Atmos. Chem. Phys. Discuss., 9, S919–S921, 2009
www.atmos-chem-phys-discuss.net/9/S919/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Kinetic modeling of nucleation experiments involving SO_2 and OH: new insights into the underlying nucleation mechanisms" *by* H. Du and F. Yu

Anonymous Referee #2

Received and published: 19 March 2009

The paper deals with a modeling study regarding the formation of new particles in the H2SO4/H2O system, i.e., a field of ongoing strong research efforts, highly important to atmospheric science. The authors used a modeling scheme on the basis of elementary steps describing dimer, trimer, etc. formation of H2SO4. By changing the rate of forward reaction, beta, (varying the H2SO4 levels) and changing the rate of the decomposition step, gamma (varying Gibbs free energy) it was tried to describe experimentally observed particle distributions. My remarks:

1) Generally, it is hard (or impossible) to reproduce the calculations done by the authors. In practice, the corresponding rate coefficients for beta and gamma are needed

explicitly. It should be described more in detail how these coefficients were obtained. Equations as a function of i would be helpful.

2) The unit of the rate of these steps is [cm(-3) s(-1)] or [molecules cm(-3) s(-1)]. In fig.1b and 3b the unit [(s-1)] is given. Please give an explanation.

3) The equation at p.1278, line 5 shows the reaction of a monomer with an existing cluster, like A + A3 = A4. Do the authors only consider forward reactions of the monomer? Are reactions like A2 + A2 = A4 neglected?

4) Comparison with Young et al.(2008): Young et al. measured H2SO4 concentrations at the outlet of the flow tube as well as simultaneously at the inlet in order to evaluate the theoretical WLF. And the measured WLF was in line with the gas kinetic limit. These measurements should be accepted! The authors should show graphically what the result of modeling is using the WLF and the H2SO4 levels detected by Young et al.. By adjusting the gamma value a description of the experimental H2SO4 profile should be possible.

5) Comparison with Berndt et al.(2008): The authors used experimental findings from runs given in Berndt et al.(2008) but for modeling an OH profile from another experiment given in Berndt et al.(2005)! Why? The way of H2SO4 determination is well described in the article. In order to discuss any discrepancies between data given in literature and own modeling results the authors should handle the literature data carefully. H2SO4 concentrations stated in Berndt et al.(2008) are average concentrations in the reactor and not peak concentrations.

6) The authors came to the conclusion that critical cluster composition as a result of their modeling is well in line with experimentally observed slopes arising from plots N over H2SO4 concentrations. It should be noted that these slopes can represent clear overestimations caused by the counting efficiency curve of the counters used, see also the notice in Berndt et al.(2005).

ACPD

9, S919–S921, 2009

Interactive Comment

7) Atmospheric measurements indicate that obviously only 1 - 2 H2SO4 molecules are needed in the critical cluster, see papers by R.Weber et al. and from the Kulmala group. The authors should discuss this topic and the consequences for the model given, the gamma values and the corresponding Gibbs free energy.

8) Personally, I guess it sounds better to say "best agreement between model and measurement is found assuming a 2 - 4 fold H2SO4 concentration" than " H2SO4 concentration was underestimated in those studies by a factor of 2 to 4."

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1273, 2009.

ACPD

9, S919–S921, 2009

Interactive Comment