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Reaction between Oxygen Difluoride and Diborane: Kinetics and a Proposed Mechanism

Robert A. Rhein*
Jet Propulsion Laboratory, Pasadena, Calif.

For the reaction between OF_2 and B_2H_6, the initial rates of consumption of OF_2 and B_2H_6 and the initial rate of formation of BF_3 (a reaction product) were experimentally determined over a range of initial partial pressures of 1–30 torr for B_2H_6 and 5–40 torr for OF_2, at 300°K. In addition, the initial consumption rates of OF_2 and B_2H_6 were determined at temperatures ranging from 300 to 330°K. These initial rates were correlated to initial reactant concentrations and to reactor temperature by the expressions

$$\left[\frac{d}{dt}(P_{BF_3})\right]_0 = 2.16 \times 10^{-3} \cdot [(P_{OF_2})]_0^{1.7} \cdot [(P_{B_2H_6})]_0^{-0.4} \text{ at } 300^\circ\text{K} -$$

$$\left[\frac{d}{dt}(P_{B_2H_6})\right]_0 = 2.82 \times 10^{6} \cdot [(P_{OF_2})]_0^{2.2} \cdot [(P_{B_2H_6})]_0^{-0.6} \cdot \exp(-11{,}000/RT) -$$

$$\left[\frac{d}{dt}(P_{OF_2})\right]_0 = 0.294 \cdot [(P_{OF_2})]_0^{1.6} \cdot [(P_{B_2H_6})]_0^{0} \cdot \exp(-2800/RT)$$

where P is partial pressure in torr at 300°K, t is time in minutes, T is temperature in degrees Kelvin, and R is 1.987 cal mole^{-1} °K^{-1}.

I. Introduction

THE propellant combination of oxygen difluoride-diborane is space-storable, and it is regarded as especially desirable for upper-stage rocket engines. Consequently, a knowledge of the reaction rates is required to enable calculation of such parameters as the hypergolic ignition limits, the ignition delay time, and others. The objective of this work was to obtain expressions relating the initial reaction rates of OF_2 with B_2H_6 to initial reactant concentration and temperature. The reaction between OF_2 and B_2H_6 at ambient temperatures was found[1] to produce H_2, BF_3, small amounts of HBF_2 and B_2F_4, and unidentified solid materials.

Reported in this paper are the initial rates of consumption of OF_2 and of B_2H_6 at ambient and at elevated temperatures (to 57°C), and the initial rate of formation of BF_3 at 300°K as measured vs various initial concentrations of OF_2 and B_2H_6.

Although the thermal decomposition of B_2H_6[2–7] and the reaction of B_2H_6 with O_2[8–10] and with H_2O[11] have been studied, there have been to the author's knowledge[†] no previous attempts to determine the rates for the OF_2–B_2H_6 reaction.

II. Experimental Procedure

The experimental setup is shown in Fig. 1. The OF_2 and the B_2H_6 were purified by standard methods[1] and were stored in the Pyrex bulbs in which the pressure was ordinarily held between 400 and 800 torr.

The initial rates were determined from measurements of infrared transmittance at prescribed time intervals following the addition of OF_2 to B_2H_6 in an infrared cell. The spectrophotometric transmittance measurements were made at the 6.88-μ band of BF_3, the 12.1-μ band for OF_2, and the 6.18-μ band for B_2H_6.

The infrared cells used for determination of the initial rates at ambient temperature were constructed of either Pyrex or 316 stainless steel. The cell windows were made of NaCl, AgCl, or IRTRAN-2 (pressed polycrystalline ZnS). Although the experiments were conducted using either cell with any of the windows, no difference due to the cell or window materials of construction was observed in the reaction rate.

Temperatures were measured in 6° intervals over the range 300°–330°K with a Beckman heated cell. The pressure of gases in the cells was measured by an electronic transducer attached directly to the cell, but could also be measured by the diaphragm gage shown on the gas-handling system attached to the cell.

The following procedure was used to conduct each experiment. 1) The cell and the attached system were evacuated to a pressure of approximately 10^{-3} torr. 2) The B_2H_6 was added to both the cell and the system, to the desired pressure as

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[*] Senior Scientist.

[†] L. Dauerman and his co-workers at New York University did some preliminary work on the high-temperature reaction between OF_2 and B_2H_6.

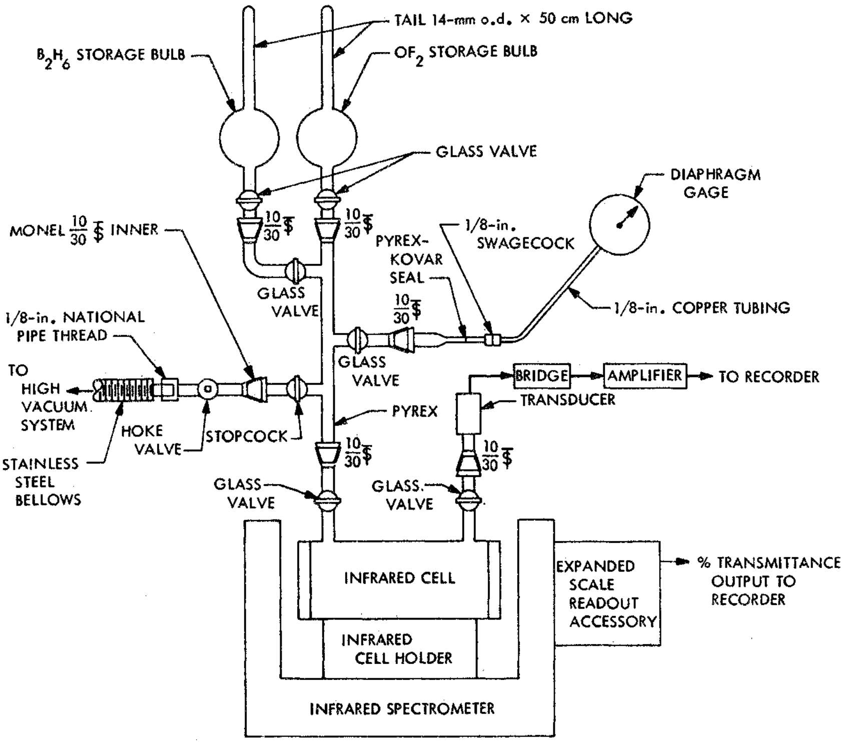

Fig. 1 Schematic of the experimental setup.

Table 1 Kinetics of the OF_2-B_2H_6 reaction: rates of consumption of B_2H_6 and OF_2 and rates of formation of BF_3 vs concentration of B_2H_6 and OF_2 reactor temperature[a]

			B_2H_6		OF_2		BF_3	
B_2H_6	OF_2		Consumption rate,	Standard deviation,	Consumption rate,	Standard deviation,	Formation rate,	Standard deviation,
Concentration, torr (Ref. 300°K)		Reactor temperature, °K	torr min^{-1} (Ref. 300°K)		torr min^{-1} (Ref. 300°K)		torr min^{-1} (Ref. 300°K)	
1.0	5.0	300	0.0357	0.0114	0.0263	0.0088	0.0291	0.0017
1.0	10.0	300	0.2130	0.0592	...	...	0.1464	0.0241
2.5	5.0	300	0.0245	0.0066	0.0368	0.0099	0.0250	0.0004
2.5	10.0	300	0.1087	0.0092	0.1181	0.0143	0.0572	0.0064
5.0	5.0	300	0.0164	0.0036	0.0151	0.0115	0.0218	0.0024
5.0	10.0	300	0.0587	0.0018	0.0828	0.0048	0.0434	0.0016
5.0	20.0	300	0.5791	0.1711	0.4262	0.0358	0.1813	0.0149
5.0	30.0	300	1.1717	0.0995	...	...	0.3050	0.2070
10.0	10.0	300	0.0563	0.0266	0.2741	0.0196	0.0432	0.0124
10.0	15.0	300	...	...	...	...	0.0581	0
10.0	20.0	300	0.4074	0.0256	0.4296	0.1010	0.1222	0
10.0	30.0	300	0.7862	0.0336	0.9127	0.0398	0.2935	0
20.0	10.0	300	0.0242	0.0093	0.1163	0.0214	0.0335	0.0154
20.0	20.0	300	0.1954	0.0655	0.2443	0.0108	0.0548	0.0013
20.0	25.0	300	...	...	...	...	0.1665	0
20.0	30.0	300	0.3183	0.0415	0.4622	0.1960	0.1790	0.0275
20.0	40.0	300	0.6685	0.0020	1.1216	0.0513	0.4674	0.0086
30.0	10.0	300	...	...	0.2124	0.1192	0.0276	0.0002
30.0	20.0	300	...	...	0.2470	0.0233	0.0691	0.0050
30.0	30.0	300	...	...	0.4252	0.0826	0.1922	0.0353
10.0	10.0	306	0.0857	0.0113	0.0783	0.0113	...	...
20.0	10.0	306	0.0767	0.0434	0.0835	0.0114	...	...
20.0	20.0	306	...	...	0.2270	0.0340	...	...
10.0	10.0	312	0.1243	0.0091	0.1115	0.0076	...	...
20.0	10.0	312	...	...	0.0820	0.0125	...	...
20.0	20.0	312	0.3793	0.1008	0.3299	0	...	...
10.0	10.0	318	0.1735	0.0111	0.1737	0.0074	...	...
20.0	10.0	318	0.1657	0.0603	0.1446	0.0071	...	...
20.0	20.0	318	0.2705	0.0491	0.2713	0.0631	...	...
10.0	10.0	324	0.2054	0.0027	0.1918	0.0051	...	...
20.0	10.0	324	0.1804	0.0608	0.1578	0.0140	...	...
20.0	20.0	324	0.4362	0.0335	0.3565	0.0086	...	...
10.0	10.0	330	0.3222	0.0320	0.1794	0.0224	...	...
20.0	10.0	330	0.3826	0.0408	0.1910	0.0321	...	...
20.0	20.0	330	0.8377	0	0.4360	0.0375	...	...

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[a] These consumption and formation rates are generally the average value over several experiments. The standard deviation refers to the data scatter about the average value.

registered by the diaphragm pressure gage. The stopcock between the cell and the system was closed and the system was evacuated. 3) The OF_2 was added to the system until its pressure was equal to the B_2H_6 pressure in the cell. The stopcock between the cell and the system was then opened and the OF_2 pressure increased until the desired pressure was achieved (the addition of OF_2 to the B_2H_6 generally took about 1 min); then the stopcock between the system and the cell was closed. It was assumed that the mixing time for the reactants in the cell was in the order of a minute or less. The mixing time, however, was not computed. Consequently, uncertainties in the experimental results due to mixing are conceivable. 4) The voltage output from the electronic equipment associated with the transducer was measured and recorded on a strip-chart recorder. This voltage output was calibrated by the pressure measured by the diaphragm gage immediately after the OF_2 was added to the B_2H_6. 5) The transmittance output from the infrared spectrometer was measured on one strip-chart recorder; and, simultaneously, the output from the electronics associated with the transducer was measured on another strip-chart recorder for the duration of the experiment. 6) The experiment lasted approximately 10 min, after which the cell was evacuated. 7) Generally, each experiment was performed three or four times for each value of initial reactants concentration and temperature.

The experimental data (transmittance vs time) were processed by a computer programed to calculate concentrations (i.e., of reactant or of BF_3 product) at prescribed intervals of time during each experiment, and then to determine the initial rates (set as equal to the slope of a linear least-squares fit of concentration vs time).[12] The average initial rate for several runs, each performed at the same value of initial reactant concentrations and reactor temperature, was computed, and the set of values of initial rates was then correlated to the corresponding set of initial reactant concentrations by rate expression (1),

$$\text{RATE} = K\cdot P_{B_2H_6}{}^{a}\cdot P_{OF_2}{}^{b} \qquad (1)$$

if the reactor temperature were the same in every experiment, or correlated to the corresponding set of initial reactant concentrations and reactor temperature by Eq. (2),

$$\text{RATE} = K'\cdot P_{B_2H_6}{}^{a}\cdot P_{OF_2}{}^{b}\cdot\exp(-E/RT) \qquad (2)$$

if the reactor temperature were not the same in every experiment. In addition, the standard error, or "goodness of fit" of the rates computed from Eq. (1) or (2) compared with the experimentally determined rates, was also obtained. For example, the coefficients K (or K'), a, b, and (where applicable) E were determined from linear multiple regression of the values of the dependent variable $\ln_e$ (RATE) vs the independent variables $\ln_e(P_{B_2H_6})$, $\ln_e(P_{OF_2})$, and (where applicable) $1/T$. The standard error of regression for the N set of variables (obtained from observation) $\ln_e$ (RATE)$_i$, $\ln_e(P_{B_2H_6})_i$, $\ln_e(P_{OF_2})_i$, and $1/T$ is

$$s = \left\{\frac{1}{N-4}\sum_{i=1}^{N} [\ln_e (\text{RATE})_i - \ln_e K' - a\cdot\ln_e(P_{B_2H_6})_i - b\cdot\ln_e(P_{OF_2})_i - E/RT]^2\right\}^{1/2}$$

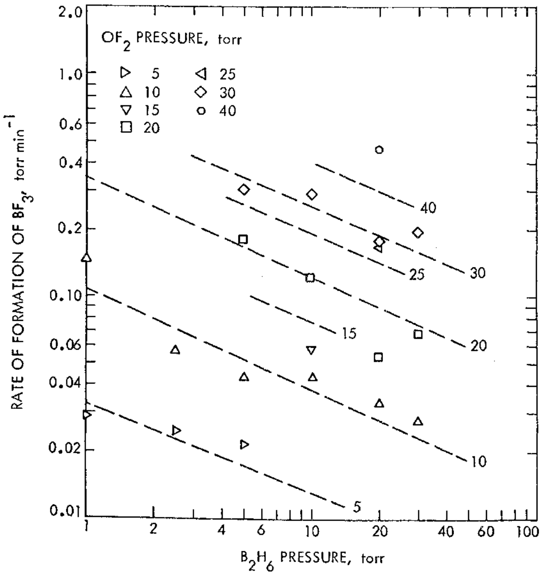

Fig. 2 Isothermal (300°K) formation rate of BF_3 vs B_2H_6 pressure for the reaction of OF_2 with B_2H_6.

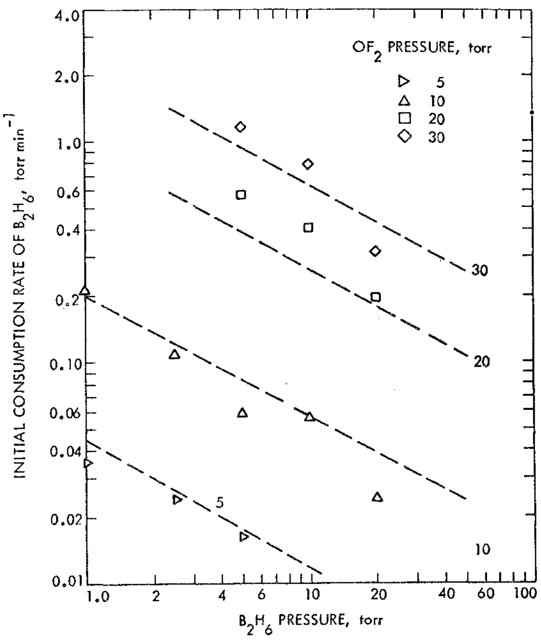

Fig. 3 Initial (isothermal, 300°K) consumption rate of B_2H_6 vs B_2H_6 pressure for the reaction of B_2H_6 with OF_2.

For the case of temperature independence,

$$s = \left\{\frac{1}{N-3}\sum_{i=1}^{N} [\ln_e(\text{RATE})_i - \ln_e K - a\cdot\ln_e(P_{B_2H_6})_i - b\cdot\ln_e(P_{OF_2})_i]^2\right\}^{1/2}$$

The standard error s can be considered as ln (RATE OBSERVED FROM EXPERIMENTS) = ln [RATE COMPUTED FROM Eq. (1) OR (2)] $\pm s$, or RATE (OBSERVED) = RATE (COMPUTED) $\times\ e^{+s}$.

III. Results

The initial rates of consumption of OF_2 and of B_2H_6, and the initial rates of formation of BF_3 are tabulated (Table 1) vs initial reactant concentrations for several reactant temperatures. These rates were empirically fit to the following expressions:

$$\left[\frac{d}{dt}(P_{BF_3})\right]_0 = 2.16 \times 10^{-3}\cdot[(P_{OF_2})]_0{}^{1.7} \times [(P_{B_2H_6})]_0{}^{-0.4} \text{ at } 300°\text{K} \qquad (3)$$

where $s = 0.247$;

$$-\left[\frac{d}{dt}(P_{B_2H_6})\right]_0 = 2.82 \times 10^{6}\ [(P_{OF_2})]_0{}^{2.2} \times [(P_{B_2H_6})]_0{}^{-0.6}\cdot\exp(-11{,}000/RT) \qquad (4)$$

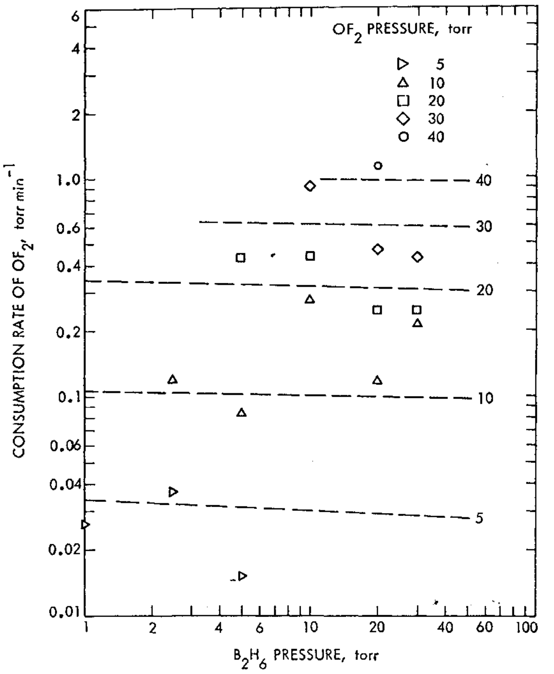

Fig. 4 Initial (isothermal, 300°K) consumption rate of OF_2 vs B_2H_6 pressure for the reaction of OF_2 with B_2H_6.

where $s = 0.312$; and

$$-\left[\frac{d}{dt}(P_{OF_2})\right]_0 = 0.294\cdot[(P_{OF_2})]_0^{1.6} \times [(P_{B_2H_6})]_0^{0}\cdot \exp(-2800/RT) \quad (5)$$

where $s = 0.385$. Here, P is partial pressure in torr at 300°K, t is time in minutes, T is temperature in degrees Kelvin, and R is 1.987 cal $mole^{-1}$ $°K^{-1}$. Equations (3–5) were plotted, along with experimental data, in Figs. 2–6.

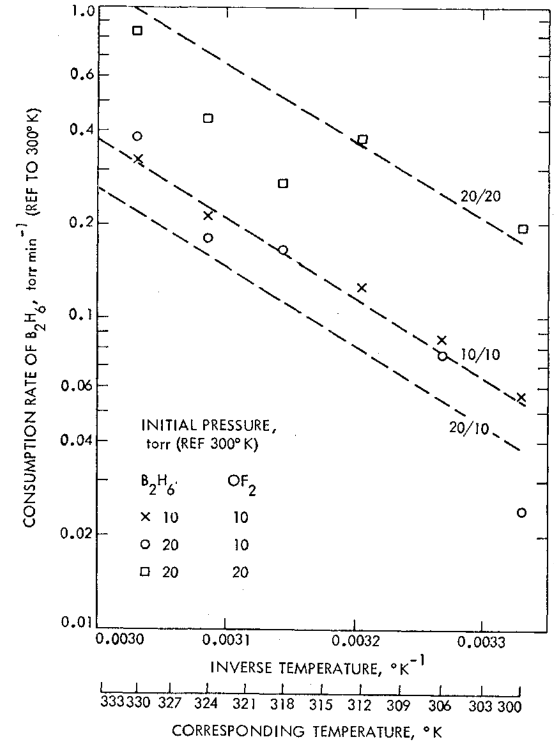

Fig. 5 Consumption rate of B_2H_6 vs inverse temperature for the reaction of B_2H_6 with OF_2.

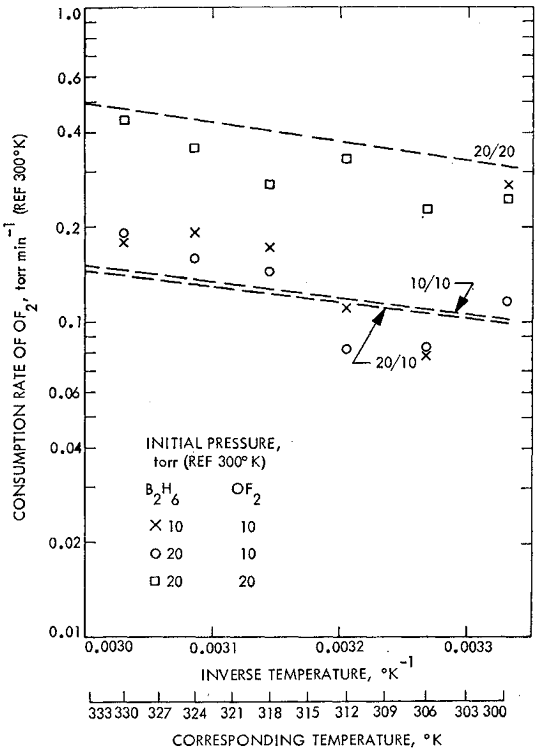

Fig. 6 Consumption rate of OF_2 vs inverse temperature for the reaction of OF_2 with B_2H_6.

Some scatter is observed in the data. One possible contributing factor to the scatter may have been inhomogeneities in the cell caused by incomplete mixing of the reactants, as previously discussed.

It is significant that rate magnitudes of B_2H_6 consumption and BF_3 formation were dependent inversely on B_2H_6 concentration, while the OF_2 consumption rate was independent of B_2H_6 concentration.

IV. Discussion and Conclusion

There were a number of features about this reaction that are interesting. The reaction rate was measurable and, in fact, rather slow at ambient temperature and in the 10–40 torr partial pressure range. The consumption rate of B_2H_6 and the formation rate of BF_3 were inversely related to the B_2H_6 partial pressure, whereas the consumption rate of OF_2 was essentially independent of the B_2H_6 partial pressure. In addition, the consumption rate of B_2H_6 was related to the partial pressure of OF_2 to an apparently higher than second order.

Although no reaction mechanism is proposed here, such a mechanism, if proposed, should explain or account for these observations. Further studies of the OF_2–B_2H_6 reaction should be directed toward determining a mechanism for this reaction. In addition, further consideration should be given to the mixing time of the reactants.

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Behavior of a Large Nonequilibrium MHD Generator

Reiner Decher*
University of Washington, Seattle, Wash.

AND

Myron A. Hoffman†
University of California, Davis, Calif.

AND

Jack L. Kerrebrock‡
Massachusetts Institute of Technology, Cambridge, Mass.

A large nonequilibrium MHD generator of the linear, segmented-electrode, Faraday type has been studied both experimentally and theoretically. Experiments have been run at the following nominal operating conditions: generator Mach number of 2.2 with a mass flow of 0.4 kg/sec^{-1} of helium seeded with about 0.3% cesium; stagnation conditions were 2000°K and about 5-atm pressure. The loaded generator exhibited several unusual features, including a very slow increase in the load currents axially and very large anode drops. The Hall voltage was a small fraction of its ideal value. At short circuit, load currents at least five times those possible with frozen ionization were drawn; but these currents were still far below those predicted by one-dimensional theory. At open circuit the transverse voltages were usually very low near the inlet and exit but as large as 0.6 of the ideal value near the channel center; negative electrode drops were measured on both cathodes and anodes. A theoretical model is proposed to explain this behavior. It is hypothesized that highly conducting layers exist along the electrode walls which short the generator through the end regions at open circuit. These layers exist because the transverse current is impeded at the insulator segments of the electrode wall, leading to a larger conductivity there than in the main flow. Under load these layers interact with a two-dimensional inlet relaxation front to couple the generator end-to-end, producing the very slow axial build-up of the load current. The proposed model is shown to explain the major features of the experimental results.

1. Introduction

THE work to be reported here is part of a continuing study of the behavior of nonequilibrium MHD generators. The generator to be discussed is of the segmented Faraday type.[1–3] Its mass flow of 0.4 kg^{-1} is large enough to prevent viscous effects from being dominant, whereas the supersonic flow and large Hall parameter ideally should result in electron temperatures well above the gas stagnation temperature with reasonable load factors.

The aims of the present investigation were mainly two. The first was to improve on the preionization. The second was to provide more detailed instrumentation than the earlier experiments, in order to more clearly delineate the current pattern in the generator. The first objective has been achieved, in part, by establishing the preionizing discharge outside of the magnetic field, ahead of the nozzle throat; and, as we shall see, this has resulted in the generator's producing large load currents near short circuit.

With the information derived from the more detailed instrumentation, it has been possible to construct a simple model which explains the behavior of the generator both at open circuit and under load in terms of shorting by end loops which are coupled to the channel center and to the loads by highly conducting layers along the electrode walls.

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* Assistant Professor, Department of Aeronautics and Astronautics.

† Professor, Department of Mechanical Engineering. Associate Fellow AIAA.

‡ Professor, Department of Aeronautics and Astronautics. Associate Fellow AIAA.