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Thermodynamic Properties of the Aqueous Sulfuric Acid System to 350 K

Frank J. Zelenik

National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44135

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Experimental measurements for aqueous sulfuric acid and its related pure, solid phases have been thermodynamically analyzed and correlated as a function of temperature and composition from pure water to pure acid. The pure phases included anhydrous sulfuric acid, five of its hydrates and ice. Experimental data which were used in the correlation included measurements of the enthalpy of dilution, both solution and pure phase heat capacities, electromotive force and solution freezing points. The correlation yielded mutually consistent expressions for the Gibbs energy of each phase and these functions generally reproduce the experimental data to ± 0.75 percent. The Gibbs energy functions of the pure solid phases were used to generate tables of their thermodynamic properties from 0 K to the melting points. The Gibbs energy function for aqueous sulfuric acid was used to produce tables of both integral and partial molar solution properties as a function of sulfuric acid mole fraction every 50° from 200 to 350 K.

Key words: aqueous; critical evaluation; electrolytes; enthalpy; Gibbs energy; heat capacity; ice; solutions; sulfuric acid; sulfuric acid hydrates; thermodynamic properties.

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		ϕ	osmotic coefficient of aqueous sulfuric acid

Symbols and Units

a_j	parameters used to describe the temperature dependence of the Gibbs energy
C_i	solution components; $C_1 = \text{H}_2\text{SO}_4$, $C_2 = \text{H}_2\text{O}$
C_p	molar isobaric heat capacity, J/mol·K
$C_p^{(r)}$	relative molar isobaric heat capacity of aqueous sulfuric acid, J/mol·K; equal to the molar isobaric heat capacity
E	electromotive force
E_0	reference energy for the pure solid phases, J/mol; equal to the enthalpy of the solid at its melting temperature
F	Faraday constant, 96484.56 A·s·mol ⁻¹
G	molar Gibbs energy, J/mol
G°	reference molar Gibbs energy for aqueous sulfuric acid, J/mol; $G^\circ = H^\circ(T_0, P; x) - TS^\circ(T_0, P; x)$
$G^{(r)}$	relative molar Gibbs energy of aqueous sulfuric acid, J/mol; $G^{(r)} = G - G^\circ(T, P; x)$
H	molar enthalpy, J/mol

1. Introduction

Aqueous sulfuric acid is an economically important chemical when judged by most standards of evaluation. It is by far the largest volume chemical commodity in the world. Its major uses include fertilizer production, petroleum refining, extraction of metals from their ores, production of inorganic pigments, pickling of iron and steel, synthesis of surface active agents, and as a reactant in the lead-acid storage battery (Donovan and Salamone).¹ Sulfuric acid has also been identified as an environmentally significant chemical. Its presence in acid rain contributes to ecological damage of lakes, corrosion of steel, attack on marble and mortar, brittleness of paper, injury to vegetation, and respiratory infections in humans (Sticksel and Engdahl).² Sulfuric acid is also thermodynamically challenging. It is a highly nonideal

binary system which displays complex physical and chemical behavior. At lower temperatures its phase diagram is characterized by the appearance of several pure solid phases including ice, anhydrous sulfuric acid, and several of its hydrates. Some of the solids melt congruently while others melt incongruently. The liquid phase exhibits a strong tendency to supercool.

Because of the obvious importance of aqueous sulfuric acid it would be reasonable to presume that its thermodynamic properties have been measured extensively and accurately, and that these measurements have been critically evaluated and correlated. This is true to some degree, but the effort expended on sulfuric acid has not been commensurate with its importance. While a moderate body of experimental knowledge has been accumulated, little of it is of recent vintage and much of it is restricted in scope. Measurements are generally confined to relatively dilute solutions near room temperature; scant attention has been given to concentrated solutions at elevated temperatures. The situation is similar with regard to the evaluation and correlation of these measurements. This has been done only at room temperature, almost exclusively for the relatively dilute acid, and has used only a small portion of the available data.

It is desirable to know the properties of aqueous sulfuric acid for both the dilute and the concentrated acid at temperatures that differ from room temperature. For example, much of sulfuric acid is produced, sold and transported as a concentrated acid. Furthermore, during its production and use the acid is often at temperatures quite removed from room temperature. The purpose of this paper is to correlate the thermodynamic measurements of aqueous sulfuric acid over an extended temperature range and for concentrations from pure water to pure sulfuric acid. This should permit cautious extrapolation of thermodynamic properties to regions where no experimental data exist. The analysis will cover not only the thermodynamic properties of aqueous sulfuric acid but also the thermodynamic properties of the relevant pure solid phases which form when the acid is cooled.

2. Experimental Measurements

Experimental thermodynamic measurements on aqueous sulfuric acid have a long history with some references dating back to before the turn of the century. However, very few such measurements have been carried out in this decade or the preceding one. Much of the very early work is of questionable accuracy and, where possible, the analysis will rely on the more recent measurements. A bibliography of sources for the thermodynamic and transport properties of aqueous sulfuric acid has been compiled by Staples and Wobbekeing.³

Data which are suitable for the thermodynamic analysis of a solution can be broadly categorized as being either single phase measurements or multiphase measurements. Examples of the former are solution heat capacity and the heat effects associated with various mixing processes such as enthalpy of dilution, and enthalpy

of solution. Typical experiments which involve more than one phase include the measurement of vapor pressure, vapor-liquid equilibria, freezing point and electromotive force (emf). Speaking pragmatically, single phase measurements are preferable over multiphase measurements for the extraction of thermodynamic information about a given phase. One need not then consider the effects of the extraneous phases nor need one be concerned about the establishment of equilibrium among the phases. Thus, ideally, one would rely exclusively on single phase measurements. But seldom do single phase measurements adequately cover the desired range of independent variables nor do they yield information about all of the thermodynamic properties of a phase. Consequently, it becomes necessary to use some multiphase measurements to supplement single phase data. Fortunately, multiphase thermodynamic measurements oftentimes can be cast into a form which eliminates the peripheral phases and their influence on the properties of the central phase. Such reformulated measurements may be regarded as pseudosingle phase properties since their values are only a function of one phase. Reliance on pseudosingle and single phase measurements insures a correlation of a phase's properties which is not biased by avoidable assumptions about the extraneous phases. One can then reserve the use of true multiphase data for establishing thermodynamically consistent connections among phases.

In this treatment of aqueous sulfuric acid I shall rely heavily, but not exclusively, on pseudosingle and true single phase data. I shall make no use of measurements based on vapor-liquid equilibrium. Thus, measurements of vapor pressure and isopiestic ratio will not be used to generate thermodynamic information about the sulfuric acid system. To use vapor pressure measurements would require assumptions about the composition and thermodynamic behavior of the vapor phase. To use isopiestic measurements would require assumptions about the properties of the various reference solutions. Both of these measurements also require the implicit assumption that equilibrium has been established between phases; a nontrivial assumption given the very low vapor pressures of aqueous sulfuric acid. The sole exception to the use of single phase data is some freezing point data which will be used to connect the solution properties to the properties of the pure phases which freeze out of solution, particularly ice and solid sulfuric acid. The properties of ice and solid sulfuric acid are reasonably well-measured and noncontroversial. By contrast, questions have been raised about the consistency between emf and vapor-liquid equilibria.

The decision to use multiphase measurements as pseudosingle phase data has the obvious advantage that the results will reflect solely the contribution of the central phase to the experimental values. That is, the results are not influenced by assumed values for the properties of other phases nor are they affected by any assumed limiting behavior of the measurements themselves. Both of these factors could easily introduce inconsistencies into the analysis which are not inherently present in the data.

But properties processed in this manner are essentially difference properties. Consequently, their values can be expected to show greater local scatter, reflecting the intrinsic scatter in the measurements themselves. This local scatter will not affect the global behavior of the thermodynamic properties, because it will cancel. There is a minor disadvantage associated with difference values. It becomes more difficult to judge the accuracy with which the data are represented. Values are now, at best, two-point functions. That is, they depend on the coordinates of the two points which are used to form the difference. Thus difference values derived from a series of experimental points will not vary in a continuous way. There may be large, seemingly random, changes in adjacent values reflecting the separation between the two points involved. Where the points are closely spaced the differences can be small even though the property may be changing rapidly and conversely. For two-point functions one cannot visualize the quality of the representation in a simple manner by plotting a dependent variable versus an independent variable.

In the following paragraphs I shall briefly review the datasets which were selected for analysis and describe how these data were used. The experimental data were processed using the 1973 CODATA recommendations for the fundamental constants (Cohen and Taylor⁴). The gas constant was $R = 8.31441 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ while the value for the Faraday constant was $F = 96484.56 \text{ A}\cdot\text{s}\cdot\text{mol}^{-1}$. Molecular weights were calculated using the 1984 atomic weights given by De Bievre, Gallet, Holden, and Barnes.⁵ All data are at a nominal pressure of 0.1 MPa. Where the necessary information was available, temperatures were converted to the International Practical Temperature Scale of 1968 (IPTS-68), energy values to absolute joules, and voltages to absolute volts. Compositions were expressed as mole fractions. Altogether 1325 data points, over the temperature range -50 to 60 °C, were processed to generate a representation for the thermodynamic properties of aqueous sulfuric acid. Of these, 819 were from galvanic cells, 166 represented enthalpies of mixing, 193 were solution heat capacities, and 147 values came from the freezing points of aqueous sulfuric acid solutions. An additional 544 heat capacities were processed to generate the thermodynamic properties of the various solid phases. These were distributed as follows: 287 for ice, 49 for sulfuric acid, 55 for the monohydrate, 41 for the dihydrate, 35 for the trihydrate, 44 for the tetrahydrate and 33 for the hemihexahydrate.

2.1 Enthalpy of Mixing

Experimental values for the heat effects accompanying the dilution of aqueous sulfuric acid with water are available in four papers, three of which describe measurements made only at 25 °C. Chronologically the first of these measurements was made by Lange, Monheim, and Robinson⁶ on very dilute solutions. They gave values at 25 °C for initial molalities from $m = 0.003$ to 0.05 which were diluted to produce an extremely dilute acid.

Groenier's measurements,⁷ also at 25 °C, dealt with slightly more concentrated solutions whose initial concentrations varied from $m = 0.003$ to 3.7. However, since Groenier was interested in the partial molar enthalpy, his dilutions were not as large as those used by Lange *et al.* and amounted to about a 10 percent reduction in molality.

Somewhat more recent measurements are those of Kunzler and Giauque⁸ who made measurements both at 25 and at -20 °C. At each temperature they covered the complete composition range available to the solution. At 25 °C this ran from pure water to pure acid and beyond. At -20 °C the composition range was more restricted because of solution freezing. Because partial molar properties of concentrated solutions motivated the work, each dilution of a concentrated solution produced a small change in the mole fraction of sulfuric acid. Typically the change was less than 5 percent for the more concentrated solutions. The percentage change for dilute solutions was considerably larger. The experimental results were extensively revised by Giauque, Hornung, Kunzler and Rubin⁹ in their recalculation of the original data. The recalculations were necessary largely to correct errors in solution compositions which were discovered subsequent to the publication of the original measurements.

The most recently published measurements are those of Wu and Young¹⁰ whose experiments were almost contemporaneous with those of Kunzler and Giauque.⁸ Their data overlap those of Groenier in composition. The initial molalities range from $m = 0.001$ to 2.5 and, like Groenier, their measurements were at 25 °C and the dilutions produced about a 10 percent change in molality. The measurements of Wu, those of Groenier and those of Kunzler and Giauque at 25 °C appear to be consistent over the region of composition overlap. Indeed, data were exchanged and compared among the experimenters.

All experimental data were converted to molar enthalpies of mixing defined as the enthalpy change accompanying the isothermal, isobaric mixing of two solutions (solution 1 and solution 2) to form 1 mole of the resulting solution (solution 3).

$$H_{\text{mix}}^{(1,2 \rightarrow 3)} = H(x^{(3)}) - [X^1 H(x^{(1)}) + X^2 H(x^{(2)})] \quad (1)$$

Here X^i represents the molar contribution of the i^{th} solution to the resulting solution and $X^1 + X^2 = 1$. The enthalpy of mixing was scaled by RT so that $H_{\text{mix}}^{(1,2 \rightarrow 3)}/RT$ was the dimensionless quantity used in the thermodynamic analysis. An advantage to using enthalpy of mixing over enthalpy of dilution is that its magnitude more nearly reflects the actual size of the heat effect measured calorimetrically. This gives greater emphasis to the larger heat effects which can be measured more accurately. Values of $H_{\text{mix}}^{(1,2 \rightarrow 3)}/RT$ ranged over five orders of magnitude for the four sets of data.

2.2 Heat Capacity

Experimental heat capacities relevant to aqueous sulfuric acid have been given in a number of papers. Osborne, Stimson and Ginnings¹¹ gave heat capacities of

liquid water from just above its freezing point to almost the boiling point. Randall and Taylor¹² measured the heat capacity of dilute solutions at 25 °C from a molality of $m = 0.04$ to 2.4. Kunzler and Giauque⁸ reported heat capacities at 25 and -20 °C for solutions containing more than 10 percent sulfuric acid by weight ($m > 1.1$). Larson, Zeeb and Hepler¹³ supplied heat capacity data at 25 °C for molalities less than $m = 0.6$.

The remaining heat capacity measurements are associated with various solid phases formed when aqueous sulfuric acid is cooled. The measurements for some of the solids were extended beyond their melting points and thus supplied heat capacity values for the liquid phase as a function of temperature at a fixed composition.

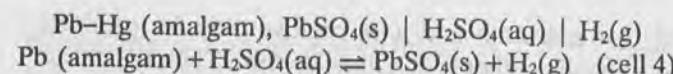
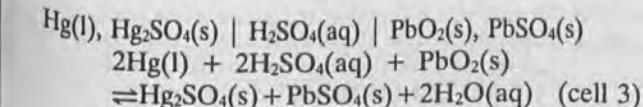
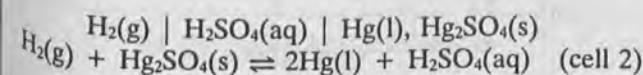
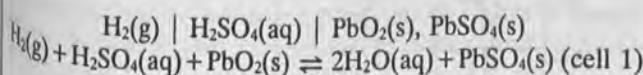
Four sets of experimental values for the heat capacity of ice are available. Giauque and Stout¹⁴ made measurements from 15 K to almost the melting point. They also cite six data points from Simon between 9 and 13 K. More recently, Flubacher, Leadbetter and Morrison¹⁵ made low temperature measurements between 2 and 27 K. The latest set of heat capacity data is from Haida, Matsuo, Suga and Seki¹⁶ who made measurements from 13 K to nearly the melting point.

Heat capacity measurements on solid sulfuric acid and its hydrates were made by Giauque and coworkers over the temperature range 15 to 300 K. The higher temperatures were above the melting points of the solids. Rubin and Giauque¹⁷ studied the monohydrate and dihydrate of sulfuric acid and sulfuric acid itself. The trihydrate and the tetrahydrate were measured by Hornung and Giauque.¹⁸ Hornung, Brackett and Giauque¹⁹ examined the hemihexahydrate and additionally measured liquid phase heat capacities at compositions corresponding to that of a hexahydrate and an octahydrate from 210 to 300 K.

Experimental heat capacities at constant pressure were converted to the molar heat capacity at constant pressure and scaled by R .

2.3 Electromotive Force

Electromotive force measurements on four electrochemical cells are relevant to the thermodynamic characterization of aqueous sulfuric acid. The cells and cell reactions are as shown below. In each case the cell and the cell reaction are written so that the negative electrode (lower potential) is on the left when the cell reaction proceeds from left to right.



Three sets of measurements of the electromotive force of cell 1 are available in the literature. The most extensive set is that of Hamer²⁰ which provides values at 23 concentrations from a molality $m = 0.0005$ to 7.0 and at 5° temperature intervals from 0 to 60 °C. Subsequently, Beck, Singh and Wynne-Jones²¹ made measurements at 10 concentrations from $m = 0.1$ to 7.2 for each of 7 temperatures from 5 to 55 °C. Covington, Dobson and Wynne-Jones²² measured the cell at 25 °C for five concentrations which ranged from $m = 0.0007$ to 0.1. The authors of this paper make a statement which implies that the results of Beck, Singh and Wynne-Jones are given in international volts whereas, from the date of the paper, one might expect the values to be in absolute volts. Since Beck *et al.* make no explicit statement about the units, the measurements were treated as international volts and converted to absolute volts for use in the correlation.

Six papers give data for cell 2. Randall and Cushman²³ made measurements at 25 °C for five molalities from $m = 0.005$ to 8.2. Trimble and Ebert²⁴ also produced values at 25 °C for six concentrations from $m = 0.005$ to 1.0. MacDougall and Blumer²⁵ listed seven data points, all at 25 °C, from $m = 0.05$ to 2.4. The most complete coverage was produced by Harned and Hamer²⁶ who studied the cell at 5° intervals from 0 to 60 °C and molalities from $m = 0.05$ to 17.5. Of somewhat more recent vintage are the data of Beck, Dobson and Wynne-Jones²⁷ at 10° intervals from 5 to 55 °C and for molalities from $m = 0.1$ to 8.0. Finally, 13 values are available from Covington, Dobson and Wynne-Jones²² at 25 °C and at concentrations from $m = 0.007$ to 0.06.

The only data for cell 3 are from the measurements of Vosburgh and Craig²⁸ at 5° intervals between 20 and 40 °C and for various concentrations from $m = 0.1$ to 3.5.

Similarly, for cell 4 we have only the values given by Shrawder and Cowperthwaite²⁹ who carried out experiments at four temperatures between 0 and 50 °C from $m = 0.001$ to 0.02.

Wynne-Jones and coworkers have asserted that Hamer's data for cell 1 and the Harned and Hamer data for cell 2 are in error. However, their conclusion is based on a calculation of standard emf and standard enthalpy of reaction for the cells at 25 °C and noting their apparent nonconstancy. These calculations used an extrapolation to infinite dilution and assumed values for solution properties derived from vapor-liquid equilibrium measurements; both are themselves open to question.

The thermodynamic analysis of electrochemical cells is based on the assumption that the emf arises from the conversion of Gibbs energy to electrical energy by means of the cell reaction. Consider the general cell reaction written for n equivalents of charge.

$$\sum r_i S_i \rightleftharpoons \sum p_i S_i \quad (2)$$

Here S_i represents the i^{th} species in the cell reaction while r_i and p_i are non-negative numbers such that r_i is positive

only for reactants and p_i is positive only for products. Additionally, either p_i or r_i must be zero. Then the Nernst equation expresses the emf of the cell in terms of the chemical potentials of the species.

$$-nFE = \sum_i (p_i - r_i) \mu_i \quad (3)$$

This expression clearly involves the chemical potentials of all species which appear in the cell reaction and thus contains contributions from all phases which go to form the cell. However, the typical experiment is a series of measurements at a fixed temperature in which the only variable is the composition of the electrolyte. Thus if one subtracts the Nernst equation for two different measurements, the second one designated by a prime, then the only surviving terms are those containing the chemical potentials of the electrolyte.

$$-nF(E - E')/RT = \sum_i (p_i - r_i)(\mu_i - \mu'_i)/RT \quad (4)$$

This form of the equation shows that solution properties depend only on the voltage difference and not on the actual value of the voltage. Thus the cell voltage could be in error by an arbitrary function of temperature and still yield good solution properties. This obviates the need to extrapolate cell measurements to infinite dilution; a problematical procedure at best. There still remains the task of choosing the composition to be used as the reference point, marked by the prime, in Eq. (4). Obviously one could choose some fixed composition. This, however, is undesirable because it over-emphasizes the importance of the chosen reference point and its associated errors. A superior choice is to imagine the set of experimental points to be laid out on the circumference of a circle and to choose as the reference point for each measurement the point which follows it on the circle or, equivalently, the point which precedes it. This allows each point, in turn, to act as a reference. Consequently each measurement appears twice in the resulting dataset; once as a data point and once as a reference point. Thus the balance among the points is maintained and no point will unduly influence the correlation. This was the method adopted in analyzing emf data.

2.4 Freezing Point

There are two important papers on isobaric freezing points of aqueous sulfuric acid. The first is a paper by Gable, Betz and Maron³⁰ who determined the phase diagram from pure water to pure acid and beyond. They determined eutectic and peritectic points in addition to the melting points of the congruently melting compounds formed on freezing. Because of supercooling they also were able to measure metastable eutectic points. Freezing point curves of concentrated sulfuric acid solutions were also determined by Kunzler and Giauque.³¹ Their measurements covered the composition range from near the $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O} - \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ eutectic to just beyond the pure acid. The two sets of measurements are largely

consistent although for sulfuric acid mole fractions greater than 0.6 there is some disagreement. The Kunzler and Giauque freezing points tend to be somewhat lower than those of Gable *et al.* in this composition range. Kunzler and Giauque suggest that this may be a result of the inability of Gable *et al.* to attain true equilibrium because of the highly viscous nature of the concentrated solution. The phase diagram for aqueous sulfuric acid is shown in Fig. 1 where the plotting symbols designate the experimental data points. Horizontal lines are drawn through the various eutectic, and peritectic points determined by Gable *et al.* while vertical lines locate the compositions of the various pure, solid phases in the system. The curves show freezing points which were calculated from the thermodynamic properties deduced in this paper. The trihydrate and the hemihexahydrate melt incongruently while all other solids shown in the phase diagram melt congruently. There is some evidence that an octahydrate exists but it has not been possible to prepare it (Hornung, Brackett, and Giauque, 1956).¹⁹

Thermodynamic analysis of freezing points is based on the assumption that an equilibrium exists between the solution and the solid phase. Suppose the solid phase is a pure compound P and the solution is composed of the components (independent species) C_i . Then the reaction and the associated equilibrium condition can be written as

$$\begin{aligned} \sum_i r_i C_i &\rightleftharpoons P \\ \sum_i r_i \mu_i &= \mu_p \end{aligned} \quad (5)$$

where μ_p is the chemical potential of the pure solid phase. This form of the equilibrium condition possesses

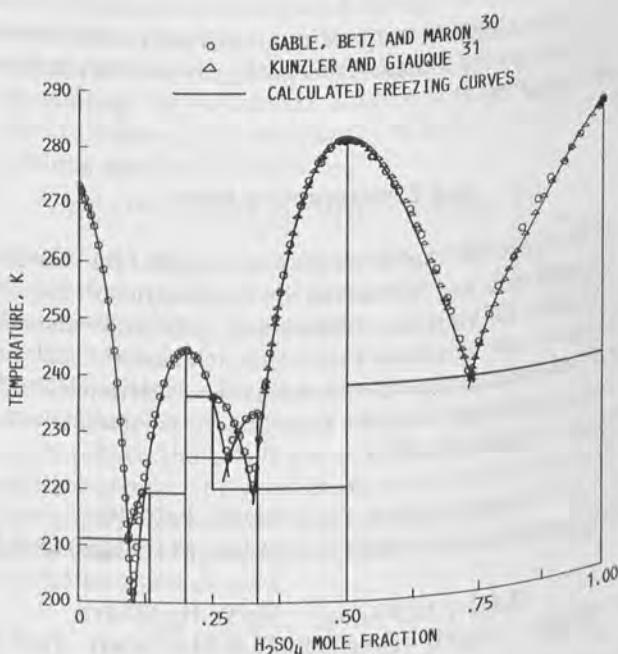


Fig. 1. Phase diagram for the sulfuric acid - water binary system. Curves are calculated from the correlations of this paper: \circ = Gable, Betz and Maron,³⁰ \triangle = Kunzler and Giauque.³¹

the distinct disadvantage that it requires a knowledge of the thermodynamic properties of the solid phase as well as the freezing point curve. Nonetheless, it was applied to the freezing out of ice and $\text{H}_2\text{SO}_4(\text{s})$ treating μ_P as known. The known values of μ_P serve to connect solution properties to the pure species properties.

Suppose, on the other hand, that P is a congruently melting solid within the composition range being studied, as is true for the monohydrate and tetrahydrate of sulfuric acid. Then its freezing temperature will be a local maximum in the isobaric freezing point curve of the solution (Fig. 1). Hence it is possible to find, for some range of temperatures below the congruent melting point, two different solution compositions which are in equilibrium with the solid at a given temperature. These solutions are on opposite sides of the solid phase composition. Subtracting the equilibrium conditions at the two points eliminates the chemical potential, μ_P , of the solid phase.

$$\sum x_i(\mu_i - \mu'_i) = 0 \quad (6)$$

The advantage of this form is that it only depends on the measured freezing curve and not on the thermodynamic properties of the solid phase. This form of the equilibrium condition was applied to the freezing out of both the monohydrate and the tetrahydrate. Fortunately, the experimental data which are available are so closely spaced that for each experimental point one can find its image point by linear interpolation of the data. Since each experimental point is paired with its interpolated image point, neither the image point nor the interpolation process should compromise the accuracy of the correlation.

2.5 Enthalpies of Fusion

The enthalpy of fusion for ice was measured by Dickinson and Osborne³² and by Haida *et al.*¹⁶ Giauque *et al.*¹⁷⁻¹⁹ measured enthalpies of fusion and melting points for sulfuric acid and its hydrates. These are estimated values for the trihydrate and the hemihexahydrate which undergo a peritectic reaction rather than melting. The ice and sulfuric acid enthalpies of fusion were used to analyze the ice and sulfuric acid equilibria with aqueous sulfuric acid. The hydrate enthalpies of fusion, together with hydrate properties and preliminary estimates of aqueous sulfuric acid properties, were only used to generate estimates for solution enthalpy and Gibbs energy at the melting points. The resulting values were used in correlating the solution properties to promote consistency between the crystalline hydrates and aqueous sulfuric acid.

2.6 Excluded Measurements

As the data were being correlated it became clear that some of the measurements were inconsistent with the bulk of the data. Accordingly these measurements were processed but were given zero weight in the analysis. The

mixing data of Kunzler and Giauque⁸ at -20°C appear to be inconsistent with the other data although the reason for the inconsistency is not obvious. The experimental enthalpies of mixing are from 20 to 50 percent lower than the predicted values. By contrast, their heat capacity data at -20°C seem quite accurate. This may simply reflect the difficulty of performing dilutions with water at temperatures below the freezing point of water. Consequently, the dilution measurements at -20°C were given zero weight. Also given zero weight were the solution heat capacities of Randall and Taylor¹² whose heat capacities clearly have an incorrect composition dependence. Similarly, the low temperature heat capacities of ice measured by Simon¹⁴ were rejected because the temperature dependence of the data seems to be somewhat in error.

The freezing point data of Gable, Betz and Maron³⁰ were used for the equilibria of solution with both ice and tetrahydrate. However, at the higher concentrations their measurements differ from those of Kunzler and Giauque³¹ whose temperatures are perceptibly lower. The Kunzler and Giauque data were used for both anhydrous acid and monohydrate equilibria with solution.

3. Previous Property Correlations

The correlation of thermodynamic properties of sulfuric acid has been going on for almost as long as the experimental data have existed. However, the earlier correlations are now only of historical interest. For example, Porter,³³ using estimation and the meager data then available, generated properties to 240°C for dilute and concentrated acid. Somewhat more recently, Craig and Vinal³⁴ calculated the partial molar enthalpy and partial molar heat capacity, at nominally room temperature, in their examination of the lead-acid storage battery. Their enthalpy table extends to a molality $m = 110$ while their heat capacity table goes to nearly $m = 400$.

In relatively more modern times the supply of experimental data has grown considerably, but much of it has gone unused. Partly this was because the newer correlations were, for the most part, limited to a few properties rather than the full spectrum of thermodynamic properties for which data existed. In part this was also due to the temperature and composition limitations of these correlations. The limitations in properties and independent variables meant that the correlations did not have to deal with the full set of consistency requirements imposed by the thermodynamic formalism. Consequently, working from essentially the same pool of experimental data, the evaluators came to very different conclusions regarding the accuracy and relevance of various measurements.

Using largely their own data, Giauque *et al.*⁹ produced tables for aqueous sulfuric acid at 25°C for the full composition range. To generate the properties they used enthalpy of dilution, heat capacity, and vapor pressure data together with some freezing points for concentrated solutions. They did not, however, make any use of data for the freezing points of dilute solutions or data from galvanic cells. Their tables give partial molar properties for Gibbs

energy, enthalpy, and heat capacity. They also produced tables for the thermodynamic properties of solid sulfuric acid and its hydrates using their own heat capacity measurements.

Rard, Habenschuss and Spedding³⁵ used 174 points to deduce the partial molar Gibbs energies for aqueous sulfuric acid to a molality of 27.7 at 25 °C. Of the 174 measurements, 142 were isopiestic ratios, 29 were vapor pressures and only 3 were emf data. They pointed to the apparent discrepancies between vapor-liquid equilibrium data and cell data to justify their exclusion of the latter. Thus they relied virtually exclusively on vapor-liquid equilibria as their source of data. Their reduction of this data required the use of information that was peripheral to aqueous sulfuric acid. They used osmotic coefficients for the various isopiestic reference solutions as well as a second virial coefficient for water vapor and the vapor pressure of pure water. To generate the parameters of their correlation they only fit osmotic coefficients, by least squares, and calculated the sulfuric acid activity coefficients by a Gibbs-Duhem quadrature.

By way of contrast, Pitner, Roy and Silvester³⁶ concluded that osmotic data were less precise than cell data. In their treatment of the very dilute acid they relied mostly on cell data supplemented with enthalpy of dilution measurements and some smoothed values for the osmotic coefficient from Robinson and Stokes³⁷ and Rard *et al.*³⁵ Parameters for their correlation were obtained by least squares and are applicable to temperatures near 25 °C, and to molalities no greater than six.

Finally, there is the evaluation of the partial molar Gibbs energy by Staples³⁸ who worked with a considerably larger set of measurements than the other evaluators. In his analysis he considered 657 data points which consisted of 80 vapor pressures, 291 isopiestic ratios, 155 freezing points of dilute acid and 131 emf values. But many of the data points (fully 25 percent) were assigned zero weight. For example, a substantial fraction of the freezing points were given zero weight and in no case were freezing points for $m > 0.65$ used. The same is true of cell measurements where sometimes low and sometimes high concentration values were considered suspect and thus rejected. The evaluation was at 25 °C and went to $m = 28$. Staples used the same kind of peripheral data employed by Rard *et al.* in their analysis. Additionally, he also used solution enthalpy and heat capacity for a 25° extrapolation of osmotic coefficients, calculated at the freezing point of ice, to 25 °C. He deduced the parameters of the correlation by a nonlinear least squares procedure applied to osmotic coefficients and the logarithm of the sulfuric acid activity coefficients.

4. The Present Correlation

The present multiproperty correlation treats both composition and temperature as independent variables. Consequently, the analysis automatically imposes stringent thermodynamic consistency requirements among Gibbs energy, enthalpy, heat capacity and their composition

derivatives. The result of the correlation of aqueous sulfuric acid properties is a function, $G^{(r)}(T, P; x)$, which gives the molar Gibbs energy of the solution relative to the pure species at 298.15 K and 0.1 MPa.

$$\left. \begin{aligned} G^{(r)}(T, P; x) &\equiv G(T, P; x) - G^\circ(T, P; x) \\ G^\circ &\equiv H^\circ(T_0, P; x) - TS^\circ(T_0, P; x) \\ H^\circ &\equiv \sum_i x_i H_i^*(T_0, P), S^\circ \equiv \sum_i x_i S_i^*(T_0, P) \end{aligned} \right\} \quad (7)$$

In these expressions $T_0 = 298.15$ K, $P = 0.1$ MPa and H_i^* , S_i^* are the pure species molar enthalpies and entropies. All other solution properties are then calculable from G by differentiation. Thus the chemical potential is obtained by partial differentiation with respect to mole fractions.

$$\left. \begin{aligned} \mu_i^r &= \mu_i(T, P; x) - \mu_i^\circ(T, P) \equiv [1 - \sum_k x_k (\partial/\partial x_k) + (\partial/\partial x_i)] G^{(r)} \\ \mu_i^\circ(T, P)/RT &= H_i^*(T_0, P)/RT - S_i^*(T_0, P)/R \end{aligned} \right\} \quad (8)$$

The relative enthalpy and heat capacity are generated by partial differentiation with respect to temperature.

$$\begin{aligned} [H(T, P; x) - H^\circ(T_0, P; x)]/RT &= H^{(r)}(T, P; x)/RT \\ &\equiv -\partial[G^{(r)}(T, P; x)/RT]/\partial \ln T \quad (9) \\ C_p(T, P; x) &= C_p^{(r)}(T, P; x) \equiv \partial H^{(r)}(T, P; x)/\partial T \end{aligned}$$

The partial molar enthalpies and heat capacities can be obtained from these by partial differentiation with respect to mole fractions in a manner identical to that used to get the chemical potentials in Eq. 8. Alternatively, they can be generated by partial differentiation of the chemical potentials with respect to temperature.

The correlation of solid phase heat capacities yields a function of temperature and pressure, $G(T, P) - E_0$, that gives the Gibbs energy of a pure species relative to an arbitrary energy level. The enthalpy and heat capacity are again obtained from the Gibbs energy by differentiation with respect to temperature.

$$\begin{aligned} [H(T, P) - E_0]/RT &\equiv -\partial[G(T, P) - E_0]/\partial \ln T \quad (10) \\ C_p(T, P) &\equiv \partial[H(T, P) - E_0]/\partial T \end{aligned}$$

For all species E_0 is chosen as the enthalpy of the crystal at its fusion temperature.

4.1 The Present Correlation and Experimental Data

Ideally, any correlation of measurements should emphasize the contributions of the more accurate values over the contributions of lower quality data. There are two reasons why this goal might not be achieved. First, one is seldom in a position to assign unequivocal quality ratings to measurements. This is especially true with multiproperty correlations where one must assign figures of merit not only to reflect the inherent errors in the measurements of each property separately, but also to quantify the thermodynamic inconsistencies among the different measurements. Second, there is the possibility that the representation of small, high quality datasets

might be compromised by large datasets of inferior quality. The contributions of a small dataset to the correlation might literally be swamped by those from a large dataset. To guard against these possibilities in the present correlation, the four categories of measurements were added to the correlation one at a time and in the sequence heat capacity, enthalpy, electromotive force and freezing points. The effects produced on the correlation by the addition of each measurement category were monitored graphically and with the statistics associated with the correlation. The results of this process led to the exclusion of the datasets mentioned in Sec. 2.6. They also suggested that the final correlation does not contain any untoward bias in the representation of the other experimental datasets. Perhaps the best indicator of this is the uniformly good representation of most of the measurements which were used to generate the correlation. In subsequent paragraphs I shall look at the representation of the measurements in some detail.

As pointed out earlier, only two types of data were not used as difference properties: (1) solution heat capacity, and (2) the chemical potential of water along the ice-solution freezing curve and the chemical potential of sulfuric acid along the $\text{H}_2\text{SO}_4(\text{s})$ -solution freezing curve. These properties can be presented graphically and so we look at them first. The results are displayed both as a plot of the property and as a plot of the residuals which are defined as the difference between the observed and predicted values. On the property plots the experimental values are shown as points while the curve is the calculated property. On the residual plots the points represent the residuals for the experimental data and the curves show $\pm 3/4$ percent of the calculated property. A horizontal line separates the positive and negative residuals and corresponds to zero error. Figures 2 to 12 show solution heat capacity and the associated residuals as a function of either composition or temperature. All data are well represented except for the clearly erroneous data of Randall and Taylor (1941)¹² shown in Fig. 2(a). In fact, the points generally lie within $\pm 3/4$ percent of the calculated curve except for isolated points.

The somewhat unusual behavior of the heat capacity of aqueous sulfuric acid at 25 °C deserves some comment. It is known that chemical reactions often make a substantial contribution to heat capacity, waxing and waning in synchrony with reaction. If the augmentation of heat capacity comes primarily from a single reaction then the maximum contribution occurs before the reaction is complete and becomes zero when the reaction reaches completion. Thus the maximum augmentation of heat capacity will occur before the maximum concentration of a species being formed in that reaction. The occurrence of simultaneous reactions will modify this behavior somewhat. Aqueous sulfuric acid is clearly a reacting system where various ionization processes are the important reactions. Its heat capacity, shown in Fig. 2(a), displays three more or less obvious enhancements which appear to maximize at mole fraction values of about 0.08, 0.54 and 0.9. There is a fourth incipient augmentation dis-

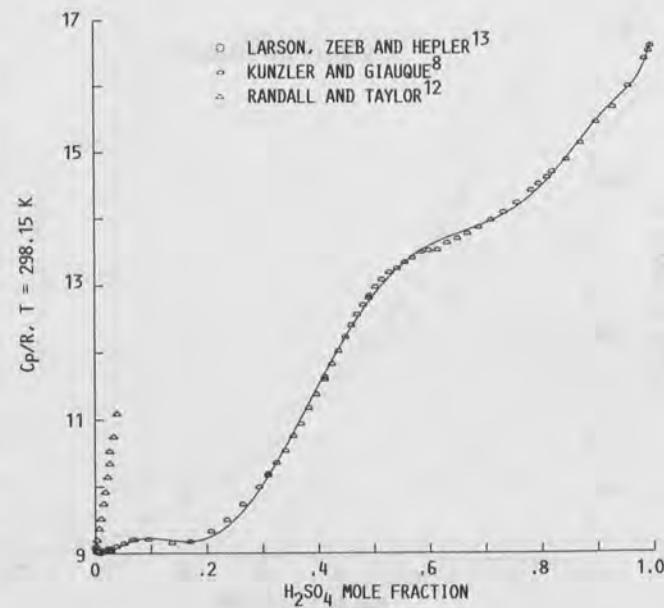


FIGURE 2(A).

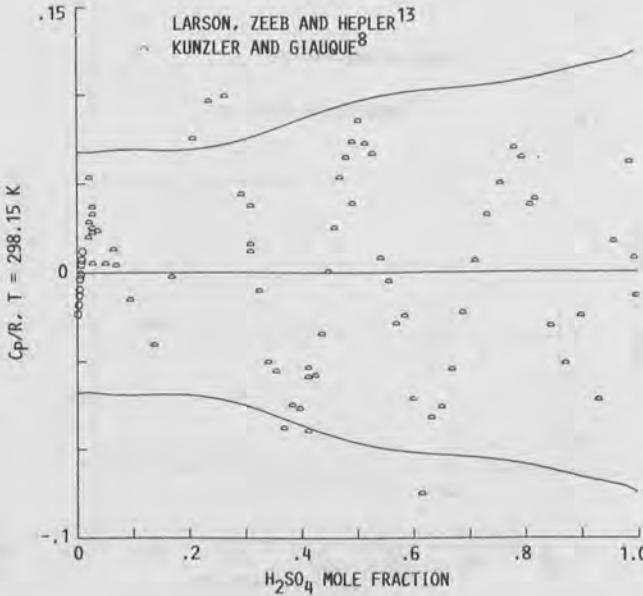


FIGURE 2(B).

Fig. 2. (a) Heat capacity of aqueous sulfuric acid at $T = 298.15$ versus sulfuric acid mole fraction: \circ = Larson, Zeeb and Hepler,¹³ \square = Kunzler and Giauque,⁸ Δ = Randall and Taylor.¹²
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for heat capacity of aqueous sulfuric acid at $T = 298.15$ K versus sulfuric acid mole fraction: \circ = Larson, Zeeb and Hepler,¹³ \square = Kunzler and Giauque.⁸

cernible near the anhydrous acid. Young and Walrafen³⁹ used Raman spectroscopy to estimate ion concentrations in aqueous sulfuric acid. They concluded that the sulfate ion peaks at an acid mole fraction near 0.15 and that the bisulfate ion peaks at a mole fraction of about 0.4. They also postulated the existence of a species, H_5SO_5^+ , whose concentration peaks near 0.9. Thus it is tempting to infer that the second and first ionizations of sulfuric acid are the major contributors to the first two heat capacity enhancements and that the formation of H_5SO_5^+ is largely responsible for the third.

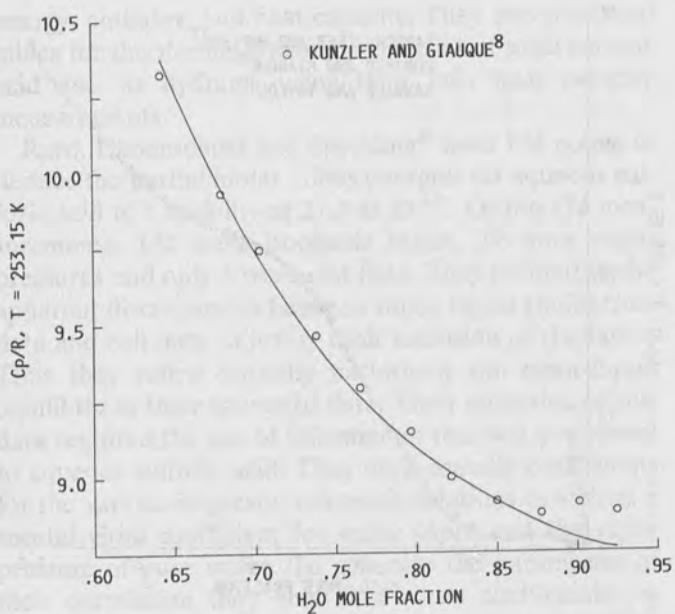


FIGURE 3(A).

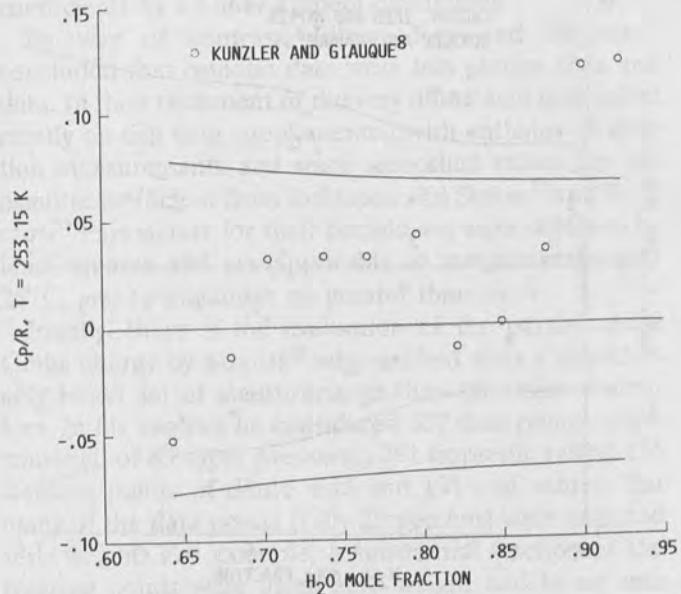


FIGURE 3(B).

Fig. 3. (a) Heat capacity of aqueous sulfuric acid at $T = 253.15\text{ K}$ versus water mole fraction: $\circ = \text{Kunzler and Giauque}^8$.
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for heat capacity of aqueous sulfuric acid at $T = 253.15\text{ K}$ versus water mole fraction: $\circ = \text{Kunzler and Giauque}^8$.

Figures 13 and 14 show the relative chemical potential of water along the ice-solution freezing curve and the relative chemical potential of sulfuric acid along the anhydrous acid-solution freezing curve. These potentials are relative to the pure species at $T = 298.15\text{ K}$. Because we are dealing with a phase equilibrium, the meaning of the experimental and calculated values is slightly different from that in Figs. 2 to 12. Here the "experimental" values are actually Gibbs energy values computed at the experimental freezing temperature from the thermodynamic

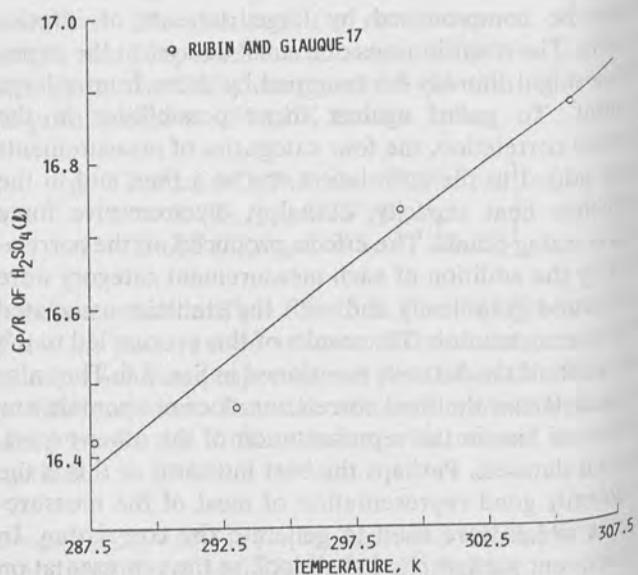


FIGURE 4(A).

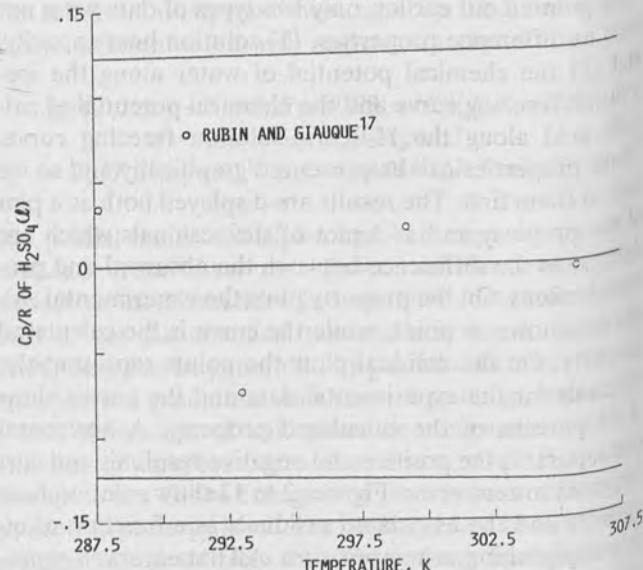


FIGURE 4(B).

Fig. 4. (a) Heat capacity of $\text{H}_2\text{SO}_4(\text{l})$ versus temperature: $\circ = \text{Rubin and Giauque}^{17}$
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4(\text{l})$ versus temperature: $\circ = \text{Rubin and Giauque}^{17}$

properties of ice or solid sulfuric acid. The calculated values are those obtained along the experimental freezing curve using the present correlation for the thermal properties of aqueous sulfuric acid. Clearly, the properties are well represented although the residuals do exceed $3/4$ percent. For ice this is largely confined to a 10° region on either side of the eutectic formed by ice and the hemihydrate (Fig. 1). This eutectic, at -62°C , is near the low temperature limit of the Gable, Betz and Maron³⁰ experiments. Furthermore, below this temperature the so

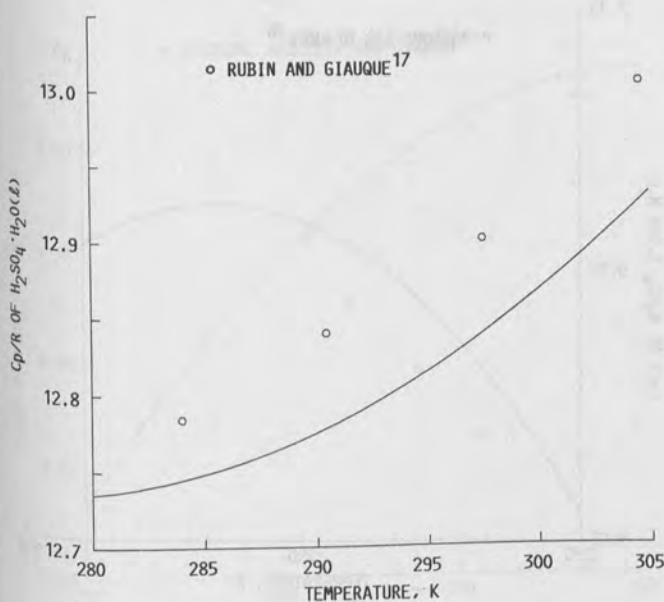


FIGURE 5(A).

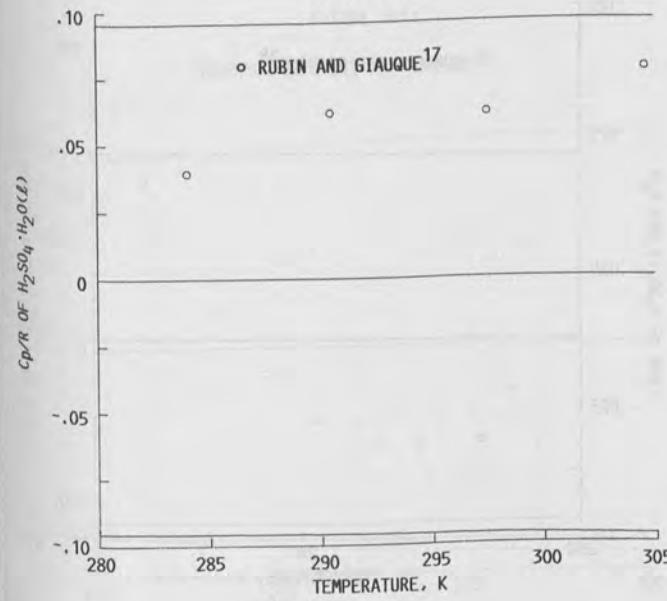


FIGURE 5(B).

Fig. 5. (a) Heat capacity of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O(l)}$ versus temperature: $\circ =$ Rubin and Giauque.¹⁷
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O(l)}$ versus temperature: $\circ =$ Rubin and Giauque.¹⁷

lution is supercooled. For the acid it occurs at the higher concentrations where solution viscosity is high and where it is very difficult to assure that phase equilibrium has been established (Kunzler and Giauque).³¹

All emf measurements were used in the form of difference values. For this data we display the residuals only to show the approximate composition range of the data for each of the cells and the general distribution of residuals. Except for cell 2, all data are confined to rather dilute acid concentrations. The residuals are plotted, grouped by cell, in Figs. 15 to 18 versus the first composition in

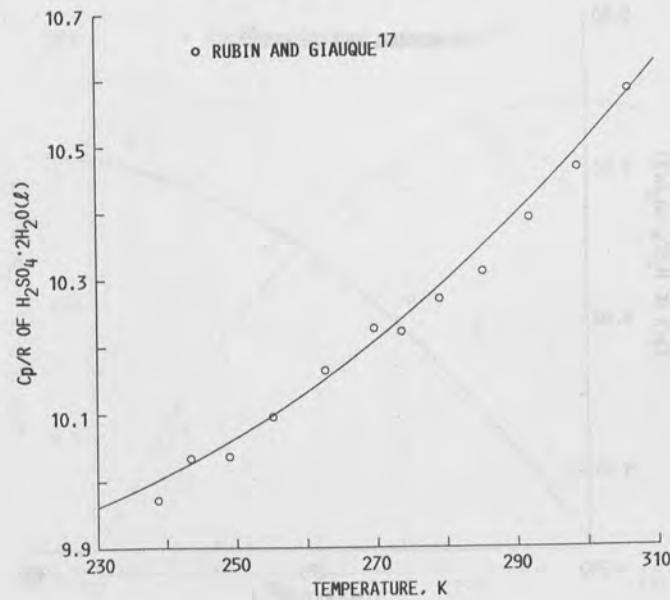


FIGURE 6(A).

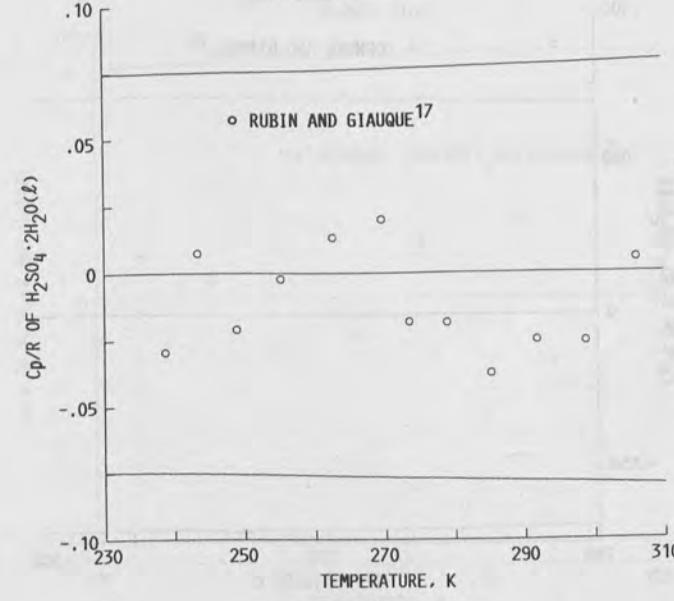


FIGURE 6(B).

Fig. 6. (a) Heat capacity of $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O(l)}$ versus temperature: $\circ =$ Rubin and Giauque.¹⁷
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O(l)}$ versus temperature: $\circ =$ Rubin and Giauque.¹⁷

Eq. (4) (the unprimed composition). Each figure displays the residuals at all temperatures. Except for isolated points, all cells seem to exhibit similarly sized residuals and to be comparably balanced between positive and negative values. One can generate a simple measure for the quality of data representation that will also quantify the relative suitability of galvanic cell data for the extraction of aqueous sulfuric acid properties. The measure is just the residual, expressed as a percentage of the voltage difference, associated with the maximum concentration difference for each dataset at a given temperature. This

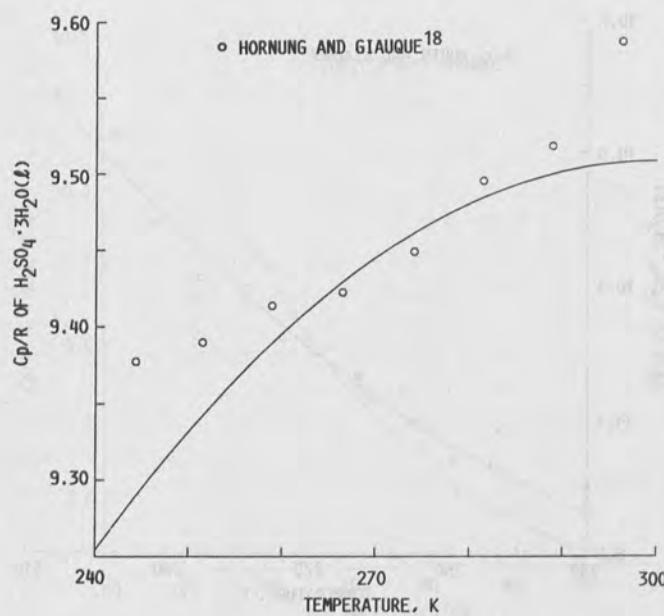


FIGURE 7(A).

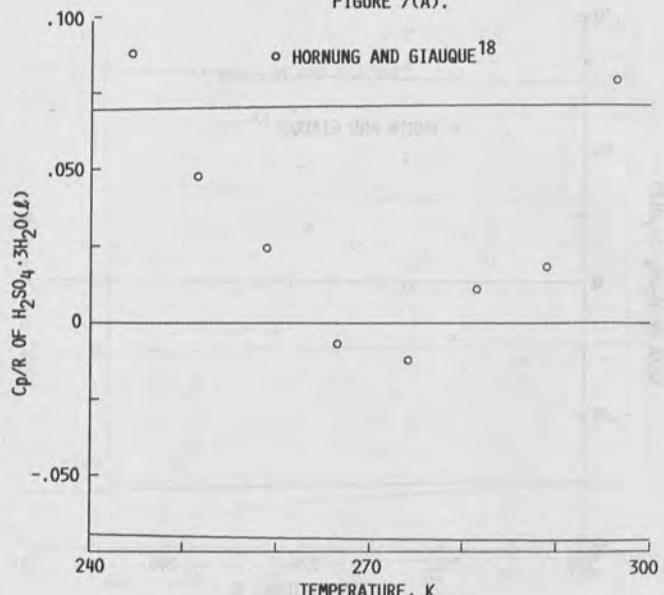


FIGURE 7(B).

Fig. 7. (a) Heat capacity of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O(l)}$ versus temperature: \circ = Hornung and Giauque.¹⁸
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O(l)}$ versus temperature: \circ = Hornung and Giauque.¹⁸

number directly gives the accuracy achieved in reproducing the voltage difference between these two concentrations. This is shown in Table 1 for $T = 298.15$ K.

From Table 1 it is clear that the maximum voltage difference is well represented at 25 °C for 7 of 11 datasets. In fact, for those datasets the accuracy is essentially within 3/4 percent. The obvious exceptions are the measurements of Covington, Dobson, and Wynne-Jones²² for both cell 1 and cell 2 and those of Trimble and Ebert²⁴ for cell 2. The latter made only a limited number of measurements for aqueous sulfuric acid. Their primary concern was the effect of ethylene glycol addition on solution

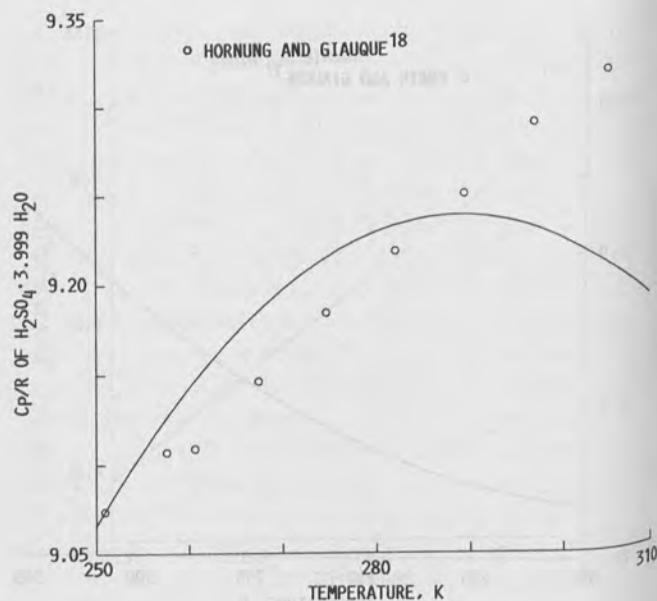


FIGURE 8(A).

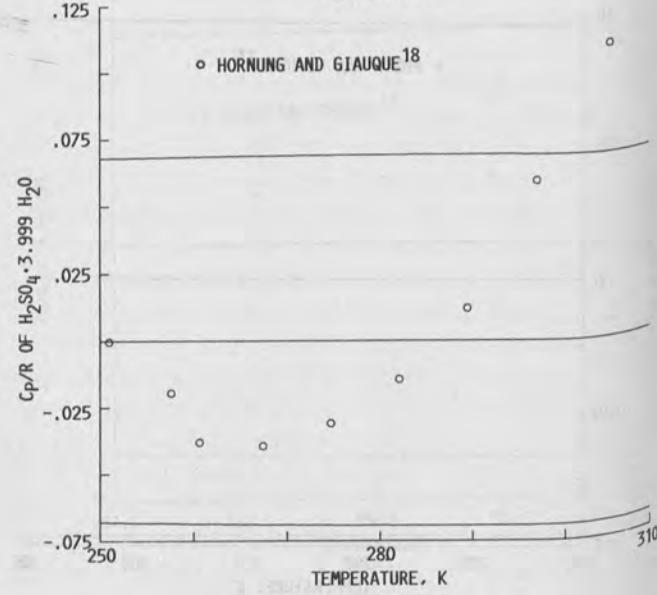


FIGURE 8(B).

Fig. 8. (a) Heat capacity of $\text{H}_2\text{SO}_4 \cdot 3.999\text{H}_2\text{O(l)}$ versus temperature: \circ = Hornung and Giauque.¹⁸
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4 \cdot 3.999\text{H}_2\text{O(l)}$ versus temperature: \circ = Hornung and Giauque.¹⁸

properties. The former carried out experiments on very dilute solutions where experiments are difficult and accuracy open to question. However, working with even more dilute solutions, Shrawder and Cowperthwaite²⁹ produced data which could be well represented. On balance it seems that the galvanic cell measurements are represented quite well at 25 °C.

The emf results at other temperatures are generally similar to those shown for 25 °C. The residual percentages generally tend to decrease at both higher and lower temperatures. Only for the measurements of Shrawder and Cowperthwaite²⁹ is there any significant deteriora-

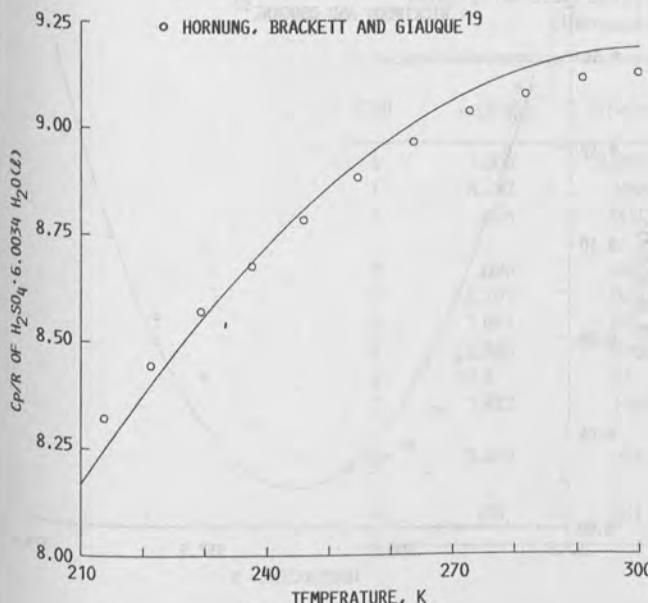


FIGURE 9(A).

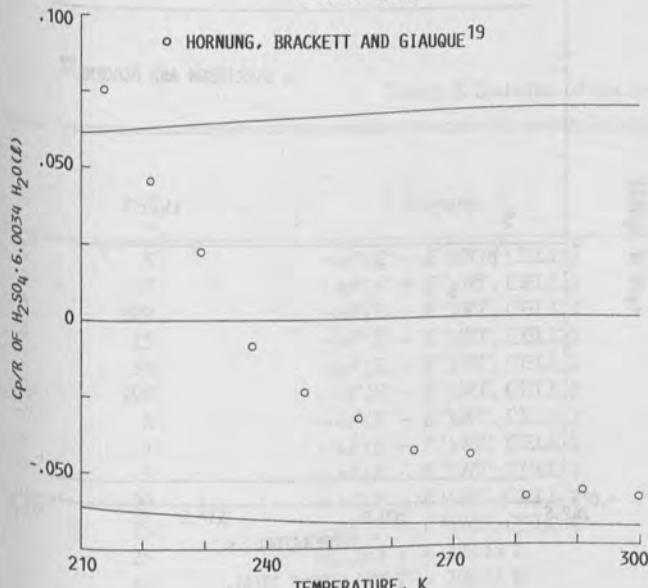


FIGURE 9(B).

Fig. 9. (a) Heat capacity of $\text{H}_2\text{SO}_4 \cdot 6.0034\text{H}_2\text{O}(l)$ versus temperature: \circ = Hornung, Brackett and Giauque.¹⁹
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4 \cdot 6.0034\text{H}_2\text{O}(l)$ versus temperature: \circ = Hornung, Brackett and Giauque.¹⁹

tion at other temperatures and even here the error remains reasonable (1.2 percent at 50 °C and 2.3 percent at 0 °C). The implication is that the correlation is generally consistent with the cell measurements to about 3/4 percent. It is interesting to note, at least on the basis of Table 1 and similar values at other temperatures, that Hamer's data²⁰ for cell 1 are not significantly less accurate than the other data for this cell with regard to aqueous sulfuric acid properties. This also applies to the measurements made by Harned and Hamer²⁶ on cell 2. These two data sets seem only moderately less accurate than those of Beck, Singh and Wynne-Jones²¹ and those of Beck, Dob-

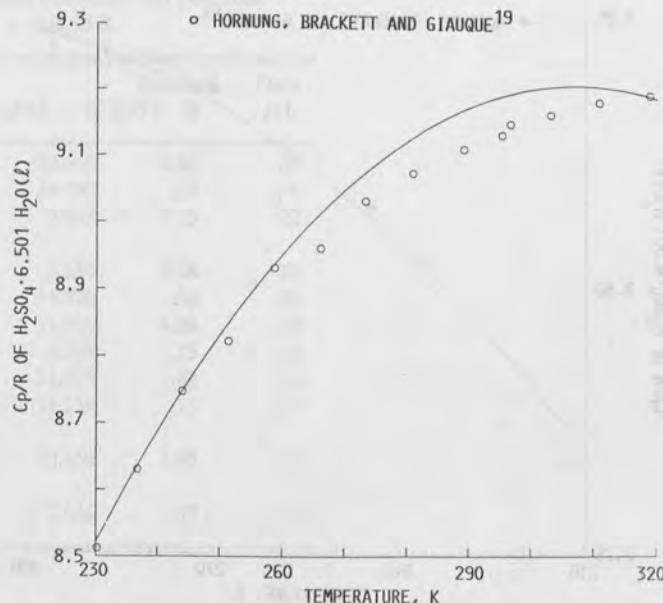


FIGURE 10(A).

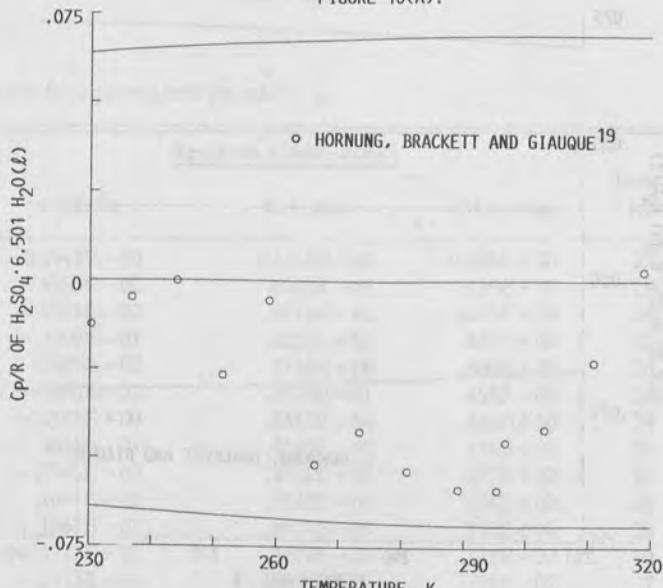


FIGURE 10(B).

Fig. 10. (a) Heat capacity of $\text{H}_2\text{SO}_4 \cdot 6.501\text{H}_2\text{O}(l)$ versus temperature: \circ = Hornung, Brackett and Giauque.¹⁹
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4 \cdot 6.501\text{H}_2\text{O}(l)$ versus temperature: \circ = Hornung, Brackett and Giauque.¹⁹

son and Wynne-Jones²⁷ for the corresponding cells. The Hamer datasets for both cells^{20,26} seem superior to the measurements of Covington, Dobson and Wynne-Jones²² if Table 1, and similar information at other temperatures, is the criterion used for the evaluation.

The residuals associated with the tetrahydrate and monohydrate freezing constraints (Eq. (6)) are shown in Fig. 19 for the experimental freezing curves. Both sets of residuals are of comparable magnitude even though the monohydrate covers temperature and mole fraction intervals about double that of the tetrahydrate. The residuals are less than 1/2-percent of the appropriate linear

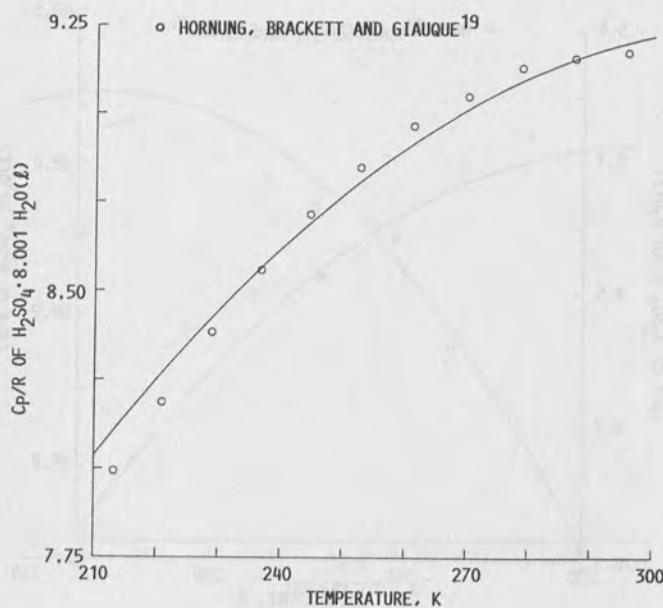


FIGURE 11(A).

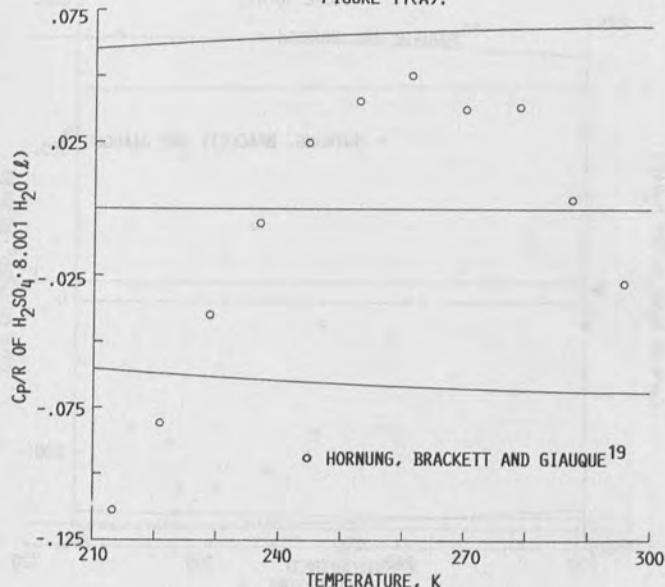


FIGURE 11(B).

Fig. 11. (a) Heat capacity of H₂SO₄·8.001H₂O(l) versus temperature: ○ = Hornung, Brackett and Giauque.¹⁹
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for heat capacity of H₂SO₄·8.001H₂O(l) versus temperature: ○ = Hornung, Brackett and Giauque.¹⁹

combination of the solution chemical potentials (Eq. (5)). The representation of the two constraints thus seems adequate.

Table 2 shows the mean residual, the standard deviation and the magnitude of the maximum residual for each of the 33 datasets used to generate the representation for the thermodynamic properties of aqueous sulfuric acid. It also gives these quantities for the Gibbs energy and enthalpy of the solution at the freezing points of the hydrates.

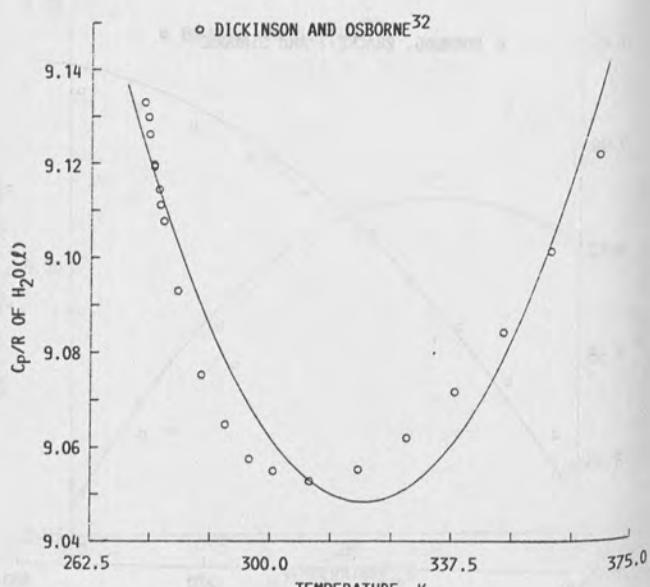


FIGURE 12(A).

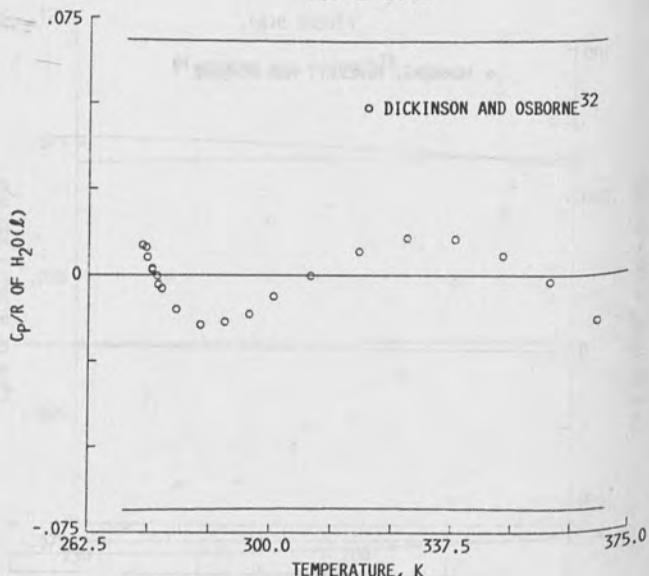


FIGURE 12(B).

Fig. 12. (a) Heat capacity of H₂O(l) versus temperature: ○ = Dickinson and Osborne.³²
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for heat capacity of H₂O(l) versus temperature: ○ = Dickinson and Osborne.³²

4.2 The Present Correlation Compared to Previous Correlations

The present correlation will be compared with the previous correlations from Giauque *et al.*, Rard *et al.*, and Staples. The correlation by Pitzer *et al.* extends only to a molality of six, and over this limited range its values and those of Rard *et al.* are virtually identical. Consequently, it will not be compared directly to the present correlation. All values from the previous correlations were taken directly from tables given in the papers.

TABLE 1. Accuracy of reproducing maximum cell potential difference at $T = 298.15\text{ K}$

Cell	$m(\max)$	$m(\min)$	$\ln F(E - E')/RT$	Residual, %	Data ref.
1	7.000	0.0005	26.668	0.85	20
1	8.272	.1096	15.885	.09	21
1	.096	.0073	5.262	9.25	22
2	.096	.0073	5.254	9.28	22
2	8.207	.005	15.870	.06	23
2	1.041	.005	11.046	4.20	24
2	2.386	.0506	8.765	.73	25
2	17.5	.05	21.975	.42	26
2	7.972	.1003	14.234	.13	27
3	3.499	.054	10.450	1.60	28
4	.02	.001	7.046	.37	29

TABLE 2. Statistics of the correlation for aqueous sulfuric acid

Points	Property	Residuals (Obsd.-Pred.)			Data ref.
		Mean	Std. dev.	Max. mag.	
1	$-nF(E - E')/RT$, CELL 1	0.1947E+00	0.1856E+00	0.486E+00	22
2	$-nF(E - E')/RT$, CELL 1	-.4383E-02	.6283E-01	.129E+00	21
3	$-nF(E - E')/RT$, CELL 1	-.8971E-02	.8113E-01	.233E+00	20
4	$-nF(E - E')/RT$, CELL 2	-.7500E-01	.1233E+00	.485E+00	22
5	$-nF(E - E')/RT$, CELL 2	.2909E-02	.1132E+00	.506E+00	27
6	$-nF(E - E')/RT$, CELL 2	-.6358E-02	.4522E-01	.165E+00	26
7	$-nF(E - E')/RT$, CELL 2	-.1545E+00	.2383E+00	.466E+00	24
8	$-nF(E - E')/RT$, CELL 2	-.1838E-01	.6383E-01	.126E+00	25
9	$-nF(E - E')/RT$, CELL 2	-.3946E-02	.1028E+00	.157E+00	23
10	$-nF(E - E')/RT$, CELL 3	.1091E-01	.7142E-01	.166E+00	28
11	$-nF(E - E')/RT$, CELL 4	-.1967E-01	.9838E-01	.176E+00	29
12	H_{mix}/RT $T = 298.15\text{ K}$	-.1327E-03	.3497E-03	.172E-02	10
13	H_{mix}/RT $T = 298.15\text{ K}$	-.5723E-05	.2620E-03	.127E-02	7
14	H_{mix}/RT $T = 298.15\text{ K}$	-.3033E-05	.1089E-04	.279E-04	6
15	H_{mix}/RT $T = 298.15\text{ K}$.9162E-02	.1273E-01	.414E-01	8
16	H_{mix}/RT $T = 253.15\text{ K}$	-.2037E+00	.1033E+00	.397E+00	8*
17	C_p/R , $T = 298.15\text{ K}$	-.4512E-02	.1112E-01	.223E-01	13
18	C_p/R , $T = 298.15\text{ K}$.2086E-02	.5203E-01	.129E+00	8
19	C_p/R , $T = 298.15\text{ K}$.7920E+00	.6580E+00	.201E+01	12*
20	C_p/R , $T = 253.15\text{ K}$.3127E-01	.5050E-01	.127E+00	8
21	C_p/R of $\text{H}_2\text{SO}_4(\text{L})$	-.5207E-02	.4169E-01	.738E-01	17
22	C_p/R of $\text{H}_2\text{SO}_4 \cdot 1.0\text{H}_2\text{O}(\text{L})$.6057E-01	.1384E-01	.781E-01	17
23	C_p/R of $\text{H}_2\text{SO}_4 \cdot 2.0\text{H}_2\text{O}(\text{L})$	-.1077E-01	.1802E-01	.373E-01	17
24	C_p/R of $\text{H}_2\text{SO}_4 \cdot 3.0\text{H}_2\text{O}(\text{L})$.3142E-01	.3498E-01	.880E-01	18
25	C_p/R of $\text{H}_2\text{SO}_4 \cdot 3.999\text{H}_2\text{O}(\text{L})$.4452E-02	.4733E-01	.112E+00	18
26	C_p/R of $\text{H}_2\text{SO}_4 \cdot 6.0034\text{H}_2\text{O}(\text{L})$	-.1674E-01	.4378E-01	.759E-01	19
27	C_p/R of $\text{H}_2\text{SO}_4 \cdot 6.501\text{H}_2\text{O}(\text{L})$	-.3003E-01	.2197E-01	.589E-01	19
28	C_p/R of $\text{H}_2\text{SO}_4 \cdot 8.001\text{H}_2\text{O}(\text{L})$	-.6397E-02	.5137E-01	.115E+00	19
29	C_p/R of $\text{H}_2\text{O}(\text{L})$	-.7916E-03	.8082E-02	.142E-01	11
30	Tetrahydrate Freezing Constraint	.5478E-02	.1781E-01	.442E-01	30
31	Monohydrate Freezing Constraint	.3563E-02	.2076E-01	.446E-01	31
32	$\mu'(\text{H}_2\text{O})/RT$ for H_2O Freezing	-.5741E-02	.9945E-02	.222E-01	30
33	$\mu'(\text{H}_2\text{SO}_4)/RT$ for H_2SO_4 Freezing	.2721E-03	.4851E-02	.103E-01	31
34	$-G^{(r)}/RT$ at Hydrate Freezing	-.5241E-01	.1376E+00	.210E+00	17,18,19
35	$H^{(r)}/RT$ at Hydrate Freezing	.1595E-01	.1086E-01	.339E-01	17,18,19

*Data were given zero weight in the correlation.

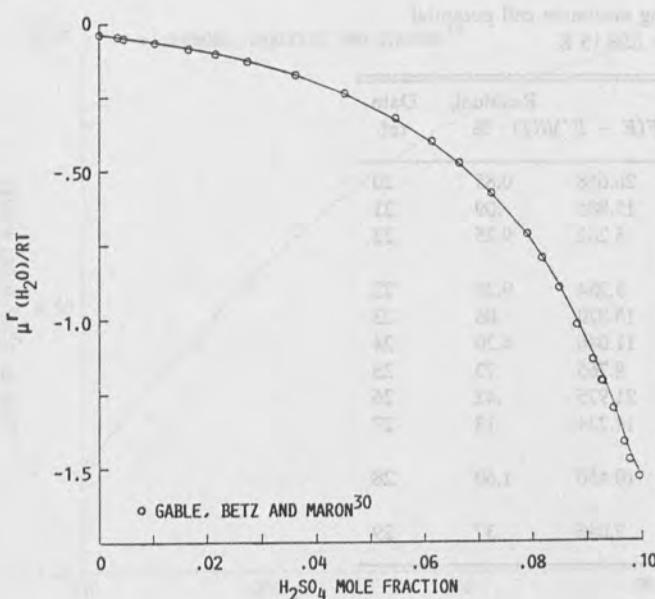


FIGURE 13(A)

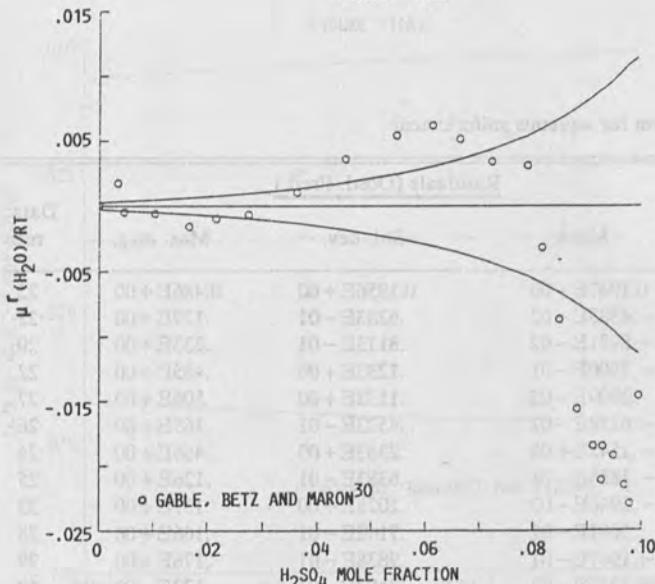


FIGURE 13(B)

Fig. 13. (a) Relative chemical potential of water along the ice-aqueous sulfuric acid freezing curve: ○ = Gable, Betz and Maron.³⁰
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for relative chemical potential of water along the ice-aqueous sulfuric acid freezing curve: ○ = Gable, Betz and Maron.³⁰

The correlations of Rard *et al.*, and Staples are restricted to a single temperature, 25 °C, and to about $m = 28$. They expressed their results as the sulfuric acid activity coefficient and the osmotic coefficient. These coefficients are directly related to the chemical potentials of sulfuric acid and water by the expressions

$$\begin{aligned} (\mu_1 - \mu_1^0)/RT &= \ln[4(m\gamma)^3] \\ (\mu_2 - \mu_2^*)/RT &= (3x_1/x_2)\phi \end{aligned} \quad (11)$$

where the subscript 1 refers to sulfuric acid, subscript 2

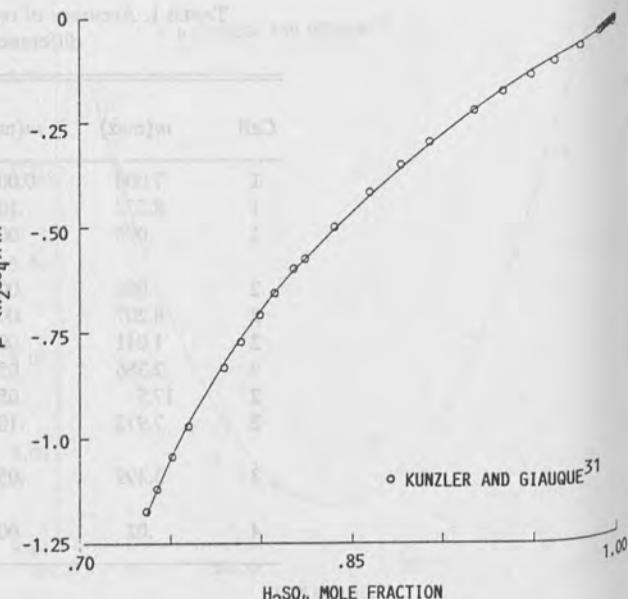


FIGURE 14(A).

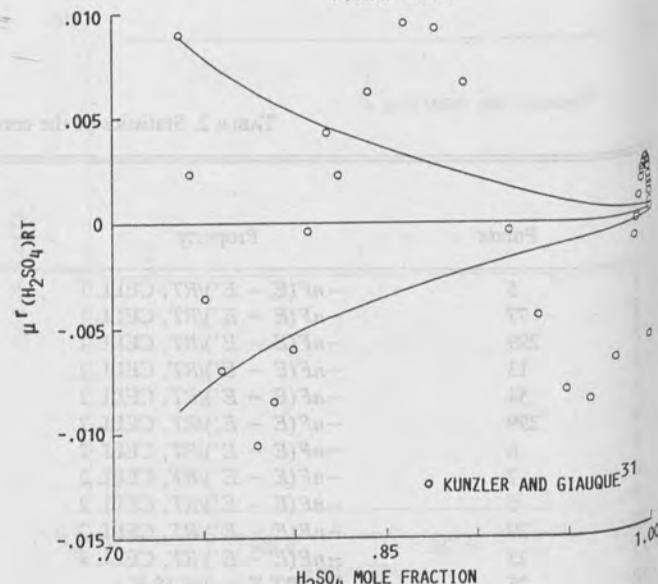


FIGURE 14(B).

Fig. 14. (a) Relative chemical potential of sulfuric acid along the $\text{H}_2\text{SO}_4(\text{s})$ - aqueous sulfuric acid freezing curve: ○ = Kunzler and Giauque.³¹
 (b) Residuals of points given nonzero weight and curves of $\pm 3/4$ percent of the predicted values for relative chemical potential of sulfuric acid along the $\text{H}_2\text{SO}_4(\text{s})$ - aqueous sulfuric acid freezing curve: ○ = Kunzler and Giauque.³¹

refers to water and where μ_1^0 is a reference value for the sulfuric acid chemical potential. Figure 20 shows the sulfuric acid activity coefficient relative to its value at unit molality since the other correlations do not give a value for the reference chemical potential of sulfuric acid. Figure 21 displays the osmotic coefficient. The agreement among the correlations is generally good although there are some differences in detail. For example, the Staples' correlation clearly deviates substantially from the other two above a molality of 15. On the other hand, the values for the activity coefficients from Rard *et al.* and those

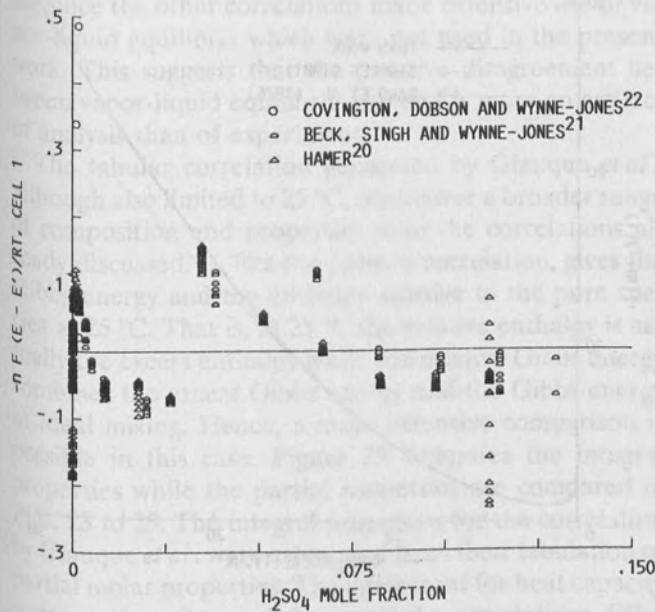


Fig. 15. Residuals for all measurements on cell 1 versus sulfuric acid mole fraction: ○ = Covington, Dobson and Wynne-Jones,²² □ = Beck, Singh and Wynne-Jones,²¹ Δ = Hamer.²⁰

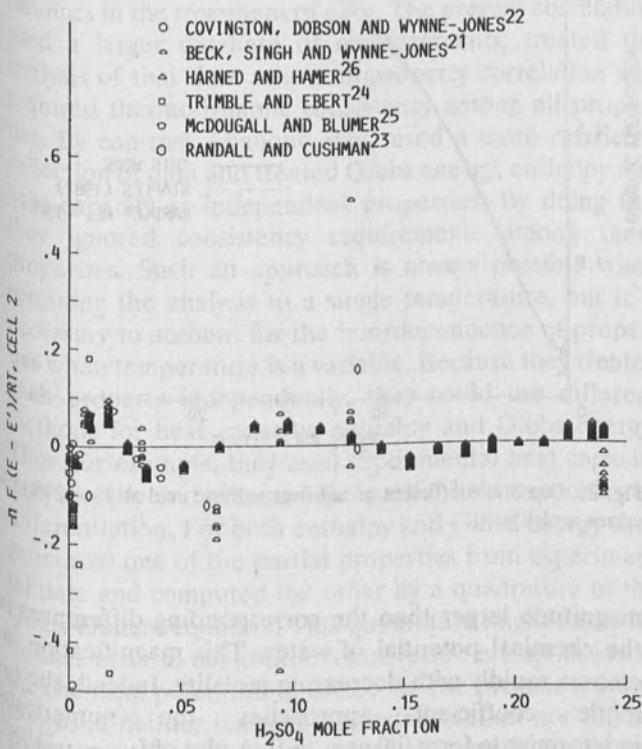


Fig. 16. Residuals for all measurements on cell 2 versus sulfuric acid mole fraction: ○ = Covington, Dobson and Wynne-Jones,²² □ = Beck, Singh and Wynne-Jones,²¹ Δ = Harned and Hamer,²⁶ ◊ = Trimble and Ebert,²⁴ ▨ = MacDougall and Blumer,²⁵ ○ = Randall and Cushman.²³

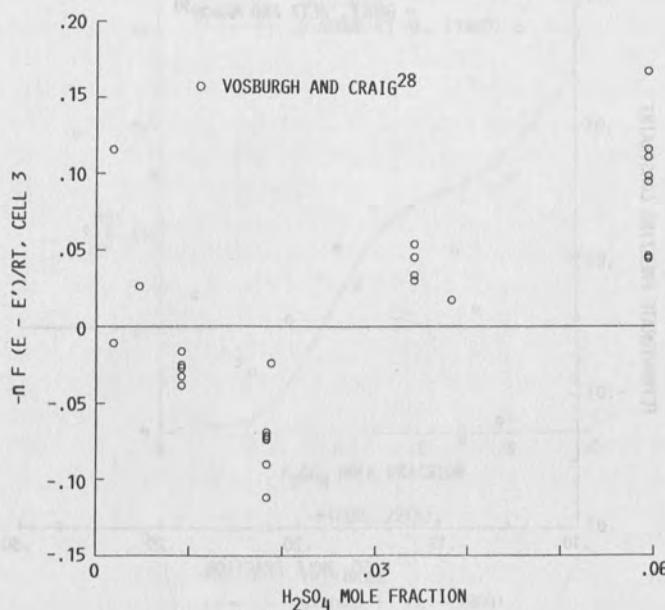


Fig. 17. Residuals for all measurements on cell 3 versus sulfuric acid mole fraction: ○ = Vosburgh and Craig.²⁸

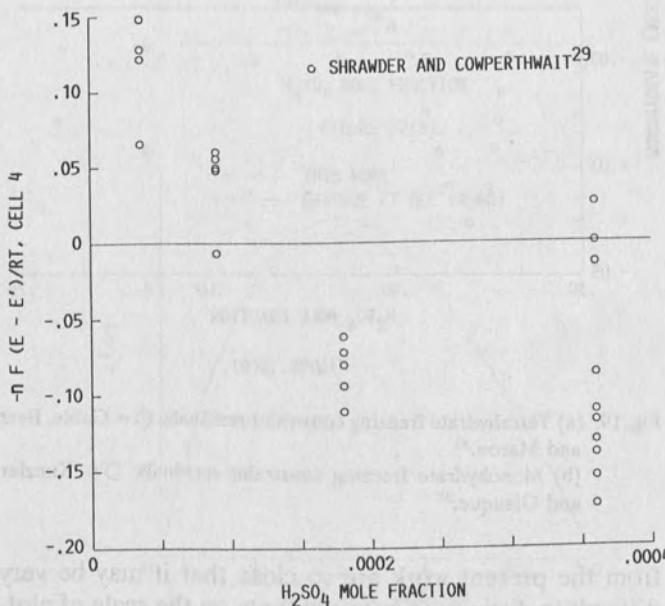


Fig. 18. Residuals for all measurements on cell 4 versus sulfuric acid mole fraction: ○ = Shrawder and Cowperthwaite.²⁹

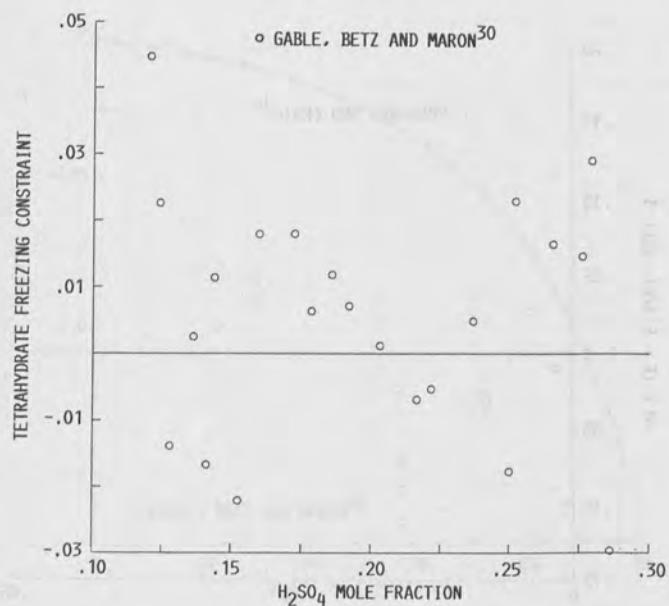


FIGURE 19(A).

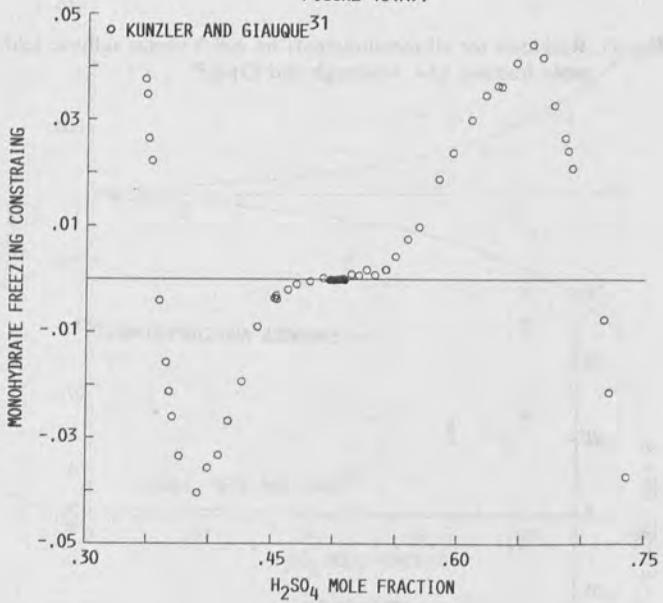
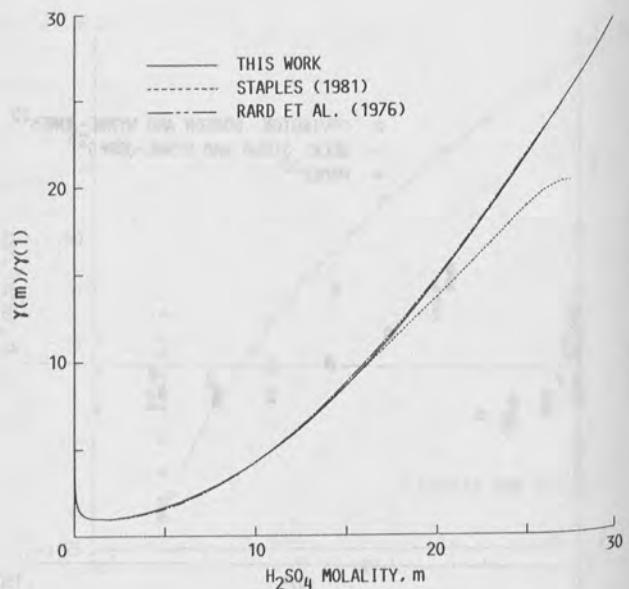
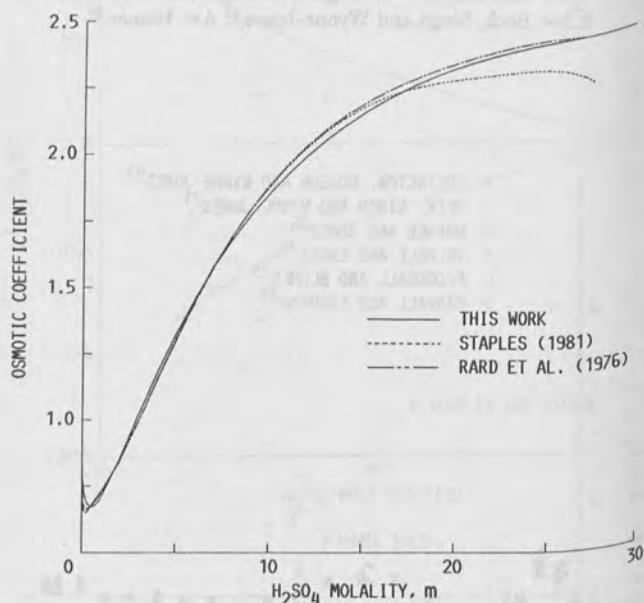


FIGURE 19(B).

Fig. 19. (a) Tetrahydrate freezing constraint residuals: ○ = Gable, Betz and Maron.³⁰(b) Monohydrate freezing constraint residuals: ○ = Kunzler and Giauque.³¹

from the present work are so close that it may be very difficult to distinguish between them on the scale of plotting in Fig. 20. The present values of the osmotic coefficient show some deviation from the other correlations in the composition region centered near $m = 15$ where they are influenced by the tetrahydrate freezing constraint. The previous correlations made no use of this data. Furthermore, there are some minor differences in the osmotic coefficient at the lowest concentrations. However, it should be noted that comparing osmotic coefficients exaggerates the importance of differences in the chemical potential of water for the dilute acid region. Differences in osmotic coefficients at $m = 2$ are almost an order of

Fig. 20. Activity coefficient of aqueous sulfuric acid at $T = 298.15 \text{ K}$ versus molality.Fig. 21. Osmotic coefficient of aqueous sulfuric acid at $T = 298.15 \text{ K}$ versus molality.

magnitude larger than the corresponding differences in the chemical potential of water. This magnification increases rapidly with decreasing molality. Indeed, the osmotic coefficient approaches the numerically indeterminate form $0/0$ as $x_1 \rightarrow 0$. A plot of $(\mu_2 - \mu_2^*)/RT$, rather than the osmotic coefficient, shows excellent agreement for the dilute sulfuric acid solutions.

The general concordance among the three correlations, especially between the present correlation and that of Rard *et al.*, is somewhat surprising because of the variability in the quantity and the type of experimental data used to produce these correlations. The good agreement for the chemical potential of water is all the more surpris-

ing since the other correlations made extensive use of vapor-liquid equilibria which were not used in the present work. This suggests that the putative disagreement between vapor-liquid equilibria and emf is more an artifact of analysis than of experiment.

The tabular correlation generated by Giauque *et al.*, although also limited to 25 °C, does cover a broader range of composition and properties than the correlations already discussed. It, like the present correlation, gives the Gibbs energy and the enthalpy relative to the pure species at 25 °C. That is, at 25 °C the relative enthalpy is actually the excess enthalpy while the relative Gibbs energy combines the excess Gibbs energy and the Gibbs energy of ideal mixing. Hence, a more extensive comparison is possible in this case. Figure 22 compares the integral properties while the partial properties are compared in Figs. 23 to 25. The integral properties for the correlation by Giauque *et al.* were calculated from their tabulation of partial molar properties. The agreement for heat capacity is generally quite good, however, the correlations differ appreciably in their values for enthalpy and Gibbs energy. This is unexpected since both correlations relied on much of the same experimental data for the more concentrated acid solutions.

Naturally, there are plausible reasons why there should be some disagreement between the present correlation and that of Giauque *et al.* Partly it can be ascribed to differences in the treatment of data. The present correlation used a larger database of measurements, treated the analysis of that data as a multiproperty correlation and required thermodynamic consistency among all properties. By contrast, Giauque *et al.* used a more restricted collection of data and treated Gibbs energy, enthalpy and heat capacity as independent properties. By doing this they ignored consistency requirements among these properties. Such an approach is always possible when confining the analysis to a single temperature, but it is necessary to account for the interdependence of properties when temperature is a variable. Because they treated each property independently, they could use different methods for heat capacity, enthalpy and Gibbs energy. Thus, for example, they used experimental heat capacity data directly and obtained the partial heat capacities by differentiation. For both enthalpy and Gibbs energy they generated one of the partial properties from experimental data and computed the other by a quadrature of the Gibbs-Duhem equation. This quadrature might easily introduce error as could their temperature extrapolation of the chemical potentials to 298.15 K. The present correlation used neither temperature extrapolation nor Gibbs-Duhem quadrature. Another contributing factor to the disagreement could well be that the present correlation relied solely on analytical tools while Giauque *et al.* probably made some use of graphical methods for differentiation and quadrature as part of their analysis. Given the complex behavior of aqueous sulfuric acid, it is easy to see that graphical techniques impose accuracy limitations over and above those dictated by data inaccuracies. The foregoing reasons are probably adequate to explain the

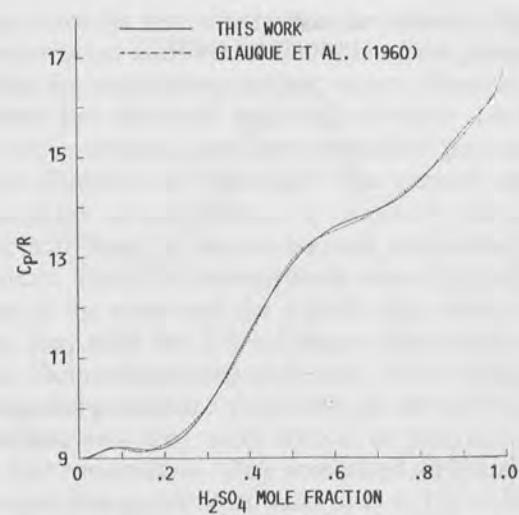


FIGURE 22(A).

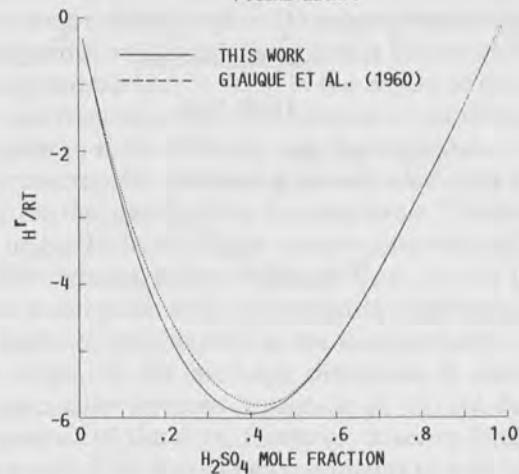


FIGURE 22(B).

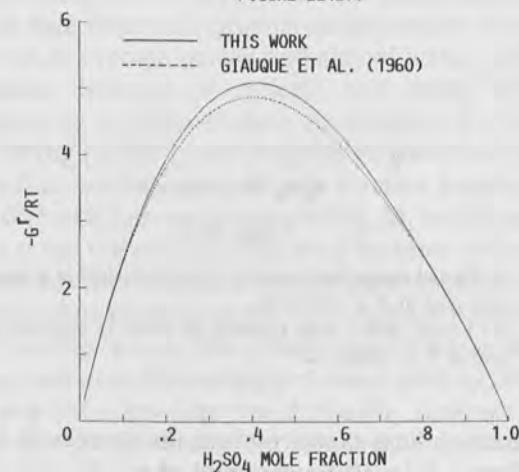


FIGURE 22(C).

Fig. 22. (a) Heat capacity of aqueous sulfuric acid at $T = 298.15\text{ K}$ versus sulfuric acid mole fraction.
 (b) Relative enthalpy of aqueous sulfuric acid at $T = 298.15\text{ K}$ versus sulfuric acid mole fraction.
 (c) Relative Gibbs energy of aqueous sulfuric acid at $T = 298.15\text{ K}$ versus sulfuric acid mole fraction.

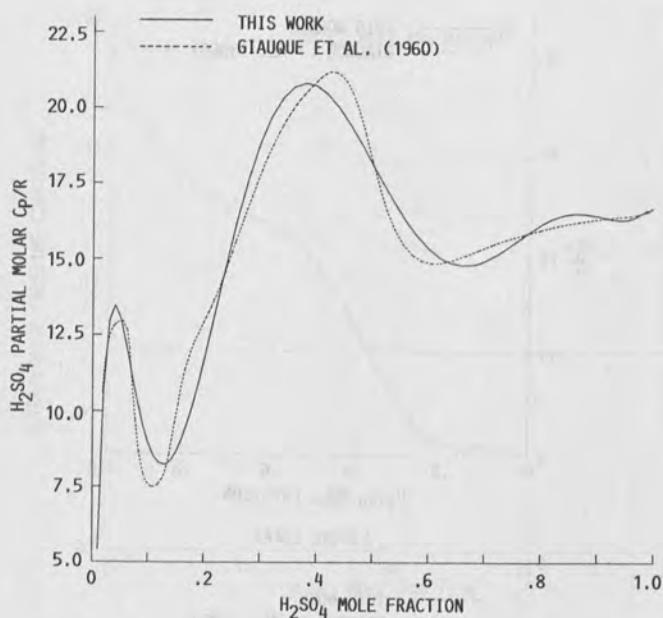


FIGURE 23(A).

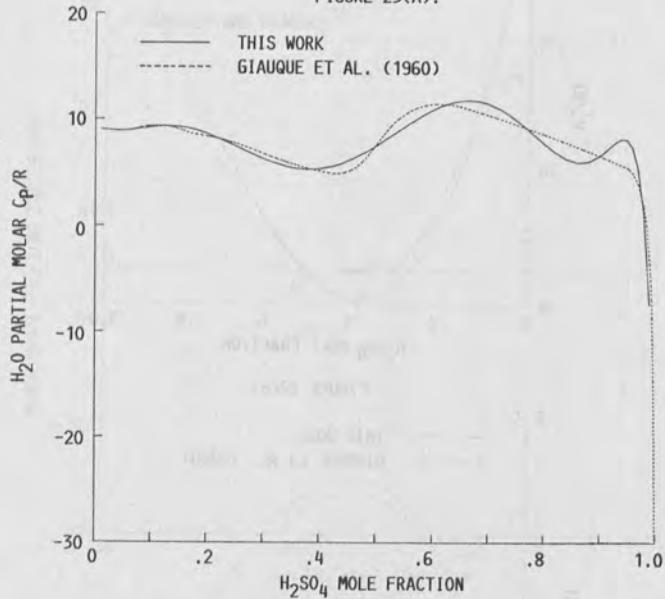


FIGURE 23(B).

Fig. 23. (a) Partial molar heat capacity of sulfuric acid in aqueous sulfuric acid at $T = 298.15\text{ K}$.
 (b) Partial molar heat capacity of water in aqueous sulfuric acid at $T = 298.15\text{ K}$.

differences in heat capacity where the agreement is generally better than 3/4 percent and where the two sets of partial properties generally display quite similar behavior. However, the magnitude of the disagreement for Gibbs energy and enthalpy is on the order of 4 to 5 percent. This invites further explanation and requires examining their methods for generating these partial molar properties.

Giauque *et al.* used vapor pressure data to establish the chemical potential of water to $x_1 = 1/3$. In this concentration range there is excellent agreement (Fig. 25) between their values and those obtained in the present work which relied on freezing points and emf measure-

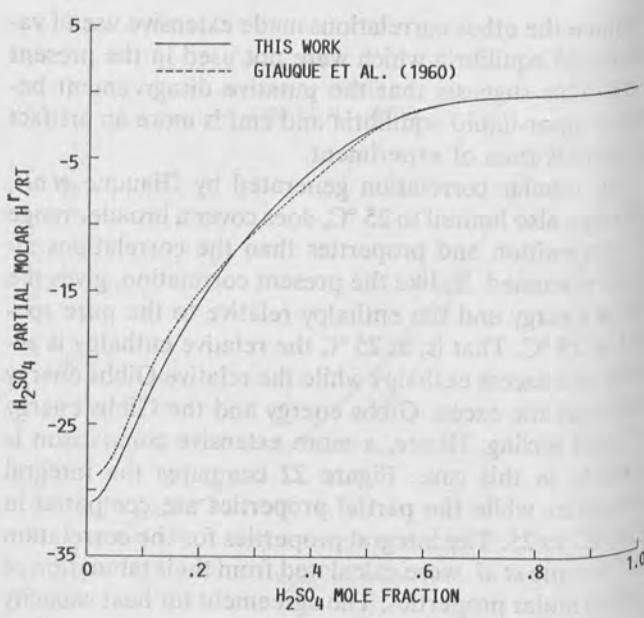


FIGURE 24(A).

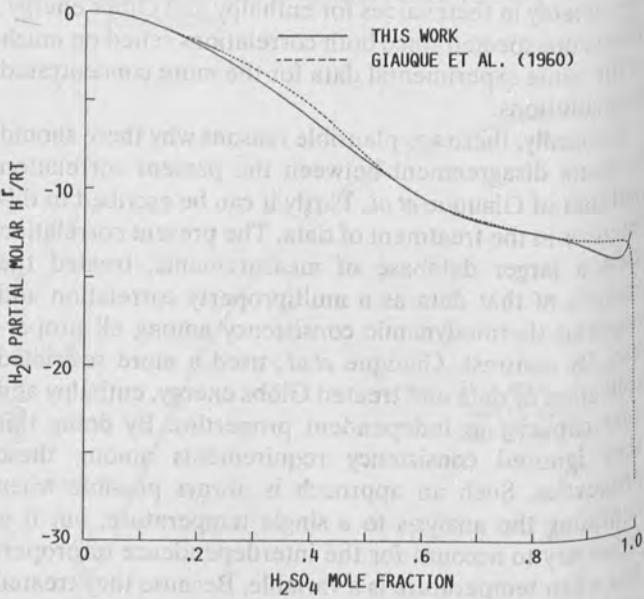


FIGURE 24(B).

Fig. 24. (a) Partial molar relative enthalpy of sulfuric acid in aqueous sulfuric acid at $T = 298.15\text{ K}$.
 (b) Partial molar relative enthalpy of water in aqueous sulfuric acid at $T = 298.15\text{ K}$.

ments. This consonance argues for the essential correctness of the values out to this composition and contrasts with the modest deviations exhibited by the other correlations in the vicinity of the tetrahydrate composition (Fig. 21). It also reinforces the conclusion that emf and vapor pressure measurements are basically in agreement relative to aqueous sulfuric acid properties. At higher acid concentrations both the present work and Giauque *et al.* used the same freezing points to establish the Gibbs energy. The sulfuric acid freezing curve from the pure acid to the monohydrate-anhydrous acid eutectic, at about $x_1 = 0.73$, directly supplies the sulfuric acid chemical potential at the solution freezing temperature. They pro-

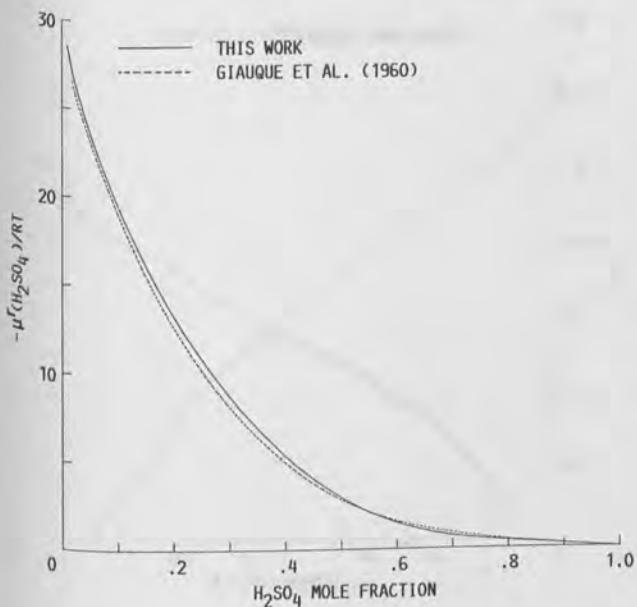


FIGURE 25(A).

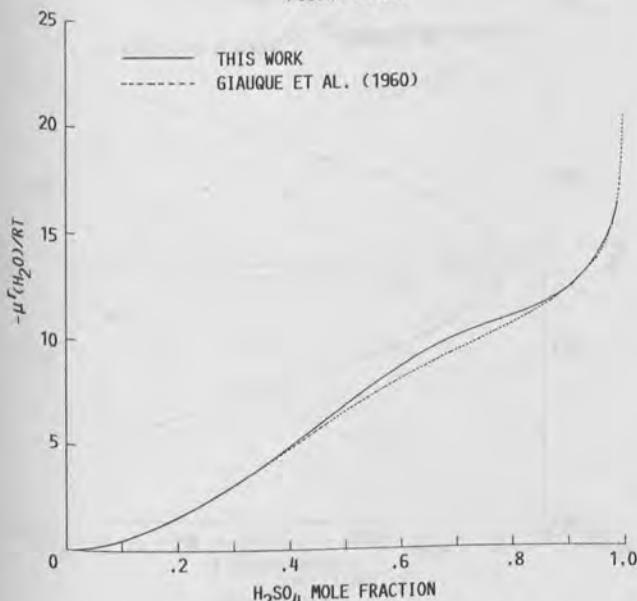


FIGURE 25(B).

Fig. 25. (a) Relative chemical potential of sulfuric acid in aqueous sulfuric acid at $T = 298.15\text{ K}$.
 (b) Relative chemical potential of water in aqueous sulfuric acid at $T = 298.15\text{ K}$.

duced the water chemical potential in this composition range from the sulfuric acid chemical potential by Gibbs-Duhem quadrature. In this region their values for both chemical potentials agree with the present values beyond an acid mole fraction of about 0.85 with differences increasing toward the eutectic composition. This seems to implicate the substantial temperature extrapolation, to 298.15 K , required by their calculation for the more dilute solutions although Gibbs-Duhem quadrature could also contribute. The remaining portion of the composition range corresponds to the monohydrate region of the phase diagram. Here both correlations used the identical

freezing curve for the monohydrate to extract Gibbs energy information and it is in this part of the phase diagram that the major disagreement occurs. Giauque *et al.* calculated the chemical potential of water from the monohydrate freezing curve by a procedure proposed by Giauque, Kunzler and Hornung.⁴⁰ The method involved the use of the monohydrate as a temporary component and explicitly used its thermodynamic properties in the calculation. Since the monohydrate can only determine the sum of the water and the sulfuric acid chemical potentials, they used the Gibbs-Duhem equation to eliminate the chemical potential of the acid. Their formula for the integrand possesses a singularity at the monohydrate composition and they were forced to patched values across that composition. They prescribed an initial value for the chemical potential of water at $x_1 = 1/3$, where values agree, and proceeded by quadrature into the more concentrated solution region. Divergence begins immediately beyond $x_1 = 1/3$ and agreement is not reestablished until approximately $x_1 = 0.85$, in the region of the anhydrous acid freezing curve. The location of the divergence thus points to some difficulty with the implementation of their procedure for generating the chemical potential of water from the monohydrate freezing curve. The problem could originate in the large temperature extrapolation from the freezing point to 298.15 K , or in the Gibbs-Duhem quadrature with its associated singularity. Most likely both are contributors to the disagreement.

The origin of the enthalpy difference is somewhat more speculative because Giauque *et al.* did not describe their analysis of the data. However, it seems likely that they generated the partial molar enthalpy of water simply by smoothing their own revised, and other, enthalpy of dilution data since their original measurements were tabulated as an average partial enthalpy of water. The partial molar enthalpy of sulfuric acid could then be generated by a Gibbs-Duhem quadrature. The differences in the partial molar enthalpy of water are largely confined to the sulfuric acid mole fraction interval from about 0.15 to 0.5 as can be seen in Fig. 24. In this concentration range the present work used the same enthalpy of dilution data as Giauque *et al.* but supplemented it with the constraints imposed by the monohydrate and tetrahydrate freezing curves. One possibility for error is that the average partial molar enthalpy of water used by Giauque *et al.* may differ from the true derivative. However, some simple calculations show that this does become significant only below a sulfuric acid mole fraction of 0.2 where the error rises above 1/2 percent. But at these dilute concentrations there is substantial agreement for the partial molar enthalpy of water. Consequently, a potential source for the discrepancy is an inconsistency between the enthalpy of dilution and the freezing curves. Yet the two independent sets of freezing point measurements confirm their essential correctness in the concentration range where the discrepancy in the water partial molar enthalpy occurs. Furthermore, their accuracy is also confirmed by the fact that the chemical potentials deduced from the freezing point data are correct for both the di-

lute and concentrated acid. By contrast, the only enthalpy data in the intermediate concentration region of the phase diagram are the uncorroborated dilution measurements of Kunzler and Giauque. This seems to imply that in this composition range the dilution data may not be as accurate as one would like and may be responsible for the inconsistency. Some additional error is probably generated by the Gibbs-Duhem quadrature to produce the partial molar enthalpy of sulfuric acid.

4.3 The Solid Phases

To complete the thermodynamic picture of the sulfuric acid-water system we must still consider the thermodynamic properties of the pure solid phases which materialize when the temperature of aqueous sulfuric acid is lowered. Except for ice, the available information is quite limited and all comes from a single source, namely, from the calorimetric measurements of Giauque and coworkers. The absence of verifying measurements makes it very difficult to judge the quality of these data. Giauque and coworkers determined the heat capacity for solid anhydrous sulfuric acid and its hydrates down to 15 K. They measured the heat capacity of all of these species on relatively pure samples except for the hemihexahydrate which could not be prepared in even moderately pure form. Hemihexahydrate values can be extracted from their heat capacity measurements for a mixture of the hemihexahydrate and the tetrahydrate with a composition of $\text{H}_2\text{SO}_4 \cdot 6.0034 \text{ H}_2\text{O}$ which corresponds to a purity of about 80 mole percent. This was done in this work using the predicted values for the tetrahydrate obtained here.

Figures 26 to 31 display the heat capacity and the heat capacity residuals for sulfuric acid and its hydrates. These figures only pertain to the heat capacities of the respective solid phases. That is, the measurements are at temperatures which are clearly below the various melting and peritectic temperatures. The liquid phase heat capacities for the corresponding compositions have already been displayed in Figs. 4 to 12. Each heat capacity plot presents all experimental data points together with the predicted curve. The corresponding residual plot shows $\pm 1/2$ percent of the predicted curve but the residuals only for those points which were assigned a nonzero weight in the analysis. To plot the residuals for the points given zero weight would have necessitated a much coarser plotting scale. As can be seen from these figures, the predicted values are generally within 1/2 percent of the experimental data which were used to generate the representation. It is also evident from the property plots that the experimental measurements are increasingly unreliable at the higher temperatures, near the melting and peritectic points. All species, except the dihydrate, exhibit some "premelting" heat capacity enhancement. The effect is most pronounced for the anhydrous acid and virtually nonexistent for the dihydrate. This is unexpected since, except for the hemihexahydrate, the dihydrate was

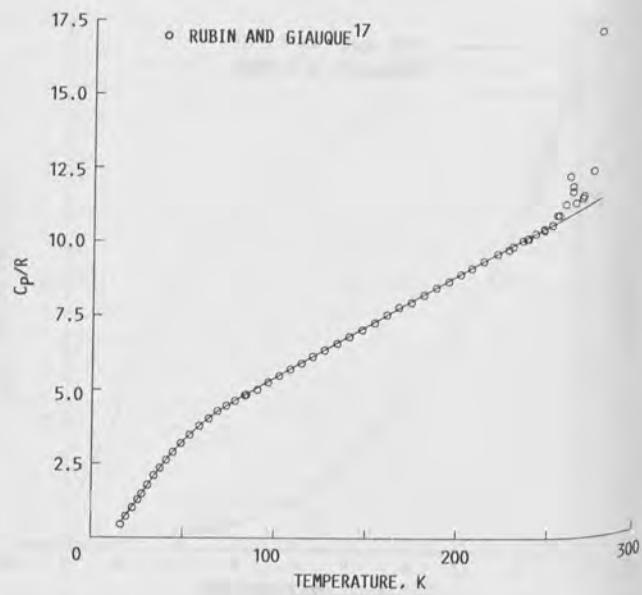


FIGURE 26(A).

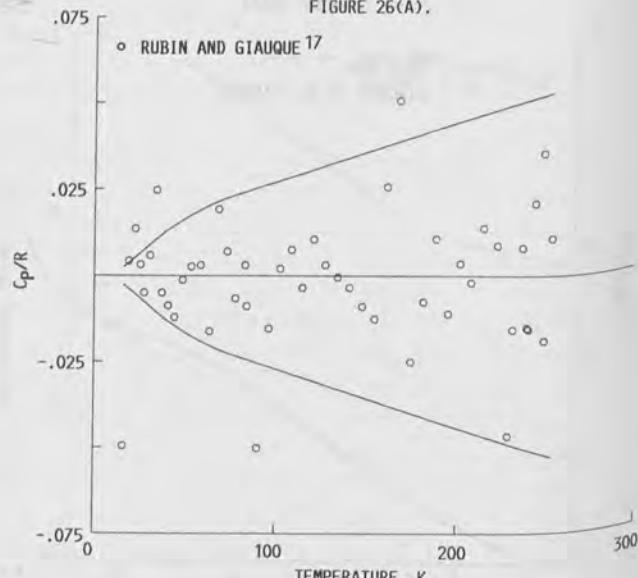


FIGURE 26(B).

Fig. 26. (a) Heat capacity of $\text{H}_2\text{SO}_4(\text{s})$ versus temperature: $\circ =$ Rubin and Giauque.¹⁷

(b) Residuals of points given nonzero weight and curves of $\pm 1/2$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4(\text{s})$ versus temperature: $\circ =$ Rubin and Giauque.¹⁷

the most impure (98.4 mole percent purity) sample measured.

In addition to premelting, each of the solid phases has some data points which are plainly in error. For example, one might speculate that one of the monohydrate points is a typographical error. Yet similarly sized excursions are visible in the anhydrous acid. Furthermore, a whole sequence of such points is apparent in the tetrahydrate measurements. These points come from a separate series of tetrahydrate heat capacity measurements (Series 2) on what was the most highly purified solid phase. Its purity even exceeded the purity of the anhydrous acid. Under

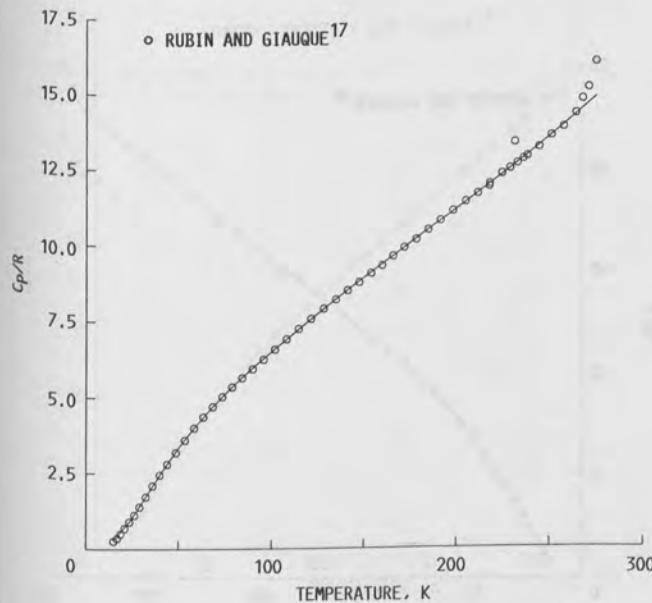


FIGURE 27(A).

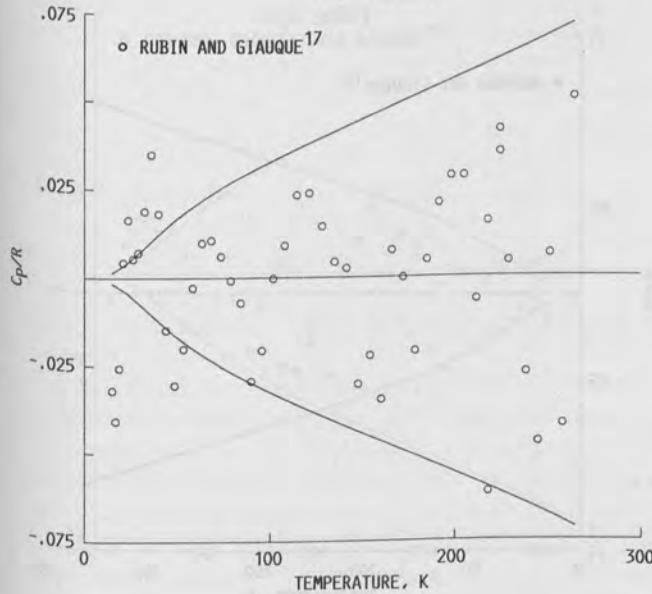


FIGURE 27(B).

Fig. 27. (a) Heat capacity of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}(s)$ versus temperature: $\circ =$ Rubin and Giauque.¹⁷

(b) Residuals of points given nonzero weight and curves of $\pm 1/2$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}(s)$ versus temperature: $\circ =$ Rubin and Giauque.¹⁷

such circumstances it is probably best to regard all of the errant values as the inevitable consequences of making measurements on such a complex and difficult system.

Giauque *et al.*⁹ prepared tables of smoothed values for the thermodynamic properties of solid anhydrous sulfuric acid and its hydrates. Since they used the same measurements that were used in the present work, it is natural that their properties should agree very well with those obtained in this work.

The thermodynamic properties of ice are more complex than those of the other solid phases but, fortunately, there are several independent sources of heat capacity

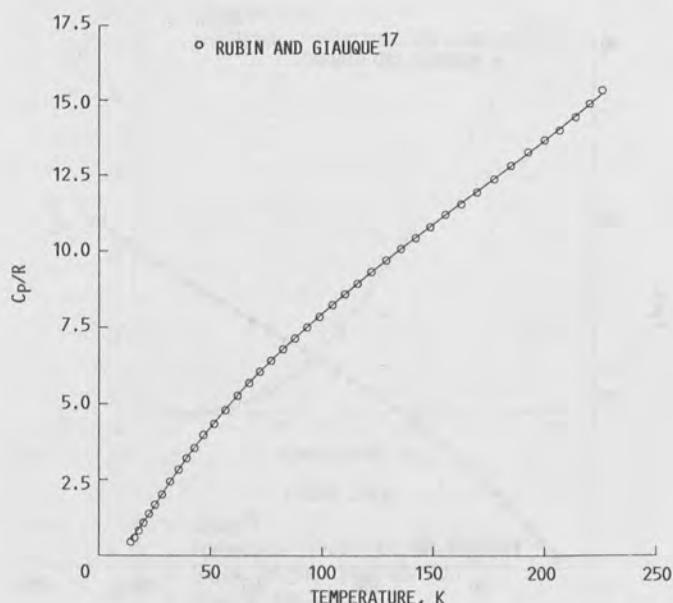


FIGURE 28(A).

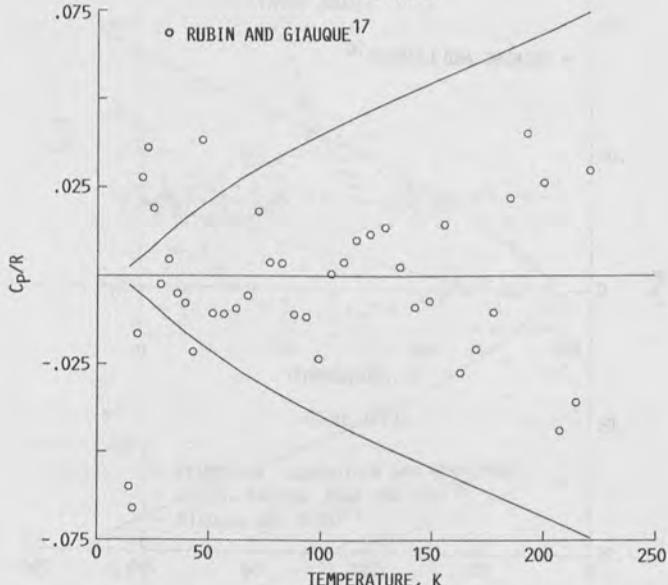


FIGURE 28(B).

Fig. 28. (a) Heat capacity of $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}(s)$ versus temperature: $\circ =$ Rubin and Giauque.¹⁷

(b) Residuals of points given nonzero weight and curves of $\pm 1/2$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}(s)$ versus temperature: $\circ =$ Rubin and Giauque.¹⁷

measurements, and these extend down to 2 K. The chief difficulty with ice originates with its propensity for freezing disorder into its crystalline structure. This makes the heat capacity of ice a function of its thermal history. Annealing ice for periods of up to a month has not succeeded in eliminating the disorder (Haida *et al.*),¹⁶ the greater the disorder, the lower the heat capacity. There are two possible choices one could make. One is to generate thermodynamic properties for the slowest possible cooling rates (annealed ice) and the other is to generate properties for the fastest possible cooling rate (quenched ice). Since quenched ice is the form that is most likely to

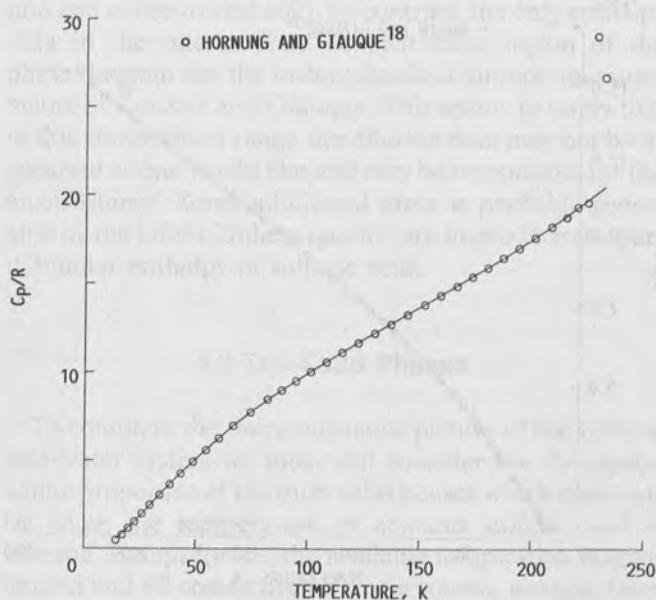


FIGURE 29(A).

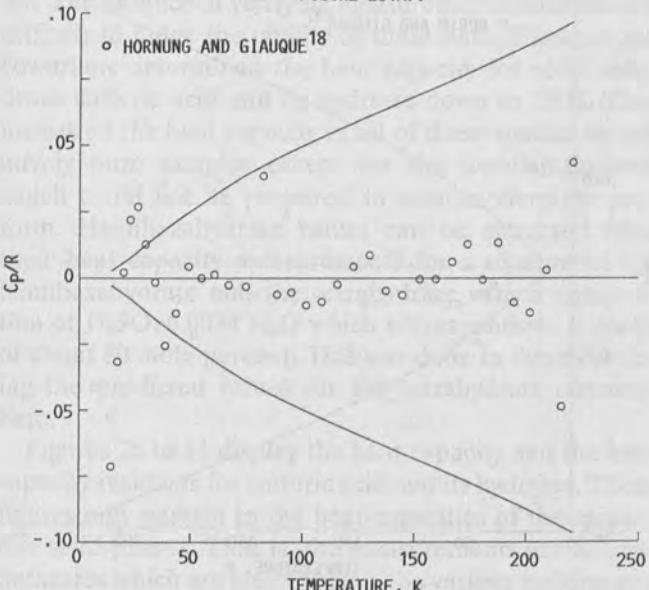


FIGURE 29(B).

Fig. 29. (a) Heat capacity of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}(s)$ versus temperature: $\circ =$ Hornung and Giauque.¹⁸

(b) Residuals of points given nonzero weight and curves of $\pm 1/2$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}(s)$ versus temperature: $\circ =$ Hornung and Giauque.¹⁸

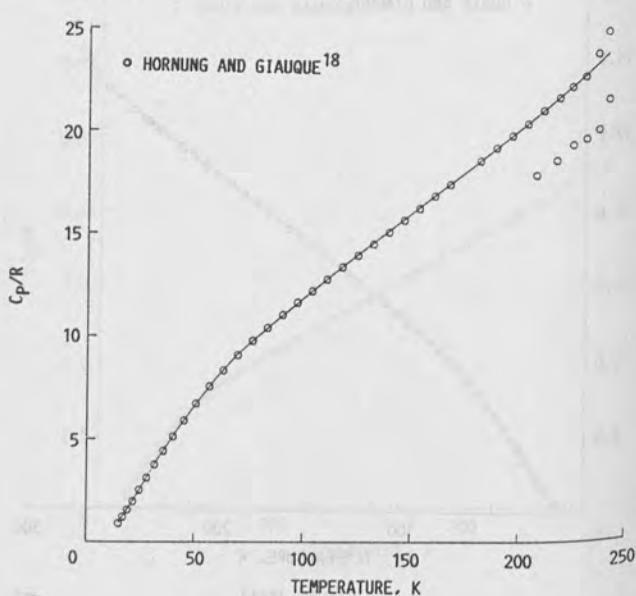


FIGURE 30(A).

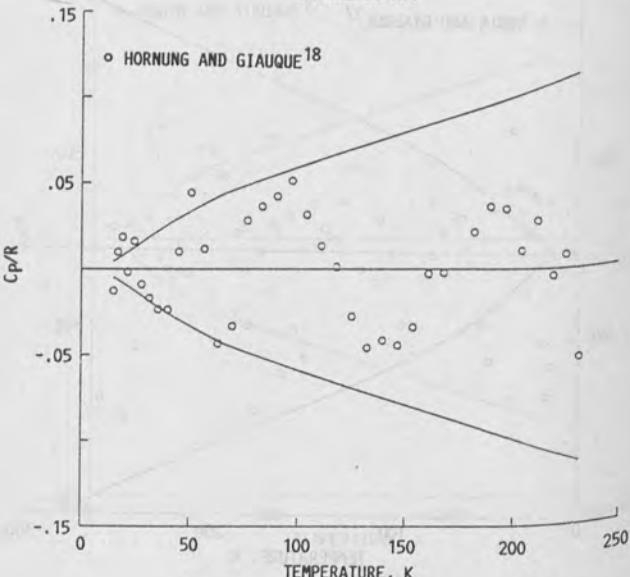


FIGURE 30(B).

Fig. 30. (a) Heat capacity of $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}(s)$ versus temperature: $\circ =$ Hornung and Giauque.¹⁸

(b) Residuals of points given nonzero weight and curves of $\pm 1/2$ percent of the predicted values for heat capacity of $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}(s)$ versus temperature: $\circ =$ Hornung and Giauque.¹⁸

be encountered in applications, its properties will be presented here. The properties of quenched ice were generated by assigning zero weight to all points in the vicinity of the order-disorder transformation which seemed to be affected by the transformation. This meant that all points between 95 and 145 K were given zero weight. Some points outside this region were also given zero weight for various other reasons.

The results for quenched ice are shown in Fig. 32. Because of the high density of points it is not possible to show simultaneously the calculated curve and all data

points. Below 30 K this is not a problem and so only the low temperature heat capacity data of Flubacher *et al.*¹⁵ and Simon¹⁴ are plotted along with the predicted curve. Two residual plots are shown for quenched ice to compensate for the absence of a heat capacity plot at higher temperatures. One shows only the residuals of those points which were given nonzero weight while the other shows the residuals for all of the data points, including those assigned zero weight. Each residual plot also displays the curves which show $\pm 1/2$ percent of the calculated heat capacity. The heat capacity spike associated

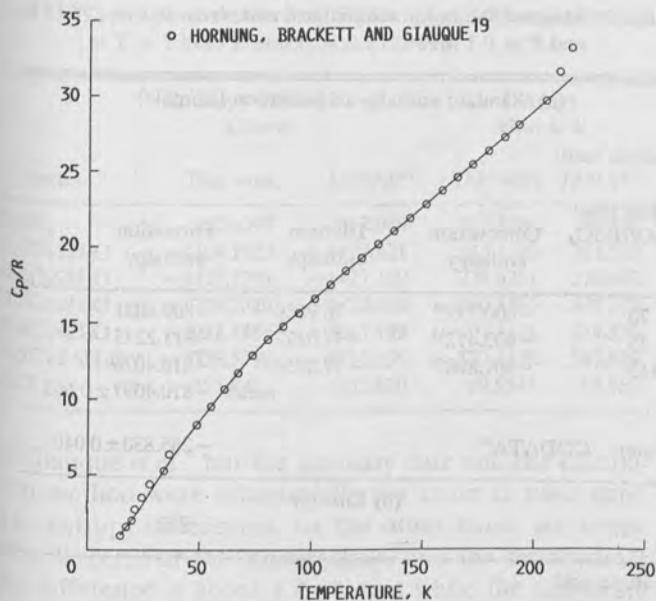


FIGURE 31(A).

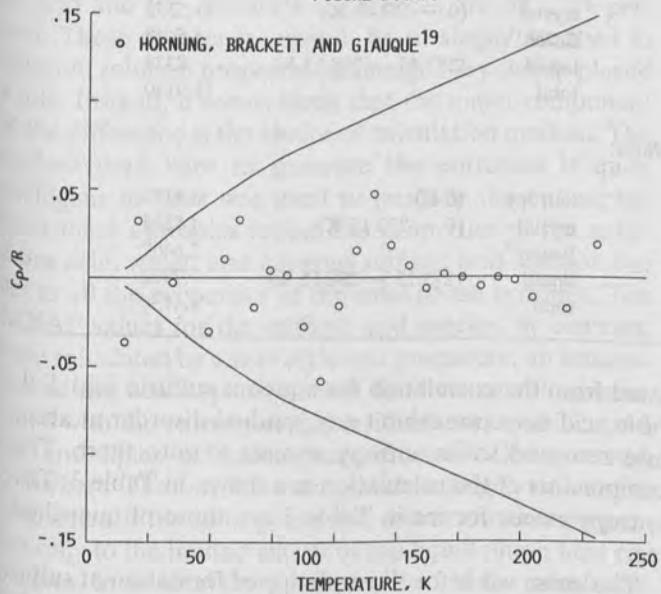


FIGURE 31(B).

Fig. 31. (a) Heat capacity of $H_2SO_4 \cdot 6.5H_2O(s)$ versus temperature: \circ = Hornung, Brackett and Giauque.¹⁹
 (b) Residuals of points given nonzero weight and curves of $\pm 1/2$ percent of the predicted values for heat capacity of $H_2SO_4 \cdot 6.5H_2O(s)$ versus temperature: \circ = Hornung, Brackett and Giauque.¹⁹

with ordering is clearly visible in the vicinity of 100 K and is manifestly a function of the samples thermal history. For ice, as for the other solid phases, the predicted values agree with the selected experimental data within 1/2 percent.

The entropy of quenched ice at 0 K is a matter of considerable interest in its own right. The present analysis gives a value of 3.4276 J/(mol·K). By comparison, the same experimental measurements yield an entropy of 3.3429 J/(mol·K) for annealed ice at 0 K. Haida *et al.*¹⁶ estimated a value of 3.41 ± 0.22 for the configurational entropy of completely disordered hexagonal ice from

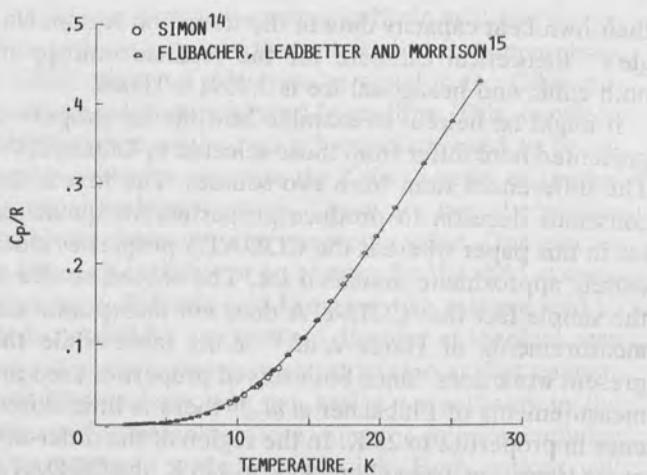


FIGURE 32(A).

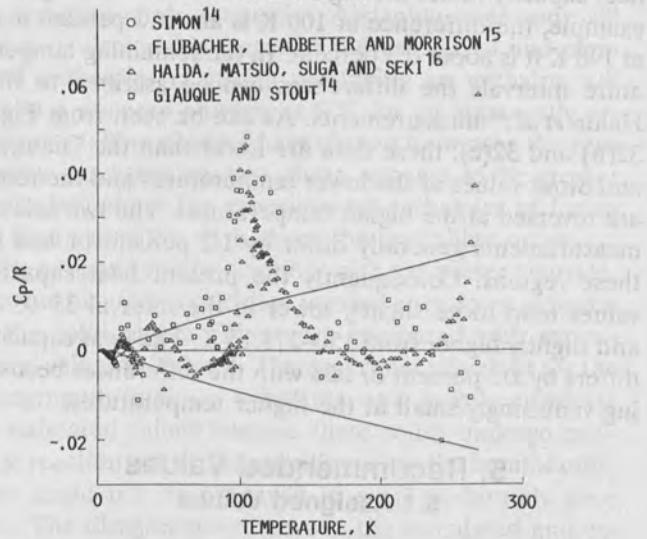


FIGURE 32(B).

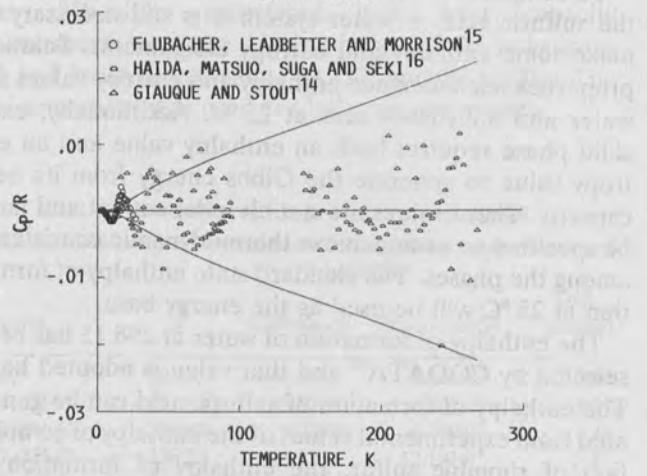


Fig. 32. (a) Heat capacity of $H_2O(s)$ -quenched versus temperature: \circ = Simon,¹⁴ \square = Flubacher, Leadbetter and Morrison.¹⁵
 (b) Residuals for all data points and curves of $\pm 1/2$ percent of the predicted values for the heat capacity of $H_2O(s)$ -quenched: \circ = Simon,¹⁴ \square = Flubacher, Leadbetter and Morrison,¹⁵ Δ = Haida, Matsuo, Suga and Seki,¹⁶ \square = Giauque and Stout.¹⁴
 (c) Residuals of points given nonzero weight and curves of $\pm 1/2$ percent of the predicted values for the heat capacity of $H_2O(s)$ -quenched: \circ = Flubacher, Leadbetter and Morrison,¹⁵ \square = Haida, Matsuo, Suga and Seki,¹⁶ Δ = Giauque and Stout.¹⁴

their own heat capacity data in the transition region. Nangle's⁴¹ theoretical estimate for the residual entropy of both cubic and hexagonal ice is 3.4091 ± 0.0008 .

It might be helpful to examine how the ice properties presented here differ from those selected by CODATA⁴². The differences stem from two sources. The first is the conscious decision to produce properties for quenched ice in this paper whereas the CODATA properties more closely approximate annealed ice. The second source is the simple fact that CODATA does not incorporate the measurements of Haida *et al.*¹⁶ in its table while the present work does. Since both sets of properties used the measurements of Flubacher *et al.*,¹⁵ there is little difference in properties to 25 K. In the region of the order-disorder transition, from about 95 K to 145 K, the CODATA heat capacity values are higher because of annealing. For example, the difference at 100 K is about 2 percent and at 140 K it is about 0.3 percent. In the remaining temperature intervals the differences can be ascribed to the Haida *et al.*¹⁶ measurements. As can be seen from Figs. 32(b) and 32(c), these data are lower than the Giauque and Stout values at the lower temperatures and the roles are reversed at the higher temperatures. The two sets of measurements generally differ by 1/2 percent or less in these regions. Consequently the present heat capacity values tend to be slightly lower in the interval 35–95 K and slightly higher from 150–273.15 K. The heat capacity differs by 1/2 percent or less with the differences becoming vanishingly small at the higher temperatures.

5. Recommended Values

5.1 Assigned Values

To complete the specification of the Gibbs energy for the sulfuric acid – water system it is still necessary to make some enthalpy and entropy assignments. Solution properties need assigned enthalpy and entropy values for water and anhydrous acid at 25 °C. Additionally, each solid phase requires both an enthalpy value and an entropy value to generate the Gibbs energy from its heat capacity. These values are not all independent and must be specified so as to achieve thermodynamic consistency among the phases. The standard state enthalpy of formation at 25 °C will be used as the energy base.

The enthalpy of formation of water at 298.15 has been selected by CODATA⁴³ and that value is adopted here. The enthalpy of formation of sulfuric acid can be generated from experimental values of the enthalpy of combustion of rhombic sulfur, the enthalpy of formation of water, and the enthalpy of dilution as calculated from the present correlation for aqueous sulfuric acid. The enthalpy of combustion of rhombic sulfur to form a dilute sulfuric acid has been measured by McCullough *et al.*,⁴⁴ by Scott *et al.*,⁴⁵ and by Good, Lacina and McCullough.⁴⁶ The entropies of sulfuric acid and water were obtained by an integration of the heat capacities of the respective solid phases from 0 K to their fusion temperatures, to which was added the entropy of fusion, and the entropy change from the fusion temperature to 298.15 K as calcu-

TABLE 3. Assigned values for sulfuric acid and water at $T = 298.15\text{ K}$ and $P = 0.1\text{ MPa}$

(a) Standard enthalpy of formation (kJ/mole)			
Sulfuric acid:			
Mole ratio	Combustion enthalpy	Dilution enthalpy	Formation enthalpy
H ₂ O/H ₂ SO ₄			
70	-600.739 ⁴⁴	-76.9669	-809.6021
75	-602.412 ⁴⁵	-77.0177	-811.2243
115	-601.868 ⁴⁶	-77.2954	-810.4026
		mean	-810.4097 ± 0.662
Water: CODATA ⁴³			-285.830 ± 0.040
(b) Entropy			
S/R			
Sulfuric acid:			
entropy	(0 K)		0.0
crystal	(0 – 283.45 K)		13.5352
fusion ¹⁷			4.5449
liquid	(283.45 – 298.15 K)		.8329
total			18.9130
Water:			
entropy	(0 K)		0.4123
crystal	(0 – 273.15 K)		4.5584
fusion ³²			2.6467
liquid	(273.15 – 298.15 K)		.7962
total			8.4136

lated from the correlation for aqueous sulfuric acid. Sulfuric acid does not exhibit any residual disorder at absolute zero and so its entropy was set to zero there. The components of the calculation are shown in Table 3. The entropy values for ice in Table 3 are those of quenched ice.

The mean value for the enthalpy of formation of sulfuric acid is -810.4097 kJ/mol , and is the value selected. It is quite close to the value derived from the measurements of Good *et al.* Also the entropy of water, $69.9541\text{ kJ/mol}\cdot\text{K}$ is in excellent agreement with the value 69.95 ± 0.03 chosen by CODATA.⁴³

The enthalpy of formation of a liquid solution, with the same composition as that of the one of the hydrates, can be obtained from the enthalpies of formation of sulfuric acid and water, and the enthalpy change for dilution as calculated from the aqueous sulfuric acid correlation. Similarly, the entropy of the hydrate liquids can be obtained from the entropies of the pure acid and water together with the entropy change accompanying dilution, again calculated from the aqueous sulfuric acid correlation. Table 4 compares these values to the values used in the JANAF thermochemical tables.⁴⁷

The enthalpies of formation agree to better than 1/2 percent and the entire difference is attributable to the use of different solution properties. The reason is that the JANAF values were based on the solution properties

TABLE 4. Liquid phase standard enthalpies of formation and entropies at $T = 298.15\text{ K}$ and $P = 0.1\text{ MPa}$

Species	Enthalpy of formation kJ/mole		Entropy kJ/mole·K	
	This work	JANAF ⁴⁷	This work	JANAF ⁴⁷
H_2SO_4	-810.4097	-813.989	157.2504	156.895
$\text{H}_2\text{SO}_4 \cdot 1\text{H}_2\text{O}$	-1124.1903	-1127.621	215.1320	211.510
$\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	-1425.2791	-1427.100	275.6751	276.363
$\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$	-1719.7820	-1720.100	340.5366	345.373
$\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$	-2011.1854	-2011.199	407.5424	414.529
$\text{H}_2\text{SO}_4 \cdot 6.5\text{H}_2\text{O}$	-2733.5796	-2733.256	579.4578	587.819
H_2O	-285.830	-285.830	69.9541	69.950

of Giauque *et al.*⁹ but the auxiliary data and the calculation method were substantially the same as used here. The entropy differences, on the other hand, are somewhat larger. For the monohydrate and the tetrahydrate the difference is about 1.7 percent while the trihydrate and hemihexahydrate differ by 1.4 percent and the sulfuric acid and the dihydrate differences are only 1/4 percent. These differences cannot be so simply ascribed to different solution properties, although they clearly played a role. Instead, it seems likely that the major component of the difference is the choice of calculation method. The method used here to generate the entropies is quite analogous to what was used to produce the enthalpies. Thus these entropies reflect the properties of the anhydrous acid, water, and aqueous sulfuric acid solution but not at all the properties of the solid phase hydrates. The JANAF values for the sulfuric acid species, by contrast, were calculated by a very different procedure; an integration of the heat capacities, at a fixed composition, combined with the entropy of fusion. The heat capacities and the enthalpies of fusion were those of Giauque and coworkers. The JANAF entropy values largely reflect the properties of the solid phase and mirror solution properties only to the limited extent of the liquid phase heat capacities. In an ideal thermodynamic world the calculation method would be irrelevant. Consequently, the greater disparity in the entropy values is probably symptomatic of an underlying inconsistency among the measured properties of the different phases.

Thermodynamic inconsistencies among the phases are to be expected in this binary system in light of the great experimental difficulties with the preparation of pure samples, supercooling, and calorimeter gradients caused by the highly viscous liquids. However, ice and $\text{H}_2\text{SO}_4(\text{s})$ properties are automatically consistent with the properties of aqueous sulfuric acid because they were used in the generation of the correlation through their freezing curves and in the calculation of the solution reference values. The five crystalline sulfuric acid hydrates, on the other hand, had only a minimal effect on the correlation. Their properties were only used to generate estimates for solution enthalpy and Gibbs energy at the melting points. The solid hydrate properties can be made consistent with the solution only by an appropriate choice of the energy reference E_0 .

Consistency between aqueous sulfuric acid and a crystalline hydrate requires that, at its fusion temperature, the Gibbs energy of a hydrate be equal to the Gibbs energy of the solution produced by melting. This, in effect, determines one of the two values which need to be assigned in order to generate the Gibbs energy of the hydrate from its heat capacity. There are two alternatives available to determine the remaining value. One can assign either an enthalpy or an entropy for the solid at some temperature. Sulfuric acid hydrates, like sulfuric acid itself, do not exhibit any residual disorder at absolute zero and so their entropies may be set to zero at that temperature. Alternatively, one can assign an enthalpy to the solid at its fusion temperature using the solution enthalpy and a measured enthalpy of fusion. Both options will point out any discrepancies between the solution properties and the hydrate properties. Assigning an entropy will lead to a discrepancy between the calculated and measured enthalpies of fusion. Assigning an enthalpy will lead to a nonzero entropy at 0 K for an apparently ordered crystalline phase. I have chosen to impose the zero entropy condition because there appears to be greater uncertainty about the experimental enthalpies of fusion and heat capacities than about the crystalline order.

The assigned values, together with the present correlations can be used to calculate implied enthalpies of fusion for the solid phases. These are compared with experimental values in Table 5. The experimental values for the incongruously melting trihydrate and hemihexahydrate are estimated values because these solids undergo peritectic reaction rather than melting. Also the hemihexahydrate could not be prepared in even moderately pure form. The disagreement between the calculated and experimental enthalpies of fusion is consistent with the obvious difficulties associated with heat capacity measurements near the melting points of the anhydrous acid and its hydrates (Figs. 26, 27, and 29 to 31). The same apparatus was used for both measurements.

TABLE 5. Enthalpies of fusion for pure solid phases

Species	T_f	H_f/RT_f		Diff., percent
		Calculated	Experimental	
H_2SO_4	283.45	4.5449	4.5449 ¹⁷	0.0
$\text{H}_2\text{SO}_4 \cdot 1\text{H}_2\text{O}$	281.63	8.7203	8.3016 ¹⁷	-5.0
$\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	233.67	9.2223	9.3895 ¹⁷	1.8
$\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$	236.76	11.5534	12.1916 ¹⁸	5.2
$\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$	244.88	14.1596	15.0465 ¹⁸	5.9
$\text{H}_2\text{SO}_4 \cdot 6.5\text{H}_2\text{O}$	220.27	17.4664	18.6467 ¹⁹	6.3
H_2O	273.15	2.6467	2.6467 ³²	.0

The validity of the choices for the assigned values, as well as the correlations themselves, may be judged by the extent of agreement between experimental and calculated freezing points. This can be seen in Fig. 1. On the whole, the agreement is quite good with the discrepancies

being confined to a small region between the monohydrate and the eutectic formed by the monohydrate and the anhydrous acid. Kunzler and Giauque ascribed the higher temperatures of Gable *et al.* to their inability to attain equilibrium in concentrated sulfuric acid solutions. This same explanation could also explain the fact that the Kunzler and Giauque temperatures are somewhat higher than the calculated curves in this region.

5.2. Functions, Parameters and Tables

The results of the correlation are a set of functions which describe the Gibbs energy of aqueous sulfuric acid and the various solid phases. The relative Gibbs energy for aqueous sulfuric acid is represented by the function

$$-G^{(r)}(T, P; x)/RT \equiv \sum_{i=1}^2 \Phi(i) \sum_{j=1}^2 \sum_{k=1}^2 (\mu_{jki} + \epsilon_{jki} \ln x_j) x_k (12)$$

where μ_{jki} and ϵ_{jki} are functions of temperature, $\Phi(1) = 1$, and $\Phi(2) = x_1 x_2$. The functions μ_{jki} are symmetric in the first pair of indices, that is, they satisfy the condition $\mu_{jki} = \mu_{kj\bar{i}}$. This function of composition is a special case of a more general representation of solution properties which is applicable to both electrolyte and nonelectrolyte multicomponent solutions. The general form of the function was derived and characterized mathematically by Zeleznik.⁴⁸ The capabilities of the function to reproduce the thermodynamic behavior of binary and ternary systems was explored by Zeleznik and Donovan⁴⁹ who tested it on the experimental data for several highly nonideal solutions.

The temperature dependence of μ_{jki} and ϵ_{jki} is here chosen to be identical in form to the function that was used to describe the temperature dependence of the Gibbs energy of the pure species.

$$\begin{aligned} -[G(T, P) - E_0]/RT &\equiv T^p \sum_{n=0}^m a_n T^n + a_{m+1}/T + a_{m+2} \ln T + a_{m+3} \\ \mu_{jki} &\equiv \sum_{n=0}^2 a_n T^n + a_3/T + a_4 \ln T \\ \epsilon_{jki} &\equiv \sum_{n=0}^2 a_n T^n + a_3/T + a_4 \ln T \end{aligned} \quad (13)$$

In all cases the temperature dependence is simply a polynomial of degree m multiplied by the temperature raised to some power, p , plus additional terms. These might include a reciprocal temperature, the logarithm of the temperature or a constant. The values of m and p differ from case to case. The parameters are given in Table 6 where only the nonzero and distinct parameters are shown.

Aqueous sulfuric acid properties from 200 to 350 K are plotted as a function of sulfuric acid mole fraction in Figs. 33 to 35. These same properties, together with those at 298.15 K, are also listed in Table 7. Extrapolation above 350 K is not recommended, especially for the concentrated acid, where there are no measured values above 25 °C. Activity coefficients and osmotic coefficients are simply alternative forms of the chemical potentials and can be calculated from them using Eq. 11. However, there may be occasions when it would be convenient to have available tabulated values of these coefficients. Con-

sequently, Table 8 gives these values, to a molality of $m = 30$, at increments of 25 degrees from 273.15 K to 348.15 K.

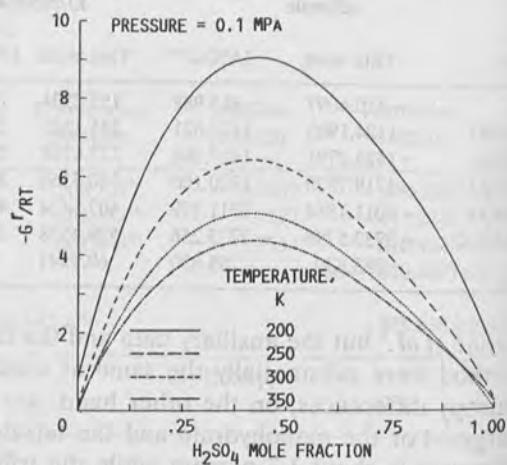


FIGURE 33(A).

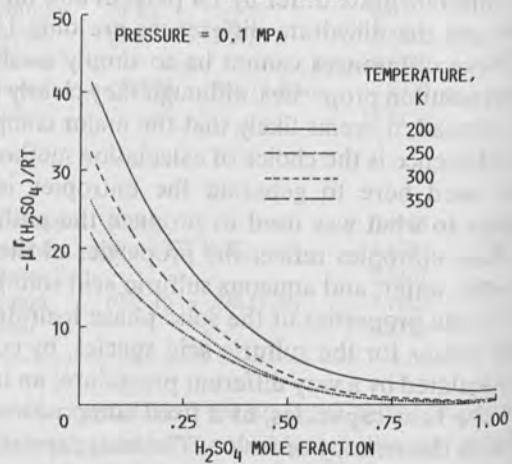


FIGURE 33(B).

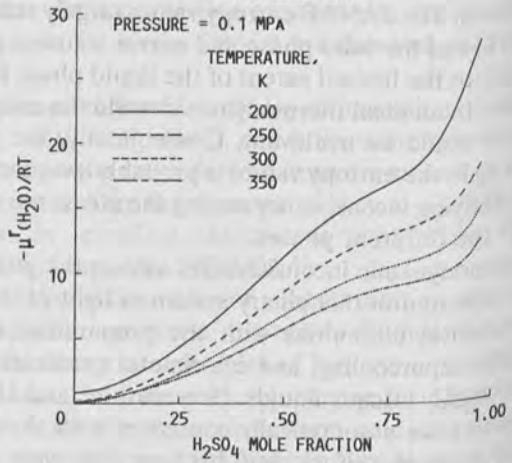


FIGURE 33(C).

Fig. 33. (a) Relative Gibbs energy of aqueous sulfuric acid versus sulfuric acid mole fraction at four temperatures and a pressure of 0.1 MPa.
 (b) Relative chemical potential of sulfuric acid in aqueous sulfuric acid versus sulfuric acid mole fraction at four temperatures.
 (c) Relative chemical potential of water in aqueous sulfuric acid versus sulfuric acid mole fraction at four temperatures.

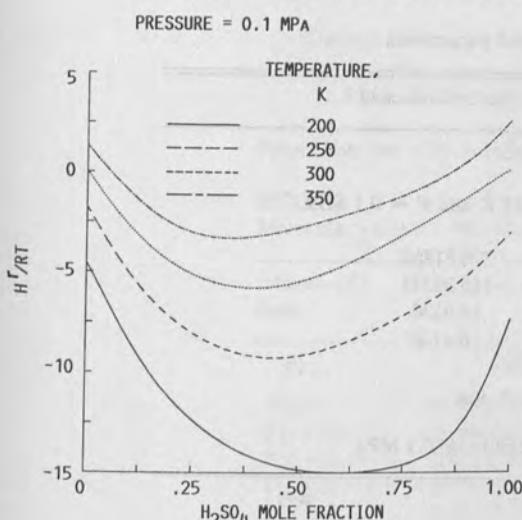


FIGURE 34(A).

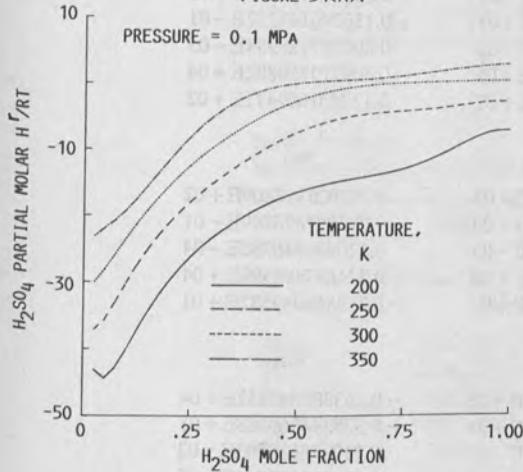


FIGURE 34(B)

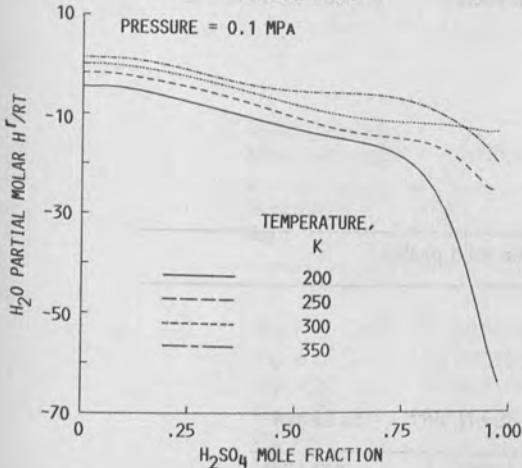


FIGURE 34(C).

Fig. 34. (a) Relative enthalpy of aqueous sulfuric acid versus sulfuric acid mole fraction at four temperatures and a pressure of 0.1 MPa.
 (b) Relative partial molar enthalpy of sulfuric acid in aqueous sulfuric acid versus sulfuric acid mole fraction at four temperatures.
 (c) Relative partial molar enthalpy of water in aqueous sulfuric acid versus sulfuric acid mole fraction at four temperatures.

The thermodynamic properties of each of the solid phases are tabulated in Tables 9 to 15 as a function of temperature from absolute zero to the melting point. If properties are required at conditions which differ from

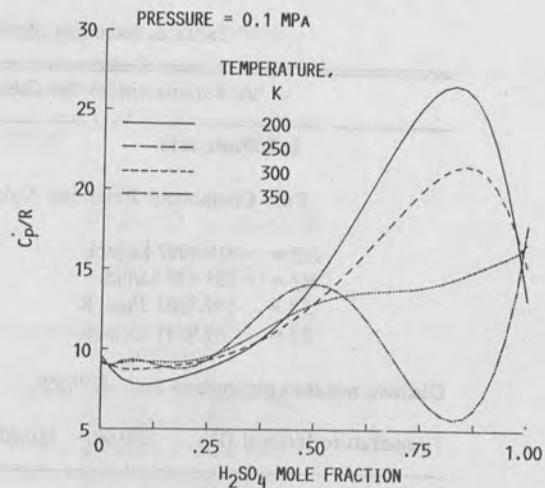


FIGURE 35(A).

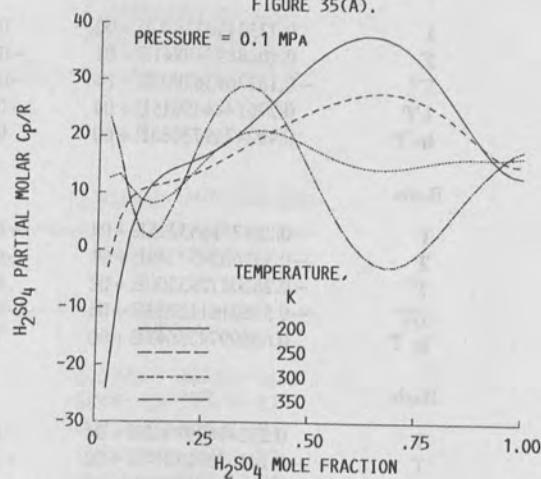


FIGURE 35(B).

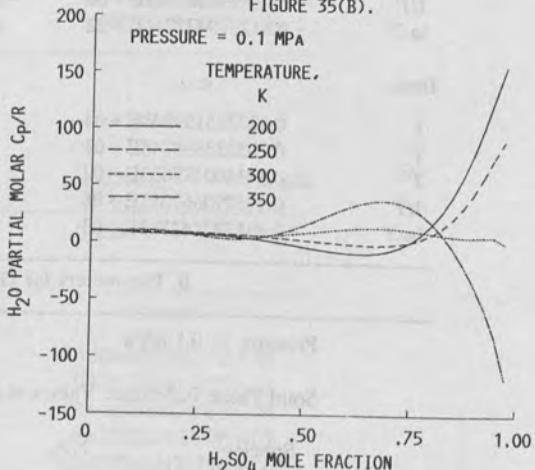


FIGURE 35(C).

Fig. 35. (a) Heat capacity of aqueous sulfuric acid versus sulfuric acid mole fraction at four temperatures and a pressure of 0.1 MPa.
 (b) Partial molar heat capacity of sulfuric acid in aqueous sulfuric acid versus sulfuric acid mole fraction at four temperatures.
 (c) Partial molar heat capacity of water in aqueous sulfuric acid versus sulfuric acid mole fraction at four temperatures.

those given in Tables 7 to 15, then they can be calculated from the Gibbs energy functions, Eq.(12) and Eq.(13), using the usual thermodynamic relations as given in Eqs.(7) to (11).

TABLE 6. Summary of reference values and parameters

A. Parameters for the Gibbs energy of aqueous sulfuric acid				
1. Sulfuric acid		2. Water		
Pure Component Reference Values at $T = 298.15\text{ K}$ and $P = 0.1\text{ MPa}$				
$H_1^* = -810.4097\text{ kJ/mol}$		$H_1^*/RT = -326.91766$		
$H_2^* = -285.830\text{ kJ/mol}$		$H_2^*/RT = -115.30325$		
$S_1^* = 157.2504\text{ J/mol}\cdot\text{K}$		$S_1^*/R = 18.9130$		
$S_2^* = 69.9541\text{ J/mol}\cdot\text{K}$		$S_2^*/R = 8.4136$		
Distinct, nonzero parameters for $-G^{(r)}/RT$,				
Temperature Interval (K)		Pressure = 0.1 MPa		
Basis	μ_{111}	μ_{121}	μ_{221}	
1	-0.235245033870E + 02	0.111458541077E + 04	-0.801488100747E + 02	
T	0.406889449841E - 01	-0.118330789360E + 01	-0.116246143257E - 01	
T^2	-0.151369362907E - 04	-0.209946114412E - 02	0.606767928954E - 05	
$1/T$	0.296144445015E + 04	-0.246749842271E + 06	0.309272150882E + 04	
$\ln T$	0.492476973663E + 00	0.341234558134E + 02	0.127601667471E + 02	
Basis	ϵ_{111}	ϵ_{121}	ϵ_{211}	
1	0.288731663295E + 04	-0.370944593249E + 03	0.383025318809E + 02	
T	-0.332602457749E + 01	-0.690310834523E + 00	-0.295997878789E - 01	
T^2	-0.282047283300E - 02	0.563455068422E - 03	0.120999746782E - 04	
$1/T$	-0.528216112353E + 06	-0.382252997064E + 04	-0.324697498999E + 04	
$\ln T$	0.686997435643E + 00	0.942682037574E + 02	-0.383566039532E + 01	
Basis	ϵ_{221}	μ_{122}	ϵ_{122}	
1	0.232476399402E + 04	0.888711613784E + 03	-0.163385547832E + 04	
T	-0.141626921317E + 00	-0.250531359687E + 01	-0.335344369968E + 01	
T^2	-0.626760562881E - 02	0.605638824061E - 03	0.710978119903E - 02	
$1/T$	-0.450590687961E + 06	-0.196985296431E + 06	0.198200003569E + 06	
$\ln T$	-0.612339472744E + 02	0.745500643380E + 02	0.246693619189E + 03	
Basis	ϵ_{212}			
1	0.127375159848E + 04			
T	0.103333898148E + 01			
T^2	0.341400487633E - 02			
$1/T$	0.195290667051E + 06			
$\ln T$	-0.431737442782E + 03			
B. Parameters for Gibbs energy of the solid phases				
Pressure = 0.1 MPa				
Solid Phase Reference Values at $P = 0.1\text{ MPa}$				
Species	r_1, r_2	T, K	$(E_0 - \sum r_i H_i^*)/RT$	$E_0\text{ kJ/mol}$
$\text{H}_2\text{SO}_4(\text{s})$	1,0	283.45	-5.3993	-823.1343
$\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}(\text{s})$	1,1	281.63	-22.1561	-1148.1201
$\text{H}_2\text{SO}_4\cdot2\text{H}_2\text{O}(\text{s})$	1,2	233.67	-39.9093	-1459.6066
$\text{H}_2\text{SO}_4\cdot3\text{H}_2\text{O}(\text{s})$	1,3	236.76	-47.6710	-1761.7410
$\text{H}_2\text{SO}_4\cdot4\text{H}_2\text{O}(\text{s})$	1,4	244.88	-52.3606	-2060.3376
$\text{H}_2\text{SO}_4\cdot6.5\text{H}_2\text{O}(\text{s})$	1,6,5	220.27	-76.6639	-2808.7081
$\text{H}_2\text{O}(\text{s})\text{-Quenched}$	0,1	273.15	-3.4788	-293.7306

TABLE 6. Summary of reference values and parameters — Continued

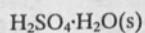
B. Parameters for Gibbs energy of the solid phases — Continued

Parameters for $-(G - E_0)/RT$ of the solid phases

Molecular weight = 98.07948

 $E_0(\text{kJ/mol}) = -823.1343$

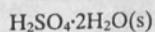
Interval (K)	0.00	80.00	80.00	283.45
Basis				
<i>p</i>	3.00000		0.00000	
<i>T(p)</i>	0.209513417696E-04		-0.937517723026E+01	
<i>T(p + 1)</i>	-0.526499356359E-06		0.168198441246E-01	
<i>T(p + 2)</i>	0.617953576113E-08		0.179957151783E-05	
<i>T(p + 3)</i>	-0.368383090168E-10		-0.292577568186E-08	
<i>T(p + 4)</i>	0.897739978818E-13		0.198704416569E+01	
<i>1/T</i>	0.186399939975E+04		0.000000000000E+00	
<i>ln T</i>	0.000000000000E+00		0.193990512985E+04	



Molecular weight = 116.09476

 $E_0(\text{kJ/mol}) = -1148.1201$

Interval (K)	0.00	90.00	90.00	281.63
Basis				
<i>p</i>	3.00000		0.00000	
<i>T(p)</i>	0.135237334699E-04		-0.266864085251E+01	
<i>T(p + 1)</i>	-0.271433961873E-06		0.397370872284E-01	
<i>T(p + 2)</i>	0.257003106068E-08		-0.326896193052E-04	
<i>T(p + 3)</i>	-0.124603123850E-10		0.307238866459E-07	
<i>T(p + 4)</i>	0.249036954092E-13		0.153155889980E+00	
<i>1/T</i>	0.227467951684E+04		0.000000000000E+00	
<i>ln T</i>	0.000000000000E+00		0.231432720591E+04	



Molecular weight = 134.11004

 $E_0(\text{kJ/mol}) = -1459.6066$

Interval (K)	0.00	75.00	75.00	233.67
Basis				
<i>p</i>	3.00000		0.00000	
<i>T(p)</i>	0.289027765084E-04		0.604443808619E+00	
<i>T(p + 1)</i>	-0.77713111063E-06		0.579024881322E-01	
<i>T(p + 2)</i>	0.986006125594E-08		-0.618363003496E-04	
<i>T(p + 3)</i>	-0.636115498524E-10		0.622828589050E-07	
<i>T(p + 4)</i>	0.167578634080E-12		-0.655841247173E+00	
<i>1/T</i>	0.197815173932E+04		0.000000000000E+00	
<i>ln T</i>	0.000000000000E+00		0.198747107654E+04	

TABLE 6. Summary of reference values and parameters — Continued

B. Parameters for Gibbs energy of the solid phases — Continued				
$\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}(\text{s})$		$E_0(\text{kJ/mol}) = -1761.7410$		
Molecular weight	= 152.12532			
Interval (K)	0.00	80.00	80.00	236.76
Basis				
<i>p</i>	3.00000		0.00000	
<i>T(p)</i>	0.299347801065E-04		0.540110012718E+00	
<i>T(p+1)</i>	-0.750745750843E-06		0.743408859682E-01	
<i>T(p+2)</i>	0.890028803487E-08		-0.873919155921E-04	
<i>T(p+3)</i>	-0.535469857197E-10		0.999853606186E-07	
<i>T(p+4)</i>	0.131126727994E-12		-0.869699692193E+00	
<i>1/T</i>	0.256132391046E+04		0.000000000000E+00	
<i>ln T</i>	0.000000000000E+00		0.258414096223E+04	
$\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}(\text{s})$				
Molecular weight = 170.14060		$E_0(\text{kJ/mol}) = -2060.3376$		
Interval(K)	0.00	75.00	75.00	244.88
Basis				
<i>p</i>	3.00000		0.00000	
<i>T(p)</i>	0.486962518106E-04		-0.916278239224E+01	
<i>T(p+1)</i>	-0.135026575456E-05		0.633712328367E-01	
<i>T(p+2)</i>	0.175469324815E-07		-0.509938896061E-04	
<i>T(p+3)</i>	-0.115168446959E-09		0.552201803973E-07	
<i>T(p+4)</i>	0.306657510197E-12		0.152059812384E+01	
<i>1/T</i>	0.318323386377E+04		0.000000000000E+00	
<i>ln T</i>	0.000000000000E+00		0.327056137013E+04	
$\text{H}_2\text{SO}_4 \cdot 6.5\text{H}_2\text{O}(\text{s})$				
Molecular weight = 215.17880		$E_0(\text{kJ/mol}) = -2808.7081$		
Interval (K)	0.00	85.00	85.00	220.27
Basis				
<i>p</i>	3.00000		0.00000	
<i>T(p)</i>	0.493060918545E-04		-0.172433321490E+02	
<i>T(p+1)</i>	-0.119938102576E-05		0.737029098304E-01	
<i>T(p+2)</i>	0.136538215188E-07		-0.300049546281E-04	
<i>T(p+3)</i>	-0.783198153045E-10		0.374194111724E-07	
<i>T(p+4)</i>	0.181877346790E-12		0.307267288403E+01	
<i>1/T</i>	0.369992150384E+04		0.000000000000E+00	
<i>ln T</i>	0.000000000000E+00		0.387572385258E+04	
$\text{H}_2\text{O}(\text{s})\text{-QUENCHED}$				
Molecular weight = 18.01528		$E_0(\text{kJ/mol}) = -293.7306$		
Interval (K)	0.00	50.00	50.00	273.15
Basis				
<i>p</i>	4.00000		0.00000	
<i>T(p)</i>	0.350462310185E-06		0.157716756765E+01	
<i>T(p+1)</i>	-0.157573711316E-07		0.169067080008E-01	
<i>T(p+2)</i>	0.300609854202E-09		-0.257488994006E-04	
<i>T(p+3)</i>	-0.273402074809E-11		0.444157502439E-07	
<i>T(p+4)</i>	0.967048529086E-14		-0.321027432499E-10	
<i>1/T</i>	0.646699573040E+03		0.642434349535E+03	
<i>ln T</i>	0.000000000000E+00		-0.424558830553E+00	
1	0.412254109268E+00		0.000000000000E+00	

TABLE 7. Aqueous sulfuric acid properties

$T = 200.000 \text{ K}, P = 0.10000 \text{ MPa}$					1. Sulfuric acid			2. Water		
x_1	Heat Capacity		Relative enthalpy		Relative Gibbs energy				x_1	
	C_P/R	$C_P(1)/R$	$C_P(2)/R$	$H^{(r)}/RT$	$H_1^{(r)}/RT$	$H_2^{(r)}/RT$	$-G^{(r)}/RT$	$-\mu_1^{(r)}/RT$	$-\mu_2^{(r)}/RT$	
0.0000	9.5666	—	9.5666	-4.5429	—	-4.5429	0.8400	—	0.8400	0.0000
.0200	8.8917	-28.1451	9.6475	-5.3349	-42.2609	-4.5812	1.7100	41.8587	.8906	.0200
.0400	8.2957	-13.1596	9.1896	-6.1153	-44.3617	-4.5217	2.5059	39.5439	.9627	.0400
.0600	7.9667	-2.6600	8.6449	-6.9111	-43.9642	-4.5460	3.2515	37.0405	1.0947	.0600
.0800	7.8181	4.0659	8.1443	-7.6832	-42.3094	-4.6721	3.9432	34.5150	1.2848	.0800
.1000	7.7864	8.2916	7.7302	-8.4127	-40.1422	-4.8871	4.5810	32.0860	1.5249	.1000
.1200	7.8294	10.9210	7.4077	-9.0921	-37.8440	-5.1713	5.1664	29.8037	1.8067	.1200
.1400	7.9198	12.5590	7.1645	-9.7197	-35.6037	-5.5059	5.7017	27.6821	2.1235	.1400
.1600	8.0409	13.6099	6.9800	-10.2967	-33.5083	-5.8754	6.1896	25.7174	2.4700	.1600
.1800	8.1827	14.3447	6.8300	-10.8260	-31.5902	-6.2679	6.6324	23.8979	2.8424	.1800
.2000	8.3405	14.9446	6.6894	-11.3107	-29.8531	-6.6751	7.0325	22.2093	3.2383	.2000
.2200	8.5129	15.5289	6.5340	-11.7542	-28.2862	-7.0913	7.3919	20.6367	3.6562	.2200
.2400	8.7010	16.1735	6.3412	-12.1595	-26.8723	-7.5133	7.7123	19.1669	4.0950	.2400
.2600	8.9073	16.9238	6.0906	-12.5294	-25.5928	-7.9395	7.9952	17.7882	4.5544	.2600
.2800	9.1357	17.8032	5.7649	-12.8664	-24.4298	-8.3695	8.2421	16.4912	5.0340	.2800
.3000	9.3904	18.8191	5.3494	-13.1725	-23.3674	-8.8032	8.4539	15.2684	5.5334	.3000
.3200	9.6760	19.9675	4.8329	-13.4495	-22.3925	-9.2410	8.6318	14.1140	6.0519	.3200
.3400	9.9973	21.2360	4.2075	-13.6990	-21.4947	-9.6830	8.7767	13.0240	6.5886	.3400
.3600	10.3586	22.6063	3.4692	-13.9224	-20.6662	-10.1290	8.8895	11.9957	7.1422	.3600
.3800	10.7640	24.0558	2.6174	-14.1209	-19.9014	-10.5780	8.9711	11.0274	7.7108	.3800
.4000	11.2172	25.5590	1.6559	-14.2958	-19.1962	-11.0287	9.0225	10.1182	8.2920	.4000
.4200	11.7210	27.0886	.5927	-14.4480	-18.5480	-11.4790	9.0445	9.2678	8.8828	.4200
.4400	12.2776	28.6160	-.5598	-14.5789	-17.9551	-11.9261	9.0382	8.4762	9.4798	.4400
.4600	12.8883	30.1123	-1.7841	-14.6896	-17.4160	-12.3670	9.0047	7.7435	10.0791	.4600
.4800	13.5534	31.5487	-3.0577	-14.7813	-16.9292	-12.7985	8.9452	7.0697	10.6764	.4800
.5000	14.2721	32.8967	-4.3525	-14.8552	-16.4930	-13.2174	8.8609	6.4547	11.2671	.5000
.5200	15.0425	34.1288	-5.6344	-14.9127	-16.1049	-13.6210	8.7532	5.8978	11.8465	.5200
.5400	15.8614	35.2189	-6.8629	-14.9550	-15.7617	-14.0079	8.6234	5.3979	12.4099	.5400
.5600	16.7240	36.1424	-7.9905	-14.9833	-15.4589	-14.3777	8.4732	4.9535	12.9528	.5600
.5800	17.6244	36.8767	-8.9623	-14.9986	-15.1910	-14.7328	8.3040	4.5621	13.4713	.5800
.6000	18.5547	37.4013	-9.7154	-15.0018	-14.9511	-15.0779	8.1174	4.2210	13.9618	.6000
.6200	19.5056	37.6988	-10.1782	-14.9937	-14.7313	-15.4216	7.9149	3.9265	14.4222	.6200
.6400	20.4657	37.7544	-10.2700	-14.9742	-14.5225	-15.7772	7.6980	3.6743	14.8512	.6400
.6600	21.4218	37.5573	-9.9001	-14.9433	-14.3148	-16.1631	7.4682	3.4596	15.2496	.6600
.6800	22.3586	37.1001	-8.9675	-14.8999	-14.0976	-16.6045	7.2268	3.2771	15.6199	.6800
.7000	23.2583	36.3803	-7.3600	-14.8423	-13.8600	-17.1340	6.9749	3.1210	15.9672	.7000
.7200	24.1011	35.4001	-4.9538	-14.7678	-13.5914	-17.7928	6.7132	2.9852	16.2994	.7200
.7400	24.8645	34.1675	-1.6136	-14.6728	-13.2817	-18.6317	6.4424	2.8637	16.6279	.7400
.7600	25.5236	32.6967	2.8080	-14.5519	-12.9222	-19.7123	6.1626	2.7505	16.9677	.7600
.7800	26.0504	31.0089	8.4697	-14.3987	-12.5065	-21.1070	5.8735	2.6399	17.3382	.7800
.8000	26.4145	29.1330	15.5400	-14.2048	-12.0310	-22.8998	5.5743	2.5271	17.7633	.8000
.8200	26.5825	27.1065	24.1951	-13.9603	-11.4962	-25.1851	5.2635	2.4081	18.2714	.8200
.8400	26.5185	24.9765	34.6135	-13.6530	-10.9077	-28.0650	4.9389	2.2805	18.8955	.8400
.8600	26.1838	22.8004	46.9674	-13.2690	-10.2777	-31.6439	4.5978	2.1438	19.6722	.8600
.8800	25.5381	20.6468	61.4069	-12.7929	-9.6260	-36.0161	4.2365	1.9998	20.6391	.8800
.9000	24.5395	18.5961	78.0306	-12.2078	-8.9817	-41.2419	3.8507	1.8530	21.8299	.9000
.9200	23.1474	16.7403	96.8295	-11.4972	-8.3841	-47.2971	3.4358	1.7117	23.2637	.9200
.9400	21.3249	15.1816	117.5716	-10.6477	-7.8829	-53.9621	2.9872	1.5872	24.9208	.9400
.9600	19.0461	14.0256	139.5409	-9.6553	-7.5351	-60.5424	2.5019	1.4942	26.6870	.9600
.9800	16.3109	13.3601	160.9145	-8.5419	-7.3892	-65.0258	1.9812	1.4457	28.2256	.9800
1.0000	13.1352	13.1352	—	-7.3879	-7.3879	—	1.4243	1.4243	—	1.0000

TABLE 7. Aqueous sulfuric acid properties — Continued

$T = 250.000 \text{ K}$, $P = 0.10000 \text{ MPa}$						1. Sulfuric acid		2. Water		
x_1	Heat Capacity			Relative enthalpy		Relative Gibbs energy			x_1	
	C_P/R	$C_P(1)/R$	$C_P(2)/R$	$H^{(r)}/RT$	$H_1^{(r)}/RT$	$H_2^{(r)}/RT$	$-G^{(r)}/RT$	$-\mu_1^{(r)}/RT$		
0.0000	9.2232	—	9.2232	-1.7584	—	-1.7584	0.1499	—	0.1499	0.0000
.0200	9.0107	-5.4941	9.3066	-2.4757	-37.0740	-1.7696	.8499	32.9346	.1951	.0200
.0400	8.8037	2.5876	9.0626	-3.1787	-36.4711	-1.7915	1.4790	30.4925	.2701	.0400
.0600	8.7271	7.1297	8.8289	-3.8544	-34.6485	-1.8888	2.0599	28.2674	.3870	.0600
.0800	8.7204	9.4067	8.6606	-4.4861	-32.4269	-2.0564	2.5950	26.1953	.5428	.0800
.1000	8.7488	10.5090	8.5531	-5.0687	-30.1688	-2.2797	3.0867	24.2733	.7327	.1000
.1200	8.7948	11.0608	8.4856	-5.6022	-28.0258	-2.5444	3.5374	22.4945	.9523	.1200
.1400	8.8504	11.4032	8.4346	-6.0889	-26.0528	-2.8389	3.9491	20.8473	1.1983	.1400
.1600	8.9134	11.7166	8.3793	-6.5318	-24.2594	-3.1551	4.3240	19.3183	1.4679	.1600
.1800	8.9844	12.0894	8.3027	-6.9341	-22.6341	-3.4877	4.6637	17.8945	1.7594	.1800
.2000	9.0657	12.5578	8.1925	-7.2986	-21.1571	-3.8339	4.9699	16.5640	2.0713	.2000
.2200	9.1600	13.1291	8.0404	-7.6278	-19.8060	-4.1928	5.2438	15.3162	2.4029	.2200
.2400	9.2702	13.7949	7.8412	-7.9237	-18.5600	-4.5648	5.4868	14.1423	2.7534	.2400
.2600	9.3990	14.5395	7.5927	-8.1880	-17.4004	-4.9512	5.6997	13.0354	3.1223	.2600
.2800	9.5488	15.3445	7.2948	-8.4220	-16.3122	-5.3536	5.8836	11.9896	3.5090	.2800
.3000	9.7216	16.1919	6.9485	-8.6267	-15.2838	-5.7736	6.0392	11.0006	3.9129	.3000
.3200	9.9190	17.0650	6.5560	-8.8027	-14.3065	-6.2126	6.1673	10.0652	4.3330	.3200
.3400	10.1423	17.9497	6.1202	-8.9506	-13.3749	-6.6714	6.2687	9.1810	4.7684	.3400
.3600	10.3924	18.8341	5.6439	-9.0709	-12.4858	-7.1501	6.3441	8.3466	5.2176	.3600
.3800	10.6701	19.7086	5.1302	-9.1642	-11.6380	-7.6479	6.3941	7.5609	5.6790	.3800
.4000	10.9757	20.5656	4.5823	-9.2307	-10.8320	-8.1631	6.4196	6.8234	6.1504	.4000
.4200	11.3095	21.3989	4.0032	-9.2711	-10.0693	-8.6931	6.4213	6.1338	6.6295	.4200
.4400	11.6715	22.2036	3.3961	-9.2860	-9.3521	-9.2340	6.4001	5.4919	7.1136	.4400
.4600	12.0617	22.9752	2.7649	-9.2761	-8.6830	-9.7813	6.3567	4.8975	7.5998	.4600
.4800	12.4798	23.7094	2.1139	-9.2424	-8.0645	-10.3297	6.2923	4.3505	8.0847	.4800
.5000	12.9254	24.4015	1.4490	-9.1859	-7.4987	-10.8730	6.2077	3.8505	8.5649	.5000
.5200	13.3976	25.0465	.7778	-9.1079	-6.9874	-11.4050	6.1041	3.3968	9.0369	.5200
.5400	13.8957	25.6386	.1104	-9.0097	-6.5313	-11.9190	5.9825	2.9887	9.4970	.5400
.5600	14.4183	26.1707	-.5396	-8.8929	-6.1305	-12.4086	5.8441	2.6247	9.9416	.5600
.5800	14.9635	26.6350	-.11546	-8.7591	-5.7838	-12.8678	5.6902	2.3034	10.3673	.5800
.6000	15.5289	27.0224	-.17115	-8.6101	-5.4890	-13.2917	5.5220	2.0227	10.7710	.6000
.6200	16.1116	27.3230	-.21808	-8.4476	-5.2427	-13.6765	5.3407	1.7802	11.1499	.6200
.6400	16.7076	27.5260	-.25253	-8.2733	-5.0405	-14.0206	5.1476	1.5733	11.5021	.6400
.6600	17.3118	27.6202	-.26988	-8.0889	-4.8766	-14.3244	4.9440	1.3986	11.8261	.6600
.6800	17.9181	27.5943	-.26443	-7.8959	-4.7448	-14.5919	4.7309	1.2529	12.1217	.6800
.7000	18.5186	27.4378	-.22933	-7.6954	-4.6376	-14.8302	4.5096	1.1324	12.3897	.7000
.7200	19.1039	27.1409	-.15633	-7.4884	-4.5473	-15.0511	4.2809	1.0331	12.6326	.7200
.7400	19.6626	26.6963	-.3571	-7.2753	-4.4659	-15.2712	4.0458	.9510	12.8543	.7400
.7600	20.1810	26.0994	1.4390	-7.0560	-4.3855	-15.5128	3.8050	.8820	13.0610	.7600
.7800	20.6432	25.3498	3.9555	-6.8298	-4.2986	-15.8041	3.5588	.8223	13.2610	.7800
.8000	21.0301	24.4524	7.3402	-6.5952	-4.1990	-16.1797	3.3074	.7680	13.4652	.8000
.8200	21.3199	23.4190	11.7566	-6.3497	-4.0819	-16.6803	3.0508	.7159	13.6875	.8200
.8400	21.4877	22.2700	17.3800	-6.0900	-3.9450	-17.3510	2.7883	.6634	13.9444	.8400
.8600	21.5057	21.0362	24.3890	-5.8118	-3.7888	-18.2390	2.5192	.6085	14.2560	.8600
.8800	21.3430	19.7605	32.9474	-5.5101	-3.6177	-19.3873	2.2419	.5506	14.6446	.8800
.9000	20.9672	18.5001	43.1698	-5.1791	-3.4411	-20.8210	1.9547	.4903	15.1345	.9000
.9200	20.3457	17.3279	55.0497	-4.8132	-3.2734	-22.5206	1.6553	.4297	15.7497	.9200
.9400	19.4501	16.3319	68.3032	-4.4084	-3.1349	-24.3592	1.3410	.3728	16.5090	.9400
.9600	18.2654	15.6102	81.9904	-3.9661	-3.0504	-25.9427	1.0089	.3252	17.4191	.9600
.9800	16.8111	15.2469	93.4626	-3.5022	-3.0411	-26.0990	.6562	.2921	18.4988	.9800
1.0000	15.1606	15.1606	—	-3.0732	-3.0732	—	.2666	.2666	—	1.0000

TABLE 7. Aqueous sulfuric acid properties — Continued

$T = 298.150 \text{ K}, P = 0.10000 \text{ MPa}$							1. Sulfuric acid	2. Water		
x_1	Heat Capacity			Relative enthalpy		Relative Gibbs energy			x_1	
	C_P/R	$C_P(1)/R$	$C_P(2)/R$	$H^{(0)}/RT$	$H_1^{(0)}/RT$	$H_2^{(0)}/RT$	$-G^{(0)}/RT$	$-\mu_1^{(0)}/RT$	$-\mu_2^{(0)}/RT$	
0.0000	9.0647	—	9.0647	0.0000	—	0.0000	0.0000	—	0.0000	0.0000
.0200	9.0144	10.7257	8.9793	-.6190	-30.5904	-.0073	.5822	26.9503	.0440	.0200
.0400	9.0894	13.4719	8.9067	-1.2179	-29.2279	-.0508	1.0961	24.6971	.1128	.0400
.0600	9.1710	12.2582	8.9737	-1.7829	-27.4306	-.1458	1.5676	22.8056	.2120	.0600
.0800	9.2164	10.3868	9.1144	-2.3083	-25.5368	-.2885	2.0010	21.1057	.3397	.0800
.1000	9.2250	8.9600	9.2542	-2.7928	-23.6759	-.4725	2.3990	19.5520	.4931	.1000
.1200	9.2101	8.2872	9.3358	-3.2368	-21.8990	-.6920	2.7640	18.1207	.6699	.1200
.1400	9.1887	8.3645	9.3227	-3.6416	-20.2237	-.9421	3.0976	16.7947	.8679	.1400
.1600	9.1767	9.0648	9.1978	-4.0086	-18.6526	-1.2192	3.4015	15.5605	1.0855	.1600
.1800	9.1872	10.2215	8.9600	-4.3394	-17.1813	-1.5205	3.6770	14.4070	1.3217	.1800
.2000	9.2298	11.6671	8.6202	-4.6355	-15.8028	-1.8437	3.9253	13.3252	1.5753	.2000
.2200	9.3105	13.2510	8.1989	-4.8982	-14.5094	-2.1873	4.1473	12.3075	1.8458	.2200
.2400	9.4323	14.8464	7.7224	-5.1288	-13.2940	-2.5503	4.3441	11.3480	2.1323	.2400
.2600	9.5950	16.3529	7.2205	-5.3283	-12.1501	-2.9315	4.5162	10.4419	2.4342	.2600
.2800	9.7964	17.6954	6.7244	-5.4978	-11.0723	-3.3300	4.6646	9.5854	2.7509	.2800
.3000	10.0322	18.8224	6.2648	-5.6383	-10.0563	-3.7449	4.7898	8.7757	3.0816	.3000
.3200	10.2967	19.7033	5.8698	-5.7506	-9.0989	-4.1749	4.8926	8.0106	3.4253	.3200
.3400	10.5832	20.3254	5.5643	-5.8355	-8.1974	-4.6188	4.9734	7.2885	3.7808	.3400
.3600	10.8847	20.6909	5.3685	-5.8940	-7.3503	-5.0749	5.0331	6.6082	4.1471	.3600
.3800	11.1937	20.8140	5.2971	-5.9269	-6.5563	-5.5411	5.0721	5.9690	4.5224	.3800
.4000	11.5030	20.7186	5.3591	-5.9349	-5.8146	-6.0151	5.0912	5.3700	4.9052	.4000
.4200	11.8059	20.4352	5.5569	-5.9191	-5.1248	-6.4944	5.0909	4.8110	5.2936	.4200
.4400	12.0962	19.9991	5.8866	-5.8805	-4.4864	-6.9758	5.0721	4.2915	5.6855	.4400
.4600	12.3688	19.4481	6.3380	-5.8199	-3.8993	-7.4560	5.0354	3.8109	6.0785	.4600
.4800	12.6194	18.8209	6.8947	-5.7386	-3.3630	-7.9314	4.9817	3.3689	6.4703	.4800
.5000	12.8450	18.1553	7.5346	-5.6376	-2.8769	-8.3983	4.9116	2.9648	6.8584	.5000
.5200	13.0438	17.4866	8.2306	-5.5181	-2.4401	-8.8526	4.8262	2.5979	7.2402	.5200
.5400	13.2153	16.8472	8.9516	-5.3815	-2.0516	-9.2905	4.7262	2.2671	7.6131	.5400
.5600	13.3601	16.2646	9.6632	-5.2290	-1.7099	-9.7079	4.6127	1.9712	7.9745	.5600
.5800	13.4802	15.7617	10.3293	-5.0620	-1.4130	-10.1013	4.4864	1.7090	8.3220	.5800
.6000	13.5786	15.3552	10.9135	-4.8820	-1.1586	-10.4670	4.3485	1.4786	8.6533	.6000
.6200	13.6594	15.0559	11.3805	-4.6902	-.9440	-10.8023	4.1998	1.2782	8.9666	.6200
.6400	13.7274	14.8686	11.6982	-4.4881	-.7661	-11.1049	4.0413	1.1056	9.2602	.6400
.6600	13.7881	14.7916	11.8398	-4.2771	-.6214	-11.3734	3.8739	.9585	9.5331	.6600
.6800	13.8474	14.8174	11.7859	-4.0584	-.5060	-11.6073	3.6986	.8344	9.7849	.6800
.7000	13.9113	14.9330	11.5271	-3.8334	-.4159	-11.8076	3.5161	.7305	10.0160	.7000
.7200	13.9855	15.1206	11.0663	-3.6031	-.3467	-11.9767	3.3274	.6439	10.2277	.7200
.7400	14.0751	15.3586	10.4213	-3.3685	-.2941	-12.1186	3.1330	.5718	10.4226	.7400
.7600	14.1842	15.6229	9.6275	-3.1303	-.2538	-12.2395	2.9335	.5112	10.6044	.7600
.7800	14.3155	15.8881	8.7395	-2.8892	-.2215	-12.3473	2.7294	.4591	10.7785	.7800
.8000	14.4701	16.1292	7.8327	-2.6454	-.1936	-12.4524	2.5208	.4130	10.9522	.8000
.8200	14.6466	16.3244	7.0022	-2.3988	-.1667	-12.5671	2.3078	.3701	11.1347	.8200
.8400	14.8413	16.4567	6.3596	-2.1492	-.1384	-12.7056	2.0901	.3286	11.3380	.8400
.8600	15.0479	16.5169	6.0231	-1.8958	-.1073	-12.8824	1.8672	.2866	11.5765	.8600
.8800	15.2578	16.5070	6.0959	-1.6378	-.0733	-13.1110	1.6381	.2431	11.8681	.8800
.9000	15.4610	16.4429	6.6215	-1.3739	-.0378	-13.3986	1.4016	.1980	12.2345	.9000
.9200	15.6482	16.3576	7.4883	-1.1030	-.0044	-13.7371	1.1560	.1520	12.7021	.9200
.9400	15.8166	16.3018	8.2138	-.8246	.0215	-14.0798	.8987	.1068	13.3054	.9400
.9600	15.9821	16.3396	7.3987	-.5400	.0326	-14.2820	.6268	.0655	14.0992	.9600
.9800	16.2104	16.5195	1.0612	-.2559	.0223	-13.8891	.3352	.0309	15.2470	.9800
1.0000	16.6818	16.6818	—	.0000	.0000	—	.0000	.0000	—	1.0000

TABLE 7. Aqueous sulfuric acid properties — Continued

$T = 300.000 \text{ K}$, $P = 0.10000 \text{ MPa}$					1. Sulfuric acid			2. Water		
x_1	Heat Capacity		Relative enthalpy			Relative Gibbs energy			x_1	
	C_P/R	$C_P(1)/R$	$C_P(2)/R$	$H^{(r)}/RT$	$H_1^{(r)}/RT$	$H_2^{(r)}/RT$	$-G^{(r)}/RT$	$-\mu_1^{(r)}/RT$		
0.0000	9.0619	—	9.0619	0.0559	—	0.0559	0.0002	—	0.0002	0.0000
.0200	9.0124	11.2394	8.9668	-.5596	-30.3340	.0481	.5785	26.7619	.0442	.0200
.0400	9.0964	13.8064	8.9000	-1.1543	-28.9635	.0044	1.0888	24.5171	.1126	.0400
.0600	9.1824	12.3712	8.9786	-1.7153	-27.1855	-.0896	1.5568	22.6366	.2112	.0600
.0800	9.2282	10.3430	9.1310	-2.2372	-25.3154	-.2304	1.9869	20.9484	.3381	.0800
.1000	9.2345	8.8283	9.2794	-2.7187	-23.4751	-.4124	2.3820	19.4062	.4904	.1000
.1200	9.2160	8.1237	9.3648	-3.1600	-21.7133	-.6300	2.7442	17.9858	.6658	.1200
.1400	9.1908	8.2101	9.3503	-3.5624	-20.0479	-.8787	3.0753	16.6701	.8622	.1400
.1600	9.1755	8.9467	9.2189	-3.9273	-18.4820	-.11549	3.3770	15.4456	1.0782	.1600
.1800	9.1838	10.1556	8.9703	-4.2560	-17.0125	-.14558	3.6505	14.3012	1.3125	.1800
.2000	9.2256	11.6604	8.6167	-4.5500	-15.6334	-.17791	3.8969	13.2279	1.5641	.2000
.2200	9.3070	13.3033	8.1797	-4.8106	-14.3381	-.21233	4.1173	12.2183	1.8324	.2200
.2400	9.4310	14.9523	7.6872	-5.0390	-13.1201	-.24870	4.3126	11.2663	2.1167	.2400
.2600	9.5971	16.5030	7.1706	-5.2363	-11.9739	-.28690	4.4836	10.3672	2.4163	.2600
.2800	9.8030	17.8781	6.6625	-5.4035	-10.8943	-.32682	4.6309	9.5175	2.7305	.2800
.3000	10.0440	19.0245	6.1950	-5.5416	-9.8776	-.36833	4.7552	8.7140	3.0586	.3000
.3200	10.3140	19.9111	5.7975	-5.6516	-8.9206	-.41132	4.8573	7.9549	3.3996	.3200
.3400	10.6060	20.5251	5.4960	-5.7342	-8.0209	-.45562	4.9377	7.2383	3.7525	.3400
.3600	10.9126	20.8696	5.3115	-5.7905	-7.1768	-.50106	4.9969	6.5633	4.1159	.3600
.3800	11.2258	20.9601	5.2594	-5.8212	-6.3870	-.54743	5.0358	5.9289	4.4883	.3800
.4000	11.5381	20.8216	5.3490	-5.8273	-5.6506	-.59450	5.0548	5.3346	4.8682	.4000
.4200	11.8424	20.4865	5.5827	-5.8097	-4.9670	-.64200	5.0547	4.7798	5.2537	.4200
.4400	12.1323	19.9921	5.9565	-5.7695	-4.3355	-.68962	5.0361	4.2642	5.6426	.4400
.4600	12.4022	19.3781	6.4595	-5.7076	-3.7556	-.73705	4.9998	3.7873	6.0326	.4600
.4800	12.6477	18.6852	7.0745	-5.6253	-3.2266	-.78394	4.9465	3.3486	6.4216	.4800
.5000	12.8658	17.9531	7.7782	-5.5235	-2.7478	-.82993	4.8771	2.9474	6.8068	.5000
.5200	13.0543	17.2194	8.5420	-5.4036	-2.3181	-.87463	4.7924	2.5832	7.1858	.5200
.5400	13.2129	16.5179	9.3329	-5.2668	-1.9361	-.91768	4.6933	2.2547	7.5560	.5400
.5600	13.3422	15.8781	10.1145	-5.1144	-1.6002	-.95871	4.5807	1.9610	7.9148	.5600
.5800	13.4443	15.3241	10.8482	-4.9478	-1.3084	-.99737	4.4555	1.7005	8.2599	.5800
.6000	13.5225	14.8741	11.4948	-4.7683	-1.0582	-.10334	4.3186	1.4717	8.5890	.6000
.6200	13.5811	14.5400	12.0162	-4.5773	-.8469	-.106636	4.1711	1.2726	8.9002	.6200
.6400	13.6254	14.3273	12.3771	-4.3761	-.6713	-.109622	4.0138	1.1012	9.1919	.6400
.6600	13.6612	14.2349	12.5472	-4.1660	-.5280	-.112281	3.8478	.9550	9.4632	.6600
.6800	13.6950	14.2555	12.5037	-3.9485	-.4132	-.114608	3.6738	.8316	9.7136	.6800
.7000	13.7335	14.3763	12.2331	-3.7245	-.3229	-.116615	3.4928	.7282	9.9434	.7000
.7200	13.7828	14.5791	11.7348	-3.4953	-.2530	-.118325	3.3054	.6421	10.1541	.7200
.7400	13.8491	14.8419	11.0227	-3.2616	-.1992	-.119778	3.1125	.5703	10.3480	.7400
.7600	13.9371	15.1397	10.1282	-3.0243	-.1574	-.121031	2.9145	.5099	10.5291	.7600
.7800	14.0505	15.4460	9.1021	-2.7839	-.1236	-.122161	2.7118	.4581	10.7025	.7800
.8000	14.1911	15.7347	8.0158	-2.5407	-.0942	-.123267	2.5047	.4121	10.8755	.8000
.8200	14.3587	15.9825	6.9609	-2.2946	-.0661	-.124466	2.2933	.3694	11.0574	.8200
.8400	14.5507	16.1705	6.0453	-2.0453	-.0370	-.125890	2.0771	.3280	11.2598	.8400
.8600	14.7616	16.2880	5.3835	-1.7922	-.0055	-.127678	1.8557	.2862	11.4972	.8600
.8800	14.9840	16.3350	5.0750	-1.5345	.0284	-.129957	1.6283	.2430	11.7874	.8800
.9000	15.2090	16.3254	5.1589	-1.2709	.0634	-.132797	1.3935	.1981	12.1520	.9000
.9200	15.4286	16.2902	5.5174	-1.0004	.0963	-.136122	1.1495	.1523	12.6175	.9200
.9400	15.6412	16.2784	5.6575	-.7225	.1218	-.139502	.8940	.1073	13.2187	.9400
.9600	15.8644	16.3520	4.1574	-.4384	.1332	-.141583	.6238	.0660	14.0112	.9600
.9800	16.1661	16.5577	-3.0265	-.1545	.1242	-.138095	.3339	.0314	15.1614	.9800
1.0000	16.7319	16.7319	—	.1030	.1030	—	.0003	.0003	—	1.0000

TABLE 7. Aqueous sulfuric acid properties — Continued

$T = 350.000 \text{ K}$, $P = 0.10000 \text{ MPa}$					1. Sulfuric acid				2. Water	
x_1	Heat Capacity		Relative enthalpy			Relative Gibbs energy			x_1	
	C_P/R	$C_P(1)/R$	$C_P(2)/R$	$H^{(r)}/RT$	$H_1^{(r)}/RT$	$H_2^{(r)}/RT$	$-G^{(r)}/RT$	$-\mu_1^{(r)}/RT$	$-\mu_2^{(r)}/RT$	
0.0000	9.0827	—	9.0827	1.3418	—	1.3418	0.1104	—	0.1104	0.0000
.0200	8.8967	22.0553	8.6280	.8010	-23.5520	1.2980	.6000	22.6005	.1511	.0200
.0400	9.1737	20.4968	8.7018	.3182	-22.3217	1.2615	1.0271	20.5641	.2131	.0400
.0600	9.3325	13.0642	9.0940	-.1442	-21.4309	1.2145	1.4163	18.8995	.3003	.0600
.0800	9.3414	6.8750	9.5556	-.5865	-20.4166	1.1378	1.7723	17.4401	.4099	.0800
.1000	9.2433	3.2496	9.9090	-.10048	-19.2124	1.0183	2.0984	16.1355	.5387	.1000
.1200	9.0932	2.1098	10.0452	-.13943	-17.8438	.8488	2.3969	14.9564	.6842	.1200
.1400	8.9411	2.9795	9.9114	-.17514	-16.3604	.6268	2.6699	13.8816	.8447	.1400
.1600	8.8274	5.3001	9.4990	-.20731	-14.8137	.3537	2.9189	12.8938	1.0189	.1600
.1800	8.7810	8.5436	8.8329	-.23576	-13.2503	.0334	3.1453	11.9794	1.2061	.1800
.2000	8.8203	12.2525	7.9620	-.26043	-11.7097	-.3279	3.3501	11.1271	1.4059	.2000
.2200	8.9541	16.0514	6.9521	-.28130	-10.2237	-.7229	3.5344	10.3279	1.6182	.2200
.2400	9.1833	19.6455	5.8792	-.29847	-8.8167	-.1430	3.6987	9.5748	1.8431	.2400
.2600	9.5018	22.8144	4.8242	-.31205	-7.5067	-.15795	3.8438	8.8622	2.0806	.2600
.2800	9.8984	25.4038	3.8682	-.32224	-6.3059	-.20234	3.9702	8.1860	2.3307	.2800
.3000	10.3575	27.3169	3.0890	-.32926	-5.2214	-.24660	4.0782	7.5431	2.5932	.3000
.3200	10.8610	28.5055	2.5574	-.33335	-4.2563	-.28993	4.1683	6.9315	2.8679	.3200
.3400	11.3885	28.9622	2.3351	-.33478	-3.4100	-.33158	4.2408	6.3498	3.1544	.3400
.3600	11.9190	28.7130	2.4721	-.3382	-2.6791	-.37090	4.2962	5.7971	3.4520	.3600
.3800	12.4311	27.8103	3.0050	-.33075	-2.0576	-.40736	4.3348	5.2731	3.7596	.3800
.4000	12.9045	26.3271	3.9559	-.32585	-1.5381	-.44054	4.3569	4.7778	4.0763	.4000
.4200	13.3199	24.3514	5.3313	-.31937	-1.1116	-.47015	4.3630	4.3113	4.4004	.4200
.4400	13.6599	21.9814	7.1214	-.31157	-0.7680	-.49603	4.3535	3.8740	4.7302	.4400
.4600	13.9097	19.3210	9.2999	-.30267	-.4970	-.51817	4.3289	3.4661	5.0639	.4600
.4800	14.0572	16.4762	11.8241	-.29289	-.2876	-.53671	4.2898	3.0879	5.3991	.4800
.5000	14.0934	13.5516	14.6349	-.28241	-.1293	-.5190	4.2366	2.7396	5.7337	.5000
.5200	14.0126	10.6473	17.6580	-.27138	-.0114	-.56415	4.1702	2.4212	6.0650	.5200
.5400	13.8129	7.8569	20.8044	-.25993	.0761	-.57399	4.0911	2.1325	6.3904	.5400
.5600	13.4959	5.2645	23.9718	-.24814	.1424	-.58209	4.0001	1.8731	6.7073	.5600
.5800	13.0670	2.9439	27.0462	-.23609	.1961	-.58920	3.8980	1.6423	7.0131	.5800
.6000	12.5355	.9564	29.9038	-.22380	.2448	-.59621	3.7856	1.4391	7.3053	.6000
.6200	11.9140	-.6501	32.4130	-.21126	.2949	-.60405	3.6637	1.2624	7.5816	.6200
.6400	11.2189	-.18416	34.4373	-.19844	.3518	-.61375	3.5331	1.1105	7.8399	.6400
.6600	10.4699	-.25986	35.8378	-.18527	.4196	-.62637	3.3948	.9818	8.0788	.6600
.6800	9.6895	-.29164	36.4765	-.17167	.5014	-.64301	3.2495	.8741	8.2972	.6800
.7000	8.9030	-.28042	36.2194	-.15750	.5988	-.6473	3.0981	.7853	8.4948	.7000
.7200	8.1381	-.22854	34.9407	-.14263	.7125	-.69262	2.9414	.7127	8.6721	.7200
.7400	7.4240	-.13957	32.5259	-.12689	.8419	-.72766	2.7800	.6540	8.8309	.7400
.7600	6.7916	-.1826	28.8758	-.11009	.9854	-.7078	2.6145	.6063	8.9738	.7600
.7800	6.2722	1.2974	23.9096	-.9205	1.1406	-.82280	2.4454	.5669	9.1054	.7800
.8000	5.8976	2.9801	17.5670	-.7255	1.3041	-.88441	2.2730	.5333	9.2318	.8000
.8200	5.6991	4.7969	9.8080	-.5138	1.4722	-.95617	2.0974	.5030	9.3612	.8200
.8400	5.7072	6.6780	.6092	-.2834	1.6407	-.10.3854	1.9186	.4737	9.5042	.8400
.8600	5.9516	8.5560	-.10.0490	-.0321	1.8054	-.11.3196	1.7360	.4438	9.6741	.8600
.8800	6.4610	10.3704	-.22.2102	.2423	1.9621	-.12.3701	1.5491	.4120	9.8876	.8800
.9000	7.2649	12.0720	-.36.0020	.5420	2.1075	-.13.5482	1.3566	.3779	10.1651	.9000
.9200	8.3961	13.6273	-.51.7674	.8694	2.2388	-.14.8789	1.1570	.3417	10.5323	.9200
.9400	9.8981	15.0210	-.70.3656	1.2280	2.3544	-.16.4201	.9481	.3050	11.0233	.9400
.9600	11.8430	16.2510	-.93.9581	1.6226	2.4530	-.18.3085	.7271	.2701	11.6946	.9600
.9800	14.3760	17.2926	-.128.5528	2.0628	2.5312	-.20.8896	.4889	.2393	12.7211	.9800
1.0000	17.8491	17.8491	—	2.5638	2.5638	—	.2085	—	1.0000	

TABLE 8. Activity and osmotic coefficients for aqueous sulfuric acid

	$T = 273.15\text{ K}$		$T = 298.15\text{ K}$		$T = 323.15\text{ K}$		$T = 348.15\text{ K}$		
m	$\gamma(m)/\gamma(1)$	$\phi(m)$	$\gamma(m)/\gamma(1)$	$\phi(m)$	$\gamma(m)/\gamma(1)$	$\phi(m)$	$\gamma(m)/\gamma(1)$	$\phi(m)$	m
0.01	3.3532	0.8514	3.8242	0.7835	4.1117	0.7594	4.7475	0.7344	0.01
0.02	2.9724	0.8380	3.2492	0.7736	3.4402	0.7506	3.9009	0.7250	0.02
0.03	2.7467	0.8269	2.9357	0.7656	3.0824	0.7434	3.4572	0.7173	0.03
0.04	2.5842	0.8171	2.7221	0.7584	2.8424	0.7370	3.1626	0.7105	0.04
0.05	2.4568	0.8083	2.5613	0.7521	2.6636	0.7313	2.9449	0.7044	0.05
0.06	2.3519	0.8003	2.4328	0.7464	2.5221	0.7262	2.7737	0.6989	0.06
0.07	2.2626	0.7930	2.3264	0.7411	2.4057	0.7215	2.6337	0.6939	0.07
0.08	2.1850	0.7862	2.2357	0.7363	2.3072	0.7172	2.5158	0.6893	0.08
0.09	2.1165	0.7799	2.1571	0.7318	2.2222	0.7132	2.4145	0.6850	0.09
0.10	2.0551	0.7740	2.0879	0.7277	2.1476	0.7095	2.3259	0.6811	0.10
0.20	1.6587	0.7309	1.6613	0.6980	1.6948	0.6831	1.7951	0.6528	0.20
0.30	1.4431	0.7059	1.4415	0.6819	1.4650	0.6689	1.5304	0.6373	0.30
0.40	1.3044	0.6917	1.3033	0.6739	1.3211	0.6618	1.3663	0.6294	0.40
0.50	1.2083	0.6848	1.2083	0.6713	1.2221	0.6597	1.2539	0.6266	0.50
0.60	1.1389	0.6833	1.1397	0.6728	1.1503	0.6612	1.1725	0.6275	0.60
0.70	1.0875	0.6858	1.0889	0.6773	1.0966	0.6653	1.1114	0.6313	0.70
0.80	1.0493	0.6916	1.0506	0.6842	1.0557	0.6716	1.0647	0.6372	0.80
0.90	1.0208	0.7000	1.0217	0.6930	1.0242	0.6795	1.0284	0.6448	0.90
1.00	1.0000	0.7105	1.0000	0.7033	1.0000	0.6889	1.0000	0.6538	1.00
1.50	0.9688	0.7833	0.9593	0.7701	0.9459	0.7487	0.9305	0.7117	1.50
2.00	1.0090	0.8742	0.9828	0.8498	0.9538	0.8197	0.9257	0.7802	2.00
2.50	1.0926	0.9714	1.0430	0.9337	0.9949	0.8941	0.9536	0.8514	2.50
3.00	1.2095	1.0696	1.1293	1.0178	1.0581	0.9685	1.0020	0.9217	3.00
3.50	1.3558	1.1658	1.2370	1.1000	1.1383	1.0409	1.0649	0.9895	3.50
4.00	1.5302	1.2585	1.3639	1.1791	1.2326	1.1104	1.1389	1.0539	4.00
4.50	1.7325	1.3471	1.5090	1.2547	1.3394	1.1767	1.2221	1.1145	4.50
5.00	1.9633	1.4312	1.6717	1.3265	1.4577	1.2394	1.3133	1.1714	5.00
5.50	2.2232	1.5107	1.8518	1.3945	1.5869	1.2987	1.4113	1.2245	5.50
6.00	2.5133	1.5856	2.0492	1.4587	1.7265	1.3547	1.5156	1.2741	6.00
6.50	2.8345	1.6562	2.2641	1.5193	1.8762	1.4073	1.6256	1.3204	6.50
7.00	3.1878	1.7226	2.4965	1.5764	2.0357	1.4569	1.7408	1.3635	7.00
7.50	3.5743	1.7850	2.7466	1.6302	2.2047	1.5035	1.8608	1.4037	7.50
8.00	3.9950	1.8437	3.0144	1.6810	2.3830	1.5474	1.9853	1.4413	8.00
8.50	4.4506	1.8989	3.3001	1.7288	2.5705	1.5887	2.1141	1.4763	8.50
9.00	4.9422	1.9508	3.6038	1.7739	2.7670	1.6275	2.2469	1.5090	9.00
9.50	5.4706	1.9997	3.9255	1.8164	2.9722	1.6642	2.3834	1.5396	9.50
10.00	6.0363	2.0456	4.2652	1.8565	3.1860	1.6987	2.5234	1.5683	10.00
10.50	6.6402	2.0889	4.6230	1.8943	3.4083	1.7313	2.6668	1.5952	10.50
11.00	7.2828	2.1297	4.9988	1.9300	3.6388	1.7620	2.8133	1.6204	11.00
11.50	7.9646	2.1681	5.3926	1.9638	3.8774	1.7910	2.9629	1.6441	11.50
12.00	8.6860	2.2043	5.8043	1.9956	4.1238	1.8183	3.1153	1.6664	12.00
12.50	9.4474	2.2385	6.2337	2.0258	4.3779	1.8442	3.2705	1.6874	12.50
13.00	10.2490	2.2707	6.6807	2.0542	4.6394	1.8686	3.4282	1.7071	13.00
13.50	11.0911	2.3011	7.1450	2.0811	4.9082	1.8917	3.5884	1.7258	13.50
14.00	11.9736	2.3299	7.6266	2.1066	5.1839	1.9135	3.7509	1.7433	14.00
14.50	12.8968	2.3570	8.1250	2.1306	5.4665	1.9342	3.9157	1.7599	14.50
15.00	13.8604	2.3826	8.6401	2.1534	5.7556	1.9537	4.0825	1.7756	15.00
15.50	14.8644	2.4068	9.1714	2.1749	6.0510	1.9722	4.2512	1.7904	15.50
16.00	15.9085	2.4297	9.7187	2.1952	6.3524	1.9897	4.4218	1.8045	16.00
16.50	16.9924	2.4512	10.2816	2.2144	6.6597	2.0062	4.5942	1.8178	16.50
17.00	18.1157	2.4716	10.8596	2.2326	6.9725	2.0218	4.7681	1.8303	17.00
17.50	19.2780	2.4909	11.4524	2.2498	7.2905	2.0366	4.9436	1.8422	17.50
18.00	20.4787	2.5090	12.0594	2.2660	7.6136	2.0505	5.1204	1.8535	18.00
18.50	21.7172	2.5262	12.6802	2.2813	7.9413	2.0637	5.2985	1.8641	18.50
19.00	22.9928	2.5423	13.3143	2.2957	8.2735	2.0762	5.4778	1.8742	19.00
19.50	24.3048	2.5576	13.9612	2.3093	8.6099	2.0879	5.6581	1.8838	19.50
20.00	25.6523	2.5719	14.6203	2.3221	8.9501	2.0990	5.8393	1.8928	20.00

TABLE 8. Activity and osmotic coefficients for aqueous sulfuric acid — Continued

$T = 273.15\text{ K}$			$T = 298.15\text{ K}$			$T = 323.15\text{ K}$			$T = 348.15\text{ K}$		
m	$\gamma(m)/\gamma(1)$	$\phi(m)$	$\gamma(m)/\gamma(1)$	$\phi(m)$	$\gamma(m)/\gamma(1)$	$\phi(m)$	$\gamma(m)/\gamma(1)$	$\phi(m)$	$\gamma(m)/\gamma(1)$	$\phi(m)$	m
20.50	27.0343	2.5854	15.2910	2.3342	9.2938	2.1094	6.0213	1.9014	20.50		
21.00	28.4500	2.5981	15.9727	2.3455	9.6409	2.1192	6.2041	1.9094	21.00		
21.50	29.8984	2.6100	16.6650	2.3562	9.9909	2.1284	6.3873	1.9171	21.50		
22.00	31.3783	2.6212	17.3671	2.3661	10.3436	2.1371	6.5711	1.9242	22.00		
22.50	32.8886	2.6316	18.0784	2.3755	10.6987	2.1452	6.7551	1.9310	22.50		
23.00	34.4281	2.6414	18.7984	2.3842	11.0558	2.1528	6.9394	1.9374	23.00		
23.50	35.9956	2.6505	19.5263	2.3923	11.4148	2.1599	7.1238	1.9434	23.50		
24.00	37.5898	2.6590	20.2615	2.3999	11.7752	2.1665	7.3082	1.9490	24.00		
24.50	39.2094	2.6669	21.0035	2.4069	12.1368	2.1726	7.4924	1.9543	24.50		
25.00	40.8531	2.6742	21.7514	2.4134	12.4994	2.1783	7.6765	1.9593	25.00		
25.50	42.5194	2.6810	22.5048	2.4194	12.8626	2.1835	7.8601	1.9639	25.50		
26.00	44.2071	2.6872	23.2628	2.4249	13.2261	2.1884	8.0433	1.9681	26.00		
26.50	45.9145	2.6929	24.0249	2.4300	13.5897	2.1928	8.2259	1.9721	26.50		
27.00	47.6404	2.6981	24.7905	2.4346	13.9530	2.1969	8.4079	1.9758	27.00		
27.50	49.3832	2.7028	25.5588	2.4387	14.3159	2.2005	8.5890	1.9792	27.50		
28.00	51.1414	2.7071	26.3293	2.4425	14.6780	2.2039	8.7693	1.9823	28.00		
28.50	52.9136	2.7109	27.1013	2.4458	15.0392	2.2068	8.9486	1.9851	28.50		
29.00	54.6983	2.7143	27.8743	2.4488	15.3990	2.2095	9.1268	1.9876	29.00		
29.50	56.4939	2.7173	28.6474	2.4513	15.7574	2.2118	9.3038	1.9900	29.50		
30.00	58.2991	2.7198	29.4203	2.4536	16.1140	2.2138	9.4795	1.9920	30.00		

TABLE 9. Properties of H₂SO₄(s)

Standard state pressure is 0.1 MPa At T = 0 K values are C _P /R, (H - E ₀)/R, S/R, -(G - E ₀)/R				
T,K	C _P /R	(H - E ₀)/RT	S/R	-(G - E ₀)/RT
0.00	0.0000	-1863.9994	0.0000	1863.9994
5.00	.0254	-372.7932	.0089	372.8022
10.00	.1632	-186.3553	.0609	186.4162
15.00	.4395	-124.1401	.1749	124.3150
20.00	.8272	-92.9486	.3523	93.3009
25.00	1.2785	-74.1489	.5846	74.7336
30.00	1.7459	-61.5387	.8591	62.3978
35.00	2.1940	-52.4656	1.1623	53.6280
40.00	2.6037	-45.6071	1.4825	47.0896
45.00	2.9706	-40.2296	1.8108	42.0404
50.00	3.3002	-35.8928	2.1411	38.0339
60.00	3.8802	-29.3111	2.7954	32.1065
70.00	4.3639	-24.5336	3.4314	27.9649
80.00	4.7293	-20.8976	4.0389	24.9365
90.00	5.0765	-18.0309	4.6160	22.6469
100.00	5.4239	-15.7028	5.1688	20.8716
110.00	5.7713	-13.7664	5.7020	19.4684
120.00	6.1186	-12.1238	6.2191	18.3429
130.00	6.4655	-10.7072	6.7226	17.4297
140.00	6.8119	-9.4682	7.2144	16.6826
150.00	7.1574	-8.3713	7.6961	16.0675
160.00	7.5020	-7.3900	8.1691	15.5591
170.00	7.8453	-6.5039	8.6342	15.1381
180.00	8.1873	-5.6972	9.0923	14.7895
190.00	8.5276	-4.9575	9.5441	14.5016
200.00	8.8660	-4.2748	9.9901	14.2649
210.00	9.2024	-3.6410	10.4308	14.0718
220.00	9.5365	-3.0496	10.8667	13.9163
230.00	9.8682	-2.4952	11.2979	13.7931
240.00	10.1972	-1.9732	11.7248	13.6980
250.00	10.5232	-1.4798	12.1477	13.6275
260.00	10.8462	-1.0119	12.5668	13.5787
270.00	11.1658	-5668	12.9821	13.5489
280.00	11.4820	-1421	13.3939	13.5360
283.45	11.5902	.0000	13.5352	13.5352

TABLE 10. Properties of H₂SO₄·H₂O(s)

Standard state pressure is 0.1 MPa At T = 0 K values are C _P /R, (H - E ₀)/R, S/R, -(G - E ₀)/R				
T,K	C _P /R	(H - E ₀)/RT	S/R	-(G - E ₀)/RT
0.00	0.0000	-2274.6795	0.0000	2274.6795
5.00	.0171	-454.9315	.0060	454.9374
10.00	.1152	-227.4370	.0420	227.4790
15.00	.3257	-151.5544	.1246	151.6790
20.00	.6447	-113.5466	.2596	113.8062
25.00	1.0488	-90.6691	.4456	91.1147
30.00	1.5070	-75.3451	.6767	76.0218
35.00	1.9887	-64.3319	.9451	65.2770
40.00	2.4689	-56.0117	1.2421	57.2538
45.00	2.9300	-49.4880	1.5598	51.0478
50.00	3.3629	-44.2243	1.8912	46.1155
60.00	4.1389	-36.2269	2.5746	38.8015
70.00	4.8202	-30.4108	3.2648	33.6755
80.00	5.4338	-25.9679	3.9492	29.9171
90.00	5.9862	-22.4476	4.6216	27.0692
100.00	6.5079	-19.5780	5.2794	24.8575
110.00	7.0128	-17.1835	5.9235	23.1070
120.00	7.5028	-15.1466	6.5548	21.7015
130.00	7.9801	-13.3859	7.1743	20.5602
140.00	8.4469	-11.8431	7.7828	19.6259
150.00	8.9055	-10.4751	8.3813	18.8564
160.00	9.3580	-9.2496	8.9705	18.2201
170.00	9.8067	-8.1418	9.5513	17.6931
180.00	10.2538	-7.1323	10.1245	17.2568
190.00	10.7015	-6.2055	10.6909	16.8963
200.00	11.1520	-5.3489	11.2512	16.6001
210.00	11.6075	-4.5523	11.8063	16.3586
220.00	12.0702	-3.8073	12.3570	16.1642
230.00	12.5423	-3.1067	12.9039	16.0106
240.00	13.0261	-2.4446	13.4479	15.8925
250.00	13.5238	-1.8159	13.9896	15.8055
260.00	14.0376	-1.2161	14.5300	15.7461
270.00	14.5696	-.6413	15.0697	15.7111
280.00	15.1221	-.0883	15.6095	15.6978
283.45	15.2143	.0000	15.6975	15.6975

TABLE 11. Properties of $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$

T,K	C_P/R	Standard state pressure is 0.1 MPa		
		$(H - E_0)/RT$	S/R	$-(G - E_0)/RT$
At T = 0 K values are C_P/R , $(H - E_0)/R$, S/R , $-(G - E_0)/R$				
0.00	0.0000	-1978.1517	0.0000	1978.1517
5.00	.0345	-395.6213	.0122	395.6335
10.00	.2184	-197.7550	.0822	197.8372
15.00	.5795	-131.7082	.2336	131.9418
20.00	1.0754	-98.5764	.4657	99.0422
25.00	1.6416	-78.5901	.7658	79.3559
30.00	2.2205	-65.1698	1.1164	66.2862
35.00	2.7754	-55.5025	1.5008	57.0034
40.00	3.2926	-48.1851	1.9056	50.0907
45.00	3.7761	-42.4382	2.3216	44.7598
50.00	4.2373	-37.7936	2.7435	40.5371
60.00	5.1193	-30.7141	3.5949	34.3090
70.00	5.9031	-25.5374	4.4447	29.9821
80.00	6.6167	-21.5629	5.2794	26.8423
90.00	7.3062	-18.3932	6.0989	24.4920
100.00	7.9619	-15.7902	6.9029	22.6931
110.00	8.5882	-13.6022	7.6913	21.2935
120.00	9.1896	-11.7278	8.4645	20.1923
130.00	9.7706	-10.0963	9.2232	19.3195
140.00	10.3358	-8.6570	9.9680	18.6250
150.00	10.8895	-7.3723	10.7000	18.0723
160.00	11.4362	-6.2138	11.4203	17.6341
170.00	11.9805	-5.1596	12.1300	17.2895
180.00	12.5269	-4.1922	12.8302	17.0224
190.00	13.0797	-3.2977	13.5223	16.8200
200.00	13.6436	-2.4648	14.2074	16.6723
210.00	14.2229	-1.6840	14.8871	16.5711
220.00	14.8222	-0.9474	15.5625	16.5099
230.00	15.4460	-0.2483	16.2350	16.4833
233.67	15.6819	.0000	16.4814	16.4814

TABLE 12. Properties of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}(\text{s})$

T,K	C_P/R	Standard state pressure is 0.1 MPa		
		$(H - E_0)/RT$	S/R	$-(G - E_0)/RT$
At T = 0 K values are C_P/R , $(H - E_0)/R$, S/R , $-(G - E_0)/R$				
0.00	0.0000	-2561.3239	0.0000	2561.3239
5.00	.0363	-512.2553	.0128	512.2681
10.00	.2336	-256.0685	.0872	256.1557
15.00	.6306	-170.5736	.2505	170.8241
20.00	1.1912	-127.7052	.5056	128.2108
25.00	1.8508	-101.8611	.8410	102.7021
30.00	2.5462	-84.5179	1.2398	85.7577
35.00	3.2317	-72.0309	1.6841	73.7150
40.00	3.8847	-62.5819	2.1587	64.7406
45.00	4.5027	-55.1621	2.6522	57.8143
50.00	5.0957	-49.1658	3.1575	52.3233
60.00	6.2514	-40.0256	4.1891	44.2146
70.00	7.3490	-33.3348	5.2366	38.5714
80.00	8.2833	-28.1892	6.2808	34.4700
90.00	9.1391	-24.0888	7.3062	31.3950
100.00	9.9548	-20.7249	8.3117	29.0366
110.00	10.7376	-17.9000	9.2974	27.1974
120.00	11.4947	-15.4819	10.2643	25.7462
130.00	12.2334	-13.3782	11.2136	24.5919
140.00	12.9608	-11.5228	12.1469	23.6697
150.00	13.6841	-9.8665	13.0658	22.9322
160.00	14.4105	-8.3719	13.9721	22.3440
170.00	15.1472	-7.0101	14.8677	21.8779
180.00	15.9014	-5.7583	15.7548	21.5131
190.00	16.6803	-4.5980	16.6353	21.2332
200.00	17.4912	-3.5139	17.5113	21.0253
210.00	18.3411	-2.4936	18.3851	20.8787
220.00	19.2374	-1.5264	19.2588	20.7852
230.00	20.1872	-.6032	20.1347	20.7379
233.67	20.8632	.0000	20.7292	20.7292

TABLE 13. Properties of $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}(\text{s})$

Standard state pressure is 0.1 MPa At $T = 0$ K values are C_P/R , $(H - E_0)/R$, S/R , $-(G - E_0)/R$				
T,K	C_P/R	$(H - E_0)/RT$	S/R	$-(G - E_0)/RT$
0.00	0.0000	-3183.2339	0.0000	3183.2339
5.00	.0577	-636.6316	.0204	636.6521
10.00	.3623	-318.2232	.1370	318.3602
15.00	.9526	-211.9369	.3868	212.3236
20.00	1.7509	-158.6179	.7665	159.3844
25.00	2.6462	-126.4553	1.2526	127.7079
30.00	3.5443	-104.8631	1.8149	106.6780
35.00	4.3904	-89.3151	2.4257	91.7408
40.00	5.1702	-77.5525	3.0635	80.6160
45.00	5.8988	-68.3203	3.7149	72.0352
50.00	6.6006	-60.8632	4.3729	65.2360
60.00	7.9610	-49.5047	5.6978	55.2025
70.00	9.1186	-41.2087	7.0161	48.2248
80.00	10.0411	-34.8596	8.2945	43.1541
90.00	10.9322	-29.8209	9.5289	39.3498
100.00	11.7979	-25.7021	10.7257	36.4278
110.00	12.6421	-22.2545	11.8899	34.1444
120.00	13.4689	-19.3119	13.0255	32.3374
130.00	14.2822	-16.7589	14.1358	30.8947
140.00	15.0860	-14.5130	15.2237	29.7366
150.00	15.8842	-12.5131	16.2917	28.8048
160.00	16.6809	-10.7134	17.3423	28.0557
170.00	17.4800	-9.0784	18.3775	27.4560
180.00	18.2856	-7.5806	19.3994	26.9801
190.00	19.1015	-6.1978	20.4099	26.6077
200.00	19.9317	-4.9122	21.4107	26.3229
210.00	20.7803	-3.7090	22.4036	26.1126
220.00	21.6511	-2.5762	23.3903	25.9665
230.00	22.5483	-1.5034	24.3724	25.8759
240.00	23.4757	-0.4820	25.3516	25.8336
244.88	23.9404	.0000	25.8288	25.8288

TABLE 14. Properties of $\text{H}_2\text{SO}_4 \cdot 6.5\text{H}_2\text{O}(\text{s})$

Standard state pressure is 0.1 MPa At $T = 0$ K values are C_P/R , $(H - E_0)/R$, S/R , $-(G - E_0)/R$				
T,K	C_P/R	$(H - E_0)/RT$	S/R	$-(G - E_0)/RT$
0.00	0.0000	-3699.9215	0.0000	3699.9215
5.00	.0602	-739.9686	.0212	739.9898
10.00	.3896	-369.8858	.1449	370.0308
15.00	1.0578	-246.3584	.4183	246.7766
20.00	2.0086	-184.3903	.8472	185.2375
25.00	3.1340	-146.9999	1.4142	148.4141
30.00	4.3236	-121.8787	2.0904	123.9692
35.00	5.4937	-103.7656	2.8454	106.6111
40.00	6.5985	-90.0384	3.6520	93.6904
45.00	7.6286	-79.2431	4.4893	83.7324
50.00	8.6008	-70.5069	5.3438	75.8507
60.00	10.4783	-57.1654	7.0783	64.2438
70.00	12.3210	-47.3693	8.8331	56.2024
80.00	13.9217	-39.8039	10.5872	50.3911
90.00	15.2083	-33.7619	12.3023	46.0642
100.00	16.4620	-28.8021	13.9696	42.7717
110.00	17.7066	-24.6306	15.5971	40.2276
120.00	18.9449	-21.0508	17.1909	38.2417
130.00	20.1795	-17.9267	18.7560	36.6828
140.00	21.4131	-15.1608	20.2966	35.4574
150.00	22.6484	-12.6814	21.8161	34.4975
160.00	23.8881	-10.4346	23.3173	33.7519
170.00	25.1349	-8.3790	24.8029	33.1819
180.00	26.3915	-6.4822	26.2751	32.7573
190.00	27.6606	-4.7187	27.7359	32.4546
200.00	28.9449	-3.0677	29.1873	32.2550
210.00	30.2471	-1.5124	30.6310	32.1433
220.00	31.5698	-0.0388	32.0685	32.1073
220.27	31.6058	.0000	32.1073	32.1073

TABLE 15. Properties of H₂O(s) - Quenched

T,K	C _P /R	Standard state pressure is 0.1 MPa At T = 0 K values are C _P /R, (H - E ₀)/R, S/R, -(G - E ₀)/R		
		(H - E ₀)/RT	S/R	-(G - E ₀)/RT
0.00	0.0000	-646.6996	0.4123	646.6996
5.00	.0031	-129.3393	.4131	129.7523
10.00	.0340	-64.6622	.4222	65.0844
15.00	.1153	-43.0847	.4496	43.5343
20.00	.2387	-32.2699	.4990	32.7689
25.00	.3758	-25.7544	.5670	26.3214
30.00	.5029	-21.3886	.6470	22.0356
35.00	.6165	-18.2530	.7331	18.9862
40.00	.7299	-15.8873	.8228	16.7101
45.00	.8493	-14.0343	.9156	14.9500
50.00	.9425	-12.5408	1.0105	13.5513
60.00	1.1549	-10.2757	1.2013	11.4770
70.00	1.3528	-8.6284	1.3944	10.0228
80.00	1.5383	-7.3691	1.5873	8.9563
90.00	1.7137	-6.3695	1.7787	8.1482
100.00	1.8806	-5.5528	1.9679	7.5207
110.00	2.0410	-4.8697	2.1547	7.0244
120.00	2.1962	-4.2873	2.3390	6.6263
130.00	2.3478	-3.7827	2.5208	6.3035
140.00	2.4971	-3.3395	2.7003	6.0398
150.00	2.6451	-2.9454	2.8776	5.8231
160.00	2.7929	-2.5914	3.0530	5.6445
170.00	2.9412	-2.2703	3.2268	5.4971
180.00	3.0907	-1.9767	3.3991	5.3758
190.00	3.2418	-1.7060	3.5703	5.2763
200.00	3.3950	-1.4548	3.7405	5.1952
210.00	3.5504	-1.2201	3.9099	5.1300
220.00	3.7081	-0.9997	4.0787	5.0784
230.00	3.8680	-0.7916	4.2470	5.0386
240.00	4.0297	-0.5941	4.4150	5.0091
250.00	4.1929	-0.4058	4.5828	4.9887
260.00	4.3570	-0.2258	4.7505	4.9763
270.00	4.5212	-0.0530	4.9180	4.9710
273.15	4.5728	0.0000	4.9707	4.9707

6. References

- ¹Donovan, J. R. and Salamone, J. M., "Sulfuric Acid and Sulfur Trioxide," in *Encyclopedia of Chemical Technology*, edited by H. F. Mark, et al. Vol. 22, Third ed. (John Wiley & Sons, 1978) pp. 190-232.
- ²Sticksel, P. R. and Engdahl, R. B., "Air Pollution," in *Encyclopedia of Chemical Technology*, edited by H. F. Mark, et al. Vol. 1. Third ed. (John Wiley & Sons, 1978) pp. 624-649.
- ³Staples, B. R. and Wobbekeing, T. F., *A Compilation of Thermodynamic and Transport Properties of Aqueous Sulfuric Acid*, (National Bureau of Standards NBSIR-81-2276, Washington, D. C., 1980).
- ⁴Cohen, E. R. and Taylor, B. N., *J. Phys. Chem. Ref. Data* 2, 663-734 (1973).
- ⁵De Bievre, P., et al., *J. Phys. Chem. Ref. Data* 13, 809-891 (1984).
- ⁶Lange, E., Monheim, J., and Robinson, A. L., *J. Am. Chem. Soc.* 55, 4733-4744 (1933).
- ⁷Groenier, W. L., "The Heats of Dilution of Sulfuric Acid Solutions," Ph. D. Thesis, Univ. of Chicago (1936).
- ⁸Kunzler, J. E. and Giauque, W. F., *J. Am. Chem. Soc.* 74, 3472-3476 (1952).
- ⁹Giauque, W. F., et al., *J. Am. Chem. Soc.* 82, 62-70 (1960).
- ¹⁰Wu, Y. C. and Young, T. F., *J. Res. Natl. Bur. Stand. (U. S.)* 85, 11-17 (1980).
- ¹¹Osborne, N. S., Stimson, H. F., and Ginnings, D. C., *J. Res. Natl. Bur. Stand. (U. S.)* 23, 197-260 (1939).
- ¹²Randall, M. and Taylor, M. D., *J. Phys. Chem.* 45, 959-967 (1941).
- ¹³Larson, J. W., Zeeb, K. G., and Hepler, L. G., *Can. J. Chem.* 60, 2141-2150 (1982).
- ¹⁴Giauque, W. F. and Stout, J. W., *J. Am. Chem. Soc.* 58, 1144-1150 (1936).
- ¹⁵Flubacher, P., Leadbetter, A. J., and Morrison, J. A., *J. Chem. Phys.* 33, 1751-1755 (1960).
- ¹⁶Haida, O., et al., *J. Chem. Thermodynamics* 6, 815-825 (1974).
- ¹⁷Rubin, T. R. and Giauque, W. F., *J. Am. Chem. Soc.* 74, 800-804 (1952).
- ¹⁸Hornung, E. W. and Giauque, W. F., *J. Am. Chem. Soc.* 77, 2983-2987 (1955).
- ¹⁹Hornung, E. W., Brackett, T. E., and Giauque, W. F., *J. Am. Chem. Soc.* 78, 5747-5751 (1956).
- ²⁰Hamer, W. J., *J. Am. Chem. Soc.* 57, 9-15 (1935).
- ²¹Beck, W. H., Singh, K. P., and Wynne-Jones, W. F., *Trans. Faraday Soc.* 55, 331-338 (1959).
- ²²Covington, A. K., Dobson, J. V., and Wynne-Jones, W. F., *Trans. Faraday Soc.* 61, 2050-2056 (1965).
- ²³Randall, M. and Cushman, O. E., *J. Am. Chem. Soc.* 40, 393-397 (1918).
- ²⁴Trimble, H. M. and Ebert, P. F., *J. Am. Chem. Soc.* 55, 958-968 (1933).
- ²⁵MacDougall, F. H. and Blumer, D. R., *J. Am. Chem. Soc.* 55, 2236-2249 (1933).
- ²⁶Harned, H. S. and Hamer, W. J., *J. Am. Chem. Soc.* 57, 27-33 (1935).
- ²⁷Beck, W. H., Dobson, J. V., and Wynne-Jones, W. F., *Trans. Faraday Soc.* 56, 1172-1178 (1960).
- ²⁸Vosburgh, W. C. and Craig, D. N., *J. Am. Chem. Soc.* 51, 2009-2019 (1929).
- ²⁹Shrawder, J. and Cowperthwaite, I. A., *J. Am. Chem. Soc.* 56, 2340-2345 (1934).
- ³⁰Gable, C. M., Betz, H. F., and Maron, S. H., *J. Am. Chem. Soc.* 72, 1445-1448 (1950).
- ³¹Kunzler, J. E. and Giauque, W. F., *J. Am. Chem. Soc.* 74, 5271-5274 (1952).
- ³²Dickinson, H. C. and Osborne, N. S., *Natl. Bur. Std. (U.S.) Bull.* 12, 49-81 (1915).
- ³³Porter, A. W., *Trans. Faraday Soc.* 13, 373-395 (1918).
- ³⁴Craig, D. N. and Vinal, G. W., *J. Res. Natl. Bur. Stand. (U. S.)*, A, 24, 475-490 (1940).
- ³⁵Rard, J. A., Habenschuss, A., and Spedding, F. H., *J. Chem. Eng. Data.* 21, 374-379 (1976).
- ³⁶Pitzer, K. S., Roy, R. N., and Sylvester, L. F., *J. Am. Chem. Soc.* 99, 4930-4936 (1977).
- ³⁷Robinson, R. A. and Stokes, R. H., *Electrolyte Solutions, the Measurement and Interpretation of Conductance, Chemical Potential, and Diffusion in Solutions of Simple Electrolytes*. Second ed. (Butterworths, London, 1959).
- ³⁸Staples, B. R., *J. Chem. Phys. Ref. Data* 10, 779-798 (1981).
- ³⁹Young, T. F. and Walrafen, G. E., *Trans. Faraday Soc.* 57, 34-39 (1961).
- ⁴⁰Giauque, W. F., Kunzler, J. E., and Hornung, E. W., *J. Am. Chem. Soc.* 78, 5482-5486 (1956).
- ⁴¹Nagle, J. F., *J. Math. Phys.* 7, 1484-1491 (1966).
- ⁴²Garvin, D., Parker, V. B., and White, H. J., *CODATA Thermodynamic Tables*. (Hemisphere Publishing, New York, 1987).
- ⁴³Cox, J. D., Wagman, D. D., Medvedev, V. A., eds., *CODATA Key Values for Thermodynamics*. (Hemisphere Publishing, New York, 1989).
- ⁴⁴McCullough, J. P., et al., *J. Am. Chem. Soc.* 75, 5075-5081 (1953).

- ⁴⁵Scott, D. W., et al., J. Am. Chem. Soc. 78, 5463-5468 (1956).
⁴⁶Good, W. D., Lacina, J. L., and McCullough, J. P., J. Am. Chem. Soc. 82, 5589-5591 (1960).
⁴⁷Chase, M. W., Jr., et al., *JANAF Thermochemical Tables*, Third ed. (American Chemical Society, New York, 1985) (also available as J. Phys. Chem. Ref. Data 14, suppl. 1, (1985)).
⁴⁸Zelegznik, F. J., *A Class of Nonideal Solutions. I. Definition and Properties*. NASA TP-1929, 1983.
⁴⁹Zelegznik, F. J. and Donovan, L. F., *A Class of Nonideal Solutions. II. Application to Experimental Data*. NASA TP-1930, 1983.