

***Interactive comment on “Commentary on
”Homogeneous nucleation of NAD and NAT in
liquid stratospheric aerosols: insufficient to
explain denitrification” by Knopf et al.” by A.
Tabazadeh***

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I thank Dr. Jungwirth for taking the time to review this letter. Below I will provide a point-by-point response to his comments.

Point 1: I agree with the statement here, but the effect of curvature has nothing to do with what is described in my letter. The reviewer is discussing the Kelvin effect here, which basically occurs when droplets get too small. I note that for the Kelvin effect there is no difference in the bulk and surface composition of the droplet, which is the issue that I am addressing and emphasizing in my letter. I believe the reviewer has

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missed the main point of my letter because the Kelvin factor is certainly not the issue being debated here.

Point 2: This may or may not be the case because HNO₃ adsorption parameters, from the aqueous phase for this ternary system, have not yet been measured in the laboratory. The current bulk data seems to indicate that molecular HNO₃, and not the ionic species are enriched at surfaces of this ternary system, which is opposite to what the reviewer is describing here. In general, because ambient air is nonpolluted, molecular rather than ionic species will be enriched at the droplet surface. Ions prefer to solvate within the bulk instead of sitting at the droplet surface, where there are less water molecules available for interactions and bonding. Again the reviewer assessment here is based on what he knows about the Kelvin effect, which becomes important for nm-sized-ranged particles, whereas the debate here is on a totally different issue. Also, the reviewer must be careful in extrapolating cluster thermodynamics to that of real particles. There are significant differences here because in clusters the number of surface molecules can exceed the number of bulk molecules and finding ions on cluster surfaces doesn't necessarily guarantee that in large droplets ions can also be found at the surface layer.

Point 3: For this comment, I will invite the reviewer to read the cited paper by Middlebrook et al.. With today's technology, it is possible to detect organic contamination in aerosol droplets, using laser mass spectrometry (LMS) techniques, to levels of about 0.02 percent by weight. In this paper, it is clearly shown that organic contamination in aerosol samples, produced in a laboratory, is larger than the 0.02 percent by weight limit, unless care is exercised in preparing the samples. I note that 0.02 percent organic contamination was consistently measured in even fresh H₂SO₄/H₂O droplet samples that were produced in the laboratory. Thus, taking the number that the reviewer cites, regarding benzene, there will be plenty of molecules to produce an equilibrium solution of benzene in the droplets with significant surface partitioning of benzene occurring. I note that if 0.01 percent of benzene is in the bulk, then the other 0.01 percent measured

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by LMS could only be at the surface of the particle. The bottom line here is that the Earth is an organic planet and there will organics in all particles, some of which tend to solely reside at the droplet surface. There is a whole body of literature on organic aerosols in the last couple of years, and I even noted a few papers in submission on organic aerosols with this journal at the ACPD stage. The question to ask here is whether tiny amounts of organic matter in aerosols can affect their freezing process. If the freezing occurs at the surface of the particle (Tabazadeh et al., 2002a, 2002b), where organics tend to get enriched, then trace amounts of organics can and will make a big difference. Thus I disagree with the reviewer stating that Knopf. et al. samples had pure surfaces because there is no evidence in this paper to support the reviewer's claim. In fact no information is given in this paper on the level of sample contamination. On the contrary, the Middlebrook et al. paper provides solid and quantitative evidence for organic contamination being present in laboratory samples.

Final Comment: My criticism is not exaggerated, and the reviewer may need to perhaps first read the cited references (Tabazadeh et al., 2002a and 2002b) before forming an opinion regarding this debate. In fact the reviewer may be debating the Kelvin effect here, which is not at all relevant to the points raised in my letter. Also, in my letter I did not discuss problems with the fact that the droplets in the Knopf et al. lab were laid on a flat surface. Real droplets in the atmosphere are constantly rotating and moving up or down in the air. There is turbulence associated with all of these motions, which is absent if the particle is constrained. The turbulence in a real particle in air causes the droplet to form vortices and evaporation often occurs at the top surface in a moving droplet. This evaporation cools the surface of the particle and enhances the rate of freezing of a real particle. Thus I disagree with the reviewer when he firmly states that the experimental results are atmospherically very relevant. First, the authors have not shown that they had pure surfaces. Second stationary droplets lack many motions that a real particle in air will no doubt experience throughout its history. The reviewer can find a full discussion on the effects of turbulence on freezing in the classical textbook of *Microphysics of Clouds and Precipitation* by Pruppacher

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and Klett.

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