OZONE BUILD-UP FROM ATOMIC OXYGEN - POSSIBILITIES AND LIMITATIONS

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ABSTRACT

A discussion is presented of the build-up of ozone from atomic oxygen. The approach is based on only three reactions between the reaction partners O, O_2, and O_3. A conversion efficiency is defined: the ratio of O_3 molecules produced to O atoms used. It is presented as a function of concentration, temperature, and number of production steps. A short discussion of the influence of the dissociation of O_3 is given.

1. INTRODUCTION

The modelling of the processes leading to ozone formation in electrical discharges has received considerable attention during the past years. The availability of large computers has brought about the possibility to cope with rather large sets of differential equations. The approaches can be divided into homogeneous stationary models (1), time dependent homogeneous models (2) which treat the temporal evolution of different particle species, and time and space dependent models (3) which try to model the complete dynamics of a discharge filament. Some of these models, (4) use up to 75 reactions between 11 reaction partners (oxygen atoms and molecules including some of their excited states, positive and negative ions, and electrons). Although the extent of these reaction systems is remarkable it should not disguise the fact that there is still considerable uncertainty about some of the rate coefficients used in these calculations.

2. PROPOSED MODEL

In this paper we want to take a completely different approach to the problem. At atmospheric pressure ozone synthesis is mainly achieved by build up from atomic oxygen. It will be shown that the simple reaction system consisting of only O, O_2, O_3 imposes certain limitations on the final ozone concentration and also on the efficiency of the process. The mechanism providing the necessary initial atomic oxygen concentration could be the dissociation of O_2 by electron collision in a discharge. It could also be a dissociation process brought about by UV-radiation, x-rays, γ-rays, electron beams or other processes.

We will try to answer the question: what amount of the originally produced oxygen can possibly be converted into ozone under different experimental conditions?
We consider the following reactions

$$O + O_2 + O_2 \xrightarrow{k_1} O_3 + O_2 \qquad (1)$$

$$O + O + O_2 \xrightarrow{k_2} O_2 + O_2 \qquad (2)$$

$$O + O_3 \xrightarrow{k_3} O_2 + O_2 \qquad (3)$$

$$O_2 + O_3 \xrightarrow{k_4} O + O_2 + O_2 \qquad (4)$$

We use the rate coefficients $k_1 = 6.75 \times 10^{-35} \exp(635/T) cm^6/s$, $k_2 = 3.8 \times 10^{-30} T^{-1} \exp(-170/T) cm^6/s$, $k_3 = 2.12 \times 10^{-11} \exp(-2337/T) cm^6/s$, $k_4 = 7.26 \times 10^{-10} \exp(-11'400/T) cm^3/s$. ($k_1$, k_3 from Ref.(5), k_2, k_4 from (6)).

Reaction (4) is the thermal decomposition of ozone which determines the decay time of ozone. From the value of k_4 it is apparent that at temperatures below 400K and residence times below 10s it can be neglected.

The remaining three reactions lead to a set of differential equations:

$$\tau \frac{dx_1}{dt} = - x_1 x_2^2 - b\, x_1^2 x_2 - a\, x_1 x_3 \qquad (5)$$

$$\tau \frac{dx_2}{dt} = - x_1 x_2^2 + \frac{b}{2} x_1^2 x_2 + 2a\, x_1 x_3 \qquad (6)$$

$$\tau \frac{dx_3}{dt} = x_1 x_2^2 - a\, x_1 x_3 \qquad (7)$$

where x_1, x_2, x_3 are the concentrations of O, O_2 and O_3, $\tau = 1/k_1 n^2$, (n = total particle density), $a = k_3/k_1 n$, $b = 2k_2/k_1$.

If we are not interested in the temporal development of O_3 we can eliminate x_2 from the equations and integrate the single differential equation

$$\frac{dx_3}{dx_1} = - \frac{(2-x_1-3x_3)^2-4ax_3}{(2-x_1-3x_3)^2+4bx_1x_2+4ax_3} \qquad (8)$$

It turns out that the "conversion efficiency"

$$E = \frac{\text{final number of } O_3 \text{ molecules}}{\text{total number of O atoms used}}$$

for a given initial pressure depends mainly on the gas temperature and the desired O_3 concentration. Results are shown in Fig.1 for an ozone concentration of 4%. For very low O_3-concentrations and moderate temperatures the conversion efficiency E approaches unity, for most conditions it will be less than 1. It can also be shown, by repeated integration of Eq.(8), that it is not very efficient to build up the desired O_3-concentration in one step. The enrichment process proves to be more efficient (less O-atoms are needed to arrive at a given O_3-concentration) if a number of smaller steps are taken (see Fig.1). The explanation is that by decreasing the initial O-concentration the reaction

$$O + O + O_2 \xrightarrow{k_2} O_2 + O_2 \qquad (2)$$

which can be considered a loss mechanism for atomic oxygen becomes less important. The limiting curve is reached if the individual steps are small enough that an oxygen atom during its life time ($\cong$ 10 µs) collides only with O_2 molecules and not with other atoms.

The other loss reaction

$$O + O_3 \xrightarrow{k_3} O_2 + O_2 \qquad (3)$$

cannot be avoided because it is related to the desired O_3-concentration. Its influence can be decreased by lowering the gas temperature or increasing the pressure. The limiting conversion efficiency for different gas temperatures is plotted in Fig.2. For each temperature there exists a maximum O_3-concentration at which the conversion process saturates. In the neighbourhood of this concentration the conversion efficiency drops to zero. Fig.2 also demonstrates how important it is to keep the gas temperature in the reaction volume as low as possible.

We would like to point out that the conversion efficiency defined here is closely related to the saturation value of the g-function presented in another publication (4) ($E=g(n_p \to \infty)x_3(1)/x_1(1)$). It should be kept in mind that the results presented here have been calculated for a constant initial pressure, whereas the results presented in (4) are given for a constant number of atoms.

3. SIMULATION OF O_3 DESTRUCTION

We have also attempted to assess the effect of an ozone destruction mechanism which normally accompanies the formation of atomic oxygen. In a discharge, for example, atomic oxygen is produced by electronic dissociation of O_2, viz.

$$e + O_2 \xrightarrow{k_5} e + O + O \qquad (9)$$

At the same time ozone is destroyed by the process

$$e + O_3 \xrightarrow{k_6} e + O + O_2 \qquad (10)$$

The rate coefficient k_6 is not known. There exist some estimates in the literature (4). It is definitely a function of E/n (electric field strength/ particle density). In our simulation we introduced a quantity

$$f = \frac{\int k_6 n_e dt}{\int k_5 n_e dt} = 0,\ 1,\ 5,\ 10,\ 20\ \ldots \qquad (11)$$

to characterize the relative importance of the two processes. Dissociation of O_3 is, of course, also present if some other mechanism than a discharge is used to provide the initial atomic oxygen (e.g. a radiation process). In this case a loss process can be included in an analog way.

Fig.3 shows some results on the effect of the loss term f on the saturation concentration of ozone (100 steps). It shows that even a small loss term (f = 1 or 5) can have a pronounced effect at higher concentrations.

There is no question that much more complex approaches are needed to model the kinetic processes in an oxygen discharge. The purpose of this contribution is, to point out that certain limitations on the ozone build-up are already incorporated in the simple reaction system between the partners O, O_2, O_3. The question of optimizing the conversion efficiency may turn out to be as important as optimizing the yield of atomic oxygen.

ACKNOWLEDGEMENT

Thanks are due to W. Egli for performing some of the numerical calculations.

REFERENCES

(1) H. Kastelewicz and P. Bachmann, Beitr. Plasmaphysik, 14, 183 (1974)

(2) B. Eliasson and U. Kogelschatz, Proc. 4th Int. Symp. on Plasma Chemistry, 729 (Zurich 1979)

(3) V.I. Gibalov, V.G. Samoilovich and Yu.V. Filipov, Vestnik Mosk. Univers., Khimiya 34, 4, 336 (1979)

(4) B. Eliasson and U. Kogelschatz, Proc. XVth Int. Conf. on Phenomena in Ionized Gases, Minsk (1981)

(5) I. Arnold and F.J. Comes, Chem. Phys. 42, 231 (1979)

(6) R.F. Hampson, Jr. and D. Garvin, "Chemical kinetic and photochemical data for modelling atmospheric chemistry", (NBS Techn. Note 866, 1975)

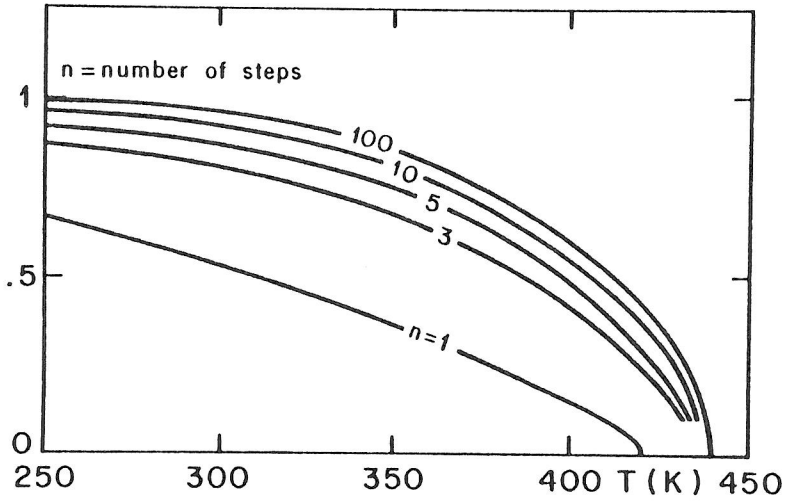

Fig.1 Conversion efficiency (final number of O_3 molecules/ total number of O atoms used) for an ozone concentration of 4%. (n: number of (equal) steps to build up the desired O_3 concentration, p_o = 1 bar.)

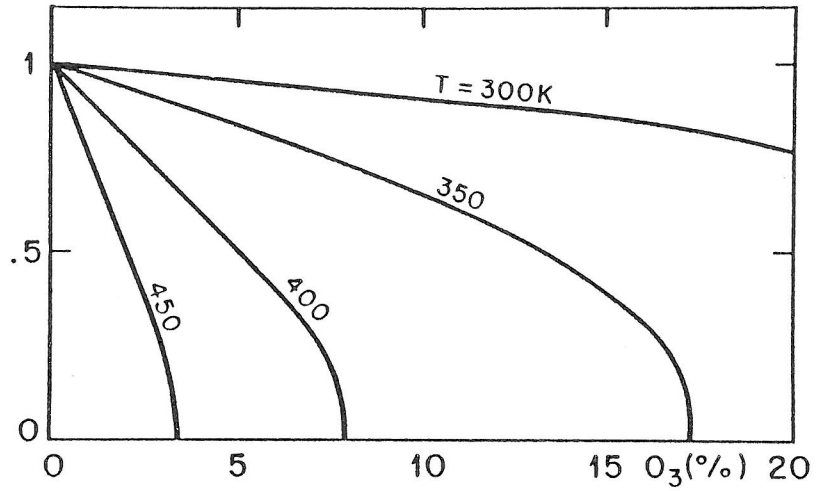

Fig.2 Limiting conversion efficiency (n = 100 steps, p_o = 1 bar)

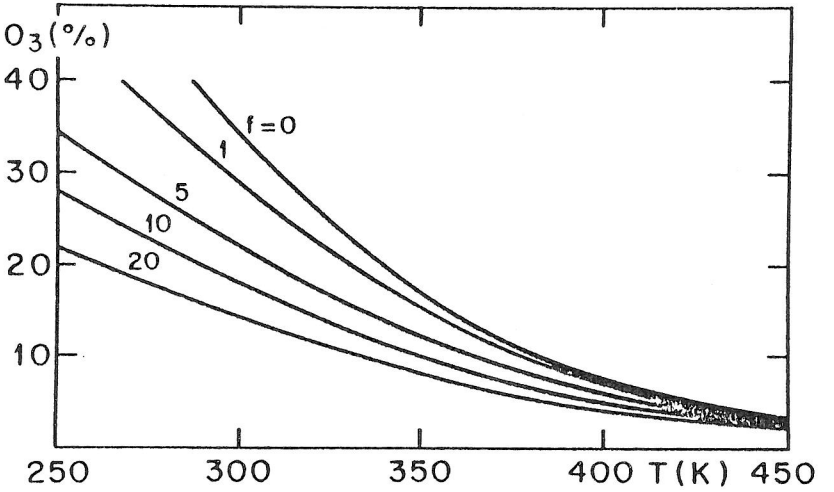

Fig.3 Saturation concentration with different loss terms f = 0,1,5,10,20 (see text)