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Updated H_2SO_4-H_2O binary homogeneous nucleation look-up tables

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[1] The calculated rates of H_2SO_4-H_2O binary homogeneous nucleation (BHN), which is the only nucleation mechanism currently widely used in global aerosol models, are well known to have large uncertainties. Recently, we have reduced the uncertainties in the BHN rates on the basis of a kinetic quasi-unary nucleation (KQUN) model, by taking into account the measured bonding energetics of H_2SO_4 monomers with hydrated sulfuric acid dimers and trimers. The uncertainties were further reduced by using two independent measurements to constrain the equilibrium constants for monomer hydration. In this paper, we present updated BHN rate look-up tables derived from the improved KQUN model which can be used by anyone to obtain the BHN rates under given conditions. The look-up tables cover a wide range of key parameters that can be found in the atmosphere and laboratory studies, and their usage significantly reduces the computational costs of the BHN rate calculations, which is critical for multidimensional modeling. The look-up tables can also be used by those involved in experiments and field measurements to quickly assess the likeliness of BHN. For quick application, one can obtain the BHN rates and properties of critical clusters by browsing through the tables. A comparison of results based on the look-up tables with those from widely used classical BHN model indicates that, in addition to several orders of magnitude difference in nucleation rates, there also exists substantial difference in the predicted numbers of sulfuric acid molecules in the critical clusters and their dependence on key parameters.

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1. Introduction

[2] Atmospheric particles perturb the Earth's energy budget directly by scattering and absorbing radiation and indirectly by acting as cloud condensation nuclei (CCN) and thus changing cloud properties and influencing precipitation. The aerosol indirect radiative forcing is largely determined by the number abundance of particles that can act as CCN [e.g., *Twomey*, 1977; *Albrecht* 1989; *Charlson et al.*, 1992]. New particle formation frequently observed throughout the troposphere is an important source of atmospheric CCN and is one of key processes that need to be accurately represented in future generations of climate models [*Ghan and Schwartz*, 2007].

[3] Among the sixteen global aerosol models considered in the AeroCom Intercomparison [*Textor et al.*, 2006], ten of them do not consider any kind of new particle formation while the other six models calculate nucleation rates based on several different H_2SO_4-H_2O binary homogeneous nucleation (BHN) models/parameterizations [*Harrington and Kreidenweis*, 1998; *Kulmala et al.*, 1998; *Pitari et al.*, 2002; *Vehkamäki et al.*, 2002]. The calculated nucleation rates based on different parameterizations may differ by orders of magnitude. Among these BHN models/parameterizations, the one given by *Vehkamäki et al.* [2002] is thermodynamically mostly updated and widely used. Since BHN theory is widely used in calculating new particle formation rates in global aerosol models, it is necessary to understand and reduce its uncertainty.

[4] The extent of H_2SO_4 monomer hydration and the accuracy of the capillarity approximation for small H_2SO_4-H_2O cluster are two major sources of uncertainties in calculated BHN rates. *Yu* [2007] found that the hydration equilibrium constants used in the most recent version of classical BHN model [*Noppel et al.*, 2002; *Vehkamäki et al.*, 2002] significantly overestimates the extent of monomer hydration. *Yu* [2007] also showed that the capillarity approximation assumed in the classical BHN models leads to a large error in the calculated Gibbs free energy change for the evaporation of H_2SO_4 molecules from small H_2SO_4-H_2O clusters. Both the overestimation of monomer hydration and the error in capillarity approximation affect the accuracy of predicted BHN nucleation rates. Previously, to address the two well-known problems associated with the classical BHN theory (that is, violation of the law of mass action and an erroneous monomer concentration [*Wilemski and Wyslouzil*, 1995]), *Yu* [2005, 2006] showed that H_2SO_4-H_2O BHN can be treated as a quasi-unary nucleation process involving H_2SO_4 in equilibrium with the H_2O vapor and developed a kinetically self-consistent model for H_2SO_4-H_2O nucleation. *Yu* [2007] improved the kinetic

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Table 1. Range of Each Dependent Variable Dimension, the Total Number of Points in Each Dimension, and the Values at Each Point for the BHN Rate Look-Up Tables Corresponding to the Conditions in Background Atmosphere and Laboratory Studies/Plumes[a]

	Range	Total Number of Points	Values at Each Point
Background atmospheric conditions			
$[H_2SO_4]$ (cm^{-3})	10^5–10^9	61	$[H_2SO_4](i) = 10^5 \times 10^{(i-1)/15}$, i = 1, 61
T (K)	190–300	111	$T(j) = 190 + (j - 1)$, j = 1, 111
RH (%)	1–99	99	$RH(k) = k$, k = 1, 99
Laboratory and plume conditions			
$[H_2SO_4]$ (cm^{-3})	10^9–10^{12}	46	$[H_2SO_4]$ $(i) = 10^9 \times 10^{(i-1)/15}$, i = 1, 46
T (K)	280–310	31	$T(j) = 280 + (j - 1)$, j = 1, 31
RH (%)	1–99	99	$RH(k) = k$, k = 1, 99

[a]$[H_2SO_4]$ is the total sulfuric acid molecule concentration (free + hydrated).

quasi-unary nucleation (KQUN) model by using two independent measurements to constrain the equilibrium constants for monomer hydration and taking into account recently measured bonding energetics of H_2SO_4 monomers with hydrated sulfuric acid dimers and trimers. The improved KQUN model is thermodynamically more robust and predicted BHN nucleation rates are in good agreement with available experimental data. The main purpose of this paper is to provide updated BHN rate look-up tables derived from KQUN model which can be used to determine the BHN rates efficiently.

2. Updated H_2SO_4-H_2O Homogeneous Nucleation Rate Look-Up Tables

[5] In order to reduce the computational costs of the nucleation rate calculations, which are very important for multidimensional modeling, *Yu* [2006] developed look-up tables for H_2SO_4-H_2O homogeneous nucleation rates based on the KQUN model (J_{KQUN}). The updated J_{KQUN} look-up tables derived from the improved KQUN model with more robust thermodynamics and reduced uncertainties [*Yu*, 2007], along with a FORTRAN code to read and interpolate the tables, are given in the AGU auxiliary material.[1] The properties of critical clusters (number of sulfuric acid molecules i_a^*, radius r^*, and sulfuric acid mole fraction x^*) are also included in the tables. J_{KQUN}, i_a^*, r^*, and x^* depend on sulfuric acid vapor concentration ($[H_2SO_4]$), temperature (T), and relative humidity (RH), and thus, the look-up tables are three-dimensional. It should be noted that the look-up tables can also be used by those involved in experiments and field measurements who want to quickly assess the likeliness of BHN or find the BHN rates under given conditions. The look-up tables are designed in such a way that, for quick application, one can find the BHN rates and properties of critical clusters just by browsing through the tables (i.e., not a single calculation is needed).

[6] Compared to the earlier version of J_{KQUN} look-up tables presented by *Yu* [2006], the updated version gives lower BHN rates when i_a^* is small (lower T, higher RH, and higher $[H_2SO_4]$) but higher BHN rates when i_a^* is large. The difference is generally within a few orders of magnitude. In addition, the updated J_{KQUN} look-up tables have higher resolution in T dimension (dT = 1 K instead of 2 K). Table 1 shows the range of each dependent variable dimension, total number of points in each dimension and values at each point for the look-up tables corresponding to conditions of the background atmosphere and laboratory studies/plumes, respectively. Values of J_{KQUN} at four different temperatures (215 K, 235 K, 255 K, and 295 K) are plotted as contours in the $[H_2SO_4]$ verse RH plane in Figure 1. The contours in Figure 1 can be used to quickly estimate the possibility of BHN under given conditions. In the upper troposphere where T can be as low as ~215 K and RH can be as high as ~40%, significant BHN ($J > 0.1$ $cm^{-3}s^{-1}$) can happen if $[H_2SO_4]$ can reach above ~2×10^6 cm^{-3}. In the middle atmosphere with T = ~255K, $[H_2SO_4]$ has to be above ~5×10^7 cm^{-3} and RH above ~70% to have significant BHN. At room temperature, significant BHN only happens when $[H_2SO_4]$ is above ~10^9 cm^{-3}.

[7] With the look-up tables and a simple interpolation subroutine, J_{KQUN} and the properties of clusters under a given condition can be decided efficiently and accurately (the differences between the interpolated values and full model results are generally within a few percentage). Figure 2 shows J_{KQUN} and i_a^* (dash-dotted lines) as a function of $[H_2SO_4]$ (Figures 2a and 2b) and T (Figures 2c and 2d) determined using the look-up tables. For comparison, experimental results from *Hanson and Eisele* [2000] and *Hanson and Lovejoy* [2006], and the values predicted on the basis of the parameterization of *Vehkamäki et al.* [2002] are also given. In Figure 2c, the data from *Hanson and Lovejoy* [2006] for $[H_2SO_4] = 10^7$ cm^{-3} and RH = 50% are the calculated net steady state fluxes between the dimer and trimer based on measured equilibrium constant. It is clear from Figure 2 that, at lower temperatures corresponding to middle and upper troposphere conditions, the CBHN model of *Vehkamäki et al.* [2002] consistently overpredicts the BHN rates by 2–3 orders of magnitude while the KQUN model of *Yu* [2007] agrees well with experimental results. Figure 2 also indicates that the numbers of sulfuric acid molecules in critical clusters (i_a^*) are generally very small (<~5) at lower temperatures (when the nucleation is significant). There also exists difference in the values of i_a^* and their dependence on key parameters predicted by the CBHN model and the KQUN model. The difference can be very large under some conditions. For example, under the condition of T = 270 K, RH = 50%, and $[H_2SO_4] = 10^7$ cm^{-3}, the number of sulfuric acid molecules in the critical cluster is ~8 based on KQUN model but is ~16 based on CBHN model. The KQUN model, which is kinetically self-consistent

[1]Auxiliary material data sets are available at ftp://ftp.agu.org/apend/jd/2008jd010527. Other auxiliary material files are in the HTML.

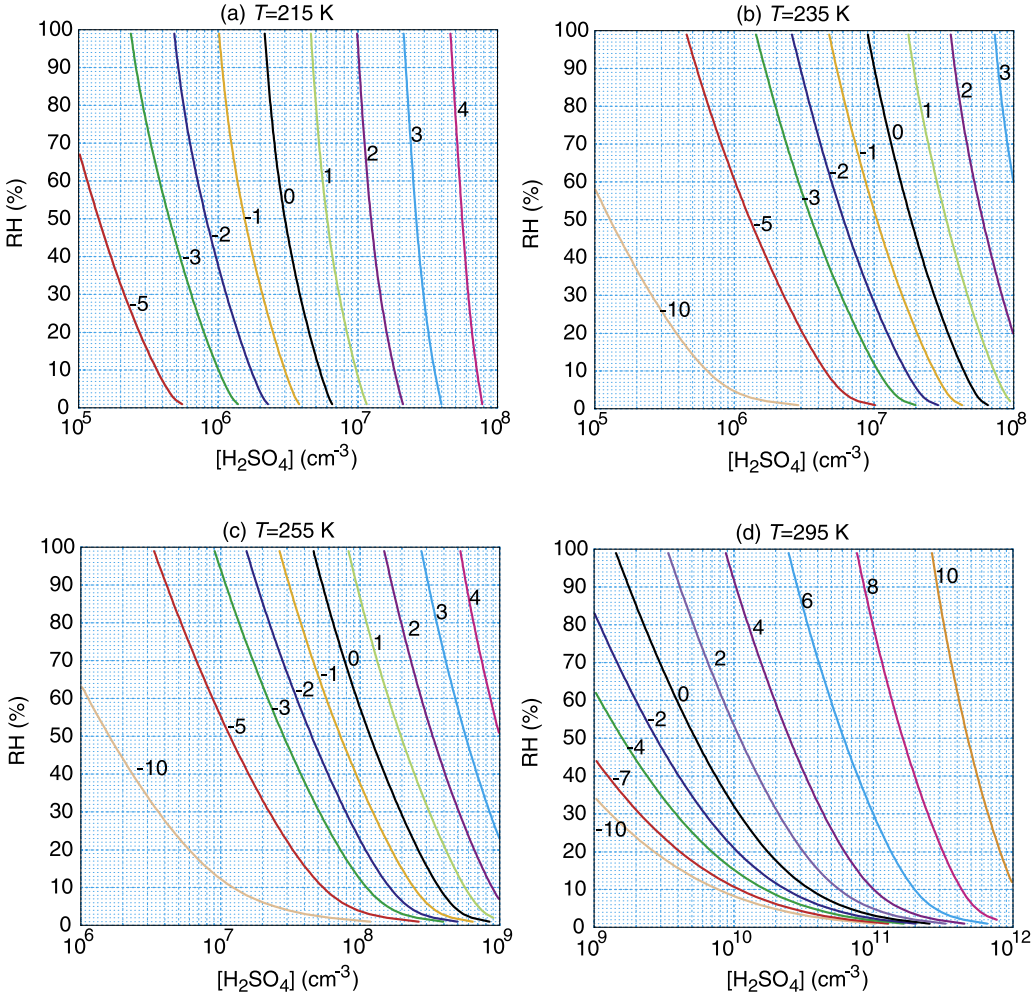

Figure 1. H_2SO_4-H_2O binary homogeneous nucleation rates for different values of $[H_2SO_4]$ and RH based on the improved kinetic quasi-unary nucleation (KQUN) model [*Yu*, 2007] at four temperatures: (a) $T = 215$ K, (b) $T = 235$ K, (c) $T = 255$ K, and (d) $T = 295$ K. Integer near each curve is the power to the base 10 of the nucleation rate in cm^{-3} s^{-1}.

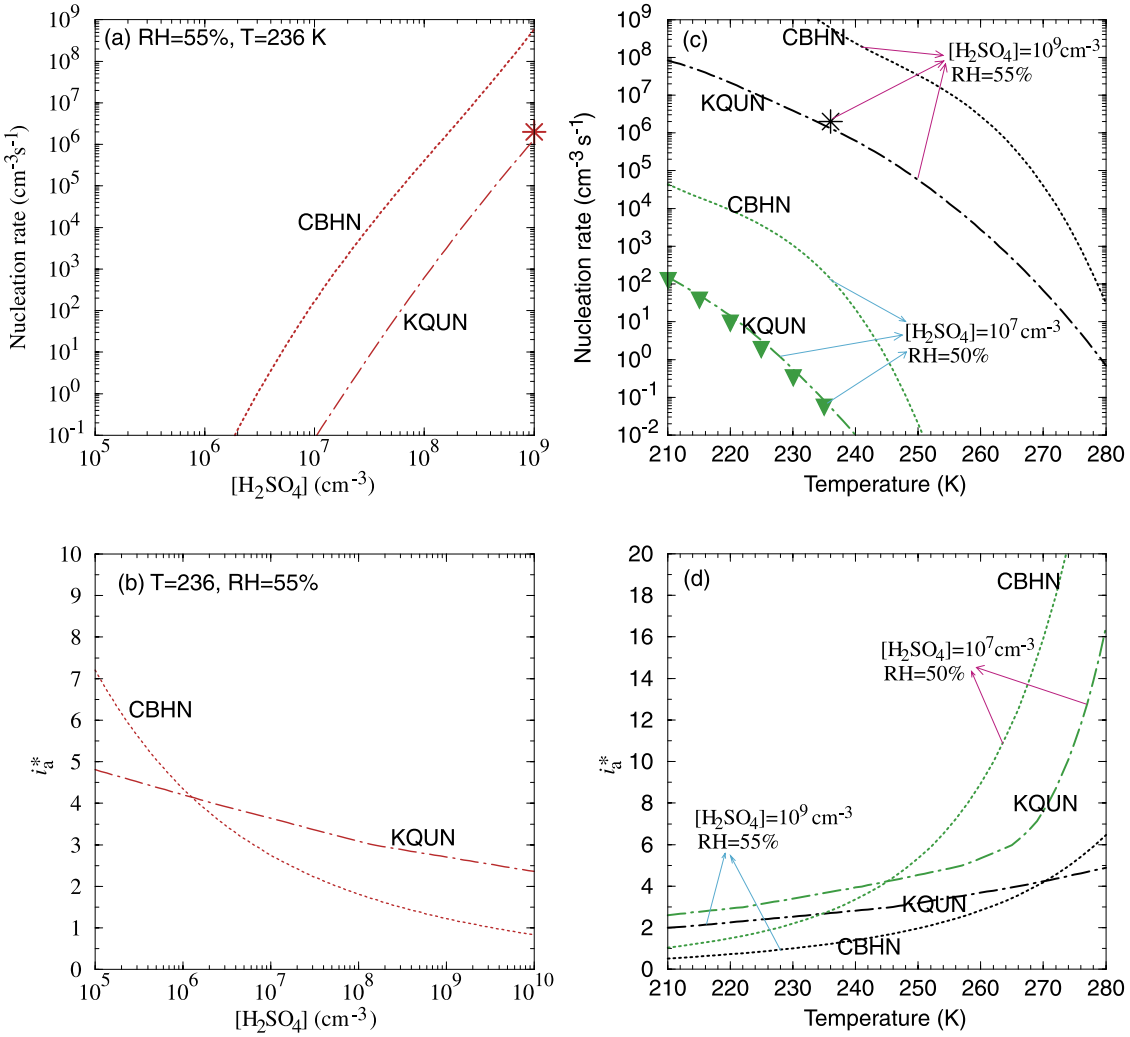

Figure 2. H_2SO_4-H_2O binary homogeneous nucleation rates and number of H_2SO_4 molecules in the critical clusters (i^*_a) as a function of (a, b) [H_2SO_4] and (c, d) T predicted by the improved kinetic quasi-unary nucleation (KQUN, dash-dotted lines) model [*Yu*, 2007] and by the classical binary homogeneous nucleation (CBHN, dotted lines) model [*Vehkamäki et al.*, 2002]. The symbols are experimental results from *Hanson and Eisele* [2000] (stars) and *Hanson and Lovejoy* [2006] (triangles). T = 236 K and RH = 55% in Figures 2a and 2b. Figures 2c and 2d show two set of conditions: [H_2SO_4] = 10^9 cm^{-3} and RH = 55%, and [H_2SO_4] = 10^7 cm^{-3} and RH = 50%.

and constrained by multiple independent experimental measurements [*Yu*, 2007], is thermodynamically more robust and its predicted values should be considered to be more accurate and reliable.

3. Summary

[8] In summary, we present updated H_2SO_4-H_2O BHN look-up tables covering a wide range of key parameters (T: 190–310 K; RH: 1–99%; [H_2SO_4]: 10^5–10^{12} cm^{-3}) in this paper. BHN of sulfuric acid and water has long been considered to be a major source of new particles in the upper troposphere and is the only nucleation mechanism currently widely used in global aerosol models that explicitly calculate nucleation rates. The updated BHN look-up tables presented here are derived from kinetically self-consistent quasi-unary nucleation model constrained by multiple independent experimental measurements [*Yu*, 2007], and thus is thermodynamically more robust and the predicted BHN nucleation rates are more accurate. With the look-up tables and a simple interpolation subroutine, the computational costs of the BHN rate calculations are significantly reduced which is critical for multidimensional modeling. For quick application, one can browse through the tables and find the BHN rates and properties of critical clusters under given conditions (i.e., without any calculation).

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References

Albrecht, B. A. (1989), Aerosols, cloud microphysics and fractional cloudiness, *Sciences*, *245*, 1227–1230.

Charlson, R. J., S. E. Schwartz, J. M. Hales, R. D. Cess, J. A. Coakley Jr., J. E. Hansen, and D. J. Hofmann (1992), Climate forcing by anthropogenic aerosols, *Science*, *255*, 423–430, doi:10.1126/science.255.5043.423.

Ghan, S. J., and S. E. Schwartz (2007), Aerosol properties and processes: A path from field and laboratory measurements to global climate models, *Bull. Am. Meteorol. Soc.*, *88*, 1059–1083, doi:10.1175/BAMS-88-7-1059.

Hanson, D. R., and F. Eisele (2000), Diffusion of H_2SO_4 in humidified nitrogen: Hydrated H_2SO_4, *J. Phys. Chem. A*, *104*, 1715–1719, doi:10.1021/jp993622j.

Hanson, D. R., and E. R. Lovejoy (2006), Measurement of the thermodynamics of the hydrated dimer and trimer of sulfuric acid, *J. Phys. Chem. A*, *110*, 9525–9528, doi:10.1021/jp062844w.

Harrington, D. Y., and S. M. Kreidenweis (1998), Simulations of sulfate aerosol dynamics: I: Model description, *Atmos. Environ.*, *32*, 1691–1700, doi:10.1016/S1352-2310(97)00452-4.

Kulmala, M., A. Laaksonen, and L. Pirjola (1998), Parameterizations for sulfuric acid/water nucleation rates, *J. Geophys. Res.*, *103*, 8301–8308, doi:10.1029/97JD03718.

Noppel, M., H. Vehkamaki, and M. Kulmala (2002), An improved model for hydrate formation in sulfuric acid–water nucleation, *J. Chem. Phys.*, *116*, 218–228, doi:10.1063/1.1423333.

Pitari, G., E. Mancini, V. Rizi, and D. T. Shindell (2002), Impact of future climate and emission changes on stratospheric aerosols and ozone, *J. Atmos. Sci.*, *59*, 414–440, doi:10.1175/1520-0469(2002)059<0414:IOFCAE>2.0.CO;2.

Textor, C., et al. (2006), Analysis and quantification of the diversities of aerosol life cycles within AeroCom, *Atmos. Chem. Phys.*, *6*, 1777–1813.

Twomey, S. (1977), The influence of pollution on the shortwave albedo of clouds, *J. Atmos. Sci.*, *34*, 1149–1152, doi:10.1175/1520-0469(1977)034<1149:TIOPOT>2.0.CO;2.

Vehkamäki, H., et al. (2002), An improved parameterization for sulfuric acid–water nucleation rates for tropospheric and stratospheric conditions, *J. Geophys. Res.*, *107*(D22), 4622, doi:10.1029/2002JD002184.

Wilemski, G., and B. E. Wyslouzil (1995), Binary nucleation kinetics. I. Self-consistent size distribution, *J. Chem. Phys.*, *103*, 1127–1136, doi:10.1063/1.469823.

Yu, F. (2005), Quasi-unary homogeneous nucleation of H_2SO_4-H_2O, *J. Chem. Phys.*, *122*, 074501, doi:10.1063/1.1850472.

Yu, F. (2006), Binary H_2SO_4-H_2O homogeneous nucleation rates based on a kinetic quasi-unary model: Look-up tables, *J. Geophys. Res.*, *111*, D04201, doi:10.1029/2005JD006358.

Yu, F. (2007), Improved quasi-unary nucleation model for binary H_2SO_4-H_2O homogeneous nucleation, *J. Chem. Phys.*, *127*, 054301, doi:10.1063/1.2752171.

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