

### Cluster evaporation and fragmentation in the APi-TOF

Evaporation (loss of single molecules) and fragmentation (fission) of clusters inside the APi-TOF mass spectrometer is not yet well characterised. However we can make the following observations.

The entry section of the APi-TOF is characterised by several chambers at successively lower pressures and the presence of an extraction voltage that accelerates the cluster ions at a reduced pressure, thereby increasing their mean free path and kinetic energy. Therefore, when charged clusters enter the APi-TOF, they are rapidly cooled by adiabatic expansion of the air and, at the same time, accelerated in the electric fields and heated by collisions with air molecules.

This environment is quite different from the equilibrium conditions that the cluster experiences while in the CLOUD chamber (Extended Data Fig. 1). Nevertheless, it is instructive to consider some simple estimates that ignore collision heating in the APi-TOF. The time interval between a cluster entering the APi-TOF and its detection is a few  $\mu\text{s}$ . This implies that molecules that evaporate from the cluster at a rate above about  $10^5 \text{ s}^{-1}$  will not be detected. For the high-evaporation-rate molecules, X, to be in equilibrium with the cluster inside the CLOUD chamber, the X arrival rate must be at least  $10^5 \text{ s}^{-1}$ . This sets a *minimum* vapour concentration in the chamber,  $[\text{X}] = 10^5/k = 5 \times 10^{13} \text{ cm}^{-3}$  (2 ppmv), where  $k = 2 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$  is the charged-neutral collision kernel.

Under these assumptions, the only molecules that could be present on the charged clusters in the CLOUD chamber and yet escape detection in the APi-TOF must be present as a vapour with a mixing ratio of at least 1 ppmv. In the CLOUD experiments the only such vapour is water (mixing ratio  $\sim 1\%$ ). Other molecules such as  $\text{H}_2\text{SO}_4$  and DMA—present at the pptv level—evaporate so slowly that there would be negligible evaporation losses in the APi-TOF. Our theoretical calculations, summarised in Table S1, indicate that certain charged DMA-SA clusters have a large negative Gibbs free energy of formation, so are not expected to fragment in the APi-TOF.

These observations suggest that water can be expected to evaporate rapidly from the clusters in the APi-TOF, but not  $\text{H}_2\text{SO}_4$  or DMA. The experimentally observed spectra (Fig. 3) support this picture. Firstly, no  $\text{H}_2\text{O}$  molecules are found on the clusters. Secondly, large  $\text{H}_2\text{SO}_4 \cdot \text{DMA}$  clusters that contain more than 10 acid-base pairs are observed in the APi-TOF, with no evidence for strong fragmentation

(which would produce pileup at low cluster masses). However partial cluster evaporation or fragmentation cannot be excluded.

These simple estimates ignore collisional heating in the API-TOF, which may be substantial. It is therefore not unlikely that some cluster evaporation and fragmentation occurs in addition to the loss of water molecules, with rates that may be sensitive to parameters such as ambient temperature, cluster composition and accelerating voltage settings. These processes are presently under active study and will be reported in a future publication.

### ACDC model

We used the Gibbs free energies calculated in our previous work<sup>25,43</sup> for neutral and positively charged clusters containing sulphuric acid, ammonia and DMA. These were then converted into evaporation rates as described by Ortega *et al.*<sup>25</sup>. The same method, B3LYP/CBSB7//RI-CC2/aug-cc-pV(T+d)Z, was used to compute the formation Gibbs free energies of negatively charged clusters as well as some remaining neutral and positive clusters. The geometry optimisations and frequency calculations were performed with the Gaussian09 program<sup>44</sup> using the B3LYP hybrid functional<sup>45</sup> and a CBSB7 basis set<sup>46</sup>. A single-point electronic energy was then calculated with the TURBOMOLE program<sup>47</sup> using the RI-CC2 method<sup>48</sup> and an aug-cc-pV(T+d)Z basis set<sup>49</sup>. Thermodynamic parameters for all studied clusters are given in Table S1 at 278 K.

In principle, all clusters with up to four sulphuric acid molecules and four base molecules are treated. However, in order to reduce the computational effort, some clusters that have extremely high evaporation rates are omitted. Tables S2-S5 show clusters explicitly included in the model. Quantum chemical data for the full set of hydrated clusters is not available at present, so water molecules have not been included in the model runs. Since pure H<sub>2</sub>SO<sub>4</sub> clusters (without stabilising molecules) are very unlikely to exist, the ACDC model cannot be applied when base concentrations are very low. According to our preliminary calculations described below, the effect of water on the simulated formation rates of DMA ternary clusters will be relatively small compared to other error sources. Moreover, estimations based on classical thermodynamics suggests that the growing clusters contain very little—if any—water under atmospheric conditions.

The ACDC model has been described and tested in detail by McGrath *et al.*<sup>24</sup>. For comparison with the

CLOUD measurements, which correspond to steady-state conditions, the base monomer concentrations and the total concentration of acid are fixed (see below) and the simulation is run until concentrations and formation rates no longer change with time.

The  $[\text{H}_2\text{SO}_4]$  value measured by the CIMS instrument may potentially contain contributions from free  $\text{H}_2\text{SO}_4$  molecules, hydrated  $\text{H}_2\text{SO}_4$  molecules,  $\text{H}_2\text{SO}_4$  clustered with base molecules, as well as possibly  $\text{H}_2\text{SO}_4$  dimers (with or without water and bases)<sup>50</sup>. When bases such as DMA are present, the concentration of free  $\text{H}_2\text{SO}_4$  may be only a small fraction of the total  $\text{H}_2\text{SO}_4$ . However, from the CLOUD measurements (Figs. 3a and 4), after charging in the CIMS, all clusters containing one  $\text{H}_2\text{SO}_4$  molecule should be detected as a free charged monomer and all clusters containing two  $\text{H}_2\text{SO}_4$  molecules should be detected as a free charged dimer—regardless of whether or not they were originally clustered with base molecules. We have therefore modelled the  $\text{H}_2\text{SO}_4$  concentration as the sum of the free  $\text{H}_2\text{SO}_4$  monomers and all clusters containing exactly one  $\text{H}_2\text{SO}_4$  molecule and any number of base molecules.

For GCR simulations, negative and positive charges are introduced as constant source terms of  $4 \text{ ion pairs cm}^{-3} \text{ s}^{-1}$  of representative primary or secondary ions, here chosen to be  $\text{O}_2^-$  and  $\text{H}_3\text{O}^+$ . When an  $\text{O}_2^-$  ion collides with a sulphuric acid molecule or any neutral cluster containing sulphuric acid, it charges the molecule or cluster negatively by removing one proton. It can also collide with a positive ion or cluster and neutralise it by removing one proton. Similarly,  $\text{H}_3\text{O}^+$  ions can either charge base molecules and base-containing neutral clusters positively or neutralise negatively-charged ions and clusters by donating a proton. Finally, the  $\text{O}_2^-$  and  $\text{H}_3\text{O}^+$  ions can neutralise each other in collisions, or be lost to the walls of the CLOUD chamber. Every time an  $\text{O}_2^-$  or  $\text{H}_3\text{O}^+$  ion loses its charge in a collision, it is removed from the system. Ionic species containing acids and/or bases cannot lose their charge by colliding with neutral air molecules.

In ref. 24 the enhancement of ion-molecule collisions due to electric charge was set to a size-independent factor. In the present study the enhancement factor is calculated from an expression that depends on cluster masses, temperature and the dipole moment and polarizability of the neutral species (Eq. 6 in ref. 51, with their recommended parameter values). This approach was shown to agree well with experimental measurements in the case of collisions between DMA and positively-charged sulphuric acid/ammonia/DMA clusters<sup>43</sup>. The dipole moments and polarizabilities of all neutral molecules and clusters, computed at the B3LYP/CBSB7 level, are presented in Table S5. Collisions of two ions of

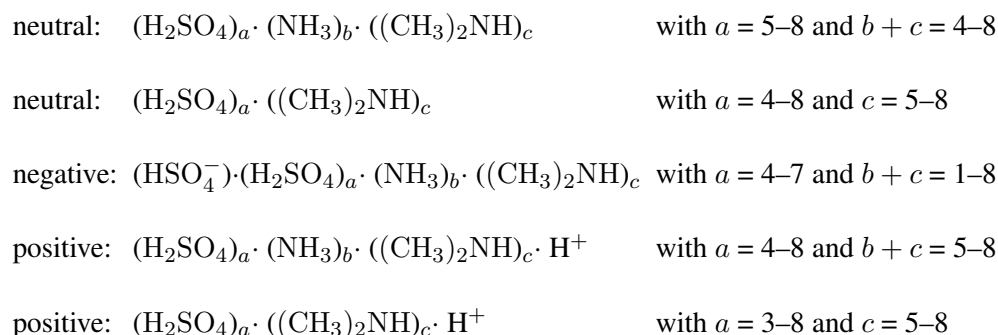
the same polarity were not allowed, and the recombination rate of ions or ionic clusters with opposite polarity was set to  $1.6 \times 10^{-6} \text{ cm}^{-3} \text{ s}^{-156}$ . In the CLOUD chamber simulations, a dilution loss rate  $0.96 \times 10^{-4} \text{ s}^{-1}$  is used and a size-dependent wall loss rate of  $S_i = (1.66 \times 10^{-3}/d_p) \text{ s}^{-1}$ , where the mobility diameter,  $d_p \text{ (nm)} = (d_m + 0.3 \text{ nm})\sqrt{1 + (28.8u/m)}$ , depends on the mass diameter,  $d_m$ , and the mass of the molecule or cluster,  $m$  (where  $u$  is the atomic mass unit)<sup>55</sup>. For ions there is an additional linear loss rate term resulting from non-uniform ion deposition in the chamber by beam  $\pi$ 's and also by beam  $\mu$ 's (which penetrate the beam stopper and contribute to ionisation under GCR conditions). To account for this extra loss term in the simulations, the size-dependent wall loss rate for ions is multiplied by an empirical factor of 3.3, determined from the experimental data.

Since the simulations are limited to clusters with up to four acids and four bases, it is assumed that clusters leaving the 4x4 simulation “box” cannot re-evaporate. ACDC simulations show that, for neutral clusters, the dominant route for growth within the simulation box falls along the diagonal. In other words, the most stable (and populous) clusters are those with a similar number of acids and bases, and they grow either by alternately adding one acid then one base molecule, or by addition of clusters containing either one or two acid-base pairs. To account for this, neutral clusters are only allowed to leave the system if they contain at least five acids and four bases or, in the case of DMA, at least four acids and five DMAs, as summarised below.

Our ACDC simulations show that the negative clusters grow first by adding acids to a bisulphate ion, but since a cluster with one bisulphate ion and four acids is not stable (evaporation rate  $\gamma = 1.6 \times 10^2 \text{ s}^{-1}$  at 278 K) the only negative clusters that are allowed to leave the system are required to have at least five acids (including the bisulphate ion) and one base. The growth of positive clusters starts by first charging a base molecule which subsequently grows by colliding with monomers or DMA-acid clusters. The most stable and abundant positively charged clusters contain more bases than acids (including the protonated ion), especially in the case of acid-DMA clusters, where the number of DMA molecules is two more than the number of acids (see Extended Data Fig. 2b). Thus, to leave the simulation box, positive clusters are required to contain at least four acids and five bases or, in the case of DMA, at least three acids and five DMAs.

When a collision results in a cluster that is outside the 4x4 box but does not satisfy the conditions for it to leave the simulation, it is forced back to the nearest boundary of the simulation box by evaporating

molecules from it. These extra molecules are returned to the simulation as free monomers. In summary, the simulated formation rate thus includes all collisions (including ion-ion recombination) leading to formation of the following clusters:



Extended Data Fig. 4 shows an example modelled distribution of steady-state cluster concentrations ( $n\text{SA}$  vs.  $m\text{DMA}$ ) for a) negative, b) positive and c) neutral clusters at  $4.0 \times 10^6 \text{ cm}^{-3} [\text{H}_2\text{SO}_4]$ , 10 pptv DMA, 4 ion pairs  $\text{cm}^{-3}\text{s}^{-1}$  and 278 K. The modelled distributions capture most of the essential features of the experimental measurements (Fig. 3), but there are some differences.

In agreement with experiment, the first negative charged cluster to which DMA binds effectively is the acid trimer, and the most abundant acid trimer contains two DMA molecules,  $(n\text{SA}, m\text{DMA}) = (3, 2)$ .

For positive clusters, the model confirms growth by accretion of SA·DMA pairs but, in comparison with experiment, indicates one additional DMA molecule in the cluster. However, our calculations (Table S1) show that the positive clusters *not* seen by CLOUD, namely  $(0, 2)$ ,  $(1, 3)$  and  $(2, 4)$ , are lightly bound and have appreciable evaporation rates ( $3 - 7 \times 10^{-4} \text{ s}^{-1}$ ). On the other hand, the positive clusters that *are* seen by CLOUD, namely  $(1, 2)$ ,  $(2, 3)$  and  $(3, 4)$  (Fig. 3b), are strongly bound and have calculated evaporation rates 7–8 orders of magnitude lower. This suggests that the discrepancy between the model and experiment may be due to loss of a single DMA molecule from the clusters by evaporation in the APi-TOF when tuned for positive clusters. Assuming this could explain the absence of positively-charged pure DMA dimers,  $(0, 2)$ , there will remain a large concentration of DMA·H<sup>+</sup> monomers,  $(0, 1)$ . However, the mass-to-charge ratio of these clusters, 46 Th, is below the APi-TOF acceptance cutoff when tuned to detect high cluster masses.

Finally, the model shows that the smallest neutral cluster is a single SA·DMA pair,  $(1, 1)$ , and it confirms a high expected concentration for the neutral acid dimer. Almost all neutral acid dimers contain exactly two SA·DMA pairs,  $(2, 2)$ . In the next step to the acid trimer,  $(2, 2) \rightarrow (3, 4)$ , the cluster favours further neutralisation of the acid by two additional DMA molecules (partial formation of

dimethylaminium sulphate). Addition of 2 DMA molecules per single SA molecule is also observed in the experimental charged cluster data (Fig. 3); for negatively-charged clusters at the  $(2, 0) \rightarrow (3, 2)$  and  $(6, 5) \rightarrow (7, 7)$  transitions, and for positively-charged clusters at the  $(2, 3) \rightarrow (3, 5)$  transition.

### Dependence of sulphuric acid-DMA nucleation on relative humidity and temperature

All the experimental measurements were performed at 38% relative humidity (RH) and 278 K. We have therefore investigated the expected dependence of the nucleation rates on RH and temperature using ACDC model simulations.

#### a) RH dependence

We simulated the sulphuric acid-dimethylamine cluster formation rate at 278 K in the presence of water vapour using a system with the clusters  $\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH}$  and  $(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_{0-2}$  along with the acid and base monomers (Table S6 shows our calculated cluster binding energies). Hydrate data for larger clusters are not yet available. Clusters were allowed to grow out of the simulation when they gained at least three acids and three bases. This smaller box together with this boundary condition reproduces almost perfectly the formation rates calculated using the 4×4 box in the absence of external losses, whereas, in the presence of wall losses, there is a small deviation due to losses of clusters with three and four acids.

For the acid molecule and all clusters we took into account hydrates containing up to five water molecules, and for the DMA molecule we included the monohydrate. The effect of hydration was taken into account via hydration-averaged collision and evaporation rates as proposed in ref. 57. The water vapour concentration as a function of relative humidity and temperature,  $T$  (K), was calculated using the parametrization of ref. 58 for the saturated water vapour pressure (Pa):

$$\ln(P_w^s) = -2991.2729 T^{-2} - 6017.0128 T^{-1} + 18.87643854 - 0.028354721 T + 0.17838301 \times 10^{-4} T^2 \\ - 0.84150417 \times 10^{-9} T^3 + 0.44412543 \times 10^{-12} T^4 + 2.858487 \ln T$$

Extended Data Fig. 2 shows the calculated neutral nucleation rates as a function of RH for 0.1 and 10 pptv DMA at  $2.0 \times 10^6 \text{ cm}^{-3} [\text{H}_2\text{SO}_4]$  and 278 K. The nucleation rates relative to their values at 38% RH are also indicated. Under saturated DMA conditions (10 pptv DMA), the nucleation rate is only

weakly dependent on RH (<5% change from its value at 38% RH). At low DMA conditions (0.1 pptv), the variation is more pronounced but still relatively small (<30% change except under the driest conditions, below 10% RH).

Using the labels  $(n, m)$  to indicate the number of sulphuric acid ( $n$ SA) and dimethylamine ( $m$ DMA) molecules in neutral clusters, we find that  $(1, 1)$  and  $(2, 0)$  clusters are further stabilised (their evaporation rates decrease) as RH increases, while the  $(2, 1)$  and  $(2, 2)$  clusters are made less stable by the addition of water (their evaporation rates increase). However, the DMA-containing clusters  $(1, 1)$ ,  $(2, 1)$  and  $(2, 2)$  are extremely stable, regardless of the relative humidity. On the other hand, addition of water molecules to the clusters increases slightly all collision rates due to the increase in cluster size. The overall effect of water vapour is a small increase in cluster formation rates, which is more pronounced at very low dimethylamine concentrations.

The fundamental reason for the insensitivity to RH is that amines drive water molecules out of the clusters due to the strong acid-base mechanism replacing the  $\text{H}_2\text{O}$  molecules, and therefore the water molecules do not play a big role. The situation may change at very high RH where we may expect some deliquescence point where the “solid” amine salt cluster becomes a liquid droplet.

In contrast with sulphuric acid-dimethylamine clusters, small sulphuric acid-ammonia clusters have appreciable evaporation rates. Therefore stabilisation of the clusters by water molecules will significantly increase the nucleation rate. In the binary sulphuric acid-water system the effect is even stronger since water is the only compound stabilising the sulphuric acid clusters against evaporation.

## b) Temperature dependence

Extended Data Fig. 3 shows the calculated GCR nucleation rates at  $2.0 \times 10^6 \text{ cm}^{-3} [\text{H}_2\text{SO}_4]$  as a function of temperature for  $2.0 \times 10^8 \text{ cm}^{-3} \text{NH}_3$  and for  $2.0 \times 10^8 \text{ cm}^{-3} \text{DMA}$ . The temperature dependence of the free energies was taken into account by re-computing them directly from the vibrational frequencies and rotational constants. The nucleation rate for sulphuric acid-DMA nucleation relative to its value at 278 K is also indicated. This shows a relatively small variation (below a factor of 2) for sulphuric acid-DMA nucleation over the range 255–300 K. In contrast, the sulphuric acid- $\text{NH}_3$  nucleation rate varies by 5 orders of magnitude over this temperature range.

Since neutral sulphuric acid-ammonia clusters are quite unstable, the nucleation rate strongly increases

at lower temperatures due to reduced evaporation rates. However, the evaporation rates of the sulphuric acid-DMA system are low over this entire temperature range due to the strong cluster binding energies, and so only a small decrease of nucleation rate is expected at the highest temperatures. Temperature does not play a large role for DMA ternary nucleation since it is approaching the kinetic limit, where every collision sticks. In this limit there is no longer any (extremely temperature dependent) barrier and the temperature dependence is mainly due merely to the changing molecular velocities (which is the reason for the small reduction in nucleation rate seen below 278 K in Extended Data Fig. 3).

In summary, the amine ternary nucleation rates are relatively insensitive to RH and temperature over most boundary layer conditions. Hence the CLOUD experimental measurements at 38% RH and 278 K presented here can be considered representative of amine nucleation in the boundary layer.



## Supplementary references

- [43] Kupiainen, O., *et al.* Amine substitution into sulphuric acid-ammonia clusters. *Atmos. Chem. Phys.* **12**, 3591–3599 (2012).
- [44] Frisch, M.J., *et al.* GAUSSIAN 09, Revision A.01, Gaussian Inc., Wallingford, CT, (2009).
- [45] Becke, A.D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648–5652 (1993).
- [46] Montgomery, J.A., Frisch, M.J., Ochterski, J.W. A complete basis set model chemistry. VI. Use of density functional geometries and frequencies. *J. Chem. Phys.* **110**, 2822–2827 (1999).
- [47] Ahlrichs, R., *et al.* Electronic structure calculations on workstation computers: The program system turbo-mole. *Chem. Phys. Lett.* **162**, 165–169 (1989).
- [48] Hättig, C., and Weigend, F. CC2 excitation energy calculations on large molecules using the resolution of the identity approximation. *J. Chem. Phys.* **113**, 5154–5161 (2000).
- [49] Dunning, T.H., Peterson, K.A., and Wilson, A.K. Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited. *J. Chem. Phys.* **114**, 9244–9253 (2001).
- [50] Kurtén, T., *et al.* The effect of H<sub>2</sub>SO<sub>4</sub>-amine clustering on chemical ionization mass spectrometry (CIMS) measurements of gas-phase sulphuric acid. *Atmos. Chem. Phys.* **11**, 3007–3019 (2011).
- [51] Su, T., and Bowers, M.T. Theory of ion-polar molecule collisions. Comparison with experimental charge transfer reactions of rare gas ions to geometric isomers of difluorobenzene and dichloroethylene. *J. Chem. Phys.* **58**, 3027–3037 (1973).
- [52] Sedo, G., Schultz, J., and Leopold, K.R. Electric dipole moment of sulphuric acid from Fourier transform microwave spectroscopy. *J. Mol. Spectrosc.* **251**, 4–8 (2008).
- [53] Nadykto, A.B., and Yu, F. Uptake of neutral polar vapour molecules by charged particles: Enhancement due to dipole-charge interaction. *J. Geophys. Res.* **108**, 4717–4723 (2003).
- [54] Lide, D., ed. *CRC Handbook of Chemistry and Physics*, 91st Edition, CRC Press/Taylor and Francis, Boca Raton, Florida (2010).
- [55] Ehn, M., *et al.* An instrumental comparison of mobility and mass measurements of atmospheric small ions. *Aerosol Sci. Technol.* **45**, 522–533 (2011).

- [56] Bates, D.R. Recombination of small ions in the troposphere and lower stratosphere. *Planet. Space Sci.* **30**, 1275–1282 (1982).
- [57] Paasonen, P., *et al.* On the formation of sulphuric acid-amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation. *Atmos. Chem. Phys.* **12**, 9113–9133 (2012).
- [58] Wexler, A. Vapor pressure formulation for water in range 0 to 100°C. A Revision. *J. Res. Nat. Bur. Stand. Sec. A: Phys. Ch.* **80A**, 775–785 (1976).

## Supplementary tables

**Table S1.** Electronic energies ( $\Delta E_{elec}$ ), enthalpies ( $\Delta H_{278K}$ ), Gibbs free energies ( $\Delta G_{278K}$ ) and entropies ( $\Delta S_{278K}$ ) of formation from monomers at 278 K and 1 atm reference pressure for all clusters used in ACDC simulations. The indices ( $n, m, k$ ) summarise the number of sulphuric acid, DMA and ammonia molecules in the cluster, respectively, including both neutral and charged species.

Cluster	( $n, m, k$ )	$\Delta E$ (kcal/mol)	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/K·mol)
<b>a) Negatively-charged clusters</b>					
$H_2SO_4 \cdot HSO_4^-$	(2,0,0)	-49.08	-48.30	-35.44	-46.25
$(H_2SO_4)_2 \cdot HSO_4^-$	(3,0,0)	-78.95	-76.47	-53.78	-81.63
$(H_2SO_4)_3 \cdot HSO_4^-$	(4,0,0)	-103.92	-100.08	-67.14	-118.49
$NH_3 \cdot HSO_4^-$	(1,0,1)	-10.94	-9.13	0.53	-34.76
$H_2SO_4 \cdot NH_3 \cdot HSO_4^-$	(2,0,1)	-61.93	-58.80	-36.66	-79.61
$(H_2SO_4)_2 \cdot NH_3 \cdot HSO_4^-$	(3,0,1)	-99.92	-96.69	-62.14	-124.28
$(H_2SO_4)_3 \cdot NH_3 \cdot HSO_4^-$	(4,0,1)	-129.49	-123.21	-80.48	-153.71
$(H_2SO_4)_2 \cdot (NH_3)_2 \cdot HSO_4^-$	(3,0,2)	-119.15	-111.68	-70.32	-148.78
$(H_2SO_4)_3 \cdot (NH_3)_2 \cdot HSO_4^-$	(4,0,2)	-157.37	-149.20	-94.53	-196.67
$(H_2SO_4)_3 \cdot (NH_3)_3 \cdot HSO_4^-$	(4,0,3)	-180.90	-168.81	-105.21	-228.80
$(CH_3)_2NH \cdot HSO_4^-$	(1,1,0)	-14.18	-12.56	-1.64	-39.26
$H_2SO_4 \cdot (CH_3)_2NH \cdot HSO_4^-$	(2,1,0)	-73.33	-69.39	-46.77	-81.38
$(H_2SO_4)_2 \cdot (CH_3)_2NH \cdot HSO_4^-$	(3,1,0)	-109.61	-104.34	-70.62	-121.27
$(H_2SO_4)_3 \cdot (CH_3)_2NH \cdot HSO_4^-$	(4,1,0)	-137.14	-130.98	-87.10	-157.86

Cluster	(n,m,k)	$\Delta E$ (kcal/mol)	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/K·mol)
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{HSO}_4^-$	(2,2,0)	-87.24	-82.71	-50.10	-117.32
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{HSO}_4^-$	(3,2,0)	-139.63	-132.17	-86.57	-164.04
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{HSO}_4^-$	(4,2,0)	-176.80	-168.02	-111.49	-203.36
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{HSO}_4^-$	(3,3,0)	-161.44	-150.52	-95.56	-197.71
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{HSO}_4^-$	(4,3,0)	-204.73	-193.12	-124.61	-246.45
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_4 \cdot \text{HSO}_4^-$	(4,4,0)	-230.44	-215.02	-137.01	-280.59
$\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{NH}_3 \cdot \text{HSO}_4^-$	(2,1,1)	-82.03	-76.29	-45.34	-111.33
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{NH}_3 \cdot \text{HSO}_4^-$	(3,1,1)	-130.67	-124.03	-79.11	-161.59
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{NH}_3 \cdot \text{HSO}_4^-$	(4,1,1)	-164.82	-155.73	-100.71	-197.92
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_2 \cdot \text{HSO}_4^-$	(3,1,2)	-144.87	-136.73	-82.83	-193.88
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_2 \cdot \text{HSO}_4^-$	(4,1,2)	-190.15	-178.15	-112.92	-234.67
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{NH}_3 \cdot \text{HSO}_4^-$	(3,2,1)	-147.41	-137.47	-84.32	-191.18
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{NH}_3 \cdot \text{HSO}_4^-$	(4,2,1)	-201.82	-189.00	-121.87	-241.50
<b>b) Positively-charged clusters</b>					
$(\text{CH}_3)_2\text{NH}_2^+ + \text{NH}_3 \rightarrow (\text{CH}_3)_2\text{NH} + \text{NH}_4^+ \#$		18.67	18.26	18.52	-0.95
$\text{H}_2\text{SO}_4 \cdot \text{NH}_3 \cdot \text{H}^{\ddagger}$	(1,0,1)	-20.90	-20.19	-15.91	-15.41
$(\text{H}_2\text{SO}_4)_2 \cdot \text{NH}_3 \cdot \text{H}^{\ddagger}$	(2,0,1)	-47.43	-45.48	-28.12	-62.42
$(\text{NH}_3)_2 \cdot \text{H}^{\ddagger}$	(0,0,2)	-26.75	-26.44	-20.99	-19.63
$\text{H}_2\text{SO}_4 \cdot (\text{NH}_3)_2 \cdot \text{H}^{\ddagger}$	(1,0,2)	-57.24	-54.21	-38.67	-55.92

Cluster	( <i>n,m,k</i> )	$\Delta E$ (kcal/mol)	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/K·mol)
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_2 \cdot \text{H}^{\ddagger}$	(2,0,2)	-84.60	-80.57	-53.94	-95.79
$(\text{NH}_3)_3 \cdot \text{H}^{\ddagger}$	(0,0,3)	-46.54	-43.98	-30.37	-48.95
$\text{H}_2\text{SO}_4 \cdot (\text{NH}_3)_3 \cdot \text{H}^{\ddagger}$	(1,0,3)	-77.48	-73.82	-49.81	-86.35
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_3 \cdot \text{H}^{\ddagger}$	(2,0,3)	-119.34	-112.02	-75.58	-131.10
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{NH}_3)_3 \cdot \text{H}^+$	(3,0,3)	-144.11	-135.85	-87.64	-173.40
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{NH}_3)_3 \cdot \text{H}^+$	(4,0,3)	-166.03	-156.18	-97.86	-209.79
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_4 \cdot \text{H}^{\ddagger}$	(2,0,4)	-138.34	-130.24	-85.04	-162.57
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{NH}_3)_4 \cdot \text{H}^+$	(3,0,4)	-175.50	-164.45	-107.40	-205.22
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{NH}_3)_4 \cdot \text{H}^+$	(4,0,4)	-199.17	-187.04	-119.81	-241.84
$\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{H}^{\ddagger\S}$	(1,1,0)	-19.97	-18.88	-11.33	-27.13
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{H}^{\ddagger}$	(2,1,0)	-43.75	-41.57	-24.15	-62.66
$((\text{CH}_3)_2\text{NH})_2 \cdot \text{H}^{\dagger}$	(0,2,0)	-26.33	-25.73	-17.49	-29.64
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{H}^{\ddagger}$	(1,2,0)	-65.60	-61.57	-45.73	-56.99
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{H}^{\ddagger}$	(2,2,0)	-94.36	-89.42	-60.91	-102.57
$((\text{CH}_3)_2\text{NH})_3 \cdot \text{H}^+$	(0,3,0)	-46.41	-43.89	-27.02	-60.70
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{H}^+$	(1,3,0)	-98.15	-91.71	-63.12	-102.84
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{H}^{\ddagger}$	(2,3,0)	-137.73	-129.13	-90.94	-137.35
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{H}^+$	(3,3,0)	-164.50	-154.79	-103.53	-184.40
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{H}^+$	(4,3,0)	-193.82	-182.95	-119.91	-226.77
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_4 \cdot \text{H}^+$	(2,4,0)	-171.25	-160.37	-108.69	-185.88

Cluster	( <i>n,m,k</i> )	$\Delta E$ (kcal/mol)	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/K·mol)
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_4 \cdot \text{H}^+$	(3,4,0)	-210.29	-196.90	-134.64	-223.95
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_4 \cdot \text{H}^+$	(4,4,0)	-229.88	-216.15	-144.83	-256.55
$(\text{CH}_3)_2\text{NH} \cdot \text{NH}_3 \cdot \text{H}^{\ddagger}$	(0,1,1)	-22.13	-20.91	-14.27	-23.89
$\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{NH}_3 \cdot \text{H}^{\ddagger}$	(1,1,1)	-52.72	-49.33	-32.96	-58.88
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{NH}_3 \cdot \text{H}^{\ddagger}$	(2,1,1)	-80.24	-76.04	-48.57	-98.79
$(\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_2 \cdot \text{H}^+$	(0,1,2)	-40.12	-37.27	-22.72	-52.33
$\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_2 \cdot \text{H}^{\ddagger}$	(1,1,2)	-72.16	-67.83	-43.01	-89.28
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_2 \cdot \text{H}^{\ddagger}$	(2,1,2)	-115.64	-108.23	-70.09	-137.19
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_2 \cdot \text{H}^+$	(3,1,2)	-140.04	-131.34	-82.36	-176.17
$((\text{CH}_3)_2\text{NH})_2 \cdot \text{NH}_3 \cdot \text{H}^+$	(0,2,1)	-43.27	-40.62	-24.96	-56.33
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{NH}_3 \cdot \text{H}^{\ddagger}$	(1,2,1)	-84.26	-78.99	-52.64	-94.80
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{NH}_3 \cdot \text{H}^{\ddagger}$	(2,2,1)	-129.23	-121.03	-81.54	-142.05
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{NH}_3 \cdot \text{H}^+$	(3,2,1)	-152.75	-143.27	-93.49	-179.09
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_3 \cdot \text{H}^{\ddagger}$	(2,1,3)	-132.06	-123.26	-76.43	-168.46
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_3 \cdot \text{H}^+$	(3,1,3)	-169.48	-158.23	-100.24	-208.59
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_3 \cdot \text{H}^+$	(4,1,3)	-194.89	-182.45	-113.79	-246.98
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{NH}_3)_2 \cdot \text{H}^{\ddagger}$	(2,2,2)	-145.57	-136.14	-87.77	-173.98
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{NH}_3)_2 \cdot \text{H}^+$	(3,2,2)	-182.26	-170.26	-111.96	-209.73
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{NH}_3)_2 \cdot \text{H}^+$	(4,2,2)	-210.17	-197.05	-126.75	-252.86
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{NH}_3 \cdot \text{H}^{\ddagger}$	(2,3,1)	-160.38	-150.13	-101.20	-175.99

Cluster	( <i>n,m,k</i> )	$\Delta E$ (kcal/mol)	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/K·mol)
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{NH}_3 \cdot \text{H}^+$	(3,3,1)	-195.81	-183.09	-123.45	-214.56
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{NH}_3 \cdot \text{H}^+$	(4,3,1)	-220.37	-207.04	-135.50	-257.36
<b>c) Neutral clusters</b>					
$(\text{H}_2\text{SO}_4)_2^*$	(2,0,0)	-19.00	-17.88	-8.56	-33.52
$(\text{H}_2\text{SO}_4)_3^*$	(3,0,0)	-38.04	-35.87	-15.75	-72.37
$(\text{H}_2\text{SO}_4)_4^*$	(4,0,0)	-56.05	-52.69	-24.80	-100.34
$\text{H}_2\text{SO}_4 \cdot \text{NH}_3^*$	(1,0,1)	-17.39	-16.01	-8.18	-28.19
$(\text{H}_2\text{SO}_4)_2 \cdot \text{NH}_3^*$	(2,0,1)	-48.44	-45.01	-25.25	-71.07
$(\text{H}_2\text{SO}_4)_3 \cdot \text{NH}_3^*$	(3,0,1)	-70.37	-66.13	-36.11	-107.96
$(\text{H}_2\text{SO}_4)_4 \cdot \text{NH}_3^*$	(4,0,1)	-92.14	-87.49	-45.36	-151.55
$(\text{NH}_3)_2^*$	(0,0,2)	-3.24	-1.68	3.80	-19.70
$\text{H}_2\text{SO}_4 \cdot (\text{NH}_3)_2^*$	(1,0,2)	-32.83	-29.73	-13.60	-58.03
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_2^*$	(2,0,2)	-70.46	-64.49	-35.42	-104.55
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{NH}_3)_2^*$	(3,0,2)	-99.64	-92.15	-52.29	-143.37
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{NH}_3)_2^*$	(4,0,2)	-124.00	-115.21	-64.16	-183.63
$(\text{NH}_3)_3^*$	(0,0,3)	-11.11	-7.82	7.58	-55.42
$\text{H}_2\text{SO}_4 \cdot (\text{NH}_3)_3^*$	(1,0,3)	-46.07	-40.51	-14.83	-92.35
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_3^*$	(2,0,3)	-87.62	-79.58	-41.04	-138.63
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{NH}_3)_3^*$	(3,0,3)	-126.84	-116.69	-67.12	-178.30
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{NH}_3)_3^\dagger$	(4,0,3)	-156.25	-145.24	-83.36	-222.60

Cluster	$(n,m,k)$	$\Delta E$ (kcal/mol)	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/K·mol)
$(\text{NH}_3)_4^*$	(0,0,4)	-17.22	-12.41	10.37	-81.94
$\text{H}_2\text{SO}_4 \cdot (\text{NH}_3)_4^*$	(1,0,4)	-58.51	-51.37	-17.50	-121.81
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_4^*$	(2,0,4)	-101.44	-91.72	-44.58	-169.58
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{NH}_3)_4^*$	(3,0,4)	-144.80	-132.89	-73.71	-212.88
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{NH}_3)_4^*$	(4,0,4)	-178.29	-164.47	-94.57	-251.43
$\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH}^*$	(1,1,0)	-27.22	-24.67	-16.03	-31.10
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH}^*$	(2,1,0)	-61.39	-57.10	-36.38	-74.56
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{CH}_3)_2\text{NH}^*$	(3,1,0)	-87.18	-81.54	-50.08	-113.18
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{CH}_3)_2\text{NH}^*$	(4,1,0)	-108.46	-101.11	-58.50	-153.28
$((\text{CH}_3)_2\text{NH})_2^*$	(0,2,0)	-4.68	-3.25	3.08	-22.77
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_2^*$	(1,2,0)	-44.09	-40.13	-21.63	-66.56
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2^{\ddagger}$	(2,2,0)	-95.06	-87.66	-56.51	-112.05
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_2^*$	(3,2,0)	-122.65	-113.69	-70.39	-155.74
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_2^*$	(4,2,0)	-150.01	-140.87	-86.71	-194.81
$((\text{CH}_3)_2\text{NH})_3^*$	(0,3,0)	-15.86	-12.81	4.35	-61.74
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_3^*$	(1,3,0)	-62.74	-57.10	-27.24	-107.41
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_3^*$	(2,3,0)	-117.81	-108.34	-65.78	-153.11
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_3^*$	(3,3,0)	-158.70	-146.73	-93.78	-190.50
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_3^*$	(4,3,0)	-186.74	-173.81	-109.73	-230.51
$((\text{CH}_3)_2\text{NH})_4^*$	(0,4,0)	-25.88	-21.50	3.58	-90.19



Cluster	$(n,m,k)$	$\Delta E$ (kcal/mol)	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/K·mol)
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_4^*$	(1,4,0)	-79.21	-72.39	-31.42	-147.36
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_4^*$	(2,4,0)	-135.97	-125.89	-72.58	-191.75
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_4^*$	(3,4,0)	-188.80	-174.86	-110.38	-231.95
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_4^*$	(4,4,0)	-221.58	-204.53	-129.48	-269.95
$(\text{CH}_3)_2\text{NH} \cdot \text{NH}_3$	(0,1,1)	-3.83	-2.50	2.62	-18.43
$\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{NH}_3^\ddagger$	(1,1,1)	-42.01	-37.71	-19.79	-64.45
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{NH}_3^\ddagger$	(2,1,1)	-82.14	-75.66	-46.03	-106.59
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{NH}_3^\ddagger$	(3,1,1)	-112.68	-104.35	-63.60	-146.59
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{NH}_3$	(4,1,1)	-136.94	-127.64	-75.99	-185.78
$\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_2^\ddagger$	(1,1,2)	-49.96	-44.41	-16.97	-98.71
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_2^\ddagger$	(2,1,2)	-100.05	-92.20	-49.53	-153.47
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_2^\ddagger$	(3,1,2)	-140.28	-129.34	-77.71	-185.73
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_2$	(4,1,2)	-167.61	-155.43	-93.22	-223.80
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{NH}_3^\ddagger$	(1,2,1)	-59.06	-53.23	-24.64	-102.85
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{NH}_3^\ddagger$	(2,2,1)	-109.67	-100.83	-61.12	-142.86
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{NH}_3^\ddagger$	(3,2,1)	-147.53	-136.18	-84.31	-186.56
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{NH}_3$	(4,2,1)	-181.47	-168.79	-104.36	-231.74
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_3$	(2,1,3)	-105.64	-96.27	-48.19	-172.95
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_3$	(3,1,3)	-160.06	-147.16	-84.16	-226.62
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{NH}_3)_3$	(4,1,3)	-191.12	-176.73	-105.64	-255.73

Cluster	$(n,m,k)$	$\Delta E$ (kcal/mol)	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/K·mol)
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{NH}_3)_2$	(2,2,2)	-117.27	-106.86	-58.79	-172.90
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{NH}_3)_2$	(3,2,2)	-172.37	-158.62	-94.49	-230.69
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{NH}_3)_2$	(4,2,2)	-208.57	-192.54	-117.55	-269.77
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{NH}_3$	(2,3,1)	-133.88	-122.64	-70.56	-187.34
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{NH}_3$	(3,3,1)	-181.90	-167.52	-102.00	-235.69
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_3 \cdot \text{NH}_3$	(4,3,1)	-213.15	-196.56	-122.01	-268.18

\* Previously published in ref. 25 at 298 K.

‡ Previously published in ref. 43 at 298 K.

† Better configuration than that of our previous work<sup>25,43</sup>.

‡ Different configuration than that of our previous work<sup>25</sup>; the earlier value was incorrect.

§ Different configuration than that of our previous work<sup>43</sup>; the previously published configuration is more stable at 298 K.

**Table S2.** Summary of neutral clusters explicitly simulated in the ACDC model. NH<sub>3</sub> indicates ammonia-containing, DMA indicates DMA-containing and M indicates mixed clusters (with both types of bases, all combinations yielding the indicated number of bases are included in the model), pure sulphuric acid clusters are also included.

	1 base	2 bases	3 bases	4 bases
0 acids		NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA	NH <sub>3</sub> DMA
H <sub>2</sub> SO <sub>4</sub>	NH <sub>3</sub> DMA	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub>	NH <sub>3</sub> DMA	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M
(H <sub>2</sub> SO <sub>4</sub> ) <sub>3</sub>	NH <sub>3</sub> DMA	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M
(H <sub>2</sub> SO <sub>4</sub> ) <sub>4</sub>	NH <sub>3</sub> DMA	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M

**Table S3.** Summary of the negatively charged clusters explicitly simulated in the ACDC model.  $\text{NH}_3$  indicates ammonia-containing, DMA indicates DMA-containing and M indicates mixed clusters (with both types of bases, all combinations yielding the indicated number of bases are included in the model), negatively charged pure sulphuric acid cluster are also included.

	1 base	2 bases	3 bases	4 bases
$\text{HSO}_4^-$	$\text{NH}_3$ DMA			
$(\text{H}_2\text{SO}_4)\cdot\text{HSO}_4^-$	$\text{NH}_3$ DMA	DMA M		
$(\text{H}_2\text{SO}_4)_2\cdot\text{HSO}_4^-$	$\text{NH}_3$ DMA	$\text{NH}_3$ DMA M	DMA M	
$(\text{H}_2\text{SO}_4)_3\cdot\text{HSO}_4^-$	$\text{NH}_3$ DMA	$\text{NH}_3$ DMA M	$\text{NH}_3$ DMA M	DMA

**Table S4.** Summary of the positively charged clusters explicitly simulated in the ACDC model. NH<sub>3</sub> indicates ammonia-containing, DMA indicates DMA-containing and M indicates mixed clusters (with both types of bases, all combinations yielding the indicated number of bases are included in the model), positively charged pure sulphuric acid clusters are not included.

	H <sup>+</sup> + 1 base	H <sup>+</sup> + 2 bases	H <sup>+</sup> + 3 bases	H <sup>+</sup> + 4 bases
0 acid	NH <sub>3</sub> DMA	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M	
H <sub>2</sub> SO <sub>4</sub>	NH <sub>3</sub> DMA	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M	
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub>	NH <sub>3</sub> DMA	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M
(H <sub>2</sub> SO <sub>4</sub> ) <sub>3</sub>			NH <sub>3</sub> DMA M	NH <sub>3</sub> DMA M
(H <sub>2</sub> SO <sub>4</sub> ) <sub>4</sub>			NH <sub>3</sub> DMA	NH <sub>3</sub> DMA M

**Table S5.** Dipole moments and polarizabilities of all studied clusters at 278 K. For molecules we used experimental values, except for the sulphuric acid polarizability, for which only a theoretical value is available, and for clusters we used values calculated for the minimum-free energy clusters (at the corresponding temperature) with the Gaussian09 program<sup>44</sup> using the B3LYP hybrid functional<sup>45</sup> and a CBSB7 basis set<sup>46</sup>.

	Dipole moment (D)	Polarizability ( $\text{\AA}^3$ )
H <sub>2</sub> SO <sub>4</sub>	2.96 <sup>a</sup>	6.2 <sup>b</sup>
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub>	0.002	9.061
(H <sub>2</sub> SO <sub>4</sub> ) <sub>3</sub>	3.692	13.710
(H <sub>2</sub> SO <sub>4</sub> ) <sub>4</sub>	3.252	18.759
NH <sub>3</sub>	1.47 <sup>c</sup>	2.81 <sup>c</sup>
H <sub>2</sub> SO <sub>4</sub> ·NH <sub>3</sub>	5.259	6.073
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> ·NH <sub>3</sub>	9.309	10.733
(H <sub>2</sub> SO <sub>4</sub> ) <sub>3</sub> ·NH <sub>3</sub>	4.580	15.482
(H <sub>2</sub> SO <sub>4</sub> ) <sub>4</sub> ·NH <sub>3</sub>	8.006	20.171
(NH <sub>3</sub> ) <sub>2</sub>	0.000	3.106
H <sub>2</sub> SO <sub>4</sub> ·(NH <sub>3</sub> ) <sub>2</sub>	3.990	7.826
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> ·(NH <sub>3</sub> ) <sub>2</sub>	6.762	12.455
(H <sub>2</sub> SO <sub>4</sub> ) <sub>3</sub> ·(NH <sub>3</sub> ) <sub>2</sub>	10.065	17.121
(H <sub>2</sub> SO <sub>4</sub> ) <sub>4</sub> ·(NH <sub>3</sub> ) <sub>2</sub>	9.769	21.828

$(\text{NH}_3)_3$	0.000	4.964
$\text{H}_2\text{SO}_4 \cdot (\text{NH}_3)_3$	7.430	9.633
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_3$	4.006	14.184
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{NH}_3)_3$	7.700	18.719
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{NH}_3)_3^\dagger$	7.163	23.637
$(\text{NH}_3)_4$	0.000	6.797
$\text{H}_2\text{SO}_4 \cdot (\text{NH}_3)_4$	5.798	11.458
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_4$	4.208	15.980
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{NH}_3)_4$	2.150	20.630
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{NH}_3)_3$	4.011	25.383
$(\text{CH}_3)_2\text{NH}$	1.01c	6.37c
$\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH}$	8.755	9.367
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH}$	7.842	13.941
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{CH}_3)_2\text{NH}$	9.113	18.640
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{CH}_3)_2\text{NH}$	7.938	23.277
$((\text{CH}_3)_2\text{NH})_2$	0.000	10.170
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_2$	6.823	14.733
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2^\ddagger$	5.843	18.876

$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_2$	7.606	23.345
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_2$	0.411	28.419
$((\text{CH}_3)_2\text{NH})_3$	0.012	15.451
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_3$	5.909	19.762
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_3$	7.030	24.141
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_3$	6.338	28.669
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_3$	8.378	33.305
$((\text{CH}_3)_2\text{NH})_4$	0.005	20.512
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_4$	1.415	25.246
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_4$	9.154	29.324
$(\text{H}_2\text{SO}_4)_3 \cdot ((\text{CH}_3)_2\text{NH})_4$	5.046	33.774
$(\text{H}_2\text{SO}_4)_4 \cdot ((\text{CH}_3)_2\text{NH})_4$	4.802	38.239
$\text{NH}_3 \cdot (\text{CH}_3)_2\text{NH}$	3.197	6.609
$\text{H}_2\text{SO}_4 \cdot \text{NH}_3 \cdot (\text{CH}_3)_2\text{NH}$	8.537	11.038
$(\text{H}_2\text{SO}_4)_2 \cdot \text{NH}_3 \cdot (\text{CH}_3)_2\text{NH}$	6.154	15.666
$(\text{H}_2\text{SO}_4)_3 \cdot \text{NH}_3 \cdot (\text{CH}_3)_2\text{NH}$	10.409	20.347
$(\text{H}_2\text{SO}_4)_4 \cdot \text{NH}_3 \cdot (\text{CH}_3)_2\text{NH}$	7.863	25.074
$\text{H}_2\text{SO}_4 \cdot (\text{NH}_3)_2 \cdot (\text{CH}_3)_2\text{NH}$	6.823	13.062



$(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_2 \cdot (\text{CH}_3)_2\text{NH}$	4.132	17.499
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{NH}_3)_2 \cdot (\text{CH}_3)_2\text{NH}$	4.861	22.072
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{NH}_3)_2 \cdot (\text{CH}_3)_2\text{NH}$	2.349	26.891
$\text{H}_2\text{SO}_4 \cdot \text{NH}_3 \cdot ((\text{CH}_3)_2\text{NH})_2$	5.752	16.342
$(\text{H}_2\text{SO}_4)_2 \cdot \text{NH}_3 \cdot ((\text{CH}_3)_2\text{NH})_2$	5.184	20.657
$(\text{H}_2\text{SO}_4)_3 \cdot \text{NH}_3 \cdot ((\text{CH}_3)_2\text{NH})_2$	6.294	25.371
$(\text{H}_2\text{SO}_4)_4 \cdot \text{NH}_3 \cdot ((\text{CH}_3)_2\text{NH})_2$	3.510	29.987
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_3 \cdot (\text{CH}_3)_2\text{NH}$	3.981	19.412
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{NH}_3)_3 \cdot (\text{CH}_3)_2\text{NH}$	8.128	24.095
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{NH}_3)_3 \cdot (\text{CH}_3)_2\text{NH}$	6.897	28.610
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{NH}_3)_2 \cdot ((\text{CH}_3)_2\text{NH})_2$	8.824	22.457
$(\text{H}_2\text{SO}_4)_3 \cdot (\text{NH}_3)_2 \cdot ((\text{CH}_3)_2\text{NH})_2$	9.046	27.355
$(\text{H}_2\text{SO}_4)_4 \cdot (\text{NH}_3)_2 \cdot ((\text{CH}_3)_2\text{NH})_2$	3.496	31.680
$(\text{H}_2\text{SO}_4)_2 \cdot \text{NH}_3 \cdot ((\text{CH}_3)_2\text{NH})_3$	5.966	25.872
$(\text{H}_2\text{SO}_4)_3 \cdot \text{NH}_3 \cdot ((\text{CH}_3)_2\text{NH})_3$	8.487	30.550
$(\text{H}_2\text{SO}_4)_4 \cdot \text{NH}_3 \cdot ((\text{CH}_3)_2\text{NH})_3$	3.140	35.001

<sup>a</sup> Sedo *et al.*<sup>52</sup>.

<sup>b</sup> Nadykto and Yu<sup>53</sup>.

<sup>c</sup> CRC Handbook of Chemistry and Physics<sup>54</sup>.

<sup>†</sup> Better configuration than that of our previous work<sup>25,43</sup>.

<sup>‡</sup> Different configuration than that of our previous work<sup>25</sup>; the earlier value was incorrect.

**Table S6.** Electronic energies ( $\Delta E_{elec}$ ), enthalpies ( $\Delta H_{278K}$ ), Gibbs free energies ( $\Delta G_{278K}$ ) and entropies ( $\Delta S_{278K}$ ) of formation from monomers at 278 K and 1 atm pressure for hydrated neutral clusters. The indices ( $n, m, w$ ) summarise the number of sulphuric acid, DMA and water molecules, respectively, in the cluster.

Cluster	( $n, m, w$ )	$\Delta E$ (kcal/mol)	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/K·mol)
H <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	(1,0,1)	-13.13	-11.46	-3.20	-29.74
H <sub>2</sub> SO <sub>4</sub> ·(H <sub>2</sub> O) <sub>2</sub>	(1,0,2)	-25.78	-22.51	-5.62	-60.75
H <sub>2</sub> SO <sub>4</sub> ·(H <sub>2</sub> O) <sub>3</sub>	(1,0,3)	-38.70	-33.52	-7.70	-92.85
H <sub>2</sub> SO <sub>4</sub> ·(H <sub>2</sub> O) <sub>4</sub>	(1,0,4)	-51.66	-44.81	-9.60	-126.64
H <sub>2</sub> SO <sub>4</sub> ·(H <sub>2</sub> O) <sub>5</sub>	(1,0,5)	-63.03	-54.57	-10.04	-160.18
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	(2,0,1)	-34.04	-31.62	-12.62	-68.36
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> ·(H <sub>2</sub> O) <sub>2</sub>	(2,0,2)	-48.02	-43.91	-16.27	-99.44
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> ·(H <sub>2</sub> O) <sub>3</sub>	(2,0,3)	-63.47	-57.26	-19.25	-136.73
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> ·(H <sub>2</sub> O) <sub>4</sub>	(2,0,4)	-79.13	-71.55	-22.42	-176.73
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> ·(H <sub>2</sub> O) <sub>5</sub>	(2,0,5)	-92.61	-82.76	-24.83	-208.37
(CH <sub>3</sub> ) <sub>2</sub> NH·H <sub>2</sub> O	(0,1,1)	-8.18	-6.23	1.37	-27.37
H <sub>2</sub> SO <sub>4</sub> ·(CH <sub>3</sub> ) <sub>2</sub> NH·H <sub>2</sub> O	(1,1,1)	-42.47	-37.94	-19.61	-65.92
H <sub>2</sub> SO <sub>4</sub> ·(CH <sub>3</sub> ) <sub>2</sub> NH·(H <sub>2</sub> O) <sub>2</sub>	(1,1,2)	-56.79	-50.16	-22.65	-98.95
H <sub>2</sub> SO <sub>4</sub> ·(CH <sub>3</sub> ) <sub>2</sub> NH·(H <sub>2</sub> O) <sub>3</sub>	(1,1,3)	-69.20	-60.48	-23.12	-134.37
H <sub>2</sub> SO <sub>4</sub> ·(CH <sub>3</sub> ) <sub>2</sub> NH·(H <sub>2</sub> O) <sub>4</sub>	(1,1,4)	-81.25	-70.84	-24.56	-166.45
H <sub>2</sub> SO <sub>4</sub> ·(CH <sub>3</sub> ) <sub>2</sub> NH·(H <sub>2</sub> O) <sub>5</sub>	(1,1,5)	-92.69	-80.68	-25.15	-199.74
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> ·(CH <sub>3</sub> ) <sub>2</sub> NH·H <sub>2</sub> O	(2,1,1)	-74.86	-69.02	-39.49	-106.23
(H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> ·(CH <sub>3</sub> ) <sub>2</sub> NH·(H <sub>2</sub> O) <sub>2</sub>	(2,1,2)	-86.20	-78.67	-40.50	-137.29

$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{H}_2\text{O})_3$	(2,1,3)	-102.59	-93.18	-44.12	-176.47
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{H}_2\text{O})_4$	(2,1,4)	-115.55	-104.40	-45.41	-212.18
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{H}_2\text{O})_5$	(2,1,5)	-125.72	-112.88	-45.76	-241.43
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{H}_2\text{O}$	(2,2,1)	-106.10	-96.75	-55.86	-147.07
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{H}_2\text{O})_2$	(2,2,2)	-118.30	-107.23	-58.31	-175.99
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{H}_2\text{O})_3$	(2,2,3)	-130.03	-116.73	-57.89	-211.65
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{H}_2\text{O})_4$	(2,2,4)	-145.52	-130.16	-60.63	-250.10
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{H}_2\text{O})_5$	(2,2,5)	-158.62	-141.12	-61.59	-286.07