Atmos. Chem. Phys. Discuss., 7, S3482–S3487, 2007
www.atmos-chem-phys-discuss.net/7/S3482/2007/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment” *by* D. Rose et al.

D. Topping

david.topping@manchester.ac.uk

Received and published: 27 July 2007

General comments

Whilst the authors present an excellent and comprehensive characterisation of the calibration procedures and measurement uncertainties in the CCN instrument, much of the terminology in the theoretical analysis of the uncertainties with respect to Köhler theory is rather confusing. It is indeed true that Köhler theory is

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

presented under various guises in the literature. However, within the manuscript there is an unfortunate lack of discussion regarding the applicability of the various approximations and no critical evaluation of the form of equation used. This leads to a rather skewed interpretation of the sources of the uncertainties in the measurements.

Starting from first principles, by minimising the Gibbs free energy of a system involving an involatile solute, considering water in the liquid and gaseous phase, and by treating the surface tension of the aqueous droplet, one arrives at the ”fundamental” Köhler equation (McFiggans et al 2006) as follows:

$((RH/100) = a_w exp(4v_w \sigma_s/RTd_d))$

Where RH is the ambient relative humidity, (a$_w$) is the water activity of the solution, (σ) is the surface tension of the solution, R the universal gas constant, T the temperature, (v$_w$) the partial molar volume of water and (d$_d$) the droplet diameter. Provided the user can provide an accurate representation of the water activity, surface tension, dry / aqueous density, surface tension and partial molar volume then this relationship will provide you with a true representation of water uptake for all inorganic systems. Common mathematical simplifications designed for ease of use are not truly accurate, despite possible ’negligible’ discrepancies for inorganic systems. True, if one applies the Köhler equation to study the onset of deliquescence then lack of consideration of the solid/air interface may introduce errors for small particles (Russell and Ming 2002). Similarly, if one cannot account for the coupling between the bulk and surface phase for systems involving a surfactant then errors may also be introduced (Sorjamaa et al 2004). However the fact remains that there is a hierarchy of approaches used for 1) representation of Köhler theory and 2) representation of parameters within Köhler theory. The authors are correct in that studies employing Köhler theory should state specifically which form has been used, but not all forms and approximations are equally valid. However, for closing laboratory studies such as the one presented, then the most accurate form of appropriate models must be used despite possible ’negligible uncertainties'. In this case, this entails use of the fundamental Köhler equation with an accurate source of (a_w) such as the Pitzer-Simonson-Clegg mole fraction based model (which can be fit online http://mae.ucdavis.edu/ wexler/aim/aim.htm (Clegg et al 1998a,b)), surface tension model and so on.

Simplifications of either the equation itself or important chemical/physical properties within the above form are useful, but mainly for larger scale modelling purposes where computational efficiency is key. Similarly, there may be organic compounds, or mixed inorganic / organic systems, for which certain variables are unknown thus requiring some form of approximation. Thus I think it is important to recognise the limitations in the applicability of approximations to Köhler theory and retain a strict 'code of practice', particularly when trying to close studies in the laboratory, and most importantly when attempting to apportion uncertainty.

For the systems investigated in the manuscript, the property which is subject to the greatest uncertainty and yet is most readily treated is the water activity. Firstly, consider the statement in the abstract "*the relative deviations between different modeling approaches were as high as 25 percent for* $(NH_4)_2SO_4$ *and 16 percent for NaCl. The deviations were mostly caused by the different parameterizations for the activity of water in aqueous solutions of* $NH_4)_2SO_4$ *and NaCl (activity parameterization,osmotic coefficient, and van't Hoff factor models).*" There is no doubt that different model approximations do indeed produce significantly different results. However, again, there is a clear methodology which can be used to calculate the water activity with great accuracy and there is no need to introduce model inaccuracies for these simple systems. It should be stressed within the paper that the errors in the approximations can be entirely overcome, leaving a clear estimate of the uncertainties resulting from the measurement techniques. A second order consideration of the error in approximations to Köhler theory could be mentioned in the discussion, but should not be a central focus of the uncertainty quantification. This can be overcome by making the critical evaluation of the approximations, establishing a definitive hierarchy in validity of modelling approaches. This is not to suggest that probing different models isn't useful. Sensitivity studies for different representation within Köhler theory are always useful, if only to highlight the dangers of using 'inaccurate' data to the community at large and to demonstrate that such inaccuracies are larger in magnitude than currently available measurements.

Even many large-scale models rely on more accurate (though inexpensive) binary fits than on older representations of the Van't Hoff model. Such fits can readily be derived from AIM online (now regarded as an accurate source for thermodynamic data for inorganic systems (Clegg et al 1998a,b)), and the older inaccurate techniques really should be consigned to history rather than being used to validate such careful measurements as reported in the manuscript. In fact, there is no mention of the Pitzer-Simonson-Clegg mole fraction activity based model (that used in AIM) in your paper, whilst you refer to a revised update of the Pitzer molality based model. You should find that both models give the same results at lower concentrations, and that both compare extremely well with measured EDB data.

Following on from this, the manuscript mentions different empirical sources for water activity as a function of concentration for inorganic compounds. The electro-dynamic-balance (EDB) is indeed regarded as an accurate source of water activity measurements and has been used quite extensively in the literature for a wide range of inorganic, organic and mixed inorganic/organic systems (e.g. Peng et al., 2001, Choi and Chan, 2002a; Choi and Chan, 2002b). In fact, more recent work by Chan and co-workers (Chan and Choi 2000) have revisited common inorganic salts in addition to those studied by Tang and Munkelwitz (1994) which you refer to in the paper. Have the measurements been compared with such up to date laboratory data? The measurements from these experimental studies and from the Pitzer-Simonson-Clegg mole fraction based semi empirical model should be equal. Have you tested this? There really should be a more extensive review of water activity measurements and comparisons with more robust theoretical tools.

The HTDMA, in its normal use, is a good field/laboratory instrument for assessing water uptake on aerosols above and below 100nm, whilst the EDB is restricted to very large particles and cannot therefore probe the influence of curvature nor be used in the field. Thus, the two instruments are of course deemed complimentary but in the end serve different purposes. The reliance on HTDMA measurements as an entirely accurate source of thermodynamic data may be questioned, particularly with respect to kinetic effects and reliance during data inversion on assumptions about the dry physical state of particles (Topping et al 2005). Whilst shown to be useful in predicting activation of certain compounds in k-Köhler theory (Petters and Kriendeweis 2007), there are limitations with this approach and it would be more appropriate to fully evaluate the measurements against an accurate Köhler model before making the approximations stated.

References

Chan, C. K., Ha, Z., and Choi, M. Y. "Study of water activities of supersaturated aerosols of mixtures of sodium and magnesium salts", Atmospheric Environment, 34, 4795-4803. 2000

Choi, M.Y., and Chan, C.K.:Continuous measurements of the water activities of aqueous droplets of water-soluble organic compounds, Journal of Physical Chemistry A, 106 (18), 4566-4572, 2002a.

Choi, M.Y., and Chan, C.K.:The effects of organic species on the hygroscopic behaviors of inorganic aerosols, Environmental Science Technology, 36 (11), 2422-2428, 2002b.

Clegg, S.L., Brimblecombe, P., and Wexler, A.S.:Thermodynamic model of the system H+-NH4+-Na+-SO42–NB3–Cl–H2O at 298.15 K, J Phys Chem A, 102 (12), 2155-2171, 1998a.

Clegg, S.L., Brimblecombe, P., and Wexler, A.S.:Thermodynamic model of the system H+-NH4+-SO42–NO3–H2O at tropospheric temperatures, J Phys Chem A, 102 (12), 2137-2154, 1998b.

McFiggans G, Artaxo P, Baltensperger U, Coe H, Facchini C, Feingold G, et al. The effect of physical and chemical aerosol properties on warm cloud droplet activation. Atmospheric Chemistry and Physics Discussions 5:8507-8647, 2006

Petters M.D. and Kreidenweis, S.M. A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. Atmos. Chem. Phys., 7, 1961-1971, 2007

Russell, L.M., and Ming, Y.:Deliquescence of small particles, J Chem Phys, 116 (1), 311-321, 2002.

Sorjamaa, R., T. Raatikainen, A. Laaksonen.:The role of surfactants in Kohler theory reconsidered, Atmospheric Chemistry and Physics Discussions, 4, 2781-2804, 2004.

Tang, I.N., and Munkelwitz, H.R.:Water Activities, Densities, and Refractive-Indexes of Aqueous Sulfates and Sodium-Nitrate Droplets of Atmospheric Importance, J Geophys Res-Atmos, 99 (D9), 18801-18808, 1994.

Topping DO, McFiggans GB, Coe H. A curved multi-component aerosol hygroscopicity model framework: Part 2 - Including organic compounds. Atmospheric Chemistry and Physics ,5:1223-1242.2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 8193, 2007.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper