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Interactive comment on "A computationally efficient inorganic atmospheric aerosol phase equilibrium model (UHAERO)" *by* N. R. Amundson et al.

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This paper describes the use of UHAERO for predicting the deliquescence and efflorescence in the chemical system of sulfate, acid, ammonium, nitrate, and water. UHAERO does two very important things: it incorporates the most accurate water activity model available in literature (namely, PSC from Clegg et al.), and it evaluates PSC and minimizes the free energy of the system rapidly enough that UHAERO is envisioned as being appropriate for inclusion in global 3D chemical transport models. CTMs presently use models that compromise accuracy for speed. Therefore, UHAERO represents an

important practical advance towards more realistic treatments of aerosol phase within CTMs. UHAERO also begins to treat particle efflorescence, and I provide below some critical thinking in regard to this aspect of the present implementation in UHAERO and the associated description in the manuscript.

A. Deliquescence The submitted paper has 21 figures on deliquescence and is very sound in its treatment of deliquescence. The paper could be strengthened by offering some comparisons between the predictions of UHAERO and those of other models in Table 1 to demonstrate why a more accurate model is important in CTMs, although perhaps the authors feel that the study of Zhang et al. was sufficient. The paper could also be strengthened by speed comparisons among UHAERO and the other models, specifically (a) UHAERO versus AIM since AIM is as accurate as UHAERO but not appropriate for incorporation in global models and (b) UHAERO versus ISORROPIA since ISORROPIA is included in global models but makes sacrifices in the accuracy of its treatment.

What do the numbers 1 through 7 mean in the figures (e.g., Figure 4a)?

B. Efflorescence In contrast to the very fine treatment of deliquescence, the treatment of efflorescence is relatively incomplete and in some cases inaccurate statements are made. On the plus side, UHAERO is the first model to begin treating efflorescence. For example, AIM offers no predictions or empirical rules about efflorescence. Other models in the past have used empirical rules. UHAERO tries to use homogeneous nucleation theory.

I. Incomplete treatment 1. The treatment of efflorescence is incomplete in this manuscript because there is only 1 figure (Figure 12) compared to the 21 figures on deliquescence. That figure considers only the sulfuric acid to ammonium sulfate compositions. The nitrate compositions are treated in deliquescence; therefore, balance in the treatment of efflorescence is missing.

2. Figure 12 is philosophically different from the figures on deliquescence in that

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the authors appear to be trying to validate the accuracy of the calculation against data whereas the treatment of deliquescence centers on the computational aspects of UHAERO.

3. An evaluation of UHAERO in its treatment of efflorescence should include a comparison to other crystallization measurements in the ammonium-sulfate-nitrate space. The efflorescence relative humidities are reported in Martin et al. (2003) cited by the authors, and the solids formed are reported in Schlenker, J.C., Malinowski, A., Martin, S.T., Hung, H.M., Rudich, Y., "Crystals Formed at 293 K by Aqueous Sulfate-Nitrate-Ammonium-Proton Aerosol Particles," Journal of Physical Chemistry A, 2004, 108, 9375-9383.

II. Inaccurate statements From my point of view, the treatment of efflorescence in this manuscript makes, in some cases, several inaccurate statements. Moreover, the treatment within the model is not yet acceptably validated through comparisons to predictions and experimental data, and the treatment based on a constant sigma(germ) for one solid but in different mother liquors may be fundamentally flawed—a shortcoming that could become apparent through model/data comparisons.

1. The abstract states, “The modelĚ computesĚ crystallization behavior without any a priori specifications of the relative humidities ofĚ crystallization.” This statement is false: page 5 under equation 12 states, “sigma(crystal/air)Ě can be determined as a parameter on one value of sigma(germ), which, in turn, can be computed from one measurement of the efflorescence RH of the corresponding crystalline salt.” In other words, the crystallization behavior is tuned; it is not determined “without any a priori specifications.” In essence, the authors use laboratory data of efflorescence to predict efflorescence, which, in the case of poles (i.e., the aqueous compositions corresponding to ammonium sulfate, letovicite, etc.), corresponds to a circular analysis.

2. Along the same lines and with the same objection, the final sentence of the manuscript states, “The model also includes a first-principles calculation ofĚ crystal-

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lization behavior."

3. The authors may want to have caution when using homogeneous nucleation theory. The way this theory has been employed in the literature of aerosol particle phase transitions is simply to reduce data: a measured efflorescence RH is converted into a sigma(germ) on a one-to-one correspondence (i.e., ERH -> f(sigma(germ))). The homogeneous nucleation theory has not been rigorously tested in the reverse: calibration once of sigma(germ) and then application to the prediction of efflorescence RH for other chemical conditions. The model of UHAERO combined with the data of Schlenker et al. (2004) presents the possibility of doing this exercise for the first time. I personally would be amazed if the predictions match observations since homogeneous nucleation theory is full of assumptions not likely to hold in crystallization of a salt from diverse mother liquors, e.g., sigma(germ) is not a constant. (The statement that sigma(crystal/air) is a constant, just after eq 12, is also not true. The surface tension of hygroscopic crystals depends on relative humidity.)

4. (a) After eq 12, the authors state that Cohen et al. (1987) measured sigma(germ). In fact, Cohen et al. measured efflorescence and used homogeneous nucleation theory to reduce their observation to the quantity sigma(germ). (b) On page 4 after eq 8, the authors imply that Cohen et al. (1987) have data on the shape of the germs of ammonium sulfate. In fact, Cohen et al. assumed that shape based upon bulk crystallography. In contrast, laboratory measurements in recent years (e.g., beam probe with AMS) suggest that 100-nm ammonium sulfate particles appear to be spherical, in contrast to the cubic shape of NaCl particles. That said, any extension from the shape of 100-nm crystals to the shape of germs would, of course, also be suspect.

5. (a) Figure 12 suggests, by comparison to data, that homogeneous nucleation theory does a good job of predicting crystallization. However, this conclusion is misleading because the maximum points in the ammonium sulfate and letovicite curves are forced by tuning (as mentioned above), and the shape of the curves coming off of them are driven by supersaturation. (b) The basis for comparison of "10^0" and "10^4" to initial

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and final crystallization should be justified and developed.

6. The UHAERO framework treats only homogeneous nucleation. As a result, there is no possibility to crystallize ammonium bisulfate. In contrast, the measurements of Schlenker et al. (2004) show that letovicite can crystallize and then acts as a heterogeneous nucleus for ammonium bisulfate to crystallize. Similarly, ammonium nitrate, which does not crystallize by homogeneous nucleation, does crystallize by heterogeneous nucleation once another crystal has formed by homogeneous nucleation.

In summary, (1) the speed and accuracy of UHAERO are important advances that will enable its incorporation in 3D CTMs and thus improve the treatment of aerosol phase in those CTMs, (2) the treatment of deliquescence is sound and the related figures in the manuscript offer an informative tutorial of the major features of the phase behavior and water uptake of this chemical system, and (3) the attempt to incorporate efflorescence is an admirable and important goal but its theoretical underpinning is not sound (e.g., homogeneous nucleation theory assuming fixed sigma(germ)), its implementation is not tested (e.g., calibrate for sigma(germ) for compositions at poles and then test predictions for nonpoles against experimental observations of Martin et al. 2003 and Schlenker et al. 2004), its treatment in the manuscript is unbalanced (e.g., 1 figure on efflorescence versus 21 on deliquescence), and its development omits heterogeneous nucleation (e.g., there is no mechanism to form ammonium bisulfate).

UHAERO has the potential to become widely used in CTMs, and I myself would be very excited to see the treatment of efflorescence successfully developed and tested.

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