

Corrigendum to

“The role of ammonia in sulfuric acid ion induced nucleation” published in Atmos. Chem. Phys., 8, 2859–2867, 2008

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We have found some numerical errors in our paper “The role of ammonia in sulfuric acid ion induced nucleation” by I. K. Ortega et al. (Atmos. Chem. Phys., 8, 2859–2867, 2008). We discovered that in some cases the convergence criteria chosen for the geometry optimization and frequency calculations (the SIESTA default values) were not tight enough to obtain reliable free energies of formation. We have recalculated all the data using tighter convergence criteria (0.01 eV/Å for force tolerance in the geometry optimization and 0.01 Bohr displacement for force constant calculation), therefore the former tables and figures given in the article have to be substituted with the ones given below.

In the most of the cases the differences ranged between 0.5 and 5.5 kcal/mol, but there are two clusters (four sulfuric acid-one ammonia neutral cluster and three sulfuric acid-one ammonia charged cluster) where the differences are larger; 14 and 12 kcal/mol, respectively. Although these differences are very large, the main conclusions of the paper are almost the same:

- Ammonia enhances the growth of sulfuric acid neutral clusters, and the ratio of ammonia to sulfuric acid is likely to be between 1:1 and 1:3, as predicted before. From the corrected version of Table 5 we can see how the addition of a fourth molecule of sulfuric acid to the ammonia-containing clusters is not favorable, suggesting that more than one ammonia molecule is probably needed to enhance the addition of a fourth acid (which is reasonable given that ammonia only forms three hydrogen bonds).
- Ammonia does not enhance ion induced nucleation at ground level conditions. On the other hand, the corrected results indicate that ammonia could play some role in high altitude conditions. If we look the formation free energy (ΔG) plot at 242 K we can see how in this case the barrier for ion induced sulfuric acid nucleation in the presence of ammonia has disappeared. In the case of charged cluster without ammonia this barrier is predicted to disappear at 220 K (Fig. 3) so ammonia could help to some extent in these conditions.

The corrected figures and tables with the new data can be found on the following pages.



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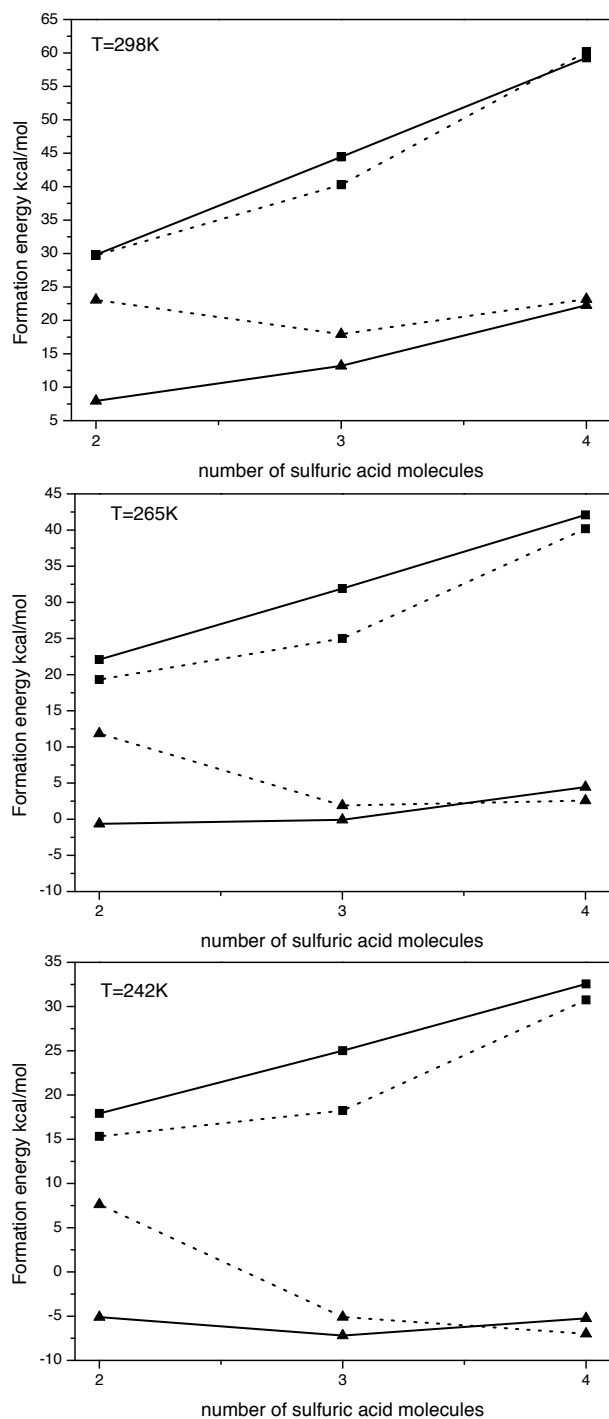


Fig. 2. Gibbs free energy of formation in function of total number of sulfuric acids in the cluster (neutral and charged), broken lines represent cluster with ammonia, solid lines represent cluster without ammonia, squares represent neutral clusters, triangles represent charged clusters. Upper panel: corresponds to upper troposphere (ΔG_1) conditions, Middle panel corresponds to mid-troposphere (ΔG_2) conditions and Lower panel: corresponds to ground level (ΔG_3) conditions, Table 3 lists the temperature and vapor pressures used.

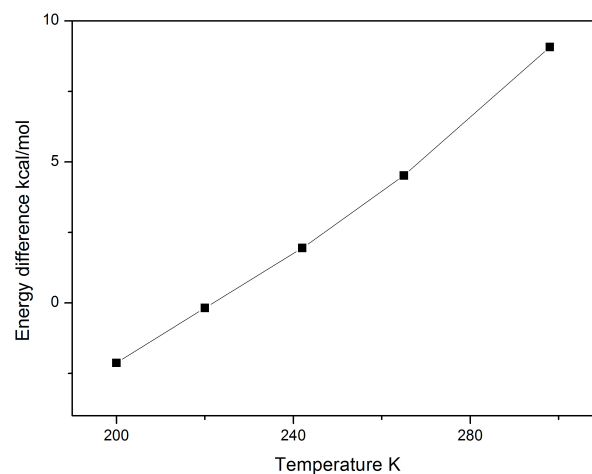


Fig. 3. Free energy difference between three and four sulfuric acid ionic clusters, for 220 K and 200 K points we used the same concentrations as given for ΔG_1 in Table 3.

Table 1. Enthalpy changes ΔH (in units of kcal/mol); comparison between experimental and calculated values.

Reaction	ΔH 295 K (Lovejoy et al., 2004)	ΔH 295 K Calculated
$\text{H}_2\text{SO}_4 + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-$	-41.8	-49.4
$\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \cdot \text{HSO}_4^- \rightarrow (\text{H}_2\text{SO}_4)_2 \cdot \text{HSO}_4^-$	-27.4	-26.6
$\text{H}_2\text{SO}_4 + (\text{H}_2\text{SO}_4)_2 \cdot \text{HSO}_4^- \rightarrow (\text{H}_2\text{SO}_4)_3 \cdot \text{HSO}_4^-$	-23.8	-21.6

Table 2. The Gibbs formation free energies (relative to free molecules with reference partial pressure 1 atm) in units of kcal/mol at 298, 265 and 242 K are listed as a function of the number of total sulfuric acid molecules and hydrogensulfate ions in the clusters.

n SA	$(\text{H}_2\text{SO}_4)_n$	$(\text{H}_2\text{SO}_4)_n \cdot \text{NH}_3$	$(\text{H}_2\text{SO}_4)_{n-1} \cdot (\text{HSO}_4^-)$	$(\text{H}_2\text{SO}_4)_{n-1} \cdot (\text{HSO}_4^-) \cdot \text{NH}_3$
298 K				
2	-6.70	-19.05	-34.01	-31.18
3	-10.33	-26.77	-47.03	-54.57
4	-13.77	-25.15	-56.22	-67.59
265 K				
2	-8.09	-21.78	-35.66	-34.08
3	-13.35	-31.17	-50.18	-59.12
4	-18.25	-31.08	-60.75	-73.53
242 K				
2	-9.05	-23.67	-36.84	-36.13
3	-15.45	-34.23	-52.42	-62.33
4	-21.39	-35.21	-63.96	-77.72

Table 4. The formation free energies for various cluster at atmospheric conditions listed in Table 3.

Cluster	Upper trop. ΔG_1	Mid-trop. ΔG_2	Ground level ΔG_3
$(\text{H}_2\text{SO}_4)_2$	17.92	22.09	29.81
$(\text{H}_2\text{SO}_4)_3$	25.01	31.91	44.44
$(\text{H}_2\text{SO}_4)_4$	32.56	42.09	59.27
$(\text{H}_2\text{SO}_4)_2 \cdot \text{NH}_3$	15.32	19.31	29.74
$(\text{H}_2\text{SO}_4)_3 \cdot \text{NH}_3$	18.25	25.00	40.28
$(\text{H}_2\text{SO}_4)_4 \cdot \text{NH}_3$	30.76	40.18	60.15
$(\text{H}_2\text{SO}_4)_1 \cdot (\text{HSO}_4^-)$	-5.10	-0.64	7.96
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{HSO}_4^-)$	-7.20	-0.07	13.20
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{HSO}_4^-)$	-5.25	4.44	22.27
$(\text{H}_2\text{SO}_4)_1 \cdot (\text{HSO}_4^-) \cdot \text{NH}_3$	7.62	11.86	23.06
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{HSO}_4^-) \cdot \text{NH}_3$	-5.09	1.90	17.93
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{HSO}_4^-) \cdot \text{NH}_3$	-6.99	2.57	23.17

Table 5. Free energies for the addition of one sulfuric acid molecule and one ammonia molecule to various clusters at different temperatures and 1 atm reference pressure.

Reaction	ΔG (242 K)	ΔG (265 K)	ΔG (298 K)
$\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightarrow (\text{H}_2\text{SO}_4)_2$	-9.05	-8.09	-6.70
$\text{H}_2\text{SO}_4 + (\text{H}_2\text{SO}_4)_2 \rightarrow (\text{H}_2\text{SO}_4)_3$	-6.40	-5.26	-3.63
$\text{H}_2\text{SO}_4 + (\text{H}_2\text{SO}_4)_3 \rightarrow (\text{H}_2\text{SO}_4)_4$	-5.93	-4.91	-3.44
$\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \cdot \text{NH}_3 \rightarrow (\text{H}_2\text{SO}_4)_2 \cdot \text{NH}_3$	-15.66	-14.53	-12.89
$\text{H}_2\text{SO}_4 + (\text{H}_2\text{SO}_4)_2 \cdot \text{NH}_3 \rightarrow (\text{H}_2\text{SO}_4)_3 \cdot \text{NH}_3$	-10.54	-9.38	-7.72
	-0.98	0.09	1.62
$\text{H}_2\text{SO}_4 + (\text{H}_2\text{SO}_4)_3 \cdot \text{NH}_3 \rightarrow (\text{H}_2\text{SO}_4)_4 \cdot \text{NH}_3$			
$\text{H}_2\text{SO}_4 + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-$	-36.84	-35.66	-34.01
$\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \cdot \text{HSO}_4^- \rightarrow (\text{H}_2\text{SO}_4)_2 \cdot \text{HSO}_4^-$	-15.58	-14.52	-13.02
$\text{H}_2\text{SO}_4 + (\text{H}_2\text{SO}_4)_2 \cdot \text{HSO}_4^- \rightarrow (\text{H}_2\text{SO}_4)_3 \cdot \text{HSO}_4^-$	-11.54	-10.57	-9.19
$\text{H}_2\text{SO}_4 + \text{HSO}_4^- \cdot \text{NH}_3 \rightarrow \text{H}_2\text{SO}_4 \cdot \text{HSO}_4^- \cdot \text{NH}_3$	-36.13	-34.08	-31.18
$\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \cdot \text{HSO}_4^- \cdot \text{NH}_3 \rightarrow (\text{H}_2\text{SO}_4)_2 \cdot \text{HSO}_4^- \cdot \text{NH}_3$	-26.20	-25.05	-23.38
$\text{H}_2\text{SO}_4 + (\text{H}_2\text{SO}_4)_2 \cdot \text{HSO}_4^- \cdot \text{NH}_3 \rightarrow (\text{H}_2\text{SO}_4)_3 \cdot \text{HSO}_4^- \cdot \text{NH}_3$	-15.38	-14.41	-13.02
$\text{H}_2\text{SO}_4 + \text{NH}_3 \rightarrow \text{H}_2\text{SO}_4 \cdot \text{NH}_3$	-8.02	-7.25	-6.16
$(\text{H}_2\text{SO}_4)_2 + \text{NH}_3 \rightarrow (\text{H}_2\text{SO}_4)_2 \cdot \text{NH}_3$	-14.63	-13.70	-12.35
$(\text{H}_2\text{SO}_4)_3 + \text{NH}_3 \rightarrow (\text{H}_2\text{SO}_4)_3 \cdot \text{NH}_3$	-18.78	-17.8	-16.44
$(\text{H}_2\text{SO}_4)_4 + \text{NH}_3 \rightarrow (\text{H}_2\text{SO}_4)_4 \cdot \text{NH}_3$	-13.82	-12.8	-11.38
$\text{HSO}_4^- + \text{NH}_3 \rightarrow \text{HSO}_4^- \cdot \text{NH}_3$	2.28	3.20	4.45
$\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^- + \text{NH}_3 \rightarrow \text{H}_2\text{SO}_4 \cdot \text{HSO}_4^- \cdot \text{NH}_3$	0.71	1.58	2.83
$(\text{H}_2\text{SO}_4)_2 \cdot \text{HSO}_4^- + \text{NH}_3 \rightarrow (\text{H}_2\text{SO}_4)_2 \cdot \text{HSO}_4^- \cdot \text{NH}_3$	-9.91	-8.94	-7.54
$(\text{H}_2\text{SO}_4)_3 \cdot \text{HSO}_4^- + \text{NH}_3 \rightarrow (\text{H}_2\text{SO}_4)_3 \cdot \text{HSO}_4^- \cdot \text{NH}_3$	-13.76	-12.78	-11.37