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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Emission of ions and charged soot particles by aircraft engines" *by* A. Sorokin et al.

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We do agree with the referee that correct determination of the ion-ion recombination coefficient kii is important, since the output of the model depend on their values.

However, we disagree with the comments of the referee stating that it is wrong to use Eq.(8) in the engine combustion zone.

The main argument of the referee is that the ion-ion recombination coefficient k_{ii} is known to first increase until it reaches a maximum, and then decrease (for a given temperature) when the total pressure P increases, while our Eq.(8) indicates that k_{ii} always increases with P. Several sets of data indeed indicates that, **at room temperature**, k_{ii} exhibit a maximum at a gas density of the order of 1.2-2 L [see for example Mächler (1937), Sayers (1938), Bates McDaniel and Mason (1973), Mendas, (1982)], where L is the Loschmidt's number (L= 2.69 10^{19} cm^{-3} i.e the number density of a gas at standard conditions).

The referee then suggested to use the Langevin's theory to calculate k_{ii} in the high pressure zone of the combustor where P = 9 atm. According to Langevin's theory, k_L in the high ambient-gas density limit is given by:

$$k_l = 4(\mu + mu_-), \tag{1}$$

where e is the elementary charge and $mu_+, _-$ the mobilities of the positive and negative ions, respectively. Since the mobilities are known to be inversely proportional to the gas density (see for example Bates, 1985), *for a given temperature*, k_L is also inversely proportional to the pressure.

However, the referee do not take into account the fact that kL is inversely proportional to the gas **density** and not only to the total pressure:

$$k_L = constT/P. \tag{2}$$

For the conditions assumed in the combustor i.e. P = 9 atm. and T = 2200 K, the Loschmidt's number L = 1.1 and the maximum of k_{ii} (total recombination coefficient) has not yet been reached i.e. k_{ii} still increases with P in agreement with Eq.(8). At the exit of the combustor, L = 2.02 and eventually the maximum has just been passed. But even for this case, k_{ii} will never be, as suggested by the referee, 4 times smaller at 9 atm. than at 1 atm. This is very well illustrated by the calculations presented in Bates (1983) where the recombination coefficient is studied both as a function of pressure and temperature (the ions are Na$^+$ and Cl$^-$). At 300 K the coefficient shows a maximum at about 1.6 L while at 2000 K, this maximum disappear and is shifted to a much higher pressure (unfortunately the calculations where stopped at 3 atm.), but even at 3 atm. the maximum was not yet reached.

We now perform the calculations suggested by the referee. The total recombination coefficient k_{ii} can be expressed as (Bates, 1985, Flannery, 1981)

$$k_{ii} = k_2 + k_3, \tag{3}$$

where k_2 is the binary (mutual) recombination coefficient and where the total three-body recombination coefficient k_3 is defined as (see for example Flannery, 1976 and 1982):

$$1/k_3 = 1/k_L + 1/k_{3T}. \tag{4}$$

In this last expression, k_L and k_{3T} are respectively the Langevin and the Thomson coefficients. Note that in our formula Eq.(8), only k_2 and k_{3T} are taken into account.

It is easy to estimate all these coefficients for the case of the combustor.

The formula to calculate kL has been given above, however, one needs to know the ion mobility given by (Raizer, 1991):

$$\mu_i \approx \frac{(1 + M/M_i)^{0.5}}{2\pi\sqrt{2}N\sqrt{\alpha M}} \tag{5}$$

where M and M_i are the molecular weight of the neutral and of the ion, N is the gas density, α is the polarisability of the neutral.

For k_2 and k_{3T}, as noted in the article we use the formula proposed by Beig and Brasseur (2000). Note that the formula given by Beig and Brasseur represents a lower estimate since the values generated in the range 1800–2400 K are about 2–4 times smaller than the experimental measurement made by Guo and Goodings (2000), and about 4–7 times smaller than those proposed by Mätzing (1991).

For the case examined by the referee, i.e. P=9 atm and T=1200K, one finds, respectively $k_2 = 3 \times 10^{-8}$ cm^3/s and k_{3T} = 1.0^{53} $\times 10^{-7}$ cm^3/s while, for these data, the coefficient used in our model and calculations is $k_{ii} = k_2 + k_{3T} = 1.35{}^{*}10^{-7}$ cm^3/s.

Let now assess the Langevin's three-body coefficient for HSO_4^- (97 amu) and H_3O^+(19 amu). Other ions can be easily chosen, but since the coefficient varies with the square root of the masses, their choice has only a limited influence on the final result.

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One finds that $k_L = 2.01{}^*10^{-6}$ cm^3 and therefore $k_L > k_{3T}$. Using Eq.(3)-(4), the total three-body recombination coefficients is $k_3 = 10^{-7}$ and $k_{ii} = 1.30{}^*10^{-7}$ cm^3/s, a value which compares favorably with the coefficient used in our study for similar conditions i.e. $1.35{}^*10^{-7}$ cm^3/s.

These calculations confirm what has been already said above e.i. that under the conditions of the present study, the increase of pressure is compensated by the increase in temperature and the high pressure limit of the three-body recombination approximation (Langevin's case) gives only a small effect, of the order of 4%.

Other comments:

1) abstract: we will add some main conclusions such as emission index, concentrations...

2) We do not intend, in this paper, to make comments about the validity or not of chemiion theory for the formation of aerosols which occurs outside the engine, but just provide an estimate of the expected number concentration at the exit of a given engine. Therefore, we will remove the phrase which goes from line 1 to 5 on page 2047.

The ion concentration measurements made by Arnold et al. (2000) were done with a simple electrostatic probe positioned in the axis of the engine exhaust. Therefore there are no losses in sampling lines and the "instrument" is rather insensitive to the mass range of the ions, as long as the voltage applied is sufficiently large. Furthermore, at the plume age where the measurement were made, clustering is extremely limited (see Sorokin and Mirabel, 2002). We think that the error bars provided by Arnold et al. are fully justified (–30%, +100% maximum). Concerning the analysis of their own data, Arnold et al. used a constant ion-ion recombination. This very crude approximation seems to be somewhat in contradiction with the above discussion about the variability of k_{ii} with temperature and pressure.

3) We just used the formula given in Rapp (2000), although they were originally ob-

tained by Natanson (1960). The main reason is that Rapp gives the Natanson's equations corrected for some typographical errors. Theoretical predictions are preferred to experimental results, based on the comment by Hoppel and Frick "Direct measurements of the attachment coefficient is so difficult that theoretical results are probably more accurate than any reported measurements.

4) the emission index will be given

Technical corrections:

The referee noted several printed mistakes which will be corrected in the final version.

The reference Yu and Turco, 1997 will also be introduced.

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