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IONIZATION IN AFTERBURNING ROCKET EXHAUSTS

CONRAD F. SCHADT
STANFORD RESEARCH INSTITUTE

QUARTERLY REPORT NO. 2, PART I
January 1962

Contract AF 04(694)-128
SRI Project PAU 4134-1

Prepared for

HEADQUARTERS
SPACE SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
Air Force Unit Post Office
Los Angeles 45, California
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Approved:

Felix T. Smith, Director
Chemical Physics Division

Copy No. 1
Calculations have been made of "flame" (or mixing) dimensions associated with afterburning in rocket exhaust at high altitudes for a hypothetical rocket and trajectory. From these and a given exhaust composition, one can estimate concentrations and times available for reactions of interest. Above some altitudes if observed flame lengths should turn out to be much greater, it would indicate that reaction rates rather than mixing rates were controlling.

Investigation of negative ion formation reactions indicates that they may not be a significant factor in removal of electrons, since dissociative recombination of polyatomic ions is much faster. However, if the production of electrons were mainly due to ionization of alkali metals (which have very low recombination coefficients), the above reactions could be an important electron-removal mechanism.

Calculations have been made of electron densities resulting from thermal ionization of potassium in a rocket engine at various altitudes to provide estimates for comparison and evaluation of the probable significance of other reactions. The estimates indicate that thermal ionization of potassium with typical solid propellants can be a very important source of electrons.

Preliminary investigation of photoionization in rocket exhaust has provided some values of radiation flux density versus altitude for various wavelengths.

Reviewed and approved:

Thomas J. Bellanca
Thomas J. Bellanca, 1st Lt., USAF
Project Administrator
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INTRODUCTION

Free electrons in a rocket exhaust stream cause interference in communications with the vehicle and increase its vulnerability to detection. An important source of free electrons is the chemionization produced in the chemical reactions of afterburning as unburned fuel in the exhaust mixes with the ambient atmosphere.

This study, which is a continuation of the work performed under Contract AF 04(647)-751, surveys existing knowledge of afterburning phenomena in rocket exhausts related to the production of ions. The objective is to provide a summary of existing information and to suggest a program of theoretical and experimental research to fill gaps in present knowledge. The over-all aim is to predict or control such ionization.

Efforts will be concentrated on two general areas: (1) fluid dynamics of exhaust jets in the atmosphere at various altitudes, and (2) ionization reactions which may occur during afterburning. The two areas are interrelated and cannot be arbitrarily separated. However, because of the complexity of each field it is desirable to treat them independently as far as possible.

During this report period, flame length calculations presented in the First Quarterly Report have been treated in more detail, and studies have been made of (a) the possible significance of negative ion formation as electron sinks, (b) the importance of alkali metal contaminants in the propellant, especially in relation to other electron sources, and (c) the possible role of photoionization in rocket exhaust.

Contributions to this report have been made by several people. The following sections are primarily the work of the following individuals:

Negative Ion Formation -- Robert C. Whitten
Thermal Ionization of Alkali Metals -- Carole R. Gatz
Photoionization -- I. G. Poppoff
DISCUSSION

A. Flame Length

The fluid dynamics of an exhaust jet is extremely complicated. However, at high altitudes certain simplifications are admissible. For example, shockwave structures within the jet can be neglected at high altitudes and high velocities. Further, at great altitudes (exceeding 60 km) the expansion of the jet to roughly a cylindrical shape is very rapid, so that the boundary of the jet can be approximated by a blunt body with a cylindrical afterbody. Thus, as an approximation the jet is assumed to expand to a cylindrical shape at a distance $b$ from the nozzle exit, and mixing is assumed to begin at $x = 0$ (see Fig. 1). A shock will be caused by the jet "blunt body," and as the diameter of the expanded jet increases (at higher altitudes due to lower ambient pressure), the shock stand-off distance may actually exceed the length of the rocket, and thus the bow shock from the expanded exhaust jet can occur ahead of the rocket itself. Shock stand-off
The distance $\Delta$ for a sphere can be calculated from

$$\Delta/R_0 = 0.143 \exp(3.24/M_\infty^2)$$

where $R_0$ = radius of the sphere, and $M_\infty$ = free-stream Mach number. For our region of interest, $\Delta$ will be roughly 0.15 times the radius of the expanded jet. For our simple model, we will neglect the effects of the rocket body, since the expanded jet will be large in comparison with it.

The pressure at the stagnation point of a hemisphere is assumed to be given by

$$p_{st}/p_\infty = \gamma_\infty M_\infty^2 + 1$$

where $p_\infty$ = free-stream pressure and $M_\infty$ = free-stream Mach number. The pressure decays around the hemisphere toward the cylinder, at the transition, corresponding to $x = 0$ (Fig. 1), the pressure is assumed to be 0.1 $p_{st}$. Decay to ambient pressure may be assumed to occur at 25-100 diameters behind a sphere, or at about 150 diameters on a cylindrical afterbody. In the model for the first calculations of flame length it was assumed that ambient pressure was attained at $x = 0$ (an unspecified distance $b$ from the front of the expanding exhaust plume) and mixing was assumed to begin at this point. However, if $x = 0$ is at about 100 expanded jet diameters downstream, one should assume that the disturbance which initiates the growth of turbulent mixing occurs at an earlier point.

For our present model, the distance $b$ to where $x = 0$ is assumed to be roughly one jet radius, i.e., the blunt portion of the jet is assumed to be roughly hemispherical, the pressure at that point is taken as 0.1 $p_{st}$, and mixing is assumed to begin there. In order to obtain some dimensions for a jet flow field at high altitudes, calculations by W.T. Lord for a particular rocket and specific trajectory have been used. The semi-divergence angle of the nozzle is 15°, the ratio of the specific heats of the jet gas is 1.2, the velocity of the jet gas at the exit plane is 3000 meters/sec, and the pressure is $1/3$ atmosphere. Diameter, $2a$, of the expanded jet is presented for different altitudes (Table I, and Fig. 2). The rocket velocity varies linearly with altitude and reaches a value of 7300 meters/sec at 150 km.
### Table I

ROCKET EXHAUST AND ATMOSPHERIC CHARACTERISTICS

<table>
<thead>
<tr>
<th>h</th>
<th>Altitude, km</th>
<th>80</th>
<th>100</th>
<th>110</th>
<th>120</th>
<th>130</th>
<th>140</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_\infty$</td>
<td>Ambient temperature, °K</td>
<td>166</td>
<td>199</td>
<td>287</td>
<td>477</td>
<td>665</td>
<td>850</td>
</tr>
<tr>
<td>$p_\infty$</td>
<td>Ambient pressure, mb</td>
<td>$1.01 \times 10^{-2}$</td>
<td>$2.14 \times 10^{-4}$</td>
<td>$4.91 \times 10^{-5}$</td>
<td>$2.04 \times 10^{-5}$</td>
<td>$1.15 \times 10^{-5}$</td>
<td>$7.50 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\rho_\infty$</td>
<td>Ambient density gm/cc</td>
<td>$2.12 \times 10^{-8}$</td>
<td>$3.73 \times 10^{-10}$</td>
<td>$5.93 \times 10^{-11}$</td>
<td>$1.48 \times 10^{-11}$</td>
<td>$5.95 \times 10^{-12}$</td>
<td>$3.02 \times 10^{-12}$</td>
</tr>
<tr>
<td>$v$</td>
<td>Rocket velocity m/sec</td>
<td>3890</td>
<td>4870</td>
<td>5350</td>
<td>5840</td>
<td>6320</td>
<td>6820</td>
</tr>
<tr>
<td>$M_\infty$</td>
<td>Free-stream Mach No.</td>
<td>14.9</td>
<td>17.1</td>
<td>15.6</td>
<td>13.3</td>
<td>12.0</td>
<td>11.4</td>
</tr>
<tr>
<td>$u_e$</td>
<td>External stream velocity, m/sec</td>
<td>2910</td>
<td>3650</td>
<td>4020</td>
<td>4380</td>
<td>4740</td>
<td>5115</td>
</tr>
<tr>
<td>$p_j$</td>
<td>Jet pressure, mb</td>
<td>$2.92 \times 10^{-1}$</td>
<td>$8.15 \times 10^{-3}$</td>
<td>$1.56 \times 10^{-3}$</td>
<td>$4.72 \times 10^{-4}$</td>
<td>$2.17 \times 10^{-4}$</td>
<td>$1.28 \times 10^{-4}$</td>
</tr>
<tr>
<td>$T_j$</td>
<td>Jet temperature, °K</td>
<td>558</td>
<td>374</td>
<td>232</td>
<td>191</td>
<td>168</td>
<td>153</td>
</tr>
<tr>
<td>$T_e$</td>
<td>External stream temp., °K</td>
<td>3500</td>
<td>4300</td>
<td>4400</td>
<td>4400</td>
<td>4420</td>
<td>4450</td>
</tr>
<tr>
<td>$u_j$</td>
<td>Jet velocity m/sec</td>
<td>1950</td>
<td>3520</td>
<td>3240</td>
<td>2480</td>
<td>1370</td>
<td>550</td>
</tr>
<tr>
<td>$u_j/u_e$</td>
<td>Velocity ratio</td>
<td>0.68</td>
<td>0.72</td>
<td>0.60</td>
<td>0.42</td>
<td>0.23</td>
<td>0.094</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Mean free path, m</td>
<td>$3.83 \times 10^{-3}$</td>
<td>$2.17 \times 10^{-1}$</td>
<td>1.36</td>
<td>5.44</td>
<td>13.5</td>
<td>26.4</td>
</tr>
<tr>
<td>$2a$</td>
<td>Jet diameter, m (for 1-meter diameter nozzle)</td>
<td>23</td>
<td>85</td>
<td>160</td>
<td>300</td>
<td>560</td>
<td>1100</td>
</tr>
<tr>
<td>$L$</td>
<td>Flame length, km (for 1-meter-diameter nozzle)</td>
<td>9.1</td>
<td>54</td>
<td>76</td>
<td>87</td>
<td>86</td>
<td>104</td>
</tr>
<tr>
<td>$L/2a$</td>
<td>Flame length/expanded jet diameter</td>
<td>395</td>
<td>635</td>
<td>476</td>
<td>289</td>
<td>154</td>
<td>95</td>
</tr>
</tbody>
</table>
Expanded jet velocity (average) is obtained from the relation for conservation of mass flux.

\[ \rho_j u_j A_j = M \]

where \( \rho_j \) = density, \( u_j \) = velocity, and \( A_j \) = cross sectional area, each referring to the expanded jet, and \( M \) is the mass flowrate at the nozzle.

Jet temperature was calculated assuming isentropic expansion. Ambient temperatures, pressures, densities, etc. were taken from the Handbook of Geophysics. External air temperature, \( T_e \), refers to the air within a few jet plume radii, which has been shock-heated in passing through the bow shock, and has been obtained from calculations by Hochstim for equilibrium air. External air velocity, \( u_e \) (adjacent to the jet) is assumed to be 0.5 - 0.75 times free-stream velocity, \( u_\infty \). For a sphere, Feldman quotes a value of 0.75 \( u_\infty \) at the downstream distance where expansion to free-stream pressure has taken place. For purposes of our calculation, we have taken \( u_e = 0.75 u_\infty \).

In order to make some specific calculations of flame lengths and diameters applicable to a rocket rising through the atmosphere, a hypothetical rocket and trajectory have been defined. Exhaust composition is given in Table II.
Table II

ROCKET EXHAUST COMPOSITION

<table>
<thead>
<tr>
<th>Constituent</th>
<th>CO</th>
<th>H₂O</th>
<th>H₂</th>
<th>CO₂</th>
<th>OH</th>
<th>H</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass % of Total</td>
<td>46</td>
<td>27</td>
<td>1</td>
<td>23</td>
<td>2</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Mass ratio air/exhaust required to complete combustion to CO₂ and H₂O -- 1.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average molecular weight of exhaust -- 22.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exhaust exit temperature -- 1800°K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A calculation of the flame shape in a jet formed by a uniform cylindrical stream of hydrogen surrounded by an ambient parallel high-speed flow of air at a pressure equal to that of the jet (see Fig. 3) has been published. This calculation is based on a theoretical analysis involving a hypothetical model for the eddy viscosity relating it to the eddy viscosity for incompressible flow. The published plot of results of the calculation is presented in Fig. 4. Here r₉ is the radius of the flame surface at the axial distance x from the plane where mixing starts (i.e., where x = 0); a is the radius of the jet at x = 0; and uⱼ/uₑ is

![Diagram](image-url)

**FIG. 3** SCHEMATIC REPRESENTATION OF FLOW (based on Reference 14)
the ratio of jet velocity to external flow velocity, relative to the nozzle. In Fig. 4 it is assumed that the chemical reaction rate is infinite and that the turbulent flow and mixing process control the flame surface location.

Flame lengths and maximum diameters can be obtained from Fig. 5 (derived from Fig. 4) as a function of $U_j/U_e$. Flame length $L$ (or $L/2a$ in dimensionless form) is defined as the value of $x$ (or $x/2a$) when $r_f/a$ is zero. However, these values refer to the following special conditions: a jet of hydrogen gas at $1300^\circ K$, external flow of air at $1600^\circ K$, both at 1-atmosphere pressure, and ambient air temperature (far from the exhaust flow field) of $282^\circ K$. Application of Libby's method to other gases and conditions (different molecular weights, concentrations, temperatures, etc.) requires very lengthy calculations, unless one can use some simple theory of mixing and assume some relation between it and Libby's theory. This has been done to provide a preliminary test of
Libby's method. Use has been made of some work by Ricou and Spalding on determination of entrainment length, $y$, for jets. The assumption is made that for two different sets of conditions for jets (identified by subscripts 1 and 2),

$$\frac{L_2}{L_1} = \frac{y_2}{y_1} \quad \text{or} \quad L_2 = \frac{y_2}{y_1} L_1 \quad (1)$$

where, $L_2$ is the flame length sought, $L_1$ is the value obtained from Fig. 5, and $y_2$ and $y_1$ are the corresponding entrainment lengths.
The calculation of the entrainment length $y$ is based upon the following equation:\(^{16}\)

\[
\frac{m_e}{m_j} + 1 = 0.32 \frac{y}{2a} \left( \frac{\rho_e}{\rho_j} \right)^{\frac{1}{2}} \tag{2}
\]

where $m_e$ is the mass flux of ambient air which has been entrained by the jet at downstream distance $y$, $m_j$ is the mass flux of the original jet (i.e., before any mixing has occurred), and $\rho_e$ and $\rho_j$ are the densities of the unmixed ambient and jet streams respectively. In this report the definitions of $y$ and $m_e/m_j$ are further restricted to the special values where $M = m_e/m_j$ represents a stoichiometric ratio for whatever gases are considered. Also let $P = \rho_e/\rho_j$. Then one can solve equation (2) for the appropriate values of $y$, and obtain

\[
\frac{y_2}{y_1} = \frac{M_2 + 1}{M_1 + 1} P_2^{-\frac{1}{2}}
\]

Substituting values corresponding to conditions for Figs. 4 and 5, one obtains

\[
\frac{y_2}{y_1} = 0.0513 (M_2 + 1) P_2^{-\frac{1}{2}} \tag{3}
\]

An indication of the maximum altitude at which continuum theory can be expected to hold can be seen from comparison of ambient mean free path, $\lambda$, with expanded jet diameter, $2a$, Table I. If one employs the criterion that the characteristic dimension should be at least 100 times the mean free path, the following conclusions can be drawn: for the jet as a simple blunt body, continuum theory may hold to an altitude of 110-120 km; for turbulent mixing assuming a typical eddy size of one-tenth the jet diameter as the characteristic dimension, continuum theory may hold only to around 90 km; for a shock standoff distance of 0.075 times the jet diameter as characteristic dimension, the corresponding altitude is somewhere near 90 km. Of course, the mean free path in the shock layer itself is much smaller than ambient (by a factor of 20-30) because of the high density. As the size of the expanded jet depends upon the size
and nature of the rocket and its trajectory, these factors must be considered in any estimate of the altitude. A quite different criterion for the maximum altitude to which continuum theory should apply is the relaxation time,\textsuperscript{17} i.e., the mean time between collisions. For large relaxation times, small disturbances will propagate in both longitudinal and transverse modes. When air density becomes less than about $10^{-10}$ atmosphere (or $10^{-7}$ mb), undamped small disturbance propagation tends to occur. For the ambient air, this corresponds to about 105 km. In the jet, because the density is higher due to higher pressure and lower temperature, the corresponding altitude is higher.

At the present time we lack field data in "flame" lengths for various altitudes in the range considered here, and so have no way of comparing with observed trends of flame lengths versus altitude. Estimates can be made of available times for reaction. Dividing the calculated lengths by the corresponding rocket velocities provides maximum times of mixing; but the reaction time must be much smaller (say not more than one-tenth as great) in order not to increase the flame length, which is calculated on the assumption of a reaction time small compared to the mixing time. Rough values of reaction times (dividing the mixing time by 10) are then found to vary from 0.23 sec at 80 km to 1.5 sec at 140 km. These times can be used at least tentatively in evaluating the significance of various electron production and removal reactions at different altitudes.

B. Negative Ion Formation

A previous study\textsuperscript{2} of ionization, including negative ions in the afterburning regions of rocket exhaust, described qualitatively some of the effects which one would expect to find there. However, it did not consider many of the finer details of the ionic processes such as the possible importance of negative ion formation as a mode of electron removal. Some of these details will be developed in the following, and from the results we shall make order of magnitude estimates of negative ion concentrations, required electron production rates for a given level of ionization, etc.
In order to compute the concentrations of negative ions present in the plume one must know or at least have a reasonable model of the rocket exhaust composition. Of the various estimates which have been made we shall employ that proposed by Boynton and Neu\textsuperscript{13} for a liquid fueled rocket (Table II). In addition we shall assume that the plume constituents mix thoroughly with the ambient atmosphere and that the pressure and temperature in the afterburning region are equal to the ambient pressure and temperature, given by the ARDC 1959 Model Atmosphere.\textsuperscript{18} Because of only partial mixing of the rocket exhaust with the atmosphere and the presence of shockwaves which result in higher pressures and temperatures in regions of the plume, these assumptions are not completely justified. However, in view of the very crude estimates of rate constants which we shall introduce later, it is considered unlikely that errors associated with these assumptions will be greater than those associated with the rate constants. The lifetime of the afterburning region is estimated to be of the order of 1 sec.

Electron removal processes are basically of two types, recombination and attachment. Before discussing the former we shall consider the formation and destruction of negative ions. The most important such processes are

\begin{align*}
\text{Radiative Attachment} \\
O_2 + e &\rightarrow O_2^- + h\nu \\
O + e &\rightarrow O^- + h\nu \\
H + e &\rightarrow H^- + h\nu \\
\text{Collisional Attachment} \\
O_2 + O_2 + e &\rightarrow O_2^- + O_2 \\
O + O_2 + e &\rightarrow O^- + O_2
\end{align*}
Photodetachment

\[ \text{O}_3^- + h\nu \rightarrow \text{O}_3 + e \]  
\[ \text{O}^- + h\nu \rightarrow \text{O} + e \]  
\[ \text{H}^- + h\nu \rightarrow \text{H} + e \]  
\[ \text{OH}^- + h\nu \rightarrow \text{OH} + e \]  
\[ \text{NO}_2^- + h\nu \rightarrow \text{NO}_2 + e \]  
\[ \text{O}_3^- + h\nu \rightarrow \text{O}_3 + e \]  

Collisional Detachment

\[ \text{O}_3^- + \text{O}_2 \rightarrow \text{O}_2 + \text{O}_2 + e \]  
\[ \text{O}_3^- + \text{O} \rightarrow \text{O}_3 + e \]  
\[ \text{O}^- + \text{O} \rightarrow \text{O}_2 + e \]  
\[ \text{H}^- + \text{H} \rightarrow \text{H}_2 + e \]  
\[ \text{OH}^- + \text{H} \rightarrow \text{H}_2\text{O} + e \]  
\[ \text{N} + \text{NO}_2^- \rightarrow \text{N}_2 + \text{O}_2 + e \]  
\[ \text{O} + \text{H}^- \rightarrow \text{OH} + e \]  
\[ \text{O} + \text{O}_3^- \rightarrow \text{O}_2 + \text{O}_2 + e \]  
\[ \text{H} + \text{O}_3^- \rightarrow \text{OH} + \text{O}_2 + e \]  

Charge Transfer and Ion-Atom Interchange

\[ \text{O}_3^- + \text{O} \rightarrow \text{O}_2 + \text{O}^- \]  
\[ \text{O}_3^- + \text{O} + \text{O}_2 \rightarrow \text{O}_2 + \text{O}_3^- \]  
\[ \text{O}_3^- + \text{N} + \text{M} \rightarrow \text{NO}_2^- + \text{M} \]  
\[ \text{O}^- + \text{OH} \rightarrow \text{O} + \text{OH}^- \]  
\[ \text{H}^- + \text{OH} \rightarrow \text{H} + \text{OH}^- \]  
\[ \text{O}_3^- + \text{OH} \rightarrow \text{O}_2 + \text{OH}^- \]  
\[ \text{O}_3^- + \text{H} \rightarrow \text{O}_2 + \text{H}^- \]  
\[ \text{O}^- + \text{O}_2 + \text{O}_2 \rightarrow \text{O}_2 + \text{O}_3^- \]  
\[ \text{H}^- + \text{O} \rightarrow \text{O}^- + \text{H} \]
Reaction \((e4)\) is energetically permitted only if the electron affinity of \(O^-\) is less than 1.8 ev. Although the photodetachment experiments of Branscomb and co-workers\(^9\) indicated that this condition is satisfied, more recent work by Schulz\(^{20}\) (1962) yields an electron affinity of 2 ev. Because we are not yet certain which value applies to the \(O^-\) in the ionosphere, we do not know whether the process is possible or not; for present purposes we shall assume that it is. Some of the rate constants associated with the reactions listed above have been measured. Estimates of others are based on typical experimental values associated with similar reactions. Temperature dependence has been neglected because of the probable absence of activation energies; the error so introduced is expected to be less than other uncertainties in the rate constants. The experimental results and estimates are shown in Table III.

### Table III

**RATE CONSTANTS**

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate Constant</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>a1</td>
<td>(\beta_1)</td>
<td>(10^{-16} \text{ cm}^3/\text{sec})</td>
<td>Branscomb et al.(^{21}) (1958), using photodetachment data and principle of detailed balancing</td>
</tr>
<tr>
<td>a2</td>
<td>(\beta_2)</td>
<td>(10^{-16} \text{ cm}^3/\text{sec})</td>
<td>Estimated by Poppoff and Whitten,(^{22}) (1962) using photodetachment data and principle of detailed balancing (Burch et al.,(^{19}) 1958)</td>
</tr>
<tr>
<td>a3</td>
<td>(\beta_3)</td>
<td>(10^{-16} \text{ cm}^3/\text{sec})</td>
<td>Same as a2, using data of Smith and Burch(^{23}) (1959)</td>
</tr>
<tr>
<td>b1</td>
<td>(k_1)</td>
<td>(10^{-30} \text{ cm}^6/\text{sec})</td>
<td>Chanin et al.(^{24}) (1959)</td>
</tr>
<tr>
<td>b2</td>
<td>(k_2)</td>
<td>(10^{-31} \text{ cm}^6/\text{sec})</td>
<td>Estimate, based on idea that b1 probably involves resonance and thus should be perhaps an order of magnitude faster</td>
</tr>
<tr>
<td>c1</td>
<td>(\rho_1)</td>
<td>0.1 sec(^{-1})</td>
<td>Estimate (Poppoff and Whitten,(^{22}) (1962))</td>
</tr>
<tr>
<td>c2</td>
<td>(\rho_2)</td>
<td>1.4 sec(^{-1})</td>
<td>Branscomb et al.(^{21}) (1958)</td>
</tr>
<tr>
<td>c3</td>
<td>(\rho_3)</td>
<td>8 sec(^{-1})</td>
<td>Computed from results of Smith and Burch(^{23}) (1959)</td>
</tr>
<tr>
<td>c4</td>
<td>(\rho_4)</td>
<td>10(^{-2}) sec(^{-1})</td>
<td>Estimate</td>
</tr>
<tr>
<td>c5</td>
<td>(\rho_5)</td>
<td>10(^{-3}) sec(^{-1})</td>
<td>Estimate</td>
</tr>
<tr>
<td>c6</td>
<td>(\rho_6)</td>
<td>10(^{-2}) sec(^{-1})</td>
<td>Estimate</td>
</tr>
</tbody>
</table>
### Table III (Concluded)

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate Constant</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>d1</td>
<td>$7_1$</td>
<td>$10^{-20}$ cm$^3$/sec</td>
<td>Phelps and Pack$^{28}$ (1961)</td>
</tr>
<tr>
<td>d2</td>
<td>$7_2$</td>
<td>$10^{-13}$ cm$^3$/sec</td>
<td>Estimate; could well be an order of magnitude larger</td>
</tr>
<tr>
<td>d3</td>
<td>$7_3$</td>
<td>$10^{-13}$ cm$^3$/sec</td>
<td>Same as d2</td>
</tr>
<tr>
<td>d4</td>
<td>$7_4$</td>
<td>$10^{-13}$ cm$^3$/sec</td>
<td>Same as d2</td>
</tr>
<tr>
<td>d5</td>
<td>$7_5$</td>
<td>$10^{-13}$</td>
<td>Same as d2</td>
</tr>
<tr>
<td>d6</td>
<td>$7_6$</td>
<td>$10^{-13}$</td>
<td>Same as d2</td>
</tr>
<tr>
<td>d7</td>
<td>$7_7$</td>
<td>$10^{-13}$</td>
<td>Same as d2</td>
</tr>
<tr>
<td>d8</td>
<td>$7_8$</td>
<td>$10^{-13}$</td>
<td>Same as d2</td>
</tr>
<tr>
<td>d9</td>
<td>$7_9$</td>
<td>$10^{-13}$</td>
<td>Same as d2</td>
</tr>
<tr>
<td>e1</td>
<td>$k_1$</td>
<td>$10^{-11}$</td>
<td>Estimate; rate constants for positive ion charge transfer processes in atmosphere have been found to be of order $10^{-11}$ cm$^3$/sec, Dickinson and Sayers,$^{26}$ (1960)</td>
</tr>
<tr>
<td>e2</td>
<td>$k_2$</td>
<td>$10^{-32}$ cm$^6$/sec</td>
<td>Estimate; maybe as large as $10^{-31}$ cm$^6$/sec</td>
</tr>
<tr>
<td>e3</td>
<td>$k_3$</td>
<td>$10^{-31}$ cm$^6$/sec</td>
<td>Estimate</td>
</tr>
<tr>
<td>e4</td>
<td>$k_4$</td>
<td>$10^{-11}$ cm$^3$/sec</td>
<td>Same as e1</td>
</tr>
<tr>
<td>e5</td>
<td>$k_5$</td>
<td>$10^{-11}$ cm$^3$/sec</td>
<td>Same as e1</td>
</tr>
<tr>
<td>e6</td>
<td>$k_6$</td>
<td>$10^{-11}$ cm$^3$/sec</td>
<td>Same as e1</td>
</tr>
<tr>
<td>e7</td>
<td>$k_7$</td>
<td>$10^{-11}$ cm$^3$/sec</td>
<td>Same as e1</td>
</tr>
<tr>
<td>e8</td>
<td>$k_8$</td>
<td>$10^{-32}$ cm$^3$/sec</td>
<td>Same as e2</td>
</tr>
<tr>
<td>e9</td>
<td>$k_9$</td>
<td>$10^{-11}$ cm$^3$/sec</td>
<td>Same as e1</td>
</tr>
</tbody>
</table>

For a given electron density [$e$] this set of constants can be used in conjunction with the corresponding rate equations and the concentrations of neutral species given in Table IV to compute the concentrations of the various species of negative ions. Actually we also need to know the ion-ion recombination coefficients $C_i$ and the positive ion concentrations [$X^+$]. For our purposes, however, neglect of this term will not materially affect the final results. After carrying out the computations for the negative ion concentrations after 1 sec, we obtain the results presented in Table V.
Table IV

CONCENTRATIONS OF NEUTRAL SPECIES (cm⁻³)
Minzner,¹⁸ (1959); Handbook of Geophysics,¹¹ (1960); Boynton and Neu,¹³ (1960)

<table>
<thead>
<tr>
<th>Altitude</th>
<th>[O₂]</th>
<th>[N₂]</th>
<th>[O]</th>
<th>[N]</th>
<th>[OH]</th>
<th>[H]</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 km</td>
<td>10¹⁴</td>
<td>4 x 10¹⁴</td>
<td>10¹²</td>
<td>10⁷</td>
<td>10¹²</td>
<td>10¹¹</td>
</tr>
<tr>
<td>100 km</td>
<td>10¹²</td>
<td>6 x 10¹²</td>
<td>3 x 10¹²</td>
<td>10⁷</td>
<td>10¹¹</td>
<td>5 x 10⁹</td>
</tr>
<tr>
<td>130 km</td>
<td>10¹⁰</td>
<td>10¹¹</td>
<td>10¹¹</td>
<td>10⁷</td>
<td>10⁹</td>
<td>5 x 10⁷</td>
</tr>
</tbody>
</table>

Table V

NEGATIVE ION CONCENTRATIONS<sup>a</sup>

<table>
<thead>
<tr>
<th>Altitude</th>
<th>[O₂⁻]</th>
<th>[O⁻]</th>
<th>[H⁻]</th>
<th>[OH⁻]</th>
<th>[NO₂⁻]</th>
<th>[O₃⁻]</th>
</tr>
</thead>
<tbody>
<tr>
<td>day&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 km</td>
<td>200</td>
<td>350</td>
<td>50</td>
<td>10⁵</td>
<td>100</td>
<td>&lt;&lt; 1</td>
</tr>
<tr>
<td>100 km</td>
<td>0.3</td>
<td>10⁴</td>
<td>0.1</td>
<td>10⁴</td>
<td>&lt;&lt; 1</td>
<td>&lt;&lt; 1</td>
</tr>
<tr>
<td>130 km</td>
<td>&lt;&lt; 1</td>
<td>10³</td>
<td>&lt;&lt; 1</td>
<td>10</td>
<td>&lt;&lt; 1</td>
<td>&lt;&lt; 1</td>
</tr>
<tr>
<td>Night&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 km</td>
<td>200</td>
<td>4 x 10³</td>
<td>10⁴</td>
<td>2 x 10⁵</td>
<td>100</td>
<td>&lt;&lt; 1</td>
</tr>
<tr>
<td>100 km</td>
<td>0.3</td>
<td>2 x 10³</td>
<td>0.1</td>
<td>2 x 10⁴</td>
<td>&lt;&lt; 1</td>
<td>&lt;&lt; 1</td>
</tr>
<tr>
<td>130 km</td>
<td>&lt;&lt; 1</td>
<td>10³</td>
<td>&lt;&lt; 1</td>
<td>10</td>
<td>&lt;&lt; 1</td>
<td>&lt;&lt; 1</td>
</tr>
</tbody>
</table>

<sup>a</sup>We are assuming that [e] = 10⁷ cm⁻³, Smith,² (1961)

<sup>b</sup>Photodetachment ceases at sunset and thus causes the negative ion concentrations to rise.
From the results of Table V we can conclude that \([\text{OH}^-]\) and \([\text{O}^-]\)
are expected to be the most important negative ions in the rocket plume. Although an increase in the charge transfer rate constants will have
the effect of increasing the relative concentrations of \(\text{NO}_2^-\) the net
effect will be small since it is extremely unlikely that the true values
of the \(k\)'s will be more than about one order of magnitude larger than
those listed in Table III. Increasing the values of the collisional
detachment coefficients \(\gamma\) will have an important effect, particularly
at night, by reducing the total negative ion concentrations, perhaps by
an order of magnitude below those given in Table V.

Recombination can occur by either of two mechanisms, dissociative,
e.g.,

\[
\text{O}_3^+ + e \rightarrow \text{O} + \text{O} \quad (5a)
\]

or ion-ion, e.g.,

\[
\text{O}_2^+ + \text{O}_2^- \rightarrow \text{O}_2 + \text{O}_2 \quad (5b)
\]

which are related to an effective recombination coefficient \(\alpha_{\text{eff}}\) by
the equation

\[
\alpha_{\text{eff}} = \alpha_D + \lambda \alpha_i \quad (6)
\]

where \(\lambda\) is the negative ion to electron concentration ratio. For some
of the ions of interest in the plume (e.g., \(\text{CHO}^+, \text{H}_3\text{O}^+\) \(\alpha_D\) is probably
of the order \(10^{-9}\) cm\(^3\)/sec while \(\alpha_i\) is expected to be considerably
smaller, i.e., \(\sim 10^{-8}\) cm\(^3\)/sec.\(^2\) Using the estimates of negative ion
concentrations in Table V, we see that the dissociative mode is much
the faster recombination mechanism for the polyatomic ions and we can
neglect negative ion formation as a deionization process in the after-
burning region except in the case of alkali metal ions which cannot
undergo dissociative recombination. Because of the unavailability of
the dissociative mode the effective recombination coefficient for these
species is expected to be much smaller, probably of the order of \(10^{-10}\) cm\(^3\)
sec\(^{-1}\).
The dominant ionization mechanism in the plume is thought to be chemionization, specifically:

\[ \text{CH} + \text{O} \rightarrow \text{CHO}^+ + \text{e} \]  \hspace{1cm} (7)

The dissociative recombination coefficient of a complex ion of this type is probably of the order $10^{-6}$ cm$^3$/sec, thus requiring an electron production rate of $\sim 10^8$ cm$^3$ sec$^{-1}$ to produce electron concentrations of the order $10^7$ cm$^{-3}$. Assuming that the rate constant of process (7) is of the order $10^{-12}$ cm$^3$ sec$^{-1}$, which is reasonable for two-body chemical reactions, one finds that concentrations of CH of $\sim 10^8$ cm$^{-3}$ are required. This is equivalent to $\sim 0.3$ ppm at 80 km, $\sim 3$ ppm at 100 km, and $\sim 5000$ ppm at 130 km. The estimates at 80 and 100 km appear reasonable but that at 130 km is undoubtedly much too large. We conclude that at an altitude in the region of about 150 km the electron density in the rocket plume probably approximates the ambient concentration.

If all of the positive ions were alkali metal ions, e.g., Na$^+$, K$^+$, a much smaller ionization rate would be required to maintain a given electron concentration; this is due to the smaller effective recombination coefficients previously discussed. Whether or not the ionization due to alkali metals in liquid fuel rockets is large enough to rival the chemionization process, equation (7), is not known. If it is, negative ions must be of great importance to the ionization properties of the plume. This point deserves further investigation. Alkali metals are present as impurities in fuels, and some atoms will be thermally ionized in the rocket engine. There is also the possibility of photo-ionization at high altitudes. Also formation of Cl$^-$ may be important for aluminum perchlorate propellants, especially at lower altitudes where Cl$^-$ concentration is much greater than O$^-$ concentration.

C. Thermal Ionization of Alkali Metals

A high concentration of electrons may be present in the exhaust gases emerging from a rocket motor. A principal source of these electrons is thermal ionization of species of low ionization potential, such as
alkali metal contaminants in the propellant. High levels of ionization presumably are attained at the high temperature of the combustion chamber; some of this ionization may be frozen during nozzle expansion and during subsequent expansion of the plume to ambient pressure.

Electrons may also be produced by interactions of the plume with the external environment. If processes such as impact ionization, photoionization, and chemionization are to be significant sources of ionization, they must produce electrons in greater concentrations than the background electron density due to thermal ionization.

We shall formulate approximate expressions for the fractional ionization of potassium in the exhaust and for the resultant electron density in the expanded plume, due to thermal ionization in the rocket. We can then estimate electron densities in the exhaust from this source under various conditions. Such estimates also provide a criterion for evaluating the significance of other sources of ionization in the exhaust plume.

The equilibrium constant $K_{\text{eq}}$ for

$$A \rightleftharpoons A^+ + e$$

(1)

can be calculated by the Saha equation, which for alkali metals is

$$K_{\text{eq}} = \left[\frac{[A^+]n_e}{[A]}\right] = 2.41 \times 10^{15} \frac{T^{3/2}}{e^{-I/kT}}$$

(2)

where $T$ is the temperature (K), $I$ is the ionization potential of $A$, $k$ is Boltzmann's constant, $n_e$ is the electron density (cm$^{-3}$), and the brackets denote concentrations per cm$^3$. 

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In the absence of any other process producing or removing electrons, 
\([A^+] = n_e\), and the electron density is given by

\[ n_e = \left( [A] 2.41 \times 10^{18} T^{3/2} e^{-I/kT} \right) \]  

(3)

and the fractional ionization of A by

\[ \frac{[A^+]}{[A]} = \left( \frac{2.41 \times 10^{18} T^{3/2} e^{-I/kT}}{[A]} \right)^{1/2} \]  

(4)

The concentration of A is

\[ [A] = f_A \frac{p}{kT} \]  

(5)

where \(f_A\) is the number fraction of A in the gas and \(p\) is the total pressure.

We assume that the ionization of potassium at the exit plane of the motor can be described as equilibrium ionization at some temperature \(T_i\). This effective ionization temperature may not be the actual temperature at the exit plane, since ionization may have been frozen at some earlier stage of nozzle expansion. Our ability to predict \(T_i\) is therefore limited, but \(T_i\) will lie between throat and exit plane temperatures.

The equilibrium constant for potassium, calculated from equation (2) for several values of \(T_i\), is given in Table VI. We combine equations (4) and (5) to obtain an expression for the fractional ionization of potassium,

\[ \frac{[K^+]}{[K]} = \left( \frac{K_{eq}}{K} \right)^{1/2} = \left( \frac{K_{eq} \frac{kT_i}{f_K}}{p_i} \right)^{1/2} \]  

(6)
Table VI

EQUILIBRIUM CONSTANT FOR $K \rightleftharpoons K^+ + e$ FOR VARIOUS TEMPERATURES

<table>
<thead>
<tr>
<th>$T_1$</th>
<th>$K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>$4.0 \times 10^5$</td>
</tr>
<tr>
<td>2000</td>
<td>$2.7 \times 10^9$</td>
</tr>
<tr>
<td>2500</td>
<td>$5.7 \times 10^{11}$</td>
</tr>
<tr>
<td>3000</td>
<td>$2.1 \times 10^{13}$</td>
</tr>
</tbody>
</table>

The fractional ionization thus depends on the potassium concentration and the effective ionization pressure as well as on $T_1$. In Table VII are given values of $[K^+]/[K]$ calculated for typical conditions, $f_K = 100$ parts per million by number, and $P_1 = 5$ psia. For conversion to other conditions, note that $[K^+]/[K]$ scales as $(f_K P_1)^{-\frac{1}{2}}$.

Table VII

FRACTIONAL IONIZATION OF POTASSIUM AT VARIOUS IONIZATION TEMPERATURES

<table>
<thead>
<tr>
<th>$T_1$</th>
<th>1500</th>
<th>2000</th>
<th>2500</th>
<th>3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[K^+]/[K]$</td>
<td>$5 \times 10^{-5}$</td>
<td>$5 \times 10^{-3}$</td>
<td>$7 \times 10^{-2}$</td>
<td>$5 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

The calculated values in Table VII, as would be expected, show a general tendency toward increasing fractional ionization as $T_1$ increases. These values should not be compared in detail because of the arbitrary assumption that $P_1 = 5$ psia. However, an alternative assumption of constant number density rather than constant pressure would change the relative values at the highest and lowest temperatures in Table VII by
a factor of only \( \sqrt{2} \). We can conclude that any other process of potassium ionization which produces a fractional ionization of less than \( 10^{-5} \) is probably not significant in comparison with thermal ionization.

If we assume the fractional ionization at the exit plane, as estimated in Table VII, is frozen during plume expansion to ambient pressure, then we can estimate typical electron densities in the plume using equation (3). The value of \([K]\) for the expanded plume is given by

\[
[K] = \frac{f_K}{T_e} P_e \times 8 \times 10^{21}.
\]

Approximate values for \( P_e \), the ambient pressure in atmospheres, are given for various altitudes in Table VIII. These data are slightly different from those used in the first section, but the differences are not significant for our purposes. The temperature of the expanded plume, \( T_e \), can be calculated for a particular motor at a particular altitude for a specific expansion model (such as assumed isentropic expansion). We shall assume \( T_e = 1000 \) K in order to calculate typical values of \( n_e \). Note that \( n_e \) scales as \( (T_e)^{-\frac{1}{2}} \). The calculated electron densities in the expanded exhaust at various ionization temperatures and altitudes are given in Table IX; as before, we have assumed \( f_K = 100 \) ppm by number and \( P_i = 5 \) psia.

Table VIII

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>( 10^{-9} )</td>
</tr>
<tr>
<td>150</td>
<td>( 3 \times 10^{-9} )</td>
</tr>
<tr>
<td>100</td>
<td>( 10^{-7} )</td>
</tr>
<tr>
<td>80</td>
<td>( 10^{-5} )</td>
</tr>
<tr>
<td>60</td>
<td>( 2 \times 10^{-4} )</td>
</tr>
<tr>
<td>40</td>
<td>( 3 \times 10^{-3} )</td>
</tr>
</tbody>
</table>
Table IX
CALCULATED ELECTRON DENSITIES (cm⁻³) IN THE EXHAUST
AT VARIOUS IONIZING TEMPERATURES AND ALTITUDES

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>T_i 1500</th>
<th>2000</th>
<th>2500</th>
<th>3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2.8 x 10^2</td>
<td>3.6 x 10^4</td>
<td>5.6 x 10^6</td>
<td>3.8 x 10^6</td>
</tr>
<tr>
<td>150</td>
<td>1.1 x 10^3</td>
<td>1.1 x 10^5</td>
<td>1.7 x 10^6</td>
<td>1.2 x 10^7</td>
</tr>
<tr>
<td>100</td>
<td>3.8 x 10^4</td>
<td>3.6 x 10^6</td>
<td>5.6 x 10^7</td>
<td>3.2 x 10^8</td>
</tr>
<tr>
<td>80</td>
<td>3.8 x 10^6</td>
<td>3.6 x 10^8</td>
<td>5.6 x 10^9</td>
<td>3.8 x 10^10</td>
</tr>
<tr>
<td>60</td>
<td>7.5 x 10^7</td>
<td>7.2 x 10^9</td>
<td>1.1 x 10^11</td>
<td>7.7 x 10^11</td>
</tr>
<tr>
<td>40</td>
<td>1.1 x 10^9</td>
<td>1.1 x 10^11</td>
<td>1.7 x 10^12</td>
<td>1.2 x 10^13</td>
</tr>
</tbody>
</table>

At a given altitude, n_e increases with ionization temperature, although the calculated values are dependent on the assumed P_i, as before. Since we have assumed a constant total number of electrons in the plume for a particular T_i, the electron density naturally decreases with ambient pressure as the altitude increases. However, since T_e also decreases with pressure, the rate of decrease of n_e with increasing altitude is not as large as indicated by the values in Table IX.

Many assumptions and approximations, in addition to those already mentioned, are implicit in the above calculations. Some of these will now be specified in more detail. Sources of electrons other than potassium have been neglected. With its relatively low ionization potential, potassium in the amounts typically present in solid propellants would quite reasonably be expected to dominate thermal ionization. Electron sinks other than K⁺ have been ignored in the formulation of equilibrium ionization. The most serious effect of this type is probably due to the presence of electron-attaching species such as Cl. The effect of equilibria such as Cl⁻ → Cl + e can be calculated in theory. The result would be lower values for n_e and higher values for [K⁺]/[K] than
given in tables VI-IX. Since equilibrium shifts toward detachment with increasing temperature, the assumption of neglecting attachment is better at higher temperatures.

It has been assumed that the potassium is available as atoms in the vapor phase. One should really consider dissociation equilibria for the potassium compounds in the fuel and other chemical sinks for potassium, such as KOH $\rightarrow$ K + OH. Neglecting such effects, as in the above calculations, can be regarded as merely a limitation on our ability to estimate [K] accurately. However, this should be given careful consideration in future studies.

The assumption that ionization is frozen during plume expansion seems reasonable for conditions of interest. If K$^+$ and electrons undergo 3-body recombination with a rate constant of about $10^{-27}$ cm$^6$ sec$^{-1}$, then the time required to reduce the electron density by one-half is given by

$$t_{\frac{1}{2}} = (10^{-27}[M]n_e)^{-1}$$

If $n_e = 10^{10}$ cm$^{-3}$ and $[M] = 10^{17}$ cm$^{-3}$ (0.01 atm at 300$^0$K), then $t_{\frac{1}{2}} \sim 1$ second, a time which is long enough compared with expansion time for recombination to be neglected.

We concluded that the amount of potassium ordinarily contained in solid propellants may produce electron densities in the exhaust plume at low altitudes which are sufficiently high to cause an attenuation problem. Nevertheless because of the uncertainties mentioned above one cannot make a positive prediction. As the exhaust temperature increases, this effect persists to higher altitudes. The lower temperature in the combustion chamber and the lower concentration of alkali metals in liquid fuel rockets lead to considerably lower calculated values for thermal ionization.

The purpose of these approximate calculations is not only to indicate conditions under which thermal ionization leads to large electron densities, but also to provide a criterion for estimating the
importance of other ionization mechanisms. Obviously, only those reactions which can produce electrons in larger concentrations than the background thermal ionization can have an important effect on the ionization level of the exhaust.

For example, consider a general process:

\[ X^* + K \rightarrow X + K^+ + e \] (10)

where \( X^* \) is an excited species whose excitation energy is greater than the ionization potential of potassium. If this process is to have a significant effect on the electron density, the concentration of \( X^* \) must obviously be larger than the background electron density, or its rate of production in the exhaust must be much larger than the required electron production rate. The electron production rate by this process must exceed the recombination rate if an increase in electron density is to occur. As an upper limit to the recombination rate assume dissociative recombination with a recombination coefficient of \( 10^{-6} \text{ cm}^3 \text{ sec}^{-1} \) can occur. Then, if the rate constant for reaction (10) is about \( 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \), we require that

\[ 10^{-12}[X^*][K] > 10^{-6}[K^+]^2. \] (11)

If \( [K^+]/[K] \sim 10^{-4} \) and \( [K] \sim 10^{10} \text{ cm}^{-3} \), then equation (11) indicates that a concentration \( [X^*] > 10^8 \text{ cm}^{-3} \) is sufficient to increase the electron density.

A more convenient method for applying this criterion may be to define a characteristic time for electron loss (by recombination or diffusion) in the plume. Then, if the electron production rate by a particular mechanism can be estimated, the total ionization per unit volume during this characteristic time can be compared directly with the background thermal ionization. For example, the rate of photoionization of potassium by solar radiation is \( \frac{FQ[K]}{I} \text{ sec}^{-1} \), where \( F \) is the total flux per cm\(^2\) per sec in the appropriate wavelength region, \( Q \) is an averaged photoionization cross section, and \( I \) is the ionization potential. If the background fractional ionization of potassium is
The time required for photoionization to increase the ionization significantly is 
\[ \frac{[K^+]}{[K]} \]. This must be less than the characteristic time, if photoionization is to be an important process.

D. Photoionization

The importance of photoionization effects in missile exhaust plumes is being explored. A preliminary look at this problem indicates that sufficient solar energy in the ultraviolet wavelengths may penetrate to altitudes at which rocket motors are still burning or outgassing. The study is, of course, restricted to those photon energies that are capable of photoionization.

Table X summarizes estimates, based on rocket data\(^{28,29,30}\), of altitudes at which 1/e of the solar flux (of given wavelength) incident to the top of the atmosphere will penetrate. The maximum ionization potentials that can be supplied at the 1/e penetration altitude by the photons are also listed, along with estimated fluxes and an indication of some common substances that could be ionized at or above the indicated altitudes. Except for Lyman-\(\alpha\) of hydrogen, the values are averages and do not represent specific strong line emission.

Calculation of ionization rates is rather lengthy and requires compilation of considerable data because the spectral distribution of radiation intensity varies with altitude, and both the spectral radiation intensity and the photoionization cross sections vary (often in a rather complicated manner) with wavelength. However it may be of interest to consider some examples of rate of ionization per unit wavelength interval for NO, K, and CO, using corresponding absorption cross sections of \(2 \times 10^{-18} \text{ cm}^2\), \(6 \times 10^{-21} \text{ cm}^2\), and \(1.6 \times 10^{-17} \text{ cm}^2\), respectively.\(^{31,32}\) These cross sections correspond to the wavelengths attenuated to 1/e of the initial flux.
### Table X

**ESTIMATES OF PHOTOIONIZATION PARAMETERS**

<table>
<thead>
<tr>
<th>Solar Radiation Attenuated to 1/e at Altitude (km)</th>
<th>Wavelength of Attenuated Radiation (Å)</th>
<th>Photon Energy of Radiation (ev)</th>
<th>Examples of Substances Ionized at or above 1/e Penetration Altitude</th>
<th>Approximate Average* Spectral Radiation Intensity 1/e Penetration Altitude (ergs/cm² sec Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>3000</td>
<td>4.1</td>
<td>Cs</td>
<td>16.5</td>
</tr>
<tr>
<td>30</td>
<td>2800</td>
<td>4.4</td>
<td>K</td>
<td>8.5</td>
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<tr>
<td>40</td>
<td>2600</td>
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<td>5.2</td>
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<tr>
<td>40</td>
<td>2400</td>
<td>5.2</td>
<td>Na</td>
<td>2.5</td>
</tr>
<tr>
<td>33</td>
<td>2200</td>
<td>5.6</td>
<td>Li</td>
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</tr>
<tr>
<td>42</td>
<td>2000</td>
<td>6.2</td>
<td>Al, Ca</td>
<td>0.51</td>
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<tr>
<td>82</td>
<td>1800</td>
<td>6.9</td>
<td></td>
<td>0.14</td>
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<td>110</td>
<td>1600</td>
<td>7.8</td>
<td>Ni, Mg</td>
<td>0.023</td>
</tr>
<tr>
<td>112</td>
<td>1400</td>
<td>8.9</td>
<td>Fe, Co</td>
<td>1.9 x 10⁻³</td>
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<tr>
<td>75</td>
<td>1,000</td>
<td>10.3</td>
<td>NO</td>
<td>1.87</td>
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<tr>
<td>70-110</td>
<td>1,200</td>
<td>12.4</td>
<td>C₂, O₂, NO₂, NH₃, Parafines</td>
<td>4.2 x 10⁻²</td>
</tr>
<tr>
<td>95</td>
<td>1,000</td>
<td>12.4</td>
<td>H, O, Cl, N, H₂, N₂, Cl₂, CO, OH, H₂O, CO₂, CH₄</td>
<td>1.3 x 10⁻³</td>
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<tr>
<td>130</td>
<td>800</td>
<td>15.5</td>
<td></td>
<td>9 x 10⁻⁴</td>
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<tr>
<td>162</td>
<td>600</td>
<td>20.6</td>
<td>F</td>
<td>7.3 x 10⁻⁴</td>
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<td>150</td>
<td>400</td>
<td>31</td>
<td></td>
<td>10⁻³</td>
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<tr>
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<td>44-60</td>
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<tr>
<td>100-115</td>
<td>8-20</td>
<td>1500-620</td>
<td></td>
<td>2 x 10⁻³</td>
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<tr>
<td>65-100</td>
<td>2-8</td>
<td>6200-1500</td>
<td></td>
<td>10⁻³</td>
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</table>

*Not uniformly averaged some 50Å, 16Å, 12Å increments.
Examples of ionization rates that may be possible to obtain at the 1/e penetration altitudes are as follows.

1. NO: Can be ionized by radiation shorter than approximately 1200A (Lyman α would be the major radiation for this reaction). Two ion pairs cm⁻³ sec⁻¹ A⁻¹ would be produced per 10⁷ cm⁻³ NO molecules.

2. K: Four ion pairs cm⁻³ sec⁻¹ A⁻¹ would be produced per 10⁸ cm⁻³ K atoms.

3. CO: Five ion pairs cm⁻³ sec⁻¹ A⁻¹ would be produced per 10¹⁰ cm⁻³ CO molecules.

During the next quarter, attempts will be made to determine the order of magnitude of concentrations of ionizable constituents that can be expected to exist in missile plumes at various altitudes. If consideration of these data still indicates that photoionization may be important, a more thorough study of the problem will be planned. In the meanwhile, compilation of radiation flux and photoionization cross section data will continue.
BIBLIOGRAPHY


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<td>Calculations have been made of &quot;flame&quot; (or mixing) dimensions associated with afterburning in rocket exhaust at high altitudes for a theoretical rocket and trajectory. From these and a given exhaust composition one can estimate concentrations and times available for reactions of interest. Above some altitudes if observed flame lengths tend to turn out to be much greater, it would indicate that reaction rates rather than mixing rates were controlling. Investigation of negative ion formation reactions indicates that they may not be a significant.</td>
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II Air Force Space Systems Division
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