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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Köhler theory for a polydisperse droplet population in the presence of a soluble trace gas, and an application to stratospheric STS droplet growth" *by* H. Kokkola et al.

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We thank the referee for the positive remarks as well as the critisizm presented, and believe that the revisions due to the critical remarks will improve the paper.

1. The main criticism is based on the fact that growth of NAT and STS aerosols in the stratosphere, in particular of large particles, is mainly determined by sedimentation processes which are completely neglected in the presented paper. If sedimentation processes are taken into account, then closed systems with limited amount of HNO_3 and water may behave like open system because falling particles (e.g. NAT rocks) experience continuously changing ambient conditions.

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Thus, probably not (only) the splitting of the distribution function but much more selective falling of the aerosols causes the formation of the bimodal size distribution.

- We certainly agree with the referee that in many cases a stratospheric air parcel cannot be considered as a closed system with respect to nitric acid, especially if the simulation times are long. This, however, does not remove the possibility that long enough periods of slow cooling unperturbed by sedimentation may sometimes occur in the stratosphere, inducing the splitting of the size distribution. The simulation regarding the stratospheric particle population we have performed is a qualitative analysis of the condensation mechanisms that may occur. The particles considered here are fairly small to be effectively sedimentated. According to Tabazadeh et al. (2000), the particles should be at least 4-6 μm in radius to be effectively sedimentated at 68 mbar. The bimodal size distribution obsereved by Voigt et al. to which we compare our calculations contains particles frozen in a lee wave, and the freezing process in itself can of course induce a splitting. By the comparison we are making we want to draw the attention to the possibility that the splitting may have occured before the freezing. We will clarify these issues in the revised version of the paper.

2. The theory presented in sections 1-5, in particular the approximations (3) and (4) are valid only for high relative humidities. The typical conditions in the stratosphere are different, mostly with moderate relative humidities. Here the question arises if the presented theory (based on equation (3) and (4)) is still applicable.

    - Equations (3) and (4) were used to describe the basics of the mechanisms of the droplet growth in a simplified manner; it is easy to see from the mathematical structure of the equations how the different Köhler curves behave

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qualitatively. For example, the Köhler curves presented in Fig. 1 were calculated using these equations.

However, in calculations presented from section 4 on, the approximations of the equations (3) and (4) have been omitted. For example, in the calculations presented in sections 4-7, the thermodynamical equilibrium of the liquid phase is calculated using an equilibrium model containing equations (1) and (2) and the degree of dissociation of the electrolytes is explicitly calculated for the whole range of RH.

The equations (3) and (4) are applicable at the low relative humidities, but only qualitatively. When the AIM thermodynamic model is used for the HNO_3-H_2SO_4-H_2O system, the Köhler curves of the largest particles are actually further lowered compared to the Köhler curves of the smaller particles, thus enhancing the splitting effect presented in this paper.

3. page 3, par 2: In the closed system .... Intuitively, one expects that the equilibrium saturation ratio derived for a closed system approaches the traditional Köhler equation if the number density of droplets decreases (i.e. every droplet contains a sufficiently amount of HNO_3 that can condensate on it). Thus, it is not clear why a closed system should behave as an open system if the droplet size growths.

   – This behavior has been previously described by Laaksonen et al (1998). The closed system does not behave as an open system, but the equilibrium size of the droplets approaches the traditional Köhler curve of the particle as the relative humidity grows, the equilibrium size increases, and the nitric acid is depleted from the gas phase. We will clarify this in the revised version of the article.

4. page 3, par 2: ...the closed system Köhler curve crosses a succession of open system curves corresponding to a smaller and smaller concentration. For

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droplets larger than about 1 mi the crossing points reside on the unstable (decreasing) side of the open system curves, however, the resulting closed system Köhler curve represents stable equilibrium This sentence needs a little bit more explanation. One method to understand this effect is to consider the Helmholtz free energy ΔF for open and closed systems, see e.g. Konopka and Vogelsberger, JGR, 1997, Vol. 102., p. 16057

- What we are describing in this sentence is similar to the considerations given by Konopka and Vogelsberger with the exception that the depleting species here is nitric acid and not water as in the Konopka and Vogelsberger article. This mechanism is described in the article by Laaksonen et al. (1998) for a monodisperse population, but it also applies to the largest size bin in a polydisperse population. We will add discussion to the revised paper along the lines suggested by the referee.

5. page 4, par 2 and 3: Explanation of the splitting effect in equilibrium These 2 paragraphs are not the explanation but rather a description of the splitting effect. To explain this effect (at least in equilibrium) one needs an energetical discussion (e.g. in terms of the Helmholtz free energy ΔF) answering the question why the splitted distribution is more favorable than an unsplitted one. Even if a complete energetical discussion is not possible in this paper, some remarks are desirable.

   - We agree with the referee that these paragraphs do not give a bottom line physical explanation of the phenomenon. However, they give an explanation in a mathematical sense of why the splitting occurs. When we first constructed the equilibrium model, we actually suspected that the “runaway” of the largest size bin is due to numerical error, see Kokkola et al. (2003). However, when the open and closed system Köhler curves are considered together, it can be immediately seen that the phenomenon is real.

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In a physical sense, the splitting of the size distribution belongs to the class of Ostwald ripening phenomena, whereby the system minimizes its free energy. We will discuss this in the revised version of the paper.

6. page 7, par 1: “fairly high number density” here some numbers should be given

   – This will be considered in the revised version

7. page 4 first par in section 5 replace “considered” through “considered as

   This will be corrected in the revised version

References

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