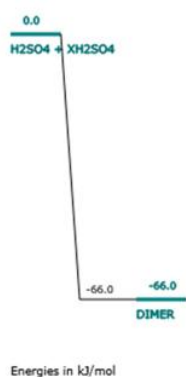


The other 2 referees are specialists in these types of calculations and have raised a number of relevant questions regarding the methodology. I take on board that this is a methodology paper and that the calculated collision rate coefficients are for new particle formation, NPF.

However, I'm still concerned about the reaction $\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ being assumed to be at its high-pressure limit at 1 atmosphere and 300 K. In the replies, you state:

increases rapidly as the number of vibrational modes ($3N - 6$, where N is the number of atoms) increases. Because the relatively large, strongly bound dimers studied here possess a large number of internal degrees of freedom to distribute the collision energy over. Consequently, the assumption of thermalization without dissociation at pressures encountered in the lower atmosphere (0.1 to 1 atm) is reasonable and represents standard practice in aerosol physics.

Now for H_2SO_4 system, 66 kJ mol⁻¹ binding energy for the dimer is NOT strongly bound; in the atmosphere the equilibrium will favour the monomer over the dimer. For this reason, I have done a basic Master Equation calculation on the system, a vibration only model using frequencies from DFT calculations, and used a high-pressure limit of 7.7e-10, based on your results.



R1 $\text{H}_2\text{SO}_4 + \text{XH}_2\text{SO}_4 \rightleftharpoons \text{DIMER}$ MesmerILT (reverse) A = 7.71e-10 E = 0kJ/mol

Energy convention is

Name	Energy kJ/mol	Rotational constants cm ⁻¹	Vibrational frequencies cm ⁻¹
He			
N ₂			
Ar			
H ₂ SO ₄	0.0	0.446 .117 0.094	3770 3710 1425 1385 1225 1180 1045 985 915 875 620 560 420 360 250
XH ₂ SO ₄	0.0	0.446 .117 0.094	3770 3710 1425 1385 1225 1180 1045 985 915 875 620 560 420 360 250
DIMER	-66	0.076 0.024 0.02	3721.4 3692.7 3184.6 2974.1 2712.5 2578.4 1418.6 1396.2 1357.8 1328.4 1206.9 1164.3 1052.7 1013.4 987.6 947.2 903.8 861.5 692.3 651.7 612.1 551.6 518.3 486.9 421.4 386.2 243.6 196.8 172.4 134.2 98.7 61.4 42.6 28.1 9.8

DIMER-deltaEDown=189.287, DIMER-deltaEDownTExponent=1.0!

At 300 K, 2.41432e+18 molecules cm⁻³ in N₂

First Order Conversion Rate Coefficients

DIMER → XH₂SO₄ 14771.6 s⁻¹

Second Order Conversion Rate Coefficients

XH₂SO₄ → DIMER 8.92947e-11 cm³molecule⁻¹s⁻¹

At 300 K, 2.41432e+19 molecules cm⁻³ in N₂

First Order Conversion Rate Coefficients

DIMER → XH₂SO₄ 46518.7 s⁻¹

Second Order Conversion Rate Coefficients

XH₂SO₄ → DIMER 2.81207e-10 cm³molecule⁻¹s⁻¹

At 300 K, 2.41432e+20 molecules cm ⁻³ in N2			
<u>First Order Conversion Rate Coefficients</u>			
DIMER	→	XH2SO4	91808.5 s ⁻¹
<u>Second Order Conversion Rate Coefficients</u>			
XH2SO4	→	DIMER	5.54986e-10 cm ³ molecule ⁻¹ s ⁻¹

At 300 K, 2.41432e+21 molecules cm ⁻³ in N2			
<u>First Order Conversion Rate Coefficients</u>			
DIMER	→	XH2SO4	116608 s ⁻¹
<u>Second Order Conversion Rate Coefficients</u>			
XH2SO4	→	DIMER	7.049e-10 cm ³ molecule ⁻¹ s ⁻¹

XH2SO2 is actually H2SO4 but is a way to make the system pseudo-first-order, which is required for the calculation. This calculation has an association rate coefficient at 1 atm ca. a factor of three below the capture rate, the high-pressure limit. Only at 100 atm is the system close to its high-pressure limit. I would also expect H2SO4 + NH(CH3)2 to be pressure dependent as its binding energy is similar. The last reaction: H2SO4 + HSO4⁻ has a binding energy about twice the other 2 reactions, so probably at its high-pressure limit. Therefore, for these first steps of NPT it should be acknowledged that assuming it is purely the capture rate coefficient might not be correct.

When you start adding more precursor, H2SO4, then it is reasonable to assume only the capture rate coefficient is required. I presume if you considered larger system, e.g. (H2SO4)2 + H2SO4 this would make it a much more costly calculation?

I note you do state this assumption:

By rejecting this assumption, the referee is inadvertently challenging the standard, widely accepted practice of modeling cluster distribution dynamics via macroscopic birth-death equations. Addressing the validity of foundational NPF kinetic frameworks falls far outside the scope of

this study, which aims specifically to evaluate the long-range physical accuracy of machine learning potentials, with the collision rate coefficient serving as the primary metric of success. This evaluation is a necessary preparatory step for large-scale, machine-learning-driven nucleation studies currently being developed within our group and the broader computational atmospheric chemistry community.

I think my above calculation challenges this assumption, but probably only for the first, dimerization step. Perhaps my model is too crude, i.e. vibration only!

The authors have done a good job replying to all the other points I made.

Overall, if the authors could recognize that the first steps of NPT may not be wholly controlled by the capture rate coefficient then I'm happy to recommend this paper for publication. I know that this assumption is outside the scope of the present study, but it should be acknowledged as a possibility.

