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Citation: Journal of Applied Physics **43**, 339 (1972); doi: 10.1063/1.1661118 View online: http://dx.doi.org/10.1063/1.1661118 View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/43/2?ver=pdfcov Published by the AIP Publishing

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## Positive Ion Species and Degree of Dissociation of SO, in dc Discharges of He-SO, Mixtures

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Positive ion sampling measurements have been conducted on dc discharges containing 0.33% and 1.2% SO<sub>2</sub> in He. Ions from SO<sub>2</sub> include S<sup>+</sup>, O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, SO<sup>+</sup>, SO<sub>2</sub><sup>+</sup>, and SO<sub>3</sub><sup>+</sup>. Studies were made of the functional dependencies on gas pressure and discharge current. Interpretation of these results led to the conclusion that appreciable dissociation of SO<sub>2</sub> occurred within the discharge. This hypothesis was confirmed by sampling the neutral gas components with and without a discharge. Measurements show the degree of dissociation increases with discharge current and reaches a limiting value which is relatively constant over the pressure range studied. For 1.2% SO<sub>2</sub> in He, the degree of dissociation can become as large as 80% at 6.5 Torr and for a 20-mA discharge current. The results moreover suggest that an appreciable fraction of the dissociated particles is in the form of SO.

### I. INTRODUCTION

SO<sub>2</sub> has recently aroused interest in many areas including music, politics, and environmental protection. Unfortunately relatively little is known concerning the basic properties of this gas. Few measurements have been reported in the literature relating to the properties of SO<sub>2</sub> when it is subjected to electrical discharges. For these reasons a study was made, using ion sampling methods, of the positive ion species resulting from SO<sub>2</sub> when mixtures of He and  $SO_2$  were subjected to dc discharges. The interpretation of the measured current and pressure dependencies of these ions led to the conclusion that appreciable dissociation of SO<sub>2</sub> occurred in the discharge. To confirm this, neutral analysis studies were conducted to determine the amount of dissociation present under discharge conditions. The present article summarizes these results.

#### II. APPARATUS

The apparatus and techniques employed in the present studies were similar to those used in previous studies of the cataphoresis effect.<sup>1</sup> However, several modifications were made in consideration of the reactive nature of SO<sub>2</sub> and also to allow studies to be made under static and flowing gas conditions. A schematic diagram of the apparatus is shown in Fig. 1. The discharge tube consisted of three sections of 2.5-cm-i.d. Pyrex tubing. The two 30-cm-length end pieces were coupled to the 80-cm-long central part using demountable O-ring joints. The central section contained a conically shaped sampling orifice.<sup>2</sup> A small cylindrical tungsten probe located opposite the orifice was used to estimate the plasma wall potential; it was monitored using a  $10-M\Omega$ input-impedance digital voltmeter (DVM). Measurements of the wall temperature on the outside of the discharge tube, using thermocouples, enabled estimates to be made of the gas temperature.

The aluminum electrodes were of a hollow cathode design and shielded to minimize undesired sputtering effects.<sup>3</sup> Both were moveable with respect to the orifice, thus permitting sampling from all regions of the discharge. Moreover, the electric field E within the discharge could be determined by measuring the potential drop across the tube at constant current for various electrode spacings. Use of two separately regulated discharge power supplies allowed the probe potential to be set at any desired value.

The quadrupole mass spectrometer was a 20-cm bakeable type which has previously been described.<sup>4</sup> The instrument was operated in a constant  $\Delta m$  mode so that transmission of the various ions would be mass independent.<sup>5</sup> Signals due to the transmitted ions could be amplified using a 10-stage Fairchild SPM-01-301 dynode structure. Both the quadrupole and the dynode structure were contained in a stainless-steel housing which was attached to the discharge tube using glass-to-metal bellows assemblies. The vacuum system, while not of the high-vacuum type, could easily be evacuated to  $\approx 10^{-7}$ Torr before measurements were undertaken.

Neutral analysis measurements were made using the analyzer shown schematically in Fig. 2. For this type of measurement the analyzer was inserted between the orifice and the quadrupole in the evacuated housing. The basic operation of the neutral analyzer involved collecting the ions which effused through the orifice with two electrodes  $(D_1, D_2)$  at the entrance of the analyzer. The remaining beam of neutral particles was then subjected to an electron beam in a field-free region. Some of the resulting ions, through the use of appropriate potentials on the grids  $G_1-G_5$ , were then accelerated into the quadrupole. In this manner the constituency of the neutral beam could be determined. To estimate the degree of dissociation of  $SO_2$  in the discharge, measurements were made of the relative values of the ion current signals of  $SO_2^+$  from the neutral beam, with and without a discharge. Obviously the functional dependence of the





dissociation on parameters such as pressure and discharge current could be estimated from this type of measurement. Moreover, from a comparison of the data for  $SO_2^*$  and  $SO^*$  information can be inferred relating to the nature of the dissociated fragments.



FIG. 2. Schematic drawing of the neutral analyzer. Electrodes  $D_1$  and  $D_2$  are used to collect ions in the beam which effuse through the orifice. Neutral particles in the beam are ionized by the electron beam. Average electron energies used in this work were  $\approx 70 \text{ eV}$ . Grids  $G_1 - G_5$  are used to control the ions which are subsequently analyzed by the quadrupole.

III. EXPERIMENTAL RESULTS

Figures 3 and 4 represent examples of the current signals due to ions which effused through the orifice from the discharge. These data refer to a concentration of 0.33% SO<sub>2</sub> in He. Ions shown are those resulting from the ionization of SO<sub>2</sub>. In Fig. 3 ion current signals are shown as a function of normalized gas pressure  $(p_0 = 273p/T)$  for a discharge current of 15 mA. It is apparent that for gas pressures increasing from 0.4 Torr, the signals increase, exhibit a maximum, and then decrease. Figure 4 indicates the dependence on discharge current at  $p_0 = 0.8$  Torr. Here it is evident that the functional dependence on current is quite different for O<sup>\*</sup> and O<sub>2</sub><sup>\*</sup> as compared to SO<sub>2</sub><sup>\*</sup> and SO<sub>3</sub><sup>\*</sup>. Data shown in Figs. 3 and 4 were obtained before the neutral analyzer was incorporated into the system.

Figure 5 gives examples of data obtained from the analysis of the neutral particles which effused through the orifice from the discharge tube. The results refer to a mixture of 1.2% SO<sub>2</sub> in He subjected to various discharge currents at pressures of p = 3.3, 6.5, and 10.2 Torr.

Figure 5 clearly shows that the  $SO_2^*$  ion current signals, which reflect the concentration of  $SO_2$  in the beam, decrease when a discharge is created in the tube. Also shown in Fig. 5 are data relating to  $SO^*$ . It is apparent that the behavior of  $SO^*$  differs somewhat from  $SO_2^*$ . The interpretation of this result will be discussed in Sec. IV.

At various times during the course of these studies, deposits formed on the inside wall of the discharge tube. A small amount of yellow elemental sulfur was observed near the cathode; however, the majority of the material observed was white and somewhat crystalline in appearance. Deposition took place along the discharge in the sections of the tube external to the evacuated housing, where the walls were cooler due to convection losses.



FIG. 3. Ion current signals from  $SO_2$  as a function of normalized gas pressure for 0.33%  $SO_2$  in He. The discharge current was 15 mA. The sampling position was 36 cm from the anode and cathode.

The process was enhanced at higher pressures or when the tube walls were externally cooled. When the tube was opened in an effort to collect a sample for analysis, the white substance immediately hydrolyzed to form a colorless liquid. Chemical analysis of this liquid showed it to be for the most part sulfuric acid. The white substance was considered to be  $\alpha$ -SO<sub>3</sub>, or a polymer of a poly-sulfur peroxide of the form (SO<sub>x</sub>)<sub>n</sub>, where  $3 \le x \le 4$ , as described by Schenk and Steudel.<sup>6</sup>

## **IV. DISCUSSION**

In these studies He<sup>+</sup> and He<sub>2</sub><sup>+</sup> were also observed. Their relative concentrations were dependent on discharge parameters such as gas pressure. The function of the helium in the mixture was to primarily serve as a buffer gas. Since O<sub>2</sub> and S have the same atomic masses, identification was made based on the natural isotopic abundances of the nuclides of oxygen and sulfur.<sup>7</sup> For example, ion signals observed at mass 50 were approximately 4.4% of the signals detected at mass 48. Since <sup>34</sup>S has a reported abundance of 4.22%, we conclude that mass 50 corresponds to <sup>34</sup>S<sup>16</sup>O<sup>+</sup>. The existence of ions such as S<sub>2</sub><sup>+</sup> and S<sub>2</sub>O<sup>+</sup> at mass 64 and 80, respectively, cannot be ruled out entirely, although the probability is believed to be small.

The functional dependence on pressure of  $SO_3^+$  was omitted

from Fig. 3, since it was detected over so narrow a range that the results were not believed significant. Results in Fig. 3 show the expected decrease of the ion-current signals at high gas pressures. Reasons for the difference between the various ions are not fully understood. The moveable electrodes enabled estimates to be made of the effective electric-field-to-pressure ratio  $(E/p_0)$  in the position column. This parameter is related to the average electron energy. Measurements of  $E/p_0$  indicated that below  $p_0 = 1.0$  Torr the values increased significantly compared to the results at higher pressure. Hence it is likely that the decrease in the data below 1 Torr shown in Fig. 3 may be related to appreciable changes in dissociation and/or ionization by electron impact.

The interpretation of results such as shown in Fig. 4 was based on the assumption that the different functional dependencies on current for O<sup>\*</sup> and O<sub>2</sub><sup>\*</sup>, compared to  $SO_2^*$  and  $SO_3^*$  implied different production processes. Specifically, at 0.8 Torr it seems clear that  $SO_2^*$  and  $SO_3^*$  must be formed in a collision including an  $SO_2$ molecule. Moreover if dissociation of  $SO_2$  increases with discharge current, the observed dependencies for  $SO_2^*$  and  $SO_3^*$  are understandable. If O<sup>\*</sup> and  $O_2^*$  are created primarily in collisions involving dissociation fragments from  $SO_2$ , their dependence could also be explained. A consistent explanation for the behavior of S<sup>\*</sup>



FIG. 4. Ion current signals from SO<sub>2</sub> for 0.33% SO<sub>2</sub> in He as a function of discharge current. The normalized pressure was  $p_0 = 0.8$  Torr. Sampling was performed 36 cm from the anode and cathode.



FIG. 5. Ion current signals of  $SO_2^+$  and  $SO^+$  obtained from the operation of the neutral analyzer, as a function of discharge current. The data refer to 1.2% SO<sub>2</sub> in He. The decrease in the ion current signals is interpreted as a measure of the dissociation of SO<sub>2</sub> in the discharge. The increase, for currents  $\approx 30$  mA, is believed to be due to the presence of impurities at high currents. Discharge instabilities prevented measurements for currents greater than 18 mA at 3.3 Torr.

and SO<sup> $\star$ </sup> in Fig. 4 leads to the conclusion that these ions may be created both by collisions involving SO<sub>2</sub> molecules and also their dissociation products.

Appearance potentials of positive ions formed by electron impact with SO<sub>2</sub> were first reported by Smyth and Mueller.<sup>8</sup> Since then several similar studies have been made. Reese, Dibeler, and Franklin<sup>9</sup> reported the appearance potentials in the following sequence of increasing electron energy:  $SO_2^* > SO^* > S^*$  (or  $O_2^* > O^*$ , ranging from  $12.4 \pm 0.1$  to 20.6 eV. In the present studies it is also apparent that ion formation by collisions of  $\text{He}^+$ ,  $\text{He}_2^+$ , or  $\text{He}^m$  (metastables) with SO<sub>2</sub> is a likely possibility. The ions observed at mass 80 in the present study are identified as SO3\*. As with the other ions formed from SO<sub>2</sub>, isotopic abundance considerations were used in identifying mass 80. Meschi and Meyers<sup>10</sup> identified ion masses at 80, 81, and 82 as being  $S_2O^{*}$ . This study was made by subjecting a mixture of  $SO_2$  and sulfur vapor to a 60-cps discharge. Gas samples were stored in 1-liter glass bulbs and then subjected to mass analysis. Because of the great differences, such as the effect of the addition of sulfur vapor,

between this study and the present experiment, a direct comparison of results is not possible. Although the formation process for  $SO_3^+$  is not known, it may possibly be created by reactions similar to those proposed to account for the production of  $SO_3^{-6}$ :  $e + SO_2 - SO_2^+ + 2e$  followed by  $SO_2^+ + SO_2 - SO_3^+ + SO$ . The decrease in the  $SO_3^+$  ion current signals with increasing discharge current shown in Fig. 4 could thus be explained on the basis that removal of  $SO_2^+$ .

To our knowledge direct measurements of the dissociation of  $SO_2$  in a discharge have not been previously reported. There is however some indirect evidence for dissociation from previous investigations involving afterglow measurements.<sup>11,12</sup> Possible dissociation reactions in the present study are

$$M + \mathrm{SO}_2 - \mathrm{SO} + \mathrm{O} + M \tag{1}$$

and

$$M + \mathrm{SO}_2 - \mathrm{S} + 2\mathrm{O} + M, \tag{2}$$

where M refers to an electron, ion, or possibly an excited particle of He or  $SO_2$ . The interpretation of the present results, as will be explained, suggests that reaction (1) is the dominant dissociation process. In the neutral measurements, shown in Fig. 5, it is apparent that for a fixed gas pressure in the discharge tube, the SO2<sup>+</sup> ion current signals rapidly decrease when the discharge is created.<sup>13</sup> As the discharge current is increased, the signals then become relatively insensitive to a further increase in current.<sup>14</sup> We assume that the observed SO<sub>2</sub><sup>+</sup> resulted solely from SO<sub>2</sub> which effused through the orifice, and was subsequently ionized in the neutral analyzer. That is, no  $SO_2$  is formed by collision processes outside the orifice. This assumption seems reasonable since the background pressure in this region is  $\approx 10^{-5}$  Torr. The decrease in the SO<sup>+</sup><sub>2</sub> ion current signals shown in Fig. 5 is interpreted as a measure of the loss of  $SO_2$  in the discharge due to dissociation. For example, at p = 6.5 Torr, and a discharge current of 20 mA, the SO<sub>2</sub> is approximately 80% dissociated.<sup>15,16</sup> It is also clear from Fig. 5 that the dependence on current for SO<sup>+</sup> differs from SO<sub>2</sub><sup>+</sup>. This difference is believed to be due to the possibility that SO<sup>+</sup> can be formed in two different ways in the neutral analyzer region. The very large SO<sup>+</sup> signals observed when ions are sampled directly from the discharge suggests the possibility of the formation of SO within the discharge. Some of these particles will then effuse through the orifice into the neutral analyzer where subsequent ionization will result in SO<sup>+</sup> current signals. The second method by which SO<sup>+</sup> could be formed would be due to the direct dissociative ionization of  $SO_2$  in the neutral analyzer. Clearly, this would be the only method possible in the limit of zero discharge current. The above interpretation would account for the apparent differences between  $SO^*$  and  $SO_2^*$  evident in Fig. 5. The initial decrease in the SO<sup>+</sup> ion current signals with increasing discharge current could be explained by the loss of  $SO_2$  due to dissociation within the discharge. However, as the dissociation increases, there will be an increasing amount of SO which effuses from the discharge into the analyzer. Hence the percent change in the signals from 0- to say 20-mA current will be greater for  $SO_2^*$  than for  $SO^*$ . This explanation is consistent with the results shown in Fig. 5. It is apparent from Fig. 5 that the degree of dissociation is relatively independent of pressure over the range investigated.

It is clear from Fig. 5 for the 6.5- and 10.2-Torr curves that as the discharge current is increased from 20 to 30 mA, the apparent degree of dissociation decreases. Analysis of the ion current signals obtained by sampling ions directly from the discharge indicates that as the discharge current is increased, impurity ions such as those resulting from water vapor become of increased importance. For example, at p = 6.5 Torr the ion peaks resulting from water vapor increase  $\approx 150\%$ as the current is increased from 20 to 30 mA. These ions will be formed by collisions with particles such as  $He^{+}$ ,  $He_{2}^{+}$ ,  $He^{m}$ . If these latter particles contribute to the dissociation of SO<sub>2</sub>, the presence of the impurities will then effectively reduce the degree of dissociation. For this reason, the apparent decrease in dissociation at high discharge currents is not believed to reflect a basic change in the dissociation mechanism, but rather an experimental difficulty which is often encountered when operating at high dc discharge currents.

It is interesting to compare the relative abundances of  $SO_2^+$  and  $SO^+$  at zero discharge current with previous magnetic mass-spectrometer results. The relative abundance of  $SO^+$  to  $SO_2^+$  for 70-V electrons was reported to be approximately 72%.<sup>9,17</sup> From Fig. 5 the relative abundance varies from 60 to 68%. In view of the differences between these two experiments, this discrepancy is not believed to be significant.

An extension of the above explanation for dissociation leads to the conclusion that, at a fixed pressure, the differences between the signals for  $SO_2^+$  and  $SO^+$  should be a measure of the amount of SO present in the discharge. Unfortunately the relative cross sections for the formation of  $SO^*$  from  $SO_2$  and the direct ionization of SO by electron impact are not known. To simplify the estimate of the amount of SO present, we assume that these cross sections are comparable.<sup>18</sup> At a given pressure and current, the current signals for SO<sup>+</sup> must be corrected by subtracting that amount which is formed directly from SO<sub>2</sub>. The data at zero current serve as a calibration point, in that they indicate the relative amounts of  $SO^*$  and  $SO_2^*$  formed, respectively, by dissociative and direct ionization of SO<sub>2</sub>. The resulting SO<sup>+</sup> current value must be further corrected if it is apparent that SO is being lost within the discharge by dissociation processes such as  $M + SO \rightarrow S + O + M$ . Evidence for this reaction was an increase in S<sup>+</sup> signals, observed from the direct ion sampling measurements. Considering this type of process one should add a rather small correction (~15%) to the SO<sup>+</sup> value. On this basis one concludes, for example, that for p=6.5 Torr and a 20-mA discharge current, approximately 65% of the neutral gas particles from  $SO_2$  are in the form of SO. In view of the above assumptions, the estimate is obviously approximate.<sup>19</sup>

The present results in SO<sub>2</sub> seem to be reasonable when

compared with CO<sub>2</sub> dissociation studies. Dissociation of CO<sub>2</sub> in the positive column of a glow discharge has been reported by Corvin and Corrigan.<sup>20</sup> Smith<sup>21</sup> observed in a flowing CO<sub>2</sub>-N<sub>2</sub>-He laser that the amount of dissociation increased with discharge current. The data in Fig. 5 are consistent with this result. Studies by Karube and Yamaka<sup>22</sup> on sealed CO<sub>2</sub> lasers indicate the fraction of decomposed CO<sub>2</sub> molecules is 60% for a 10-mA dc discharge at 10 Torr. Buser and Sullivan<sup>23</sup> report that for dc discharges in He-CO<sub>2</sub> mixtures, under certain conditions up to 80% dissociation is observed.<sup>24</sup>

#### V. CONCLUSIONS

The major positive ions observed from  $SO_2$  in dc discharges containing 0.33 and 1.2%  $SO_2$  in He are S<sup>+</sup>, O<sup>+</sup>,  $O_2^+$ ,  $SO^+$ ,  $SO_2^+$ , and  $SO_3^+$ . Identification is based on the known isotopic abundances of S and O. The explanation of the current and pressure dependencies of these ions is consistent with the belief that appreciable dissociation of SO<sub>2</sub> occurs within the discharge. Measurements of the neutral species confirm this interpretation. Data indicate that as much as 80% dissociation occurs for a 20-mA discharge. The results also imply that a considerable amount of the dissociated particles are in the form of SO.

- <sup>6</sup>P. W. Schenk and R. Steudel, in *Inorganic Sulphur Chemistry*, edited by G. Nickless (Elsevier, New York, 1968), Chap. 11. <sup>7</sup>R. L. Heath, in *Handbook of Chemistry and Physics*, 47th ed. (Chemical Rubber Co., Cleveland, Ohio, 1966).
- $^8{\rm H.}$  D. Smyth and D. W. Mueller, Phys. Rev. 43, 121 (1933).  $^9{\rm R.}$  M. Reese, V. H. Dibeler, and J. L. Franklin, J. Chem.
- Phys. 29, 880 (1958). <sup>10</sup>D. J. Meschi and R. J. Myers, J. Am. Chem. Soc. 78,
- 6220 (1956).
  <sup>11</sup>M. A. A. Clyne, C. J. Halstead, and B. A. Thrush, Proc. Roy. Soc. (London) 295A, 355 (1966).
- <sup>12</sup>A. G. Gaydon, Proc. Roy. Soc. (London) 146, 908 (1934).
- <sup>13</sup>Measurements of the ions and the neutral particles from the discharge as a function of axial distance from the cathode confirmed that the data given in Fig. 5 were obtained under conditions such that cataphoresis effects were minimized (see, for example, Ref. 1.) This was achieved by operating at a high SO<sub>2</sub> concentration and relatively low pressures and discharge currents. From previous investigations in other gas mixtures it is known that the above conditions greatly reduce the cataphoresis effect.
- <sup>14</sup>Data shown in Fig. 5 were obtained under flowing gas conditions  $\approx 0.5 \text{ cm}^3/\text{sec.}$  This comparatively small flow rate was used to ensure minimum removal of SO<sub>2</sub> by gas clean up at the cathode. Operation at the relatively high SO<sub>2</sub> concentration would also minimize the over-all effect. Studies of clean up in He-N<sub>2</sub> mixtures [R. B. Tombers, J. P. Gaur, and

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<sup>&</sup>lt;sup>1</sup>J. P. Gaur and L. M. Chanin, J. Appl. Phys. 40, 256 (1969). <sup>2</sup>Initial measurements (Figs. 3 and 4) were made using a discharge tube having a  $125-\mu$ -diam orifice. To obtain reliable data at high pressures, later studies were made using a tube having a  $30-\mu$ -diam orifice.

<sup>&</sup>lt;sup>3</sup>J. P. Gaur and L. M. Chanin, Rev. Sci. Instr. **39**, 1948 (1968).

<sup>&</sup>lt;sup>4</sup>G. F. Sauter, R. A. Gerber, and H. J. Oskam, Physica 32, 1921 (1966).

<sup>&</sup>lt;sup>5</sup>C. E. Woodward and C. K. Crawford, Laboratory of Insulation Research, MIT, Technical Report No. 194 1964 (unpublished).

L. M. Chanin, J. Appl. Phys. 42, 4855 (1971)] show that when this effect is important, the ion current signals are strongly dependent on time. In the present studies, measurements indicated the ion signals were essentially time independent. Hence while some  $SO_2$  removal probably occurred at the cathode, the effect was believed quite small. No deposition of material was observed on the walls of the discharge tube during the time interval necessary to acquire the results given in Fig. 5.

- <sup>15</sup>Gas pressures given in Fig. 5 are not normalized pressures. For the data referring to p = 10.2 Torr, normalized pressures varied from  $p_0 = 9.3$  to 6.2 Torr as the current varied from 0 to 30 mA, respectively. For p = 6.5 Torr,  $p_0$  varied from 6.0 to 3.9 Torr for currents from 0 to 30 mA, respectively. For p = 3.3 Torr,  $p_0$  varied from 3.0 to 2.3 Torr for currents from 0 to 18 mA, respectively.
- <sup>16</sup>One can readily show that the reduction in the ion current signals with increasing current, evident in Fig. 5, is not due to the dependence of the orifice conductance on gas temperature.
- <sup>17</sup>Data shown in Fig. 5 were obtained using electron energies  $\approx 70$  eV. Significant differences in the results were not observed for electron energies 70-100 eV. This suggests that this range is close to the maximum in the total ionization

cross section. To our knowledge measurements of this quantity have not been reported. A maximum in the total ionization cross section for  $CO_2$  was reported by R. K. Asundi, J. D. Craggs, and M. V. Kurepa, [Proc. Phys. Soc. (London) 82, 967 (1963)] to be 80-100 eV.

- <sup>18</sup>At 100 eV for CO<sub>2</sub> this assumption is not unreasonable. Compare J. T. Tate and P. T. Smith, Phys. Rev. 39, 270 (1932), for CO<sup>+</sup>: and for CO<sub>2</sub><sup>+</sup>, H. S. W. Massey, *Electronic and Ionic Impact Phenomena* (Clarendon, Oxford, England, 1969), Vol. 2, p. 1046.
- <sup>19</sup>If the reactions  $e + SO \rightarrow S^* + O + 2e$  or  $\rightarrow O^* + S + 2e$  are important in the neutral analyzer region, this would also add a corresponding correction to the SO<sup>\*</sup> value. On this basis the estimate of the percent of SO<sub>2</sub> in the form of SO probably represents a lower limit.
- <sup>20</sup>K. Kutszegi Corvin and S. J. B. Corrigan, J. Chem. Phys. 50, 2570 (1969).
- <sup>21</sup>A. L. S. Smith, Brit. J. Appl. Phys. 2, 1129 (1969).
- <sup>22</sup>N. Karube and E. Yamaka, J. Appl. Phys. 41, 2031 (1970).
- <sup>23</sup>R. G. Buser and J. J. Sullivan, J. Appl. Phys. 41, 475 (1970).
- $^{24}$ C. J. Chen, J. Appl. Phys. 42, 1016 (1971), has recently reported that during the current pulse in a high-current pulsed CO<sub>2</sub> laser, the CO<sub>2</sub> is totally dissociated into CO and O.

# A New Analysis of Space-Charge-Limited Emission between Concentric Spheres and Concentric Cylinders\*

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Space-charge-limited current flow between a small spherical cathode and a concentric spherical anode has been reexamined, taking into account the full energy and angle distribution of the emitted thermoelectrons. A similar analysis has been carried out for concentric cylindrical electrodes. On the basis of the theory thus developed, self-consistent iterative computations have been carried out to determine the variation of the potential and the space charge with radius at various cathode temperatures and fixed anode potential. The important effect of the initial angular motion of the thermoelectrons is demonstrated, and a comparison with other calculations is presented.

#### INTRODUCTION

The flow of space-charge-limited thermionic electron currents between concentric spheres and concentric cylinders has been studied for many years.<sup>1</sup> The usual purpose of such investigations has been the design of electron guns of large current density for electron beam devices.<sup>2</sup> However, the aim of our work was the simulation of an effective point source of electrons diverging from an inner cathode sphere toward an outer anode sphere, and current density was of secondary importance. The electron source is used in a Purcell-type electron monochromator in which a chromatic (energydispersed) image of the apparent source is produced by a double-focussing electrostatic prism consisting of sectors of two concentric spheres.<sup>3</sup>

The effective source from which the electrons appear to diverge can be described by extrapolating the tangents to electron trajectories reaching the anode backward toward the cathode. The region of space in which the extrapolated tangents intersect, located near the center of the cathode, can be regarded as the apparent source. For good energy resolution, the size of this source should be as small as possible.

In practice, an electron gun of this type will be operated under space-charge-limited conditions. In order to design the electron source, a numerical solution to Poisson's equation is required, taking full account of the initial energy and angle distribution of the thermoelectrons. In the course of a search through the extensive literature on this subject, we have not been able to find such a solution. The published solutions all contain approximations, normally in the treatment of the initial energy and angle distribution, that make them difficult to apply to our problem.<sup>4</sup> For these reasons, we decided to reanalyze space-charge-limited current flow between concentric spheres by a self-consistent method in which the physical situation is described exactly, and the only approximations made are those necessary in the numerical solution of differential equations and in nu-

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