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THE PHOTOIONIZATION OF NITRIC OXIDE

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Abstract

The photostationary concentration of ions in gaseous nitric oxide has been measured using a Langmuir probe. The ion concentration depends on the square root of the ion production rate, which indicates that ions and electrons disappear predominately by dissociative recombination. In addition, the rate of decay of the electron concentration in the gas after interruption of the ionizing radiation has been measured. The data indicate that the ion-electron dissociative recombination rate constant is no greater than 2×10^{-6} cm^3/ion sec, and may be as low as 4×10^{-7} cm^3/ion sec.

The photoionization of nitric oxide has been studied by Tanaka and Steacie[1] and by Zelikoff and Aschenbrand.[2] Tanaka and Steacie were primarily interested in using the ion current produced by krypton photosensitization as a means of measuring the quenching cross-section of various added gases for the krypton excitation. Zelikoff and Aschenbrand showed that the application of strong electric fields increased the rate of destruction of a photoionized sample of nitric oxide, presumably through acceleration of the free electrons to ionizing energies. However, no attempt has yet been made to examine the detailed processes by which the ions and electrons disappear from the gas. It seems very probable that the de-ionization of the gas is dominated by the ion-electron dissociative recombination reaction

$$NO^+ + e \longrightarrow N + O \qquad (1)$$

The purpose of this work was to measure the rate constant for this reaction, which is a quantity of interest in upper atmospheric chemistry and in radiation chemistry. Two quite different techniques were employed. In the first method, the rate of ionization, denoted by q, was combined with the photostationary concentration of ions n, as measured by a Langmuir probe, to give α, the second order rate constant of reaction 1, by the relation

$$\alpha = q/n^2$$

The second method involved a measurement of the rate of decay of the electron concentration after the photoionization source was interrupted. These two complementary methods yield values of α which are in satisfactory agreement, considering the uncertainty of the measurements.

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1 I. Tanaka and E.W.R. Steacie, Can. J. Chem., 35, 821(1957).

2 M. Zelikoff and L. Aschenbrand, J. Chem. Phys., 25, 674 (1956).

EXPERIMENTAL

The vacuum ultraviolet light source for these experiments has been previously described.[3] The krypton resonance line at 1236 A was used as the ionizing radiation. The reaction vessel was a pyrex tube 65 mm in diameter which contained a probe and two parallel plate electrodes surrounded by guard rings. The probe consisted of a tungsten wire 0.0025 cm in diameter and was 1.0 cm long. It was supported midway between the parallel plates by a large tungsten wire enclosed in a glass sheath. The parallel plates and guard rings were made of stainless steel. The inner electrodes proper were 2 cm in diameter and were surrounded by annular guard rings 1 cm wide. The separation between the parallel plates was 2 cm. Light entered the cell from the lamp through a lithium fluoride window 25 mm in diameter.

In order to determine the rate of production of ions, one of the parallel plates and its guard ring was grounded. The other plate was connected to a battery to which potentials up to 135 volts could be applied. The second guard ring was charged to a potential equal to that of its electrode by means of a separate battery. Current drawn from the vessel by the electrode and battery was measured with a Keithley 610A electrometer. A reduction in the current to the electrodes by a factor of two was observed when the guard rings were connected, indicating that they were functioning properly. From the known volume between the center electrodes from which a saturation current was drawn, the rate of production of ions per cc per second could be calculated.

For the probe measurements, all the parallel plates and guard rings were connected together and grounded and a potential of up to 90 volts, of reversible polarity, was applied between the probe and the electrodes. The current

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[3] B.H. Mahan, J. Chem. Phys. 33,959(1960).

drawn was again measured with the electrometer.

For the charge decay measurements, the plates and guard rings were again connected together at ground potential and the probe was made 1.5 volts positive. The electron current drawn by the probe returned to ground through a one megohm resistor, and the resulting voltage was observed as a function of time on a Tektronix Type 555 oscilloscope with a Model H preamplifier. In order to interrupt the ionizing radiation in a short time compared to the decay time of the ion concentration in the cell, a 6130 thyratron was connected from the magnetron high voltage supply to ground. At zero bias, the thyratron did not conduct and the magnetron operated normally. However, when interruption of the lamp was desired, the grid of the thyratron was made approximately 50 volts positive with respect to the cathode and the thyratron fired, dropping the high voltage to zero in a very short time. Provision was made to trigger an oscilloscope sweep from the firing of the thyratron. The output of the lamp was examined with a photomultiplier and oscilloscope and it was found that the intensity of the lamp dropped to one-half its original value within 20 microseconds of the time of the firing of the thyratron.

The gases used were handled in a conventional mercury-free vacuum system. The tank nitric oxide was purified by passing through a trap at -78°C and evacuation at -195°C. High purity nitrogen was used without further purification as were hydrogen and helium. The impurity level in the nitrogen was found mass spectrometrically to be less than one part per million and the hydrogen and helium were pure to within one part in ten thousand. Pressures in the vacuum system were measured either by a thermocouple gauge or mercury manometer. The pressure of nitric oxide was kept low enough in the reaction vessel that uniform ionization was insured, with at most two percent of the initial radiation being absorbed.

RESULTS AND DISCUSSION

The current-voltage characteristic obtained using the parallel plate electrodes and a nitric oxide pressure of 0.05 mm is shown in Fig. 1. As the voltage increases it appears that a saturation region is encountered, in which the current is limited by the rate of ionization in the volume elements between the electrodes. Actually, true saturation is only encountered when the mean free path of the ions approaches the vessel dimension, which is not the case in our measurements. One can interpret the current-voltage curves by a theory developed by Thomson.[4] Detailed treatment of our data shows the current observed at 90 volts is within 25 percent of a true saturation current. Therefore, we have used the value of the current at 90 volts to calculate q, the number of ion-electron pairs produced per second per cubic centimeter. Higher applied voltages were not used in order to avoid electron multiplication processes.

Many attempts were made to measure the steady-state ion concentration by use of the conventional Langmuir[5] probe and the floating double probe method of Johnson and Malter.[6] However, both these techniques depend on surrounding a negative probe with a well-defined sheath of positive ions which completely neutralizes the charge on the electrode. Because of the relatively small rate of ionization employed in our experiments a sheath of small, well defined radius could not be obtained without seriously depleting the concentration of ions in the bulk of the gas. Therefore we made use of another probe method, also proposed by Langmuir, in which no sheath exists and the current to the

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[4] J.J. Thomson and G.P. Thompson, Conduction of Electricity Through Gases, Cambridge University Press, 1928.

[5] I. Langmuir and H. Mott-Smith, Gen. Elect. Rev., 27, 449, 538, 616, 762(1924).

[6] E.O. Johnson and L. Malter, Phys. Rev., 80, 58 (1950).

probe electrode is determined by the orbital motion of ions in the field of the probe. This method is applicable only in situations where the mean free path of the ions is large compared to the radius of the probe, and therefore measurements must be made at relatively low total pressures. The mathematical analysis of this method was first given by Mott-Smith and Langmuir[7] as a special case of a more complicated general situation. Therefore we present here a shorter derivation which exposes the assumptions more clearly.

Consider a long cylindrical probe parallel to the z axis. Positive ions having just made a collision at a distance of approximately one mean free path may have trajectories which carry them near or to the probe. It is assumed that at the start of the trajectory the ions have only kinetic energy, and that they are attracted by the probe. Since the field of the probe is cylindrically symmetric the initial velocity component parallel to the z axis will be a constant of the motion. Conservation of total energy and of angular momentum then give

$$\tfrac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + U(r) = \tfrac{1}{2} mg^2$$

$$b (g^2 - \dot{z}^2)^{1/2} = r (\dot{x}^2 + \dot{y}^2)^{1/2}$$

where g is the magnitude of the initial velocity vector, $U(r)$ is the potential energy of an ion of mass m at a perpendicular distance r from the wire, and b is the impact parameter, or aiming error in the x-y plane. Evaluation of these expressions at $r = R$, the probe radius, and elimination of all but the constants of motion gives

$$b_m^2 = R^2 \left\{ 1 - \frac{2\,U(R)}{m(g^2 - \dot{z}^2)} \right\}$$

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[7] I. Langmuir and H. Mott-Smith, Phys. Rev., 28, 727 (1926).

as the critical or maximum impact parameter which will allow an ion to reach the probe. The factor $\frac{1}{2} m (g^2 - \dot{z}^2)$ is just the initial total kinetic energy in the x-y plane. If the space potential, as determined by the large plate electrode, is taken as zero then the potential energy of an ion at the probe surface is $-eV$, where V is the voltage difference between the plate and the probe. Since the measurements are made in such a way that $eV \gg \frac{1}{2} m(g^2 - \dot{z}^2)$, we can write

$$b_m = R \left(\frac{2eV}{m(g^2 - \dot{z}^2)} \right)^{1/2}$$

The collision cross-section of an ion with the probe is $2b_m \ell$, where ℓ is the length of the wire probe. The total collision rate with the wire is obtained by multiplying this quantity by the speed in the x-y plane and the concentration of ions n, to give

$$2 R \ell \left\{ \frac{2eV}{m(g^2 - \dot{z}^2)} \right\}^{1/2} (g^2 - \dot{z}^2)^{1/2} n$$

The two velocity factors cancel, and the current at the probe is given by

$$i = 2\sqrt{2} \frac{R \ell e^{3/2}}{m^{1/2}} n V^{1/2}$$

Therefore a plot of i^2 as a function of probe potential should be linear, with a slope which measures the ion concentration. It has been assumed that the collision cross-section of electrons with the probe is essentially zero due to the electrostatic repulsion.

Our data were obtained at a total pressure of 0.05 mm, which should correspond to a mean free path of approximately 0.02 centimeters. This is large compared with the probe radius which was 0.00125 centimeters. Fig. 2 shows that the predicted linear dependence of i^2 on V is observed over most of the voltage range. At higher pressures noticeable deviations from linearity occur as expected. In order for the slope to yield reliable values of the

ion concentration, each collision of an ion with the probe must result in charge neutralization. It seems probable that this is the case, since ions which strike the probe but are not discharged will almost certainly lose some of their kinetic energy and then describe closed orbits about the probe. These closed orbits inevitably lead to another collision with the probe, and a second possibility of neutralization. Another requirement is that the plasma potential be set by the large electrode so that the potential difference between the large electrode and the probe measures the difference between the potential energies of an ion at the beginning and end of its trajectory. As long as the mean free path is large, and the current drawn by the probe is small, this condition should be satisfied, since no disturbing local space charges are to be expected in such a situation. However, there is a noticeable curvature in the probe characteristic as the potential difference between the plate and probe approaches zero. This is probably caused by preferential diffusion of the electrons to the walls of the vessel which results in raising the plasma potential with respect to the probe even when there is no applied voltage. When the probe is first made negative with respect to ground the plasma becomes less positive with respect to ground due to the fact that positive ions are being lost to the probe.[6] The effective change in the probe potential with respect to the plasma is therefore less than the change in the applied voltage, so the increase in current for a given voltage change is small. As the probe is made still more negative this effect will become progressively less important since the plasma potential attains a small but essentially constant value which is positive with respect to ground. The voltage change in the linear portion of the characteristic should then faithfully represent a change in probe potential with respect to the plasma.

In addition to ion-electron recombination, ions are lost by diffusion to the walls of the vessel and by conduction to the probe. The latter effect will be small if the current drawn to the probe is small compared with the saturation current to the plates. The currents used to obtain the linear portion of the probe characteristic were never more than one tenth of the saturation currents, so that the measuring current perturbed the ion concentration only slightly. The question of diffusional loss was treated by Sayers[8] in connection with experiments on ion-ion recombination. Diffusional loss will make a contribution to an assumed second order ion-electron recombination coefficient amounting to

$$\alpha' = \frac{3}{2} D/nd^2$$

where D is the diffusion coefficient of the positive ion, n is its concentration, and d is the minimum vessel dimension. For the nitrosonium ion D is approximately 0.05 cm^2/ sec at NTP, d is two centimeters and in our experiments the ion concentration was never much higher than 10^9 ions/cc, so the effective diffusional correction to α is at least 2×10^{-7} cc/ion sec, at the lower pressures. It is seen that the success of the probe method at low pressures depends on having the highest possible ion concentration. It must not be assumed that the probe measurement will be valid only if the value of α is large, however. If we make the substitution

$$n = (q/\alpha)^{1/2}$$

$$\alpha' = \frac{3}{2} D\alpha^{1/2} / d^2 q^{1/2}$$

we see that the correction becomes less important as the true α becomes smaller, if q is kept constant. Although it would appear that diffusion

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8 J. Sayers, Proc. Roy. Soc., A169, 83 (1938).

does not dominate the charge loss, a test of this assumption is provided by plotting n^2 as a function of q. If ion-electron combination were the dominant method of charge loss a straight line should result, while if diffusional loss were important deviation from linearity should result. If diffusional loss were dominant, a plot of n as a function of q should be linear. Fig. 3 shows that n^2 is a linear function of q in the region of high ion concentration. Fig. 4 shows that a plot of n as a function of q is noticeably curved. The slope of the linear portion of Fig. 3 can be taken as a measure of α, and the result is $\alpha = 1.8 \times 10^{-6}$ cc/ion sec. This number should be accepted as an upper limit since all the possible errors which have been mentioned tend to make the measured value of α too large.

In order to further confirm the validity of the probe measurement of α, experiments were carried out which were designed to measure the rate of decrease of the ion concentration after the ionizing radiation was extinguished. This was accomplished by measuring the current collected by a positive probe as a function of the time elapsed after interruption of the light. The probe current should be proportional to the first power of the electron concentration if the current drawn is so small as to avoid polarization effects. Therefore, if a fixed voltage is applied to the probe, the second order ion-electron recombination coefficient can be derived from a plot of the reciprocal of the current as a function of time, if the proportionality constant between current and electron concentration is known. However, this proportionality constant involves electron temperature and is poorly defined for electrons in the small fields employed here, so another relation between current and concentration was used to allow the calculation of absolute values of α. The conductivity of the gas in the photostationary condition provides this relationship. If we express all ion concentrations as a fraction f of the initial photostationary

concentration n_o, we have

$$n_o^2 = q/\alpha$$

$$1/n - 1/n_o = \alpha t$$

$$1/f - 1 = (q\alpha)^{1/2} t$$

The value of f is directly calculated from the deflection of the oscilloscope trace produced by the probe current. Fig. 5 shows the results of typical experiments done with nitric oxide in the absence and presence of added nitrogen. At pressures above 0.1 mm diffusional loss should be negligible in the early stages of the decay, and it is seen that the reaction follows the second order rate law for more than two half-lives. Deviations from the second order kinetics are to be expected as the ion concentration decreases, since the fraction of ions lost to the measuring circuitry increases as time increases. Moreover, diffusional loss should become more important in the later stages of the reaction. In experiments done with 0.05 mm of nitric oxide alone in the cell it is apparent that deviations from second order kinetics occur somewhat earlier than in experiments done at higher pressures. However, it is possible to conclude that even at the lower pressures diffusional loss does not make a major contribution when the initial ion concentration is greater than 5×10^8 ions/cc. This conclusion is consistent with the results of the low pressure probe measurements.

The observed second order kinetics also show that the loss of ions to the measuring circuitry did not seriously affect the decay rate, at least in the initial stages of the reaction. This is to be expected, since only five percent of all the ions present in the cell at the time of the interruption of the light were lost to the measuring circuitry in the first two half-lives. It was possible, however, to observe serious deviations from second order kinetics if the current drawn from the cell in the measurement was increased

by an order of magnitude.

At total pressures above one millimeter it is possible that attachment of electrons to nitric oxide and subsequent ion-ion reactions might become an important mechanism for charge loss. The probe measurements, while having no quantitative significance in this pressure range, provided a way of demonstrating that free electrons are still the predominant negative species present in the decay measurements. Due to the difference in the mobilities of positive ions and electrons, the current-voltage characteristic of the probe immersed in an ion-electron gas is highly asymmetric about zero applied voltage. This asymmetry could be eliminated by adding molecular oxygen, which converts the electrons to negative ions. The asymmetry expected for an ion-electron gas persisted, however, in the mixtures used in the decay measurements. A further indication of the unimportance of negative ions in our experiments can be obtained if it is assumed that the electron attachment coefficient of nitric oxide is no greater than that of oxygen. The electron attachment coefficient for oxygen has been reported by Biondi[9] to be 2×10^{-30} cc^2/sec. Therefore the ratio of the electron attachment rate to the ion-electron recombination rate is given by

$$\frac{k\,(NO)(M)(e)}{\alpha\,(NO^+)(e)}$$

where k is the attachment coefficient, (M) is the concentration of inert gas, and (e) is the electron concentration. In our experiments, the attachment rate is one tenth the recombination rate at a total pressure of one millimeter, if the nitric oxide pressure is 0.05 millimeter, and α is taken as 10^{-6}. Naturally the later stages of the reaction attachment will become more important. It seems that while below one millimeter pressure the measured α is relatively unaffected by attachment processes, at higher pressure this effect can become

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9 M. Biondi, Symposium on Chemical Reactions in the Lower and Upper Atmosphere, San Francisco, California, 1961. Proceedings to be published.

important. Therefore the most reliable measurements are those in the pressure range from 0.05 to 1.5 millimeters. These data are contained in Table 2. There is no discernable trend in the measured value of α in this pressure range, although the imprecision of the data make detection of systematic variation difficult. The inherent imprecision of this method is due to the electrical disturbances which necessarily occur when the photolysis lamp is extinguished and make it difficult to obtain a precise value of the initial deflection of the oscilloscope trace.

The average value of α as determined by the decay experiments is 3.2×10^{-7}, while the probe method gives 2×10^{-6} cc/ion sec. The value determined by the probe method might be expected to be high, since diffusional loss is apt to be most important in these low pressure experiments. Furthermore, the probe method is very sensitive to small errors in the ion concentration, since the square of this factor enters the calculation. Similarly the concentration decay method is seriously affected by errors in the choice of the initial steady state concentration. Considering these sources of imprecision, the agreement between the two methods is all that can be expected. An ion-electron recombination coefficient of approximately 3×10^{-7} is consistent with previously reported values for several molecular gases,[10] and somewhat less than the recently reported values for the ions produced by an electrical discharge through water.[11]

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10 L.B. Loeb, Basic Processes of Gaseous Electronics, Univ. of California Press, Berkeley, 1955.

11 S. Takeda and A.A. Dougal, J. Applied Phys., 31, 412 (1960).

ACKNOWLEDGEMENT

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TABLE I

Determination of α by the Steady State Method [a]

Run	NO Pressure	$q \times 10^{-12}$	$n \times 10^{-8}$	$\alpha \times 10^{6}$
3	0.050	1.2	8.6	1.6
4	0.050	1.4	7.9	2.2
6	0.050	0.75	6.3	1.9
7	0.050	1.0	7.7	1.7
8	0.050	0.42	4.5	2.1
9	0.120	0.50	4.5	2.5
10	0.120	0.25	2.4	4.2
11	0.120	0.50	3.5	4.0
12	0.020	0.32	2.9	3.4
13	0.020	0.15	1.7	5.0
14	0.020	0.44	3.6	3.3
15	0.070	1.8	9.2	2.2
16	0.070	0.71	5.7	2.1
17	0.070	1.4	8.3	2.0
18	0.055	1.7	10	1.7
19	0.055	1.8	11	1.5
20	0.055	0.58	5.8	1.7
21	0.055	0.34	3.7	2.4
22	0.060	1.3	7.7	2.1
23	0.060	1.4	8.9	1.7
24	0.150	6.6	14	3.2
25	0.150	3.8	13	2.2
26	0.150	2.4	10.5	2.2
27	0.150	4.3	14	2.1
28	0.070	2.1	11	1.8
29	0.070	2.5	12	1.8

[a] Pressures are given in millimeters; the units of q are ions/cc sec; those of n are ions/cc, and α is in cc/ion sec.

TABLE II

Determination of α by the Dynamic Method [b]

Run	Pressure NO	Pressure N_2	Probe Voltage	$\frac{d}{dt}(1/f)$	$q \times 10^{12}$	$\alpha \times 10^{6}$
120	0.130	-	3.0	1.6×10^{3}	3.2	8.0
121	0.130	-	1.5	1.2	3.2	4.5
122	0.130	-	6.0	(first order)	-	-
123	0.110	-	0.7	1.2	2.9	5.2
124	0.050	-	1.5	1.3	1.3	14.0
125	0.073	-	1.5	0.79	1.9	3.2
126	0.140	-	1.5	1.0	3.8	2.6
127	0.190	-	1.5	1.23	5.1	2.9
128	0.050	-	1.5	1.15	1.33	9.8
129	0.210	-	1.5	1.43	4.4	4.7
130	0.250	-	1.5	1.13	5.4	2.4
133	0.050	1.3	1.5	0.78	1.06	5.7
136	0.050	1.0	1.5	0.66	1.15	3.8
137	0.050	0.6	1.5	0.54	1.12	2.6
138	0.050	1.7	1.5	0.53	1.12	2.5
141	0.050	1.1	1.5	0.57	1.11	3.4
142	0.050	0.8	1.5	0.50	1.11	2.3

[b] Pressures are given in millimeters; the units of the time derivative of 1/f are seconds^{-1}; q is given in ions/cc sec, and α in cc/ion sec.

Figure Captions

Fig. 1 - The current to the parallel plates as a function of applied voltage.

Fig. 2 - The square of the positive ion current collected by the probe as a function of voltage.

Fig. 3 - The square of the steady state ion concentration as a function of the rate of production of ions, q.

Fig. 4 - The steady state concentration of ions n as a function of the rate of production of ions, q.

Fig. 5 - The quantity 1/f as a function of time for the ion decay experiments. Open circles correspond to run 126, done with 0.14 mm of nitric oxide alone, and solid points represent run 136, done with a mixture of 0.05 mm of nitric oxide and 1.0 mm of nitrogen.

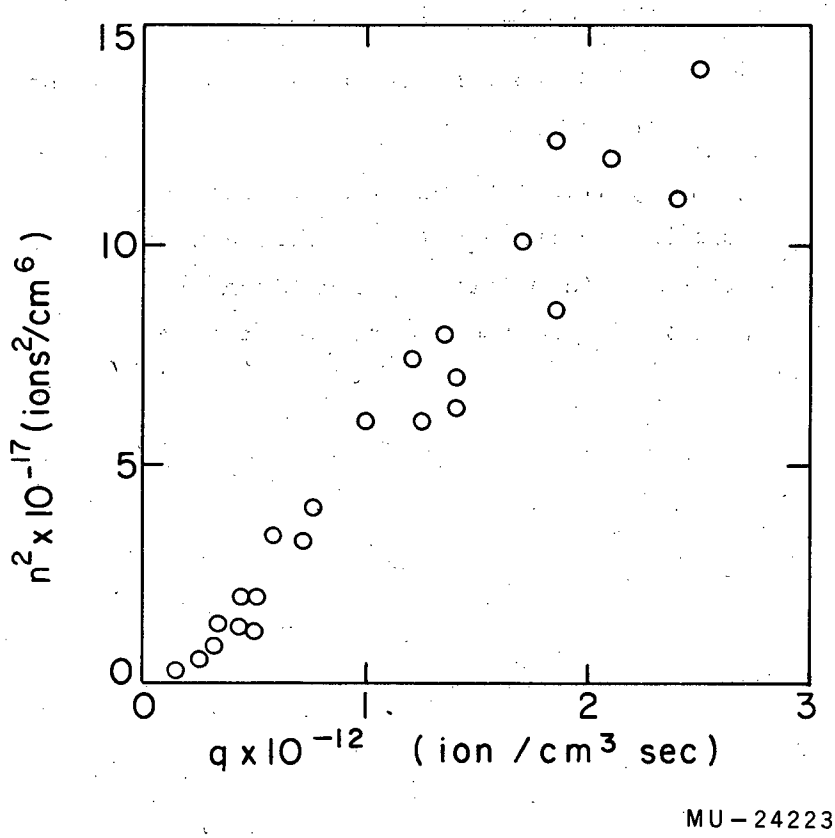
15
10
5
0
0
1
2
3
$n^2 \times 10^{-17}$ (ions^2/cm^6)
$q \times 10^{-12}$ (ion / cm^3 sec)
MU-24223

Fig. 1

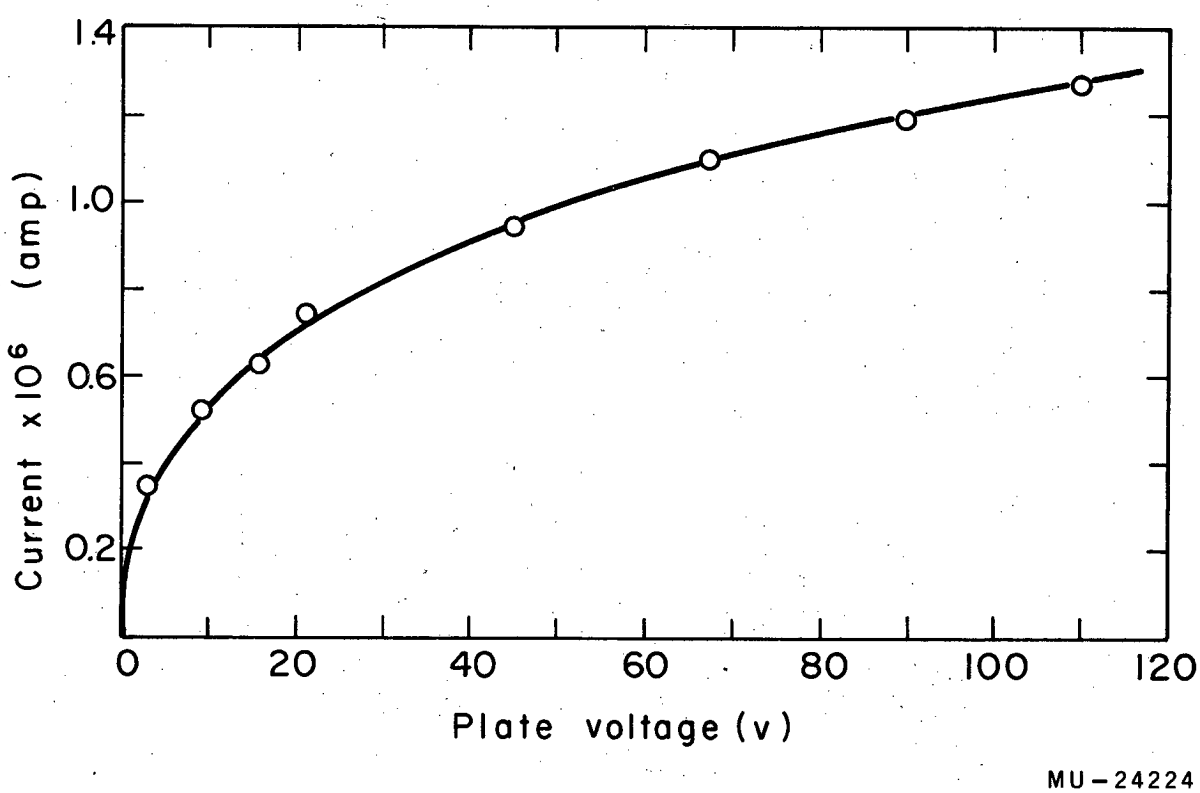
1.4
1.0
0.6
0.2
Current x 10^6 (amp)
0
20
40
60
80
100
120
Plate voltage (v)
MU-24224

Fig. 2

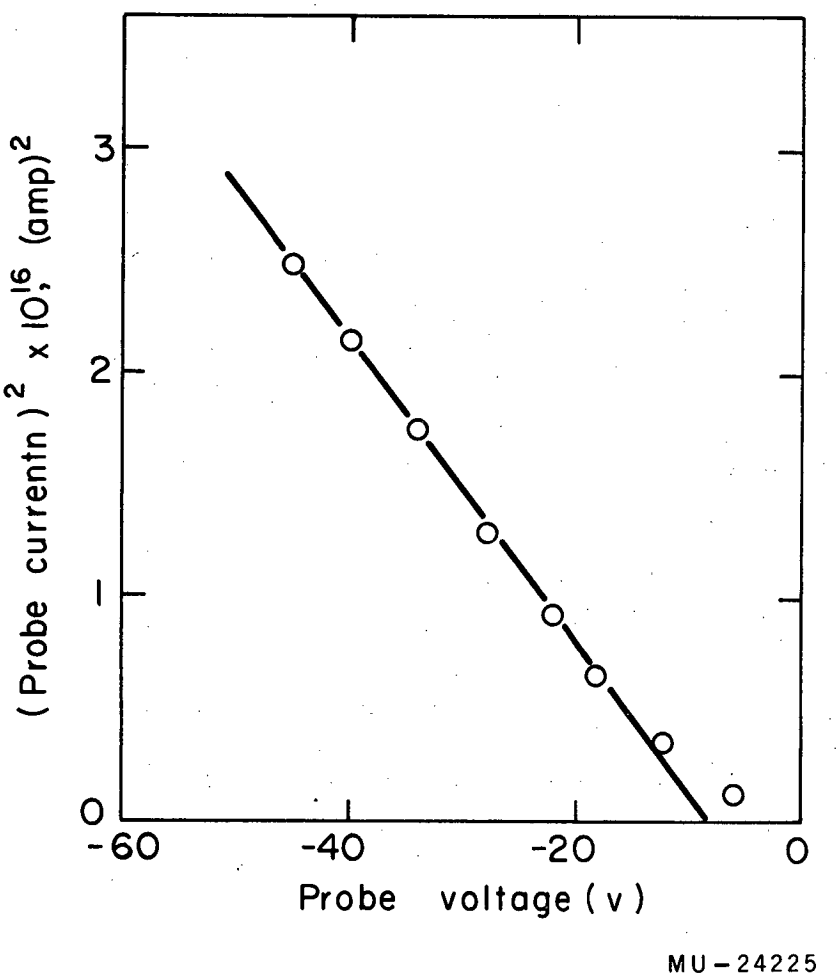
(Probe currentn)^2 x 10^{16}, (amp)^2
3
2
1
0
-60
-40
-20
0
Probe voltage (v)
MU-24225

Fig. 3

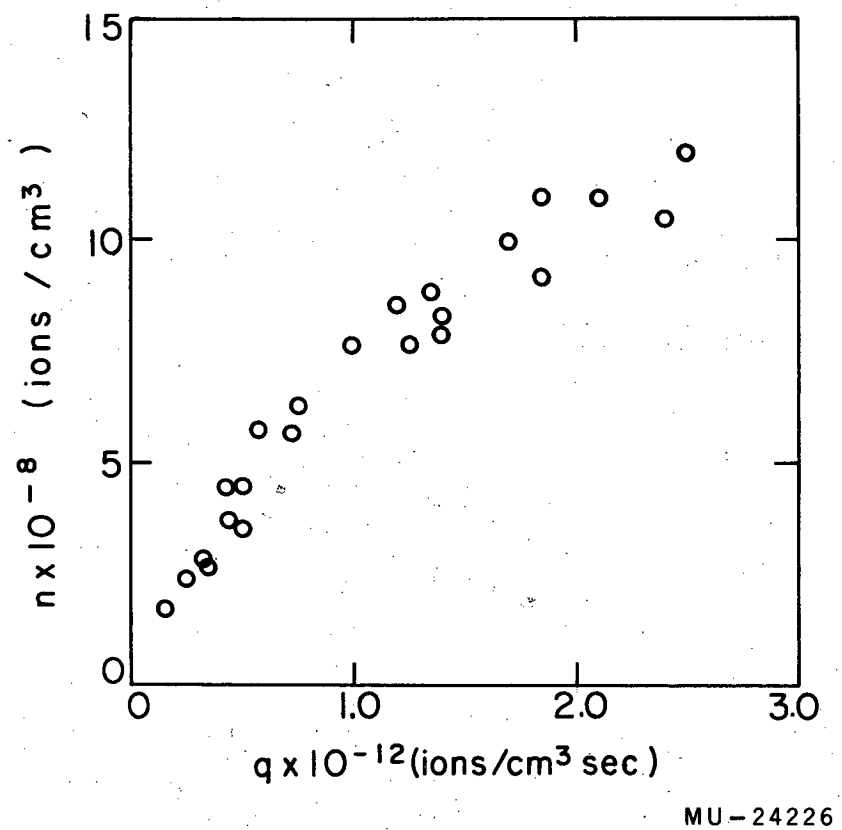

Fig. 4

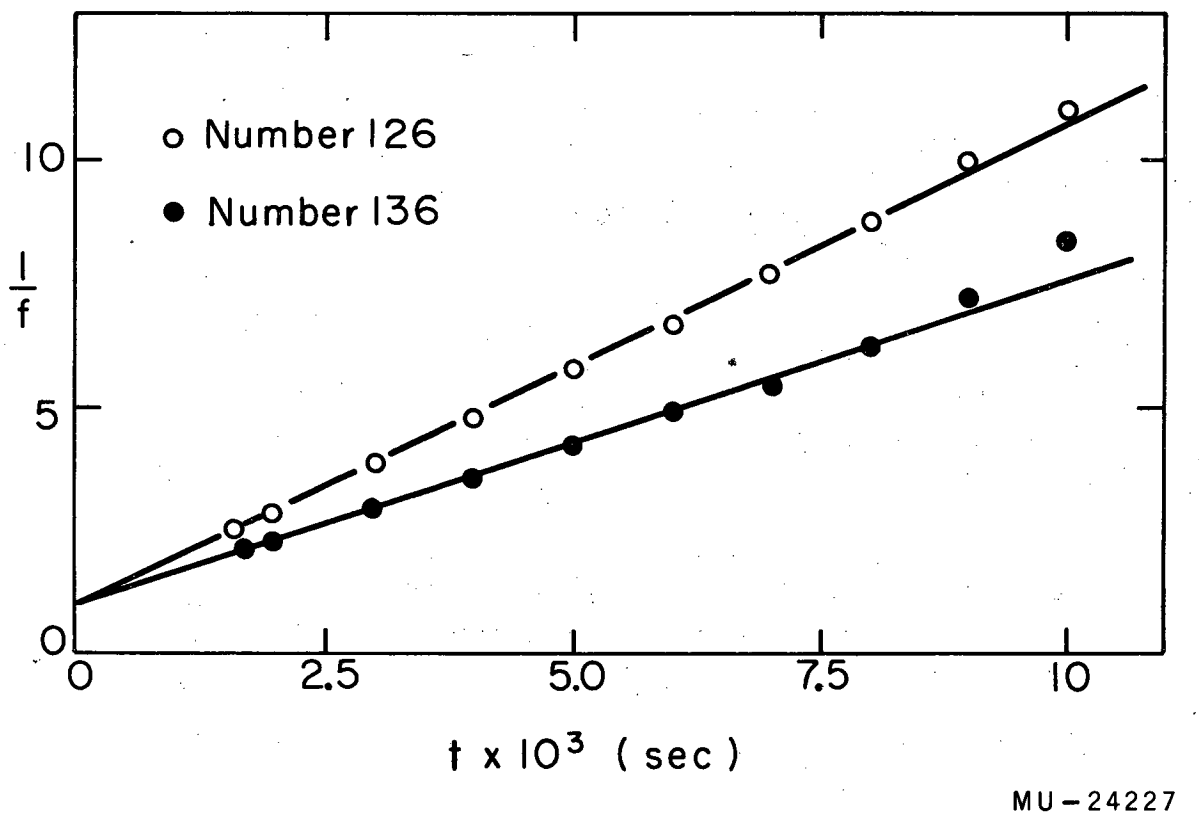

Fig. 5

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