

## ***Interactive comment on “Mass-based hygroscopicity parameter interaction model and measurement of atmospheric aerosol water uptake” by E. Mikhailov et al.***

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### **General comment on the relevance of the KIM approach**

In this comment we explain the motivation and objectives of the KIM approach in comparison to earlier model approaches.

The existing thermodynamic models require that the properties of all involved compounds in the mixed particles are known. All of them are complex multi-parameter ion- and molecule interaction models. Thus, 7 parameters (3- short range and 4- long range) have to be known to describe the water activity of a simple NaCl particle using the rigorous Aerosol Inorganic model (AIM; Clegg et al., 1998). More complex models

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for organic-inorganic mixed particles basically are different combinations of AIM and UNIFAC models with poor-defined mixture parameters. Application of these thermodynamic models to atmospheric aerosols containing a multitude of generally unspecialized organic compounds remains under question especially at low RH (Petters and Kreidenweis, 2007; Tong et al., 2008). In addition, by definition, the thermodynamic models are equilibrium models and thus they are not able to describe phase state of non-equilibrium (metastable) solutions.

The KIM was basically developed to describe the hygroscopic properties of atmospheric particles with poorly defined chemical composition. Therefore, in the KIM the following three basic approaches have been used:

1. Mole (fraction) scale was replaced by mass (fraction) basis.
2. Concentration-dependent  $\kappa_m$  parameter was introduced to account for the relationship between water activity and mass of water absorbed by solid particles.
3. Depending on particle evolution stage the solute concentrations are expressed in explicit form either as solubilities or as mass fractions of solutes.

In the KIM we use a self-interaction coefficient  $\alpha_{i,i}$  instead of an activity coefficient to account for the non-ideal behavior of the pure solutes and the solvent in concentrated solutions. This simple approach eliminates the necessity to involve complex multi-parameter models such as AIM (for inorganics and dissociated organics) or UNIFAC (for water soluble organics). The same simplified approach was used to treat the interaction between different solutes. Only one mixed term, i.e. the cross-interaction coefficient  $\alpha_{i,j}$  is used to consider interaction between pairs of solutes. It should be noted that both coefficients have a reasonable physical interpretation indicating the strength of interaction between solutes in solution.

In the thermodynamic models equilibrium between solutions and solid phases is calculated based on a solubility constant (or activity product ( $K_s$ ), Clegg et al., 1998; Clegg

and Seinfeld, 2006). This approach can be used only for equilibrium systems where the activity product of the dissolved species (ions) is constant. This rule is not valid for metastable systems. As a result non-equilibrium phase transitions cannot be taken into account. The KIM equations contain a particle solubility parameter in an explicit form and its quantity can be used to characterize metastable or semi-solid solutions.

The framework of KIM is close to the extended ZSR model (Clegg et al., 2003; Clegg and Seinfeld, 2004). Both models are expressed in terms of properties of solutions of individual salts or uncharged molecules and include interaction parameters for pairs of solute. However, several significant differences exist. First, in case of KIM the hygroscopic growth and phase transitions (eutonic, deliquescence, efflorescence) of the mixed particles can be quantitatively characterized for particles with unknown composition. That is in contrast to the extended ZSR model where thermodynamic properties of the individual components have to be known before (Clegg et al., 2003). Second, the extended ZSR model involves molality-based Debye-Hückel expressions for osmotic and activity coefficients of salts, and models such as UNIFAC for uncharged solutes (Clegg and Seinfeld, 2004). In addition, three empirical parameters are introduced in the ZSR to account for the interaction between pairs of solutes (Clegg et al., 2003). As mentioned above, KIM does not require this kind of information and only one interaction parameter is used. That is, the  $\kappa_m$ -mass model minimizes the number of interaction parameters. Thus, for pure (single) particles only two coefficients ( $\kappa_m^0$ ,  $\alpha$ ) are needed to describe water uptake including the metastable solution RH range (Eq.29). Modeling results have also shown that water uptake observed upon deliquescence and efflorescence transitions is well captured by KIM using the same parameters ( $\kappa_m^0$ ,  $\alpha$ ) supplemented with solubility,  $C_m$  (Eq.28). Finally, the KIM provides a good fit for complex ambient particles with poor-defined composition, covering the multiphase area at low relative humidity. The set of derived fit parameters (Eqs. 35-40, or Eqs. 39-44 in the updated manuscript) is to some extent different for the SPB and AMAZE samples. It is reasonable to expect that an individual set of such parameters can be used to characterize ambient aerosol from different locations. Thus, we believe that KIM is an

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appropriate tool for description of the hygroscopic properties of atmospheric samples. Besides, the KIM model can be also useful to interpret the water uptake measured by mass-based methods, like electrodynamic balance (EDB), particle mass analyzer (Khalizov et al., 2009), microbalance (Hatch et al., 2008), micro-Raman spectroscopy (Yeung and Chan, 2008), and filter-based methods (Mikhailov et al. 2011; Speer, et al., 2003; Lee and Hsu, 2000) We are testing now volume based KIM as applied to pure and mixed organic-inorganic particles using HTDMA data set. The obtained KIMV modeling results will be presented soon.

## References

- Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: A thermodynamic model of the system  $\text{H}^+ - \text{NH}_4^+ - \text{Na}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl} - \text{H}_2\text{O}$  at 298.15 K, *J. Phys. Chem. A*, 102, 2155–2171, 1998. Clegg, S.L., Seinfeld, J. H., and Edney E. O.: Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds. II. An extended Zdanovskii–Stokes–Robinson approach, *Aeros. Sci.*, 34, 667–690, 2003.
- Clegg, S. L., and Seinfeld, J. H.: Improvement of the Zdanovskii-Stokes-Robinson model for mixtures containing solutes of different charge types, *J. Phys. Chem. A*, 108, 1008-1017, 2004.
- Clegg, S. L., and Seinfeld, J. H.: Thermodynamic models of aqueous solutions containing inorganic electrolytes and dicarboxylic acids at 298.15 K. 1/ The acids as nondissociating components, *J. Chem. Phys.*, A., 110, 5692-5717, 2006.
- Hatch, C. D., Gierlus, K. M. Schuttlefield, J. D., and Grassian V. H.: Water adsorption and cloud condensation nuclei activity of calcite and calcite coated with model humic and fulvic acids, *Atmos. Environ.*, 42, 5672-5684, 2008.
- Lee, C. T., and Hsu, W. C.: The measurement of liquid water mass associated with collected hygroscopic particles, *Aerosol Sci.*, 31, 189-197, 2000.

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Khalizov, A. F, Zhang, R., Zhang, D., Xue, H., Pagels, J., and McMurry, P. H.: Formation of highly hygroscopic soot aerosols upon internal mixing with sulfuric acid vapor, *J. Geophys. Res.*, 114, D05208, doi:10.1029/2008JD010595, 2009.

Mikhailov, E. F., Merkulov, V. V., Vlasenko, S. S., Ryshkevich, N. I., and Pöschl, U. J.: Filter-based differential hygroscopicity analyzer of aerosol particles, *Izvestiya, Atmospheric and Oceanic Physics* 47, 747-759, 2011.

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, doi:10.5194/acp-7-1961-2007, 2007.

Speer, R.E., Edney, E.O., and Kleindenst, T.E.: Impact of organic compounds on the concentrations of liquid water in ambient PM<sub>2.5</sub>, *Aerosol. Sci.*, 34, 63–77, 2003.

Tong, C., Clegg, S. L. and Seinfeld, J. H.: Comparison of activity coefficient models for atmospheric aerosols containing mixtures of electrolytes, organics, and water, *Atmos. Environ.*, 42, 54-59-5482, 2008.

Yeung, M. C., and Chan, C. K.: Water content and phase transitions in particles of inorganic and organic species and their mixtures using micro-Raman spectroscopy, *Aerosol Sci. and Technol.*, 44, 269-280, 2010.

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