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TECHNICAL REPORT ECOM-01354-F

6 IONIZATION AND ELECTRON LOSS SIMULATION
IN ATMOSPHERIC GASES

Report No. 3

1 December to 1 March 1966

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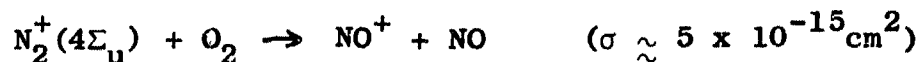
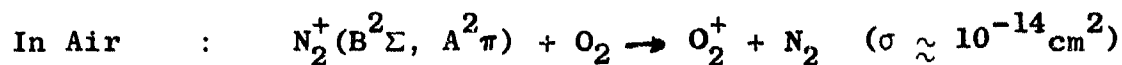
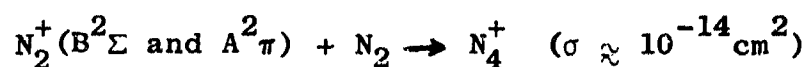
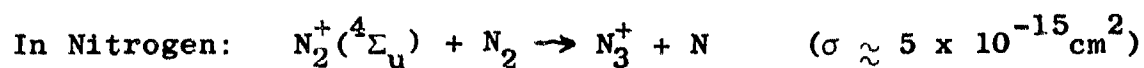
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where $\alpha_{e1}(O_2^+, NO^+ \text{ in air}) = (3 \pm 2) \times 10^{-7} \text{ cm}^3/\text{sec}$

f) Ion-Molecule Reactions



Optical studies of the fluorescent emission from irradiated nitrogen and air show collisional quenching of the $N_2(B^3\pi_g \rightarrow A^3\Sigma_u^+)$ Second Positive System and $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ First Negative System, with cross sections given by:

State	Quencher	σ ($\times 10^{-16} \text{ cm}^2$)
$N_2:B^3\pi_g(v' = 0)$	N_2	$1.2 \pm .6$
$B^3\pi_g(v' = 0)$	O_2	39 ± 11
$(v' = 1)$	O_2	52 ± 18
$(v' = 2)$	O_2	81 ± 32
$N_2^+:B^2\Sigma_u^+(v' = 0)$	N_2	69 ± 10
$B^2\Sigma_u^+(v' = 0)$	O_2	123 ± 21

ACKNOWLEDGEMENTS

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I. INTRODUCTION

A. Purpose of the Experimental Program

This report summarizes work performed during the period 1 July 1961 to 31 March 1966 on a program entitled "An Experimental Investigation of the Effects of Radiation on the Propagation of Electromagnetic Signals in Air." This work was performed for the Defense Atomic Support Agency at the G. C. Dewey Corporation Space Physics Laboratory in New York City, under the technical supervision of the Atomics Branch of the Applied Physics Division, U. S. Army Signal Research and Development Laboratories at Fort Monmouth, New Jersey.

There are two traditional approaches to an experimental study of the processes occurring in the upper atmosphere. One can try to deduce atmospheric reaction models from in situ observations of the chemical, ionic, and electronic composition of the atmosphere obtained with rocket-borne instruments or ground-based measurements. Alternatively, one can create a situation in the laboratory in which a specific reaction is dominant, then study this reaction as a function of the various parameters at the control of the experimenter. Each method has its advantages and limitations. Thus, the interpretation of direct atmospheric measurements suffers from the incompleteness of our knowledge of the composition of the atmosphere and the nature of all the external influences exerted on it in general, and at the time and location of the experiment in particular. Also, the complexity of atmospheric processes is so great that it is difficult to correlate a given observation with a particular process. Finally, the experimenter cannot control the pressure,

2.

temperature, and chemical composition independently, to study the dependence of the process under investigation on these parameters. Despite these difficulties, direct atmospheric measurements are still attractive and important in that they represent the ultimate in relevance, that is, they relate directly to the phenomena which are to be explained. In the laboratory, on the other hand, one has nearly complete control over the chemical composition, pressure, and temperature of the gas being studied, and can choose these parameters so that a given reaction will dominate the observed phenomena. One can then study this reaction in great detail. It is well known, however, that not only the rates, but even the mechanisms, of many charged particle reactions depend strongly on the internal energy states of the reactants. Due to the dissimilarities between most laboratory experiments and the atmospheric environment, it is unreasonable to assume that the excited state distribution is characteristic of the upper atmosphere. Hence, one cannot know a priori the relevance of a given reaction studied in the laboratory to the upper atmosphere.

In July, 1961, the G. C. Dewey Corporation began work on an experimental program designed to study ionization and deionization processes in the upper atmosphere arising from prolonged irradiation by beta particles from trapped fission debris subsequent to the detonation of a nuclear device at high altitudes. The objectives of the program were to create a laboratory environment which closely resembles the beta-irradiated upper atmosphere, then to study the processes common to the laboratory and ionospheric situations as closely as possible. The experiment was visualized as an approach to ionospheric reactions which stands midway between direct atmospheric measure-

ments and traditional laboratory studies. By suitable choices of experimental parameters, one could study individual reactions in typical laboratory detail, then vary the parameters to produce a close approximation to the ionospheric situation, and determine the relevance of these reactions to the phenomenology of the ionosphere. Thus the experimental program was planned to combine the best features of the traditional approaches described above. As the results to be presented in this report indicate, the experimental program has been extremely successful in both aspects of the problem.

B. Nature of the Experiment

The ionosphere differs from any laboratory simulation in several ways. Most obvious is the necessity of confining the laboratory environment in some sort of container. The container walls can then modify the test environment by various means, including the removal of electrons and ions by surface recombination and the de-excitation of otherwise long-lived states by wall collisions. The laboratory experiment is never completely free from system-contributed impurities which are not present in the ionosphere, but which may participate in the laboratory phenomenology. These dissimilarities are greatly minimized in the present experiment, the first by the use of an extremely large reaction chamber, four feet in diameter and two feet long, to provide a large volume-to-surface ratio, and the second by the use of ultrahigh vacuum techniques and clean gases.

Three diagnostic techniques are used to study the irradiated gas. The densities of free secondary electrons are deduced by resonant cavity methods. A mass spectrometer studies the

positive and negative ions which diffuse to the container walls. An optical spectrometer examines the light emitted by the fluorescing gas. The simultaneous application of these three techniques provides unusually detailed information on the instantaneous state of the irradiated gas.

C. Summary of This Report

Chapter II describes the experimental equipment and techniques in detail. In Chapter III, the various processes which can occur in weakly ionized atmospheric gases are discussed, along with means for treating experimental data obtained from the measurements. Chapters IV and V contain the results obtained to date. Chapter IV describes the optical studies in nitrogen, while Chapter V presents the results of electron density and mass spectrometric studies in pure oxygen, pure nitrogen and airlike mixtures. The report closes with Chapter VI, which includes a summary of experimental results and suggestions for further work.

D. Administrative Details

The work described in this report was conducted over the period between 1 July 1961 and 31 March 1966, under the following contracts:

<u>Contract Number</u>	<u>Dates</u>
DA-36-039-SC-87318	1 July 1961 - 30 June 1963
DA-36-039-AMC-03278 (E)	1 July 1963 - 31 June 1964
DA-28-043-AMC-00457 (E)	1 July 1964 - 28 February 1965
DA-28-043-AMC-01354 (E)	1 June 1965 - 31 March 1966

The following G. C. Dewey Corporation personnel contributed to the project for the approximate fraction of the total available time indicated:

Merle N. Hirsh, Senior Associate (Project Director)	75-100%
Philip N. Elsner, Research Associate	75-100%
James A. Slevin, Research Associate	50- 75%
David R. Maerz, Senior Technical Assistant	50- 75%
Alexander S. Walker, Jr., Senior Technical Assistant	50- 75%
Walter G. Chesnut, Senior Associate	0- 25%
Gerald M. Halpern, Research Associate	0- 25%
Neil S. Wolf, Research Associate	0- 25%
J. Warren Blaker, Research Associate	0- 25%
Howard Zwiren, Technical Assistant	0- 25%

6.

II. EXPERIMENTAL TECHNIQUES

A. General Description

The present experiment is a study of electron production and loss in air and atmospheric gases subjected to ionizing radiation, under conditions approximating those at altitudes in the atmosphere between 40 to 100 km. Three diagnostic tools are used for these studies. The density of free electrons for a wide variety of experimental conditions is determined by the measurement of the radio-frequency properties of a resonant cavity containing the ionized gas, and mass and optical spectrometry provide information on the ions present and the density distribution of excited states. All three techniques are applied simultaneously to the study of the ionized gas, thereby providing as detailed a characterization of the state of the gas as possible.

A schematic diagram of the experimental system is shown in Figure 2.1. A divergent beam of 1.5 Mev electrons from a Van de Graaff accelerator traverses a thin foil window which serves as one end of a cylindrical uhf cavity containing the gas to be studied. The cavity has been made extremely large, four feet in diameter, two feet in length, to minimize the role of diffusion in the charged particle removal processes. The geometry of the beam divergence is chosen to provide a flux of electrons which is nearly uniform throughout the volume of the cavity, so that the gas contained in the cavity is ionized by a spatially uniform source.

Two types of experiments are performed. In one, the electron beam irradiates the gas continuously, setting up a steady-state distribution of charged particles and excited neutral species.

Electron and ion densities and optical emission intensities are measured as functions of the pressure and chemical composition of the gas and of fast electron beam current. In the second type of experiment, the electron beam is pulsed on and off periodically, and time-resolved measurements of electron density are made during the approach to in-beam equilibrium and during the radiation afterglow. These two types of experiments provide complementary information as will be seen in Chapters V and VI.

Because of the high gamma intensity in the Van de Graaff room, it is necessary for the operator to be located some distance away from the experimental area. All parts of the experiment which require adjustment, tuning, or observation during the course of an experiment are therefore located in an adjacent room also containing the operator. This room is shielded from the Van de Graaff irradiation area by $4\frac{1}{2}$ foot thick walls of extremely dense bluestone masonry. In the operator area, radiation surveys are unable to detect any radiation in excess of normal background during an experiment.

B. The Electron Beam

The source of electrons for the irradiation experiments is a Van de Graaff electron accelerator, Model GS (horizontal), produced by High Voltage Engineering Corporation, Burlington, Massachusetts. The accelerator produces 1.5 Mev electrons at currents up to 1.7 milliamperes. The electrons emerge from the accelerator in a collimated beam of roughly elliptical cross section, 3 mm long by 1 mm wide. This collimated beam maintains a cross-sectional dimension of less than 10 mm after traversing a path 10 meters in length in vacuum of the order of 10^{-5} Torr. The

energy spread of the beam is guaranteed by the manufacturer to be no more than 40 kev; since ionization cross-sections for fast electrons in gases are quite insensitive to electron energy in the Mev range, there was no attempt made to measure the actual energy spread.

Upon emerging from the accelerator, the beam passes into a beam switching section, shown in Figure 2.2, which consists of a straight-through arm of 2" diameter tubing to which a second tube at an angle of 12° from the beam axis is attached. A Helmholtz coil, capable of producing a field of 300 Oersteds quite uniform over a cylindrical volume 3" in diameter by 1" in height, is located at the junction of the two tubes. A Faraday cup is attached to the side arm through an insulating flange. To read total current from the Van de Graaff one switches the beam into this side arm by applying the magnetic field. With the help of a second Faraday cup located at the end of the straight-through section (E' in Figure 2.2) it was determined that the current into the side arm with the field on is equal to the straight-through current observed in the absence of a magnetic field to within about 1%.

The collimated beam emerging from the Van de Graaff is passed through a thin metallic foil, which diffuses it by multiple scattering. For small scattering angles, the electrons can be described by the angular distribution function

$$P(\theta) = K e^{-\theta^2/\bar{\theta}^2} \quad (21.)$$

Here $\bar{\theta}$ is the rms scattering angle characteristic of the thickness and composition of the foil, and is determined by

10.

$$\theta^2 = \left(\frac{Z}{E}\right)^2 \frac{x}{x_0} \quad (2.2)$$

Here E is the energy of the electron in Mev, x the "thickness" of the foil in gm/cm², and x₀ a characteristic "length" for the foil material given by

$$1/x_0 = 1.37 \times 10^{-3} \frac{Z(Z+1)}{A} \log_e 183Z^{-1/3} \text{ gm/cm}^2 \quad (2.3)$$

Foils are chosen so that only a small central spread in θ strikes the cavity, providing a nearly uniform flux across the cavity face. Electrons scattered through larger angles are removed at the collimator C. The length of the beam tube (10 meters) has been chosen to keep the r^{-2} loss in flux due to the beam divergence less than 10% from front to back of the cavity (0.6 meters).

Direct measurements of the spatial distribution and absolute flux of the Van de Graaff beam within the cavity were made with a Faraday cup which could be scanned along vertical and horizontal diameters of the cavity. Figure 2.3 shows the Faraday cup itself, which is made from a cylinder of aluminum 12" long and 1 1/8" in diameter, so that the collection area of the cup is 1 square inch. The back of the cylinder is closed with a 1/8" thick aluminum disc, and the open front end is guarded by a fine wire repeller grid insulated from the body of the cup, to which a large negative voltage is applied. The combination of the repeller grid and the large ratio of length to diameter of the cup prevents the loss of secondary electrons from the cup. To avoid electron collection on the outer walls, the cup is enclosed in a 1 3/4" diameter grounded aluminum tube, and the front edge of the cup is guarded from the direct beam by a 3 1/2" diameter grounded frontal disc. Collected electron current is measured with an electrometer-

tube microammeter and chart recorder.

The cup is driven at constant speed along the rod by means of a motor assembly which automatically reverses at each end of the travel. The cup thus scans continually back and forth, each traversal requiring about three minutes. At one end of the rod, the Faraday cup moves behind a heavy shield which blocks the incident beam. The residual current observed with the cup behind the shield is due to the collection of backscattered electrons at the cable feedthrough; this background is subtracted from all readings.

Beam profiles were measured with the scanning Faraday cup along the vertical and horizontal diameters of the cavity, for a beryllium foil scatterer 0.004" thick. The current distributions are shown in Figure 2.4. From these data, the total current to the cavity has been computed for a 100 μ amp beam from the Van de Graaff. It was found that this current amounts to 28.7% of the total incident beam. It will be noticed that the current distribution along the vertical axis is quite nonuniform. It is believed that the bottom of the scattered electron distribution is shadowed by an obstacle in the collimating section. A new collimator has been designed, and will be incorporated into subsequent experiments.

Indirect measurements of the foil scattering were also made. The geometry of the second Faraday cup E' and the collimator C in Figure 2.2 is chosen so that the collection area of E' intercepts the same solid angle at the foil as does the cavity in its normal position. The total current intercepted by E' should then be the same as the total current incident on the cavity.

Measurements made in this manner for the 0.004" beryllium foil used above give a value of 28.8% of the total incident beam, in fortuitously good agreement with the total current obtained above. Because of their simplicity, the indirect measurements were used for relative calibrations between foils.

Because of inadequate filtering in the pentode emission control circuit, the amplitude of the electron beam has a small 400 cps modulation, of the order of 5%. This normally presents very little difficulty in the experiments, particularly when the electron loss frequency is small compared to 400 sec^{-1} . At high pressures in oxygen, however, some difficulty is encountered in the transient measurements due to the arbitrary phasing of the 400 cps modulation relative to the beam switching times, to which the afterglow densities show a marked response. It is planned to improve the beam stability in the near future. During the present program, however, there was considerable reluctance to open and repair an otherwise well-functioning accelerator, for fear of the time which could be lost in getting the Van de Graaff operating well again.

C. Electron Density Measuring System

Figure 2.5 is a block diagram of the circuit used for the measurement of electron density. A uhf oscillator, crystal-controlled at $387 \text{ Mcps} \pm 400 \text{ cps}$, is fed into the rf input of a General Radio 1000 - P6 crystal modulator. A General Radio Model 1211B low frequency oscillator drives the modulator at a frequency f_m , typically on the order of 1 to 6 Mcps. The output of the modulator then occurs at $387 \text{ Mcps} \pm f_m$. The high-frequency sideband is used to drive a hybrid ring bridge which contains the cavity

and an adjustable reference impedance in opposite arms. The reference impedance is balanced for maximum output at frequencies off cavity resonance. In the vicinity of cavity resonance, the voltage reflection coefficient of the cavity decreases, thus unbalancing the bridge so that the output signal goes through a minimum at the cavity resonant frequency. The signal from the rf bridge is detected by a crystal diode, and the resulting envelope is displayed on an oscilloscope. Balancing the bridge for maximum signal off resonance biases the crystal onto a sensitive part of its characteristic, and optimizes the signal observed at cavity resonance. This scheme allows one to measure all frequency shifts in the cavity in terms of changes in f_m , due to the stability of the 387 Mcps oscillator. Changes in f_m are measured with a digital counter to an accuracy of 1 kcps.

The heart of the rf circuit is the resonant cavity in which the gas is contained. The cavity has been made large, to minimize the loss of charged particles to the walls by diffusion. The principal concern of the present experiments lies with processes occurring in the volume of the gas, away from the walls. Therefore, a cavity mode was chosen which has vanishing electric fields at the walls, thus weighting the electrons in the volume more heavily.

In the measurements, the cylindrical TE_{011} is used; the electric field lines in this mode are azimuthal circles with the intensity variation

$$E = E_0 J_1 \left(3.832 \frac{r}{R} \right) \sin \frac{\pi z}{h} \quad (2.4)$$

Here R , h are the radius and height of the cavity, both equal to 60 cm. A false electrical end plate, in the form of a circular

disc set off on legs from the back of the cavity structure, separates this mode from the TM_{211} , with which it would be degenerate in an ideal cylindrical resonator. The cavity has a loaded Q of about 16,000.

The presence of a distribution of $n(r, z)$ free electrons per cm^3 in a gas contained in a microwave resonant cavity changes with the resonant frequency and quality factor from their electron-free values ν_0 , Q_0 by an amount [Van Lint et al, 1965]

$$\Delta\left(\frac{1}{Q}\right) - 2i \frac{\Delta\nu}{\nu_0} = \frac{1}{2\pi\epsilon_0\nu_0} \frac{\int_V \sigma E^2 dV}{\int_V E^2 dV} \quad (2.4)$$

Here $\Delta\left(\frac{1}{Q}\right) = \frac{1}{Q_e} - \frac{1}{Q_0}$, $\Delta\nu = \nu_e - \nu_0$, the subscript "e" referring to values in the presence of free electrons. E is the rf electric field in the cavity, and σ is the complex conductivity of the free electrons, given by

$$\sigma = \frac{ne^2}{m} \frac{\nu_c - i\omega}{\nu_c^2 + \omega^2} \quad (2.5)$$

where ν_c is the electron-neutral atom collisional frequency, ω the radian frequency of the applied rf field, and e and m are the charge and mass, respectively, of the electron. The integrals in 2.4 extend over the volume of the resonant cavity. If we write $n(r, z) = n_0 f(r, z)$, then 2.4 becomes

$$\Delta\left(\frac{1}{Q}\right) - 2i \frac{\Delta\nu}{\nu_0} = \frac{n_0 e^2 (\nu_c - i\omega)}{2\pi m \epsilon_0 \nu_0 (\nu_c^2 + \omega^2)} \frac{\int_V f E^2 dV}{\int_V E^2 dV} \quad (2.6)$$

where the ratio of integrals is the effective "filling factor" of the electrons in the cavity, which for convenience can be abbreviated ϕ . For $\nu_0 = 390$ Mcps and $\nu_c = 1.35 \times 10^8$ p sec⁻¹ [Van Lint, 1959], 2.6 can be written

$$\nu \cdot \Delta\left(\frac{1}{Q}\right) - 2\lambda \Delta\nu = \frac{(0.054 p + i) 0.1 \phi n_e}{1 + (0.054 p)^2} \quad (2.7)$$

Thus a uniform distribution of electrons ($\phi = 1$) of density $n_0 = 10^7 \text{ cm}^{-3}$ at 10 Torr in oxygen gives $\Delta\nu = 770 \text{ kcps}$, $Q_e = 500$. At low pressures, where $Q_e \approx Q_0$, $\Delta\nu = 0.1 \phi n_0$.

With no gas in the cavity, it is not possible to detect a shift in the resonant cavity due to the beam electrons alone. Since the velocity of these electrons is so high (effectively equal to the speed of light), the density of beam electrons in the cavity at the highest available current is only about 100 cm^{-3} , which is two orders of magnitude below the detection limit of the instrumentation. Thus, during continuous irradiation of the gas-filled cavity, one can relate all observed changes in resonant frequency to secondary electrons and ions produced in the gas.

The usual precautions have been taken to prevent heating of the free electrons by the rf probing field. Measurements of electron density have been performed at various probe power levels. The results indicate that the power levels used in all measurements reported here (about $0.1 \mu \text{ watt}$) is at least 15 db below those required to produce detectable changes in the measured electron densities.

Direct measurements of cavity Q have not been made because of the beam modulation mentioned above. The noise observed in the oscilloscope display off cavity resonance is severe enough to prevent an accurate measurement of the inflection points of the cavity resonance curve. The cavity band width, from which the Q is deduced, is the small difference between the two large frequencies at the inflection points. With even a small error on each inflection frequency, the Q value is quite seriously in error.

D. Timing Circuits and Transient Measurements

Time-resolved electron density measurements have been performed in experiments in which the electron beam is repetitively switched on and off the cavity. Time intervals are selected at fixed positions within the beam switching sequence; the electron density measurements are performed at these intervals. The circuit also possesses a manual operating mode to be used in steady-state measurements.

A block diagram of the timing system is shown in Figure 2.6. The cycle is initiated by a one second time mark from a Tektronix Model 180 A Time Mark Generator, which initiates the beam irradiation and recycles the Berkeley Preset Counter. The electron beam is switched off at a subsequent 10 or 100 msec time mark selected by the coincidence circuit, so that the beam on and off times are rigidly fixed to within about 1 μ sec.

The selection of a time interval during the sequence at which measurements are to be made is accomplished by the preset counter. 100 μ sec time marks are counted up to a number preselected on the front panel, at which time a trigger pulse is delivered to the oscilloscope used to observe the output of the uhf bridge used for electron density measurements. The counter is recycled by the next one second pulse and the process is then repeated. In this manner, the oscilloscope sweep is activated at integral numbers of 100 μ sec intervals after the one second time mark. The duration of the oscilloscope sweep is kept short compared with the time over which the cavity resonance frequency changes appreciably. Measurements are then made by adjusting f_m to

produce a minimum signal on the oscilloscope, which then gives the cavity resonant frequency at that time.

E. Mass Spectroscopy

Ions from the volume of the gas diffuse to the container walls under the influence of ambipolar space charge fields (see Chapter III). If a small aperture is placed in one of the walls, a representative sample of the ions arriving at the walls can be drawn off and injected into a mass analyzer to determine and identify the densities of the various ionic species produced in the irradiated gas.

A common technique of ion sampling makes use of an accelerating field at the aperture which attracts ions of a given polarity, to increase the collection efficiency of a given aperture. It was feared that this technique would produce disastrous results in the present experiment. Even a few volts of energy opens many new channels to the ions for chemical reactions which are not representative of those occurring in the volume of the gas for thermal ions [Keller et al, 1965]. It was therefore decided to forego ion acceleration in the relatively high pressure cavity, reserving it for use in the low-pressure regions of the mass analyzer where collisions are infrequent enough to minimize the distortion of the ion spectra by chemical reactions.

A very important, but quite elusive, aspect of the mass spectroscopy involves the detailed prediction of the ion sampling efficiency as a function of charge density and gas pressure. If the ions were sampled strictly by diffusion, they would enter the aperture at a rate proportional to their diffusion loss rate, that is, roughly proportional to the central density of the ions in the cavity divided by the gas pressure. In fact, the data

indicate that the inverse p dependence is not observed, and the measured ion currents vary as the central ion densities. To interpret this result requires detailed consideration of the space charge field at the walls, and the neutral gas flow field in the region of the aperture. Sufficient data do not exist at this time to warrant such an analysis.

Mass analyses of ions are performed with an rf monopole mass filter [Von Zahn, 1963]. The monopole, which is actually one quadrant of the Paul quadrupole spectrometer [Paul and Raether, 1955], consists of a circular cylindrical rod electrode and an electrode in the shape of a "vee" (Figure 2.7). In principle, the quadrupole field requires that the rod electrodes have a hyperbolic cross section, but a correctly designed circular pole piece can approximate the hyperbolic field quite well [Dayton et al, 1954].

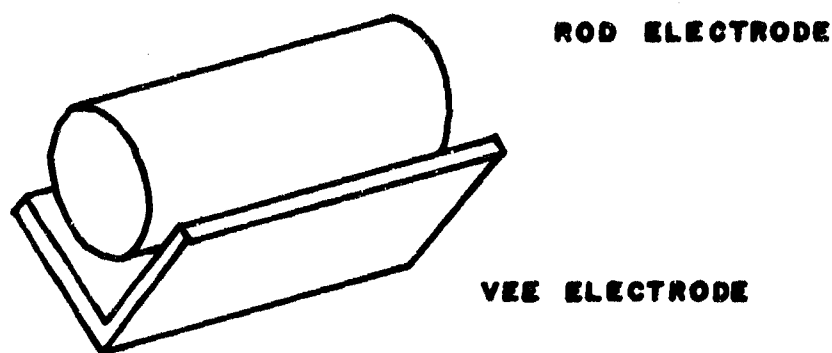


Figure 2.7 R.F. MONOPOLE

Figure 2.8 is a simplified cross-sectional view of the spectrometer, showing the salient features of its design. The front chamber A is defined by the entrance aperture plates into the cavity and the monopole housing B. This region provides the first stage of differential pumping required to maintain the necessary low pressures in the monopole and detector sections. Chamber A contains a simple aperture lens for focussing ions into the analyzing region, and an electron gun of conventional design for use in the study of neutral species. Great care has been taken to remove all insulating surfaces from Chamber A. These insulators were found to be particularly troublesome because they accumulate charge in the gamma field produced by the Van de Graaff electrons which defocusses the ion beam entering the spectrometer.

The monopole housing contains the analyzing electrodes. A ceramic ring seal C insulates the front section of the housing, which is at the potential of the Vee electrode, from the rear section, which is maintained at ground potential.

The rear chamber of the spectrometer houses the detector and a nude ionization vacuum gauge. This chamber is evacuated by its own diffusion pump and is maintained at the lowest pressure in the spectrometer system. The ion detector is mounted on the flange at the rear of the chamber. Electrical feedthroughs in the flange make connection to the electrodes of the detector.

The vacuum system for the mass spectrometer consists of two 4" NRC oil diffusion pumps isolated from the spectrometer by a combination water cooled chevron-molecular sieve baffle manufactured by Kane Engineering Labs. The pumps are connected

to the main foreline used by the diffusion pumps on the cavity and beam tube. Without baking, the detector section of the mass spectrometer reaches an ultimate pressure of 2×10^{-8} Torr. This vacuum system enables the spectrometer to maintain a low internal pressure despite high cavity pressure. For example, with a gas flow of 150 micron-liters/sec through the entrance aperture the pumping system maintains a pressure of 10^{-3} Torr in the lens chamber, 3×10^{-6} Torr in the monopole section, and 5×10^{-7} Torr at the detector. (This gas flow is obtained with an entrance aperture of 0.0135 inch diameter and a cavity pressure of 10 Torr)

Figure 2.9 is a block diagram of the electronics for the mass spectrometer. The rf oscillator is a Hartley type tunable from 730 kcps to 9.39 Mcps, with a peak rf voltage of 1100 volts over the entire frequency tuning range. The rf oscillator is rigidly but demountably attached to the mass spectrometer by a brass coaxial coupler between the oscillator chassis and the rf feedthrough on the monopole housing. This arrangement minimizes the capacitance seen by the oscillator yet provides good rf shielding.

The mode of operation for this spectrometer maintains constant amplitudes of the electric fields, but changes the frequency of the rf field to scan the range of mass-to-charge ratios. The oscillator is tuned remotely from the operator by a selsyn drive which changes the capacitance and inductance in the tank circuit simultaneously. The selsyn master is itself driven by a multispeed motor to permit mass scans to be made at various speeds. Oscillator frequency is continuously monitored on a digital counter for mass identification.

An additional output from the oscillator is rectified to produce the dc potential required for the rod electrode; the polarity of this potential can be chosen by means of a front panel switch, depending on the polarity of the ion being studied. After suitable voltage division, the same rectified output is also used to supply the required voltages for the focussing electrodes. Derivation of the dc voltages from the rf output provides a first-order stability correction for variations in oscillator output power.

The ion detector is a 10-stage Dumont electron multiplier with copper-beryllium dynodes. Dynode voltages are supplied from a regulated Keithley high voltage supply. In the detection of negative ions the entire Keithley supply is floated 1000 volts positive with respect to ground by means of an additional voltage supply. The detector is typically operated at 350 volts per stage.

Two detection schemes have been employed. In the first, the output from the electron multiplier is measured on a Keithley Model 600 A electrometer, and, after suitable integration, is displayed on a strip chart recorder. In the second, the ion lens is driven by a square wave at several hundred cycles per second. The output from the electron multiplier is amplified by an electrometer amplifier with a frequency response flat to 1 kcps and then capacitively coupled to the input of a Princeton Applied Research Model JR-5 Lock-in Amplifier. The lock-in has an internal Oscillator which provides both the reference signal for the detector and a modulation signal which is applied to the ion lens. The ion current is thus coherently modulated at the reference frequency.

The largest source of noise results from the bremsstrahlung generated by the electron beam, which produce photoelectrons within the electron multiplier. The signal-to-noise ratios for the ac and dc techniques outlined above were found to be about the same. However, since the electron multiplier must be biased to a high positive potential for the detection of negative ions, the ac technique must be used in this case.

F. Optical Spectroscopy

The optical spectrometer used is a Jarrell-Ash 0.5 meter Fastie-Ebert monochromator [Fastie, 1952]. This instrument provides good resolution (0.3 Å in the visible first order) and a relatively high geometrical speed ($f/10$) for moderate cost. Other advantages include its ability to scan the entire spectral range without being refocussed, and the linearity of its wavelength drive with time.

Figure 2.10 shows the optical system of the monochromator. Light from the entrance slit is collimated by the spherical mirror, and strikes the plane grating as a plane wave. Depending on the angle between the direction of propagation of the light and the normal to the grating, light at a particular wavelength is reflected back to the spherical mirror, where it is refocussed to pass through the exit slit and strike the detector. Wavelength scanning is accomplished by rotating the grating about a vertical axis while maintaining fixed light paths in space. The grating is equipped with a motor drive which produces wavelength scans linear with time, at any of eight speeds from 2 Å/min to 500 Å/min, as well as a manual drive for setting by hand to any given wavelength. Wavelength indications are displayed on a counter to within the nearest Angstrom, both alongside the spectrometer

itself and on a remote servo-driven counter located in the operator area. Two modes of operation are possible with the monochromator. First, the grating can be scanned at some fixed rate through a given wavelength range to determine the general appearance of the spectrum. Alternatively, the grating rotation and slit widths can be set to transmit a given wavelength interval and the variation of intensity at that wavelength can be measured as a function of external parameters such as time or beam current.

The grating used for the work reported below is a Bausch and Lomb plane replica grating with 30,000 lines per inch, blazed for maximum intensity in the first order at 5,000 Å. The grating is 52 mm square.

The detector is an RCA Type 1P21 photomultiplier contained in a light-tight housing. As in the mass spectrometer detecting system, bremsstrahlung generated by the electron beam from the Van de Graaff accelerator produce photoelectrons within the photomultiplier, and reduce the overall sensitivity of the system. Consequently, it is necessary to shield the photomultiplier with lead in order to reduce the beam-contributed signal. To obtain the necessary 4π shielding, the photomultiplier housing was removed from the exit slit of the spectrometer, and mounted some distance away from it.

The complete optical system is shown in Figure 2.10. Light from the cavity falls on the entrance slit of the spectrometer with no intervening optical elements. (It can be shown [Nielsen, 1930; 1947] that the geometry of the extended source of light provided by the cavity affords optimum illumination of the spectrometer which cannot be improved by the use of focussing lenses.) After traversing the spectrometer, the light is collimated by a convex

lens A and falls onto plane mirrors B and C. The light is then focussed by lens D onto the photocathode of the photomultiplier, which is contained in a light-tight housing. All optical elements are mounted in a brass tube which is in turn rigidly attached to the spectrometer. By surrounding the light pipe on all sides with lead, it is possible to reduce the bremsstrahlung signal to zero. The photomultiplier output is measured with an electrometer amplifier, then displayed on a strip-chart recorder.

The relative response of the optical system versus wavelength was measured in the following way. Measurements (described in Chapter IV below) were made of the intensity distribution of several molecular band systems in nitrogen, and of the relative intensities of several multiplets from a mercury capillary discharge. The detailed distribution of excited states in a radiating system depends very critically on the nature of the excitation process and the physical environment of the system. In the absence of selective absorption, however, the relative intensities of lines or bands arising from a common upper state depend only on the density of that state, and not on external conditions. The ratios of measured photocurrents to theoretical intensities for these lines or bands are then determined by the transmission of the optical system.

Ratios of measured photocurrents to theoretical intensities were plotted as a function of wavelength for various bands in the First Negative and Second Positive Systems in nitrogen, and for several multiplets in mercury. Values of relative intensities in nitrogen were obtained from Bates [1949], and those in mercury from Crosswhite and Dieke [1957]. Intensity ratios for bands or lines arising from the same upper level were found to lie on smooth curves. By appropriate normalization of groups of

transitions arising from different upper states, it was possible to construct a smooth curve covering the entire wavelength region between 3000 and 6000 Å. The resulting curve is shown in Figure 2.11.

G. Vacuum and Gas Handling Systems

It is well known that concentrations of certain impurities in atmospheric gases as small as one part per million may cause marked alterations in the electron removal processes occurring in the pure gas. Standard ultra-high vacuum techniques are employed in order to reduce to a minimum the contamination of the experimental gas by outgassing of the vacuum system.

In addition to the clean system, an evacuated region is provided for the diverging electron beam. The beam tube vacuum and the uhf chamber are separated by a thin metal foil to avoid distortions of the beam homogeneity by multiple Coulomb scattering. The beam tube is operated at about 10^{-5} Torr, somewhat below the pressure required from considerations of beam dynamics alone, in order to reduce the chance of contamination of the experimental gas through possible pinhole leaks in the foil.

A schematic of the vacuum system is shown in Figure 2.1. A Kinney fore-pump with a speed of 80 cfm is used to rough out both the cavity and the beam tube. A 1500 liters/sec NRC diffusion pump followed by a water cooled chevron baffle and 6" gate valve is used to evacuate the beam tube and beam scattering section. The clean experimental chamber is evacuated by an 1800 liters/sec Dresser diffusion pump isolated from the chamber by a water cooled baffle and sorbent trap containing zeolite. The net pumping speed at the cavity is reduced to about 150 liters/sec by the

various traps.

The rf cavity and gas handling system are constructed from non-magnetic type 304 stainless steel. Due to the difficulty of machining flanges of the order of 48" I.D. to sufficient accuracy for crush metal seals, the foil window is sealed to the cavity and beam tube with double viton O-rings. The space between the two O-rings is evacuated through a connection to the beam tube. A 6" Granville-Phillips valve is used to seal off the cavity from the pump when the latter is filled with gas during experiments. The 4" optical window, made from Spectrosil quartz to prevent color-centre formation in the intense radiation field, is sealed to the cavity opposite the optical port, is attached to the cavity by a Varian Conflat seal.

The gas handling system, constructed from $\frac{1}{2}$ " diameter stainless steel tubing, is evacuated separately by a 200 liters/sec CVC diffusion pump equipped with a water-cooled baffle and zeolite sorbent trap. The system is attached to the cavity through a GE 1.5" bakeable valve, and a similar valve is used to seal it off from the pump when gas is to be admitted to the cavity. The gases used in the experiments are research grade oxygen and nitrogen contained in steel cylinders filled to 500 psi, and supplied by the Matheson Corporation, New Jersey. Gas from the bottles is admitted to the cavity through a pressure regulator and Granville-Phillips variable-leak pressure controller. The variable leak is capable of controlling flow rates from more than 100 standard cc per second to less than 10^{-8} standard cc per sec, and is used to admit gas continuously to the cavity to compensate for that lost through the mass spectrometer aperture.

All seals are made with Varian conflat flanges, and the entire gas handling system is bakeable to 450° C.

Figure 2.12 shows the system used for the measurement of gas pressures. A Granville-Phillips capacitance manometer is mounted onto the cavity with its reference side connected, as shown in the figure, to a system containing an oil manometer, a CVC McLeod Gauge, and a needle valve air inlet. The system, which is constructed from Pyrex, is evacuated by a Cenco diffusion pump and Welsh forepump, which provide an ultimate pressure of less than 10^{-5} Torr. With the cavity and reference system both evacuated, the capacitance bridge is balanced. Air is then admitted to the reference side at the pressure at which the cavity is to be filled, which unbalances the capacitance bridge. This pressure is then determined on the McLeod Gauge between 10^{-3} Torr and 10 Torr, and on the oil manometer, which uses Octoil as the working fluid, at pressures greater than 10 Torr. Alternatively, two Hastings-Raydist thermocouple pressure gauges, calibrated against the McLeod Gauge, are used as rough monitors of this pressure. Gas is then admitted slowly to the cavity and the bridge is rebalanced. This technique permits pressure measurements to be made with absolute manometers without allowing the clean experimental gas to come in contact with the manometric fluid.

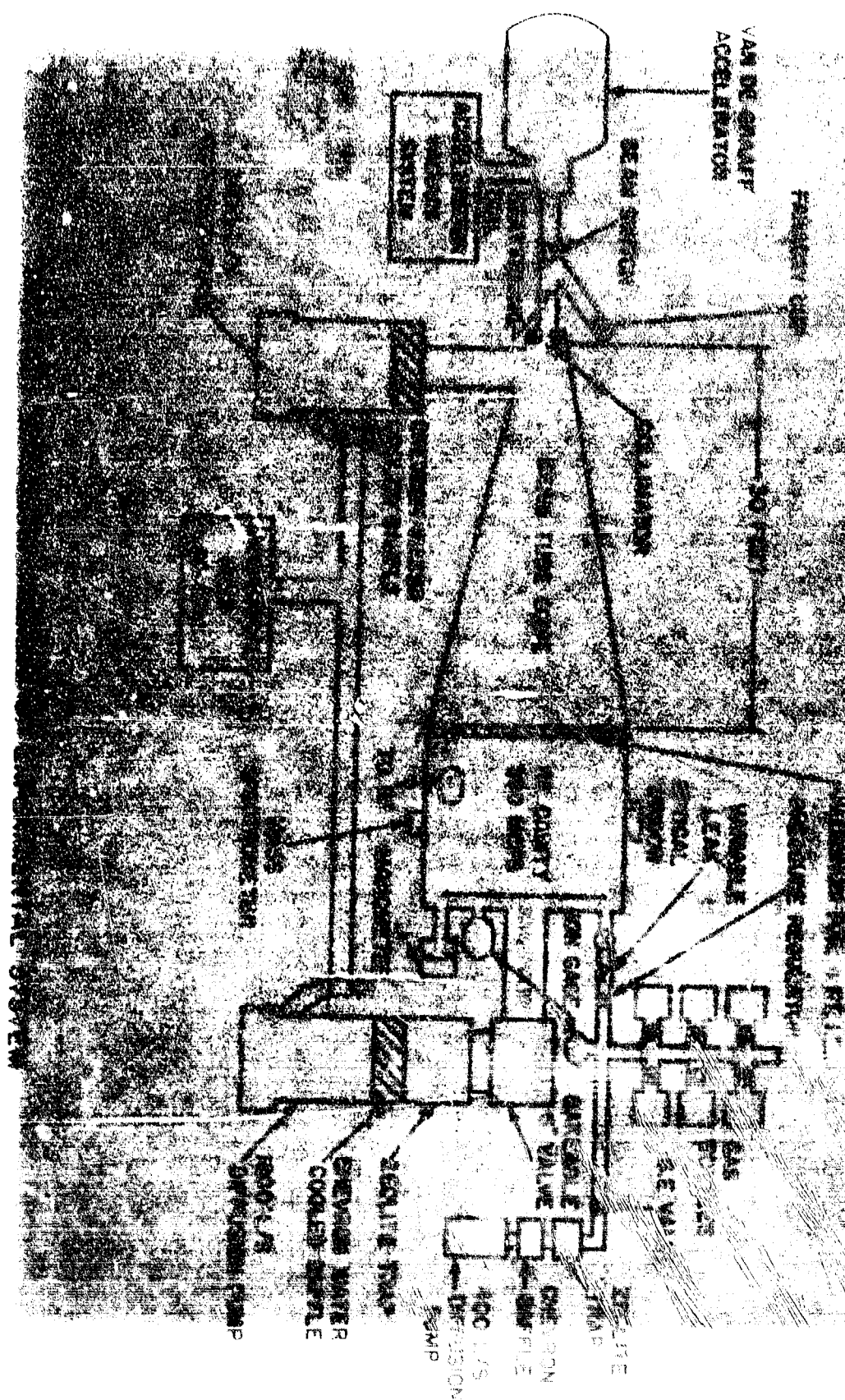
To minimize the effects of wall-occluded impurities, it is necessary to bake the cavity at high temperatures while evacuating prior to filling with experimental gas. A serious wall contaminant in the cavity is water released from the zeolite sorbent trap during its activation. To remove water effectively from steel surfaces, a wall temperature of at least 200°C is required.

The oven used to bake the experimental chamber consists of twelve 2.5 kilowatt Calrod heaters wound around the cavity, and twelve 0.5 kilowatt Calrod heaters attached to the back. Several chromel-alumel thermocouples are attached to various parts of the cavity in order to monitor the temperature during bakeout. The cavity is insulated thermally by wrapping it with a thick layer of fibre glass wool. The temperature of the oven is controlled by varying the current through the Calrods by means of variacs. Heating tapes are used to bake the gas handling system. Because of the various Viton O-rings, the cavity cannot be baked at temperatures higher than 250°C . The gas handling system, however, which is baked separately can withstand temperatures up to 450°C .

After cavity bakeout at 250°C for 24 to 48 hours, the background pressure in the cavity is on the order of 1.0×10^{-8} Torr or less, with a rate of rise of about 1.0×10^{-8} Torr/minute when the cavity is shut off from the pumps. For a gas load of 5×10^{-3} Torr the cavity contributed impurity level is about 1 part in 10^4 after thirty minutes, which represents the least favorable conditions under which the data on the following pages were collected.

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A - HELIUM VALVES

B - VAC. DIFFUSER

C - COLL. CUP

DD - INSULATED LANCES

EE - THERMION CUPS



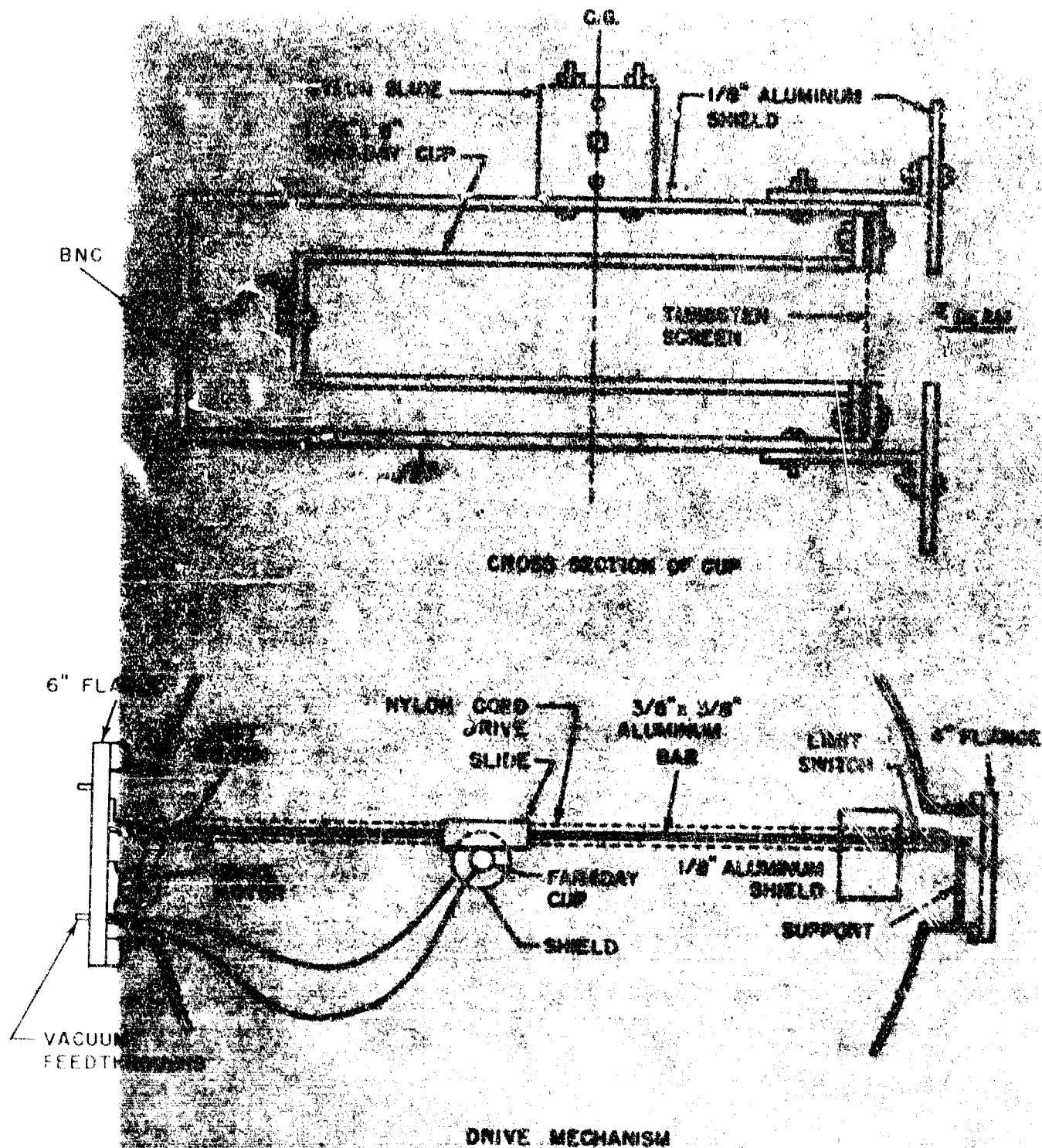
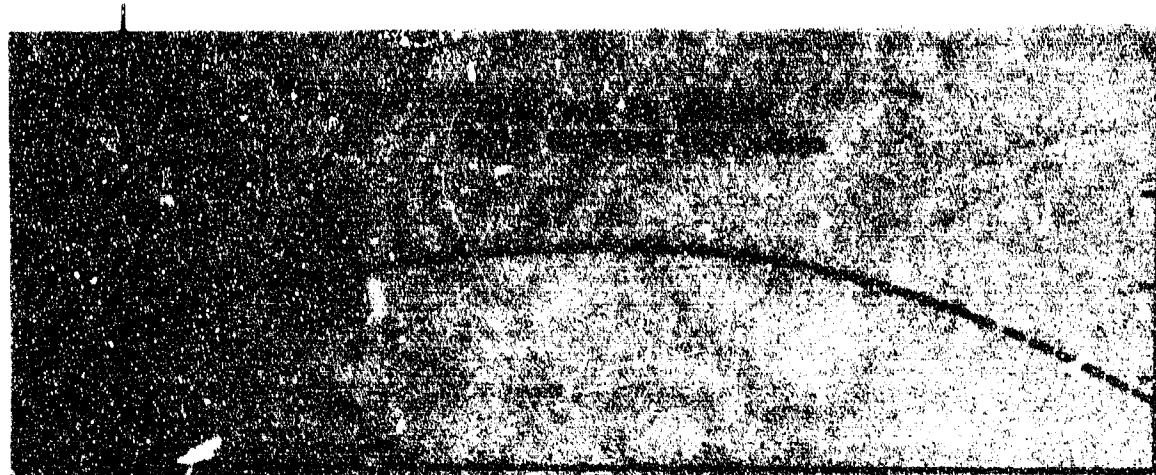
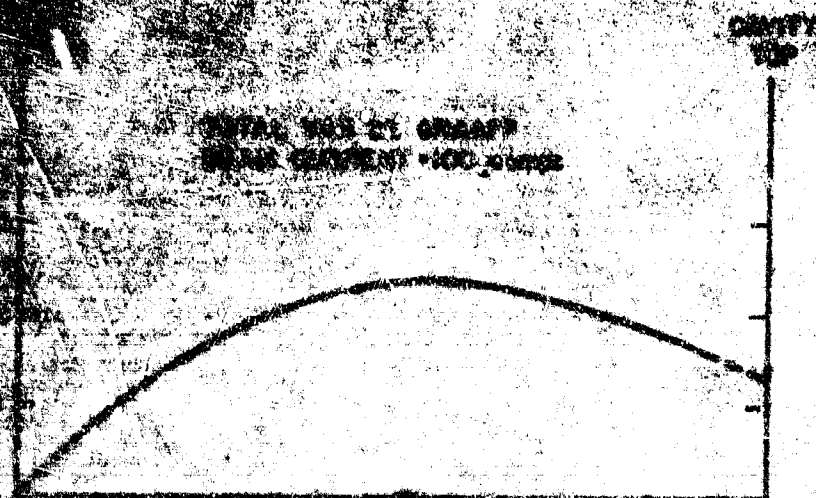


FIGURE 2.3- FARADAY CUP FOR BEAM CALIBRATION

MASS
SPECTROMETER
PORT



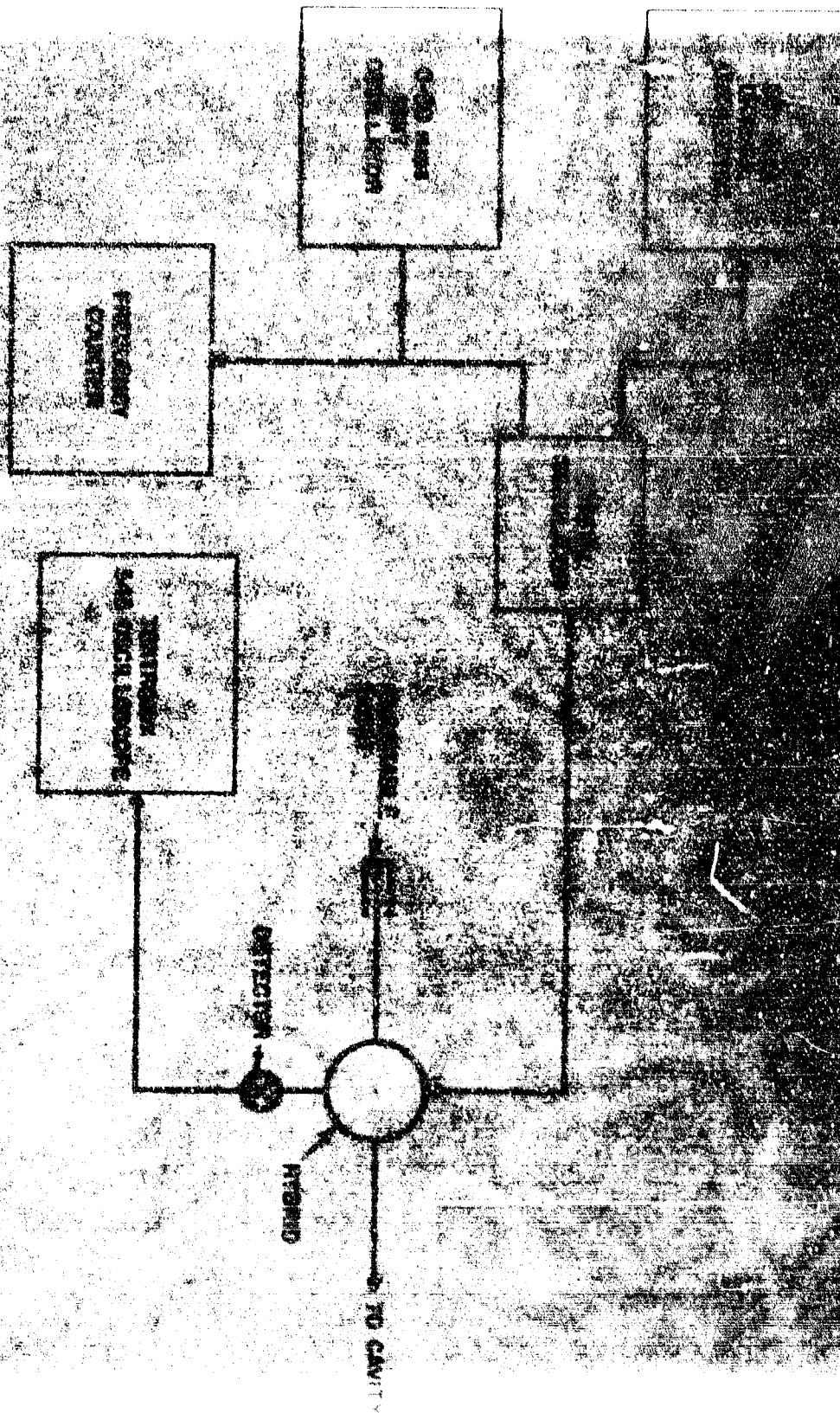
VERTICAL PROFILE OF ELECTRON BEAM



VERTICAL PROFILE OF ELECTRON BEAM

FIGURE 2A

FIGURE 10-10 RF CIRCUITS



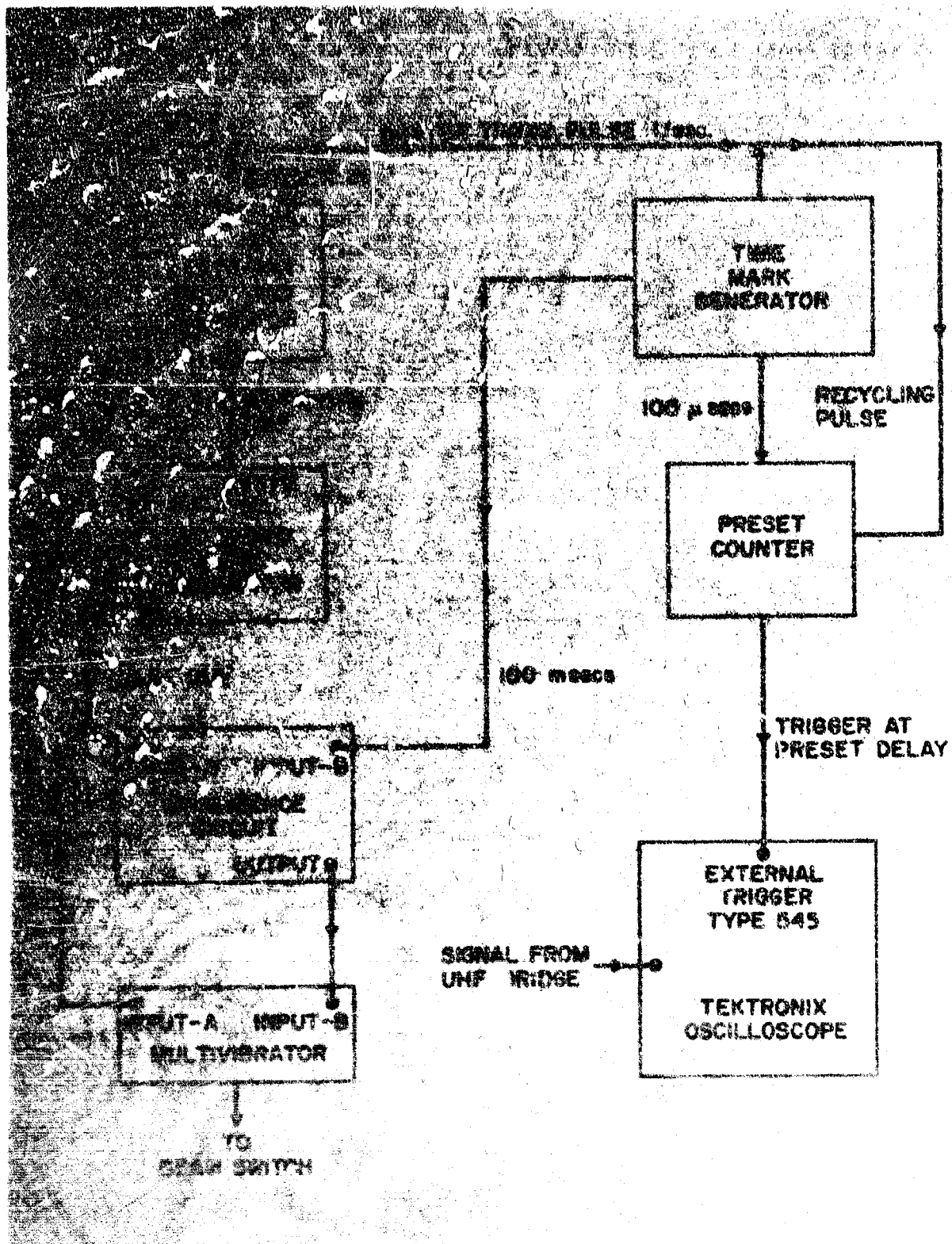


FIGURE 2.6- BLOCK DIAGRAM OF TIMING CIRCUIT

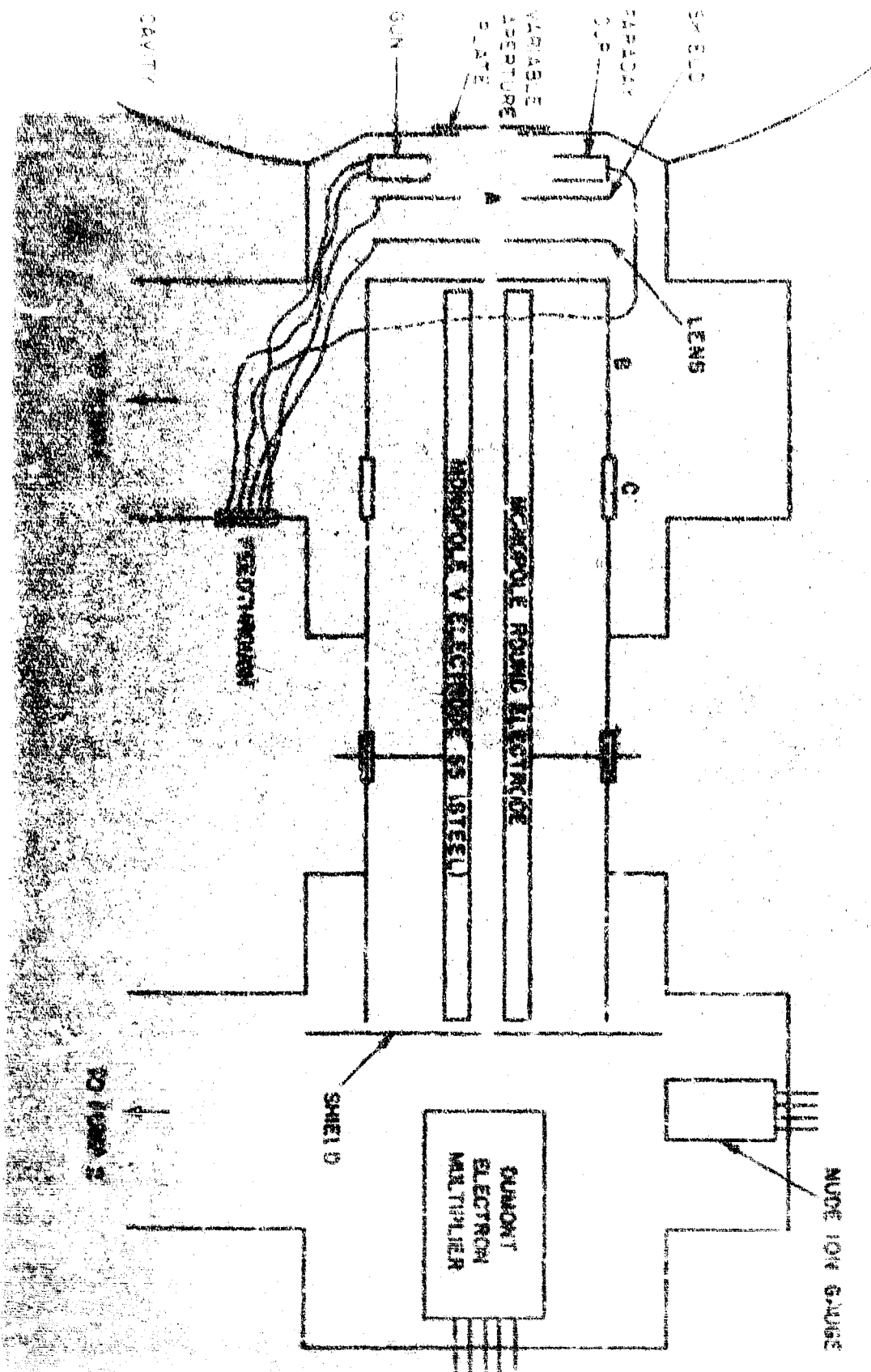


FIGURE 2.8 CROSS SECTION SCHEMATIC OF MONOPOLE STRUCTURE AND HOUSING

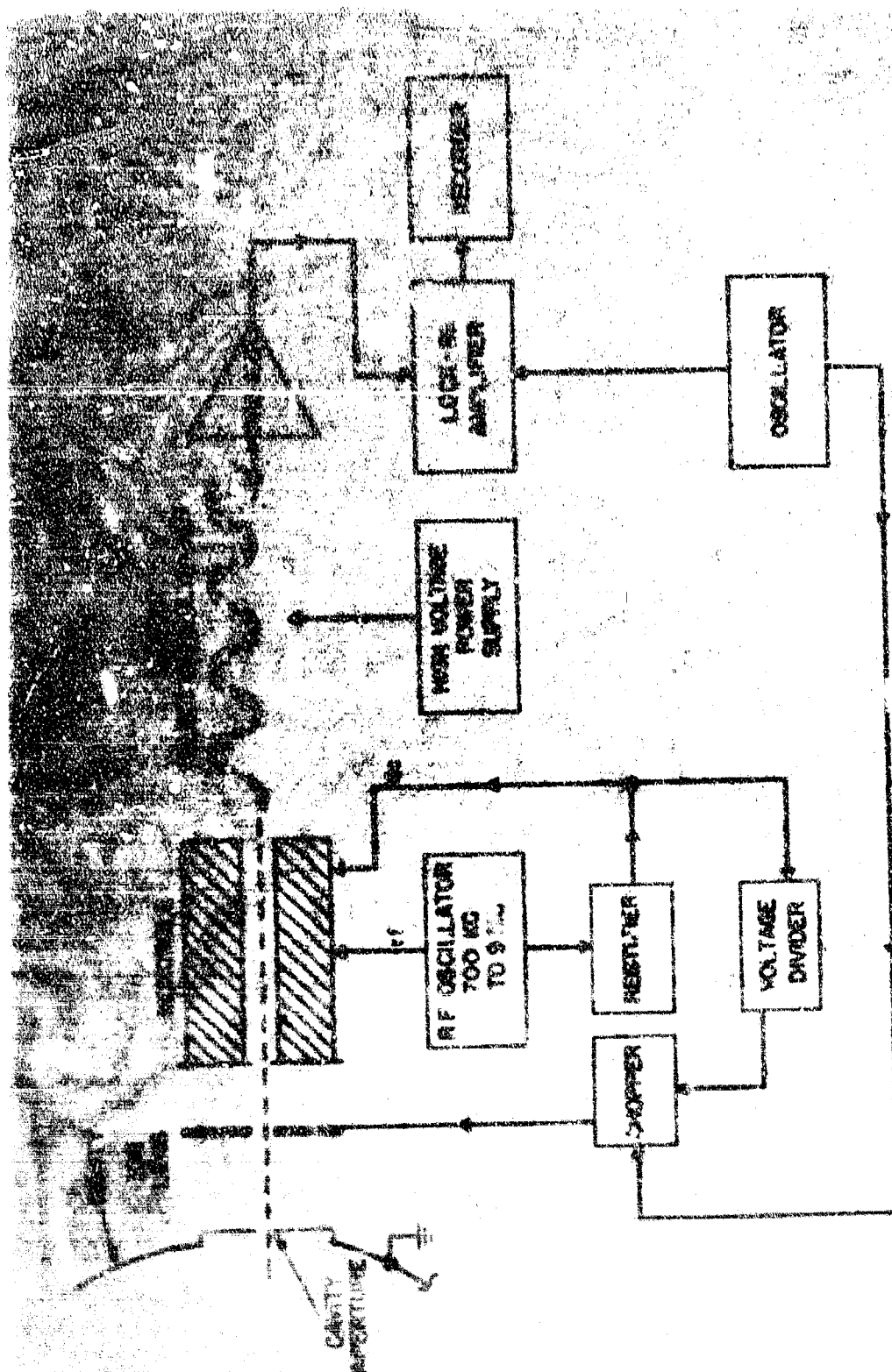


FIGURE 2.9- ELECTRONICS FOR MASS SPECTROMETER

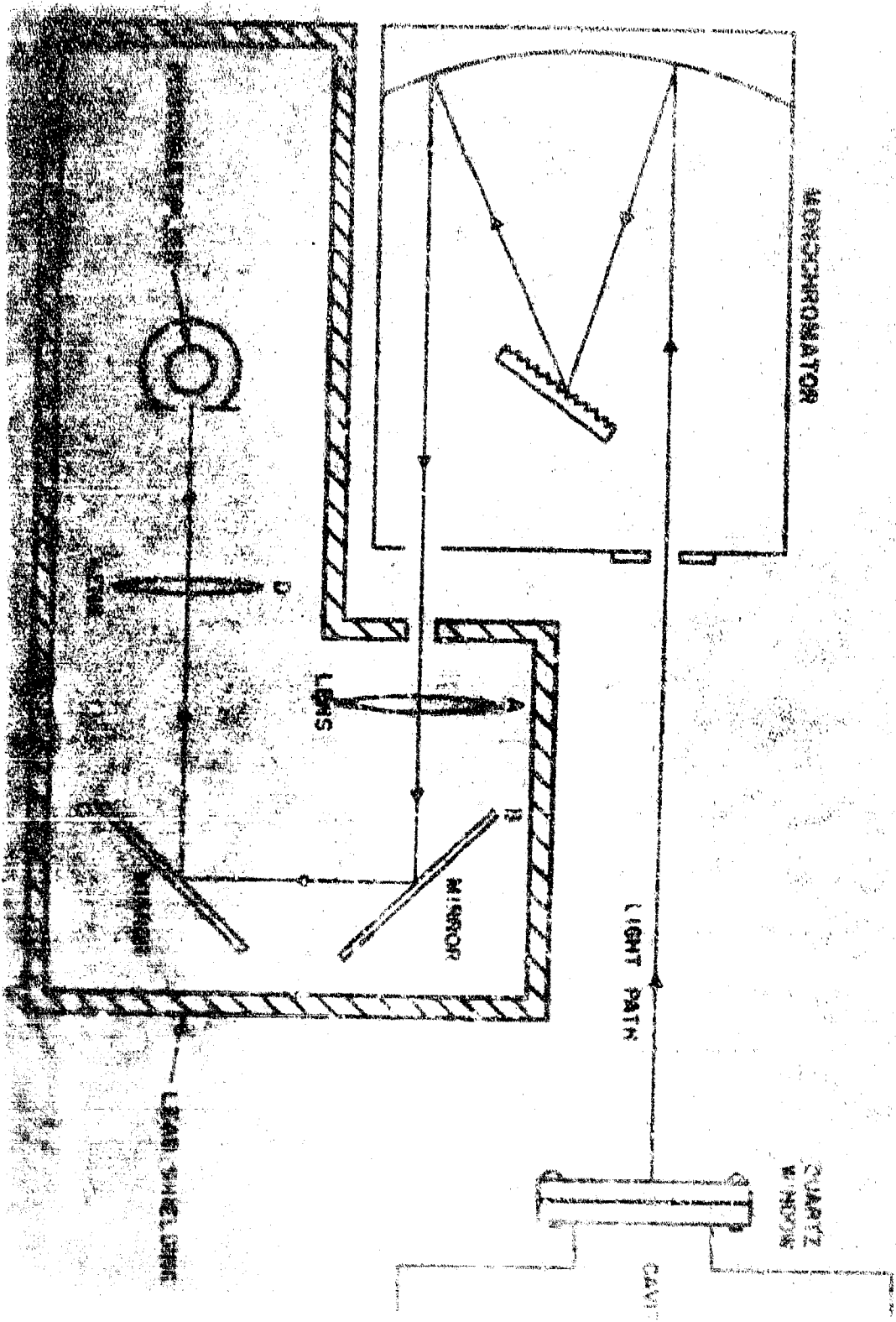


FIGURE 2.10 OPTICAL SYSTEM

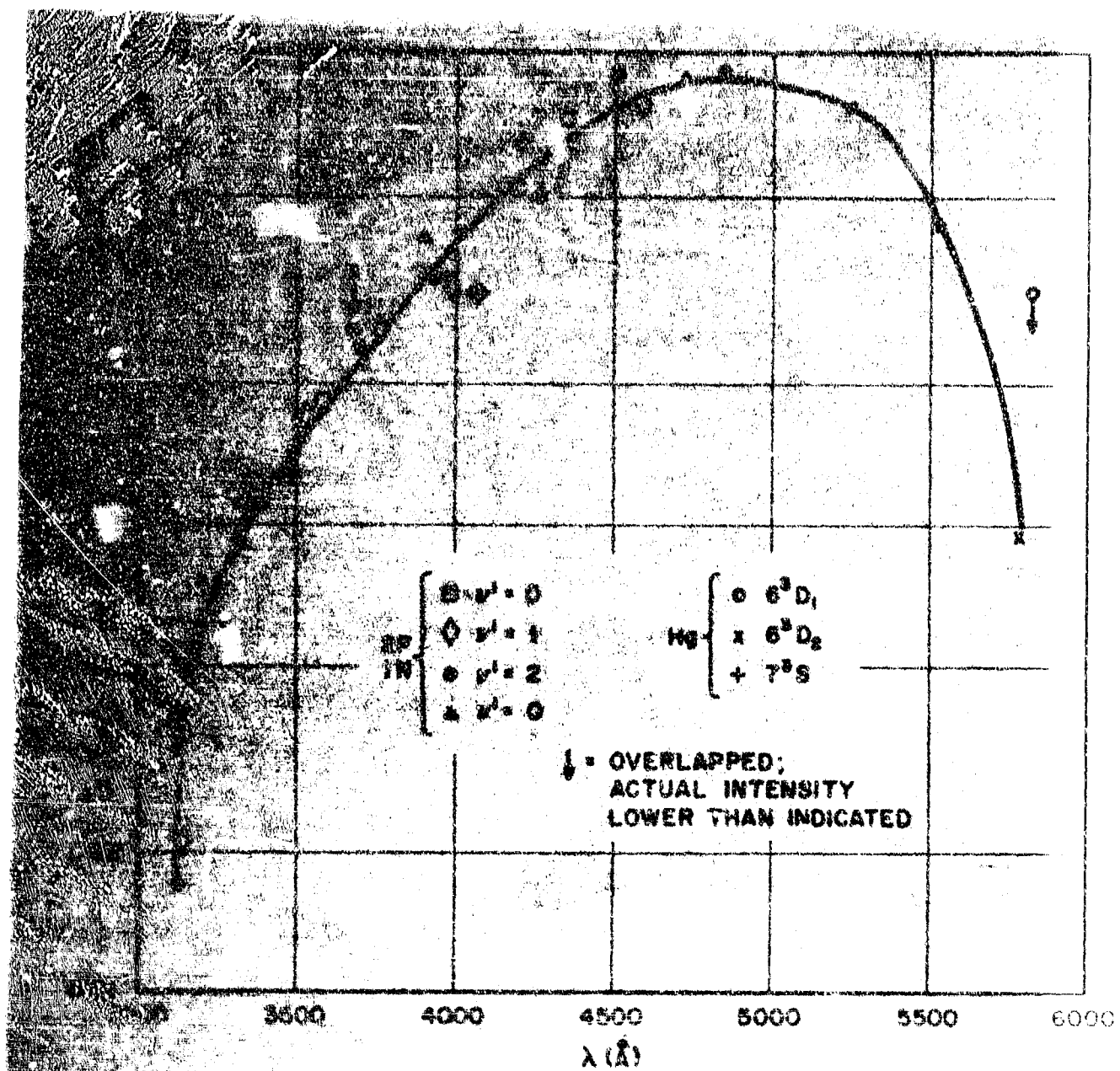


FIGURE 2.11 - RELATIVE RESPONSE OF SPECTROMETER

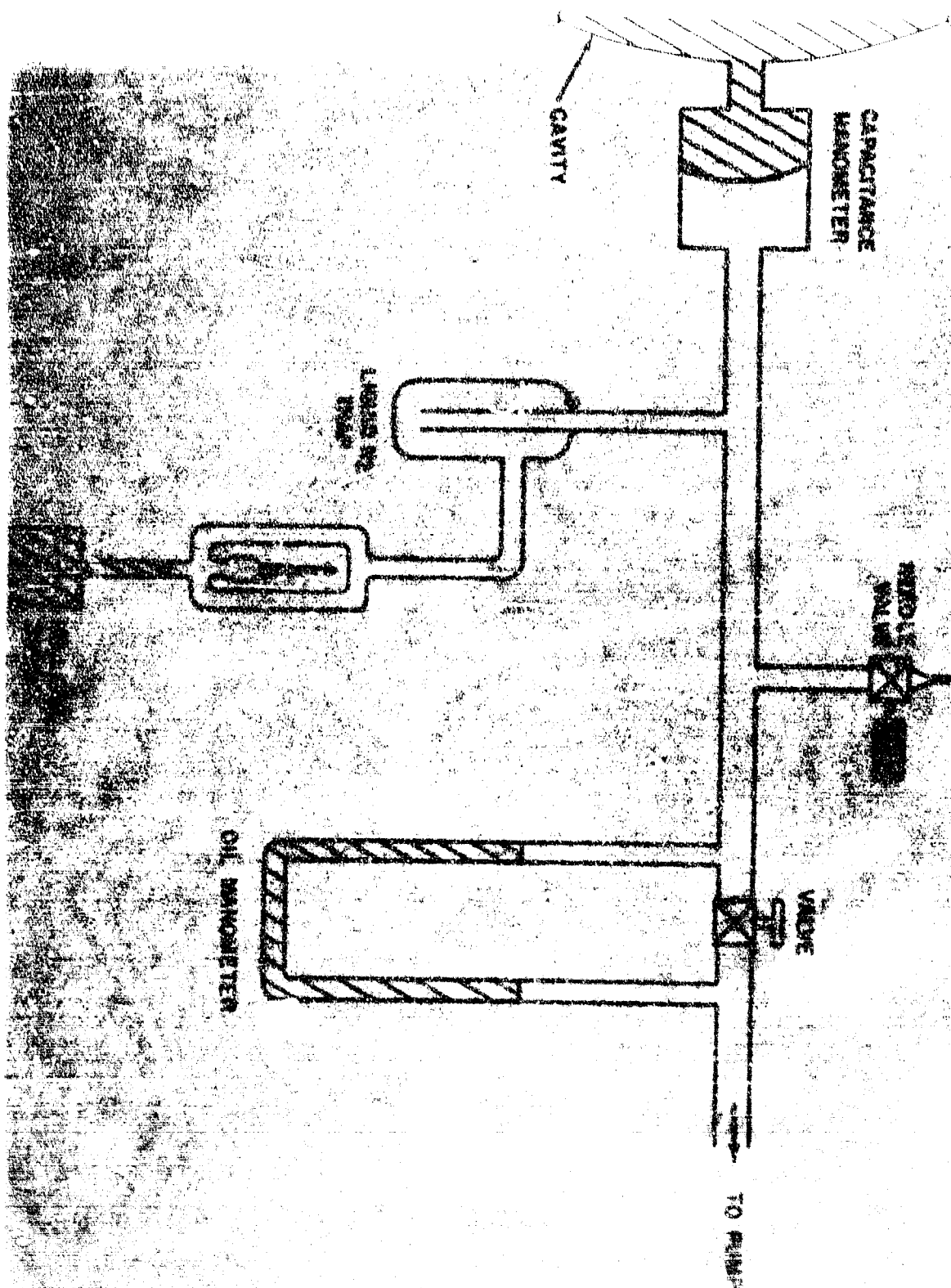


FIGURE 2.12- REFERENCE PRESSURE MEASURING SYSTEM

III. THEORETICAL BACKGROUND

A. Introduction

This chapter provides the theoretical framework in which to view the experimental results presented in the remainder of this report. The chapter includes descriptions of the various processes by which charged particles and excited neutral species are created and destroyed in atmospheric gases subjected to irradiation by 1.5 Mev electrons. The discussion will be on an empirical level, aimed at developing a phenomenological description of the behavior of a gas in which the various reactions are occurring. In addition, experimental tests will be derived by which the data can be examined for evidence that a given type of reaction is taking place. Detailed accounts of the reaction mechanisms will not be included, for reasons of brevity; for these, the reader is referred to the excellent treatises by McDaniel [1964], Hasted [1964], and Bates [1962]. The chapter concludes with a description of the problems in extrapolating laboratory results to ionospheric situations.

B. Ionization by Beam Electrons

A relativistic electron traversing a molecular gas can interact directly with one of the bound electrons of a neutral gas molecule, imparting sufficient energy to it to excite it to either a higher bound state or the ionization continuum. A calculation by Bethe [1936] of the distribution of various kinds of collisions for electrons in the Mev range with hydrogen molecules suggests that approximately 50% of the collisions produce molecules excited into electronic states with principal quantum number 2, 8% into states with quantum number 3, and 5%

into all higher states; 4% of the collisions are elastic. The remaining 33% of the collisions result in ionization, in which the molecular ion may be left in an excited state. Figure 3.1 shows the calculated energy spectrum of secondary electrons produced by 1 Mev electrons incident on H_2 . It can be seen that many of the secondary electrons are sufficiently energetic to produce further excitation and ionization in the gas. It is reasonable to expect that the calculation for hydrogen should display the general features which can be expected for other diatomic gases. Although the cross-sections for various processes may vary somewhat differently with energy.

The production of electron-ion pair in a gas by electron impact can be written as a binary collision between the incident electron and a gas molecule. For convenience in comparison with laboratory measurements, this reaction can be expressed by the rate equation

$$\frac{\partial x^+}{\partial t} = \frac{\partial n}{\partial t} = K p i \quad (3.1)$$

where x^+ is the number density of ions produced per cm^3 , n the number density of the electrons per cm^3 , p the pressure of the target gas in Torrs, and i the beam current density in micro-amperes/ cm^2 . For an a priori calculation of the rate coefficient K , one must resort to a mixture of theory and experiment. If a fast electron loses V volts in traversing one centimeter of a gas at STP, and if an expenditure of W volts of primary electron energy results in one ion pair under condition where all secondaries are stopped in the gas, then $K = 7.55 \times 10^9 W/V$ at $25^\circ C$. From

a calculation by Nelms [1957], the stopping power V/ρ where ρ is the gas density in gram cm^{-3} , is 1.66 Mev cm^2/gm in air, N_2 , and O_2 for electrons at 1.5 Mev. Because of the complication of ionization by energetic secondary electrons, it is difficult to compute W from first principles. However, values of W have been determined experimentally for these gases by Jesse and Saudauskis [1953] and Jesse [1958] under conditions in which all secondary electrons are stopped in the gas. Table I presents these results, together with the calculation for K.

Laboratory measurements are frequently complicated by the presence of back-scattered and secondary electrons produced at the chamber walls, in addition to those in the primary beam. For the aluminum back plate used in the reaction chamber, one can expect about 7% of the incident electron beam to be back-scattered with energies of 50 ev or greater [Bakish, 1962]. The last column in Table I includes the full 7% correction on K; this correction provides an upper limit for K, since many of the back-scattered electrons have insufficient energy to traverse the cavity completely. "True" secondary electrons in the energy range below 50 ev are also emitted from the back plate, but it is expected that their total number above the ionization potential of the gas is not significant.

Of particular interest in the present experiment is the rate of energy relaxation of the secondary electrons. In some of the measurements reported below, a steady-state electron distribution is established in equilibrium between continuous ionization (hence production at high energies) and electron removal and energy relaxation processes. For this distribution to approximate gas temperatures, the free electron removal rates must be low compared to the energy relaxation frequencies, so

T A B L E I

GAS	$\frac{U}{\rho} \left(\frac{\text{Mev cm}^2}{\text{gm}} \right)$	$\rho \left(\frac{\text{gm}}{\text{cm}^3} \right)$	$U \left(\frac{\text{kev}}{\text{cm}} \right)$	$W \text{ eV/ion pr}$	$\frac{U}{W} \frac{\text{ion pr}}{\text{cm}}$	$K \frac{\text{cm}^2}{\text{Torr uamp}}$	Back K + Scattering
Air	1.66	1.19×10^{-3}	1.98	33.9	58	$\frac{\text{ion pr}}{\text{cm}^3 \text{sec}}$ $4.4 \times 10''$	$47 \times 10''$
N ₂	1.66	1.15	1.91	35.0	54.5	$4.1 \times 10''$	$4.4 \times 10''$
O ₂	1.65	1.31	2.16	30.9	70	$5.3 \times 10''$	$5.7 \times 10''$

CALCULATION OF RATE COEFFICIENT FOR IONIZATION
by BEAM ELECTRONS

that the electrons spend most of their free lifetimes at thermal energies. The correct approach to the analysis of this problem requires a solution to the Boltzmann transport equation for the secondary electrons, in which elastic and all pertinent inelastic collisions are included. This would be a staggering task even if all relevant cross-sections were known over the energy range of interest, which they in fact are not. A very promising approximate approach in the current literature is a technique described by Frost and Phelps [1962]. In this work the frequency of energy exchange collisions is obtained from comparisons of theoretical and experimental values for mobility and diffusion coefficients, by adjusting a set of assumed elastic and inelastic collision cross-sections for optimum fit. For nitrogen, their value for the frequency of energy exchange collisions at thermal energies is $\nu_u \approx 6.5 \times 10^5 p$, where p is the gas pressure in Torr. This is to be compared with the ordinary elastic collision-frequency model for energy exchange, defined by

$$\frac{\partial u}{\partial t} = \frac{m}{M} \nu_c u \quad (3.2)$$

where u is the electron energy in excess of that corresponding to the ambient gas, m and M are the masses of electrons and neutral molecules, respectively, and ν_c is the frequency for elastic collision with energy transfer. For nitrogen, this gives an elastic rate of about $3 \times 10^3 p$, which is considerably smaller than the rate obtained by Frost and Phelps. One ordinarily expects inelastic collisions to bring the electrons very quickly down to energies below the lowest available state of the neutral molecule. The major part of the electron cooling time is then assumed to be spent in elastic collisions as described by Equation (3.2). As will be reported below, however, observations have been made in

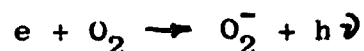
which the electrons are apparently thermal although their lifetimes are shorter than the elastic-collision cooling time, but are still within the lifetime specified by the results of Frost and Phelps.

C. Electron and Ion Loss Mechanisms

The charged particles produced by the primary ionization of $O_2 - N_2$ mixtures are subject to various possible loss mechanisms. These loss mechanisms can be conveniently classified into three general types: attachment, recombination and diffusion.

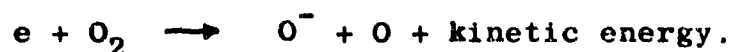
1. Electron attachment

Electrons can be removed from the volume of certain gases by combining with neutral molecules to form negative ions. Various mechanisms are available to stabilize the resulting negative ion by removing the excess binding energy from the electron-molecule system. The energy may be radiated as a photon; This process, referred to as radiative attachment, is written

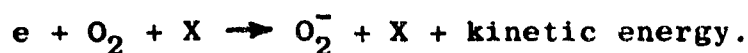


If the electron energy and the inter-nuclear distance in the neutral molecule are appropriate, the electron may be captured into an excited state of the ion from which it very rapidly makes a transition to a repulsive ionic state. This process, called dissociative attachment, produces a neutral atom and a negative atomic ion, the excess energy being carried off as kinetic energy

of the atomic fragments. Thus



Finally, a ternary (3-body) collision may occur between an electron, a neutral molecule to which the electron will ultimately attach, and a second molecule (not necessarily of the same species) which carries off the excess energy. Thus



Electron attachment losses are described quantitatively by the rate equation

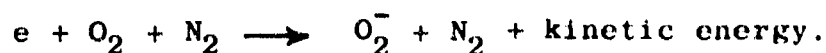
$$\left(\frac{\partial n_e}{\partial t}\right)_{\text{attachment}} = -\nu_a n_e, \quad (3.3)$$

where ν_a is the net attachment frequency, and is the sum of contributions from the radiative, dissociative, and three-body processes. For thermal electrons in pure oxygen, the best current estimates in the literature give:

$$\begin{aligned} \nu_{\text{rad.}} &\cong 4 \times 10^{-21} [O_2] \text{ sec}^{-1} && [\text{Archer, 1963}] \\ \nu_{\text{3-body}} &\cong 2 \times 10^{-30} [O_2]^2 \text{ sec}^{-1} && [\text{Pack and Phelps, 1966}] \\ \nu_{\text{diss.}} &\cong 0 && [\text{Pack and Phelps, 1966}] \end{aligned} \quad (3.4)$$

[Dissociative attachment becomes important only for electron energies above ~ 1.3 ev.] Thus three-body attachment is the only important process at pressures above 10^{-5} Torr.

In mixtures of oxygen with nitrogen, the ground-state N_2 molecule can also serve as a stabilizing third body:



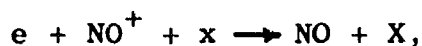
The total three-body attachment rate equation in nitrogen-oxygen mixtures can be written

$$\left(\frac{\partial n}{\partial t}\right)_{3\text{-body}} = -\beta_0 [O_2] ([O_2] + \xi [N_2]) \quad (3.5)$$

where ξ , the efficiency of an N_2 molecule in stabilizing the negative ion relative to an O_2 molecule, is of the order of a few percent [Chanin et al, 1962].

2. Recombination

Electrons can recombine with positive ions to form neutral molecules in various stages of excitation. The energetics of the disposal of binding energy in the recombination process are similar to the attachment reactions described above. Radiative, dissociative and three-body recombination are all at least theoretically possible. For the low ionization levels which we encounter, three-body recombination in which the third body is a charged particle is very unlikely. A process such as



however, in which the stabilizing third body is a neutral molecule, may be expected to dominate the recombination mechanisms at sufficiently high pressures. Radiative recombination seems to have a very small probability; a theoretical estimate of the rate of the reaction



yields the result [McDaniel, 1964]

$$\frac{\partial n_e}{\partial t} \sim 10^{-12} P n_e$$

where P is the density of positive ions. It is presently believed that dissociative recombination is an important electron-ion process in the upper atmosphere [Kasner and Biondi, 1965]. For this case we write

$$e + P_{2j}^+ \rightarrow P_j + P + \text{kinetic energy} \quad (3.6)$$

and $\left(\frac{\partial n_e}{\partial t}\right)_{\text{recomb.}} = \left(\sum_j \alpha_{je}\right) n_e$

where P_j is the density of the "jth" positive ion and α_{je} is the pertinent two-body coefficient for its recombination with electrons.

In addition to the electron-positive ion reactions described above, negative ions may also charge-exchange with positive ions. Here there can be a two-body process in which the excess energy appears as excitation of the resulting species:



A three-body ion-ion recombination also occurs, and is of great importance in ionized air at low altitudes. The loss of negative ions from oxygen by recombination can be written [Sayers, 1938]

$$\frac{\partial N}{\partial t} = - \left[10^{-[8 \pm 0.5]} + 7.2 \times 10^{-[9 \pm 0.5]} p \right] P N \quad (3.7)$$

3. Diffusion

Charged particles can be removed from the volume of a gas by diffusion to the walls of the experimental container. Experiments indicate that the charge species readily recombine at the walls by utilizing the latter as an efficient medium for energy and momentum disposal. This imposes the boundary conditions that all charged particle densities vanish at the walls [cf. however McDaniel, 1964 pp 496 ff]. The vanishing of the particle densities at the walls guarantees the existence of a concentration gradient for the charge species, which makes diffusion possible.

The equation describing the current of the jth particle species under the combined influence of a concentration gradient and an electric field E is

$$\Gamma_j = - D_j \nabla n_j + \mu_j n_j E , \quad (3.8)$$

where D_j and μ_j are the free diffusion and mobility coefficients of the jth species. These quantities satisfy the Einstein Relation [Jeans, 1954]

$$\frac{D_j}{\mu_j} = \frac{k T_j}{e} \quad (3.9)$$

where T_j is the "temperature" of the jth species. The diffusion coefficient is defined for a Maxwellian distribution by the equation

$$D_j = \frac{1}{3} \lambda_j \bar{v}_j , \quad (3.10)$$

where λ_j is the mean free path of the j th species for elastic collisions with momentum transfer with gas molecules and $\bar{v}$ is the mean thermal speed of the j th species. As a result, D_j and λ_j are both inversely proportional to the gas pressure, and diffusion can dominate any volume process at sufficiently low pressures. Even in the absence of external electric fields E does not, in general, vanish. The initially unequal rates at which the various charged particle species diffuse out of the volume of the chamber sets up space charge fields (E) which profoundly influence further diffusion. To study this influence in greater detail, one must consider specific plasmas containing the kinds and numbers of ion species of interest. In the work to be described in the body of this report, three situations are of particular interest:

- a) Plasmas containing electrons and a single species of positive ions;
- b) Plasmas containing electrons and two species of positive ions;
- c) Plasmas containing electrons and one species each of positive and negative ions.

Case a) represents the situation leading to the well-known ambipolar diffusion problem [Biondi and Brown, 1949]. As long as $n = P$ everywhere in the plasma, both electrons and positive ions will diffuse at a common rate according to the equation

$$\frac{\partial n}{\partial t} = \frac{\partial P}{\partial t} = D_a \nabla^2 n = D_+ \left(1 + \frac{T_e}{T_i}\right) \nabla^2 n \quad (3.11)$$

where D_a is the ambipolar diffusion coefficient, $T_e = T_i$, as the electron and ion temperatures, respectively. If $T_e = T_i$, as

appear to be the case in the work discussed below, then $D_a = 2D_+$ [cf. however, Allis and Rose, 1954].

Case b) represents a more complex situation, in that charge neutrality considerations above do not fix the relative spatial distribution of the electrons and the two ion species, P_1 , P_2 , as they did in Case a). If one imposes the assumption of spatial congruence [Phelps, 1952], that is, that

$$\frac{\nabla n}{n} = \frac{\nabla P_1}{P_1} = \frac{\nabla P_2}{P_2}$$

then

$$\left. \begin{aligned} \frac{\partial P_1}{\partial t} &= D_{a1} \nabla^2 P_1 \\ \frac{\partial P_2}{\partial t} &= D_{a2} \nabla^2 P_2 \\ \frac{\partial n}{\partial t} &= \frac{\partial P_1}{\partial t} + \frac{\partial P_2}{\partial t} \end{aligned} \right\} \quad (3.12)$$

where D_{a1} , D_{a2} are the ambipolar diffusion coefficients which would be obtained if each ion species were diffusing in the absence of the other. In some cases, particularly those involving strong recombination of electrons with one of the ion species, the assumption of a spatial congruity is difficult to justify, and a more complete theory must be used [McDaniel, 1964].

Case c) presents a similar complexity, in that relatively simple solutions can be obtained only with the assumption of spatial congruence of all species. In this latter case, one finds for the effective diffusion coefficients for the electrons, positive ions, and negative ions [Oskam, 1958]

$$\begin{aligned}
D_{e, \text{eff}} &= 2D_+ (1 + N/n) \\
D_{+, \text{eff}} &= 2D_+ \\
D_{-, \text{eff}} &\cong 0
\end{aligned}
\tag{3.13}$$

As will be seen in Chapter V, the assumption of spatial congruence of all the particle species is frequently difficult to justify on physical grounds. In this case, one must go back to the set of Equations 3.8, and find the complete self-consistent solution for the currents subject to the conditions

$$\sum_j n_{j+} = \sum_K n_{K-} \quad ; \quad \sum_j \Gamma_{j+} = \sum_K \Gamma_{K-} \quad , \tag{3.14}$$

that is, that the total local positive and negative charge and current densities vanish. This then leads to a rate equation for the diffusion of each particle species of the form

$$\frac{\partial N_j}{\partial t} = - \nabla \cdot \Gamma_j \quad , \tag{3.15}$$

which in general must be solved numerically on a high-speed electronic computer.

For many situations of interest, it is sufficiently accurate to make the replacement

$$\nabla^2 n_j \Rightarrow \frac{1}{\Lambda_{||}^2} n_j$$

where $\Lambda_{||}$, the fundamental diffusion length, is the largest eigen-value of the equation

$$\frac{\partial n_j}{\partial t} = D_j \nabla^2 n_j \tag{3.16}$$

subject to the boundary conditions that n_j vanish at the container

boundary. For a right circular cylindrical container of radius R , height h ,

$$\frac{1}{\Lambda_{11}^2} = \left(\frac{2.405}{R} \right)^2 + \left(\frac{\pi}{h} \right)^2 \quad (3.17)$$

D. Production and Loss of Excited States

In this section, the mechanisms by which excited states of neutral and ionic species can be created or destroyed is considered. One must know the excited state distribution in the irradiated gas, both to interpret the observed optical emission from these states, and to account for the profound effect that excited states can have on measured rate coefficients [McDaniel, 1964, pp. 250,255].

The rate equation governing the population N_j of the j th excited states is [Fowler, 1954]

$$\frac{\partial N_j}{\partial t} = P_j + D_j \nabla^2 N_j + B_{oj} \rho_{oj} N_o - \sum_{i=0}^{j-1} A_{ji} N_j + \sum_{k=j+1}^{\infty} A_{kj} N_k \quad (3.18)$$

Here D_j is the diffusion coefficient for state j , B_{oj} the Einstein absorption coefficient for radiation corresponding to transitions between state j and the ground state (denoted by the subscript "o"),

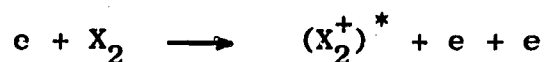
ρ_{oj} is the flux density of this radiation, and A_{jk} is the Einstein spontaneous emission coefficient for a downward transition from state j to state k . P_j includes all other mechanisms for the production and loss of N_j from the volume of the gas. The diffusion term in Equation 3.17 is only significant when state j is metastable; for short-lived states, diffusion is a negligible

loss mechanism relative to the radiative processes. For a weakly ionized gas, only the ground state is present in sufficient density to produce appreciable population of upper states by absorption; the only states which can be affected by the process described by the third term are therefore those for which $B_{0j} \neq 0$. The first summation in Equation (3.17) represents the radiative loss out of N_j to all lower states; it is convenient to define the radiative lifetime τ_{kj} of the state by

$$\tau_{kj}^{-1} = \sum_{i=0}^{j-1} A_{ji} \equiv A_j. \quad (3.19)$$

The second summation represents the population of N_j by radiative cascading from all higher states N_k ; the relative importance of this term must be examined separately in each experimental situation.

Consider now the term P_j . A binary inelastic collision between an energetic electron and a gas molecule will produce an excited state of either the neutral molecule or the molecular ion, so that the reaction can be represented by one of the following:



The rate equation for this process can be written

$$\left(\frac{\partial N_j}{\partial t} \right)_{\text{impact}} = K_j n_i \quad (3.20)$$

Excited molecular states may also be populated by the recombination of a molecular ion in a radiative or three-body process:



if the recombination mechanism is dissociative, an excited atomic state may result:



In either case, the population of an excited state by recombination is proportional to the recombination rate:

$$\left(\frac{\partial N_j}{\partial t} \right)_{\text{recomb.}} = \alpha_j [X_2^+] n \quad (3.21)$$

The proportionality constant obviously satisfies

$$\sum_{j=0}^{\infty} \alpha_j \leq \alpha \quad (3.22)$$

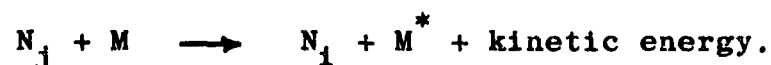
where α is the electron-ion recombination coefficient, since not all of the recombination events may populate excited states.

It should be noted that dissociative recombination may also populate a molecular state indirectly, by way of a reassociation reaction such as the process

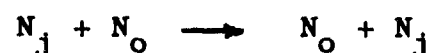


If this reaction occurs rapidly enough, its rate is still controlled by the rate of the initial dissociative recombination (Equation 3.20).

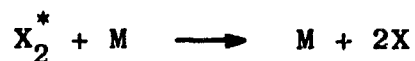
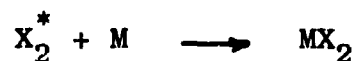
Excited molecules can also be lost to the volume of the gas by collisions with ground state neutral molecules. These collisions can result in the transfer of excitation (either rotational, vibrational or electronic) from the excited molecule to the neutral molecules, leaving the former in some lower state i :



If M is the ground state of the neutral molecule from which N_j was produced, then the resonant exchange



makes no change in N_j . Another type of collision which can remove excitation is one which changes the identity of the excited molecule in a chemical reaction, such as



All these collision processes compete with radiation as the depopulating mechanism of N_j , and are therefore referred to as quenching reactions, for which the rate equation can be written

$$\left(\frac{\partial N_j}{\partial t}\right)_{\text{quenching}} = - C_p N_j \quad (3.23)$$

The optical measurements to be presented in this report are concerned with band systems originating on one of two electron states, the First Negative System of N_2^+ , resulting from the transition $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$, and the Second Positive System of N_2 , $C^3\pi_u \rightarrow B^3\pi_g$. Neither initial state is radiatively coupled to the ground state of the neutral molecule, and both are sufficiently short-lived that diffusion is negligible. For the $B^2\Sigma$ level of N_2^+ , radiative cascading can almost certainly be ignored [Stewart, 1956]. For lack of specific information to the contrary, it will be assumed that cascading can be neglected for the $C^3\pi_u$ state of N_2 as well. If the measurements are confined to a regime of ionization levels where recombination can be ignored, then

$$\frac{\partial N_j}{\partial t} = K_j p_i - A_j N_j - C_p N_j \quad (3.24)$$

This equation is easily generalized to the case of a gas mixture. If the parent gas of the excited molecule (or ion) is denoted by subscript a and the other constituents of the mixture by b, c, ..., then

$$\frac{\partial N_j}{\partial t} = K_j p_a i - (C_a p_a + C_b p_b + \dots) N_j - A_j N_j \quad (3.25)$$

where $p_a, p_b, \dots$ are the respective partial pressures.

For a binary mixture in steady-state,

$$N_j = \frac{K_j p_a i}{C_a p_a + C_b p_b + A_j} \quad (3.26)$$

The intensity of light emitted during a transition from state j to a given lower state will be proportional to the population N_j . Consequently

$$\frac{p_a}{I_j} \propto C_a p_a + C_b p_b + A_j \quad (3.27)$$

where I_j is the intensity of the radiation under consideration. The quenching coefficients can be determined by an analysis of (p_a/I_j) versus p_a plots for various values of p_b . In particular, a pure gas plot ($p_b = 0$) should yield a straight line for which the ratio of slope to intercept is given by

$$R_a = \frac{C_a}{A_j} \quad (3.28)$$

with C_a thus determined, C_b can be found in an entirely analogous manner.

To conclude this section, consider how K_j can be calculated in terms of known quantities. By definition $K_j p_i$ gives the number of molecules per cm^3 raised to a specific state j in one second. The designation j fixes both the electronic and vibrational configurations; rotational fine structure may be included if desired. If p is sufficiently low that collisional quenching is negligible, the steady-state population reduces to

$$N_j = \frac{K_j p_i}{A_j} \quad (3.29)$$

The number of photons ϕ_{je} emitted from each cm^3 of the gas per second in a downward transition from state j to some specific state i is then given by

$$\phi_{ji} = A_{ji} N_j = \frac{A_{ji}}{A_j} K_j p_i \quad (3.30)$$

In the absence of an absolute intensity calibration for the optical spectrometer, ϕ_{je} cannot be evaluated directly. One can relate ϕ_{je} , however, to the total energy U deposited in one cm^3 in the gas per second by the beam if the fluorescence efficiency η_{je} for the excitation of the specific transition is known. η_{je} is defined by

$$\eta_{ji} = \phi_{ji} h \nu_{ji} / U \quad (3.31)$$

U can be evaluated for the present experiment by a measurement of the ionization production rate (Section III.B):

$$U = K p_i W, \quad (3.32)$$

where K is the rate coefficient for ionization by the beam. This yields

$$K_j = \frac{\eta_{ji} A_j W \times K}{A_{ji} h \nu_{ji}} \quad (3.33)$$

One can then determine the absolute density of excited state N_j ; from this one can determine quantities such as the total number of quenching collisions per cm^3 per second for state j :

$$\left(\frac{dN_j}{dt} \right)_q = -C_p N_j \quad (3.34)$$

E. Treatment of Experimental Data

In this section some of the techniques by which information is extracted from the basic measurements are developed. In addition to afterglow measurements, which have been widely treated in the literature, the experiment employed here permits the study of thermal electrons and ions in the steady state during continuous irradiation. Several techniques not described elsewhere in the literature have been applied to the data analysis, and are therefore included here.

The results of electron density measurements appear as a set of frequency shifts which are functions of the experimental parameters. These frequency shifts can be related to local electron density in the cavity only if the spatial distribution of electrons is known. To do this, one must have a model which describes the various processes occurring in the gas, from which the spatial dependence can be deduced. In order to arrive at a model, the individual reactions occurring in the gas must be identified. We have proceeded by first making the assumption that the electron density differs from the measured frequency shift by a constant factor, then studied the variations of the density which results from this assumption with experimental parameters. When the processes have been identified qualitatively, they are then assembled into a complete mathematical model from which the correct spatial dependences can be obtained. This model is then solved accurately, at least in principle, for the correct frequency shift - electron density relation.

The steady-state density n_s can be written

$$n_s = K p i / \nu_s \quad (3.34)$$

where the loss frequency in the steady-state is, in general, a function of gas pressure and temperature, beam current, and electron and ion densities and their gradients. (In the following, the gas temperature will be considered constant at 300° K.) For ν_s a function only of pressure, which is taken as a power law dependence,

$$\nu_s = a p^b \quad (3.35)$$

then

$$n_s / i = K p / \nu_s \sim p^{1-b} \quad (3.36)$$

The ratio n_s/i is found from the slope of the linear plot of n_s vs i at a fixed pressure, then b is evaluated from a plot of $\log (n_s/i)$ vs $\log p$. Cases have been observed in which ν_s is constant for low ionization levels, but is a function of n_s at larger n_s . Then the data have been found to obey a relation of the form

$$i = A n + B n^c \quad (3.37)$$

where A is the reciprocal of n_s/i in the linear regime. With this relationship, the entire beam current dependence at a fixed pressure can be characterized by only three number, the coefficients A and B and the exponent c .

In the linear regime, the time-resolved electron density rises toward n_s after the irradiation has begun according to

$$n_r(t) = n_s(1 - e^{-\nu_r t}) \quad (3.38)$$

Following a beam pulse of duration T , the density in the after-glow falls according to

$$n_a(t) = \{n_s(1 - e^{-\nu_r T})\} e^{-\nu_a(t-T)} \quad (3.39)$$

If n_s is sufficiently large to lie in the non-linear regime, Equations 3.38 and 3.39 are no longer valid. One can evaluate n_s in this case by studying the early portion of the electron density rise. This is done by replacing n_s in 3.38 with the extrapolation of the linear density to the beam current actually employed in the transient experiment:

$$n_r(t) = i/A (1 - e^{-\nu_r t}) \quad (3.40)$$

ν_r is then found from the characteristic frequency at early times, that is, for t' such that $n_2(t < t')$ is linear.

The transient frequencies are evaluated from the time-resolved densities by the usual graphical techniques. If ν_j , ($j=A,R$) varies as p^b , where b is evaluated from the steady-state data, one is tempted to identify that transient frequency with ν_s . To establish this identity, calculate K_j , which is defined by

$$K = \nu_j n_s / i p \quad (3.41)$$

(Cf. Equation 3.36). If K_j is independent of pressure, and has a numerical value in reasonable agreement with the predictions of K given in Table I, then one may safely assume $\nu_j = \nu_e$, $K_j = K$. All subsequent distinctions between the transient and steady-state values may then be used without further distinction.

If ν_e is a strong function of electron temperature, then the result $\nu_j = \nu_e$ implies a common temperature (T_{gas}) for the electrons in both the steady-state and afterglow experiments (Section III.B). In fact, if the electrons were epithermal in the steady-state, one could expect ν_e to change with time in the afterglow as the electrons cool; thus the afterglow decay of electron density would not appear to be exponential.

The complete general equations describing the production and loss of charged particles in the cavity may be written for ions as

$$\frac{\partial X_j}{\partial t} = P_j + D_{j,\text{eff}} \nabla^2 X_j - \alpha_{ej} n_e X_j - \alpha_{ij} X_j X_k \quad (3.42)$$

and for electrons as

$$\frac{\partial n_e}{\partial t} = P_e + D_{e,\text{eff}} \nabla^2 n_e - \nu_a n_e - \alpha_{ej} X_j n_e \quad (3.43)$$

Here X_j is the j th species of ion, P_j and P_e are production rates for ions and electrons. $D_{j,\text{eff}}$ and $D_{e,\text{eff}}$ are the effective diffusion coefficients for ions and electrons, and the other terms are as defined in earlier sections. Equations 3.42 for each X_j

and 3.43 form a set of simultaneous non-linear partial differential equations which cannot in general be solved in closed form. Solutions can be obtained by rewriting these equations as difference equations, then solving the set numerically as a function of space and time on a high-speed electronic computer. In general, computer programs of this magnitude were outside the scope of the present contract, so that other means have had to be devised to obtain information from the measurements.

The technique used most frequently in the present work has been based on the approximation that the spatial distribution of all particles is characteristic of the fundamental diffusion mode; thus

$$X_i \approx X_{i0} J_0(2.405 \frac{r}{R}) \sin \frac{\pi z}{h} \quad (3.44)$$

where R, h are the radius and height, respectively, of the experimental cavity. This technique allows 3.42 and 3.43 to be rewritten as total differential equations:

$$\frac{dX_{i0}}{dt} = P_{i0} - \frac{D_{i,eff}}{\Lambda_{ii}^2 p} \cdot p X_{i0} - \alpha_{ej} n_{e0} X_{i0} - \alpha_{ij} X_{j0} X_{i0} \quad (3.45)$$

$$\frac{dn_{e0}}{dt} = P_{e0} - \frac{D_{e,eff}}{\Lambda_{ee}^2 p} \cdot p n_{e0} - \bar{\nu}_a n_{e0} - \alpha_{ej} X_{j0} n_{e0} \quad (3.46)$$

The subscript "0" applied to a quantity is defined by

$$N_0(t) = \frac{\int_c N(\vec{r}, t) J_0(2.405 \frac{r}{R}) \sin \frac{\pi z}{h} dv}{\int_c J_0^2(2.405 \frac{r}{R}) \sin^2 \frac{\pi z}{h} dv} \quad (3.47)$$

where the integrals extend over the volume of the cavity.

To evaluate a specific reaction rate coefficient, one chooses experimental conditions which cause the desired reaction to predominate. Thus at high pressures and low ionization levels, the electron equation (3.46) reduces to

$$\frac{dn_{eo}}{dt} = P_{eo} - \gamma_a n_{eo}, \quad (3.48)$$

which, by virtue of its linearity, can be extended to all other coefficients in the Fourier-Bessel expansion and eventually to the summation of these coefficients into the original quantities:

$$\frac{dn_e}{dt} = P_e - \gamma_a n_e \quad (3.49)$$

For a spatially uniform source term, as is the case in the present experiments, n_e is also uniform, and the relationship between Δf and n_e is given by

$$n_e (\text{cm}^{-3}) = 10^4 \Delta f (\text{kcps}) \quad (3.50)$$

From transient measurements γ_a can be determined; steady-state measurements then give P_e .

At higher ionization levels at high pressures, electron-positive ion recombination can also be studied. The pertinent

rate equation still refers to uniform spatial distributions of particles, since recombination will not destroy the spatial uniformity:

$$\frac{dn_e}{dt} = P_e - \nu_a n_e - \alpha_{ei} X_j n_e \quad (3.51)$$

In these measurements, the actual ion density X_j is usually not identical with n_e , due to the presence of other ions. A useful technique for steady-state measurements involves the use of mass spectrometer ion currents, in the following way. From (3.51) in the steady-state,

$$\frac{P_e}{n_e} = \nu_a + \alpha_{ei} X_j \quad (3.52)$$

A plot of the ratio P_e/n_e vs X_j can be made, using measured values of n_e and X_j , and computed values of P_e (usually Kp_i). If the mass spectrometer ion current is known only in relative units, then such plots at least identify electron-ion recombination as the responsible process. If an absolute calibration of the ion current has been obtained, so that X_j is known in units of ions per cm^3 , α_{ei} can be evaluated from the ratio of slope to intercept of the straight-line plot resulting from (3.52).

At low pressures, where diffusion becomes important, the particles have a spatial distribution midway between the uniform distribution imposed by the beam and that of the fundamental diffusion mode. In the absence of the complete calculation, we have resorted to the fundamental-mode approximation (Equation 3.44). This is particularly justified for electrons, since the measured frequency shift is dominated by the contribution from the funda-

mental-mode component of the actual electron distribution. To see this in more detail, consider a fictitious electron density, $n(\vec{r}, t)$ expressed as a Fourier-Bessel series with equal coefficients. The net frequency shift is then given by $\Delta f = \sum_{kl} \Delta f_{kl}$ where

$$\Delta f_{kl} = C \int_0^R \int_0^{\pi} J_0(\alpha_{kl} \frac{r}{R}) J_1^2(3.832 \frac{r}{R}) \sin(\frac{l\pi z}{h}) \sin^2(\frac{\pi z}{h}) r dr dz \quad (3.54)$$

α_{kl} is the k^{th} zero of $J_0(x)$ and C is a constant. The Table below gives $g_{kl} \equiv |\Delta f_{kl} / \Delta f_{11}|$. Consideration of this table along with the fact that the Fourier-Bessel coefficient for the fundamental mode ($k = l = 1$) of a physically realizable density distribution is always larger than any of the higher order coefficients justifies the inclusion of only fundamental-mode contributions to the frequency shift.

TABLE II

RELATIVE FREQUENCY SHIFT CONTRIBUTIONS FROM
WEIGHTED FOURIER-BESSEL MODES

k	l	1	3	5	7	
1		1.000	.200	.029	.001	(Symmetry requires that even- l contributions vanish)
2		.230	.046	.007	.000	
3		.146	.029	.004	.000	
4		.001	.000	.000	.000	

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70.

TABLE III

Observed Bands and Their Identification

<u>λ (observed)</u>	<u>Identification</u>	<u>λ observed</u>	<u>Identification</u>
3120	2P (3,2)	3999	2P (1,4)
3135	2P (2,1)	4059	2P (0,3)
3159	2P (1,0)	4091	2P (4,8)
*3275	2P (4,4); 2P(3,3)	4141	2P (3,7)
*3309	2P (2,2); 1N(2,0)	4200	2P (2,6)
3340	2P (1,1)	4239	1N (1,2)
3371	2P (0,0)	4278	1N (0,1)
*3463	2P (4,5); 2P(3,4)	4346	2P (0,4)
3501	2P (2,3)	4415	2P (3,8)
3537	2P (1,2)	4488	2P (2,7)
3578	2P (0,1)	4574	2P (1,6)
3660	Unidentified	4656	1N (1,3)
3671	2P (3,5)	4667	2P (0,5)
3710	2P (2,4)	4709	1N (0,2)
3755	2P (1,3)	4813	2P (2,8)
3804	2P (0,2)	5230	1N (0,3)
3894	2P (3,6)		
3914	1N (0,0)		
3943	2P (2,5)		

the wavelength at the peak intensity is given, and both overlapping bands are identified. All other bands are degraded to the violet, and are listed by the wavelength₀ of the bandhead. Except for a single unidentified band at 3630 Å, all other bands have been assigned to either the N₂ Second Positive or the N₂⁺ First Negative system. The absence of N₂ First Positive bands is in keeping with the observations of other workers [Davidson (1964), Fan (1956)] on the low intensity of the N₂ First Positive bands excited by fast electron bombardment.

As a further verification of the band identifications, the relative response of the system as a function of wavelength has been determined from the measured intensity distributions using a technique described in Section II.F. The identified nitrogen bands, when compared with the theoretical intensity distributions, can be made to lie on a smooth curve by a suitable normalization of each of the common upper vibrational levels. Figure 2.11 shows data from a high pressure nitrogen beam experiment together with a similar treatment of several multiplets measured in a mercury capillary discharge, using published intensity ratios [Crosswhite (1957)], as a secondary verification of the reasonableness of the results. The smoothness and general agreement of the shape of the curve with expectations based on the known photomultiplier response and grating blaze suggest that the identifications are correct.

C. Emission Intensities

The only published quantitative experimental data with which one can compare the emission intensities reported here are from Davidson and O'Neil (1964). Air-like mixtures of $N_2:O_2$ at 5 Torr and higher total pressures were bombarded by 50 kev electrons at high current densities in their experiment. Their reported intensities are integrated intensities rather than peak heights as in the present report. However, the ratio of peak height to integrated intensity should be reasonably constant over the limited wavelength interval of a given band system. This fact has been confirmed for a few bands in this laboratory as well as by Brocklehurst [1964]. Therefore the intensity comparisons of the various 2P bands between Davidson's results and those presented here can properly be made. Furthermore, one would expect the excitation due to 50 kev electrons to be similar to 1.5 Mev electrons, [Davidson, 1964].

From the air data shown in Figure 4.3, emission intensities at 5 Torr have been determined and are listed in Table IV. The 2 P intensities observed by Davidson have been normalized to agree at the 2P (0,0) band ($3371 \text{ \AA}$) and are also tabulated there. The last column of Table IV lists the relative intensities predicted by Bates [1949] under the assumption that the parent state concerned is populated by direct electron excitation from the ground state of the neutral molecule. Bates' 2₀P intensities are also normalized to the 5 Torr data at $3371 \text{ \AA}$.

RELATIVE INTENSITIES OF SECOND POSITIVE BANDS

TABLE IV

<u>Identification</u>	<u>λ(A)</u>	<u>5 Torr Intensities</u>	<u>Davidson</u>	<u>Bates</u>
2P(1,0)	3159	2600	-	2340
2P(0,0)	3371	3200	3200	3200
2P(1,2)	3537	690	668	634
2P(0,1)	3577	2250	2260	1970
2P(2,4)	3710	155	132	127
2P(1,3)	3755	600	566	514
2P(0,2)	3804	770	821	710

In order to compare 1N and 2P intensities with those of Davidson, it is necessary to compute the ratio of the peak intensity to the area under the band for each of the band systems and correct Davidson's intensities accordingly. This has been done from measurements made in the laboratory; the ratios of peak heights to integrated area are 0.4 for the 3371 Å 2P band and 0.28 for the 1N band at 3914 Å. With this information Davidson's integrated intensities have been converted to peak heights and are listed in Table V. Bates' values for electron excitation from the ground state of the neutral molecule are also listed in Table V, after normalization to the measured 3914 Å intensity for this table.

The rather good agreement, especially in the 2 Positive intensities, with both the measured values from Davidson and the theoretical values from Bates displayed in Tables IV and V suggests several conclusions.

RELATIVE INTENSITIES OF FIRST NEGATIVE BANDS

TABLE V

Identification	λ Å	5 Torr Intensities	Davidson	Bates
1N(0,0)	3914	1700	2090	1700
1N(1,2)	4237	32	-	63.5
1N(0,1)	4278	330	-	480
1N(0,2)	4709	45	100	71

First, the procedure outlined above for the computation of the relative spectral response curve, Figure 2.11, is reasonably valid. Second and more important, the agreement lends credence to the theory that the light observed from both the 2 P and 1 N band systems is produced by direct excitation of ground state neutral molecules.

Another test for the direct excitation mechanism was made by examining the afterglow of both the 1 N and 2 P emission. The output of the photomultiplier was applied directly to the 1 Megohm input of a Tektronix 545 oscilloscope. The Van de Graaff beam was pulsed periodically on for 15 milliseconds, off for 10 milliseconds. From photographs of the traces it would have been possible to detect afterglows with decay times of 2 milliseconds or longer. Measurements in pure nitrogen (no oxygen added) at 5 and 12 Torr failed to reveal any afterglow light from nitrogen band systems which decayed at least this slowly. (The cyanogen bands, however, were observed to have afterglow lifetimes of the order of one second at 12 Torr.) Thus it must be concluded that the $B^2\Sigma$ and $C^3\pi$ states are not populated by long-lived

processes, in keeping with their assumed excitation by the electron beam.

D. Collisional De-excitation of $B^2\Sigma$ and $C^3\pi$ States

Measurements have been made of the dependence of the peak intensities of various bands as a function of pressure and chemical composition of the irradiated gas and of Van de Graaff beam current. From these measurements one can expect to obtain some indication of the processes by which a given excited state is populated and depopulated.

The intensity of the $3914 \text{ \AA}$ First Negative (0,0) band has been measured in nitrogen and 4:1 ("airlike") mixtures of $N_2:O_2$ as a function of beam current and gas pressure. In nitrogen, the intensity is linear with Van de Graaff current up to the highest currents used, 1 milliampere, over the pressure range 1 to 10 Torr, as illustrated in Figure 4.4. At a fixed beam current, the intensity increases smoothly with pressure, as shown in Figure 4.5, and exhibits the well known non-linear behavior associated with collisional quenching [Mitchell, 1961].

The $3914 \text{ \AA}$ band has also been studied in 4:1 mixtures of $N_2:O_2$. At 10 Torr, the intensity is also linear with beam currents less than 1 milliampere, but departs from linearity in this current range at lower pressures, as shown in Figure 4.6. The variation of intensity in the linear region with total "air" pressure at a fixed beam current is shown in Figure 4.7.

From the theory developed in III.D one can extract collisional de-excitation coefficients from data such as those

shown in Figures 4.5 and 4.7. The intensity I_{jk} of a given band of frequency ν_{jk} was shown to be given by (Equation 3.25)

$$I_{jk} = A_{jk} N_j = \frac{K_j p_n \lambda}{A_j + C_N p_n + C_o p_o} \quad (4.1)$$

where

- A_{jk} = Einstein spontaneous emission coefficient for the transition
- N_j = Population density of state j
- K_j = Production coefficient for state j
- p_n, p_o = Partial pressures of N_2, O_2
- A_j = Reciprocal of radiative lifetime of state j
- $C_N p_n, C_o p_o$ = De-excitation frequencies for collisions with N_2, O_2 molecules.

In pure N_2 (and in N_2 with a trace of O_2 for cyanogen quenching) the quenching coefficients for the 2P and 1N systems are found from the ratio of slope to intercept R_n of a plot of p_n/I vs p_n , such as Figure 4.8; (Equation 3.26).

$$\frac{p_n}{I} \sim A_j + C_N p_n \quad (4.2)$$

From Equation 3.27, this yields

$$C_N = R_n A_j \quad (4.3)$$

In binary $N_2:O_2$ mixtures

$$\frac{p_n}{I} \sim A_j + C_N p_n + C_o p_o \quad (4.4)$$

In airlike mixtures, for which $p_n = 4p_o$, so that the total pressure $p_t = p_n + p_o$ can be written

$$p_n = 0.8 p_t, \quad p_o = 0.2 p_t \quad (4.5)$$

Equation 4.4 becomes

$$\frac{p_n}{I} \sim A_j + (0.8 C_n + 0.2 C_o) p_t \quad (4.6)$$

Thus the ratio of slope to intercept for the airlike mixtures, R_a , can be written

$$R_a = \frac{0.8 C_n + 0.2 C_o}{A_j} \quad (4.7)$$

so that

$$C_o = \frac{A_j R_a - 0.8 C_n}{0.2} \quad (4.8)$$

Substituting for C_n its value determined from the pure N_2 data (Equation 4.3), one obtains

$$C_o = 5A_j (R_a - 0.8 R_n) \quad (4.9)$$

This analysis has been applied to the observed band intensities of the 2P and 1N systems of N_2 . Figure 4.9 presents the results which have been obtained for the $v' = 0$ level of the N_2^+ 1N system, with both N_2 and O_2 as the quenching molecule, for the

$v' = 0$ level of the N_2 2P system with N_2 as the quenching molecule, and the $v' = 0, 1, 2$ levels of the 2P system with O_2 as the quenching molecule. Although other bands were observed, their relative intensities were too weak for accurate quantitative study. Values for A_j were obtained from Bennet and Dalby [1958].

There has been some confusion in the literature as to an appropriate definition of the effective cross-section for quenching, $\sigma_{o,n}$. The definition used in this report is:

$$C_a p_a = \sigma_a \bar{v}_a N$$

where

$$\bar{v}_a = (v_N^2 + v_a^2)^{1/2}$$

The values for N_2 and O_2 as the quenching gases at $25^\circ C$ and 1 Torr are

$$\bar{v}_N = 6.71 \times 10^4 \text{ cm-sec}^{-1}$$

$$\bar{v}_O = 6.50 \times 10^4 \text{ cm-sec}^{-1}$$

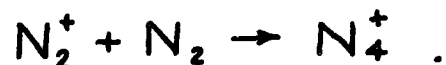
$$N = 3.24 \times 10^{16} \text{ cm}^{-3}$$

yielding

$$\sigma_N = \frac{C_N p_N}{\bar{v}_N N} = \frac{C_N}{2.17 \times 10^{21}} \text{ cm}^2; \quad \sigma_O = \frac{C_O p_O}{\bar{v}_O N} = \frac{C_O}{2.11 \times 10^{21}} \text{ cm}^2$$

The cross-section results of Davidson and O'Neil are of the form $\sigma = \pi r^2/4$, and therefore should be multiplied by 4 for $\pi r^2/4$ comparison with our data. If this same procedure is applied to Brocklehurst's data, then all three sets of results are substantially in agreement. There is a discrepancy between Brocklehurst and this laboratory of a factor of two in the cross-section for O_2 quenching of the 1 Negative (0,0) band. A possible cause of this discrepancy may be the effects of impurities present in Brocklehurst's unpurified O_2 .

Some comments must be made regarding the very large cross-sections tabulated in Figure 4.9 for collisional de-excitation. First, quenching cross-section of this magnitude ($2 \times 10^{-14} \text{ cm}^2$) have been reported for N_2 on the $\text{A } ^2\pi$ state of N_2^+ , the upper state of the transition responsible for the Meinel bands [Sheridan et al, 1962]. It is not too surprising to find these two states of N_2^+ behaving similarly. Second, evidence is offered in Chapter V, Section B.3, that the rate of quenching collisions between N_2 and N_2^+ ($\text{A } ^2\pi$) is quite nearly equal to the rate at which N_4^+ ions appear to be produced from the reaction



This suggests that the quenching mechanism may be a chemical reaction, rather than a simple excitation transfer, which might account for the large cross-section.

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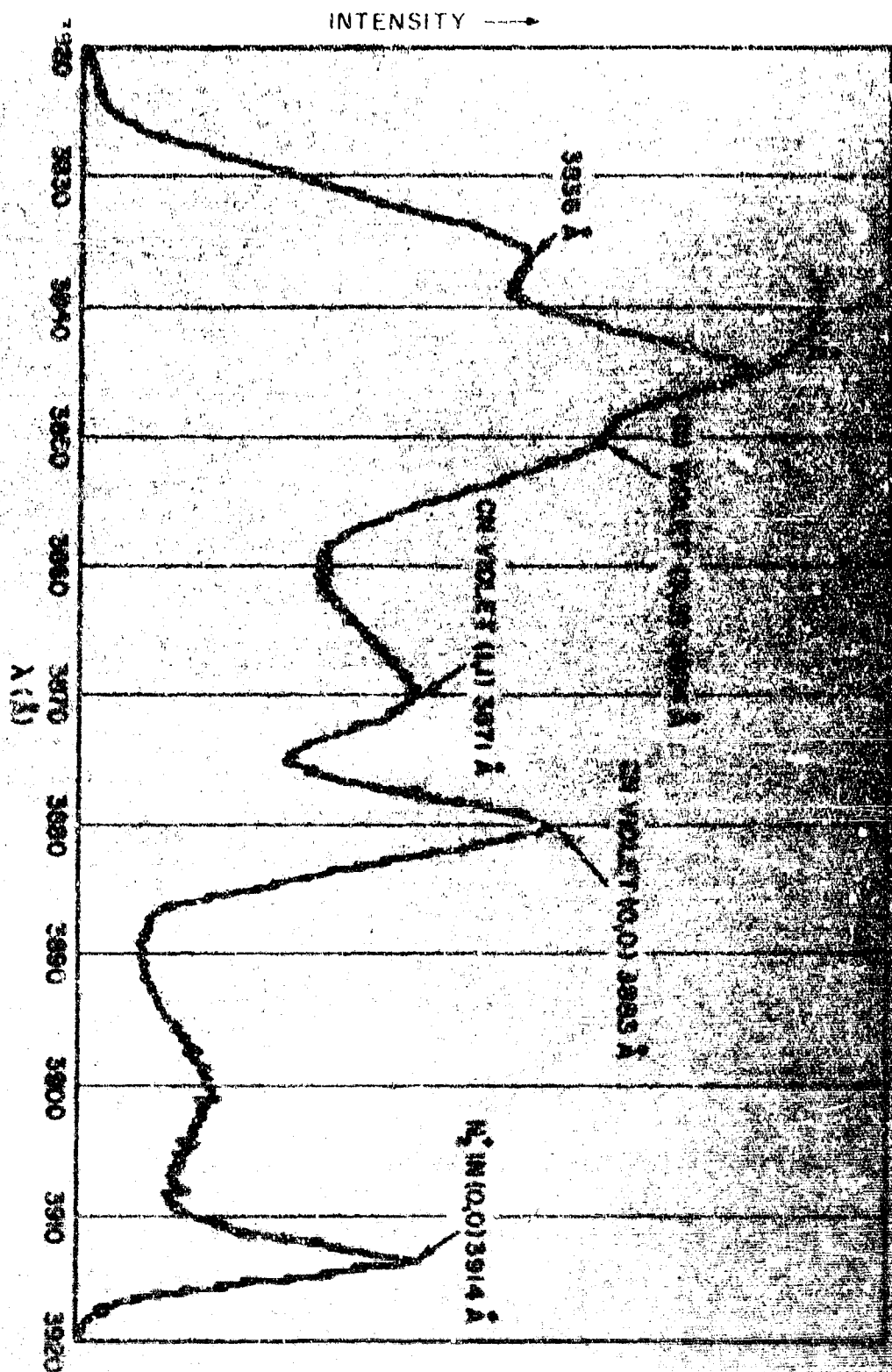
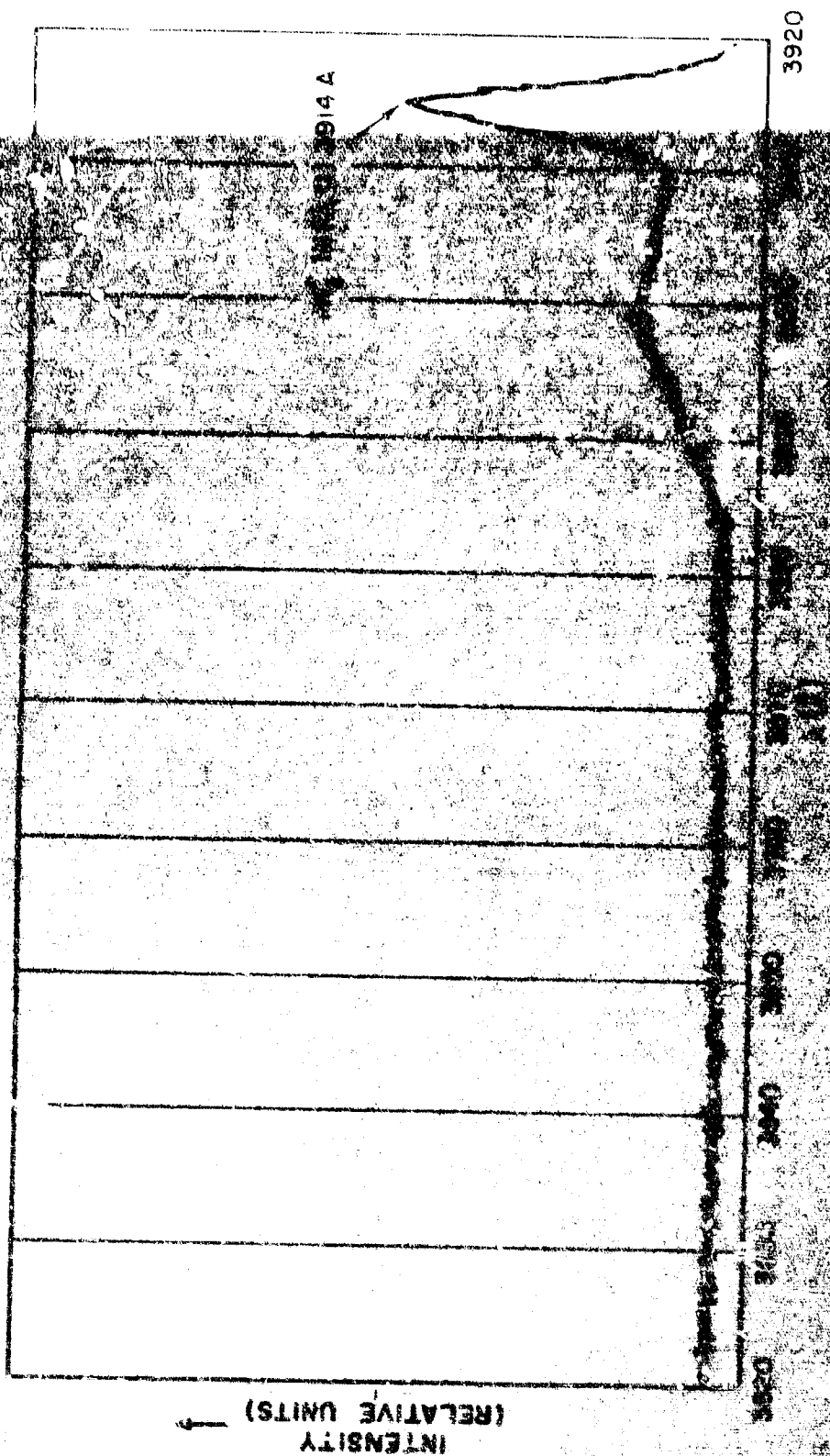


FIGURE 41- SPECTRAL SCAN IN 10.5 TORR OF N_2 (3920 Å-3820 Å)



3820 Å

3920

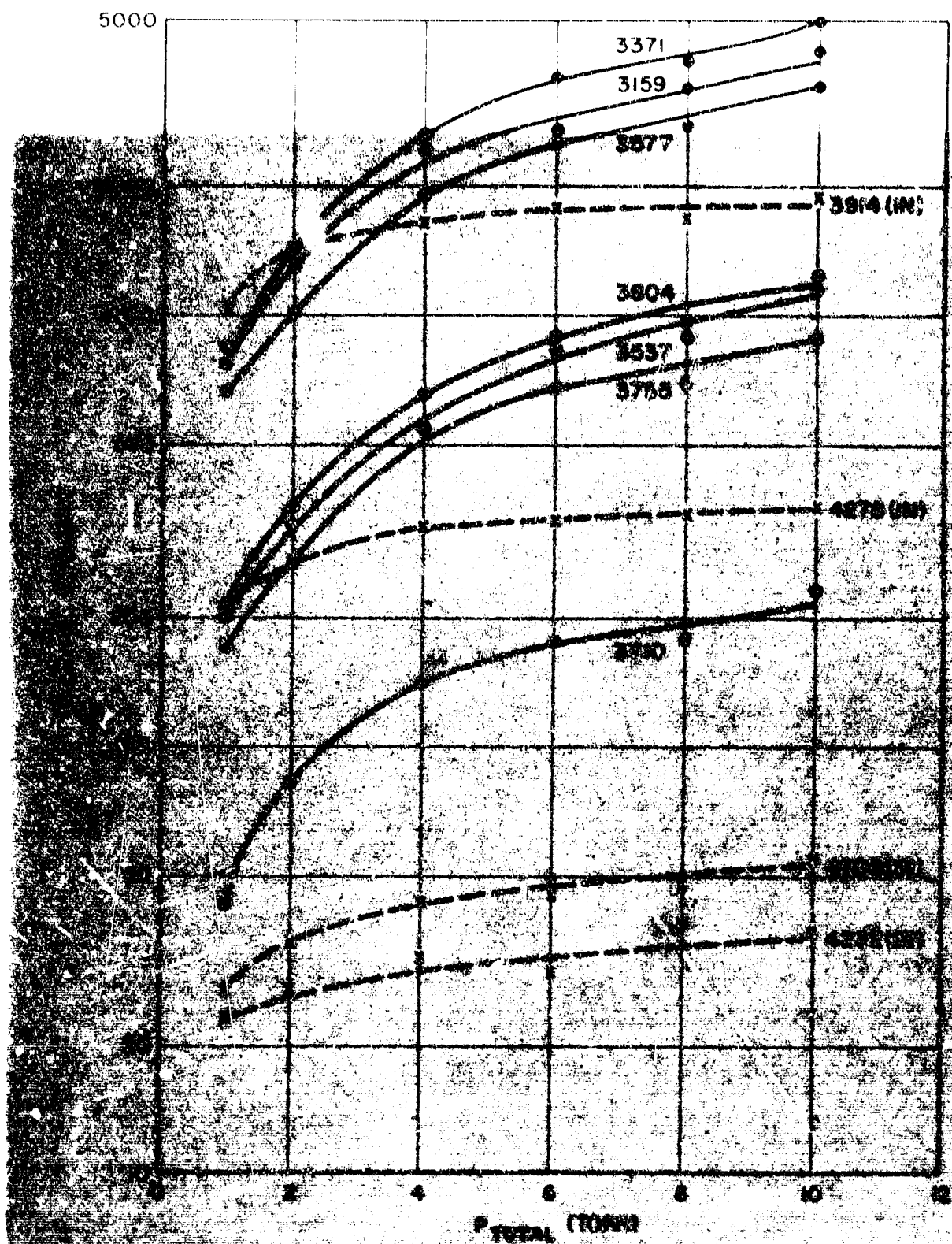


FIGURE 4.5. RELATIVE INTENSITIES OF PROMINENT BANDS VS. PRESSURE IN MIXTURES N_2/O_2

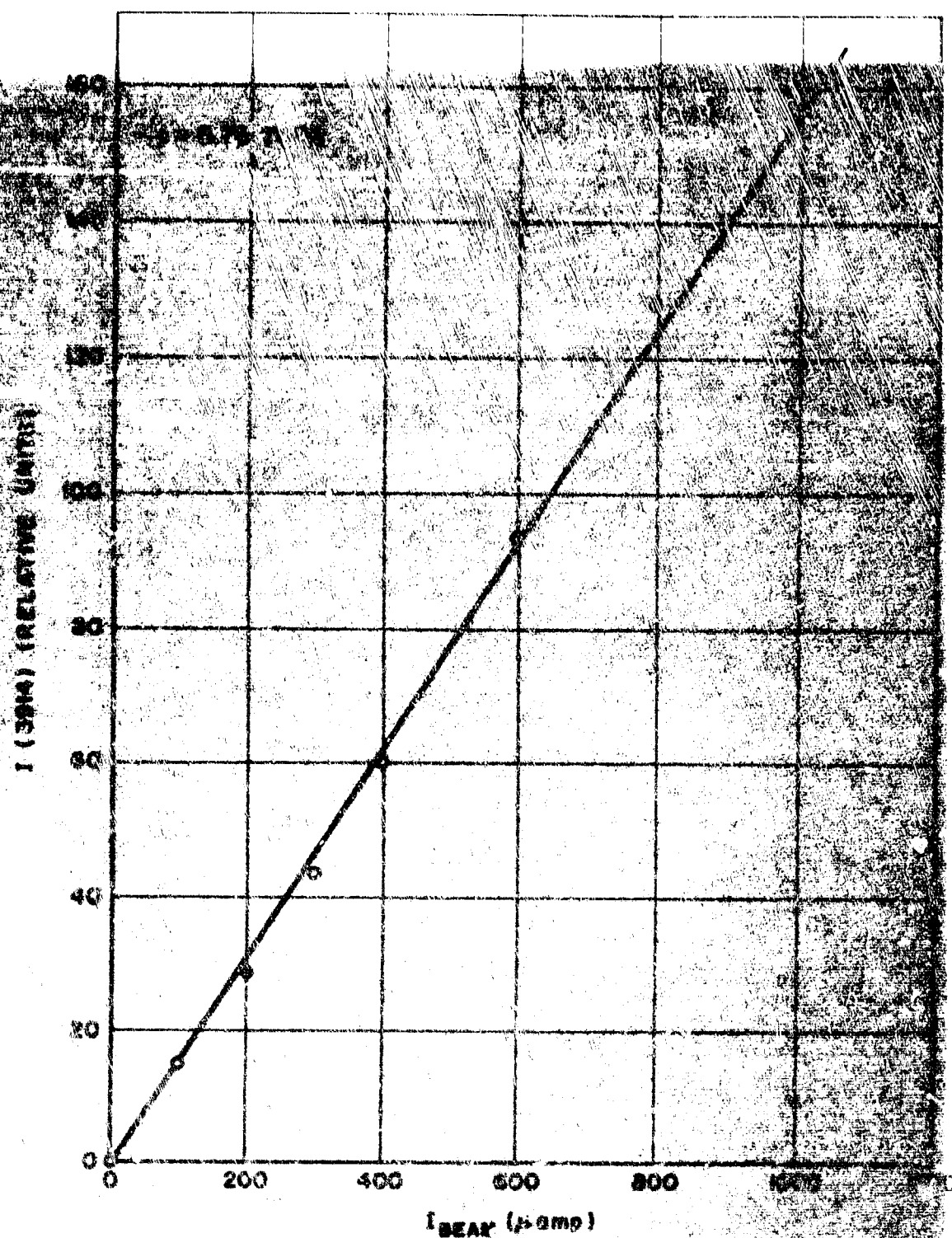


FIGURE 4.4 - $I (3914 \text{ \AA})$ VS. BEAM CURRENT IN NITROGEN

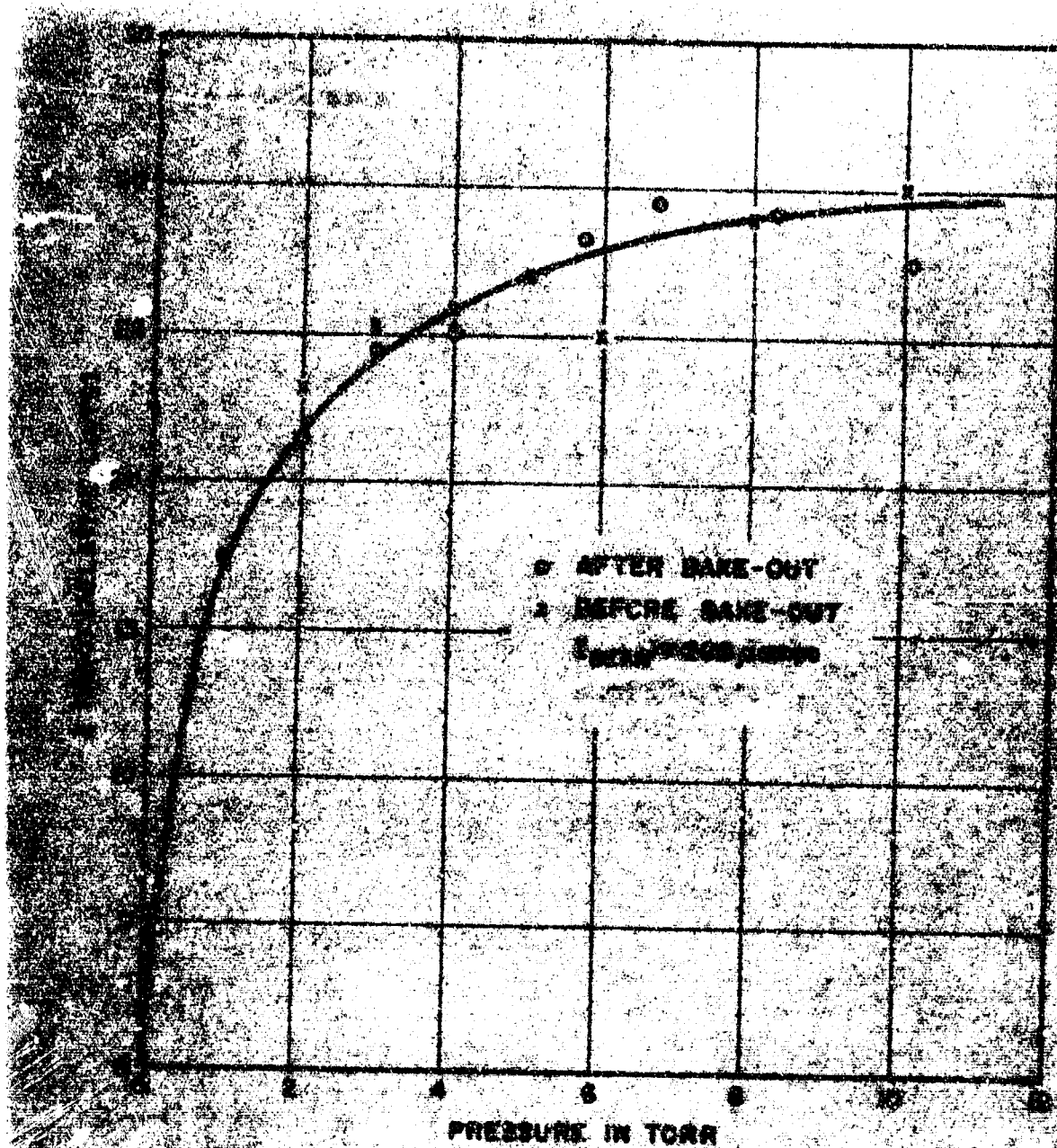


FIGURE 4.5- I (3214) VS. PRESSURE IN "PURE" N_2

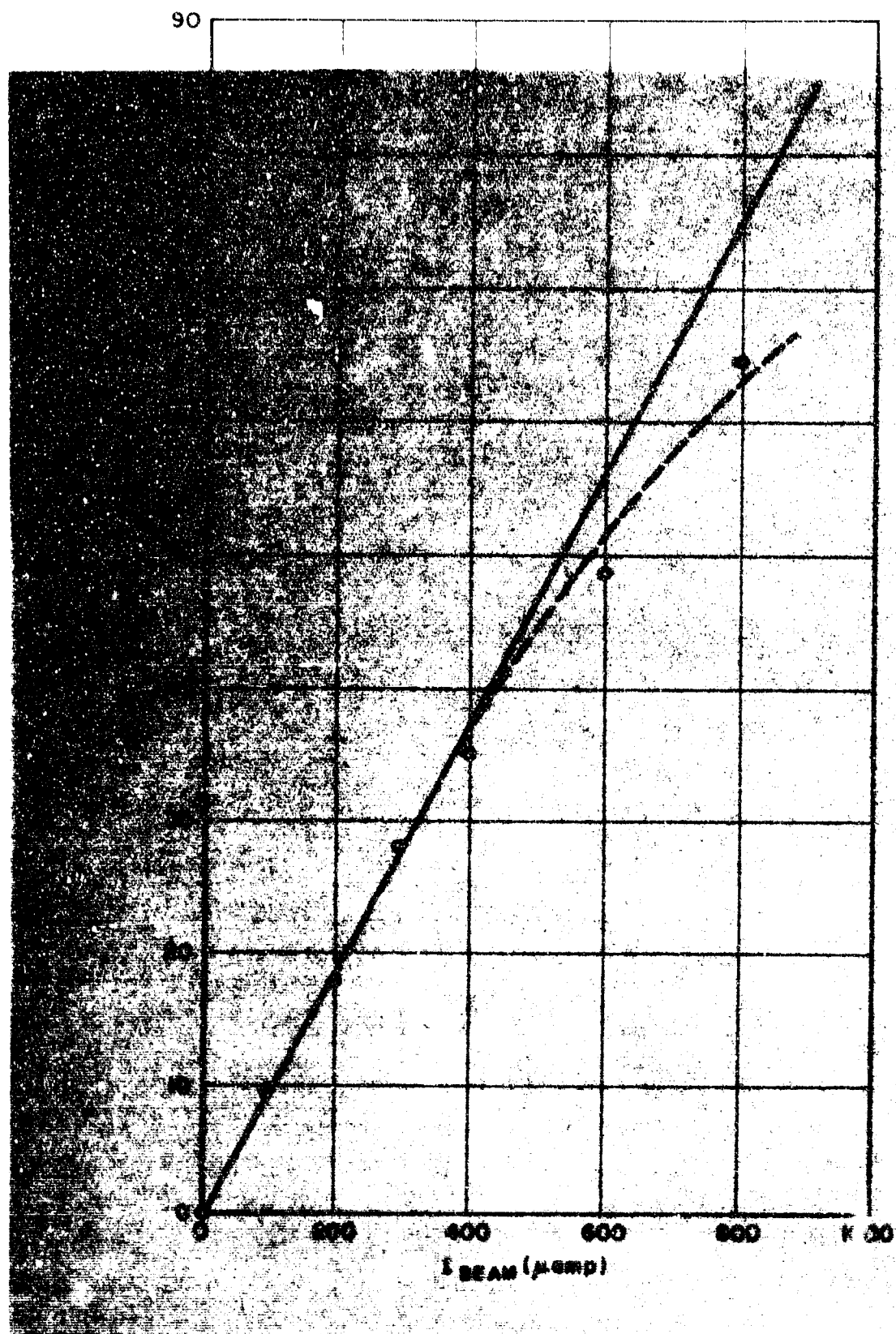
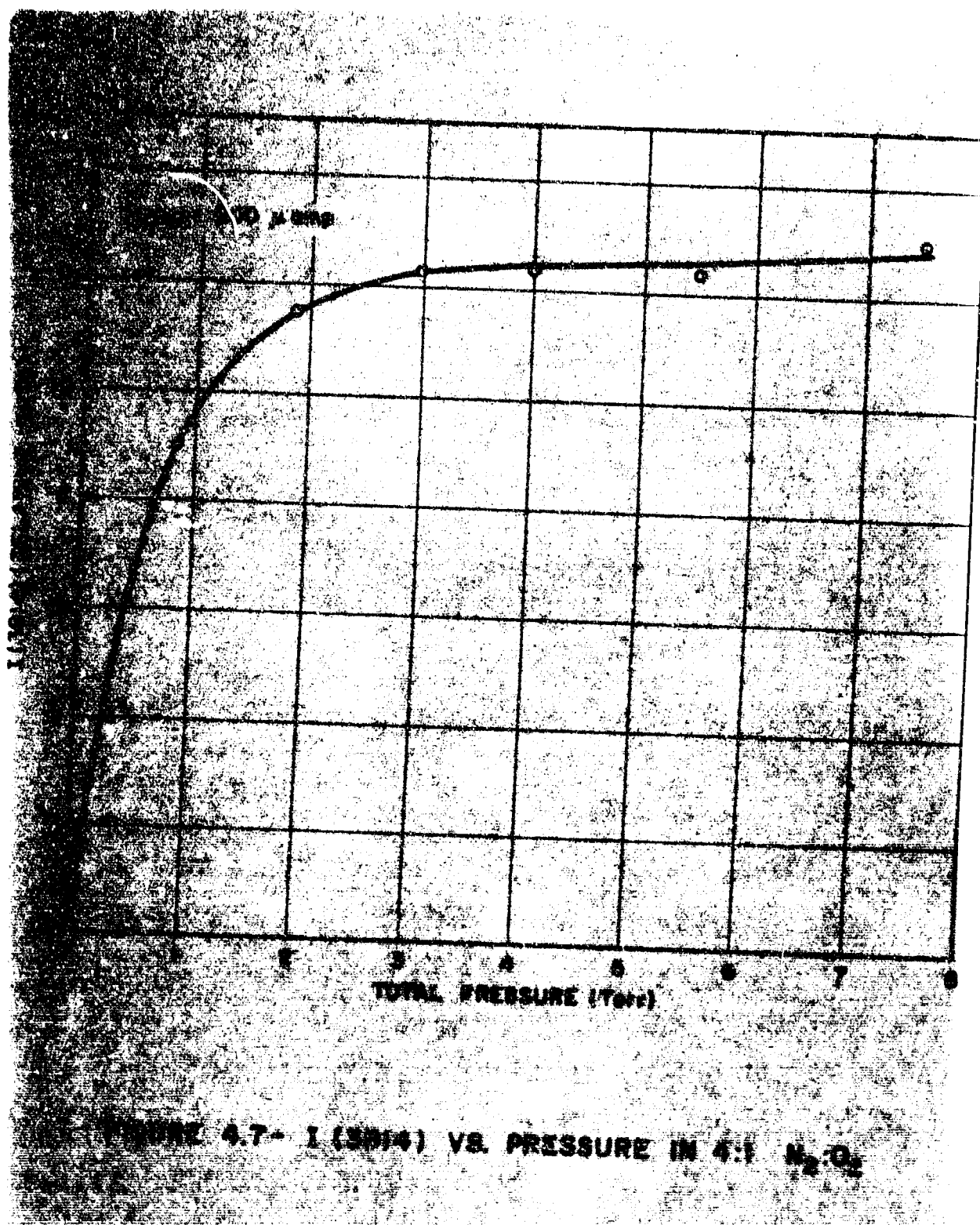


FIGURE 4.6- $I (3914)$ VS. I_{BEAM} IN 4:1 $\text{N}_2:\text{O}_2$



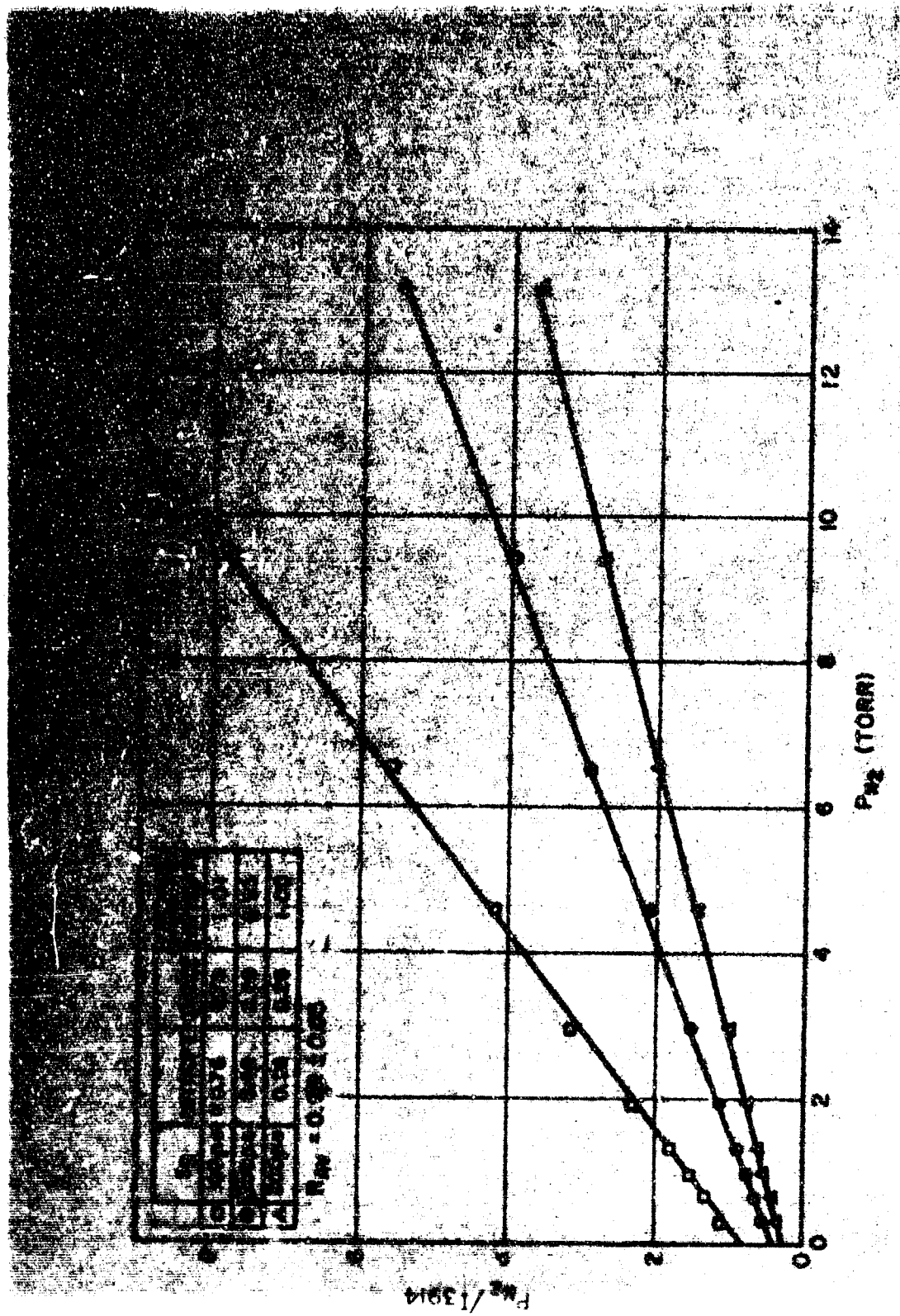


FIGURE 4.8- 3914 Å QUENCHING PLOT IN NITROGEN

INITIAL STATE	QUENCHER	k_1 (10^3 sec^{-1})	DYE IN SOLUTION		DYE IN MELT	
			C_{Dye} / A	ρ_{Dye} (10^{-10} cm^{-1})	C_{Dye} / A	ρ_{Dye} (10^{-10} cm^{-1})
(0,0)	O_2	1.25 ± 0.08	1.2 ± 0.5	152 ± 51	0.8 ± 0.4	80 ± 50
(0,0)	N_2		1.0 ± 0.1	80 ± 10	0.62 ± 0.2	60 ± 50
(0,0)	N_2					$\{ 80 \pm 50 \}$
(5,5,3)	O_2	5.52 ± 0.34	0.12 ± 0.5	81 ± 25	0.012 ± 0.005	1.2 ± 0.4
(0,0,5,2)	O_2		0.9 ± 0.1	25 ± 18		
(0,0,1,5,2)	O_2		0.92 ± 0.04	30 ± 11		
(0,0)	N_2	5.52 ± 0.34	0.011 ± 0.004	1.5 ± 0.6	0.012 ± 0.005	1.2 ± 0.4
(0,0)	N_2					
(0,0)	N_2					

$\{ 80 \pm 50 \}$
 $\{ 30 \pm 10 \}$

V. EXPERIMENTAL RESULTS AND INTERPRETATIONS

A. Introduction

This chapter presents the results of laboratory studies of electron and ion densities in pure oxygen, pure nitrogen, and 4:1 (airlike) mixtures of $N_2:O_2$ subjected to ionizing radiation. From these measurements and the optical studies described in Chapter IV, many specific reactions which participate in the deionization of the disturbed ionosphere have been identified, and their mechanisms and rates have been determined. These gases have afforded a relatively simple medium in which the techniques developed for the lumped-parameter experiment were tested. By avoiding the full complexity of atmospheric chemistry at the early stages of this program, it has been possible to concentrate on the techniques themselves, and on the kinds of information which can be expected from these measurements. As a result, the pure gas and simple mixture studies have established the range of validity of the lumped-parameter measurements more thoroughly, and more rapidly, than would have been possible had the experiments been confined to air from the outset.

B. Measurements in Oxygen

1. Electron density measurements

Steady-state electron densities have been measured during continuous irradiation in oxygen over the pressure range 0.025 to 10 Torr. Figure 5.1 shows several measurements of the shift of resonant frequency in the cavity as a function of Van

de Graaff beam current, which typify the observations made at pressures above 0.3 Torr. The measured points lie on straight lines passing through the origin. The slopes of these lines, in $\text{kcps}/\mu\text{ amp}$, are shown as a function of pressure in Figure 5.2. The data for Figure 5.2 have been obtained under various conditions, including the use of both 0.0015" beryllium and 0.0005" titanium foil beam scatterers (corrected for relative transmission) with the cavity both baked and unbaked prior to the measurements. All data obtained in the baked cavity were reproducible even after prolonged irradiation of the gas at high beam currents. Similar experiments in the unbaked cavity show a permanent decrease in the ionization per unit beam current following the irradiation of a given gas load at high currents, probably due to contamination by the evolution of occluded impurities from the chamber walls.

From Figure 5.2 it can be seen that the measured values of the specific ionization are well approximated by a p^{-1} dependence at pressures greater than 0.9 Torr. From Section III.E, this implies that $\nu_s \sim p^2$.

Below 0.3 Torr, n_s is not linear with beam current. Instead, the measured frequency shifts appear as shown in Figure 5.3. At high beam currents, the data lie on straight lines which do not, however, intersect the origin. The low current data have been examined carefully to insure that the offset of the straight-line fit is not due to instrumental errors, but is in fact a reproducible, pressure-dependent phenomenon. The inherently non-linear nature of the electron loss process at low pressures is borne out in the transient results as well, as will be described below.

Transient electron density measurements were made in oxygen at both high and low pressures, using a pulsed beam with a repetition rate of either 10 or 1 per second. For the measurements described below, the beam remained on the cavity for times which varied between 10 and 90% of the beam switching cycle.

Measurements above 0.7 Torr were originally made with a beam duty cycle of 50%, that is, 0.05 seconds into the cavity and 0.05 seconds off. A typical afterglow decay obtained from these measurements is shown in Figure 5.4. The frequency shifts appear to fall exponentially early in the afterglow, but then deviate into a long-lived "tail." The frequency shift at which this deviation occurs is related, although erratically, to the pressure and to the gas history of the cavity since its most recent bakeout. If these measurements are repeated in the afterglow of a 0.01 second beam pulse, the tail disappears and the frequency shifts decrease exponentially for well over a decade, as shown by the circles in Figure 5.5. Furthermore, one can duplicate the short-pulse measurements by subtracting a constant frequency shift from the data obtained in the afterglow of the long pulse, such as those in Figure 5.4, as shown by crosses in Figure 5.5. This suggests that the afterglow frequency shifts can be described as the sum of an exponentially decaying component independent of beam duty cycle and a constant, or at least much more slowly varying, component related to the the duty cycle.

The loss frequencies obtained from the exponential decays at high pressures are shown in Figure 5.6 as a function of oxygen pressure, after correction for the cavity bandwidth.

Above 0.9 Torr, the data are well approximated by a p^2 -dependence, as had been predicted from the steady-state measurements of specific ionization. The decay frequency can be expressed as

$$\nu = (2.12 \pm 0.15) \times 10^{-30} [O_2]^2 \text{ sec}^{-1} \quad (5.1)$$

It would be more desirable to have a much wider pressure range over which to deduce the decay frequency. Unfortunately, the p^2 dependent loss process no longer controls the electron lifetimes below 0.9 Torr, and the decay frequencies above about 2.0 Torr are as large as or larger than the cavity bandwidth, thus restricting the range over which data may be obtained. From the steady-state measurements, however, one can infer that the p^2 process dominates the electron removal at least at pressures up to 10 Torr. Indirect evidence also exists for the persistence of the p^2 process at pressures as low as 25 millitorr with the same coefficient as that deduced from the data in Figure 5.6. This is discussed below in connection with the interpretation of the low pressure transient data.

The nonlinearity observed in the low-pressure steady-state data is seen in the transient measurements as well. Figure 5.7 shows typical time resolved measurements of electron density during the in-beam phase of a repetitively pulsed beam switching cycle; in this cycle, the beam spends 0.5 seconds in the cavity, 0.5 seconds off. The overshoot at early times characterizes all the measurements below 0.3 Torr, although the peak is more pronounced at the lower pressures, as can be seen from the figure. Following the overshoot, the electron density

decays toward the equilibrium value obtained in the steady-state measurements. The decay of electron density in the afterglow at low pressures is typified by the data shown in Figure 5.8. At early times, the densities decay more or less exponentially with time, but soon break away and fall at an increasingly rapid rate at the late times.

The detailed behavior of the transient in-beam measurements at low pressures is a very sensitive function of the duty cycle of the electron beam. Figure 5.9 shows the effect of varying the duty cycle from 10 to 90% at 0.1 Torr. In general, the ratio of peak overshoot height to equilibrium in-beam density decreases as the afterglow period is shortened.

2. Mass spectrometric observations

Ion measurements have been made in oxygen during continuous electron irradiation over the pressure range 0.01 to 10 Torr. Studies above 1 Torr were performed early in the experimental program. At that time, the mass spectrometer data were not quantitatively reproducible, due to the presence of inadequately shielded insulators in the ion lens chamber. These insulators accumulated charge during the Van de Graaff irradiation which defocussed the slow incident ions in an unpredictable way. No quantitative information could be obtained concerning the pressure and beam current dependence of the various ions during that period, although the ion identifications appear to be reliable. Not until the last quarter of the present program was it possible to arrive at a design for the front end of the spectrometer which was free of these charging problems, yet provided the necessary operating characteristics. The quantitative

studies of mass-identified ions presented in this report have all been performed during the last month of this program. These latter studies were performed at pressures below 0.3 Torr; re-examination of the high-pressure regime was not possible during the time remaining on this contract.

Two detection systems were used during the earlier mass spectrometer measurements. The dc current from the electron multiplier could be read directly with an electrometer-tube picoammeter. Alternatively, the ion current could be modulated by a square-wave voltage applied to the ion lens, then the modulated component of the ion current ac amplified and synchronously detected. Both techniques were used for the positive ion studies, and gave comparable results. For studies of negative ion spectra, only the ac scheme could be employed because of the high dc voltage (about 4.5 kv) on the electron multiplier dynode with the spectrometer operating in the negative-ion mode. Following the elimination of the spectrometer charging problem mentioned above, there was insufficient time remaining to set up the ac detection system, so that only positive ions were studied during the last series of measurements.

At pressures in the range 1 to 10 Torr, several positive ions were observed in pure oxygen. The largest ion currents were observed for O_4^+ at these pressures. O_3^+ appeared with about one-third to one-fourth the ion current observed for O_4^+ . Traces of O_2^+ were also observed during these measurements. On several occasions at the higher pressures, possibly the first observations of O_5^+ reported in the literature were made.

During this early period, mass scans were also made in the pressure range 0.01 to 0.30 Torr. O_2^+ was the only positive ion observed in this pressure range. Similar scans for negative ions were also made during this period. A single ion, O_2^- , was observed with a signal-to-noise ratio of about 5. It is possible that other negative ions were present in appreciable density which were not seen due to the low sensitivity which the instrument then had for negative ions. There is, however, no reason to believe that other ions were indeed present.

Since the modification of the mass spectrometer, a series of measurements of positive ions was made in oxygen below 0.1 Torr. As was the case earlier, only O_2^+ was observed during continuous irradiation over this pressure range. Figure 5.10 shows several measurements of the O_2^+ ion current as a function of beam current, shown on a logarithmic plot. It can be seen that O_2^+ is not linear with beam current, which would then be evidenced by a straight line of unit slope on the graph, except for an "accidental" linearity somewhere between 25 and 50 millitorr.

3. Discussion of Oxygen results

Consider first the electron density measurements at high pressures. From the agreement between the pressure dependence measured in the afterglow ($\nu_a \sim p^2$) and that deduced from the steady-state n_s/i plots, it is reasonable to assume that the dominant electron loss mechanism in both time domains is the same. The afterglow decay frequencies yield the value

$$\nu_a = (2.12 \pm 0.15) \times 10^{-30} [O_2]^2 \text{ sec}^{-1} \quad (5.1)$$

This is in excellent agreement with the value obtained by Pack and Phelps [1966] for the frequency of three-body attachment of electrons to neutral O_2 molecules at 300° K , of $(2.0 \pm 0.2) \times 10^{-30} [O_2]^2 \text{ sec}^{-1}$, and with that of Van Lint [1959] of $2.1 \times 10^{-30} [O_2]^2 \text{ sec}^{-1}$. From this numerical agreement, it is reasonable to conclude that the reaction being studied is



The identification of O_2^- as the negative ion at low pressures supports the reaction proposed in 5.2. This does not imply that O_2^- is also the dominant ion at high pressures, for subsequent ion chemistry may alter the identity of the ion produced in the attachment process.

From the measured value of the decay frequency, the ionization production coefficient can be evaluated as discussed in Chapter III. From Figure 5.2, the specific ionization over the pressure range 0.9 to 10 Torr is given by $(1.35 \pm 0.14) \times 10^3/p$

electrons/cm³ μ a, referred to total current from the Van de Graaff accelerator. In terms of actual flux of electrons at the cavity, the specific ionization should be corrected by the factor appropriate to the scattering foil used:

$$\frac{\lambda_{\text{cavity}} (\mu\text{a}/\text{m}^2)}{\lambda_{\text{K.K.G.}} (\mu\text{a})} = 0.58 \pm 0.02 \quad (5.3)$$

This yields a corrected specific ionization at 1 Torr of

$$(\eta/\lambda) = (2.33 \pm 0.33) \times 10^3 \text{ electrons } [\text{cm}^2 \frac{\mu\text{a}}{\text{m}^2}]^{-1} \quad (5.4)$$

From the decay frequency given by Equation (5.1) the production coefficient is now evaluated; one finds

$$K = \frac{\lambda (\eta/\lambda)}{p} = (5.1 \pm 0.1) \times 10^7 [\text{cm}^3 \text{ sec Torr } (\frac{\mu\text{a}}{\text{m}^2})]^{-1} \quad (5.5)$$

With the assumption of the value $W = 30.9$ ev/ion pair measured by Jesse and Saudauskis [1953], the energy loss rate of 1.5 Mev electrons per unit path length in oxygen at STP (Section III.B) is

$$U = (2.1 \pm 0.4) \text{ kev/cm} \quad (5.6)$$

which is to be compared with the theoretical value 2.2 kev/cm computed by Nelms (1957).

At pressures above 0.9 Torr, it has been shown that diffusion does not play an important role in electron removal. As a consequence, for a spatially uniform electron-beam excitation function the electron density will also be spatially uniform,

both during irradiation and in the afterglow. This justifies the conversion of cavity frequency shifts to electron densities by the relation

$$n = 10^4 \times \Delta f(\text{kcps}) \quad [\text{cm}^{-3}] \quad (5.7)$$

implicit in which is the assumption of uniform electron density (Section II.C).

As the pressure is reduced, one expects diffusion to play an increasingly important role in electron removal. Three-body attachment can be expected to persist down to the lowest pressures, although it is no longer the dominant electron removal mechanism. Nevertheless, the attachment process should still produce appreciable densities of negative ions even at the lowest pressure employed in these experiments. This necessitates the use of the positive ion-negative ion ambipolar diffusion treatment for oxygen (Section III.C), and the model of the low-pressure oxygen plasma used to interpret the data must follow the density of negative ions as well as of electrons and positive ions.

From the mass spectroscopic results, it is apparent that the only significant positive ion at pressures below 300 millitorr is O_2^+ . The mass data also suggest that O_2^- is the only negative ion to be considered. If a complete account of the density of O_2^- is to be kept, some assumption must be made regarding the lifetime-controlling processes for O_2^- . It is reasonable to assume that O_2^- is produced by three-body attachment. From Equation 3.13, diffusion cannot be the limiting removal mechanism for the negative ion. Also, from the variation of

electron density with beam current, it is apparent that the negative ions must be lost in a non-linear process. This non-linear process is assumed to be mutual neutralization with O_2^+ , that is



For the purposes of the model, the production coefficient K and the three-body attachment frequency ν are assumed to have the values found at high pressures.

The model defined by the above consideration can be described by the system of equations

$$\frac{\partial n_e}{\partial t} = K p i - \beta p^2 n_e + D_a \left(1 + \frac{[O_2^-]}{n_e} \right) \nabla^2 n_e \quad (5.9)$$

$$\frac{\partial [O_2^-]}{\partial t} = \beta p^2 n_e - \alpha [O_2^+] [O_2^-] \quad (5.10)$$

$$[O_2^+] = [O_2^-] + n_e \quad (5.11)$$

This set of equations can now be solved numerically on an electronic computer for the electron and ion densities as functions of space and time, using assumed values for D_a and $\alpha_{O_2^+, O_2^-}$. The electron densities obtained from the solution should then be convoluted with the square of the rf measuring field in the cavity, from which the frequency shifts are predicted which can then be compared with experiment. A computation of this magnitude was felt to be beyond the scope of the present program, so that exact solutions have not yet in fact been obtained. The complete numerical solutions are included in plans for future work, however.

A great deal of information can be extracted from a simplified analysis which proceeds from the substitution

$\nabla^2 n_e \rightarrow -n_e / \Lambda_n^2$, where Λ_n is the fundamental diffusion length for the cavity. (In this work, $\Lambda_n^2 = 230 \text{ cm}^2$.) With this substitution, the steady-state model becomes

$$K p i = \frac{D_a p}{\Lambda_n^2} \left(1 + \frac{[O_2^+]}{n_e}\right) n_e + \beta p^2 n_e \quad (5.12)$$

$$\beta p^2 n_e = \alpha_{ii} [O_2^+][O_2^-] \quad (5.13)$$

$$[O_2^+] = [O_2^-] + n_e \quad (5.14)$$

The error inherent in the assumption that all charged particles are distributed in the fundamental diffusion mode can be seen from Equation 5.13, where in essence a single species is assumed proportional to the product of the other two. The error introduced by this simplification can only be evaluated by comparison of the solutions of the approximate model with the complete solutions, when the latter have been obtained.

From the measurements of Sampson and Weissler [1965] of the drift velocity of O_2^+ in oxygen, the zero-field mobility of O_2^+ is $2.4 \text{ cm}^2/\text{volt sec}$. This corresponds to an ambipolar diffusion coefficient $D_a p = 110 \text{ Torr cm}^2/\text{sec}$ at 300° K , or a free diffusion coefficient for O_2^+ just half that value ($D_+ p = 55 \text{ Torr cm}^2/\text{sec}$), which is the value used in the following computations. With the help of 5.14, Equation 5.12 can be written

$$\frac{D_a p}{\Lambda_n^2} [O_2^+] = K p i - \beta p^2 n_e = G(i) \quad (5.15)$$

G(1) has been calculated at 88 millitorrs from measured electron densities. Using the $D_a p$ given above, one can then predict $[O_2^+]$ in density units. This prediction is compared with the values of O_2^+ ion current measured simultaneously with the electron densities used in the above computation in Figure 5.11, where it can be seen that the linearity is excellent. This implies that the values for K and β determined at high pressures are still reasonable below 100 millitorr.

Equations 5.12 and 5.13 can be combined to yield an expression for the beam current as a function of electron density:

$$i_b = \left[\frac{\beta p}{K} + \frac{D_a p}{2\Lambda_n^2 p^2 K} \right] n_e + \frac{D_a p}{2\Lambda_n^2 p^2 K} n_e \left(1 + \frac{4\beta p^2}{\alpha_{ii} n_e} \right)^{1/2} \quad (5.16)$$

A value for α_{ii} has been determined for one pressure and for a single beam current. Figure 5.12 is a plot of Δf versus beam current for oxygen at a pressure of 0.17 Torr. For $i_b = 30 \mu\text{amp}$, $\Delta f = 106 \text{ kcps}$. Substitution of these values into 5.16 yields a value $\alpha_{ii} = 9.86 \times 10^{-8} \text{ cm}^3/\text{sec}$. Equation 5.16 can now be plotted, as shown in Figure 5.13. The electron beam currents required to produce electron densities of 5×10^5 , 10^6 , and $5 \times 10^6 \text{ cm}^{-3}$ have been calculated and are shown in Figure 5.13. Experimental data are shown by open circles. The agreement between experiment and calculation is quite good over the pressure range shown with the use of a single value of α_{ii} , considering the inadequacies of the simplified model. The value $\alpha_{ii} \approx 9.86 \times 10^{-8} \text{ cm}^3/\text{sec}$ is in agreement with numbers reported in the literature [Sayers, 1962]. The process is probably a

two-body recombination since the calculations agree so well with the data over nearly two decades of pressure.

The values of the coefficients obtained from the steady-state data can now be applied to the transient situation. The time-dependent simplified model can be written

$$\frac{dn_e}{dt} = K p i - \frac{D_a p}{\Lambda_{ii}^2 p} \left(1 + \frac{[O_2^-]}{n_e}\right) n_e - \beta p^2 n_e \quad (5.17)$$

$$\frac{d[O_2^-]}{dt} = \beta p^2 n_e - \alpha_{ii} [O_2^+][O_2^-] \quad (5.18)$$

$$[O_2^+] = [O_2^-] + n_e \quad (5.19)$$

These equations apply when electrons are present as well as positive and negative ions. From the increasingly rapid electron removal rate in the afterglow, it is apparent that the ratio $[O_2^-]/n_e$ becomes large as the electrons disappear. When $[O_2^-]/n_e \gg \mu_e/\mu_- \approx 10^4$, Equations 5.17 through 5.19 are no longer appropriate. Instead, one must set $n_e = 0$, then permit the residual positive and negative ions to diffuse freely; thus, for late times in the afterglow, Equations 5.18 and 5.19 must be replaced by

$$\frac{d[O_2^+]}{dt} = \frac{d[O_2^-]}{dt} = \alpha_{ii} [O_2^+][O_2^-] - \frac{D_a p}{\Lambda_{ii}^2 p} [O_2^-] \quad (5.20)$$

Equations 5.17 through 5.20 have been programmed and solved numerically on an IBM 1620 electronic computer for the case of a transient experiment with a 50% electron beam duty cycle (500 msec on, 500 msec off). Calculations were performed for a beam current of 100 μ amperes and oxygen pressures of 50, 100, 200, and 300 millitorrs, for the initial conditions

$n_e = [O_2^-] = [O_2^+] = 0$. The calculations trace n_e vs time during the in-beam phase of the cycle, then into the electron afterglow, using Equations 5.17, 5.18, and 5.19. When $[O_2^-]/n_e \approx 10^4$, the calculation switches over to Equation 5.20 to compute the ion density decays. The residual ion densities at the end of the afterglow are then used as initial conditions for the next beam cycle. It was found that the calculations converged after two cycles for all cases tried.

The results of the calculations for the in-beam electron density are shown in Figures 5.14 through 5.17, for two pairs of values for α_a and $D_a p$. Agreement between theory and experiment is surprisingly good. In addition to supplying general qualitative agreement, the model capably predicts both the location and height of the electron density overshoot over the entire pressure range. There are still some limitations to the model, however, as can be seen from the afterglow results shown in Figures 5.18 through 5.21. Perfect agreement can hardly be expected, in light of the following weaknesses of this calculation:

- (a) There is no reason to believe that n_e , $[O_2^+]$, and $[O_2^-]$ are spatially congruent. In fact, the differential equations indicate that they are not.
- (b) The spatial variation of the electron beam has not been properly taken into account.
- (c) It must be remembered that the solution

to the electron equation must be convoluted with the square of the cavity field before comparison with experiments can be made.

The variation of the in-beam behavior of the time-resolved electron density at low pressures with electron beam duty cycle has been referred to in Section V.B.1 and Figure 5.9. The origin of this variation can now be understood immediately. As long as the afterglow time is short compared to the positive and negative ion lifetimes, the second and all subsequent beam cycles begin with a finite density of negative ions. This changes the initial diffusion coefficient from its value $2D_+$ at $t = \Delta t$ during the first cycle to $2D_+ \left(1 + \frac{[O_2^- (R)]}{n_0(\Delta t)}\right)$, where $[O_2^- (R)]$ is the residual negative ion density at the end of the preceding pulse. This is illustrated by the computation shown in Figure 5.22, in which the early behavior of the electron density is calculated for initial ion densities $[O_2^-] = 0$, $[O_2^-] = 1.5 \times 10^7 \text{ cm}^{-3}$, and $[O_2^-] = 2 \times 10^7 \text{ cm}^{-3}$ for an oxygen pressure of 80 millitorr. These assumptions are compared with experimental measurements made for afterglow times of 20 and 100 milliseconds, respectively. It can be seen that, with a correct calculation of electron density in oxygen as outlined above, it should be possible to determine the time variation of negative ion density in the afterglow by terminating the afterglow at selected times and studying the early-time behavior of the next in-pulse electron density measurement.

An important consequence of the duty cycle effects reported above is the fact that the negative ions survive for at least one second in the wall-controlled laboratory environment. In the atmosphere, where the diffusion loss rate is greatly reduced, one can expect the ions to survive for a considerably longer period. Thus, even if the recombination coefficient is in fact as large as $10^{-7} \text{ cm}^3/\text{sec}$, then

$$\nu_{\text{eff}} = \alpha_{ii} [\text{O}_2^+] \quad (5.21)$$

At an ion density of 10^6 cm^{-3} , the effective loss frequency of O_2^- is 10^{-1} sec^{-1} ; at 10^5 cm^{-3} , the loss frequency is reduced to 10^{-2} sec^{-1} . Densities of positive and negative ions as high as 10^4 cm^{-3} can last for times the order of 15 to 20 minutes following the disappearance of electrons by attachment. If the correct computation proves that α_{ii} is lower than $10^{-7} \text{ cm}^3/\text{sec}$, the ions will last even longer. The military consequences of this persistence of negative ions in the atmosphere will be discussed in Chapter VI.

In summary, it has been shown that the behavior of oxygen over the pressure region 0.025 to 10 Torr can be explained by the following processes, using the indicated rate coefficients:

- (a) Production of electrons and O_2^+ ions in binary collisions between beam electrons and O_2 molecules in the ground state.
 Production rate = $K_{pi} \text{ ion pairs/cm}^3 \text{ sec}$,
 where

$$K = (5.1 \pm 0.1) \times 10^7 \text{ [cm}^3 \text{ sec Torr } (\frac{\mu\text{amp}}{\text{meter}^2})]^{-1}$$

At the higher pressures O_2^+ is rapidly converted to O_4^+ ; O_3^+ is also observed, although its origin is uncertain. At pressures below 0.3 Torr, O_2^+ and O_2^- appear to be the only ions present.

- (b) Loss of electrons and production of O_2^- ions by three-body attachment.

The reaction is



with a rate constant

$$\nu_a = (2.12 \pm 0.15) \times 10^{-30} [O_2]^2 \text{ sec}^{-1}$$

- (c) Diffusion controlled by the space-charge field of electrons, positive ions, and negative ions. For the O_2^+ ions, a value

$$D_a p \approx 110 \text{ cm}^2 \text{ Torr/sec}$$

is consistent with the measurements.

- (d) Loss of O_2^+ and O_2^- by two-body mutual neutralization, via the reaction



$$\alpha_{ii} \approx 1 \times 10^{-7} \text{ cm}^2/\text{sec}$$

is consistent with the measurements.

- (e) Duty-cycle effects on the in-beam densities at low pressures can be interpreted as the effect of residual ions left over from the preceding afterglow on the initial rate of electron diffusion. Negative ions persist for more than 1 second in the laboratory environment.

C. Measurements in Nitrogen

1. Electron density measurements

Measurements of electron densities in nitrogen were made over the pressure range 6 to 300 millitorr. The results were reproducible and consistent to a degree not usually encountered in experiments with pure nitrogen.

During the measurement of steady-state electron densities in oxygen, it was necessary to wait for about a minute after each beam current setting to allow the frequency shift to reach its equilibrium value. Figures 5.23 and 5.24 show results of several measurements of these equilibrium cavity frequency shifts as a function of total electron current from the Van de Graaff. At low currents, the measured points lie on straight lines which intersect the origin. At higher currents, the data break away from the extrapolation of these lines, suggesting the onset of another loss mechanism at the higher ionization levels. The frequency shift at which the breakaway occurs decreases with increasing pressures, as can be seen from the figure.

Figure 5.25 shows a compilation of the slopes of the linear portions of the steady-state measurements, in units of $\text{electrons/cm}^3 \mu\text{amp}$, where the slopes have been corrected for the transmission of the foil scattering system. For this graph, it has been assumed that the electron density has a uniform spatial distribution in the cavity, so that $f(\text{k cps})$ has simply been replaced by $10^4 \frac{\Delta f \text{ electrons}}{\text{cm}^3}$. It can be seen that the data display

a p^2 variation up to about 100 millitorr. From equation 3.36, this suggests that the rate coefficient for the controlling electron removal process in the linear regime varies as p^{-1} .

Figure 5.26 shows a typical decomposition of the electron density into an expression of the form (Equation 3.37).

$$i = A n + B n^c \quad (5.22)$$

This expression fits all the steady-state measurements quite accurately. From graphs such as Figure 5.26 the exponent c has been determined as well as the electron density at which the linear and the non-linear terms are equal, that is, n_{int} such that

$$B n_{int}^{c-1} = A \quad (5.23)$$

(From Figure 5.25, $A = 9.5 \times 10^{-9} p^{-2} \mu\text{amp cm}^3$, where p is in Torr.) Figure 5.27 is a summary of the values of c and of n_{int} for nitrogen which characterizes the measurements at all beam currents used.

Time-resolved measurements of the rise of the electron density to in-beam equilibrium, and of its decay in the radiation afterglow, were also made over the pressure range 5 to 300 millitorr in switched-beam experiments. Typical afterglow measurements are shown in Figure 5.28. Data at lower pressures are linear throughout the entire afterglow period, beginning with the time the beam is switched off. At higher pressures, the electron densities at late times show an exponential decay as well, although at earlier times the data lie above the backward extrapolation of the late-time linear decay. The early data at high pressures seem to follow a relationship of the form

$$\frac{1}{n} = \frac{1}{n_0} + \alpha t \quad (5.24)$$

the well-known "recombination plot" (See Chapter III), as shown in Figure 5.29. From the data, the slopes are given by

$\alpha = (6 \pm 2) \times 10^{-7} \text{ cm}^3/\text{sec}$. Unfortunately, the range of electron densities over which the data appear to satisfy Equation 5.24 is less than a factor of 2, so that it is dangerous to draw inferences from this plot about both mechanisms and rates. See Section C.3 below, however.

From the exponential afterglow decays one can compute lifetimes for the linear loss mechanism at various pressures. The data are summarized in Figure 5.30 in which the product of decay frequency and nitrogen pressure is shown as a function of pressure (solid circles).

Time-resolved measurements have also been made of the buildup of the electron density following beam turn-on. As mentioned in Section III.E, one must be careful in the analysis of the early-time data. Plots of the exponential rise toward equilibrium in-beam density should be referred not to the actual steady-state density characteristic of the beam current used, but to an extrapolation to the density which would occur if only linear processes were operating. When this is done according to Equation 3.40, one obtains plots of Δn vs time following beam turn-on which at least at early times characterize the linear process in-beam, as shown in Figure 5.31. This non-linearity at large $n(t)$, hence small $\Delta n(t)$, is exactly analogous to the early-time nonlinear behavior in the afterglow. The products of the gas pressures and characteristic frequencies of the exponential rise are shown in Figure 5.30 as open circles.

2. Mass spectrometric measurements

Mass spectrometric studies of positive ions in nitrogen have been made over the pressure range 0.005 to 10 Torr. These measurements have the same general history as those in oxygen (See Section V.B.2). At pressures between 1 and 10 Torr, only ion identifications have been made; quantitative results have been confined to the region below 0.1 Torr.

Between 1 and 10 Torr, several positive ions were seen in pure nitrogen. The largest ion currents were observed for N_4^+ , with N_3^+ appearing at currents about 0.2 to 0.3 times as large. At the highest pressures, traces of N_5^+ have also been seen. Small currents corresponding to ions of mass 44 (N_2O^+ or CO_2^+), 46 (NO_2^+), and 30 (NO^+) have also been detected at various times, as well as a broad unidentified peak in the neighborhood of mass 72. As mentioned in Section IV.A, when 0.1 to 1% O_2 is added to the nitrogen to quench cyanogen emission, peaks are observed at masses 48 (O_3^+) and 52 ($C_2N_2^+$). N_2^+ is not observed in pure nitrogen at these pressures.

Below about 0.1 Torr, the positive ion spectrum observed during continuous irradiation is dominated by N_2^+ , N_3^+ , N_4^+ . Near 0.1 Torr, NO^+ and NO_2^+ have also been observed, but their intensities decrease more rapidly at lower pressures than do those of N_2^+ , N_3^+ and N_4^+ . Most of the quantitative data which have been collected relate to these latter three ions, and the remainder of this section will be devoted to their discussion.

A series of measurements was performed of the relative ion currents for N_2^+ and N_4^+ at fixed pressures as a function of

Van de Graaff beam current. Figure 5.32 shows typical results for the N_2^+ currents at several pressures. The ion currents are linear with bombarding current over the range of beam currents employed. In Figure 5.33 the results of similar measurements for N_4^+ are shown. These data are linear at low beam currents, but depart from linearity at higher Van de Graaff flux, in a manner reminiscent of the high-current electron density behavior shown in Figure 5.24. The similarity between the N_4^+ and electron densities is borne out by Figure 5.34, in which logarithmic plots of N_4^+ ion current and electron density are shown at several pressures.

Another set of experiments was performed in which ion currents were measured at a fixed beam current as a function of gas pressure. Figure 5.35 shows the results of these measurements for N_2^+ at a beam current of 100 μ amperes. The N_2^+ ion currents vary as p^2 at low pressures, but approach a constant value at pressures above 0.035 Torr. At the highest pressures a slight decrease in ion current is observed, corresponding to the departure from linearity of the N_2^+ vs i data at 100 μ amperes. This behavior is quite different from the N_4^+ pressure dependence at 100 μ amperes, shown in Figure 5.36. There is no evidence of saturation at high pressures in the N_4^+ current, so that the N_2^+ saturation seen in Figure 5.35 is not due to instrumental limitations. The ratio of N_4^+ current to N_2^+ current at 100 μ amperes is shown in Figure 5.37 as a function of pressure. Below 40 millitorr the ratio varies as p^2 , but at higher pressures the ratios are smaller than predicted by the p^2 dependence. Included in Figure 5.37 are values of the N_4^+/N_2^+ ratio at 10 μ amperes, at which the individual N_4^+ measurements are linear. These ratios are somewhat larger at high pressures than those obtained at

100 μ amperes, but are still too small to agree with the p^2 dependence extrapolated from lower pressures.

The behavior of N_3^+ can be described simply by the statement that, for all cases observed, the ion current due to N_3^+ is exactly one-fourth the N_4^+ current. Thus N_3^+ varies with both pressure and beam current in the manner indicated above for N_4^+ , except for the absolute magnitude of the ion current. At the highest pressures studied, at which N_4^+/N_2^+ is largest, $I(N_2^+)$ is still more than twice as large as $I(N_3^+)$.

3. Discussion of nitrogen results

The principal experimental facts to be explained are summarized below.

- a) The steady-state electron densities can be expressed as

$$I_{\text{beam}} = An + Bn^c$$

where $A = 9.5 \times 10^{-9} / p^2 \text{ } \mu\text{amp cm}^2$
and $C \approx 2$.

- b) In transient measurements in the linear regime, the electron densities rise exponentially in-beam, and decay exponentially in the afterglow. Between 0.1 and 0.3 Torr, the rise and decay frequencies are equal, and satisfy the relation

$$\nu p = (0.65 \pm 0.03) \text{ Torr sec}^{-1}.$$

At low pressures, the product of transient frequency and pressure is smaller than this value, with the rise frequency smaller than the afterglow decay frequency at the lowest pressures.

- c) For beam-current in the non-linear regime, the early afterglow electron densities satisfy a relation of the form

$$\frac{1}{n} - \frac{1}{n_0} = (6 \pm 2) \times 10^{-7} \times t ,$$

but only over a range of densities smaller than a factor of two.

- d) Below 0.1 Torr, three positive ions, N_2^+ , N_3^+ , and N_4^+ dominate the mass spectrum in the steady-state. The N_2^+ ion currents are linear with Van de Graaff beam current. At a fixed beam current, $I(N_2^+)$ varies as p^2 at the lowest pressures then appears to flatten off at about 0.035 Torr. The N_4^+ ion current is linear with beam current at low currents, then breaks away from linearity at high beam currents. The ratio N_4^+/N_2^+ varies as p^2 below 0.040 Torr. $I(N_3^+)$ is always one-quarter of $I(N_4^+)$ under all conditions investigated.

From the results summarized above, it is possible to identify several processes occurring in the nitrogen plasma.

Consider the following model of the low-pressure nitrogen plasma. The plasma consists of electrons and N_2^+ , N_3^+ , and N_4^+ ions as well as neutral N_2 molecules. N_2^+ is produced by binary collisions between beam electrons and neutral molecules, and is removed from the plasma by ambipolar diffusion and ion-molecule reactions producing N_3^+ and N_4^+ . The latter two ions are produced by the ion-molecule reactions which remove N_2^+ , and are lost by ambipolar diffusion and by recombination with electrons. To simplify the treatment of the diffusion controlled by several positive ion species, the assumption is made that all charged particle species are spatially congruent, that is, that

$$\frac{\nabla N_2^+}{N_2^+} = \frac{\nabla N_3^+}{N_3^+} = \frac{\nabla N_4^+}{N_4^+} = \frac{\nabla n_e}{n_e} \quad (5.25)$$

Then Equations 3. may be used for the effective diffusion coefficients. The model can then be described by

$$\frac{\partial N_2^+}{\partial t} = K p i + D_{a,2} \nabla^2 N_2^+ - \{C_3(p) + C_4(p)\} N_2^+ \quad (5.26)$$

$$\frac{\partial N_3^+}{\partial t} = C_3(p) N_2^+ + D_{a,3} \nabla^2 N_3^+ - \alpha_{3,e} n_e N_3^+ \quad (5.27)$$

$$\frac{\partial N_4^+}{\partial t} = C_4(p) N_2^+ + D_{a,4} \nabla^2 N_4^+ - \alpha_{4,e} n_e N_4^+ \quad (5.28)$$

$$n_e = N_2^+ + N_3^+ + N_4^+ \quad (5.29)$$

Here D_{aj} is the ambipolar diffusion coefficient which would be observed for the ion N_j^+ in the absence of all other ions. $\alpha_{j,e}$

is the electron- N_j^+ recombination coefficient, and $C_j(p)$ is the frequency of ion-molecule reaction producing N_j^+ . Equations 5.26 to 5.29 are non-linear partial differential equations which cannot be solved in closed form. A numerical solution can be obtained through the use of a high-speed electronic computer. A computer program of sufficient complexity to provide accurate solutions was beyond the scope of the present contract, however, although it is included in plans for future work.

Much information can be obtained from the model without an exact solution, if we make an additional approximation. Assume not only spatial congruence, but that the ions and electrons are all distributed spatially according to the fundamental diffusion mode:

$$n_e, N_j^+ \sim J_0(2.405 \frac{r}{R}) \sin \frac{\pi z}{h} \quad (5.30)$$

Then the equations reduce to

$$\frac{dN_2^+}{dt} = K p i - \left(\frac{D_{a,2} p}{\Lambda_{ii}^2 p} + C_3(p) + C_4(p) \right) N_2^+ \quad (5.31)$$

$$\frac{dN_3^+}{dt} = C_3(p) N_2^+ - \left(\frac{D_{a,3} p}{\Lambda_{ii}^2 p} + \alpha_{3,e} n \right) N_3^+ \quad (5.32)$$

$$\frac{dN_4^+}{dt} = C_4(p) N_2^+ - \left(\frac{D_{a,4} p}{\Lambda_{ii}^2 p} + \alpha_{4,e} n \right) N_4^+ \quad (5.33)$$

$$\frac{dn_e}{dt} = K p i - \frac{1}{\Lambda_{ii}^2 p} \sum_j D_j p N_j^+ - \sum_j (\alpha_{j,e} N_j^+) n_e \quad (5.34)$$

In the above equations n_e , N_j^+ are the amplitudes of the fundamental-mode distribution, and i is the coefficient of the first term in the expansion of the uniform current in a Fourier-Bessel series. In the remainder of this treatment, the density coefficients are identified with the measured particle densities. Equations for the steady-state are derived from 5.31 - 5.34 by setting all time derivatives equal to zero.

Consider first the steady-state equations in the limit of low ionization, so that electron-ion recombination can be neglected. Then Equations 5.32 and 5.33 give

$$\frac{N_2^+}{N_2^+} = \frac{p C(p)}{\frac{D_{a,2} p}{\Lambda_{II}^2}} ; \quad \frac{N_4^+}{N_2^+} = \frac{p C_4(p)}{\frac{D_{a,4} p}{\Lambda_{II}^2}} \quad (5.35)$$

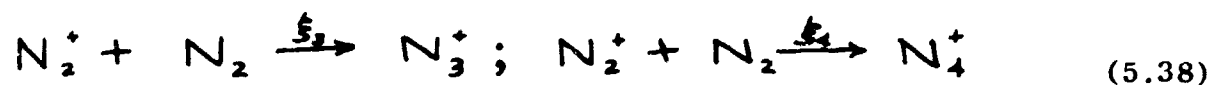
Since $D_{aj}p/\Lambda_{II}^2$ is independent of pressure, then the pressure dependence of the indicated ion current ratios can be used to deduce the pressure dependence of $C_j(p)$. From the low-pressure p^2 dependence of N_4^+/N_2^+ shown in Figure 5.37,

$$C_4(p) = \xi_4 p \quad (5.36)$$

from the similarity of N_3^+ and N_4^+ it is also apparent that

$$C_3(p) = \xi_3 p \quad (5.37)$$

This linear dependence of the ion-molecule reaction rates on gas pressure implies that the reactions are of the form



For further confirmation of 5.36 and 5.37, and for evaluation of the rate coefficients, Equation 5.31 is rewritten

$$\frac{p^2}{N_2^+} = \frac{1}{K_i} \left\{ \frac{D_{a,2} p}{\Lambda_{ii}^2} + (\xi_3 + \xi_4) p^2 \right\} \quad (5.39)$$

A plot of p^2/N_2^+ , at fixed beam current vs p^2 should yield a straight line, for which the ratio of slope to intercept is

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{\xi_3 + \xi_4}{\frac{D_{a,2} p}{\Lambda_{ii}^2}} \quad (5.40)$$

Figure 5.38 shows the N_2^+ vs p data of Figure 5.35 replotted in accordance with Equation 5.39. The data below 0.04 Torr lie on a straight line; from the data and Equation 5.43,

$$\xi_3 + \xi_4 = 4 \times 10^3 \frac{D_{a,2} p}{\Lambda_{ii}^2} . \quad (5.41)$$

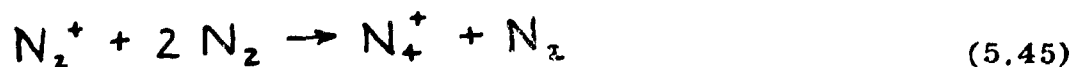
The data at pressures above 0.04 Torr are well approximated by a straight line on the p^2 plot which passes through the origin. This high pressure behavior of the data has not yet been explained. It may represent a change in the mode of ion sampling by the mass spectrometer, since at 0.04 Torr the gas-kinetic mean free path is equal to the aperture diameter 1.25 mm. This problem requires more detailed study with apertures of various sizes, to determine the role of the aperture on ion sampling. Below 0.09 Torr, however, it appears that the ion current is representative of the central ion density. Gas-kinetic considerations of ion sampling should not be a problem in

coefficient through its effect on the excited state populations. Cress et al [1966] have also measured the lifetime of the excited state responsible for the two-body N_3^+ production. They obtain a value on the order of 6×10^{-6} sec.

Two reactions have been proposed in the literature for the production of N_4^+ from N_2^+ . The first is the Hornbeck-Molnar process,



proposed by Curran [1963] to explain his observed ion chemistry in nitrogen; the excited state of N_2 involved in 5.44 is not specified. At higher pressures, an additional source of N_4^+ is the three-body process



[Munson et al, 1962; Knewstubb and Tickner, 1962]. The present results show no evidence for the three-body process below 0.1 Torr. It is somewhat more difficult to make a definitive statement concerning the applicability of 5.44 to the present situation. Several points should be made, however. First, the similarity of the pressure variation of the N_3^+ and N_4^+ ion currents suggest that these ions arise from states having similar pressure dependences. Second, as will be mentioned in the next section, the addition of oxygen to nitrogen to 20% partial pressure depletes N_2^+ through the rapid charge exchange reaction



[Stebbing et al, 1966]. Traces of N_2^+ , but no N_3^+ or N_4^+ are seen in the nitrogen-oxygen mixtures. The latter fact suggests that N_4^+ production must be related to N_2^+ rather than to neutral N_2 . From the former, it is possible to relate the N_4^+ production to a definite state of the N_2^+ ion, as follows.

First, we observe N_4^+ currents four times as large as the N_3^+ currents; Cermak and Cress do not observe N_4^+ from binary collisions. Hence it would appear that N_3^+ and N_4^+ arise from two different states, the relative excitation of which is different in this experiment from that which results from low-energy electrons. The state from which N_4^+ is derived must be lost by radiation at low pressures and by ion-molecule reaction at high pressures; the ratio of the reaction rate coefficient to the spontaneous emission probability for this state must be the same as for the $^4\Sigma_u$ state. Sheridan et al [1964] have shown that the $A^2\Pi$ state of N_2^+ has a radiative lifetime of the order of 3×10^{-6} sec, much the same as the result of Cress et al for $^4\Sigma_u$. Since no estimate of the rate coefficient for $^4\Sigma_u$ conversion to N_3^+ is forthcoming it is not possible to compare the rate with that for $A^2\Pi$. One can estimate, however, the number of quenching collisions suffered by $A^2\Pi$ in one second, then compare this with the observed production rate of N_4^+ .

The quenching coefficients obtained by Sheridan et al for $A^2\Pi$, as well as our own results for $B^2\Sigma$, are of the order of $5 \times 10^{-9} \text{ cm}^3/\text{sec}$, referred to the excited state density. We observe N_2^+ destruction at a rate of the order of $5 \times 10^{-14} \text{ cm}^3/\text{sec}$, so that these rates give equal numbers of events for values of the ratio

$$\frac{[A^2\Pi]}{N_2^+} \approx 10^{-5} \quad (5.47)$$

This ratio in the steady-state can be estimated from a knowledge of the fluorescence efficiency for one of the Meinel bands (which arise from $A^2\pi$) in the following manner. The density of $A^2\pi$ states is given by (Equation 3.26)

$$[A^2\pi] = \frac{K_A p i}{A_A + C_A p} \quad (5.48)$$

where $C_A = 130 A_A$, the ratio $[A^2\pi]/N_2^+$ is then given by

$$\frac{A^2\pi}{N_2^+} = \frac{K_A}{K} \frac{D_{2,2} p / \Lambda^2 p + (\xi_2 + \xi_4) p}{A_A + C_A p} \quad (5.49)$$

From 3.33,

$$\frac{K_A}{K} = \frac{\eta_{(2,0)} A_A W}{A_{(2,0)} h \nu_{(2,0)}} \quad (5.50)$$

The various symbols are as defined in Chapter III. From Davidson [1966], $\eta_{(2,0)} \approx 1 \times 10^{-5}$, the ratio $A_A/A_{(2,0)}$ is of the order of 2; for nitrogen, $W = 35$ ev; $h \nu_{(2,0)} \approx 1.5$ ev. Then

$$\frac{K_A}{K} \approx 0.05 ; \quad (5.51)$$

since $A \approx 3 \times 10^5 \text{ sec}^{-1}$ this gives [Sheridan et al., 1964]

$$\frac{A^2\pi}{N_2^+} \approx 1.7 \times 10^{-7} \frac{[D_{2,2} p / \Lambda^2 p + (\xi_2 + \xi_4) p]}{1 + 130 p} \quad (5.52)$$

Over the pressure range 0.01 to 0.1, the quantity in brackets

varies from 70 sec^{-1} at 0.01 Torr to 200 sec^{-1} at 0.1 Torr, so that

$$\frac{A^2\pi}{N_2^+} \approx 10^{-5} \text{ to } 10^{-6} \quad (5.53)$$

Hence the number of $A^2\pi$ quenching reactions is nearly equal to the observed production rate for N_3^+ and N_4^+ ions, to within the accuracy of the calculation. This suggests the reactions



The assignment of $A^2\pi$ to the reaction 5.54 is consistent with Varney's [1953] estimate of the binding energy of N_4^+ of 0.5 eV ($A^2\pi$ lies 1 eV above the $X^2\Sigma$ ground state of N_2^+). The apparent rates for these reactions, without corrections for mass spectrometer relative sensitivity for N_3^+ and N_4^+ , or difference in $D_{a,p}$ and $D_{a,4p}$ are

$$\xi_3 \approx 6 \times 10^{-15} \text{ cm}^3/\text{sec} \quad (5.56)$$

$$\xi_4 \approx 2.4 \times 10^{-14} \text{ cm}^3/\text{sec} \quad (5.57)$$

The observation of such small rate coefficients compared with those observed by Creswell must be attributed to the different experimental

considerations of the ratio of two ion currents, however, unless specific chemical reactions occurring at or in the aperture are involved.

Although a numerical evaluation of the rate coefficients ξ_3 and ξ_4 requires a knowledge of $D_{a,2} p$, several considerations concerning the reaction are in order at this point. First, a two-body rate coefficient for the reaction



has been reported [Cress et al, (1966)]; its value is about 5×10^{-11} cm³/sec. From 5.41 and the knowledge that $D_{a,2} p$ cannot be much different from 100 Torr cm²/sec, the total conversion coefficient is of the order of

$$\xi_3 + \xi_4 \approx \frac{2 \times 10^3}{3.2 \times 10^{16}} \frac{[10^{-10} \text{ sec}]^{-1}}{\frac{\text{Molecules}}{\text{cm}^3 - \text{Torr}}} \approx 6 \times 10^{-14} \text{ cm}^3/\text{sec} \quad (5.43)$$

The rate constant reported by Cress for the reaction 5.42 which is believed to proceed from the $^4\Sigma_u$ state of N_2^+ [Cermak and Herman, 1962] is referred to the total density of N_2^+ . Thus in the present experiment in which the ions are observed during continuous irradiation by fast electrons, it appears that the $^4\Sigma_u$ state (or whichever state of N_2^+ is in fact involved in 5.42) has a fractional density some three orders of magnitude lower than in Cress's work. This illustrates the difficulties encountered in the characterization of reactions which proceed through excited states; the experimental technique employed for ionization can control the apparent rate

conditions employed here. The high energy electrons which are used for the excitation, may be less likely to induce the spin transition required for $^4\Sigma$ excitation. Also, the observations were made during continuous irradiation; thus whatever $^4\Sigma$ was produced could be destroyed in collisions with the beam electrons. Any of the proposed reactions 5.42, 5.44 and 5.45 could be occurring in the afterglow, although the similarity of the electron density turn-on and turn-off rates suggests that nothing unusual happens in the afterglow.

To summarize, it appears that N_3^+ is produced from N_2^+ in the $^4\Sigma$ state by binary collisions with ground-state N_2 molecules, with a rate of $1 \times 10^{-14} \text{ cm}^3/\text{sec}$, N_4^+ is produced from the $A^2\pi$ state of N_2^+ in similar collisions; both excited states behave in a similar manner with pressure. The ion-molecule reaction is responsible for the observed optical quenching of $A^2\pi$. From the equality of the cross-sections for $A^2\pi$ and $B^2\Sigma$ quenching, it appears reasonable to assign the $B^2\Sigma$ quenching to N_4^+ production, as well. The cross-sections for the quenching collisions are also the ion-molecule cross-sections referred to the excited state, of the order of 10^{-14} cm^2 .

For several reasons, we are hesitant to deduce ambipolar diffusion coefficients from the electron density data. First, the transient decay frequencies do not vary inversely as the pressure, as the steady-state slopes suggest they should. The high-pressure asymptote of $\tau p = 0.65 \text{ Torr sec}^{-1}$ (Figure 5.30) is consistent with a $D_a p$ of about $150 \pm 10 \text{ Torr cm}^2/\text{sec}$. If this is used in Equation 3.41, a value for the production coefficient $K = 6.8 \times 10^{11} (\text{cm}^3 \text{ Torr sec})^{-1}$ is obtained from the steady-state slopes shown in Figure 5.25. From air measurements to be

presented in the next section, a value of $K = 5.7 \times 10^{11}$ ($\text{cm}^3 \text{Torrsec} \frac{\text{pAmp}}{\text{cm}^2}^{-1}$) is found corresponding to a $D_a p$ of about $110 \text{ Torr cm}^2/\text{sec}$ which agrees with the low pressure limit of ηp . In no case does the transient electron decay follow an exponential plot for significantly more than a decade of electron density, so that these plots may be gravely misleading. In view of the recent dispute over ionic mobilities in nitrogen [Keller et al, 1965] it is desirable to avoid entering the controversy until better measurements are obtained. At this point it will suffice to say that the measurements are consistent with a value of $D_a p$ between 110 and $150 \text{ Torr cm}^2/\text{sec}$, which can probably be attributed to the N_3^+ and N_4^+ ions. For N_2^+ , the best estimate from mobility measurements [Keller et al, 1965; Saproshenko, 1965] give $D_{a,2p} \approx (60 \pm 20) \text{ Torr cm}^2/\text{sec}$. This value may explain the apparently low ηp observed in the turn-on at low pressures, before the N_2^+ has had an opportunity to convert to N_3^+ and N_4^+ in any significant amounts.

To summarize the results in nitrogen, the following should be listed:

- a) The dominant electron loss mechanism at low pressures is ambipolar diffusion. The following coefficients are consistent with the measurements:

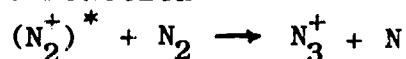
$$D_{a,2p} \approx (60 \pm 20) \text{ Torr cm}^2/\text{sec}$$

$$D_{a,3p}, D_{a,4p} \approx 110 \text{ to } 150 \text{ Torr cm}^2/\text{sec}$$

The steady-state data suggest that $D_{a,4p}$ is probably $110 \text{ Torr cm}^2/\text{sec}$.

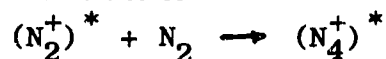
- b) N_2^+ is produced directly by the beam, and is lost by diffusion and conversion to N_3^+ and N_4^+ .

- c) The reaction



has been observed. The evidence is consistent with the assignment of the $^4\Sigma_u$ metastable state of N_2^+ as the one participating in the reaction. The cross-section for the reaction is on the order of $5 \times 10^{-15} \text{ cm}^2$.

- d) The reaction



has been observed. It is suggested that the dominant excited state involved is the $A^2\pi$, and that the conversion to N_4^+ is responsible for the observed optical quenching of both $A^2\pi$ and $B^2\Sigma$. The cross-section for the reaction, as deduced from optical quenching measurement, is about 10^{-14} cm^2 .

D. Measurements in Airlike Mixtures of N_2 and O_2

1. Introduction

A series of measurements of electron and ion densities has been performed in 4:1 mixtures of $N_2:O_2$ subjected to bombardment by 1.5 Mev electrons. Optical emission studies in these gas mixtures have also been performed, and are presented in Chapter IV. The measurements described in this section were performed over the pressure range 0.035 to 10 Torr, which corresponds to the altitude range from 30 to 70 km in the atmosphere.

The gas mixtures used in this work, 80% N_2 and 20% O_2 by pressure, have been chosen as a first approximation to the complex chemistry of the upper atmosphere. As will be seen below, much of the gross phenomenology of the atmosphere deduced from weapon test data is reproduced by this simple mixture. Future work directed toward a study of the detailed aspects of the response of the atmosphere to ionizing radiation can use these binary mixtures as a starting point for more sophisticated chemical approximations to the atmosphere. The results of those measurements will probably consist of small changes in the results observed in the present work.

The section opens with a discussion of the measurements performed in the $N_2:O_2$ mixtures. This is followed by the interpretation of the results with reference to the laboratory environment. The section closes with an extrapolation of the laboratory results to the upper atmosphere, in which comparisons are made with current lumped-parameter models of the disturbed ionosphere.

2. Electron density measurements

Electron densities were measured during continuous irradiation of 4:1 mixtures of $N_2:O_2$ at fixed pressures between 0.035 and 10 Torr. Figure 5.39 shows several examples of these measurements at pressures above 0.6 Torr. It can be seen that the data are linear over the beam current range measured. The slopes of these linear plots are compiled in Figure 5.40 as a function of pressure; the measured slopes, in $kcps/\mu$ ampere, have been converted to $electrons/cm^3 \mu$ ampere with the use of Equation 2.7. The correction for electron-neutral collisions was made for the assumption $\nu_c = 1 \times 10^8 p \text{ sec}^{-1}$ [Phelps, 1962]. The slopes are referred to total beam current from the accelerator. It can be seen that n_s/i varies as p^{-1} quite accurately for pressures greater than 1.5 Torr. This implies that the electron loss mechanism varies with pressure as p^2 (Equation 3.34).

Figure 5.41 shows several measurements of electron density at pressures below 0.1 Torr. Here the curvature at low beam currents is reminiscent of the steady-state oxygen data at low pressures (Section V.B). At somewhat higher beam currents, the electron densities fall onto a straight line which does not intersect the origin, as was also observed in oxygen. At higher currents and pressures, however, the electron density breaks away below this line in the mixtures; in oxygen the straight line represented the data up to the highest beam currents.

Transient measurements of electron density were performed in the radiation afterglow at pressures above 0.6 Torr. Figure 5.42 shows several examples of the observed decays, which are quite accurately exponential over the pressure range inves-

tigated. The characteristic frequencies deduced from these decays are compiled in Figure 5.43 as a function of gas pressure. These frequencies accurately follow a p^2 dependence at least down to 1.5 Torr, and can be represented in this range by

$$\gamma_A = (1.10 \pm 0.05) \times 10^{-21} [M]^2 \text{ sec}^{-1} \quad (5.58)$$

where $[M]$ is the number density of neutral air molecules.

3. Mass spectrometric measurements

Quantitative mass data have been obtained in 4:1 mixtures of $N_2:O_2$ over the pressure range 0.025 to 0.1 Torr. Above 1 Torr, positive ions have been identified, but no quantitative results are available at this time.

At pressures above 1 Torr, the positive ion spectra observed in 4:1 mixtures are dominated by two species, N_2^+ and NO^+ . In addition, other ions have been seen from time to time, particularly N_3^+ , N_2O^+ , and O_4^+ , although at much smaller peak currents.

Below 0.1 Torr, two peaks dominate the positive ion spectrum, O_2^+ and NO^+ . N_2^+ is also observed at these pressures, but its peak current is about an order of magnitude smaller than either NO^+ or O_2^+ , and remains nearly constant over the pressure range. Figure 5.44 shows O_2^+ peaks as a function of beam current at several pressures. At low currents the data lie on straight lines passing through the origin. The slopes of these lines are linear with pressure, as shown in Figure 5.45. The deviation of

the ion currents from the straight line increases with increasing pressure.

In Figure 5.46 the NO^+ peak currents are shown as a function of beam current at several pressures. The data are linear at low beam currents, but show a departure from linearity at the highest pressure. In general, this departure is not as marked as that observed for O_2^+ under these conditions. The slopes of the straight-line portions are not linear with pressure, but vary as illustrated in Figure 5.45.

4. Interpretation of laboratory measurements

The coincidence of the p^2 dependence of the electron loss processes deduced from the steady-state and afterglow measurements at high pressures suggests that these in fact represent the same process. From the analogy with the measurements in oxygen, the dominant removal mechanism can be identified as three-body attachment of electrons to neutral O_2 molecules, with both O_2 and N_2 acting as third bodies. The attachment frequency

$$\nu_a = (1.10 \pm 0.05) \times 10^{-31} [M]^2 \text{ sec}^{-1} \quad (5.58)$$

deduced from the measurement is in excellent agreement with the value quoted by other workers [Pack and Phelps, 1966] for electron attachment in airlike mixtures of nitrogen and oxygen. The efficiency of N_2 relative to O_2 as a third body in stabilizing the newly formed negative ion is given by (Equation 3.5)

$$\eta = (3 \pm 1) \times 10^{-2} \quad (5.59)$$

From the measured slopes of the linear n_s vs i plots, a value for the ionization production coefficient K may be deduced. From Equation 3.34,

$$K = \frac{\partial_a n_s}{p i} = \frac{\partial_a}{p} S \quad (5.60)$$

where S is the value of the slope referred to incident beam current density. From Figure 5.40, the slope referred to total beam current from the accelerator is

$$S_T = 1.45 \times 10^5 \cdot p^{-1} \quad (\text{cm}^3 \mu\text{amp})^{-1} \quad (5.61)$$

After correction for the scattering foil used in these measurements, (foil transmission = 0.288), this yields

$$S = (5.0 \pm 0.2) \times 10^5 \cdot p^{-1} \quad (\text{cm}^3 \frac{\mu\text{amp}}{\text{cm}^2})^{-1} \quad (5.62)$$

Thus the production coefficient for the airlike mixture is given by

$$K_{\text{air}} = \frac{S \partial_a}{p} = (5.55 \pm 0.35) \times 10'' \quad (\text{cm}^3 \frac{\mu\text{amp}}{\text{cm}^2} \text{ Torr} \cdot \text{sec})^{-1} \quad (5.63)$$

This is to be compared with the value obtained for the production coefficient for oxygen (Section V.B):

$$K_{\text{oxygen}} = 5.1 \times 10'' \quad (\text{cm}^3 \frac{\mu\text{amp}}{\text{cm}^2} \text{ Torr} \cdot \text{sec})^{-1} \quad (5.64)$$

From the relation

$$K_{\text{air}} = 0.8K_{\text{nitrogen}} + 0.2K_{\text{oxygen}},$$

it follows immediately that

$$K_{\text{NITROGEN}} = (5.6 \pm 0.4) \times 10'' \left(\text{cm}^3 \frac{\mu\text{amp}}{\text{cm}^3 \text{ Torr sec}} \right) (5.65)$$

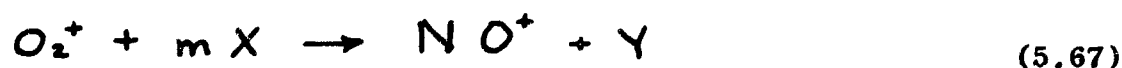
These values are in general agreement with the calculated production coefficients shown in Section III.B, and in good agreement with each other.

From the mass spectrometer data at low pressures, several statements can be made concerning the origins of the positive ions observed during continuous irradiation. The primary ions produced by the electron beam are N_2^+ and O_2^+ , in the ratios of the partial pressures of neutral N_2 and O_2 , respectively. It is known that N_2^+ undergoes a rapid charge exchange with O_2 to produce O_2^+ (Equation 5.46). Referred to their total N_2^+ density, which was known to be very rich in $\text{A}^2\Pi$, Stebbings et al [1966] deduce a rate coefficient for the charge exchange reaction given by

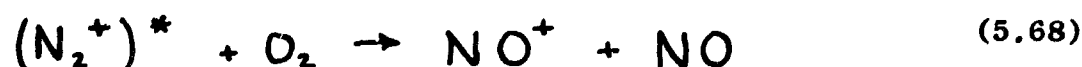
$$R_x = 2 \times 10^{-10} \text{ cm}^3/\text{sec} \quad (5.66)$$

Our measurements of the rate coefficient for the quenching of $\text{B}^2\Sigma$ by collisions with O_2 molecules (Chapter IV) gives a value when referred to $\text{B}^2\Sigma$ density of about $10^{-9} \text{ cm}^3/\text{sec}$. This suggests

that similar rates should hold for the quenching of $A^2\pi$ by O_2 as well. Furthermore, both quenching reactions can probably be attributed to the charge exchange reaction. The origin of NO^+ in the experiments is somewhat uncertain. From the observation that NO^+ shows less departure from linearity with beam current than does O_2^+ , reactions of the form

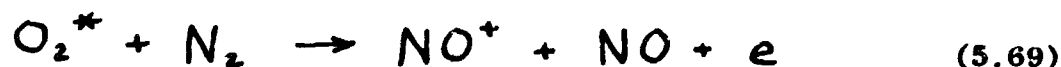


can probably be ruled out. NO^+ could be produced in an ion-molecule reaction of the form

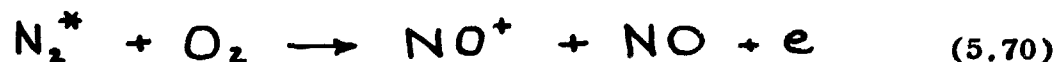


It is necessary to invoke an excited state for this reaction. Stebbings and his group do not observe this reaction for ionizing electron energies of the order necessary to populate just the $A^2\pi$ and $X^2\Sigma$ states of N_2^+ ; 5.58 must therefore come from a higher-lying state than $A^2\pi$. Since N_3^+ is not observed in the air mixtures, the $^4\Sigma$ state responsible for N_3^+ production might be quenched by reaction 5.58.

NO^+ could also be produced from a modified Hornbeck-Molnar reaction



or



It would be very convenient to invoke Reaction 5.60 to explain the observed quenching of Second Positive Bands, which originate from the $C^3\pi$ state of N_2 , by neutral oxygen. This reaction cannot however, be a major source of NO^+ , since the resulting production of free electrons would be in disagreement with the electron density measurements, which show an electron production term which varies as p over the entire pressure range. Thus reactions 5.69 and 5.70 cannot explain most of the observed NO^+ , which we therefore tentatively ascribe to 5.68.

To describe the mixture data in its most convenient form, a lumped-parameter model is used. This model assumes a single species each of "average" positive and negative ions, as well as electrons, so that it is very similar to the model used for oxygen (Section V.B). The equations for three-component plasma at low pressures will be presented for the steady-state, with the assumption that all particles are distributed in the fundamental diffusion mode. Then

$$K p_i = \frac{D_a p}{\Lambda^2 p} P + \alpha_i N P + \alpha_e n P \quad (5.71)$$

$$\beta p^2 n = \alpha_i N P \quad (5.72)$$

$$P = N + n \quad (5.73)$$

In the limit of low electron density, where the electron-positive ion recombination term in 5.61 can be neglected, the above equations can be rearranged to give

$$P = \frac{K p_i - \beta p^2 n}{\frac{D_{ap}}{\Lambda^2 p}} \quad (5.74)$$

$$N = P - n \quad (5.75)$$

$$\alpha_i = \frac{\beta p^2 n}{NP} \quad (5.76)$$

Both K and β have been evaluated from the high pressure data. One can therefore arrive at a value for α_i by assuming a value for D_{ap} (say $\overline{D_{ap}}$) calculating P and N for this value, then finally α_i . $\overline{D_{ap}}$ is then varied until the calculated ion recombination coefficient is independent of beam current. The ion densities predicted by one such calculation are shown in Figure 5.47. From calculations of this type, all the data obtained at low pressures have been found to be consistent with the values

$$D_{ap} = (160 \pm 15) \text{ Torr} \cdot \text{cm}^2 / \text{sec} \quad (5.77)$$

$$\alpha_i = (2.5 \pm 1.5) \times 10^{-7} \text{ cm}^3 / \text{sec} . \quad (5.78)$$

A simple extension of the above technique permits an estimate of the electron-positive ion recombination coefficient. From Equations 5.71 and 5.72 one obtains

$$\frac{K p_i - \beta p^2 n}{P} = \frac{D_{ap}}{\Lambda^2 p} + \alpha_e n \quad (5.79)$$

Thus a plot of the quantity $(K p_i - \beta p^2 n)/P$ vs n should yield a straight line; the ratio of the slope to intercept of this line

is given by

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{\alpha_e}{\frac{D_{ap}}{\Lambda^2 p}} \quad (5.80)$$

Figure 5.48 shows a plot of Equation 5.79 made for a mixture pressure of 0.083 Torr. From the limited data thus far available, α_e has been found to be consistent with

$$\alpha_e = (3 \pm 2) \times 10^{-7} \text{ cm}^2/\text{sec} \quad (5.81)$$

Several comments should be made concerning the above computations of recombination coefficients. First, the techniques described above yield more consistent results in air than they did in oxygen (section B). This is because the lower attachment rate for air than for oxygen at the same pressure results in fewer negative ions, hence in a closer approximation to the true situation by the fundamental-mode model, Equations 5.71 to 5.73. Second, the predicted values of α_e are in very good agreement with other laboratory measurements for $\alpha_e(O_2^+)$ and $\alpha_e(NO^+)$ which can be summarized as

$$\alpha_e(O_2^+) = (2 \pm 1.5) \times 10^{-7} \text{ cm}^2/\text{sec} \quad [\text{Kasner and Biondi, 1965}] \quad (5.82)$$

$$\alpha_e(NO^+) = 4.6 \times 10^{-7} \text{ cm}^2/\text{sec} \quad (5.83)$$

[Gunton and Shaw, 1965]

Finally, the pair of numbers α_i, α_e obtained above is in good agreement with deductions made from analyses of the disturbed ionosphere [Knapp, 1966], which are consistent with the sets of

values

$$\begin{aligned}
 \alpha_e = \alpha_i &= 3 \times 10^{-7} \text{ cm}^2/\text{sec} \\
 \alpha_e = 2^+ \times 10^{-7} \text{ cm}^2/\text{sec}; \alpha_i &= 1 \times 10^{-7} \text{ cm}^2/\text{sec} \\
 \alpha_e = 2^- \times 10^{-7} \text{ cm}^2/\text{sec}; \alpha_i &= 3 \times 10^{-8} \text{ cm}^2/\text{sec}
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} \alpha_e = \alpha_i &= 3 \times 10^{-7} \text{ cm}^2/\text{sec} \\ \alpha_e = 2^+ \times 10^{-7} \text{ cm}^2/\text{sec}; \alpha_i &= 1 \times 10^{-7} \text{ cm}^2/\text{sec} \\ \alpha_e = 2^- \times 10^{-7} \text{ cm}^2/\text{sec}; \alpha_i &= 3 \times 10^{-8} \text{ cm}^2/\text{sec} \end{aligned}} \right\} (5.84)$$

From the results presented above, we are inclined to accept the first set of values, the so-called equal-coefficient model.

The laboratory measurements in air-like mixtures can be summarized as follows:

- a) At pressures above 1.4 Torr, the linear electron loss process is dominated by the three-body attachment of thermal electrons to neutral O_2 molecules. The rate coefficients for attachment and for production of electron-ion pairs by 1.5 Mev electrons are given by

$$\beta_{air} = (1.10 \pm 0.05) \times 10^{-31} \text{ cm}^6/\text{sec}$$

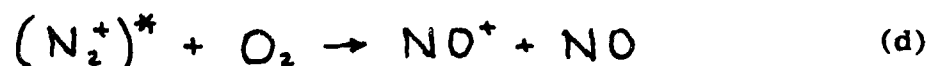
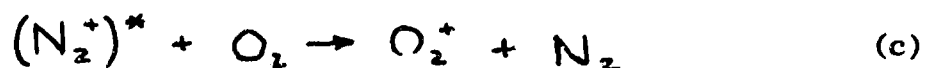
referred to the total density of neutral molecules, and

$$K = (5.55 \pm 0.35) \times 10^{-11} \left(\text{cm}^3 \frac{\text{Kamp}}{\text{cm}^2} \text{Torr-sec} \right)^{-1}$$

The attachment coefficient is consistent with a value of the efficiency of N_2 relative to O_2 as the third body stabilizing the newly formed negative ion is

$$\eta = (3 \pm 1) \%$$

- b) At pressures below 0.1 Torr, three species of positive ions are found, NO^+ , O_2^+ , and N_2^+ . The ion densities are consistent with the following scheme:



The charge-exchange reaction (c) has been identified as the quenching mechanism observed in the optical spectra from N_2^+ states, with a cross-section of the order of 10^{-14} cm^2 .

- c) The ionization at pressures below 0.1 Torr is controlled by electron diffusion in the presence of positive and negative ions, three-body attachment of electrons to O_2 molecules, electron-ion recombination, and ion-ion mutual neutralization. The apparent values for the various rate coefficients are

$$D_{AP} = (160 \pm 15) \text{ Torr} \cdot \text{cm}^2/\text{sec}$$

$$\alpha_i = (2.5 \pm 1.5) \times 10^{-7} \text{ cm}^3/\text{sec}$$

$$\alpha_e = (3 \pm 2) \times 10^{-7} \text{ cm}^3/\text{sec}$$

E. Ionospheric Implications of the Laboratory Measurements

The phenomenology of airlike mixtures of nitrogen and oxygen reported in the previous section strongly resembles that observed in the disturbed ionosphere. The positive ion spectrum observed in the laboratory experiment, consisting of O_2^+ , NO^+ , and N_2^+ , is the same as has been observed in the upper atmosphere [Narcisi, 1965]. The measured rate coefficient for three-body attachment is in agreement with that deduced from conductivity measurement in the O_2 dominated D region [Knapp, 1966]. Electron-ion and ion-ion recombination has been observed in the laboratory at simulated altitudes between 60 and 75 km, with rates which are in substantial agreement with atmospheric data [Knapp, 1966].

Several important ionospheric reactions have not yet been studied in the laboratory. First, since all experiments to date have been performed at 300°K , no information on temperature dependence of the various rate coefficients has been obtained. In particular, the collisional detachment of negative ions, the rate coefficient for which is negligible below 400°K , has not been observed. Second, no indications have been seen of the production of significant densities of free atoms over the

pressure range investigated. Thus reactions depending on free atoms, such as radiative attachment,



associative detachment,



and ozone formation,



have not been studied. The laboratory measurements are therefore characteristic of the upper atmosphere at altitudes below about 80 km, where the neutral O density is negligible. Third, measurements of ionic recombination have not been made for simulated altitudes lower than 60 km; in particular, three-body ionic recombination, which is expected to be of significance below 45 km [Knapp, 1966] has not been studied. Finally, the effects of minority constituents of the normal atmosphere are not included in the laboratory experiments. These constituents are expected to play a significant role in the phenomenology of the disturbed atmosphere only at very low ionization levels [Knapp, 1966]. Thus the laboratory measurements should be substantially representative of the real atmosphere over the altitude range 45 to 80 km.

Within the above limitations, it is possible to construct a model of the ionosphere based on the laboratory measurements. As before, a three-component "lumped-parameter" model (electrons, positive ions, and negative ions) will be used. The equations describing the simulated ionosphere are

$$\frac{dn_e}{dt} = P_e - \beta[M]^2 n_e - \alpha_e P n_e \quad (5.85)$$

$$\frac{dP}{dt} = P_e - \alpha_e n_e P - \alpha_i N P \quad (5.86)$$

$$\frac{dN}{dt} = \beta[M]^2 n_e - \alpha_i P N \quad (5.87)$$

The production term P_e is the same for positive ions and electrons. For ionization due to a flux of ϕ beta particles/cm² sec in the energy range 1 to 2 Mev, which corresponds to a current density of relativistic electrons given by

$$J = 1.6 \times 10^{-13} \phi \text{ amp/cm}^2 \quad (5.88)$$

The production rate is (Equation 5.63)

$$P_e \equiv K_p J = 8.8 \times 10^{-2} p \phi \text{ (cm}^3 \text{sec)}^{-1} \quad (5.89)$$

or, in terms of neutral molecule number density,

$$P_e = 2.7 \times 10^{-18} [M] \phi \quad (5.90)$$

Figure 5,49 summarizes the production rate as a function of altitude for a uniform beta flux of $1(\text{cm}^2 \text{sec})^{-1}$.

No information on the temperature dependence of the three-body attachment coefficient has yet been obtained in this experiment. Instead, we use the expression given by Knapp [1966], modified upward 10% to agree with our value of β at 300°K:

$$\beta = 2.2 \times 10^{-30} \left(\frac{300}{T}\right)^{1/2} \exp\left[1.8\left(1 - \frac{300}{T}\right)\right] \text{ cm}^6 \text{sec}^{-1} \quad (5.91)$$

The resulting loss frequency due to three-body attachment is calculated from the U.S. Standard Atmosphere [1962], and is shown in Figure 5.50.

One can now calculate expected electron and ion densities from Equations 5.85 through 5.87 as a function of altitude and beta flux. From the results presented in Section V.D.3, $\alpha_e \approx \alpha_i$, so that 5.76 can be rewritten as

$$P = (P_e / \alpha_e)^{1/2} \quad (5.92)$$

N and n_e can then be computed in a straightforward manner.

In a realistic situation in the disturbed upper atmosphere, a uniform beta flux is not to be expected. Instead, the production model given by Crain [1964], is used. Assume a nuclear detonation at high altitudes with the fission debris spread into a circular area of radius $R(\text{km})$, all at altitudes above 90 km. Then the normalized production distribution P_e at lower altitudes is as shown in Figure 5.51. Ionization is due primarily to betas above 65 km, and to gammas below 30 km. Between 30 and 65 km, both betas and gammas contribute to the ionization.

The ionization at 65 km is related to weapon parameters by

$$P_e (65 \text{ km}) = \frac{5 \times 10^{13} Y}{R^2 t^{1.2}} \text{ electrons/cm}^2 \text{ sec} \quad (5.93)$$

where Y is the fission yield of the weapon in megatons, and t is the time in seconds after the detonation. For a weapon with a fission yield of 1 megaton, with the debris spread over a radius

100 km, the production rate one hour after detonation is given by

$$P_e(65 \text{ km}) = 2.5 \times 10^6 \text{ electrons/cm}^3\text{sec} \quad (5.94)$$

to which the curve in Figure 5.51 is normalized. The model then yields the particle densities shown in Figure 5.2. The rapid attachment of electrons to O_2 molecules below about 60 km is responsible for the strongly developed electron layer peaked at 75 km. At 45 km, the ratio of ion to electron density is sufficiently high that the propagation of electromagnetic signals through this region is controlled by the ions rather than by the electrons [Crain, 1946 ; Johler, 1965]. It should be remembered that the curve is valid only for night-time conditions, that is, in the absence of photodetachment.

If one includes the effects of three-body recombination with a coefficient given by [Crain, 1961]

$$\alpha_{i,3} \approx 6 p(\text{atm}) T^{-5/2} \quad (5.95)$$

where the pressure is expressed in atmosphere, the ion densities are reduced at low altitudes, as shown by the dotted curve in Figure 5.52.

From atmospheric measurement, it is difficult to evaluate α_e and α_i separately. For both quantities one must study the ion densities at high ionization levels. It should be pointed out that in the laboratory it is possible to separate the effects of electron-ion and ion-ion recombination, in a rather surprising way. At low ionization levels, electron-positive ion recombination

can be neglected relative to the linear processes of attachment and diffusion. For the negative ions however diffusion is greatly suppressed by the electrons, so that their only available loss mechanism is ionic recombination, even at low ionization levels. In the laboratory, electron diffusion rates have been shown to be strongly dependent on the negative ion density, hence indirectly on the ionic recombination coefficient which controls the negative ion density. By studying electron diffusion at low ionization levels, one can deduce α_i (as was in fact done in the preceding section) without interference from electron-ion recombination. Thus the hitherto "undesirable" diffusion of charged particles to the walls of the laboratory container is in fact a valuable diagnostic method for a process which cannot presently be studied directly in the atmosphere.

As mentioned in Section V.B, one can expect to find negative ions in a post-weapon environment at densities of 10^4 cm^{-3} or greater for times of the order of 30 minutes. One is tempted to inquire into the fate of these negative ions when subjected to the high rf field of a modern area-defense radar beam. The field strengths contemplated for such systems are certainly small enough to avoid breakdown in normal air. It is not difficult to contemplate that a small electron residuum could be heated in the radar field sufficiently to detach appreciable densities of electrons from the negative ions. Thus a premature resumption of radar surveillance following a period of weapon-induced blackout could result in the radar's blacking itself out again as soon as it is turned on. It is recommended that radar breakdown studies in air rich in negative ions be carried out to establish safe-working limits for radar field strengths.

In summary, the laboratory measurements have given general agreement with measurements obtained in the disturbed ionosphere over the altitude range between 45 and 80 km. It should be possible to extend the range of agreement by means of further work using the same general techniques described in the present report. In the next chapter, specific recommendations are made for experimental studies by which the reaction rates deduced from laboratory measurements can be extended to other altitude ranges and ionization conditions.

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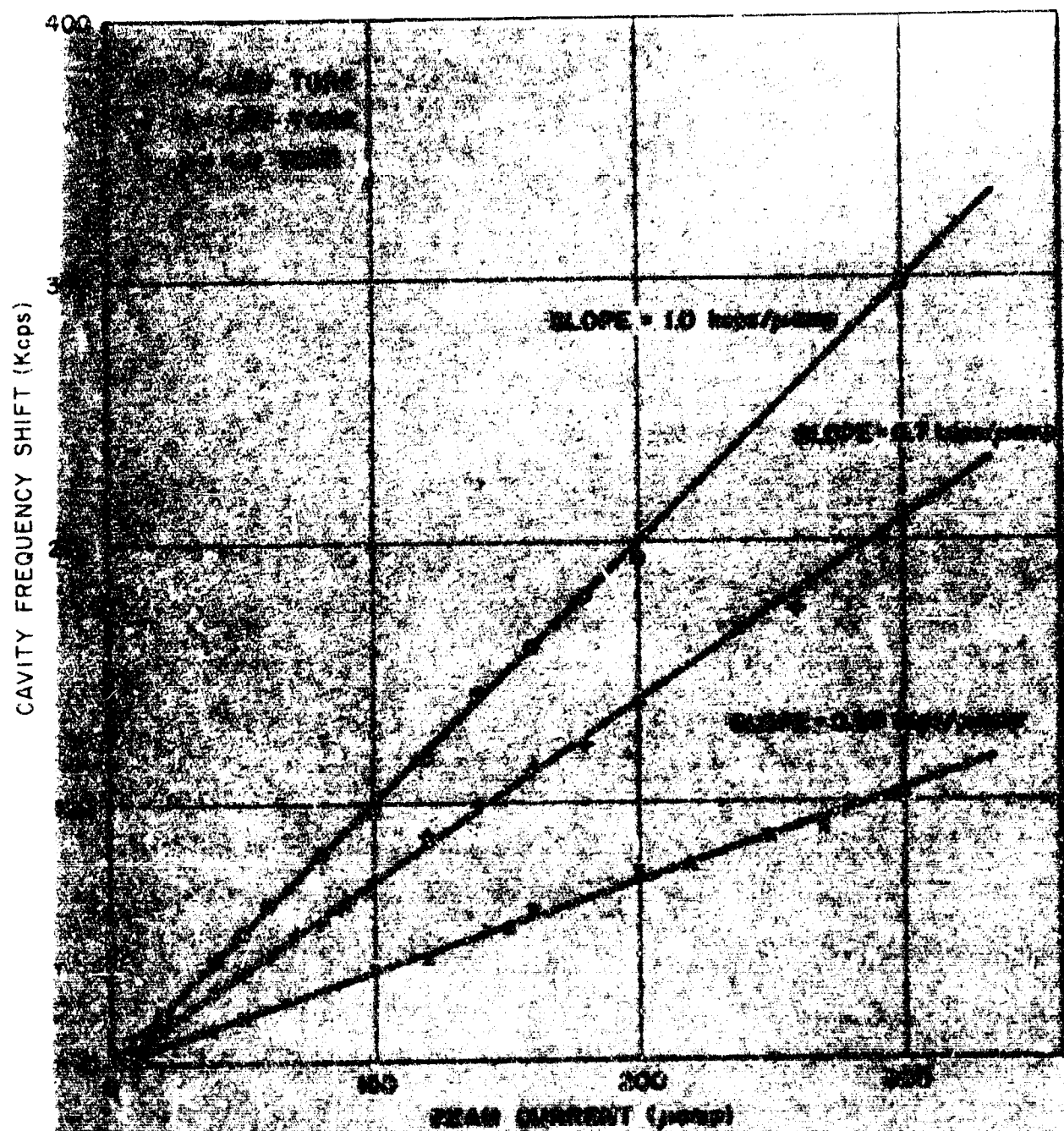


FIGURE 3.1- EQUILIBRIUM ELECTRON DENSITY IN OXYGEN VS. BEAM CURRENT FOR HIGH PRESSURES

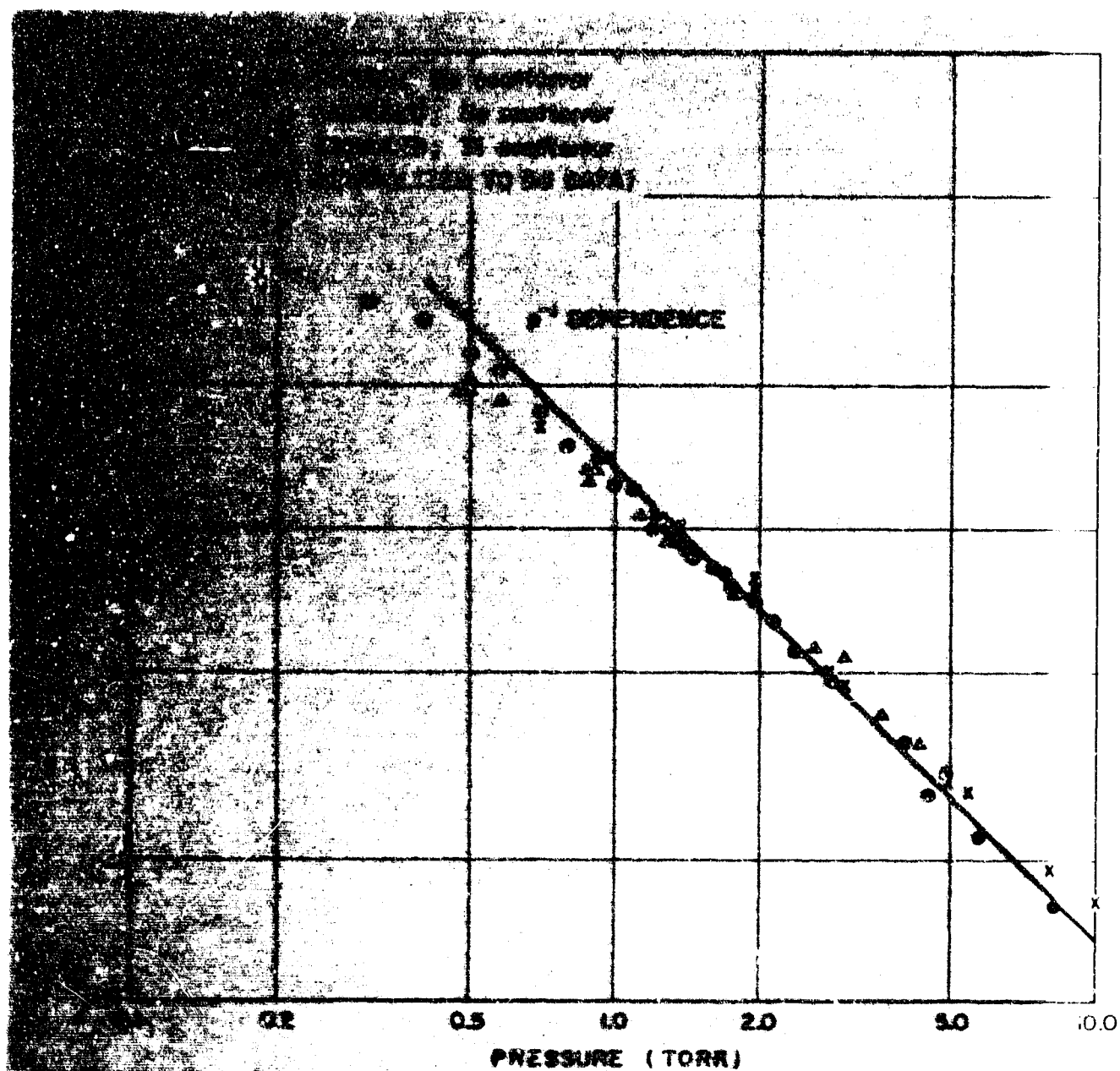


FIGURE 312- PRESSURE DEPENDENCE OF SPECIFIC IONIZATION IN PURE OXYGEN

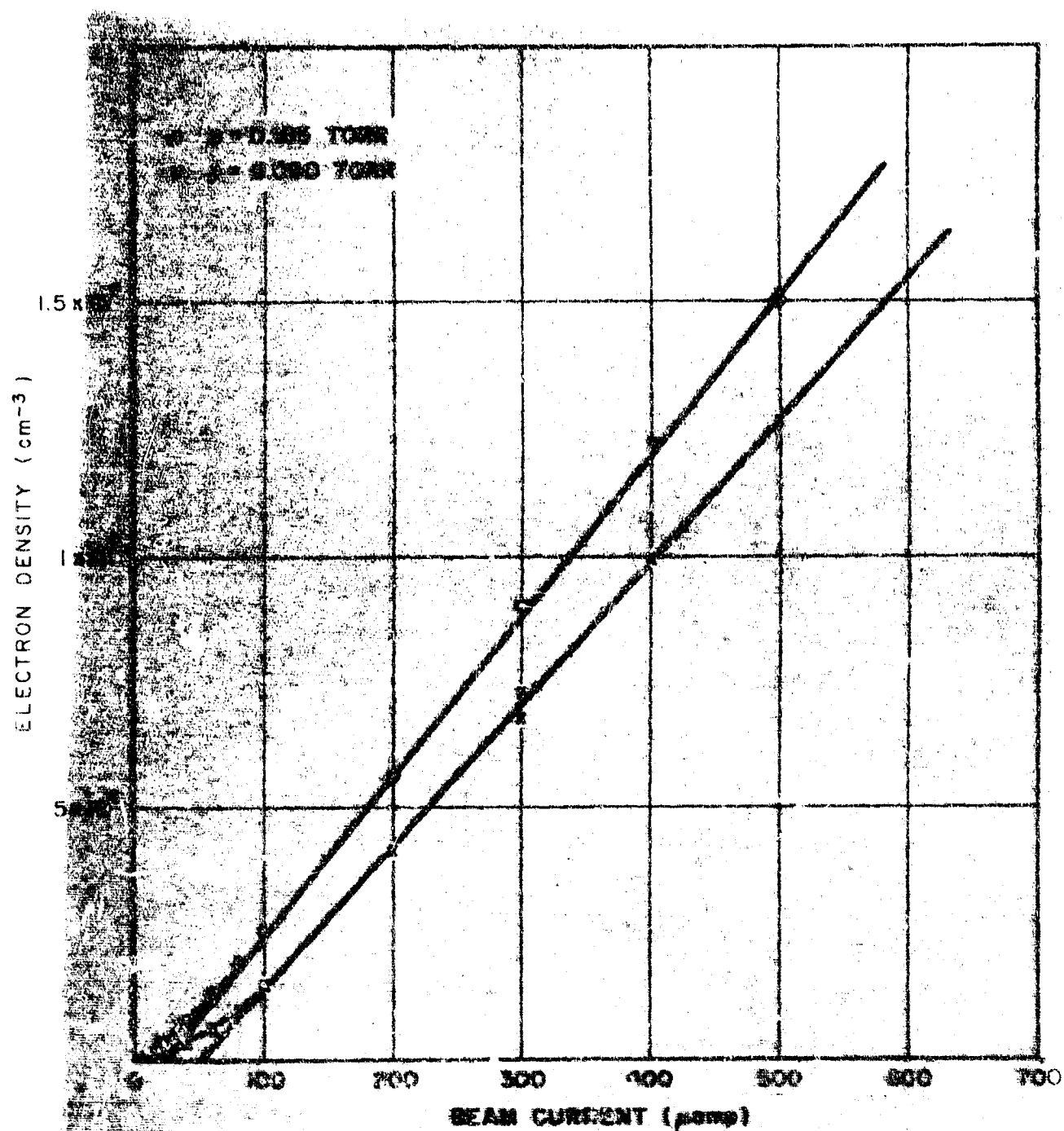


FIGURE 5.3- EQUILIBRIUM ELECTRON DENSITY IN OXYGEN VS. BEAM CURRENT FOR LOW PRESSURES

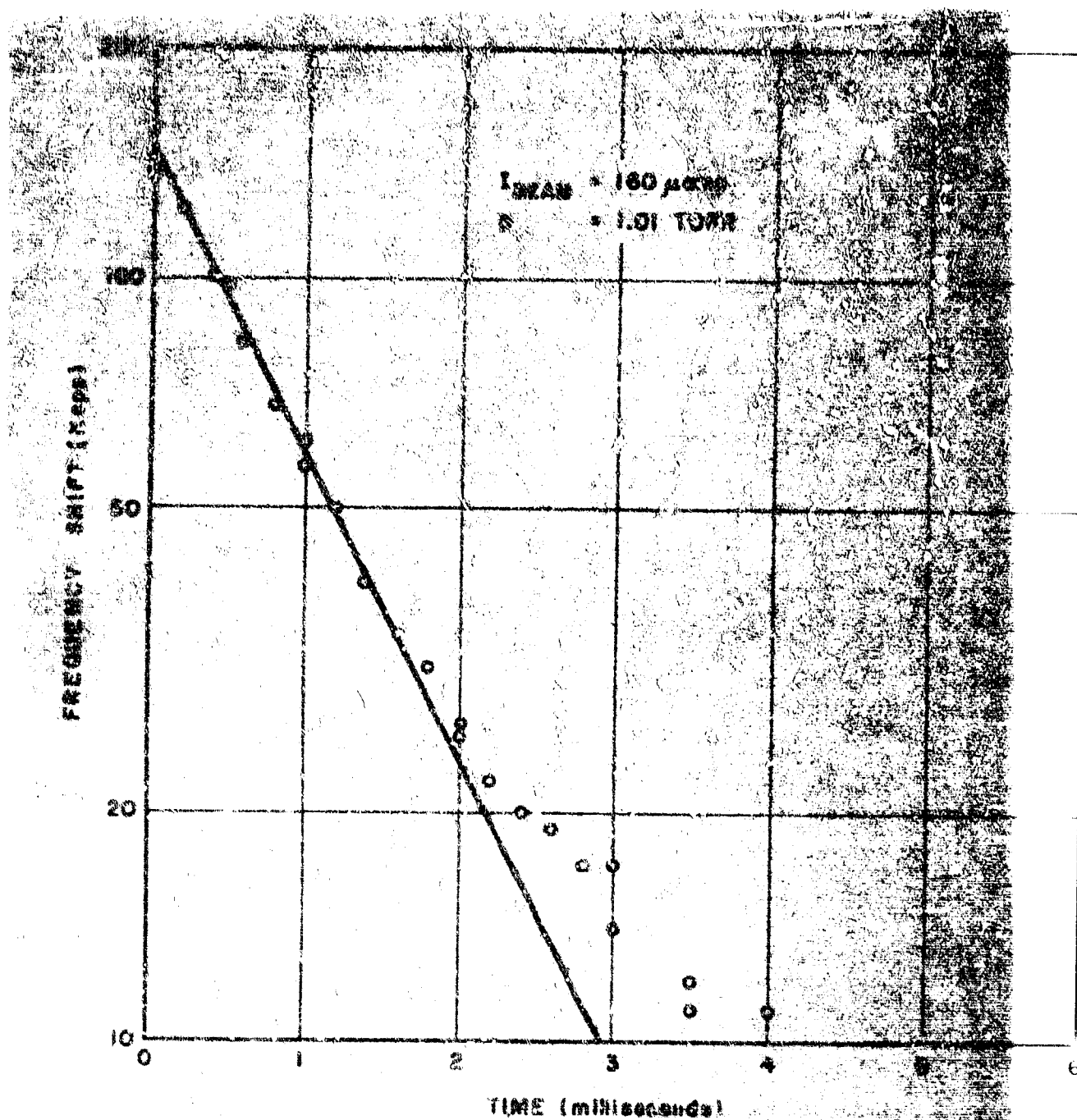


FIGURE 5.4 - CAVITY FREQUENCY SHIFT VS. TIME IN AFTERGLOW OF 50 msec IRRADIATION IN OXYGEN

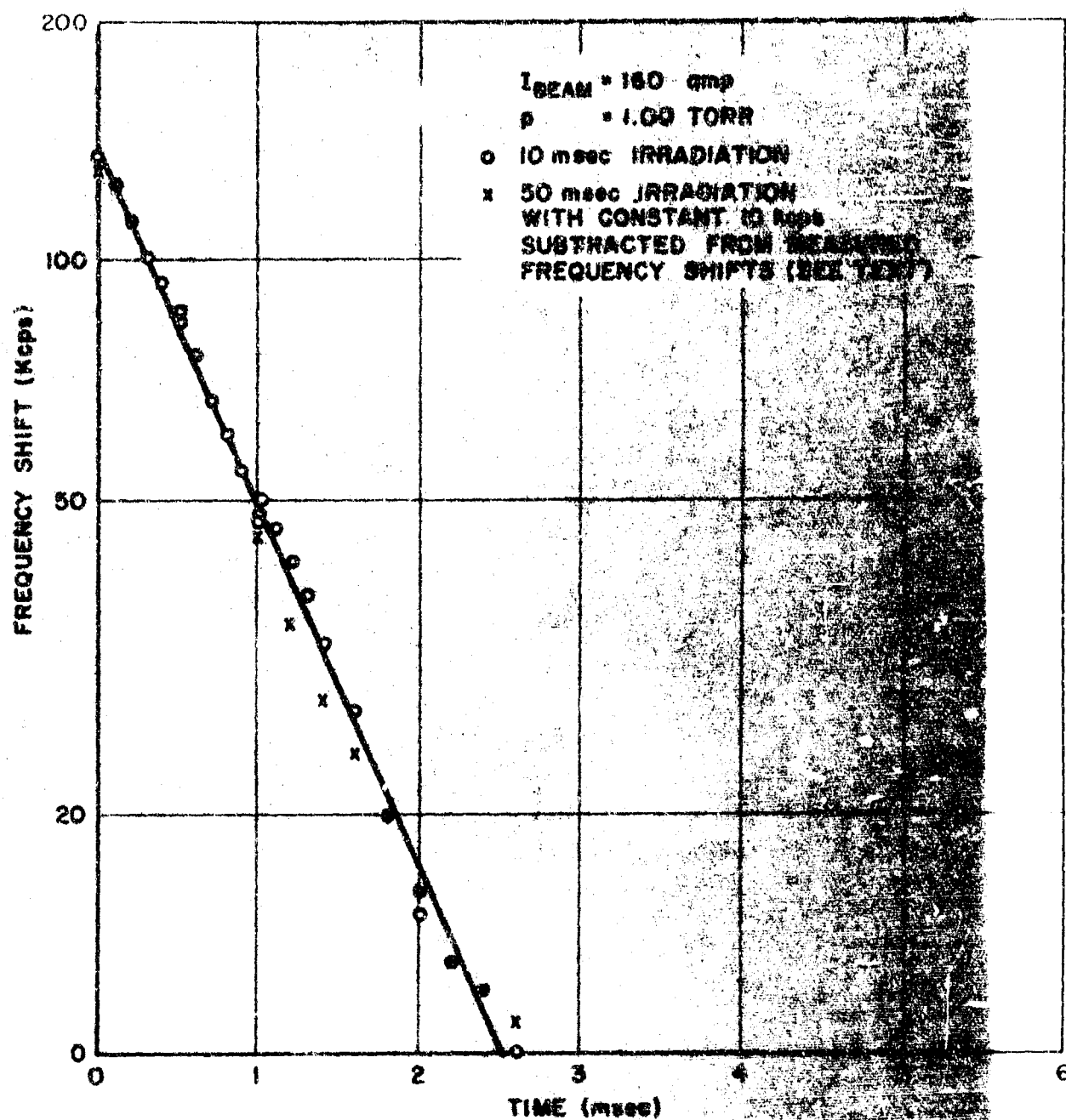


FIGURE 5.5- CAVITY FREQUENCY SHIFT VS. TIME IN AFTERGLOW OF 10 msec IRRADIATION IN OXYGEN

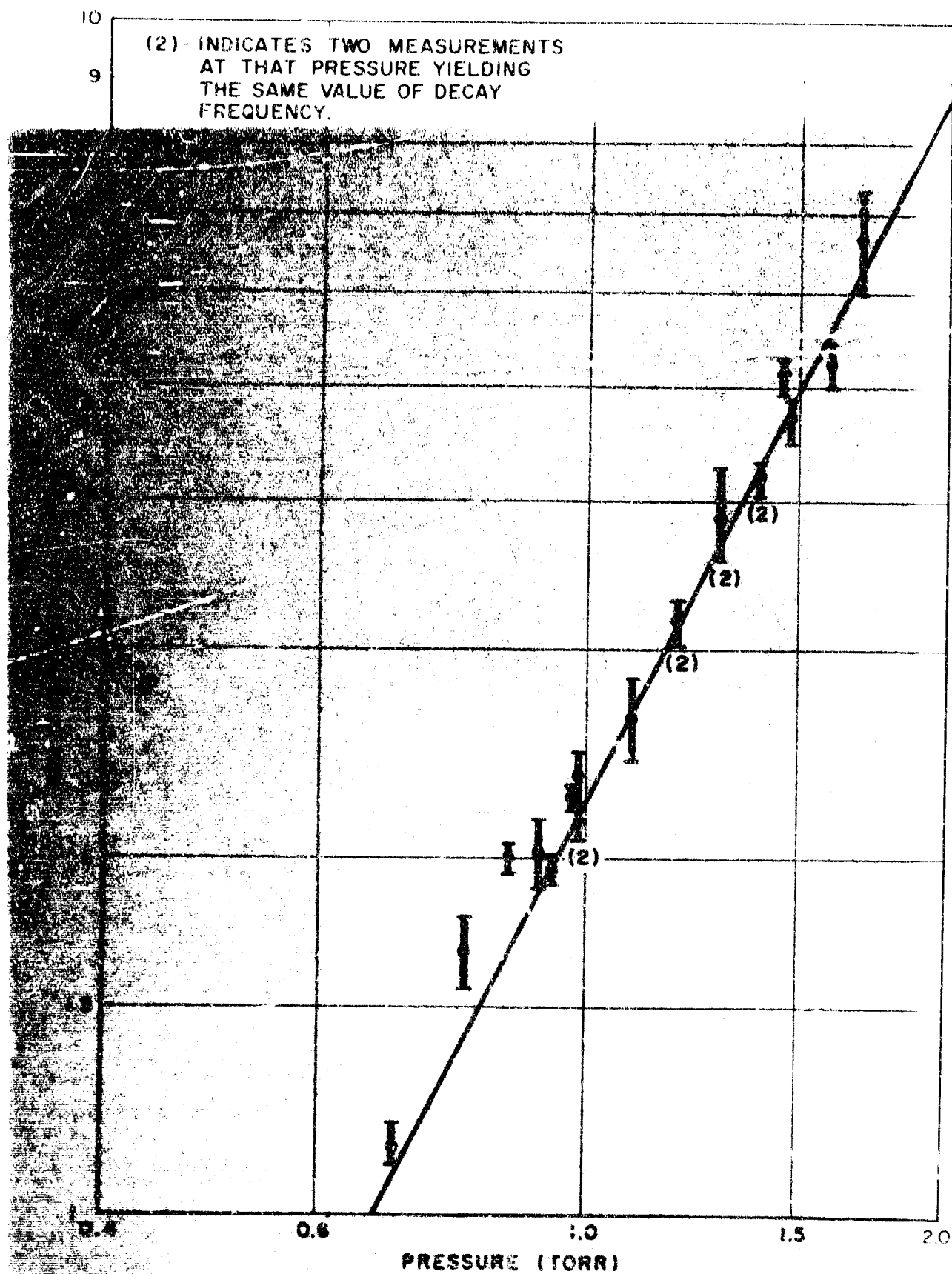


FIGURE 5.6 - AFTERGLOW DECAY FREQUENCY VS. PRESSURE IN OXYGEN

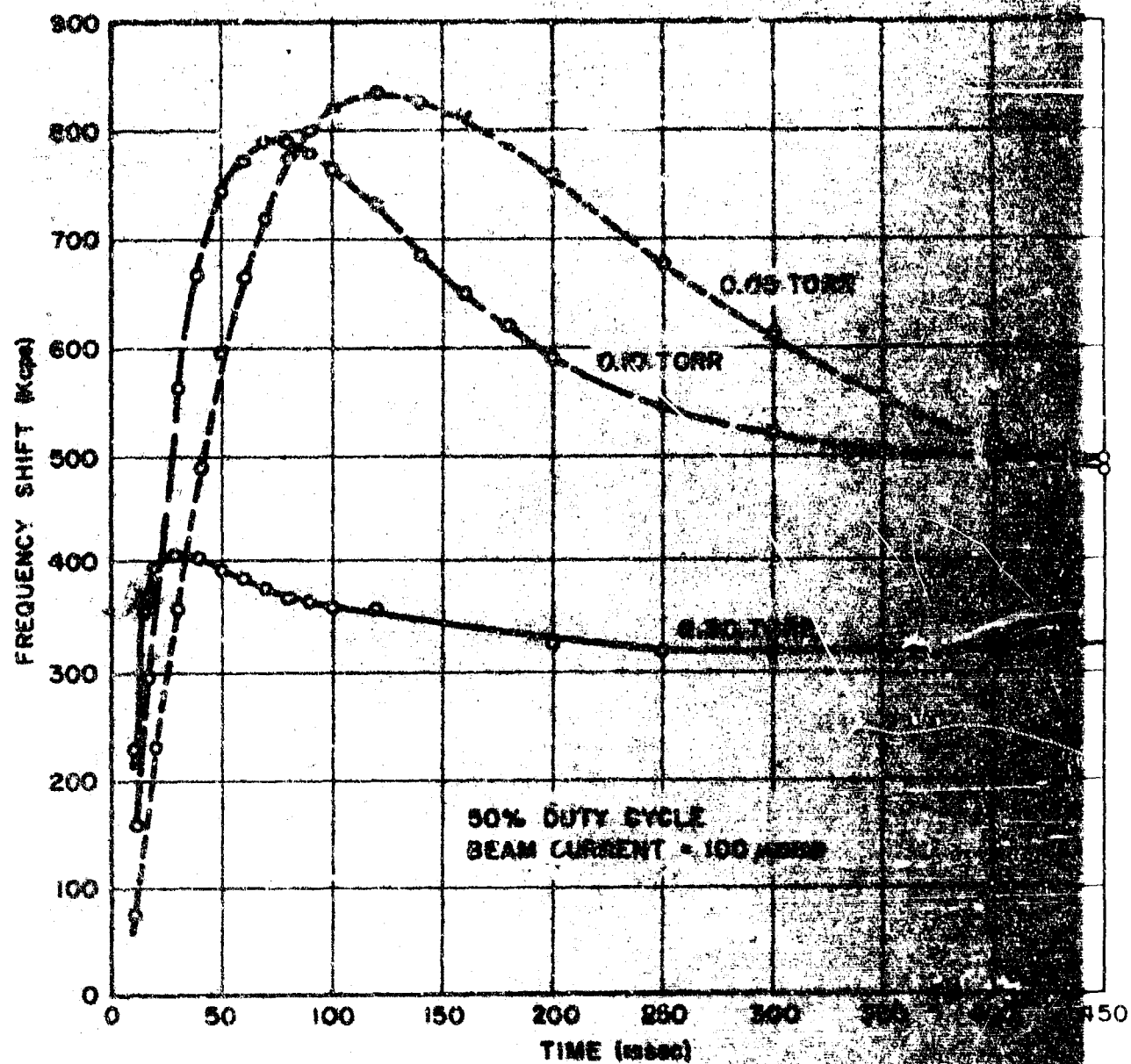


FIGURE 5.7- TURN-ON DATA IN OXYGEN AT SEVERAL PRESSURES

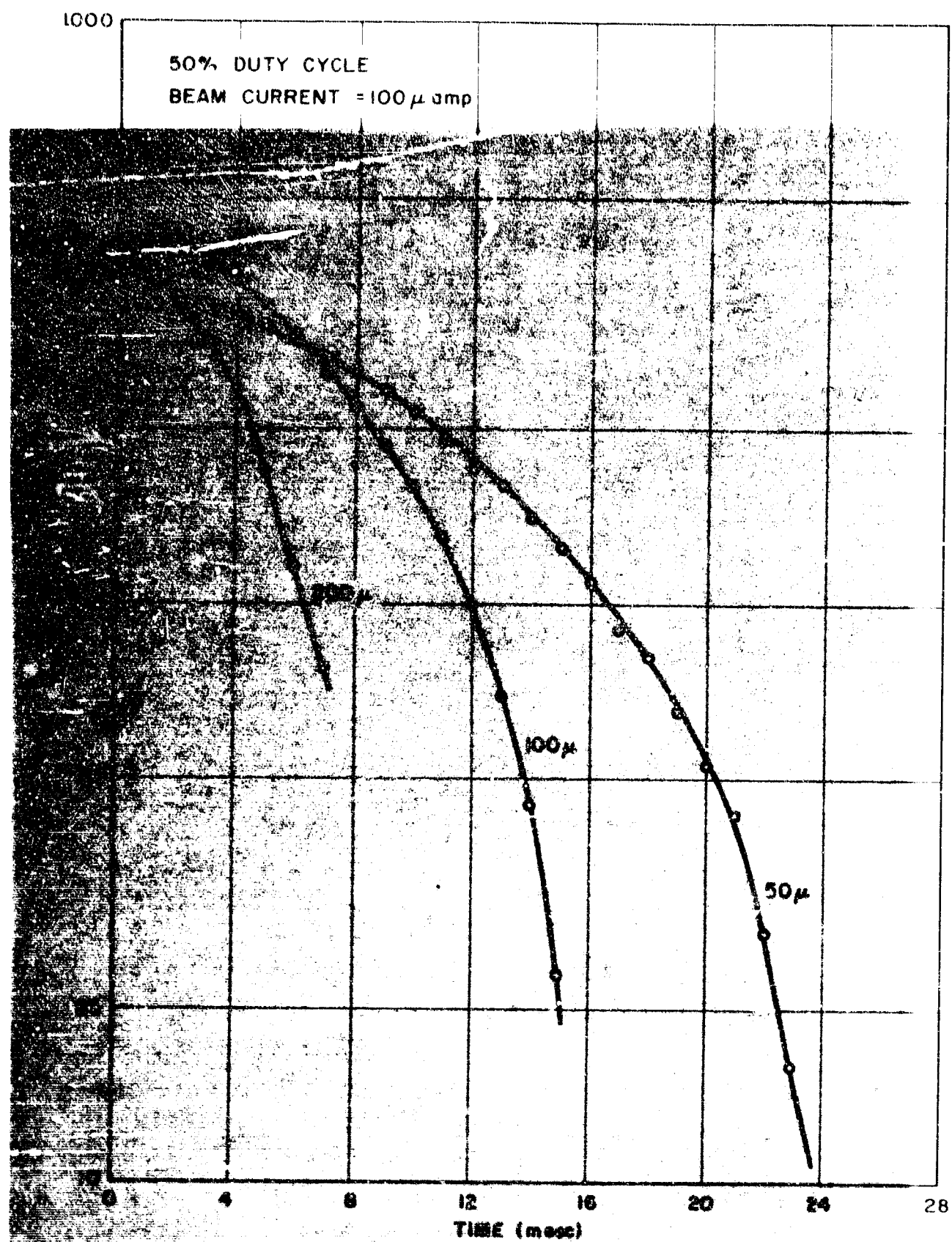
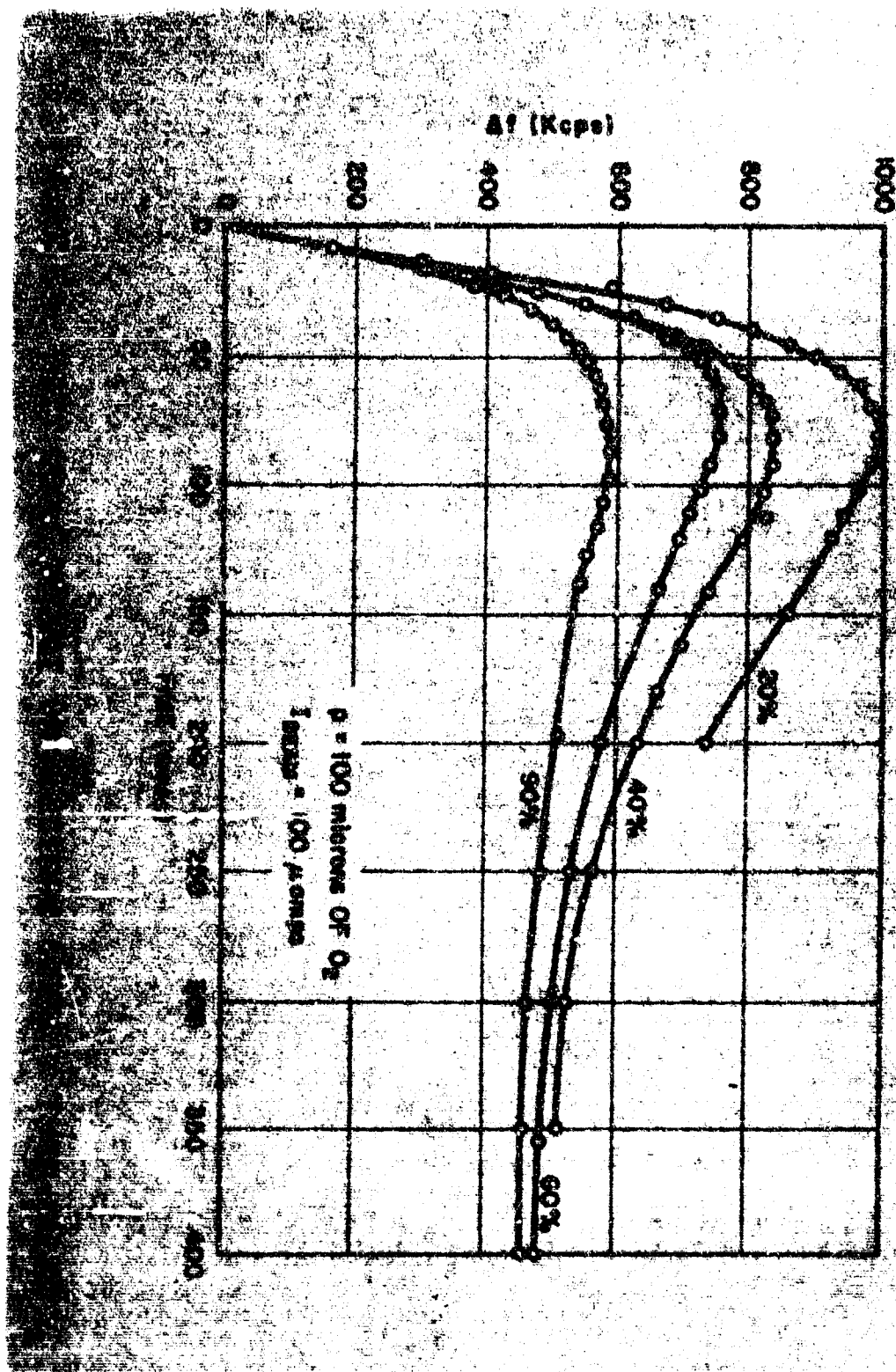


FIGURE 5.8- AFTERGLOW DATA IN OXYGEN AT LOW PRESSURES



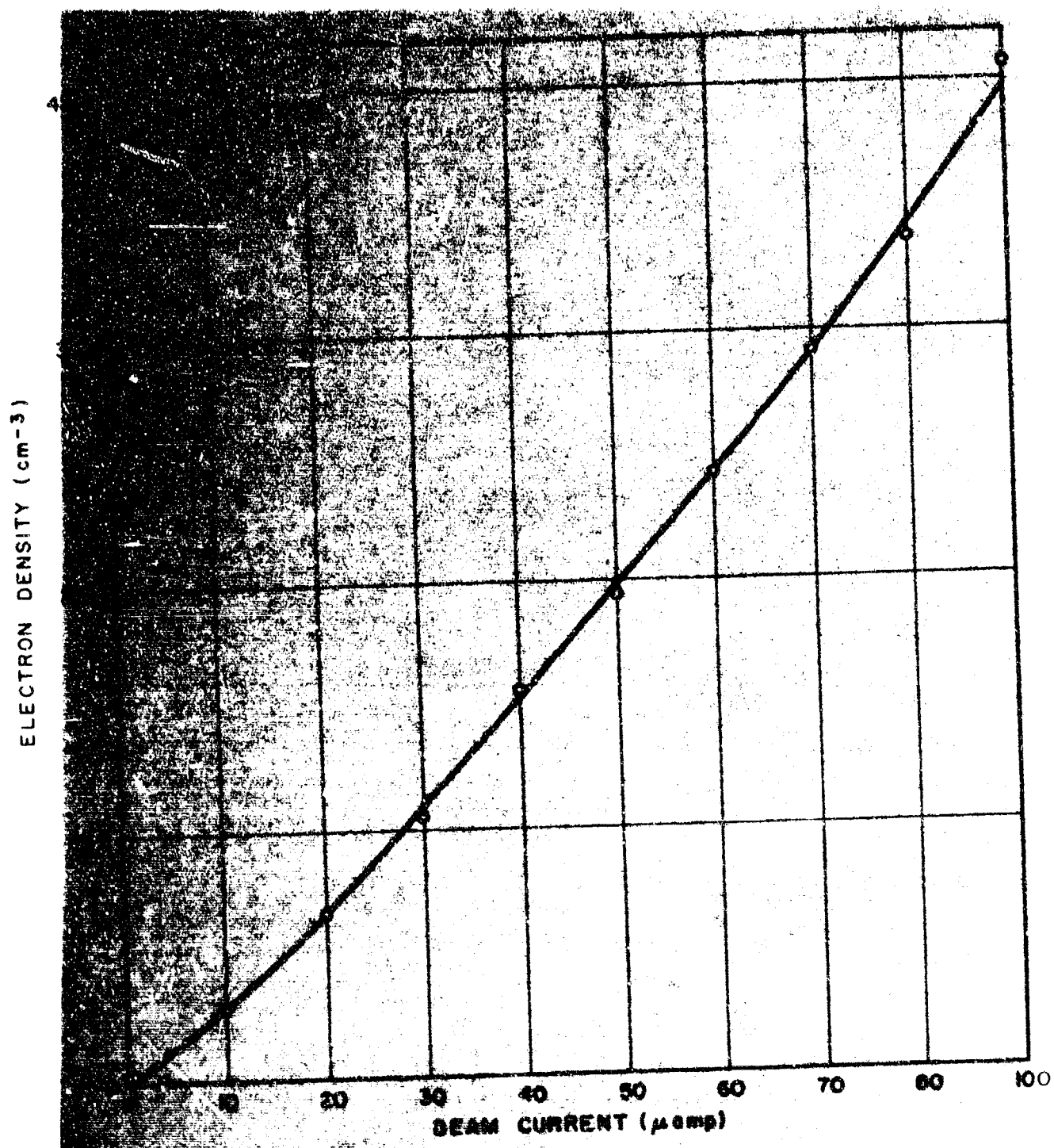


FIGURE 8.12 - ELECTRON DENSITY VS. BEAM CURRENT IN OXYGEN

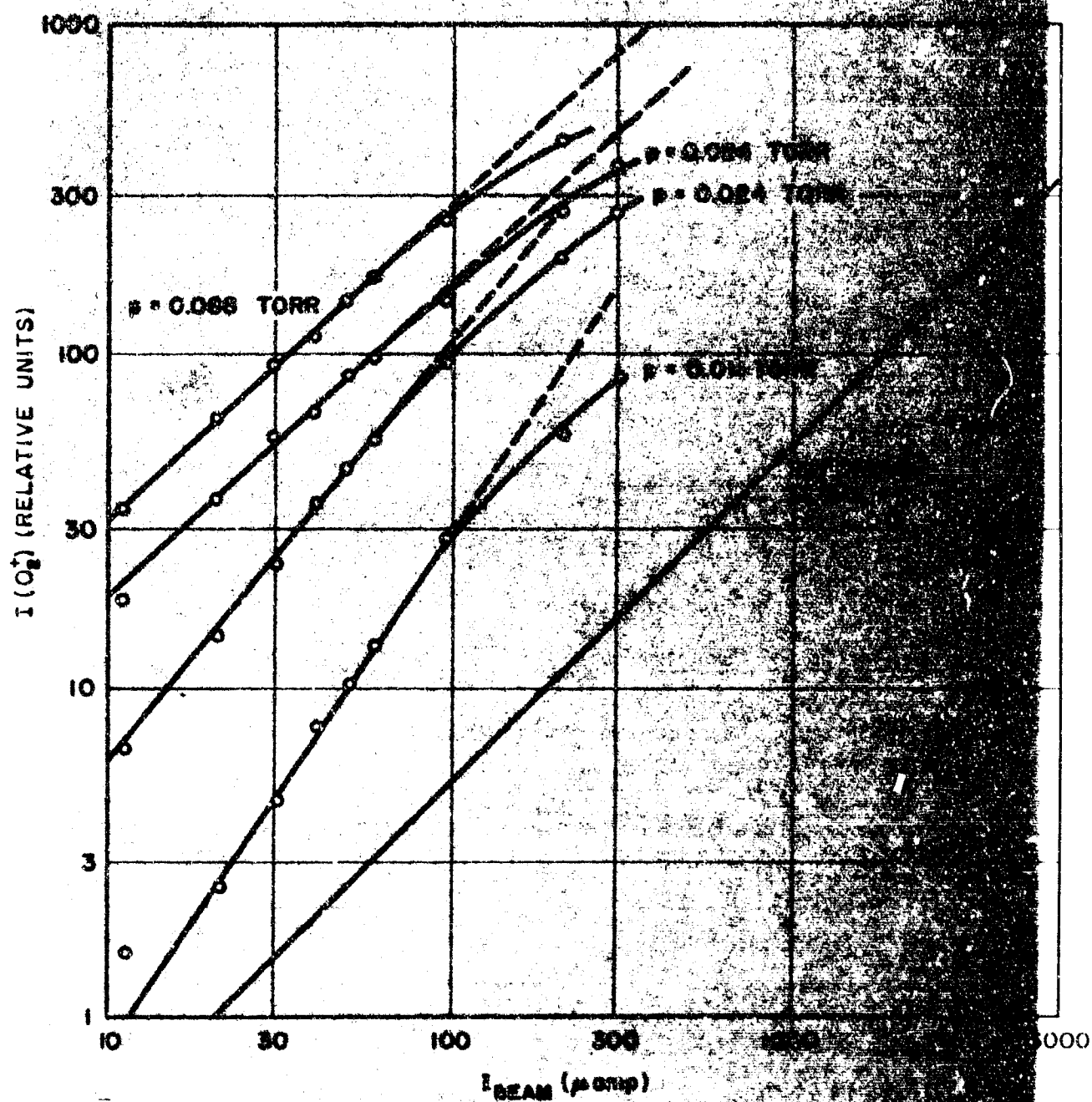


FIGURE 5.10- O_2^+ ION CURRENT VS. I_{BEAM} IN TORR

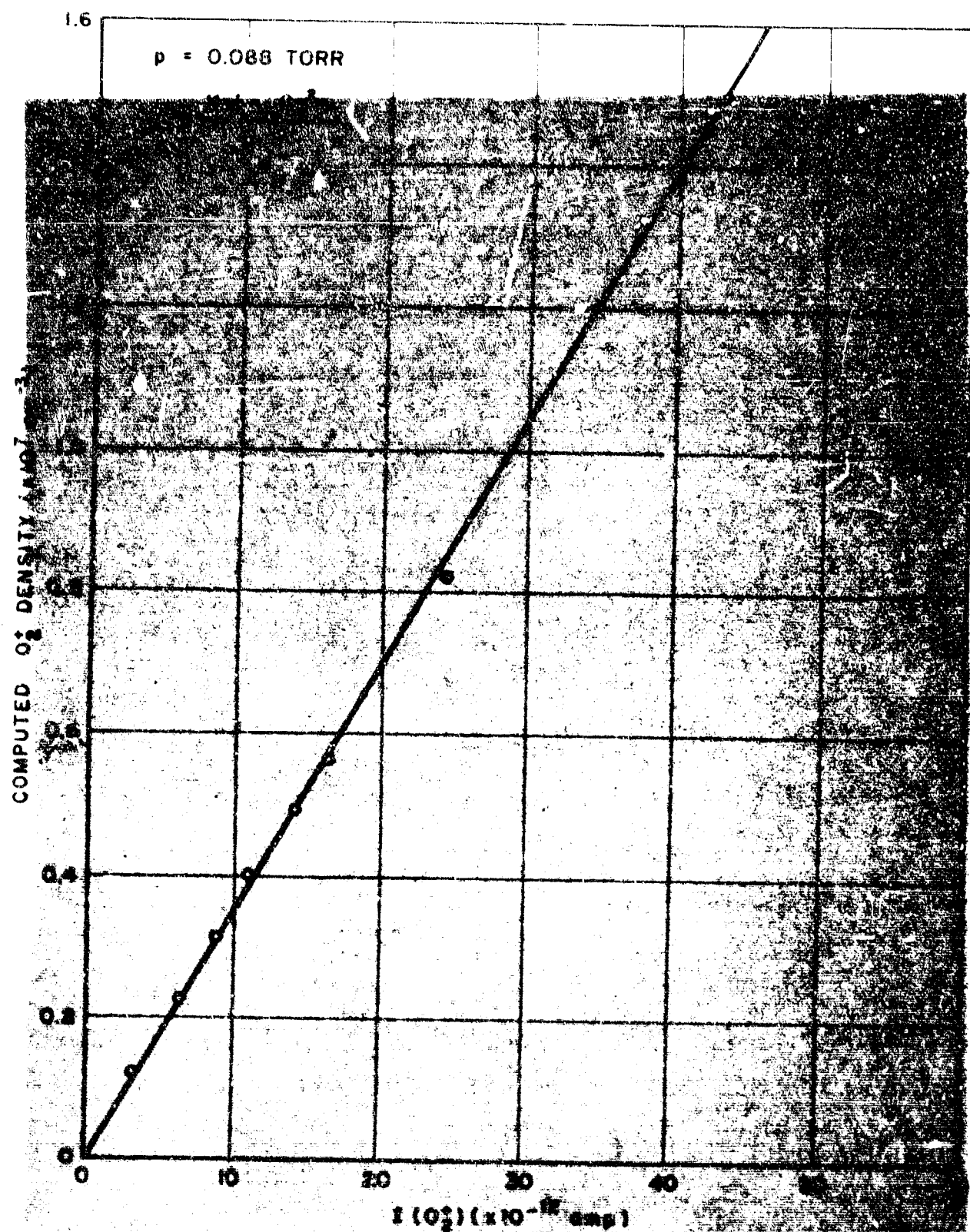


FIGURE 5.11 - COMPARISON BETWEEN MEASURED AND CALCULATED O_2^+ DENSITIES FROM EQUATION 5.15

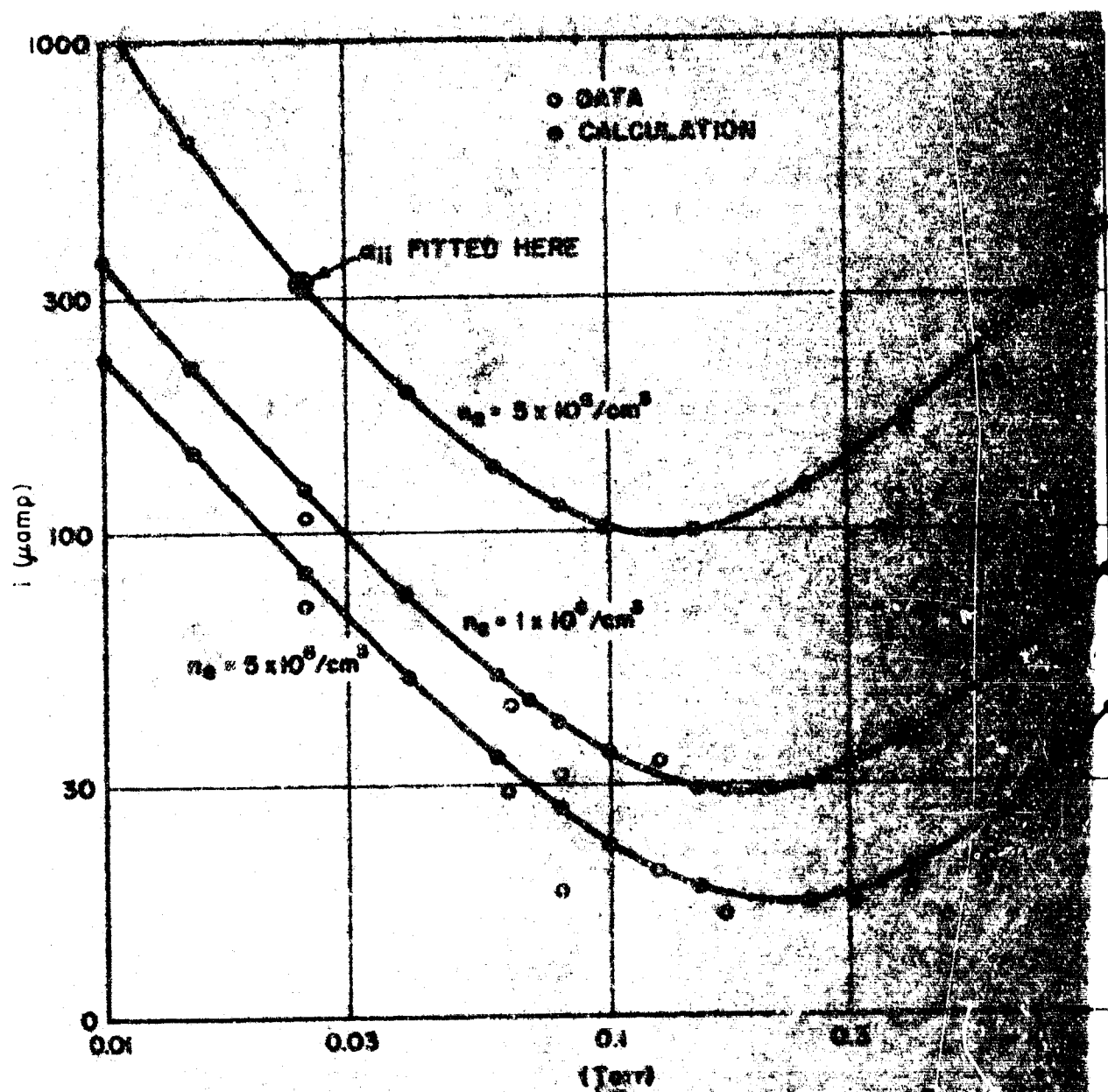
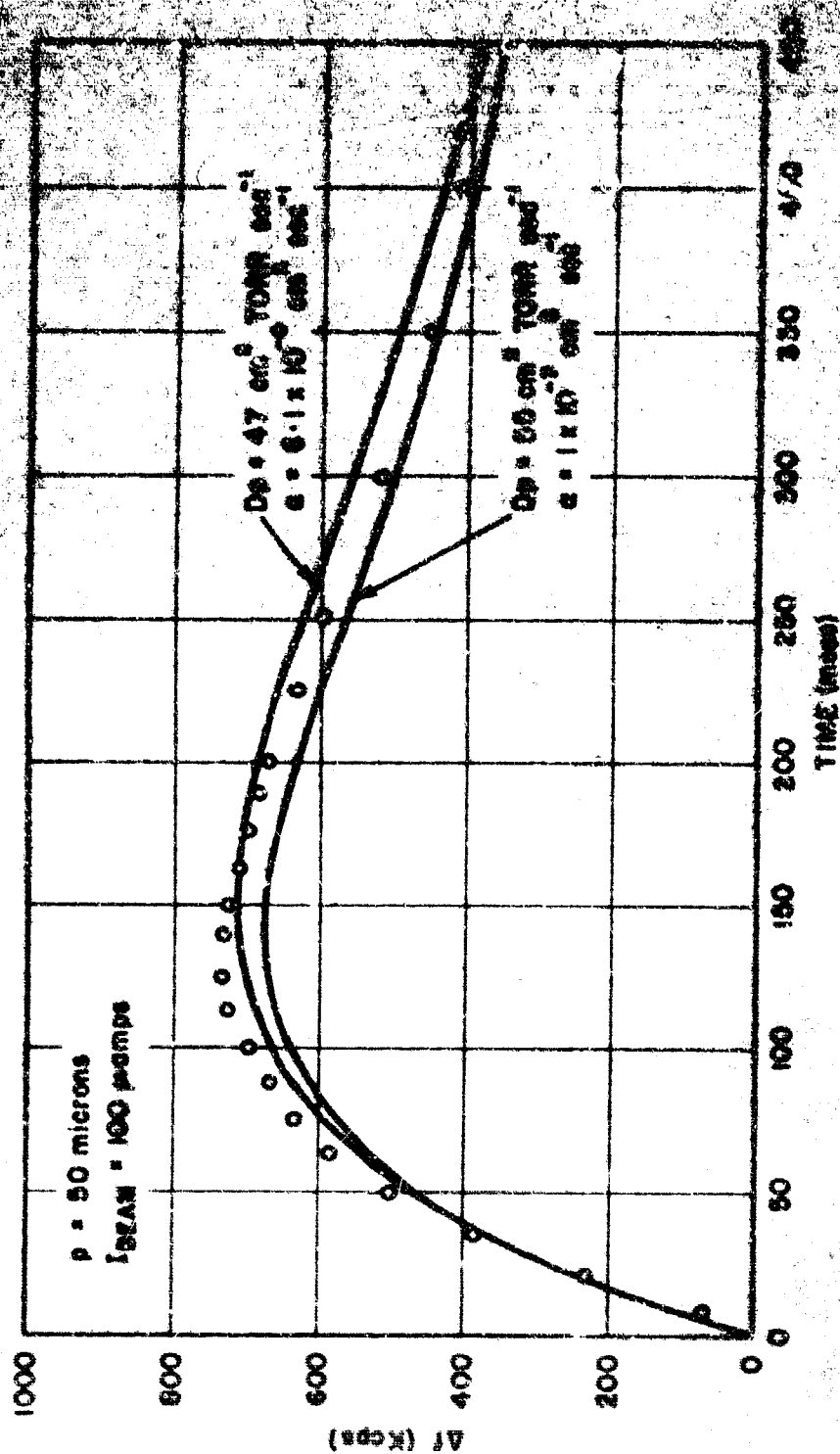
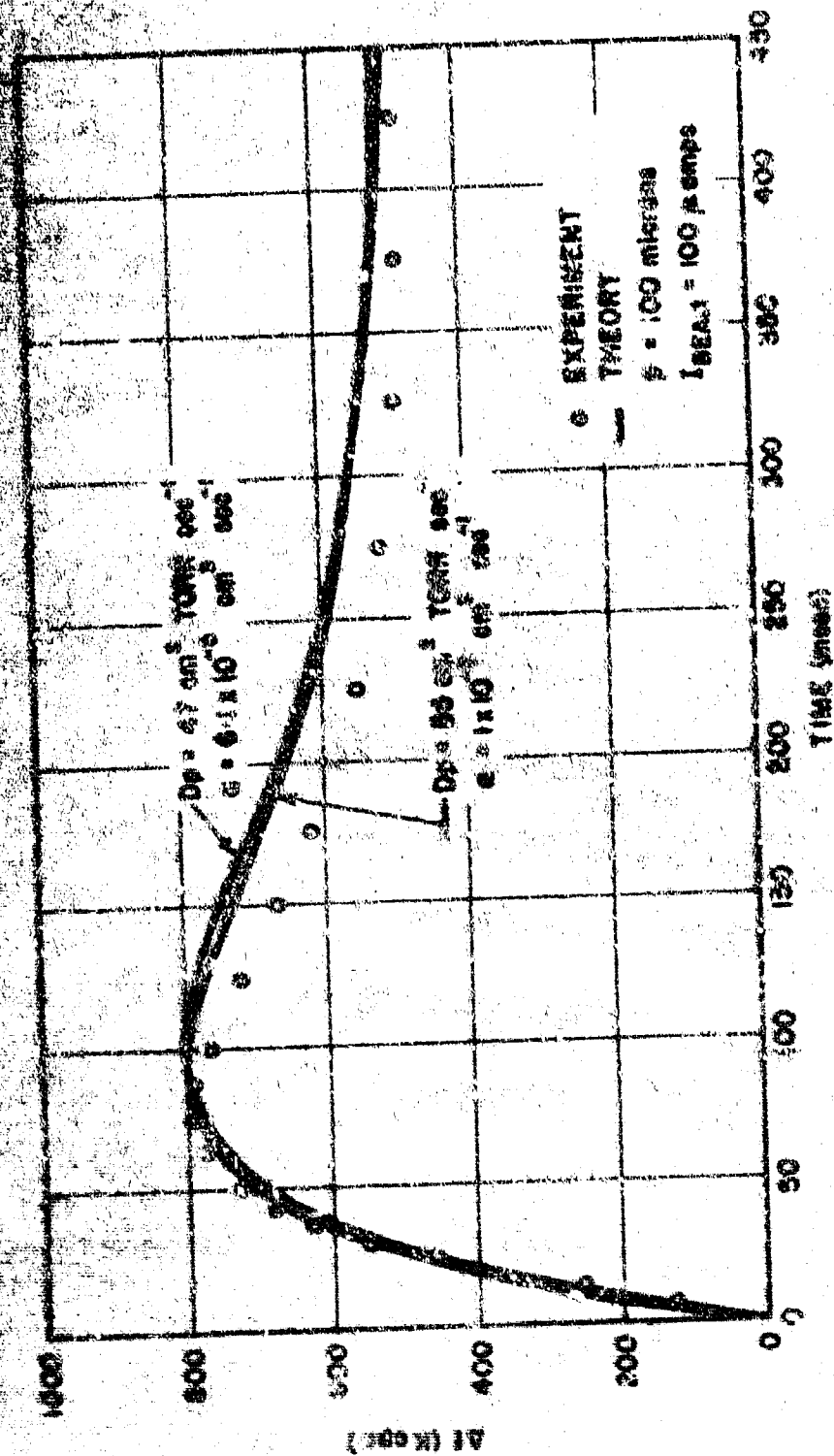
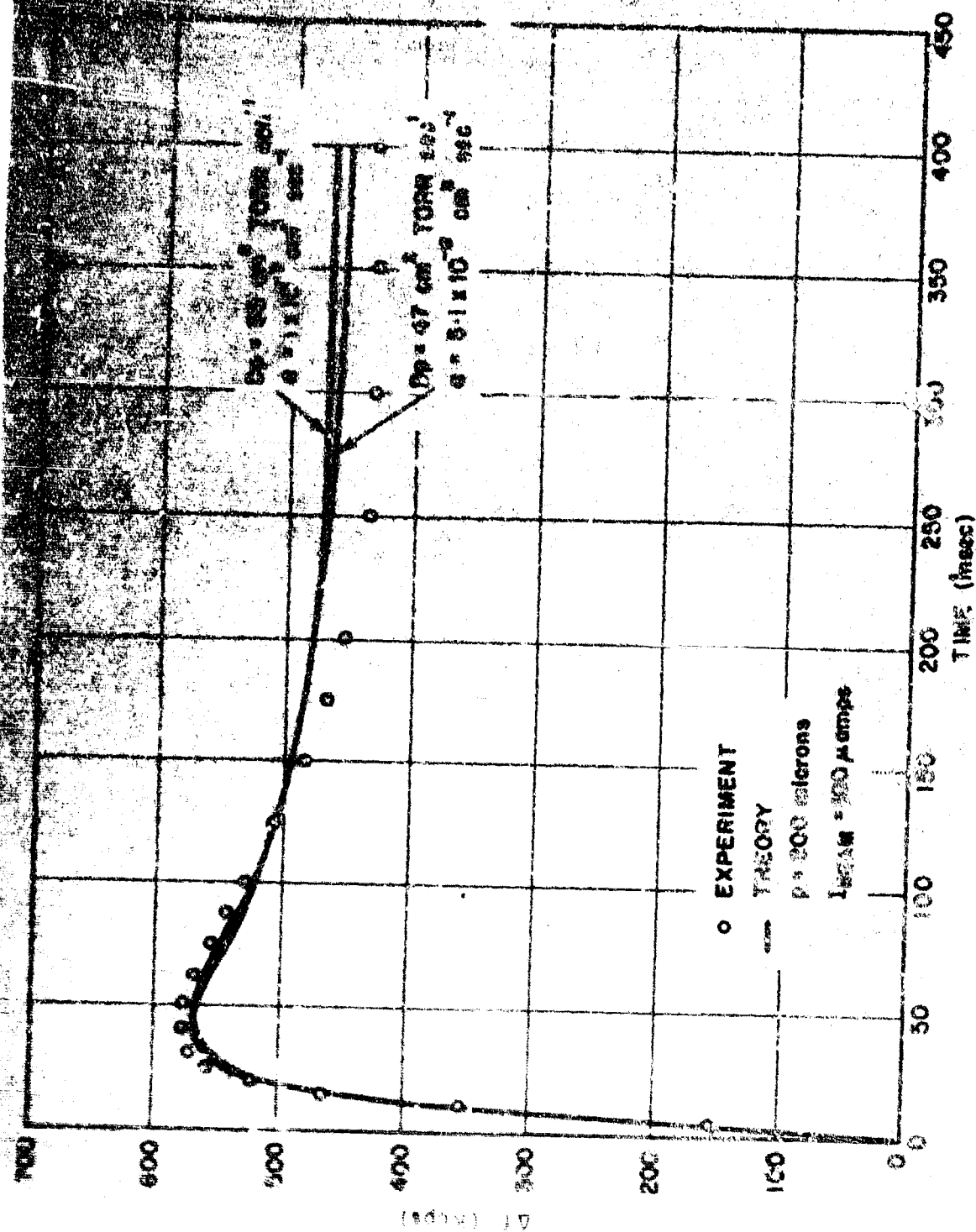


FIGURE 5.13- PLOT OF EQUATION 3.29 AND COMPARISON WITH DATA.

FIGURE 6.14 - FREQUENCY SHIFT VS. TIME AFTER BEAM TURN-ON IN G_1

FIGURE 0.13- FREQUENCY SHIFT VS. TIME AFTER BEAM TURN-ON IN O_2

FIGURE 5.16- FREQUENCY SHIFT VS. TIME AFTER BFAM TURN-ON IN O_2

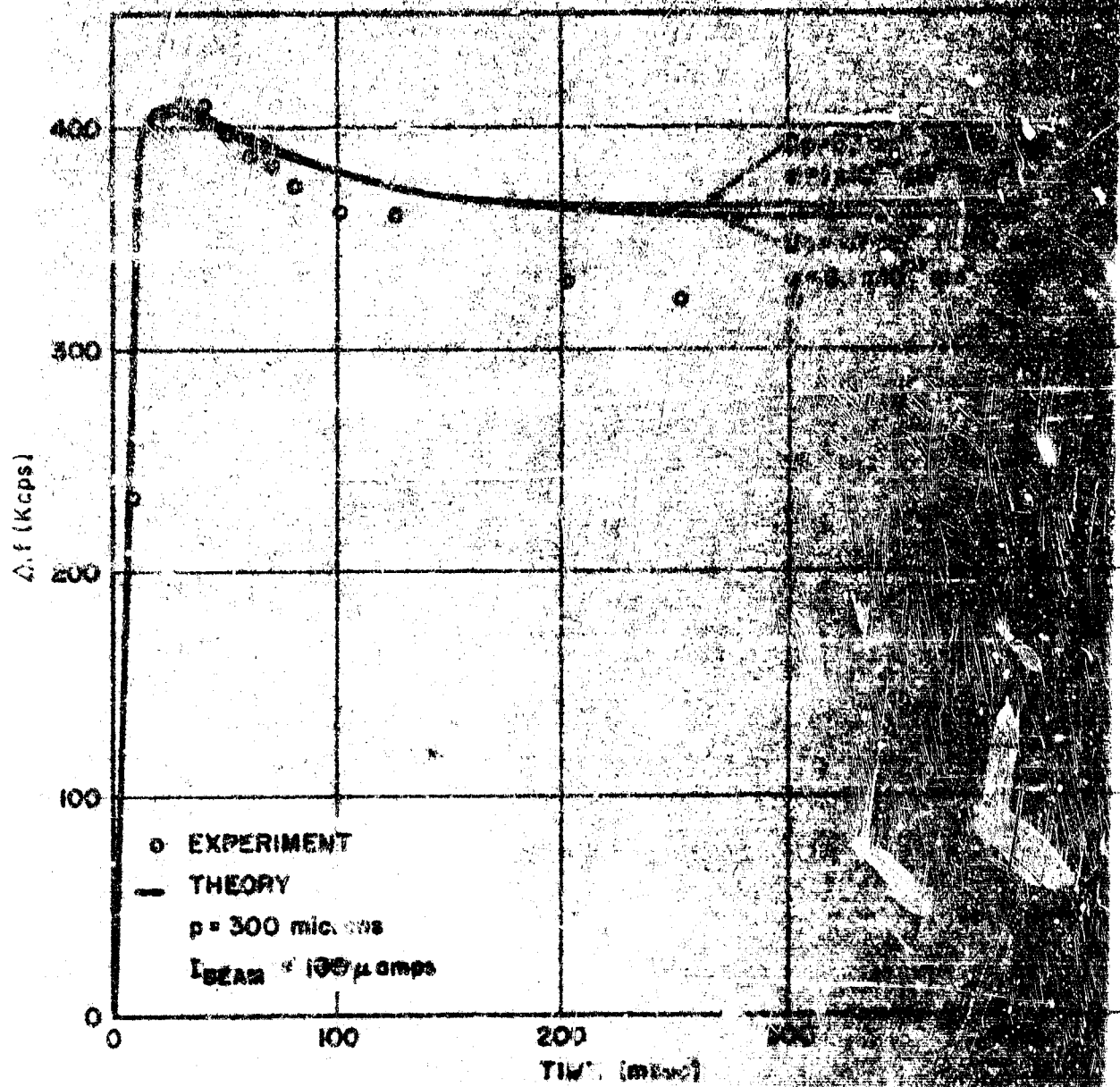


FIGURE 5.17- FREQUENCY SHIFT VS. TIME AFTER PUMP
TURN-ON IN O_2

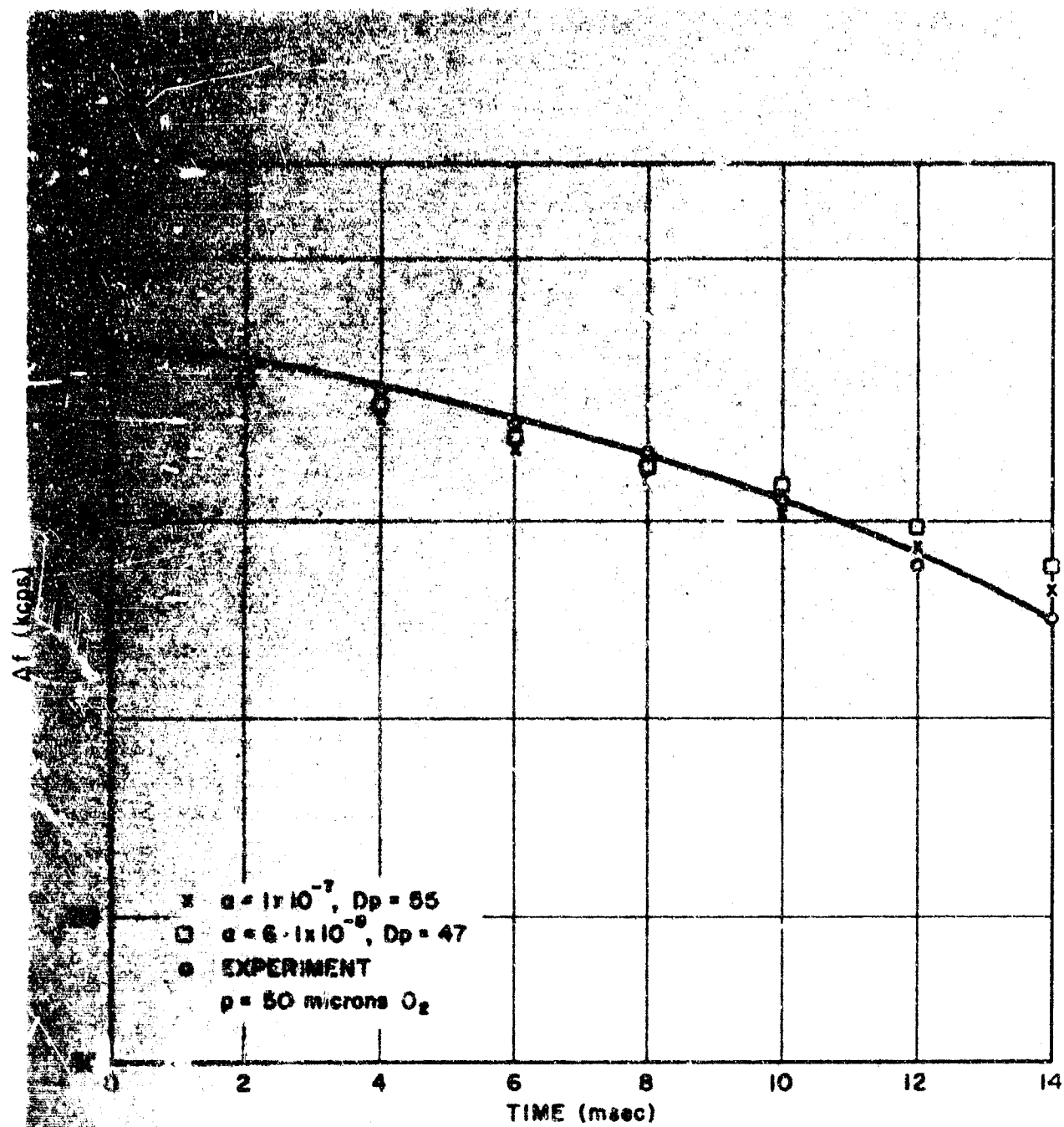


FIGURE 5.18 - ELECTRON AFTERGLOW

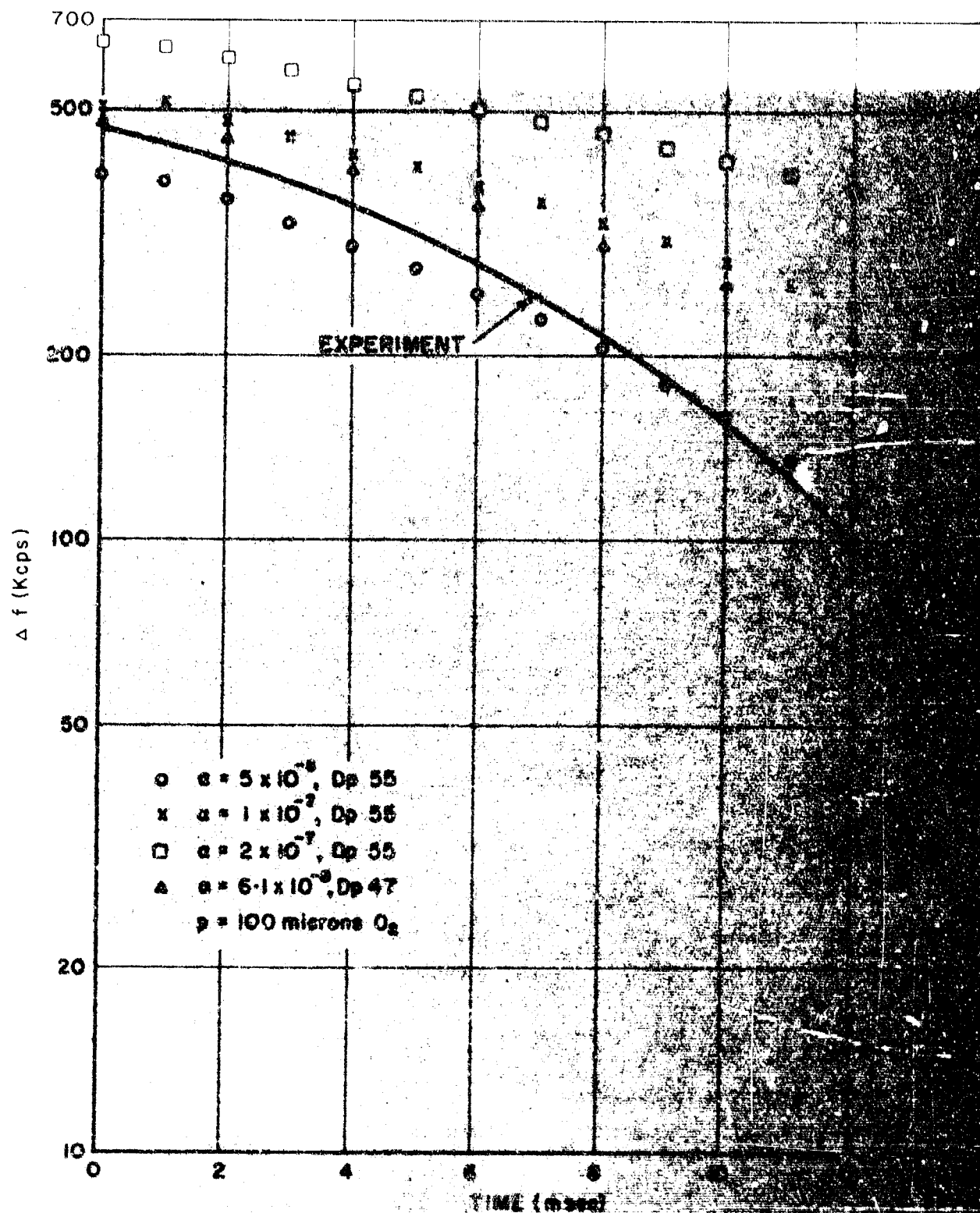


FIGURE 5.19- ELECTRON AFTERGLOW

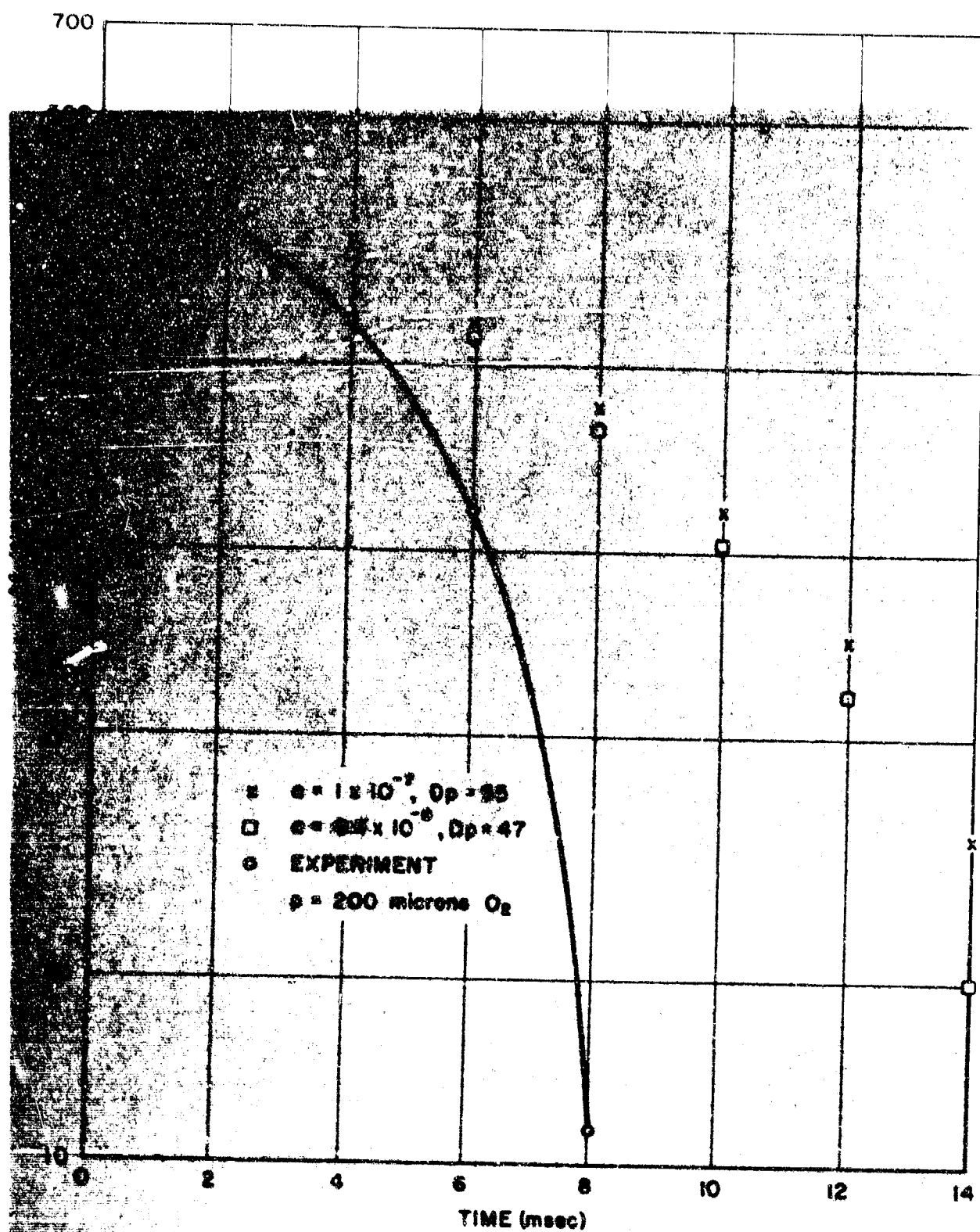


FIGURE 5.20- ELECTRON AFTERGLOW

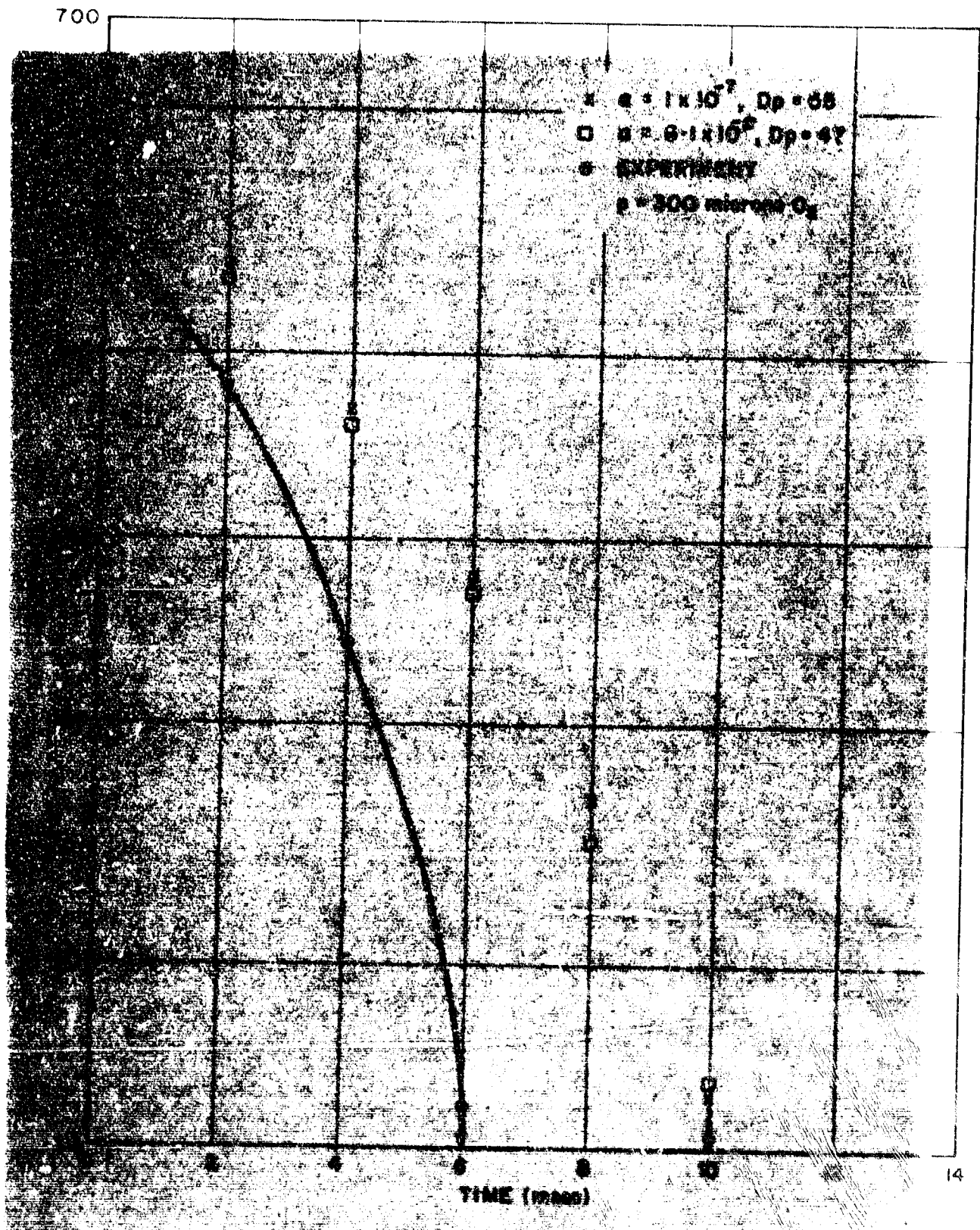


FIGURE 5.21- ELECTRON AFTERGLOW

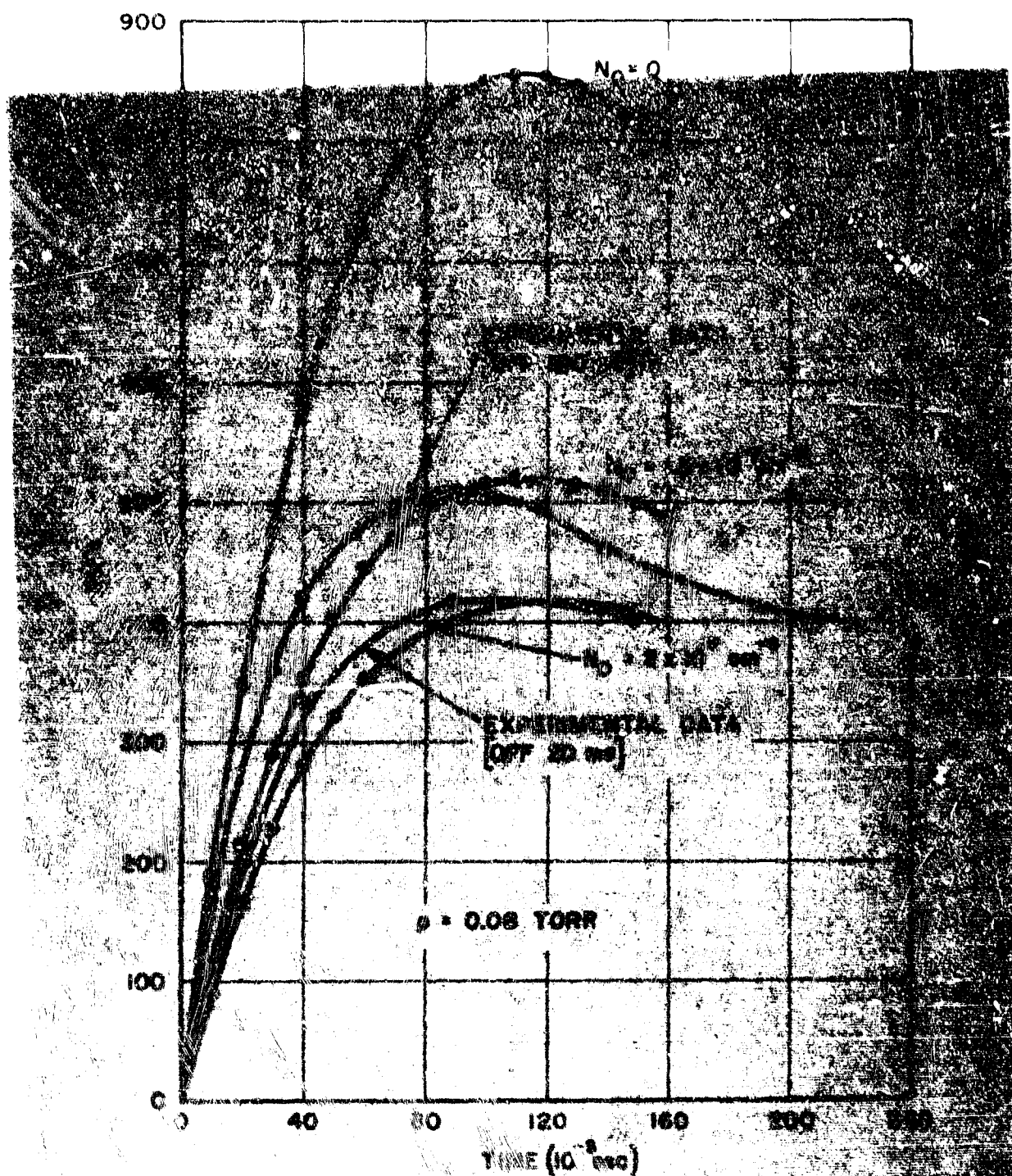


FIGURE # 22 - EFFECT OF INITIAL NEGATIVE ION DENSITY ON CALCULATED ELECTRON DENSITIES DURING TURN-ON IN OXYGEN.

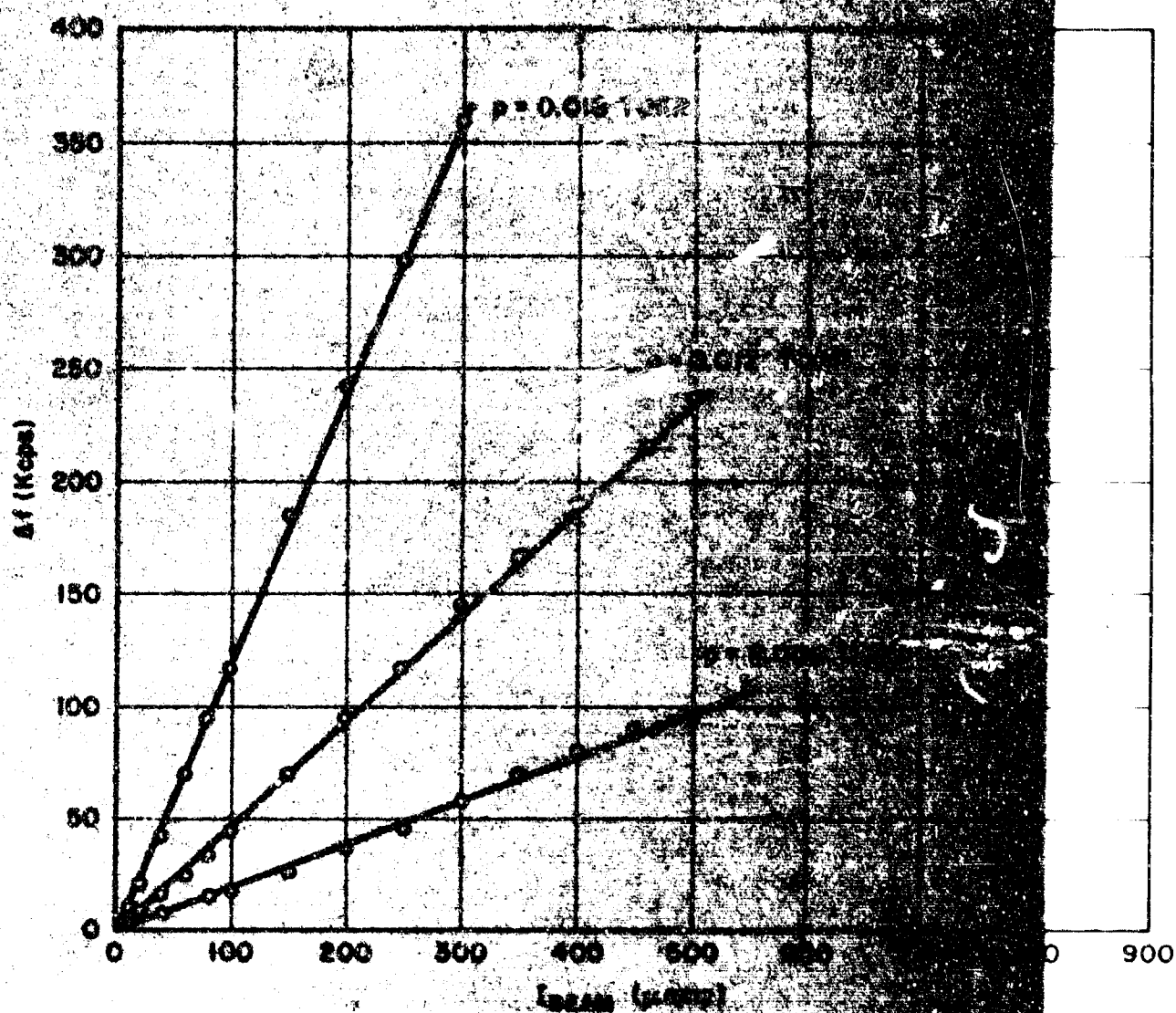


FIGURE 5.23- STEADY-STATE ELECTRON BEAM CURRENT IN NITROGEN

BEAM

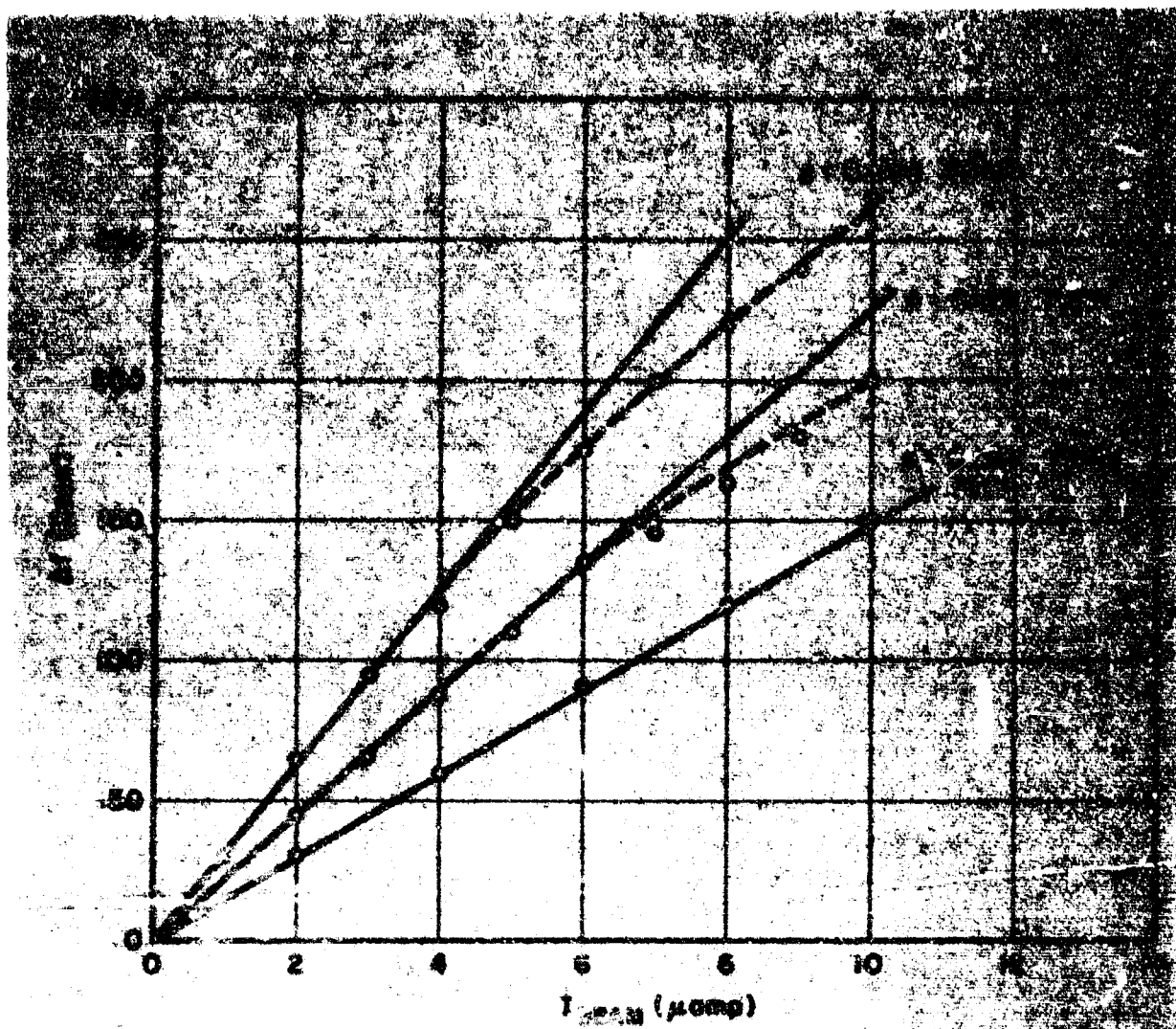
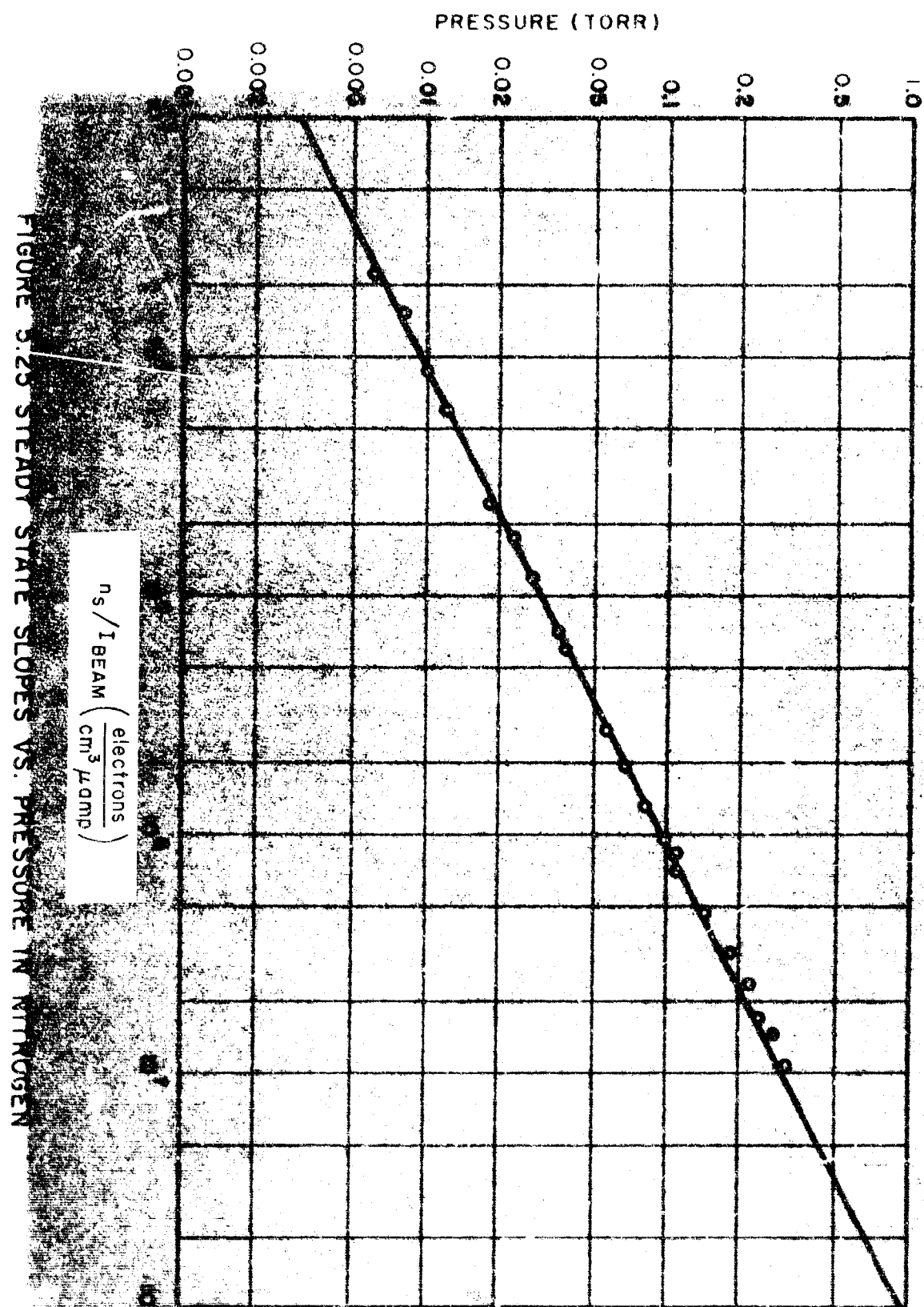


FIGURE 5.24- STEADY-STATE ELECTRON DENSITY VS. BEAM CURRENT IN NITROGEN



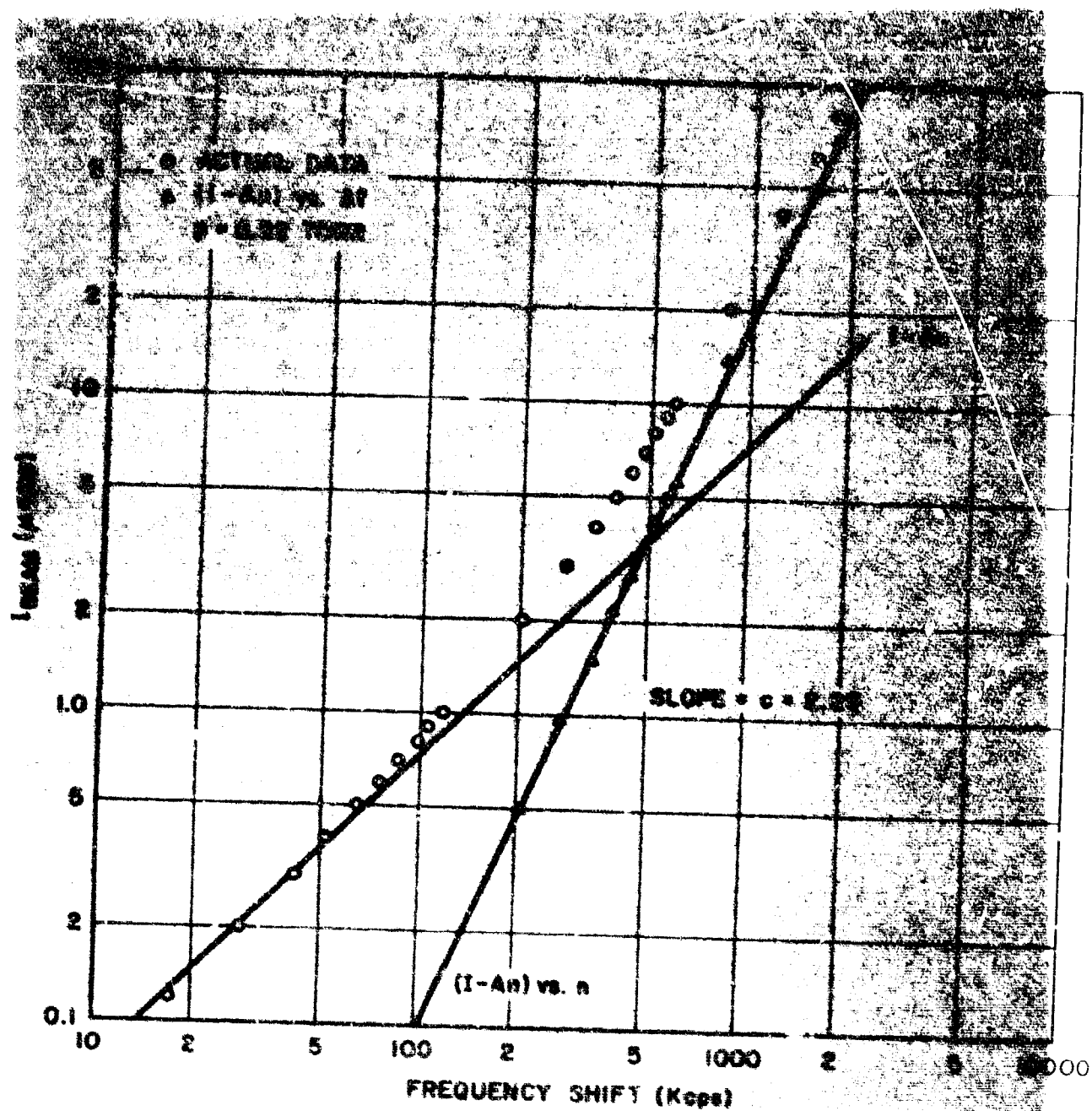


FIGURE 5.26- DECOMPOSITION OF ELECTRON DENSITY DATA
INTO $Kp_i = A n + B n^c$

RESULTS OF DECOMPOSITION OF STEADY-STATE
ELECTRON DENSITIES INTO THE FORM

$$K_{pi} = A_n + B_n^c$$

PRESSURE (Torr)	$n_{\text{intersection}}$	c
0.057	1.25×10^7	2.07
0.067	1.25×10^7	2.20
0.081	7.7×10^6	2.60
0.098	9.4×10^6	2.26
0.110	8.2×10^6	2.24
0.145	9.5×10^6	2.24
0.185	9.5×10^6	2.92
0.220	5.5×10^6	2.38
0.240	8.5×10^6	2.32
0.275	9.0×10^6	2.53
0.310	8.1×10^6	2.50

NOTE: $(n_{\text{intersection}})^{c-1} = A/B$

FIGURE 5.27

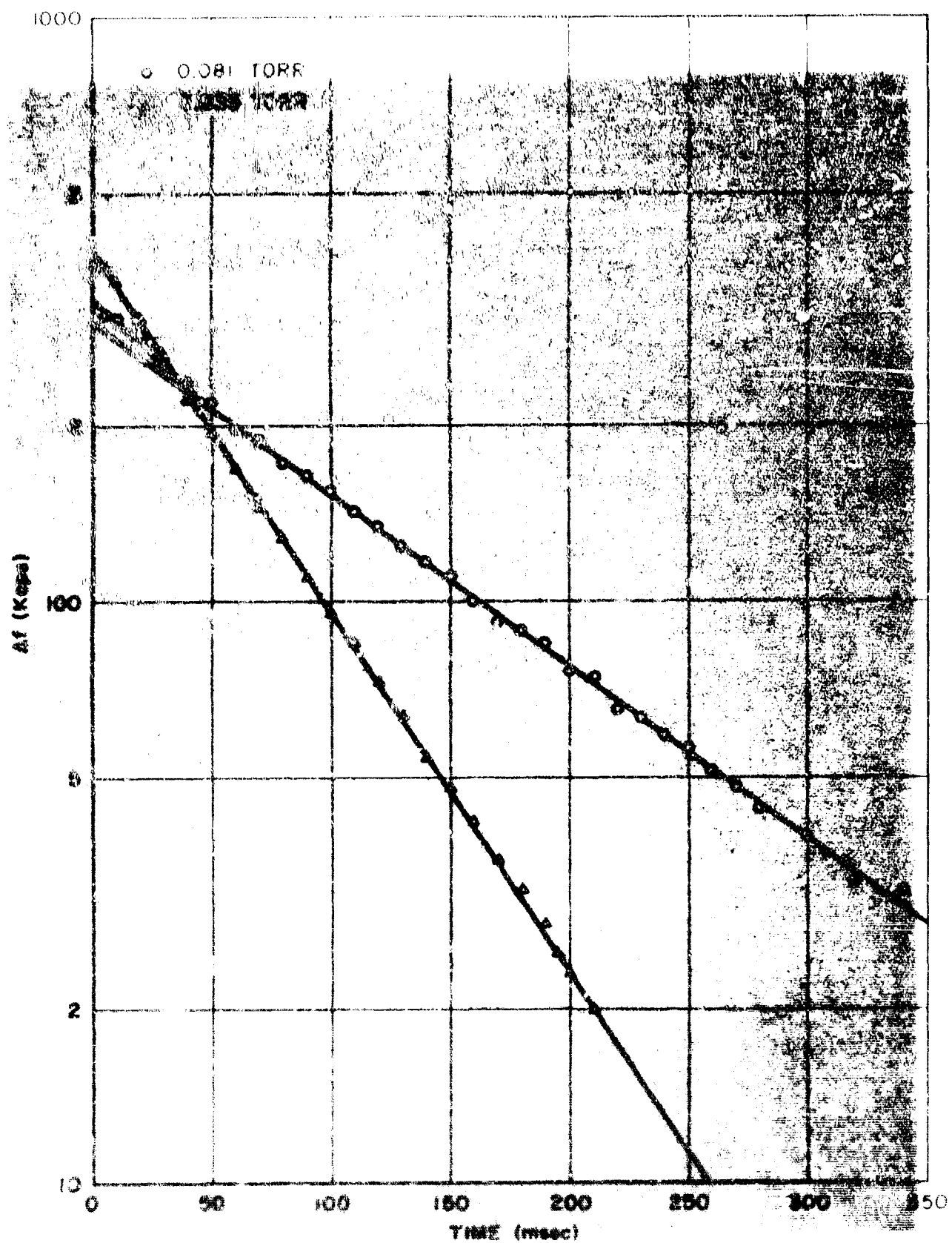


FIGURE 5-28- ELECTRON DENSITY DECAY IN NITROGEN AT 0.081 TORR AND 0.035 TORR

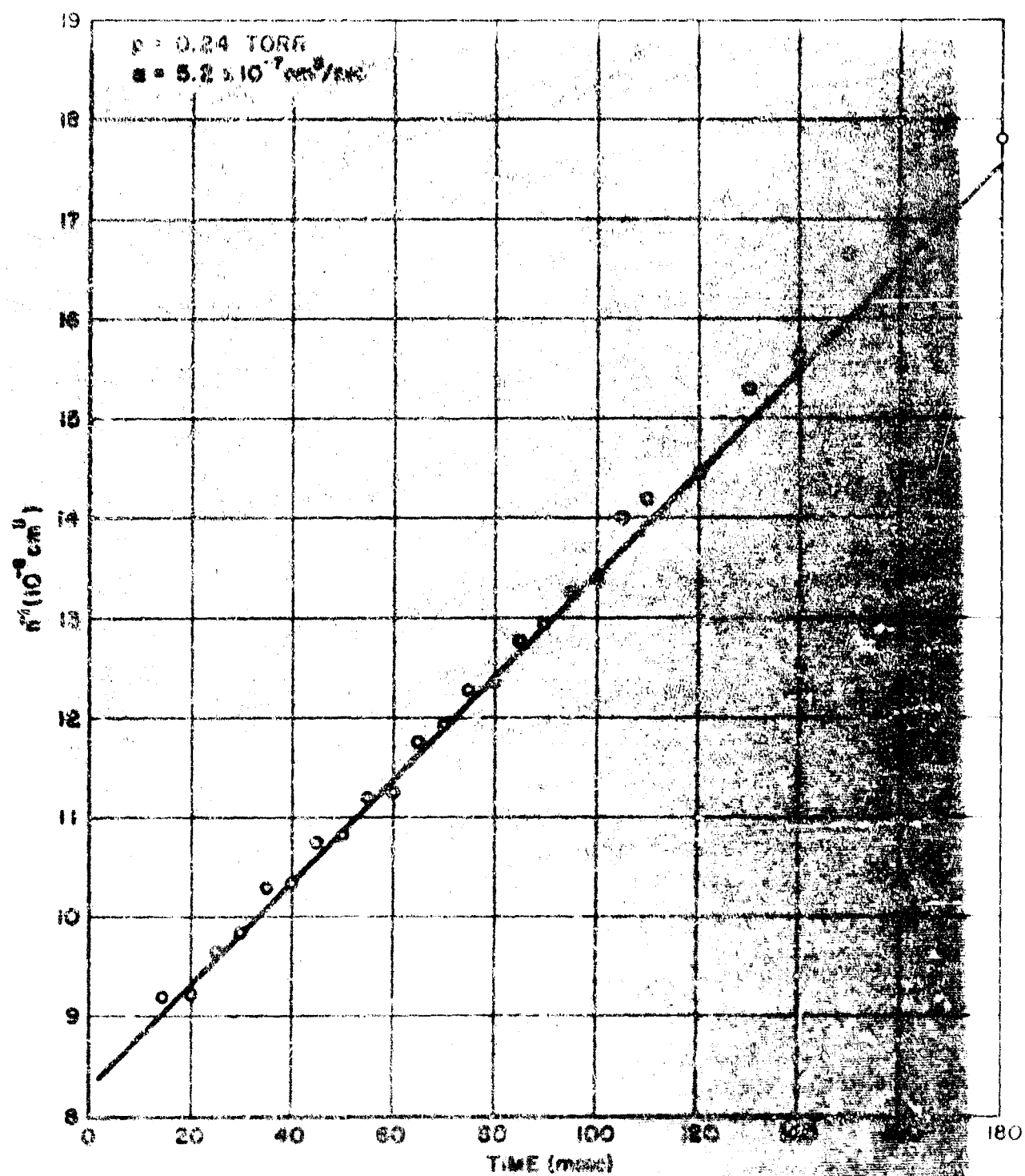


FIGURE 5.29 - RECOMBINATION PLOT FOR NITROGEN AT 1750°K

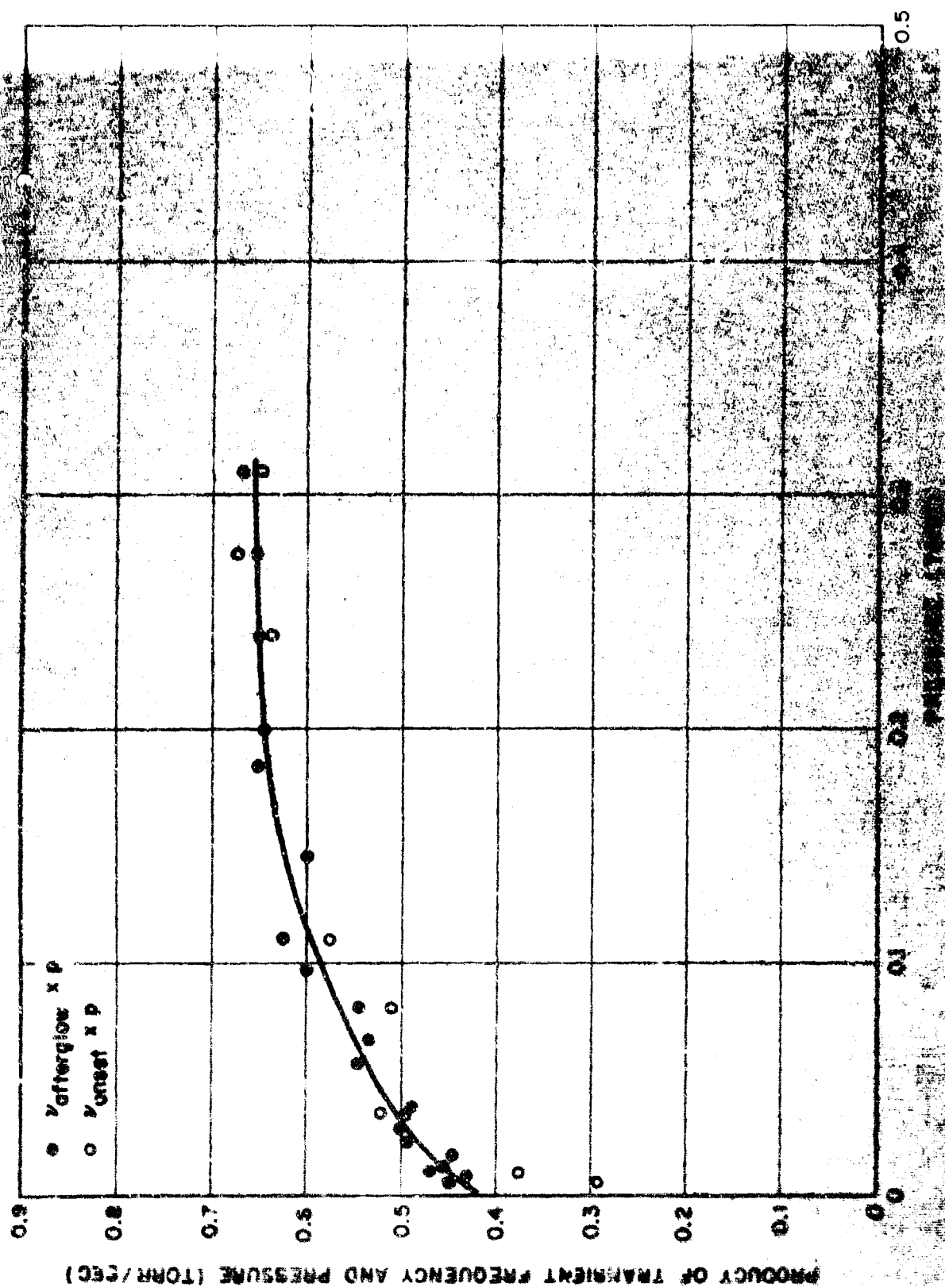


FIGURE 5.30- LINEAR BEHAVIOR OF TRANSIENT ELECTRON DENSITIES IN NITROGEN

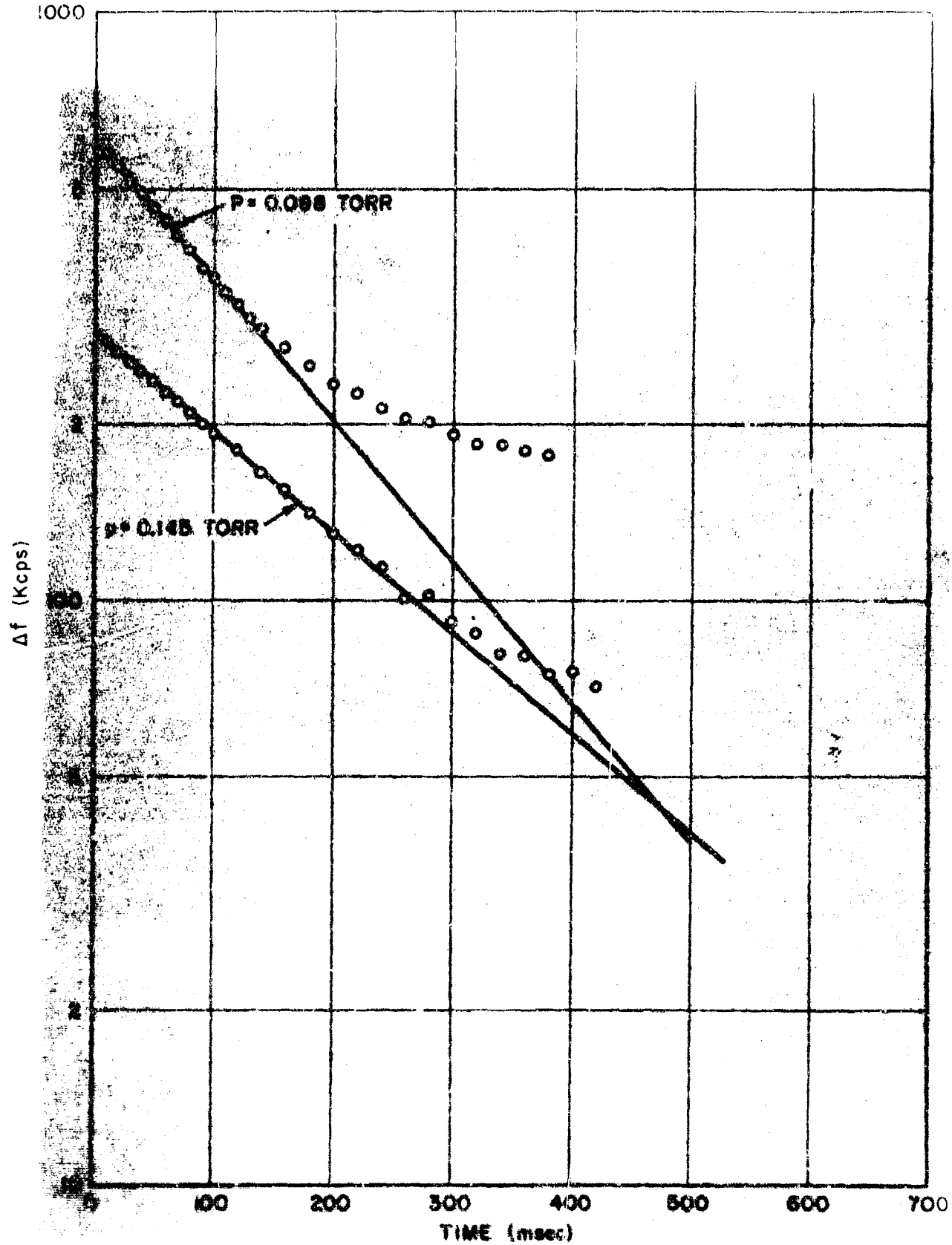


FIGURE 5.31- ELECTRON DENSITY BUILD-UP IN NITROGEN

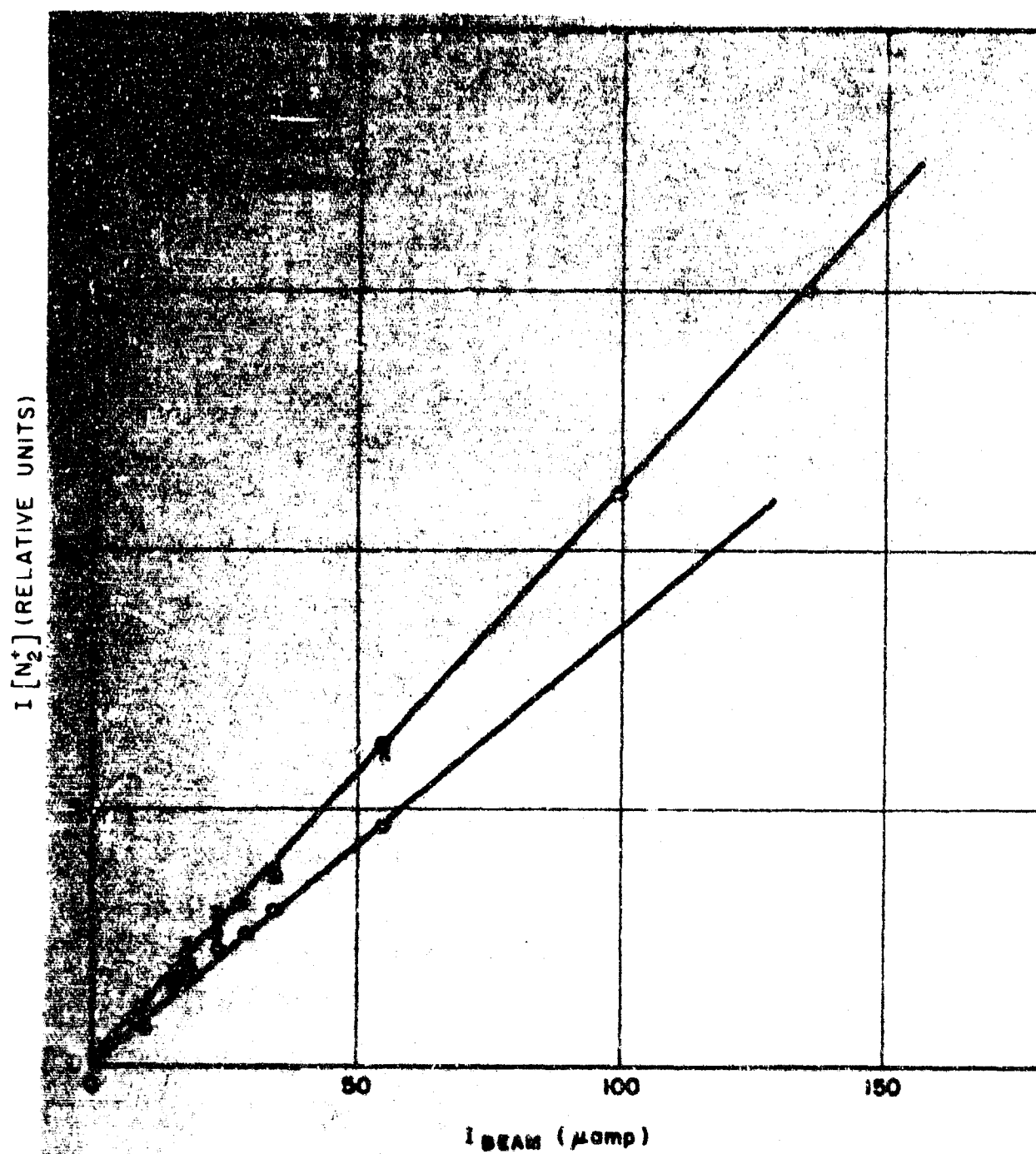


FIGURE 5.32- N_2^+ CURRENT VS. I_{BEAM} AT SEVERAL PRESSURES

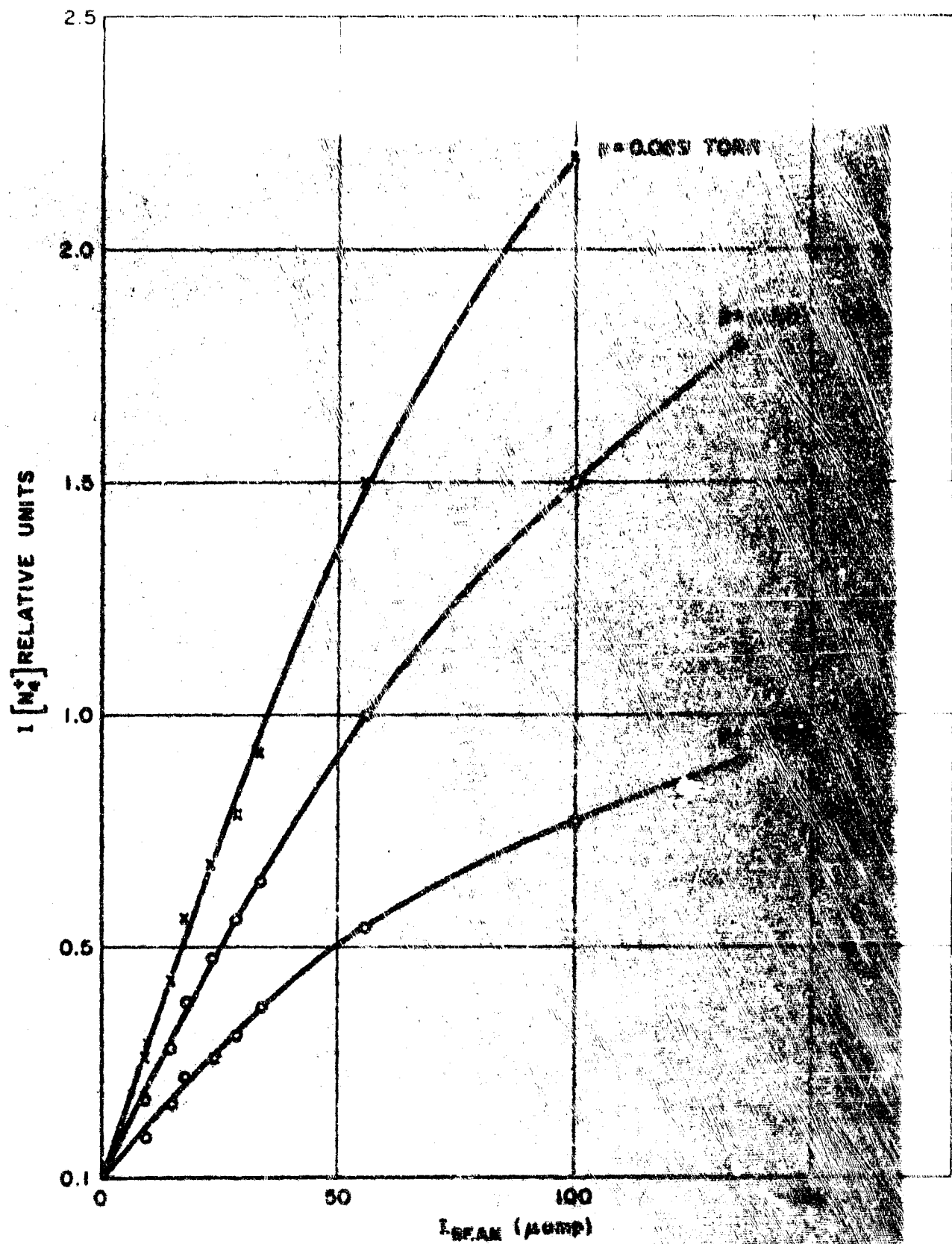


FIGURE 5.33- N_4^+ CURRENT VS. I_{BEAM} AT SEVERAL PRESSURE

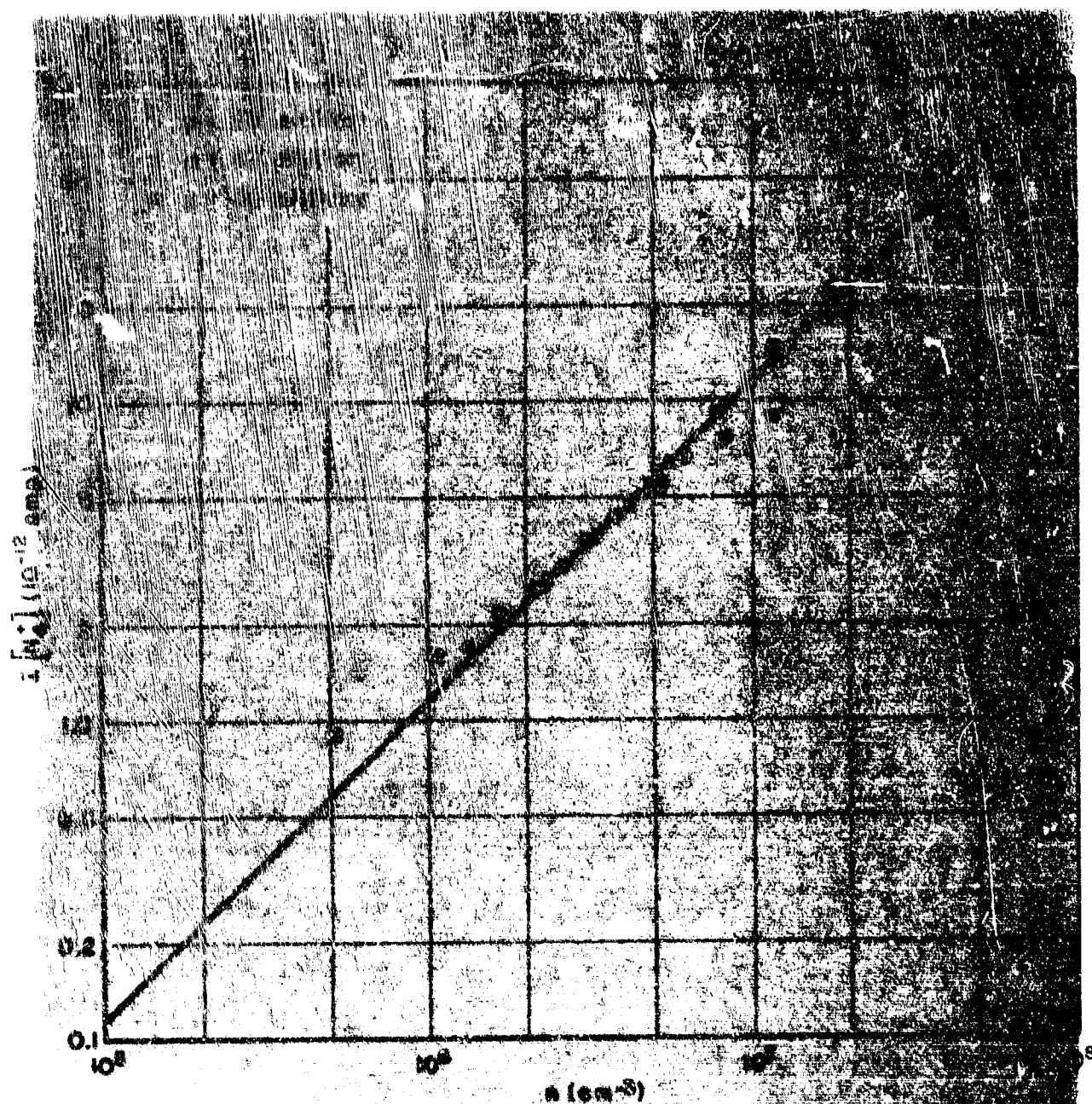


FIGURE 5.34- N_1^+ ION CURRENT VS. ELECTRON DENSITY AT SEVERAL PRESSURES

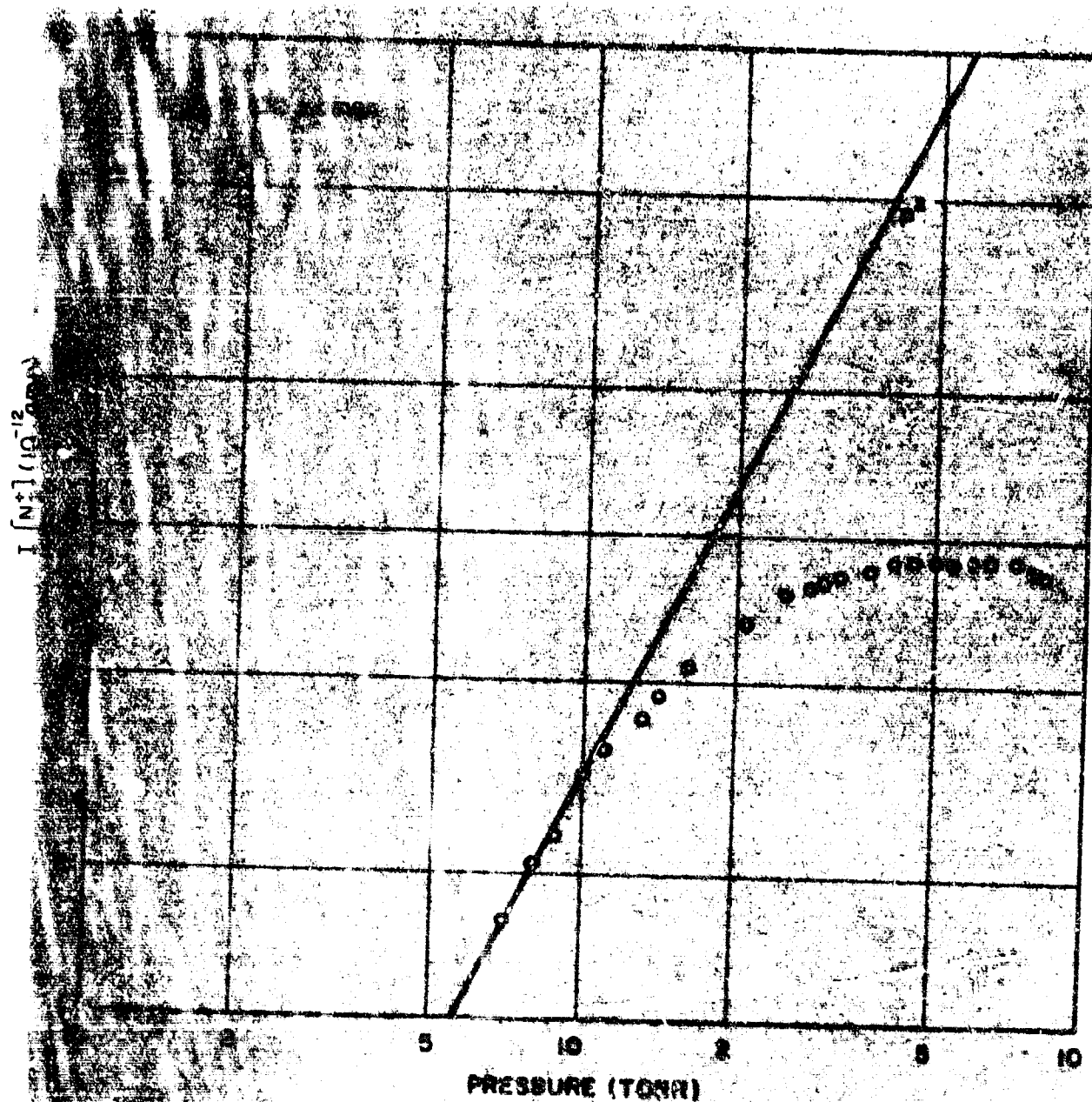
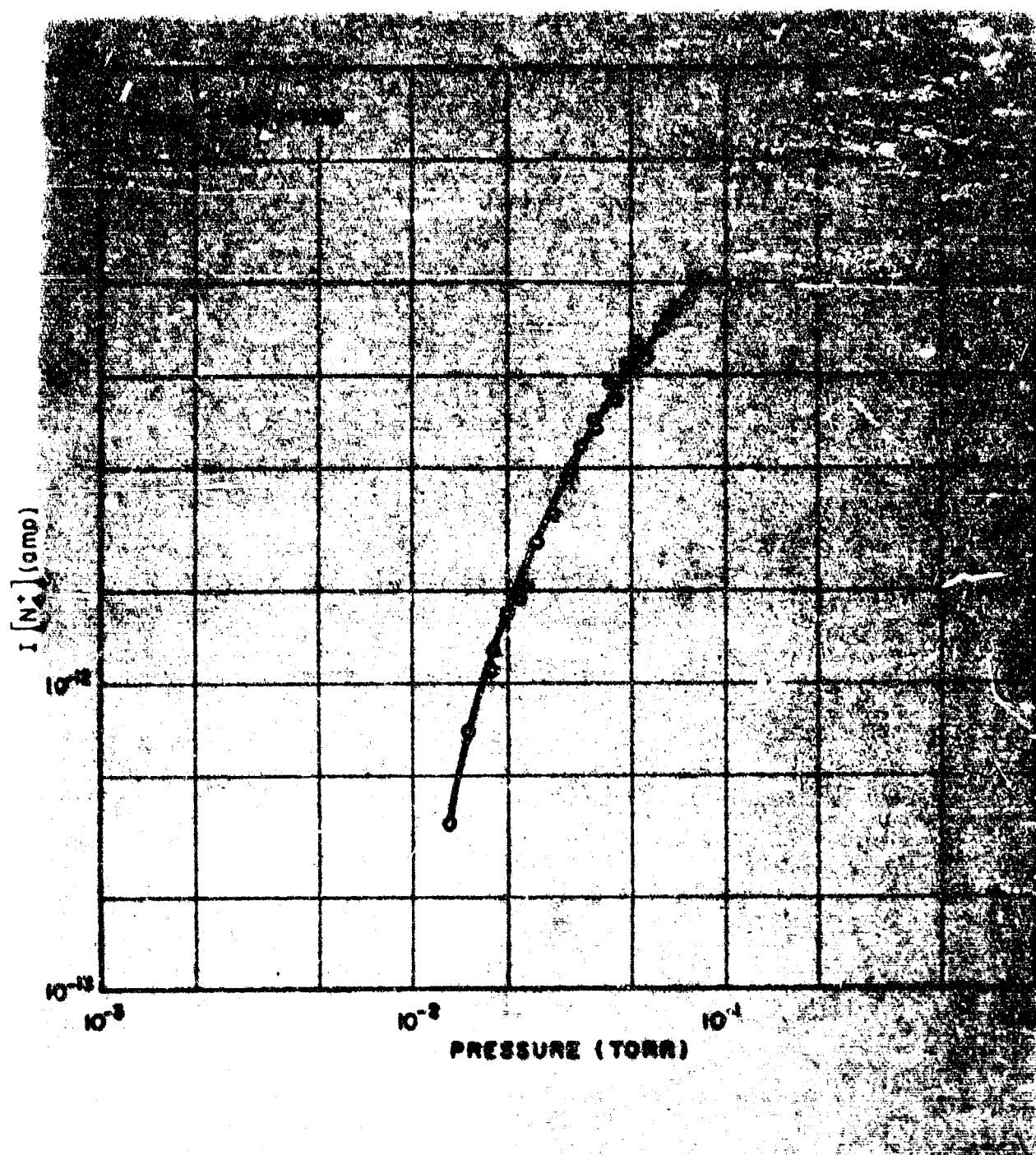


FIGURE 5.35 - $I[N_2^+]$ VS. PRESSURE IN PURE NITROGEN



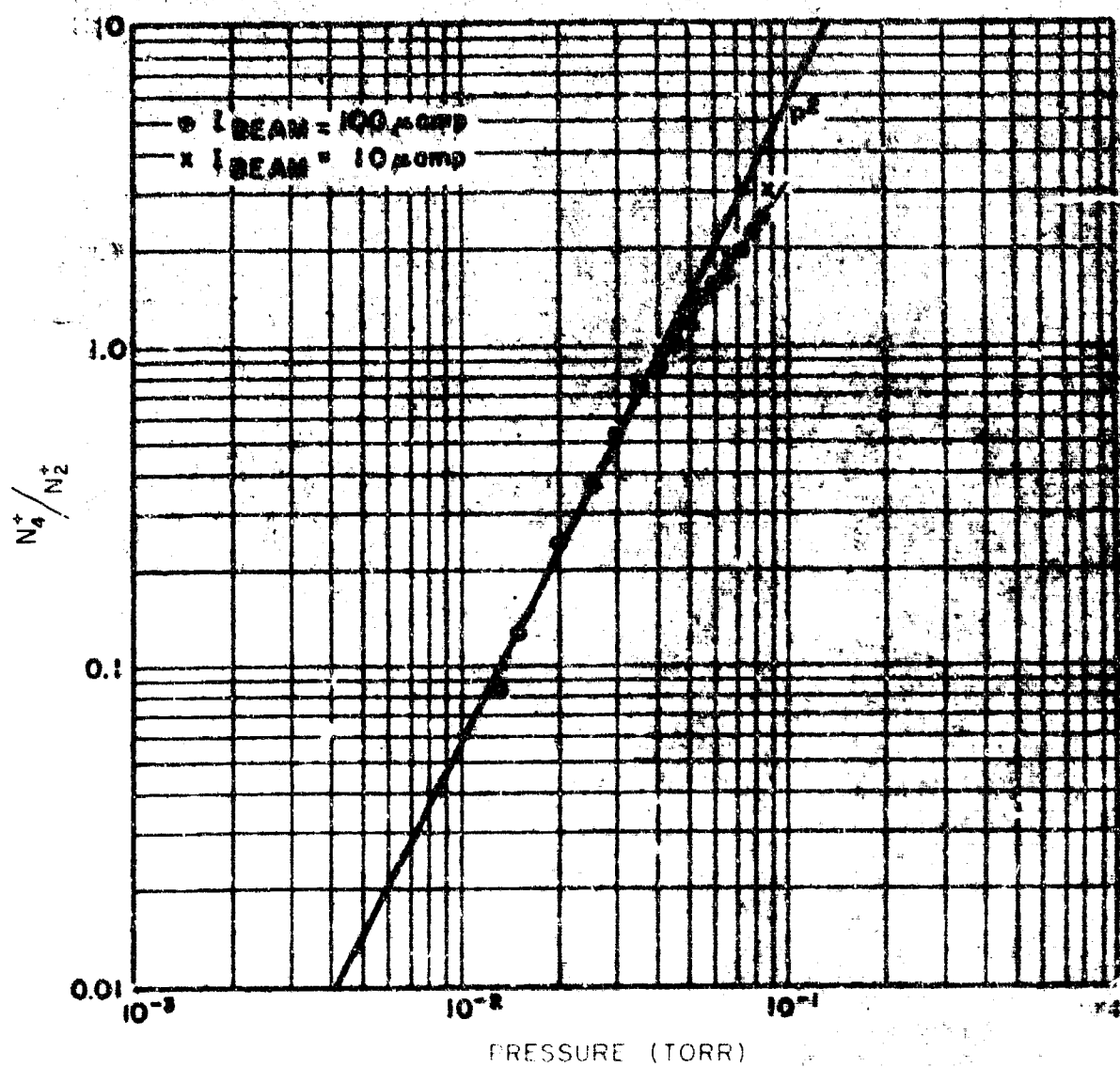
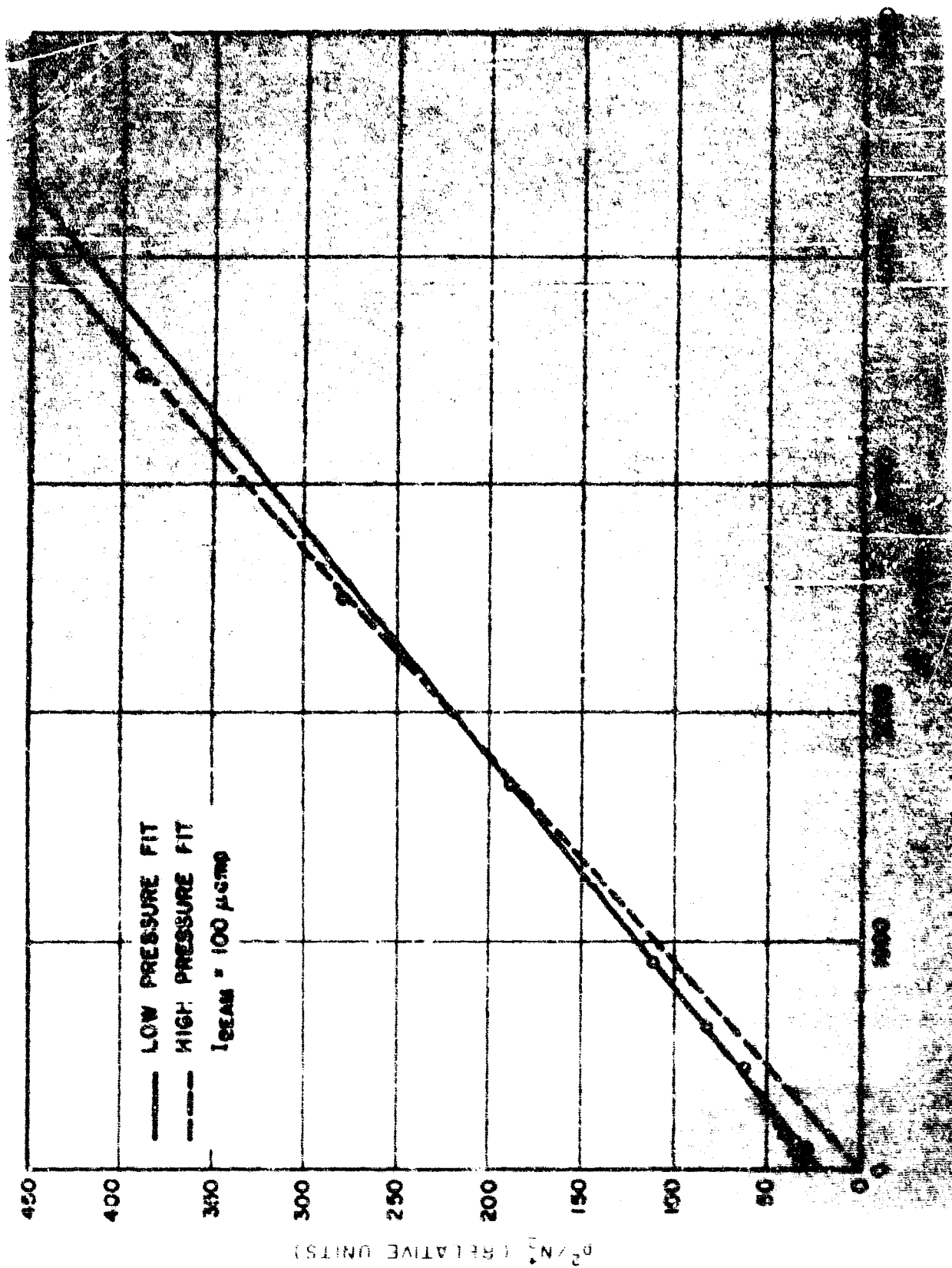


FIGURE 5.37- RATIO OF N_4^+ TO N_2^+ ION CURRENT VS. PRESSURE

FIGURE 5.38 p^2/N_2 VS. p^2

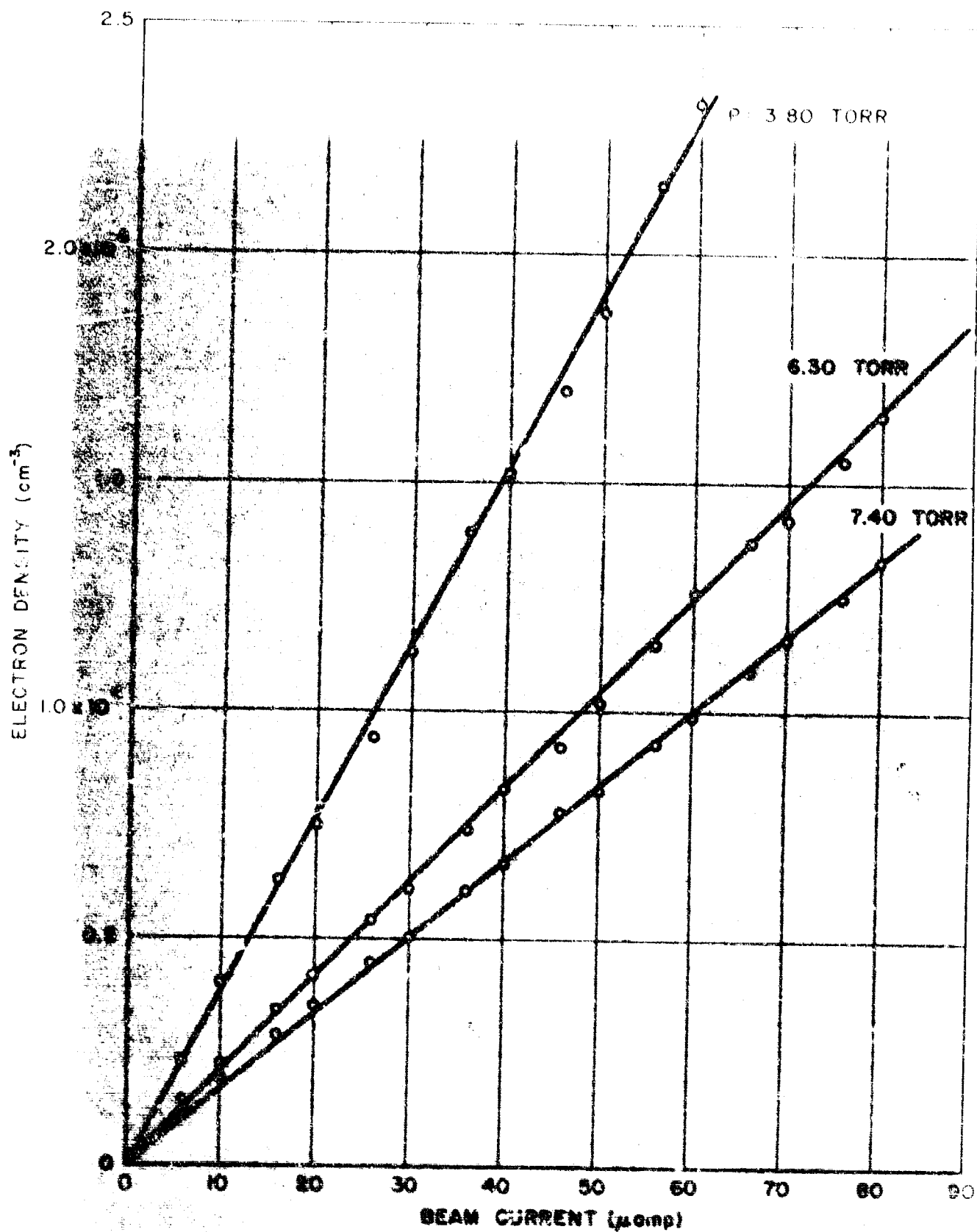


FIGURE 5.39- ELECTRON DENSITY VS. I_{BEAM} IN 4:1 N_2O_2

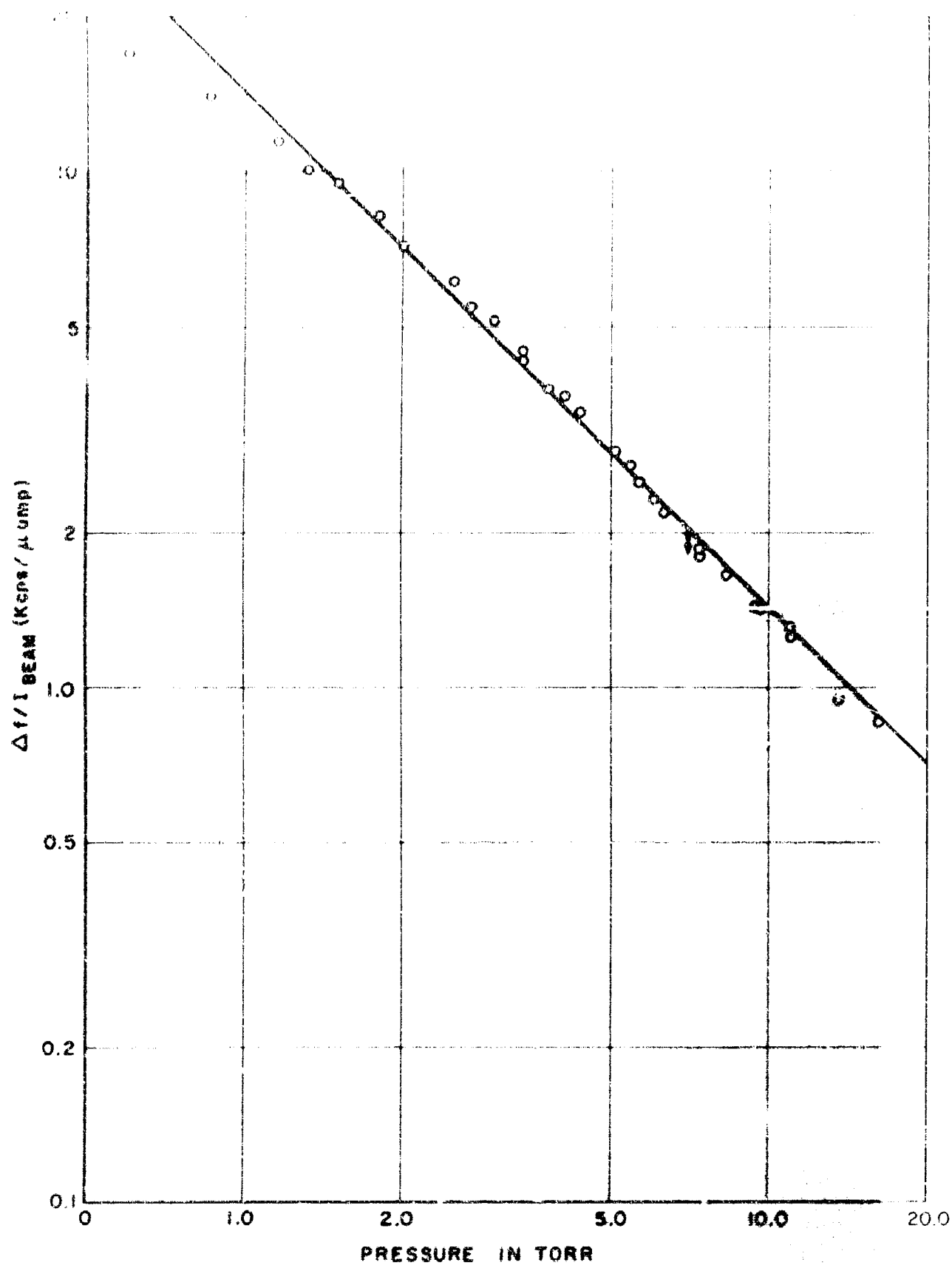


FIGURE 5.40- SLOPES OF LINEAR PLOTS OF ELECTRON DENSITY VS. I_{BEAM} AS A FUNCTION OF PRESSURE IN 4:1 N_2 : O_2 MIXTURES

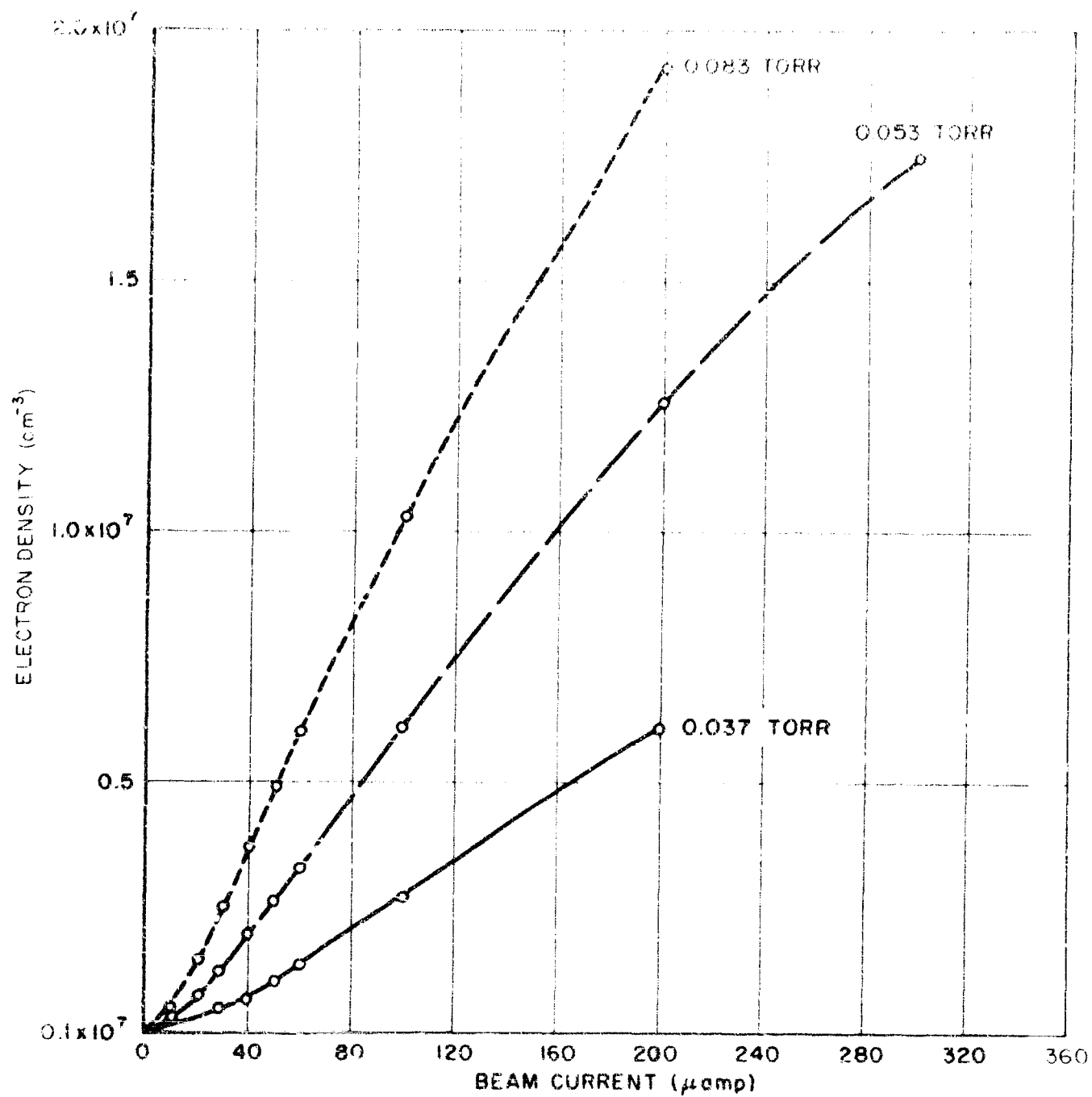


FIGURE 5.41- STEADY STATE ELECTRON DENSITY VS. BEAM CURRENT IN 4:1 N₂:O₂

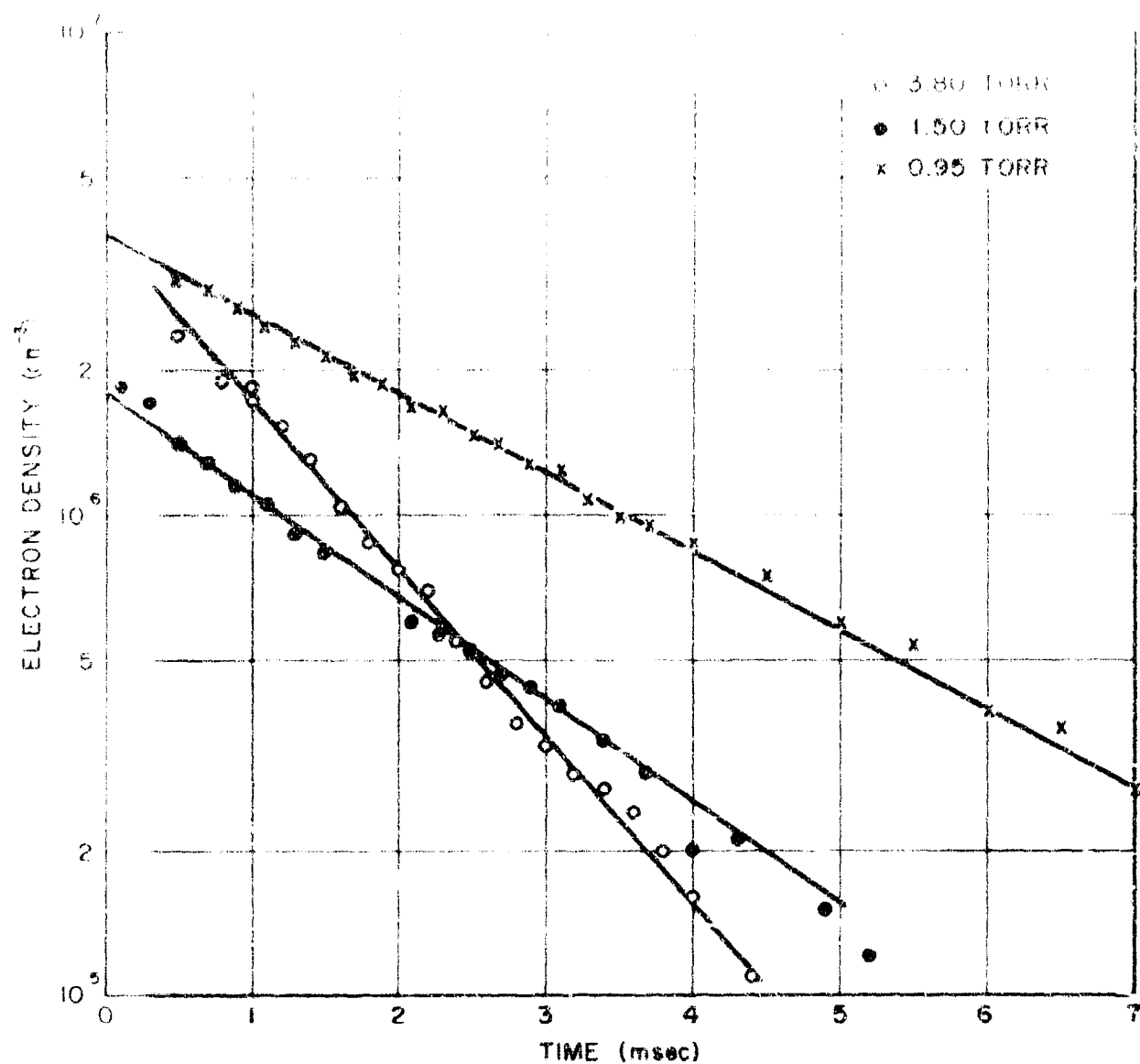


FIGURE 5.42- AFTERGLOW DECAY OF ELECTRON DENSITY IN
4:1 N₂:O₂

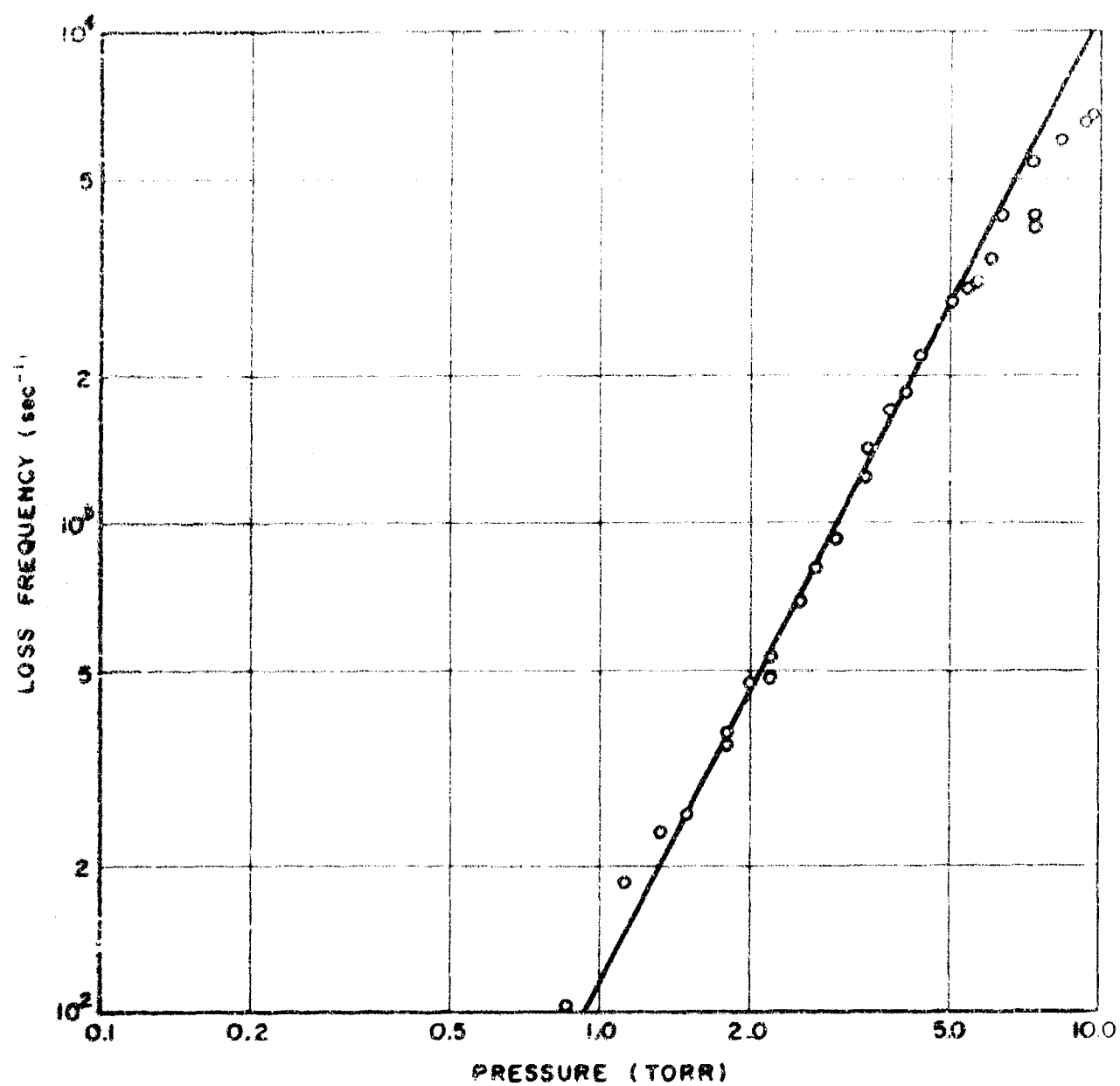


FIGURE 5.43- ELECTRON LOSS FREQUENCY VS. PRESSURE
IN 4:1 $N_2:O_2$

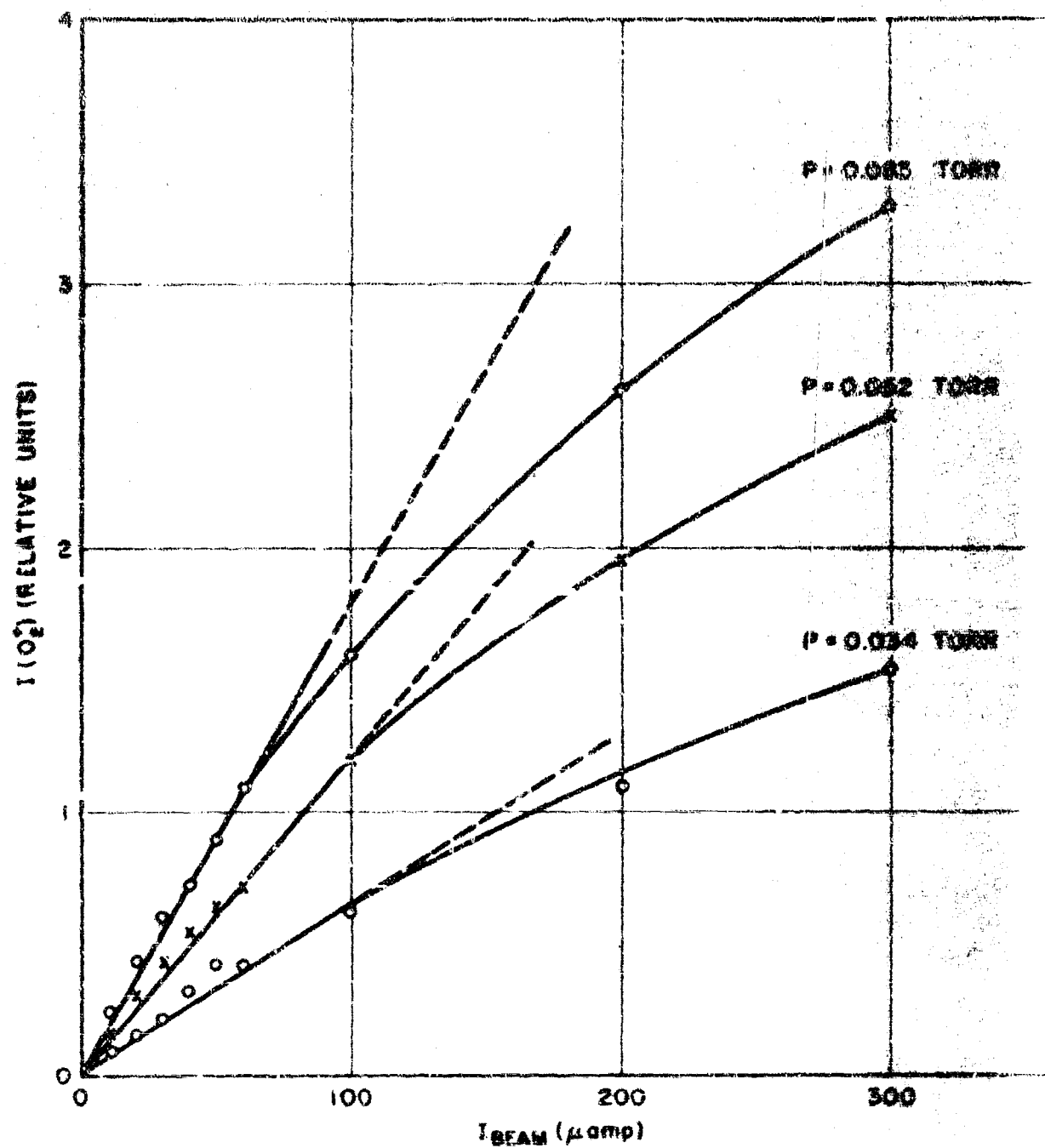


FIGURE 5.44- O_2^+ CURRENTS VS. I_{BEAM} IN 4:1 $N_2:O_2$

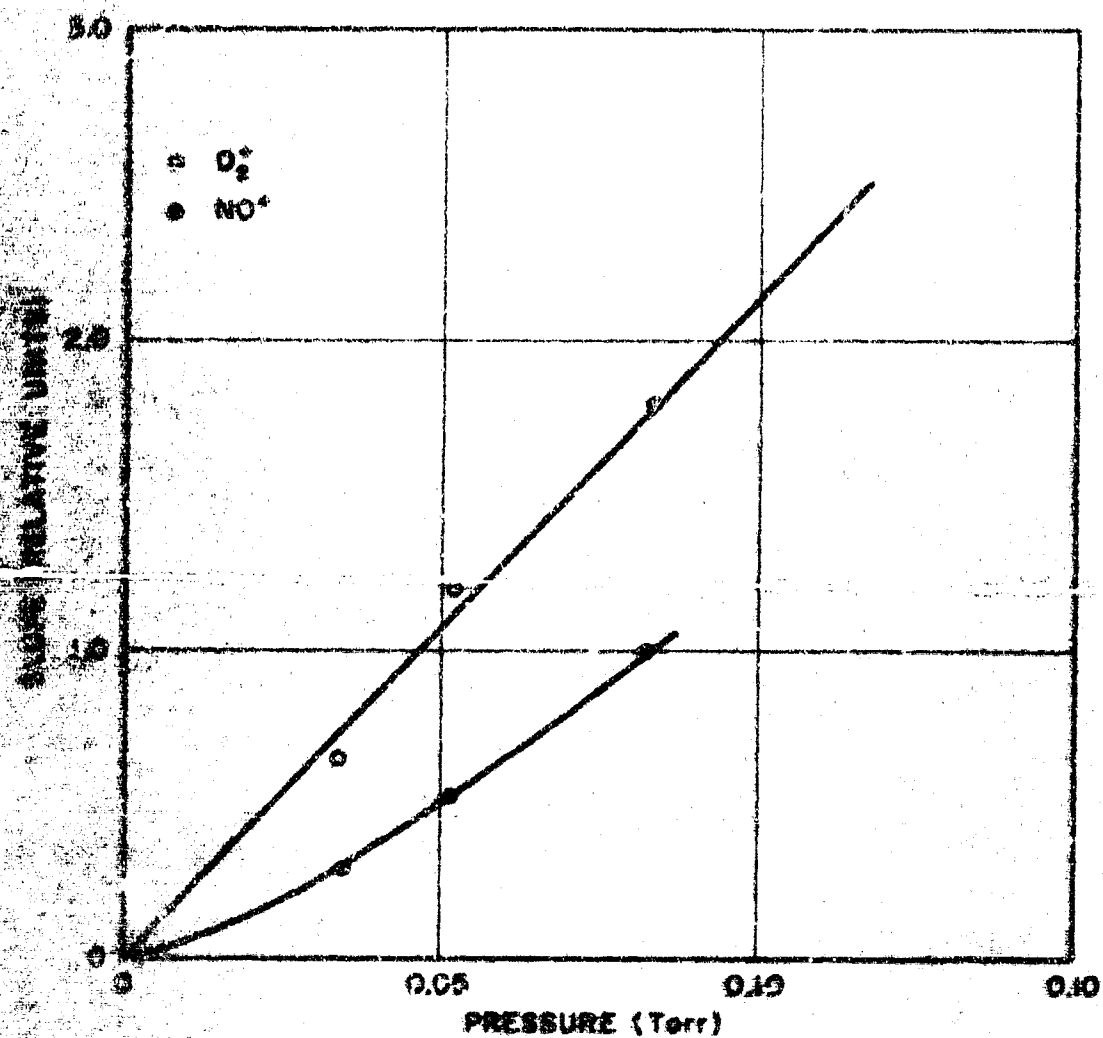


FIGURE 5.45- SLOPES OF LINEAR PORTION OF ION CURRENT VS. I_{beam} PLOT AS FUNCTION OF PRESSURE

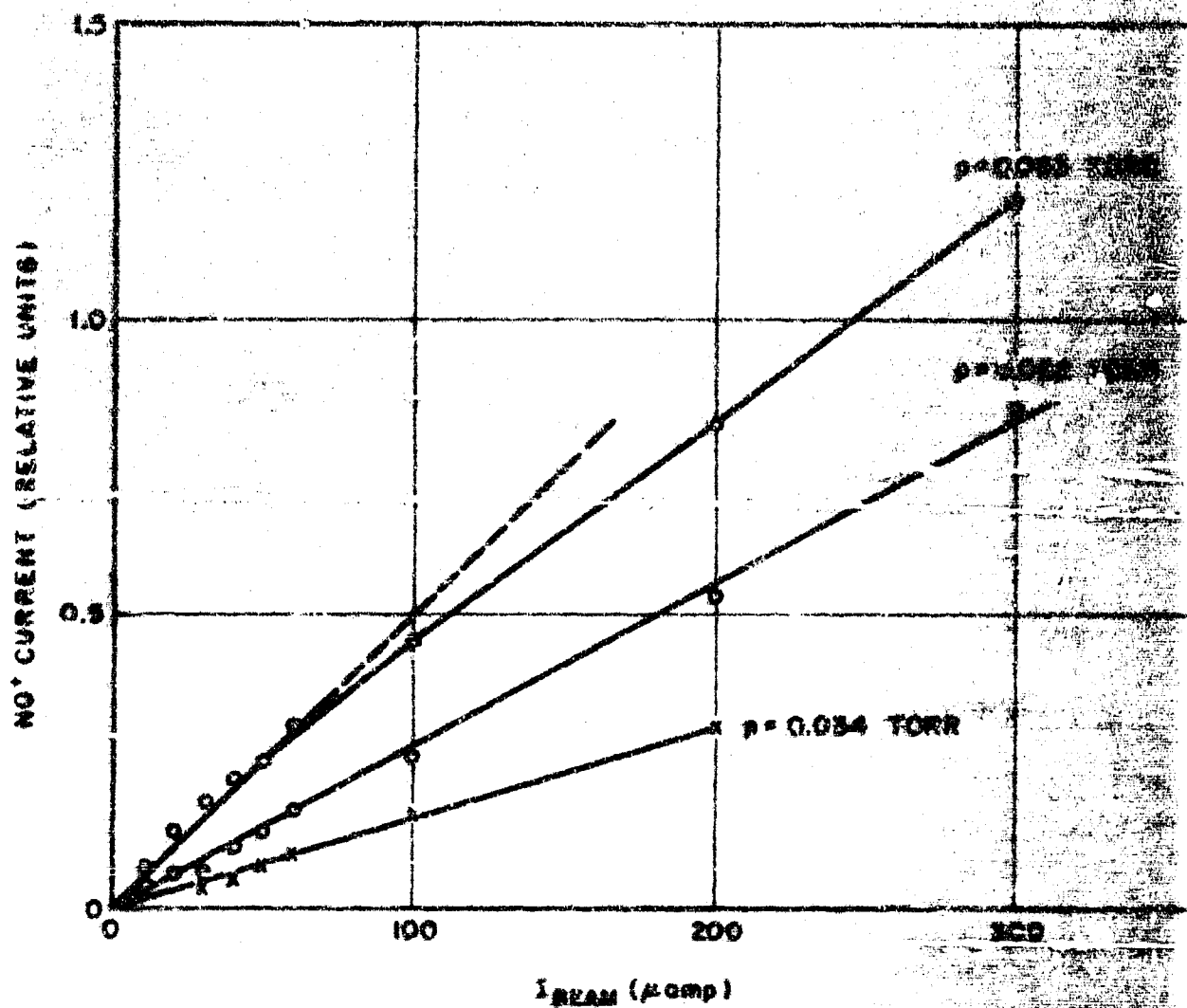


FIGURE 5.46- NO^+ ION CURRENT VS. I_{beam} IN 4:1
 $\text{N}_2:\text{O}_2$

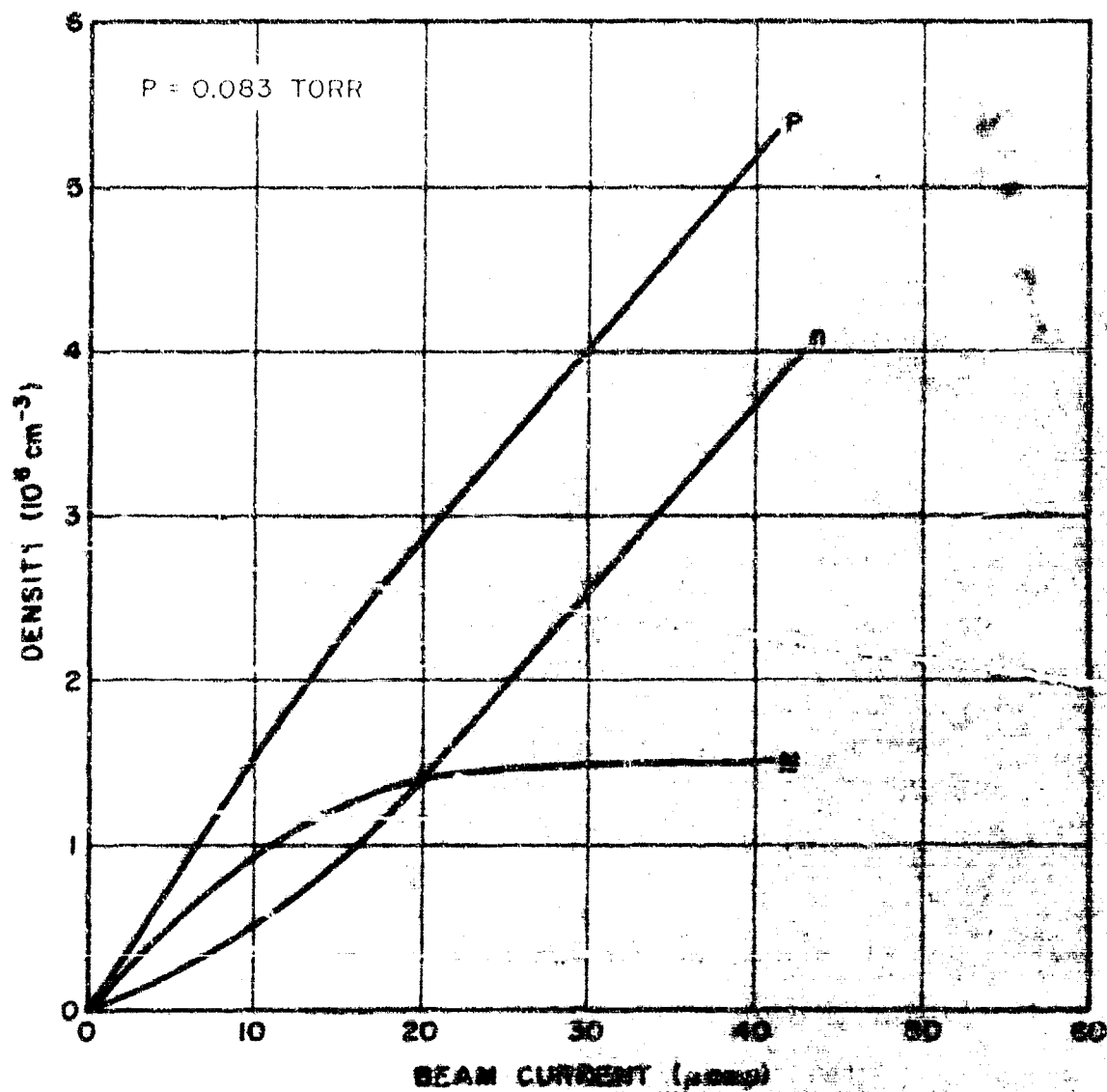


FIGURE 5.47- PARTICLE DENSITIES VS. BEAM CURRENT
IN 4:1 $N_2:O_2$ MIXTURE

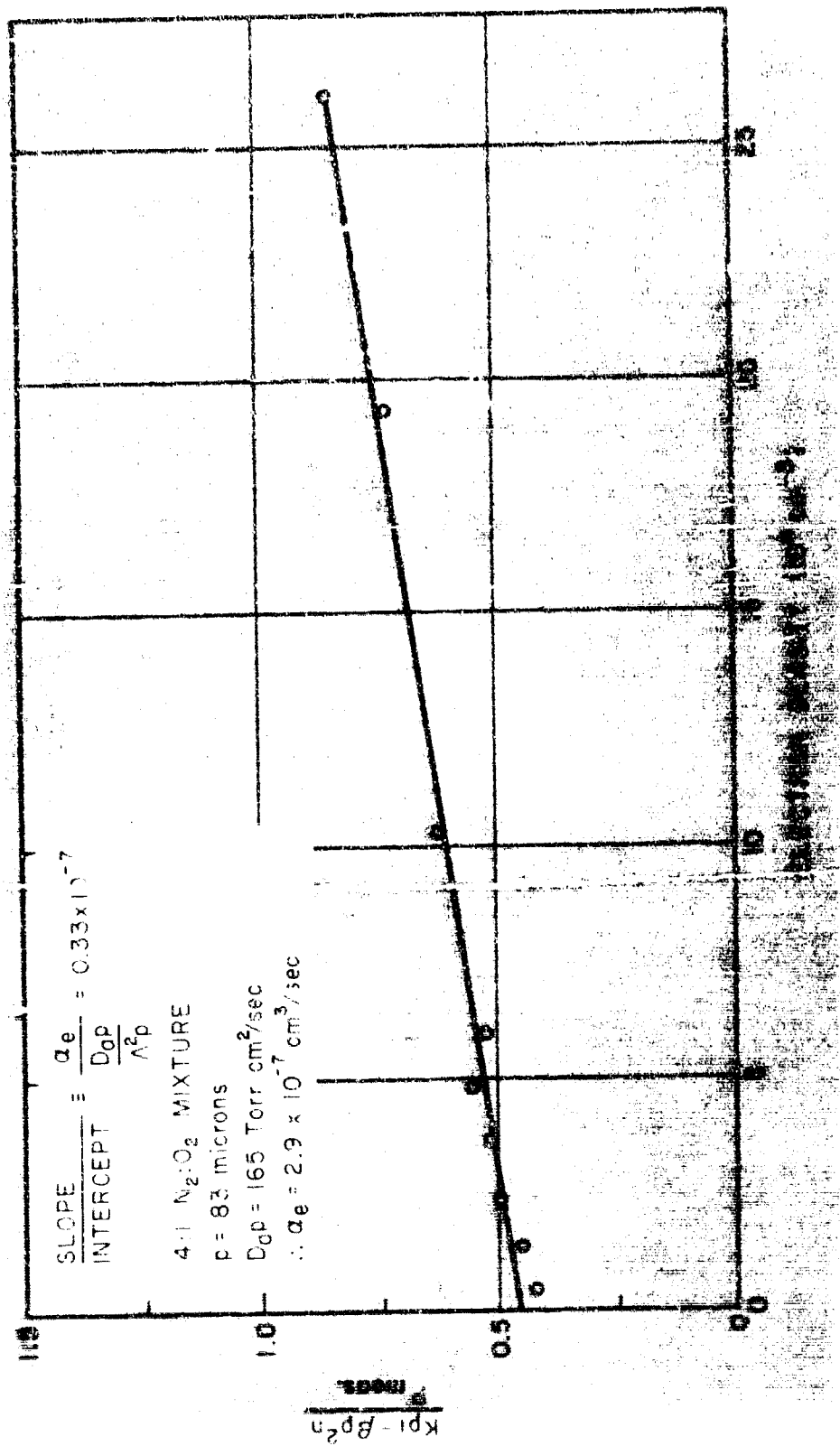


FIGURE 5.48- EVALUATION OF α_e IN N₂O₂ MIXTURES

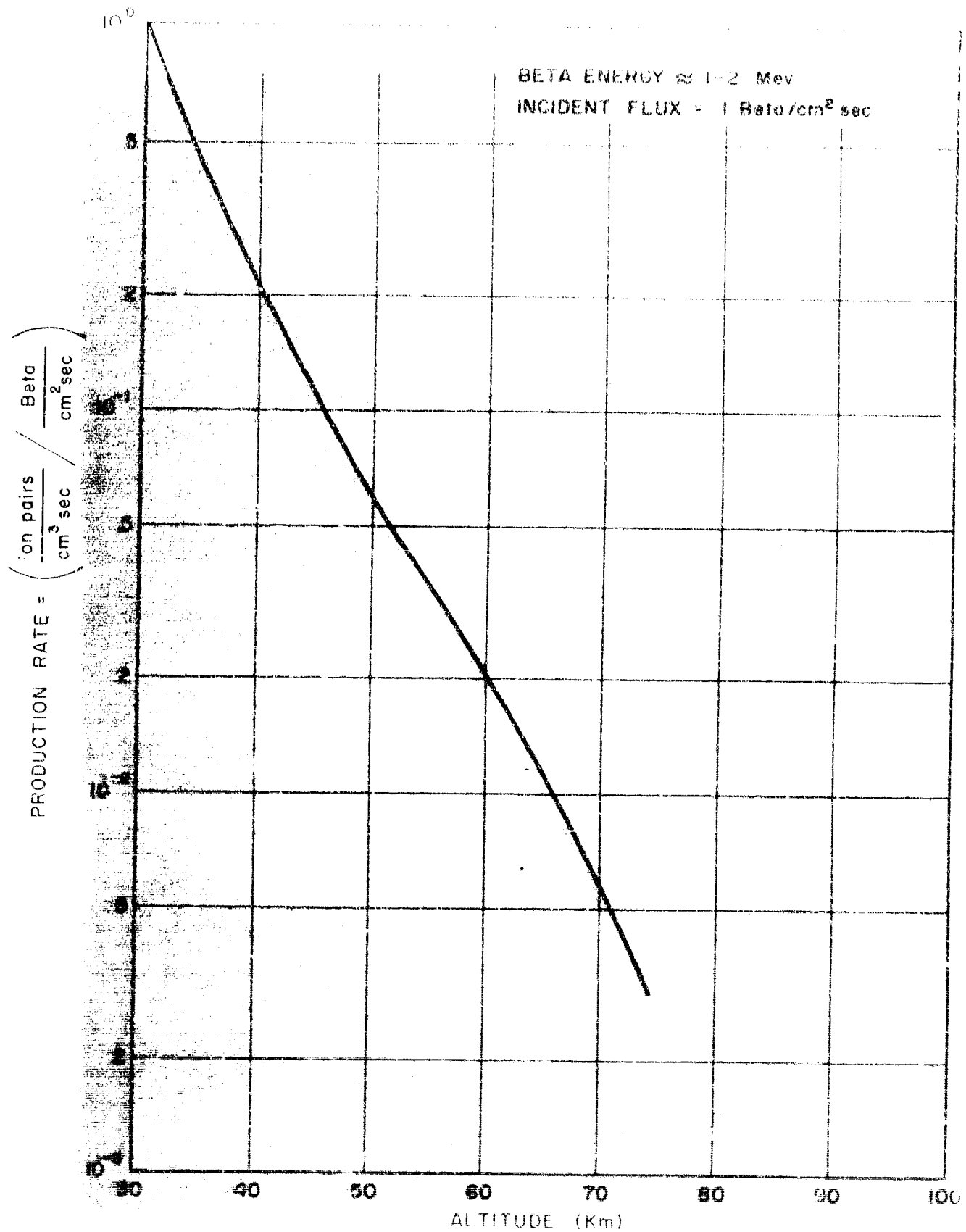


FIGURE 5.49- IONIZATION RATE OF AIR BY BETA PARTICLES
VS. ALTITUDE

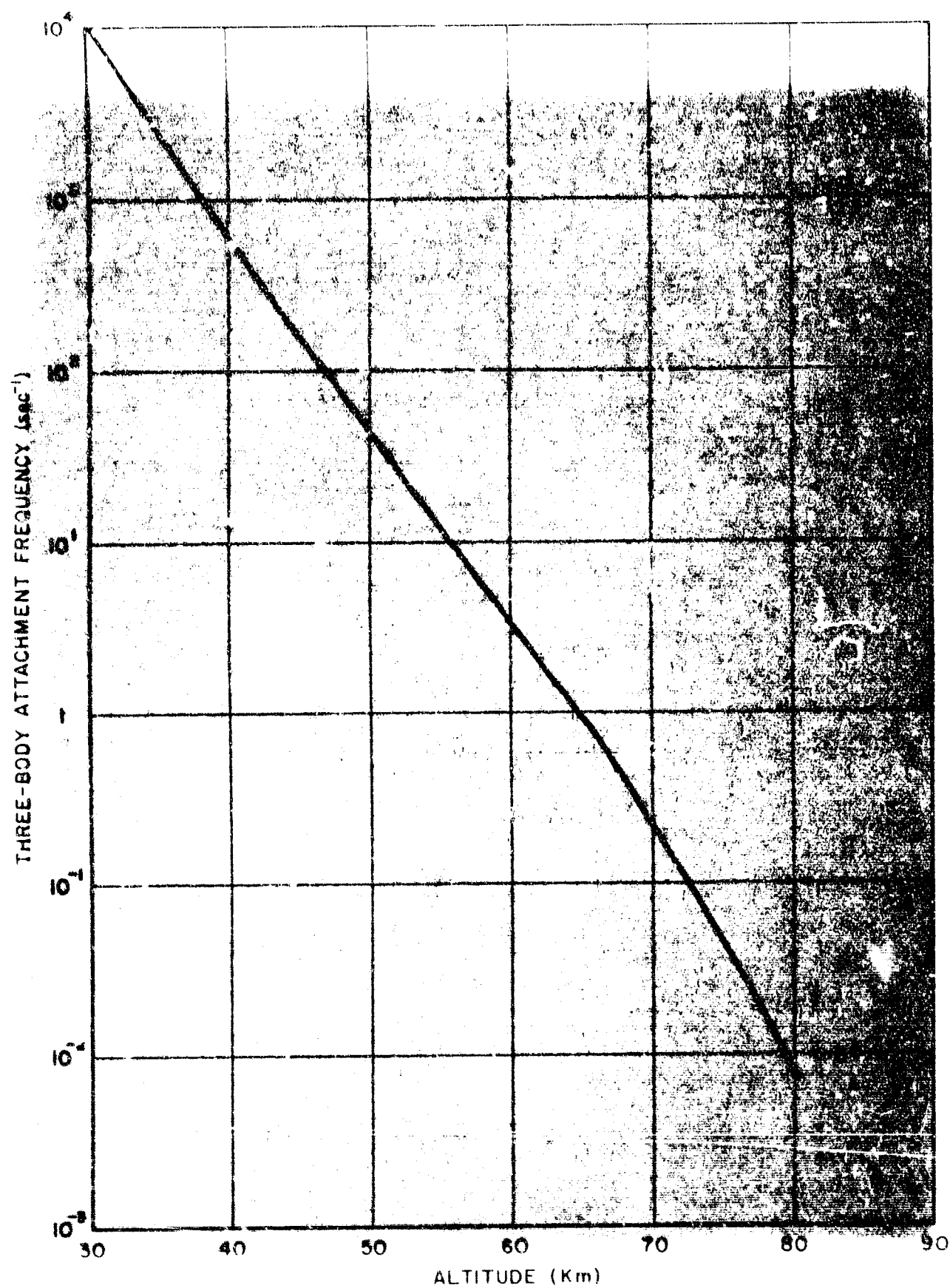


FIGURE 5.50- THREE-BODY ATTACHMENT LOSS FREQUENCY AS A FUNCTION OF ALTITUDE

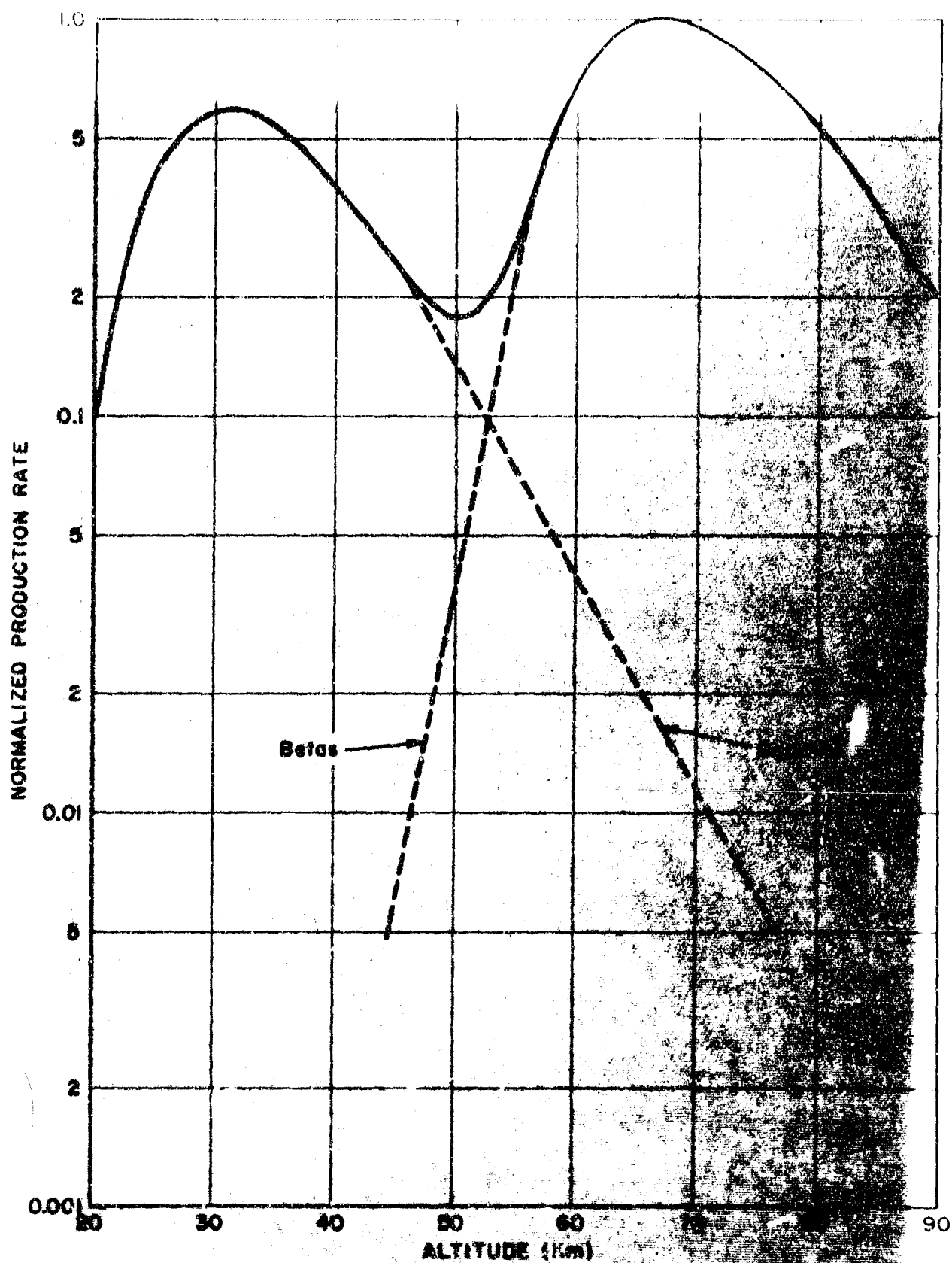


FIGURE 5.51- TYPICAL ELECTRON PRODUCTION DISTRIBUTION
FOR HOMOGENEOUS FISSION DEBRIS LAYER
ABOVE 90 Km

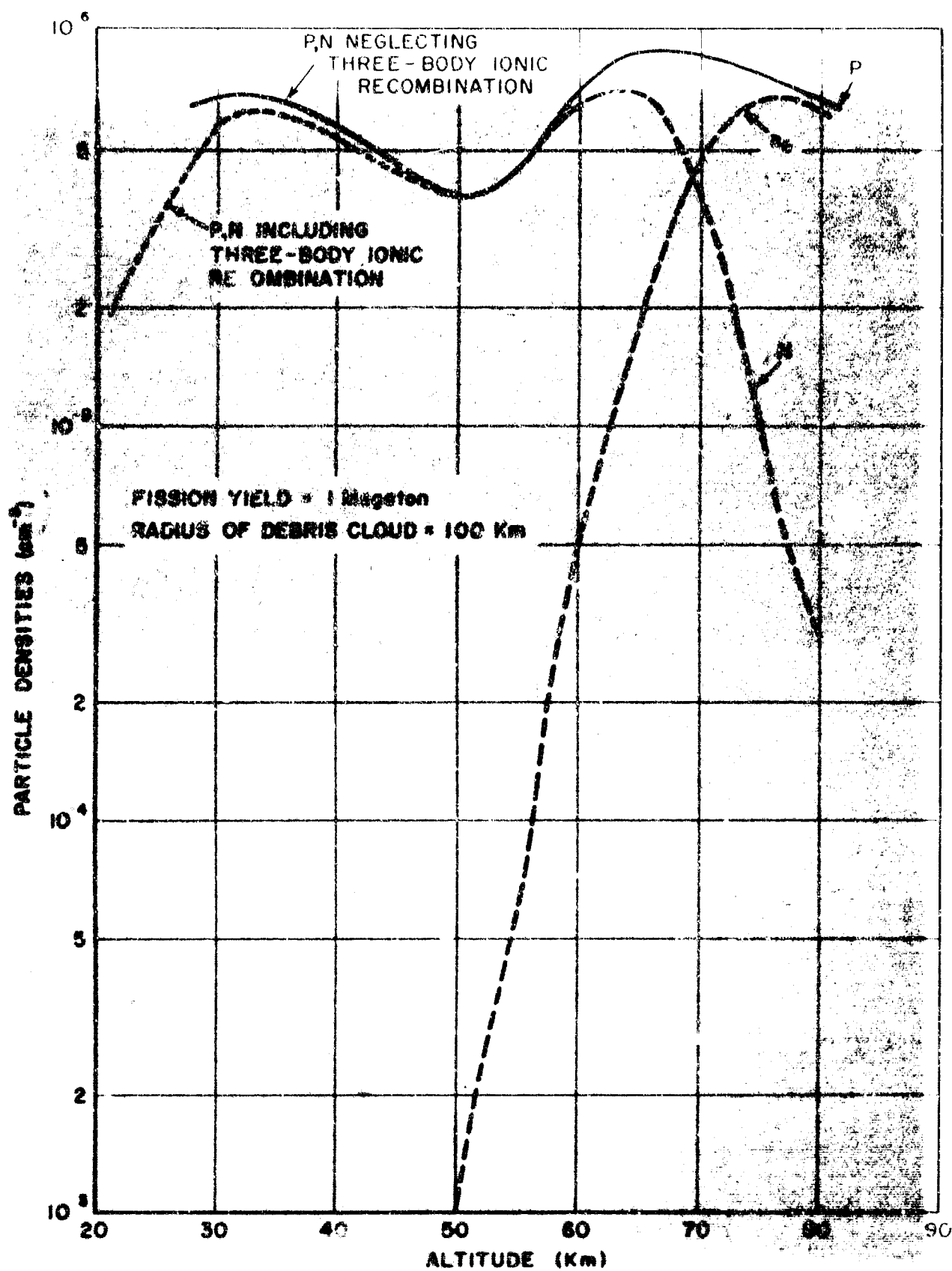


FIGURE 5.52- COMPUTED PARTICLE DENSITIES 1 HOUR AFTER
 DETONATION OF NUCLEAR DEVICE AT HIGH
 ALTITUDE

VI. SUMMARY OF RESULTS AND SUGGESTIONS FOR FURTHER WORK

A. Summary of Experimental Results

A laboratory experiment was developed to study the response of atmospheric gases to ionizing radiation under conditions resembling those in the D region of the ionosphere subjected to beta particles from trapped fission debris. The experiment, described in Chapter II, uses a large reaction chamber to minimize the effects of particle diffusion and wall-induced chemistry, neither of which is pertinent to the atmospheric processes under study. A spatially uniform beam of 1.5 Mev electrons, which approximates the mean energy of the fission-debris betas, irradiates the gas in the chamber. The subsequent behavior of the gas is then determined from simultaneous electron density, ion analysis, and optical emission measurements. As shown by the results described in the body of the report (summarized below), the information obtained from the laboratory measurements is in excellent agreement with that deduced from the limited atmospheric data which are currently available. In addition, one can study certain processes, notably ionic recombination, more directly in the experiment than can be done in the atmosphere or in other laboratory apparatus. As a result of the similarity between this laboratory environment and the disturbed upper atmosphere, which is borne out by the measurements described in this report, the experiment promises to provide detailed information concerning ionospheric processes over a wide range of atmospheric conditions.

Measurements were performed in oxygen, nitrogen, and 4:1 airlike mixtures of $N_2:O_2$, over the pressure range 0.005 to 10 Torr.

The principal processes observed include:

1. Production of electron-ion pairs by collisions of beam-electrons with neutral molecules; the rate equation is

$$\left(\frac{\partial n_e}{\partial t}\right) = K p i$$

where p is the gas pressure in Torr, i the current density of the incident beam in microamperes/cm². The values found for K in the three gases studied are

$$\left. \begin{aligned} K(\text{oxygen}) &= (5.1 \pm 0.) \times 10'' \\ K(\text{nitrogen}) &= (5.7 \pm 0.) \times 10'' \\ K(\text{air}) &= (5.5 \pm 0.) \times 10'' \end{aligned} \right\} (\text{cm}^3 \text{ sec Torr } \frac{\mu\text{amp}}{\text{cm}^2})^{-1}$$

These are the first direct measurements of total ion production coefficients for 1.5 Mev electrons reported in the literature. They are in excellent agreement with theoretical predictions.

2. Three-body attachment of electrons to neutral O₂ molecules; the rate equation is

$$\left(\frac{\partial n_e}{\partial t}\right)_{3\text{-body}} = -\beta n_e [O_2][X]$$

where $[O_2]$ is the number density of neutral O₂ molecules, and $[X]$ is the density of molecules serving as third bodies. In pure oxygen, where $[X] = [O_2]$, and in airlike mixtures, where $[X] = [N_2] + [O_2]$, the measurements yield

$$\beta_{\text{OXYGEN}} = (2.12 \pm 0.15) \times 10^{-30} \text{ cm}^6/\text{sec}$$

$$\beta_{\text{AIR}} = (1.10 \pm 0.05) \times 10^{-31} \text{ cm}^6/\text{sec}$$

These values are in excellent agreement with attachment rates deduced from atmospheric data [Knapp, 1966] and from laboratory measurements obtained with different ionization techniques [Pack and Phelps, 1966] indicating that the excitation technique does not critically affect the observed rate.

3. Diffusion of electrons controlled by the presence of negative and/or positive ions; the rate equation is

$$\left(\frac{\partial n_e}{\partial t}\right)_{\text{diff}} = D_{\text{eff}} \nabla^2 n_e$$

where the form of D_{eff} depends on the types and densities of the ions present. In oxygen the measurements are consistent with the value

$$(D_{\text{eff}} p)_{\text{OXYGEN}} = 110 \left\{ 1 + \frac{[O_2^-]}{n_e} \right\} \text{ Torr cm}^2/\text{sec}$$

in good agreement with the value derived from the measured validity of O_2^+ [Sampson, 1965].

The diffusion measurements in oxygen are among the few well-documented cases cited in the literature for the influence of negative ions on ambipolar diffusion. In air, the measurements are consistent with

$$(D_{\text{eff}} p)_{\text{AIR}} = 165 \pm 15 \left\{ 1 + \frac{N}{n} \right\} \text{ Torr cm}^2/\text{sec}$$

where N is the density of (unidentified)

negative ions. In nitrogen, the measurements

indicate that at low pressures, where N_2^+ is the dominant ion, $(D_{eff} p)_{NITROGEN} = (60 \pm 20) \text{ Torr cm}^2/\text{sec}$. At high pressures, where the dominant ions are a mixture of N_3^+ and N_4^+ ,

$$(D_{eff} p)_{NITROGEN} = (130 \pm 20) \text{ Torr cm}^2/\text{sec}$$

These are in general agreement with values computed from the best available mobility measurements [Keller, 1965].

4. Electron positive-ion recombination; the rate equation is $\left(\frac{\partial n_e}{\partial t}\right)_{\text{recomb.}} = -\alpha_e P n_e$

where P is the density of recombining ions. A value for α_e was determined from the air measurements;

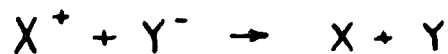
$$\alpha_e = (3 \pm 2) \times 10^{-7} \text{ cm}^3/\text{sec}$$

This is in excellent agreement with the results obtained by other workers for individual ions

$$\alpha_e(O_2^+) \approx 2 \times 10^{-7} \text{ cm}^3/\text{sec} \text{ [Kasner, 1961]}$$

$$\alpha_e(NO^+) \approx 4 \times 10^{-7} \text{ cm}^3/\text{sec} \text{ [Gunton, 1965]}$$

5. Mutual neutralization of positive and negative ions by the reaction



The rate equation is

$$\frac{dX^+}{dt} = \frac{dY^-}{dt} = -\alpha_i X^+ Y^-$$

In pure oxygen at low pressures, where the ions O_2^+ and O_2^- , the measurements are consistent with

$$(\alpha_i)_{O_2} = 1 \times 10^{-7} \text{ cm}^2/\text{sec}$$

to within a factor of two. This is believed to be the first reported laboratory value for $\alpha_i(O_2^+, O_2^-)$. In the airlike mixtures

$$(\alpha_i)_{\text{air}} = (3 \pm 2) \times 10^{-7} \text{ cm}^2/\text{sec}$$

where the positive ions are O_2^+ and NO^+ . The negative ions have not yet been identified.

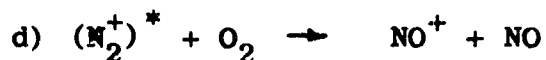
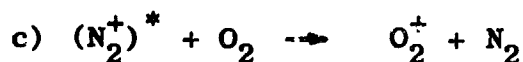
6. Quenching of optical radiation from the states $N_2(C^3\pi)$ and $N_2^+(B^2\Sigma)$ in binary collisions with ground-state N_2 and O_2 molecules. The observed two-body quenching cross-sections are:

	STATE	QUENCHER	CROSS-SECTION
N_2^*	$C^3\pi(v'=0)$	N_2	$(1.2 \pm 0.6) \times 10^{-16} \text{ cm}^2$
	$C^3\pi(v'=0)$	O_2	$(39 \pm 11) \times 10^{-16} \text{ cm}^2$
	$C^3\pi(v'=1)\dagger$	O_2	$(52 \pm 18) \times 10^{-16} \text{ cm}^2$
	$C^3\pi(v'=2)\dagger$	O_2	$(81 \pm 32) \times 10^{-16} \text{ cm}^2$
$(N_2^+)^*$	$B^2\Sigma(v'=0)$	N_2	$(69 \pm 10) \times 10^{-16} \text{ cm}^2$
	$B^2\Sigma(v'=0)$	O_2	$(123 \pm 21) \times 10^{-16} \text{ cm}^2$

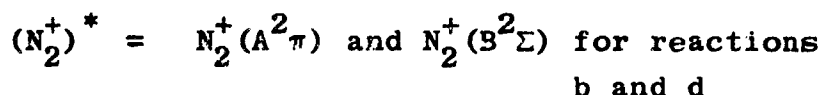
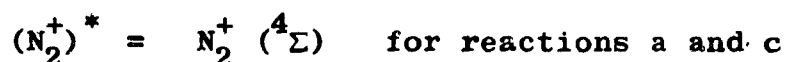
Measurements for states labelled with a dagger have not previously been reported in the literature. For the other states, the results for quenching by N_2 are in excellent agreement with values reported in the literature [Davidson, 1964; Brocklehurst, 1964]. The cross-sections for quenching by O_2 are about a factor

of two higher than reported by Brocklehurst, but appear to be in better agreement with atmospheric data [Hoerlin, 1966]

7. Ion-molecule reactions have been studied in nitrogen and airlike mixtures. The measurements suggest the following reactions and rate coefficients referred to total N_2^+ density:



Tentative assignments have been made of the excited states of N_2^+ participating in the various reactions. These are



Reactions b and d appear to account for the observed quenching of optical radiation from $N_2^+ (B^2\Sigma)$

The experimental results cited above show broad areas of agreement with in situ measurements of the properties of the disturbed ionosphere. The situation is not so straightforward with regard to the agreement of this work with that of other laboratories using different modes of excitation of the gas. Several reactions, notably three-body attachment and positive ion-electron recombination, appear to have the same rates as are found in electron swarm and microwave afterglow studies. Ion-molecule reactions, however, which are strongly dependent on the excited state configuration of the ion, are qualitatively different in this experiment from those observed by other workers using low-energy electrons. Some reactions, such as ion-ion two-body recombination, have not been studied in sufficient detail by other workers to permit comparison with the present results.

The lumped-parameter experiment thus appears to serve three functions which are of great importance to DASA's overall program. First, it provides a good approximation to the phenomenology of the disturbed upper atmosphere, at least at altitudes between 30 and 80 kilometers. Second, by taking advantage of the unique characteristics of this experimental facility (such as the large size of the chamber and the variety of available diagnostic techniques) one can use the experiment to study individual reactions in detail. Finally, by virtue of the similarity of the excitation employed here to that occurring in the beta-irradiated upper atmosphere, the lumped-parameter experiment will be useful in determining which reactions observed under various laboratory conditions are likely to be important in the disturbed ionosphere.

B. Suggestions for Further Work

Several modifications could profitably be made to the program which would improve the accuracy of the measured reaction rates and extend the range of atmospheric conditions which can be studied by the lumped-parameter experiment.

The single greatest improvement in the accuracy of the measured reaction rates can be brought about by the use of a numerical computation of the complete set of reaction equations. By taking proper account of the spatial distributions of the charged particles, one can expect to obtain better fits to the low pressure data, both in-beam and afterglow. The rate coefficients deduced from complete solutions will be more accurate than those derived in the report from an approximate analysis. From these solutions, it will be possible to determine the error introduced by the spatial congruence assumption in specific laboratory situations.

Future experiments should be performed on gas mixtures which more closely approximate the neutral composition of the D region. The inclusion of CO_2 , water vapor, and the nitrogen oxides should yield particularly interesting results in their effect on attachment and detachment, on ionic composition, and on the effective rates for ion-ion and ion-electron recombination. The temperatures at which the experiments are performed should be varied between 200 and 500°K. This will permit the observation of collisional detachment, as well as the evaluation of temperature dependences of the various rate coefficients in a range directly comparable to ionospheric conditions. More effort should be spent measurements at high beam fluxes to evaluate electron-positive ion recombination coefficients with greater accuracy.

Two modifications should be made to existing experimental apparatus which would increase the detail with which the state of the gas can be determined. First, time resolved mass spectrometric measurements should be made available, so that the transient production and loss of mass-analyzed ions can be studied in detail. This will permit the assignment of a diffusion coefficient to each ionic species. It will also permit the observation of gross differences in the ionic constitution of the gas during and after irradiation. Time-resolved optical absorption studies should also be made to determine the densities of those excited states of the neutral and ionized molecules which are believed to participate in ion-molecule reactions.

The lumped-parameter experiments should also be repeated in chambers of vastly different sizes from the one used here. With a chamber of linear dimensions some ten times smaller than the one used in this work, it should be possible to study electron densities in diffusion-controlled situations up to pressures of 10 Torr in air. From measurements of this type at low beam currents, one can evaluate ion-ion recombination coefficients in a pressure region where the three-body process dominates. Conversely, a much larger chamber could make that altitude range above 80 km, in which atomic oxygen is an important neutral constituent, accessible to laboratory study. This would permit the study of associative detachment, radiative attachment to O, and various ion-molecule reactions which depend on atomic oxygen.

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