# Plasma Chemical Model for Decomposition of SF<sub>6</sub> in a Negative Glow Corona Discharge

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Received January 28, 1994; accepted March 23, 1994

#### Abstract

A zonal plasma chemical model is proposed to account for the observed oxidation and decomposition of sulfur hexafluoride (SF<sub>6</sub>) by a negative, point-to-plane glow-type corona discharge in pressurized SF<sub>6</sub>/O<sub>2</sub>/H<sub>2</sub>O gas mixtures. The model yields dependencies of stable neutral oxidation by-products such as SOF<sub>2</sub>, SO<sub>2</sub>F<sub>2</sub>, SOF<sub>4</sub>, S<sub>2</sub>F<sub>10</sub>, and SO<sub>2</sub> on time, discharge current, and O<sub>2</sub> and H<sub>2</sub>O concentrations which are consistent with measured results. Electron-impact-induced dissociation of SF<sub>6</sub> in the glow region of the discharge is the decomposition rate-controlling process. The relative roles played by different reactions involving neutral free radicals and ions in different zones of the discharge are examined, and in some cases, reaction rate coefficients have been adjusted within reasonable limits to give best fits to observed production rates of various by-products. Problems of uniqueness that arise because of gaps in our knowledge about important processes that should be included in the model are also discussed.

#### 1. Introduction

Compressed sulfur hexafluoride (SF<sub>6</sub>) is widely used as an electrical-insulating medium in equipment that operate at high-voltage such as found in electric-power transmission systems, high-energy particle accelerators, pulse-power switches, and X-ray machines. Previous work [1–6] has shown that when corona discharges occur in SF<sub>6</sub>, a host of corrosive and/or toxic by-products can be formed which are obviously of concern from the points-of-view of system reliability and safety. The stable gaseous by-products formed in SF<sub>6</sub> corona include: SO<sub>2</sub>F<sub>2</sub>, SOF<sub>2</sub>, SOF<sub>4</sub>, SO<sub>2</sub>, S<sub>2</sub>F<sub>10</sub>, S<sub>2</sub>OF<sub>10</sub>, S<sub>2</sub>O<sub>5</sub>, and HF. The absolute yields of all except SF<sub>4</sub> and HF have been measured for corona generated in point-to-plane electrode gaps under a variety of conditions [2, 7–16].

Determinations have been made of the dependencies of the by-product yields and production rates on various parameters including: absolute gas pressure, discharge current and polarity, duration of the discharge, and the concentrations of water vapor and molecular oxygen. The predominant sources of oxygen for formation of the oxyfluoride species SOF<sub>2</sub>, SO<sub>2</sub>F<sub>2</sub>, and SOF<sub>4</sub> were identified from massspectrometric analyses of SF<sub>6</sub> decomposed by corona discharges for cases where normal <sup>16</sup>O<sub>2</sub> or H<sub>2</sub><sup>16</sup>O were substituted respectively with <sup>18</sup>O<sub>2</sub> and H<sub>2</sub><sup>18</sup>O (see Ref. [8]). It was found, for example, that SOF<sub>2</sub> derives its oxygen predominantly from H<sub>2</sub>O, while SO<sub>2</sub>F<sub>2</sub> derives its oxygen predominanly from  $O_2$ . The species SOF<sub>4</sub> acquires its oxygen from either H<sub>2</sub>O or O<sub>2</sub>, where the predominant source depends on which of these two gases is the more abundant. Surprisingly, once H<sub>2</sub>O and O<sub>2</sub> are present in the gas at trace levels, it is found that rates for oxyfluoride production are relatively insensitive to the concentrations of these gases [2, 6-10].

For constant-current negative-glow corona in sufficiently large gas volumes, the production rates of the predominant by-products tend to be nearly constant with time. Any deviations from constancy usually occur during early stages of the discharge [2, 9], and in the case of some species like  $S_2F_{10}$ , these deviations appear to be correlated with "electrode conditioning" as discussed in Ref. [16]. Significant deviations from a constant production rate have been reported [14] for SOF<sub>2</sub> and SO<sub>2</sub>F<sub>2</sub> in cases where the gas volume is relatively small, the water vapor content is high  $(\geq 2000 \text{ parts in } 10^6 \text{ by volume, ppm}_v)$  and the degree of decomposition exceeds more than about 0.1 percent of the original SF<sub>6</sub>. Under such conditions, it is found that SOF, can actually be consumed during the discharge after a sufficiently long period of time, i.e, it has a "negative production rate". Deviations from constant production can be expected to occur as the concentrations of the by-products increase and secondary reactions begin to become more important. Heating of the gas by the discharge can also introduce changes in by-product production rates with time.

Previous interpretations [11] of measured SF<sub>6</sub> decomposition rates in negative-glow corona generated in SF<sub>6</sub>/O<sub>2</sub>, SF<sub>6</sub>/N<sub>2</sub>, and SF<sub>6</sub>/Ne mixtures containing less than 20% SF<sub>6</sub> suggest that recombination of the SF<sub>6</sub> dissociation fragments back into SF<sub>6</sub> predominates and typically less than 3% of the SF<sub>6</sub> molecules initially dissociated within the discharge by electron impact form measurable gaseous decomposition products. The production rates for oxyfluorides in positive corona are typically an order-of-magnitude higher than in negative corona at comparable average discharge currents [2]. Positive corona in SF<sub>6</sub> tends to exhibit rapidly fluctuating or pulsating current with filamentary structure and is thus less easily controlled or quantified than negative corona. In the case of negative point-plane corona in SF<sub>6</sub>, the discharge current is very constant with time and the glow region is restricted and clearly defined from optical observations. The positive corona in SF<sub>6</sub> appears to be a higher temperature discharge than negative corona and the dominant decomposition mechanisms are probably more like those that occur in a spark discharge [17-19]. At the present time, the negative-corona discharge appears to be more amenable to modeling.

The processes that should be considered in a model for discharge-induced chemistry of  $SF_6$  decomposition and oxidation in low-temperature glow and corona discharges have been compiled and reviewed [20]. Since the time of this review, additional information has become available and revisions have been made in the rates for some key processes that need to be considered in formulating a model for  $SF_6$  discharge chemistry. The model discussed in the present

work includes new information about reaction rate coefficients and can be considered as an extension of our earlier model [20, 21]. The present model calculations include many more reactions than previously considered. Two slightly different versions of the model are used to demonstrate the problem of uniqueness.

#### 2. Zonal model of negative corona

# 2.1. Definition of zones

The assumptions upon which the proposed zonal model for negative glow-type point-plane corona discharge chemistry is based were introduced in earlier publications [8, 20, 21]. In this model, three zones of differing chemical activity are defined as shown in Fig. 1. Zone-1 corresponds to the volume of the discharge glow in which ionization and excitation of molecules by electron collisions is important. It is within this region that molecules dissociate and that fast reactions involving the dissociation products (free radicals) occur with highest probability. Zone-2 is defined as the region between the glow and the planar anode in which charge transport by negative ions occurs. The chemistry in this zone is dominated by ion-molecule reactions. The third zone (zone-3) is assigned to the main gas volume surrounding the point-plane gap and is the zone in which the chemistry is characterized by slow gas-phase or surface reactions.

In the present model, the relatively small cathode-fall region between the glow and point cathode is not considered to be a separate zone from the point-of-view of chemical activity. The relatively strong electric field in the cathode fall will accelerate ions from the glow toward the cathode and secondary electrons away from the cathode toward the glow. These accelerated ions and electrons are expected to make only minor contributions to the initial gas dissociation by ion-molecule or electron-molecule collisions



Fig. 1. Diagram of a negative point-plane glow-type corona discharge showing the three different zones of chemical activity postulated in the present model.

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in the cathode fall. The discharge is sustained by the secondary electrons released at the cathode by processes such as electric-field emission or impact of positive ions, metastable excited species, and photons. The basic assumptions that apply to each of the zones defined above are discussed in the next section. The transport of species between zones is governed by diffusion, which in the case of negative ions, is influenced by the electric field in the gap.

## 2.2. Basic assumptions

2.2.1. Zone-1 (glow region). The glow region for negative point-plane corona corresponds to the small volume which is observed to be of nearly uniform luminosity near the tip of the point electrode. The glow region is assumed, in the present model, to be spherical with a radius R and volume  $\tau_c$ . The actual size of the glow is determined from optical observations [12]. For the experimental conditions to which this model applies,  $\tau_c$  is much smaller than the main gas volume  $\tau_t$ , i.e.,  $\tau_c/\tau_t \simeq 10^{-9}$ .

Within the glow, the electron temperature  $(T_e)$  is much greater than the gas temperature  $(T_g)$ , i.e.,  $T_e \ge T_g$ . The value of  $T_g$  within  $\tau_c$  is assumed to be the same as that of the gas in the main volume. This is justified by the small ratio  $\tau_c/\tau_t$ . The electric field-to-gas density ratio (E/N) within the glow is assumed to satisfy the condition

$$E/N \simeq (E/N)_{\rm c}, \quad r < R, \tag{1}$$

where  $(E/N)_c$  is the critical value of E/N at which the electron-impact ionization rate equals the electron-molecule attachment rate. This assumption is justified by theoretical models [22] of discharge development in SF<sub>6</sub> and measurements [23] of electric fields within constricted gas discharges in SF<sub>6</sub>. It is possible that at high currents (greater than a milliampere) E/N can exceed  $(E/N)_c$  within the glow [23], however, large deviations of the field from the critical value in a highly electronegative gas like SF<sub>6</sub> will lead to discharge instabilities. As noted by Morrow [24] in discussing a model for streamer propagation in SF<sub>6</sub>, the electron density in the discharge will drop by more than an order-of-magnitude as E/N is decreased from  $1.03(E/N)_c$  to  $0.97(E/N)_c$ . It can be expected that when the discharge is initiated, the space charge associated with ions and electrons in a stable glow will build up to the point where the electric field acquires a value at or slightly above the minimum value,  $(E/N)_{c}$ , needed to sustain ionization.

Dissociation or ionization of SF<sub>6</sub> and other "contaminant" molecules such as O<sub>2</sub> and H<sub>2</sub>O is confined to the glow region, since for  $E/N < (E/N)_c$ , energetic electrons are quickly thermalized by collisions and subsequently removed by attachment processes [25, 26]. It is additionally assumed that all biomolecular reactions of neutral or ion species in the glow region are at their high-pressure limit and are sufficiently fast (greater than about 10<sup>-15</sup> cm<sup>3</sup>/s) that they go to completion in or near this region. The reaction times are therefore short compared to the times required for diffusion of the active species out of the volume  $\tau_c$ . These assumptions are reasonable for highly reactive free radicals and high absolute gas pressures equal to or greater than 100 kPa. The previous measurements [2, 8, 13-16] of SF<sub>6</sub> decomposition in corona discharges to which the predictions of the present model can be compared were performed for pressures in the range of 100 to 500 kPa.

A consequence of the above assumptions is that the highly reactive intermediates that result directly or indirectly from dissociation of  $SF_6$  such as F and  $SF_5$  are not only confined to  $\tau_c$ , but are also in a steady-state condition within that volume, i.e.,

$$\frac{\mathrm{d}[\mathrm{F}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{SF}_{5}]}{\mathrm{d}t} = 0, \quad r \leq R$$
$$[\mathrm{F}] = [\mathrm{SF}_{5}] = 0, \quad r > R, \tag{2}$$

where t denotes time. It will be argued in Section 3.1.1 that in order to make the additional asumption that species such as F and SF<sub>5</sub> have a spatially uniform density distribution within the glow, the radius of this zone should be assigned an effective value that is somewhat smaller than the measured value R. This assumption is used in calculating the quantities in moles of the by-products that are formed. When considering neutral diffusion rates out of the glow, it is desirable to choose an effective value for the radius that is greater than R. As will be discussed in Section 3.3.2, the choice of a large value for R to calculate the diffusion loss rates tends to compensate for the "trapping" of neutral species near the glow by turbulent effects.

2.2.2. Zone-2 (ion-drift region). In this zone, E/N decreases from the critical value at the glow boundary to a lower value at the anode which depends on the point-to-plane spacing. As noted above, once the electrons exit zone-1 they rapidly attach to form stable or quasi-stable negative ions through processes such as three-body attachment, e.g.,

$$e + SF_6 + M \to SF_6^- + M \tag{3}$$

where M is an arbitrary molecular species in the gas, or dissociative attachment, e.g.,

$$e + \mathrm{SF}_6 \to \mathrm{SF}_5^- + \mathrm{F},\tag{4}$$

where  $SF_5^-$  is formed in an energetically stable state.

The negative ions formed outside of the glow region are responsible for nearly all of the charge transport in zone-2. At electric-field strengths below the critical value, it is known that negative ions such as  $F^-$ ,  $SF_5^-$ , and  $SF_6^-$  will not readily relinquish the extra electron by collisional detachment processes [27, 28]. Photodetachment processes are also known to be unimportant [29]. However, various ion-conversion processes such as charge exchange, and Fexchange are known [9, 30-34] to be fast at the low fields and gas temperatures associated with zone-2. In particular, reactions of  $SF_6^-$  with discharge by-products like  $SOF_4$  and SiF<sub>4</sub> have rates at or close to the collision limit, and have the potential for significantly influencing the overall discharge chemistry. The possible importance of these reactions is enhanced by the fact that they take place in a volume that is much larger than that of the glow region. The effects of ion-molecule reactions in the drift region are assessed here assuming that once a negative ion hits the anode surface it is destroyed, e.g., either deposited or consumed, so that it does not result in formation of a neutral species that is returned to the main gas volume. Implications of this assumption are considered later in Section 3.2.

2.2.3. Zone-3 (main gas volume). The discharge occurs in a gas volume that is much larger than the volume of the glow region. This main gas volume is assumed to be at ambient temperature ( $T_g \sim 300 \text{ K}$ ). The gas in this volume is static and consists of SF<sub>6</sub> with initial low levels of water vapor

and oxygen, where  $[H_2O]/[SF_6] \le 4 \times 10^{-4}$  and  $[O_2]/[SF_6] \le 0.01$ . Both  $[H_2O]$  and  $[O_2]$  are maintained at constant levels. This is justified by the additional assumption that the maximum level of SF<sub>6</sub> decomposition is weak, i.e.,  $[X_i]/[SF_6] \le 2 \times 10^{-4}$ , where  $X_i$ , i = 1, 2, ... is any stable gaseous by-product of the discharge. These assumptions conform to the conditions of experiments with which the results of the present model are to be compared [2].

The fact that the decomposition is weak is of significance in that it allows one to neglect second-order reactions resulting from diffusion of the by-products  $X_i$  back into the small volume of the discharge. It is assumed that once a neutral by-product reaches a boundary at or near that of  $\tau_e$ , it essentially escapes into the main gas volume, never to return. There they either remain as stable components of the gas or undergo reactions with the minor gas constituents,  $H_2O$  and  $O_2$ , or with contaminants on the walls of the containment vessel. The possible effect on diffusion of species out of the glow region from perturbations of the gas flow near the point electrode are also considered but not specifically included in the model. These effects are manifested by vortex formation in gas flow resulting from local ion transport. [35].

Gas-phase reactions that occur in the main gas volume are necessarily much slower than those that occur in or near the glow. Surface reactions are limited by the times required for species to diffuse from the glow region to the walls, and will be relatively unimportant when the experiment observation times is shorter than this diffusion time.

## 3. Reaction scheme

# 3.1. Glow region (zone-1)

It is within the glow region of the negative corona that most of the significant and complex chemistry occurs. In the following subsections, the chemistry of zone-1 is discussed in terms of four different types of processes, namely: (1) dissociation by electron impact, (2) recombination reactions involving the fragment species produced by dissociation of  $SF_6$ , (3) oxidation reactions of  $SF_6$  fragments with the molecules  $H_2O$  and  $O_2$  or fragments from the breakup of these molecules, and (4) losses from the glow region due to diffusion into the other zones.

3.1.1. *Electron impact dissociation*. The electron-impact induced dissociation reaction

$$e + SF_6 \to SF_{6-n} + nF + e, n \ge 6 \tag{5}$$

is the process that controls the rate of SF<sub>6</sub> decomposition in the glow, and therefore it is important to make a reasonable estimate of this rate. It has been shown previously [2, 11] that the net SF<sub>6</sub> dissociation rate from all reactions of the type indicated by process (5) determines the upper limit on the SF<sub>6</sub> decomposition rate in the discharge. This means that the net decomposition rate,  $r_t$ , must satisfy the condition  $r_t < r_d$ , where  $r_d$  is the net SF<sub>6</sub> dissociation rate in the discharge. The net decomposition rate is that corresponding to the sum of the production rates for all observed sulfurcontaining by-products, i.e.,

$$r_{\rm t} = \sum j d[\mathbf{X}_{ij}]/dt \tag{6}$$

where  $X_{ij}$  is a by-product containing j sulfur atoms,  $j \ge 1$ .

The net equivalent unimolecular  $SF_6$  dissociation rate by electron impact can be estimated by the formula [2, 11, 21].

$$r_{\rm d} \simeq (Ilk_{\rm d}/ev_{\rm d}\,\tau_{\rm c})[\rm{SF}_{6}],\tag{7}$$

where I is the discharge current associated with electron transport in the glow, l is the effective mean path length for electron motion in the glow, e is the electron charge, and  $k_d$ and  $v_d$  are, respectively, the SF<sub>6</sub> dissociation rate constant and electron drift velocity at  $E/N = (E/N)_c$ . The quantity in parentheses has the units of a unimolecular rate constant and will be denoted here by  $k_D$ , i.e.,  $r_d \simeq k_D[SF_6]$ . The form of eq. (7) implies a uniform electron density within the volume  $\tau_c$ . In general, the electron density is not uniform. Allowing that E/N can slightly exceed the critical value  $(E/N)_c$  within parts of the glow, it is expected that the density will vary and that at any position x < R, it will be approximately proportional to the factor

$$\exp\left\{\int_0^x \left[\alpha_i(x') - \eta_a(x')\right] \, \mathrm{d}x'\right\}$$

where  $\alpha_i$  and  $\eta_a$  are respectively the ionization and attachment coefficients of the gas [2]. It can be expected, therefore, that the mean electron path length, l, will be less than implied by the size of the glow. Assuming that  $l = \gamma R$ , where  $\gamma$  is an adjustable constant such that  $\gamma < 1.0$ , we obtain

$$k_{\rm D} = \frac{3\gamma I k_{\rm d}}{4ev_{\rm d}(\pi R^2)}.$$
(8)

A value of  $\gamma = 0.33$  has been selected for the present calculations. This is equivalent to assuming that the electron density is uniform within a sphere that has about half the radius of the observed glow, i.e.,  $R_{eff} \simeq 0.01$  cm. This adjustment is significant but also within the experimental uncertainties of the measured values for R at different discharge currents [21]. The value for  $k_d$  and  $v_d$  at  $(E/N)_c$  have been calculated from numerical solutions to the Boltzmann transport equation using a set of electron-impact collision cross sections derived by Phelps and Van Brunt [36] from fits to measured electron-transport data. The Boltzmann transport-equation yields electron kinetic-energy (ɛ) distribution functions  $f(\varepsilon, E/N)$  that depend on E/N. The distribution function for  $E/N = (E/N)_c$ , denoted here by  $f_c(\varepsilon)$ , can then be used to compute  $k_d$  and  $v_d$ .

Summing over the cross sections  $\sigma_{xi}(\varepsilon)$  for excitation by electron collision to all antibonding electronic states of SF<sub>6</sub>, one obtains a net dissociation rate coefficient  $k_d$  given by [36]

$$k_{\rm d} = (2/m_{\rm e})^{1/2} \int_0^\infty \varepsilon f_{\rm c}(\varepsilon) \sum_i \sigma_{xi}(\varepsilon) \, \mathrm{d}\varepsilon, \qquad (9)$$

where  $m_e$  is the electron mass. In selecting the cross sections for inclusion in eq. (9), it was assumed that SF<sub>6</sub> behaves like CF<sub>4</sub> in that all electronic excitation leads to dissociation [37]. It was previously argued [20] that this assumption is supported by optical-emission data [38]. At electron-impact energies high enough for electronic excitation, the SF<sub>6</sub> emission spectrum is dominated by atomic fluorine lines and broad featureless peaks indicative of dissociative excitation. It is not yet certain that the weak emission band at 480 nm recently observed by Casanovas and coworkers [39] from corona discharges in "pure" SF<sub>6</sub> is really due to SF<sub>6</sub> itself. It

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was noted [39] that this radiation might come from an  $SF_n$  (n < 6) fragment or an unknown contaminant.

The electron drift velocity at  $(E/N)_c$  was computed from  $f_c(\varepsilon)$  using

$$v_{\rm d} = (-e/3)(2/m_{\rm e})^{1/2}(E/N)_{\rm c} \int_0^\infty \sigma_{\rm m}(\varepsilon)^{-1} \frac{\mathrm{d}f_{\rm c}(\varepsilon)}{\mathrm{d}\varepsilon} \,\mathrm{d}\varepsilon, \tag{10}$$

where  $\sigma_m(\varepsilon)$  is the electron momentum transfer cross section. The calculated values for  $v_d$  are in agreement with experimental results such as reported by Aschwanden [40] and Nakamura [41].

It was shown from previous calculations [20, 36] that the presence of H<sub>2</sub>O or O<sub>2</sub> in SF<sub>6</sub> at low levels (below 10% concentration by volume), has a negligible effect on the electron-energy distribution  $f_{c}(\varepsilon)$ . Therefore, the dissociation rate determined for pure SF<sub>6</sub> is assumed also to apply for all the gas mixtures considered here that contain small quantities of H<sub>2</sub>O and O<sub>2</sub>. If all dissociation processes are included in the calculation using eq. (9), i.e., all processes leading to ions as well as neutral fragments, one obtains the value  $k_d$  (max) = 7.43 × 10<sup>-9</sup> cm<sup>3</sup>/s at the critical field,  $(E/N)_{\rm c} = 3.57 \times 10^{-19} \,{\rm V}\,{\rm m}^2$ . This value was shown [20] to be consistent with the results of Masek and coworkers [42] obtained at a lower E/N and agrees to within a factor of 2 with resuls of a similar calculation by Kline [43] who used a different SF<sub>6</sub> cross-section set. (Uncertainties of about a factor of 2 are considered to be reasonable for this calculation [36].)

It can be expected that processes leading to ion formation such as dissociative ionization and dissociative attachment will make less of a contribution to chemistry in the glow region than processes leading to neutral fragment formation. This is because ions are swept out of the glow more rapidly by the field and will thus have less time to react. If ion-formation processes are completely excluded, one obtains  $k_d$  (min) =  $5.7 \times 10^{-9}$  cm<sup>3</sup>/s.

The net SF<sub>6</sub> dissociation rate constants used for the two versions of the model (model-1 and model-2) considered were selected to lie within the range  $k_d$  (min)  $< k_d < k_d$ (max), namely  $k_d = 6.55 \times 10^{-9}$  cm<sup>3</sup>/s for model-1 and  $k_d =$  $6.70 \times 10^{-9}$  cm<sup>3</sup>/s for model-2. The difference in these values is of no significance and is due to the choice of a higher rate for SF<sub>6</sub> dissociation into the SF<sub>2</sub> fragment in model-2 than in model-1 when the rates for all other dissociation channels are kept the same. More will be said about the differences between the two models later. Again, the purpose of considering two models is to demonstrate that, to within the uncertainties of the information about various rates, it is possible to construct more than one version of the model that yields nearly the same results.

Although the value of  $k_d$  given by eq. (9) using known cross sections is considered to be a reliable estimate, there is no information about the relative contributions to  $k_d$  from the various possible dissociation channels leading to different SF<sub>n</sub> fragments. Four different dissociation channels are included as indicated in Table I. Of these, it is assumed that the channel leading the SF<sub>5</sub> predominates and accounts for more than 90 percent of the dissociation in both versions of the model. Listed in Table I are equivalent unimolecular rate constants calculated using  $k_d$  and  $v_d$  [determined from eq. (10) to be  $2.0 \times 10^7$  cm/s at  $(E/N)_c$ ] in eq. (8) for a current of 40 µA and R = 0.02 cm. The rates for the individTable I. Equivalent unimolecular  $SF_6$  dissociation rates for model-1 and model-2 calculated using eq. (8) with  $I = 40 \,\mu A$  and  $R = 0.02 \,cm$ 

Rate Coefficients (1/s)		
Model-1	Model-2	
$k_1 = 60.5$	$k_1 = 60.5$	
$k_2 = 2.9$	$k_2 = 2.9$	
$k_3 = 0.85$	$k_3 = 0.85$	
$k_4 = 0.87$	$k_4 = 2.37$	
	Rate Coefficients Model-1 $k_1 = 60.5$ $k_2 = 2.9$ $k_3 = 0.85$ $k_4 = 0.87$	

ual channels,  $k_i$ , satisfy the requirement that

$$k_{\rm d} = \sum_{j=1}^{4} k_j. \tag{11}$$

It should be noted that the summation of eq. (11) is not necessarily the same as that in eq. (8), since it is possible that a particular  $SF_n$  fragment is formed from excitation of more than one electronic state of  $SF_6$ .

No distinction is made between dissociation leading to fragments in their ground state and to fragments in excited states. The subsequent chemistry assumes a predominance of interactions involving species in their ground electronic state and with internal energies consistent with gas-kinetic conditions at 300 K. This is equivalent to the assumption that all dissociation fragments have been thermalized, i.e., have undergone deexcitations, before entering into a chemical reaction.

It must be emphasized that the rate coefficients in Table I are model specific and may not be applicable to conditions that deviate from a glow-type corona discharge considered here. The rate coefficients were adjusted to give results that agree with experimental observations. The rates for dissociation into  $SF_4$  and  $SF_2$  fragments were found, for example, to be significant in affecting the production rates for  $SOF_2$  and  $SO_2F_2$  respectively. The higher rate for  $SF_2$  formation in model-2 is more consistent with observations of Ryan and Plumb [44, 45] in a microwave plasma which suggests that  $SF_6$  breaks down as far as  $SF_2$  in a single-step collision process.

The electron-impact dissociation rates assumed for other species are listed in Table II. These rates correspond to the same discharge conditions used to obtain the rates for  $SF_6$  dissociation given in Table I. As will be shown in Section 5.4, dissociation of the  $SF_6$  fragments such as  $SF_5$  into smaller fragments is generally of minor significance. The multistep fragmentation of  $SF_6$  was omitted from earlier versions of the model [20, 21]. Neglect of multistep frag-

Table II. Equivalent unimolecular dissociation rates assumed for  $SF_6$  dissociation products and the minor constituents  $O_2$ and  $H_2O$ . These rates are used in both versions of the model and apply to the condition  $I = 40 \,\mu A$  and  $R = 0.02 \,cm$ 

Reaction	Rate coefficient (1/s)	
$SF_5 \rightarrow SF_4 + F$	$k_{5} = 65$	
$SF_4 \rightarrow SF_3 + F$	$k_{6} = 65$	
$SF_3 \rightarrow SF_2 + F$	$k_7 = 88$	
$SF_2 \rightarrow SF + F$	$k_8 = 55$	
$S_2F_{10} \rightarrow SF_5 + SF_5$	$k_{9} = 135$	
$S_2F_{10} \rightarrow SF_6 + SF_4$	$k_{10} = 80$	
$0_2 \rightarrow 0 + 0$	$k_{11} = 50$	
$H_2O \rightarrow H + OH$	$k_{12} = 50$	

mentation can usually be compensated for by small adjustments in the rates for other processes.

Provided the concentrations of  $H_2O$  and  $O_2$  are low, electron-impact dissociation of these molecules does not play an important role in the overall oxidation chemistry of SF<sub>6</sub> (see Section 5.4). Because of the insensitivity of the model predictions to the assumed rates given in Table II, no attempt was made to determine these rates more accurately. Although the rates in Table II are physically reasonable, they are model specific and should therefore not be used in cases where these processes are more important such as in SF<sub>6</sub>/O<sub>2</sub> mixtures containing more than 10% O<sub>2</sub>.

3.1.2. Recombination of  $SF_6$  dissociation fragments. Following the dissociation of  $SF_6$  by electron impact in the glow region, the next most important class of reactions are those among the  $SF_6$  dissociation fragments that either lead to reformation of  $SF_6$  or other long-lived stable sulfur-fluoride compounds such as  $SF_4$  and  $S_2F_{10}$ . Table III lists the radical recombination reactions that have been considered together with their recently estimated rate coefficients and the rate coefficients actually used in models-1 and -2.

Of particular importance in determining the net  $SF_6$  decomposition rate is the reaction

$$\mathbf{F} + \mathbf{SF}_5 + M \xrightarrow{\kappa_{15}} \mathbf{SF}_6 + M, \tag{12}$$

where again M is a third body required for stabilization. The important role played by this reaction is expected because of the assumption that  $SF_5$  and F are the primary products of  $SF_6$  dissociation. From a reanalysis of the data relevant to determination of the S-F bond energy in  $SF_6$ , Tsang and Herron [46] have argued that the rate constant for reaction (12) at the high-pressure limit should have a temperature dependence given by

$$k_{15} = 1.1 \times 10^{-11} (T_g/300)^{-1} \,\mathrm{cm}^3/\mathrm{s}.$$
 (13)

This yields a rate constant at 300 K (see Table III) that is more than an order-of-magnitude smaller than that used in our earlier model [20]. In both versions of the present model, we have selected a rate for process (12) of  $1.5 \times 10^{-11}$  cm<sup>3</sup>/s which is close to that predicted by eq. (13). In the process of adjusting  $k_{15}$  downward, it was necessary to make compensating changes in other rates that will be discussed later.

Most of the reactions listed in Table III involve the radicals  $SF_3$  and  $SF_5$  that are known [47, 48] to be the least energetically stable of the  $SF_n$  fragments and therefore likely to be the most reactive. The rates for reactions involving  $F_2$ such as [49]

$$SF_4 + F_2 \rightarrow SF_5 + F, \quad k = 5.3 \times 10^{-22} \text{ cm}^3/\text{s},$$
  
 $SF_5 + F_2 \rightarrow SF_6 + F, \quad k = 7.3 \times 10^{-16} \text{ cm}^3/\text{s},$  (14)

are too low to be of any consequence in the glow region. In both versions of the model, the species  $F_2$  is assumed, after being formed by the reaction

$$F + F + M \rightarrow F_2 + M, \quad k = 2.9 \times 10^{-16} \text{ cm}^3/\text{s},$$
 (15)

to drift without further reaction into the main gas volume where it remains. At the present time, there have been no determinations of the  $F_2$  production rate in corona discharges.

Table III.	High-pressure	limit for radica	l recombination rate	constants at 300 K
		2		

		$k_i (\mathrm{cm}^3/\mathrm{s})$		the first the future we
i	Reaction	tion Calculated	Model-1	Model-2
13	$SF + F \rightarrow SF_2$	$(2.0 \times 10^{-11})^{a}$	$1.0 \times 10^{-12}$	$2.0 \times 10^{-11}$ *
14	$SF_3 + F \rightarrow SF_4$	$(2.4 \times 10^{-11})^{b}$	$2.0 \times 10^{-13}$	$2.4 \times 10^{-11}$ *
15	$SF_5 + F \rightarrow SF_6$	$(1.1 \times 10^{-11})^{c,d}$	$1.5 \times 10^{-11}$	$1.5 \times 10^{-11}$
16	$SF + SF \rightarrow S + SF_2$	$(1.8 \times 10^{-11})^{c}$	$2.5 \times 10^{-11}$	$2.5 \times 10^{-11}$
17	$\rightarrow$ S <sub>2</sub> F <sub>2</sub>		$1.0 \times 10^{-14}$	$1.0 \times 10^{-14}$
18	$SF_3 + SF_3 \rightarrow SF_2 + SF_4$	$(2.2 \times 10^{-12})^{c}$	$2.0 \times 10^{-13}$	$2.2 \times 10^{-12}$ *
19	$SF_5 + SF_5 \rightarrow S_2F_{10}$	$(1.8 \times 10^{-12})^{c}$	$1.4 \times 10^{-12}$	$1.4 \times 10^{-12}$
20	$\rightarrow$ SF <sub>4</sub> + SF <sub>6</sub>		$1.5 \times 10^{-14}$	$1.5 \times 10^{-14}$
21	$SF + SF_3 \rightarrow S + SF_4$	$(1.3 \times 10^{-11})^{b}$	$5.0 \times 10^{-11}$	$5.0 \times 10^{-12}$ *
22	$SF_2 + SF_2$		$6.0 \times 10^{-19}$	$6.0 \times 10^{-14}$ *
23	$SF + SF_5 \rightarrow SF_4 + SF_2$	$(1.1 \times 10^{-10})^{b}$	$1.0 \times 10^{-15}$	$1.0 \times 10^{-15}$
24	$SF_3 + SF_5 \rightarrow SF_6 + SF_2$	$(4.0 \times 10^{-12})^{b}$	$5.0 \times 10^{-12}$	$5.0 \times 10^{-12}$
25	$\rightarrow$ SF <sub>4</sub> + SF <sub>4</sub>		$7.0 \times 10^{-14}$	$7.0 \times 10^{-14}$
26	$SF_4 + F \rightarrow SF_5$	$(2.3 \times 10^{-15})^{e}$	$1.0 \times 10^{-16}$	$1.0 \times 10^{-16}$

\* Different rates for models-1 and -2

\* From Ryan and Plumb (Ref. [50])

<sup>b</sup> From Refs [51] and [52], estimated using geometrical mean rule:  $k_{A+B} = 2\{(k_{A+A})(k_{B+B})\}^{1/2}$ 

<sup>c</sup> From Refs [51] and [53] estimated using Benson's geometrical model

<sup>d</sup> From Tsang and Herron (Ref. [46])

<sup>e</sup> From Herron (Ref. [49])

As seen from Table III, the recombination reaction

$$F + SF_4 + M \to SF_5 + M \tag{16}$$

was assumed to have a rate coefficient in both versions of the model that is more than an order-of-magnitude lower than that suggested by Herron [49]. It is presently believed that the rate for process (16) is probably smaller than originally suggested. Nevertheless, if its rate is increased in model-2 to the value recommended in Ref. [49], then it has a small effect in reducing the SOF<sub>2</sub> yield to give a better agreement between the predictions of model-1 and model-2 (see Section 5.1).

Because the density of the SF radical in the glow region is typically much smaller than that of the other SF, radicals, the reactions involving SF such as  $SF_n + SF$ , which are estimated [50-53] to be fast, generally have little or no consequence on the predicted yields of the major by-products and can therefore be neglected (see Section 5.4). The present model allows for the formation of stable S<sub>2</sub>F<sub>2</sub> from SF reactions. Although this species has been identified from mass spectrometric observations [54, 55] as a product of SF<sub>6</sub> decomposition in discharges, there is no information about its formation rate in high-pressure corona with which the present predictions can be compared. Moreover, the mechanism for its formation may be more complex than suggested by the present model [55]. The predicted  $S_2F_2$  yield is, in any case, much smaller than that of the major by-products, and the inclusion or exclusion of the process that leads to its formation does not affect the yields of the major byproducts.

Other than the differences in the dissociation rates for  $SF_6 \rightarrow SF_2 + 4F$  given in Table I, the difference between model-1 and model-2 are those rates for the recombination reactions marked with an asterisk in Table III. The recombination rate coefficients used for model-2 tend to agree more closely with the estimated [50-53] rate coefficients.

The rates for the  $SF_5 + SF_5$  reactions are important in determining the  $S_2F_{10}$  yield from discharge-induced decomposition. It is desirable to obtain reasonable predictions of

the  $S_2F_{10}$  yield in light of the recent experimental results reported in Ref. [16]. The rate coefficients for the  $SF_5$ -self reactions shown in Table III have been revised and differ significantly from those used in earlier versions of our model [20, 21].

The rate for  $SF_5 + SF_5 \rightarrow S_2F_{10}$  used previously was based in part on an interpretation [49] of measurements by Tait and Howard [56] in nonaqueous solvents over the temperature range of 153 to 233 K. In retrospect, the positive temperature coefficient that they reported for this reaction raises questions about its relevance to the related gas-phase process because radical-radical association reactions usually have a negative temperature coefficient. It is suspected that the rates reported by Tait and Howard are diffusion limited.

Although it is not easy to quantify the contribution of diffusion, it can be shown [51] that the positive activation energy reported by Tait and Howard is not incompatible with that estimated for a diffusion controlled reaction with a small temperature coefficient given by

$$k_{\rm diff} = 8 \times 10^{-10} \exp\left(-1500/T_{\rm g}\right) \,{\rm cm}^3/{\rm s.}$$
 (17)

Shown in Fig. 2 is an extrapolation of the data of Tait and Howard [56] compared with the diffusion rate coefficient given by eq. (17). The results shown in Fig. 2 suggest that equating gas and solution phase rate constants is probably invalid in this case.

The rate for  $S_2F_{10}$  formation by  $SF_5$  combination can be estimated with the geometric method of Benson [53] used by Ryan and Plumb [45] and Tsang and Herron [46] to treat the  $SF_5 + F$  recombination reaction. The method is based on a collision model in which the rate constant is defined as the product of the ratio of electronic degeneracies of the product (adduct) and reactants,  $g_e$ , the collision rate,  $Z_b$ , and a steric factor  $\alpha_s$ , i.e.,

$$k = q_e Z_b \alpha_e. \tag{18}$$

Each of the terms in eq. (18) is readily obtained from spectroscopic tables, bond energies and molecular geometry.



Fig. 2. Temperature dependence of the rate coefficient for the  $SF_5 + SF_5$  reaction. Shown are the data of Tate and Howard (Ref. [56], open points and solid line) compared with an estimated diffusion limited rate coefficient (dot-dashed line) and results of present calculation based on the geometric model of Benson (solid points and dashed line).

The values for these parameters are tabulated in detail elsewhere [51]. The rate coefficient for the  $SF_5 + SF_5$  reaction predicted by the model of Benson is shown in Fig. 2 as a function of temperature. The predicted rate coefficient has an expected negative temperature coefficient, further supporting the argument that the experimental results obtained in solution give an unreliable estimate of the gas-phase rate.

The Tait and Howard [56] measurements, irrespective of their applicability to gas-phase reactions, refer to the rate of decay of SF<sub>5</sub> radicals, and give no information about the reaction products. In the present model, it is important to known the ratio of the rates leading to  $S_2F_{10}$  formation and to disproportionation into  $SF_4 + SF_6$ . This ratio,  $k_{19}/k_{20}$ (see Table III) was derived previously [49] from modeling of the pyrolysis of  $S_2F_{10}$  in the presence of NO which serves as a radical scavenger. This led to a value for  $S_2F_{10}$ unimolecular decomposition rate constant, and ultimately to a value for  $k_{19}/k_{20}$  at 444 K of 1.9. There are conflicting data that can be used to argue that this number is too small. In particular, the data of Leary and coworkers [57] on infrared multiphoton photolysis of  $SF_5Cl$  leads to a much higher value for  $k_{19}/k_{20}$ .

In pure SF<sub>5</sub>Cl, photolysis gives:

$nhv + SF_5Cl \rightarrow SF_5 + Cl,$	(19)
---------------------------------------	------

$$nhv + SF_5 \to SF_4 + F, \tag{20}$$

 $Cl + SF_5 \rightarrow SF_5Cl,$  (21)

 $F + SF_5 \to SF_6, \tag{22}$ 

 $SF_5 + SF_5 \rightarrow S_2F_{10}, \tag{23}$ 

$$SF_5 + SF_5 \rightarrow SF_4 + SF_6, \tag{24}$$

where nhv corresponds to n photons. In this case, the primary products of the photolysis are  $SF_4$ ,  $SF_6$ , and

 $S_2F_{10}$ . When  $H_2$  is added, the following processes occur:

$$Cl + H_2 \rightarrow HCl + H,$$
 (25)

$$F + H_2 \rightarrow HF + H, \tag{26}$$

 $SF_5 + H \rightarrow SF_4 + HF,$  (27)

 $SF_5Cl + H \rightarrow SF_5 + HCl.$  (28)

Reactions (25) and (26) are particularly significant because they remove the Cl and F radicals and thereby inhibit the recombination reactions (21) and (22). It is found experimentally [57] that the addition of  $H_2$  strongly reduces the SF<sub>6</sub> yield and enhances the S<sub>2</sub>F<sub>10</sub> yield. This observation suggests that the disproportionation [reaction (24)] is a minor process. Recently Willner [58] studied photolysis of SF5Cl in the presence of H<sub>2</sub> using infrared spectroscopy and also found that the yield of  $SF_6$  was much less than that of  $S_2F_{10}$ . There are additional sources of data on the SF<sub>5</sub> combination/disproportionation ratio that are discussed in more detail elsewhere [51]. It can be concluded from this analysis that the ratio  $k_{20}/k_{19}$  at 300 K should be no greater than 0.01. In both versions of the present model we assume that  $k_{20}/k_{19} = 0.01$ . In fact, the disproportionation reaction can be completely omitted without significant effect on the yields of the major by-products.

Schested and coworkers [59] have recently estimated that the rate coefficient  $k_{19}$  for process (23) is about  $2.3 \times 10^{-13}$  cm<sup>3</sup>/s from recent measurements of SF<sub>6</sub> gasphase chemistry using a pulsed radiolysis ultraviolet absorption technique. This is about a factor of 0.16 smaller than the rate coefficient used in the present model, although closer to that used in our previous work [20]. This lower rate is not completely inconsistent with the present model since a decrease in the rate for process (23) can be at least partially offset by decreasing the assumed dissociation rates for S<sub>2</sub>F<sub>10</sub> by electron impact ( $k_9$  and  $k_{10}$  in Table II).

3.1.3. Oxidation reactions. The relatively fast oxidation reactions that are assumed to occur in the glow region are tabulated in Tables IV and V. In order to identify the major sources of oxygen in the formation of the various oxyfluoride by-products such as SOF<sub>2</sub>, SO<sub>2</sub>F<sub>2</sub>, and SOF<sub>4</sub>, a distinction is made between oxygen originating from O<sub>2</sub> and that originating from H<sub>2</sub>O. In the former case, it is assumed that the normal <sup>16</sup>O<sub>2</sub> is replaced with isotopically pure <sup>18</sup>O<sub>2</sub>, and in the latter case, the water vapor is assumed to contain only <sup>16</sup>O. The model predictions can therefore be compared with results from experiments in which isotopic substitutions were made [8]. The rate coefficients are not allowed to have an isotope dependence, e.g., the rates for the S<sup>18</sup>O<sub>2</sub>F + SF<sub>5</sub> and S<sup>16</sup>O<sub>2</sub>F + SF<sub>5</sub> reactions are the same.

The basis for the selection of rate coefficients given in Tables IV and V is the same as used in our earlier work [20]. When possible, we have selected data available in the literature. In other cases, recourse was made to estimates based on analogy. Unfortunately, for many of the radicals of interest here, there are few experimental data available. In cases where the reactions can be treated as the reverse of simple bond breaking reactions, the rate constants can be expected to fall in the range of  $10^{-10}$  to  $10^{-12}$  cm<sup>3</sup>/s depending on steric factors. Because most of the reactions listed in Tables IV and V are of minor importance, it is generally sufficient to estimate their rates to within an order-of-magnitude (see Section 5.4).

Table IV. Radical-radical reactions involving <sup>16</sup>O from H<sub>2</sub>O

i (* 19	Reaction	$k_i (\mathrm{cm}^3/\mathrm{s})$
27	$F + H_2^{16}O \rightarrow {}^{16}OH + HF$	$9.0 \times 10^{-12}$
28	$^{16}OH + SF_5 \rightarrow S^{16}OF_4 + HF$	$1.1 \times 10^{-12}$
29	$^{16}OH + SF_4 \rightarrow S^{16}OF_3 + HF$	$3.6 \times 10^{-15}$
30	$F + S^{16}OF_3 \rightarrow S^{16}OF_4$	$5.0 \times 10^{-11}$
31	$H + {}^{16}OH \rightarrow H_2 {}^{16}O$	$5.0 \times 10^{-13}$
32	$S^{16}OF_3 + {}^{16}OH \rightarrow S^{16}O_2F_2 + HF$	$5.0 \times 10^{-13}$
33	$^{16}OH + F \rightarrow F^{16}OH$	$5.0 \times 10^{-13}$
34	$^{16}OH + ^{16}OH \rightarrow H_2  ^{16}O + ^{16}O$	$2.0 \times 10^{-12}$
35	${}^{16}O + {}^{16}OH \rightarrow {}^{16}O_2 + H$	$3.3 \times 10^{-11}$
36	$^{16}O + SF_5 \rightarrow S^{16}OF_4 + F$	$2.0 \times 10^{-11}$
37	$S^{16}OF_3 + {}^{16}O \rightarrow S^{16}O_2F_2 + F$	$5.0 \times 10^{-13}$
38	$SF_2 + {}^{16}O \rightarrow S {}^{16}OF + F$	$8.0 \times 10^{-14}$
39	$S^{16}OF + {}^{16}O \rightarrow S^{16}O_2F$	$1.0 \times 10^{-13}$
40	$S^{16}O_2F + F \rightarrow S^{16}O_2F_2$	$1.0 \times 10^{-14}$
41	$S^{16}OF + F \rightarrow S^{16}OF_2$	$2.0 \times 10^{-12}$
42	$SF_3 + {}^{16}O \rightarrow S {}^{16}OF_2 + F$	$1.0 \times 10^{-12}$
43	$SF + {}^{16}O \rightarrow S {}^{16}OF$	$1.0 \times 10^{-11}$
44	$SF_3 + {}^{16}OH \rightarrow S {}^{16}OF_2 + HF$	$8.1 \times 10^{-14}$
45	$SF_2 + {}^{16}OH \rightarrow S {}^{16}OF + HF$	$6.0 \times 10^{-14}$
46	$SF + {}^{16}OH \rightarrow S {}^{16}OF + H$	$5.0 \times 10^{-13}$
47	$SF + {}^{16}OH \rightarrow HF + S {}^{16}O$	$1.0 \times 10^{-11}$
48	$S^{16}O + F \rightarrow S^{16}OF$	$1.0 \times 10^{-12}$
49	$S^{16}O + {}^{16}O \rightarrow S^{16}O_2$	$1.0 \times 10^{-11}$
50	$SF_5 + {}^{16}O \rightarrow S {}^{16}OF_5$	$1.0 \times 10^{-11}$
51	$SF_{5} + S^{16}OF_{5} \rightarrow S_{2}^{16}OF_{10}$	$1.0 \times 10^{-13}$
52	$S^{16}OF_5 + S^{16}OF_5 \rightarrow S_2^{16}O_2F_{10}$	$1.0 \times 10^{-13}$
53	$S^{16}O_2F + SF_5 \rightarrow SF_6 + S^{16}O_2$	$1.0 \times 10^{-12}$
54	$S^{16}O_2F + SF_3 \rightarrow SF_4 + S^{16}O_2$	$1.0 \times 10^{-11}$
55	$S^{16}OF_3 + F \rightarrow S^{16}OF_4$	$1.0 \times 10^{-10}$
56	$S^{16}OF_3 + SF_5 \rightarrow SF_6 + S^{16}OF_2$	$1.0 \times 10^{-12}$
57	$S^{16}OF_3 + SF_3 \rightarrow SF_4 + S^{16}OF_2$	$1.0 \times 10^{-12}$
58	$S^{16}OF_5 + SF_5 \rightarrow S^{16}OF_4 + SF_6$	$5.0 \times 10^{-13}$
59	$S^{16}OF + SF_5 \rightarrow S^{16}O + SF_6$	$1.0 \times 10^{-13}$

In some cases we have used rate coefficients that differ slightly from recommended values. For example, the rate coefficient recommended [60] for the important  $F + H_2O$ reaction (reaction 27 in Table IV) is  $1.4 \times 10^{-11}$  cm<sup>3</sup>/s. The best fits to observed oxyfluoride production rates were obtained using a lower value of  $0.9 \times 10^{-11}$  cm<sup>3</sup>/s which lies

Table V. Radical-radical reactions involving <sup>18</sup>O from <sup>18</sup>O<sub>2</sub>

i gai	i Reaction	
60	$S^{18}O_5 + SF_5 \rightarrow S^{18}OF_4 + SF_6$	$5.0 \times 10^{-13}$
61	$S^{18}OF + SF_5 \rightarrow S^{18}O + SF_6$	$1.0 \times 10^{-13}$
62	$S^{18}O_2F + SF_3 \rightarrow S^{18}O_2 + SF_4$	$1.0 \times 10^{-11}$
63	$S^{16}O^{18}OF + SF_3 \rightarrow SF_4 + S^{16}O^{18}O$	$1.0 \times 10^{-11}$
64	$S^{18}O_2F + SF_5 \rightarrow SF_6 + S^{18}O_2$	$5.0 \times 10^{-12}$
65	$S^{18}O^{16}OF + SF_5 \rightarrow SF_6 + S^{16}O^{18}O$	$1.0 \times 10^{-12}$
66	$S^{16}OF + {}^{18}O \rightarrow S^{16}O^{18}OF$	$1.0 \times 10^{-13}$
67	$S^{18}OF_5 + S^{18}OF_5 \rightarrow S_2^{18}O_2F_{10}$	$1.0 \times 10^{-13}$
68	$SF_5 + {}^{18}O \rightarrow S {}^{18}OF_5$	$1.0 \times 10^{-11}$
69	$SF + {}^{18}O \rightarrow S {}^{18}OF$	$1.0 \times 10^{-11}$
70	$SF_3 + {}^{18}O \rightarrow S {}^{18}OF_2 + F$	$1.0 \times 10^{-12}$
71	$S^{18}OF + F \rightarrow S^{18}OF_2$	$2.0 \times 10^{-11}$
72	$S^{16}O^{18}OF + F \rightarrow S^{16}O^{18}OF_2$	$1.0 \times 10^{-14}$
73	$S^{18}O_2F + F \rightarrow S^{18}O_2F_2$	$1.0 \times 10^{-14}$
74	$S^{18}OF + {}^{16}O \rightarrow S^{16}O^{18}OF$	$1.0 \times 10^{-13}$
75	$SF_2 + {}^{18}O \rightarrow S {}^{18}OF + F$	$8.0 \times 10^{-14}$
76	$S^{16}OF_3 + {}^{18}O \rightarrow S^{16}O^{18}OF_2 + F$	$5.0 \times 10^{-13}$
77	$^{18}O + SF_5 \rightarrow S^{18}OF_4 + F$	$2.0 \times 10^{-11}$
78	$^{18}O + ^{16}OH \rightarrow ^{16}O^{18}O + H$	$3.3 \times 10^{-11}$
79	$S^{18}OF + {}^{18}O \rightarrow S^{18}O_2F$	$1.0 \times 10^{-13}$
80	$SF_5 + S^{18}OF_5 \rightarrow S_2^{18}OF_{10}$	$1.0 \times 10^{-13}$
81	$S^{18}OF_5 + S^{16}OF_5 \rightarrow S_2^{18}O^{16}OF_{10}$	$1.0 \times 10^{-13}$

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within the estimated uncertainty [60] for  $k_{27}$ . This is also lower than the rate used in our earlier model [20]. The rate coefficients for reactions of O atoms with SF<sub>2</sub>, SF<sub>5</sub>, and SOF are assigned values close to those measured by Plumb and Ryan [61].

As in our earlier calculation [20], we use a rate for the reaction

$$F + SOF_3 \rightarrow SOF_4$$
 (29)

that is close to the collision limit suggested by Ryan [62]  $(k_{55} = 1.0 \times 10^{-10} \text{ cm}^3/\text{s in Table IV})$ . However, if the rate for this reaction is reduced by two orders-of-magnitude to  $1.0 \times 10^{-12} \text{ cm}^3/\text{s}$ , the yields for the major by-products SOF<sub>2</sub> and SOF<sub>4</sub> change by less than 0.35% and 0.33% respectively. The insensitivity of the model predictions to this reaction can be explained by the relatively low steadystate SOF<sub>3</sub> concentration in the glow. Other radicals that tend to have low steady-state concentrations are S<sup>18</sup>OF, S<sup>18</sup>OF<sub>5</sub>, S<sup>16</sup>O<sup>18</sup>OF, S<sup>18</sup>O<sub>2</sub>F, S<sup>16</sup>O<sub>2</sub>F, <sup>18</sup>O, <sup>16</sup>O, SF<sub>3</sub> and SF. Therefore, as will be seen from the sensitivity analysis discussed in Section 5.4, reactions involving these species are usually of less importance than other reactions. Among the radicals that appear with highest density in the glow are: SF<sub>5</sub>, SF<sub>4</sub>, SF<sub>2</sub>, F, H, <sup>16</sup>OH, S<sup>16</sup>OF<sub>5</sub>, and S<sup>16</sup>OF. The fast reactions involving these species are usually among the most significant in determining by-product yields.

Although the reaction scheme shown in Tables IV and V applies to  $SF_6$  that contains low levels of  $O_2$  and  $H_2O$ , it should not be applied to gas mixtures that contain higher concentrations of  $O_2$ . Consistent with experimental observations, the present model predicts yields for oxygenated products like  $SO_2$ ,  $S_2O_2F_{10}$ , and  $S_2OF_{10}$  that are an order-of-magnitude or more below those of the major byproducts. When oxygen is present at higher levels (>10%), reactions involving  $O_2$ , O, and  $O_3$  become more important and yields of the minor products can significantly increase [11, 12]. At higher  $O_2$  levels, it may be necessary to consider processes presently omitted from the reaction scheme such as those involving formation of  $O_3$  and reactions affecting  $S_2O_2F_{10}$  production such as

$$SF_5 + O_2 + M \to SF_5O_2 + M, \tag{30}$$

$$SF_5O_2 + SF_5 + M \rightarrow SF_5O_2SF_5 + M, \tag{31}$$

which are relatively fast [59, 63, 64] and can significantly affect the  $S_2F_{10}$  yield [16].

In constructing the reaction scheme shown in Tables IV and V, it was necessary to make assumptions about the predominant reaction paths that are often difficult to justify and should therefore be subjected to future investigations. For example, the reaction of SF<sub>3</sub> with OH is assumed to predominantly yield the stable products  $SOF_2 + HF$  rather than the intermediate SF<sub>3</sub>OH which is of questionable stability, but may have a long lifetime in the glow. The reaction of SF<sub>5</sub> with O is assumed to yield both SOF<sub>5</sub> and SOF<sub>4</sub> + F with nearly equal probability. Here the SOF, is formed initially with sufficient internal energy to either decompose back to the reactants or decompose into  $SOF_4 + F$ . However, it is assumed here that under the high-pressure conditions considered, the initially formed SOF<sub>5</sub> radicals are stabilized about 30% of the time by collisions. The choice of predominant pathways for reactions must necessarily take into account the fact that the reaction rates are at their high-pressure limit. In our earlier model [20], the possibility of forming SOF<sub>5</sub> was ignored.

In addition to the reactions given in Tables III, IV, and V, both versions of the model also include the following radical-radical reactions:

$$H + H + M \rightarrow H_2 + M, \quad k_{82} = 1.0 \times 10^{-15} \text{ cm}^3/\text{s}, \quad (32)$$

 $F + H + M \rightarrow HF + M$ ,  $k_{83} = 0.9 \times 10^{-15} \text{ cm}^3/\text{s}$ , (33)

$$F + F + M \rightarrow F_2 + M, \quad k_{84} = 0.2 \times 10^{-15} \text{ cm}^3/\text{s.}$$
 (34)

These reactions are relatively slow and tend to be of minor importance. The rate coefficients for reactions among the radicals F, H, O, and OH are based on values given in the literature [60, 65, 66].

3.1.4. Diffusion losses from the glow. Species formed in the glow region that do not experience subsequent reactions after formation are assumed to drift into the main gas volume and eventually become uniformly distributed within that volume. Among the products in this category are the compounds SOF<sub>4</sub>, HF, H<sub>2</sub>, F<sub>2</sub>, FOH, SO<sub>2</sub>, S<sub>2</sub>O<sub>2</sub>F<sub>10</sub>,  $S_2OF_{10}$ , and  $S_2F_2$ . Of these, only  $SOF_4$  is a major byproduct for which production rates have been experimentally determined. The only other major by-product in this category is HF, for which (although experimentally identified as a discharge by-product) [1, 67] no data exist about its production rate. The species SO<sub>2</sub>, S<sub>2</sub>O<sub>2</sub>F<sub>10</sub>, and S<sub>2</sub>OF<sub>10</sub> have been detected from corona discharges, but make minor contributions to the total decomposition of SF<sub>6</sub> under the conditions considered here. The compounds SOF<sub>4</sub>, SO<sub>2</sub>, and HF can undergo gas-phase or wall reactions in either the main gas volume or the ion-drift region.

The highly reactive intermediate species such as  $SF_5$ , F,  $SF_3$ , SF,  $SOF_3$ ,  $SO_2F$ , SOF, and  $SOF_5$  are confined to the glow region. However, the moderately reactive species that include  $SF_2$ ,  $SF_4$ , and  $S_2F_{10}$  are allowed to escape the glow region. Although these species undergo subsequent reactions in the glow after being formed, it is required that they attain a steady-state condition within the glow so that  $[SF_2]$ ,  $[SF_4]$ , and  $[S_2F_{10}]$  are constant in time for r < R.

In this reaction scheme for the glow, the loss of species  $SF_2$ ,  $SF_4$ , and  $S_2F_{10}$  from the glow region by diffusion is represented by effective unimolecular rate constants. These rate constants are pressure dependent. The values that apply at an absolute gas pressure of 200 kPa are listed in Table VI. The method used to estimate these rate coefficients is discussed in Section 3.3.2. The diffusion rates of the species listed in Table VI from zone-1 into zone-3 are significant in determining the production rates for  $SOF_2$ ,  $SO_2F_2$ , and  $S_2F_{10}$ .

## 3.2. Ion drift region (zone-2)

The processes that occur in the ion-drift region are limited to negative ion-molecule reactions. These reactions are

Table VI. Unimolecular rate coefficients for diffusion loss from the glow region at a pressure of 200 kPa

i	Species	Rate coefficient
85	SF <sub>2</sub>	$k_{85} = 140.0 \ 1/s$
86	SF4	$k_{86} = 94.0 \ 1/s$
87	S2F10	$k_{87} = 33.5 \ 1/s$

found to be of minor importance in affecting the overall corona chemistry in  $SF_6$ . Fast reactions that are potentially significant in zone-2 are listed in Table VII. Given in this table are the rate coefficients measured at two different gas temperatures [29]. These rate constants are consistent with data obtained by different methods [30–32] and with expectations based on F<sup>-</sup> affinities of the various molecules [33, 34]. All of the reactions given in Table VII involve F<sup>-</sup> transfer from  $SF_6^-$ , which is expected to be the predominant initial charge carrier that enters zone-2 from zone-1. The ion  $SF_6^-$  does not appear to react with the oxyfluorides  $SOF_2$  and  $SO_2F_2$  [30].

There are other fast ion-molecule reactions that are likely to occur in the ion-drift region such as [29, 68]

$$SO_2F^- + SOF_4 \rightarrow SOF_5^- + SO_2,$$
 (35)

$$O_2^- + SO_2 \rightarrow SO_2^- + O_2$$
,  $C_2^- = C_2^- C$ 

$$O_2^- + S \to O_2 + S^-.$$
 (37)

However, these reactions have not been considered in the model because they involve minor ion or neutral species. It has been suggested [11] that reaction (37) might be responsible for the formation of circular sulfur deposits observed on the anode in some experiments [2]. Sulfur dimer formation has also been observed [69] in low-pressure glow discharges in SF<sub>6</sub>. These observations suggest the formation of S atoms either directly from dissociation of SF<sub>6</sub> molecules or by subsequent reactions as considered in the present model.

Of the reactions shown in Table VII, only the first two are likely to be important in affecting the concentrations of SOF<sub>4</sub> and SF<sub>4</sub> in the main gas volume. A detailed analysis of the influence of the SF<sub>6</sub><sup>-</sup> + SOF<sub>4</sub> reaction on SF<sub>6</sub> chemistry in glow-type corona has already been made [9]. It was shown in Ref. [9] that the rate equation for SOF<sub>4</sub> production that includes the effect of the SF<sub>6</sub><sup>-</sup> + SOF<sub>4</sub> reaction can be written as

$$\frac{d[SOF_4]}{dt} = r_s - \frac{\beta I k_{89} [SOF_4]}{e \bar{v} \tau_t} \\ \times \left\{ \frac{\exp\left[-(k_{89} [SOF_4]/\bar{v} - k')Z_0\right] - 1}{k_{89} [SOF_4]/\bar{v} - k'} \right\}, \quad (38)$$

where  $\beta$  is the fraction of the current at the boundary between zones-1 and -2 corresponding to SF<sub>6</sub><sup>-</sup> charge carriers,  $\bar{v}$  is the mean drift velocity of SF<sub>6</sub><sup>-</sup>, Z<sub>0</sub> is the distance between  $\tau_c$  and the anode,  $r_s$  is the production rate for SOF<sub>4</sub> within  $\tau_c$  and k' is a decay constant associated with competing SF<sub>6</sub><sup>-</sup> removal or deactivation processes that can also occur in the ion-drift zone.

The effect of the  $SF_6^- + SOF_4$  reaction is to introduce an initial nonlinearity in the  $[SOF_4]$  vs. time curve. At t = 0,  $d[SOF_4]/dt$  is given by  $r_s$ , and after a sufficiently long time

Table VII. Rate constant for fast  $F^-$  transfer reactions at 298 K and 373 K (see Ref. [29])

i		$k_i (\mathrm{cm}^3/\mathrm{s})$		
	Reaction	298 K	373 K	
88	$SF_6 + SF_4 \rightarrow SF_5 + SF_5$	$7.4 \times 10^{-10}$	$5.0 \times 10^{-10}$	
89	$SF_6^- + SOF_4 \rightarrow SOF_5^- + SF_5$	$8.5 \times 10^{-10}$	$4.0 \times 10^{-10}$	
90	$SF_6^- + SO_2 \rightarrow SO_2F^-SF_5$	$1.06 \times 10^{-9}$	$8.1 \times 10^{-10}$	

it approaches a lower constant value of  $r_s - \beta I/e\tau_t$  that represents the limit where all available SF<sub>6</sub><sup>-</sup> is consumed by reaction with SOF<sub>4</sub>. This latter condition is likely to be reached for the experimental conditions considered here.

Using a calculation based on eq. (38) to fit the measured yields of SOF<sub>4</sub> from corona in SF<sub>6</sub> and its mixtures with  $O_2$ ,  $N_2$ , and Ne gave relatively high values for the SF<sub>6</sub> decay constant k'. This indicates the importance of competing reactions that effectively remove SF<sub>6</sub><sup>-</sup> from the ion drift zone. It has been speculated that a mechanism that could deactivate SF<sub>6</sub><sup>-</sup> is the formation of hydrated complexes such as SF<sub>6</sub><sup>-</sup> (H<sub>2</sub>O). These complexes are known to form under high-pressure conditions when water vapor is present [70]. Although this possibility is consistent with the measured data, no information exists about the reactivity of hydrated SF<sub>6</sub><sup>-</sup> toward species like SOF<sub>4</sub>. It was also shown [20, 29] that the competing reactions

$$SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5 \tag{39}$$

and

 $SOF_5^- + SiF_4 \rightarrow SiF_5^- + SOF_4 \tag{40}$ 

can be effective in inhibiting the  $SF_6^- + SOF_4$  reaction if  $SiF_4$  is present at trace levels. This species was observed in corona discharges for the experimental conditions used by Van Brunt [2, 29].

The experimental results of Sauers and Harmon [71] clearly show the dramatic influence of  $SOF_4$  on ion transport after the discharge has been on for relatively short times (<500 s). Within about 300 s of discharge initiation, the predominant charge carrier changes from  $SF_6^-$  to  $SOF_5^-$ . However, data were not obtained for longer times needed to reveal the possible effect of  $SiF_4$ . It is significant that the ion clusters  $SF_6^- \cdot (HF)$  and  $SOF_5^- \cdot (HF)$  are observed to attain relatively high abundances within a short time. These cluster ions together with possible formation of  $SF_6^- \cdot (SF_6)$  and  $SF_6^- \cdot (SF_6)_2$  reported by Patterson [72] could also significantly affect the  $SOF_4$  chemistry in zone-2.

It is interesting to note that fits to experimental results using eq. (38) consistently yielded values for  $\beta$  that were close to unity [9]. This is consistent with the results of Sauers and Harman [71] and Sieck and Van Brunt [29] which indicate that SF<sub>6</sub><sup>-</sup> is the predominant initial negativeion charge carrier. This was also shown [9] to indicate that there is no significant conversion of SOF<sub>5</sub><sup>-</sup> back into SOF<sub>4</sub> at the anode.

Because of the relatively high values that were obtained for k', the overall effect of the  $SF_6^- + SOF_4$  reaction in reducing the yield of  $SOF_4$  measured in the main gas volume is not significantly greater than the effect of slow gas-phase hydrolysis discussed in the next section. This conclusion is especially true in the case considered here of  $SF_6$ that contains only low levels of  $O_2$  and  $H_2O$ . Moreover, a small effect on the  $SOF_4$  yield implies an even smaller effect on the  $SF_4$  concentration in zone-3 because  $SF_4$  is expected to be at a much lower level that that of  $SOF_4$  due to its conversion into  $SOF_2$  by hydrolysis (see next section).

## 3.3. Main gas volume (zone-3)

3.3.1. Gas-phase reactions. The gas-phase reactions in zone-3 that are considered in the present model and that can affect the yields of the major oxyfluoride products

 $SOF_2$ ,  $SO_2F_2$ , nd  $SOF_4$  are listed in Table VIII. The rate coefficients given in this table are those estimated for a gas temperature of 300 K. The rate coefficient,  $k_{91}$ , for the  $SF_4$  hydrolysis reaction was determined by Sauers and coworkers [73] to be  $1.7 \times 0.9 \times 10^{-19} \text{ cm}^3/\text{s}$  at 350 K which agrees to within the uncertainties with the value of  $2.0 \pm 0.6 \times 10^{-19} \text{ cm}^3/\text{s}$  obtained by Ruegsegger and coworkers [74] at 340 K. We assume that a slightly lower value of  $1.5 \times 10^{-19} \text{ cm}^3/\text{s}$  applies at 300 K; although, as shown below, the model prediction is not sensitive to the precise value selected for  $k_{91}$  even though this reaction is important in determining the SOF<sub>2</sub> yield.

It should be noted that, although the rate assumed for the  $SF_4 + H_2O$  reaction appears to be consistent with measured data, there are remaining questions about the temperature dependence of this reaction. Results from measurements in the aqueous phase [75] give a rate for the SF<sub>4</sub> hydrolysis of  $2.8 \times 10^{-19}$  cm<sup>3</sup>/s at 291 K which is also consistent with the value assumed here. However, the fact that the data taken over a temperature range of 60 K all yield the same rate suggests that the activation energy for the reaction is close to zero. Hydrolysis reactions in the aqueous phase usually have activation energies between 50 to 100 kJ mol<sup>-1</sup>. If we use a value of 75 kJ mol<sup>-1</sup> for estimation purposes, we predict [51] a rate constant that changes by about a factor 200 for a temperature change of 60 K. It can thus be argued that the apparent agreement between the  $SF_4 + H_2O$  reaction rates obtained in the gas phase and in solution is probably fortuitous.

It was suggested earlier [76] that the reaction of  $SF_4$  with  $H_2O$  in the gas phase is likely to be a two step process, i.e.,

$$SF_4 + H_2O \rightarrow SF_3OH + HF, \tag{41}$$

$$SF_3OH \rightarrow SOF_2 + HF,$$
 (42)

which may differ from the process that occurs in solution. Sauers and coworkers [73] have argued that the  $SF_3OH$  intermediate could react with water in the aqueous phase to give final products that do not include  $SOF_2$ .

The rate coefficients given in Table VIII for the reactions of SOF<sub>2</sub> and SOF<sub>4</sub> with H<sub>2</sub>O are those measured by Van Brunt and Sauers [77] at 298 K. In the case of SOF<sub>2</sub>, the rate constant given in Table VIII is a factor of  $3 \times 10^{-4}$ smaller than the rate reported by Ruegsegger and coworkers [74] at 340 K. It was suggested that this large difference may have been a consequence of contributions from wall reactions in the latter work. However, as in the case of SF<sub>4</sub> hydrolysis, nothing is known about the temperature dependence of the SOF<sub>2</sub> + H<sub>2</sub>O reaction. At least part of the difference in reported rates for this reaction could merely reflect the fact that the reaction has an appreciable activation energy. If one assumes, for example, an activation energy of about 120 kJ mol<sup>-1</sup>, then it would be possible for

Table VIII. Gas-phase reactions considered to occur in the main gas volume at 300 K

	Reaction	Rate coefficient (cm <sup>3</sup> /s)
91	$SF_4 + H_2O \rightarrow SOF_2 + 2HF$	$k_{91} = 1.5 \times 10^{-19}$ , Refs [73,74]
92	$SF_2 + O_2 \rightarrow SO_2F_2$	$k_{92} \leq 5 \times 10^{-16}$ , Ref. [61]
93	$SOF_{2} + H_{2}O \rightarrow SO_{2} + 2HF$	$k_{93} = 1.2 \times 10^{-23}$ , Ref. [75]
94	$SOF_4 + H_2O \rightarrow SO_2F_2 + 2HF$	$k_{94} = 2.0 \times 10^{-21}$ , Ref. [75]

the rate to increase by two orders-of-magnitude for a 40 K increase in temperature. A strong dependence of  $k_{93}$  on temperature could account for the observed destruction of SOF<sub>2</sub> reported by Casanovas and coworkers [14] if the experimental conditions are such as to allow a significant heating of the gas with time by the discharge. Significant heating of the gas by the discharge did not occur in the experiments with which the present model calculations are compared due to the sheer size of the main gas volume and the fact that the discharge power dissipation was always less than 1 W [2].

The reaction of SF<sub>2</sub> with O<sub>2</sub> is the least known of those listed in Table VIII. An upper limit of the rate constant is estimated by Plumb and Ryan [61] to be less than  $5 \times 10^{-16}$  cm<sup>3</sup>/s. In the present model, SF<sub>2</sub> is the only species that is assumed to react directly with O<sub>2</sub> in the main gas volume. There is no evidence that SF<sub>2</sub> reacts with H<sub>2</sub>O, and the possibility of such a reaction is not considered in this model.

None of the gas-phase measurements upon which the rates given in Table VIII are based have been carried out under conditions which convincingly prove that the reactions are entirely homogeneous. This would require, at a minimum, very extensive studies of the role of wall materials and surface- volume ratios. Even then, the distinction between heterogeneous and homogeneous reactions is difficult to establish. Because of the difficulty in making these kinds of measurements, the "gas-phase" hydrolysis rate constants given in Table VIII should be treated as upper limits.

In the present model, the distinction between heterogeneous and homogeneous reactions in the main gas volume is not a major concern because it is simply assumed that once  $SF_4$  and  $SF_2$  enter the main gas volume, they convert respectively to  $SOF_2$  and  $SO_2F_2$ . In the case of  $SOF_2$ , the oxygen is derived from  $H_2O$ , and in the case of  $SO_2F_2$ , it is derived from  $O_2$  independent of where or how the reactions occur in the volume. The reactions involving hydrolysis of  $SOF_2$  and  $SOF_4$  are, as will be shown below, of relatively minor significance and have been neglected in the final calculation of oxyfluoride production rates.

Estimates of decreases in the concentrations of  $SF_4$ ,  $SOF_4$ , and  $SOF_2$  from hydrolysis in the main gas volume can be made using a rate equation that neglects spatial non-uniformities due to diffusion (see next section):

$$\frac{\mathrm{d}[X_j]}{\mathrm{d}t} = r_{\mathrm{s}j} - k_j [X_j] [\mathrm{H}_2 \mathrm{O}], \tag{43}$$

where  $X_j$  corresponds to one of the compounds SF<sub>4</sub>, SOF<sub>4</sub>, or SOF<sub>2</sub> and  $k_j[X_j][H_2O]$  and  $r_{sj}$  are respectively the rate for hydrolysis and the rate for production for  $X_j$  in the glow plus the main gas volume. Integrating this equation gives:

$$[X_{j}]_{t} = \frac{r_{sj}}{k_{j}[H_{2}O]} [1 - \exp(-k_{j}[H_{2}O]t)].$$
(44)

The fractional loss of  $X_j$  due to hydrolysis at time t is defined by

$$\Delta[X_j]_t \equiv (r_{sj}t - [X_j]_t)/r_{sj}t.$$

$$\tag{45}$$

Using eq. (44) gives

$$\Delta[X_j]_t = \frac{1}{t} \left\{ t - \frac{[1 - \exp(-k_j [H_2 O] t)]]}{k_j [H_2 O]} \right\}.$$
 (46)

The calculated fractional losses using the rate coefficients from Table VIII are shown in Table IX for two different times measured from the start of discharge operation. The calculations were made using a typical H<sub>2</sub>O concentration of 100 ppm<sub>v</sub> in 200 kPa SF<sub>6</sub> ([H<sub>2</sub>O] =  $0.5 \times 10^{-16}$  cm<sup>-3</sup>). The shorter time of  $1 \times 10^3$  s corresponds to the normal minimum time interval used for gas sampling in some experiments [2], and the longer time of  $7.5 \times 10^4$  s corresponds to the maximum time used in the model calculation and the typical maximum time for most experiments with which the calculations are compared. These calculations show that nearly all the SF<sub>4</sub> is converted to SOF<sub>2</sub> during the time of discharge operation, whereas only a small fraction of the SOF<sub>4</sub> and SOF<sub>2</sub> are removed by reaction with H<sub>2</sub>O. Under most of the conditions considered here, the total SOF<sub>4</sub> yield is estimated to be reduced by less than 30% during the course of an experiment due to the combined effects of hydrolysis and ion-molecule reactions in zone-2.

The SOF<sub>4</sub> + H<sub>2</sub>O process will introduce nonlinearities in the yield-vs.-time curves for SOF<sub>4</sub> and SO<sub>2</sub>F<sub>2</sub>. The effect of this reaction on the SOF<sub>4</sub> yield curve is similar to that of the reaction SOF<sub>4</sub> + SF<sub>6</sub> as discussed in Ref. [9]. The modification of the yield curve for SO<sub>2</sub>F<sub>2</sub> is represented by its slope at any time, namely:

$$\frac{d[SO_2F_2]}{dt} = r_{s1} + r_{s2}[1 - \exp(-k_{94}[H_2O]t)],$$
(47)

where  $r_{s1}$  is the production rate for SO<sub>2</sub>F<sub>2</sub> excluding the SOF<sub>4</sub> hydrolysis reaction and  $r_{s2}$  is the production rate of SOF<sub>4</sub> from the glow region. The SO<sub>2</sub>F<sub>2</sub> production rate will thus increase from an initial value of  $r_{s1}$  at t = 0 to a final value of  $r_{s1} + r_{s2}$  as  $t \to \infty$ . Although this type of behavior appears to be consistent with experimental data on SO<sub>2</sub>F<sub>2</sub> yields [2, 8], no attempt was made to use eq. (47) to fit experimental data. Nonlinearities of the type observed in the SO<sub>2</sub>F<sub>2</sub> yield curves would also be explained in part by the slowness of the SF<sub>2</sub> + O<sub>2</sub> reaction. Since only an upper limit is known for the rate of the SF<sub>2</sub> + O<sub>2</sub> reaction, it is not possible to estimate this contribution to nonlinearities. The nonlinearities in both the SOF<sub>4</sub> and SO<sub>2</sub>F<sub>2</sub> yield curves tend to be minor when the O<sub>2</sub> and H<sub>2</sub>O concentrations in SF<sub>6</sub> are within the relatively low ranges considered here.

3.3.2. Diffusion and surface reactions. In this section the effects of diffusion and surface reactions within the main gas volume will be considered. It will first be shown how the diffusion rates of species from zone-1 into zone-3 (see Table VI) have been estimated. The diffusion coefficients,  $D_i$ , for the relevant neutral species given in Table VI are estimated

Table IX. Calculated fractional losses in concentration due to gas-phase hydrolysis in zone-3 for two indicated times measured from the start of discharge operation ( $[H_2O] = 0.5 \times 10^{16} \text{ cm}^{-3}$ )

		Discharge time	(s)
Species	$\Delta[X_i]_i$	$1.0 \times 10^{3}$	7.5 × 10 <sup>4</sup>
SF4	$\Delta[SF_4],$	0.30	0.98
SOF	$\Delta[SOF_4],$	$2.5 \times 10^{-3}$	0.16
SOF <sub>2</sub>	$\Delta[SOF_2]_r$	$2.5 \times 10^{-5}$	$1.8 \times 10^{-3}$

using the classical expression [78]

 $D_i = \frac{1}{2}\lambda_i \langle v_i \rangle \tag{48}$ 

where  $\lambda_i$  and  $\langle v_i \rangle$  are respectively the mean-free path and mean molecular speed of the *i*th species. Assuming ideal-gas kinetics, eq. (48) can be written as

$$D_i = \frac{2}{3} \frac{\left[ (k_{\rm B} T_{\rm g})^3 / \pi m_i \right]^{1/2}}{\sigma_i P}$$
(49)

where  $k_{\rm B}$  is the Boltzmann constant, P is the absolute gas pressure, and  $\sigma_i$  and  $m_i$  are respectively the collision cross section and mass of the *i*th species.

Within the glow region (r < R), the species SF<sub>2</sub>, SF<sub>4</sub>, and S<sub>2</sub>F<sub>10</sub> satisfy rate equations of the form

$$\frac{\partial [X_i]}{\partial t} = k_{ie} [SF_6] + \sum_{n, m} k_{nm} [Y_n] [Y_m] -\sum_l k_{il} [X_i] [Y_l] - k_{id} [X_i] - k_{is} [X_i],$$
(50)

which are coupled to corresponding rate equations for the species  $Y_i$ . In eq. (50),  $[X_i]$  corresponds to one of the compounds  $SF_2$ ,  $SF_4$ , or  $S_2F_{10}$ . The unimolecular rate coefficients  $k_{ie}$ ,  $k_{id}$ ,  $k_{is}$  correspond respectively to those given in Tables I, II, and VI. In the case of  $S_2F_{10}$ ,  $k_{ei} = 0$ . The bimolecular rate coefficients  $k_{nm}$  and  $k_{ii}$  correspond to processes in Tables III-V that respectively form and consume the compound  $X_i$ . In the main gas volume (r > R),  $[X_i]$  depends on r and the rate equation for  $X_i$  is

$$\frac{\partial [X_i]}{\partial t} = D_i \nabla^2 [X_i] - k_{ih} [Z_i] [X_i], \qquad (51)$$

where  $k_{ih}$  corresponds to the appropriate gas-phase reaction in Table VIII and  $Z_i$  is either H<sub>2</sub>O or O<sub>2</sub>. For S<sub>2</sub>F<sub>10</sub>,  $k_{ih} =$ 0 since this species does not appear to react directly with H<sub>2</sub>O or O<sub>2</sub> in the gas phase at 300 K. The possible effect of reactions that are known [79] to occur between S<sub>2</sub>F<sub>10</sub> and H<sub>2</sub>O adsorbed on surfaces will be considered below.

The coefficient  $k_{is}$  for the surface diffusion loss rate from  $\tau_c$  is found by matching the solutions to eqs (50) and (51) at r = R. For the species SF<sub>2</sub> and SF<sub>4</sub>, it is assumed that a steady-state condition applies within the main gas volume, i.e.,  $\partial [X_i]/\partial t = 0$  ( $R_W > r > R$ ) where  $r = R_W$  at the wall. It was previously noted that a steady-state condition for these species also applied within zone-1. For a spherically symmetric gas volume under steady-state conditions, the following boundary condition must also be satisfied at the wall:

$$-D_i \frac{\partial [X_i]}{\partial r} = K_i [X_i], \quad r = R_{\rm W},$$
(52)

where  $K_i \ge 0$  is an effective wall absorption coefficient  $(K_i = 0 \text{ implies total reflection and } K_i \rightarrow \infty \text{ implies total}$ 

Table X. Predicted relative <sup>16</sup>O, <sup>18</sup>O isotope content of the major oxyfluoride by-products from model-2 for different relative <sup>18</sup>O<sub>2</sub> and  $H_2$  <sup>16</sup>O concentrations and  $I = 40 \,\mu A$ 

$\frac{[^{18}O_2]}{[SF_1]}$	[H <sub>2</sub> <sup>16</sup> O]	$\frac{[S^{16}OF_4]}{[S^{18}OF_4]}$	$\frac{[S^{16}OF_2]}{[S^{18}OF_2]}$	$\frac{[S^{16}O_2F_2]}{[S^{18}O_2F_2]}$
[01 6]	[01 6]	[0 01 4]		
$1 \times 10^{-4}$	$2 \times 10^{-4}$	$1.70 \times 10^{3}$	$8.18 \times 10^{3}$	$2.83 \times 10^{-3}$
$1 \times 10^{-4}$	$0.5 \times 10^{-4}$	$1.00 \times 10^{3}$	$4.43 \times 10^{3}$	$0.57 \times 10^{-3}$
$1 \times 10^{-2}$	$2 \times 10^{-4}$	16.7	80.9	$2.76 \times 10^{-3}$
$1 \times 10^{-2}$	$0.5 \times 10^{-4}$	9.55	42.8	$0.54 \times 10^{-3}$

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absorption). It can be shown [80, 81] that this parameter is related to the reflection coefficient,  $\xi_i$ , by

$$K_i = \frac{\langle v_i \rangle (1 - \xi_i)}{2\kappa (1 + \xi_i)},\tag{53}$$

where  $\kappa$  lies in the range of 0.5 to 1.0, and  $\xi_i$  lies in the range of 0 to 1.0. Here,  $\xi_i = 0$  corresponds to perfect absorption and  $\xi_i = 1.0$  to total reflection.

The general solution to eq. (51) for r > R, assuming steady-state and a spherically symmetric volume, is:

$$[X_{i}] = \frac{R[X_{i}]_{R}[(1 + K_{i}) e^{\Lambda_{i}(R_{W}-r)} + (1 - K_{i}) e^{-\Lambda_{i}(R_{W}-r)}]}{r[K_{i}/(\Lambda_{i} + R_{W}^{-1}) (e^{\Lambda_{i}(R_{W}-R)} - e^{-\Lambda_{i}(R_{W}-R)}) + e^{-\Lambda_{i}(R_{W}-R)} + e^{\Lambda_{i}(R_{W}-R)}]}$$
(54)

where

$$\Lambda_i^2 \equiv k_{ih}[Z_i]/D_i. \tag{55}$$

When  $R_{W} \ge R$  and wall effects are negligible, the solution reduces to

$$[X_i] = \frac{R[X_i]_R}{r} e^{-\Lambda_i(r-R)}.$$
(56)

In both eqs (54) and (56),  $[X_i]_R$  is the density of  $X_i$  at the boundary (r = R) between zones 1 and 3. In cases where eq. (56) is a good approximation, the matching of solutions at r = R under steady-state conditions allows a determination of  $k_{is}$  that gives the following expressions for the rates of SOF<sub>2</sub> and SO<sub>2</sub>F<sub>2</sub> production in the main gas volume:

$$\frac{\mathrm{d}[\mathrm{SOF}_2]}{\mathrm{d}t} = \frac{4\pi R D_1 [\mathrm{SF}_4]_R}{\tau_t} (\Lambda_1 R + 1), \tag{57}$$

$$\frac{d[SO_2F_2]}{dt} = \frac{4\pi R D_2[SF_2]_R}{\tau_c} (\Lambda_2 R + 1),$$
(58)

where  $D_1$  and  $D_2$  are the diffusion coefficients for SF<sub>4</sub> and SF<sub>2</sub> respectively that are estimated using eq. (49). The appropriate expression for  $k_{is}$  that corresponds to eqs (57) and (58) is:

$$k_{\rm is} = \frac{3D_i}{R} \left[ R^{-1} + \Lambda_i \right].$$
(59)

For the conditions to which the model applies, it is found that  $\Lambda_i \ll R^{-1}$ , so that, to a good approximation

$$k_{\rm is} \simeq \frac{3D_i}{R^2}.\tag{60}$$

This is a consequence of the relatively small values for both R and the product  $k_{ih}[Z_i]$ . The implication of eq. (60) is that the observed production rates for SOF<sub>2</sub> and SO<sub>2</sub>F<sub>2</sub> are insensititive to the precise values of the rate coefficients given in Table VIII. As noted above, this permits one to assume that once SF<sub>4</sub> and SF<sub>2</sub> enter the main gas volume they will, within a reasonably short time, convert entirely to SOF<sub>2</sub> and SO<sub>2</sub>F<sub>2</sub>.

The diffusion loss rate coefficients given in Table VI are smaller than those used in the earlier version of our model [20]. The present values are considered to be more realistic because they are based on better estimates for  $D_i$  and because allowance has been made for longer retention times

of neutral species in the glow due to vortex formation resulting from momentum transfer to the gas from positive and negative ions moving in opposite directions [35]. Vortex formation can be at least partly compensated for by increasing the effective radius of the glow region used in eqs (59) and (60). The effective radius for the diffusion calculation is allowed to be up to 50% larger than that which defines the actual glow. Localized turbulence is therefore assumed to reduce the rate of neutral species diffusion out of the glow.

Equation (60) was also used to estimate the  $S_2F_{10}$  diffusion loss rate from the glow even though the steady-state condition required to derive this equation does not strictly apply in this case. There is experimental evidence that  $S_2F_{10}$  is slowly destroyed by surface reactions in the main gas volume [79]. One of the products of  $S_2F_{10}$  decomposition on surfaces is SOF<sub>2</sub> which enters the gas phase. At 300 K, the reactions that destroy  $S_2F_{10}$  on surfaces are evidently too slow to allow development of a steady-state condition in the main gas volume, i.e.,  $[S_2F_{10}]$  continues to build up with time during discharge operation. Only for very low discharge currents (less than  $2\mu A$ ) is there evidence that the production rate of  $S_2F_{10}$  from the discharge is low enough that a steady-state condition is approached [15, 16].

Even in the extreme case where  $S_2F_{10}$  is completely destroyed at the walls of the containment vessel by surface reactions, there is a minimum time required to reach an equilibrated condition in the main gas volume. This minimum time is determined by the time it takes the  $S_2F_{10}$ molecules to diffuse to the wall from the glow region, and as will be shown below, this time can be comparable to the total time of the experiment in some cases.

If an extreme case is assumed where  $S_2F_{10}$  is completely destroyed at the wall and has a constant concentration of  $[S_2F_{10}]_R$  at r = R, the solution of eq. (51) with  $k_{ih} = 0$  is [82]

$$C(r, t) = [S_2 F_{10}]_R \frac{R}{r} \left\{ 1 - \frac{(r-R)}{(R_W - R)} + \frac{2}{\pi} \sum_{j=1}^{\infty} \frac{1}{j} \sin \left[ j\pi \frac{(r-R)}{(R_W - R)} \right] \exp \left[ \frac{[D_3(j\pi)^2 t}{(R_W - R)^2} \right] \right\},$$
(61)

where C(r, t) is the time and position dependent concentration of  $S_2F_{10}$  for  $R_W > r > R$  and  $D_3$  is the  $S_2F_{10}$  diffusion coefficient. Spherical symmetry was assumed in deriving this equation together with the initial condition C(r, 0) = 0 for  $R_W > r > R$ . The flux of the diffusing species at the wall is given by

$$F_{\mathbf{w}}(t) = -D_{3} \left[ \frac{\partial C(r, t)}{\partial r} \right]_{r=R_{\mathbf{w}}}$$
$$= \frac{D_{3} \left[ S_{2} F_{10} \right]_{R}}{R_{\mathbf{w}}(R_{\mathbf{w}} - R)} R$$
$$\times \left\{ 1 - 2 \sum_{j=1}^{\infty} \cos\left(j\pi\right) \exp\left[ \frac{-D_{3}(j\pi)^{2} t}{(R_{\mathbf{w}} - R)^{2}} \right] \right\}.$$
(62)

The net  $S_2F_{10}$  loss rate at the wall is then

$$L_{\rm W}(t) = -4\pi R_{\rm W}^2 F_{\rm W}(t).$$
(63)

The fractional loss rate of  $S_2F_{10}$  in the main volume is defined by

$$f_{\rm L} \equiv \frac{|L_{\rm W}(t) - L_{\rm R}|}{L_{\rm R}},\tag{64}$$

where  $L_R$  is obtained from the flux of  $S_2F_{10}$  released from  $\tau_c$  and is approximated here by

$$L_R \cong -4\pi [S_2 F_{10}] D_3 R \tag{65}$$

using eq. (60). From eqs (62)–(65), the fractional loss rate can be written as

$$f_L(t) = 2\sum_{j=1}^{\infty} \cos(j\pi) \exp\left[\frac{-D_3(j\pi)^2 t}{R_W^2}\right],$$
 (66)

for  $R_{\rm W} \ge R$ . Under steady-state conditions it is required that  $f_L = 0$ , i.e., the rate of release of  $S_2 F_{10}$  molecules from the glow should equal the rate of loss at the walls.

Shown in Fig. 3(a) are plots of normalized  $\log_{10} C(r, t) vs.$ radius at different indicated times after the start of the discharge. The values for C(r, t) were calculated using eq. (61) with R = 0.01 cm,  $R_W = 10$  cm, and  $D_3 = 0.007$  cm<sup>2</sup>/s corresponding to an absolute gas pressure of 200 kPa. The data plotted in the figure have been normalized to the value of C(r, t) at r = R and t = 0, i.e.,  $C(R, 0) = [S_2F_{10}]_R$ . Figure 3(b) shows corresponding values for  $f_L(t)$ -vs.-time calculated for three different indicated values of  $R_W$ . It is seen from these results that the time required to reach steady state depends significantly on the value of  $R_W$ . In the experiments



*Fig. 3.* (a) Normalized concentration of  $S_2F_{10}$  calculated using eq. (61) for different radial distances from the glow at different times in the range of 1 to 10<sup>4</sup> seconds assuming  $R_w = 10 \text{ cm}$  and  $C(t, R_w) = 0$  for all  $t \ge 0$ ; (b) fractional loss rate of  $S_2F_{10}$  calculated using eq. (66) for different indicated values of  $R_w$ .

with which the present model are compared,  $R_w$  was in the range of 10 to 15 cm. For  $R_w = 15$  cm, the equilibration time exceeds  $10^4$  s, which is comparable to the total time of some experiments. The calculations also show that equilibration time increases significantly with pressure. The results of Fig. 3(a) indicate that diffusion of a molecule to the wall from the source can take more than  $10^3$  s if  $R_w =$ 10 cm. The above analysis suggests that, even under extreme conditions of total  $S_2F_{10}$  destruction, reactions on the wall will not have a significant effect on  $S_2F_{10}$  yields during early stages of discharge operation. It is found experimentally that the half-life of  $S_2F_{10}$  in the main gas volume due to wall reactions at 300 K is typically more than  $10^6$  s, even under conditions where the container is highly contaminated with water vapor [79, 83].

Of greater significance to S<sub>2</sub>F<sub>10</sub> production in corona discharges is the possibility of  $S_2F_{10}$  decomposition on the surface of the point electrode. This surface is, of course, much closer to the glow region and can be at significantly higher temperatures than the surrounding walls due to heating by ion bombardment. There is experimental evidence [15, 16] that as the tip of the point electrode is roughened by ion bombardment it becomes more effective in catalyzing the destruction of S<sub>2</sub>F<sub>10</sub>. This "conditioning" of the electrode by the discharge appears to account for the initial nonlinearity in measured S<sub>2</sub>F<sub>10</sub> yield curves. In the calculations described in the next section, we allow for a possible 25% reduction in the  $S_2F_{10}$  yield from reactions on a fully conditioned electrode surface. This is considered to be a reasonable upper limit even when account is taken of possible enhancement of electrode-gas interactions due to vortex formation [35].

#### 4. Calculations

The set of coupled rate equations for the reactions listed in Table I-VI were solved numerically using a chemical kinetics code known as ACUCHEM which was developed by Braun and coworkers [84]. The rate coefficients for some of the key processes discussed in the previous section were adjusted to within acceptable limits to give calculated yield curves for the major species SOF2, SO2F2, SOF4, and S<sub>2</sub>F<sub>10</sub> that correspond closely to experimental data. Shown in Fig. 4 are examples of calculated yield curves compared with measured results [2] for a pressure of 200 kPa, a discharge current of  $40 \mu A$ , and the indicated amounts of  $O_2$ and H<sub>2</sub>O expressed in percent of the SF<sub>6</sub> content. The yields in micro-moles are plotted vs. net charge transported, Q, in coulombs which is given by Q = It, where I is always a constant for the discharge conditions considered here. It is convenient to express the production rates in terms of quantity produced per unit-of-charge transported. The charge rateof-production of species  $X_i$  is related to the time rate-ofproduction by

$$\frac{\mathrm{d}[X_i]}{\mathrm{d}Q} = I^{-1} \frac{\mathrm{d}[X_i]}{\mathrm{d}t}.$$
(67)

The current dependence of the production rates is determined by the electron-impact dissociation rates. The rate coefficients for those processes given in Tables I and II apply specifically to  $I = 40 \,\mu$ A. The dissociation rate coefficients



Fig. 4. Calculated (lines) and measured (Refs [8] and [20], points) absolute yields of the oxyfluorides (SOF<sub>4</sub>, SOF<sub>2</sub>, and SO<sub>2</sub>F<sub>2</sub>) vs. net charge transported for a discharge current of 40  $\mu$ A, pressure of 200 kPa, and the indicated relative concentrations of H<sub>2</sub>O and O<sub>2</sub>.

for other values of the current are found using eq. (7), i.e., the dissociation rates are directly proportional to I.

Once the rate coefficients are determined from fits to the yield curves shown in Fig. 4 for a specific current and  $H_2O$  and  $O_2$  content, no further changes are made and these rate coefficients are then used to compute yields for other values of *I*,  $[H_2O]$ , and  $[O_2]$ . All of the calculations performed here apply to an absolute gas pressure of 200 kPa for which the optical measurements of the glow region are considered to be most reliable.

At this pressure, the size of the glow was not found to change significantly with discharge current in the range of 10 to  $100 \mu A$  [12]. Therefore, the parameter R is assumed here to be independent of I.

The spatial extent of the glow region can change significantly with gas pressure, generally becoming more constricted as pressure increases. The dependence of R on Pwould have to be considered in any attempt to extend the model to other pressures. Assuming that R is proportional to  $P^{-\eta}$ , where  $\eta$  is a positive constant, it can be shown from considering eq. (7) that the number of SF<sub>6</sub> molecules dissociated per unit of time by electron-impact for a given current will be proportional to  $P^{2-\eta}$ . The measured yields of  $SOF_2$ ,  $SOF_4$ , and  $SO_2F_2$  are found [2] to be relatively insensitive to changes in P within the range of 100 to 400 kPa. For example, the experimentally determined production rate for SOF<sub>2</sub> decreases by about a factor of 2.0 as P is increased from 144 to 300 kPa. These results suggest that  $\eta$  has a value slightly greater than 2.0. A consideration of eq. (59) suggests that the diffusion rate coefficients (see Table VI) will increase with pressure by a factor of  $P^{\eta-1}$ . However, the effect of changes in the diffusion rates on the yields of the major by-products is not nearly as significant as the effect of changes in the dissociation rates.

As noted previously, the calculations were performed assuming that the concentrations of SF<sub>6</sub>, H<sub>2</sub>O, and O<sub>2</sub> are all constant during the time of discharge operation, i.e., as these molecules are consumed by dissociation in the glow, they are replenished by molecules that diffuse in from the main gas volume. The ACUCHEM code yields the number densities of the products within the volume  $\tau_c$ . Those products whose concentrations build up in time are assumed to enter the main gas volume and become uniformly distributed within that volume at the time of measurement. The absolute quantities that are present at time t in the main volume are given by  $[X_i]_t \tau'_c N_A$  where  $[X_i]_t$  is the number density of the species  $X_i$  predicted by ACUCHEM in the glow at time t,  $N_A$  is the Avogadro's constant, and  $\tau'_c < \tau_c$  is the assumed effective glow volume of radius  $R_{eff} = 0.5R$ within which the electrons and products can be assumed to have a uniform density distribution as discussed in Section 3.1.1.

All of the rate coefficients are independent of time, i.e., possible effects due to local heating by the discharge are neglected. The species  $SF_4$  and  $SF_2$  are allowed to convert immediately to the by-products of  $SOF_2$  and  $SO_2F_2$  respectively (see previous section). This means that the rates for the relatively slow gas-phase processes given in Table VIII are not included directly in the calculation. Allowance is made for small reduction in the  $SOF_4$  yield due to the  $F^-$  transfer reaction in the ion-drift zone.

## 5. Results and discussion

## 5.1. Dependencies of production rates on $[H_2O]$ and $[O_2]$

The predicted dependencies of the production rates for the major species  $SOF_4$ ,  $SOF_2$ ,  $SO_2F_2$ , and  $S_2F_{10}$  on the concentrations of  $H_2O$  and  $O_2$  in the discharge cell are shown in Figs 5 and 6 respectively for models 1 and 2. Similar results are obtained from both models. The trends shown in Figs 5 and 6 are also consistent with those found using the much simpler model discussed in our earlier work [13, 20, 85].

All versions of the model give the following ordering of the magnitudes for the production rates:  $d[SOF_4]/dQ > d[SOF_2]/dQ > d[SO_2F_2]/dQ > d[S_2F_{10}]/dQ$ , when  $5 \times 10^{-4} > [H_2O]/[SF_6] > 5 \times 10^{-5}$ . This ordering is in agreement with experimental results [2].

The present model gives a rate for  $S_2F_{10}$  production that is lower than that from our earlier model and in better agreement with measured data [13]. The biggest difference between the results from the two versions of the present model is in the predicted rate for SOF<sub>2</sub>. Although the SOF<sub>2</sub> rate from model-1 is in better agreement with the data shown in Fig. 4, model-2 gives results that are in better agreement with most of the other available experimental data as shown in the next section. The SOF<sub>2</sub> production rates predicted by model-2 can be brought into agreement with those predicted by model-1 by increasing the rate coefficient  $k_{26}$  for SF<sub>4</sub> + F (see Table III) by an order-of-magnitude in model-2. This increase would make the rate coefficient more consistent with the value originally suggested by Herron [49].

The predicted production rates for the oxyfluorides and  $S_2F_{10}$  are seen to be insensitive to the oxygen concentration for  $[O_2]/[SF_6] \leq 0.01$ . This is consistent with results [2, 8,



Fig. 5. Predicted dependencies of the SOF<sub>4</sub>, SOF<sub>2</sub>, SO<sub>2</sub>F<sub>2</sub>, and S<sub>2</sub>F<sub>10</sub> production rates on [H<sub>2</sub>O] for the indicated oxygen concentrations from model-1. The results correspond to a current of 40  $\mu$ A and pressure of 200 kPa.

11] which show that the effect of  $O_2$  content does not become significant until its level exceeds about 10% of the SF<sub>6</sub> concentration (see Fig. 4). In the case of SOF<sub>4</sub> and SOF<sub>2</sub>, the insensitivity to  $O_2$  content is expected because



Fig. 6. Predicted dependencies of the  $SOF_4$ ,  $SOF_2$ ,  $SO_2F_2$ , and  $S_2F_{10}$  production rates on [H<sub>2</sub>O] for the indicated oxygen concentrations from model-2. The results correspond to a current of 40  $\mu$ A and pressure of 200 kPa.

oxygen simply does not play an important role in the formation of these species. This is shown by the predicted oxygen isotope content of these species given in Table X. It is found experimentally [8, 11] and by the present calculations that  $O_2$  has its biggest effect on  $SO_2F_2$  production. This is not too surprising since  $SO_2F_2$  derives its oxygen predominantly from  $O_2$  (see Table X). However, even in this case, the dependence of the production rate on  $[O_2]$  is not significant. This is due to the fact that  $SO_2F_2$  is formed predominantly in the main gas volume by reaction of  $SF_2$  with  $O_2$ , and consequently the  $SO_2F_2$  production rate is governed primarily by the rate of  $SF_2$  release into this volume from the glow region (see Table XI).

Even though  $SOF_2$  derives it oxygen predominantly from  $H_2O$  (see Table X), its rate of production is not sensitive to the  $H_2O$  concentration. As in the case of  $SO_2F_2$ , this is due to the fact that it is primarily formed in the main gas volume (see Table XI). Its rate of formation is governed to a large extent by the rate of  $SF_4$  production in the glow.

The species  $SOF_4$  and  $S_2F_{10}$ , which are formed entirely within the glow region, exhibit a greater dependence on [H<sub>2</sub>O]. In the case of  $SOF_4$ , the increase in its production rate with increasing [H<sub>2</sub>O] is due mainly to the combined effect of the three reactions:

 $F + H_2O \rightarrow OH + HF$ , (68)

$$SF_5 + OH \rightarrow SOF_4 + HF,$$
 (69)

$$SF_5 + F \to SF_6. \tag{70}$$

As  $[H_2O]$  increases so does [OH] due to the first of these reactions. Also [F] decreases thereby allowing [SF<sub>5</sub>] to increase. The combined increases in [OH] and [SF<sub>5</sub>] give a higher yield for SOF<sub>4</sub> through the second reaction. Similarly the S<sub>2</sub>F<sub>10</sub> production rates will also increase with [H<sub>2</sub>O] due to the corresponding increase in [SF<sub>5</sub>].

The predicted increase in the  $S_2F_{10}$  production rate with increasing  $H_2O$  concentration is not consistent with some experimental results that show the opposite trend [13], i.e., the measured  $S_2F_{10}$  yields seem to decrease as water content increases. It should be kept in mind, however, that the predicted behavior shown in Figs 5 and 6 is based entirely on gas-phase chemistry. It can be expected that the previously observed [79] surface catalyzed reactions of  $S_2F_{10}$  with  $H_2O$  could become significant with the addition of water vapor, particularly in a relatively small discharge cell such as described in Ref. [13].

Table X shows the predicted <sup>16</sup>O and <sup>18</sup>O isotope content of the oxyfluorides for different concentrations of oxygen and water vapor. The results given in this table are

Table XI. Percentages of the total oxyfluoride yields that come from processes in the main gas volume for the different indicated relative  $O_2$  and  $H_2O$  concentrations and for  $I = 40 \,\mu A$ 

[0,]	[H-O]	Percentage of yield from zone-3			
[SF <sub>6</sub> ]	[SF <sub>6</sub> ]	SOF <sub>4</sub>	SOF <sub>2</sub>	SO <sub>2</sub> F <sub>2</sub>	
$1 \times 10^{-4}$	$2 \times 10^{-4}$	0.0	71	99	
$1 \times 10^{-4}$	$0.5 \times 10^{-4}$	0.0	76	99	
$1 \times 10^{-2}$	$2 \times 10^{-4}$	0.0	71	99	
$1 \times 10^{-2}$	$0.5 \times 10^{-4}$	0.0	75	99	

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consistent with experimental results [8] which show that for relatively low oxygen concentrations both  $SOF_4$  and  $SOF_2$ derive oxygen predominantly from H<sub>2</sub>O, whereas  $SO_2F_2$ derives its oxygen from O<sub>2</sub>. As the oxygen content increases, it makes an increasingly greater contribution to  $SOF_4$  and  $SOF_2$  formation. The results shown in Table XI indicate that both  $SOF_2$  and  $SO_2F_2$  are predominantly formed in the main gas volume whereas  $SOF_4$  and  $S_2F_{10}$ are formed entirely within the glow region.

# 5.2. Dependence of production rates on current

The predicted charge rates-of-production of the predominant by-products as a function of the discharge current are shown in Fig. 7 in comparison with experimental results from different sources [2, 8, 10, 13-16, 20]. The predicted production rates indicated by the various solid and dashed lines were calculated using both versions of the model for  $[H_2O]/[SF_6] = 2 \times 10^{-4}$ , and  $[O_2]/[SF_6] = 1 \times 10^{-4}$ . The error bars associated with the theoretical curves correspond to the variations of the rates for different H<sub>2</sub>O content from  $0.5 \times 10^{-4}$  to  $3.0 \times 10^{-4}$ . This is the range of water-vapor concentrations that best corresponds to the experimental results shown in Fig. 7. Since it is known [2] that water-vapor content can change during the course of an experiment, it is impossible to know precisely what value of [H<sub>2</sub>O] applies best to a particular set of experimental data.

The upper set of curves for  $S_2F_{10}$  were obtained from a consideration of gas-phase chemistry only and do not include possible effects of surface chemistry. The lower set of



Fig. 7. Calculated current dependencies of the charge rates-of-production for SOF<sub>4</sub>, SOF<sub>2</sub>, SO<sub>2</sub>F<sub>2</sub>, and S<sub>2</sub>F<sub>10</sub> compared with the experimental results from different sources  $(1 ( V ) - \text{Ref. [13]}, 2 ( \nabla ) - \text{Ref. [14]}, 3 ( I I ), <math> \bullet$ ,  $\bullet ) - \text{Refs [8]}$  and [20],  $4 ( \nabla , V ) - \text{Refs [15]}$  and [16],  $5 ( \Box , \bigcirc , \bigtriangleup ) - \text{Ref.}$ [2],  $6 ( \bullet - \text{Ref. [10]})$ . The lines correspond to an H<sub>2</sub>O concentration of 0.02% and an O<sub>2</sub> concentration of 0.01% and the bars corresponds to variations of [H<sub>2</sub>O] from 0.005% to 0.03%.

curves for this species allow for an estimated 25% reduction in the yields due to reactions on the point electrode surface. The upper curves should be compared with the solid points marked with the number 4 that correspond to the initial experimentally determined rates from Refs [15] and [16] at t = 0. The lower curves should be compared with the open points marked with a 4 that correspond to the S<sub>2</sub>F<sub>10</sub> production rates determined from the measured data at a time when the yield curve becomes linear. At this time the electrode surface is fully conditioned by the discharge and becomes most efficient as a catalyzer of S<sub>2</sub>F<sub>10</sub> destruction.

The calculations have been performed for currents in the range of 10 to 80 µA. This is the range in which the glow is known to be stable and its size does not change significantly with current. At currents below about 1 to 2µA, the discharge assumes a pulsating characteristic, and at currents above about 100 µA, the discharge can become unstable with development of fluctuations in the size and shape of the glow [86]. If R were to increase with current by a factor of  $I^{\eta}$ , where  $\eta$  is a positive constant, then it can be shown using eq. (7) that the number of  $SF_6$  molecules dissociated per unit time will increase by a factor of  $I^{n+1}$ . This would mean that the charge rate-of-production of the by-products should also increase with I. It is seen in Fig. 7, however, that the measured charge rates-of-production for the major byproducts do not change significantly with current over the range considered. This suggests that  $\eta \ll 1$ . The predicted charge rates-of-production of SOF<sub>2</sub> and SO<sub>2</sub>F<sub>2</sub> from both model-1 and model-2 are nearly independent of I and in agreement with experimental results. This means that the time rates-of-production for these species are approximately proportional to I. Model-2 gives results for SOF<sub>2</sub> that are in better agreement with those reported in Ref. [2], whereas model-1 gives results in better agreement with those reported in Ref. [10].

The predicted rates for SOF<sub>4</sub> and S<sub>2</sub>F<sub>10</sub> both of which are formed entirely in the glow region, show a decrease with increasing current which is not entirely consistent with the experimental results, especially in the case of  $S_2F_{10}$ . The failure of the experimentally determined rates for these species to show a decrease with I is most likely due to the increasing role played by destruction processes in the main gas volume as I decreases. When the discharge current is reduced, the time required to observe a given yield for SOF<sub>4</sub> and S<sub>2</sub>F<sub>10</sub> increases (approximately in direct proportion to I). This means that there is more time available for the gasphase hydrolysis or, surface reactions to take effect in reducing the yields for these species as discussed in Sections 3.3.1 and 3.3.2. Other than to consider the reduction of  $S_2F_{10}$  yield due to reactions on the point cathode, no attempt has been made to use the reactions in the main gas volume (zone-3) to reduce the production for either  $S_2F_{10}$ or SOF<sub>4</sub>. From eq. (46) it is found that,

$$\Delta[\text{SOF}_4]_t / \Delta[\text{SOF}_4]_{2t} \simeq 2.0, \tag{71}$$

provided  $k_{94}[H_2O]t < 1$ . This means that the predicted 17% increase of d[SOF<sub>4</sub>]/dQ in going from  $I = 40 \,\mu\text{A}$  to  $I = 20 \,\mu\text{A}$  can be at least partly offset by an 18% decrease in the SOF<sub>4</sub> yield due to destruction by hydrolysis assuming that the 20  $\mu\text{A}$  experiment requires twice the time of the 40  $\mu\text{A}$  experiment. At this time, not enough is known about the reactions that destroy  $S_2F_{10}$  on surfaces to estimate the possible changes in the yield of this species due to changes in the duration of the experiment.

## 5.3. Recombination efficiency

From a consideration of eqs (6), (7), (8) and (67), the  $SF_6$  recombination efficiency,  $E_{\rm ff}$ , can be estimated by the formula

$$E_{\rm ff} = 100 \left\{ 1 - \frac{I \sum_{i} j \, d[X_{ij}]/dQ}{k_{\rm D}[\rm{SF}_6]} \right\}.$$
 (72)

The recombination efficiency represents the percentage of the SF<sub>6</sub> molecules dissociated by electron impact that convert back into SF<sub>6</sub>. In the case where H<sub>2</sub>O and O<sub>2</sub> are maintained at levels respectively of 200 and 100 ppm<sub>v</sub>, it is found from the calculated production rates using model-2 that  $E_{\rm ff}$  varies from 85% at 80 µA to 73% at 10 µA (see Table XII). Keeping the current fixed at 40 µA and the O<sub>2</sub> content at 100 ppm<sub>v</sub>, it is seen from Table XII that  $E_{\rm ff}$ increases from 76% to 89% as H<sub>2</sub>O content decreases from 400 ppm<sub>v</sub> to 50 ppm<sub>v</sub>. Under most of the conditions considered here, the recombination efficiency is greater than 75%.

The values for  $E_{\rm ff}$  obtained from the present calculations are lower than the value of 97% estimated using the earlier version of our model [11, 20]. The lower value for  $E_{\rm ff}$  are a consequence of the lower estimates of the SF<sub>6</sub> dissociation rates used here. The dissociation rates estimated for the models discussed here are considered to be more reasonable and are required to offset the lower rate used for the SF<sub>5</sub> + F recombination reaction.

In estimating  $E_{\rm ff}$ , it is sufficient to include only the production rates for the major sulfur-containing by-products in eq. (72), namely: SOF<sub>4</sub>, SOF<sub>2</sub>, SO<sub>2</sub>F<sub>2</sub>, and S<sub>2</sub>F<sub>10</sub>. The predicted production rates of the other sulfur-containing byproducts tend to be too small to be of any consequence in calculating the total SF<sub>6</sub> decomposition rate. The relative yields for the minor oxygenated products are seen from Table XIII to fall an order-of-magnitude or more below the yields of the major oxyfluoride products. The relative yields

Table XII. Calculated  $SF_6$  recombination efficiency  $(E_{ff})$  for the different indicated conditions

	[H <sub>2</sub> O]	[O <sub>2</sub> ]	
Ι (μΑ)	[SF <sub>6</sub> ]	[SF <sub>6</sub> ]	$E_{\rm ff}$ (%)
40	$4 \times 10^{-4}$	$1 \times 10^{-4}$	76
40	$2 \times 10^{-4}$	$1 \times 10^{-4}$	81
40	$5 \times 10^{-4}$	$1 \times 10^{-4}$	89
80	$2 \times 10^{-4}$	$1 \times 10^{-4}$	85
10	$2 \times 10^{-4}$	$1 \times 10^{-4}$	73

Table XIII. Predicted yields of the minor sulfur-containing by-products relative to the yield of  $SOF_2$  from model-2 at  $I = 40 \,\mu A$  and for the indicated  $H_2O$ ,  $O_2$  levels

$\frac{[H_2O]}{[SF_6]}$	$\frac{[O_2]}{[SF_6]}$	$\frac{[S_2F_2]}{[SOF_2]}$	$\frac{[SO_2]}{[SOF_2]}$	$\frac{[S_2OF_{10}]}{[SOF_2]}$	$\frac{[S_2O_2F_{10}]}{[SOF_2]}$
$2 \times 10^{-4}$	$1 \times 10^{-4}$	$2.2 \times 10^{-7}$	$1.1 \times 10^{-2}$	$2.9 \times 10^{-2}$	$1.3 \times 10^{-3}$
$1 \times 10^{-4}$	$1 \times 10^{-2}$	$1.2 \times 10^{-7}$	$4.2 \times 10^{-3}$	$2.3 \times 10^{-2}$	$1.5 \times 10^{-2}$
$4 \times 10^{-4}$	$1 \times 10^{-2}$	$3.2 \times 10^{-7}$	$2.3 \times 10^{-2}$	$4.3 \times 10^{-2}$	$1.7 \times 10^{-2}$

shown in Table XIII are consistent with comparable experimental results [2, 16].

# 5.4. Sensitivity analysis

In an attempt to assess the relative importance of the different reactions included in the model described here, the rate coefficient for each was either increased or decreased by two orders-of-magnitude and the corresponding relative changes in the yields for the major by-products were recorded. Examples of results from this type of analysis are given in Tables XIV and XV. The indicated percent changes in the yields of the major sulfur-containing by-products correspond to the change in the rate coefficient for a single reaction from a value  $k_i$  used in the model to a value  $k'_i = bk_i$ , where  $b = 10^{-2}$  or  $10^{+2}$ . Table XIV show results for some reactions that are considered to be relatively important in the sense that a two order-of-magnitude change in the rate for the reaction results in a  $\pm 20\%$  or more change in the yield of at least one of the major by-products. Table XV shows results for selected reactions that do not meet this criterion and are therefore considered to be relatively unimportant.

More than half of the radical-radical type reactions listed in Tables III-V are found to be sufficiently unimportant that they could be excluded from the model without significant effect on the predicted yields of the major by-products. This observation explains why simpler models [20, 21, 85] that contain fewer processes can be adjusted within reasonable limits to yield results that are comparable to those obtained with the much more complex model considered here.

Most of the secondary electron-impact induced dissociation reactions in Table II are also unimportant as illustrated by the results for SF5 dissociation [process (5) in Table XV]. The only exceptions are the process corresponding to electron-impact dissociation in S<sub>2</sub>F<sub>10</sub> which can have a significant effect on the yield for this compound [see results for process (4) in Table XIV]. The assumed  $S_2F_{10}$ dissociation rate is higher than that of the other species given in Table II. This was justified because of the relatively weak S-S bond that suggests a low threshold energy for  $S_2F_{10}$  dissociation [87]. This is further supported by the measured appearance poentials of fragment ions from dissociative ionization of  $S_2F_{10}$  which are found to be much lower than those for corresponding ions from SF<sub>6</sub> [88]. It was previously noted that the present model can accommodate a lower rate for  $S_2F_{10}$  formation by the SF<sub>5</sub> + SF<sub>5</sub> reaction (see Table III), such as found by Sehested and coworkers [59], by making a downward adjustment in the assumed electron-impact dissociation rate for S<sub>2</sub>F<sub>10</sub>.

The dissociation rates for  $SF_6$  given in Table I are the most important in controlling the overall rate of  $SF_6$ decomposition in the discharge. The rate of  $SF_5$  formation is particularly important in determining the production rates for  $SOF_4$  and  $S_2F_{10}$ . It can be seen from Table XIV that the rates for formation of  $SF_4$  and  $SF_2$  from dissociation of  $SF_6$  are significant in determining the production rates respectively for  $SOF_2$  and  $SO_2F_2$ .

Table XIV. Examples of relatively significant reactions revealed from sensitivity analysis calculations made using model-2 with  $I = 40 \,\mu A$ ,  $[H_2O]/[SF_6] = 2 \times 10^{-4}$  and  $[O_2]/[SF_6] = 1 \times 10^{-2}$ 

	Reaction	Rate constant change	Percent change in yields			
religios			SOF <sub>4</sub>	SOF <sub>2</sub>	SO <sub>2</sub> F <sub>2</sub>	S <sub>2</sub> F <sub>10</sub>
1	$SF_5 + F \rightarrow SF_6$	$k_{15}' = 10^{+2} k_{15}$	-85.8	- 12.7	-11.9	- 99.9
2	$F + H_2O \rightarrow OH + HF$	$k'_{27} = 10^{-2}k_{27}$	-95.6	- 5.3	+19.2	- 99.9
3	$S_2F_{10}(zone-1) \rightarrow S_2F_{10}(zone-3)$	$k'_{87} = 10^{-2}k_{87}$	+1.4	+3.5	+1.6	-98.9
4	$S_2F_{10} \rightarrow 2SF_5$	$k'_{0} = 10^{-2}k_{0}$	+0.28	+18.7	-1.8	+ 77.5
5	$SF_6 \rightarrow SF_4 + 2F$	$k_2' = 10^{-2}k_2$	-8.1	-40.0	-0.41	+28.7
6	$SF_6 \rightarrow SF_2 + 4F$	$k'_{A} = 10^{-2}k'_{A}$	+ 3.4	-13.4	-74.0	+ 50.0
7	$SF_5 + O \rightarrow SOF_4 + F$	$k'_{50,77} = 10^{-2} k_{50,77}$	-27.8	+ 3.9	+ 3.0	+20.3
8	$SF_5 + OH \rightarrow SOF_4 + HF$	$k'_{28} = 10^{-2}k_{28}$	- 36.3	+ 3.0	+0.88	+21.5
9	$SF_4 + OH \rightarrow SOF_3 + HF$	$k_{29}^{\prime} = 10^{+2} k_{29}^{\prime}$	+ 43.1	- 72.6	-1.4	+ 30.2

Table XV. Examples of relatively insignificant reactions revealed from sensitivity analysis calculations made using model-2 with  $I = 40 \,\mu A$ .  $[H_2O]/[SF_6] = 2 \times 10^{-4}$  and  $[O_2]/[SF_6] = 1 \times 10^{-2}$ 

		Pote constant	Percent cha	Percent change in yields			
	Reaction	change	SOF <sub>4</sub>	SOF <sub>2</sub>	SO <sub>2</sub> F <sub>2</sub>	S <sub>2</sub> F <sub>10</sub>	
1	$H_2O \rightarrow OH + H$	$k_{12}' = 10^{-2}k_{12}$	0.00	0.00	0.00	0.00	
2	$SOF_3 + OH \rightarrow SO_2F_2 + HF$	$k'_{32} = 10^{-2}k_{32}$	+0.07	0.00	0.00	0.00	
3	$SOF_3 + F \rightarrow SOF_4$	$k_{55}' = 10^{-2} k_{55}$	-0.08	+0.06	-0.02	-0.06	
4	$SOF + F \rightarrow SOF_2$	$k'_{41,71} = 10^{-2} k_{41,71}$	-4.2	-15.3	-0.10	-8.5	
5	$SF_5 \rightarrow SF_4 + F$	$k_5' = 110^{-2}k_5$	0.00	-0.26	0.00	+0.11	
6	$SF + SF_3 \rightarrow SF_4 + S$	$k'_{21} = 10^{-2}k_{21}$	0.00	0.00	0.00	0.00	
7	$SF + F \rightarrow SF_2$	$k'_{13} = 10^{-2}k_{13}$	-9.45	+2.4	-11.4	+0.52	
8	$SOF_3 + O \rightarrow SO_2F_2 + F$	$k'_{37,76} = 10^{-2} k_{37,76}$	0.00	0.00	0.00	0.00	
9	$SOF + O \rightarrow SO_2F$	$k'_{39,74,79} = 10^{-2}k_{39,74,79}$	+ 0.04	0.00	0.00	0.00	
10	$SF_3 + SF_5 \rightarrow 2SF_4$	$k'_{25} = 10^{+2} k_{25}$	+1.4	+11.6	-2.2	-4.5	
11	$SF_5 + O \rightarrow SOF_5$	$k_{50,68}' = 10^{-2} k_{50,68}'$	- 5.5	+2.5	+1.1	+9.9	