

Review ACP-2017-610

The authors answered the comments of both reviewers correctly, with some exceptions listed below.

Reviewer 1.

Comment 8. [lines 232-236] The concentrations of HSO_3^- , SO_3^{2-} and H_2SO_3 in equilibrium with gaseous SO_2 (75 ppm ?, specify the constants used, please, not the reference alone) may not be the actual concentrations in the droplets due to chemical reactions involved. Good answer needs some modeling.

Comment 9. [lines 247-263] Unanimously with Reviewer 1, I think that SO_2 should react with NO_2 not only in $\text{Ca}(\text{NO}_3)_2$ droplets but also in NaNO_3 and NH_4NO_3 ones. The authors claimed any sulfate produced was below the limit of detection in the latter systems. Their Raman spectra included only SO_4^{2-} ions from anhydrite (CaSO_4). No crystals were observed in the absence of calcium ions, clearly because the solubility of sodium or ammonium sulfate in water is much higher than that of CaSO_4 .

Thus, the experiments presented in the manuscript are inadequate to conclude on the reactive uptake of SO_2 and NO_2 in NaNO_3 and NH_4NO_3 droplets and formation of sulfate therein. We just do not know how much sulfate was formed in these experiments. N.B., it would be interesting to know all the limits of detection involved as there were other species undetected in the droplets, e.g. sulfite ion, SO_3^{2-} and CaSO_3 [lines 239-244].

The comment on using eqn (5) and Gibbs free energy of the reaction is provided just below (Reviewer 2).

Reviewer 2.

Major concern 2. The authors are right that eqn (5) is valid for all reactions (an equilibrium takes place when $\Delta G = 0$). However, it is difficult if possible to use eqn (5) to prove that precipitation of CaSO_4 crystals promotes sulfate formation by reducing the concentration of sulfate in the reaction environment. The authors claimed [lines 257-263] that some backward reaction yet unknown can bring back SO_2 from sulfate so that increased concentration of sulfate ions can slow down the formation of sulfate ions while precipitation keeps the concentration of sulfate ions low. In my opinion, under conditions of their experiments, such backward reaction is just impossible. The sulfate ions could slow down the formation of sulfate only by crowding the reaction environment and reducing the encounter probability for the reactants. Maybe, by decreasing the uptake of reagents from the gas phase as well. Precipitation to CaSO_4 crystals removed the nuisance, naturally.

[line 253] Replace “Reaction (R2)” with “Reactions (R6) and (R7)”.

Comment: *Will the presence of SO_2 influence the uptake of NO_2 ?*

The authors somehow missed their response [lines 201-2014] that the influence of SO_2 on NO_2 uptake was not significant. Following their line, it was, probably, not significant when calcium carbonate was

present. When there was no carbonate anymore, the reaction of SO₂ with NO₂ plausibly increased the uptake of both gases by Ca(NO₃)₂ solution.

My own comments:

- (1) The role or fate of NO₂⁻/HONO (reactions R2, 6 and 7) has not been commented in the manuscript, even though this product is quite reactive.
- (2) The uncertainties of uptake coefficients in Table 2 should be explained.
- (3) [Lines 226-229] R6 and R7 are overall stoichiometric reactions but not a reaction mechanism.

The question whether the studies of SO₂ oxidation by NO₂ (acp-2017-610) and on SO₂ oxidation by O₂ (acp-2017-900) should be combined together or not.

I support Reviewer 1 in her/his opinion that the two manuscripts should be combined in one well-structured work. It is a natural desire of a reader, when exploring the first paper, to compare immediately and easily the experiments presented to those including oxygen, a common atmospheric reactant. The authors had right to divide their work as they wished. They stated their reasons for doing so but they did not convince me. There are many common parts in both manuscripts while discussion and conclusions are complementary. However, I do not hesitate to remind that researchers are evaluated basing on the number of papers and citations, and the Hirsch index. Especially when they apply for grants or positions. Therefore, we are often tempted to produce 2 or 3 papers rather than a single well-structured publication.