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IONIZATION IN ROCKET FLAMES
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by

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ABSTRACT

The temperature in the combustion chamber of a rocket motor can be sufficiently high to maintain a relatively large degree of thermal ionization when small quantities of an alkali metal are added to the flame gases. This paper describes a series of measurements of ion concentrations obtained under various conditions in a rocket motor combustion chamber.

In certain fast flame reactions the observed ionization is several orders of magnitude larger than that predicted by equilibrium considerations, and at first sight it might be expected that the conditions in a rocket combustion chamber would be particularly conducive to excess ionization. Arguments are presented, however, which demonstrate that for highly ionized flames at high pressure there should be only slight deviations from the equilibrium ionization. These arguments are based on the following considerations:

1. Disturbances in the high energy portion of the Maxwell-Boltzmann distribution should have a decreasing effect on ionization as the temperature increases.
2. The thermalization times for electrons and ions are extremely small under typical rocket combustion chamber conditions if the equilibrium ionization is increased by the presence of alkali metals.

In the experimental study a small (10 pounds nominal thrust) rocket motor was used with the following propellant combinations:

1. Hydrogen (gaseous) - oxygen (gaseous)
2. Methane (gaseous) - oxygen (gaseous)
3. Methanol (liquid) - oxygen (gaseous)

The stoichiometric combustion of these propellants produces temperatures of about 3000 K and, with alkali metal additives, yields positive ion concentrations in excess of $10^{14}$/cc.
The additives were introduced into the chamber as aqueous solutions of the alkali metal nitrates, and the flow rate of the solution was controlled to maintain the alkali metal atom concentration at one per cent (by weight) of the flame gases.

Ion concentrations in the chamber were obtained by the Langmuir probe technique. A water-cooled probe has been developed which performs quite reliably under combustion chamber conditions. A simple correction, based on the ionic mean free path, is applied to reduce the effects of pressure on the accuracy of the probe data.

Data are presented on the variation of ion concentration with pressure and the oxidizer to fuel ratio. The measured ion concentrations in the "seeded" flames are less than or equal to the values calculated by the Saha equation for the equilibrium ionization, and there is at least order of magnitude agreement.

The slopes of the individual curves suggest that the free alkali metal atom concentration is influenced to a significant degree by some chemical equilibria. This interpretation is supported by the work of Sugden, who has demonstrated that the alkali metal hydroxides are comparatively stable in high temperature flames. If it is assumed that the alkali metal hydroxide formation was significant in our experiments, then the curves, except for that of rubidium ionization, at least qualitatively behave as predicted.

It seems reasonable to expect that if accurate thermo-chemical data were available, the correlation between the experimental and calculated values of ionization would be improved by including such equilibria in the calculations.
INTRODUCTION

The electrical properties of flames have been the subject of repeated investigations. Although many experimental facts have been uncovered, large areas of uncertainty exist. It is known, for example, that the reaction zone of organic fuel-air mixture is the seat of very high ionization (1, 2, 3); however, the causes of this chemi-ionization are little known. The burnt gases of fuel-air mixtures above the reaction zone generally show a level of ionization in agreement with theoretical expectations as derived from the Saha equation if materials of known and rather low ionization potential are introduced into the flame (4). The burnt gases of flames containing no "seeded" materials should have an exceedingly low degree of ionization as the ionization potential of all product gases such as CO, CO₂ and H₂O have ionization potentials above 12 e volt with the sole exception of NO whose value is 9.23. However, even this latter value cannot explain the ionization in Bunsen flames which is usually about 10⁸ ions/cc.

Further uncertainty exists, especially in the explanation of the effects caused by the interaction of electrical and magnetic fields with flames. "Seeded" rocket flames are carriers of a high degree of ionization because of the high temperature in the chamber. The interaction of electromagnetic fields with the fast moving rocket gases is an interesting and potentially useful field of investigation. This paper reports on a first series of experiments conducted to throw light on this question. Measurement of the ionization in rocket chambers is described using Langmuir probes. Theoretical considerations are presented that are relevant to the use of these probes at high pressure.
THE EXPERIMENTAL SETUP

The primary emphasis in this program was on the determination of the maximum ion concentrations available in rocket combustion chambers. The measurements were obtained in the chamber of a motor, which employs a conventional injection system that is believed to be representative of rocket combustion. The details of motor and injector can be seen in figure 1.

LEGEND

1. Probe housing
2. Spark plug housing
3. Chamber-injector mounting holes
4. Cooling water inlet
5. Connection for bourdon gage
6. Water outlet
7. Chamber wall
8. Coolant jacket
9. Additive inlet
10. Fuel inlet
11. Oxidizer inlet
12. "O" ring groove
13. Fuel and oxidizer outlets

Figure 1. Water cooled rocket engine of 10lb nominal thrust, showing also injector and injector face.

The measurement of probe current as a function of probe potential is obtained automatically by using a low frequency signal generator to apply the probe potential and an X-Y recorder to plot the current versus potential. The signal generator provides a triangular wave form at 0-30 volts. The frequency may be varied between 0.008 and 1100 cps. The horizontal axis of the X-Y plotter is driven by the signal generator. The vertical axis has a maximum sensitivity of 0.3 millivolt per inch and is used to record probe current as a function of the potential with respect to the chamber wall.
The Langmuir probe used in this program was slowly developed by trial and error until a configuration was obtained which was reliable in combustion chamber measurements. The water-cooled "hairpin" probe (figure 2) was the most reliable type. For high pressure measurements, however, it was necessary to substitute boron nitride for the ceramic insulator to avoid electrical breakdown.

**Figure 2.** Hairpin probe for ionization measurements.

**PROBE THEORY**

The basic theory of the Langmuir probe is readily available in the literature (5, 6, 7, 8) and is consequently only outlined briefly in the following discussion. When a probe is immersed in an ionized gas at a sufficiently negative potential with respect to the gas, all of the electrons are repelled by the probe, and the current to the probe is simply due to the random positive ion current density in the gas. By assuming a Maxwellian velocity distribution for the ions, the current reaching a probe of area $A$ is then

$$J = \frac{N_i e c A}{4} = N_i e A \left( \frac{KT}{2 \pi M_i} \right)^{1/2}$$
where:  
\( J \) is the current in amperes  
\( N_i \) is the positive ion concentration per m\(^3\)  
\( \bar{e} \) is the arithmetic mean velocity of the ions in m/sec  
\( A \) is the area of the immersed probe in in\(^2\)  
\( e \) is the electronic charge (in coulombs) of the ion  
\( K \) is the Boltzmann constant  
\( T \) is the absolute temperature of the gas °K  
\( M_i \) is the mass of the positive ion in kgm.

Solving for the positive ion concentration:

\[
N_i = \frac{J}{Ae} \left( \frac{2\pi M_i}{KT} \right)^{1/2}
\]

Thus, if the mass of the ion is known, a simple measurement of the current to the probe and the gas temperature will yield the positive ion concentration in the gas. In practice, of course, the current to the probe is plotted as a continuous function of the probe potential. The value of the current, \( J \), used above is taken as the positive ion saturation current.

This rather simple technique is quite accurate for the purposes for which it was designed—ion concentration measurements at low pressures. In the analysis for the probe current, it is implicitly assumed that the probe creates a negligible disturbance in the gas which is being studied. It has been shown (8) that this assumption is valid only under the following conditions:

1. The radius of the probe must be much smaller than the ionic mean free path.
2. The collision parameter as a function of the probe potential must not differ appreciably from the probe radius. The collision parameter is defined as the maximum distance from the center of the probe for which ions will be collected.

The first condition can never be satisfied in rocket combustion chambers where the ionic mean free path is typically less than 10\(^{-6}\) meter. An analysis by Bohm, Burhop and Massey (8) does, however, yield appropriate correction factors for this situation and also for the case of large collision parameters. The mean free path correction
factor is approximately \( r/\lambda \) where \( r \) is the probe radius and \( \lambda \) is the ionic mean free path. All data on ion concentrations in this report have been modified by the factor \( r/\lambda \).

**THERMAL IONIZATION**

The relationship developed by Saha yields quantitative values of ion concentrations in a gas in thermal equilibrium if the ionization potentials and temperature are known.

\[
\log \frac{x^2}{1 - x^2} P = -\frac{5040 V_i}{T} + \frac{5}{2} \log T - 6.49 + \log \frac{g_i g_e}{g_0}
\]

where \( x \) is the degree of ionization, \( P \) is the sum of the partial pressures, i.e., \( P = P_A + P_e + P_{A^+} \) in atmospheres. 

\([A^+]/[A]\) is the mole fraction of the positive ion, 

\([A]\) is the mole fraction of the neutral atom (for example potassium),

\([e]\) is the mole fraction of electrons,

\(V_i\) is the ionization potential of the atom in e volts,

\(T\) is the absolute temperature in OK,

\(g_i, g_e, \text{ and } g_0\) are the statistical weights of the positive ion, the electron and neutral atom respectively.

The exponential dependence of ionization upon the ionization potential of the atom in this equation explains the fact that even small amounts of alkali metal impurities in the flame gases will have a very strong effect in increasing the equilibrium ionization; the \(V_i\) for the alkali metals are all less than 6 e volts, and the ionization potentials of typical equilibrium flame species are, on the other hand, rather high (12-16 e volts).

Although the equilibria of each ionizable species in the flame gases should be considered in computing the total ionization, it is evident that for cases when an alkali metal is present the contributions from other species are negligible. Any additional equilibria which control the free metal atom concentration in the flame must, however, be considered for evaluation of electron or ion concentrations. The work of Sugden...
and Smith (9) and Sugden (10) has shown, for example, that LiOH and 
CsOH are comparatively stable in certain flames, and their formation 
greatly reduces the concentrations of Li and Cs atoms available for 
ionization.

Saha's equation predicts ionization in a rocket chamber only if 
thermal equilibrium is installed. As rocket chambers are designed to 
contain very rapid chemical reactions, this question needs further 
investigation. It is known that ionization in the reaction zone of a 
premixed flame is many orders of magnitudes larger than theoretically 
expected. This effect is very similar to the excess electronic excita-
tion observed in the reaction zones of flames (2) and this relationship 
is not unexpected as ionization is basically an electronic excitation.
The following facts are known about the excess electronic excitation: 
The higher the pressure the less observable is this disturbance of the 
Maxwell-Boltzmann distribution. Also this disturbance is only present 
in premixed flames but not in diffusion flames. As all rocket flames 
are basically diffusion flames (except for monopropellants), one would 
expect that the ionization is not far from thermal. If local excess 
ionization does occur, then the rate of recombination has to be con-
sidered.

Although no data are available on recombination rates for conditions 
appropriate to flames in a rocket combustion chamber (high pressure 
and high temperature), a rough estimate for the ion recombination 
relaxation time may be obtained by employing data from electric arcs 
which have similar temperatures. These data show typical recombi-
nation coefficients of \( \alpha = 10^{-10} \text{ cm}^3/\text{sec} \) (2). Since the relaxation time 
constant is approximately \( \alpha \cdot n_e \), where \( n_e \) is the electron concentration 
per cm\(^3\), the relaxation time in a "seeded" flame for which \( n_e = 10^{14} \) 
per cm\(^3\) will be less than \( 10^{-4} \) second.

This relaxation time seems small enough to prevent any large 
deviations from ionization equilibrium in the chamber. In the exhaust, 
however, the gas temperature drops very quickly due to the rapid expansion 
process, and the ionization could possibly remain above the equi-
librium value for some distance downstream of the throat.
The arguments above are, unfortunately, valid only when the recombination process is that of direct recombination of ions with electrons. The probability of direct recombination decreases as the electron concentration decreases (2), and the process becomes primarily dependent upon three-body collisions. The electrons first become attached to neutral molecules, and these negative molecular ions recombine readily with the positive ions. The recombination coefficient is consequently increased by several orders of magnitude. For example, in methane-air flames at 66 mm Hg = 2.5 x 10^{-7} cm^{3}/sec (11).

In rocket flames which are not seeded with alkali metals, the equilibrium electron concentrations are rather low and the recombination relaxation time is probably greater than 10^{-3} second. Thus, if excess ionization is produced in the reaction, the ionization should be greater than the equilibrium value throughout the entire flame. Experimental work on such questions would be quite valuable, but the abnormal effects of minute traces of easily ionizable impurities makes experimental data on ionization values in "pure" rocket flames quite questionable. For example in a rocket flame at 3000 K at 1 atmosphere where the equilibrium ionization is 10^{9} ions/cc the introduction of 1 part in 10^{5} of potassium would increase the ionization to about 10^{12} ions/cc.

EXPERIMENTAL RESULTS AND DISCUSSION

The most significant data on ion concentrations are summarized in figures 3 through 6. All of these data were obtained in the chamber of the rocket motor described previously.

The curves in figure 3 present the experimental and calculated values of ion concentration as a function of chamber pressure for stoichiometric combustion of gaseous CH_{4} and gaseous O_{2}. The additive was a solution of CsNO_{3} which resulted in a cesium concentration of 1 per cent by weight in the flame gases.

The Saha equation may be modified to the following form by assuming that the electron concentration and positive ion concentration are approximately equal:

\[ 2 \log n_{i} = - \frac{5040 \, V_{i}}{T} + 1.5 \log T + 15.38 + \log \frac{e_{i} e_{e}}{e_{o}} + \log n_{o} \]

\[ n_{i} \text{ and } n_{o} \text{ are the ion and neutral atom concentration per cm}^{3}. \]
This equation reveals that the ion concentration is dependent only on the temperature and neutral cesium atom concentration.

If it is assumed that the neutral cesium atom concentration is not influenced by chemical equilibria, then the cesium atom concentration will be directly proportional to the pressure and inversely proportional to the temperature (except for the small percentage of atoms which are ionized).

The variation of flame temperature with pressure is as follows:

1. As pressure increases above one atmosphere, the flame temperature rapidly increases.

2. At higher pressures the rate of increase of flame temperature with pressure decreases.

The calculated values for ion concentrations in this report have been obtained by calculating the flame temperature (assuming that the additive has negligible effect on the enthalpy). The neutral atom concentration is then calculated at the pressure and temperature from the original concentration in the gas mixture. The Saha equation is then employed to obtain the ion concentration. The discussion which follows shows that the discrepancy between the experimental and calculated values in figure 3 can be at least partially attributed to the invalidity of the assumption that the cesium atom concentration is uninfluenced by chemical equilibria.

The curves in figures 4 and 5 show the variation of ion concentration with O/F ratio for a CH₄ - O₂ flame at a chamber pressure of one atmosphere and an H₂ - O₂ flame at a chamber pressure of one atmosphere. In each case the fuel and oxidizer were introduced in the gaseous state and the additives produced alkali metal concentrations of one per cent by weight in the flame.
In figure 5 the dashed line represents the calculated values for the potassium ion concentration. Stoichiometric ratio is at an O/F ratio of 7.95 for the H₂-O₂ flame and 4.0 for CH₄-O₂. Table 1 gives the relation between O/F ratio and flame temperature at 1 atmosphere for H₂-O₂ flames.

![Graph showing calculated values for potassium ion concentration.](image)

The experimental values exhibit order of magnitude agreement with simple calculations based upon the Saha equation, and the curves are in the relative order which is predicted by the ionization potentials of the respective atoms (table 2). The slopes of the individual curves, however, are in substantial disagreement with those calculated with the assumption that the alkali metal atoms are not involved in any chemical equilibria at these flame temperatures.

**TABLE 1**

<table>
<thead>
<tr>
<th>O/F Ratio</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>2370°K</td>
</tr>
<tr>
<td>4.0</td>
<td>2778°K</td>
</tr>
<tr>
<td>5.0</td>
<td>2980°K</td>
</tr>
<tr>
<td>6.0</td>
<td>3030°K</td>
</tr>
<tr>
<td>7.0</td>
<td>3076°K</td>
</tr>
<tr>
<td>8.0</td>
<td>3081°K</td>
</tr>
</tbody>
</table>

**TABLE 1**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>4.67 e volt</td>
</tr>
<tr>
<td>Ra</td>
<td>4.15 e volt</td>
</tr>
<tr>
<td>K</td>
<td>4.32 e volt</td>
</tr>
<tr>
<td>Na</td>
<td>5.12 e volt</td>
</tr>
<tr>
<td>Li</td>
<td>5.36 e volt</td>
</tr>
</tbody>
</table>
In all cases, if the curves are plotted as ion concentration versus flame temperature, the experimental slopes \((d n_i/dT)\) are less than those calculated from the derivative of the Saha equation at temperatures below \(3000^\circ\text{K}\). A possible explanation for this behavior is based on the work of Sugden and Wheeler (10) (12) who studied the formation of alkali metal hydroxides in high temperature flames. The formation of the hydroxide will, of course, reduce the concentration of free atoms available for ionization.

If the derivative of the logarithm of the ion concentration with respect to temperature is obtained from the Saha equation, then

\[
\frac{d \log_{10} n_i}{dT} = \frac{2520 V_i}{T^2} + \frac{0.75 \log_{10} e}{T} + \frac{0.5 \log_{10} e d n_o}{n_o dT}
\]

Simple calculations reveal that even at \(3000^\circ\text{K}\) the last term on the right hand side will have only a minor effect if the neutral atom concentration is reduced only by the production of ions. If however, the free atom concentration is controlled by chemical equilibria, e.g. hydroxide formation, this term would become significant and reduce the slope of the ionization curve below that predicted on the assumption that \(n_o\) is reduced only by ion formation. Hydroxide formation is, of course, more likely for higher \(O/F\) ratios than on the fuel rich side.

Sugden (10) has obtained the following estimates for the gas phase heats of formation for alkali metal hydroxides:

- LiOH \(102\) kcal/mole
- CsOH \(91\) kcal/mole
- KOH \(86\) kcal/mole
- NaOH \(81\) kcal/mole

If a value of \(88\) kcal/mole for the heat of formation of RbOH, estimated from the values above, is added, then the slopes of the curves should be less than the predicted slopes in the following order of significance: \(Li^+\), \(Cs^+\), \(Rb^+\), \(K^+\) and \(Na^+\). The data exhibit this trend at temperatures below about \(2800^\circ\text{K}\) if they are compared individually with the theoretical slopes.
At higher temperatures the slopes of the Na\(^{+}\), K\(^{+}\) and Cs\(^{+}\) curves approach the predicted values. The slopes of the Rb\(^{+}\) and Li\(^{+}\) curves, however, become negative at temperatures above 3000\(^{0}\)K.

In figure 6 the ion concentration is plotted as a function of O/F for a CH\(_3\)OH-O\(_2\) flame at one atmosphere chamber pressure. In these measurements the CH\(_3\)OH was injected as a liquid through a conventional "shower head" injector; the oxidizer was gaseous O\(_2\). For this system the alkali metal ion concentrations are again in order of magnitude agreement with values predicted by the Saha equation, but the individual curves show evidence of variations in the neutral atom concentration which could probably be explained by additional chemical equilibria if the pertinent thermo-chemical data were available. The rather anomalous behavior of the rubidium ionization curve is as prominent in this system as in the other systems.

CONCLUSIONS

It has been demonstrated that the measured ion concentrations in a "seeded" rocket combustion chamber may be predicted within an order of magnitude by a simple application of the Saha equation. In all cases the ion concentrations measured by the Langmuir probe are less than or equal to calculated values. No evidence of chemi-ionization was found in "seeded" flames, although it may be present in "pure" flames. In this latter case however our data are not conclusive because of the possible presence of minute quantities of impurities. The data suggest that the correlation will be improved if the chemical equilibria which control the alkali metal atom concentration are included in the calculations. At the present time, however, the necessary thermo-chemical data are not known to a sufficient degree of accuracy to
justify more tedious calculations. Furthermore, even an order of magnitude estimate of the degree of ionization in a rocket flame is sufficient to evaluate the basic feasibility of certain magnetohydrodynamic applications which have been proposed for chemical rockets.
REFERENCES


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