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Equilibrium Vapor Pressure of H_2O above Aqueous H_2SO_4 at Low Temperature

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Equilibrium partial pressures of water ($p(H_2O)$) over solutions of (5.054 to 26.18) mol kg^{-1} H_2SO_4 from (314.2 to 196.5) K have been determined using capacitance manometers in order to (1) obtain data for compositions relevant to the stratospheric aerosol and (2) extend and test present knowledge of the thermodynamic properties of aqueous H_2SO_4 at low temperature. Current approaches to calculating $p(H_2O)$ from existing thermodynamic data are critically examined and compared to measurements made in this study and others in the literature. The reliability (to within about ±10% at the lowest temperatures) of predictions of $p(H_2O)$ using liquid phase thermodynamic properties determined by Giauque and co-workers is confirmed for solutions from 4.37 mol kg^{-1} to at least 25 mol kg^{-1}.

1. Introduction

The importance of stratospheric H_2SO_4 aerosols (e.g., Steele and Hamill, 1981; Molina *et al.*, 1993), and the widespread industrial use of H_2SO_4, has led to a number of evaluations and correlations of the thermodynamic properties of the aqueous acid (Giauque *et al.*, 1960; Gmitro and Vermeulen, 1964; Bolsaitis and Elliott, 1990; Zeleznik, 1991; Clegg and Brimblecombe, 1995). Treatments of vapor−liquid equilibria involving aqueous H_2SO_4 have traditionally emphasised behaviour at relatively high temperatures (e.g., Greenewalt, 1925; Gmitro and Vermeulen, 1964; Bolsaitis and Elliott, 1990). However, for stratospheric applications, equilibrium partial pressures of water over solid hydrates and aqueous solutions (up to about 30 mol kg^{-1}) from 240 K to <200 K are required. These have recently been measured by Zhang *et al.* (1993a), who have also determined partial pressures over aqueous mixtures of H_2SO_4 with HNO_3 and HCl (Zhang *et al.*, 1993b), and by Becker *et al.* (1995), supplementing the early data of Daudt (1923). Our own approach to the problem has so far been theory-based, developing first a model of the H_2- + H_2O system using existing measurements of liquid phase properties (Clegg and Brimblecombe, 1995) and then extending this further to acid mixtures (Carslaw *et al.*, 1995).

There are significant discrepancies in terms of liquid phase water activity and equilibrium partial pressures of water ($p(H_2O)$) at low temperatures between both the available data, which remain sparse, and the various thermodynamic correlations. For example, Clegg and Brimblecombe (1995) noted differences in calculated water activities for 40 mol kg^{-1} H_2SO_4 between their model and the earlier correlation of Zeleznik (1991) of >10% at 298.15 K, and 30% at 250 K. By contrast, water vapor pressures calculated using the model of Clegg and Brimblecombe agree with values based on the thermodynamic properties tabulated by Giauque *et al.* (1960) to within ±5% for molalities less than 35 mol kg^{-1} and to temperatures as low as 193 K. The equations of Gmitro and Vermeulen (1964), based mostly on the results of Giauque *et al.* (1960), agree only to within about ±10% and yield vapor pressures that are inconsistent with the observed freezing curve of H_2SO_4 with respect to ice. Water partial pressures measured by Becker *et al.* (1995) for 35 mass % H_2SO_4 agree to within experimental error with our model predictions for temperatures below about 225 K. However, the measurements of Zhang *et al.* (1993a) deviate systematically from predictions using the correlations of both Clegg and Brimblecombe (1995) and Zeleznik (1991) by up to 20% or more (Clegg and Brimblecombe, 1995).

In view of these differences there is a need, first, to establish the vapor−liquid equilibrium of aqueous H_2SO_4 and its mixtures with other acids at low temperature and for compositions relevant to the stratosphere. Second, it is important to resolve the disagreements between existing thermodynamic property correlations noted above, and hence validate models for practical calculations. We have therefore measured equilibrium vapor pressures over (5 to 26) mol kg^{-1} H_2SO_4 from <200 K to about 315 K as part of a larger study of aqueous acid mixtures at low temperatures. Correlations of the thermodynamic properties of the aqueous acid are then reviewed and compared with our experimental results and those of other workers. Recommendations are made as to the most accurate method of calculating equilibrium partial pressures of H_2O over aqueous H_2SO_4 at low temperature, based on current data.

2. Experiments

Equilibrium pressures of water were measured using a method similar to that described by Hanson and Mauersberger (1988) for HNO_3 and Miller (1983) for HCl. In this method the pressure over the aqueous test solution, which has been previously degassed to remove dissolved air, is determined directly at a known temperature using capacitance manometers.

The concentrations of the test solutions were chosen, first, to match those thought to occur in the stratospheric aerosol during winter—about 7.5 mol kg^{-1} at 195 K for a water partial pressure of 5×10^{-4} mbar (Steele and Hamill, 1981)—and to obtain measurements at the lowest possible temperature subject to the constraints of the freezing properties of the aqueous acid. Second, two higher molalities (about 25 mol kg^{-1}) were measured as a specific test of the theoretical methods of calculating $p(H_2O)$, because existing predictions differ by >10% for temperatures below 233 K (section 5).

(a) Apparatus. The experimental setup is shown in Figure 1 and consists of a twin walled glass cell connected to a vacuum line, thermostatic bath, pressure gauges, and an acid solution reservoir. In a typical experiment, the

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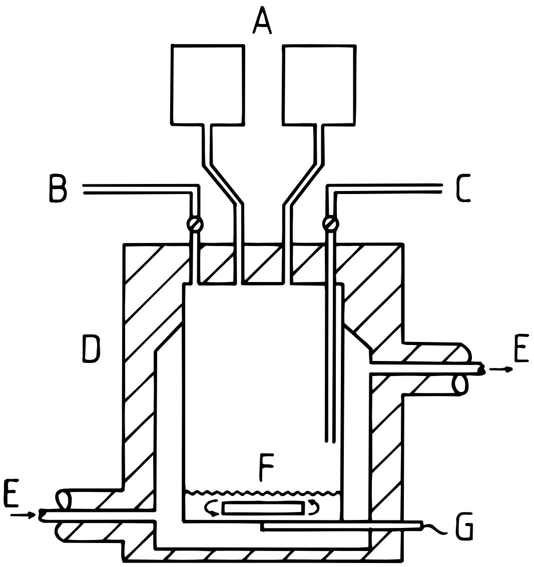

Figure 1. Schematic diagram of the apparatus: A, pressure gauges; B, connection to vacuum line; C, connection to solution reservoir; D, test cell with thermal insulation; E, connections to refrigerating bath/circulator; F, test solution with magnetic stirring bar; G, platinum resistance thermometer.

$_2$O) over a solution of fixed composition is first measured over a range of temperatures. The solution concentration in the cell is then increased by adding more concentrated acid from the reservoir, and the cycle is repeated.

Vapor pressures were measured using two capacitance manometers (Edwards High Vacuum, type 655 Barocell) covering the range (10 to 0.001) Torr and (0.1 to 10^{-5}) Torr (Torr $\simeq$ 133.3 Pa). The gauges were internally heated to 45 °C to minimize the effect of variations in ambient temperature on the measurement of pressure. The gauges measure total pressure, independent of the species present, and give a direct voltage output which is linear in response with respect to pressure. The gauges were used as supplied, only requiring the output to be zeroed at a suitably low pressure. This was achieved by pumping the system down to 1.3×10^{-4} Pa. The output linearity of the gauges was factory certified as being better than 0.1% over the whole pressure range. The (0 to 10) V output of the capacitance gauges was checked against a direct current millivolt source (Model 404s, Time Electronics Ltd, ±0.05% accuracy) for the (0.0 to 1.0) V range and a digital bench multimeter (Thurlby model 1905a, ±0.015% accuracy) for the (0.0 to 10.0) V range.

The temperature of the solution in the heavily insulated cell was maintained by ethanol coolant passed between the inner and outer walls of the cell. This was circulated from a mechanical refrigeration unit (Julabo F81 bath and VC circulator) which controlled the temperature to ±0.025 K. The temperature of the cell during experimental runs was monitored by a platinum resistance probe located between the cell walls, and in contact with the inner wall. Probe readings, together with the stability of the observed water vapor pressure, confirmed that the cell temperature was maintained to within ±0.025 K at each setting of the bath thermostat. The probe had been previously calibrated against the internal temperature sensor in the bath itself, which has a specified accuracy equivalent to about ±0.1 K at 273 K falling to ±0.5 K at the lowest temperature measured.

The capacitance manometers and thermometers monitoring the thermostatic bath and the cell were connected to a personal computer via a 16 bit A/D converter (Pico Technology Pico ADC-16) with measurements taken at 1 min intervals. The A/D converter was set to 14 bits when recording temperatures which resulted in an indicated resolution of 0.015 K. A higher resolution (16 bits) was used for recording the output from the manometers so that pressure measurements could be resolved to 0.015% of the full scale reading.

The vacuum line was wrapped in heating tape, and the fluid circulation between the cell walls could be switched from cold ethanol to hot water from a second thermostatic bath to enable the cell and vacuum line to be heated and degassed prior to the introduction of the test solution. This enabled much more rapid zeroing of the capacitance manometers than if the system was pumped down at room temperature.

Sulfuric acid test solutions were prepared from 98% acid stock (BDH, Aristar grade), diluted with laboratory distilled water. Test solutions were prepared gravimetrically and samples were titrated against aqueous sodium hydroxide (Aldrich Volumetric Standard) both before and after each experiment. The uncertainty in the molality of each test solution was better than 0.015 mol kg^{-1}.

(b) Procedure. A 50 cm^3 aliquot of freshly prepared acid solution was introduced into the cell at room temperature, and the cell was sealed. The solution was then cooled to 200 K and the resulting solid or supercooled acid solution de-aerated using rotary and diffusion pumps capable of maintaining pressures down to 1.3×10^{-4} Pa. On the first pass the cell was evacuated slowly to prevent explosive decompression of the dissolved air. The cell was then warmed to room temperature to release further dissolved gas. The process of cooling and de-aeration was repeated until there was no change in the observed vapor pressure at low temperature over several cycles, thus ensuring that the solution was air free. With the bulk of the dissolved air removed at the first cycle, a liquid nitrogen cooled trap was used in series with the pumps to facilitate the process.

The vapor pressure of the liquid test solution, which was magnetically stirred from below, was measured as follows. The initial temperature of the thermostatic bath was first set and a pathway opened between the cell and the manometers. The cell temperature and vapor pressure were then allowed to stabilize, with values of both quantities being logged to the PC. Using 5 K or 10 K steps equilibration with respect to temperature was achieved in approximately 1 h, except at the lowest bath temperatures where refrigeration efficiency is lowest. Stabilization of water vapor pressure took about 2 h, after which the temperature was reset. The onset of freezing of the solution was monitored visually through a removable section of the thermal insulation, and also through the sharp rise in cell temperature caused by the release of enthalpy of crystallization.

After each series of measurements a small sample of acid was removed from the test solution and its concentration checked by titration to ensure that the quantity of water removed during de-aeration was not significant. A weighed amount of a second (more concentrated) acid solution was then added to the cell to adjust the concentration for the next run. After thorough mixing, a small sample was again removed and the new composition determined. The experimental cycle was then repeated.

(c) Results. The temperature of the cell and the capacitance manometers differ in the experiments by up to 120 K. A correction to the indicated pressure is therefore required to take account of thermal transpiration. This is a function of pressure, gauge and vapor temperatures, and the size of the constriction between the gauge and the system being monitored. An empirical model for this effect has been proposed by Takaishi and Sensui (1963) and was

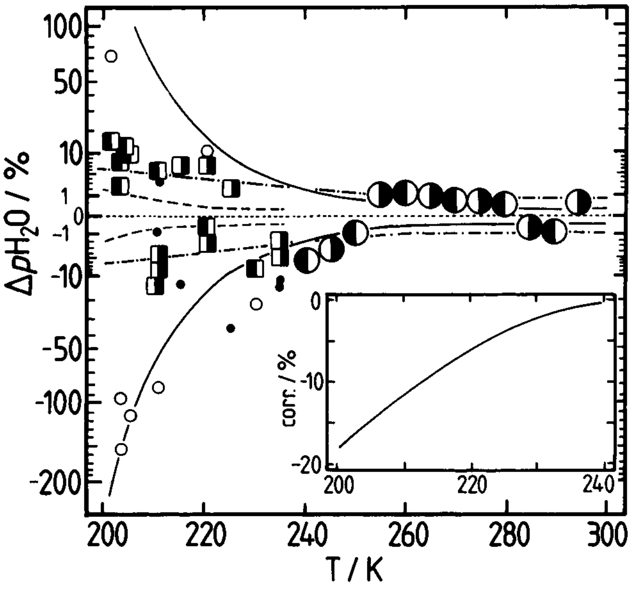

Figure 2. Results for a typical experimental run (8.05 mol kg^{-1} SO$_4$), showing percentage differences in partial pressure from theoretical values (based on liquid phase thermodynamic properties tabulated by Giauque *et al.*, 1960). Symbols: (◐), 10 Torr gauge and downward temperature scan; (◑) 10 Torr gauge and upward temperature scan; (◧), 0.1 Torr gauge and downward temperature scan; (◨) 0.1 Torr gauge and upward temperature scan; (○) 10 Torr gauge (downward temperature scan, data not used); (•) 10 Torr gauge (upward temperature scan, data not used). Lines: (solid) uncertainty in $p(H_2O)$ determination for the 10 Torr gauge expected from the observed signal to noise ratio and accuracy specified by the manufacturer; (dashed) same for 0.1 Torr gauge; (dash-dot) uncertainty in $p(H_2O)$ due to possible errors in temperature determination (the greater of 0.5% or 0.1 °C between 100 °C and +100 °C). Inset: transpiration correction as a percentage of the true pressure in the test cell.

used here with parameters for water vapor listed by Yasumoto (1980).

Results for a typical experimental run are illustrated in Figure 2. Pressures determined by each of the two capacitance manometers are distinguished, as is the direction of the temperature change associated with each measurement. It is clear that values of $p(H_2O)$ obtained on the upward and downward temperature scans do not differ significantly, which gives confidence in their reliability.

Data from the 10 Torr gauge below 1% of the full scale reading exhibit increasing scatter as the measured pressure falls toward the lower limit of about 0.13 Pa near 200 K. The values are broadly consistent with the unbroken lines in Figure 2, which show the uncertainty in the measured pressure for the 10 Torr gauge associated with the signal-to-noise ratio of the gauge output (determined when the gauge was zeroed and during experimental runs), and the resolution of the A/D converter. Data from the 10 Torr gauge for pressures below 13.3 Pa (within the range of the second gauge) were discarded. Uncertainties in results from the 0.1 Torr gauge, calculated in a similar way, are also shown in Figure 2. These reach a maximum of only about 2%, even at 200 K, which is much less than the observed scatter in the data. The cause of the scatter is unclear. It is of similar magnitude to the errors expected due to possible absolute inaccuracies in the measured temperature (up to ±0.5 K, see subsection a above), but these would be expected to be systematic rather than random. Certainly output from the gauges was stable after temperature equilibration to within 1 or 2% even at very low pressures. Errors in the molalities of the test solutions would produce only systematic changes in pressure, which should in any case be less than 0.5%.

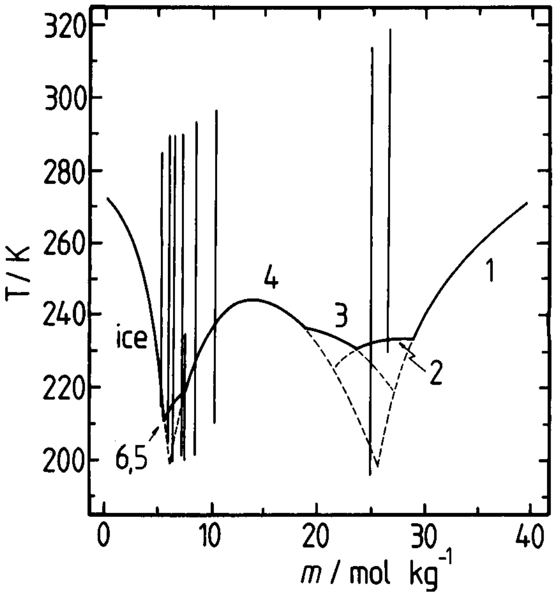

Figure 3. Range of temperature and composition (vertical lines) of the vapor pressure determinations carried out in this study. The freezing curve of aqueous H_2SO_4 is also shown (Gable *et al.*, 1950). Numbers "*n*" indicate the precipitating solid phases $H_2SO_4 \cdot nH_2O$.

The inset in Figure 2 illustrates the extent of the transpiration correction to the data, which is about 20% at 200 K decreasing to a negligibly small value above 240 K. Uncertainties in the transpiration correction are thought to contribute no more than about 1% to the total error in the measured pressures.

The molalities of the test solutions were chosen with two objectives in mind. First, to investigate the low temperature (~200 K) and low concentration (6 to 10) mol kg^{-1} regime thought to be typical of aerosols in the winter polar stratosphere. Second, two higher molalities were measured in order to validate the predictions of thermodynamic property correlations, some of which differ significantly at high concentration. The extent of the measurements in terms of composition and temperature are illustrated in Figure 3, which also shows the H_2SO_4 freezing curve. Experimental results for all test solutions are listed in Table 1.

3. Thermodynamic Properties of Aqueous H_2SO_4 to Low Temperature

In this section the available correlations and evaluations of the properties of aqueous H_2SO_4 are briefly summarized.

Giauque et al. (1960). The first comprehensive evaluation of the thermodynamic properties of aqueous H_2SO_4 and its solid phase hydrates was that of Giauque *et al.*, who present a table covering the entire liquid phase composition range, derived from the results of extensive earlier researches by that group. Each of the later models and correlations summarized below are based to some extent upon the tabulation of Giauque *et al.* (1960), or on their original experimental measurements.

Gmitro and Vermeulen (1964). These authors present equations for calculating the vapor–liquid equilibrium of aqueous H_2SO_4 using the results of Giauque *et al.* (1960), though also incorporating data on the gas phase properties of the acid (including dissociation into SO_3(g) and H_2O(g)). Critically, temperature coefficients of partial molar heat capacities were optimized in order to obtain agreement with high-temperature vapor pressure data. Gmitro and

Table 1. Measured Equilibrium Partial Pressures of Water ($p(H_2O)$) over Pure Aqueous H_2SO_4 to Low Temperature

$m(H_2SO_4)$/mol kg^{-1}	T/K	$p(H_2O)$/Pa	$m(H_2SO_4)$/mol kg^{-1}	T/K	$p(H_2O)$/Pa	$m(H_2SO_4)$/mol kg^{-1}	T/K	$p(H_2O)$/Pa
5.05	284.8	9.27×10^{2}	6.10	203.5	2.31×10^{-1}	10.02	225.4	2.05
5.05	284.6	9.22×10^{2}	6.10	201.6	1.68×10^{-1}	10.02	220.4	1.16
5.05	279.9	6.59×10^{2}	6.10	200.6	1.77×10^{-1}	10.02	220.4	1.07
5.05	279.8	6.57×10^{2}	6.10	200.6	1.88×10^{-1}	10.02	220.4	1.02
5.05	275.0	4.62×10^{2}	7.01	289.6	1.01×10^{3}	10.02	220.3	1.06
5.05	274.9	4.60×10^{2}	7.01	284.7	7.19×10^{2}	10.02	215.7	6.34×10^{-1}
5.05	269.8	3.13×10^{2}	7.01	279.8	5.08×10^{2}	10.02	215.7	5.95×10^{-1}
5.05	264.9	2.15×10^{2}	7.01	274.9	3.54×10^{2}	10.02	215.7	5.52×10^{-1}
5.05	264.9	2.14×10^{2}	7.01	269.8	2.42×10^{2}	10.02	210.6	2.79×10^{-1}
5.05	260.0	1.43×10^{2}	7.01	264.9	1.63×10^{2}	10.02	230.1	3.68
5.05	255.1	9.43×10	7.01	260.0	1.09×10^{2}	10.02	240.1	1.13×10
5.05	255.1	9.38×10	7.01	255.1	7.08×10	10.02	240.1	1.10×10
5.05	250.2	6.07×10	7.01	250.2	4.65×10	10.02	215.6	6.41×10^{-1}
5.05	245.3	3.94×10	7.01	245.3	2.98×10	10.02	215.5	6.56×10^{-1}
5.05	245.2	3.97×10	7.01	240.6	1.89×10	10.02	215.4	6.26×10^{-1}
5.05	245.2	3.88×10	7.01	240.5	1.86×10	10.02	215.4	5.81×10^{-1}
5.05	245.2	3.90×10	7.01	235.3	1.09×10	10.02	213.9	4.95×10^{-1}
5.05	240.5	2.49×10	7.01	235.2	1.10×10	10.02	213.9	4.41×10^{-1}
5.05	240.5	2.49×10	7.01	230.3	6.26	10.02	211.9	3.44×10^{-1}
5.05	240.6	2.55×10	7.01	230.3	6.22	10.02	210.3	2.61×10^{-1}
5.05	240.6	2.53×10	7.01	225.6	3.57	10.02	210.3	2.78×10^{-1}
5.05	235.3	1.56×10	7.01	225.6	3.53	24.61	314.2	3.89×10^{2}
5.05	235.3	1.57×10	7.01	225.5	3.53	24.61	309.3	2.82×10^{2}
5.05	235.3	1.55×10	7.01	220.5	2.24	24.61	309.3	2.83×10^{2}
5.05	233.2	1.24×10	7.01	220.5	2.04	24.61	304.4	2.04×10^{2}
5.05	230.3	9.01	7.01	220.5	2.08	24.61	304.4	2.04×10^{2}
5.05	230.3	8.90	7.01	220.5	2.08	24.61	304.4	2.03×10^{2}
5.05	230.3	8.89	7.01	215.4	1.11	24.61	304.4	2.03×10^{2}
5.05	230.2	8.95	7.01	215.4	1.06	24.61	304.4	2.04×10^{2}
5.05	230.2	8.89	7.01	211.2	6.10×10^{-1}	24.61	299.5	1.44×10^{2}
5.05	225.4	5.02	7.01	211.2	6.02×10^{-1}	24.61	299.5	1.45×10^{2}
5.05	225.4	5.07	7.01	211.2	6.71×10^{-1}	24.61	294.6	1.02×10^{2}
5.05	225.4	5.07	7.01	205.5	2.81×10^{-1}	24.61	294.6	1.02×10^{2}
5.05	225.4	5.08	7.01	203.5	2.04×10^{-1}	24.61	294.6	1.02×10^{2}
5.05	220.5	2.83	7.01	201.6	1.63×10^{-1}	24.61	289.7	7.04×10
5.05	220.5	2.88	7.07	235.2	1.08×10	24.61	289.7	7.03×10
5.05	220.5	2.79	7.07	225.4	3.52	24.61	289.7	7.12×10
5.05	218.5	2.20	7.07	225.3	3.62	24.61	284.8	4.86×10
5.05	217.9	2.35	7.07	225.3	3.49	24.61	279.9	3.34×10
5.05	217.9	1.92	7.07	220.6	2.03	24.61	279.9	3.32×10
5.05	216.3	1.74	7.07	220.6	1.93	24.61	279.9	3.32×10
5.05	215.3	1.63	7.07	216.0	1.32	24.61	279.9	3.44×10
5.94	289.6	1.14×10^{3}	7.07	215.9	1.22	24.61	275.0	2.27×10
5.94	284.6	8.17×10^{2}	7.07	216.0	1.26	24.61	269.9	1.49×10
5.94	284.6	8.15×10^{2}	7.07	215.9	1.14	24.61	265.0	9.37
5.94	279.8	5.81×10^{2}	7.07	215.8	1.15	24.61	260.1	5.77
5.94	279.8	5.82×10^{2}	7.07	215.8	1.27	24.61	260.1	5.80
5.94	274.9	4.06×10^{2}	7.07	215.7	1.24	24.61	260.0	5.77
5.94	274.9	4.07×10^{2}	7.07	211.2	7.00×10^{-1}	24.61	255.0	3.65
5.94	269.8	2.76×10^{2}	7.07	211.0	6.80×10^{-1}	24.61	250.1	2.17
5.94	265.0	1.93×10^{2}	7.07	205.8	3.08×10^{-1}	24.61	245.2	1.33
5.94	264.8	1.89×10^{2}	7.07	205.6	3.11×10^{-1}	24.61	240.2	7.19×10^{-1}
5.94	260.0	1.25×10^{2}	7.07	205.6	3.04×10^{-1}	24.61	235.2	4.42×10^{-1}
5.94	255.1	8.32×10	7.07	205.6	3.03×10^{-1}	24.61	230.3	2.32×10^{-1}
5.94	255.1	8.70×10	7.07	204.6	2.65×10^{-1}	24.61	230.2	2.24×10^{-1}
5.94	250.2	5.41×10	7.07	203.8	2.16×10^{-1}	24.61	230.2	2.29×10^{-1}
5.94	245.5	3.49×10	7.07	203.6	2.23×10^{-1}	24.61	225.3	1.35×10^{-1}
5.94	245.4	3.48×10	7.07	202.8	1.73×10^{-1}	24.61	225.3	1.32×10^{-1}
5.94	240.4	2.14×10	7.07	202.7	1.81×10^{-1}	24.61	225.3	1.46×10^{-1}
5.94	240.4	2.14×10	7.07	201.9	1.55×10^{-1}	24.61	225.2	1.29×10^{-1}
5.94	235.4	1.34×10	7.07	201.7	1.60×10^{-1}	24.61	225.2	1.41×10^{-1}
5.94	235.3	1.47×10	7.07	201.0	1.34×10^{-1}	24.61	220.3	8.29×10^{-2}
5.94	235.3	1.45×10	7.07	200.8	1.42×10^{-1}	24.61	220.3	8.11×10^{-2}
5.94	230.4	8.24	8.05	294.4	1.18×10^{3}	24.61	220.2	7.28×10^{-2}
5.94	225.6	4.99	8.05	289.6	8.77×10^{2}	24.61	220.1	7.52×10^{-2}
5.94	225.6	4.87	8.05	284.7	6.25×10^{2}	24.61	215.3	4.21×10^{-2}
5.94	220.5	2.63	8.05	279.8	4.41×10^{2}	24.61	215.3	4.34×10^{-2}
5.94	220.4	2.67	8.05	274.9	3.06×10^{2}	24.61	215.3	3.66×10^{-2}
5.94	215.7	1.62	8.05	269.8	2.08×10^{2}	24.61	215.3	3.20×10^{-2}
5.94	211.4	7.21×10^{-1}	8.05	264.9	1.40×10^{2}	24.61	215.2	4.39×10^{-2}
5.94	211.4	7.77×10^{-1}	8.05	260.0	9.26×10	24.61	210.0	2.42×10^{-2}
5.94	207.6	4.13×10^{-1}	8.05	255.0	6.06×10	24.61	210.0	1.82×10^{-2}
5.94	205.4	3.30×10^{-1}	8.05	250.1	3.96×10	24.61	210.0	2.03×10^{-2}
6.10	289.7	1.13×10^{3}	8.05	245.3	2.57×10	24.61	210.0	2.37×10^{-2}
6.10	284.7	8.12×10^{2}	8.05	240.4	1.63×10	24.61	207.3	1.74×10^{-2}
6.10	274.9	4.01×10^{2}	8.05	235.1	9.34	24.61	205.8	1.19×10^{-2}
6.10	279.9	5.79×10^{2}	8.05	235.1	9.12	24.61	205.7	1.38×10^{-2}
6.10	265.0	1.86×10^{2}	8.05	230.2	5.65	24.61	204.1	9.07×10^{-3}
6.10	255.1	8.06×10	8.05	225.4	2.99	24.61	201.8	6.28×10^{-3}
6.10	245.3	3.37×10	8.05	220.5	1.74	24.61	196.7	2.81×10^{-3}

Table 1 (continued)

$m(H_2SO_4)$/mol kg^{-1}	T/K	$p(H_2O)$/Pa	$m(H_2SO_4)$/mol kg^{-1}	T/K	$p(H_2O)$/Pa	$m(H_2SO_4)$/mol kg^{-1}	T/K	$p(H_2O)$/Pa
6.10	269.9	2.75×10^{2}	8.05	220.5	1.56	24.61	196.5	2.23×10^{-3}
6.10	260.0	1.24×10^{2}	8.05	220.5	1.71	26.18	319.0	4.36×10^{2}
6.10	250.2	5.26×10	8.05	215.6	8.58×10^{-1}	26.18	314.2	3.21×10^{2}
6.10	240.5	2.15×10	8.05	211.1	5.50×10^{-1}	26.18	309.2	2.32×10^{2}
6.10	235.3	1.33×10	8.05	211.1	5.40×10^{-1}	26.18	304.4	1.67×10^{2}
6.10	235.2	1.27×10	8.05	210.9	4.71×10^{-1}	26.18	299.5	1.18×10^{2}
6.10	235.2	1.27×10	8.05	210.8	5.60×10^{-1}	26.18	294.6	8.25×10
6.10	225.5	4.23	8.05	205.3	2.08×10^{-1}	26.18	289.7	5.72×10
6.10	225.3	4.10	8.05	204.4	1.76×10^{-1}	26.18	284.8	3.98×10
6.10	225.3	4.07	8.05	203.4	1.72×10^{-1}	26.18	279.9	2.74×10
6.10	220.5	2.32	8.05	203.4	1.61×10^{-1}	26.18	274.9	1.83×10
6.10	220.4	2.26	8.05	201.6	1.15×10^{-1}	26.18	270.0	1.21×10
6.10	220.6	2.40	10.02	297.4	1.10×10^{3}	26.18	265.0	7.40
6.10	220.5	2.56	10.02	297.3	1.11×10^{3}	26.18	260.0	4.58
6.10	220.5	2.55	10.02	294.4	9.12×10^{2}	26.18	255.0	2.88
6.10	218.4	1.97	10.02	289.6	6.60×10^{2}	26.18	250.1	1.66
6.10	215.4	1.22	10.02	289.6	6.58×10^{2}	26.18	245.1	9.94×10^{-1}
6.10	215.4	1.20	10.02	284.7	4.70×10^{2}	26.18	240.1	5.63×10^{-1}
6.10	215.4	1.26	10.02	284.7	4.70×10^{2}	26.18	235.1	3.09×10^{-1}
6.10	215.3	1.29	10.02	279.9	3.29×10^{2}	26.18	235.1	3.21×10^{-1}
6.10	215.3	1.24	10.02	274.8	2.30×10^{2}	26.18	235.1	3.29×10^{-1}
6.10	211.5	7.30×10^{-1}	10.02	269.8	1.54×10^{2}	26.18	230.2	1.75×10^{-1}
6.10	211.3	7.01×10^{-1}	10.02	264.9	1.06×10^{2}	26.18	230.2	1.83×10^{-1}
6.10	211.2	7.10×10^{-1}	10.02	259.9	6.79×10	26.18	230.1	1.89×10^{-1}
6.10	211.2	8.30×10^{-1}	10.02	255.0	4.70×10	26.18	230.1	1.90×10^{-1}
6.10	211.2	7.18×10^{-1}	10.02	250.1	2.94×10	26.18	230.1	1.85×10^{-1}
6.10	205.4	3.70×10^{-1}	10.02	235.1	6.48			
6.10	205.5	3.17×10^{-1}	10.02	230.1	3.64			
6.10	205.4	3.18×10^{-1}	10.02	230.1	3.57			

Vermeulen (1964) used their correlation to calculate partial pressures of H_2O over aqueous H_2SO_4 to temperatures as low as −50 °C, and their equations were adopted by Steele and Hamill (1981) for the prediction of the composition of aqueous stratospheric aerosols as functions of temperature and water partial pressure.

Bolsaitis and Elliott (1990). These authors pointed out the continued uncertainty in the thermodynamic properties of the concentrated acid, including vapor−liquid equilibria and the vapor pressure of pure H_2SO_4, and reexamined available data to obtain a revised set of thermodynamic parameters enabling the calculation of phase equilibrium at and above 298.15 K. Bolsaitis and Elliott adopt the azeotrope measurements of Kunzler (1953), and water activities at 298.15 K compiled by Giauque *et al.* (1960) to $x(H_2SO_4) = 0.4$ ($\sim$37 mol kg^{-1}), as being the most reliable of all available data. Consequently, partial pressures of water calculated from the work of Gmitro and Vermeulen (1964) and Bolsaitis and Elliott (1990) agree closely for the acid concentrations of interest here and at temperatures close to 298.15 K.

Zeleznik (1991). In this work, experimental data for aqueous H_2SO_4 and related pure solid phases are correlated for the entire composition range, and thermodynamic quantities from 200 K to 350 K are tabulated as a function of composition. A notable feature of Zeleznik's analysis is that no vapor pressure or isopiestic measurements were used. This choice probably accounts for the fact that water activities in highly concentrated solutions derived from Zeleznik's correlation deviate from those obtained from the work of Gmitro and Vermeulen (1964), and given by Bolsaitis and Elliott (1990) and Clegg and Brimblecombe (1995), all of which rely to some degree on the free energies of H_2O tabulated by Giauque *et al.* (1960). Zeleznik made extensive use of the emf data of Hamer (1935) and Harned and Hamer (1935), which yield the mean activity coefficient of H_2SO_4 in aqueous solution. Rard and Clegg (1995) have since shown that the graphical smoothing techniques used by Harned and Hamer (1935) introduce some error in the reported emfs (in most cases, the original measurements are not given). More important, it is believed that the cells did not behave reversibly above (2 to 3) mol kg^{-1}, which implies that the thermodynamic quantities derived from them will be in error (Rard and Clegg, 1995).

Clegg et al. (1994). These authors, and earlier Pitzer *et al.* (1977), used the molality-based "Pitzer" model to correlate thermodynamic measurements of liquid phase properties (osmotic coefficients, heat of dilution, heat capacities, and degrees of dissociation of the HSO_4^- ion in the work of Clegg *et al.*) from about 278.15 K to 328.15 K and for molalities to 6 mol kg^{-1}. While these studies yield very accurate values of thermodynamic properties, including the standard potentials of several electrochemical cells, the ranges of composition and temperature are too restricted for use in calculations involving the solutions studied here and for applications involving stratospheric aerosols.

Clegg and Brimblecombe (1995). In this work a mole-fraction-based thermodynamic model is used to correlate available data for the aqueous acid to 40 mol kg^{-1} H_2SO_4 and from 328.15 K to <200 K. Modeled properties below 273.15 K are constrained chiefly by heats of dilution (at 253.15 K) and heat capacities (to 240 K) determined by Giauque and co-workers. The modeling framework adopted by Clegg and Brimblecombe (1995) allows a straightforward extension of the treatment to mixtures (Carslaw *et al.*, 1995), which are important for a variety of applications including the stratosphere, where there is thought to be significant condensation of HNO_3 to the (supercooled) liquid phase below 200 K (Tabazadeh *et al.*, 1994a; Carslaw *et al.*, 1994).

4. Comparison of Correlations and Models of the Thermodynamic Properties of Aqueous H_2SO_4

Here we examine in detail the principal models and thermodynamic correlations from which liquid phase activities and equilibrium water vapor pressures over aqueous H_2SO_4 at low temperature can be calculated.

(a) Giauque et al. (1960). These authors list free energies and partial molar enthalpies and heat capacities at 298.15 K and from 1 mol kg^{-1} to >100 mass % acid. The tabulation is based upon the extensive measurements of liquid and solid phase properties to low temperatures made by Giauque and co-workers, and also other determinations in the literature. We note that the available data for liquid phase properties, relating to the calculation of $p(H_2O)$ over the aqueous acid, have not been significantly extended since the publication of Giauque *et al.* (1960).

The work of Gmitro and Vermeulen (1964) is based directly upon the thermodynamic properties tabulated by Giauque *et al.* (1960). Many of the original measurements of Giauque and co-workers have been also used in the correlation of Clegg and Brimblecombe (1995) and, with some omissions, that of Zeleznik (1991). Here, we compare the free energies and partial molar enthalpies and heat capacities of water tabulated by Giauque *et al.* (1960) with original measurements. This is in order to check their (presumably graphical) evaluation of the partial molar properties and to set a reference against which the expressions of Gmitro and Vermeulen (1964), the correlation of Zeleznik (1991), and the model of Clegg and Brimblecombe (1995) can be compared. We limit the maximum molalities considered to about 40 mol kg^{-1}, which is well above those encountered in environmental applications. However, we note that recent studies suggest that the free energies listed by Giauque *et al.* (1960) for more concentrated solutions require adjustment (Bolsaitis and Elliott, 1990; Zeleznik, 1991).

First we examine the tabulated partial molar free energies of water at 298.15 K. Below 6 mol kg^{-1} values agree with water activities obtained from the critical evaluation of Clegg *et al.* (1994) (based upon extensive isopiestic and emf data) to within (−0.3 to +0.2)%. At higher molalities, direct comparisons with available isopiestic and vapor pressure data used in the model of Clegg and Brimblecombe (1995) (see their Table 11) yield agreement to within (−0.40 to +0.87)% in water activity with a mean deviation of only 0.05%. The vapor pressures, available to a maximum molality of about 27 mol kg^{-1}, include determinations by Hornung and Giauque (1955) which were used to fix the partial molar free energy of water to the pure substance as the standard state. At higher concentrations the tabulated partial molar free energies of Giauque *et al.* (1960) were determined by extrapolation and application of the Gibbs−Duhem equation. Bolsaitis and Elliott (1990) judged the values of Giauque *et al.* to be reliable to about 37 mol kg^{-1}, and it is only above about 40 mol kg^{-1} that significant differences between water activities derived from the two studies arise.

Next, tabulated partial molar enthalpies of water (L_1) were compared (by integration) with available differential heats of dilution ($\Delta_{dil}H$) above 2 mol kg^{-1} concentration. A value of 23 732 J mol^{-1} was adopted for the apparent molar enthalpy of aqueous H_2SO_4 at 2 mol kg^{-1} (Clegg *et al.*, 1994). The principal data set for dilutions for which the final molality is >2 mol kg^{-1} is that of Kunzler and Giauque (1952). This comparison is therefore only a test of the method used by Giauque *et al.* (1960) to obtain L_1 from their own measurements, since the data that were later published by Wu and Young (1980) were known to Giauque *et al.* (1960) and there have been no further measurements since. Agreement was within (−0.1 to +0.5)% and without systematic deviation for all dilutions for mean molalities in the range (4 to 40) mol kg^{-1}, and to within ±1.5% at lower molalities—with the latter values probably influenced by uncertainties in our interpolation of L_1 from Table I of Giauque *et al.* (1960).

A similar comparison was carried out for apparent molar heat capacities at 298.15 K for molalities above 1.4 mol kg^{-1}, by integrating the partial molar heat capacities (J_1) listed by Giauque *et al.* (1960). The principal source of experimental data is again Kunzler and Giauque (1952). Agreement between apparent molar heat capacities derived from the measurements, and values calculated from the tabulated partial molar values, was within (−1.70 to +1.53)%.

Giauque *et al.* (1960) also tabulate differentials of the partial molar heat capacities of water and H_2SO_4 with respect to temperature. We have not attempted to verify directly these values. However, calculated equilibrium water partial pressures along the freezing curve of aqueous H_2SO_4 (section 5), which are sensitive to the values of the differentials, agree well with estimates for the pure ice solid phase. This gives confidence in their accuracy for molalities up to 6 mol kg^{-1}.

We conclude that the partial molar properties of water in aqueous H_2SO_4 at 298.15 K from about 2 mol kg^{-1} to 27 mol kg^{-1} (water activity) and 40 mol kg^{-1} (enthalpy and heat capacity) as tabulated by Giauque *et al.* (1960) are essentially an exact fit to the experimental data. Furthermore, water activities are probably reliable to 40 mol kg^{-1}.

(b) Gmitro and Vermeulen (1964). As noted above, the expressions of Gmitro and Vermeulen for equilibrium partial pressures of H_2O and H_2SO_4 above aqueous H_2SO_4 adopt the partial molar properties tabulated by Giauque *et al.* (1960), though with adjustments to the variation of partial molar heat capacities with temperature. Liquid phase properties predicted from the equations of Gmitro and Vermeulen are thus essentially the same close to 298.15 K, but there are increasing differences at low temperature: up to about 10% in equilibrium $p(H_2O)$ (hence water activity) at 193 K over a range of compositions. This is discussed further in section 5, where partial pressures of water calculated using the different approaches are compared.

(c) Clegg and Brimblecombe (1995). The correlation of these authors is based upon much of the same data as the tabulation of Giauque *et al.* (1960), though with the inclusion of the results of many isopiestic studies (yielding ϕ, mostly at 298.15 K), and emf measurements (giving H_2SO_4 and water activities to 8.272 mol kg^{-1}, from 278.15 K to 328.15 K). The use of equations representing activities and other thermodynamic properties to the limit of infinite dilution, and the inclusion of large numbers of measurements made at very low concentrations means that the model accurately represents properties below the 1 mol kg^{-1} limit of the evaluation of Giauque *et al.* (1960).

Differences between the fitted model of Clegg and Brimblecombe (1995) and the tabulated properties of Giauque *et al.* (1960) are shown in Figure 4 for water activity (a_1) and partial molar enthalpies (L_1) and heat capacities (J_1) of water at 298.15 K. Water activities agree to within ±0.8% up to the 40 mol kg^{-1} limit of the Clegg and Brimblecombe model. For L_1 there is agreement to within ±1% (150 J mol^{-1}) between 4 mol kg^{-1} and 35 mol kg^{-1}, with a difference of 4% (600 J mol^{-1}) at 40 mol kg^{-1}; see Figure 4b. Examination of the fits to apparent molar enthalpies at 298.15 K (Figures 4 and 13 of Clegg and Brimblecombe, 1995) suggests that these small differences are due simply to the fact that the model is not able to represent heat of dilution data to within experimental uncertainty at high concentrations. Partial molar heat capacities (J_1, Figure 4c) calculated using the model agree to within +10% (1.5 J mol^{-1} K^{-1}) and −20% (4 J mol^{-1} K^{-1}) above 15 mol kg^{-1}, and with deviations of (+1 to −2) J mol^{-1} K^{-1} close to 10 mol kg^{-1}. Again, these are attributable to limitations in the model fit (see Figures 5 and 14 of Clegg and Brimblecombe, 1995).

Inaccuracies in the representation of L_1, J_1, and to a lesser extent $(\partial J_1/\partial T)_P$ will influence calculated H_2O and H_2SO_4 activities far from the reference temperature of 298.15 K: thus the small difference in a_1 at 298.15 K shown in Figure 4a at about 40 mol kg^{-1} increases to −10% for a

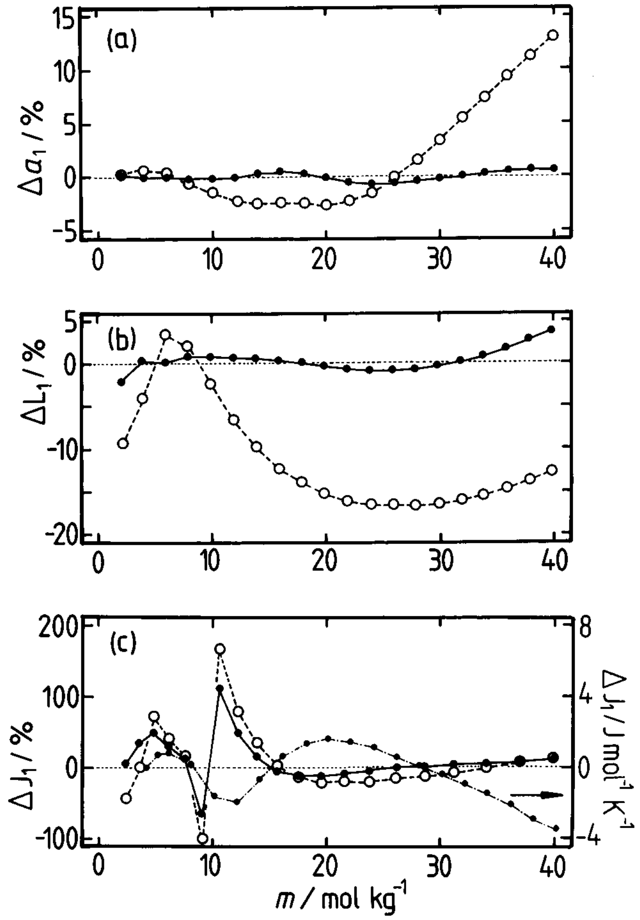

Figure 4. Comparison of calculated thermodynamic properties of aqueous H_2SO_4 at 298.15 K with reference values of Giauque *et al.* (1960). Plots show percentage differences, given as 100· $_{\text{Giauque}} - X_{\text{calc}})/X_{\text{Giauque}}$, and also the absolute difference in the case of partial molar heat capacity (right hand scale in (c)): (a) water activity (a_1); (b) partial molar enthalpy (L_1); (c) partial molar heat capacity (J_1). Symbols: (●, •) model of Clegg and Brimblecombe (1995); (○) correlation of Zeleznik (1991).

hypothetical liquid solution at 200 K. However, overall the model of Clegg and Brimblecombe (1995) conforms closely to the evaluation of Giauque *et al.* (1960).

(d) Zeleznik (1991). This correlation of the thermodynamic properties of aqueous H_2SO_4 and solid phase hydrates to 350 K excludes vapor–liquid equilibrium and isopiestic data from consideration on the grounds of concern over the establishment of equilibrium and, for isopiestic measurements, dependence on the properties of the reference solution. Activities close to 298.15 K are constrained most directly by emf measurements. Of the 819 data points used, 598 are from the work of Hamer (1935) and Harned and Hamer (1935) which extend to a maximum molality of 17.5 mol kg^{-1}. Figure 4a shows that water activities calculated from Zeleznik's correlation are greater than those of both Giauque *et al.* (1960) and Clegg and Brimblecombe (1995) between 8 mol kg^{-1} and 25 mol kg^{-1} but are lower thereafter. We have tested the dependency of the water activities obtained from Zeleznik's correlation at 298.15 K on the data of Hamer (1935) and Harned and Hamer (1935) by integrating mean activity coefficients of H_2SO_4 listed in Table IV of Harned and Hamer (1935) to obtain a_1 up to 17.5 mol kg^{-1}. Water activities were found to agree closely with values obtained from Zeleznik's correlation and are therefore the cause of the difference noted above for the lower molality range. As stated previously, Rard and Clegg (1995) have shown that the emf measurements of Hamer (1935) and Harned and Hamer (1935) are probably in error above a few mol kg^{-1}, and we conclude that water activities from Zeleznik's correlation are too high by up to 2.5% between (8 and 25) mol kg^{-1}. Thus Zeleznik's statement that "...emf and vapor pressure measurements are basically in agreement relative to aqueous sulphuric properties" is only true where the emf measurements of Hamer (1935) and Harned and Hamer (1935) are excluded from the comparison. Deviations similar to those shown in Figure 4a can be expected at other temperatures because the emf measurements of Hamer (1935) and Harned and Hamer (1935) cover the range (273.15 to 333.15) K.

Zeleznik (1991) suggested that the large positive deviations shown in Figure 4a above 25 mol kg^{-1} could be associated with the determination of the chemical potential of water (by Giauque and co-workers) from the monohydrate freezing curve. We have compared water activities at 298.15 K from Zeleznik's correlation with values given by Bolsaitis and Elliott (1990) in their study of vapor–liquid equilibrium data for the azeotrope and other solution compositions. As noted above, Bolsaitis and Elliott (1990) assign a high degree of reliability to the water activities given by Giauque *et al.* (1960) to 37 mol kg^{-1}, and the azeotrope data of Kunzler (1953). Water activities from Table VII of Bolsaitis and Elliott (1990) agree with those of Giauque *et al.* (1960) to within <1% to 50 mol kg^{-1}. Above this molality the water activities of Bolsaitis and Elliott (1990) are greater than those of Giauque *et al.* (1960), by about 30% at 100 mol kg^{-1}. In contrast, a_1 predicted by Zeleznik's equations at these concentrations are significantly lower than those from *both* other studies—continuing the trend shown in Figure 4a.

More direct comparisons with equilibrium water partial pressures are also possible. Greenewalt (1925) presents simple equations (as $\log p = a - b/T$) yielding $p(H_2O)$ from (0 to 95) mass % acid, based largely on the high-temperature measurements of Burt (1904). Partial pressures agree with predictions of the equations of Gmitro and Vermeulen (1964) to within ±7.5% to 90 mass % acid at 373.15 K and (+7.5 to −40)% at 298.15 K. Values are higher than those obtained using Zeleznik's correlation at 298.15 K by about 15% at 80 mass % acid, rising to 90% at 85 mass % and 160% at 90 mass % acid. While some of these differences are probably attributable to the large temperature extrapolation of Greenewalt's equations to 298.15 K, they tend to support the thermodynamic properties as derived by Giauque *et al.* (1960) rather than those obtained by Zeleznik (1991).

Partial molar enthalpies of water (L_1) are compared in Figure 4b, showing that values from Zeleznik's correlation are significantly greater than those tabulated by Giauque *et al.* (1960) over most of the concentration range shown. Values of L_1 above about 2 mol kg^{-1} are based mainly upon the heats of dilution of Kunzler and Giauque (1952), which agree well with other data at the lower concentrations. Zeleznik (1991) discussed the differences and suggested that the heats of dilution in the intermediate region of the phase diagram may be inaccurate. If this refers to the data of Kunzler and Giauque (1952) at 253.15 K, which were omitted from Zeleznik's correlation, then it is incorrect: after adjustment to the appropriate reference basis (see Table 13 of Clegg and Brimblecombe, 1995) these measurements are consistent with other data. We note that Bolsaitis and Elliott (1990) include the partial molar enthalpies of Giauque *et al.* (1960) in their correlation of vapor pressure data without any inconsistency being found. It is possible that the correlation of enthalpies in Zeleznik's model is influenced by the fit to the emf data of Hamer (1935) and Harned and Hamer (1935).

Finally, Figure 4c shows that partial molar heat capacities (J_1) of water obtained from Zeleznik's correlation agree satisfactorily with those of Giauque *et al.* (1960) and values predicted by the model of Clegg and Brimblecombe (1995). The principal data for all correlations, except at very low molalities, are the results of Giauque and co-workers (e.g., Table 14 of Clegg and Brimblecombe, 1995).

5. Predicted Equilibrium $p(H_2O)$ over Aqueous H_2SO_4 at Low Temperatures

Partial pressures of water were calculated using the liquid phase models of Clegg and Brimblecombe (1995) and Zeleznik (1991) as $p(H_2O) = a_1p^o(H_2O(l))$. Values of p^o(H_2O(l)), the vapor pressure of water over the pure liquid, are taken from Carslaw *et al.* (1995). Water partial pressures based on the liquid phase properties tabulated by Giauque *et al.* (1960) were calculated using the equations by Gmitro and Vermeulen (1964), but retaining the original $(\partial C_{p1}/\partial T)_P$ listed by Giauque *et al.* (1960).

The freezing curve with respect to ice provides a well-defined reference for $p(H_2O)$ because the equilibrium vapor pressure of water over ice ($p(H_2O(s))$) is known (Goff, 1957; Jancso *et al.*, 1970). The lowest temperature reached on the curve is 201.9 K at 6.02 mol kg^{-1} (Gable *et al.*, 1950). Water partial pressures calculated using the model of Clegg and Brimblecombe (1995), the correlation of Zeleznik (1991), and thermodynamic properties tabulated by Giau- *et al.* (1960), all agree with $p(H_2O(s))$ to within (+1.5 1.0)% from 273.15 K to 201.9 K, a satisfactory result. However, values obtained using the expressions of Gmitro and Vermeulen (1964), and their associated set of constants, are too low by about 1% at 240 K and 9% at 201.9 K. This error is caused by their optimization of $(\partial C_{p1}/\partial T)_P$ to improve agreement with high-temperature vapor pressure data.

A broader comparison of predicted $p(H_2O)$, using values based on the tabulated properties of Giauque *et al.* (1960) as a reference, is shown in Figure 5. Deviations are $<\pm1\%$ for the model of Clegg and Brimblecombe (1995) over much of the concentration range, but increase to 10% at the lowest temperature for 40 mol kg^{-1} acid. This is a consequence of the imperfect representation of L_1(298.15 K) at very high concentrations (Figure 4b). The positive deviations of (3 to 5)% in water activity for temperatures below 213.15 K are probably caused by the fact that Giauque *et al.* (1960) did not evaluate $(\partial C_{p1}/\partial T)_P$ below 30 mass % acid (4.37 mol kg^{-1}), and our calculations therefore involve an interpolated estimate. It is likely that the model of Clegg and Brimblecombe (1995) is more accurate at these low molalities.

Deviations in partial pressures predicted using liquid phase properties from the study of Zeleznik (1991) are shown in Figure 5b. Below about 10 mol kg^{-1} the results are similar to those obtained using the model of Clegg and Brimblecombe, but deviations are large and positive above 15 mol kg^{-1}. This is due both to the differences in derived water activities at 298.15 K (Figure 4a) and especially to the fitted partial molar enthalpies (Figure 4b).

Differences between $p(H_2O)$ calculated using the expressions of Gmitro and Vermeulen (1964) (with their adjusted $(\partial C_{p1}/\partial T)_P$) and values derived from the tabulation of Giauque *et al.* (1960) are shown in Figure 5c. Deviations range between about +12% and −10%, and the large differences at low molalities explain the poor agreement with the freezing curve noted above.

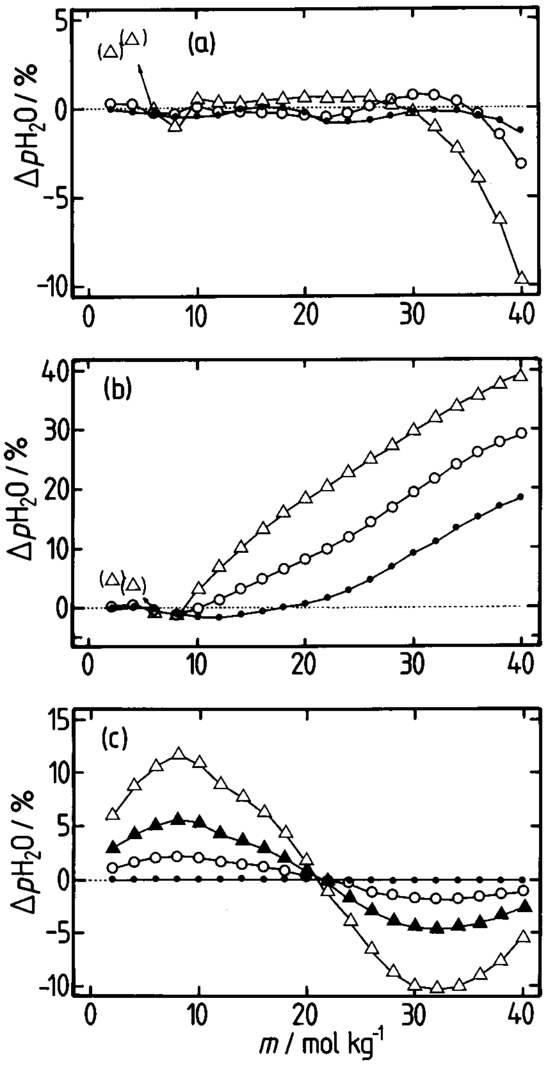

Figure 5. Comparison of calculated equilibrium $p(H_2O)$ over aqueous H_2SO_4 with reference values based on the tabulated thermodynamic properties of Giauque *et al.* (1960). Plots show percentage differences, given as $100(p(H_2O)_{Giauque} - p(H_2O)_{calc})/p(H_2O)_{Giauque}$: (a) model of Clegg and Brimblecombe (1995); (b) correlation of Zeleznik (1991); (c) expressions of Gmitro and Vermeulen (1964). Symbols: (•) 273.15 K; (○) 233.15 K; (▲) 213.15 K (c only); (△) 193.15 K.

The following can be concluded from the comparisons presented in this and the previous section. First, activities calculated using the model of Clegg and Brimblecombe (1995) closely agree with the thermodynamic analysis of Giauque *et al.* (1960), except for very high molalities where inaccuracies in the representation of enthalpy data result in differences in predicted water activity of up to 10% at very low temperatures. However, this difference should not prove significant because 40 mol kg^{-1} H_2SO_4, for example, is saturated with respect to $H_2SO_4 \cdot H_2O$ above 273.15 K for which the model error is <1.5%. Activities calculated by the model for low temperature and <4 mol kg^{-1} acid are likely to be more accurate than those derived from the properties tabulated by Giauque *et al.* (1960).

Second, the expressions of Gmitro and Vermeulen (1964) for $p(H_2O)$, though based on the results of Giauque *et al.* (1960), use coefficients that are optimized for best agreement with high-temperature vapor pressure data. This gives rise to errors of about ±5% in $p(H_2O)$ at around 213 K, and up to 9% over solutions saturated with respect to ice at about 202 K.

Third, the correlation of Zeleznik (1991), from which vapor pressure data were excluded, agrees satisfactorily with the results of Giauque *et al.* (1960) below about 10 mol kg^{-1} (to within 5% in predicted water activity—Figure 4) but with large deviations in water partial pressure at all temperatures for higher concentrations. This is at-

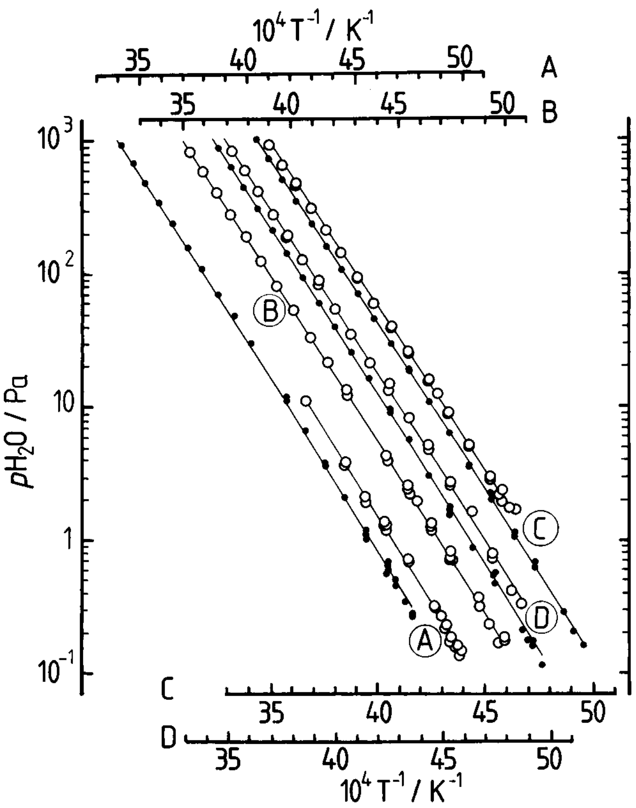

Figure 6. Measured and predicted equilibrium $p(H_2O)$ for (5.054 to 10.019) mol kg^{-1} H_2SO_4 (data from this study). Upper case letters A–D on the plot associated with each acid concentration identify the corresponding temperature scale. Symbols: (A) (○) 7.074 mol kg^{-1}; (A) (•) 10.019 mol kg^{-1}; (B) (○) 6.103 mol kg^{-1}; (C)) 5.054 mol kg^{-1}; (C) (•) 7.011 mol kg^{-1}; (D) (○) 5.940 mol kg^{-1}; •) 8.053 mol kg^{-1}. Lines: predicted partial pressures based upon liquid phase thermodynamic properties tabulated by Giauque *et al.* (1960).

tributed partly to the high degree of reliance on emf data and also to the poor fit to the available enthalpy data for the aqueous acid.

6. Data Comparison

The partial pressures of water listed in Table 1 significantly increase the number of measurements available for low temperatures. It is one of the aims of the present study to resolve the disagreements between the thermodynamic property correlations discussed in the previous section, in particular between the results of Giauque *et al.* (1960) and of Zeleznik (1991). In addition, we wish to determine whether any revisions of the models used for practical calculations (for example, that of Clegg and Brimblecombe, 1995) are required. In this section each set of experimental measurements is therefore compared with theoretical predictions of $p(H_2O)$ using liquid phase properties from the tabulation of Giauque *et al.* (1960).

(a) Measurements from this Study. Values of $p(H_2O)$ for $m(H_2SO_4) \leq 10$ mol kg^{-1} (Table 1) are shown in Figure 6, together with predictions based upon the thermodynamic properties tabulated by Giauque *et al.* (1960). There is close agreement, with none of the systematic deviations that are apparent for the data of Zhang *et al.* (1993a) (subsection b), although there is some increase in scatter at the lowest temperatures. Differences between measured and predicted partial pressures are shown in Figure 7. The estimates of experimental uncertainty shown on the plots are rms values derived from the combined data set from (5.054 to 10.019) mol kg^{-1}, based on individual fits to the measurements at each concentration (as $\ln(p) = a + b/T + c\ln(T)$). Comparisons with predictions of the expressions of Gmitro and Vermeulen (1964) are included in the figure, as the work of these authors has previously been compared with experimental data (Zhang *et al.*, 1993a) and used for calculations of the state of liquid stratospheric aerosols (Steele and Hamill, 1981). Values of $\Delta p(H_2O)$ obtained using the models of Clegg and Brimblecombe (1995) and Zeleznik (1991) are close to those shown for the Giauque *et al.* predictions in Figure 7, differing by averages of only −0.36% and −0.90%, respectively.

The measured equilibrium $p(H_2O)$ values cover 4 orders of magnitude of pressure, and experimental uncertainty increases significantly in the final decade (below about 220 K). Differences between the predictions of the various models are greatest close to 200 K, but are below 10%. This is less than the scatter in the data for the range of concentrations shown in Figures 6 and 7. We conclude that these data confirm that the predictions of the models and correlations considered here are accurate to within ±10% from (5 to 10) mol kg^{-1} H_2SO_4 and for temperatures to about 200 K.

A minor feature of plots (a) to (d) in Figure 7 is a rising trend in $\Delta p(H_2O)$ of ~4% from the highest experimental temperatures to around 250 K. The reason for this is not known, but it is probably an experimental artifact because the trend is evidently not continued to lower temperatures but is followed by a fall in $\Delta p(H_2O)$ of a few percent around 240 K. If the deviations reflected errors in the calculations of liquid phase properties, then differences of the order of 50% in L_1 are implied. These are highly unlikely, given the consistency of thermal data with direct measurements of activity from about (278 to 328) K (Clegg *et al.*, 1994). A systematic error in the measured temperature of the cell coolant is a possibility, given that a temperature change of only 0.5 K causes $p(H_2O)$ to change by about 4%. However, we have no evidence for this, as temperature was not monitored independently of the bath thermostat.

Measurements made for 24.61 mol kg^{-1} and 26.18 mol kg^{-1} H_2SO_4 fall between the tetra- and monohydrate saturation curves, and the results are shown in Figures 8 and 9. The data extend to a minimum partial pressure of about 2×10^{-3} Pa, a factor of 50 below those obtained for the lower acid molalities discussed above. There is good agreement between measured and predicted partial pressures to about 0.1 Pa, but below this the measured partial pressures are higher than predicted values for the 24.61 mol kg^{-1} acid. These data do not appear to follow a simple $1/T$ proportionality with values at higher temperatures and are probably affected by an experimental error. For the 26.18 mol kg^{-1} acid, deviations at low temperature were much larger, amounting to about a factor of 10 at 200 K, and data for $T < 230$ K were therefore discarded. There could be several causes for such errors. At first a shift in the manometer zero pressure baseline was suspected, but on isolation of the gauge no such shift was found. Second, some residual air may have remained dissolved in solution (which only became apparent at the lowest pressures), despite the fact that the solution was degassed several times prior to vapor pressure measurements being made. However, since the measurements themselves were made over several cycles, with the cell evacuated after the solution was warmed to room temperature overnight between cycles, it would be expected that the effect of dissolved air in the solution would diminish. Third, prior to measurements on these last two solutions, several of the "O" rings in the stopcocks and connectors were replaced and their degassing may have been the effect observed at the lowest temperatures.

Differences between measured and calculated partial pressures are shown in Figure 9. For 24.61 mol kg^{-1} acid

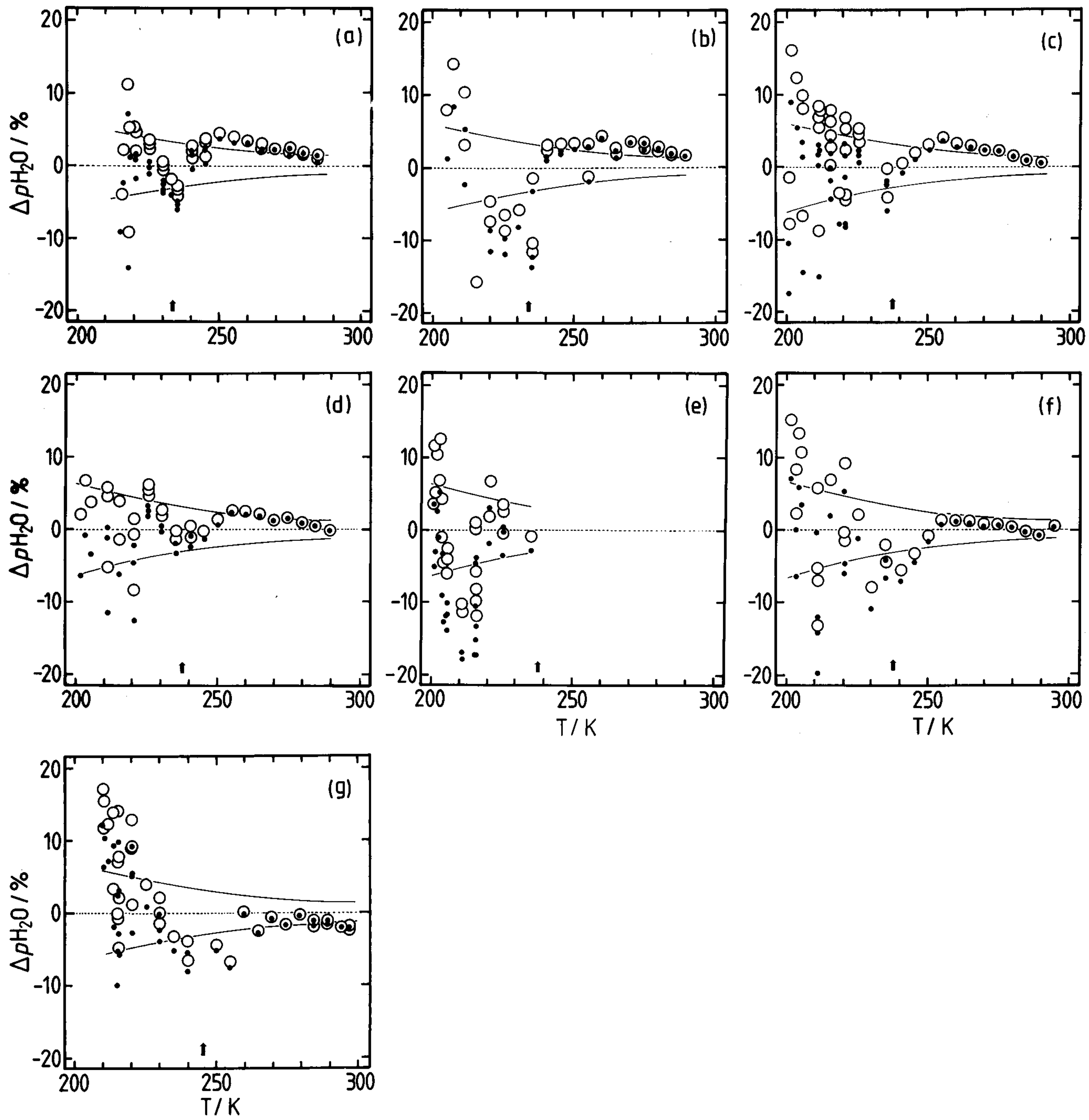

Figure 7. Deviations between measured and calculated $p(H_2O)$ for (5.054 to 10.019) mol kg^{-1} H_2SO_4, given as $100(p(H_2O)_{calc} -$ $O)_{meas})/p(H_2O)_{calc}$: (a) 5.054 mol kg^{-1}; (b) 5.940 mol kg^{-1}; (c) 6.103 mol kg^{-1}; (d) 7.011 mol kg^{-1}; (e) 7.074 mol kg^{-1}; (f) 8.053 mol kg^{-1}; (g) 10.019 mol kg^{-1}. Symbols: (○) with $p(H_2O)_{calc}$ obtained using the thermodynamic properties listed by Giauque *et al.* (1960); (•) $p(H_2O)_{calc}$ predicted from expressions of Gmitro and Vermeulen (1964). Lines show estimates of experimental uncertainty.

the data from Table 1 agree well with values predicted using thermodynamic properties tabulated by Giauque *et al.* (1960) to about 230 K, although a small negative deviation of about 4% is apparent. Partial pressures calculated using liquid phase properties from the correlation of Zeleznik (1991) are also compared with those derived from the work of Giauque *et al.* (1960) in Figure 9. Here a consistent negative trend with temperature is shown for both molalities, and it is clear that the measured partial pressures most closely support the work of Giauque *et al.* (1960). In particular these results suggest that the partial molar enthalpies derived by Giauque *et al.* (1960) are correct and that the correlation of Zeleznik (1991) does not accurately represent the thermodynamic properties (activity and enthalpy) of aqueous H_2SO_4 at the concentrations of interest here.

(b) Measurements of Zhang et al. (1993a). These authors have measured equilibrium $p(H_2O)$ over aqueous H_2SO_4, including solutions saturated with respect to ice and two solid phase hydrates, to temperatures as low as 200 K. Zhang *et al.* (1993a) compared their data for various fixed acid concentrations with predictions of the model of Jaecker-Voirol *et al.* (1990) and the work of Gmitro and Vermeulen (1964). There was reasonable agreement with the latter for dilute solutions, but larger differences above ~60 mass % acid. This is illustrated in Figure 10 where we show the data of Zhang *et al.* (1993a) (from their Figure 2), and partial pressures based upon both the equations of Zeleznik (1991) and the tabulation of Giauque *et al.* (1960). Except for the 33.9 mass % acid, predicted partial pressures are higher than measured values in both cases—by averages of 22% (Giauque *et al.*) and 18% (Zeleznik). The

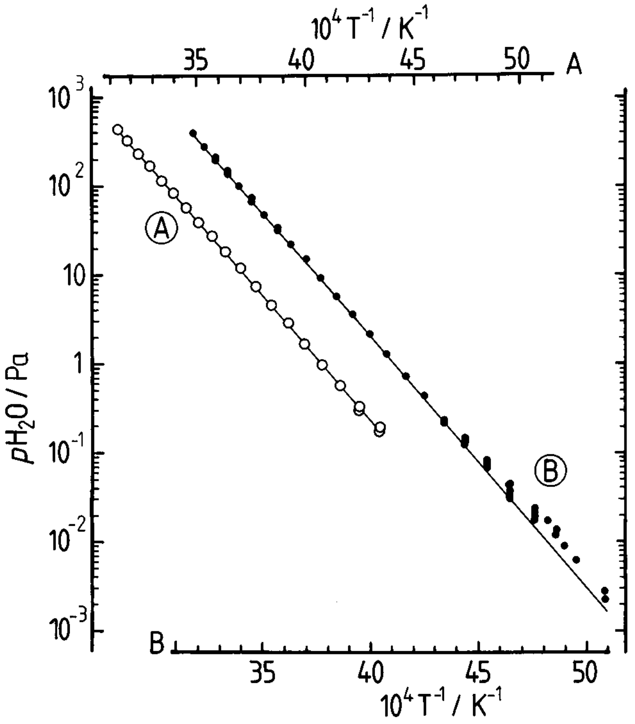

Figure 8. Measured and predicted equilibrium $p(H_2O)$ for 24.61 mol kg^{-1} and 26.18 mol kg^{-1} H_2SO_4 (data from this study). Upper case letters A and B, associated with each acid concentration, identify the corresponding temperature scale. Symbols: (A) (○) 26.18 mol kg^{-1}; (B) (•) 24.61 mol kg^{-1}. Lines: predicted partial pressures based upon liquid phase thermodynamic properties tabulated by Giauque *et al.* (1960).

model of Clegg and Brimblecombe (1995) yields similar deviations of 23%. These differences (as $\Delta \log p(H_2O)$) are almost invariant with temperature. Consequently, extrapolation to a higher temperature such as 273.15 K yields essentially the same result (see Figure 11 of Clegg and Brimblecombe, 1995). However, the models are tightly constrained by other thermodynamic data close to room temperature and are likely to be accurate to within a few percent or better. It is therefore concluded that the measurements of Zhang *et al.* (1993a) for >37.5 mass % acid are probably subject to small systematic errors, being (10 to 30)% low for (44.2 to 67.8) mass % H_2SO_4, and about 40% too high for 70 mass % acid (Clegg and Brimblecombe, 1995).

Zhang *et al.* (1993a) also measured equilibrium $p(H_2O)$ over partially frozen mixtures containing the solid phases ice, $H_2SO_4{\cdot}6.5H_2O$, and $H_2SO_4{\cdot}4H_2O$. Initial comparisons showed best agreement with the models at the lowest measured partial pressures, with positive deviations at the highest temperature (~240 K). The fact that this was also true of the solutions containing ice, whose vapor pressure is well established, suggested the possibility of a systematic error in the measurements. (The determination of temperature in the experiments appears to be accurate, as the measured and predicted temperature of maximum $p(H_2O)$ over $H_2SO_4{\cdot}4H_2O$ freezing mixtures agree almost exactly.) We derived a tentative correction factor for the full data set equivalent to the true $p(H_2O(s))$ over ice at temperature T divided by the value from the results of Zhang *et al.* (1993a), which was determined from a fit to measurements for the lowest and three highest temperatures. Both original and adjusted data are compared in Figure 11 with predictions from the correlation of Zeleznik (1991) and the model of Clegg and Brimblecombe (1995). (Here the model of Clegg and Brimblecombe was used in preference to the work of Giauque *et al.* (1960) simply for ease of calculation of the freezing curve.) The adjusted data agree well at all temperatures with both sets of predictions, which are similar over the measured range of solution compositions. Values of $p(H_2O)$ over solutions saturated with respect to $H_2SO_4{\cdot}4H_2O$, estimated directly from our own measurements and freezing point data, are also shown in Figure 11. These agree well with the calculated curve. Differences between the models are greatest for the highly concentrated solutions in equilibrium with $H_2SO_4{\cdot}H_2O$, as expected from the comparisons shown earlier in Figure 5a,b.

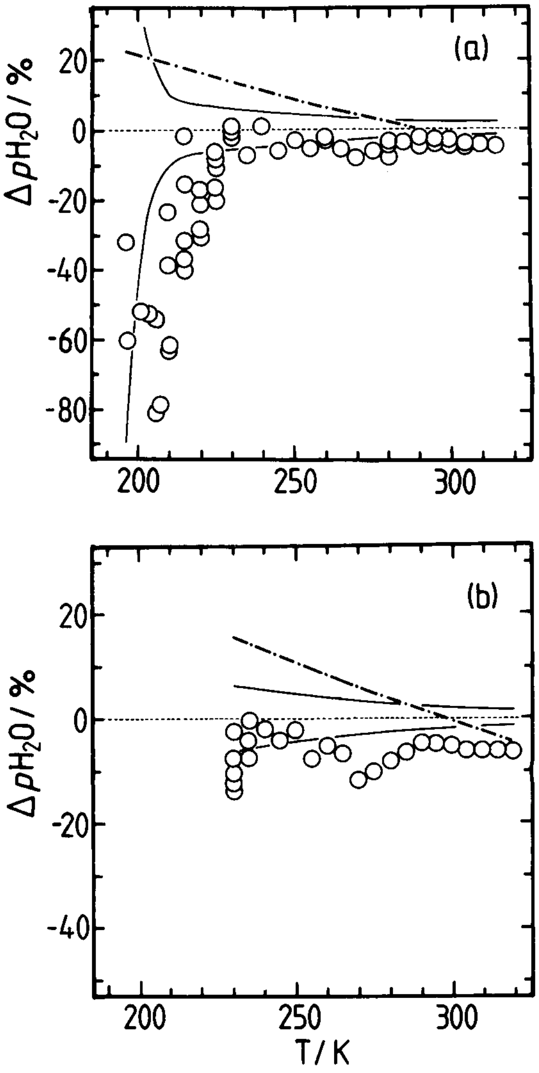

Figure 9. Deviations between measured and calculated $p(H_2O)$ for (24.61 and 26.18) mol kg^{-1} H_2SO_4, given as $100(p(H_2O)_{calc} - p(H_2O)_{meas})/p(H_2O)_{calc}$: (a) 24.61 mol kg^{-1}; (b) 26.18 mol kg^{-1}. Symbols: deviations between data from this study and partial pressures calculated using the thermodynamic properties listed by Giauque *et al.* (1960). Lines: (dash-dot) deviations between partial pressures predicted using the correlation of Zeleznik (1991) and values calculated using the thermodynamic properties listed by Giauque *et al.* (1960); (solid) estimates of experimental uncertainty. The steep rise in this quantity below 210 K is related to the resolution of the A/D converter and properties of the manometer (whose contribution to the overall uncertainty is equivalent to 0.15% of measured pressure + 0.015% of full scale deflection (13.3 Pa, or 0.1 Torr)).

In conclusion, the measurements of Zhang *et al.* (1993a) as presented show small systematic deviations from partial pressures predicted using the correlation of Zeleznik (1991), thermodynamic properties tabulated by Giauque *et al.* (1960) and the model of Clegg and Brimblecombe (1995). Comparisons of extrapolated partial pressures and model predictions at 273.15 K, and with vapor pressures of H_2O

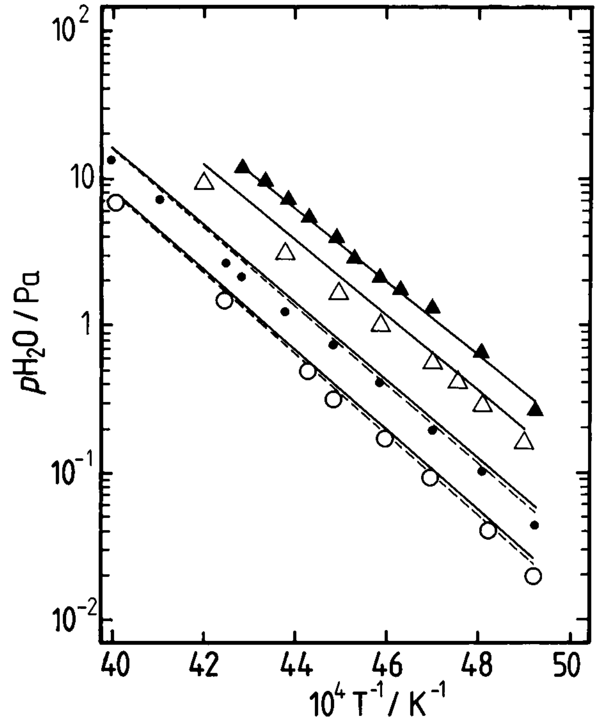

Figure 10. Predicted equilibrium $p(H_2O)$ over aqueous H_2SO_4 compared with the data of Zhang *et al.* (1993a). Symbols: (▲) 33.9 mass %; (△) 44.4 mass %; (•) 56.6 mass %; (○) 62.6 mass %. Lines: (solid) from thermodynamic properties tabulated by Giauque *et* (1960); (dashed) correlation of Zeleznik (1991). Note that for the two lower mass % H_2SO_4 the predicted lines overlie each other.

over ice, suggest that these deviations are not due to model errors but are present in the data. A small adjustment to the data for freezing mixtures brings models and data into good agreement. These measurements are not sufficiently extensive or precise to favour one model or set of thermodynamic properties over any other.

(c) Measurements of Becker et al. (1995). These authors have determined equilibrium partial pressures of O, HNO_3, HCl, and HBr above aqueous acid mixtures at low temperatures by laser spectrometric methods. In Figure 12 we present a comparison with measured $p(H_2O)$ over 35 mass % H_2SO_4. There is excellent agreement with model predictions, which for this relatively low concentration of acid agree closely, although a (3 to 8)% difference between predictions of the Gmitro and Vermeulen (1964) expressions and the other correlations is noted. Measured partial pressures also agree well with the results of Zhang *et al.* (1993a) for 33.85 mass % and 35.7 mass % H_2SO_4.

We note that Becker *et al.* (1995) also carried out experiments on 16 mass % H_2SO_4. However, such solutions should be highly supersaturated with respect to ice, and this appears to have formed as the partial pressures are grossly discordant with theoretical predictions.

(d) Measurements of Daudt (1923). This author has determined equilibrium $p(H_2O)$ over (68.4 to 85) mass % H_2SO_4 from (295 to 223) K, using a bithermal technique in which ice (at low temperature) is the source of reference $p(H_2O)$. After recalculation of the partial pressures to more recent values (involving changes of <2.5% from those listed by Daudt), the experimental data were compared with predictions based on thermodynamic properties tabulated by Giauque *et al.* (1960), and the correlation of Zeleznik (1991)—see Figure 13. The model of Clegg and Brimblecombe (1995) yields very similar partial pressures to the Giauque *et al.* values, agreeing to within (+0.4 to −0.8)% for the two lower concentrations and (+5 to −6)% for those above the 40 mol kg^{-1} limit of fit of the model.

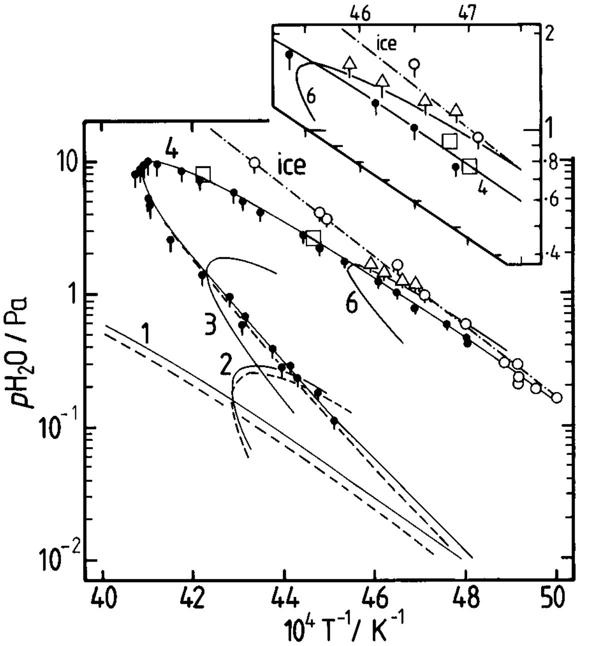

Figure 11. Predicted equilibrium $p(H_2O)$ over freezing mixtures of aqueous H_2SO_4, compared with the data of Zhang *et al.* (1993a). Symbols (corrected data): (○) solid phase ice; (△) solid phase $H_2SO_4{\cdot}6.5H_2O$; (•) solid phase $H_2SO_4{\cdot}4H_2O$; (□) partial pressures for solid phase $H_2SO_4{\cdot}4H_2O$ estimated from data in Table 1 and available freezing point measurements. The vertical line associated with each data point indicates the extent of the correction of the original measurements of Zhang *et al.* (1993a). The inset shows the detail of $H_2SO_4{\cdot}6.5H_2O$ saturation. Lines: (solid) model of Clegg and Brimblecombe (1995); (dashed) correlation of Zeleznik (1991); (dash-dot) ice solid phase. Calculated saturation curves for some additional solid phases to those given above are shown on the plot, all of which are numbered as follows: (1) $H_2SO_4{\cdot}H_2O$; (2), $H_2SO_4{\cdot}2H_2O$; (3) $H_2SO_4{\cdot}3H_2O$; (4) $H_2SO_4{\cdot}4H_2O$; (6) $H_2SO_4{\cdot}6.5H_2O$.

Measured and calculated $p(H_2O)$ for the 68 mass % acid agree well to about 260 K, but measured values are higher than predicted $p(H_2O)$ below this temperature. The lowest temperature measured (223.85 K) corresponds to a solution saturated with respect the $H_2SO_4{\cdot}4H_2O$. From Figure 11 it is seen that the data of Zhang *et al.* (1993a) yield $p(H_2O)$ equal to 20.2 Pa for this temperature—close to the values predicted by the models. Further examination of the pattern of differences between Daudt's measured partial pressures and predicted values showed that these were quite simply related to the temperature of the reference ice phase in the experiments: there is agreement with the models to within about 20% to an ice temperature of 225 K, worsening to a difference of a factor of 2.6 at about 207 K. This suggests errors in the experiments, and it is concluded that the measurements of Daudt (1923) for 82.31 mass % and 85 mass % acid, and for pressures less than about 1 Pa, are probably inaccurate.

7. Summary and Recommendation

We have determined equilibrium partial pressures of water over (5.054 to 26.18) mol kg^{-1} H_2SO_4 from (314.2 to 196.5) K by a direct method, and have critically examined current approaches to calculating this quantity theoretically.

This study confirms the reliability of theoretical predictions of $p(H_2O)$ to about 25 mol kg^{-1} H_2SO_4 based upon thermodynamic properties determined by Giauque and coworkers and tabulated by Giauque *et al.* (1960). The model of Clegg and Brimblecombe (1995) was fitted from (0 to 40) mol kg^{-1} to much of the same data used by Giauque *et*

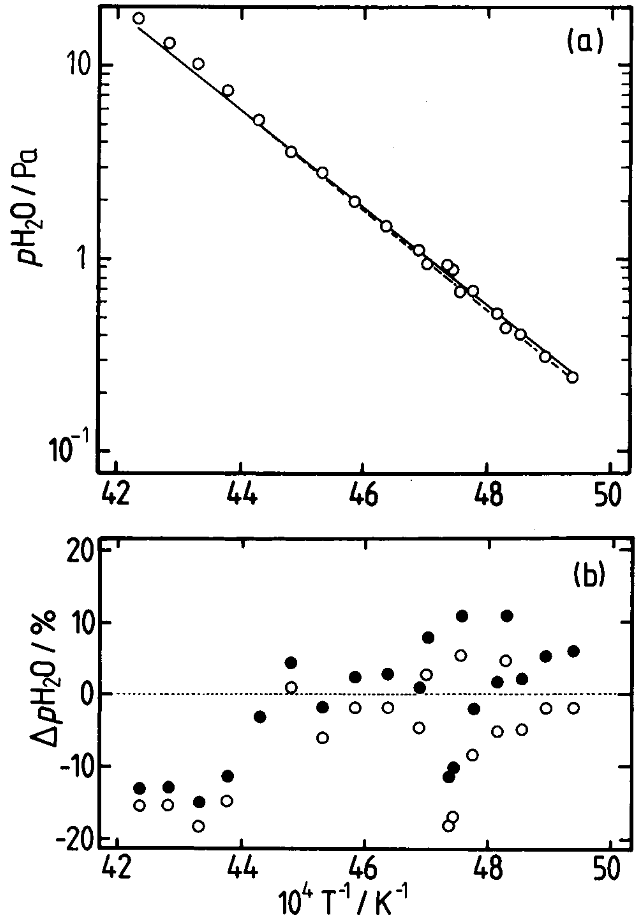

Figure 12. (a) Predicted equilibrium $p(H_2O)$ over 35 mass % aqueous H_2SO_4 compared with the data of Becker *et al.* (1995):) measured values; (solid line) model of Clegg and Brimblecombe (1995), correlation of Zeleznik (1991), and predictions based upon thermodynamic properties tabulated by Giauque *et al.* (1960); (dashed line) equations of Gmitro and Vermeulen (1964). (b) Percentage deviation in partial pressure (calculated − observed)) model of Clegg and Brimblecombe (1995), correlation of Zeleznik (1991), and predictions based upon thermodynamic properties tabulated by Giauque *et al.* (1960); (○) expressions of Gmitro and Vermeulen (1964).

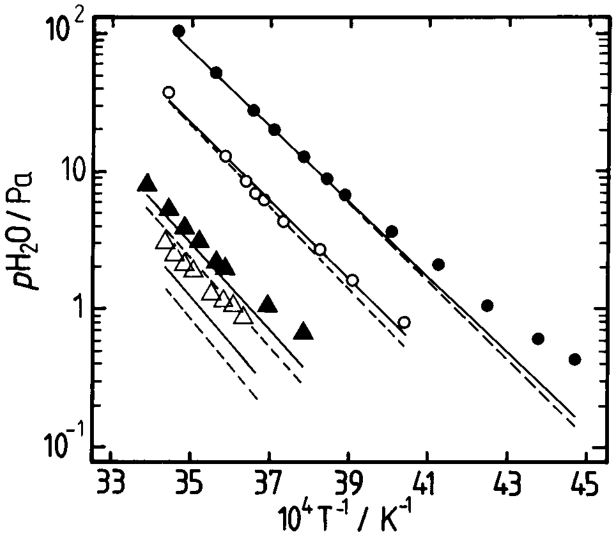

Figure 13. Predicted equilibrium $p(H_2O)$ over aqueous H_2SO_4 compared with the data of Daudt (1923). Symbols: (●) 68.4 mass % H_2SO_4; (○) 74.8 mass %; (▲) 82.31 mass %; (△) 85 mass %. Lines: (solid) based upon thermodynamic properties tabulated by Giauque *et al.* (1960); (dashed) correlation of Zeleznik (1991).

(1960) and consequently yields values of $p(H_2O)$ that are in close agreement for most molalities. These two approaches to calculating $p(H_2O)$ at low temperature (and about 40 mol kg^{-1} H_2SO_4) are recommended as the most accurate currently available. For dilute solutions (<30 mass % acid) the model of Clegg and Brimblecombe (1995) is to be preferred due to the limited coverage of this part of the concentration range by Giauque *et al.* (1960). Conversely, at molalities close to 40 mol kg^{-1} thermodynamic properties from the tabulation of Giauque *et al.* (1960) are probably more accurate due to limitations in the representation of enthalpy data by the model of Clegg and Brimblecombe (1995).

The expressions of Gmitro and Vermeulen (1964) utilize directly the thermodynamic quantities tabulated by Giauque *et al.* (1960). However, thermal quantities were optimized for best agreement with high-temperature vapor pressures, and this causes differences of ±5% in calculated values of $p(H_2O)$ for molalities up to 40 mol kg^{-1} and a temperature of 213 K, with greater deviations occurring at lower temperatures.

The correlation of Zeleznik (1991), for (0 to 100)% H_2SO_4 and temperatures to 350 K, appears strongly biased toward the emf data of Hamer (1935) and Harned and Hamer (1935) which are now known to be in error. This causes predicted water activities to be too great by about 2% between 10 mol kg^{-1} and 20 mol kg^{-1} at 298.15 K. By contrast, calculated values of $p(H_2O)$ at 273.15 K and below, and for molalities greater than 10 mol kg^{-1}, are significantly lower than those obtained from the other models and equations referred to above (by up to 17% for 25 mol kg^{-1} H_2SO_4 at about 213 K). Much of this difference can be attributed to the fact that the available enthalpy data are poorly fitted by the correlation of Zeleznik (1991) for molalities above 10 mol kg^{-1}. Measurements of $p(H_2O)$ over 24.62 mol kg^{-1} and 26.18 mol kg^{-1} acid made in this study confirm that the work of Zeleznik (1991) is inaccurate in this region of concentration.

The measurements of Zhang *et al.* (1993a), Becker *et al.* (1995), and those from the present study for molalities up to 10 mol kg^{-1} agree satisfactorily with model predictions. The small systematic deviations that exist between experimental and predicted $p(H_2O)$ for the data of Zhang *et al.* (1993a) are attributed to experimental artifacts.

The partial pressures determined in the present study are not sufficiently precise to draw detailed conclusions about the relative accuracy of the models below about the 10% level. A worthwhile improvement in this area would require about a factor of 5 increase in precision for measurements in the (0.1 to 1.0) Pa region close to 200 K. In terms of practical gains such measurements would probably not be justified, and the problem might in any case be better approached indirectly, by measuring enthalpies for example. However, uncertainties in liquid phase activities at room temperature above about 40 mol kg^{-1} are likely to be more important, especially as these also affect the vapor−liquid equilibrium of H_2SO_4. Further vapor pressure measurements at low temperature should focus on mixed acid solutions, again thought to be significant in the chemistry of the stratospheric aerosols. For such systems (e.g., $HCl + HNO_3 + H_2SO_4 + H_2O$) the data remain relatively sparse, although predictive models of vapor−liquid equilibrium have been produced (Tabazadeh *et al.*, 1994b; Carslaw *et al.*, 1995).

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