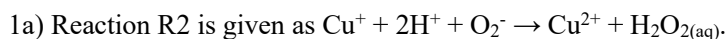Response to Comment of Theodore S. Dibble

We thank a lot for the short comment by Prof. Theodore S. Dibble on the chemical reaction equations and rates in Table 2 and Table 3.

Comment:

1) Being a kineticist, I looked at the Table 2 (Kinetic data for the simulation of reactions in aqueous aerosols). I found that Table confusing:

      1a) Reaction R2 is given as $Cu^+ + 2H^+ + O_2^- \rightarrow Cu^{2+} + H_2O_{2(aq)}$.

Is the rate expression for this reaction $v = k[Cu^+][H^+]2[O_2^-]$? If so, that should be made clear, but the reaction would be unimportant given the value of the rate constant. It seems more likely that the rate expression is $v = k[Cu^+]2[O_2^-]$; if so, then perhaps the reaction should be written: $Cu^+ + (2H^+) + O_2^- \rightarrow Cu^{2+} + H_2O_{2(aq)}$ with a note on the Table specifying that species in parentheses do not contribute to the rate equation.

Similar questions apply to R5.

      1c) Reactions R1 and R3 do not exhibit mass balance.

Response:

Thanks a lot for pointing out the possible problems in the chemical reaction equations. The box model ensures the mass balance of interrelated chemical reactions. Reaction rates of R1, R2 and R5 are not affected directly from the concentration of H^+ ion while the ratio of different valence state of the copper ion is affected by the solution acidity. In Table 2, R1, R2, R3 and R5 are corrected accordingly.

Table 2: Kinetic data for the simulation of reactions in aqueous aerosols.

No.	Reactions	k_{298}	E_a
R1	$Cu^+ + HO_{2(aq)} + (H^+) \rightarrow Cu^{2+} + H_2O_{2(aq)}$	2.2×10^9	
R2	$Cu^+ + (2H^+) + O_2^- \rightarrow Cu^{2+} + H_2O_{2(aq)}$	9.4×10^9	
R3	$Cu^+ + OH_{(aq)} \rightarrow Cu^{2+} + OH^-_{(aq)}$	3×10^9	
R5	$Cu^+ + (H^+) + O_{3(aq)} \rightarrow Cu^{2+} + O_{2(aq)} + OH_{(aq)}$	3×10^7	

Comment:

      1b) Reaction R9 has O_2^- reducing Cu^{2+} to Cu^+ while reaction R2 has O_2^- oxidizing Cu^+ to Cu^{2+}, both with rate constants at the diffusion limit. Perhaps I am exhibiting my ignorance of aqueous-phase chemistry, but I find this hard to believe.

Response:

O_2^- can be catalytically dismutated by metals and metal complexes thus can function either as a univalent oxidant or reductant with transition metal ions such as iron, copper and manganese (Bielski and Cabelli, 1991). Among the transition metals, Cu is the most likely catalytic sink of O_2^-. The rate constant of R2 and R9 are from CAPRAM 2.4 and Jacob, 2000 based on the aerosol bulk estimated pH range (Ervens et al., 2003; Jacob, 2000).

Comment:

Some minor points:

a) In my experience "K" (upper case) is used for equilibrium constants and "k" (lower case) for rate constants, while the present manuscript uses the opposite convention.

b) Table 3 appears to have equilibrium data but no kinetic data. Also, I assume that the redox chemistry of iron is included in the model, even though it is not included in Table Perhaps the table should be retitled something like "Equilibria for copper and HOx chemistry in aqueous aerosols"

c) I noticed on line 94 that "ironic" is used for "ionic"

Response:

a) Rate symbol "K" (upper case) and "k" (lower case) in Table 2 and Table 3 are corrected accordingly.

b) The redox chemistry of iron is not included in the present model for the diagnosis of copper influence but we indeed studied the iron chemistry in separate model runs which don't have observations to compare. Nevertheless, we think your proposed tile for Table 3 is more accurate and we changed as suggested.

c) We revised accordingly.

Bielski, B., and Cabelli, D.: Highlights of current research involving superoxide and perhydroxyl radicals in aqueous solutions, International journal of radiation biology, 59, 291‑319, 1991.

Ervens, B., George, C., Williams, J. E., Buxton, G. V., Salmon, G. A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., and Herrmann, H.: CAPRAM 2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application, J. Geophys. Res.‑Atmos., 108, 10.1029/2002jd002202, 2003.

Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, Atmos. Environ., 34, 2131‑2159, 10.1016/s1352‑2310(99)00462‑8, 2000.