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Rate Coefficient for $X^+ + 2X \rightarrow X_2^+ + X$ in Neon and Argon*

J. P. Gaur and L. M. Chanin
Department of Electrical Engineering, University of Minnesota, Minneapolis, Minnesota 55455
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A method is described of determining three-body conversion coefficients for the production of homonuclear diatomic ions. The technique involves ion sampling from the positive column of a dc discharge. For neon, values of the rate coefficient vary from $5.7–8.9 \times 10^{-32}$ cm^6/sec depending on the values of a number of experimental parameters. In argon values range from $3.0–4.7 \times 10^{-31}$ cm^6/sec. The present results are compared with values obtained using other techniques.

I. INTRODUCTION

Homonuclear diatomic ion formation in noble gases is believed to occur primarily by two types of collisions. At low pressures the dominant formation process is a two-body association involving an interaction between an excited atom and one in the ground state.[1] At high pressures molecular ion formation generally takes place by three-body conversion. Here the collision complex involves two atoms and an atomic ion.

The first reliable measurement of three-body conversion frequencies in the noble gases was that reported by Phelps and Brown.[2] These studies using mass analysis, involved measurements of positive ions in the afterglow of a low-pressure helium discharge. Versions of this technique have been used by a number of investigators[3–6] to evaluate conversion frequencies or rate coefficients in helium, neon, and argon. Within the past few years three-body conversion coefficient values have also been reported from studies of the conversion of ions drifting in a gas.[7]

In the course of recent cataphoresis studies[8] involving ion sampling from dc discharges, we attempted to measure the three-body conversion coefficient for pure neon and argon. The measurements involved sampling of the atomic and molecular ions from the positive column of a high-pressure dc discharge. The method is relatively direct by comparison with other techniques. Moreover comparison of conversion coefficient values inferred from active discharges and afterglows provides important information as to whether or not the plasma environment significantly affects the formation process.[9,10] The present article describes the method of measurement, the analysis and results obtained for neon and argon.

II. APPARATUS

The apparatus used in the present studies is a modified version of the system used for studies of the cataphoresis effect.[8] A block diagram of the equipment is shown in Fig. 1. That portion of the apparatus shown within the dashed line was mounted on a standard high-vacuum-gas handling station.[11] The cylindrical discharge tube consisted of a 100 cm length of precision bore 2.22-cm Pyrex tubing. The molybdenum electrodes were identical, of the hollow cathode design, and the cathode was shielded so as to minimize sputtering effects.[12] The cathode was movable relative to the sampling orifice. The discharge tube had a conically-shaped sampling orifice with the smallest diameter of approximately 35 μ. All ion signal measurements were made in the positive column and sufficiently far removed from the cathode region so that trace impurities if any, due to cataphoretic pumping, were not detectable. The use of a movable cathode permitted electric field measurements to be made by measuring the potential drop across the discharge tube for a constant current value. A number of thermocouples, not shown in Fig. 1, were used to monitor the temperature of the walls of the discharge tube, and thus could be used to estimate the gas temperature. Measurements of the gas pressure were made using a bakeable capacitance manometer. An automatic pressure controller was used to compensate for gas loss through the sampling hole. Gas samples used in the study were research-grade neon and argon. The quadrupole mass spectrometer was a 20-cm bakeable type which has been described previously.[13] It was operated at a constant Δm mode to minimize mass discrimination caused by radial entrance momentum.[14] Ion signals from the quadrupole were amplified by a ten-stage SPM 01-301 Dumont multiplier. As shown in Fig. 1 a small cylindrical probe P was located opposite to the sampling hole. The potential of this probe was used to estimate the wall potential of the discharge tube.

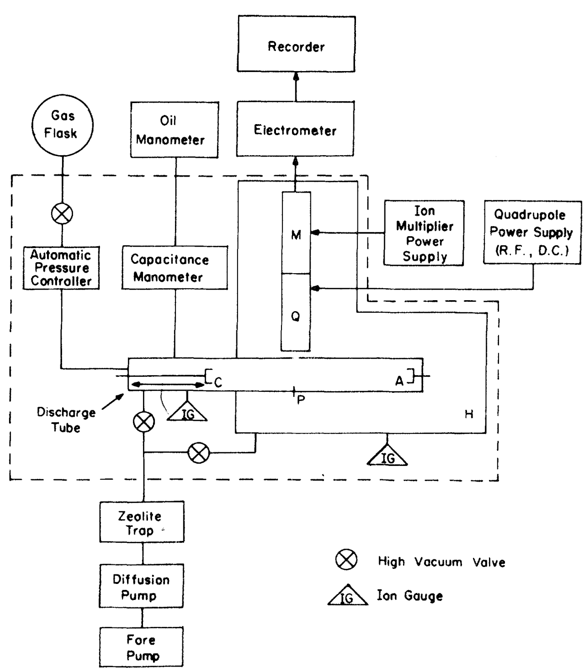

FIG. 1. Schematic drawing of the experimental apparatus.

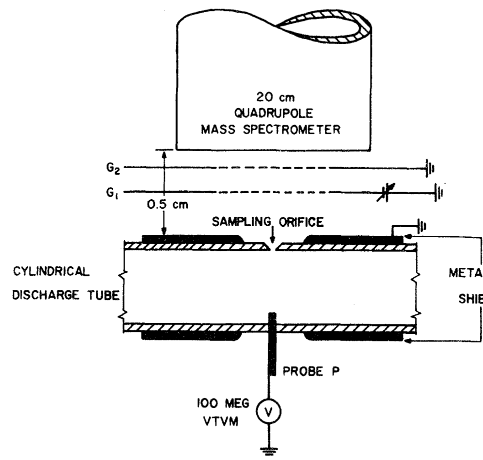

FIG. 2. Schematic drawing of the sampling orifice region.

Figure 2 shows schematically (not to scale) the configuration close to the sampling orifice. The metallic shield shown in Fig. 2 consisted of a metallic sheet which was wrapped around the discharge tube in the vicinity of the orifice and the probe. This served as a shield for the discharge tube and also as a reference electrode. Grid G_2 at the entrance to the quadrupole was used to shield the rf quadrupole power, while the second grid G_1 was used for ion acceleration. In general measurements were made using potentials applied to G_1 such that the atomic and molecular ion current signals were maximized. Under certain conditions G_1 was also used to estimate effusing ion energies from retarding potential measurements. The discharge was maintained by two separate, regulated power supplies connected in series with the common terminal grounded. The two power supplies were used to obtain desired probe potential values. As indicated in Fig. 2, the probe potential was measured by a high-input impedance voltmeter (HP model 412 AR). Measurements of the ion signals as a function of probe potential are discussed in Sec. V. It should be noted that the entrance to the quadrupole was 0.5 cm from the orifice. Under these conditions possible preferential selection of the ions due to collisions outside the orifice was minimized.

III. THEORY

The major production processes of the atomic and molecular ions in the positive column of a dc discharge, in pure noble gases are assumed to be given by[15]

$$X + e \to X^* + e \qquad (K_e), \qquad (1)$$

$$X + e \to X^+ + 2e \qquad (K_i), \qquad (2)$$

$$X^* + X \to X_2^+ + e \qquad (K_2), \qquad (3)$$

$$X^+ + 2X \to X_2^+ + X \qquad (\beta), \qquad (4)$$

In the above, K_i, K_2, β, are the rate coefficients for the reactions (2)–(4). K_e is the effective rate coefficient for the production of excited states which participate in reaction (3).[16]

The steady-state continuity equation for the molecular ions X_2^+, assuming losses by ambipolar diffusion and electron-ion recombination is given by

$$K_2[X^*][X] + \beta[X^+][X]^2 = -D_{a2}\nabla^2[X_2^+] + \alpha n_e[X_2^+] . \qquad (5)$$

The quantities in the brackets denote number densities; D_{a2} and α are the ambipolar diffusion coefficient and the recombination coefficient of the molecular ions, respectively, and n_e is the electron density. Here it is assumed that the electron temperature is constant over the tube cross section. Assuming the ions and electrons have a zeroth-order Bessel-function density distribution J_0, and approximating[17,18] the nonlinear term αJ_0^2 by $\alpha C_0 J_0$ yields

$$K_2[X^*][X] + \beta[X^+][X]^2 = \{D_{a2}/\Lambda^2 + C_0\alpha n_e(0)\}[X_2^+] , \qquad (6)$$

where Λ is the characteristic diffusion length, $n_e(0)$ is the electron density at the tube axis, and $C_0 \approx 0.67$.[18] From the steady-state continuity equations of X^* and X^+, it can be shown that

$$\frac{[X^*]}{[X^+]} = \tau \frac{K_e}{K_i} \frac{D_{a1}/\Lambda^2 + \beta[X]^2}{1 + \tau K_2[X]} , \qquad (7)$$

where τ is the average radiative lifetime of X^*, and D_{a1} is the ambipolar diffusion coefficient of the atomic ions.[19] Using Eqs. (6) and (7), one obtains

$$\{D_{a2}/\Lambda^2 + C_0\alpha n_e(0)\}[X_2^+]/[X^+]$$

$$= K_2[X]\tau \frac{K_e}{K_i} \frac{D_{a1}/\Lambda^2 + \beta[X]^2}{1 + \tau K_2[X]} + \beta[X]^2 . \qquad (8)$$

X_2^+ by three-body conversion can be neglected, Eq. (8) becomes

$$\left\{1 + \frac{C_0\alpha n_e(0)}{D_{a2}/\Lambda^2}\right\} \frac{I(X_2^+)}{I(X^+)} = \frac{K_e}{K_i} \qquad (9)$$

since the radial ion current $I(X^+)$ arriving at the wall is proportional to $D_{a1}\nabla[X^+]|_{\text{wall}}$. The validity of the assumption that $\tau K_2[X] \gg 1$ is discussed in Sec. V and VI. It should be noted that when the recombination loss of X_2^+ is small compared to loss by diffusion, the ion current ratio is just K_e/K_i. In argon this behavior has previously been observed by Pahl.[20] Using Eq. (9) K_e/K_i can be evaluated from measurements of the relative ion signals at a given discharge current and pressure.

At higher pressures when the production of X_2^+ is primarily due to three-body conversion and when $\tau K_2[X] \gg 1$, Eq. (8) yields

$$\{D_{a2}/\Lambda^2 + C_0\alpha n_e(0)\} I(X_2^+)/I(X^+)$$

$$= \frac{D_{a2}}{\Lambda^2}\frac{K_e}{K_i} + \frac{D_{a2}}{D_{a1}}\left(1 + \frac{K_e}{K_i}\right)\beta[X]^2 . \qquad (10)$$

The three-body rate coefficient β can be calculated from measurements of the relative ion currents for a given pressure and discharge current, when values are known for the various parameters. Values of K_e/K_i can be obtained using Eq. (9) as previously indicated. Other values that must be used to calculate β include $\alpha, n_e(0)$, diffusion coefficients and the electron temperature. Equation (10) may be re-expressed in the form

$$\frac{I(X_2^+)}{I(X^+)} = \frac{K_e/K_i}{1 + AP_0} + \frac{BP_0^3}{1 + AP_0} , \qquad (11)$$

where A, B are constants for a fixed current E/P_0 and electron temperature. The first term on the right-hand side of (11) represents contributions to X_2^+ formation from the two-body process. At high pressures this term is small compared to the second term. Hence $I(X_2^+)/I(X^+)$ will have a quadratic or cubic dependence on P_0 depending on whether recombination or diffusion losses are respectively dominant.

IV. EXPERIMENTAL CONSIDERATIONS

To obtain meaningful values of the ratio of the currents due to the molecular and the atomic ions, it is clear that a number of conditions must prevail in the positive column. In particular, the column must be relatively free of striation phenomena. For example, when standing striations are present the ion signals are observed to be strongly dependent on the position of the orifice relative to the striations. The requirement that there be no striations present in the column is, in general, equivalent to specifying a particular current and pressure range of operation for the discharge.[21] Further, pronounced constrictive effects if present, would also probably alter the observed molecular and atomic ion current signals, this also restricts the pressure and current range investigated. In addition the studies must either be conducted on very pure-gas samples or sufficiently far removed from the cathode region of the discharge so that the plasma in the sampling region is free from possible trace impurities as the result of cataphoresis. In the present studies reproducible data were only obtained after all of these effects had been taken into consideration.

Other factors also limit the range of several experimental parameters. For example, an increase of the current obviously increases the relative importance of recombination losses. The increased recombination loss will alter the distribution of the molecular ions to a greater extent than that of the atomic ions. This will result in larger observed values of $I(X_2^+)/I(X^+)$ due to different gradients at the wall of the tube. Also these losses will result in an overestimate of $n_e(0)$ values. From Eq. (10) it will be noted that the net effect will be to overestimate values of β. Unfortunately these effects cannot be easily included in the analysis, however, the observed variation with discharge current is consistent with this interpretation. The effects of plasma boundary sheaths must also be considered. Assuming that the sheath thickness is on the order of a few Debye lengths, operation at high currents would be desirable. However operation at very high currents, would have a deleterious effect due to the introduction of phenomena such as appreciable temperature gradients across the tube diameter and constriction of the discharge, etc. On the basis of these considerations, the most reliable data are believed to be obtained at moderate discharge currents.

Another important experimental parameter whose values must be properly selected is the probe potential V_p. In general the ratio of the molecular to the atomic ion currents is observed to decrease strongly as the probe potential is increased from very small values ≈ 1 V. As V_p is increased to approximately 10 V, the ratio becomes insensitive to further increase of the probe potential to values as high as 50 V in neon for example, if the background pressure outside the orifice is sufficiently low. With increasing pressure in the discharge and hence increased background pressure, the ratio shows a slight dependence on probe potential. Retarding potential measurements at moderate pressures clearly show that the mean ion energies are approximately given by the corresponding values of V_p. At high pressures, however, the ion energies are reduced, presumably due to collisions. As the probe potential is increased from 10 to 30 V, the atomic ion signals increase much more rapidly with V_p than the molecular ion signals. This is probably related to the dependence on ion energy of the cross section for charge exchange of the atomic ions, and increased collisional dissociation of the molecular ions thereby producing low-energy atomic ions. Hence at high pressures changes in the probe potential have a significant effect on the ion current ratios. To minimize the loss of atomic ions due to charge exchange, it would be desirable to operate the probe at high potentials. However increased dissociation of molecular ions under this condition is an additional limiting factor. On the basis of these considerations, data obtained at moderate probe potential values are believed to be the most significant for β determinations.

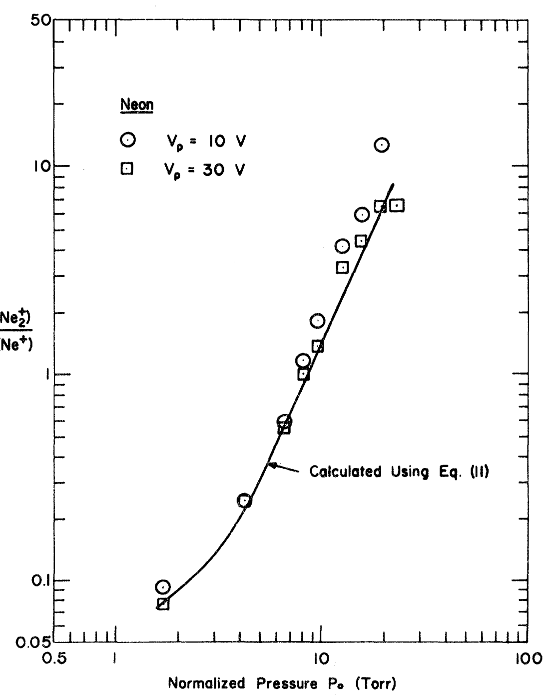

FIG. 3. Ratio of the ion currents of Ne_2^+ and Ne^+ as a function of normalized gas pressure. Data shown were obtained using probe potentials $V_p = 10$ and 30 V, and a discharge current of 50 mA. The solid curve was calculated from Eq. (11), using a value of $\beta = 7.3 \times 10^{-32}$ cm^6/sec and $K_e/K_i = 0.06$.

TABLE I. Comparison of values of β obtained in neon as a function of pressure for a discharge current of 50 mA. Values are given corresponding to probe potentials of 10 and 30 V. At the lowest pressure the K_e/K_i term is the major contribution to the ratio given by Eq. (11). At this pressure $K_e/K_i = 0.06$ is obtained from Eq. (11) by extrapolation of β values obtained at higher pressures. At $P_0 = 4.2$ Torr, the value of β is calculated using $K_e/K_i = 0.06$, at higher pressures K_e/K_i terms are neglected.

P_0 (Torr)	T (°K)	E/P_0 (V/cm Torr)	V_p (V)	$I(Ne_2^+)/I(Ne^+)$	β (10^{-32} cm^6/sec)
1.69	323	1.66	10	0.093	
			30	0.076	
4.2	326	0.57	10	0.25	7.5
			30	0.25	7.5
6.6	333	0.40	10	0.59	7.6
			30	0.56	7.2
8.12	336	0.35	10	1.17	10.2
			30	1.0	8.6
9.63	340	0.36	10	1.8	10.0
			30	1.35	7.5
12.8	343	0.31	10	4.1	12.2
			30	3.3	8.9
15.7	348	0.30	10	5.8	10.7
			30	4.4	8.1
19.4	352	0.30	10	12.4	14.0
			30	6.4	7.3

V. EXPERIMENTAL RESULTS

Figure 3 shows examples of measurements in neon of the ratio of the ion signal current due to Ne_2^+ and Ne^+ as a function of the normalized gas pressure ($P_0 = 273\,P/T$). Measurements are shown corresponding to probe potentials of 10 and 30 V. The data were obtained for a discharge current of 50 mA. Also shown in Fig. 3 is a solid curve calculated using Eq. (11). The curve is drawn using an averaged value of $\beta = 7.3 \times 10^{-32}$ cm^6/sec and $K_e/K_i = 0.06$ taken from the present measurements. The data shown in Fig. 3 are expressed in tabular form in Table I. The β values are calculated from Eq. (10) using measured values of the ion current ratios.[22] Figure 4 shows the variation of β with normalized pressure P_0 for a probe potential $V_p = 30$ V. As discussed in Sec. IV a probe potential of 30 V rather than 10 V provides a more reliable estimate of β. From Fig. 4 it will be noted that within the experimental errors β is independent of P_0 as would be expected for the limited E/P_0 range investigated.

Studies were also conducted on the dependence of β on discharge current I. Examples of these results are shown in Fig. 5. The data given in this figure were obtained using a probe potential $V_p = 30$ V. Data plotted in Fig. 5 are given in tabular form in Table II. Here it will be noted that E/P_0 values vary from 0.57 to 0.37 V/cm × Torr as the current is increased from 6 to 60 mA, a corresponding gas temperature increase from 310°K to 345°K is also observed.

Measurements were also made to determine the effect on the ratio of the molecular to the atomic ion signals, of the Δm mode of operation of the quadrupole mass spectrometer. The effect was observed to be negligible, corresponding at low

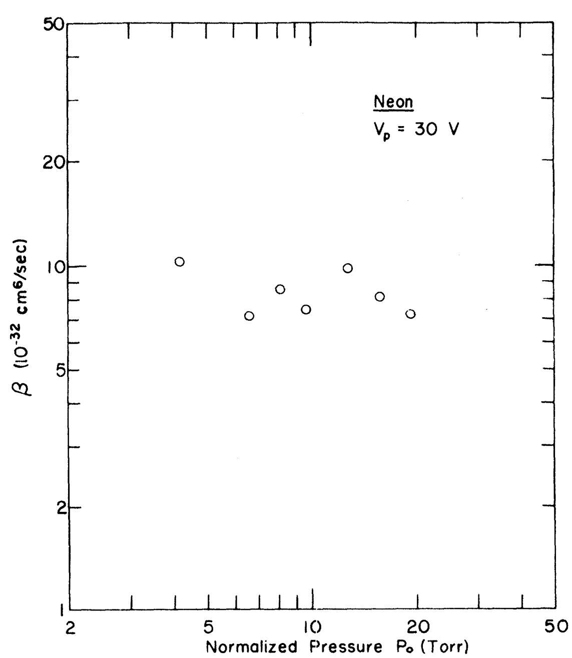

FIG. 4. The variation of β with P_0 for neon. The data shown were obtained using a probe potential of 30 V and a discharge current of 50 mA.

TABLE II. Comparison of values of β in neon as a function of discharge current, for an approximately fixed P_0. Data were obtained using a probe potential of 30 V.

I (mA)	P_0 (Torr)	T (°K)	E/P_0 (V/cm Torr)	$I(Ne_2^+)/I(Ne^+)$	β (10^{-32} cm^6/sec)
6	10.6	310	0.57	2.7	5.7
10	10.4	316	0.41	2.5	6.3
20	10.2	321	0.41	2.16	6.8
40	9.85	332	0.39	1.45	6.6
50	9.63	340	0.36	1.35	7.5
60	9.5	345	0.37	1.2	7.6

pressures to a reduction of approximately 2% as Δm was increased from 2 to 8. All measurements reported here were obtained using $\Delta m = 4$.

Figure 6 shows examples of measurements of the ratio of the current signals of Ar_2^+ to Ar^+ as a function of P_0 obtained in argon. The data shown were obtained using a probe potential $V_p = 30$ V, and a discharge current of 50 mA. Also shown in Fig. 6 is a curve calculated using Eq. (11). The curve was calculated using an averaged value of $\beta = 3.6 \times 10^{-31}$ cm^6/sec and $K_e/K_i = 0.42$ obtained from the present studies. From Fig. 6 it will be noted that the ion current ratio for P_0 values between 2.5 and 5.0 Torr exhibits approximately a quadratic dependence, while for $P_0 < 2$ Torr the ratio is essentially independent of pressure. Data shown in Fig. 6 are given in tabular form in Table III.

Previous studies[10, 20, 23] indicate that values of K_e/K_i for argon are not small compared to unity. Hence the neglect of K_e/K_i terms in Eq. (10) can cause significant errors in calculating β. To evaluate K_e/K_i, the ratio $I(Ar_2^+)/I(Ar^+)$ was measured in the present studies at 1 Torr and for discharge currents varying from 10 to 50 mA. Pahl[20] observed that $I(Ar_2^+)/I(Ar^+)$ becomes pressure independent for gas pressures from 1 to 2 Torr and a current $I = 3$ mA. This implies that the assumption that $K_2\tau[X] \gg 1$ made in obtaining Eq. (9) is reasonably valid at 1 Torr. The ratio K_e/K_i is evaluated from Eq. (9) using the measured values of $I(Ar_2^+)/I(Ar^+)$. The K_e/K_i value is calculated to be 0.42.[24] The β values calculated from Eq. (10) and using $K_e/K_i = 0.42$ are shown in the last column of Table III.[24] When $K_2\tau[X]$ is not very large compared to unity, the resulting K_e/K_i and β values are slightly modified. These effects are considered in the next section.

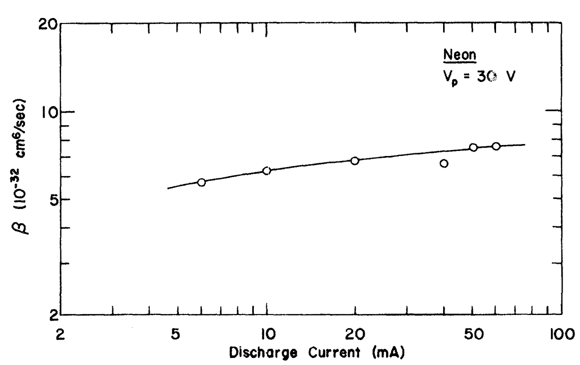

FIG. 5. The variation of β observed in neon with discharge current. Data were obtained using a probe potential of 30 V.

VI. DISCUSSION OF RESULTS

In Figs. 3 and 6 the observed variation of $I(X_2^+)/I(X^+)$ at low and intermediate pressures may be explained using Eq. (11)

$$\frac{I(X_2^+)}{I(X^+)} = \frac{K_e/K_i}{1 + AP_0} + \frac{BP_0^3}{1 + AP_0}. \quad (11)$$

For neon at low pressures (< 2 Torr) where three-body conversion is small, since recombination losses are small compared to diffusion losses

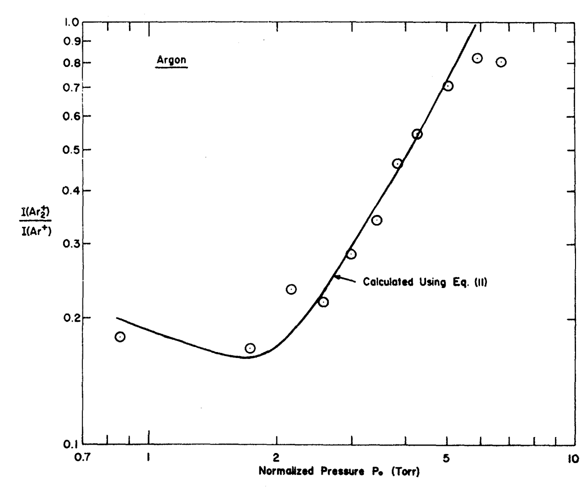

FIG. 6. The ratio of ion currents of Ar_2^+ and Ar^+ as a function of P_0. The data were obtained using a probe potential $V_p = 30$ V and a discharge current of 50 mA. The solid curve was calculated from Eq. (11) using a value of $\beta = 3.6 \times 10^{-31}$ cm^6/sec and $K_e/K_i = 0.42$.

TABLE III. Comparison of values of β obtained for argon as a function of pressure for a discharge current of 50 mA. and a probe potential of 30 V. Values of β are not given at the pressure extremes for reasons given in the text.

P_0 (Torr)	T (°K)	E/P_0 $\left(\frac{\text{V}}{\text{cm Torr}}\right)$	$\frac{I(Ar_2^+)}{I(Ar^+)}$	β $\left(\frac{10^{-31}}{\text{cm}^6/\text{sec}}\right)$
0.85	316	1.61	0.18	
1.73	316	0.76	0.17	3.83
2.16	316	0.65	0.23	4.74
2.58	317	0.59	0.22	3.17
3.0	318	0.52	0.29	3.38
3.43	318	0.47	0.34	3.28
3.85	319	0.39	0.47	3.80
4.28	320	0.39	0.54	3.61
5.06	320	0.38	0.71	3.42
5.93	322	0.34	0.83	3.0
6.75	324	0.31	0.81	

the ratio should approach a constant value essentially given by K_e/K_i. However, for argon at low pressures, recombination losses can be comparable to diffusion losses depending on the discharge current value. In this case ($AP_0 \simeq 1$) the first term on the right of (11) decreases, and the second term increases with pressure. Calculations indicate that for the pressure range of interest one term compensates for the other, such that the ratio $I(Ar_2^+)/I(Ar^+)$ becomes essentially pressure independent.[25] Moreover these estimates verify the assumption made in obtaining Eq. (9) that three-body conversion may be neglected at low pressures. At pressures greater than 2.5 Torr, the second term starts to dominate, clearly then the dependence of the ratio is determined by the second term. From Fig. 6 it will be noted that at high pressures, the ion current ratio becomes pressure independent. This effect is also evident at high pressures in Fig. 3 for neon. In general the saturation occurs at lower pressures as the discharge current is reduced. This behavior may be understood on the basis of the increased importance of molecular ion collisions in the space charge sheaths which produce dissociation.

An additional effect which occurs at high pressures, is the onset of striations, thus for example in Table I measurements were not conducted above $P_0 \approx 20$ Torr, due to the appearance of striations. In the limit of very low pressures $P_0 < 2$ Torr in neon for example, standing and moving striations were also observed and thus prevented reliable measurements. On the basis of the above considerations meaningful values of β could only be obtained over a restricted range of gas pressures.

To obtain Eq. (9) the assumption was made that $K_2\tau[X]$ was large compared to unity. If one calculates K_e/K_i without assuming $K_2\tau[X] \gg 1$, using the values of $K_2\tau$ obtained by Pahl,[20] the resulting K_e/K_i value is increased by $\approx 40\%$. The corresponding β values are then reduced by $\approx 10\%$. Values of $K_2\tau$ reported in the literature vary over a considerable range. With the exception of Hornbeck's[23] result, the value reported by Pahl is the smallest. Hence by assuming $K_2\tau[X] \gg 1$, β values are overestimated at the most of 10%.

It will be noted from Table II that for $V_p = 30$ V, the values of β for neon vary from 5.7×10^{-32} to 7.6×10^{-32} cm^6/sec as the current is increased from 6 to 60 mA. A similar, but more pronounced current dependence was also observed for β values in argon. For argon as the current was increased from 25 to 90 mA, calculated β values increased from 2.6×10^{-31} to 5.1×10^{-31} cm^6/sec. The stronger current dependence in argon, compared to neon may be explained, since for argon recombination losses are more important than in neon. The current dependence is believed to be primarily determined by the influence of recombination losses and plasma sheath boundary effects are discussed in Sec. IV. In principle the observed current dependence may in part be attributed to changes in gas temperature and E/P_0, however such changes are not very large and hence are not believed to be significant.

The present results for the rate coefficient obtained in neon are compared in Fig. 7 with data obtained previously using different experimental methods. The data of Beaty and Patterson[7] are

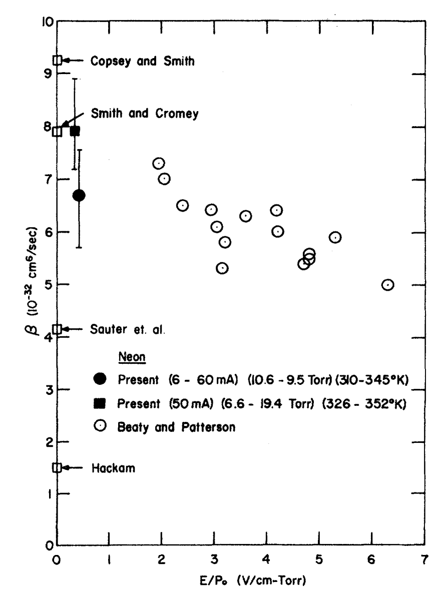

FIG. 7. Comparison of experimental measurements of β for neon. The present values indicated by the ● symbols were taken from Table I; the ■ data were taken from Table II.

expressed as a function of E/P_0, all other values[4, 6, 26, 27] were obtained at E/P_0 values corresponding to thermal energies. The present data shown in Fig. 7 represent averaged values taken from Tables I and II, corresponding to the most reliable data in the sense that they were obtained in the middle of the experimental pressure range and at moderate values of the probe potential and discharge currents.

Data reported by Beaty and Patterson[7] were obtained from drift-tube ion-conversion studies at room temperature. All other data shown in Fig. 7, with the exception of the present results, were obtained from investigations of decaying plasmas. While differences exist in the pressure ranges and gas temperatures used in the afterglow studies, it seems unlikely that they could account for the discrepancies. In particular by comparison, the value reported by Hackam[27] appears low. The present results are in reasonable agreement with the data of Beaty and Patterson. It should be emphasized that the present results are obtained by ion sampling from active plasmas, hence the plasma environment is considerably different compared to other experimental methods. At the present time it is not obvious that these differences can be completely discounted. Perhaps the most serious difficulty associated with the present results is the fact that sampling is performed through plasma boundary sheaths, which are not collisionless. While the measurements are made under conditions such that these effects are believed to be minimized, the effect of molecular ion collisions in the sheath could have the effect of reducing the effective value of β due to collisional dissociation.

Several theoretical estimates have been made of the conversion rate constant for neon. Mahan[28] has reported a value of 6.2×10^{-32} cm^6/sec, while Beaty and Patterson[7] calculate a value of 6.4×10^{-32} cm^6/sec, and also using Thomson's[29] theory they estimate $\beta\approx10^{-31}$ cm^6/sec. Smirnov[30] has reported a value of 11×10^{-32} cm^6/sec. Clearly these values are in order of magnitude agreement with the experimental observations.

Table IV shows a comparison of some of the reported values of the three-body conversion rate constant for argon.

The results of Cronin and Sexton[5] and Smith and Cromey[6] were obtained from afterglow studies. The value given by Kretschmer and Peterson[31] was estimated from Langmuir probe studies of pulsed argon discharges. Peterson and Beaty's[32] value was obtained from drift-tube studies.

TABLE IV. Comparison of values of β obtained for argon. The comparison shows both theoretical estimates and some of the more reliable experimental values.

	β (10^{-31} cm^6/sec)
THEORETICAL	
Smirnov (Ref. 30)	4.2
Loeb (Ref. 32)	4.5
Mahan (Ref. 33)	2.3
EXPERIMENTAL	
Cronin and Sexton (Ref. 5)	3.0
Smith and Cromey (Ref. 6)	2.5
Kretschmer and Peterson (Ref. 31)	1.46
Peterson and Beaty (Ref. 31)	2.3
Present Experiment	3.0–4.7

Theoretical values of β for argon have been given by several investigators. Loeb[33] using Thomson's three-body collision theory has estimated $\beta\simeq4.5\times10^{-31}$ cm^6/sec, Mahan[34] has calculated a value of 2.3×10^{-31} cm^6/sec and Smirnov[30] estimates $\beta\simeq4.2\times10^{-31}$ cm^6/sec.

VII. CONCLUSIONS

Direct ion sampling from the positive column of a dc discharge in a noble gas permits estimates to be made of the three-body conversion coefficient for homonuclear diatomic ion formation. Values obtained in this manner are found to be in rough agreement with measurements made using other techniques. The analysis involves a number of simplifying assumptions. Moreover sampling through the plasma boundary sheath raises the problem of possible preferential ion transmission. In principle, however the apparent agreement of the present data with generally accepted values, strongly suggests that previously reported orders of magnitude discrepancies[9, 10] in such rate coefficients cannot be primarily attributed to different plasma environments. The present studies are believed to be the first extensive measurements that have been made of three-body conversion coefficient for dc discharges in neon and argon.

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$$n_e(0) = 2.3I/\pi r_0^2 q v_{de},$$

where I is the discharge current, r_0 is the radius of the discharge tube, and v_{de} is the drift velocity of the electrons. The values of v_{de} were obtained from the data of Pack and Phelps, Phys. Rev. 121, 798 (1961).

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