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PROPERTIES OF AMMONIATED SULFATE AEROSOLS AT LOW TEMPERATURES: WHY ARE THE MODELS SO FAR OFF?

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PROPERTIES OF AMMONIATED SULFATE AEROSOLS AT LOW TEMPERATURES: WHY ARE THE MODELS SO FAR OFF?

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Natural and anthropogenic aerosols play a major role in determining the climate on earth either by scattering solar radiation back to space, or by altering cloud radiative properties when they act as CCNs. To incorporate aerosols into GCMs it is essential to know their thermodynamic and optical properties over a temperature and humidity range that prevail in the troposphere. We will present a study of the properties of ammoniated sulfate aerosols ($(NH_4)_2SO_4$, NH_4HSO_4, and in-between mixtures), the most common class of anthropogenic aerosols from –35 ^oC to 35 ^oC.

Using our low temperature single particle levitation apparatus we mapped out all of the phase transformations in ammoniated sulfate aerosols, ones that take place at equilibrium as well as those from metastable; super-saturated or super-cooled solutions. On the basis of the observed transitions we derived equilibrium and metastable phase boundaries. The former are commonly available for many substances, while the latter are a map of conditions in water pressure, composition, and temperature where homogeneous nucleation occurs. Figures 1 and 2 illustrate the phase diagrams in the temperature compositions domains for $(NH_4)_2SO_4$ and NH_4HSO_4. Combined, these diagrams can be used to predict the phases of $(NH_4)_2SO_4$ or NH_4HSO_4 aerosols under any atmospheric condition provided the path - in water pressure and temperature - is known.

In the process of deriving the phase diagram we discovered new phases that are stable at low temperatures: below –19.35^oC and at high RH the stable phase of $(NH_4)_2SO_4$ is $(NH_4)_2SO_4{\cdot}4H_2O$, and below –30.5 ^oC the stable phase of NH_4HSO_4 is $NH_4HSO_4{\cdot}8H_2O$. The data show that once these hydrate phases form, they persist for many days even when the %RH is reduced to 1^{-10}. It would therefore not be surprising to find that in the mid to upper troposphere NH_4HSO_4 aerosols are commonly in the octahydrate phase.

Our results show that because of a lack of data, many of the assumptions that are used in radiative transmission models can be rather inaccurate. For example it is generally assumed that the RH at deliquescence and efflorescence is temperature independent. In contrast, we find that the efflorescence point in $(NH_4)_2SO_4$ increases from 37 %RH to 70 %RH as the temperature is reduced from 25^oC to –30.5 ^oC, and that the deliquescence RH of NH_4HSO_4 increases from 40 to 70 over a similar temperature range.

A comparison between observations and the latest thermodynamic model (S. Clegg et al. 1998) derived equilibrium phase diagram for ammonium sulfate shows excellent agreement. Similar agreement with the model is found over a wide range of solution compositions at temperatures higher than 15 ^{o}C. This is not surprising given that the high temperature data were used as input to the thermodynamic model. However, when the same model is extrapolated to low temperatures a significant discrepancy between data and model is uncovered. Similar comparisons between data and model for NH_4HSO_4 show even larger disparity.

A detailed examination of the data and its temperature dependence reveals a liquid-liquid phase transition at 5^{o}C which could not have been predicted by the model. We are at present in the process of deriving a new comprehensive model that incorporates the physics of such a liquid-liquid phase transition.

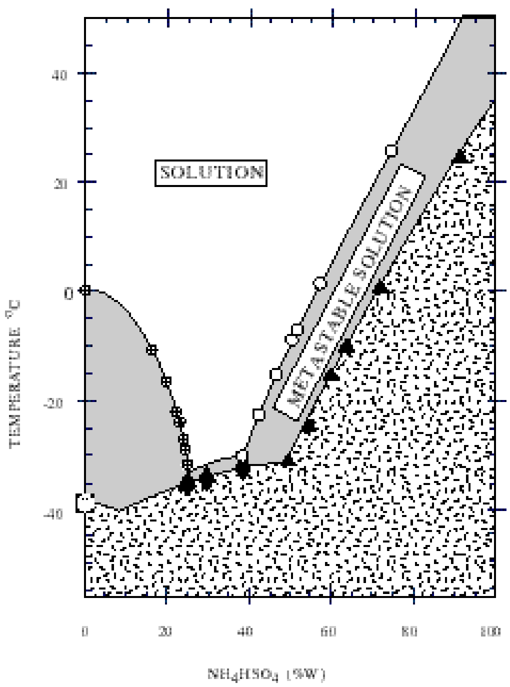

Figure 1. The ammonium bisulfate phase diagram in the composition vs. temperature domain. The metastable solution is the gray area. The dotted area indicates solid phases. The solid triangles and diamonds indicate efflorescence into anhydrous and octahydrate respectively.

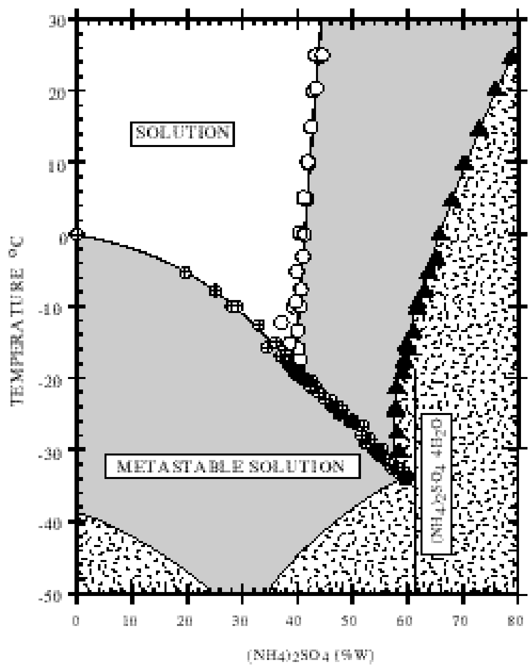

Figure 2. The ammonium sulfate phase diagram in the composition vs. temperature domain. The metastable solution is the gray area. The dotted area indicates solid phases. The solid triangles indicate efflorescence into anhydrous.