THE RADIANT OUTPUT OF GRENADE GLOW CLOUDS IN THE LOWER THERMOSPHERE

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Summary

Records of the behaviour of aluminized grenade glow clouds at twilight and at night were obtained using cameras and photometers. From these records the radiance, radiant power, and radiant energy have been deduced for the altitude range 100–200 km. The twilight observations show that the absorption cross section of aluminium monoxide is about 3×10^{-14} cm². From the night-time results it is concluded that the glow probably arises from a chemiluminescent reaction with atomic oxygen. A set of reactions consistent with the observations above 120 km altitude is

 $\begin{aligned} AlO_2+O &\rightarrow AlO+O_2, \\ AlO+O &\rightarrow AlO_2+h\nu, \\ AlO+O &\rightarrow Al+O_2, \end{aligned}$

with the rate constants being 5×10^{-12} , 1×10^{-13} , and 4×10^{-13} cm³ molecule⁻¹ sec⁻¹ respectively.

I. INTRODUCTION

Various authors (Woodbridge 1961; Armstrong 1963; Johnson and Low 1967) have discussed observations made of the glowing clouds that result when grenades containing aluminium are exploded at night or at twilight in the region of the upper atmosphere between 100 and 200 km altitude. Armstrong (1963) and Johnson and Low (1967) have shown that the night-time spectra are continua and that the twilight spectra are dominated by aluminium monoxide (AlO) bands due to resonant scattering of sunlight. The night-time continuum also appears as a weak feature underlying the AlO bands.

We have made observations of these clouds using a special spectroradiometer, described by Johnson (1965) and Johnson and Low (1967), a scanning photometer, described by Johnson and Lloyd (1963), and a total radiation photometer with a 2° field of view. All instruments use logarithmic amplifiers (Groves 1965), with response times of a few milliseconds. Various cameras using calibrated film have also been used to photograph the glow clouds.

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The present paper forms part of a series describing observations of glow clouds formed by chemical releases in the upper atmosphere. The observations were originally undertaken to determine atmospheric properties, using molecular diffusion and temperature measurements (Lloyd and Sheppard 1966; Low 1967), and to investigate the reactions that occur following the chemical releases. The latter give information on chemical reactions in a low pressure, wall-free environment, which cannot be duplicated in the laboratory, and on the chemical composition of the upper atmosphere (Cook, Drummond, and Sheppard 1966).

II. VARIATION OF RADIANT OUTPUT WITH TIME

(a) Night-time Glow Clouds

Armstrong (1963) has observed, in night-time releases, that the $A^2\Sigma^+-X^2\Sigma^+$ bands of AlO are emitted by the flashes of exploding grenades, but that they become less prominent as the altitude of the explosion increases. At an altitude of about 90 km, these bands are no longer evident and a brief luminescence appears. The present photometer records show that further transition phenomena occur, as exemplified by Figure 1, which is a partial record of the results of a night-time firing of a sequence of grenades. Unfortunately, because of the greater difficulty of tracking the rocket at twilight, we have no similar record for a twilight firing.



Fig. 1.—Variation of radiant power P with time for night-time clouds.

Figure 1 shows that, after the initial very rapid decay of the flash, the output behaviour falls into three patterns with a smooth transition between them. Up to about 100 km altitude there is a monotonic decay. At about 100 km a small build-up occurs before decay sets in, while above an altitude of about 125 km, there is a short initial decay before the build-up. All build-up and decay rates decrease with increasing altitude. Photographic observations of twilight clouds show that this trend continues to higher altitudes. Eventually, near 200 km altitude, the final decay stage is not observed. The results shown in Figure 1 are limited in time after detonation for two reasons. The grenades are released at intervals of a few seconds and, since the instrument tracks the ascending rocket, lower clouds pass out of the field of view. Secondly, in many cases the clouds overlap so as to prevent measurement of the behaviour of any one of them. Lloyd and Sheppard (1966) have given a curve showing the variation of radiant power for longer times.

(b) Twilight Glow Clouds

Two types of grenades were exploded. Both were essentially the same, but one (described as the Ba-type grenade) contained some barium nitrate and potassium perchlorate, while the other (described as the K-type grenade) contained a similar quantity of potassium nitrate. The only difference in observed behaviour was that, in addition to the AlO bands and the K and Al lines, the Ba⁺ 455 \cdot 4 nm line was produced by the first type. Figure 2 shows the later time histories of the various resonant emissions of some sunlit glow clouds near 180 km altitude. Because rapid decreases in radiance due to diffusion would be expected, only the behaviour of the resonant emissions relative to AlO is shown. For clarity the curves have not been plotted at the correct relative positions on the ordinate scale and only the slopes of the curves are significant. Johnson and Low (1967) have given some curves showing the relative strengths of the various emissions.



Fig. 2.—Decay of resonant emissions relative to those of AlO emissions for twilight clouds near 180 km altitude.

The significant features of Figure 2 are that the K 404–5 nm emissions decay more rapidly than those of AlO and K 770 nm. With the Ba-type grenade at 167 km there is a build-up of the K 770 nm line before a slight decay sets in. This is the only observation of such a cloud, but the effect could be corroborated by the fact that the line was not detected during the short time that the Ba-type grenade at 182 km was observed, and that there was a slight rise for the K-type grenade at 189 km. The Al 396 nm line decays more rapidly than the AlO emissions. With both Ba-type grenades the Ba⁺ 455 nm line decayed very rapidly.

To obtain more information on the relative rates of decay a multifilter photometer has been built. This instrument will be used to make measurements at the K, Al, and AlO (0,0) wavelengths together with wavelengths representing the underlying continuum and the sky foreground.

III. RADIANT OUTPUT OF CLOUDS

After allowing for the known spectral distribution of the radiation from the clouds (Johnson and Low 1967) and for the spectral response of the detectors (which

were calibrated in absolute terms against a standard lamp) it was possible to calculate the absolute value of the radiant output of the clouds. Figures 3, 4, and 5 show curves plotted against altitude, which are the means of many observations with the various



Fig. 3.—Centre-point radiance R_{centre} at 1, 10, 30, 60, and 120 sec after detonation (note that 1 rayleigh = $10^{6}/4\pi$ photons sec⁻¹ cm⁻² steradian⁻¹).

instruments. The ordinate scales are also calibrated in terms of the equivalent number of photons emitted at the (0,0) bandhead wavelength of AlO ($\lambda = 484 \cdot 2 \text{ nm}$) for twilight clouds, and at a representative wavelength ($\lambda = 550 \text{ nm}$) for night-time



Fig. 4.—Total radiant power emitted by the clouds at 1, 10, 30, 60, and 120 sec after detonation. The curve for $P_{\text{max}} = 2 \cdot 5 \times 10^{11} n(\text{O})$ is shown, where the values of n(O) were taken from CIRA (1965).

clouds. Similar calibrations would be obtained for the actual numbers of photons emitted.

Figure 3 shows the centre-point radiance for various times after detonation. For the higher altitude twilight clouds the centre-point radiance decreases by about one order of magnitude in 120 sec. Figure 4 shows the total radiant power emitted by the whole cloud. Above 120 km altitude at night, the radiant power decreases in a similar manner to the atomic oxygen concentration. From the variation of the radiant power with time, overall rate constants can be calculated. These rate constants are related to the chemical reactions that occur and are considered in Section V. The curves for radiance and radiant power of twilight clouds refer to the case when the full intensity of the Sun's radiation is falling on them. Since absorption by the Earth's atmosphere reduced the intensity of the Sun's radiation, the effects of absorption had to be removed from the observations before the results could be plotted in Figures 3 and 4. At lower altitudes the absorption effects are large; at higher altitudes the changes in the number N of AlO molecules are small. This means that



Fig. 5.—Total radiant energy *E'* emitted during the lifetime of night-time clouds.

at all altitudes the change in radiant power with time was as much due to variation in the intensity of the Sun's radiation incident on the cloud as it was due to a change in N. Thus curves for twilight clouds in Figures 3 and 4 must be treated as tentative. It may be noted, however, that the increase in radiant power with time at higher altitudes (Fig. 4) is a real effect, since it was observed at evening twilight.

Figure 5 shows the total radiant energy emitted by night-time glow clouds during their lifetime. Above 120 km the curve is very tentative, but it appears that the total radiant energy is constant. The peak energy output of about 3×10^5 J should be compared with 2.95×10^6 J, which is the total chemical energy available in the explosion of the standard 1 lb Skylark grenade. This suggests that the cloud traps energy in the ambient atmosphere by reaction of the explosion products with some constituent of it.

No curve similar to Figure 5 is given for twilight glow clouds since the output depends on the incident sunlight, and hence the total radiant energy has no meaning.

IV. Absorption Cross Section of AlO

If N is the total number of AlO molecules in a sunlit cloud, P is the total observed radiant power from the cloud, and ϕ is the incident solar irradiance on the cloud then, for an optically thin cloud, the absorption cross section σ of AlO is given by

$$\sigma = P/\phi N \, .$$

From an analysis of the power and energy emitted by night-time clouds in terms of the kinetics of the reactions (see Section V(b)) it was found that approximately half the aluminium available is in the form of AlO and half in the form of AlO₂. Consequently 140 g of AlO gives $N = 2 \cdot 0 \times 10^{24}$ molecules. The radiant power P for a grenade at 155 km and 1 sec after detonation is 10^{23} photons/sec (Fig. 4); variations from 140 to 200 km altitude for times after detonation of 1–30 sec are small. The solar irradiance ϕ can be calculated by assuming that all the energy emitted by the cloud falls into one line of rectangular shape equivalent to the real profile of the line due to natural and Doppler widths. Most of the energy falls near $484 \cdot 2$ nm in the (0,0) band of the $A^2\Sigma^+-X^2\Sigma^+$ transition of AlO and the variation of solar flux over this band can be neglected.

Following the method used by Authier (1964), let $\Delta \nu$ be the half-intensity width of the real line profile. Then the natural width $\Delta \nu_n$ is equal to $(2\pi\tau)^{-1}$, where τ is the lifetime in the excited state. For a permitted transition τ is greater than 10^{-8} sec, so that $\Delta \nu_n$ is less than 10^9 sec^{-1} . The Doppler width of the line is (Chamberlain 1961)

$$\Delta \nu_{\rm D} = 1 \cdot 67 (2RT/\mu)^{\frac{1}{2}},$$

where μ is the molecular weight, *R* the gas constant, and *T* the absolute temperature. For $T = 687^{\circ}$ K, which corresponds to 155 km altitude (CIRA 1965), and $\mu = 43$ for AlO, $\Delta \nu_{\rm D}$ is equal to 1.78×10^9 sec⁻¹. Hence $\Delta \nu_{\rm D}$ is greater than the natural width and is the dominant contribution to the actual line profile. The rectangle with area equivalent to the profile has width

$$egin{aligned} \delta &
u = \int_{-\infty}^\infty \exp(-
u/\Delta
u_{
m D})^2 \, {
m d}
u \ &= \pi^{rac{1}{2}} \Delta
u_{
m D} = 3 \cdot 17 imes 10^9 \, {
m sec}^{-1} \end{aligned}$$

and, at a wavelength of $484 \cdot 2$ nm, this corresponds to $\delta \lambda = (\lambda^2/c)\delta \nu = 2 \cdot 47 \times 10^{-3}$ nm, where c is the velocity of light. Allen (1963, p. 172) gives the solar radiation above the Earth's atmosphere as $2130 \text{ erg cm}^{-2} \text{ nm}^{-1} \text{ sec}^{-1}$. Hence the solar irradiance through a window $2 \cdot 47 \times 10^{-3}$ nm wide at $484 \cdot 2$ nm is

$$\phi = (2130/h\nu) \times 2.47 \times 10^{-3} = 1.29 \times 10^{12} \text{ photons cm}^{-2} \text{ sec}^{-1}$$
.

Consequently, the absorption cross section for AlO in a typical cloud at 155 km and at 1 sec after detonation is

$$\sigma = 10^{23}/1 \cdot 29 \times 10^{12} \times 2 \times 10^{24} = 3 \cdot 9 \times 10^{-14} \text{ cm}^2$$

a not unreasonable value.

 $N\sigma$ can also be determined from observation of the radial distribution of output across the cloud. Lloyd (1965) has examined theoretically the effect of absorption on the radiance profiles of glow clouds. His results indicate that the radiance profile is essentially Gaussian when the optical thickness parameter $gb^2 (= \sigma N/\pi r_e^2)$, where r_e is the effective radius of the cloud) is less than unity and that the profile is markedly non-Gaussian when gb^2 is greater than 2. Thus the glow cloud is optically thick when r_e^2 is less than $\sigma N/2\pi$.

Observations of twilight clouds have enabled the region of non-Gaussian radiance profiles to be identified. Combining the results of Figures 3 and 4 of Lloyd and Sheppard (1966) shows that this region is described by $r_{\rm e}^2 < 0.6 \pm 0.2 \,\rm km^2$ for the altitude range 100–160 km. The absorption cross section can now be deduced from the two results for $r_{\rm e}^2$. We find that $\sigma N/2\pi = 0.6 \,\rm km^2$, giving for $N = 2 \times 10^{24}$, $\sigma = 1.9 \times 10^{-14} \,\rm cm^2$. This result is in good agreement with the earlier result for σ . We conclude that the absorption cross section of AlO is about $3 \times 10^{-14} \,\rm cm^2$.

An alternative method of describing scattering is to use the oscillator strength f, which gives the equivalent number of classical scattering electrons per molecule. The relation between σ and f is (Allen 1963, p. 55)

$$\sigma = \frac{\int \sigma_{\nu} \, \mathrm{d}\nu}{\delta \nu} = \frac{\pi e^2}{mc} \frac{f}{\delta \nu}.$$

This gives f = 0.005 for AlO, which compares well with those values of f for NO₂ (0.002) and CO⁺ (0.003) quoted by Allen (1963, p. 78).

V. CHEMICAL REACTIONS

(a) Overall Rate Constants

The data in Figures 1 and 4 describe the variation of radiant power P with time. Generally P decreases with time, then increases, and subsequently decreases. The variation of P with time is represented by $\exp Kt$, using three different values for K as shown in Figure 6. The constants K_1 , K_2 , and K_3 are overall rate constants related to the chemical reactions that occur. Figure 7 shows the time after detonation at which the radiant power is a maximum, so that the ordinate gives an indication of $1/K_2$. Figure 8 presents the results for K_1 , K_2 , and K_3 , with the actual data points shown. It should be noted that the results for K_1 and K_2 are generally much less accurate than those for K_3 because the observation times were much smaller. Some of the results for $\log(-K_1)$ are shown as lower limits, as the time resolution on these particular records was inadequate for K_1 to be calculated.

The overall rate constant K_1 is dependent upon the initial behaviour of the explosion products. From the analysis of Brode (1959), who examined theoretically a TNT explosion at sea level, it follows that the explosion products first reach a density near that of the atmosphere at a time of about $10^{-1} E_0^{1/3} \rho_0^{1/2} p_0^{-5/6}$, where E_0 is the energy released in the explosion, ρ_0 is the atmospheric density, and p_0 is the atmospheric pressure. From 100 to 200 km altitude, the value of this expression is about 0.3 sec for the 1 lb Skylark grenades. Thus all observations for times earlier

than 0.3 sec after detonation of the grenade will represent a chemical reaction (or reactions) occurring under conditions of rapidly decreasing pressure and temperature. All the photometer observations in Figure 8(*a*) refer to times from 10^{-2} to 1 sec and so should be discarded. The photographic observations refer to later times when the explosion products had mixed with the atmosphere and had reached atmospheric temperature. Typically, the radiant power decreased by 30% in about 30 sec and then increased. The present observations do not enable the variation of K_1 with



Fig. 6.—Variation of radiant power Pwith time t showing the overall rate constants K_1 , K_2 , and K_3 (note that K_1 and K_3 are negative). Curve 1 $P = P_1 \exp K_1 t$

Curve 2 $P = P_2 \exp K_2 t$ Curve 3 $P = P_3 \exp K_3 t$

altitude to be determined satisfactorily. Consequently, no explanation of the cause of this initial decrease in radiant power is offered here and the chemical reactions associated with K_1 are not considered in the following discussions.

The rate constants K_2 and K_3 both decrease with altitude in a manner similar to the concentration of atomic oxygen, n(O). Included in Figure 8 are curves proportional to the atomic oxygen concentrations given in CIRA (1965). The behaviour



Fig. 7.—Values showing the time after detonation t_{max} at which the total radiant power of night-time clouds is a maximum. The curve is a plot of $3 \times 10^{11}/n(\text{O})$, where the values of n(O) were taken from CIRA (1965).

- Photometer measurements
- ▲ Photographic measurements

of K_3 above 140 km altitude at night (Fig. 8(c)) has not been measured satisfactorily. However, it seems that K_3 may increase with altitude, thus showing that it is no longer proportional to n(O); this would mean that another chemical reaction becomes important above 130 km altitude or, possibly, that the overall rate constant depends on both n(O) and temperature. In order to resolve this uncertainty, further grenade experiments above 140 km altitude at night are planned.

The indication that K_2 and K_3 are proportional to n(O), at both twilight and night-time, suggests that the products of the grenade explosion react with atomic

oxygen to give AlO. Resonant radiation from AlO is observed at twilight. The reactions with atomic oxygen probably give the continuum radiation observed at night.



Fig. 8.—Overall rate constants of the chemical reactions: (a) first reactions, P decreasing; (b) second reactions, P increasing; (c) third reactions, P decreasing. Values of n(O) for the curves were taken from CIRA (1965). Note that in (a) the lower limits were due to poor resolution on some records (observation time less than 1 sec). K_1 , K_2 , and K_3 are measured in units of sec⁻¹.

The twilight results above 150 km altitude show that the radiant power increases with time, i.e. the number of AlO molecules increases. Such an effect would be observed if aluminium dioxide existed and then reacted with atomic oxygen to give AlO. Thus the overall rate constant K_2 is identified with the reaction (Rosenberg 1963)

$$AlO_2 + O \xrightarrow{k_2} AlO + O_2, \qquad (1)$$

so that $K_2 \simeq k_2 n(O)$. From Figure 8(b) it follows that

 $k_2 \simeq 4 \times 10^{-12}$ cm³ molecule⁻¹ sec⁻¹.

The overall rate constant K_3 describes the decrease in radiant power with time. For twilight glows this must mean that AlO is being destroyed. A simple reaction with atomic oxygen is

$$AlO + O \xrightarrow{k_3} Al + O_2.$$
 (2)

Provided that AlO is not regenerated in subsequent reactions of Al with O or O_2 this reaction would explain the destruction of AlO (an alternative reaction is presented in Section V(c)). Thus $K_3 = -k_3 n(O)$ and it follows from Figure 8(c) that

$$k_3 = 4 \times 10^{-13}$$
 cm³ molecule⁻¹ sec⁻¹.

Reaction (2) is about 10 times slower than reaction (1). Reactions (1) and (2) are

the simplest reactions that can be invoked to explain the present observations of twilight glow clouds.

(b) Light Emission

Results for the radiant power of night-time glow clouds are given in Figure 4. From these results it can be shown that the maximum radiant power could be produced by reaction (2) were it chemiluminescent. However, this would give Al line emissions at night and, since they are not observed, we prefer to use the chemiluminescent reaction (Rosenberg 1963)

$$AlO + O \xrightarrow{k_4} AlO_2 + h_{\nu}, \qquad (3)$$

and this is consistent with the observations of Johnson and Low (1967), who showed that the night-time continuum is detectable in twilight clouds as a weak feature underlying the strong AlO band emissions.

The rate F of emission of photons in reaction (3) is given by

$$F = k_4 n(O) n(AlO)$$
 photons sec⁻¹ cm⁻³

and the maximum radiant power is

$$P_{\max} = k_4 n(0) \times 2 \times 10^{24}$$
 photons/sec,

since, as already noted in Section IV, the number of AlO molecules is approximately 2×10^{24} . The observations in Figure 4 give $P_{\text{max}} = 2.5 \times 10^{11} n(\text{O})$ photons/sec above 120 km altitude. Hence $k_4 = 1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, which is comparable with k_3 .

We have seen that the present observations are consistent with the set of reactions

$$AlO_2 + O \xrightarrow{k_2} AlO + O_2, \qquad (1)$$

$$AlO + O \xrightarrow{k_3} Al + O_2, \qquad (2)$$

$$AlO + O \xrightarrow{k_4} AlO_2 + h\nu .$$
(3)

A detailed analysis of the kinetics of these three reactions^{*} shows that the result for k_2 in Section V(a) must be modified to obtain agreement with the data for K_2 , K_3 , and P_{max} . The rate constants are

$k_2 = 5 imes 10^{-12}$	$\mathrm{cm}^{3}\mathrm{molecule}^{-1}\mathrm{sec}^{-1}$,
$k_3=4\! imes\!10^{-13}$	${ m cm^3molecule^{-1}sec^{-1}}$,

and

$$k_4 = 1 \times 10^{-13}$$
 cm³ molecule⁻¹ sec⁻¹.

* See Johnson et al. (1967).

In addition, it is found that $n(AlO) \simeq n(AlO_2)$ initially. The above findings are consistent with the present results for the time t_{\max} at which P_{\max} occurs. From an analysis of the kinetics of reactions (1), (2), and (3), and using the above values for the rate constants, it can be shown that

$$t_{\rm max} = 3.6 \times 10^{11}/n(0)$$
 sec.

This is in good agreement with the result shown in Figure 7, namely

$$t_{\max} = 3 \times 10^{11} / n(O)$$
 sec.

A similar analysis of the radiant energy can also be made. For a total of 4×10^{24} molecules of AlO and AlO₂, the total energy emitted by the cloud, with the above rate constants, is calculated to be $1 \cdot 0 \times 10^{24}$ photons. This agrees well with the value of 1×10^{24} photons indicated by the results of Figure 5 above 120 km altitude.

It should be noted that the discussion in this section only applies to altitudes above 120 km. Below 120 km the behaviour of the radiant power no longer follows the atomic oxygen profile and the total energy emitted decreases rapidly with altitude. The reason for this is that mixing due to diffusion is less effective and that reactions different from those presented in this section become dominant at lower altitudes; in particular, reactions with molecular oxygen become important. Furthermore, the altitude differences in the behaviour of the radiant power at very early times suggest that the products of the grenade explosion change with altitude, the higher oxides of aluminium becoming more important at lower altitudes. Below 90 km all the aluminium is rapidly changed to Al_2O_3 and no persistent glow is produced at night; at twilight the solid particles of Al_2O_3 are visible as a small patch of smoke.

(c) Alternative Reactions

Chemiluminescent reactions emitting the light observed at night have been proposed by Woodbridge (1961), Armstrong (1963), and Drummond (1967), as well as by Rosenberg (1963). Woodbridge suggested the scheme

$$Al+O \rightarrow AlO+h\nu,$$

$$AlO+O \rightarrow AlO_2+h\nu,$$

$$AlO_2+AlO \rightarrow Al_2O_3.$$
 (2a)

This is not consistent with the present results for k_2 and k_4 , but would be so if no light were emitted by the first reaction. The third reaction (2a) may be significant and, like (2), would destroy AlO. However, the initial radius of the glow clouds increases with altitude so rapidly (Lloyd and Sheppard 1966) that $n(AlO_2)$ must decrease from a value comparable with n(O) at 120 km altitude to about $10^{-2}n(O)$ at 200 km altitude. Hence, the product of $n(AlO_2)$ with the rate constant for reaction (2a), which gives a value for K_3 , decreases with altitude more rapidly than does the present observed value of K_3 (shown in Fig. 8(c)). We thus conclude that reaction (2a) is probably unimportant. However, we note that this reaction does provide a mechanism for the eventual conversion of the aluminium sub-oxides to alumina and, were it chemiluminescent, it could be coupled with reaction (1) to give a possible reaction scheme.

Armstrong (1963) considered the possibilities that monoxides of aluminium, barium, potassium, or nitrogen might react with atomic oxygen in the manner of nitric oxide, namely

$$\mathrm{NO}+\mathrm{O}
ightarrow \mathrm{NO}_2+h
u$$
,
 $\mathrm{NO}_2+\mathrm{O}
ightarrow \mathrm{NO}_2+\mathrm{O}_2^*$.

The barium, potassium, and nitrogen possibilities must be eliminated since we did not observe a glow cloud following the detonation of a grenade containing no aluminium. We agree with Armstrong that reactions involving AlO must be significant. Armstrong also suggested as a possibility the reaction

$K+OH \rightarrow KOH + h\nu$.

This also must be rejected since aluminium is an essential constituent of grenades that produce glow clouds at night-time.

A detailed discussion of possible chemical reactions involving the various oxides of aluminium has been given by Drummond (1967). He suggests that below 120 km altitude light emission arises from the reactions

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. . .

$$AIO + AIO \rightarrow Al_2O + O,$$

$$Al_2O + O_2 \rightarrow (AIO)_2 + O,$$

$$Al_2O + O_2 \rightarrow Al_2O_3 + h\nu,$$

$$(AIO)_2 + O \rightarrow Al_2O_3 + h\nu.$$

These reactions give a difference between twilight clouds, which are observed because of resonant scattering of sunlight by AlO molecules, and night-time clouds. The present observations show that twilight glow clouds are not observed below 100–110 km altitude, but that night-time clouds are observed above 80–90 km altitude. Consequently, Drummond's reaction scheme seems to be valid below about 110 km altitude. Above 120 km altitude, Drummond suggests that the dominant reactions are

 $\begin{aligned} \text{AlO}+\text{AlO} &\to \text{Al}_2\text{O}+\text{O} ,\\ \text{Al}_2\text{O}+\text{O} &\to (\text{AlO})_2+h\nu ,\\ (\text{AlO})_2+\text{O} &\to \text{Al}_2\text{O}+\text{O}_2 ,\\ (\text{AlO})_2+\text{O} &\to \text{Al}_2\text{O}_3+h\nu ,\\ \text{Al}_2\text{O}+\text{O}_2 &\to \text{Al}_2\text{O}_3+h\nu . \end{aligned}$

Again, there will be a difference between night-time and twilight clouds. Thus the overall rate constants K_2 and K_3 , describing the increase and subsequent decrease in

radiant power, would be different at night and at twilight. This does not seem to be so from the observations given in Figures 8(b) and 8(c). We conclude that Drummond's second reaction scheme is probably unsatisfactory.

It is clear that further observations of grenade glow clouds in the upper atmosphere and of relevant chemiluminescent glows in the laboratory are needed. Such observations will help in determining those chemical reactions that are likely to occur in the clouds and in deciding whether reactions (1), (2), and (3) are still the most appropriate ones to use.

VI. ACKNOWLEDGMENTS

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