Supplementary Material to:


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The published Comment contains our calculations for the two example concentrations chosen by Knopf et al.,¹ which can be compared directly with the figures in their original paper. It is also important to assess differences between the models and the thermodynamic properties to which they have been fitted over a broader range of compositions. In this document we compare calculated equilibrium relative humidities (RH) above 0 to 80 mass% H₂SO₄, from 180 to 320 K. We also offer some further comments regarding the measurements of Knopf et al., which they have not previously compared with the results of earlier studies. Finally, in a note² we describe how the mole fraction activities of Giauque et al.³ were converted to the infinite dilution reference state in order to determine activity coefficients for inclusion in Figures 1 and 2 of our Comment.

1. Equilibrium Relative Humidities above 0 to 80 mass% H₂SO₄

Figure 1 shows equilibrium RH humidities calculated from the work of Giauque et al.³ (symbols), and both AIM⁴ and Knopf et al.¹ models (lines), superimposed on the H₂SO₄-H₂O phase diagram. Temperatures below the homogeneous ice nucleation temperature are again shown by hatching. A line corresponding to a typical trajectory of a stratospheric H₂SO₄ particle (5 ppmv H₂O, 100 mbar altitude) is included, indicating that the combination of very high mass% H₂SO₄ and very low temperature is not relevant atmospherically. Overall, the AIM model agrees most closely with the available thermodynamic data, with the exception of about 30 mass% to 50 mass% acid and the lowest temperatures, for which differences are comparable.

These results are consistent with the comparisons shown in the Comment, and confirm that the AIM model more closely agrees with the evaluated thermodynamic
properties of Giauque et al. to which both models have been fitted. These properties must be subject to some uncertainty in the supersaturated region of the phase diagram, as we noted in the Comment, though the inclusion of extensive low temperature thermal measurements in the work of Giauque et al. suggests that these uncertainties will not be large except at very high supersaturations with respect to the equilibrium solid phases.

2. Dissociation Constant Measurements

In their paper Knopf et al.\(^1\) did not present any comparisons of their measurements with the quite extensive data that already exist, particularly at 298.15 K (see Table 15 of Clegg and Brimblecombe\(^4\)). They now do so in their Response, and it is clear that their experiments yield the highest values of the dissociation constants of all the studies (except for two which are clearly erroneous). Knopf et al. are unable to explain the differences, and we do not investigate them here. However, it should be possible to assess the accuracy of the data indirectly, at least at 298.15 K, using a model and the extensive osmotic and activity coefficient data that exist for aqueous H\(_2\)SO\(_4\) in the 0 to 6 mol kg\(^{-1}\) range. We note that values of the degree of dissociation given in the critical review of Clegg, Rard, and Pitzer at 298.15 K are 0.21 at 0.5 mol kg\(^{-1}\), and 0.33 (the maximum) at 4.0 mol kg\(^{-1}\). These values are both significantly lower than determined by Knopf et al. It remains unclear whether the dissociation constants determined by Knopf et al. can be reconciled with the available activity data, and also thermal data which are strongly influenced by the dissociation (see Figures 5 and 6 of Clegg et al.\(^5\)).

References and Notes


(2) H\(_2\)SO\(_4\) activities calculated from Table 1 of Giauque et al.\(^3\) have a reference state of pure liquid H\(_2\)SO\(_4\). The correction factor to a reference state of infinite dilution is a function of temperature only. Because the tabulation of Giauque et al. does not extend to dilute solutions (in which the mean activity coefficient of H\(_2\)SO\(_4\) varies strongly with molality) we have determined the reference state correction as follows: the mean activity coefficient of H\(_2\)SO\(_4\) was calculated relative to both a reference state of infinite dilution (Clegg and Brimblecombe\(^4\) model) and pure liquid H\(_2\)SO\(_4\) (Table 1 of Giauque et al.) at five molalities from 5.0 to 25.0 mol kg\(^{-1}\) from 330 to 180 K. For temperatures above 250 K, for which the
Clegg and Brimblecombe model agrees closely with Giauque et al., and also agrees reasonably well with the Knopf et al. model for 50 mass% acid, the reciprocal of the H$_2$SO$_4$ activities relative to the two reference states agree very closely at all temperatures and molalities. The following equation was fitted:

\[
\ln(a_{\text{H}_2\text{SO}_4})^{\text{Giauque}} - \ln(4\gamma_2^3 m_{\text{H}_2\text{SO}_4}^3) = -420.662511 + 7975.95687/T + 65.31953\ln(T)
\]

This was used to estimate $\gamma_2$ for temperatures below 250 K from H$_2$SO$_4$ activities calculated from Table 1 of Giauque et al., and are the values plotted in Figures 1b and 2b in the Comment.


Figure Caption

Fig. 1. Equilibrium relative humidities, from 1% to 98%, above aqueous H$_2$SO$_4$ as a function of temperature and mass% H$_2$SO$_4$. Symbols: calculated from the thermodynamic evaluation of Giauque et al.$^3$ Lines: solid - AIM model;$^4$ dashed - model of Knopf et al.;$^1$ thick solid - saturation of aqueous H$_2$SO$_4$ with respect to ice (furthest left) and H$_2$SO$_4$ hydrates; dotted - trajectory of a typical stratospheric H$_2$SO$_4$ droplet for 5 ppmv H$_2$O and 100 mbar altitude. Hatched area: the upper boundary marks the practical limit of supercooling of dilute aqueous solutions before ice nucleation occurs.$^6$