

Interactive comment on “Water activity and activation diameters from hygroscopicity data – Part I: Theory and application to inorganic salts” by S. M. Kreidenweis et al.

Anonymous Referee #3

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Kreidenweis et al., Water Activity and Activation Diameters from Hygroscopicity Data - Part I: Theory and Application to Inorganic Salts. Review date: 20050317

The authors develop a technique that utilizes growth factor (GF) measurement for inferring critical dry diameters. The approach consists of fitting GF measurements versus relative humidity (RH), correcting for the Kelvin effect, and validating the derived water activities against parameterizations based on gravimetric (i.e., results from the Tang laboratory) and computational methods (Clegg, Debye-Huckel etc.). This manuscript focuses on results for NaCl and ammonium sulfate. The manuscript is Part I of a two-

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part series; Part II is in preparation. As such, I feel that a solid foundation should be set for Part II and I am thus critical of aspects of Part I. This criticism is elaborated on below.

Comment 1 - The authors compare against published assessments of the Sc based on laboratory CCN measurements. Most (all ?) of these are linked to models of supersaturation in the cloud chamber which itself is dependent on a priori knowledge of the Sc - D_{dry} relationship. There are two consequences: 1) The “uncertainty ranges” emphasized at the end of sections 3.1.2 and 3.2.2 do not include bias coming from the predicted Sc - D_{dry} relationship, and 2) the “uncertainty ranges” referred to, may reflect the width of a Gaussian used to fit data consisting of activation fraction and D_{dry} and as such the uncertainties are more a consequence of broadening in an electrostatic classifier rather than measurement error.

Comment 2 - I feel that more attention should be given to the GF measurements. First, I do not think that the introduction is the place to include a description of the apparatus. Second, how confident are the authors that the particles are equilibrated in the Perma Pure tubing? Have experiments been conducted with differing lengths of Perma Pure tubing, different residence times, etc?

Comment 3 - Since calculations for bulk systems, for which the Kelvin effect can be ignored, are the basis for your $aw-x$ validation, I feel that the Kelvin correction should be explicit in Equation 17. In contrast, you discuss three different results: 1) the uncorrected activities, 2) the Kelvin-corrected activities assuming pure water surface tension, and 3) the Kelvin corrected activities assuming concentration-dependent solution tensions. I feel that these three options overburden both the discussion (bottom of page 296 and the end of section 4 on page 305) and the graphics (Figures 4, 5 and 6). In my opinion the Kelvin effect be accounted for using concentration-dependent solution tensions and presented as such without recourse to the intermediate step of Kelvin-uncorrected activities.

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Comment 4 - Section 6 (Summary and Conclusions) left me with several questions. Clearly, the proposed approach does not require dry particle density to predict critical dry size but this result is expressed in the following way, “It also does not require the dry particle density to predict CCN activity”. I find this vague and recommend a more direct statement. I have the same comment about the usage “dry material”. Perhaps “solute mass” is more definitive. Finally, the terminology “dry particle weight percent” is confusing because I believe you are referring the composition of the dry particle, not the liquid solution, but you use weight percent to describe the composition of both. My general comment is that the semantics both here (Conclusions) and in the body of the text need to be coordinated.

Comment 5 - I have several comments about the formulism. First, the authors present Equation (2) without any reference or justification. Specifically, I am referring to the use of the partial molar volume in the Kelvin term; what is the basis for this? Second, below Equation (12) we are presented the formulation , and are told that Equation (12) “is the same expression that would be obtained from ” in the dilute limit. Are you sure about this? Third, in Equation (13) the Kelvin term is formulated inversely with temperature but the authors comment above this that “a parameterization for the change in surface tension of water with temperature” is applied. If the temperature parameterization is applied should not both temperature-independent and temperature-dependent terms be present in the middle equation of Equation (13)? Fourth, the transition from Equation (17) to Equation (18) is not clear. Does this follow from Equations (14) and (17)? Further, what is the relevance of Equation (18)? Fifth, Equation (25) uses “chi” for a shape factor but “chi” is also common notation for the dynamic shape factor seen in Stoke’s Law for aspherical particles. A dynamic shape factor equal to 1.08 is often referenced as the correct value for cubes leading to a mobility/sphere size ratio of 1.04. Recent work by Martin Geisel (EST) is relevant to your discussion of this issue. Sixth, the comment following Equation (26) would be more accessible if expressed in terms of molality, not weight percentage.

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Comment 6 - Your data is for the RH interval 75 to 90% RH, and only includes a few data values, but you are extrapolating to larger RH to infer Sc. Could the extrapolation introduce significant uncertainty in the Ddry-Sc relationship?

Comment 7 - We are told that the proposed technique avoids the need for knowledge of the molecular weight and degree of dissociation. This is an important advance, if it can be applied to ambient particles. What assumptions will be necessary to accomplish such a characterization, and how will these assumptions limit inferred ambient aerosol Sc values?

Details -

Why D_p , and not D with appropriate subscripting to indicate "wet", "dry", "critical" etc?

At the bottom of page 306 there is a "Dcrits"

You are plotting continuous functions, but I see kinks and wobbles (i.e. Figures 2, 3, 5, 7 and 8)

Figures 4 and 6 are difficult to interpret - where is the "AIM" line in Figure 6, where is "Low" in Figure 4b, how to distinguish between Debye-Huckel and "Uncorrected" in Figures 4 and 6? Since you are plotting continuous functions should not the use of "data points" be avoided?

The usage "stable cloud droplets" is contradictory in the sense that such particles are experiencing changing size with time, as opposed to the "stable" particles whose size constrained by the Kohler curve and ambient RH.

Why not MKS dimensions for surface tension, etc.?

Is the last paragraph of section 2 relevant to the NaCl and AS covered in this paper?

Perhaps "metastable" for what you refer to as "crystallization (hysteresis)"?

Section 4.2 should be revised. Specifically, the last part of the first sentence of this sec-

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tion ("Essentially extrapolates the volume ratios to dilute solutions) and the following sentence ("Thus, the Kohler curves") are perhaps too complex.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 287, 2005.

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