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SUMMARY

Theoretically, the hydroxyl airglow (and possibly also the sodium airglow) could be artificially stimulated by the release of ozone into the upper atmosphere near 90 kilometers. Calculations indicated that the light intensity expected from an ozone release was so low as to be invisible from the ground. Consequently, photometers and a telemetry system were mounted on the rocket that carried the ozone. Two Nike-Cajun rockets were fired; each carried 2 pounds of ozone dissolved in 18 pounds of Freon-12, along with photometers monitoring 6260 Å (9-3 hydroxyl band), 6205 Å (red continuum background), 5890 Å (sodium D lines), and 5760 Å (green continuum). The ozone - Freon-12 mixture was released near 74 kilometers in one case and 68 kilometers in the other, rather than the intended 90 kilometers. As a result, no information about the sodium airglow was obtained since this layer was not penetrated. It was found from the photometer data that the ozone was released inside the hydroxyl airglow layer in the 74-kilometer release, but at the lower edge in the 68-kilometer release. A faint luminosity was observed in both cases. For the release at the lower edge of the airglow layer, this luminosity was attributed mainly to light scattered from Freon-12 "ice" particles into the photometers. The luminosity for the rocket that did penetrate the airglow layer was attributed to chemiluminescence plus scattered light. The scattered light contribution was estimated from the photometer data for the release at the lower edge of the airglow layer and was subtracted leaving chemiluminescence. The chemiluminescence was observed at 6260 Å, which corresponds to the 9-3 hydroxyl band. It was concluded that release of ozone into the hydroxyl airglow layer produces a faint red chemiluminescence due to reaction of the ozone with atmospheric atomic hydrogen.

The upper limit of the total intensity of the chemiluminescence was estimated to be of the order of 10^{-9} watt. This intensity was much less than might have been expected for complete mixing of the ozone with the ambient atmosphere. Evidently, mixing was very imperfect in the experiment.

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INTRODUCTION

In 1956, Pressman, et al. (ref. 1) showed that atomic oxygen in the upper atmosphere could be detected by a chemiluminescent reaction with nitric oxide. They released $18\frac{1}{2}$ pounds of nitric oxide gas at 106 kilometers at night. The resulting chemiluminescent reaction of NO + O produced a luminous cloud, which was visible for about 10 minutes. The experiment was simple and produced such a clear-cut result that it stimulated interest in the use of chemical releases to explore the properties of the upper atmosphere. A number of different chemicals have been released with varying degrees of success (ref. 2).

This report is concerned with an attempt to detect atomic hydrogen in the upper atmosphere by a chemiluminescent reaction with ozone released from a rocket. The atomic hydrogen-ozone reaction is believed to be the origin of the hydroxyl airglow (ref. 3), so that the experiment also may provide some evidence for the correctness of this belief.

The estimated brightness of the luminosity expected from the ozone release was very low, so that ground observations were not possible. Instead, phototubes were mounted on the rocket, and the brightness monitored at the point of ozone release. A telemetry system was to read the phototube outputs. Two almost identical experiments were performed (rockets 10.79 and 10.80). One (10.80) ozone release occurred in the atmospheric layer where atomic hydrogen can be expected, while the other (10.79) occurred at the lower edge of this layer. The latter served as a blank from which the results of the former could be interpreted.

THEORETICAL BACKGROUND

When ozone is released into the atmosphere at 70 to 100 kilometers, the following chemical reactions may occur with the emission of light:

(a) For OH bands,

$$H + O_3 \rightarrow OH + O_2 + \text{red and infrared light}$$

(b) For nitric oxide continuum,

$$NO + O_3 \rightarrow NO_2 + O_2 + \text{yellow-red light}$$

(c) For nitric acid continuum,

$$N + O_3 \rightarrow NO + O_2$$

followed by

$$NO + O \rightarrow NO_2 + \text{yellow-red light}$$

(d) For sodium D lines,

$$O + O_3 \rightarrow O_2{}^* + O_2$$

followed (possibly) by

$$Na + O_2{}^* \rightarrow Na + O_2 + \text{yellow light}$$

If the light from these four processes could be observed, the following information can be deduced:

(1) The presence of atomic hydrogen

(2) The presence of nitric oxide or atomic nitrogen

(3) Whether or not the sodium airglow is produced by the interaction of sodium (already present) with excited oxygen produced from the reaction of O and O_3

Theory indicates that there should be sufficient atomic hydrogen to produce an observable luminescence, so that the outlook for a satisfactory result for item (1) was good. Theoretical estimates of the concentrations of atomic nitrogen and nitric oxide are so low that it was doubtful that any chemiluminescence could be observed. The success or failure of item (3) could not be predicted. This was one of the reasons for doing the experiment. Semiquantitative estimates of the light intensities expected from the cloud of ozone released into the upper atmosphere are now given.

Intensity of Hydroxyl Band Emission from Ozone Cloud

The intensity I of light emission from the ozone cloud is

$$I = \Phi R \tag{1}$$

where Φ is the quantum yield, the number of quanta emitted in the spectral range of interest per reaction event, and R is the total rate of reaction.

Here, the reaction of interest is

$$H + O_3 \rightarrow OH + O_2 + h\nu$$

The light produced by this reaction consists of vibration-rotation bands covering the spectral range from the visible to the infrared. The bands are strongest in the infrared, but most multiplier phototubes are most sensitive in the visible. As an optimum compromise, the 9-3 hydroxyl band at 6257 Å was selected for study. The quantum yield Φ at 6257 Å can be estimated in two ways - from laboratory measurements of the light emitted from the $H + O_3$ reaction, and from the intensity of the hydroxyl airglow at 6257 Å. The former yields a lower limit, the latter an upper limit. The details of the laboratory measurements and the airglow calculations are given in appendix A. The resulting quantum yields are as follows:

(a) Airglow (upper limit) $\Phi = 10^{-4}$ quantum at 6257 Å/reaction event

(b) Laboratory (lower limit) $\Phi = 5\times10^{-8}$ quantum at 6257 Å/reaction event

An upper bound to the total rate of hydroxyl production R can be found by assuming that the ozone is instantly mixed with the atmosphere upon release. Then,

$$R = kn[H] \tag{3}$$

where k is the rate constant for the reaction of H and O_3 (3×10^{-12} cm^3/(molecule)(sec), ref. 4), n is the total number of ozone molecules released, and [H] is the atomic hydrogen concentration (atoms/cc).

About 2 pounds or 1.2×10^{25} molecules of ozone can be released. By assuming (refs. 5 and 6) that [H] is 10^9 atoms per cubic centimeter in the hydroxyl airglow layer (70 to 90 km), it is seen that $R = 3.6\times10^{22}$ molecules of OH produced per second. Then, substitution in equation (1) gives, for the intensity,

$$I = 3.6\times10^{18} \text{ quanta/sec} \approx 1 \text{ W} \quad \text{(upper limit)}$$

$$I = 1.5\times10^{15} \text{ quanta/sec} \approx 5\times10^{-4} \text{ W} \quad \text{(lower limit)}$$

Intensity of Other Possible Chemiluminescent Emissions

Great uncertainty is attached to intensity estimates of other chemiluminescent reactions. Calculations similar to those for ozone-atomic hydrogen were performed for the glow anticipated at 90 kilometers from atomic nitrogen and from the sodium D lines, if excited. The results indicated that about 10^{-3} watt could be expected from each at 90 kilometers for perfect mixing (assuming the atomic nitrogen concentration to be 10^9 atoms/cm^3). At lower altitudes, the intensities were negligibly small.

Reduction of Light Output by Imperfect Mixing

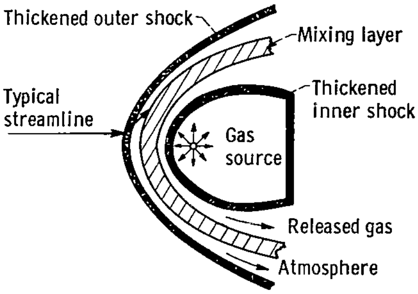


Figure 1. - Viscous flow pattern for gas release from a body moving at supersonic velocity (ref. 7).

The light intensities calculated previously are for perfect mixing of ozone with the atmosphere. Unfortunately, the ozone cannot be mixed instantly with the atmosphere. The physics and aerodynamics of a chemical released into the atmosphere from a moving body are such that the mixing process is imperfect and the released material is spread into a long trail, rather than a small cloud. Hill and Alden (ref. 7) have made an aerodynamic analysis of the flow generated by the release of a gas from a supersonic vehicle into the upper atmosphere. This analysis is applicable to the experiment discussed here, since range safety limitations required the rocket to be fired at such an angle as to give a slightly supersonic horizontal velocity. Thus, even at trajectory peak, where the vertical velocity is zero, the vehicle is still traveling at supersonic velocity. In order to gain a qualitative understanding of the circumstances surrounding the release, it is helpful to examine the flow pattern schematic given by Hill and Alden, which is reproduced in figure 1. There exist two shocks, an inner shock in the released gas and an outer shock in the atmosphere. Between the two shocks exists a mixing layer in which the atmosphere and the released gas mix. The mixing region will extend for a long distance downstream, comprising a wake. This is far from the idealized case discussed up to now, where the released gas is assumed to be instantly and completely mixed with the atmosphere. It is not possible to estimate how rapid and complete the mixing is for any particular case without a much more extensive study of the problem. However, it is certain that mixing will be imperfect, and the light intensity produced by the release will be less than the perfect mixing value.

EXPERIMENTAL

The general experimental plan was to carry a quantity of ozone to an altitude of about 90 kilometers, release it into the atmosphere, and observe the resulting luminescence by means of photometers mounted on the rocket vehicle.

Thus, the rocket payload consisted of two parts, an ozone tank and a photometer-telemetry section. A sketch and photograph of the payload are given in figure 2.

The ozone was carried in the tank as a dilute (10 percent) solution in liquid Freon-12 (CCl_2F_2). The Freon-12 was required to inert the ozone, which in pure form detonates easily. A disadvantage of Freon-12 is that it forms a cloud of "ice" crystals when

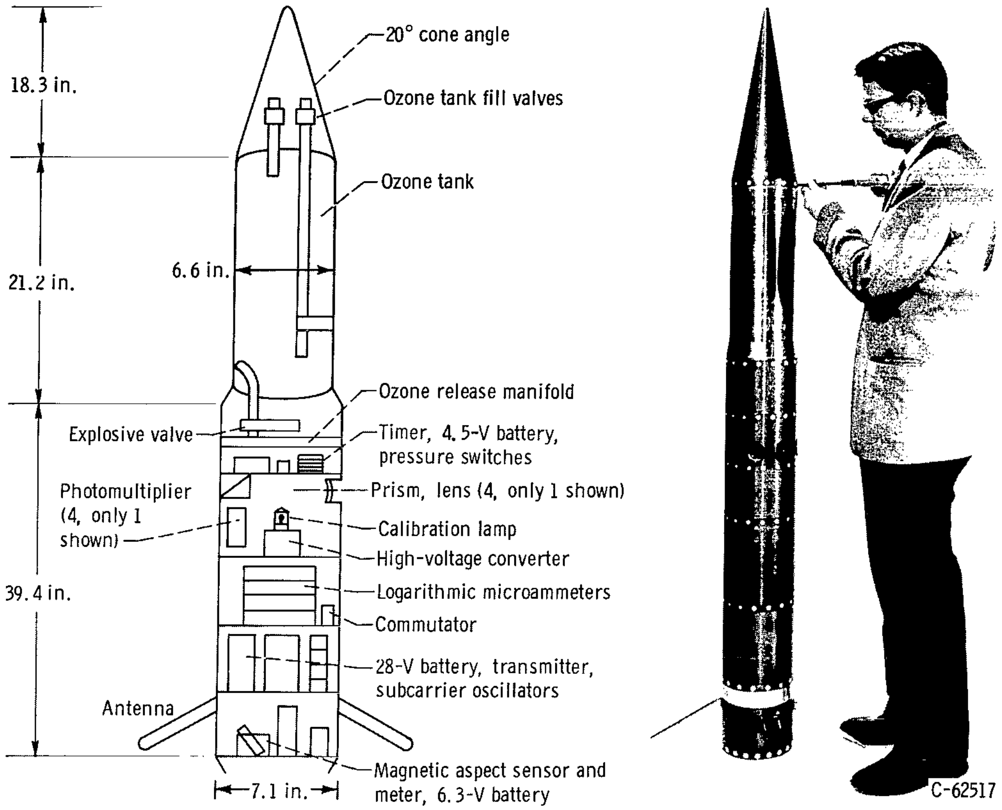


Figure 2. - Payload configuration for ozone release (Nike-Cajuns 10.79, 10.80).

released into the upper atmosphere. This and other details of the preparation and handling of the ozone solution are described in detail in appendix B. The photometer-telemetry section, flight sequence, and predicted trajectory will now be described.

Photometer-Telemetry System

A sketch of the photometer-telemetry system as attached to the ozone tank is shown in figure 2(a). A block diagram is shown in figure 3 and a circuit diagram is given in figures 4(a) and (b) for the payload and associated test console. A brief description of the system follows, beginning with the entrance of light into the payload and ending with the telemetry signal.

Four separate similar optical systems were installed in the payload. Each consisted of a lens, a prism, and a field stop. Light entered the lenses mounted on the side of the payload, traveled to the prisms, was reflected parallel to the rocket axis through the field stops, and then through interference filters to end-on multiplier phototubes. In the first payload (rocket 10.79), concave lenses were used so as to yield a field of view

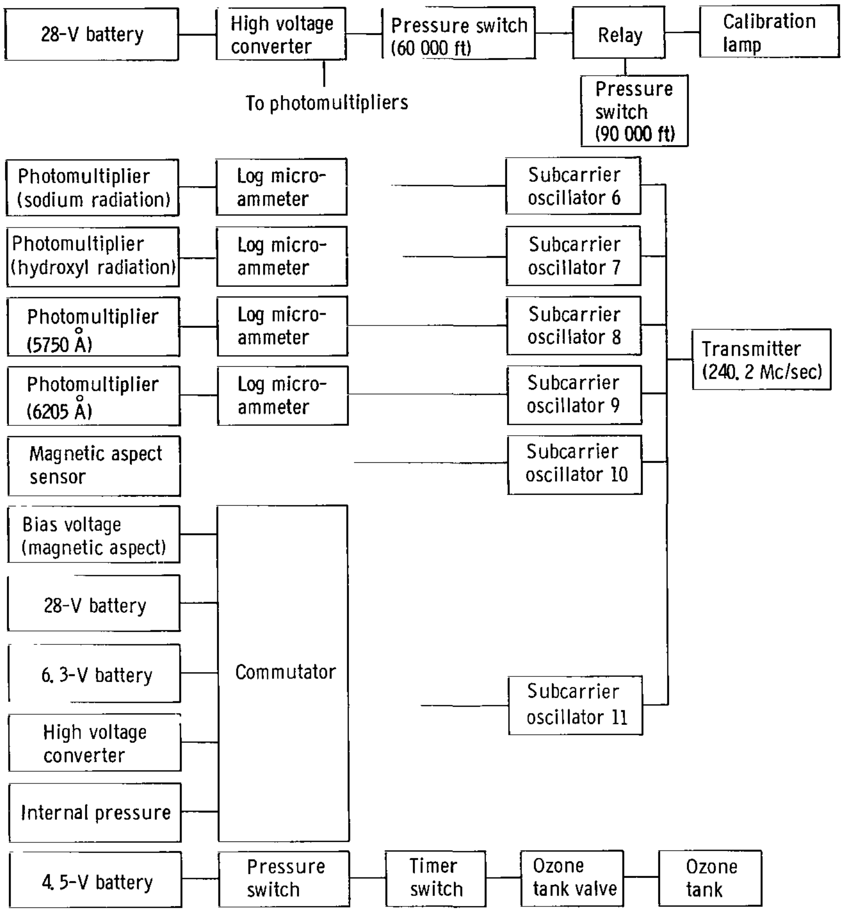
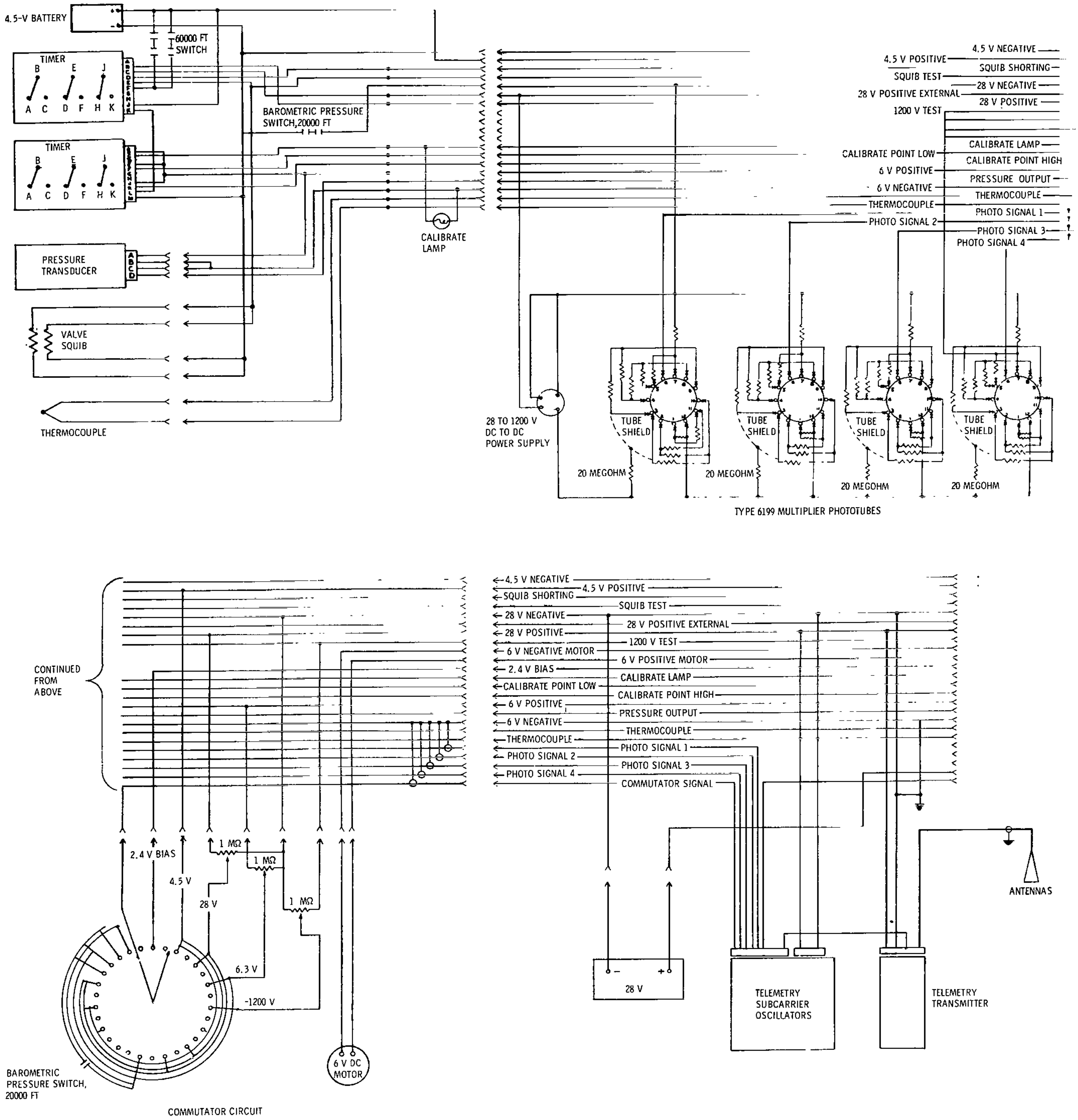


Figure 3. - Block diagram of ozone release payload for Nike-Cajuns 10.79 and 10.80.

of about 20° (0.1 sr) for each optical system. In the second payload (rocket 10.80), convex lenses were used so as to yield a field of view of 4.5° (0.005 sr). The interference filters were designed to pass 5890 Å (±5 Å half-power bandwidth, HPB), 5760 Å (±33 Å HPB), 6260 Å (±23 Å HPB), and 6205 Å (±10 Å HPB). The airglow features that the various filters were intended to isolate were 5890 Å (sodium D lines), 5760 Å (green continuum), 6260 Å (9-3 hydroxyl band), and 6205 Å (starlight and continuum background). The 6205 Å filter was flown only on the second rocket (10.80). The first rocket (10.79) had no interference filter at all in this particular optical system. Both rockets 10.79 and 10.80 carried 5890, 5760, and 6260 Å filters cut (by a sandblast technique) from the same large filter, so as to make them as nearly identical as possible.

The four multiplier phototubes used in each payload were ruggedized 6199-type tubes with S-11 photosensitive surfaces. The spectral responses of a number of tubes were measured, and those tubes with high yellow and red sensitivities were picked for use in the payload. After assembly of the optical system and the multiplier phototube section of the payload, an absolute calibration was performed by using a National Bureau of


4.5-V BATTERY
60000 FT SWITCH
TIMER
B E J
A C D F H K
TIMER
B E J
A C D F H K
BAROMETRIC PRESSURE SWITCH, 20000 FT
CALIBRATE LAMP
PRESSURE TRANSDUCER
A B C D
VALVE SQUIB
THERMOCOUPLE
4.5 V NEGATIVE
4.5 V POSITIVE
SQUIB SHORTING
SQUIB TEST
28 V NEGATIVE
28 V POSITIVE EXTERNAL
28 V POSITIVE
1200 V TEST
CALIBRATE LAMP
CALIBRATE POINT LOW
CALIBRATE POINT HIGH
6 V POSITIVE
PRESSURE OUTPUT
6 V NEGATIVE
THERMOCOUPLE
THERMOCOUPLE
PHOTO SIGNAL 1
PHOTO SIGNAL 2
PHOTO SIGNAL 3
PHOTO SIGNAL 4
28 TO 1200 V DC TO DC POWER SUPPLY
TUBE SHIELD
TUBE SHIELD
TUBE SHIELD
TUBE SHIELD
20 MEGOHM
20 MEGOHM
20 MEGOHM
20 MEGOHM
TYPE 6199 MULTIPLIER PHOTOTUBES
CONTINUED FROM ABOVE
2.4 V BIAS
4.5 V
1 MΩ
1 MΩ
1 MΩ
28 V
6.3 V
-1200 V
BAROMETRIC PRESSURE SWITCH, 20000 FT
6 V DC MOTOR
COMMUTATOR CIRCUIT
4.5 V NEGATIVE
4.5 V POSITIVE
SQUIB SHORTING
SQUIB TEST
28 V NEGATIVE
28 V POSITIVE EXTERNAL
28 V POSITIVE
1200 V TEST
6 V NEGATIVE MOTOR
6 V POSITIVE MOTOR
2.4 V BIAS
CALIBRATE LAMP
CALIBRATE POINT LOW
CALIBRATE POINT HIGH
6 V POSITIVE
PRESSURE OUTPUT
6 V NEGATIVE
THERMOCOUPLE
THERMOCOUPLE
PHOTO SIGNAL 1
PHOTO SIGNAL 2
PHOTO SIGNAL 3
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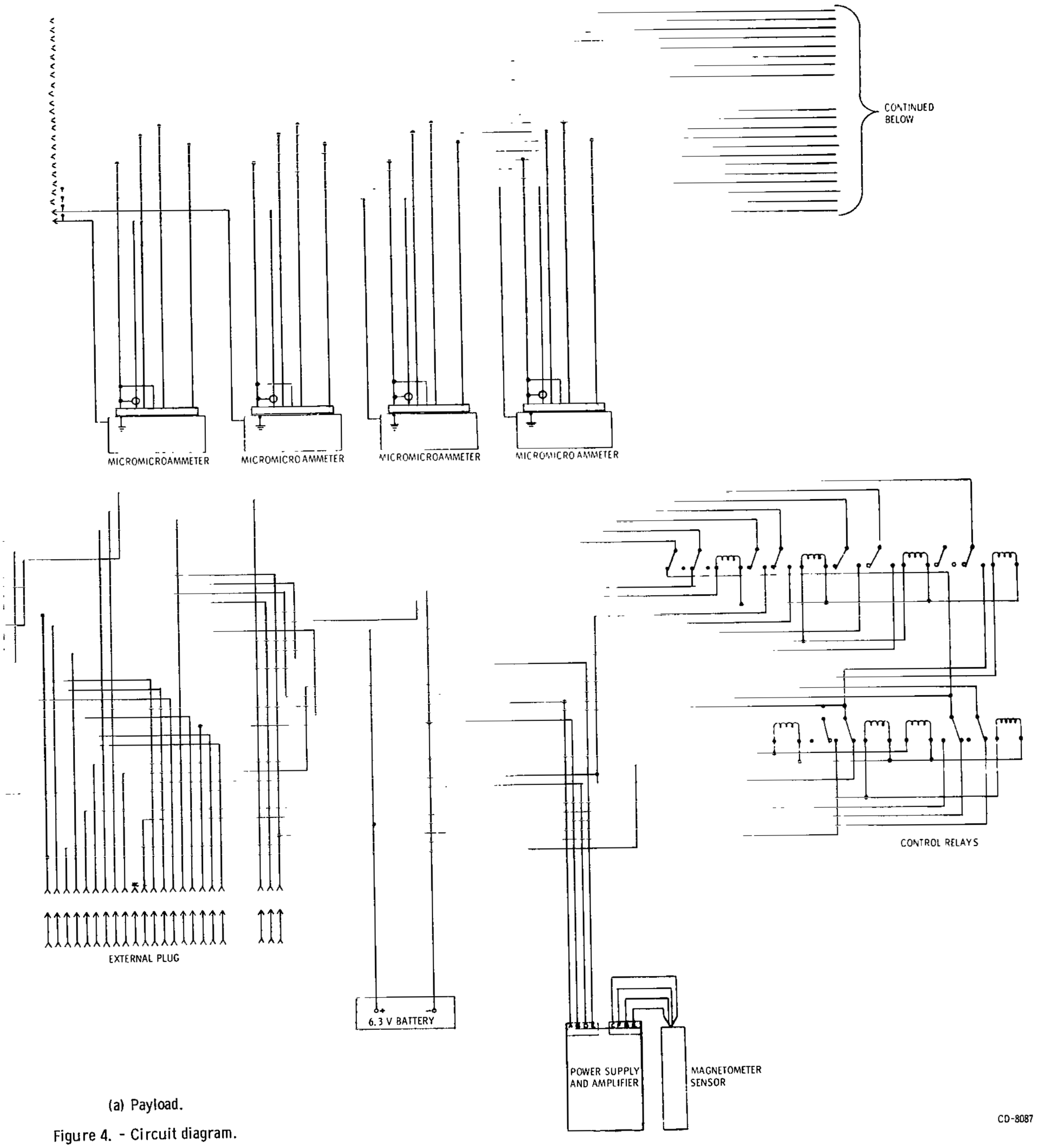
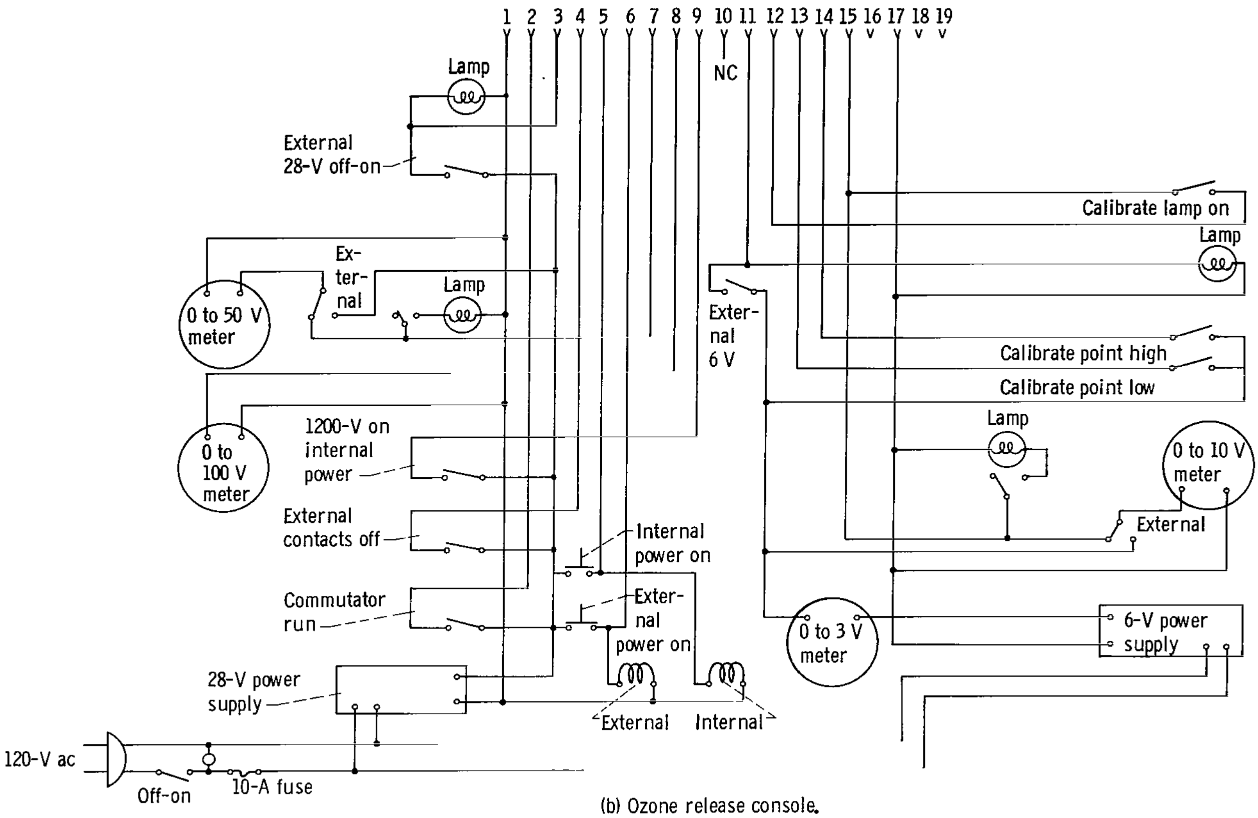
COMMUTATOR SIGNAL
ANTENNAS
- +
28 V
TELEMETRY SUBCARRIER OSCILLATORS
TELEMETRY TRANSMITTER



(a) Payload.

Figure 4. - Circuit diagram.



(b) Ozone release console.

Figure 4. - Concluded.

Standards standard lamp. From the spectral distribution of the light from the lamp, and the spectral transmission curves of the interference filters, the absolute sensitivity was found for each of the four detectors in terms of amperes photocurrent produced per watt of light energy in the pass band of the filter incident on the lens.

A secondary standard for in-flight calibration of the system was provided by a small tungsten lamp placed in the optical system. Multiplier phototube outputs produced by this lamp were measured at the same time that the absolute calibrations were being made.

In order to determine how well the photometer system could detect hydroxyl radiation from the $H + O_3$ reaction, light from a low-pressure flame of $H + O_3$ was measured. The photometer currents were converted to watts by using the calibrations described previously. The results, shown in table I, are expressed relative to the amount of light received by the 6260 Å (9-3 hydroxyl band) photometer.

The light intensity at 5890 Å is 11 to 13 percent of the intensity at 6260 Å. The light at this wavelength is probably due to the 8-2 hydroxyl band. Some light (6 to 7 percent of that at 6260 Å) was detected by the 5760 Å photometer. This may be due to poor light blocking in the light filter, since there is no hydroxyl band at this wavelength. The 6205 Å photometer detected nothing, as it should. There is no hydroxyl radiation at 6205 Å. It

TABLE I. - RELATIVE AMOUNTS OF LIGHT RECEIVED AT THREE WAVELENGTHS FROM THE H + O_3 FLAME

Wavelength, λ, Å	(W at λ)/(W at 6260 Å)	
	10.79 Optical system	10.80 Optical system
6260 (9-3 Hydroxyl band)	1.00	1.00
5890 (Sodium D lines)	.11	.13
5760 (Green background)	.06	.07
6205 (Red background)	--	.00

was concluded that the photometer system functioned properly, and that hydroxyl radiation could easily be distinguished.

The photocurrents from the multiplier phototubes were passed to logarithmic microammeters. These units provided outputs ranging from 0 to 5 volts for inputs ranging from 10^{-8} to 10^{-5} ampere. The outputs from the logarithmic microammeter were passed to subcarrier oscillators in the telemetry system.

The telemetry system was an FM/FM type, operating at 240.2 megacycles at a rated power of 1 watt with subcarrier frequencies at the IRIG channels 6, 7, 8, 9, 10, and 11. A dipole antenna was used and was tuned by "stubbing". Each element of the antenna projected 7.7 inches from the payload and was swept back 30° from the normal to the payload.

As mentioned previously, four of the six telemetry channels were used to monitor output from the phototubes. The output from an aspect magnetometer was applied to one of the remaining channels. The last channel was used for "housekeeping", checking various voltages in the payload by means of a commutator.

Calibration circuits were provided in rocket 10.80 so that relays could switch currents of 5×10^{-8} and 5×10^{-6} ampere successively into the logarithmic microammeters. In 10.79, a single calibration current of 3×10^{-7} ampere was used.

The entire electrical section of the payload was pressurized with dry nitrogen to about 20 pounds per square inch absolute.

Sequence of Events During Rocket Flight

The payload was launched with the telemetry on, but with high voltage to multiplier phototubes off. At T + 30 seconds, after second-stage burnout, the phototubes were turned on. At T + 145 seconds, just before the predicted peak time of 147 seconds, the explosive valve on the ozone tank was fired. At T + 210 seconds, the calibration lamp was turned on. At T + 215 seconds, a microammeter low current calibration was turned on. The entire sequence was initiated and controlled by two g-actuated spring-wound timers.

TABLE II. - TRAJECTORY ELEMENTS FOR NIKE-CAJUN ROCKETS

Trajectory element	Rocket	
	10. 79	10. 80
Launch site	Wallops Island, Va.	Wallops Island, Va.
Launch time	23:31 EST, April 4, 1962	20:44 EST, Jan. 16, 1963
Peak altitude, km	69. 5	74. 5
Peak time, sec	129	135
Impact time, sec	258	273
Impact range, km	73. 0	64. 1
Ozone release altitude, km	67. 8	74. 0
Ozone release time, sec	145. 2	146. 2

Vehicle, Payload Weights, and Predicted Trajectory

The vehicle used in both experiments was the Nike-Cajun two-stage solid-propellant rocket. The total weights of the payloads when filled with the ozone solution were 132 pounds for 10. 79 and 130 pounds for 10. 80. The elements of the predicted trajectory for an 83° launch angle from sea level were a peak altitude of 91 kilometers and a peak time of 147 seconds.

RESULTS

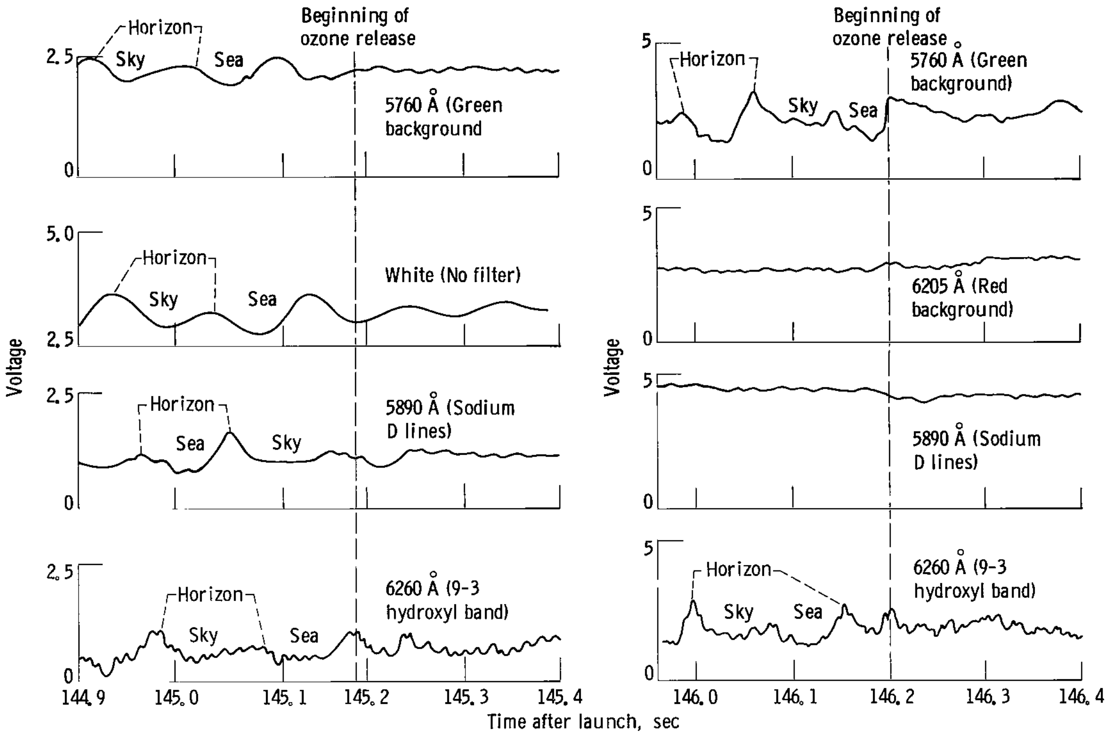
Vehicle Performance

The observed trajectories of rockets 10. 79 and 10. 80 are summarized in table II. The peak altitudes in both cases (69. 5 and 74. 5 km, respectively) were well below the predicted peak of 91 kilometers, the difference mounting to about 20 and 16 kilometers for 10. 79 and 10. 80, respectively. The fact that the rockets did not achieve the predicted altitude affected the outcome of the experiment, since the sodium airglow layer was not penetrated in either case.

Study of the magnetic aspect data from the magnetometer on board the rockets revealed that both rockets flew stably, rolling on their long axes, until after trajectory peak was passed. After ozone release, precession rates increased and complex motions occurred before turnover. The roll rate was intended to be 5 revolutions per second, and approximately this rate was achieved through most of both flights.

Ozone Release

The releases were timed to release at near the calculated time of trajectory peak.



(a) Rocket 10.79.

(b) Rocket 10.80.

Figure 5. - Telemetry records during ozone release.

Unfortunately, trajectory peak occurred earlier in both rockets, so that release occurred as the rocket was falling. The release altitudes were 67.8 kilometers for rocket 10.79 and 74.0 kilometers for rocket 10.80. Tracings of the telemetry records during the time of ozone release are shown in figure 5(a) for rocket 10.79 and in figure 5(b) for rocket 10.80. The early parts of the photometer readings, before ozone release, show a cyclic variation in photocurrent as the vehicle spins. The spin causes the photometers to view in sequence the bright horizon, a less bright sky, the bright horizon again, and then the dark sea. These regions are identified for one cycle on the figures. A change in appearance of the photometer output cycles can be seen at the instant that the ozone release begins. The ozone release continued well past the time period shown in figure 5. The principal effects of the ozone release are a reduction of the light peaks at the two horizons, and an increase in the intensities in the light minima occurring at the seal and sky view angles.

For rocket 10.80, the 5890 Å (sodium D lines) and 6205 Å (red background) photometers malfunctioned. Their outputs were high and varied occasionally during the flight, but not in the cyclic pattern associated with the vehicle spin. Several possibilities exist for the malfunction, including corona discharge and microammeter malfunction. The tubes responded to the calibration light, indicating partial functioning of the photometer system, but the high background output that fluctuated erratically during the flight make the data from these tubes of no value. It is possible that a similar phenomenon was noted in reference 8, where a 5890 Å photometer yielded a saturated output until 70 kilometers was reached.

As noted previously, the ozone releases occurred at too low an altitude to expect any effect on the sodium airglow. Indeed, the release altitude was so low as to cast doubt that even the hydroxyl airglow layer had been penetrated. The first task in data reduction was to answer this question.

Penetration of Airglow Layer by Rockets

To determine whether or not the releases occurred in the hydroxyl airglow layer, where chemiluminescence might be expected, the altitude of the layer at the time and place of the releases must be known. A procedure suggested by the work of Nicodemus, et al. (ref. 9) was used to find the altitude of the bottom of the layer.

It may be shown (ref. 9) that in the absence of absorption by dust or gas, that is above 40 kilometers, the maximum intensity of the airglow (the airglow horizon) will be observed at an angle of exactly 90° from the zenith, provided the observation is made below the airglow layer. Above the airglow layer, it is obvious that the maximum airglow intensity will be observed below the geometric horizon, or at zenith angles greater than 90°. Thus, a plot of the zenith angle of the airglow horizon against altitude should show a constant value of 90° with increasing altitude, until the airglow layer is entered. Then, the angle should increase with altitude. Analysis of the angle as a function of altitude plot should yield the airglow layer profile. This technique is particularly well suited to this experiment, in which the photometers were pointed at right angles to the axis of the spinning rocket. Each revolution of the rocket brought successively into view the airglow horizon, the sky, the other airglow horizon, and then the dark sea. The angle from zenith of the airglow horizon was determined from the photometer output throughout one revolution by the procedure shown in figure 6. In practice, three cycles were measured and the results averaged. For both rockets on the down leg below 60 kilometers, a light emission peak was observed on the sea, or normally dark portion of the cycle. This peak can be attributed to a luminous shock wave in front of the vehicle. The luminous shock made exact location of the airglow horizon difficult or impossible. For this reason, no horizon angles from below 60 kilometers on the down leg could be

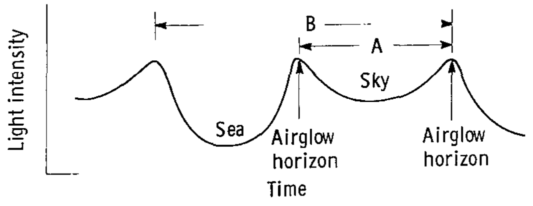


Figure 6. - Calculation of angle from zenith of airglow horizon, $\frac{A}{2B}(360^\circ)$.

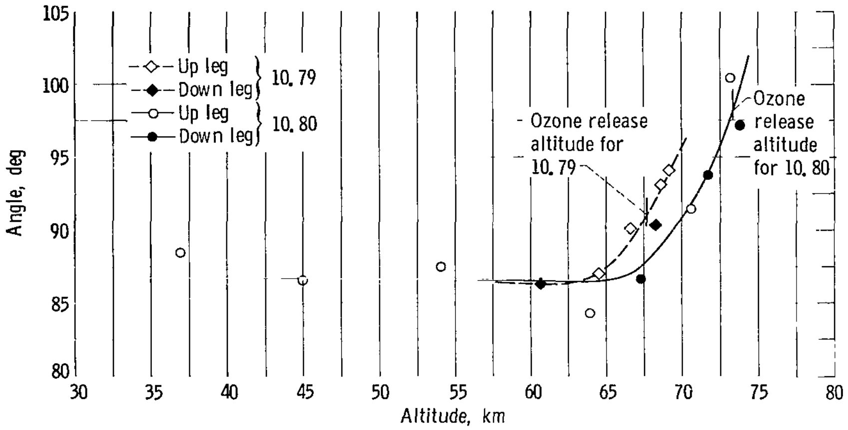
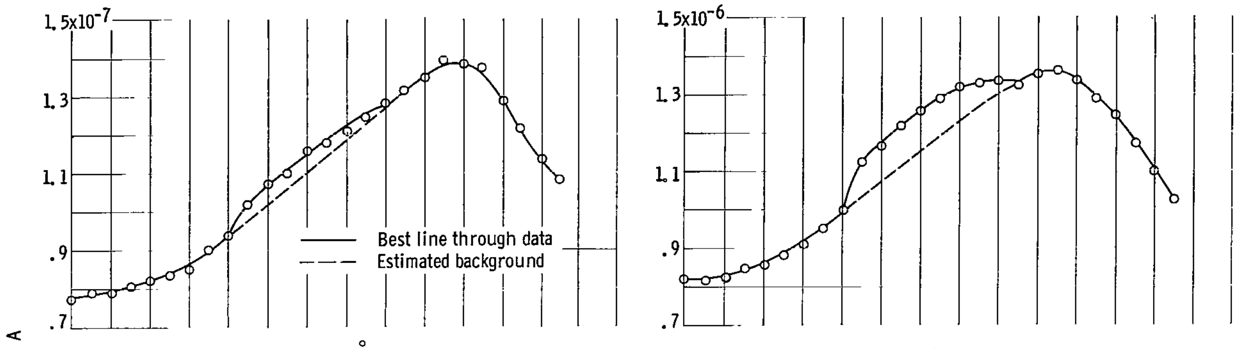


Figure 7. - Angle from zenith of hydroxyl airglow horizon as function of altitude.

calculated. Zenith angles were computed for rocket 10.80 from about 35 kilometers on the up leg. Zenith angles were computed for rocket 10.79 only from about 65 kilometers on the up leg, because the photometers turned on late on account of a delay in the closing of an altitude switch. The results of these calculations are shown in figure 7, where the zenith angle of the hydroxyl airglow horizon is plotted against altitude for both rockets. The zenith angle is found to be approximately constant at 87° up to about 65 kilometers for both rockets. It is not understood why the zenith angle is slightly less than 90°. Possibly absorption by ozone in the Chappuis bands is responsible. Above 65 kilometers, the zenith angle for rocket 10.79 increases abruptly, which indicates the rocket entered the airglow layer at about this altitude. A similar sharp increase in zenith angle occurred for rocket 10.80 above 67 kilometers. The altitudes at which the ozone releases were initiated are also shown in figure 7. The ozone release for rocket 10.79 began when the airglow zenith angle was 90° and ended when the zenith angle was 89°. It is concluded that the 10.79 ozone release occurred at the lower boundary of the airglow layer. The ozone release for rocket 10.80 was initiated at a zenith angle of 97°, definitely within the airglow layer.

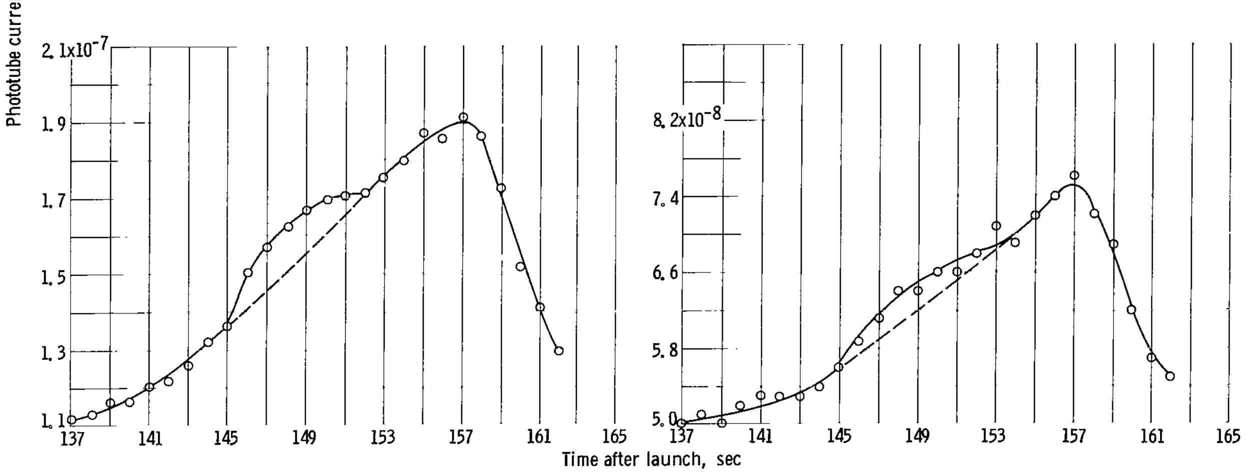
Luminescence Associated with Ozone Releases

Examination of the telemeter records shown in figure 5 shows that if luminosity was produced by the ozone releases, it had to be very slight. In an attempt to distinguish any faint luminosity from the fluctuating background light, the photocurrents were averaged over periods of 1 second. The photocurrent was sampled at 1/125-second intervals, so that each 1-second average was the average of 125 photocurrent readings. The roll rate was about 5 rps, so that each 1-second average included about five complete sky and



(a) Wavelength, 5890 Å (sodium D lines).

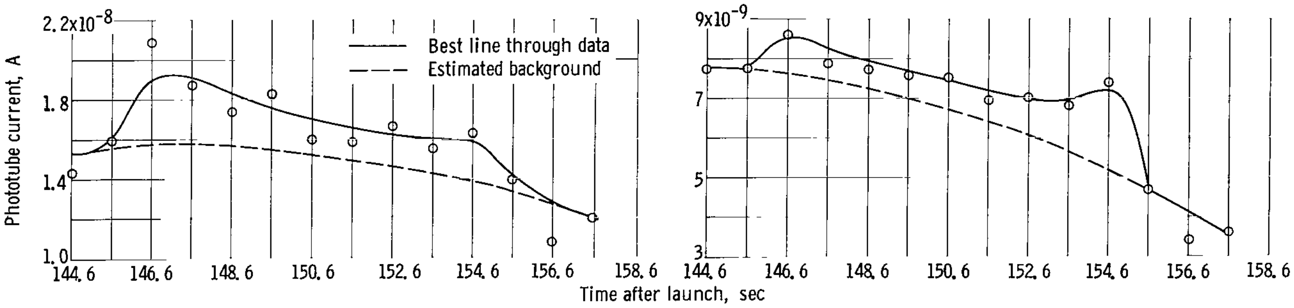
(b) White (no filter).



(c) Wavelength, 5760 Å (green continuum and starlight).

(d) Wavelength, 6260 Å (9-3 hydroxyl band).

Figure 8. - Phototube current during ozone release for Nike-Cajun 10.79. Currents averaged over 1-second intervals.



(a) Wavelength, 5760 Å (green continuum and starlight).

(b) Wavelength, 6260 Å (9-3 hydroxyl band).

Figure 9. - Phototube current during ozone release for Nike Cajun 10.80.

ground scans. The results for rockets 10.79 and 10.80 are plotted in figures 8 and 9, respectively. An increase in light intensity due to the ozone release can be clearly distinguished in these plots.

The length of time that the intensity increase can be detected is about 8 seconds in both releases. In ground tests, the measured time for 90 percent of the tank contents to be expelled was about 4 seconds. Either the flight release took longer, due to the different condition of the liquid in the zero-gravity condition, or the material expelled in the initial phases of the release moved to a considerable distance ahead of the vehicle.

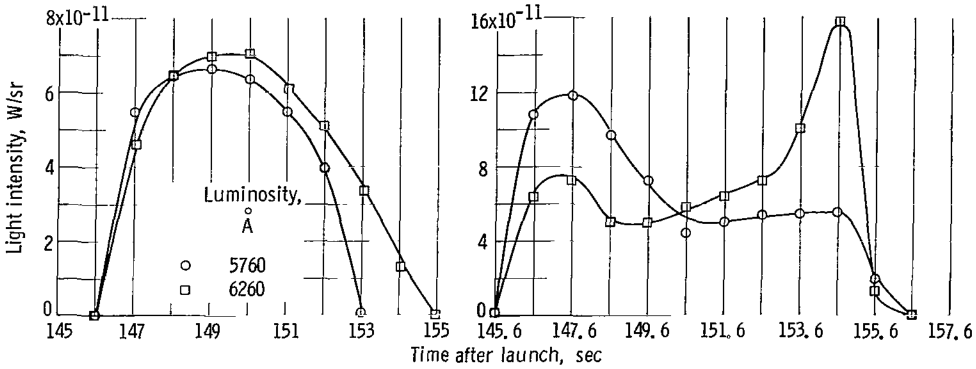
In order to properly interpret the results, it is necessary to find the intensity of the light received from the ozone cloud in terms of absolute units, watts per steradian. For this, the photocurrents were converted to watts by use of calibration factors determined in the laboratory prior to flight. Dividing the intensity in watts by the solid angle of the optical system yielded the intensity in watts per steradian. The light intensity from the release alone was found by subtracting the background light intensity from the total light intensity during the time that the release was observed. The background intensities were estimated by interpolation, as shown by dotted lines in figures 8 and 9.

Some results of these calculations are shown in table III, where mean release intensity values are shown for both rockets 10.79 and 10.80. This table shows the mean photocurrent from the release, the corresponding mean intensity in watts per steradian, and the mean intensity per angstrom, watts per steradian angstrom. The latter was calculated by dividing the intensities by the band width of the interference filters. It is interesting to note that the intensity per angstrom for rocket 10.79 is almost independent of wavelength. The table also shows that the mean intensity of the ozone cloud was similar for both releases.

The absolute intensities at 6260 Å (OH) and 5760 Å (green) of the release as a function

TABLE III. - MEAN VALUES OF OZONE RELEASE LUMINOSITY

Rocket	Wavelength, λ, Å	Mean photocurrent due to cloud, A	Absolute mean intensity from cloud	
			W/sr	W/(sr)(Å)
10.79	6260 (9-3 Hydroxyl band)	2×10^{-9}	4.7×10^{-11}	5.0×10^{-13}
	5890 (Sodium D lines)	4	1.2	4.3
	5760 (Green background)	11	5.8	4.6
	No filter	900	---	---
10.80	6260 (9-3 Hydroxyl band)	1×10^{-9}	7.2×10^{-11}	7.6×10^{-13}
	5890 (Sodium D lines)	----	---	---
	5760 (Green background)	2	6.4	5.0
	6205 (Red background)	----	---	---



(a) Rocket 10.79. (b) Rocket 10.80.

Figure 10. - Intensity of light at 5760 and 6260 Å from ozone release.

of time are shown in figures 10(a) and (b) for rockets 10.79 and 10.80, respectively. Comparison of these two figures shows a distinct difference between the release at the airglow boundary (10.79) and the release inside the airglow layer (10.80). The latter shows an excess of red 6260 Å (OH) light just at the end of the release. A similar excess is not seen for rocket 10.79.

DISCUSSION OF RESULTS

The release from rocket 10.79 occurred at the lower boundary of the airglow layer, so that little or no chemiluminescence is expected. Yet, the apparent light intensity from this release was similar to that from the 10.80 release, which occurred inside the airglow layer. The most plausible origin of the apparent increase in light intensity measured by the 10.79 photometers is light scattered by Freon-12 "ice" crystals from bright parts of the sky. Appendix B gives a brief discussion of the origin of the Freon-12 "ice" cloud produced by release of the solution of ozone in Freon-12 into the atmosphere. The photograph in figure 11 shows an actual Freon-12 ice cloud.

The ice crystals will diffuse light, such that a photometer situated in the center of a cloud of crystals will tend to measure the same intensity in all directions. If the field of view of the photometers does not encompass the brightest parts of the sky, the cloud will diffuse light from these parts into the photometers. The averaged photometer currents for rocket 10.79 show the luminosity from the ozone release superimposed on a changing background light level. The background light increases to a maximum, then decreases, as precession of the rocket moves bright portions of the sky in and out of the photometer field of view. The ozone release occurred at a median background light level, so that one might expect that light scattered from bright regions would increase the photometer reading, as was observed.

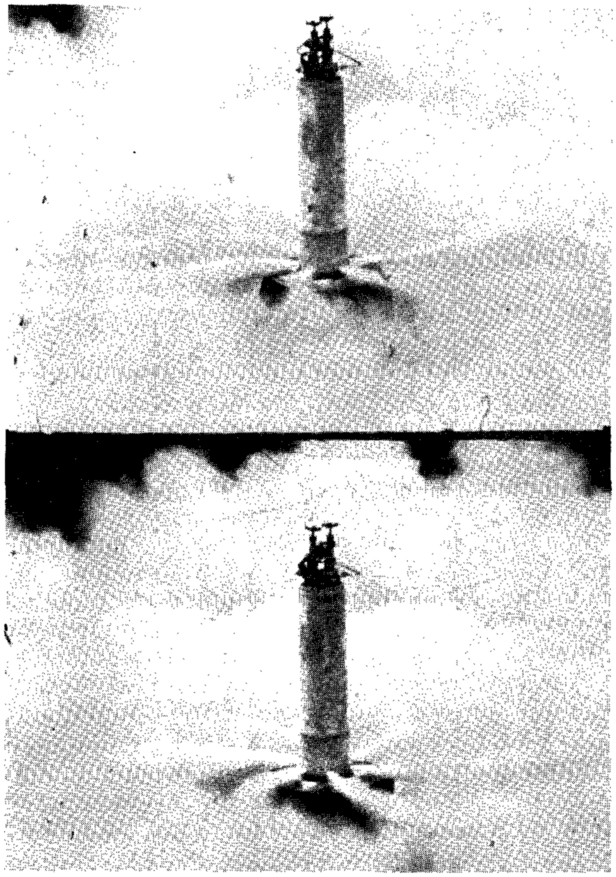


Figure 11. - Spinning ozone release test.

Two additional points support this interpretation. First, the airglow horizon light intensity maxima were sharply reduced, and the dark sea intensity minimum was increased (as shown in fig. 5) by the release. The existence of a cloud of scattering particles around the rocket explains this effect very well. Second, the spectral distribution of the light increase was very uniform, as shown in table III. This is consistent with scattering of sky and starlight as the origin of the light.

Consider now the results for rocket 10.80, which entered the airglow layer. For this rocket, the 6205 Å (red background) and 5890 Å (sodium D lines) photometers malfunctioned, and useful data exist only from the 6260 Å (OH) and 5760 Å (green background) photometers. These data are shown in figure 10(b). By examining this figure it can be seen that the luminosity in this release was qualitatively similar to that in 10.79 (fig. 10(a)) during the first few seconds. Near the end of the release, the intensity at 6260 Å (OH) increased abruptly to a peak which was large relative to the 5760 Å (green background) intensity. Much of the light must be due to light scattered from Freon-12 ice crystals, as in rocket 10.79. However, since this release occurred in the airglow layer, some part of the light, particularly near the end of the release, may be due to chemiluminescence.

An easy test of the presence of the chemiluminescence from the $H + O_3$ reaction would have been comparison of the outputs of the 6260 Å (OH) and the 6205 Å (red background) photometers, and this is why the latter was included. Unfortunately, the 6205 Å (red background) photometer malfunctioned. Another way of testing for chemiluminescence becomes possible if it is assumed that the contribution of chemiluminescence to the light observed for the 10.79 release is negligible. This seems to be a reasonable assumption, since this release occurred at the lower boundary of the airglow layer. Then, the data from rocket 10.79 may be used to estimate the scattered light contribution to the light observed in the 10.80 release. This was done in the following way. Reference to table I shows that the 5760 Å (green background) photometer is nearly insensitive to light generated from the $H + O_3$ reaction, while the 6260 Å (OH) photometer is most sensitive

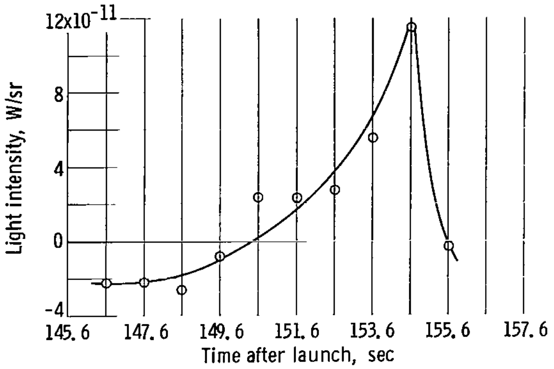


Figure 12. - Chemiluminescence. Luminosity, 6260 Å; rocket 10.80; less estimated contribution from scattered light.

to the hydroxyl radiation. Consequently, the 5760 Å (green background) photometer output is due almost entirely to scattered light, while the 6260 Å (OH) photometer output is due to scattered light plus any possible chemiluminescence. The data from rocket 10.79 were used to calculate the ratio of light scattered at 6260 Å (OH) to light scattered at 5760 Å (green background), since it is presumed that no chemiluminescence accompanied this release. The mean ratio is shown in table III. Multiplying the 5760 Å (green background) photometer output for rocket 10.80 by this ratio gives the scattered light intensity at 6260 Å for rocket 10.80. Subtracting this from the observed light intensity yields the chemiluminescent intensity, if any. The curve resulting from this calculation is shown in figure 12. The red-green ratio from 10.79 apparently overestimates the scattered light for 10.80 because some negative values result. However, figure 11 shows that there is a definite excess of 6260 Å (OH) light over the scattered light, and that the excess light reaches a sharp maximum just as the vehicle leaves the cloud. The simplest explanation of this result is that the chemiluminescence can be detected only near the end of the release, when the flow rates are low, and the mixing region shown in figure 1 is closest to the photometers.

It is not possible to calculate accurately the total light emitted by the release, since the release cloud dimensions and the distribution of light within the release cloud are unknown. However, an upper limit to the total intensity can be obtained by assuming that the peak light intensity I (W/sr) observed as the release ended represents the surface brightness. The total light emitted by the cloud would then be $4\pi I$ watts. The peak light intensity I was 1.2×10^{-10} watt per steradian, which yields 1.4×10^{-9} watt at 6260 Å for the total chemiluminescent brightness of the release.

In the theoretical part of this report, the anticipated release brightness for perfect mixing was estimated to be a maximum of 1 and a minimum of 5×10^{-4} watt. The observed intensity near 10^{-9} watt indicates that very imperfect mixing was achieved.

CONCLUDING REMARKS

A 10-percent solution of ozone in Freon-12, when released into the hydroxyl airglow layer of the upper atmosphere, appears to produce a very faint red chemiluminescence. This chemiluminescence is attributed to the reaction of ozone with atmospheric atomic hydrogen and is evidence for the existence of atomic hydrogen in the hydroxyl airglow layer. An estimated upper limit to the total light intensity of the chemiluminescence at 6260 Å was 10^{-9} watt. This was much less than the value predicted for perfect mixing, which indicated poor mixing of the ozone with the atmosphere in this experiment.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, May 3, 1965.

APPENDIX A

QUANTUM YIELD FOR THE H + O_3 REACTION

Quantum Yield Based on Airflow Intensity (Upper Limit)

The estimated zenith intensity of the 9-3 hydroxyl band at 6257 Å is 110 Rayleighs (ref. 10) or 1.1×10^8 quanta per square centimeter column per second. The estimated total rate of excited hydroxyl production in the hydroxyl airglow is 1.2×10^{12} molecules per square centimeter column per second (ref. 10). The ratio of these two is 10^{-4} quantum per excited hydroxyl. This represents an upper limit to the quantum yield, since it would equal the quantum yield if every reaction event yielded an excited hydroxyl molecule.

Quantum Yield Based on Laboratory Measurements (Lower Limit)

The arrangement for experimental measurement of the quantum yield of the H + O_3 reaction at 6257 Å is shown in figure 13. A stream of oxygen containing about 3 percent ozone was mixed in a spherical reactor with a stream of hydrogen gas partly dissociated to atomic hydrogen in a microwave discharge. A large excess of partly dissociated hydrogen was provided so as to react completely with the ozone. At a pressure of about 1 millimeter, a slow flow of the oxygen-ozone mixture into the reactor produced a small atomic "flame" as shown in figure 13. Light from the "flame" was measured with the calibrated optical system of rocket 10.80. The flow rate of the oxygen-ozone mixture was measured from the rate of pressure drop in a calibrated volume. The concentration of ozone in the mixture was measured by standard analytical techniques. The light source was small enough so that it could be considered as a point source. Then the quantum yield per atom of hydrogen reacted with ozone was

$$\Phi = \frac{4\pi}{\Omega} \frac{IS}{F}$$

where

4π	number of steradians in a sphere
Ω	solid angle subtended by the optical system of rocket 10.80
I	light intensity, quanta at 6257 Å/sec
F	flow rate of ozone, molecules/sec
S	molecules of ozone destroyed per atom of hydrogen reacted

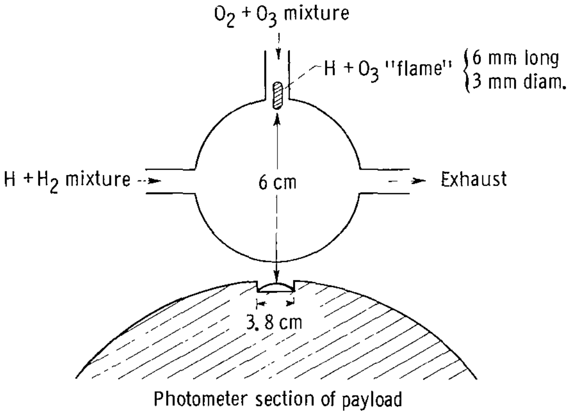


Figure 13. - Experimental arrangement for measuring quantum yield for H + O_3 chemiluminescence.

A value of 3 for S was taken from reference 4. The radiant power from the atomic flame at 6257 Å was 1.8×10^{-11} watt, and the flow rate of ozone was 2.48×10^{-7} mole per second. The dimensions of the optical system as shown in figure 13 were such that $4\pi/\Omega = 43$. These data yield $\Phi = 5\times10^{-8}$ quantum per hydrogen atom. It seems likely that considerable quenching of excited hydroxyl occurs in this experiment. Indeed, indirect evidence for quenching is given in reference 4. Consequently, the quantum yield found in this experiment probably represents a lower limit. The value applicable to the airglow can only be found by measurements at much lower pressures than in this experiment.

APPENDIX B

THE OZONE SOLUTION, ITS PROPERTIES, PREPARATION, AND USE

Ozone Handling

Because 100 percent ozone is easily detonable, it must be diluted in some fashion before it can be carried on a rocket. Three possible means exist: (1) "dilution" with solid particles (i.e., storage of 100 percent ozone in a vessel packed with minute hollow alumina spheres); (2) dilution with liquid oxygen; and (3) dilution with liquid Freon-12 (dichlorodifluoromethane). For case (1), the amount of ozone that can be carried is small, amounting to only 1 pound of ozone for 75 pounds of container. For case (2), since O_2 is more volatile than O_3, a heat exchanger would be required to provide the heat of vaporization of O_3. For case (3), the ozone will evaporate readily from the Freon-12 solution, since it is more volatile than Freon-12.

This last technique was adopted, since it appeared to be the most desirable dilution method from a practical point of view. Extensive tests on the detonability of ozone - Freon-12 solutions were performed to find the safe range of ozone concentrations. It was concluded that up to 10 percent ozone the solutions were completely inert so that a 10-percent solution was chosen for the experiment.

A problem with the use of ozone solutions is that while the solution itself may be inert, the vapor pressure of ozone above the solution may be so high as to produce a hazardous gaseous ozone concentration. In order to reduce the gaseous ozone concentration, it was necessary to chill the solution to a low temperature. For field operations, it was considered impractical to cool the solution below the temperature of solid carbon dioxide (dry ice). At dry ice temperature (-78° C), the partial pressure of ozone gas was estimated to be 1084 millimeters above a 10-percent solution. In order to make the ozone nondetonable, it must be diluted with an inert gas to a concentration below the flammability limit, or about 2 percent. This was accomplished by pressurizing the gas space with helium to pressures in excess of 1200 psi. The high-pressure helium also served to expel the contents of the tank into the ambient atmosphere when release was initiated.

Effect of Freon-12 on Experiment

The necessity of releasing a large amount of Freon-12 with the ozone raises the question as to whether Freon-12 might produce undesirable effects on the experiment. In order to detect possible interference by chemical reactions, laboratory studies of the reactions of Freon-12 were made. Gaseous Freon-12 was mixed with gas streams containing about 10 percent atomic oxygen, 2 percent atomic nitrogen, and 20 percent atomic hydrogen, respectively. The reaction vessel was a stirred reactor of the type described in reference 11 for the study of reactions of atomic species. At room temperature, residence times of about 0. 2 second, and pressures of about 1. 5 torr, no reaction whatsoever could be detected with the mass spectrograph attached to the stirred reactor. This indicates that the reaction rate constant is $\leq 10^{-16}$ cubic centimeter per second in all cases. This is 10^3 or more times less than for the $H + O_3$ reaction. Consequently, it appeared that chemical reactions involving Freon-12 could be neglected.

Physical effects of the Freon-12 on the ozone release were more difficult to assess. When a solution of ozone in Freon-12 is released into a vacuum, the ozone will evaporate first because its vapor pressure is much higher than Freon-12. The heat of vaporization for the ozone is supplied from the heat capacity of the liquid Freon-12. Freon-12 will also vaporize, again with the heat of vaporization being supplied from the heat capacity of the remaining liquid. Consequently, as evaporation proceeds, the remaining liquid cools until it freezes. About half the Freon-12 freezes. The final result is a cloud of ozone - Freon-12 vapor containing many small particles of Freon-12 "ice". These particles of Freon-12 ice have an important effect on the experiment, since they obscure and scatter light. A photograph of the Freon-12 ice cloud is shown in figure 11 (p. 19).

Ozone Tank

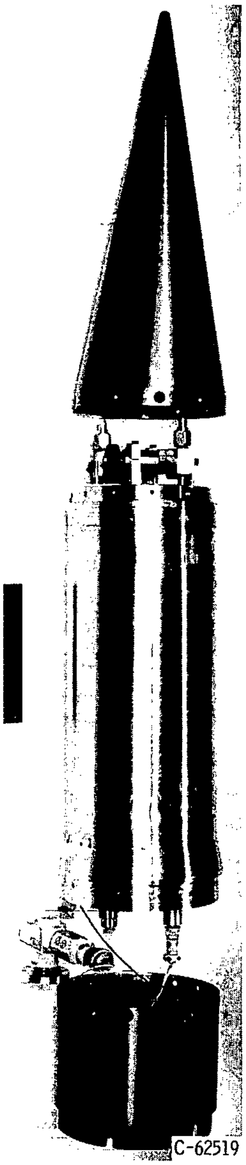


Figure 14. - Ozone tank.

The ozone tank is shown in cross section in figure 2 (p. 6) and in a photograph in figure 14. It was made from stainless steel, had a volume of about 450 cubic inches, and was pressure tested to 2250 psi, with an ultimate burst pressure in excess of 3000 psi. A pressure transducer was mounted in the wall of the tank to monitor tank pressure after filling (for rocket 10. 80, but not for 10. 79). Considerable difficulty was encountered in making the tanks leak free to helium to 1000 psi at low temperatures. Leak-free operation was achieved by the use of Teflon tape to seal all pipe joints and stainless-steel cryogenic valves for fill and vent. The ozone solution was released from the tank by opening of an electrically activated explosive valve. The ozone solution then flowed into a manifold with six vents mounted 60° apart and then out into the atmosphere at right angles to the tank axis. In flight, the ozone solution was made to flow to the tank walls by spinning the vehicle to 5 rps. The dip tube, through which the ozone solution flowed to the release manifold, was curved to touch the tank wall as a consequence of this. A photograph of the tank during a spinning release of the ozone - Freon-12 mixture is shown in figure 11 (p. 19). The time required to release 90 percent of the tank contents was about 4 seconds.

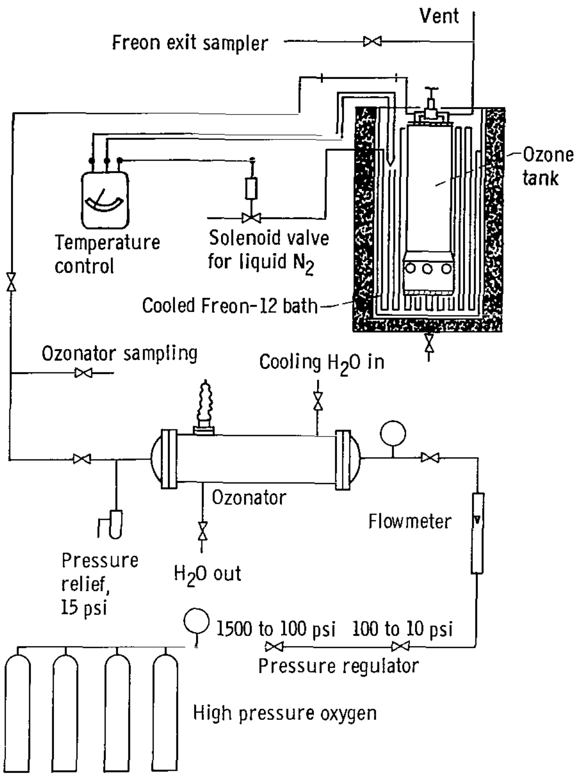


Figure 15. - Freon-12 ozonization flow diagram.

Filling the Tank with Ozone - Freon-12 Solution

The flow diagram for the method of preparation of the ozone - Freon-12 solutions is shown in figure 15. A typical successful filling operation proceeded as follows. To begin the preparation of a tank of solution, the tank and associated hardware were first passivated by passing 3 to 4 percent ozonated oxygen through them for a period of 5 hours. The ozone tank was then filled with 17.5 pounds of Freon-12, immersed in the liquid-nitrogen-cooled Freon-12 cold bath, and cooled to -150° C. At this point the ozonator was turned on and allowed to stabilize for a period of 1 hour under the flow conditions to be used in the ozonization of the Freon-12. Then, the ozonated oxygen from the ozonator was allowed to flow into the Freon-12 contained in the ozone flight tank. The ozone inlet concentration varied from about 3.0 to 5.8 percent, and the outlet ozone concentration varied from 0.05 to 1.1 percent. The oxygen flow through the ozonator was held at about 10 liters per minute. Temperature of the Freon-12 in the ozone tank was maintained at $-150^{\circ}\pm2^{\circ}$ C all during the process. By integrating the inlet and outlet ozone concentrations, the concentration of dissolved ozone in the Freon-12 at any time could be found by difference. Oxygen dissolved in Freon-12 to the extent of 2 percent at -150° C. The oxygen concentration reached 2 percent rather quickly and remained constant thereafter. After about 18 hours of operation, the ozonation process was stopped. At this time, 1.92 pounds of ozone and about 0.35 pound of oxygen were dissolved in the 17.5 pounds of Freon-12, which made about a 9.9-percent solution of ozone. The tank was then slowly pressurized with helium to 755 psig at -147° C and the fill and vent valves closed. The filled tank was then allowed to warm very slowly up to a temperature of -78° C. The ullage at this temperature was about 25 percent. The solution was stable at -78° C, and no decomposition could be detected in a period of 5 days.

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