac{A_T\, k_f\, 0_2}{(k_f\, 0_2 + k_r\, 0)} \left[1 - \exp - (k_f\, 0_2 + k_r\, 0)t\right] \quad (23)$$

where:

$(A10)_T$ = total amount of A10 present in the cloud.

The time variation of $A10_T$ can be used in conjunction with Equation (23) to derive an experimental value for $(k_f\ 0 + k_r\ 0_2)$. This was done by means of a least squares procedure and gave $(k_f\ 0 + k_r\ 0_2) = 0.085$. To obtain a rate constant from this result, the equilibrium constant, $K_{eq} = \frac{k_r}{k_f}$, was taken from Table III and atmospheric densities for 0 and 0_2 were used (Reference 6). The value derived from the release data was $k_f = 5.3 \times 10^{-12}$ cm^3/sec which compares well with a laboratory measurement of $k_f = 3 \times 10^{-11}$ (Reference 4). It is concluded from the A10 observations that Al was the released species which reacted with the ambient atmosphere to form A10. The rate constant for the oxidation process as deduced from the release data was in good agreement with laboratory measurements.

The interpretation of the Al resonance line data is complicated by optical thickness effects and other theoretical difficulties. Consequently, we decided to estimate the total Al concentration in the cloud by a comparison between the data and theory assuming the cloud is optically thin. When the cloud is thick, the theory will over predict the measurements. However, at that point where theory and data first agree, the optical thickness at the cloud center should be approximately unity. The intensity of resonance fluorescence per unit volume in the optically thin limit is proportional to the Al number density, i.e. for a Gaussian cloud.

$$N \propto \frac{(Al)_T}{\pi^{3/2} (r_o^2 + 4Dt)^{3/2}} \exp \frac{-r^2}{r_o^2 + 4Dt} \qquad (24)$$

Equation 24 now must be integrated over the line of sight and over the slit width of the spectrometer. The result as given by Dr. D. F. Kitrosser of AFCRL for the particular geometry and spectrometer of interest is

$$N \propto (Al)_T/r_o^2 + 4Dt)^{1/2} \qquad (25)$$

Before comparison with data, an additional correction for the chemical removal of Al and AlO must be applied. The removal process which was assumed is

$$AlO + O_2 \xrightarrow{k_1} AlO_2 + O$$

This reaction is fast in comparison to the competing chemilumenescent process

$$AlO + O \longrightarrow AlO_2 + h\nu$$

The appropriate correction using $k_1 = 3 \times 10^{-13}$ (Reference 4) becomes

$$N \propto \frac{(Al)}{(r_o^2 + 4Dt)^{1/2}} \exp \frac{-t}{505} \qquad (26)$$

Equation 26 was plotted on Figure 11 ($r_o = 5 \times 10^4$ cm, $0 = 1.23 \times 10^8 \frac{cm^2}{sec}$) for comparison with the aluminum resonance line measurements. Also shown on the figure is that point where the cloud becomes optically thin for both lines, t - 70 sec (3940), t - 100 sec (2961). Assuming that the optical thickness is unity at this point, Equation 23 gives

$$(Al)_T = \frac{\pi^{3/2} (r_o^2 + 4Dt)}{k_o} \qquad (27)$$

This provides an estimate for the total amount of aluminum in the cloud of 4.8×10^{23} and 5.9×10^{23} for the 3961 and 3940 lines respectively. The average value is 5.35×10^{23} molecules.

It is of interest to compare the ratio of Al/AlO derived from the release measurements to that obtained theoretically as shown in Table III. Referring to Figure 13, $(AlO)_T = 1.17 \times 10^{24}$. This gives $(Al)_T/(AlO)_T = 5.35 \times 10^{23}/1.17 \times 10^{24} = 0.46$. The theoretical value computed using the equilibrium constant and standard atmospheric densities for O and O_2 is $(Al)_T/(AlO)_T = 0.6$. This is considered excellent agreement.

The following conclusions have been drawn from optical measurements of Al resonance line fluorescence and AlO(0,0) band radiation produced by an atmospheric release.

1. Al atoms were vaporized by the reaction of $Ti + 2B \longrightarrow TiB_2$ + heat.
2. The Al atoms diffused through and were oxidized by the ambient atmosphere to form AlO. The time constant derived for the oxidation process agreed reasonably well with estimates based on available chemical rate constants and standard atmospheric properties.
3. The ratio of Al/AlO derived from the release data agreed very well with estimates based on thermodynamic calculations and on standard atmospheric properties.

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