

Comment on the "Thermodynamic Dissociation Constant of the Bisulphate Ion from Raman and Ion Interaction Modelling Studies of Aqueous Sulphuric Acid at Low Temperature" by D. A. Knopf, B. P. Luo, U. K. Krieger, and Thomas Koop (*J. Phys. Chem. A* **2003**, *107*, 4322-4332)

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Knopf *et al.*<sup>1</sup> have recently determined the degrees of dissociation of the bisulphate ion ( $\alpha_{\text{HSO}_4}$ ) in aqueous sulphuric acid to low temperature. The results, together with similar measurements of Myrhe *et al.*,<sup>2</sup> are a valuable addition to the available data for the acid and will enable more reliable models of aqueous mixtures containing sulphuric acid to be developed.

The authors use an ion-interaction model, in which individual species molalities and activity coefficients are calculated, to estimate the value of the thermodynamic dissociation constant ( $K_{II}$ ) for bisulphate dissociation 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.*<sup>3</sup> which was used in the Aerosol Inorganics Models (*AIM*) of Clegg and co-workers for the systems  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ ,<sup>4</sup>  $\text{H}^+\text{-HSO}_4^-\text{-SO}_4^{2-}\text{-NO}_3^-\text{-Cl}^-\text{-Br}^-\text{-H}_2\text{O}$ ,<sup>5-7</sup> and  $\text{H}^+\text{-NH}_4^+\text{-HSO}_4^-\text{-SO}_4^{2-}\text{-NO}_3^-\text{-H}_2\text{O}$ .<sup>5,6</sup> Knopf *et al.* go on to compare their own model with *AIM* for  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ <sup>4</sup> (not cited by Knopf *et al.*) in terms of bisulphate 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  $\text{H}_2\text{SO}_4$  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 sulphate aerosols, for which the *AIM* models are 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  $\text{H}_2\text{SO}_4$  activities. We show that the *AIM* model appears to yield more accurate predictions of water and  $\text{H}_2\text{SO}_4$  activities under most conditions, including low temperatures. We determine the reasons for this and offer some general comments on the limitations of the models.

## 1. $\text{HSO}_4^-$ Dissociation and Thermodynamic Properties

While it is generally desirable that solution models represent the observed speciation in solution (in this case the equilibrium  $\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$ ), it is not a necessary condition for the accurate representation of solute and solvent activities. When developing the *AIM*  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  model Clegg and Brimblecombe<sup>4</sup> included the degree of dissociation data that were available at the time (at 273.15 K, 298.15 K, and 323.15 K - see their Table 15), but otherwise allowed the calculated  $\text{HSO}_4^-/\text{SO}_4^{2-}$  speciation to vary freely in order to most accurately represent the available activity and thermal data. Consequently, while the calculated degrees of dissociation, and  $m\text{SO}_4^{2-}/m\text{HSO}_4^-$  ratios, predicted by the *AIM* model differ from the measurements and model of Knopf *et al.* at high molality (their Figures 6 and 7) this does not reflect the relative accuracies of the models in the prediction of water and  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  activities.

We have a further comment regarding Figures 6 and 7 of Knopf *et al.* At molalities below about  $4 \text{ mol kg}^{-1}$  their experimental results and  $\alpha_{\text{HSO}_4}$  calculated using *AIM* agree quite well at all  $T$ , apart from a roughly constant offset of about 0.075 to 0.1. Comparisons at 298.15 K both with the recent experiments of Myrhe *et al.*,<sup>2</sup> and with five earlier studies (not cited by Knopf *et al.*, see Table 15 of Clegg and Brimblecombe<sup>4</sup>), suggest that both experimental and fitted  $\alpha_{\text{HSO}_4}$  of Knopf *et al.* are high by about 0.1.

The *AIM*  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  model uses the equation of Dickson *et al.*<sup>3</sup> for  $K_{II}$ , which is based upon data covering the temperature range 283.15 K to 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.*<sup>3</sup> equation only differs significantly from their own below about 225 K. In order to determine whether this has an effect on the prediction of water and  $\text{H}_2\text{SO}_4$  activities these quantities must be compared directly with 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 $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$

The model developed by Knopf *et al.* to estimate  $K_{II}$  from their experimental data is based upon the ion-interaction equations of Pitzer,<sup>8</sup> including a one parameter extension

originally proposed by Archer.<sup>9</sup> It is essentially the same as that used by Clegg, Rard and Pitzer<sup>10</sup> in their critical review of the thermodynamic properties aqueous H<sub>2</sub>SO<sub>4</sub> from 0-6 mol kg<sup>-1</sup> and 273.15 K ≤ T ≤ 328.15 K. The model of Knopf *et al.* is stated to be valid from 0 to 40 mol kg<sup>-1</sup>, although the Harned and Hamer<sup>11</sup> activity coefficient data on which it is based are limited to an upper molality of 17.5 mol kg<sup>-1</sup>. 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 calculated  $\alpha_{\text{H}_2\text{SO}_4}$ , and H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O 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 ( $\phi$ ), vapour pressure, electromotive force (EMF), and  $\alpha_{\text{H}_2\text{SO}_4}$  data at 298.15 K (and including osmotic coefficients from the evaluation of Giaque *et al.*<sup>12</sup> from 16 to 40 mol kg<sup>-1</sup>). The results suggest the causes of the different predictions of the *AIM* and Knopf *et al.* models, and are also relevant to the application of any ion-interaction model to the H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O system. The key factors are as follows:

(1) *Use of activity coefficients from the work of Harned and Hamer*<sup>11</sup>. The work of Harned and Hamer<sup>11</sup>, and of Hamer,<sup>13</sup> has been shown to be in error (see Rard and Clegg,<sup>14</sup> and references therein) due to irreversible behaviour of the electrochemical cell used, and to further errors introduced by the least-squares smoothing of original data. Activity coefficients at 298.15 K in Table IV of Harned and Hamer<sup>11</sup> are too high at all molalities, by >30% in  $\gamma_{\pm}^3$  at 5-9 mol kg<sup>-1</sup>, decreasing to about 13% above 12 mol kg<sup>-1</sup>. Adjusting the values to correspond to a different standard EMF of the electrochemical cell, as Knopf *et al.* have done (pers. comm.), brings only a small improvement: errors are still positive, and about 8% lower than those noted above.

(2) *The molality range over which the model is applied.* Clegg *et al.*<sup>10</sup> found that the molality-based equations were able to represent activity and thermal data for aqueous H<sub>2</sub>SO<sub>4</sub> to within the experimental uncertainty only to about 6 mol kg<sup>-1</sup>, just over 1/7 of the maximum molality adopted by Knopf *et al.* Using the same characteristic weights ( $w_c$ ) as Clegg *et al.*<sup>10</sup> 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 two or greater, and  $\alpha_{\text{H}_2\text{SO}_4}$  are very poorly represented (predicted values are too high by about 0.2 at 3-4 mol kg<sup>-1</sup>, and too low at all molalities >10 mol kg<sup>-1</sup>). 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% ( $\phi$ ), 46% (EMF) and 20% ( $\alpha_{\text{H}_2\text{SO}_4}$ ) of the values obtained with the molality-based equations.

(3) *The relative weighting applied to different types of fitted data.* Both Clegg *et al.*<sup>10</sup> and Clegg and Brimblecombe<sup>4</sup> 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  $\alpha_{\text{H}_2\text{SO}_4}$  data (their Figure 7) could only be achieved by assigning a very high weight, resulting in deviations of the fitted osmotic coefficients that exceed the experimental uncertainty by up a factor of 10. These deviations are equivalent to water activities that are too high at 1 mol kg<sup>-1</sup> by 0.0012, too low at 4 mol kg<sup>-1</sup> by -0.0016, and too high at 10 mol kg<sup>-1</sup> 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.

We also note that the model of Knopf *et al.* does not include unsymmetrical mixing terms<sup>8</sup> which are important in dilute solutions. However, this omission has a negligible effect compared to (1) to (3) above.

An important general result of our calculations it appears not to be possible to represent both activity *and*  $\alpha_{\text{H}_2\text{SO}_4}$  data within experimental uncertainty to 40 mol kg<sup>-1</sup> using either model (and assumed ionic species H<sup>+</sup>, HSO<sub>4</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>). *AIM* is intended primarily for phase equilibrium calculations (which require water and H<sub>2</sub>SO<sub>4</sub> activities), and does not accurately predict  $\alpha_{\text{H}_2\text{SO}_4}$  at high molality. By contrast the Knopf *et al.* model best represents their own  $\alpha_{\text{H}_2\text{SO}_4}$  measurements, and is likely to predict solute and solvent activities much less well for the reasons given above. Water activities, and H<sub>2</sub>SO<sub>4</sub> activity coefficients, predicted by the two models are compared in the following section.

### 3. Water Activities and H<sub>2</sub>SO<sub>4</sub> Activity Coefficients

Meaningful comparisons of the activity coefficient product  $\gamma_{\text{H}^+}^2\gamma_{\text{SO}_4^{2-}}$  (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<sub>2</sub>SO<sub>4</sub> 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. Using values supplied by Knopf *et al.* we have adjusted both their activity coefficients and those from the *AIM* model to a stoichiometric basis using the equation:

$$(\gamma_{\text{H}^+}m_{\text{H}^+})^2\gamma_{\text{SO}_4^{2-}}m_{\text{SO}_4^{2-}} = 4(\gamma_{\pm}m_{\text{H}_2\text{SO}_4})^3 \quad (1)$$

where the activity coefficients ( $\gamma$ ) and species molalities ( $m$ ) on the left hand side are those predicted by the models, and  $m\text{H}_2\text{SO}_4$  on the right hand side is the stoichiometric molality of  $\text{H}_2\text{SO}_4$  in solution. The quantity  $\gamma_{\pm}$  is therefore the stoichiometric mean activity coefficient of  $\text{H}_2\text{SO}_4$ . We do not consider the single ion activity coefficients plotted in Figure 10 and 11 of Knopf *et al.* as, individually, they do not have particular thermodynamic significance.

As noted above, Clegg *et al.*<sup>10</sup> have critically reviewed the available thermodynamic data for aqueous  $\text{H}_2\text{SO}_4$  solutions for 0 to 6.0 mol kg<sup>-1</sup> and 273.15 K to 328.15 K, and presented both a model and recommended values that have been used as a reference in many other studies. Massucci *et al.*<sup>15</sup> have reviewed the available models covering a wider range of temperature and composition and concluded that the studies of Giaque and co-workers are the most reliable. The publication of Giaque *et al.*<sup>12</sup> summarises the evaluated thermodynamic properties of the  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  system and is the culmination of eight years of exceptionally precise experimental work at low temperature. The model of Knopf *et al.* is partially based upon thermal properties from Table 1 of Giaque *et al.*,<sup>12</sup> and the *AIM* model was fitted to much of the original experimental data of Giaque and co-workers. Both models thus appear to share a common data set at low temperature.

In Figure 1 we compare predicted  $a_w$  and  $\gamma_{\pm}$ <sup>3</sup> for a 10 mass% solution with values from Clegg *et al.*<sup>10</sup> and Giaque *et al.*<sup>12</sup> (see also Figure 10 of Knopf *et al.*). The boundary between the hatched and open areas of the plot is the temperature at which homogeneous ice nucleation occurs in aqueous  $\text{H}_2\text{SO}_4$ .<sup>16</sup> 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.*<sup>10</sup> at temperatures above that of saturation with respect to ice (268.5 K) is about  $\pm 0.0001$  to  $\pm 0.0002$  - less than the dimensions of the symbols on the plot. Furthermore, the fact that Clegg *et al.*<sup>10</sup> included heat capacity data (for  $283.15 \leq T \leq 328.15$  K) in their evaluation make it likely that the calculated  $a_w$  and  $\gamma_{\pm}$ <sup>3</sup> will be accurate for  $T$  well below saturation. Water activities predicted using the *AIM* model agree very closely with both the critical review of Clegg *et al.*<sup>10</sup> and the work of Giaque *et al.*<sup>12</sup> However, it is clear that both 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  $\text{H}_2\text{SO}_4$  solutions are well established. Activity coefficients for the 10 mass% case are compared in Figure 1b. Again, the *AIM* model agrees very closely with both the critical

review of Clegg *et al.*<sup>10</sup> and the work of Giaque *et al.*<sup>12</sup> The Knopf *et al.* model yields  $\gamma_{\pm}^3$  that are about 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 Giaque *et al.* to about 210 K, and at 180 K yields  $a_w$  that higher by about 0.01. The model of Knopf *et al.* agrees better at the lowest temperatures, but predicts  $a_w$  that are high by about 0.01 at all higher temperatures. This is consistent with results of the test calculations discussed in the previous section, particularly item (3). Activity coefficients are compared in Figure 2b.<sup>17</sup> In this case both models disagree, at low T, with the thermodynamic properties of Giaque *et al.*<sup>12</sup> Predictions of the *AIM* model are too low by a factor of about x2 at 200 K rising to x5 at 180 K. The predictions of the Knopf *et al.* model appear to be too high by a somewhat larger factor.

These limited comparisons suggest that, contrary to the impression given by Knopf *et al.*, the *AIM* model yields  $a_w$  and H<sub>2</sub>SO<sub>4</sub> activities that are more accurate than that of Knopf *et al.* despite predictions of bisulphate dissociation that differ from measured values at low temperatures. A more complete assessment can be made from Figure 3. This shows equilibrium relative humidities calculated from the work of Giaque *et al.*<sup>12</sup> (symbols), and both *AIM* and Knopf *et al.* models (lines), superimposed on the H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O phase diagram. Temperatures below the homogeneous ice nucleation temperature are again shown by hatching. A line corresponding to a typical trajectory of a stratospheric H<sub>2</sub>SO<sub>4</sub> particle (5 ppmv H<sub>2</sub>O, 100 mbar altitude) is included, indicating that the combination of very high mass% H<sub>2</sub>SO<sub>4</sub> 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.

#### 4. Discussion

Knopf *et al.* are aware that experimental degrees of dissociation of the HSO<sub>4</sub><sup>-</sup> ion do not uniquely constrain ion-interaction models with respect to the prediction of activities and activity coefficients (p.4327 and p.4328 of Knopf *et al.*). Our comparisons - particularly in Figures 2b and 3 - suggest that their model is subject to similar or greater errors than *AIM* at low temperature despite the use of improved values of  $K_{II}$  and a better representation of  $\alpha_{\text{HSO}_4}$ . We attribute this to two main factors: the high weighting given to  $\alpha_{\text{HSO}_4}$  data, and use of molality-based model equations to a very high concentration.

One of the most important practical applications of the *AIM* models is the calculation of  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{HBr}$  solubilities in low temperature  $\text{H}_2\text{SO}_4$  aerosols. The thermodynamic properties of aqueous solutions of these acids at low temperature, and of other important aerosol components such as  $(\text{NH}_4)_2\text{SO}_4$ , are required for such calculations but are poorly known compared to those of  $\text{H}_2\text{SO}_4$ . This is likely to remain a significant limitation for some time, and should be born in mind when using the models.

As stated earlier, future thermodynamic models of  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  at low temperature should include the degree of dissociation data of Knopf *et al.* (including their  $K_{II}$ ), and of Myrhe *et al.* and earlier workers, in the fitted datasets. Based on the calculations we have carried out here we would expect a more accurate representation of the trend in  $\alpha_{\text{HSO}_4}$  with  $T$  at all molalities using the two ion-interaction models. However, predicted values  $\alpha_{\text{HSO}_4}$  above about  $12 \text{ mol kg}^{-1}$  would still be low (as in the current *AIM* model) where the data have been weighted such that water and  $\text{H}_2\text{SO}_4$  activities are accurately reproduced. For applications in which a knowledge of  $\alpha_{\text{HSO}_4}$  itself is important then the available experimental data should be consulted.

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<sup>5,15,6</sup> of our models with the available data for solid formation, effective Henry's law constants, and equilibrium vapour pressures show that these properties are predicted satisfactorily within the uncertainties of the experimental measurements.

## References and Notes

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- (17) H<sub>2</sub>SO<sub>4</sub> activities calculated from Table 1 of Giauque *et al.*<sup>12</sup> have a reference state of pure liquid H<sub>2</sub>SO<sub>4</sub>. 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<sub>2</sub>SO<sub>4</sub> varies strongly with molality) we have determined the reference state correction as follows: the mean activity coefficient of H<sub>2</sub>SO<sub>4</sub> was calculated relative to both a reference state of infinite dilution (Clegg and Brimblecombe<sup>4</sup> model) and pure liquid H<sub>2</sub>SO<sub>4</sub> (Table 1 of Giauque *et al.*) at five molalities from 5.0 to 25.0 mol kg<sup>-1</sup> 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<sub>2</sub>SO<sub>4</sub> activities relative to the two reference states agree very closely at all temperatures and molalities. The following equation was fitted:

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

This was used to estimate  $\gamma_{\pm}$  for temperatures below 250 K from H<sub>2</sub>SO<sub>4</sub> activities calculated from Table 1 of Giauque *et al.*, and are the values plotted in Figure 2b.

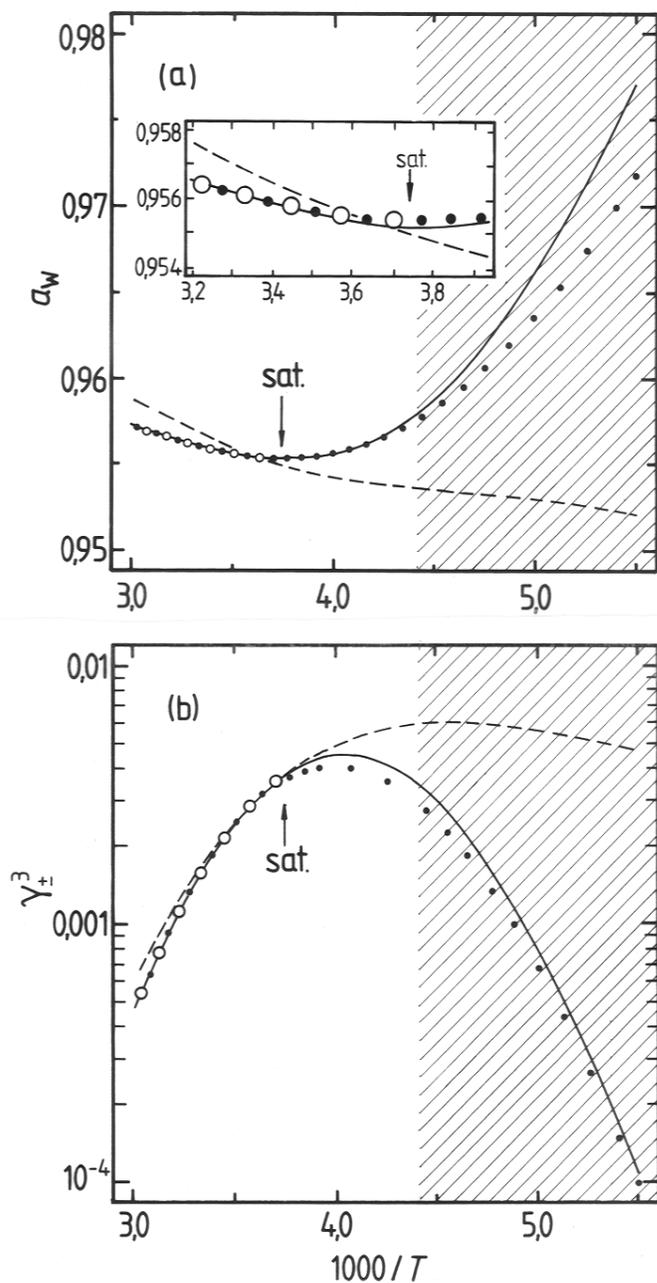


Fig. 1. Thermodynamic properties of 10 mass% ( $1.133 \text{ mol kg}^{-1}$ ) aqueous H<sub>2</sub>SO<sub>4</sub> as a function  $1/T$ , where  $T$  (K) is temperature. (a) Water activity ( $a_w$ ), inset gives detail at high temperature. (b) Cube of the stoichiometric mean activity coefficient of H<sub>2</sub>SO<sub>4</sub> ( $\gamma_{\pm}^3$ ). Symbols: open circles - critical review of Clegg *et al.*<sup>10</sup>; dots - Giauque *et al.*<sup>12</sup>. Lines: solid - AIM model<sup>4</sup>; dashed - model of Knopf *et al.*<sup>1</sup>

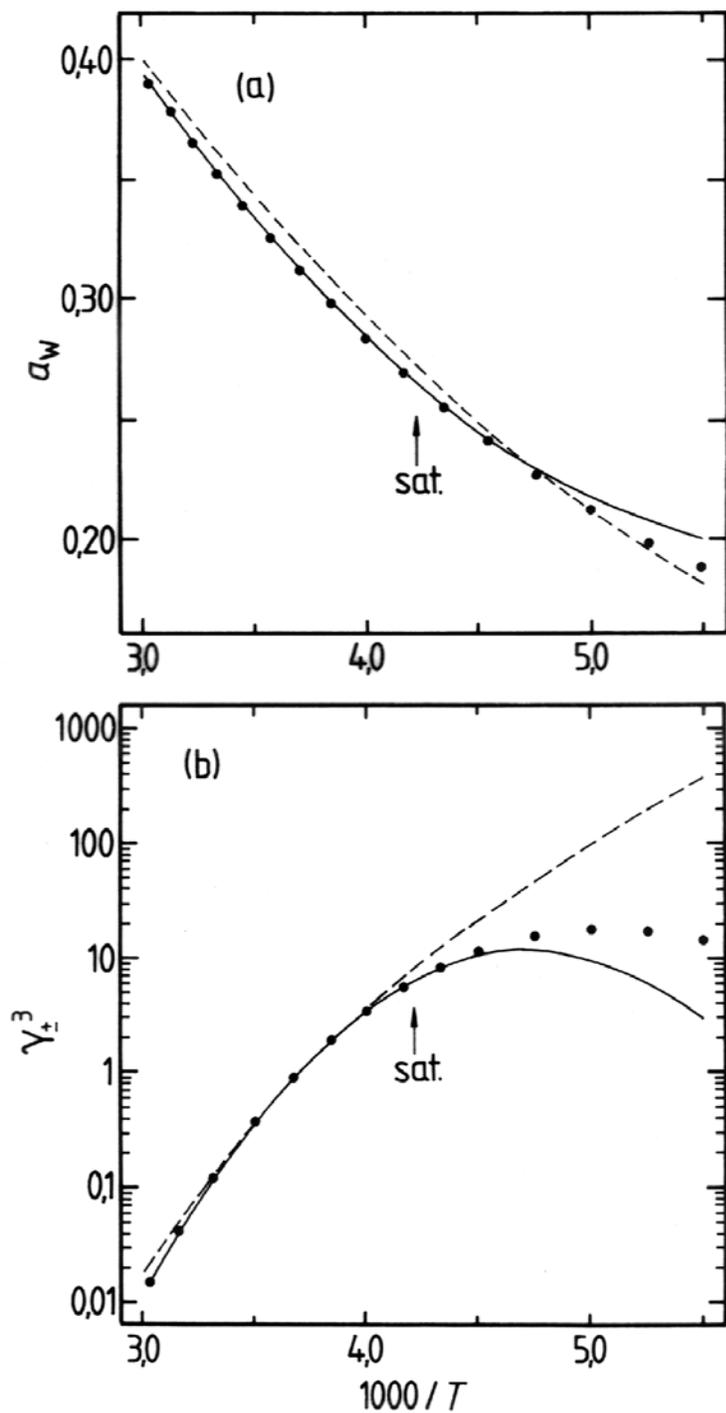


Fig. 2. Thermodynamic properties of 50 mass% ( $10.196 \text{ mol kg}^{-1}$ ) aqueous  $\text{H}_2\text{SO}_4$  as a function  $1/T$ , where  $T$  (K) is temperature. (a) Water activity ( $a_w$ ). (b) Cube of the stoichiometric mean activity coefficient of  $\text{H}_2\text{SO}_4$  ( $\gamma_{\pm}^3$ ). Symbols: - Giaque *et al.*<sup>12</sup>. Lines: solid - model of Clegg and Brimblecombe<sup>4</sup>; dashed - model of Knopf *et al.*<sup>1</sup>

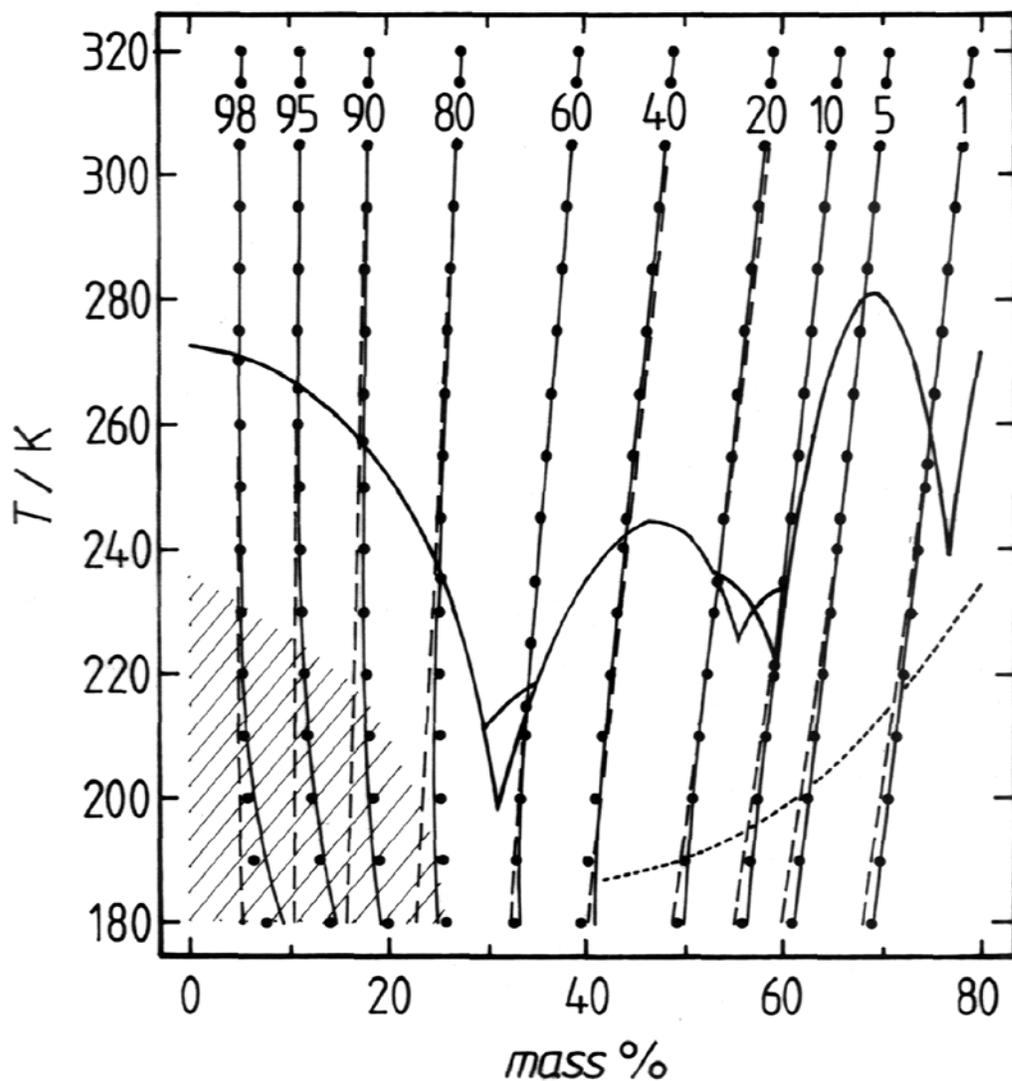


Fig. 3. Equilibrium relative humidities, from 1% to 98%, above aqueous  $\text{H}_2\text{SO}_4$  as a function of temperature and mass%  $\text{H}_2\text{SO}_4$ . Symbols: calculated from the thermodynamic evaluation of Giauque *et al.*<sup>12</sup> Lines: solid - AIM model;<sup>4</sup> dashed - model of Knopf *et al.*<sup>1</sup> thick solid - saturation of aqueous  $\text{H}_2\text{SO}_4$  with respect to ice (furthest left) and  $\text{H}_2\text{SO}_4$  hydrates; dotted - trajectory of a typical stratospheric  $\text{H}_2\text{SO}_4$  droplet for 5ppmv  $\text{H}_2\text{O}$  and 100 mbar altitude. Hatched area: the upper boundary marks the practical limit of supercooling of dilute aqueous solutions before ice nucleation occurs.<sup>16</sup>