region where the quantum effects are important, both from the point of view of diffraction and exchange effects. For interparticle separations much greater than $\lambda\!\!\!^{-}$ the r.d.f. is given by the classical result.

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Ion Energies at the Cathode for Conduction Through Rarefield Gases

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The characteristics of ion energies at the cathode are derived from collisional ionization cross sections for conduction between plane, parallel electrodes in rarefied gases, where the mean-free path is much greater than the cathode-anode separation. Expressions are given for the electron ionization efficiency, the ion particle-current density striking the cathode, the power density transferred to the cathode by the ions, and the average impacting ion energy. These expressions are given both for a homogeneous (single species) gas and for a heterogeneous mixture of gases. The latter can be obtained additively from the results obtained by treating each of the constituent gases individually. The maximum impacting ion energy is equivalent to the potential applied across the cathode and the anode; the minimum impacting ion energy is equivalent to the smallest first ionization potential of the gases present in the cathode-anode space.

The amount of ionization is discussed in terms of an "ionization volume" swept out by each of the bombarding electrons. By maximizing this volume with respect to the applied potential, the maximum amount of collisional ionization occurs in the cathode-anode space (a potential of approximately 200 V for most gases). Drawings of the typical shape of the ionization volume are given for applied potentials much less than, equal to, and much greater than, the applied potential which yields maximum ionization. A specific example demonstrating an application of the derivations is given, using argon as a model.

INTRODUCTION

The molecules of a gas can be ionized when subjected to bombardment by electrons which are accelerated through the gas by the electric field of an applied potential. The ions, which are generated by collisional ionization, are accelerated toward the cathode by the same applied electric

field. The energy absorbed from the electric field by these ions is dissipated at the cathode. A knowledge of the energy characteristics of the ions as they strike the cathode provides an insight for interpreting the surface phenomena (e.g., sputtering, implantation, etc.) occurring at the cathode. An analysis is presented below describing these energy characteristics at the cathode for conduction between plane, parallel electrodes in a rarefied gas when a constant potential gradient (including a Townsend discharge, but excluding other electrical discharges) exists throughout the cathode-anode space.

To determine the energy characteristics of the ions striking the cathode, it is necessary to know the relative amount of ionization occurring in the cathode-anode space as a function of distance from the cathode. For the motion of ions, most theories are based on the assumption that the cathode anode separation, L, is related to the mean-free path, λ, by

$$L \gg \lambda \ . \tag{1}$$

For this condition, the ions have an average drift velocity determined by the mobility of the ions and the magnitude of the applied electric field. For single ionization, the number of ions impinging on the cathode are equal to the difference between the number of electrons reaching the anode, ν_a, and the number of electrons leaving the cathode, ν_c. Therefore, the amount of ionization can be approximated indirectly from the relationship[1]

$$\nu_a = \nu_c e^{\gamma V} \ , \tag{2}$$

where γV is the average number of ionizing collisions experienced by each electron falling through the applied potential difference, V.

As the energy distribution of the electrons leaving the cathode becomes steady only after the electrons have traveled a distance of several λ, detailed investigations require a modification of Eq. (2) to the form[1]

$$\nu_a = \nu_c e^{\gamma (V - V_0)} \ , \tag{3}$$

where V_0 is a constant. With Eq. (3), analyses can be conducted as if the electron-energy distribution were steady throughout the entire region between the cathode and the anode.

For the case of rarefied gases, however, just the reverse of Eq. (1) applies, i.e., $L \ll \lambda$. The nonsteady electron energy-distribution condition which was more or less confined to the region immediately adjacent to the cathode for situations obeying Eq. (1) now extends throughout the cathode-anode space. Therefore, ionization in a rarefied gas cannot be adequately described by the preceding equations. Instead, an analysis for determining the ion energies at the cathode for conduction through rarefied gases must be based on the fundamental concept of ionization cross sections.

THEORY

One of the fundamental measurements in the field of electronic-impact phenomena is the absolute total cross section for ionization of molecules in a gas by electron impact. A cross section is a measure of the probability that a given type of reaction (in our case, ionization) will occur under stated conditions. The magnitude of a cross section depends on the nature of the colliding particles, their mutual velocity of approach, the impact parameter, and the particular reaction considered.[2] Due to the relatively large number of events occurring in collision phenomena, an average cross section is sufficient to account for all the parameters which affect the magnitude of the cross section with the exception of the dependency on the mutual velocity of approach. In turn, since the velocity and energy are directly related, the cross section is considered to be a function of energy. The ionization cross sections for various gases as a function of the energy of monoenergetic electrons are shown in Fig. 1.[3] It is evident from Fig. 1 that the maximum values for ionization cross sections occur for electrons which have an energy of approximately 100 eV. A monoenergetic electron which has an energy greater than, or less than, approximately 100 eV will, on the average, generate fewer ions than an electron with an energy of approximately 100 eV.

Since the electrons between the plane, parallel electrodes are not monoenergetic but are accelerated by the applied electric field, the probability of an ionization collision at any given point in the cathode-anode space depends on the energy possessed by the particular bombarding electron at that point. For the subsequent analysis, the following model for ionization in the cathode-anode space is assumed:

(1) The potential gradient between the cathode and the anode is constant.

(2) The energies of the conduction electrons initially leaving the cathode and the thermal energies (approximately $\frac{1}{40}$ eV at room temperature) of the gas molecules are negligible compared to the energies absorbed by the electrons from the applied electric field.

(3) An ionization collision results in the formation of singly-charged positive ions. Although some multiple ionization does occur, the amount

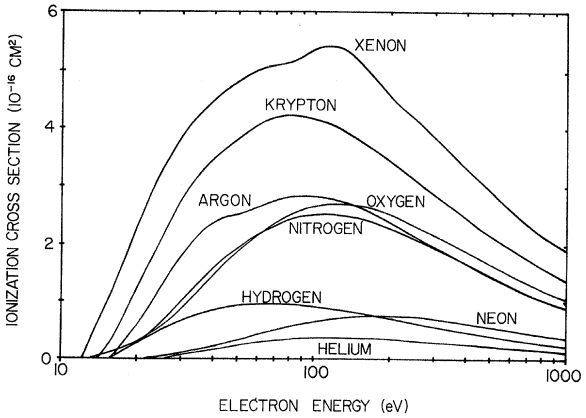

FIG. 1. Ionization cross sections of various gases when bombarded by monoenergetic electrons (data for these curves taken from Ref. 3).

is small compared to that of single ionization. However, the cross sections used in the calculations are those experimentally determined for total ionization cross section.

(4) The generated ions do not interact with other atomic systems. Although some electron exchange may take place between an ion and another molecule (whereby the ion is neutralized and another ion formed without there being, necessarily, any exchange of energy),[4] the cross sections and energy losses for this and other collisional processes experienced by the ions as they are accelerated toward the cathode are negligible in rarefied gases, where $L \ll \lambda$. Elastic collisions are predominantly small-angle scattering and thus do not affect the velocity of the ion to any great extent.[5] Further, any photo-ionization is assumed to be negligible.

(5) Electron losses due to attachment, electron-ion recombination, and space- or surface-charge effects are negligible.

(6) The average energy lost by an electron during an ionization event is negligible. This is justified since the fraction of electrons which actually cause an ionizing collision in a rarefied gas is small, and the resulting average energy loss per electron due to ionization is negligible.

With the foregoing assumptions, the bombarding electrons at any given equipotential "plane" (see Fig. 2) between the cathode and the anode are monoenergetic (disregarding the energies of the small number of electrons generated by ionization). Thus, for a gas composed of a single species, the number of electrons generated per second by collisional ionization in unit area of an infinitesimal planar element situated a distance of x cm from the cathode is

$$dn = nN(x)q(\epsilon)dx \text{ electrons/cm}^2 \text{ sec}; \quad (4)$$

where n is the number of electrons impinging on unit area of the planar element per second, $N(x)$ is the density of gas molecules as a function of displacement from the cathode, $q(\epsilon)$ is the ionization cross section which corresponds to the energy of the bombarding electrons at the equipotential plane represented by the planar element, and dx is the thickness of the element. Integrating Eq. (4),

$$\int_{n_c}^{n_a} dn/n = \int_0^L N(x)q(\epsilon)dx \ , \quad (5)$$

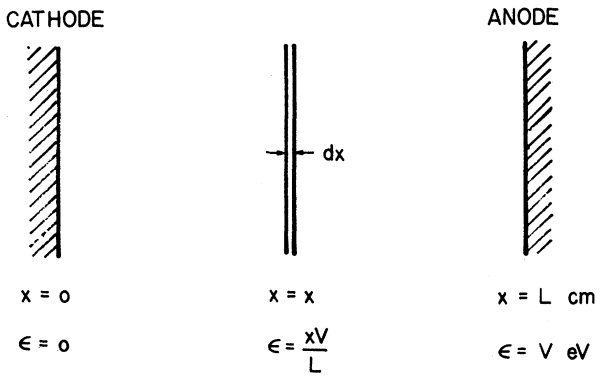

FIG. 2. Model used in the derivation of the ionization characteristics in rarefied gases.

where n_c is the particle-current density of electrons leaving the cathode, n_a is the particle-current density of electrons reaching the anode, and L is the cathode-anode separation.

The energy, ϵ, of the bombarding electrons at any given equipotential plane between the cathode and the anode is a function of the displacement of that plane from the cathode. These two quantities are related by

$$\epsilon = \mathcal{E}x \quad (6)$$

$$= (V/L)x \text{ eV} \quad (7)$$

where the energy is measured in electron volts, $\mathcal{E}$ is the strength of the applied electric field, and V is the magnitude of the externally applied potential. Substituting Eq. (7) into Eq. (5)

$$\int_{n_c}^{n_a} dn/n = (L/V)\int_0^V N(L\epsilon/V)q(\epsilon)d\epsilon \quad (8)$$

$$\text{or } n_a/n_c = \exp[(L/V)\int_0^V N(L\epsilon/V)q(\epsilon)d\epsilon] \quad (9)$$

$$\text{and } (n_a - n_c)/n_c = \exp[(L/V)\int_0^V N(L\epsilon/V)q(\epsilon)d\epsilon] - 1 . \quad (10)$$

The term in brackets in Eq. (10) is positive. Therefore, assuming

$$(n_a - n_c)/n_c \ll 1 \quad (11)$$

(which is subsequently shown to be a valid assumption), then the bracketed term is small. Since

$$e^{\alpha} \approx 1 + \alpha \quad (12)$$

for $\alpha \ll 1$, Eq. (10) can be approximated by

$$(n_a - n_c)/n_c = (L/V)\int_0^V N(L\epsilon/V)q(\epsilon)d\epsilon \ . \quad (13)$$

For the condition assumed in Eq. (11), the error introduced by using the approximation given in Eq. (12) is of the order

$$[\text{error in } (n_a - n_c)/n_c] \sim \tfrac{1}{2}[(L/V)\int_0^V N(L\epsilon/V)q(\epsilon)d\epsilon]^2 \quad (14)$$

The term, $n_a - n_c$, represents the number of electrons generated per second in a rectangular parallelopiped with unit cross-sectional area which extends from the cathode to the anode. Since single ionization was assumed, $n_a - n_c$ also represents the number of ions impinging on unit area of the cathode per second, or, from Eq. (13),

$$J = n_a - n_c = (n_c L/V)\int_0^V N(L\epsilon/V)q(\epsilon)d\epsilon \ , \quad (15)$$

where J is the ion particle-current density impinging on the cathode. The average number of ions generated for each electron leaving the cathode is the electron ionization efficiency, η, where

$$\eta = J/n_c = (L/V)\int_0^V N(L\epsilon/V)q(\epsilon)d\epsilon \quad (16)$$

The power density delivered to the substrate by the generated ions can be determined similarly.

The energy transferred by each ion depends on the distance at which the ion was generated from the cathode, and the strength of the applied electric field. The power density transferred to the cathode by the ionization which occurs in a planar element situated x cm from the cathode is given by

$$dQ = ne\epsilon N(x)q(\epsilon)dx , \tag{17}$$

where $e(=1.6\times10^{-19}\,\mathrm{C})$ is the fundamental electronic charge. Assuming the total amount of ionization is small, then

$$n \approx n_c \tag{18}$$

and Eq. (17) becomes

$$dQ = n_c e\epsilon N(x)q(\epsilon)dx . \tag{19}$$

Substituting Eq. (7) into Eq. (19), and integrating,

$$Q = (n_c eL/V)\int_0^V \epsilon N(L\epsilon/V)q(\epsilon)d\epsilon . \tag{20}$$

The power density can also be described by the product of the ion particle-current density and the average impacting ion energy, $\bar{\epsilon}$,

$$Q = J\bar{\epsilon} . \tag{21}$$

or, from Eqs. (15) and (20),

$$\bar{\epsilon} = \frac{\int_0^V \epsilon N(L\epsilon/V)q(\epsilon)d\epsilon}{\int_0^V N(L\epsilon/V)q(\epsilon)d\epsilon} . \tag{22}$$

When several gases are present in the cathode-anode space, the molecules of each gas act independently. Thus, the number of free electrons generated per second by ionization in a unit-area planar element situated x cm from the cathode is

$$dn = nN_1(x)q_1(\epsilon)dx + nN_2(x)q_2(\epsilon)dx + \cdots , \tag{23}$$

where $N_i(x)$ is the density of the ith species of molecules at x, and $q_i(\epsilon)$ is the corresponding ionization cross section for the energy of the bombarding electrons at x. Again, assuming the total amount of ionization is small, then from Eqs. (18) and (23)

$$dn = n_c[N_1(x)q_1(\epsilon)dx + N_2(x)q_2(\epsilon)dx + \cdots] . \tag{24}$$

Substituting Eq. (7) into Eq. (24) and integrating, the ion particle-current density in a mixture of m species of gas is

$$J = n_a - n_c = (n_c L/V)[\int_0^V N_1(L\epsilon/V)q_1(\epsilon)d\epsilon + \cdots + \int_0^V N_m(L\epsilon/V)q_m(\epsilon)d\epsilon] \tag{25}$$

$$= \frac{n_c L}{V}\sum_i^m \int_0^V N_i(L\epsilon/V)q_i(\epsilon)d\epsilon . \tag{26}$$

The electron ionization efficiency for this heterogeneous mixture of rarefied gases is

$$\eta = \frac{J}{n_c} = \frac{L}{V}\sum_i^m \int_0^V N_i(L\epsilon/V)q_i(\epsilon)d\epsilon . \tag{27}$$

Similarly, the power density transferred to the cathode is

$$Q = \frac{n_c eL}{V}\sum_i^m \int_0^V \epsilon N_i(L\epsilon/V)q_i(\epsilon)d\epsilon , \tag{28}$$

and the average impacting ion energy is

$$\bar{\epsilon} = \frac{\sum_i^m \int_0^V \epsilon N_i(L\epsilon/V)q_i(\epsilon)d\epsilon}{\sum_i^m \int_0^V N_i(L\epsilon/V)q_i(\epsilon)d\epsilon} . \tag{29}$$

The immediately preceding analysis reveals that the modifications in J, η, and Q due to heterogeneity can be obtained additively from the results obtained by treating each constituent gas individually.

DISCUSSION

Since the impacting ion-energy characteristics of a gas mixture can be obtained from the results of treating each constituent gas separately, only a single species need be considered for the following discussion. Further, the residual pressure is assumed to be uniform throughout the cathode-anode space:

$$N(x) = N = \text{constant} . \tag{30}$$

During a collision, a "point" electron is generally assumed to collide with the finite cross section of a gas molecule; however, it is immaterial whether the target molecule or the energetic electron possesses the cross section. Therefore, the bombarding electrons can be assumed to possess the cross sections, and the gas molecules can be assumed to be "points", without altering the final results. As an electron traverses the cathode-anode space, the ionization cross section possessed by the electron sweeps out a volume. Since the velocities of the accelerated electrons are much greater than the thermal velocities of the gas molecules, the points representing the gas molecules can be considered as fixed in space. The average number of fixed points (molecules) enclosed by this "ionization volume" represents the average number of ionization events which occur when a single electron travels from the cathode to the anode. From Eqs. (7), (15), and (30),

$$\int_0^L q(\epsilon)dx = (L/V)\int_0^V q(\epsilon)d\epsilon = J/n_c N . \tag{31}$$

The term at the left of Eq. (31) represents the volume swept out by a cross section. Since L represents the distance between the cathode and the anode, then

$$V^{-1}\int_0^V q(\epsilon)d\epsilon \tag{32}$$

is the ionization volume per unit cathode-anode separation. Values of this term as a function of applied potential are given in Fig. 3 for the various gases depicted in Fig. 1. The values for the curves in Fig. 3 were determined by numerically

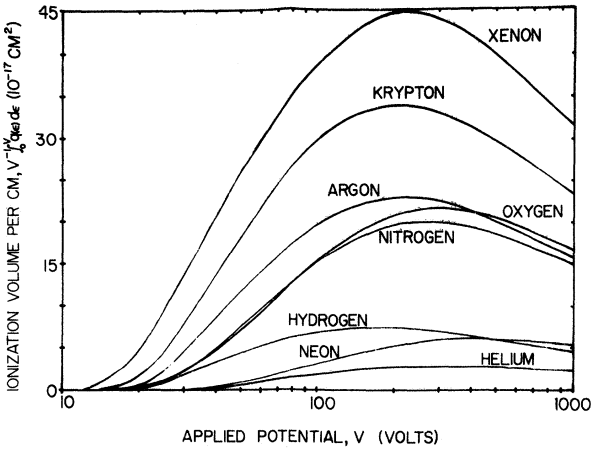

FIG. 3. Ionization volume per unit cathode-anode separation as a function of applied potential for various gases.

integrating (Simpson's Rule) the corresponding curves of Fig. 1.

Since cross sections are a function of energy and since the bombarding electrons are continuously accelerated by the applied electric field, the shape of the ionization volume swept out by each of the electrons in a given gas is not cylindrical, but has a characteristic shape which is dependent on the magnitude of the potential applied across the cathode and the anode. Therefore, if the ionization volume could be maximized as a function of the applied potential so as to contain a maximum number of fixed points (molecules), then maximum collisional ionization occurs. For this maximum ionization, the equation

$$(d/dV)[(L/V)\int_0^V q(\epsilon)d\epsilon]_{V=V_m}=0 \qquad (33)$$

must be satisfied. Inspection of Fig. 3 shows that Eq. (33) does have a solution; for the gases considered,

$$V_m \sim 200 \text{ V}. \qquad (34)$$

If a potential much greater than, or much less than V_m is applied across the cathode and the anode, a smaller electron ionization efficiency and a smaller ion particle-current density results. Figure 4a shows the typical shape of an ionization volume, where $V \approx V_m$. Figures 4a and 4b show the typical shapes of the ionization volume for $V \ll V_m$, and $V \gg V_m$, respectively. The phenomenon apparent near the cathode in Figs. 4b and 4c is due to the fact that the bombarding electrons cannot produce ions by collisional ionization until the electrons have fallen through a potential difference equivalent to the first ionization potential of the gas. Therefore, the minimum impacting ion energy is equal to the ionization potential of the gas because the ions, while traveling to the cathode, must fall through (at least) this same potential difference. The maximum impacting ion energy is equivalent to the magnitude of

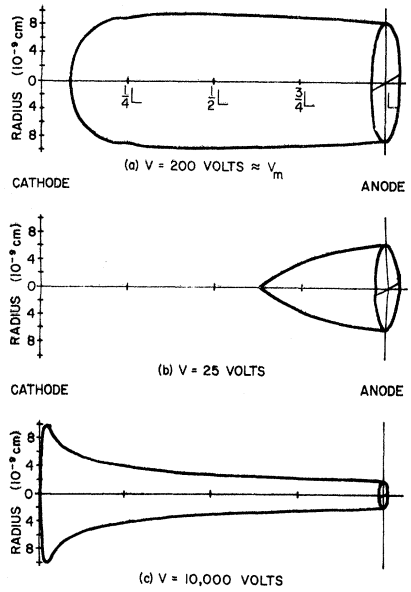

FIG. 4. Typical shapes of an ionization volume for applied potentials of (a) $V \approx V_m$, (b) $V \ll V_m$, and (c) $V >> V_m$, using argon as a model.

the applied potential. From Eqs. (4), (7), and (30), and assuming the total amount of ionization is small, then

$$dn/d\epsilon \approx (n_c NL/V)q(\epsilon)$$

which shows that the distribution of impacting ion energies for a single gaseous species has the form of the corresponding cross section, $q(\epsilon)$ (see Fig. 1).

For determining the power density delivered to the cathode, values of the term

$$V^{-1}\int_0^V \epsilon\, q(\epsilon)d\epsilon$$

must be calculated. These values as a function of applied potential are given in Fig. 5 for the various gases shown in Fig. 1. Data for the curves plotted in Fig. 5 were obtained by weighting each point of the curves shown in Fig. 1 by the energy which corresponds to that point, and numerically integrating (Simpson's rule) the resulting function.

EXAMPLE

To demonstrate the numerical magnitudes represented by the preceding derivations, consider a rarefied gas composed of a single species – argon. Since the pressure is assumed to be uniform, the molecular density is given by[1]

$$N = N_L p_0 = 3.54\times10^6 p_0 \text{ molecules/cm}^3, \qquad (35)$$

where p_0 is the reduced pressure in Torr (mm Hg) and N_L is a constant, known as Loschmidt's number, which is the number of molecules per cm^3 per unit reduced pressure,

$$p_0 = (273/T)p, \qquad (36)$$

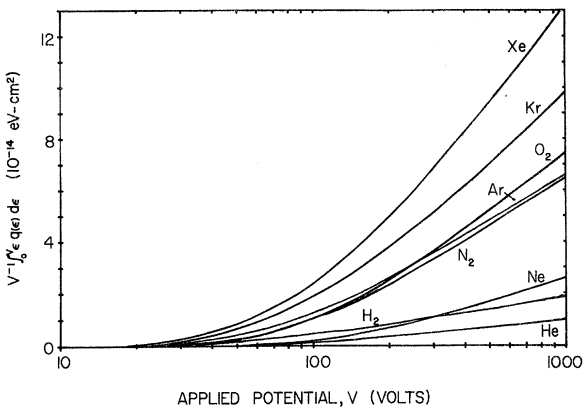

FIG. 5. $V^{-1}\int_0^V \epsilon q(\epsilon)d\epsilon$ vs applied potential for various gases.

where T is the absolute temperature in degrees Kelvin. (For a mixture of gases, p is the partial pressure.) If the electron particle-current density is expressed as an electrical current density, j, and assuming the electron ionization efficiency is small, then

$$j = n_a e \approx n_c e \quad . \tag{37}$$

Substituting Eqs. (35) and (37) into Eqs. (15), (16), (20), and (22), and recasting the resulting equations in the form of (32), then for a single species (with j in A cm^{-2}, p_0 in Torr, L in cm, q in cm^2)

$$J = 2.21\times10^{35} j p_0 L\left[V^{-1}\int_0^V q(\epsilon)d\epsilon\right]$$

$$\text{ions/cm}^2 - \text{sec}\,, \tag{38}$$

$$\eta = 3.54\times10^{16} p_0 L\left[V^{-1}\int_0^V q(\epsilon)d\epsilon\right], \tag{39}$$

$$Q = 3.54\times10^{16} j p_0 L\left[V^{-1}\int_0^V \epsilon\, q(\epsilon)d\epsilon\right]\text{W/cm}^2\,, \tag{40}$$

$$\bar{\epsilon} = V^{-1}\int_0^V \epsilon q(\epsilon)d\epsilon \Big/ V^{-1}\int_0^V q(\epsilon)d\epsilon\,. \tag{41}$$

For purposes of demonstration, consider the following values:

$$V = 200\ V,\ p_0 = 10^{-5}\ \text{Torr},\ L = 10\ \text{cm}, j = 1\ \text{mA/cm}^2. \tag{42}$$

From the curve shown for argon in Fig. 3,

$$\tfrac{1}{200}\int_0^{200} q(\epsilon)d\epsilon = 2.3\times10^{-16}\ \text{cm}^2 \tag{43}$$

and the ion particle-current density striking the cathode is

$$J = 5.1\times10^{12}\ \text{ions/cm}^2\ \text{sec}. \tag{44}$$

Similarly, the electron ionization efficiency is

$$\eta = 8.1\times10^{-4} \tag{45}$$

$$= 0.08\% \tag{46}$$

which indicates that, on the average, approximately 80 ions are generated for every 10^5 electrons leaving the cathode. From Eqs. (14) and (43), the errors introduced by using the approximation shown in Eq. (12) are approximately

$$\text{error in } J \sim 2.1\times10^{9}\ \text{ions/cm}^2\,\text{sec}\,,$$

$$\text{error in } \eta \sim 3.3\times10^{-7}. \tag{47}$$

Since these errors are negligible compared to Eqs. (44) and (45), the approximation shown in Eq. (13) is valid.

From the curve shown for argon in Fig. 5,

$$\tfrac{1}{200}\int_0^{200} \epsilon\, q(\epsilon)d\epsilon = 2.6\times10^{-14}\ \text{eV cm}^2 \tag{48}$$

and the power density transferred to the cathode by the generated ions is

$$Q = 9.2\times10^{-5}\ \text{W/cm}^2\,, \tag{49}$$

and $$\bar{\epsilon} = \int_0^{200} \epsilon\, q(\epsilon)d\epsilon \Big/ \int_0^{200} q(\epsilon)d\epsilon = 110\ \text{eV} \tag{50}$$

is the average impacting ion energy. The maximum impacting ion energy is equivalent to the magnitude of the applied potential, or 200 eV. The minimum impacting ion energy is equivalent to the first ionization potential of argon, or approximately 15 eV.

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