

STUDIES SUPPORTING AN
UPPER-ATMOSPHERIC CHEMICAL
RELEASE PROGRAM

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Final Report

Part I. Experimental Studies on Chemiluminescence

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Part II. A Model of Releases Leading to
Upper-Atmospheric Chemi-Ion Formation

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ABSTRACT

The goal of the work discussed in Part I of this report was to find one or more chemical compounds whose release in the upper atmosphere would have a unique suitability for studying this medium by observation of chemiluminescence. Most of the work was performed near room temperature at pressures of from 3 to 8 milli Torr, in a cylindrical flow reactor. The work has indicated that diborane, B_2H_6 , would have unique advantages as a release agent, especially (but not only) at altitudes where $[O_2] \gg [O]$ and it is recommended that an upper-atmospheric diborane release be carried out. The chemiluminescent reactions of diborane have been compared to those of two presently successfully used chemiluminescent release agents, NO and trimethyl aluminum (TMA), and two reagents which have given rise to only a weak upper-atmospheric luminescence of short duration, CS_2 and C_2H_2 .

Over a wide range of concentrations the intensity of the O- B_2H_6 reaction was close to that of the O-NO reaction but was strongly enhanced by $O_2(X^3\Sigma_g^-)$ --ground-state--molecules. None of the other reagents tested showed a similar behavior. The enhancement by excited O_2 molecules, predominantly $O_2(a^1\Delta_g)$, is some 10 times stronger than that of $O_2(X^3\Sigma_g^-)$ in the same concentration. No glow was observed in the reaction of B_2H_6 with these O_2 species in the absence of O atoms.

TMA produced a very weak chemiluminescence in its reaction with O atoms but a much more intense luminescence upon reaction with $O_2(a^1\Delta_g)$ molecules (both in the absence and in the presence of O atoms). It appears quite possible that the upper-atmospheric chemiluminescence of TMA is due primarily to excited O_2 molecule reactions.

The O- C_2H_2 reaction produced a weak luminescence only. The O- CS_2 reaction showed the previously observed high initial intensity; however, this intensity decreased at least 10 times as fast with distance along the reaction tube as that of any of the other reagents at similar concentrations. It seems likely that its failure as a chemiluminescent release agent is related to this observation.

In Part II of this study an atmospheric model for point (spherical) chemical releases has been developed in order to test the feasibility of producing observable electron clouds by chemi-ionization reactions. Based on the model, a digital computer program has been developed and used for the feasibility study. With minor modification this program can be easily adapted to the study of chemiluminescent releases. A chemi-ionization reaction mechanism for acetylene releases has been developed which is consistent with existing laboratory data at ≈ 1 Torr (laboratory data at lower pressures are presently unavailable). Electron recombination and attachment reactions are also included in the reaction mechanism used in this upper atmospheric model.

Predictions of the electron density profile in space and time following an acetylene release have been made. These indicate that chemi-ionization, as observed by ground-based ionosondes, can be used to study the upper atmosphere in a manner similar to the observation of chemiluminescence by optical techniques. It is shown that the electron cloud can be sustained for a time well in excess of 10 minutes. This is due, in large part, to the continual electron production via chemi-ionization.

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NOMENCLATURE

Part I. Experimental Studies on Chemiluminescence

- []₀ = Initial reactant concentration
 a. i. u. = Arbitrary intensity units, i. e., phototube current
 TMA = Trimethyl aluminum

Part II. A Model of Releases Leading to Upper-Atmospheric Chemi-Ion Formation

- A = Avogadro's number
 D = diffusion coefficient
 k_j = rate constant for jth reaction
 M = mass of release agent
 N = total number of molecules released
 \dot{n} = rate of production
 n_i = species concentration
 (n_i)₀ = initial value of ith species
 r = radial distance from center of release
 r₀ = Gaussian half-width
 t = time
 W = molecular weight of release agent

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PART I. EXPERIMENTAL STUDIES ON CHEMILUMINESCENCE

A. Fontijn and P.H. Vree

I. INTRODUCTION

The purpose of this phase of the program was to find chemical compounds whose release in the upper atmosphere would be uniquely suitable for studying this medium by optical techniques. At the outset, two release agents, trimethyl aluminum (TMA) and NO, were known to give a luminescence of sufficient brightness and duration to allow performance of mass motion studies.^{1,2} Moreover, TMA has been used to determine upper-atmospheric temperatures by analysis of the AlO resonance radiation,^{3,4} and NO is potentially useful for O-atom concentration determinations.^{5,6} We were therefore looking for agents that either had superior qualities to these agents for the study of some upper-atmospheric properties or else would yield data to serve as a check on the results obtained with NO and Al(CH₃)₃.

Boron compounds were chosen for our first investigations for a number of reasons:

1. The observed bright luminescence of long duration following Al(CH₃)₃ releases makes it of interest to study compounds of elements similar in chemical properties to Al.
2. For upper-atmospheric diffusion measurements, it is desirable to observe luminescent species of molecular weight comparable to that of species present in the undisturbed atmosphere. Boron compounds can more closely approximate this condition than can aluminum compounds.
3. Light-element compounds are also preferred to heavy-element compounds because the light emitters produced from them will usually diffuse in the upper atmosphere at speeds comparable to most of the other reaction products. The fact that hydrocarbon free radicals diffuse faster than a species like PbO has been suggested as one possible explanation⁷ for the short duration of the light emission observed in NASA-Langley's lead tetramethyl releases; i. e., upper-atmospheric O atoms were scavenged by hydrocarbon free radicals and may have been no longer available to react with lead atoms or lead oxide molecules.
4. The spectrum of BO--observed in many boron oxidation reactions⁸--shows many transitions originating from different vibrational levels emitted in relatively narrow wavelength intervals. This spectrum, therefore, appears promising for lending itself to upper-atmospheric temperature determinations during twilight. A comparison with the AlO resonance radiation results would be valuable.[†]

[†] It must be pointed out, however, that very recent theoretical studies at AFCRL⁹ have indicated that it will be easier to determine upper-atmospheric temperatures from releases leading to MgO or BeO rather than BO or AlO.

The initial studies were performed at pressures around 2 Torr. It very quickly became evident that the reaction of O atoms with diborane not only gave far higher intensities than were obtained with any other boron compounds used (BF_3 , BCl_3 , $\text{B}(\text{CH}_3)_3$) but was also one of the brightest chemiluminescent reactions which we had ever observed in this pressure regime. These observations, combined with the fact that the molecular weights of B_2H_6 (28) and of the principal emitter BO (27) are very close to that of the ambient atmosphere (25 to 29 over the altitude region of potential interest, *i. e.*, from 200 to 30 km),¹⁰ suggested diborane to be a good release agent. It was therefore decided to build a facility to study the O- B_2H_6 reaction in the 1 to 10 milli-Torr pressure regime, which is comparable to that encountered in the actual releases[†] in the 90 to 110 km altitude region, rather than look for further release agents in the ≈ 1 -Torr pressure range. In the milli-Torr facility we have studied B_2H_6 and compared the behavior of this reagent to that of NO and TMA as well as to two compounds, CS_2 and C_2H_2 , which--as upper-atmospheric observations have shown--give rise to luminescence of relatively low intensity and short duration only.¹¹⁻¹³ In this way a more reliable prediction of the suitability of B_2H_6 for a release could be obtained. Only relative measurements have been made in this facility, *i. e.*, for a constant (but not measured) O-atom concentration the relative light intensities obtained with the test reagents were measured. By proceeding in this manner, sufficient experience with and understanding of the low-pressure facility have been obtained, so that in any future work detailed absolute measurements can be made on most compounds of interest.

II. STUDIES AT PRESSURES OF ≈ 2 TORR

The preliminary work made in this relatively high-pressure regime is briefly described here. The reaction tube used for this work is shown in Fig. I-1. This facility and the general experimental procedure have previously been described in several places; *e. g.*, Refs. 14 to 16. In most of the experiments a 97% He-3% O_2 mixture was passed through a microwave discharge and then mixed with the test reagent in a 22-mm i. d. Pyrex reaction tube. The chemiluminescent glows were observed visually and with a Jarrell-Ash 0.5-meter Ebert monochromator, equipped with a 1P28 photomultiplier tube and associated electronics. The pressure in these experiments was ≈ 2 Torr, the temperature $\approx 300^\circ\text{K}$, the initial O-atom concentration, $[\text{O}]_0$, $1.2 \times 10^{15} \text{ cc}^{-1}$, and the average gas velocity 13 m sec^{-1} . In a few experiments under otherwise identical conditions prepurified N_2 was passed through the discharge, and the reaction with N atoms and atomic N-O mixtures was investigated; $[\text{N}]_0$ in these experiments was $4 \times 10^{14} \text{ cc}^{-1}$. The N-O mixtures were produced by partial

[†]The ambient pressure at 90 km is ≈ 1 milli-Torr and at 110 km ≈ 0.05 milli-Torr.^{10a} Pressures on the mixing layer--were a considerable amount of the observed chemiluminescence can be produced--are typically about an order of magnitude higher.⁵

titrations of N atoms with NO, as in some of our earlier work.^{15,17} The reactions of the boron compounds gave rise to the BO- α and β band systems⁸ and the BO₂ fluctuation bands;⁸ the BH 4332 Å system was also present. The relative intensities were different for each of the compounds used: B₂H₆, BCl₃, BF₃, and B(CH₃)₃.

Attempts were also made to establish whether chemi-ionization occurred in any of these reactions; if so, these compounds might also be used for releases leading to ionization (cf. Part II of this report). All the reactions involving boron compounds led to coating of the (stationary) Langmuir probe¹⁴⁻¹⁶ with solids, which made it impossible to establish the occurrence of chemi-ionization with that tool. The reactions of B₂H₆ with O atoms and with N atoms were therefore also investigated using our ion mass spectrometer flow system (cf. Fig. 2 of Ref. 15) where such a coating did not interfere with ion detection, as verified by studying the O-C₂H₂ reaction immediately after the O-B₂H₆ reaction. The results indicated no chemi-ionization in the O-B₂H₆ and N-B₂H₆ reactions.

We will now discuss the results obtained with each of the boron compounds mentioned above.

a. O-B₂H₆: Diborane was supplied by the Callery Chemical Co. The reaction of O-B₂H₆ showed emission in three distinct zones which were in sequence: (1) a blue zone immediately following mixing of the reagent with the O-atom stream; the emission in this zone was predominantly due to BO bands with the BH bands also clearly present. (2) A very bright blue zone, approximately 3 to 5 cm long. In this zone the total intensity was about one order of magnitude higher, but the spectral distribution was about the same as that in zone 1. The position of this zone could be continuously and reproducibly varied from near the B₂H₆ inlet nozzle to the inlet of the pump line (some 2 meters downstream) by varying the B₂H₆ flow rate. (3) Immediately following the bright blue zone 2 a bluish-green zone extending all the way to the pump line was observed which had an initial intensity about two orders of magnitude less than that of zone 2, decreasing further with reaction time. In this zone BO, BH, and also BO₂ emission were present.

b. N-B₂H₆: This reaction produced a blue glow which at its brightest point had an intensity about two orders of magnitude less than that of the O - B₂H₆ reaction in zone 2.

c. O-BCl₃: Boron trichloride was supplied by the Matheson Co. and was used without further purification. The intensity of O - BCl₃ at its brightest point was two orders of magnitude less than that of the O - B₂H₆ reaction in zone 2. The reaction produced a green glow of which the BO₂ fluctuation bands were the dominant component.

d. N-BCl₃: In the reaction of N - BCl₃, a blue glow was observed which was weaker in intensity than that of the O - BCl₃ reactions. When partially substituting O atoms for N atoms in this system, the green glow of BO₂ gradually replaced the blue glow of BO as the [O]/[N] ratio increased.

e. O-BF₃ and N-BF₃: Boron trifluoride was obtained from the Matheson Co. and was used without further purification. At flow rates similar to those used for BCl₃ and B₂H₆, no visible glow could be observed. Only at much higher flow rates (some 20 times higher than the O-atom flow rate) were some weak emissions seen; these may have been due to impurities.

f. O-B(CH₃)₃: B(CH₃)₃ is unavailable as an off-the-shelf chemical and was therefore synthesized in situ. A modification of a procedure described by Brown,¹⁸ i. e., introduction of BF₃ into an n-hexyl ether solution of CH₃MgBr, was used. The B(CH₃)₃ thus formed was trapped with (CH₃)₃N in a dry ice trap. A controlled flow of B(CH₃)₃ was then obtained by passing a known flow of HCl through the trap. Excess HCl was trapped out with Indicarb and the efficiency of conversion was determined by analysis for B(CH₃)₃ downstream from the Indicarb traps, using 1,1-Dianthrimide in aqueous solution as the colorimetric agent.¹⁹

Emission from the O-B(CH₃)₃ reaction at flow rates similar to those used in the B₂H₆ work was some two to three orders of magnitude less than that obtained in the O + B₂H₆ reaction, zone 2.

III. STUDIES AT PRESSURES IN THE 3 TO 30 MILLITORR REGIME

A. Apparatus

A schematic diagram of the flow system is given in Fig. I-2 and a photograph of the apparatus in Fig. I-3. The central part of this system is the 130-cm long, 15-cm i. d., cylindrical Pyrex reaction tube. The flanges on either end of the tube accommodated the gas inlet tubes, pressure measurement stations, and quartz window for end-on observation of the glows. The gas flows were regulated by needle valves. For those materials that have boiling points below room temperature, the inverted pipet method²⁰ was used for measuring flows. For compounds having higher boiling points, CS₂ and Al(CH₃)₃, the flow rate was obtained by measuring the drop of the liquid level in a small pipet; the saturated vapor of these compounds flowed into the vacuum system through a needle valve located above the pipet.

Oxygen atoms were produced by passing either O₂ or a 95% Ar-5% O₂ mixture through the 2450 MHz microwave discharge. The pressure in the discharge zone was always about 0.8 Torr. The partially dissociated gas stream was then expanded through a sonic orifice into the low-pressure reaction vessel. The purpose of the sonic orifice was to keep the flow conditions in the discharge tube constant when the pressure in the reaction tube was varied by throttling the vacuum pumps. By proceeding in this manner, the initial O-atom partial pressure in the reaction tube remained a constant fraction of the total pressure, which made it possible to determine the reaction order by throttling the pump (by partially closing the valve upstream from the pumps). A baffle was placed immediately downstream from the nozzle in such a manner that any "beam" emanating from the nozzle was broken up; this

prevented any beam effects in the observation zone (downstream from the baffle) and guaranteed that the reactions took place near room temperature.^{††}

Initial reaction pressures for each new flow condition were measured with a Pirani gauge (at stations P_1 and P_2), calibrated against the McLeod gauge. The final reported pressure measurement was always made with the McLeod gauge (no measurable pressure drop occurred over the length of the reaction tube).

A 2-in CVC oil diffusion pump backed by a 5 CFM Welch Duo-Seal pump completed the flow system.

Light intensities were measured with a 1P28 tube which viewed the reaction tube directly (Fig. I-3) and could be moved along the length of the reaction tube. The wavelength region detected was about 3000 to 6500 Å. The former limit is due to the short wavelength cut-off of the Pyrex tubes used (roughly corresponding to the atmospheric ozone cut-off)²¹ and the latter is the long wavelength cut-off of the phototube.

B. Procedure and Flow Conditions

As far as possible, all test reagents were studied with the other gases present at the same pressure and concentrations to allow meaningful comparison of the results. The intensity of the O-NO glow for an $[\text{NO}]_0$ of 8×10^{12} molecule cc^{-1} was measured at regular intervals throughout the work to insure unchanging conditions. Small variations in the intensity of this glow occurred, but these did not exceed $\pm 25\%$ of

[†]The kinetic temperature in a molecular beam created by expansion through a nozzle is lower than that of the gas upstream from the nozzle. The gas returns to the latter temperature when the beam is scattered.

^{††}For future work it is recommended that a small baffle (e.g., of about the diameter of the discharge tube) be used instead of the present large baffle because the baffle prevented us from making throttling experiments for the faster reactions (those involving CS_2 and TMA). When for such reactions the system was throttled, the intensity immediately upstream from the baffle--as suggested by visual observation--was one order of magnitude higher than that immediately downstream of the baffle.

the average O-NO glow intensity.[†] The atom concentration obtained with the 95% Ar-5% O₂ discharge was, within experimental error, the same as that obtained with the O₂ discharge, as indicated by the O-NO glow intensity upon NO addition (Fig. I-8). Any major difference in intensity of reactions of the other reagents between the two discharges can therefore be attributed to reactions involving O₂ molecules in the ground ($X^3\Sigma_g^-$) and electronically excited states. Some 10% of the O₂ emanating from an O₂ discharge may be in the a $^1\Delta_g$ state^{22, 23} and a smaller percentage (typically 0.2%, but depending on the "age" of the active oxygen)^{22, 24, 25} in the b $^1\Sigma_g^+$ state. The absolute concentration of excited O₂ molecules produced from a 95% Ar-5% O₂ discharge is of necessity smaller because of the lower O₂ content of the discharge gas.[‡] § By comparing the results of both types of discharges with and without added (ground-state) O₂, one can distinguish between the effect of O₂($X^3\Sigma$) and of O₂(a $^1\Delta$) + O₂(b $^1\Sigma$) on the reactions. This is of importance since appreciable quantities of these species, especially O₂(a $^1\Delta$), are present at release altitudes.^{26, 27}

After the experiments in the absence of additive gas were completed, O₂ was added through the additive nozzle (Fig. I-2). To ascertain that any major effect of added O₂ was due to a chemical rather than a flow effect, these experiments were followed by experiments in which Ar was added at the same flow rates used for O₂ addition. In a few experiments mercury was distilled through the discharge during operation; this led to the deposition of a mercuric oxide mirror which removes the O atoms but not the excited molecules, whose concentration may actually be enhanced.^{22, 28}

In further experiments we studied (1) glow intensity as a function of test reagent flow rate and (2) glow intensity as a function of pressure for constant-volume flow rates.

[†] During the TMA work, no such comparison was made.

[‡] In this report we shall refer to reactions between a compound X and (1) the products of an Ar-O₂ discharge as an Ar-O-O₂-X system, (2) the products of an O₂ discharge as an O-O₂-X system, and (3) the products of an O₂ discharge when an HgO mirror had been deposited as an O₂*-O₂-X system.

[§] The experiments discussed in Section III.G indicate that the concentration of excited O₂ molecules from the Ar-O₂ discharge is vanishingly small.

Except for the experiments in which the total pressure was varied, the pressure was always about 3 milliTorr in the absence of additive gas and was 8 milliTorr[†] at the highest additive flow rates used. The O-atom concentration was not measured in this work. The concentrations in the reaction tube[‡] at 3 milliTorr, were $[\text{Ar}]_0 = 8 \times 10^{13}$, $[\text{O}_2]_0 = 4 \times 10^{12}$ for the Ar-O₂ discharge and $[\text{O}_2]_0 = 8 \times 10^{13}$ for the O₂ discharge (all in molecule cc⁻¹).[§] This corresponded to a total gas flow through the discharge of 5×10^{-2} cc (STP) sec⁻¹. For the experiments with the full pumping capacity in the 3 to 8 milliTorr range, the average gas velocity was about 1 m sec⁻¹, and the average residence time in the reaction tube was thus about 1 sec. The increase in residence time for the throttled pump situation is proportional to the increase in pressure. Because of the rapid axial diffusion at low pressure, one cannot simply relate distance to reaction time--unlike in experiments in the 1-Torr regime.²⁹ For slow reactions one should in fact approach stirred flow reactor conditions.³⁰ However, fast reactions still cause a decrease in intensity with distance from the baffle, from which a qualitative knowledge of relative reaction rates can be obtained. In any given cross section of the reaction tube no intensity nonuniformities (such as those found at milliTorr pressures for very fast reactions in spherical reactors)³¹ could be detected.

The most extensive series of experiments was performed for B₂H₆. Since the work on the other reagents was performed primarily to allow their comparison with the B₂H₆ results, not all the experiments discussed above were carried out for them.

C. Diborane Studies

Diborane was obtained from the Callery Chemical Co. The storage cylinder was kept in a dry ice container from the time of manufacture throughout the course of the work to prevent slow decomposition of this material, which takes place at room temperature.^{32, 33}

In Fig. I-4 the observed light intensities as a function of distance from the baffle (Fig. I-2) are shown for various values of $[\text{B}_2\text{H}_6]_0$. Figure I-4 includes the results obtained with both the Ar-O₂ and the O₂ discharges and the effect of added O₂ on these intensities.^{††}

[†] The pressure in the reaction tube in this regime is proportional to the total volume flow.

[‡] Airco argon and U. S. P. oxygen were used throughout this work.

[§] These values for $[\text{O}_2]_0$ and those given elsewhere in this report neglect the decrease in $[\text{O}_2]_0$ due to dissociation.

^{††} A more tangible idea of the intensities shown can be obtained from the observation that at the highest intensity shown, 2×10^{-6} a. i. u., the chemiluminescence could be seen in a partly lit room, whereas the other glows could be observed only in a completely darkened room. Intensities in the 10^{-9} and 10^{-10} a. i. u., ranges were visually detectable only after an extended period, 10 to 20 min, of dark adaptation.

It can be seen from these results that, except for the very high $[B_2H_6]_0$ value of 4.5×10^{13} molecule cc^{-1} , no appreciable decay in intensity takes place over the length of the reaction tube, which indicates that the reaction is a relatively slow one (compare the results of a fast reaction, $O + CS_2$, which shows a factor of ≈ 50 decay in intensity over the same distance, cf. Section III. F and Fig. I-11).

The reaction is strongly enhanced by the addition of ground-state O_2 as well as by the presence of excited O_2 molecules, as may be seen by comparing the results obtained at $[B_2H_6]_0 = 8 \times 10^{12}$ molecule cc^{-1} for the two discharges in the absence and presence of added ground-state O_2 . The addition of argon instead of O_2 (but at the same flow rates as the O_2) had no noticeable effect on the observed intensities. The effect of added O_2 , for an Ar- O_2 discharge, is also shown in Fig. I-5 for various O_2 concentrations.

By comparing Figs. I-4 and I-5, it may be seen that the intensity of the Ar-O- O_2 - B_2H_6 system for an O_2 concentration of 8×10^{13} molecule cc^{-1} is 4×10^{-8} a. i. u., whereas for an O- O_2 - B_2H_6 system at the same O_2 concentration it is 3×10^{-7} a. i. u. Since the O-atom content for both systems is about the same (cf. Sections III-B and III-D), this difference has to be attributed to the presence of appreciable quantities of excited O_2 molecules (cf. Sections III-B) which apparently enhance the O- B_2H_6 reaction some ten times more strongly[†] than do ground-state O_2 molecules. To ascertain that O atoms are needed to initiate the chemiluminescent B_2H_6 reaction, a mercuric oxide mirror was deposited in the discharge arm. Such mirrors destroy the O atoms but not the excited O_2 molecules (Section III-B). No luminescence could be observed under these circumstances.

Figure I-6 gives the intensity of the Ar-O- O_2 - B_2H_6 system as a function of B_2H_6 flow and shows that the intensity passes through a maximum. This is typical for a reaction in which one of the reactants (O atoms in this case) is involved both in an initial attack step and in one or more of the subsequent steps leading to light emission; i. e., several reaction steps compete for the O atoms and, once their consumption in some initial step becomes appreciable, less atoms are available for the subsequent steps. Similar maxima were obtained using the other reagents, except for NO (Fig. I-9), which reacts directly with O atoms to produce chemiluminescence.

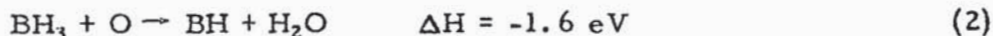
[†]We can assume^{22, 28} the O_2^* concentration for the O_2 discharge to be about 1×10^{13} , i. e., about 10% of the total O_2 . As Fig. I-5 shows, the increase in intensity for addition of a comparable quantity of ground-state O_2 , i. e., an $[O_2]_0$ increase from 7 to 8×10^{13} molecule cc^{-1} , is from about 3.5×10^{-8} to 4×10^{-8} a. i. u.

In Fig. I-7 the intensity of the Ar-O-O₂-B₂H₆ system is shown as a function of the system pressure. Very similar plots were obtained for lower B₂H₆ concentrations (down to 8 x 10¹⁰ molecule cc⁻¹) and for an O₂ instead of an Ar-O₂ discharge. These plots show that the intensity is approximately proportional to the square of the pressure, probably indicating a rate-determining reaction first order in each of the major reactants, *i. e.*, $I \propto [B_2H_6]_0 [O]_0$.

Visual observation of the chemiluminescence in these reactions showed the glow to be pale blue and of similar appearance as observed at 2 Torr (Section II). This observation suggests that the dominant emission is again the BO- α system: BO (A²II-X²Σ). Crude spectral distribution measurements using the phototube with various filters also indicated BO- α bands to be the principal emission. Some speculation regarding the mechanism leading to this emission appears to be in order at this point. No previous studies of the chemiluminescence in the active oxygen-diborane reaction have been reported. However, Fehlner and Strong³⁴ have photochemically studied the mechanism of the overall reaction between O atoms and B₂H₆ near 200 Torr in N₂O. Wolfhard, *et. al.*³⁵ have reported on the chemiluminescence in B₂H₆-O₂ combustion flames at 1 to 15 Torr, which exhibit the BO- α and β bands, BO₂ fluctuation bands, and BH 4332 Å system. These are the same bands found in our 2-Torr work (Section II) and in many other systems involving boron reactions.⁸ Apparently, no mechanisms for the formation of these emitters has yet been suggested. Following Fehlner and Strong,³⁴ we can write the attack step as:



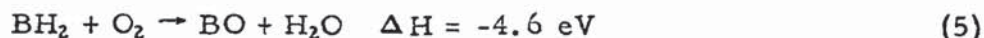
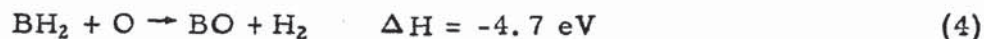
This highest observed vibrational level of the A²II state ($v = 5$) of BO is 3.7 eV above the X²Σ, $v = 0$ level.⁸ Hence, we need a reaction forming BO which is at least 3.7 eV exothermic; reactions between BH₃ and O or O₂ (X³Σ, a¹Δ or b¹Σ) leading to BO all fall short of this goal.[†] We therefore assume hydrogen-stripping reactions as the second step. Such reactions involving O₂ (X³Σ, a¹Δ) are endothermic and hence could not proceed rapidly at ambient temperature, while there probably are insufficient amounts of O₂ (b¹Σ) present to account for much reaction. O-atom reactions, however, are exothermic:



However, Reaction (2) leading to ground-state BH (X¹Σ⁺) is spin-forbidden, which leaves Reaction (3) as the most likely process.[‡] Reaction (3) can now be followed by the sufficiently exothermic reactions:

[†]The heats of formation used in this work are those given in the JANAF Tables. The electronic ground state of the BH compounds involved are: BH (X¹Σ⁺), BH₂ (X²II_u), and BH₃ (X¹A), *cf.* JANAF Tables and Ref. 36.

[‡]There exists³⁷ a relatively low-lying triplet (a³II) of BH whose excitation energy is not known. If it could exothermically be formed in Reaction (2), then reactions involving BH would also have to be considered. BH (X¹Σ⁺; a³II) can produce BO (A²II) by O-atom and O₂-molecule reactions analogous to Reactions (4) and (5).



In the above scheme a three-step mechanism leads to light emission, but it is quite possible that a shorter route exists. Fehlner³⁸ has recently presented evidence that the pyrolysis of diborane proceeds via



instead of via



as had been previously assumed. If we now, by analogy, postulate



followed by Reactions (4) and/or (5), then the light emission would occur in a two-step process. In either event, the proposed scheme can explain the enhancement of the observed emission by O_2 , since once the BH_2 has been formed by O-atom reactions, O_2 as well as O atoms can produce BO in a sufficiently exothermic reaction. The greater efficiency of the excited O_2 molecules relative to ground state molecules can then be explained by a higher reaction rate in Reaction (5) for the former compared to the latter.

The above scheme, of course, is highly speculative, but it explains our (few) observations.

A discussion of the anticipated properties of an upper-atmospheric diborane release is postponed until Section IV. We will now first discuss the observations made with the other compounds to provide the necessary background for that discussion.

D. The O-NO Reaction

The reaction had the familiar whitish-green appearance which increased in visual intensity upon throttling of the pump line. The NO was obtained from the Matheson Co. and was passed through an Indicarb trap for removal of NO_2 . In Fig. I-8 the intensity of the O-NO reaction is shown as a function of distance from the baffle plate (Fig. I-2) for various flow conditions. Little or no decrease in intensity is apparent over the length of the reaction tube, indicating a relatively slow reaction. Comparison between the results of the Ar- O_2 and O_2 discharges for the same NO flow rate shows that both give about an equal intensity. This indicates that the same atom concentration is obtained from both discharges, since, as discussed below, $I \propto [\text{O}][\text{NO}]$. No increase in intensity could be observed upon Ar or O_2 addition to this reaction.

Figure I-9 shows that the glow intensity is, in good approximation, proportional to $[\text{NO}]$, and Fig. I-10 shows that the glow is proportional to the square of the pressure over the 3 to 30 milli-Torr range. These results indicate that the glow intensity I is proportional to $[\text{O}][\text{NO}]_0$ --in agreement with earlier work in this pressure range.^{39, 40} Thus the reaction is--as in the 1-Torr regime⁴¹--of second order; this does not necessarily imply however that the reaction has the same rate constant and mechanism in these two pressure regimes, as has been suggested by other workers.^{39, 40}

E. The O-C₂H₂ Reaction

Airco C₂H₂, purified by passage over silica gel for acetone removal, was used. Figure I-11 shows that at the "standard" concentration ($[\text{C}_2\text{H}_2]_0 = 8 \times 10^{12}$ molecule cc⁻¹) the reaction has a low intensity and is again relatively slow, *i. e.*, little or no decay occurs along the length of the reaction tube. For the Ar and O₂ concentrations given in the figure, the chemiluminescence reached a peak intensity of 3×10^{-9} a. i. u. for $[\text{C}_2\text{H}_2]_0 = 1.6 \times 10^{14}$ molecule cc⁻¹ and decreased again for higher C₂H₂ flows. The low intensity observed (relative to *e. g.*, O-NO) is in agreement with, but not necessarily the complete explanation of, the low intensity of short duration observed in upper-atmospheric releases of this compound.¹² Addition of Ar or O₂ to the reaction resulted in a slight increase in intensity which at the highest additive concentrations used (1.7×10^{14} molecule cc⁻¹) was less than a factor of 2 and was the same for both additives. Hence, no chemical enhancement effect from O₂ appears to occur.

The reaction intensity was too low to allow any visual observation of the color of the glow. The predominant emitters in the O-C₂H₂ reaction at ≈ 1 Torr are CH and C₂; the chemiluminescence in that pressure regime has been discussed in several places, *e. g.*, Refs. 14, 16, and 42, and no further remarks on it appear to be in order.

F. The O-CS₂ Reaction

Merck reagent-grade CS₂ was used without further purification, and a blue luminosity was observed upon its introduction to the reaction vessel. Figure I-11 gives the intensities as a function of distance along the reaction tube. It is immediately apparent that the Ar-O-O₂-CS₂ system differs in one important aspect from all the other reactions studied, *i. e.*, a very pronounced decrease in intensity along the reaction tube occurs. For $[\text{CS}_2]_0 = 1.6 \times 10^{13}$ molecule cc⁻¹, this decrease is by a factor of ≈ 50 over the length of the reaction tube. The B₂H₆ and NO reactions, Figs. I-4 and I-8 show by contrast decreases at even higher concentrations which range from less than a factor of two (B₂H₆) to no observable decrease at all (NO). These results thus indicate that the O-CS₂ reaction is very fast, as has also previously been observed.⁴³ A decrease in CS₂ concentration caused a decrease in the rate of reaction and hence in the rate of intensity change along the reaction tube. This is illustrated by the data for $[\text{CS}_2]_0 = 3.2 \times 10^{11}$ molecule cc⁻¹, which show (within experimental error) no decrease in intensity along the reaction tube. Addition of O₂ or Ar up to a concentration of 1.7×10^{14} molecule cc⁻¹ had no measurable effect upon the chemiluminescent intensity.

The initial intensity of the CS₂ reaction is at least an order of magnitude higher than that of the NO and B₂H₆ reactions under the same reaction conditions (Ar-O₂ discharge).[†] This confirms the findings by Harteck *et. al.*^{31, 43} that this reaction is accompanied by an exceedingly bright chemiluminescence. On the basis of Harteck's observations, upper-atmospheric releases of this compound have been performed. These were unsuccessful,^{11, 13} as the luminescence was too weak to be visible to the naked eye, although detection for about 60 sec by instruments was possible. The present observations show that a very fast decay of the luminescence can occur within a very short period of time (average residence time in our reaction vessel is ≈1 sec). Hence, the number of photons ultimately produced per CS₂ molecule can quite possibly be lower than that of the other reactants even though the initial intensity is much higher. While this may not be the only explanation[‡] for the failure of CS₂ as a release agent, it at least indicates that a high initial intensity is an unreliable measure for making upper-atmospheric release predictions.

G. Trimethyl Aluminum Study

TMA was obtained from the Ethyl Corporation and was used without further purification. The glow from an Ar-O₂ discharge was too weak for visual detection; the glow for an O₂ discharge was bluish-white. The intensities obtained for various flow conditions are shown in Fig. I-12. For both discharges (Ar-O₂ and O₂) the [TMA]₀ given is that which gives a maximum intensity in the absence of additive gas. It was noted, however, that these intensity maxima were not very strongly dependent on flow rate. With the equipment and time available it was impossible to determine complete plots of intensity vs. [TMA]₀. The intensity of the Ar-O-O₂-TMA system is slightly enhanced by addition of a small amount of O₂ (4 x 10¹³ molecule cc⁻¹). As Fig. I-12 shows, addition of further O₂ had no effect on the initial intensity but caused a more rapid decrease in intensity along the reaction tube. Addition of Ar instead of O₂ had no effect on intensity. A similar result was obtained for the O₂ discharge: addition of O₂ showed no enhancement[§] in the initial intensity but caused a decrease in intensity further downstream.

[†] The lower [CS₂]₀ value has to be compared to extrapolated data for B₂H₆ (Fig. I-6) and NO (Fig. I-9).

[‡] Only a complete gas dynamic/chemical kinetic release model, such as is discussed in Part II of this report, would allow a definitive explanation. It is conceivable, for example, that the O-CS₂ reaction--because of its high rate--locally depletes the atmospheric O atoms and that, before further mixing occurs, undesirable side reactions take place that remove the light emitter precursor (SO).⁴³

[§] Probably because of the high O₂ concentration already present.

As in the diborane reactions, the intensity obtained from the O_2 discharge is considerably higher than that obtained from an Ar- O_2 discharge for the same $[O]_0$ and $[O_2]_0$ concentrations (the latter obtained by adding further O_2 through the additive arm). However, contrary to the diborane behavior, electronically excited O_2 molecules by themselves can also produce chemiluminescence with TMA; this was shown in experiments in which an HgO mirror was deposited for removal of the O atoms.[†] These experiments are indicated[‡] as the $O_2^*-O_2$ -TMA system in Fig. I-12, where it may be seen that the intensity of the $O_2^*-O_2$ -TMA system was subject to wide fluctuations. The intensity of 2.5×10^{-8} a. i. u. was obtained with a fresh HgO surface and remained steady for several days. The lower intensity, 3.0×10^{-9} a. i. u., was obtained after the system had been opened to the atmosphere. This apparently affects the capability of the system to produce excited molecules; distilling further Hg through the discharge did not affect this intensity. Addition of 1.7×10^{14} O_2 molecules cc^{-1} had no effect on the chemiluminescent intensity of the $O_2^*-O_2$ -TMA system.

Addition of water vapor between the discharge and the sonic orifice in concentrations in excess of the total O_2 concentration (as judged by the pressure rise in the system) had no effect on the chemiluminescent intensity. Since $O_2(b^1\Sigma)$ molecules are--contrary to $O_2(a^1\Delta)$ --effectively de-excited²² by H_2O , this demonstrates that the observed glow is due to $O_2(a^1\Delta)$ molecules. When the discharge was extinguished no glow could be detected. If we assume^{22, 28} that the discharge produced a 90% ground-state ($X^3\Sigma$) O_2 -10% ($a^1\Delta$) O_2 mixture, then these results show that $O_2(a^1\Delta)$ molecules produce at least 10^4 times as intense a glow as do $O_2(X^3\Sigma)$ molecules in the same concentration. A glow due to the latter species has been observed in earlier work at higher pressures.⁴⁴

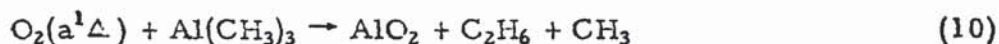
In the presence of the HgO mirror no glow could be detected from an Ar- O_2 discharge i. e., the intensity was at most 10^{-3} times that from the O_2 discharge. This experimentally demonstrates the absence in any appreciable concentration of excited O_2 molecules in the products of an Ar- O_2 discharge and makes it likely that the chemiluminescence in the Ar-O- O_2 -TMA system (in the absence of the HgO mirror) is due to an O-atom reaction, somewhat enhanced by O_2 molecules. While no O and $O_2(a^1\Delta)$ concentrations have been measured in this work, the results given in Fig. I-12 suggest that although reactions of either of these species can produce chemiluminescence, the latter is probably the most efficient in producing the glow. The extent to which each of these species will contribute to the chemiluminescence

[†] The effectiveness of the mirror in removing O atoms was tested with NO addition (instead of TMA addition). No emission could be detected under these circumstances; this showed that the O-atom concentration had been reduced by at least a factor of 10^4 by depositing the mercuric oxide mirror.

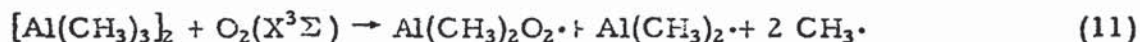
[‡] When O atoms are present the O_2^* molecules are not explicitly mentioned in the figures, e. g., the O- O_2 -TMA system could more exactly have been called an O- O_2 - O_2^* -TMA system.

observed in an upper-atmospheric TMA release will depend in part on their relative concentrations. However, the fact that the Ar-O-TMA system gives an intensity an order of magnitude less than that of the Ar-O-NO system, combined with the fact that TMA produces at least as bright a chemiluminescence in the upper atmosphere as does NO, seems an argument in favor of $O_2(a^1\Delta)$ reactions being the most important in an upper-atmospheric release.

Speculative mechanisms by which O atoms produce a luminescence with TMA have been discussed in the literature.^{3, 44} It seems in order to make some speculations regarding mechanisms by which $O_2(a^1\Delta)$ can produce a glow; we offer the following two processes for consideration:



Reaction (9) involves TMA in the dimeric form, whereas Reaction (10) involves this compound in the monomeric form. It is likely that part of the TMA released in the upper atmosphere is present in the dimeric form.⁴⁵ Some 3 to 4 eV are needed² to excite the unknown emitter of the upper-atmospheric releases. Reaction (9) can therefore adequately describe the formation of the emitter, and no facts presently known about the emission preclude Al_2O_2 as the (an) emitter. Thus, if Reaction (9) is correct, a one-step process describes the formation of the emitter. The monomer, which is present to some unknown extent in the released material, can react following Reaction (10) to produce emission. Its concentration could be enhanced by slow dissociation, following the release. Other reactions can also be considered. For example, the slow oxidation of $[Al(CH_3)_3]_2$ has been suggested⁴⁷ to proceed via the initiation step:



The $Al(CH_3)_2\cdot$ radical could then react with $O_2(a^1\Delta)$ to produce the light emitter. However, such a process seems unlikely since O_2 addition to the $O_2^*-O_2$ -TMA system did not enhance the intensity of the glow.

In the absence of more detailed data on the production of chemiluminescence, any discussion such as the above has to be considered as highly speculative.

† The values of the heats of formation of $Al(CH_3)_3$ and $[Al(CH_3)_3]_2$ are -0.58 and -2.0 eV, respectively.^{45, 46} The heat of formation of AlO_2 is unknown; it has been assumed³ that this compound exists, but this has never been proven.

H. Boron Trimethyl Study

Early in our investigations a brief study of the Ar-O-O₂-B(CH₃)₃ system was performed. As in the work at 2 Torr (Section II), B(CH₃)₃ gave rise to a chemiluminescent intensity at least one order of magnitude less than that of B₂H₆. This work was therefore discontinued. However, these observations do not rule this compound out altogether as a potential release agent, since the effects of O₂(X³Σ) and O₂(a¹Δ) addition were not investigated.

IV. COMPARISON OF DIBORANE WITH PREVIOUSLY USED RELEASE AGENTS; RECOMMENDATIONS

The results of Section III allow us to compare diborane with the other release agents studied. On the basis of this comparison, some reasonable predictions on the upper-atmospheric behavior of diborane can be made. In the present discussion we will use NO as a primary comparison standard. It should be stated first that highly reliable release predictions cannot be made from laboratory experiments alone but can be made only by incorporating the laboratory data into a realistic gas dynamic/chemical kinetic release model. A limited effort in this direction is made in Part II of this report for a release leading to chemi-ionization.

Comparison of Figs. I-6 and I-9 shows that over a large range of concentrations ($[B_2H_6]_0$ or $[NO]_0 \lesssim 3 \times 10^{13}$ molecule cc⁻¹)[†] the intensity of the Ar-O-O₂-B₂H₆ system is very close to that of the Ar-O-O₂-NO system. It therefore appears likely that, due to O-atom reactions alone, B₂H₆ would produce a chemiluminescence with an intensity at least comparable to that of NO.[‡]

Figure I-4 shows, as discussed in Section III.C, that ground-state and excited O₂ molecules cause orders of magnitude enhancements in the intensity of the O-B₂H₆ reaction. It is quite probable that, due to the presence of excited O₂ molecules in the upper atmosphere, cf. Sections III.B and G, the intensity of a B₂H₆ release would exceed that of an NO release at all altitudes. Certainly, however, at altitudes where

[†] The higher concentrations considerably exceed the O-atom concentration which was $\leq 8 \times 10^{12}$ molecule cc⁻¹, i.e., twice the O₂ concentration if no dissociation had occurred in the discharge zone.

[‡] The small amount of O₂ present in the products of an Ar-O₂ discharge due to incomplete dissociation does not affect this conclusion. O₂ does not influence the intensity of the O-NO reaction, and extrapolation to $[O_2]_0 = 0$ molecule cc⁻¹ of the Ar-O-O₂-B₂H₆ intensity in Fig. I-5 shows that the enhancement in intensity due to this amount of O₂ is too small to affect our interpretation. As discussed in Section III.G, excited O₂ molecules are virtually absent in the products of an Ar-O₂ discharge and, hence, do not influence these results.

[O₂] considerably exceeds [O]--i. e., below about 100 km--⁴⁸ diborane should give rise to a much higher intensity than NO or any of the other release agents studied, since it is the only agent whose intensity is continuously enhanced by O₂(X³Σ) molecules in their ground state. It thus appears likely that diborane can be used down to altitudes lower than those at which previously used agents have been successful, i. e., below 78 to 90 km, which is the latitude-dependent⁶ altitude limit of NO and TMA chemiluminescence. Hence, in diborane we may for the first time have a suitable release agent for the mesopause and possibly even for part of the mesosphere. It appears desirable, therefore, that a trail release of diborane be performed, starting at an altitude some 10 to 15 km lower than where chemiluminescence has been observed previously and extending up to the highest altitude practical for a release starting at this lower level. If a bright glow is still observed near the lower limit, further releases could be attempted at even lower altitudes.

These conclusions are further fortified by the fact that the diborane reactions are relatively slow--little decrease in intensity occurs along the length of the reaction tube, cf. Fig. I-4. As discussed in Section III. F, it appears likely that the failure of CS₂ as a release agent is related to its fast decrease in chemiluminescent intensity along the length of the reaction tube; this decrease far exceeds that of any other agent tested.

As already discussed in Section I, the fact that the molecular weights of B₂H₆ (28) and of the principal emitter BO (27) are so close to that of the ambient atmosphere constitutes another strong argument in favor of diborane as a release agent.

It is also possible to produce an argument against diborane as a release agent: The chemiluminescence following an NO release is due to a one-step process:



As discussed in Section III. G, it is conceivable that the TMA chemiluminescence also occurs as a one-step process, i. e., Reaction (9). If this were correct, then both of the presently known successful chemiluminescent release agents undergo one-step chemiluminescent reactions. Because of the rapid diffusion in the upper atmosphere, multistep processes such as the diborane reactions would seem to be at a disadvantage. However, in view of the highly speculative nature of Reaction (9), this presently appears to be a weak argument against a diborane release. In the opinion of the authors, the arguments in favor of diborane presented above appear strong enough to make it worthwhile to attempt a release of this material.

V. CONCLUSIONS

Our major conclusions from this work are:

1. The chemiluminescent intensity of the O-B₂H₆ reaction is strongly enhanced by the presence of O₂ molecules. Excited O₂ molecules, predominantly in the (a¹Δ_g) state, are about 10 times as effective in causing this increase as are electronic ground-state O₂ molecules. Oxygen atoms are needed to initiate the chemiluminescent reaction.
2. This strong enhancement by ground-state O₂ molecules is typical for B₂H₆; no such enhancement was observed for the other release agents tested (NO, TMA, C₂H₂, and CS₂).
3. At altitudes where [O] < [O₂], it is expected that the brightness of a diborane release will be comparable to that of an NO release. At altitudes where [O₂] >> [O]--i. e., below about 100 km--it is expected that a diborane release would yield a chemiluminescent intensity much higher than that of any previously used release agent. It appears likely therefore that diborane can be used down to altitudes lower than those at which those previously used agents have been successful.
4. The molecular weights of B₂H₆ (28) and of the principal emitter BO (27) are very close to that of the ambient atmosphere over the altitude region of potential interest (30 to 200 km), which suggests that diborane is a good release agent for making diffusion measurements.
5. In view of the above, it is recommended that a release of diborane be attempted.
6. TMA produces a very weak chemiluminescence in its reaction with O atoms but a much more intense luminescence upon reaction with O₂(a¹Δ_g) molecules (both in the absence and in the presence of O atoms). O₂(a¹Δ_g) molecules produce at least 10⁴ times as intense a glow as do ground-state O₂ molecules in the same concentration. It appears quite possible that the well-known upper-atmospheric chemiluminescence following TMA releases is due primarily to excited O₂ molecule reactions.

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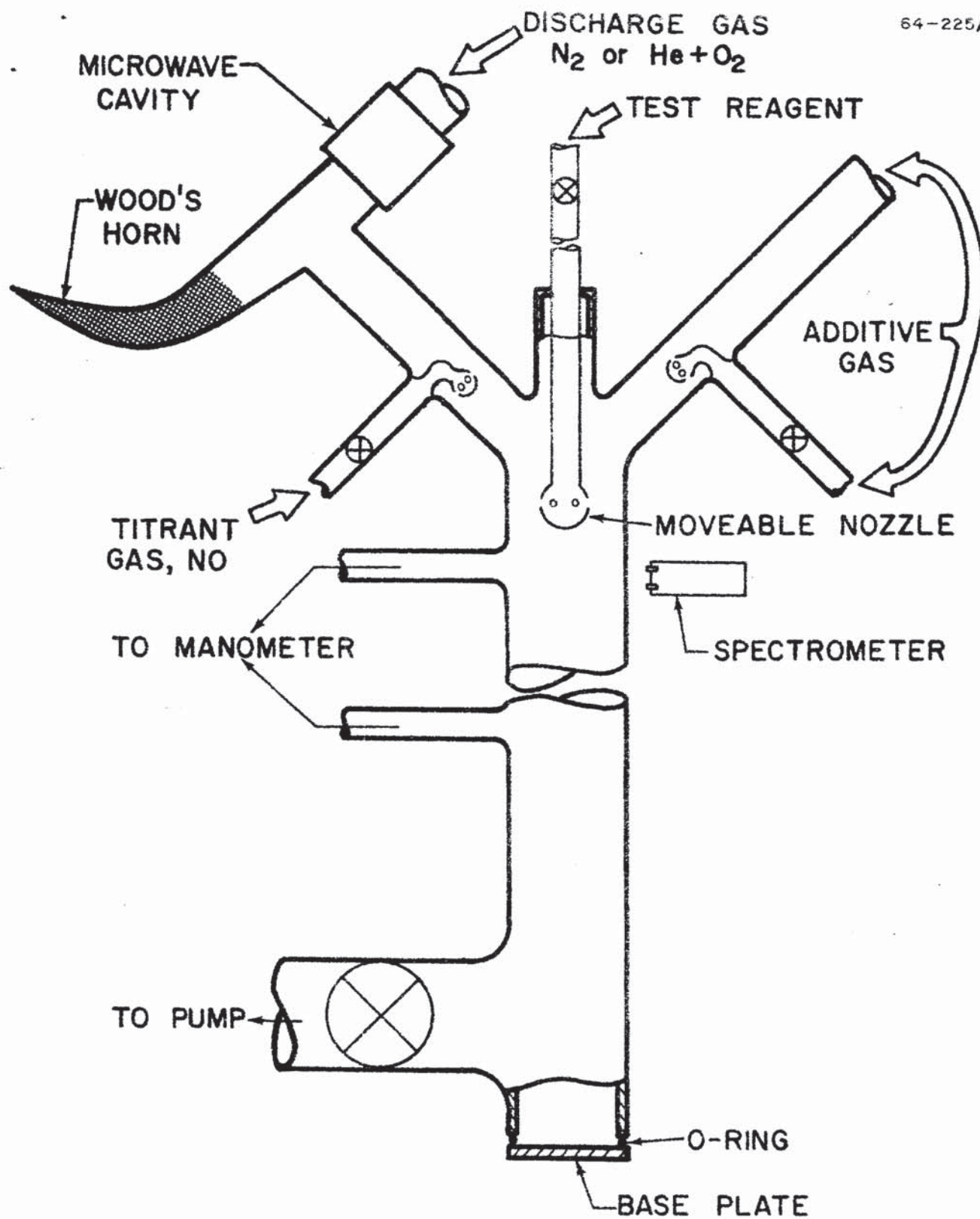


FIG. I-1 SCHEMATIC DIAGRAM OF REACTION TUBE FOR STUDIES AND PRESSURES OF ≈ 2 TORR

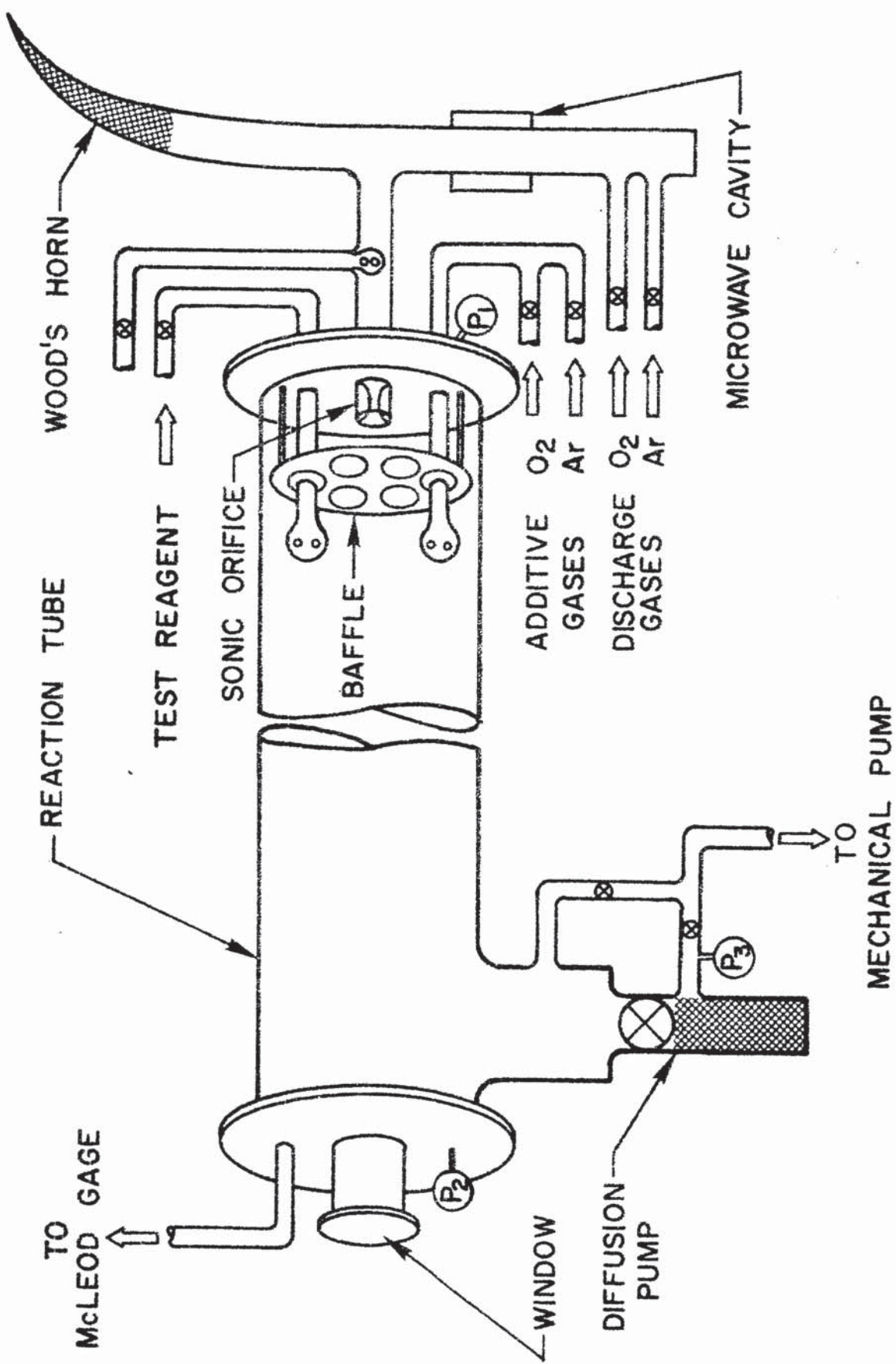


FIG. I-2 SCHEMATIC DIAGRAM OF APPARATUS FOR STUDIES AT LOW PRESSURES

Reaction tube is made from 15-cm diam Pyrex pipe.
 P₁, P₂, and P₃ indicate Pirani gauge stations.

66-66

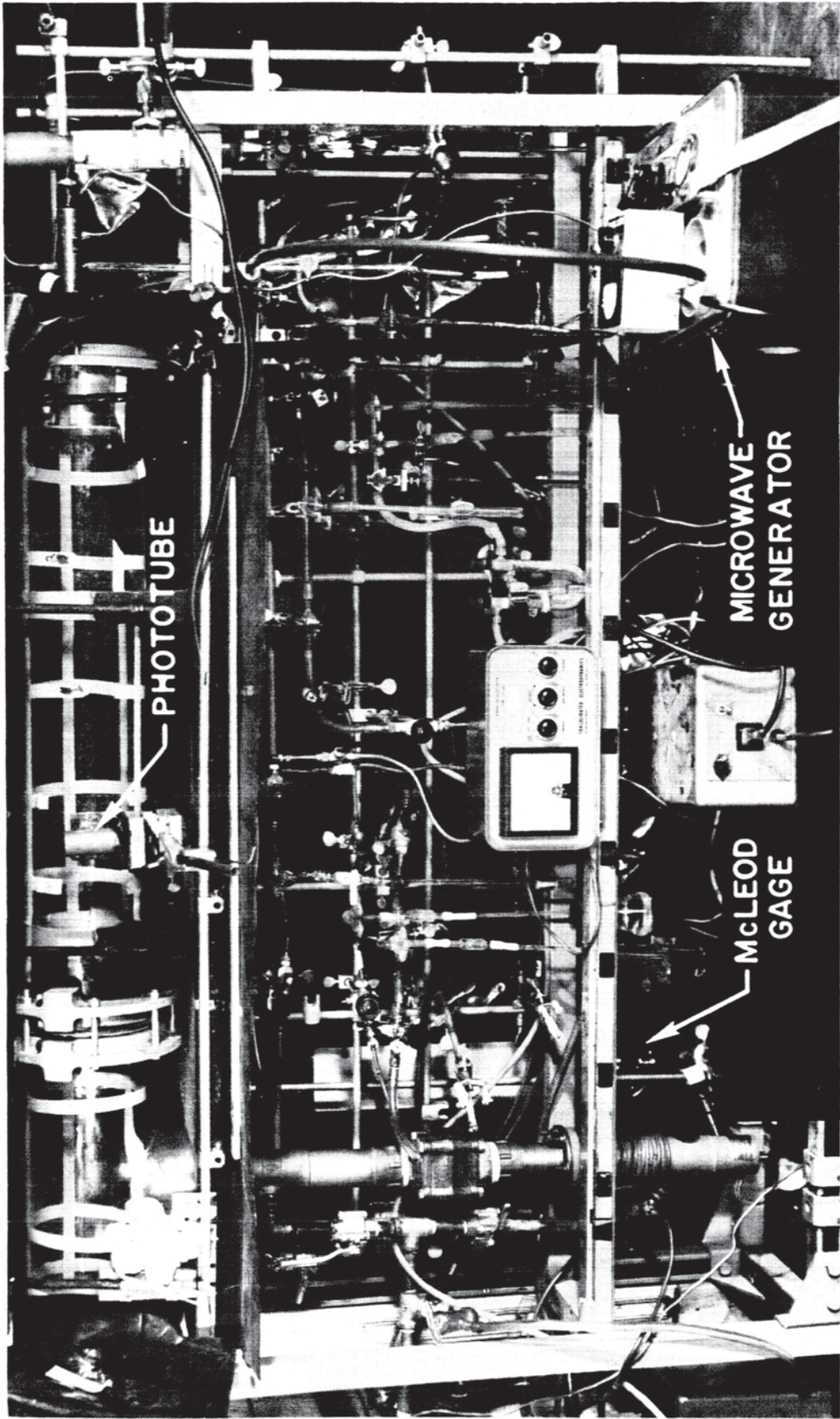


FIG. I-3 APPARATUS FOR STUDIES AT LOW PRESSURES

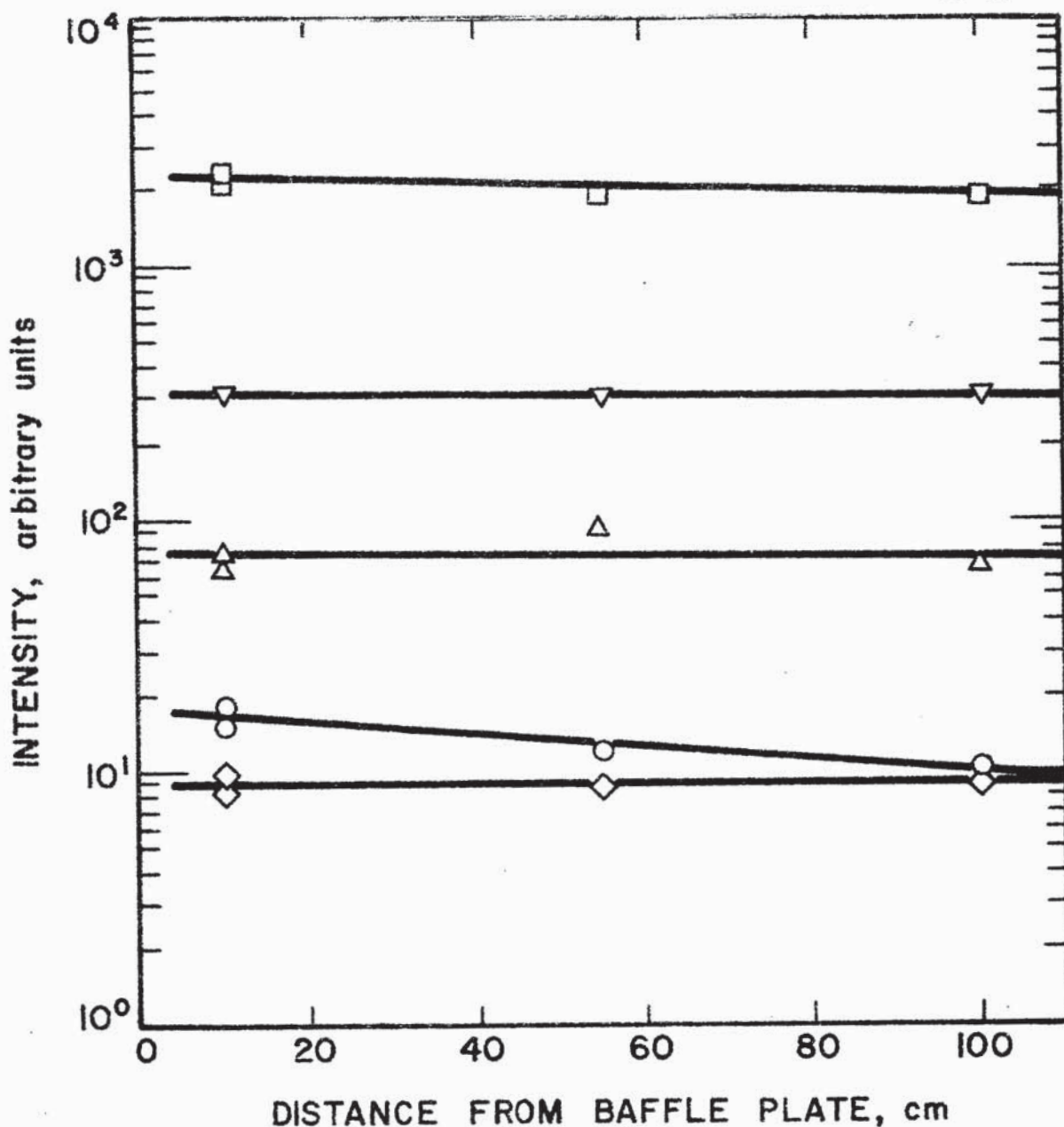


FIG. I-4 INTENSITY OF THE B_2H_6 REACTIONS AS A FUNCTION OF DISTANCE ALONG THE REACTION TUBE FOR VARIOUS FLOW CONDITIONS

The intensity is expressed in arbitrary units, *i. e.* phototube current $\times 10^9$.

Concentrations are given below in molecule cc^{-1} . Unless otherwise mentioned, P without added O_2 is 3 milliTorr and with added O_2 is 8 milliTorr.

- ◇: Ar- O_2 - B_2H_6 system: $[Ar]_0 = 8 \times 10^{13}$; $[O_2]_0 = 4 \times 10^{12}$; $[B_2H_6]_0 = 8 \times 10^{12}$
- : Ar- O_2 - B_2H_6 system: $[Ar]_0 = 8 \times 10^{13}$; $[O_2]_0 = 4 \times 10^{12}$; $[B_2H_6]_0 = 4.5 \times 10^{13}$; P = 5 milliTorr
- △: Ar- O_2 - B_2H_6 system with added O_2 : $[Ar]_0 = 8 \times 10^{13}$; $[O_2]_0 = 1.7 \times 10^{14}$; $[B_2H_6]_0 = 8 \times 10^{12}$
- ▽: O_2 - B_2H_6 system: $[O_2]_0 = 8 \times 10^{13}$; $[B_2H_6]_0 = 8 \times 10^{12}$
- : O_2 - B_2H_6 system with added O_2 : $[O_2]_0 = 2.5 \times 10^{14}$; $[B_2H_6]_0 = 8 \times 10^{12}$

66-33A

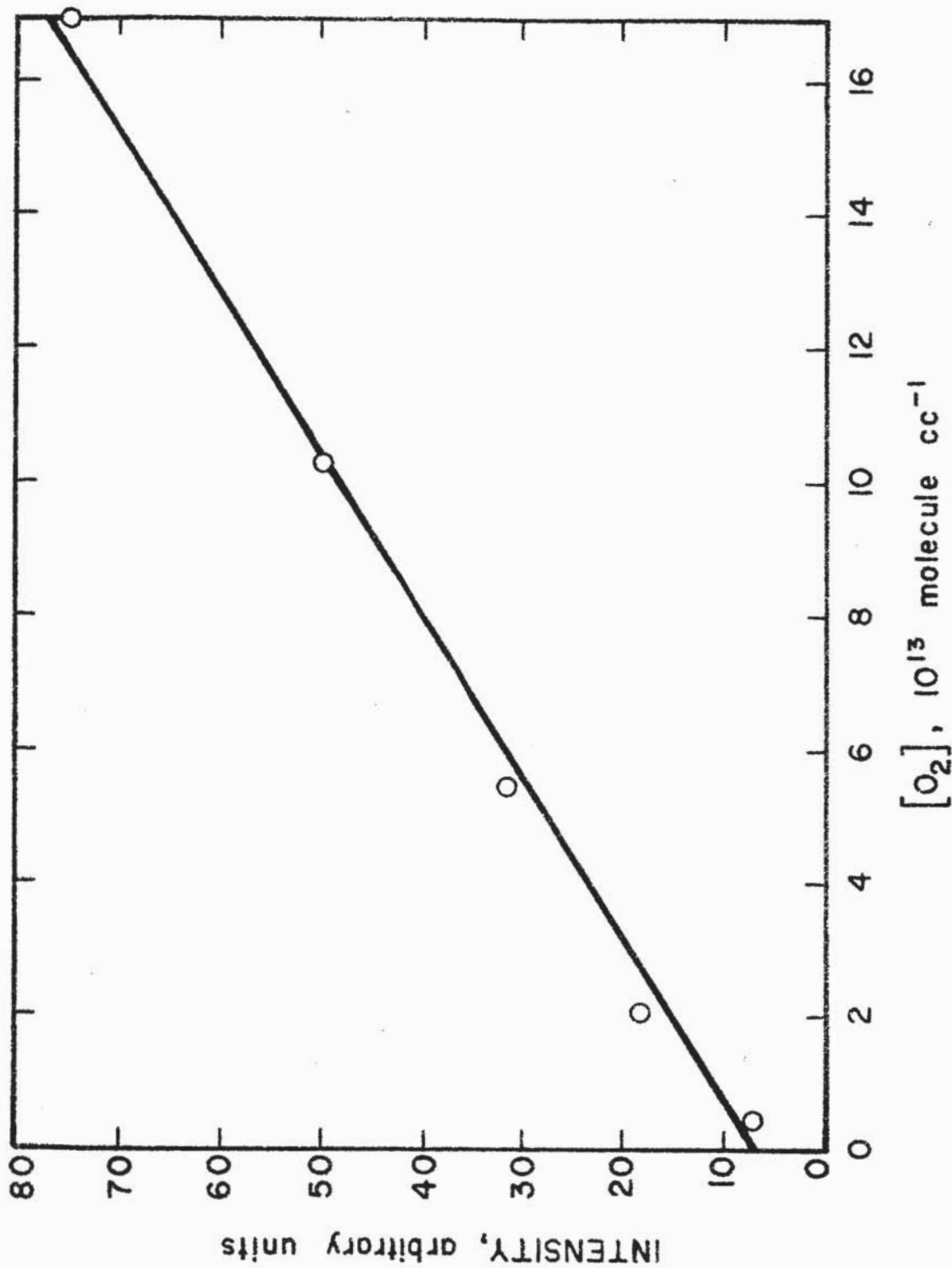


FIG. 1-5 EFFECT OF O₂ ON LIGHT INTENSITY OF THE Ar-O₂-B₂H₆ SYSTEM

Intensity is expressed in arbitrary units, i. e. phototube current $\times 10^9$.

The abscissa gives the total O₂ concentration (discharge gas + additive gas).

The point closest to the ordinate is thus that for no O₂ addition, for which $P = 3$ milli Torr.

Other concentrations: $[Ar]_0 = 8 \times 10^{13}$; $[B_2H_6]_0 = 8 \times 10^{12}$ molecule cc⁻¹; phototube position: 10 cm from baffle plate.

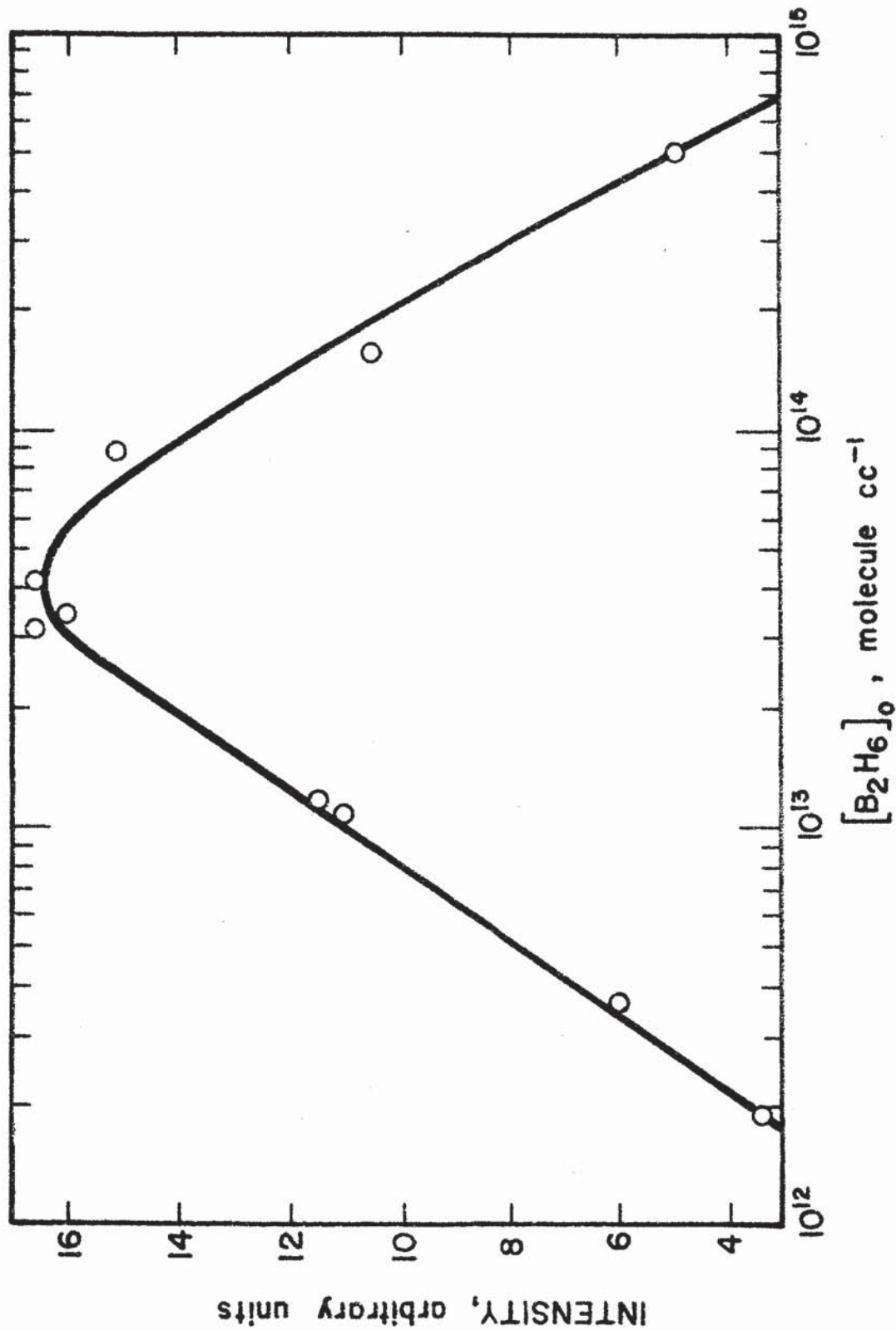


FIG. I-6 INTENSITY AS A FUNCTION OF $[B_2H_6]_0$ FOR THE Ar-O₂-B₂H₆ SYSTEM

Intensity is expressed in arbitrary units, i. e. phototube current $\times 10^9$.

Other concentrations: $[Ar]_0 = 8 \times 10^{13}$; $[O_2]_0 = 4 \times 10^{12}$ molecule cc^{-1} .

Pressure in the absence of B₂H₆ is 3 milli Torr. Phototube position:
10 cm from baffle plate.

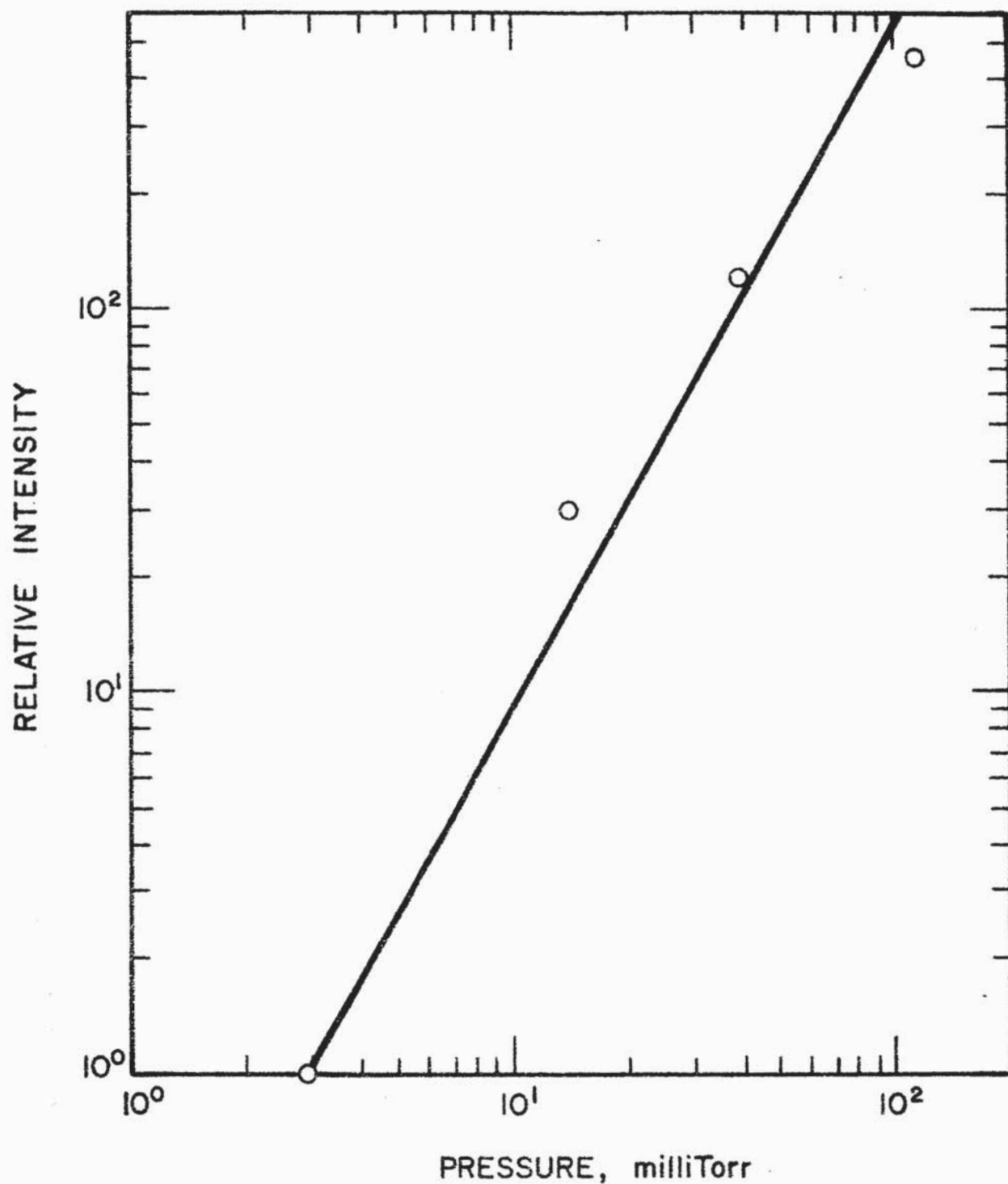


FIG. I-7 EFFECT OF PRESSURE INCREASE AT CONSTANT VOLUME FLOW RATE ON LIGHT INTENSITY OF THE Ar-O₂-B₂H₆ SYSTEM

Light intensities are relative to their 3-milliTorr value. Concentrations at 3 milliTorr: [Ar]₀ = 8 × 10¹³; [O₂]₀ = 4 × 10¹²; [B₂H₆]₀ = 8 × 10¹² molecule cc⁻¹. Phototube position: 10 cm from baffle plate.

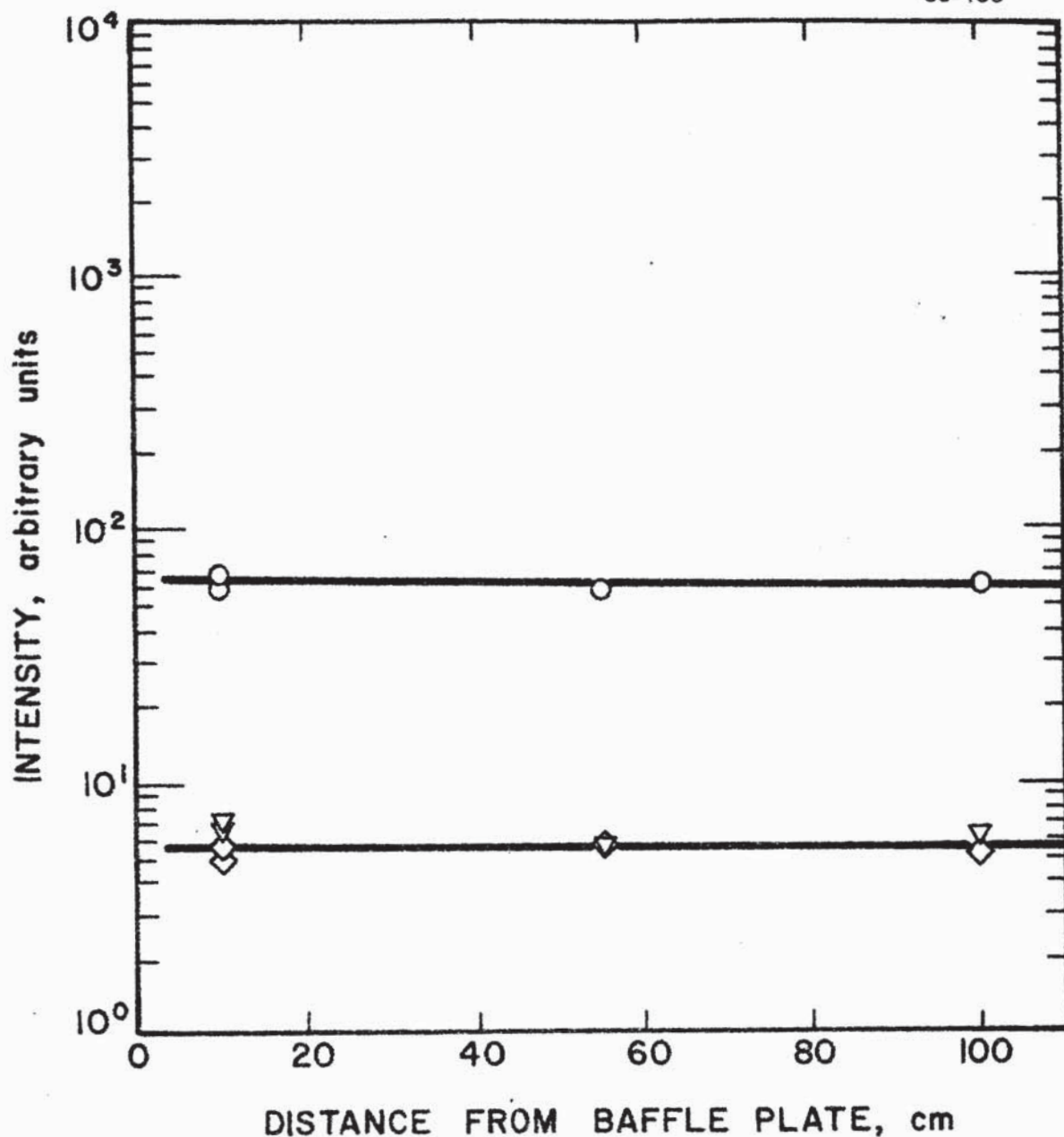


FIG. I-8 INTENSITY OF THE NO-O₂ REACTION AS A FUNCTION OF DISTANCE ALONG THE REACTION TUBE FOR VARIOUS FLOW CONDITIONS

Intensity is expressed in arbitrary units, *i. e.* phototube current $\times 10^9$. Concentrations are given below in molecule cc^{-1} .

- ◇: Ar-O₂-NO system: $[\text{Ar}]_0 = 8 \times 10^{13}$; $[\text{O}_2]_0 = 4 \times 10^{12}$; $[\text{NO}]_0 = 8 \times 10^{12}$; $P = 3$ milliTorr.
- : Ar-O₂-NO system: $[\text{Ar}]_0 = 8 \times 10^{13}$; $[\text{O}_2]_0 = 4 \times 10^{12}$; $[\text{NO}]_0 = 8 \times 10^{13}$; $P = 6$ milliTorr.
- ▽: O₂-NO system: $[\text{O}_2]_0 = 8 \times 10^{13}$; $[\text{NO}]_0 = 8 \times 10^{12}$; $P = 3$ milliTorr.

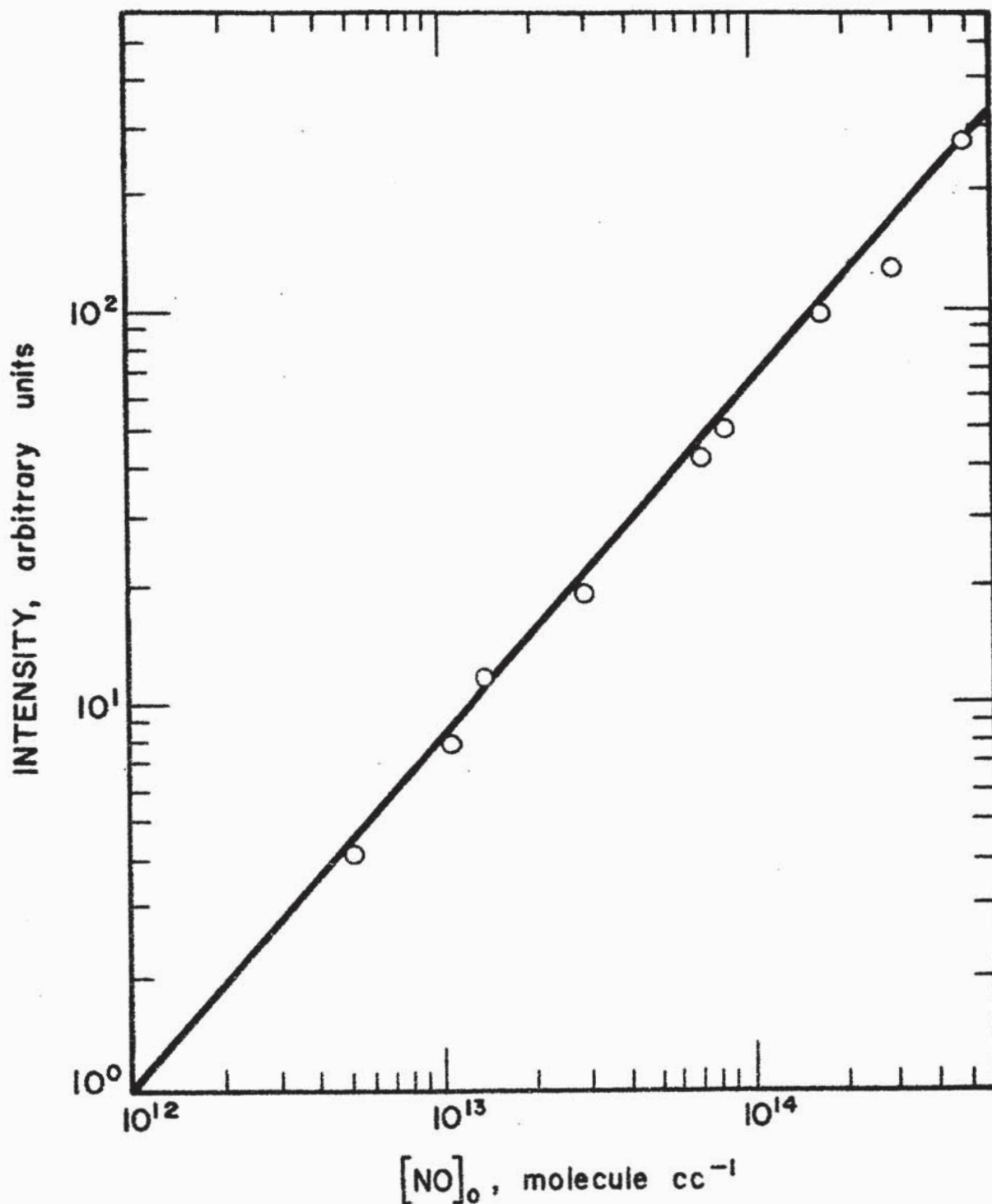


FIG. I-9 INTENSITY AS A FUNCTION OF $[\text{NO}]_0$ FOR THE Ar-O-O₂-NO SYSTEM
 Intensity is expressed in arbitrary units, *i. e.* phototube current $\times 10^9$.
 Other concentrations: $[\text{Ar}]_0 = 8 \times 10^{13}$; $[\text{O}_2]_0 = 4 \times 10^{12}$ molecule cc^{-1} .
 Pressure in the absence of NO is 3 milli Torr. Phototube position:
 10 cm from baffle plate.

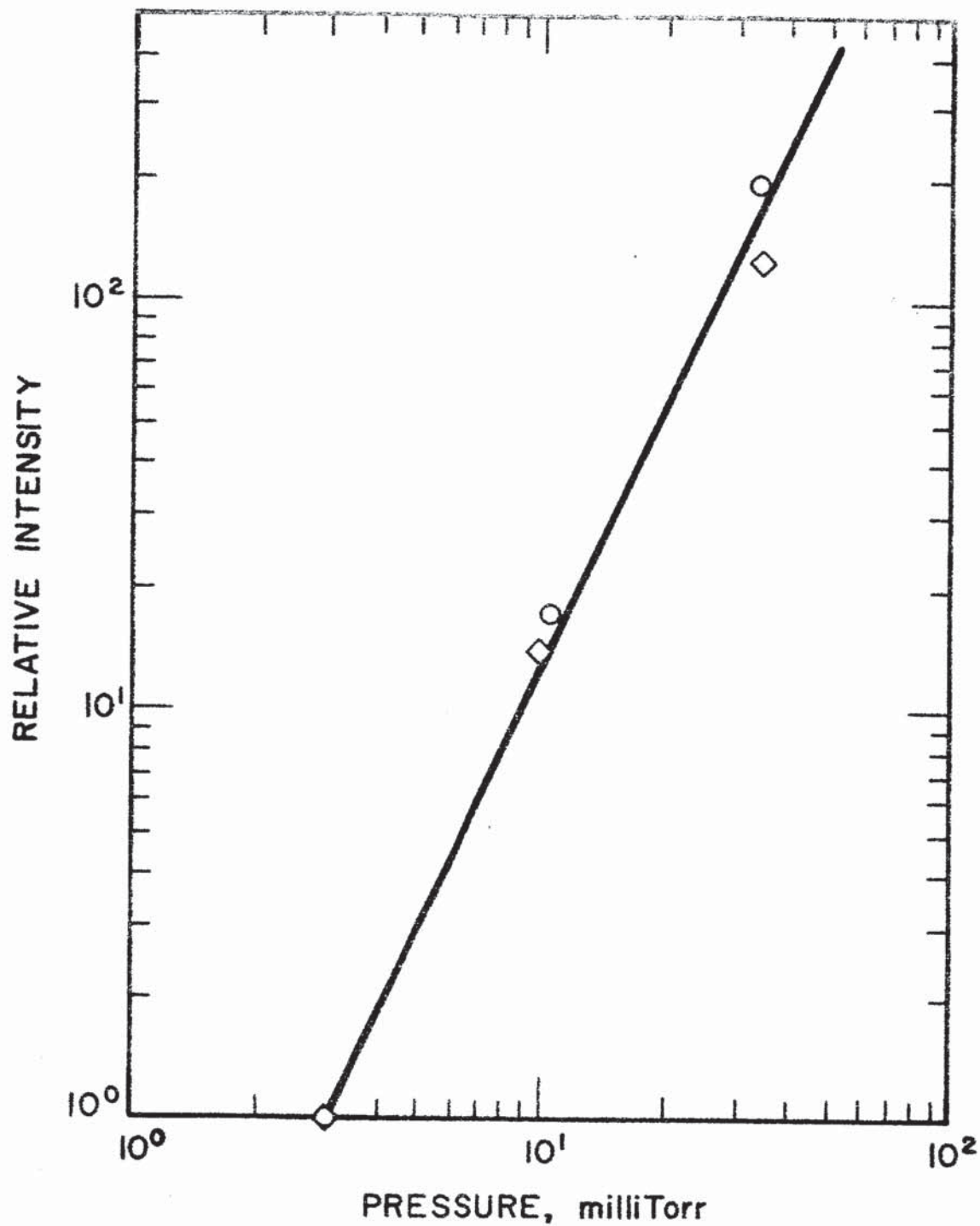


FIG. I-10 EFFECT OF PRESSURE INCREASE AT CONSTANT VOLUME FLOW RATE ON LIGHT INTENSITY OF THE Ar-O-O₂-NO SYSTEM

Light intensities are relative to their 3 milliTorr values.

Concentrations at 3 milliTorr in molecule cc⁻¹: [Ar]₀ = 8 × 10¹³;
[O₂]₀ = 4 × 10¹².

◇: [NO]₀ = 8 × 10¹² molecule cc⁻¹

○: [NO]₀ = 8 × 10¹¹ molecule cc⁻¹

Phototube position: 10 cm from baffle plate.

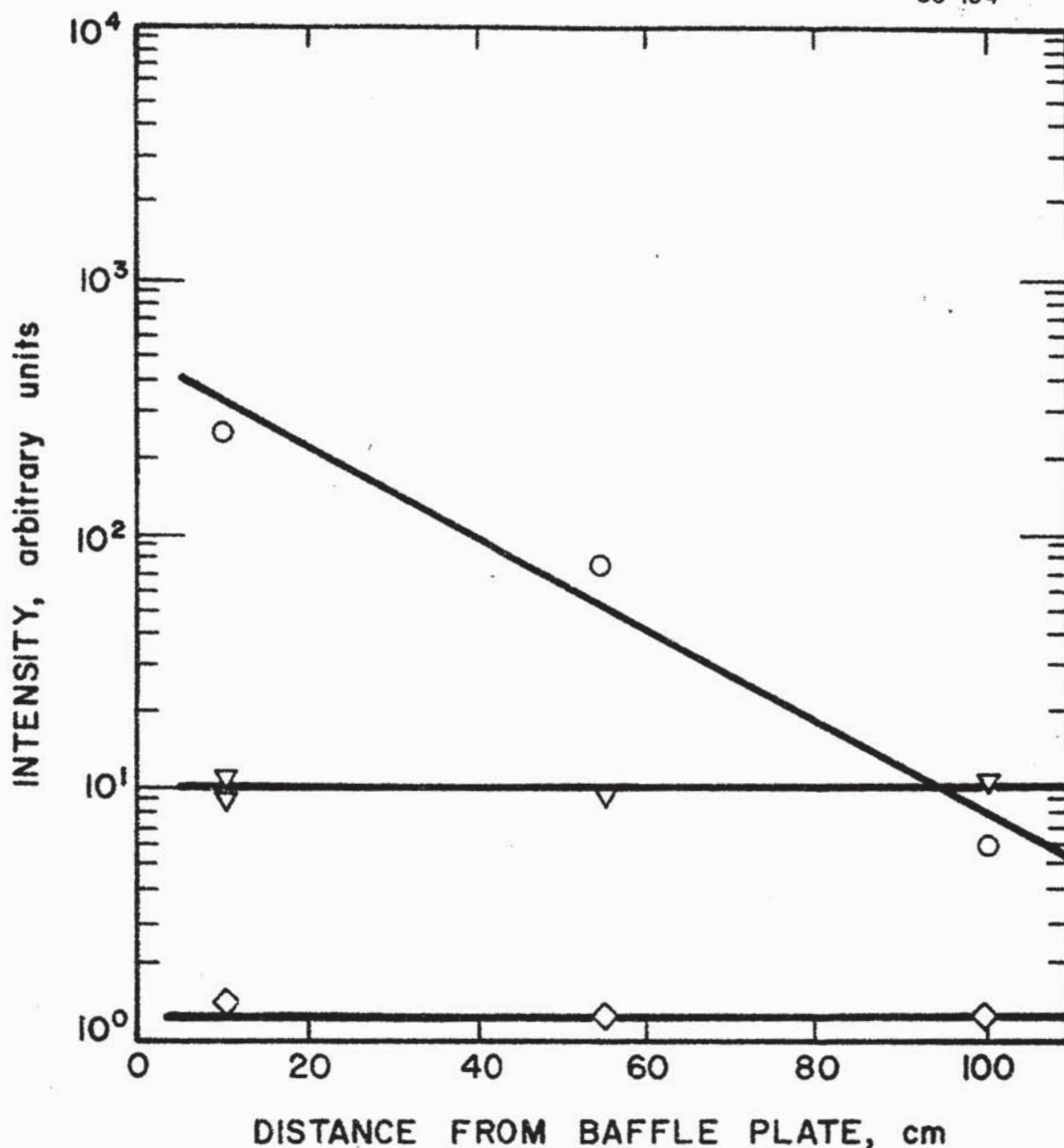


FIG. I-11 INTENSITY OF THE Ar-O-O₂-C₂H₂ AND Ar-O-O₂-CS₂ SYSTEMS AS A FUNCTION OF DISTANCE ALONG THE REACTION TUBE FOR VARIOUS FLOW CONDITIONS

Intensity is expressed in arbitrary units, *i.e.* phototube current $\times 10^9$.

Concentrations are given below in molecule cc^{-1} . $P = 3$ milli Torr.

- ◇: Ar-O-O₂-C₂H₂ system: $[\text{Ar}]_0 = 8 \times 10^{13}$; $[\text{O}_2]_0 = 4 \times 10^{12}$; $[\text{C}_2\text{H}_2]_0 = 8 \times 10^{12}$
- : Ar-O-O₂-CS₂ system: $[\text{Ar}]_0 = 8 \times 10^{13}$; $[\text{O}_2]_0 = 4 \times 10^{12}$; $[\text{CS}_2]_0 = 1.6 \times 10^{13}$
- ▽: Ar-O-O₂-CS₂ system: $[\text{Ar}]_0 = 8 \times 10^{13}$; $[\text{O}_2]_0 = 4 \times 10^{12}$; $[\text{CS}_2]_0 = 3.2 \times 10^{11}$

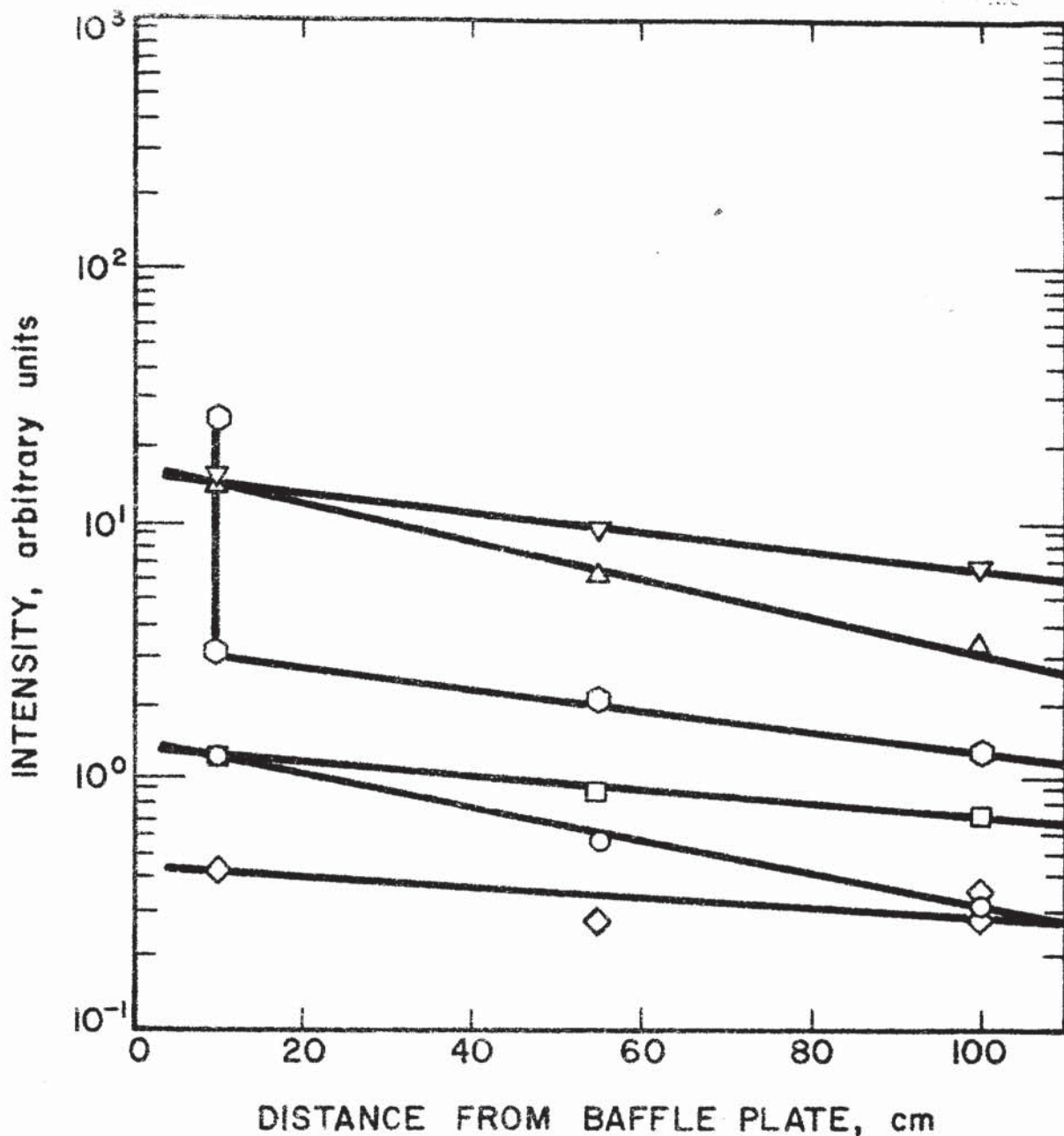


FIG. I-12 INTENSITY OF THE TMA REACTIONS AS A FUNCTION OF DISTANCE ALONG THE REACTION TUBE FOR VARIOUS FLOW CONDITIONS

Intensity is expressed in arbitrary units, *i.e.*, phototube current $\times 10^9$.

Concentrations are given below in molecule cc^{-1} .

- ◇: Ar-O-O₂-TMA system: $[\text{Ar}]_0 = 8 \times 10^{13}$; $[\text{O}_2]_0 = 4 \times 10^{12}$; $[\text{TMA}]_0 = 1.4 \times 10^{13}$; $P = 3$ milliTorr
- : Ar-O-O₂-TMA system with added O₂: $[\text{Ar}]_0 = 8 \times 10^{13}$; $[\text{O}_2]_0 = 4.0 \times 10^{13}$; $[\text{TMA}]_0 = 1.4 \times 10^{13}$; $P = 4$ milliTorr
- : Ar-O-O₂-TMA system with added O₂: $[\text{Ar}]_0 = 8 \times 10^{13}$; $[\text{O}_2]_0 = 1.7 \times 10^{14}$; $[\text{TMA}]_0 = 1.4 \times 10^{13}$; $P = 8$ milliTorr
- ▽: O-O₂-TMA system: $[\text{O}_2]_0 = 8 \times 10^{13}$; $[\text{TMA}]_0 = 4.3 \times 10^{13}$; $P = 4$ milliTorr
- △: O-O₂-TMA system with added O₂: $[\text{O}_2]_0 = 2.5 \times 10^{14}$; $[\text{TMA}]_0 = 4.3 \times 10^{13}$; $P = 8$ milliTorr
- : O₂*-O₂-TMA system: $[\text{O}_2]_0 = 8 \times 10^{13}$; $[\text{TMA}]_0 = 1 \times 10^{13}$; $P = 3$ milliTorr

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PART II. A MODEL OF RELEASES LEADING TO UPPER-
ATMOSPHERIC CHEMI-ION FORMATION

H. S. Pergament, A. Fontijn and G. D. Bleich

I. INTRODUCTION

This phase of the program was designed to establish whether observation of upper-atmospheric chemical releases leading to enhanced ionospheric free electron concentrations by chemi-ionization is feasible. This type of release offers several unique advantages over existing techniques:

1. Chemiluminescence can only be observed at night and resonance radiation measurements are restricted to twilight hours, whereas electron clouds can be observed at any time. Hence, mass motion studies and hopefully--after development of a suitable upper-atmospheric model--atom concentration measurements can also be made in the daytime.
2. Electrons can also be produced by explosive releases of cesium,¹ but they can be observed at night for relatively short periods only, since all the electrons are produced at the instant of release. In the daytime, where photo-ionization of the cesium also occurs, the electron distribution depends on the rate of diffusion of this heavy element (molecular weight 133), which is quite different from that of the ambient species. By contrast, the production of electrons from C_2H_2 (the chemi-ionizing release agent considered in this study) proceeds for a long time, and this species (molecular weight 26) will diffuse at a rate comparable to that of the ambient species; hence, meaningful daytime diffusion measurements could be made with it.

An analysis of a point (spherical) release, including diffusion and chemical kinetics, is presented here. An exact numerical solution is obtained for the equations describing the electron density distribution in time and space. C_2H_2 was selected as the release agent for this feasibility study because it offers the highest known chemi-ionization rate with upper-atmospheric constituents.² Its selection needs justification, however, since no enhanced ionization was observed³ in Project Firefly releases of this compound (NETTY and OLGA). There are two reasons why chemi-ionization, which was not observable at that time, might still have occurred in these releases.

1. NETTY and OLGA were trail releases. An elongated cylinder, formed in a trail release, presents a difficult target for ionosonde observations.³ We have therefore made our calculations for a point release, which is far easier to observe.
2. Sporadic E-layer ionization occurred simultaneously with the Project Firefly releases. This ionization was sufficiently strong to blank out any expected effect from the trail release.⁴ For a future release it is necessary that no sporadic E activity be present in the last minutes preceding the release.

In developing the upper-atmospheric model it is necessary to utilize a chemical reaction mechanism which describes the electron formation, recombination, and attachment processes. Since no ionization kinetic data are available at the pressures of interest (≈ 1 milli Torr), we have utilized laboratory data at 1 Torr to infer a

reaction mechanism. The development of this mechanism is discussed in the next section. In the remainder of this report we derive the equations for the upper-atmospheric model, outline the development of a digital computer program used to obtain a solution to these equations, and make specific calculations which show the feasibility of using C_2H_2 as a chemi-ionizing release agent.

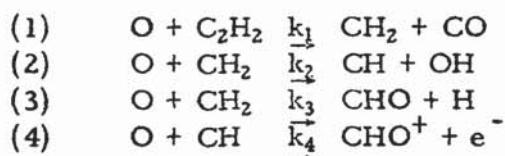
II. REACTION MECHANISM

Generally, the reactions needed to describe the upper-atmospheric release chemistry can be divided into two categories: A set of reactions that produces electrons and one that removes electrons. It is certainly possible to a priori prescribe a reasonable (but unsubstantiated) set of reactions that will describe both processes. However, the accuracy of the predicted upper-atmospheric results will depend upon the adequacy of the mechanism and the accuracy of the rate constants.

Since laboratory data are available for the acetylene-atomic oxygen reaction at 1 Torr, we chose to develop an ion (electron)-producing reaction mechanism which is consistent with the available data at this pressure. The two primary pieces of information available were (1) the rate of ion production for O-atom-rich mixtures⁵ and (2) the observation^{2,6} that the peak rate of ion production in the laboratory occurs at about 1 millisecond after the initial reactants are mixed. While it is realized that these data are meager, they can still be utilized, with proper interpretation, to get reasonable values for the rate constants of the electron production mechanism.

The following procedure was used to obtain the mechanism and rate constants: First, an ion-producing reaction mechanism consistent with present knowledge was chosen and a set of rate constants assumed. Next, the conditions under which the laboratory data were taken were described mathematically by a set of ordinary differential equations which describe the time rate of concentration change of individual species. A standard Runge-Kutta/predictor-corrector integration procedure was used to obtain the solution to these equations.[†] Finally, a solution to the set of ordinary differential equations was obtained (using an IBM 7090/94) and the rate of ion production examined as a function of time. When a set of rate constants was found that duplicated the aforementioned laboratory data, the procedure was completed. We then utilized this mechanism and rate constants for the electron-producing reactions following the upper-atmospheric release of C_2H_2 .

The following basic mechanism was selected to describe the ion production:



[†]This integration package may be found in the IBM SHARE program library (Subroutine RWINT, Distribution No. 602).

k_1 has been measured in the laboratory⁷ to be about 1×10^{-13} cc sec⁻¹ and was fixed at this value; k_4 has been estimated both theoretically and experimentally⁸ to be on the order of 10^{-11} to 10^{-12} cc sec⁻¹. Moreover, the experimental results indicate that one chemi-ion is formed for about every 10^2 to 10^3 C₂H₂ molecules reacted; this fixes $k_3/k_2 > 10^2$.

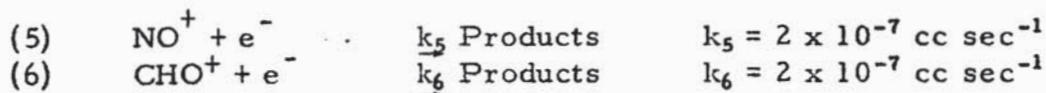
In the computer experiments k_2 , k_3 , and k_4 were systematically varied in order to get agreement with the laboratory data. The desired results have been obtained with the following set of rate constants:

$$\begin{aligned} k_2 &= 5 \times 10^{-14} \text{ cc sec}^{-1} \\ k_3 &= 1 \times 10^{-10} \text{ cc sec}^{-1} \\ k_4 &= 3 \times 10^{-12} \text{ cc sec}^{-1} \end{aligned}$$

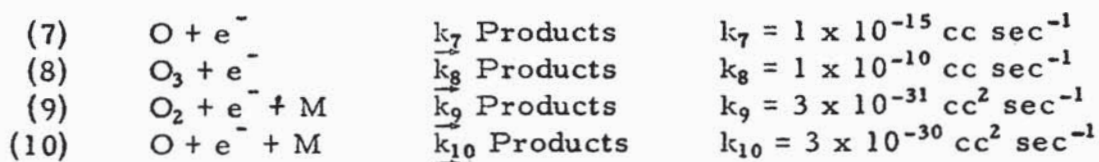
Using the above rate constants in the computer program gives the results shown in Fig. II-1 for the rate of positive ion production (dn_{CHO^+}/dt). The initial acetylene and O-atom concentrations are listed in the figure. The laboratory measurements for these initial concentrations gave⁵ $dn_{\text{CHO}^+}/dt = 7.2 \times 10^{12}$ ions cc⁻¹ sec⁻¹ at 4×10^{-3} sec. Thus, since the peak rate of ion production occurs at about 1 millisecond, the two essential pieces of laboratory data have been accounted for with the above mechanism and rate constants. A study of the uniqueness of this solution indicates that: (1) the time at which the peak rate of ion production occurs is relatively independent of k_2 and (2) the rate of ion production at times greater than about 1 millisecond is a function of k_3/k_2 , for fixed values of k_1 and k_4 . Thus, other solutions could be obtained which would match the given data. However, the rate constants listed above are all reasonable in view of present chemical kinetic knowledge. Considering that this comparison was made at pressures of 1 Torr (rather than 1 milli-Torr) and that we are only making a feasibility study, the rate constants found by this method are considered to be quite adequate.

The following set of electron-depletion reactions have been included in the upper-atmospheric model:

Recombination Reactions⁹⁻¹¹



Attachment Reactions^{12, 13}



where M is an arbitrary third body. The above values have been taken from the best available experimental data.

III. FORMULATION OF A MODEL FOR UPPER-ATMOSPHERIC POINT RELEASES

Previous theoretical treatments of diffusion and chemical reactions with spherical symmetry have been motivated primarily by the problem of predicting the light emission from chemiluminescent reactions.¹⁴ The mathematical formulation of the problem can be divided into two parts, viz. (1) the period immediately following the release, during which pressure equilibration is achieved, and (2) the subsequent analysis of diffusion and chemical reaction once the ambient pressure has been reached. Part (1) has been extensively studied by Groves,¹⁵ who extended the earlier work of Brode¹⁶ and compared his own results with data obtained from Project Firefly releases. Previous analyses^{14,17} of Part (2) have used analog computer techniques to solve the set of partial differential equations. A recent study of closed-form solutions for idealized upper-atmospheric chemical releases has been carried out by Rosner,¹⁸ who examined two limiting cases for a one-step irreversible chemical reaction: first, the diffusion-controlled ("thin flame") limit in which reaction rates are fast compared to diffusion and, second, in the other extreme, very slow reaction rates.

The set of differential equations which describe the diffusion process with chemical reactions are formulated with the following assumptions:

1. spherical symmetry
2. constant pressure (equal to the ambient pressure at the center of the release)
3. a single diffusion coefficient (taken to be constant) can describe the diffusion of all species
4. upper-atmospheric turbulence can be neglected
5. convective effects are negligible

The governing equations are:

$$\frac{\partial n_i}{\partial t} = D \left[\frac{\partial^2 n_i}{\partial r^2} + \frac{\partial n_i}{\partial r} \right] + \dot{n}_i \quad (i = 1, 2, \dots, k) \quad (1)$$

where $\dot{n}_i = \dot{n}_i(n_1, n_2, \dots, n_k)$, and

- n_i = concentration of species i
- \dot{n}_i = net rate of production of species i
- t = time
- r = radial distance from center of release
- D = diffusion coefficient

In order to solve Eq. (1) initial species concentration profiles must be specified, along with a complete chemical reaction mechanism (cf. Section II). The method of finite differences was used to cast the above equations into a form convenient for solution on a digital computer. The complete set of finite difference equations as well as a discussion of the computer program is given in, AeroChem TN-95, (Appendix A of this report).

IV. FEASIBILITY STUDY

In order to test the feasibility of obtaining a large electron cloud of long duration, calculations were made for a nighttime acetylene release at 100 km. This altitude was selected because the ambient electron concentration^{19, 20} is relatively low and the absolute oxygen atom concentration^{21, 22} is near its maximum. These conditions are the most favorable for producing electron densities significantly greater than the ambient. Once it has been established that observations are possible under these favorable conditions, further work can be undertaken to establish the limiting conditions.

As discussed previously, initial species concentration profiles must be assumed in order to start the calculations. Earlier studies^{14, 17} have assumed either Gaussian or square-wave profiles after the pressure equilibration period. We have arbitrarily assumed, for this study, that the release agent (C_2H_2) has an initial Gaussian profile, i. e.,

$$n_{C_2H_2} = (n_{C_2H_2})_0 e^{-(r/r_0)^2} \quad (2)$$

and the ambient species have an inverted Gaussian profile,[†]

$$n_i = (n_i)_0 \left[1 - e^{-(r/r_0)^2} \right] \quad i = e^-, NO^+, O_2, O_3 \quad (3)$$

The half-width, r_0 , is determined from the total amount of acetylene released, i. e.,

$$N = 4\pi \int_0^\infty (n_{C_2H_2})_0 e^{-(r/r_0)^2} r^2 dr \quad (4)$$

where N is the total number of molecules in the release. By performing the required integration in Eq. (4) and employing the equation of state, we obtain the following expression for the Gaussian half-width,

[†]The exception to this is the O-atom profile, which is assumed to be on the order of 10^8 atoms cc^{-1} at the center of the release rather than the zero value required by the inverted Gaussian profile; this was done for computational convenience.

TABLE II-1

INPUT DATA FOR CHEMI-IONIZATION FEASIBILITY STUDY

Mass of C₂H₂ Released = 20 kg
 Gaussian half-width,^a r₀ = 0.23 km

Ambient Properties at Release Altitude, 100 km (night)			Ref.
Species Concentration, molecule cc ⁻¹	O ₃	<1 x 10 ⁷ b	23
	O	6 x 10 ¹¹	21, 22, 24, 25
	O ₂	1 x 10 ¹²	
	N ₂	5 x 10 ¹²	
	e ⁻	<1 x 10 ⁴ b	9, 19, 20
	NO ⁺	1 x 10 ⁴	
Temperature, °K		200	21
Pressure, milliTorr		0.14	calculated
Diffusion coefficient, cm ² /sec		2 x 10 ⁵	14, 26

^aComputed from Eq. (5)

^bFor calculation purposes these upper limits were used.

$$r_0 = \pi^{-1/2} \left(\frac{A}{W}\right)^{1/3} \left[\frac{m}{(n_{C_2H_2})_0}\right]^{1/3} \text{ cm.} \quad (5)$$

where m is the mass of acetylene released in grams and (n_{C₂H₂)₀) is in molecule cc⁻¹. The initial value of the C₂H₂ concentration at the center of the release (n_{C₂H₂)₀) is assumed to be equal to the ambient concentration.†}}

The input data for the feasibility study given in Table II-1 were used as input to the computer program outlined in Appendix A (AeroChem TN-95). The results of the calculations for the species e⁻, C₂H₂, and O for a release of 20 kg of C₂H₂ at 100 km (at night) are shown in Figs. II-2 through II-4. Because only limited computer use was allowed for under the present contract, calculations were performed only for a 10-min. period following pressure equilibration.

Figure II-2 demonstrates (1) the feasibility of using C₂H₂ to produce, via chemi-ionization, a region in the upper atmosphere in which the electron concentration exceeds the ambient concentration, (2) that the diameter of this (spherical) region is greater than 1 km, and (3) that this "electron cloud" exists for at least 10 min (and certainly much longer, considering the slow diffusion and recombination). A cloud of about 1 km in which the electron concentration exceeds the ambient concentration by some 10% is all that is required for observation by standard ionosonde equipment.⁴ Hence, the electron cloud produced via chemi-ionization can easily be monitored by such equipment. There are several further interesting points to be made regarding the electron profiles:

† Thus, in effect, we assumed an expansion to ambient density rather than ambient pressure and consequently neglect the effects of temperature equilibration on the solution. This assumption is not expected to grossly affect the electron density profiles and is therefore adequate for this feasibility study.

1. The rapid (almost instantaneous) achievement of the peak electron density in the cloud indicates the rapidity of the chemi-ionization process. It must be pointed out that the initial distributions of C_2H_2 and O affect the initial rate of production. Therefore, if square-wave initial profiles¹⁴ were assumed, the results would differ at early times but should not affect the gross behavior of the cloud over the longer periods.
2. An examination of the computer output shows that the main process responsible for the electron density decay is, initially, $CHO^+ + e^- \rightarrow$ Products. Of course, diffusion controls the electron decay after long times.
3. The peak recombination rate of electrons with CHO^+ (which occurs at $t = 3.5$ sec) is about 4×10^6 molecules $cc^{-1} sec^{-1}$, while at $t = 600$ sec the rate has decreased to about 1×10^5 molecules $cc^{-1} sec^{-1}$.
4. The two-body recombination with NO^+ (Reaction (5)) and the two-body attachment reactions (Reactions (7) and (8)) make a minor contribution to the electron decay, while the three-body attachment reactions (Reactions (9) and (10)) can be completely neglected.

The profiles of C_2H_2 and O over the 10-min time period are shown in Figs. II-3 and II-4, respectively. The effect of chemistry on the C_2H_2 concentration at the center of the release is negligible, and the slow diffusion rates decrease this concentration by about a factor of 3 in 10 min. Chemistry has a stronger influence in regions of the cloud with lower concentrations of C_2H_2 . Since the chemi-ionization process continues as long as a sufficient amount of C_2H_2 is present, the results shown in Fig. II-3 imply that the production of electrons will continue for a time period considerably in excess of 10 min.

The O-atom profiles show the significant effects of chemistry at the center of the release where the assumed initial concentration of 1×10^8 molecule cc^{-1} is drastically reduced. These effects continue for about 6 min, when diffusion begins to take over and the slow process of achieving the ambient O-atom concentration up to the center of the release is initiated.

V. DISCUSSION AND RECOMMENDATIONS

The calculations have shown (cf. Fig. II-2 and Section IV) that a nighttime point release of 20 kg of acetylene at an altitude of 100 km would yield peak electron concentrations of about 5×10^6 electrons cc^{-1} . The total electron concentration would be high enough and cover a sufficient volume to be observable with standard ground-based ionosonde equipment for periods well in excess of 10 min. Hence, the use of C_2H_2 for releases leading to meaningful upper-atmospheric measurements using the free electrons produced appears feasible. Establishing the feasibility of observing electrons

produced in the upper atmosphere by chemi-ionization achieves the limited objective of Part II. It should be pointed out, however, that because no kinetic data at pressures comparable to those encountered in actual releases are available one cannot predict the success of an upper-atmospheric release with a high degree of certainty. Clearly, laboratory chemi-ionization data at pressures in the 1 to 10 milli Torr range are badly needed.

It is also desirable to extend these calculations to daytime conditions. Since chemiluminescent techniques cannot be used in the daytime, chemi-ionization techniques would be especially useful during that period. Daytime ambient electron densities^{19, 20} at 100 km are on the order of 10^5 cc^{-1} . Since electron concentrations some 20% higher than ambient concentrations are detectable by ionosonde equipment, the results of Fig. II-2 strongly indicate that electrons produced by chemi-ionization can also be measured in daytime.

It is further recommended that in future work additional calculations be made, in the form of a parametric study, in order to test the effect of varying:

1. initial species concentration profiles
2. rate constants for the important ionization and electron recombination reactions
3. release altitude
4. amount of C_2H_2 released

In addition, a critical investigation into the validity of the assumptions employed in formulating the model should be made. It is especially important to evaluate the possible effects of the diffusion and kinetic processes occurring during the pressure equilibration period and the influence of upper-atmospheric turbulence on the electron cloud.

VI. CONCLUSIONS

An upper-atmospheric acetylene release can lead to sufficiently high electron concentrations to make observation by ground-based ionosondes possible. The electron cloud produced can be used in the study of upper-atmospheric properties in a manner similar to the observation of chemiluminescence by optical techniques. Because of the lack of laboratory input data in the correct pressure range and the limited use made of the theoretical model developed in the present study, this conclusion must be considered a tentative one.

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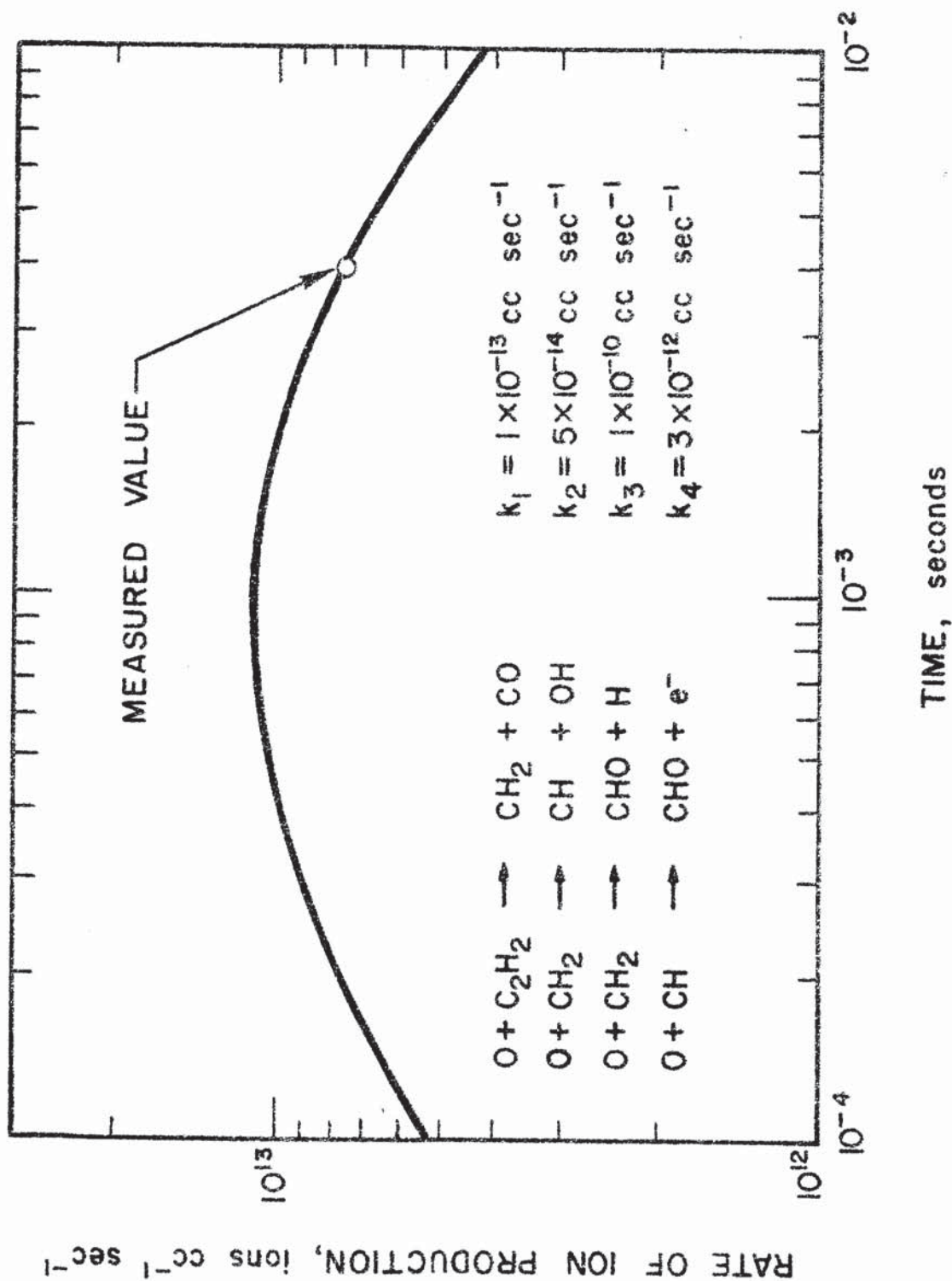


FIG. II-1 PREDICTED RATE OF ION PRODUCTION IN LABORATORY ATOMIC OXYGEN-ACETYLENE REACTIONS; A COMPARISON OF DIGITAL COMPUTER RESULTS WITH LABORATORY DATA

Initial concentrations: $n_{C_2H_2} = 2.7 \times 10^{14}$ and $n_O = 9.8 \times 10^{14}$ molecule cc⁻¹

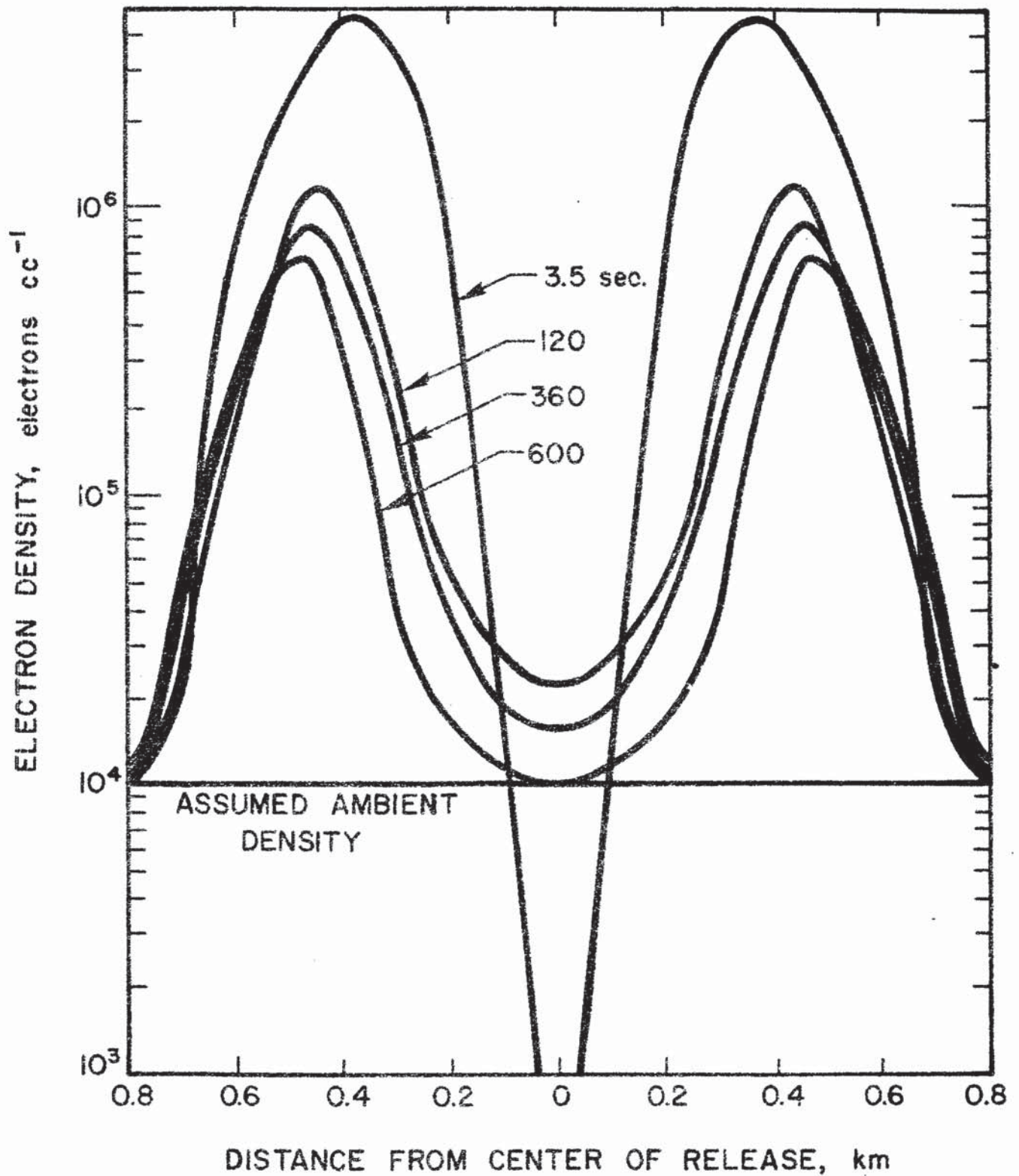


FIG. II-2 ELECTRON DENSITY PROFILES FOLLOWING AN ACETYLENE POINT RELEASE

Release altitude = 100 km (night)

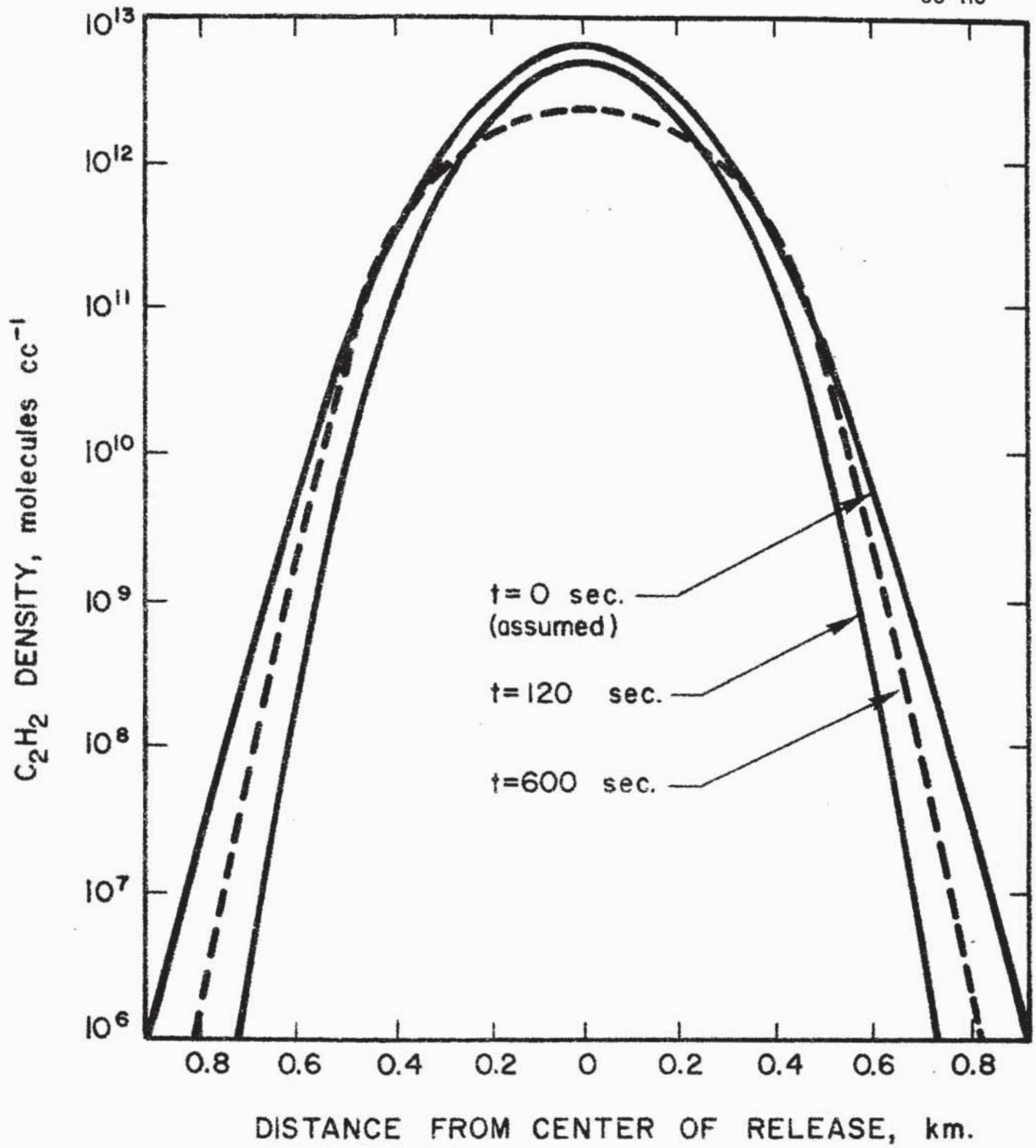


FIG. II-3 ACETYLENE DENSITY PROFILES FOLLOWING AN ACETYLENE POINT RELEASE
Release altitude = 100 km (night)

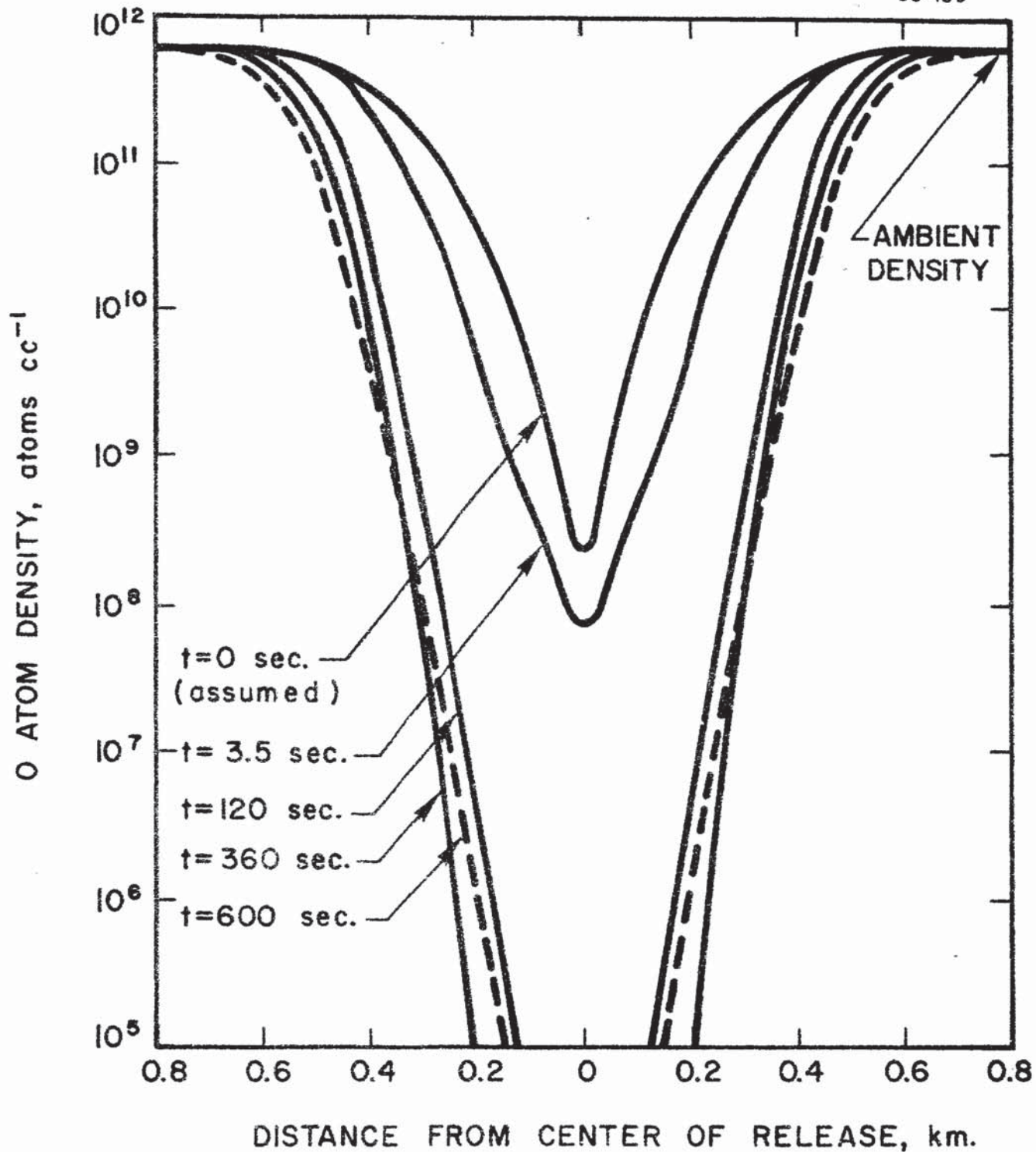


FIG. II-4 OXYGEN ATOM DENSITY PROFILES FOLLOWING AN ACETYLENE POINT RELEASE

Release altitude = 100 km (night)

APPENDIX A
THE AEROCHEM UPPER-ATMOSPHERE CHEMICAL
RELEASE COMPUTER PROGRAM

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ABSTRACT

This digital program can be used to determine the species concentration profiles following an upper-atmospheric chemical point release which diffuses with spherical symmetry and chemically reacts with ambient species. The release of acetylene, which reacts with atomic oxygen to give chemi-ions, is considered here. However, the program can easily be modified to handle any release agent which results in chemi-ionization or chemiluminescence. Up to 20 species involved in as many as 20 reactions can be treated.

This note describes the governing equations, numerical analysis, and input format of the program.

NOMENCLATURE

D	=	diffusion coefficient
k	=	reaction rate constant
n	=	species concentration
\dot{n}	=	rate of production
r	=	space coordinate (radial)
R	=	reaction rate
t	=	time coordinate

Subscripts

e	=	outer edge of release (ambient)
i	=	i^{th} species
j	=	j^{th} reaction
m	=	radial coordinate grid point
n	=	time coordinate grid point

Governing Equations

The diffusion-chemical kinetic model considered here is applicable after the release material has expanded to ambient density. Initial profiles must be specified which take into account the physical processes occurring during the density equilibration period. Spherical symmetry is then assumed for the subsequent interaction of the release material with the ambient species.

The following equations are used to obtain the complete solution to the aforementioned problem:

$$\frac{\partial n_i}{\partial t} = D \left[\frac{\partial^2 n_i}{\partial r^2} + \frac{2}{r} \frac{\partial n_i}{\partial r} \right] + \dot{n}_i$$

where

$$\dot{n}_i = \sum_j (R_j)_i$$

The diffusion coefficient for each species are assumed to be equal and constant.

Boundary and Initial Conditions

$$t = 0: n_i = n_i(r)$$

$$r = 0: \frac{\partial n_i}{\partial r} = 0$$

$$r \rightarrow \infty: n_i = (n_i)_e$$

Finite Difference Formulation

The governing parabolic equations are cast in an explicit finite difference formulation by applying a backward difference technique in the axial direction and a central difference technique radially. The notation is shown schematically in Fig. 1. In the following equations the species subscript "i" is dropped for clarity.

Backward Difference

$$\left(\frac{\partial n}{\partial t} \right)_{n+1, m} = \frac{n_{n+1, m} - n_{n, m}}{\Delta t}$$

Central Difference

$$\left(\frac{\partial n}{\partial r} \right)_{n, m} = \frac{n_{m+1, n} - n_{m-1, n}}{2\Delta r}$$

$$\left(\frac{\partial^2 n}{\partial r^2} \right)_{n, m} = \frac{n_{m+1, n} - 2n_{m, n} + n_{m-1, n}}{(\Delta r)^2}$$

The final difference equation is:

$$n_{m,n+1} = n_{m,n} + \frac{(\Delta t)D}{(\Delta r)^2} \left[n_{m+1,n} - 2n_{m,n} + n_{m-1,n} + \frac{1}{m} (n_{m+1,n} - n_{m-1,n}) \right] + \dot{n} \Delta t$$

At the center of the release, $r = 0$, the term $\frac{2}{r} \frac{\partial n_i}{\partial r}$ is indeterminate. By applying L'Hopital's rule the equation becomes

$$\frac{\partial n_i}{\partial t} = 3D \frac{\partial^2 n_i}{\partial r^2} + \dot{n}_i$$

the resulting difference equation is:

$$n_{o,n+1} = n_{o,n} + \frac{6D\Delta t}{(\Delta r)^2} (n_{1,n} - n_{o,n}) + \dot{n} \Delta t$$

Stability Criterion

The preceding difference formulation subjects the resulting algebraic equations to a stability criterion which governs the maximum permissible time step (Δt). The stability criterion is approximately

$$\Delta t \leq \frac{(\Delta r)^2}{6D} \quad r = 0$$

and

$$\Delta t \leq \frac{(\Delta r)^2}{2D} \quad r > 0$$

The maximum permissible step size is the smaller of the above values; namely, $(\Delta t)_{r=0}$.

Step-Size Determination

Extremely small time steps were utilized to start the solution, and a step-size control was incorporated so that the solution can seek out a "large" step size consistent with a desired accuracy.

The procedure utilized is one which tests all dependent variables at all radial grid points by comparing the values after a nominal step size has been taken with values using one-half the nominal step size--after taking two steps. If the two values agree to within a certain tolerance (ϵ_1) the step size is doubled; if the percentage difference is outside another tolerance (ϵ_2) the step size is halved; and if the agreement lies within the two tolerances the step size is not altered.

For this program ϵ_1 was taken to be 0.001, and ϵ_2 was taken as 0.01. No attempt has yet been made to determine the best values of ϵ_1 and ϵ_2 .

Mesh Growth

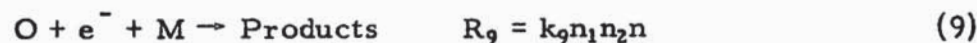
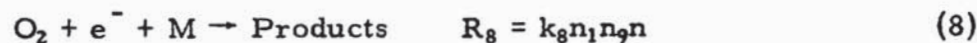
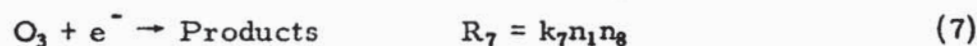
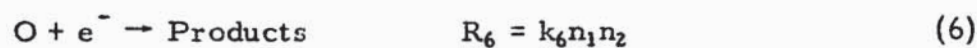
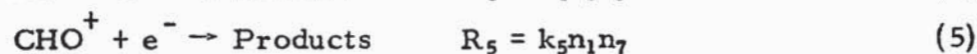
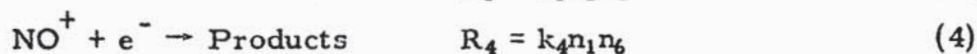
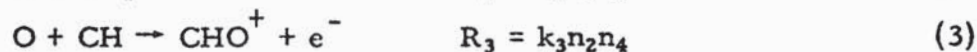
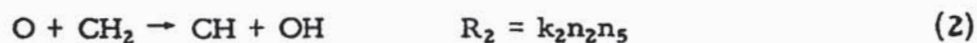
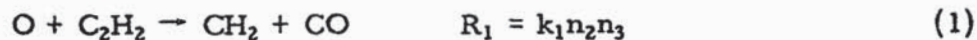
An additional radial mesh point (at ambient conditions) is added whenever the current penultimate radial point of any non-zero free stream species differs by more than one-tenth of one percent from the corresponding free stream value. In order to minimize computer time, the radial mesh is halved whenever it expands to twice its original size.

Reaction Mechanism[†]

The program presently incorporates the following nine species:

1. e^-	4. CH	7. CHO^+
2. O	5. CH_2	8. O_3
3. C_2H_2	6. NO^+	9. O_2

involved in the following reactions.



where $n = \sum_i n_i$, $i = 1, 2, \dots, 9$.

The net rates of production for each species are

$$\dot{n}_1 = R_3 - R_4 - R_5 - R_6 - R_7 - R_8 - R_9$$

$$\dot{n}_2 = -R_1 - R_2 - R_3 - R_6 - R_9 - R_{10}$$

$$\dot{n}_3 = -R_1$$

$$\dot{n}_4 = R_2 - R_3$$

$$\dot{n}_5 = R_1 - R_2 - R_{10}$$

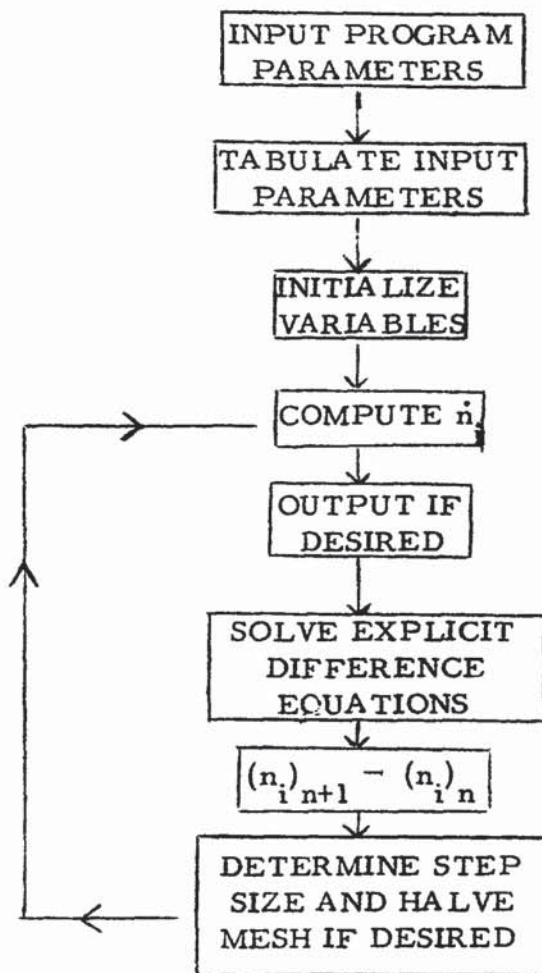
$$\dot{n}_6 = -R_4$$

$$\dot{n}_7 = R_3 - R_5$$

$$\dot{n}_8 = -R_7$$

$$\dot{n}_9 = -R_8$$

[†]The species and reaction numbers listed in this section correspond to the notation in the computer output.

Program Flow ChartInput Format

Card 1 is an identification card which may contain any 72 characters. The information on the card will be printed at the top of each output page (Format 72H).

Card 2 contains three control parameters:

1. the initial number of radial grid points
2. the number of reactions
3. the number of species (Format 3I5).

Card 3 contains six variables:

1. initial time, t_0 (usually 0)
2. final time, sec
3. initial step size (Δt) (usually 10^{-7} sec)
4. desired print increment (Δt_{print} , sec)
5. tolerance to halve the step size ($\epsilon_1 = 0.01$)
6. tolerance to double the step size ($\epsilon_2 = 0.001$) (Format 6E10.8).

Card 4 contains two variables:

1. initial radial step size (Δr)
2. diffusion coefficient (D) (Format 2E10.8).

Card 5 contains the reaction rate constants. A maximum of seven to a card is permitted. If more than seven are required they are continued onto a second and even a third card, if there are more than 14 reactions (Format 7E10.8).

Card 6 contains the initial species profiles. The values are punched seven to a card (if more than seven species are considered, then two or even three cards can be used), beginning with the value at $r = 0$ and continuing out to the ambient condition (Format 7E10.8).

Output Format

The first page contains a tabulation of the input data. The following pages contain the radial profiles of species concentration (n_i), reaction rate (R_j), and rate of production (\dot{n}_i) at various times (t) during the release. In addition, the time step (Δt) presently being used in the computations is listed.

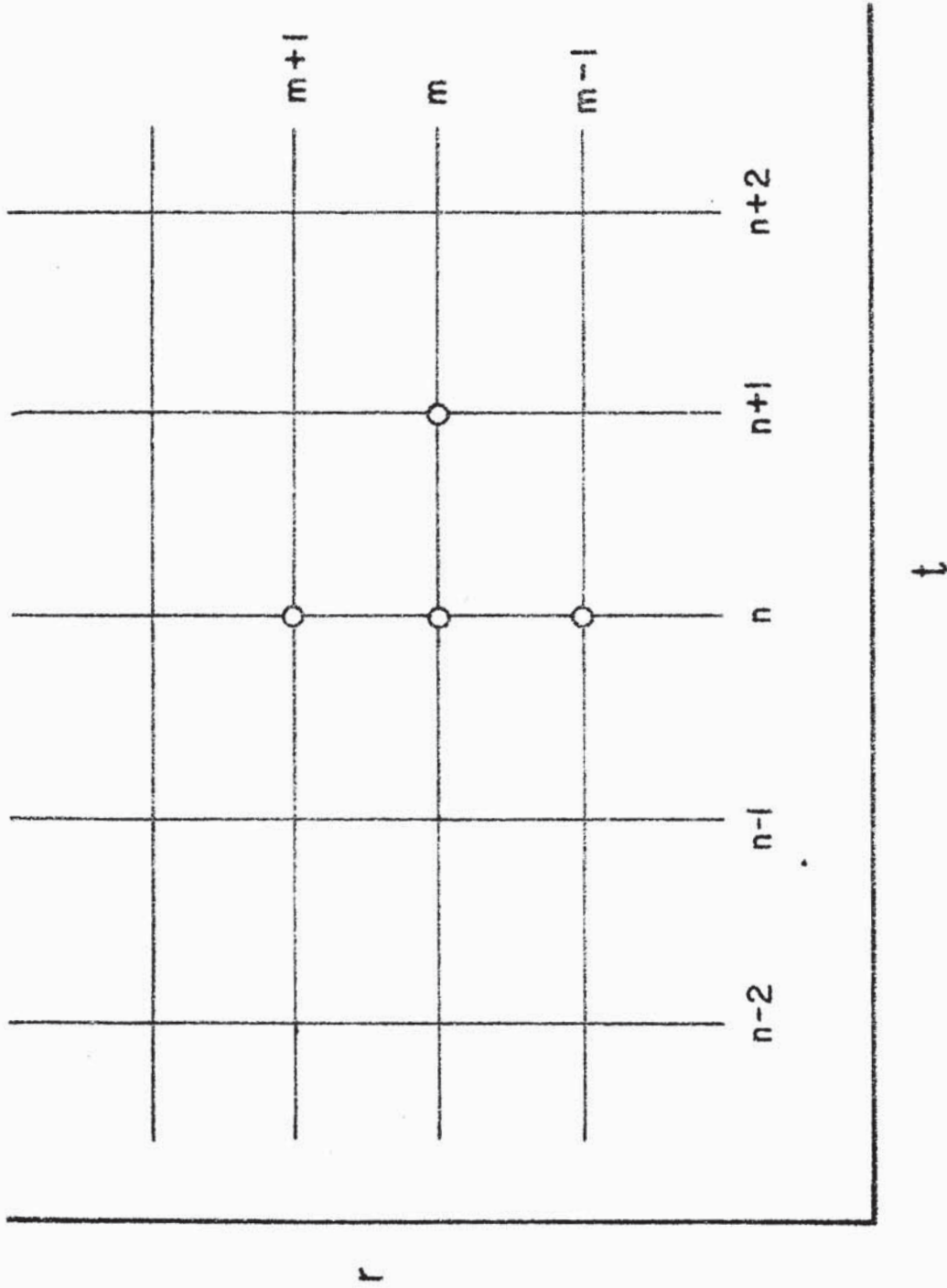


FIG. 1 SCHEMATIC OF GRID NETWORK IN $r-t$ PLANE