J. Phys. Chem. A **2005,** *109,* 2707−2709

Reply to "Comment on the 'Thermodynamic Dissociation Constant of the Bisulfate Ion from Raman and Ion Interaction Modeling Studies of Aqueous Sulfuric Acid at Low Temperatures'"

D. A. Knopf,* B. P. Luo, U. K. Krieger, and
Thomas Koop

Institute for Atmospheric and Climate Science,
Swiss Federal Institute of Technology, Honggerberg HPP,
8093 Zurich, Switzerland

Received: April 20, 2004; In Final Form: June 25, 2004

In their comment, Clegg and Brimblecombe[1] question the validity of both the data and the model of Knopf et al.[2] and conclude that their own "AIM appears to yield more accurate predictions of water and H_2SO_4 activities under most conditions, including low temperatures". In the following, we respond to these criticisms and discuss why we do not agree with these conclusions.

Degree of Dissociation

Clegg and Brimblecombe[1] state that the experimental and modeled values for the degree of dissociation, $\alpha_{HSO_4^-}$, by Knopf et al.[2] are too high when compared to recent experimental data by Myhre et al.,[3] earlier data,[4−8] and the aerosol inorganics model (AIM).[9−13] In Supporting Information Figure 1, we provide a comprehensive overview of available data for $\alpha_{HSO_4^-}$ between 0.5 and 15 mol kg^{-1} at temperatures between 289 and 298 K. The open symbols indicate experimental data that were available before the AIM[9−13] was developed. Only three of these data sets (open squares, triangles, and circles) were obtained in Raman studies,[5,7,8] while the data shown as stars and asterisks were obtained from NMR[4] and density measurements,[6] respectively. Both of the latter studies are only indirect determinations of $\alpha_{HSO_4^-}$, because they did depend on the Raman data by Young et al.[5] (open squares, see discussion in Chen and Irish[7]).

The solid symbols indicate data obtained very recently in four independent Raman studies.[2,3,14,15] Apart from the early Raman data by Turner[8] which are much larger than any of the other data sets, there appears to be a systematic difference between earlier[4−7] and newer[2,3,14,15] data. We do not know the reasons for these differences; however, we note that the older Raman studies by Young[5] (open squares) and Chen and Irish[7] (open circles) were obtained without laser light sources. Such measurements are very difficult because of the low irradiance of mercury arc lamp illumination compared to one by a focused laser beam.[16] In contrast, all of the recent studies[2,3,14,15] (solid symbols) have employed modern laser techniques and provide a consistent picture of the behavior of $\alpha_{HSO_4^-}$.

Also shown in Supporting Information Figure 1 are the results from the AIM[9−13] (dashed lines) and the model by Knopf et al.[2] (solid lines) at 290 and 298.15 K (the upper line belongs to the lower temperature in both cases). The AIM[9−13] deviates from the model of Knopf et al.[2] by 0.1 at 3−4 mol kg^{-1} and is closer to the earlier measurements, while our predictions[2] are consistent with the recent data.[2,3,14,15] This is despite the fact that neither the data of Myhre et al.[3] nor those of Minogue et al.[15] were published when our work was submitted. We note that all of the newer experimental studies,[2,3,14,15] not just that of Knopf et al.[2] (contrary to the impressions given by Clegg and Brimblecombe in the supplement to their Comment[1]), indicate values for the degree of dissociation that are higher than that of 0.33 at 4.0 mol kg^{-1} as given by Clegg et al.[20]

Model Results

Clegg and Brimblecombe[1] argue that three key factors cause the differences between the model of Knopf et al.[2] and existing thermodynamic data: (1) the use of activity coefficients from the work of Harned and Hamer,[17] (2) the molality range over which the model is applied, and (3) the relative weighting applied to the different types of fitted thermodynamic data sets during fitting.

We have used only part of the electromotive force data by Harned and Hamer,[17] namely, those of the cell Pt|H_2(g,p^0)|H_2SO_4(aq)|Hg_2SO_4(s)|Hg(l)|Pt for solutions of H_2SO_4 with concentrations of 0.05−17.5 mol kg^{-1} at temperatures of 273−323 K. We did not use the $E°$ value given by Harned and Hamer[17] but instead fitted $E°$ within our model, resulting in a value of $E° = 0.613\,43$ V. This is much closer to the value recommended by Rard and Clegg[18] (0.612 52 V) than the original value of Harned and Hamer[17] (0.615 52 V). In addition, the data by Giauque et al.[19] were used at H_2SO_4 concentrations of 20−40 mol kg^{-1}.

We agree with Clegg and Brimblecombe[1] that the use of the Harned and Hamer[17] data has contributed to the observed small differences between their critical evaluation[20] and our model at higher temperatures where data are available. However, as Clegg and Brimblecombe[1] point out, "it appears not to be possible to represent both activity and $\alpha_{HSO_4^-}$ data within experimental uncertainty to 40 mol kg^{-1} using either model", that is, even when the data by Harned and Hamer[17] are excluded and a mole-fraction-based model is used.

Following the request by Clegg and Brimblecombe,[1] we show a comparison between water activities predicted by our model and those derived from the evaluated thermal data by Giauque et al.[19] at 298.15 K in Supporting Information Figure 2. The relative differences are always below 10% over the entire concentration range up to 40 mol kg^{-1}. Similar comparisons including predictions by the AIM[9−13] are shown in Figures 1a and 2a and Supporting Information 1 of Clegg and Brimblecombe,[1] over a larger temperature range. The data points in Figures 1 and 2 and Supporting Information Figure 1 as well as the text of Clegg and Brimblecombe[1] imply that the data by Giauque et al.[19] have been measured over the indicated temperature range (180−330 K). However, this is not the case. Therefore, a discussion is in order about the evaluated thermodynamic data set by Giauque et al.[19] These data are based predominantly on thermal measurements of liquid H_2SO_4/H_2O solutions.[21−25] Measurements of the isobaric heat capacity, c_p, have been performed over the entire concentration range at 298 K and between ∼4.5−30.9 mol kg^{-1} H_2SO_4 (∼30−75 wt %) at 253 K. In addition, at several individual compositions larger than 6.9 mol kg^{-1}, the c_p values of liquid solutions have been measured to even lower temperatures. On the basis of these c_p measurements, Giauque et al.[19] provided a detailed table of the thermodynamic properties of H_2SO_4/H_2O solutions at 298.15 K, together with a linear temperature dependent term for the heat capacity, dc_p/dt. The latter are based predominantly on the

---

* To whom correspondence should be addressed. E-mail: knopf@chem.ubc.ca.

10.1021/jp040300t CCC: $30.25

data by Kunzler and Giauque[21] at 253 K. Furthermore, for solutions more dilute than ~4.3 mol kg^{-1}, Giauque et al.[19] do not provide any dc_p/dt data because they did not perform any low temperature c_p measurements in this concentration range. We do not know how Clegg and Brimblecombe[1] derived the "Giauque points" for a 1.13 mol kg^{-1} solution in Figure 1 and those for solutions below 30 wt % shown in Supporting Information Figure 1. We can only speculate that this extrapolation was performed using dc_p/dt values at higher temperatures from other sources. In contrast, it is well established that several thermodynamic properties of water and aqueous solutions behave very nonlinear at temperatures where the liquid is supercooled with respect to ice.[26,27] For example, c_p of water and aqueous solutions increases very strongly when approaching the homogeneous ice nucleation limit,[28–29] a behavior that cannot be inferred by extrapolation of data from higher temperatures. Clegg and Brimblecombe[1] are aware of the nonlinearities in water and aqueous solutions and expect that the evaluation of the Giauque et al. data yields accurate predictions down to ~240−250 K.[19] Therefore, for those solutions at temperatures below ~250 K, any comparison of the AIM[9–13] and the model by Knopf et al.[2] with extrapolated "data" from higher temperatures is inconclusive.

Our Raman measurements show that at low temperatures (also in the range supercooled with respect to ice) the dissociation of the bisulfate ion increases strongly, and hence, the ionic strength also increases. Therefore, it appears to be more reasonable that a_w decreases with decreasing temperature, in disagreement with the strong increase predicted by the AIM.[9–13]

Clegg and Brimblecombe[1] state that comparisons of the models below the homogeneous ice nucleation limit,[30] T_f, have no practical relevance. We certainly agree with this notion; we note, however, that even the observed differences above T_f at H_2SO_4 concentrations between 11 and 25 wt % might have implications for ice nucleation studies.

In their Figures 1b and 2b, Clegg and Brimblecombe[1] show the cube of the stoichiometric mean activity coefficient of H_2SO_4, $\gamma_{\pm}^3$, as a function of temperature for 10 wt % and 50 wt % H_2SO_4/H_2O solutions. $\gamma_{\pm}^3$ is directly related to the excess Gibbs free energy, $G^{ex} = RT \ln \gamma_{\pm}^3$, of the ions $2H^+ + SO_4^{2-}$ in an aqueous H_2SO_4 solution. G^{ex} is the difference between the Gibbs free energy in a real solution, G^r, and in an ideal solution, G^{id} (see Knopf et al.[2] and Pitzer[31]). With the Gibbs–Helmholtz relationship, also the excess entropy, S^{ex}, of $2H^+ + SO_4^{2-}$ ions in the solution can be derived. The Nernst heat theorem[32] says that the entropy of an ideal system, S^{id}, approaches 0 as the temperature approaches 0 K, while, for nonideal substances, a positive residual in S^r may remain. It follows that the excess entropy of a real solution $S^{ex} = S^r - S^{id}$ approaches a positive value at lower temperatures. Supporting Information Figure 3 shows this excess entropy as a function of temperature for a 50 wt % H_2SO_4/H_2O solution, calculated using both models. The negative values of S^{ex} calculated with the AIM[9–13] (dashed line in Supporting Information Figure 3) imply a negative entropy of S^r, as the entropy of the ideal solution, S^{id}, approaches zero when $T \rightarrow 0$ K, in contradiction with the Nernst heat theorem.[32] In contrast, the entropy derived from the Knopf et al.[2] model obeys the thermodynamic law and shows a residual entropy, just as expected for a real solution.

Conclusion

We agree that the AIM[9–13] is probably more accurate than our model at describing activities for temperatures at which data are available. We also agree with Clegg and Brimblecombe[1] that the inclusion of the new dissociation data makes it impossible to fit the model with the same accuracy to the thermodynamic data because of the additional constraints. However, we believe that the incorporation of $\alpha_{HSO_4^-}$ and the new evaluation of thermodynamic dissociation constant K_{II} do make our model[2] more realistic in terms of the underlying physics. Both these facts are likely to improve the ability of our model to extrapolate to lower temperatures, while making it somewhat less accurate than the AIM[9–13] at higher temperatures.

Clegg and Brimblecombe[1] state that "while it is generally desirable that solution models represent the observed speciation in solution ..., it is not a necessary condition for the accurate representation of solute and solvent activities". This is true. However, whether such an approach is desirable or even preferable to a model that is only slightly less accurate in terms of activities but agrees with measured ion concentrations is a matter of debate. It appears that Clegg and Brimblecombe[1] consider speciation data to be less important than activities; in contrast, we think both are equally important. One reason for our opinion is that laboratory work often depends crucially on the ion concentrations rather than on the ion activities, for example, spectroscopic work aimed at determining the real and imaginary parts of the refractive indices of aerosols or IR flow tube studies to determine phase changes in aqueous aerosols at low temperatures. Obviously, for such purposes, it would be more reasonable to use the model of Knopf et al.[2]

For these reasons, we agree with Clegg and Brimblecombe[1] that a revision of the existing models is desirable and that future models should include the degree of dissociation data of Knopf et al.[2] and Myhre et al.[3] as well as the thermodynamic dissociation constant K_{II} derived in Knopf et al.[2]

Supporting Information Available: Figures showing experimentally determined and modeled degrees of dissociation, $\alpha_{HSO_4^-}$, water activity, a_w, and the excess entropy, S^{ex}, of $2H^+ + SO_4^{2-}$ ions in a 50 wt % H_2SO_4 solution. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Clegg, S. L.; Brimblecombe, P. *J. Phys. Chem. A* **2005**, *109*, 2703–2706.

(2) Knopf, D. A.; Luo, B. P.; Krieger, U. K.; Koop, T. *J. Phys. Chem. A* **2003**, *107*, 4322–4332.

(3) Myhre, C. E. L.; Christensen, D. H.; Nicolaisen, F. M.; Nielsen, C. J. *J. Phys. Chem. A* **2003**, *107*, 1979–1991.

(4) Hood, C. D.; Reilly, C. A. *J. Chem. Phys.* **1957**, *27*, 1126–1128.

(5) Young, T. F.; Maranville, L. F.; Smith, H. M. Raman Spectral Investigations of Ionic Equilibria in Solutions of Strong Electrolytes. In *The Structure of Electrolyte Solutions*; Hamer, W. J., Ed.; Wiley: New York, 1959.

(6) Lindstrom, R. E.; Wirth, H. E. *J. Phys. Chem.* **1969**, *73*, 218–223.

(7) Chen, H.; Irish, D. E. *J. Phys. Chem.* **1971**, *75*, 2672–2681.

(8) Turner, D. J. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 1346–1356.

(9) Wexler, A. S.; Clegg, S. L. *J. Geophys. Res.* **2002**, *107*, 4207–4221.

(10) Carslaw, K. S.; Clegg, S. L.; Brimblecombe, P. *J. Phys. Chem.* **1995**, *99*, 11557–11574 (http://www.hpc1.uea.ac.uk/e770/aim.html).

(11) Massucci, M.; Clegg, S. L.; Brimblecombe, P. *J. Phys. Chem. A* **1999**, *103*, 4209–4226 (http://www.hpc1.uea.ac.uk/e770/aim.html).

(12) Clegg, S. L.; Brimblecombe, P.; Wexler, A. S. *J. Phys. Chem. A* **1998**, *102*, 2137–2154 (http://www.hpc1.uea.ac.uk/e770/aim.html).

(13) Clegg, S. L.; Brimblecombe, P.; Wexler, A. S. *J. Phys. Chem. A* **1998**, *102*, 2155–2171.

(14) Tomikawa, K.; Kanno, H. *J. Phys. Chem. A* **1998**, *102*, 6082–6088.

(15) Minogue, N.; Riordan, E.; Sodeau, J. R. *J. Phys. Chem. A* **2003**, *107*, 4436–4444.

(16) Hawes, R. C.; George, K. P.; Nelson, D. C.; Beckwith, R. *Anal. Chem.* **1966**, *38*, 1842–1847.

(17) Harned, H. S.; Hamer, W. J. *J. Am. Chem. Soc.* **1935**, *57*, 27−35.

(18) Rard, J. A.; Clegg, S. L. *J. Chem. Thermodyn.* **1995**, *27*, 69−98.

(19) Giauque, W. F.; Hornung, E. W.; Kunzler, J. E.; Rubin, T. R. *J. Am. Chem. Soc.* **1960**, *82*, 62−70.

(20) Clegg, S. L.; Rard, J. A.; Pitzer, K. S. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1875−1894.

(21) Kunzler, J.; Giauque, W. *J. Am. Chem. Soc.* **1952**, *74*, 3472−3476.

(22) Kunzler, J.; Giauque, W. *J. Am. Chem. Soc.* **1952**, *74*, 797−800.

(23) Rubin, T.; Giauque, W. *J. Am. Chem. Soc.* **1952**, *74*, 800−804.

(24) Hornung, E.; Giauque, W. *J. Am. Chem. Soc.* **1955**, *77*, 2983−2987.

(25) Hornung, E.; Brackett, T.; Giauque, W. *J. Am. Chem. Soc.* **1956**, *78*, 5747−5751.

(26) Franks, F. The properties of aqueous solutions at subzero temperatures. In *Water a comprehensive treatise*; Franks, F., Ed.; Plenum Press: New York, 1982; Vol. 7.

(27) Angell, C. A. Supercooled water. In *Water a comprehensive treatise*; Franks, F., Ed.; Plenum Press: New York, 1982; Vol. 7.

(28) Oguni, M.; Angell, C. A. *J. Chem. Phys.* **1980**, *73*, 1948−1954.

(29) Archer, D. G.; Carter, R. W. *J. Phys. Chem. B* **2000**, *104*, 8563−8584.

(30) Koop, T.; Luo, B. P.; Tsias, A.; Peter, T. *Nature* **2000**, *406*, 611−614.

(31) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; CRC Press: Boca Raton, FL, 1991.

(32) Nernst, W. *Nachr. Ges. Wiss. Goettingen, Math.-Phys. Kl.* **1906**, 1−40.