

Interactive comment on “Thermodynamic characterization of Mexico City aerosol during MILAGRO 2006” by C. Fountoukis et al.

Anonymous Referee #2

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General comments

The authors have applied the bulk equilibrium model ISORROPIA II to Mexico City aerosols sampled at the T1 site to examine the gas-particle partitioning of semi-volatile inorganic species, deliquescence behavior, and the particle phase state. They conclude that the bulk equilibrium assumption is appropriate for the complex Mexico City aerosols, with the equilibration time scales ranging between 6 and 20 min. They also infer from their model analysis that Mexico City aerosols prefer the stable state when particulate $\text{SO}_4/\text{NO}_3 < 1$ and the metastable state when $\text{SO}_4/\text{NO}_3 > 1$. Another major conclusion they draw from their analysis is that crustal species (Ca, Mg, K) must be explicitly treated in models for accurately predicting gas-aerosol partitioning and phase state.

While some of these conclusions may or may not be correct, I question the entire approach used to arrive at them. I recommend that this manuscript be rejected due to specific issues listed below.

Specific comments

First of all, I would like to echo all the specific comments and concerns raised by Referee #3. I completely agree with each and every one of them. My specific concerns are as follows:

1. Line 10, page 9205, the authors state “*An important question regarding the partitioning of semi-volatile inorganic aerosol phase is whether the assumption of thermodynamic equilibrium is adequate to predict chemical composition.*”

In my opinion the assumption of [bulk] thermodynamic equilibrium is *not* adequate to predict chemical composition. The approach adopted in this study (and several other similar studies in the past) is at odds with the conclusions from a number of studies that have used dynamic models to simulate partitioning of semi-volatile inorganic gases to size- and composition-resolved aerosols. While the authors cite some of these studies here, they simply proceed further to test the bulk equilibrium assumption anyway.

It is now pretty clear that a dynamic mass transfer treatment is needed for simulating size-resolved aerosol composition, especially when significant compositional differences exist between different sized particles. Therefore any attempt to test the bulk equilibrium assumption, especially for complex aerosol such as found in Mexico City, is a meaningless exercise.

However, if the authors still wish to examine the equilibrium assumption, then they must at least solve the “size-resolved equilibrium” problem instead of the “bulk equilibrium” problem (e.g., see Jacobson, M. Z., Studying the effects of calcium

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and magnesium on size-distributed nitrate and ammonium with EQUISOLV II, Atmos. Environ., 33, 3635- 3649, 1999).

2. The second issue with this study is the use of an approximate thermodynamic model to examine the phase state of complex aerosols. While ISORROPIA has been widely applied and used in a number of 3-D models, the fact still remains that it is an approximate model which cannot accurately simulate multicomponent deliquescence and phase transitions in complex aerosol particles. This is because, ISORROPIA does not explicitly solve the solid-liquid phase equilibria, but rather simply tries to approximate it using an ad-hoc approach. This can introduce significant errors in the equilibrium phase-state, water content, and composition of aerosol particles.

To illustrate this point, I show below a comparison of aqueous-phase concentrations of various ions predicted by ISORROPIA and AIM2 as a function of RH for a relatively simple aerosol particle composed of:

$\text{SO}_4 = 1 \mu\text{mole}/\text{m}^3$, $\text{NO}_3 = 1 \mu\text{mole}/\text{m}^3$, $\text{Cl} = 0.2 \mu\text{mole}/\text{m}^3$, and $\text{NH}_4 = 3.2 \mu\text{mole}/\text{m}^3$.

AIM2 serves as the "truth" model because it uses a highly accurate activity coefficient model and employs a direct Gibbs free energy minimization approach for solving multicomponent phase equilibria. ISORROPIA was run in the "reverse" mode while gas-particle partitioning in AIM2 as turned off so that the results from both the models can be directly compared. Also, formation of double salts in AIM2 was turned off to maintain consistency between the two models. Temperature was 298 K.

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RH (%)	Liquid-Phase Concentrations in $\mu\text{mole}/\text{m}^3$ air									
	AIM2					ISORROPIA				
	NH4	SO4	NO3	Cl	H2O	NH4	SO4	NO3	Cl	H2O
40	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
42	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
44	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
46	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
48	0.0	0.0	0.0	0.0	0.0	0.29	0.08	0.13	0.0	0.41
50	0.0	0.0	0.0	0.0	0.0	0.81	0.25	0.25	0.05	1.34
52	0.0	0.0	0.0	0.0	0.0	1.21	0.38	0.38	0.08	2.16
54	1.35	0.08	1.0	0.2	2.33	1.62	0.51	0.51	0.10	3.08
56	1.38	0.09	1.0	0.2	2.62	2.02	0.63	0.63	0.13	4.12
58	1.42	0.11	1.0	0.2	2.94	2.43	0.76	0.76	0.15	5.29
60	1.46	0.13	1.0	0.2	3.33	2.83	0.88	0.88	0.18	6.61
62	1.53	0.16	1.0	0.2	3.79	3.20	1.0	1.0	0.2	8.01
64	1.61	0.21	1.0	0.2	4.37	3.20	1.0	1.0	0.2	8.59
66	1.73	0.27	1.0	0.2	5.11	3.20	1.0	1.0	0.2	9.23
68	1.90	0.35	1.0	0.2	6.10	3.20	1.0	1.0	0.2	9.93
70	2.17	0.48	1.0	0.2	7.52	3.20	1.0	1.0	0.2	10.7
72	2.59	0.69	1.0	0.2	9.68	3.20	1.0	1.0	0.2	11.6
74	3.20	1.0	1.0	0.2	12.9	3.20	1.0	1.0	0.2	12.6
76	3.20	1.0	1.0	0.2	14.1	3.20	1.0	1.0	0.2	13.8
78	3.20	1.0	1.0	0.2	15.5	3.20	1.0	1.0	0.2	15.2
80	3.20	1.0	1.0	0.2	17.2	3.20	1.0	1.0	0.2	16.8

The above results show that the mutual deliquescence RH (MDRH) predicted by ISORROPIA is 48% instead of the correct value of 54% as predicted by AIM2. But more importantly, the composition of the liquid-phase predicted by ISORROPIA is completely wrong between 42 and 72% RH.

For instance, according to AIM2, NH_4NO_3 and NH_4Cl are completely deliquesced at 54% RH while $(\text{NH}_4)_2\text{SO}_4$ is partially deliquesced. More $(\text{NH}_4)_2\text{SO}_4$ dissolves as RH increases, and it is completely dissolved at 74% RH. On the other hand, ISORROPIA gradually dissolves all three salts starting at 48% RH until they are all completely dissolved at 62% RH. This is thermodynamically incorrect. Large errors can also be seen in the water content predicted by ISORROPIA. Clearly, there is no resemblance between the approximate aerosol phase state, water content, and composition predicted by ISORROPIA and the true thermodynamic equilibrium composition predicted by AIM2 for this aerosol case. According to the species concentrations listed in Table 1 of this manuscript, Mexico City aerosols should have similar or more complex compositions.

Ansari and Pandis (Aerosol Sci. and Technol., 31, 129-153, 1999) also showed that ISORROPIA has difficulty in reproducing the complex multistage deliquescence behavior in multicomponent aerosols. How can then one expect ISORROPIA to give reliable answers when applied to examine equilibrium assumption and the deliquescence behavior and phase state of real atmospheric aerosols as complex as the ones found in Mexico City?

Thus, if the authors still wish to examine the bulk equilibrium assumption and the deliquescence behavior and phase state of the complex Mexico City aerosols, then they must at least use a true thermodynamic aerosol model such as EQUISOLV II, which includes the crustal species that the even more accurate thermodynamic models such as AIM2 and GFEMN currently lack.

3. Plots of “predicted” - “observed” in Figure 3 show many points with large positive values for both for $\text{NH}_{4(p)}$ and $\text{NO}_{3(p)}$ for $\text{RH} > 50\%$. Doesn't this automatically mean that the bulk equilibrium assumption is invalid for those points?
4. What is the physical basis for the SO_4/NO_3 ratio in determining the phase state preference of aerosol particles (i.e., stable vs. metastable branch)? In any case,

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the statement in Conclusion 4 (line 10, page 9219) that “*This can serve as an important constraint for three-dimensional air quality models that simulate ambient particle concentrations under conditions characteristic of Mexico City*” is a stretch in the light of above arguments.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 9203, 2007.

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