A new parameterization of H_2SO_4/H_2O aerosol composition: Atmospheric implications

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Abstract. Recent results from a thermodynamic model of aqueous sulfuric acid are used to derive a new parameterization for the variation of sulfuric acid aerosol composition with temperature and relative humidity. This formulation is valid for relative humidities above 1 % in the temperature range of 185 to 260 K. An expression for calculating the vapor pressure of supercooled liquid water, consistent with the sulfuric acid model, is also presented. We show that the *Steele and Hamill* [1981] formulation underestimates the water partial pressure over aqueous H_2SO_4 solutions by up to 12% at low temperatures. This difference results in a corresponding underestimate of the H_2SO_4 concentration in the aerosol by about 6 % of the weight percent at approximately 190 K. In addition, the relation commonly used for estimating the vapor pressure of H_2O over supercooled liquid water differs by up to 10 % from our derived expression. The combined error can result in a 20 % underestimation of water activity over a H_2SO_4 solution droplet in the stratosphere, which has implications for the parameterization of heterogeneous reaction rates in stratospheric sulfuric acid aerosols. The influence of aerosol composition on the rate of homogeneous ice nucleation from a H_2SO_4 solution droplet is also discussed. This parameterization can also be used for homogeneous gas phase nucleation calculations of H_2SO_4 solution droplets under various environmental conditions such as in aircraft exhaust or in volcanic plumes.

Introduction

The equilibrium compositions of H_2SO_4/H_2O aerosols representative of the stratosphere are often calculated using the *Steele and Hamill* [1981] parameterization, which is based on equations given by *Gmitro and Vermeulen* [1964] for the partial pressure of H_2O above aqueous H_2SO_4 [e.g., *Anthony et al.*, 1995; *Bertram et al.*, 1996]. These equations utilize thermodynamic properties tabulated by *Giauque et al.* [1960], though with adjustment of some quantities to improve predictions at temperatures above 298.15 K. This optimization leads to errors of up to 10% in the equilibrium partial pressure of water around 200 K [*Massucci et al.*, 1996]. In contrast, the aqueous sulfuric acid model of *Clegg and Brimblecombe* [1995] agrees very closely, at stratospheric temperatures, with both the original thermodynamic analysis of *Giauque et al.* [1960] and the recent vapor pressure measurements of *Massucci et al.* [1996]. Our purpose here is to

draw attention to this significant revision to the fundamental water partial pressure/composition relationship for the atmospheric aerosol, and to provide equations that can be used in practical applications. Here we parameterize the output of the *Clegg and Brimblecombe* [1995] model into simple functions and compare the results, in terms of the equilibrium partial pressure of water, with that of the *Steele and Hamill* [1981] formulation. The effects of the parameterization on predicted probabilities of $ClONO_2$ hydrolysis in aqueous H_2SO_4 aerosols, and on ice nucleation in the atmosphere, are explored. The use of this parameterization is likely to be most important for the reactions whose rates vary sharply with H_2SO_4 concentration *Hanson and Ravishankara* [1994] or H^+ activity in the aerosol [*Robinson et al.*, 1997]. Another area that this parameterization can be used would be in homogeneous gas phase nucleation calculations of atmospheric sulfate particles in aircraft exhaust or in volcanic plumes. We do not discuss the latter application in this paper, however, it is clear that different vapor pressures would alter the critical supersaturations at which ultrafine particles (assumed to be aqueous H_2SO_4 solution droplets) would nucleate in the atmosphere.

Data and Parameterization

For a thorough survey of the similarities and differences between vapor pressure data sets and models of the H_2SO_4/H_2O binary system see the work of *Zhang et al.* [1993] and, particularly, *Massucci et al.* [1996]. Here we note first that the model of Clegg and Brimblecombe and the tabulation of Giauque *et al.* yield water and H_2SO_4 activities in close agreement for aqueous H_2SO_4 solutions under stratospheric conditions. Second, predicted partial pressures of H_2O from both studies agree with values measured recently by Massucci *et al.* to temperatures below 200 K, which gives confidence in the results.

Figure 1 illustrates differences between water partial pressures calculated using the Clegg and Brimblecombe model and the equations of Gmitro and Vermeulen for a number of different acid compositions. This difference is caused primarily by the fact that Gmitro and Vermeulen optimized the heat capacities tabulated by Giauque *et al.* to obtain better agreement for calculations above 298.15 K. Values of $\Delta P H_2O$ increase with decreasing temperature and are greatest for a 40 wt % H_2SO_4 solution (see also Figure 5 of Massucci *et al.*).

Based on the work of *Massucci et al.* [1996] and the results shown in Figure 1, we do not recommend the expressions of Gmitro and Vermeulen for calculating water partial pressures over aqueous sulfuric acid solutions. However, the model of Clegg and Brimblecombe is complex, and there is a need for a simpler (but still accurate) representation of the water partial
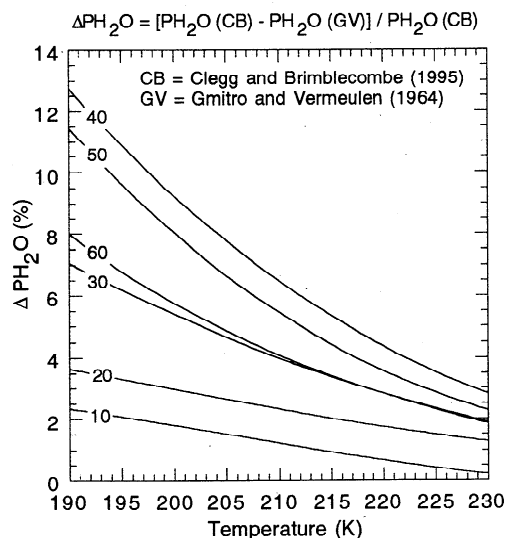
$$\Delta PH_2O = [PH_2O\,(CB) - PH_2O\,(GV)]\,/\,PH_2O\,(CB)$$

Figure 1. Differences between equilibrium water partial pressures over aqueous H_2SO_4 calculated using the model of *Clegg and Brimblecombe* [1995] and the expressions of *Gmitro and Vermeulen* [1964] (as used by *Steele and Hamill*, [1981]). The numbers on the curves indicate the H_2SO_4 weight percent of the solution.

pressure/composition relationship for stratospheric and upper tropospheric temperatures. Below we derive a series of polynomial functions for this purpose, fitted to properties calculated using the model (see Table 1).

We found that the most efficient way to parameterize the variation of aerosol composition with temperature and water partial pressure was to express the composition as a function of water activity. This is defined as the ratio of the equilibrium water partial pressure to the saturation water vapor pressure over (supercooled) liquid water. The following relation gives the saturation water vapor pressure, $P^o_{H_2O}$, consistent with that used by Clegg and Brimblecombe (see their Table 2) though in simpler form:

Table 1. Water Vapor Pressure Coefficients

$$P_{H_2O}(mb) = EXP\left[a + b/T + c/T^2\right]$$

weight %	a	b	c
10	19.726	-4364.8	-147620
15	19.747	-4390.9	-144690
20	19.761	-4414.7	-142940
25	19.794	-4451.1	-140870
30	19.883	-4519.2	-136500
35	20.078	-4644.0	-127240
40	20.379	-4828.5	-112550
45	20.637	-5011.5	-98811
50	20.682	-5121.3	-94033
55	20.555	-5177.6	-96984
60	20.405	-5252.1	-100840
65	20.383	-5422.4	-97966
70	20.585	-5743.8	-83701
75	21.169	-6310.6	-48396
80	21.808	-6985.9	-12170

Coefficients *a-c* are fitted to partial pressures generated using the model of Clegg and Brimblecombe for 0 to 75 % acid, and to values calculated using thermodynamic properties tabulated by Giauque et al. for 80 % acid. The results are valid over a temperature range of 185 to 260 K. Water partial pressures can be obtained for intermediate compositions by linear interpolation. This procedure will yield values that differ from those of Clegg and Brimblecombe model by no more than 2 %.
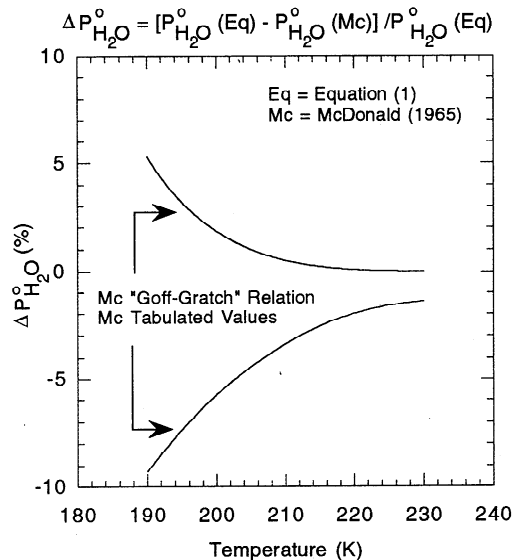
$$\Delta P^o_{H_2O} = [P^o_{H_2O}\,(Eq) - P^o_{H_2O}\,(Mc)]\,/P^o_{H_2O}\,(Eq)$$

Figure 2. The difference between the saturation vapor pressure of water calculated using Eq. (1), and values given by *McDonald* [1965]. Two curves are shown for this comparison since different results are obtained if ones uses the Goff-Gratch relation in the McDonald article versus his tabulated values. *Hanson and Ravishankara* [1994] fitted the latter values in a simple function and used this function in their parameterization of heterogeneous reaction rates.

$$\ln P^o_{H_2O} = 18.452406985 - 3505.1578807\,/\,T - 330918.55082\,/\,T^2$$
$$+\,12725068.262\,/\,T^3 \tag{1}$$

where $P^o_{H_2O}$ is in mbar. This relation is valid over the temperature range of 185 to 260 K. Figure 2 illustrates the difference between saturation water vapor pressures given by equation (1) and values tabulated by *McDonald* [1965], as used recently by *Hanson and Ravishankara* [1994]. It is important to note that the $P^o_{H_2O}$ listed in Table 1 by McDonald are inconsistent with the "Goff-Gratch" equation which was presented in the same paper. Comparisons with other literature sources suggest that the equation, and not the Table, gives the values intended by the author. Hanson and Ravishankara have expressed the reactive uptake coefficient of $ClONO_2$ at low temperature in aqueous H_2SO_4 solutions as a function of water activity, calculated using the expressions of Gmitro and Vermeulen for the partial pressure of water over aqueous H_2SO_4 and $P^o_{H_2O}$ from Table 1 of McDonald. It is clear from the discussion above that these choices will lead to water activities that differ from the best available estimates. In the next section we discuss the implications of such differences for calculations using the parameterization scheme of Hanson and Ravishankara.

The Clegg and Brimblecombe sulfuric acid model was used to generate equilibrium $P^o_{H_2O}$ from 185 to 260 K for a wide range of solution compositions. Table 1 summarizes the results of such runs for 15 selected weight percentages of H_2SO_4. The water partial pressures calculated for each solution composition in Table 1 yield the water activity of the solution when divided by the value of $P^o_{H_2O}$ from equation (1) for the same temperature. The water activities obtained this way agree with the water activities calculated directly from the thermodynamic model of Clegg and Brimblecombe to within the fourth significant digit. The generated data set, which contained columns of composition, temperature and water activity, was fitted to the following function:

$$m_s(a_w,T) = y_1(a_w) + \frac{(T-190)\left[y_2(a_w) - y_1(a_w)\right]}{70} \tag{2}$$

Where m_s is the sulfuric acid molality, a_w is the water activity and y functions are given in Table 2. Note that the acid weight percent (wt_s) and molality are related by

Table 2. Composition Functions

$$y = Aa_w^B + Ca_w + D$$

	A	B	C	D
$0.01 < a_w < 0.05$				
y_1	1.2372089320e+1	-1.6125516114e-1	-3.0490657554e+1	-2.1133114241e+0
y_2	1.3455394705e+1	-1.9213122550e-1	-3.4285174607e+1	-1.7620073078e+0
$0.05 < a_w < 0.85$				
y_1	1.1820654354e+1	-2.0786404244e-1	-4.8073063730e+0	-5.1727540348e+0
y_2	1.2891938068e+1	-2.3233847708e-1	-6.4261237757e+0	-4.9005471319e+0
$a_w > 0.85$				
y_1	-1.8006541028e+2	-3.8601102592e-1	-9.3317846778e+1	2.7388132245e+2
y_2	-1.7695814097e+2	-3.6257048154e-1	-9.0469744201e+1	2.6745509988e+2

Read 1.2372089320e+1 as 1.2372089320 x 10^1. The minimum water activity of 0.01 (corresponding to 30 mol kg^{-1} H$_2$SO$_4$ at ~ 260 K) is set by the limit of validity of the Clegg and Brimblecombe sulfuric acid model.

$$wt_s = \frac{9800m_s}{98m_s + 1000} \qquad (3)$$

Weight percents calculated using equations (2) and (3) differ by at most 0.05 % from the model results of Clegg and Brimblecombe in the temperature range of 185 to 260 K for relative humidities greater than 1 %.

Results

Differences between aerosol compositions calculated using equations (2) and (3) and the tabulated values of Steele and Hamill are shown in Figure 3 for four constant water vapor pressure profiles. The typical ranges for the variation of water partial pressure in the lower stratosphere and upper troposphere are shown in Figure 3. For stratospheric water partial pressures, and temperatures above 200 K, the aerosol compositions given by Steele and Hamill are low by at most 1 %. However, below 200 K the difference in the calculated composition grows rapidly as temperature decreases. This deviation is caused by the fact that Gmitro and Vermeulen water vapor pressure relations are accurate to only about 10 % at low temperatures (see Figure 1). Under upper tropospheric

conditions, the H$_2$SO$_4$ weight percent in solution is underestimated by about 5 % near the ice nucleation point (Figure 3). The effect of this compositional difference on the nucleation of ice crystals from a H$_2$SO$_4$ solution droplet is discussed below.

Hanson and Ravishankara [1994] have shown that the rate of heterogeneous chemical reactions in sulfuric acid aerosols can be scaled as a function of water activity. In order to convert the composition of a solution into a water activity, these authors divided water partial pressures calculated using the Gmitro and Vermeulen expressions by the saturated water vapor pressures tabulated by McDonald. However, Figure 1 shows that the equilibrium water partial pressures over aqueous H$_2$SO$_4$ are underestimated by up to about 10% for stratospheric aerosol compositions (40 to 60 wt%). In addition, Figure 2 shows that the saturated water vapor pressure appears to be overestimated in McDonald's table by almost 10 % at 190 K. Consequently, the water activities derived by Hanson and Ravishankara are likely to be in error. Figure 4 illustrates the difference between our calculated water activities and those of Hanson and Ravishankara. At 190 K, the water activity estimated by Hanson and Ravishankara deviates from our value by about 20 %.

We have also calculated reaction probabilities for ClONO$_2$ hydrolysis in aqueous H$_2$SO$_4$ using the old (Hanson and Ravishankara) and new (this work) water activities. Figure 4 shows the ratio of these revised reaction probabilities to those presented by Hanson and Ravishankara. Differences are small
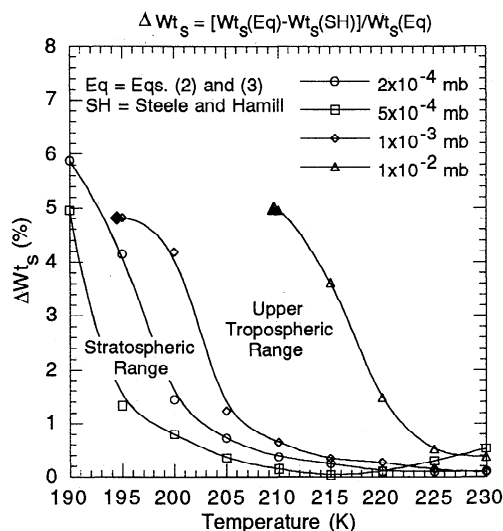

Figure 3. Difference between the sulfuric acid compositions calculated using equations (2) and (3), and values tabulated by *Steele and Hamill* [198]. This difference is shown for four constant water vapor pressure profiles, which bracket the water partial pressure variations in the lower stratosphere and upper troposphere. The solid symbols show the point at which ice crystals will nucleate in solution (see *Tabazadeh et al.*, [1997]).
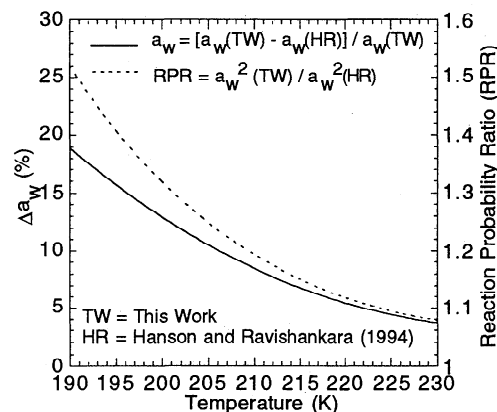

Figure 4. The difference in the calculated water activity between this work and that described by *Hanson and Ravishankara* [1994] for a 50 % sulfuric acid solution composition (see text for more detail). Also shown is the ratio for the change in the reaction probability of ClONO$_2$ hydrolysis as compared to those reported by Hanson and Ravishankara for a 50 % sulfuric acid solution composition.
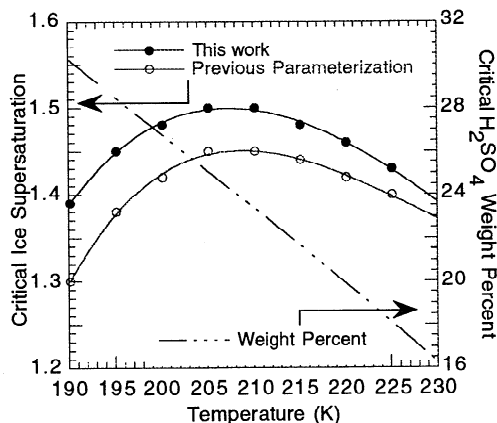
Figure 5. The critical ice saturation of H_2SO_4 droplets as a function of critical temperature (see text for more detail). Also shown are the critical H_2SO_4 acid composition, from the laboratory measurements of *Bertram et al.* [1996]. The relation given by *Buck et al.* [1981] was used for the determination of the equilibrium water vapor pressure over ice.

for temperatures above 230 K, but grow sharply below this temperature. For example, at 190 K the reaction probability for $ClONO_2$ hydrolysis calculated from the parameterization of Hanson and Ravishankara is about 50% lower than our estimate.

To fully assess the effect of this new parameterization on heterogeneous reactions involving HCl, the laboratory data should be refitted using water activities calculated from the relations given here. However, we predict a similar or slightly higher sensitivity to heterogeneous reactions involving HCl since the water activity determines the aerosol composition and hence the HCl solubility. In fact, under conditions where the errors in determining the reaction probability for the $ClONO_2$ hydrolysis become large [*Hanson and Ravishankara*, 1994; *Robinson et al.*, 1997], the $ClONO_2$ reaction with HCl is the major sink for the loss of $ClONO_2$. Thus we suggest that it would be worthwhile revising the rates of $ClONO_2$ reaction with HCl as reported by *Hanson and Ravishankara* [1994] by using the new H_2SO_4 compositions, instead of those tabulated by Steele and Hamill.

It is important to remember that other uncertainties remain in the calculations of heterogeneous reaction rates, such as diffusivities and rate coefficients, and their variation with temperature and aerosol composition [e.g., *Hanson and Ravishankara*, 1994; *Robinson et al.*, 1997]. Also the extrapolation of measured heterogeneous reaction rates to conditions outside of those used in the laboratory may introduce errors. Nevertheless, the relationship between ambient water partial pressure and stratospheric aerosol composition remains fundamental to accurate predictions of heterogeneous processes in the stratosphere.

The relationship between water partial pressure and aerosol composition is also important in calculations of homogeneous ice nucleation [*Tabazadeh et al.*, 1997]. Figure 5 illustrates the critical composition and temperature at which ice crystals were formed in an aqueous H_2SO_4 solution droplet in the laboratory [*Bertram et al.*, 1996]. Using relations (2) and (3) we have converted the aerosol composition into a critical ice saturation ratio (see *Tabazadeh et al.*, [1997] for more detail). The ice saturation is defined as the ambient water partial pressure divided by the equilibrium vapor pressure over ice [*Buck et al.*, 1981] at the temperature where ice nucleated in the laboratory. In the second parameterization we used the Steele and Hamill compositions instead of equation (2) and (3) in order to convert the composition into an ice saturation ratio. Figure 5 shows that a slightly higher nucleation barrier is calculated using the parameterization described here as compared to the second scheme. This difference is caused by the fact that near the ice nucleation point (see Figure 3), the

Steele and Hamill weight percentages are about 5 % smaller than our estimates, and at the same temperature ice will nucleate more readily from a less concentrated solution.

Summary

In this work we present a new parameterization for the variation of H_2SO_4 aerosol composition with temperature and relative humidity, which is consistent with the model of Clegg and Brimblecombe and thermo-dynamic properties of aqueous H_2SO_4 tabulated by Giauque *et al.*. Comparisons with the widely used aerosol compositions given by Steele and Hamill show differences which increase with falling temperature and are greatest for solutions of 40 to 50 wt % composition. Water activities derived from the Steele and Hamill parameterization and saturated water vapor pressures presented by McDonald also differ from our estimates. We showed that such differences can result in an underestimation of the reaction probability for $ClONO_2$ hydrolysis in sulfate aerosols by up to 50 % at low temperatures. Finally, we calculate a slightly larger barrier to the formation of ice in an aqueous H_2SO_4 droplet by homogenous nucleation using our revised water activities and compositions.

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