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Comment on the “Thermodynamic Dissociation Constant of the Bisulfate Ion from Raman and Ion Interaction Modeling Studies of Aqueous Sulfuric Acid at Low Temperatures”

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Knopf et al.[1] have recently determined the degrees of dissociation of the bisulfate ion (α_{HSO_4}) in aqueous sulfuric acid at low temperatures. They also use an ion-interaction model, in which the molalities and activity coefficients of individual species are calculated, to estimate the value of the thermodynamic dissociation constant (K_{II}) for bisulfate as a function of temperature. In their Figures 8 and 9, Knopf et al. compare K_{II} with values from the equation of Dickson et al.[2] which was used in the aerosol inorganics models (AIM) of Clegg and coworkers.[3] Knopf et al. go on to compare their own model with the AIM model for $H_2SO_4-H_2O$[4] (not cited by Knopf et al.) in terms of bisulfate dissociation, single ion activity coefficients, activity coefficient products, and water activities (their Figures 6, 7, 10, and 11). Very large differences are found at low temperatures, implying that AIM is inaccurate for aqueous H_2SO_4 and its mixtures with other electrolytes. If true, this would have important implications for calculations of gas solubilities and phase equilibria in tropospheric and stratospheric acid sulfate aerosols, for which the AIM model is used extensively.

Here, we compare AIM and the model of Knopf et al., on the correct basis, with the best available data for water and H_2SO_4 activities. We show that the AIM model appears to yield more accurate predictions of water and H_2SO_4 activities under most conditions, including low temperatures. We determine the reasons for this and offer some general comments on the limitations of the models. A brief discussion of the available data for the dissociation of the bisulfate ion in aqueous H_2SO_4 (addressed by Knopf et al. in their response), and a comparison of relative humidities predicted by the models over a wide range of temperatures and concentrations, can be found in the Supporting Information for this Comment.

1. HSO_4^- Dissociation and Thermodynamic Properties

While it is desirable that solution models represent the observed speciation in solution (in this case, the equilibrium $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$), it is not a necessary condition for the accurate representation of solute and solvent activities. When developing the $H_2SO_4-H_2O$ AIM model, Clegg and Brimblecombe[4] included the degree of dissociation data that were available at the time (see their Table 15), but otherwise allowed the calculated HSO_4^-/SO_4^{2-} speciation to vary freely in order to most accurately represent the available activity and thermal data. Consequently, while the calculated degrees of dissociation and $mSO_4^{2-}/mHSO_4^-$ ratios predicted by the AIM model differ from the measurements and model of Knopf et al. at high molalities (their Figures 6 and 7), this does not reflect the relative accuracies of the models in the prediction of water and H_2SO_4 activities. Furthermore, our own tests, discussed in the section below, suggest that the close fit of the Knopf et al. model to their degree of dissociation data was obtained at the expense of an accurate representation of H_2SO_4 and H_2O activities.

The $H_2SO_4-H_2O$ AIM model uses the equation of Dickson et al.[2] for K_{II}, which is based upon data covering the temperature range 283.15−523 K. Knopf et al. show that this expression, when extrapolated to 0 K, does not obey the Nernst heat theorem. However, the Dickson et al.[2] equation only differs significantly from their own below ~225 K. To determine whether this has an effect on the prediction of water and H_2SO_4 activities, these quantities must be compared directly with the available thermodynamic data. We do this in section 3, at the same time correcting errors made by Knopf et al. in their Figures 10 and 11.

2. Thermodynamic Models of $H_2SO_4-H_2O$

The model developed by Knopf et al. to estimate K_{II} from their experimental data is essentially the same as that used by Clegg, Rard, and Pitzer[5] in their critical review of the thermodynamic properties of aqueous H_2SO_4 from 0 to 6 mol kg^{-1} and 273.15 K $\leq T \leq$ 328.15 K. The model of Knopf et al. is stated to be valid from 0 to 40 mol kg^{-1}, and is based on the electromotive force data of Harned and Hamer[6] to an upper molality of 17.5 mol kg^{-1} and the evaluated thermodynamic properties of Giauque et al.[7] at higher molalities and at low temperatures. Knopf et al. do not present any comparisons with the evaluated thermodynamic data (activities and thermal properties) to which their model was fitted.

There are several possible sources of error and uncertainty that will influence the accuracy of fitted models in terms of the calculated α_{HSO_4} values and H_2SO_4 and H_2O activities. We have assessed these sources of error by carrying out test fits of both AIM and the equations of Knopf et al. to primary osmotic coefficient (ϕ), vapor pressure, electromotive force (EMF), and α_{HSO_4} data at 298.15 K (and including osmotic coefficients from the evaluation of Giauque et al.[7] from 16 to 40 mol kg^{-1}). The results suggest the causes of the different predictions of the AIM and the Knopf et al. models, and are also relevant to the application of any ion-interaction model to the $H_2SO_4-H_2O$ system. The key factors are as follows:

(1) *Use of activity coefficients from the work of Harned and Hamer.*[6] The work of Harned and Hamer[6] has been shown by Rard and Clegg[8] to be in error due to the irreversible behavior of the electrochemical cell used, and to further errors introduced by the least-squares smoothing of original data. The activity coefficients at 298.15 K in Table 4 of Harned and Hamer[6] are too high at all molalities, by >30% in $\gamma_\pm^3$ at 5−9 mol kg^{-1}, decreasing to ~13% above 12 mol kg^{-1}. Adjusting the values to correspond to a different standard EMF ($E°$) of the electrochemical cell, as Knopf et al. have done, brings only a small improvement: the errors are still positive and ~8% lower than those noted above.

(2) *The molality range over which the model is applied.* Clegg et al.[5] found that the molality-based model equations, as used by Knopf et al., were able to represent activity and thermal data for aqueous H_2SO_4 to within the experimental uncertainty only to ~6 mol kg^{-1}, just over $^1/_7$ of the maximum molality adopted by Knopf et al. Using the same characteristic weights (w_c) as Clegg et al.[5] for the different data types, we find that deviations of fitted osmotic coefficients from measured values exceed the uncertainty in the data by a factor of 2 or greater when the model

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is fitted to 40 mol kg^{-1}. Degrees of dissociation (α_{HSO_4}) are also very poorly represented (the predicted values are too high by ∼0.2 at 3−4 mol kg^{-1} and too low at all molalities >10 mol kg^{-1}). As expected, the mole-fraction-based equations of AIM yield an improved fit over such an extended molality range, with sums of squared deviations that are only 33% (ϕ), 46% (EMF), and 20% (α_{HSO_4}) of the values obtained with the molality-based equations.

(3) *The relative weighting applied to different types of fitted data.* Both Clegg et al.[5] and Clegg and Brimblecombe[4] adopted weightings determined by the uncertainty and/or probable error in each type of measurement. Our calculations show that the close fit obtained by Knopf et al. to their α_{HSO_4} data (their Figure 7) could only be achieved using an unrealistically high weighting, resulting in deviations of the fitted osmotic coefficients that exceed the experimental uncertainty by up to a factor of 10. These deviations are equivalent to water activities that are too high at 1 mol kg^{-1} by 0.0012, too low at 4 mol kg^{-1} by −0.0016, and too high at 10 mol kg^{-1} by 0.005. They are similar in both sign and magnitude to some of the differences between the Knopf et al. and AIM models that will be shown in the following section.

An important general result of our calculations is that it is not possible to represent both activity *and* α_{HSO_4} data (from whatever source) within experimental uncertainty to 40 mol kg^{-1} using either model. AIM is intended primarily for phase equilibrium calculations (which require water and H_2SO_4 activities) and does not accurately predict α_{HSO_4} at high molalities. By contrast, the Knopf et al. model best represents their own α_{HSO_4} measurements and predicts solute and solvent activities much less well for the reasons given above.

3. Water Activities and H_2SO_4 Activity Coefficients

Meaningful comparisons of the activity coefficient product $\gamma_H{}^2\gamma_{SO_4}$ (Figures 10 and 11 of Knopf et al.) can only be made on the basis of the same ionic speciation at each *total* or stoichiometric H_2SO_4 molality. This correction was not made in the work of Knopf et al. and is the cause of some of the apparent differences between the AIM and Knopf et al. models at higher temperatures. We have therefore adjusted both their activity coefficients and those from the AIM model to a stoichiometric basis using the equation $(\gamma_H mH)^2\gamma_{SO_4}mSO_4 = 4(\gamma_\pm mH_2SO_4)^3$, where the activity coefficients (γ) and species molalities (m) on the left-hand side are those predicted by the models and mH_2SO_4 on the right-hand side is the stoichiometric molality of H_2SO_4 in solution. The quantity $\gamma_\pm$ is the stoichiometric mean activity coefficient of H_2SO_4. We do not consider the single ion activity coefficients plotted in Figures 10 and 11 of Knopf et al. as, individually, they do not have particular thermodynamic significance.

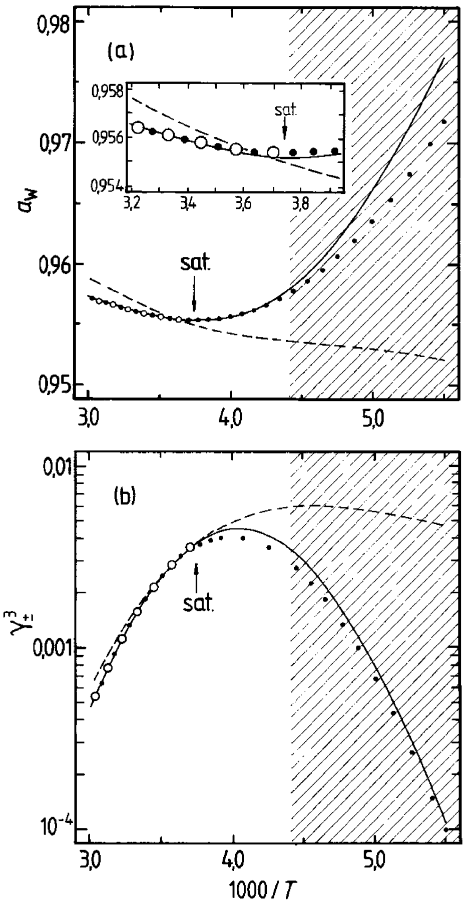

Figure 1. Thermodynamic properties of 10 mass % (1.133 mol kg^{-1}) aqueous H_2SO_4 as a function 1/*T*, where *T* (K) is temperature: (a) water activity (a_w), inset gives detail at high temperatures; (b) cube of the stoichiometric mean activity coefficient of H_2SO_4 ($\gamma_\pm{}^3$). Symbols: open circles, critical review of Clegg et al.;[5] dots, Giauque et al.[7] Lines: solid, AIM model;[4] dashed, model of Knopf et al.[1] Sat.: saturated with respect to ice.

In their review, Clegg et al.[5] present both a model and recommended thermodynamic properties of 0−6.0 mol kg^{-1} aqueous H_2SO_4, from 273.15 to 328.15 K, which have been used as a reference in many other studies. Massucci et al.[9] have reviewed the available models covering a wider range of temperatures and compositions and concluded that the studies of Giauque and co-workers are the most reliable. The publication of Giauque et al.[7] summarizes the evaluated thermodynamic properties of the H_2SO_4−H_2O system and is the culmination of 8 years of exceptionally precise experimental work at low temperatures. The model of Knopf et al. is partially based on the thermal properties from Table 1 of Giauque et al.,[7] and the AIM model was fitted to much of the original experimental data of Giauque and co-workers. Both models thus share a common data set at low temperatures.

In Figure 1, we compare predicted a_w and $\gamma_\pm{}^3$ values for a 10 mass % solution with values from Clegg et al.[5] and Giauque et al.[7] (see also Figure 10 of Knopf et al.). The values from Clegg et al. and Giauque et al. are plotted as points, rather than as lines, because both evaluations have been fitted to a wide range of primary data which they represent to within experimental uncertainty. We are well aware of the sources of data on which the evaluation of Giauque et al. is based (contrary to the impression given by Knopf et al. in their response), as we used all of those original data to develop the AIM model.[4] The evaluation of Giauque et al. provides an accurate representation of thermodynamic properties over the entire liquid range and also agrees well with our own experimental measurements of water vapor pressures for supersaturated solutions.[9] However, calculated water activities for such solutions (including those below the freezing point) are subject to some uncertainty, which is likely to increase with decreasing temperature. The boundary between the hatched and open areas of the plot is the temperature at which homogeneous ice nucleation occurs in aqueous H_2SO_4.[10] This represents the practical limit of supercooling, and comparisons of the model results in the hatched area therefore have little relevance.

The uncertainty in the critically assessed water activities of Clegg et al.[5] at temperatures above that of saturation with respect to ice (268.5 K) is about ±0.0001 to ±0.0002, which is less than the dimensions of the symbols on the plot. Furthermore, the fact that Clegg et al.[5] included heat capacity data (for 283.15 K $\leq T \leq$ 328.15 K) in their evaluation makes it likely that the calculated a_w and $\gamma_\pm{}^3$ values for 1.13 mol kg^{-1} acid in Figure 1 will be accurate for T well below saturation. These heat capacity data were also used to generate dc_p/dT values to improve the accuracy of predictions based on the work of Giauque et al. for this composition. Knopf et al. appear to be unaware of this and do not take it into account in their response. Water activities predicted using the AIM model agree very closely with both the critical review of Clegg et al.[5] and the work of Giauque et al.[7] However, it is clear that both the absolute values of a_w predicted by the Knopf et al. model, and their trend with respect to temperature, are in error even for those conditions ($T \geq$ 273.15 K) for which the thermodynamic properties of dilute H_2SO_4 solutions are well established. The nonlinearities in water and aqueous solution behavior to which Knopf et al. refer in their response are likely to have an effect only at very low temperatures, and we expect the evaluation of Giauque et al. to yield accurate predictions to around 240−250 K.

Activity coefficients for the 10 mass % case are compared in Figure 1b.[11] Again, the AIM model agrees very closely with both the critical review of Clegg et al.[5] and the work of Giauque et al.[7] The Knopf et al. model yields $\gamma_\pm{}^3$ values that are ~40% too high at 330 K, with large deviations also at low temperature.

The comparisons for 50 mass % are shown in Figure 2 (see Figure 11 of Knopf et al.). The AIM model agrees well with the work of Giauque et al. to ~210 K, and at 180 K yields a_w values that are higher by ~0.01. The model of Knopf et al. agrees better at the lowest temperatures but predicts a_w values that are high by ~0.01 at all higher temperatures. This is consistent with the results of the test calculations discussed in the previous section, particularly item 3. Activity coefficients are compared in Figure 2b.[11] In this case, both models disagree, at low T, with the thermodynamic properties of Giauque et al.[7] Predictions of the AIM model are too low by a factor of ~2 at 200 K, rising to ×5 at 180 K. The predictions of the Knopf et al. model appear to be too high by a somewhat larger factor.

These comparisons suggest that, contrary to the impression given by Knopf et al., the AIM model yields a_w values and H_2SO_4 activities that are more accurate than those of the model of Knopf et al. despite predictions of bisulfate dissociation that differ from measured values at low temperatures. A more complete assessment for the 0−40 mol kg^{-1} range, which confirms this result, can be found in the Supporting Information.

Knopf et al. present some comparisons of calculated entropies in their response, although they once more do not include the data to which their model was fitted. We doubt the usefulness of comparisons in terms of a quantity that is difficult to relate to solvent and solute activities directly, and to a relationship (the Nerst heat theorem) that applies only in the limit $T \rightarrow 0$. Our own calculations, in terms of the more useful *total* entropies of solutions (S) which can be compared directly with values listed by Giauque et al.,[7] confirm that: (a) AIM begins to deviate from activities based on the evaluation of Giauque et al. at ~240 K (as is already clear from Figures 1 and 2); (b) Giauque et al.'s evaluation of thermodynamic properties yields reasonable low temperature extrapolations as expected.

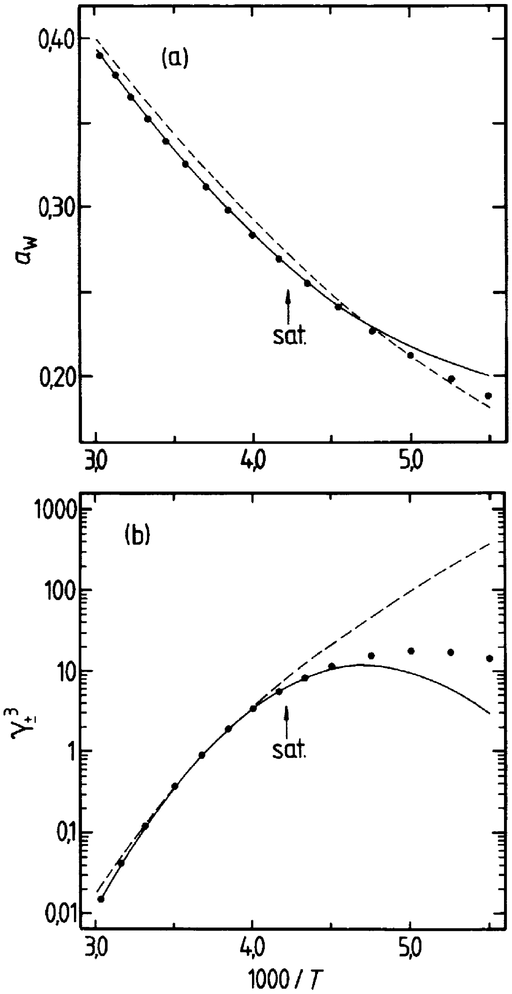

Figure 2. Thermodynamic properties of 50 mass % (10.196 mol kg^{-1}) aqueous H_2SO_4 as a function 1/T, where T (K) is temperature: (a) water activity (a_w); (b) cube of the stoichiometric mean activity coefficient of H_2SO_4 ($\gamma_\pm{}^3$). Symbols: dots, Giauque et al.[7] Lines: solid, model of Clegg and Brimblecombe;[4] dashed, model of Knopf et al.[1] Sat.: saturated with respect to $H_2SO_4 \cdot 4H_2O$(cr).

4. Discussion

Knopf et al. are aware that experimental degrees of dissociation of the HSO_4^- ion do not uniquely constrain ion-interaction models with respect to the prediction of activities and activity coefficients (pp 4327 and 4328 of Knopf et al.). Our comparisons, particularly in Figure 2b and Figure 1 in the Supporting Information, suggest that their model is subject to similar or greater errors than AIM at low temperatures despite the use of improved values of K_{II} and a better representation of α_{HSO_4}. We attribute this to two main factors: the high weighting given to α_{HSO_4} data, and the use of molality-based model equations to a very high concentration. Knopf et al. accept, in their response, that it is not possible to represent both activity *and* α_{HSO_4} data accurately to high molalities with either model. However, contrary to the statement attributed to us, we must point out that this applies to the available degree of dissociation data from all sources and not just to recent measurements.

Future thermodynamic models of H_2SO_4−H_2O at low temperatures should include the degree of dissociation data of Knopf et al. (including their K_{II}) and the recent results of Myrhe et al.[12] in the fitted data sets. On the basis of the calculations carried out here, we would expect a more accurate representation of the trend in α_{HSO_4} with T at all molalities using the two ion-interaction models, but with the predicted α_{HSO_4} values above ~12 mol kg^{-1} likely to be low (as in the current AIM model) where the data have been weighted such that water and H_2SO_4

activities are accurately reproduced. For applications in which a knowledge of α_{HSO_4} itself is important, then the available experimental data should be consulted directly.

It is likely that a revision of models of Clegg and co-workers would result in improved predictions of activities in multicomponent solutions at low temperatures, especially for compositions beyond the range of the single-solute or mixture data to which the models have been fitted. Nonetheless, extensive comparisons[9,13,14] of our models with the available data for solid formation, effective Henry's law constants, and equilibrium vapor pressures show that these properties are predicted satisfactorily within the uncertainties of the experimental measurements.

Supporting Information Available: Comparison of equilibrium relative humidities above 0−80 mass % H_2SO_4 over a wide range of temperatures (including a figure), a brief discussion of available degree of dissociation data, and a note on the adjustment of H_2SO_4 activities from Giaque et al. to an infinite dilution reference state. This material is available free of charge via the Internet at http://pubs.acs.org.

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