The system has 10 degrees of freedom, and therefore, we represent the experimental results with equilibrium K values as shown in Figures 1-4. K values decreased with increasing pressures and tended to increase with increasing temperature except for H_2.

Literature Cited

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Thermodynamic Activities and Equilibrium Partial Pressures for Aqueous Sulfuric Acid Solutions

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Published room-temperature and azeotropic composition data for solutions together with recently published high-temperature *P-T-X* data and room-temperature values for the equilibrium vapor pressure of sulfur-bearing species over concentrated sulfuric acid-water solutions are evaluated critically for self-consistency. The adjusted data are used to calculate activity coefficients at 0 °C and at the normal azeotropic boiling temperature and to generate expressions for the partial molar heat capacities in H_2SO_4-H_2O solutions. These partial molar properties, calculated for temperatures between 25 and 320 °C and spanning the composition range from pure water to the azeotropic composition, are used as interpolation formulas for the calculation of basic thermodynamic parameters of H_2SO_4-H_2O solutions that are specifically needed for nucleation and precipitation phenomena involving vapors with a high sulfur oxide and/or sulfuric acid content.

(1) Introduction

It is generally recognized that the oxidation of sulfur dioxide to SO_3 and subsequent nucleation, in the presence of H_2O, of liquid droplets is the principal mechanism for the formation of sulfuric acid aerosol found in the atmosphere. Elaborate mechanisms have been postulated by which the heterogeneous or homogeneous nucleation of H_2SO_4 could take place under tropospheric or stratospheric conditions (*19*, *26*, *34*, *39*), and measurements of nucleation rates under such conditions have been reported (*5*, *9*, *30a*, *33*, *34*). Also, studies have been conducted of the formation of sulfuric acid aerosols in combustion processes where exhaust gases contain solid aerosol particles that may serve as catalysts for the oxidation of SO_2 and/or as nucleation sites for the condensation of sulfuric acid (*3*, *31*, *36*, *47*).

A quantitative interpretation of the conditions leading to the formation of sulfuric acid by nucleation and condensation requires knowledge of the thermodynamic properties of aqueous sulfuric acid solutions under the conditions of temperature and partial pressures at which the liquid phase is likely to form. Surprisingly, in light of the importance of sulfuric acid in industrial technology, such data are scarce and largely inconsistent. This problem has been recognized by authors who have tried to generalize the representation of thermodynamic properties of aqueous sulfuric acid solutions through correlations (*1*, *13*, *14*, *43*, *44*) and also by those who have attempted to use available data and data correlations to arrive at quantitative estimates of rates of formation of sulfuric acid in the atmosphere and in combustion processes. Specifically, the data required are liquid-phase activity coefficients and vapor pressures of the various species that are in equilibrium with aqueous solutions of sulfuric acid, for specified conditions of temperature and composition of the liquid phase. The inconsistencies in reported values of the vapor pressure of sulfuric acid and the lack of high-temperature heat capacity data have been the main obstacles in calculating accurate activity coefficients, vapor pressures, and degrees of supersaturation.

The measurement of activities and vapor pressures in solutions with compositions approaching pure sulfuric acid are extremely difficult. Even the vapor in equilibrium with "pure" sulfuric acid includes $H_2O(v)$ and $SO_3(v)$ as well as $H_2SO_4(v)$, and dissociation of H_2SO_4 into H_2 and SO_3, coupled with the very low vapor pressure of sulfuric acid near room temperature, complicates the measurement of the partial pressures of the various species. A relatively recent report (*6*) on the reasons for the failure of an attempted series of measurements in the sulfuric acid-water system at high acid concentrations dramatically illustrates such difficulties. Recent publications dealing with calculation of nucleation rates in the sulfuric acid-water system (*5*, *19*, *33*, *34*, *36*, *47*) most commonly use a value for the vapor pressure of pure sulfuric acid given by the correlation of Gmitro and Vermeulen (*13*) of 3.6×10^{-4} Torr (0.048 Pa), although it has been suggested that this value may be in error by several hundred percent (*43*), and more recently, the authors themselves have revised significantly their previous correlation (*44*). Another value in use, 10^{-6} Torr (1.3×10^{-4} Pa), is derived from estimations by LaMer et al. based on observed nucleation rates of aqueous sulfuric acid from the vapor phase (*9*, *30a*).

Such inconsistencies prevail not only among reported values of vapor pressures but also for azeotropic compositions, boiling points, and other thermodynamic parameters, as has been pointedly summarized by Myers in a recent article (*35*).

The purpose of the analysis reported here has been to reexamine the available thermodynamic data and to derive therefrom a framework of self-consistent values of basic thermodynamic parameters that may be used to calculate with some degree of consistency levels of supersaturation, dew points, and phase equilibria related to the precipitation of aqueous sulfuric acid droplets for various conditions of temperature, humidity, and partial pressure of SO_3.

(2) Thermodynamic Data for the H_2SO_4-H_2O System

Thermodynamic activities can be determined experimentally from several different properties of solutions. In the case of H_2O-H_2SO_4 solutions, properties such as vapor pressure, electromotive force, osmotic pressure, and freezing point depression have been used to determine the activities of one or the other component over various ranges of composition and temperature.

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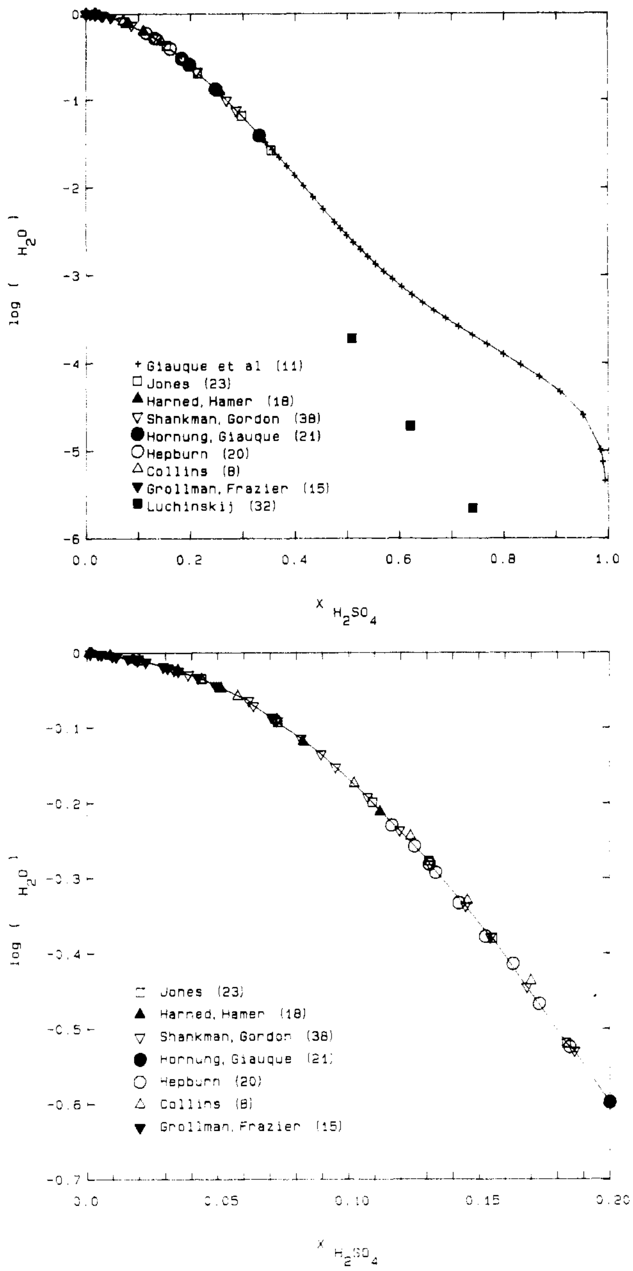

Figure 1. Activity coefficient of H_2O in H_2O-H_2SO_4 solutions at 25 °C.

Table I. Sources of Experimental Data on Activity Coefficients for the H_2O-H_2SO_4 System at 25 °C

composition (X)	species analyzed	method[a]	ref
0.020-0.258	H_2O	vp	8
0.333-1.000	H_2O	fp	11[b]
0.001-0.049	H_2O	vp	15
9.0×10^{-4}-0.112	H_2O, H_2SO_4	EMF	18
0.117-0.185	H_2O	dew pt	20
0.200-0.333	H_2O	vp	21
0.020-0.424	H_2O	vp	23
0.511-0.914	H_2O, H_2SO_4	vp	32
0.464, 0.815	H_2SO_4	vp	37
0.033-0.290	H_2O	vp	38

[a] Abbreviations: vp, vapor pressure; fp, freezing point.

Table II. Sources of Experimental Data on Activity Coefficients for the H_2O-H_2SO_4 System at $T > 25$ °C

temp range	composition (X)	species analyzed	method[a]	ref
65-170	0.9005	H_2SO_4	vp	2
55-235	0.057-0.813	H_2O	vp	7
25-140	0.020-0.300	H_2O	vp	8
100-193	0.256-0.410	H_2SO_4	vp	16
40-60	9.0×10^{-4}-0.112	H_2O, H_2SO_4	EMF	18
40-200	0.511-0.914	H_2O, H_2SO_4	vp	32
180-315	0.604-0.960	H_2O, H_2SO_4	vp	42

[a] vp, vapor pressure.

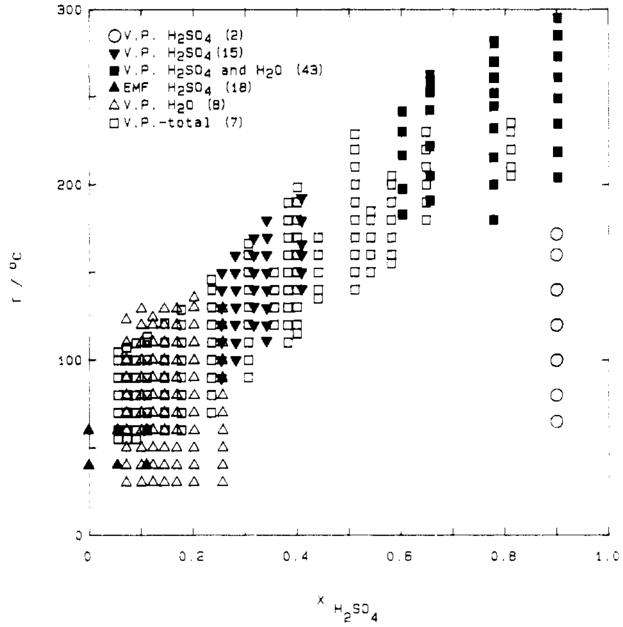

Figure 2. Available vapor pressure and EMF data for H_2O-H_2SO_4 system at temperatures above 25 °C.

In general, if data are available for the activity of one component of a binary system over the entire composition range, the activity of the second component can be calculated through integration of the Gibbs-Duhem equation. This calculation requires that the activity of a related property be established at some composition for the second component. The difficulty for calculating thermodynamic activities of sulfuric acid in the H_2SO_4-H_2O system lies in the establishment of a proper reference state. The H_2SO_4-H_2O system is not a true two-component system but rather a section of the more general H_2O-SO_3 system: the fact that pure sulfuric acid (an intermediate compound in the H_2O-SO_3 system) has an incongruous boiling point makes that composition an inconvenient reference state, especially at higher temperatures where the partial pressure of SO_3 in equilibrium with the liquid phase is appreciable.

A critical evaluation of the data on the activity coefficient of water in H_2SO_4-H_2O solutions at 25 °C has been published by Staples (*40*). Figure 1 summarizes available room-temperature data for H_2SO_4-H_2O solutions, and the sources are listed in Table I. This summary shows that values for the activity coefficient of water in dilute solutions, $X_2 < 0.3$ where X_2 is the mole fraction of H_2SO_4 in solution, reported by different authors are in close agreement. These data are the basis for the values of partial molar free energies at dilute concentrations in a critical compilation by Giauque et al. (*11a*). For higher sulfuric acid concentrations, a considerable discrepancy exists between the data reported by Giauque et al. (based on an interpolation of freezing point data) and the values derived from vapor pressures measured by Luchinskij (*32*).

Figure 2 and Table II summarize the compositions and temperatures (above 25 °C) for which measurements of vapor pressures and/or activities in the H_2SO_4-H_2O system have been reported in the literature. A wealth of data on vapor pressures and activities of water in H_2SO_4-H_2O solutions is available along a band of concentration values following the normal boiling temperature of H_2SO_4-H_2O solutions to about 200 °C. These data, which are generally self-consistent, especially at the lower temperatures, are, however, insufficient for integration of the Gibbs–Duhem equation. Direct measurements of sulfuric acid activities (or vapor pressures) are much scarcer and cover a smaller range of concentrations and temperatures. Very few measurements have been attempted in the range of low temperatures and high sulfuric acid concentrations. The accuracy of the results of the only study reported that has attempted to cover this range of temperatures and concentrations (*32*) has been questioned (*2*, *43*).

Two more recently reported sets of data are helpful for filling this gap: The high-temperature P–T–X data of Giazitzouglou and Wuster (*12*) are useful for bridging room-temperature activity data and vapor pressures near the boiling point of H_2SO_4–H_2O solutions. The partial pressures of sulfuric acid over two concentrated solutions (X_2 = 0.464, 0.815) measured by Roedel (*37*) allow an estimate of the activity coefficients and vapor pressures for concentrated H_2SO_4 solutions and define the vapor pressure of the room-temperature azeotrope that is a convenient thermodynamic "reference" state for the treatment of data.

There are also two other sets of thermodynamic data to be considered: One set is the particularly accurate measurements of azeotropic compositions as a function of boiling pressure reported by Kunzler (*28*). Another set is data on the equilibrium constant for the decomposition of sulfuric acid in the vapor phase ($H_2SO_4(v) = H_2O(v) + SO_3(v)$) over a wide temperature range, which was measured by Bodenstein and Katayama (*4*) nearly 80 years ago. Although no confirmation of these data has been reported in later literature, they have been used extensively for thermodynamic calculations and correlations pertaining to the H_2SO_4–H_2O system (*1*, *2*, *13*, *43*).

However, there are inconsistencies among the aforementioned data. The total vapor pressures at 25 °C, calculated from the partial molar free energies (activities) listed by Giauque et al. (*11a*), the H_2SO_4 vapor pressures determined by Roedel (*37*), and the equilibrium constant of Bodenstein and Katayama (*4*), do not result in a vapor pressure minimum (i.e., azeotrope) in the H_2O–H_2SO_4 composition range, contrary to other experimental evidence, especially the extrapolation of Kunzler's data (*28*) to room temperature, shown in Figure 3. This discrepancy may be due to the necessary approximations involved in Giauque's correlation for concentrated solutions that is based on freezing point depressions in a two-component representation of the system, i.e., H_2O and H_2SO_4, which ignores the partial pressure of SO_3.

A similar discrepancy with Kunzler's azeotrope is found in the high-temperature P–T–X data of Giazitzouglou and Wuster. These data, interpolated to the normal boiling point of 1.013 bar, result in an azeotropic composition of 0.8995 mol % H_2SO_4 and a boiling temperature of 315 ± 2 °C, whereas the azeotrope composition determined by Kunzler is 0.9222 mol % H_2SO_4. We found no evident explanation for this discrepancy, except that, for the reasons outlined above, accurate measurement for compositions high in H_2SO_4 are exceedingly difficult.

A critical evaluation and adjustment of the data becomes necessary if they are to be used for calculation of self-consistent, derived parameters. It is deemed that Kunzler's azeotrope data and the activities of water in dilute solutions ($X < 0.4$) at 25 °C, as compiled by Giauque et al., are the most reliable of all available data. Giauque's activity data for concentrated solutions are corrected with use of Roedel's vapor pressure measurements for solutions of X = 0.464 and 0.815 and the room-temperature azeotrope composition (X = 0.9402) obtained from extrapolating Kunzler's data. The partial molar free energy of water, G_1, in solutions in the concentration range ($0.464 < X < 1.00$) was expressed as a polynomial function of the form

$$\bar{G}_1 = A_0 + A_1X + A_2X^2 + A_3X^3 + A_4X^4 \qquad (1)$$

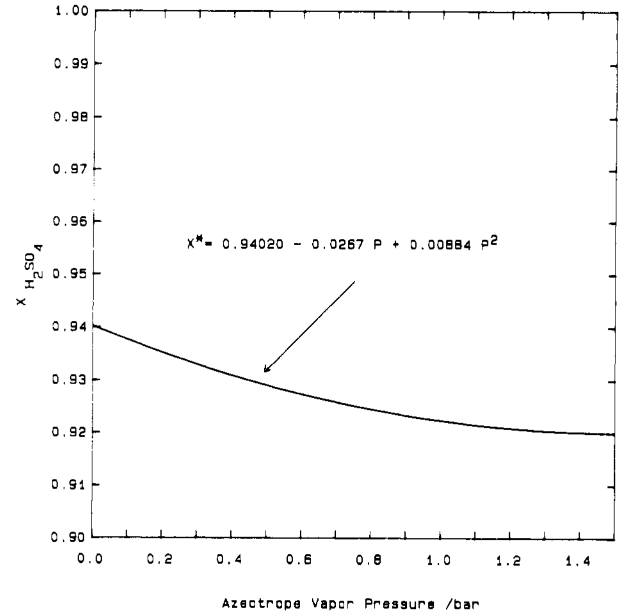

Figure 3. Azeotropic composition and vapor pressure (after Kunzler (*28*)).

The corresponding partial molar free energy of sulfuric acid, G_2, calculated by a Gibbs–Duhem integration with X = 1 as the reference state is

$$\bar{G}_2 = A_1(X - 1 - \ln(X)) + A_2(X - 1)^2 + A_3(X^3 - 1.5X^2 + 0.5) + A_4(X^4 - 1.333X^3 + 0.333) \qquad (2)$$

The five constants of eq 1 and 2 were determined from the following conditions

$$\bar{G}_1(X{=}0.464) = \bar{G}_1(X{=}0.464,\text{Giauque}) = -14.714\ \text{kJ/mol} \qquad (3a)$$

$$\frac{d\bar{G}_1}{dX}(X{=}0.464) = \frac{d\bar{G}_1}{dX}(X{=}0.464,\text{Giauque}) = -43.15\ \text{kJ/mol} \qquad (3b)$$

$$\frac{P_{H_2SO_4}(X{=}0.464,\text{Roedel})}{P_{H_2SO_4}(X{=}0.815,\text{Roedel})} = \exp\left[\frac{\bar{G}_2(X{=}0.464) - \bar{G}_2(X{=}0.815)}{RT}\right] = 0.0464 \qquad (3c)$$

and, at the azeotropic composition, $X = Y = 0.9402$

$$\frac{dP_t}{dX}(X{=}0.9402) = \frac{d(P_{H_2O} + P_{H_2SO_4} + P_{SO_3})}{dX} = 0 \qquad (3d)$$

$$\frac{P_{H_2O} - P_{SO_3}}{P_{H_2SO_4} + P_{H_2O}}(X{=}0.9402) = 1 - X_a = 0.0598 \qquad (3e)$$

From the simultaneous solution of eq 3 were obtained the following values for the constants of eq 1 and 2:

$$A_0 = 23.99\ \text{kJ/mol}$$

$$A_1 = -102.7\ \text{kJ/mol}$$

$$A_2 = -52.63\ \text{kJ/mol}$$

$$A_3 = 308.2\ \text{kJ/mol}$$

$$A_4 = -226.9\ \text{kJ/mol}$$

The molar free energies calculated from eq 1 and 2 are compared to the values in the correlation by Giauque et al. in Figure 4. The difference in total vapor pressure resulting from this adjustment of the partial molar free energies is illustrated in Figure 5.

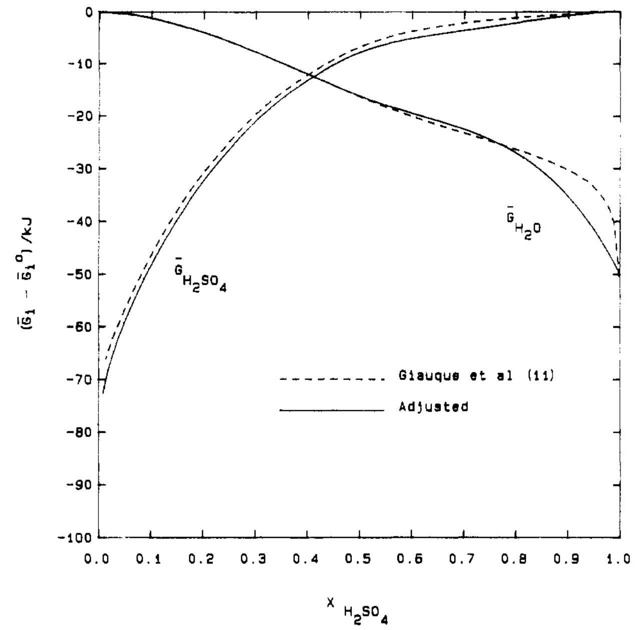

Figure 4. Partial molar free energies of Giauque et al. (*11a*) adjusted to Roedel's vapor pressures and Kunzler's azeotrope (*28*, *37*).

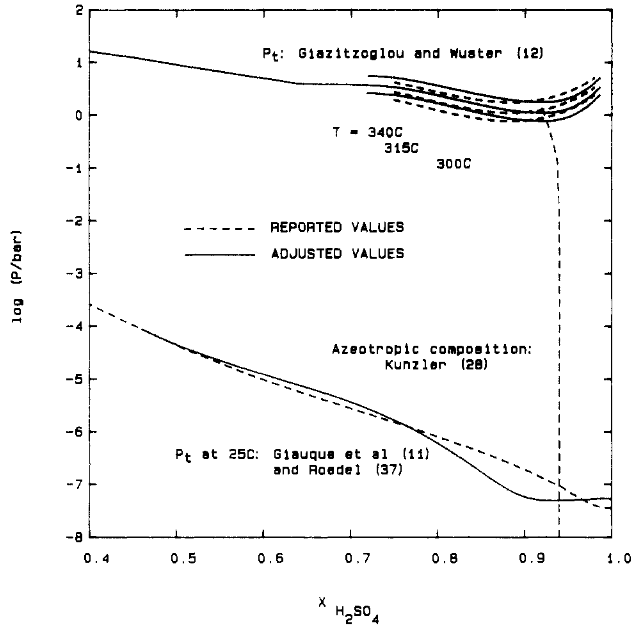

Figure 5. Reported and adjusted vapor pressure and azeotropic composition values (*11a*, *12*, *28*).

The P-T-X data reported by Giazitzouglou and Wuster were adjusted to coincide with Kunzler's azeotropic composition (X_a = 0.9222 at P = 1.0133 bar). Thus, for the hypoazeotropic composition range

$$X = \frac{0.9222}{0.8995}X' \qquad (4)$$

where X' is the reported concentration and X the corrected value. The analysis of the P-T-X data for the normal azeotropic boiling temperature is discussed in section 4(iv).

(3) Reference States for H_2SO_4-H_2O Solutions

The calculation of activities for solutions requires the definition of a reference state (state of unit activity) for each of the components. The thermodynamic activity of a substance is defined as the ratio of its fugacity in a given state and its fugacity in a reference state. In the present treatment, we shall assume that the deviations from ideality in the vapor phase are negligible and that the fugacities may be replaced by the corresponding partial pressures

$$a_i = f_i/f_i^{\circ} = P_i/P_i^{\circ} \qquad (5)$$

where P_i° is the vapor pressure of the species in the reference state at the temperature in question.

Particular attention is required in the selection of the sulfuric acid reference state. Sulfuric acid dissociates in the gas phase according to the equilibrium

$$H_2SO_4(g) \leftrightarrow H_2O(g) + SO_3(g) \qquad (6)$$

with an equilibrium constant (*4*)

$$K_p = P_{H_2O}P_{SO_3}/P_{H_2SO_4} \qquad (7a)$$

$$\log (K_p/\text{bar}) = 3.00 - 5000/T + 1.75 \log T - 5.70 \times 10^{-4}T \qquad (7b)$$

Thus, the vapor phase in equilibrium with an aqueous sulfuric acid solution consists of three chemical species: H_2SO_4, SO_3, and H_2O. The thermodynamic properties of the H_2SO_4-H_2O system may, in principle, be also represented as an H_2O-SO_3 binary system (with H_2SO_4 as an intermediate compound), or as a three-component system with a constraint expressed by the equilibrium of eq 6.

(i) Azeotrope Reference State. For the present analysis, three considerations are important for the selection of convenient reference states:

(a) The thermodynamic activity data available for the system are predominantly in the form of water vapor pressures over aqueous sulfuric acid solutions of various compositions. To obtain the liquid-phase activity of H_2SO_4 and partial pressures of the other two species (H_2SO_4 and SO_3) in the gas phase, these data must be integrated by use of the Gibbs-Duhem equation.

(b) The system of interest is delimited by temperatures and pressures where a two-phase equilibrium exists, i.e., liquid plus vapor. The composition range of interest extends from pure water to the azeotropic composition. Solutions of hyperazeotropic compositions are better represented in terms of an H_2SO_4-SO_3 binary system and will be covered in a subsequent paper.

(c) The vapor pressure at the reference state should be experimentally measurable or calculable for the temperature range of interest.

On the basis of these considerations, it was found that the most convenient form of activities for integration by the Gibbs-Duhem equation is obtained if liquid water (X = 0) and a solution of azeotropic composition ($X = X^*$) are used as the reference states. The liquid and vapor phases in equilibrium at the azeotropic point have the same overall composition: The partial pressures of the third species (SO_3) can be easily related to the partial pressure of sulfuric acid by the equilibrium condition of eq 7.

Solutions of azeotropic composition are in equilibrium with a gas phase that consists of water vapor and sulfuric acid partly decomposed into sulfur trioxide and water. The fraction of total sulfuric acid decomposed in the gas phase equilibrated with liquid of azeotropic composition according to the equilibrium of eq 6, "y^*", is calculated as follows

$$P_{H_2SO_4} = (1 - y^*)P_{H_2SO_4}{}^* \qquad (8a)$$

$$P_{SO_3} = y^*P_{H_2SO_4}{}^* \qquad (8b)$$

$$P_{H_2O} = P_{H_2O}{}^* + y^*P_{H_2SO_4}{}^* \qquad (8c)$$

$$P_t = P_{H_2O}{}^* + (1 + y^*)P_{H_2SO_4}{}^* \qquad (8d)$$

where $P_{H_2SO_4}$, P_{SO_3}, P_{H_2O} are the partial pressures of the individual species in the vapor phase in equilibrium with the azeotropic mixture and $P_{H_2SO_4}{}^*$ and $P_{H_2O}{}^*$ the total water and sulfuric acid vapor pressures defined by liquid-phase activities.

By stoichiometry

$$\frac{P_{H_2SO_4}{}^*}{P_{H_2O}{}^* + P_{H_2SO_4}{}^*} = X^* \tag{9}$$

and, from the equilibrium constant of eq 7

$$P_{SO_3}P_{H_2O}/P_{H_2SO_4} = K_p \tag{10}$$

Equations 8–10 may be combined to calculate for the azeotropic composition, $X_a{}^*$, the fraction of sulfuric acid decomposed in the gas phase, y^*, in terms of the total vapor pressure, P_t, and the equilibrium constant K_p:

$$y^{*2}[X_a{}^*(P_t + K_p)] + y^*(1 - X_a{}^*)(K_p + P_t) - K_p = 0 \tag{11}$$

(II) Vapor Pressure of Azeotropic Solutions. The vapor pressure of solutions of azeotropic composition for temperatures between 25 °C and the normal azeotropic boiling were calculated from the partial molar enthalpies, specific heats, and temperature derivatives of specific heats given by Giauque et al. (*11a*, *29*); the composition of the azeotropic solutions of Kunzler (*28*); the azeotrope vapor pressure at 25 °C calculated from Roedel's data (*37*) in section 2; and the normal azeotropic boiling temperature (315 ± 2 °C) interpolated from the P–T–X data of Giazitzouglou and Wuster (*12*).

The vapor pressure at any temperature may be expressed in the form of the Van't Hoff equation as

$$\ln\frac{P_t}{P_t{}^\circ} = -\int_{T_0}^{T}\frac{\Delta\bar{H}^v}{RT^2}\,dT \tag{12a}$$

where $P_t{}^\circ$ is the vapor pressure at the reference temperature T_0 and the enthalpy of vaporization, H^v, is calculated from its value at room temperature, $H^{v,\circ}$, and the molar heat capacities of the liquid and vapor phases in equilibrium:

$$\Delta\bar{H}^v = \Delta\bar{H}^{v,\circ} + \int_{T_0}^{T}(\bar{C}^v{}_p - \bar{C}^l{}_p)\,dT \tag{12b}$$

The heat capacity of the vapor phase, $\bar{C}^v{}_p$, per mole of vaporized liquid phase, was calculated from the known molar heat capacities of the individual vapor-phase species and the fraction, y^*, of H_2SO_4 decomposed at each temperature given by eq 11:

$$\bar{C}^v{}_p = X^*(1 - y^*)\bar{C}^v{}_{p,H_2SO_4} + (1 - X^* + X^*y^*)\bar{C}^v{}_{p,H_2O} + X^*y^*\bar{C}^v{}_{p,SO_3} \tag{13}$$

The molar heat capacity of the liquid phase, $\bar{C}^l{}_p$, was then expressed by a relation of the form

$$\bar{C}^l{}_p = a + bT + cT^2 \tag{14}$$

The constants a–c were determined by matching experimental data for the molar heat capacity and its temperature derivative at 25 °C with the values tabulated by Giauque et al. and by numerically integrating eq 12a between 298.15 (25 °C) and 588.15 K (315 °C) to match the change in vapor pressure from 25 to 315 °C, i.e.

$$\bar{C}^l{}_{p,298.15} = a + b(298.15\ \text{K}) + c(298.15\ \text{K})^2 = 131.9\ \text{J/(mol·K)} \tag{15a}$$

$$(d\bar{C}^l{}_p/dT)_{298.15} = b + 2c(298.15\ \text{K}) = 0.1983\ \text{J/(mol·K}^2) \tag{15b}$$

$$\ln\frac{P_{t,588.15\,K}}{P_{t,298.15\,K}} = \ln\frac{1.0133}{4.87 \times 10^{-8}} = 16.85 \tag{15c}$$

Other experimental data used in this calculation were the following:

(a) Molar heat capacities of the vapor species (*22*, *25*)

$$\bar{C}^v{}_{p,H_2SO_4}(g) = 0.900 + 0.390T - 4.751 \times 10^{-4}T^2 + 2.33 \times 10^{-7}T^3 \quad \text{J/(mol·K)} \tag{16a}$$

$$\bar{C}^v{}_{p,H_2O}(g) = 30.0 + 10.7 \times 10^{-3}T + 0.33 \times 10^5T^{-2} \quad \text{J/(mol·K)} \tag{16b}$$

$$\bar{C}^v{}_{p,SO_3}(g) = 57.3 + 26.9 \times 10^{-3}T - 13.1 \times 10^5T^{-2} \quad \text{J/(mol·K)} \tag{16c}$$

(b) The enthalpy of vaporization of the azeotropic solution at 25 °C was calculated from the enthalpies of vaporization of water, $\Delta\bar{H}_w{}^\circ$ = 44.04 kJ/mol (*24*), and the enthalpy of vaporization of sulfuric acid determined by Ayers et al. (*2*). Ayers et al. measured the temperature dependence of the vapor pressure of a 90.05 mol % (98.0 wt %) sulfuric acid solution. From these data and the partial molar free energies of Giauque et al., they estimated the enthalpy of vaporization for 100% H_2SO_4 to be 84.4 kJ/mol. This value was corrected with the adjustments to Giauque's free energies outlined in section 2. The resulting adjusted value for the heat of vaporization of 100% H_2SO_4 is 84.15 kJ/mol. This value, combined with the enthalpy of vaporization of water and the partial molar enthalpies of mixing given by Giauque et al., results in an enthalpy of vaporization, $\Delta\bar{H}^{v,\circ}$ = 82.9 kJ/mol for an azeotropic solution (X_a = 0.9402) at 25 °C.

The values for the constants of eq 14 calculated from these data are a = −476.1 J/(mol·K), b = 3.880 J/(mol·K^2), and c = −6.175 × 10^{-3} J/(mol·K^3). The total vapor pressures of solutions of azeotropic composition at various temperatures were calculated with eq 12 and the partial pressures of the individual vapor phase species from eq 8 and 11. The partial and total vapor pressures calculated for the temperature range of 0–320 °C are listed in Table III.

(4) Thermodynamic Parameters of the H_2O–Azeotrope System at 25 °C and 315 °C

(I) Partial Molar Free Energies and Activity Coefficients at 25 °C. The partial molar free energies for the H_2SO_4–H_2O system at 25 °C, compiled by Giauque et al. (*11a*) and adjusted at higher H_2SO_4 concentration range (section 2), were used to calculate the corresponding partial molar quantities for the water–azeotrope binary system. The partial molar quantities in the water–azeotrope system (subscripts "w" and "a") are related to the corresponding values in the water–sulfuric acid system (subscripts "1" and "2") and the azeotropic composition X^* by equations of the form

$$\bar{G}_w - \bar{G}_w{}^\circ = \bar{G}_1 - \bar{G}_1{}^\circ - X^*X^2\frac{d(\bar{G}_2 - \bar{G}_2{}^\circ)}{dX} - X(1 - X^*X)\frac{d(\bar{G}_1 - \bar{G}_1{}^\circ)}{dX} \tag{17a}$$

$$\bar{G}_a - \bar{G}_a{}^\circ = X^*(\bar{G}_2 - \bar{G}_2{}^\circ) + (1 - X)(\bar{G}_1 - \bar{G}_1{}^\circ) - \Delta G^* + (1 - X)\left[X^*\frac{d(\bar{G}_2 - \bar{G}_2{}^\circ)}{dX} + (1 - X^*)\frac{d(\bar{G}_1 - \bar{G}_1{}^\circ)}{dX}\right] \tag{17b}$$

where

$$\Delta G^* = X^*(\bar{G}_2 - \bar{G}_2{}^\circ)_{X=X^*} + (1 - X^*)(\bar{G}_1 - \bar{G}_1{}^\circ)_{X=X^*} \tag{17c}$$

X represents the mole fraction of H_2SO_4 in the H_2SO_4–H_2O system and X_a the mole fraction of azeotrope in the water–azeotrope system. Relations of the form of eq 17 are generally applicable to any partial molar quantity, i.e., H_i, S_i, V_i, etc.

The activity coefficients and activities for the water–azeotrope system are then calculated from the definitional equation

$$a_i = \gamma_i X_i = \exp\left(\frac{\bar{G}_i - \bar{G}_i{}^\circ}{RT}\right) \tag{18}$$

Table III. Calculated Vapor Pressures for Solutions of Azeotropic Composition

T/°C	P_{H_2O}/bar	$P_{H_2SO_4}$/bar	P_{SO_3}/bar	P_t/bar
0.0	0.1830×10^{-09}	0.1952×10^{-08}	0.6887×10^{-10}	0.2191×10^{-08}
10.0	0.7393×10^{-09}	0.7140×10^{-08}	0.2899×10^{-09}	0.8156×10^{-08}
20.0	0.2669×10^{-08}	0.2368×10^{-07}	0.1117×10^{-08}	0.2745×10^{-07}
25.0	0.4888×10^{-08}	0.4167×10^{-07}	0.2123×10^{-08}	0.4870×10^{-07}
30.0	0.8770×10^{-08}	0.7178×10^{-07}	0.3945×10^{-08}	0.8453×10^{-07}
40.0	0.2642×10^{-07}	0.2009×10^{-06}	0.1285×10^{-07}	0.2404×10^{-06}
50.0	0.7447×10^{-07}	0.5236×10^{-06}	0.3864×10^{-07}	0.6368×10^{-06}
60.0	0.1963×10^{-06}	0.1276×10^{-05}	0.1084×10^{-06}	0.1581×10^{-05}
70.0	0.4887×10^{-06}	0.2931×10^{-05}	0.2844×10^{-06}	0.3698×10^{-05}
80.0	0.1153×10^{-05}	0.6368×10^{-05}	0.7031×10^{-06}	0.8222×10^{-05}
90.0	0.2594×10^{-05}	0.1321×10^{-04}	0.1648×10^{-05}	0.1746×10^{-04}
100.0	0.5585×10^{-05}	0.2618×10^{-04}	0.3681×10^{-05}	0.3548×10^{-04}
110.0	0.1153×10^{-04}	0.4989×10^{-04}	0.7852×10^{-05}	0.6934×10^{-04}
120.0	0.2291×10^{-04}	0.9162×10^{-04}	0.1607×10^{-04}	0.1306×10^{-03}
130.0	0.4406×10^{-04}	0.1629×10^{-03}	0.3170×10^{-04}	0.2388×10^{-03}
140.0	0.8222×10^{-04}	0.2812×10^{-03}	0.6039×10^{-04}	0.4236×10^{-03}
150.0	0.1486×10^{-03}	0.4732×10^{-03}	0.1114×10^{-03}	0.7328×10^{-03}
160.0	0.2624×10^{-03}	0.7780×10^{-03}	0.2000×10^{-03}	0.1242×10^{-02}
170.0	0.4519×10^{-03}	0.1253×10^{-02}	0.3499×10^{-03}	0.2056×10^{-02}
180.0	0.7621×10^{-03}	0.1982×10^{-02}	0.5984×10^{-03}	0.3342×10^{-02}
190.0	0.1262×10^{-02}	0.3090×10^{-02}	0.1000×10^{-02}	0.5346×10^{-02}
200.0	0.2046×10^{-02}	0.4753×10^{-02}	0.1641×10^{-02}	0.8433×10^{-02}
210.0	0.3273×10^{-02}	0.7228×10^{-02}	0.2642×10^{-02}	0.1315×10^{-01}
220.0	0.5164×10^{-02}	0.1089×10^{-01}	0.4198×10^{-02}	0.2028×10^{-01}
230.0	0.8035×10^{-02}	0.1633×10^{-01}	0.6561×10^{-02}	0.3090×10^{-01}
240.0	0.1239×10^{-01}	0.2432×10^{-01}	0.1014×10^{-01}	0.4688×10^{-01}
250.0	0.1888×10^{-01}	0.3622×10^{-01}	0.1549×10^{-01}	0.7063×10^{-01}
260.0	0.2858×10^{-01}	0.5370×10^{-01}	0.2344×10^{-01}	0.1057
270.0	0.4295×10^{-01}	0.7962×10^{-01}	0.3508×10^{-01}	0.1577
280.0	0.6412×10^{-01}	0.1183	0.5212×10^{-01}	0.2346
290.0	0.9528×10^{-01}	0.1761	0.7691×10^{-01}	0.3484
300.0	0.1414	0.2630	0.1126	0.5171
310.0	0.2092	0.3944	0.1639	0.7675
320.0	0.3086	0.5942	0.2375	$0.1140 \times 10^{+01}$
330.0	0.4523	0.9008	0.3444	$0.1697 \times 10^{+01}$
340.0	0.6507	$0.1377 \times 10^{+01}$	0.5073	$0.2535 \times 10^{+01}$

where i = a,w for the water–azeotrope system.

(ii) Partial Molar Enthalpies at 25 °C. The partial molar enthalpies for the water–azeotrope system were calculated from the H_2O–H_2SO_4 system values of Giauque et al. by the relations equivalent to eq 17 rewritten in terms of enthalpies. The calculated partial molar free energies and enthalpies for hypoazeotropic solutions are shown in Figure 6.

(iii) Molar Heat Capacities and Their Temperature Derivatives at 25 °C. The molar heat capacities and their temperature derivatives for the two components of the water–azeotrope system were also calculated from the H_2O–H_2SO_4 system values of Giauque et al. by applying Kopp's law and the lever rule

$$[\bar{Q}_w]_X = [\bar{Q}]_X - X(d\bar{Q}/dX)_X \tag{19a}$$

$$[\bar{Q}_a]_X = [\bar{Q}]_X - (X^* - X)(d\bar{Q}/dX)_X \tag{19b}$$

where $\bar{Q}$ represents either the molar heat capacity $\bar{C}_p$ or its temperature derivative $d\bar{C}_p/dT$. Equations 19 can be rewritten in terms of the azeotrope composition coordinate

$$[\bar{Q}_w]_{X_a=X/X^*} = [\bar{Q}]_{X_a=X/X^*} - X_a(d\bar{Q}/dX)_{X_a=X/X^*} \tag{20a}$$

$$[\bar{Q}_a]_{X_a=X/X^*} = [\bar{Q}]_{X_a=X/X^*} - (1 - X_a)(d\bar{Q}/dX)_{X_a=X/X^*} \tag{20b}$$

The calculated values of the 25 °C thermodynamic parameters of the water–azeotrope system are listed in Table IV.

(iv) Activity Coefficients, Free Energies, and Partial Pressures at 315 °C. The activity coefficients, partial molar free energies, and partial pressures at the normal azeotropic boiling temperature were calculated by a Gibbs–Duhem integration of the P–T–X data of Giazitzouglou and Wuster (*12*). The normal boiling temperature and the P–X relation at this temperature were determined by interpolation of Giazitzouglou and Wuster's data as is illustrated in Figure 7a. Different interpolation procedures for the same data set were found to give a variation of approximately ±2 °C in the normal boiling temperature and of ±0.001 in the mole fraction of H_2SO_4 at the azeotrope. The calculated azeotropic composition $X^{*\prime}$ = 0.900 ± 0.001 at the normal azeotropic boiling temperature (for P_t = 1.0133 bar), 315 ± 2 °C, was subsequently adjusted to match Kunzler's value for the azeotropic composition, X^* = 0.9222, as is discussed in section 2. The resulting P_t–X_a relation at 315 °C after adjusting to the water–azeotrope com-

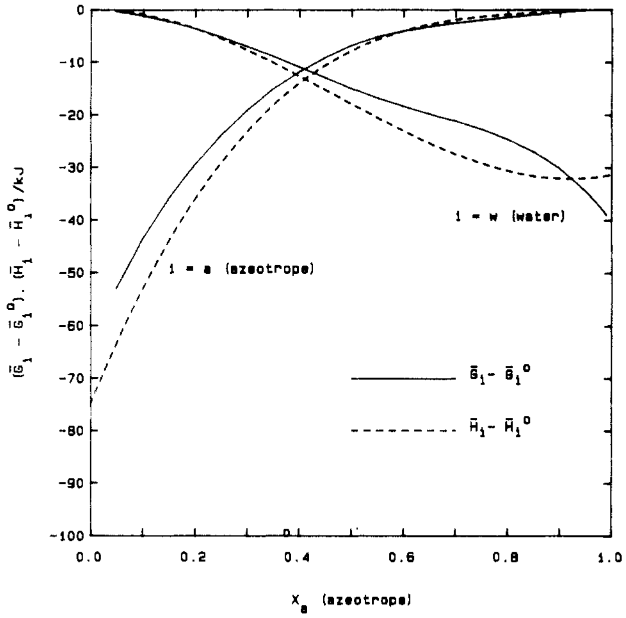

Figure 6. Partial molar free energies of water–azeotrope binary system at 25 °C (from adjusted H_2O–H_2SO_4 data).

Table IV. Thermodynamic Parameters for the Water–Azeotrope System at 25 °C

X_a	$\bar{G}_w - \bar{G}_w°$/ (kJ/mol)	$\bar{G}_a - \bar{G}_a°$/ (kJ/mol)	$\bar{H}_w - \bar{H}_w°$/ (kJ/mol)	$\bar{H}_a - \bar{H}_a°$/ (kJ/mol)	$\bar{C}_{p,w}$/ (J/(K·mol))	$\bar{C}_{p,a}$/ (J/(K·mol))	$d\bar{C}_{p,w}/dT$/ (J/(K²·mol))	$d\bar{C}_{p,a}/dT$/ (J/(K²·mol))
1.00	-39.48	0.00	-31.72	0.00	50.28	131.90	-0.0379	0.1984
0.99	-38.98	-0.01	-31.58	0.00	51.40	131.00	-0.0668	0.2002
0.98	-37.77	-0.02	-33.39	-0.09	52.54	130.60	-0.1069	0.1899
0.97	-36.63	-0.05	-31.39	-0.01	53.67	130.80	-0.0571	0.1968
0.96	-35.55	-0.09	-31.89	-0.09	54.80	131.00	-0.0366	0.2020
0.95	-34.53	-0.14	-31.49	-0.10	55.58	131.20	-0.0953	0.1997
0.90	-30.19	-0.49	-31.11	-0.08	63.84	130.10	-0.1307	0.2037
0.85	-26.94	-0.95	-31.31	0.00	73.66	128.80	-0.1563	0.2008
0.80	-24.51	-1.46	-29.55	-0.42	78.33	127.90	-0.1877	0.2126
0.75	-22.64	-2.00	-29.47	-0.72	86.80	125.50	-0.1920	0.2098
0.70	-21.11	-2.58	-26.69	-1.75	92.36	123.40	-0.1727	0.2046
0.65	-19.73	-3.24	-26.16	-2.01	94.93	122.20	-0.1309	0.1862
0.60	-18.34	-4.08	-24.90	-2.79	89.77	125.40	-0.0031	0.1070
0.55	-16.80	-5.23	-21.83	-5.08	72.76	138.10	0.4085	-0.2028
0.50	-14.98	-6.88	-17.87	-8.68	48.83	159.60	0.3854	-0.1717
0.45	-12.90	-9.14	-14.29	-12.63	41.38	167.60	0.0515	0.1937
0.40	-10.86	-11.91	-11.61	-16.24	44.49	163.20	-0.1252	0.4299
0.35	-8.86	-15.24	-9.50	-19.77	51.56	151.30	-0.1359	0.4460
0.30	-6.95	-19.22	-7.42	-24.13	59.11	135.60	-0.0498	0.2651
0.25	-5.17	-23.92	-5.51	-29.04	66.28	116.90	0.0310	0.0545
0.20	-3.57	-29.46	-3.84	-34.84	70.35	102.60	0.0588	-0.0411
0.15	-2.19	-35.97	-2.43	-41.51	76.51	73.50	0.1036	-0.2418
0.10	-1.10	-43.66	-1.15	-50.65	77.46	68.80	0.0671	0.0091
0.05	-0.34	-53.03	-0.26	-61.45	74.43	106.50	0.1226	-0.7082
0.00	0.00	-∞	0.00	-79.52	75.36	88.00	-0.0075	9.1250

position coordinate system is shown in Figure 7b.

The activity coefficients for the water and azeotrope components at 315 °C were calculated by numerical integration of the Gibbs–Duhem relation along the P_t–X_a line (Figure 7b). The effects of nonideal mixing in the vapor phase were neglected by equating partial pressures to fugacities. For the integration process, the activity of one of the components (azeotrope) was represented in each composition interval between a pair of measured total vapor pressure values by a relation of the form

$$\ln \gamma_a = \Omega(1 - X_a)^2 \tag{21a}$$

where Ω is a constant to be determined by matching the experimental vapor pressure data. The activity of the other component (water) is calculated by integrating the Gibbs–Duhem equation over each composition interval

$$\ln \gamma_w = \int_1^{X_a} \frac{\Omega X_a}{1 - X_a}\, dX_a \tag{21b}$$

where the constant Ω is determined at each composition interval from the condition that

$$P_t = X_a \gamma_a P_a° + X_w \gamma_w P_w° \tag{22}$$

The partial pressures of the individual species in the vapor phase and the degree of decomposition, "y", of sulfuric acid can be calculated at each composition from the value of the dissociation constant K_p (eq 7) and the stoichiometric relations

$$P_{H_2O} = X_w \gamma_w P_w° + X_a \gamma_a P_w^a \tag{23a}$$

$$P_{SO_3} = \frac{K_p(P_t - P_{H_2O})}{K_p + P_{H_2O}} \tag{23b}$$

and

$$P_{H_2SO_4} = \frac{P_{H_2O} P_{SO_3}}{K_p} \tag{23c}$$

where $P_w° = 105.60$ bar is the vapor pressure of water at 315 °C (*24*) and $P_w^a = 0.276$ bar (from Table III), the water vapor component of the total vapor pressure of azeotrope at the same temperature.

Table V. Total Vapor Pressure and Calculated Partial Molar Free Energies of Water–Azeotrope System at 315 °C

X_a	P_t/bar	$\bar{G}_s - \bar{G}_w°$/ (kJ/mol)	$\bar{G}_a - \bar{G}_a°$/ (kJ/mol)
1.00	1.01		0.00
0.99	1.03	-40.59	-0.07
0.98	1.08	-35.41	-0.14
0.97	1.15	-32.50	-0.22
0.96	1.23	-29.87	-0.32
0.95	1.32	-27.76	-0.41
0.90	1.84	-22.98	-0.78
0.85	2.50	-20.39	-1.14
0.80	3.25	-18.55	-1.53
0.75	4.04	-17.08	-1.96
0.70	4.92	-15.82	-2.44
0.65	5.95	-14.66	-2.99
0.60	7.28	-13.55	-3.66
0.55	9.08	-12.43	-4.49
0.50	11.55	-11.26	-5.55
0.45	14.88	-9.83	-7.14
0.40	19.22	-8.42	-9.05
0.35	24.58	-7.28	-10.94
0.30	30.86	-6.22	-13.15
0.25	37.99	-5.20	-15.84
0.20	46.15	-4.21	-19.29
0.15	56.10	-3.21	-24.03
0.10	69.19	-2.19	-31.29
0.05	86.75	-1.13	-45.05
0.00	108.64	0.00	

The calculated activity coefficients and partial molar free energies for water and azeotrope at 315 °C are listed in Table V.

(5) Thermodynamic Parameters at Other Temperatures Calculated by Interpolation

The change in partial molar free energies (hence activity coefficients) with temperature is given by the Gibbs–Duhem relation

$$\frac{d(\bar{G}_i/T)}{dT} = -\frac{\bar{H}_i}{RT^2} \tag{24a}$$

or, expressed in terms of activity coefficients

$$\frac{d \ln \gamma_i}{dT} = -\frac{\bar{H}_i - \bar{H}_i°}{RT^2} \tag{24b}$$

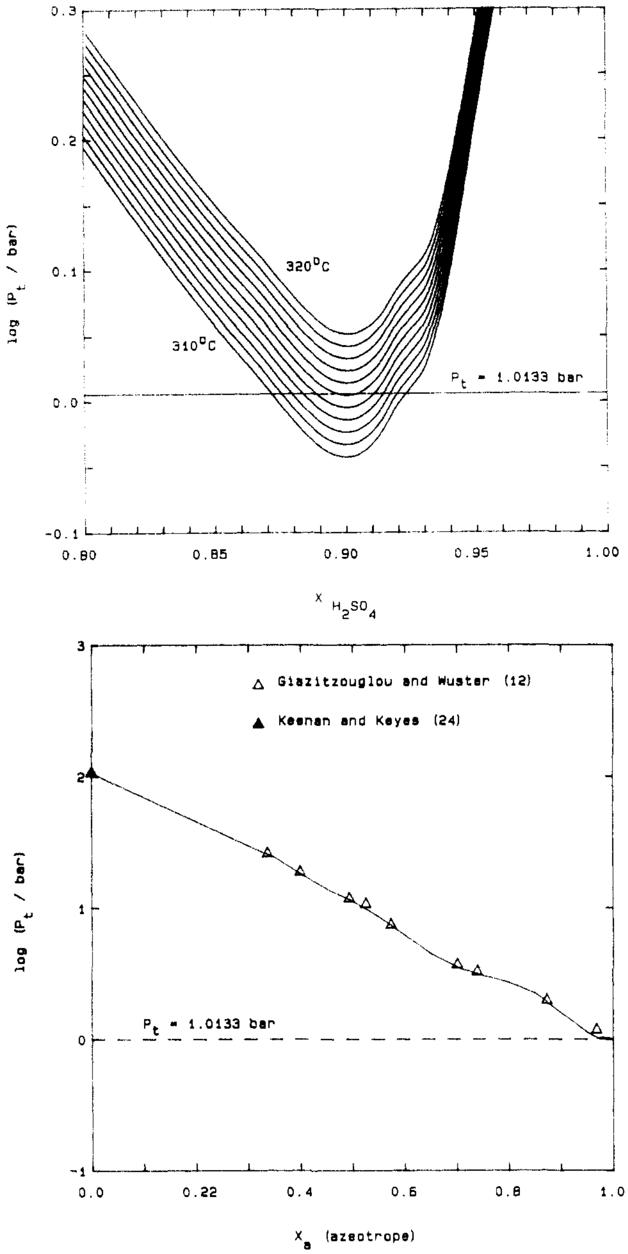

Figure 7. (A) Evaluation of normal azeotropic composition and temperature by cubic spline fit of P_t–X' data (*12*). (B) P–X_a relation at normal boiling temperature of azeotrope (315 °C).

At each composition, the change in the activity coefficients between 25 and 315 °C can be calculated as

$$\ln\left(\frac{\gamma_{i,588.15\,\mathrm{K}}}{\gamma_{i,298.15\,\mathrm{K}}}\right) = \int_{298\,\mathrm{K}}^{588\,\mathrm{K}} \frac{\bar{H}_i - \bar{H}_i^\circ}{RT^2}\,\mathrm{d}T \qquad (25)$$

where $\bar{H}_i^\circ$ is the partial molar enthalpy at 298.15 K and

$$\bar{H}_i = \bar{H}_i^\circ + \int_{298\,\mathrm{K}}^{T} \bar{C}_{p,i}\,\mathrm{d}T \qquad (26)$$

The values of the molar heat capacities $\bar{C}_{p,\mathrm{w}}$ and $\bar{C}_{p,\mathrm{a}}$ and their temperature derivatives at 298.15 K are known (Table IV). These values, together with the integral eq 25 can be used to calculate the constants in three-parameter equations for the temperature dependence of the partial molar heat capacities at each composition:

$$\bar{C}_{p,\mathrm{a}} = A_\mathrm{a} + B_\mathrm{a}T + C_\mathrm{a}T^2 \qquad (27\mathrm{a})$$

$$\bar{C}_{p,\mathrm{w}} = A_\mathrm{w} + B_\mathrm{w}T + C_\mathrm{w}T^2 \qquad (27\mathrm{b})$$

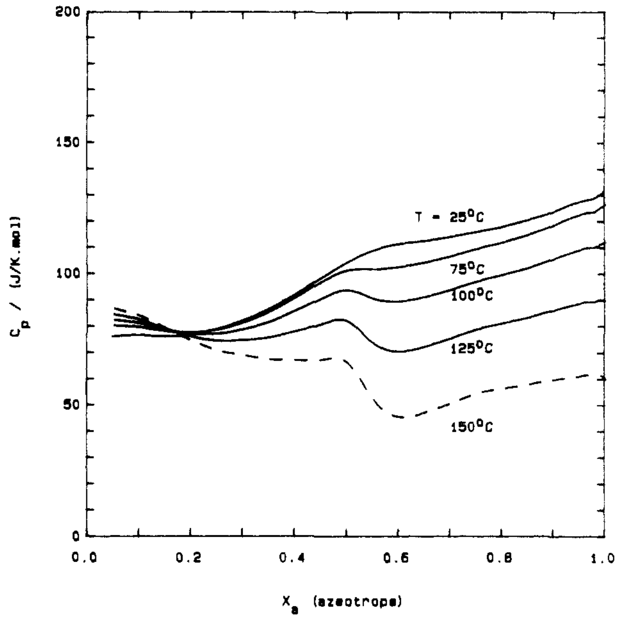

Figure 8. Calculated molar heat capacities of hypoazeotropic aqueous sulfuric acid solutions for various temperatures.

These partial molar heat capacities can then be used to calculate partial molar enthalpies by eq 26, partial molar free energies by eq 23, and activity coefficients by eq 24. The total and partial pressures of the vapor species in equilibrium with the liquid phase at each composition and temperature are calculated from the equilibrium constant for sulfuric acid decomposition (eq 7), the partial pressures of water and azeotrope at the temperature in question, and the stoichiometric relations of eq 23.

Table VI lists the constants in eq 27 calculated from the 25 and 315 °C parameters given in Tables IV and V. The calculated molar heat capacities for several temperatures in the 25–320 °C range are illustrated in Figure 8, and Table VII lists the calculated activity coefficients for the water–azeotrope system.

Table VIII lists the total vapor pressures and the corresponding partial pressures of the individual species in equilibrium with solutions in the 0–320 °C temperature range.

(6) Comparisons with Experimental Data and Other Correlations

It was noted in the Introduction that significant discrepancies exist among various experimental data reported for the H_2O–H_2SO_4 system. Table IX lists commonly cited values for vapor pressures for concentrated aqueous sulfuric acid solutions and azeotropic compositions derived from experiments or data correlations and compares them with the values adopted for the present analysis. One of the reasons for the large discrepancies in these data must surely be the decomposition of sulfuric acid in the vapor phase and the resulting variation of the SO_3:H_2SO_4 ratio with composition. Correlations of vapor pressure data are, on the other hand, quite sensitive to the azeotrope compositions and normal boiling temperatures selected.

The most substantial uncertainty in the reported experimental data is in the normal boiling temperature. Early measurements of the H_2O–H_2SO_4 azeotrope by Knietsch (*27*) resulted in an normal azeotrope at 317 °C and $X_{H_2SO_4}$ = 0.925. This value was subsequently superseded by a value of 326 °C, which was cited in many textbooks and data tabulations and correlations (*2*, *10*, *13*). This latter value is based on tabulations in the International Critical Tables derived from data correlations established by Greenewalt (*14*, *45*). More recently, the com-

Table VI. Calculated Constants for Partial Molar Heat Capacities of Water and Azeotrope as Function of Temperature (Equations 27)

X_a	$10^{-3}A_w$/ (J/mol)	B_w/ (J/(mol·K))	10^3C_w/ (J/(mol·K^2))	$10^{-3}A_a$/ (J/mol)	B_a/ (J/(mol·K))	10^3C_a/ (J/(mol·K^2))
1.00	0.513	-3.067	5.080	-0.476	3.880	-6.175
0.99	0.151	-0.600	0.893	-0.466	3.807	-6.049
0.98	-0.032	0.673	-1.309	-0.448	3.692	-5.874
0.97	-0.151	1.431	-2.495	-0.451	3.706	-5.886
0.96	-0.232	1.961	-3.351	-0.452	3.712	-5.887
0.95	-0.209	1.869	-3.295	-0.448	3.685	-5.845
0.90	-0.081	1.009	-2.063	-0.448	3.677	-5.824
0.85	0.029	0.454	-1.024	-0.456	3.724	-5.909
0.80	0.117	-0.075	-0.188	-0.487	3.909	-6.200
0.75	0.102	0.093	-0.478	-0.494	3.948	-6.268
0.70	0.048	0.473	-1.084	-0.503	3.997	-6.361
0.65	-0.023	0.924	-1.769	-0.503	4.005	-6.405
0.60	-0.123	1.430	-2.403	-0.464	3.848	-6.273
0.55	-0.396	2.739	-3.908	-0.198	2.460	-4.465
0.50	-0.161	1.025	-1.072	-0.279	3.111	-5.506
0.45	0.147	-0.761	1.363	-0.613	5.040	-8.127
0.40	0.295	-1.557	2.401	-0.811	6.104	-9.516
0.35	0.310	-1.599	2.453	-0.833	6.159	-9.580
0.30	0.225	-1.062	1.698	-0.652	5.019	-7.972
0.25	0.145	-0.558	0.987	-0.453	3.767	-6.227
0.20	0.129	-0.451	0.854	-0.392	3.356	-5.697
0.15	0.069	-0.056	0.267	-0.123	1.558	-3.018
0.10	0.091	-0.155	0.373	-0.260	2.195	-3.665
0.05	0.027	0.196	-0.123	0.569	-2.395	2.829
0.00	0.098	-0.143	0.228			

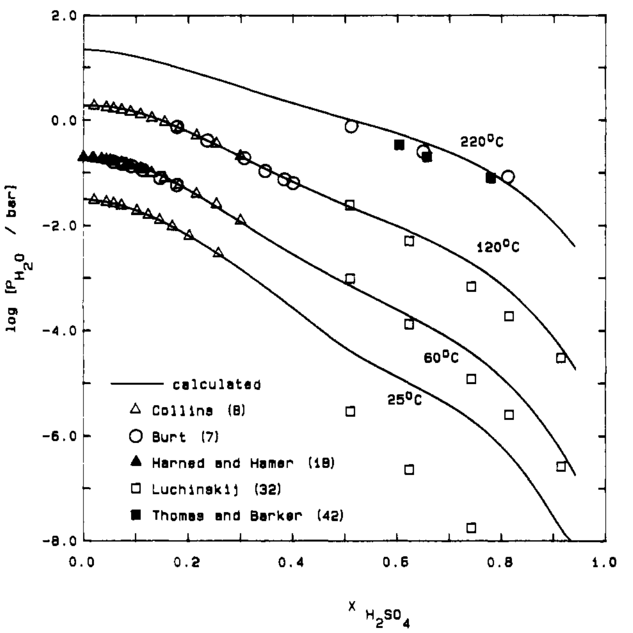

Figure 9. Partial pressure of H_2O at different temperatures: experimental data and calculated values.

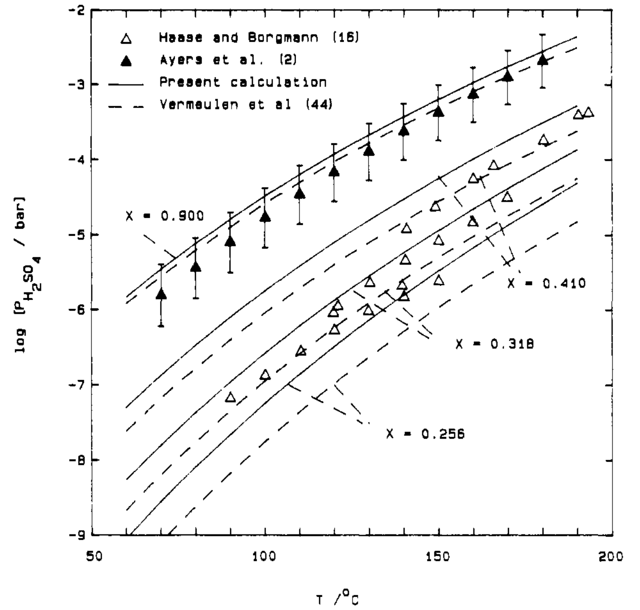

Figure 10. Partial pressure of H_2SO_4 at various liquid compositions and temperatures: experimental data and calculated values.

monly cited normal azeotropic temperature is 338.8 °C at $X_{H_2SO_4}$ = 0.915 (98.33 wt %) (*46*), based on data reported by Luchinskij (*32*). The recent measurements by Giazitzouglou and Wuster are, however, in closer agreement with Knietsch's values. Knietsch's azeotropic composition at the normal boiling point is also closest to the accurate measurements of this parameter by Kunzler (*28*).

Evidently, the selection of the normal azeotropic temperature and composition is subject to considerable uncertainty, until definitive measurements of these parameters are made. As was discussed above, the azeotropic boiling point of Giazitzouglou and Wuster and the azeotropic compositions of Kunzler were selected for the present calculations.

The accuracy of the calculated thermodynamic parameters may be best evaluated by comparing calculated and experimental values at temperatures and compositions where data are available. Figure 9 shows such comparisons for three intermediate temperatures (60, 120, and 220 °C) of calculated and measured partial pressures of water in equilibrium with H_2O-H_2SO_4 solutions. It is noted that the partial pressures reported by Luchinskij are systematically lower than other data, which are consistent with a relatively higher normal boiling temperature.

Calculated values of partial pressures of sulfuric acid are compared in Figure 10 to partial pressures measured by Ayers et al. (*2*) and by Haase and Borgmann (*16*). This figure also includes, for comparison, values derived from the most recent correlation by Vermeulen et al. (*44*). The calculated values are well within the experimental uncertainty range of the vapor pressures reported by Ayers (*2*). The calculated vapor pressures also show good agreement with Haase and Borgmann's values in the higher temperature range. The discrepancy increases somewhat at the lower temperatures. It must be noted, however, that the different slope of the log *P* versus *T*

Table VII. Calculated Activity Coefficients in the Water–Azeotrope Binary System

A

ln (γ_w), ln (γ_a)

x_a	T = 0.0 C		10.0 C		20.0 C		25.0 C		30.0 C	
	x^*=0.9402		x^*=0.9402		x^*=0.9402		x^*=0.9402		x^*=0.9402	
1.00	-12.421	0.000	-11.880	0.000	-11.372	0.000	-11.130	0.000	-10.895	0.000
0.99	-12.410	0.006	-11.873	0.006	-11.370	0.007	-11.130	0.007	-10.897	0.008
0.98	-12.608	0.007	-12.077	0.008	-11.578	0.010	11.340	0.010	-11.109	0.011
0.97	-12.537	0.003	-12.010	0.005	-11.516	0.008	-11.280	0.009	-11.051	0.010
0.96	-12.375	-0.004	-11.853	-0.001	-11.364	0.002	-11.130	0.003	-10.903	0.005
0.95	-12.174	-0.015	-11.656	0.011	-11.171	-0.008	-10.940	-0.006	-10.716	-0.004
0.90	-11.060	-0.111	-10.565	-0.103	-10.103	-0.095	-9.883	-0.092	-9.670	-0.088
0.85	-10.098	0.249	-9.626	-0.237	-9.187	-0.226	-8.978	-0.220	-8.776	-0.215
0.80	-9.339	0.405	-8.892	0.389	-8.477	-0.374	-8.280	-0.367	-8.090	-0.360
0.75	-8.746	-0.568	-8.324	0.549	-7.933	-0.530	-7.748	-0.521	-7.569	-0.512
0.70	8.249	-0.741	-7.853	-0.719	-7.487	-0.696	-7.314	-0.686	-7.147	-0.675
0.65	-7.781	-0.949	-7.412	-0.920	-7.072	-0.893	-6.912	-0.879	-6.758	-0.865
0.60	-7.282	-1.237	-6.945	-1.196	-6.633	-1.156	-6.485	-1.137	-6.343	-1.118
0.55	-6.697	1.705	-6.395	-1.623	-6.113	-1.548	-5.979	-1.513	-5.849	-1.479
0.50	-5.997	2.418	-5.728	-2.273	-5.474	-2.143	-5.351	-2.083	-5.232	-2.026
0.45	5.125	3.377	-4.913	-3.169	-4.711	-2.981	-4.613	-2.893	-4.517	-2.810
0.40	-4.291	-4.507	4.119	4.245	-3.955	-4.005	-3.876	-3.893	-3.798	-3.785
0.35	3.490	-5.845	-3.349	-5.532	-3.215	-5.242	-3.150	-5.106	-3.086	-4.975
0.30	-2.720	-7.448	2.609	-7.072	-2.504	-6.721	2.453	-6.555	-2.403	-6.394
0.25	-2.001	9.338	1.918	8.891	1.840	-8.472	-1.802	-8.272	-1.765	-8.078
0.20	-1.359	-11.554	-1.301	-11.020	1.246	-10.519	-1.220	-10.280	-1.194	-10.048
0.15	0.815	14.138	-0.777	-13.509	-0.741	-12.915	-0.725	-12.630	-0.708	-12.353
0.10	-0.383	-17.162	-0.365	-16.393	-0.348	-15.668	-0.340	-15.320	-0.333	-14.982
0.05	-0.100	-20.672	0.096	-19.721	0.093	-18.833	-0.091	-18.410	-0.089	-18.000
0.00	0.000	-24.549	0.000	-23.356	0.000	-22.216	0.000	-21.670	0.000	-21.140

B

ln (γ_w), ln (γ_a)

x_a	T = 40.0 C		50.0 C		60.0 C		70.0 C		80.0 C	
	x^*=0.9402		x^*=0.9402		x^*=0.9402		x^*=0.9402		x^*=0.9402	
1.00	-10.445	0.000	-10.020	0.000	-9.617	0.000	-9.236	0.000	-8.876	0.000
0.99	-10.451	0.009	-10.030	0.009	-9.631	0.010	-9.253	0.011	-8.893	0.012
0.98	-10.667	0.013	-10.250	0.014	-9.855	0.016	-9.479	0.017	-9.122	0.019
0.97	-10.614	0.012	-10.201	0.014	-9.809	0.016	-9.438	0.018	-9.085	0.020
0.96	-10.470	0.008	-10.061	0.010	-9.674	0.013	-9.307	0.015	-8.957	0.018
0.95	-10.287	0.000	-9.881	0.003	-9.498	0.006	-9.134	0.009	-8.787	0.012
0.90	-9.263	-0.081	-8.879	-0.074	-8.516	-0.068	-8.173	-0.062	-7.847	-0.056
0.85	-8.391	-0.204	-8.030	-0.194	-7.690	-0.184	-7.368	-0.174	-7.064	-0.165
0.80	-7.727	-0.346	-7.387	-0.332	-7.068	-0.319	-6.766	-0.306	-6.481	-0.293
0.75	-7.230	-0.494	-6.913	-0.477	-6.616	-0.460	-6.336	-0.443	-6.073	-0.427
0.70	-6.832	-0.653	-6.537	-0.632	-6.261	-0.611	-6.003	-0.591	-5.760	-0.570
0.65	-6.465	-0.839	-6.193	-0.812	-5.939	-0.787	-5.701	-0.761	-5.477	-0.736
0.60	-6.073	-1.082	-5.822	-1.047	-5.588	-1.014	-5.368	-0.981	-5.162	-0.949
0.55	5.602	-1.415	-5.370	-1.356	-5.153	-1.299	-4.949	-1.246	-4.757	-1.194
0.50	-5.002	-1.919	-4.784	-1.821	-4.577	-1.732	-4.381	-1.649	-4.195	-1.573
0.45	4.332	-2.654	-4.154	-2.512	-3.983	-2.383	-3.819	-2.265	-3.662	-2.156
0.40	-3.647	-3.584	-3.501	-3.398	-3.361	-3.228	-3.225	-3.072	-3.094	-2.927
0.35	-2.963	-4.727	-2.844	-4.497	-2.729	-4.283	-2.619	-4.085	-2.512	-3.900
0.30	-2.307	-6.089	-2.215	-5.803	-2.127	-5.535	-2.042	-5.283	-1.960	-5.045
0.25	-1.694	-7.708	-1.627	-7.359	-1.562	-7.029	-1.501	-6.715	-1.443	-6.418
0.20	-1.145	-9.602	-1.098	-9.180	-1.054	-8.780	-1.012	-8.399	-0.973	-8.036
0.15	-0.678	-11.819	-0.649	-11.310	-0.623	-10.825	-0.599	-10.361	-0.577	-9.915
0.10	-0.318	-14.332	-0.305	-13.714	-0.293	-13.126	-0.283	-12.566	-0.273	-12.030
0.05	0.086	-17.218	-0.083	-16.479	-0.080	-15.780	-0.078	-15.117	-0.077	-14.487
0.00	0.000	-20.132	0.000	-19.196	0.000	-18.334	0.000	-17.545	0.000	-16.830

C

ln (γ_w), ln (γ_a)

x_a	T = 90.0 C		100.0 C		110.0 C		120.0 C		130.0 C	
	x^*=0.9402		x^*=0.9402		x^*=0.9402		x^*=0.9402		x^*=0.9402	
1.00	8.533	0.000	-8.209	0.000	-7.901	-0.001	-7.610	-0.001	-7.334	-0.001
0.99	-8.551	0.013	-8.226	0.013	-7.915	0.014	-7.618	0.015	-7.334	0.015
0.98	-8.782	0.021	-8.457	0.022	-8.145	0.024	-7.846	0.025	-7.558	0.026
0.97	-8.749	0.022	-8.427	0.024	-8.118	0.026	-7.822	0.027	-7.536	0.029
0.96	-8.624	0.020	-8.305	0.022	-7.999	0.024	-7.705	0.025	-7.421	0.027
0.95	-8.456	0.014	-8.140	0.016	-7.835	0.018	-7.543	0.020	-7.260	0.022
0.90	7.537	-0.050	-7.240	-0.045	-6.956	-0.040	-6.684	-0.036	-6.421	-0.032
0.85	-6.775	-0.156	6.500	-0.147	-6.238	0.139	-5.987	-0.131	-5.747	-0.123
0.80	-6.211	-0.281	5.954	-0.270	-5.710	-0.258	-5.477	-0.247	-5.254	-0.237
0.75	5.824	-0.411	5.587	-0.396	-5.363	-0.381	-5.149	-0.366	-4.945	-0.351
0.70	-5.530	-0.550	-5.313	0.531	5.107	-0.512	-4.911	-0.492	-4.724	-0.474
0.65	-5.266	-0.712	-5.067	-0.687	-4.879	-0.663	-4.699	-0.639	-4.527	-0.616
0.60	-4.967	0.918	-4.784	-0.887	4.610	-0.857	-4.444	-0.827	-4.286	-0.798
0.55	4.577	1.145	4.407	-1.096	4.246	1.050	-4.094	-1.004	-3.949	-0.960
0.50	4.018	-1.501	-3.850	-1.434	3.691	-1.371	-3.539	-1.311	-3.395	-1.254
0.45	-3.510	-2.056	3.365	-1.965	-3.225	1.879	3.091	-1.801	-2.961	-1.727
0.40	-2.967	-2.794	-2.845	-2.671	-2.726	-2.557	-2.612	-2.451	-2.501	-2.352
0.35	-2.408	3.727	2.308	-3.566	-2.212	-3.415	2.119	-3.272	-2.030	-3.138
0.30	1.882	-4.821	-1.807	-4.609	-1.734	-4.408	-1.665	-4.216	-1.599	-4.034
0.25	1.387	6.134	1.334	-5.864	-1.284	-5.605	-1.236	-5.358	-1.191	-5.121
0.20	-0.935	-7.689	-0.900	-7.357	-0.867	-7.038	-0.836	-6.732	-0.807	-6.437
0.15	-0.557	-9.488	0.538	-9.077	0.521	-8.681	-0.507	-8.299	-0.493	-7.931
0.10	-0.265	-11.518	-0.258	-11.028	-0.252	-10.558	-0.247	-10.107	-0.243	-9.674
0.05	0.076	-13.887	-0.075	-13.315	-0.076	12.769	-0.076	-12.248	-0.078	-11.751
0.00	0.000	16.186	0.000	-15.611	0.000	15.102	0.000	-14.656	0.000	-14.270

D

ln (γ_w), ln (γ_a)

x_a	T = 140.0 C		150.0 C		160.0 C		170.0 C		180.0 C	
	x^*=0.9402		x^*=0.9402		x^*=0.9402		x^*=0.9402		x^*=0.9402	
1.00	-7.074	0.001	-6.828	-0.001	-6.597	-0.001	-6.380	-0.001	-6.177	-0.001
0.99	-7.062	0.016	-6.801	0.016	-6.551	0.016	-6.311	0.016	-6.081	0.016
0.98	-7.280	0.027	-7.012	0.028	-6.752	0.029	-6.500	0.029	-6.255	0.030
0.97	-7.261	0.030	-6.993	0.031	-6.734	0.031	-6.481	0.032	-6.235	0.032
0.96	-7.146	0.028	-6.880	0.028	-6.620	0.029	-6.367	0.029	-6.118	0.029
0.95	-6.986	0.023	-6.719	0.024	-6.459	0.024	-6.205	0.024	-5.956	0.024
0.90	-6.168	-0.028	-5.923	-0.025	-5.685	-0.022	-5.454	-0.020	-5.228	-0.018
0.85	-5.516	-0.116	-5.294	-0.109	-5.079	-0.102	-4.871	-0.096	-4.669	-0.091
0.80	-5.041	-0.226	-4.836	-0.216	-4.638	-0.206	-4.448	-0.197	-4.264	-0.188
0.75	-4.750	-0.337	-4.563	-0.323	-4.383	-0.309	-4.209	-0.296	-4.041	-0.282
0.70	-4.545	-0.455	-4.373	-0.436	-4.208	-0.418	-4.048	-0.400	-3.893	-0.382
0.65	-4.363	-0.592	-4.205	-0.569	-4.053	-0.546	-3.905	-0.523	-3.761	-0.499
0.60	-4.135	-0.769	-3.989	-0.739	-3.849	-0.710	-3.712	-0.682	-3.580	-0.653
0.55	-3.811	-0.916	-3.679	-0.874	-3.552	-0.832	-3.429	-0.791	-3.310	-0.751
0.50	-3.258	-1.199	-3.127	-1.147	-3.003	-1.096	-2.884	-1.047	-2.771	-1.000
0.45	-2.838	-1.658	-2.719	-1.593	-2.605	-1.531	-2.495	-1.472	-2.391	-1.415
0.40	-2.394	-2.259	-2.292	-2.171	-2.193	-2.088	-2.099	-2.009	-2.008	-1.933
0.35	-1.943	-3.011	-1.861	-2.890	-1.781	-2.774	-1.706	-2.663	-1.633	-2.557
0.30	-1.535	-3.860	-1.474	-3.694	-1.417	-3.534	-1.362	-3.380	-1.310	-3.231
0.25	-1.148	-4.892	-1.107	-4.673	-1.069	-4.461	-1.033	-4.257	-1.000	-4.059
0.20	-0.780	-6.154	-0.756	-5.880	-0.733	-5.615	-0.712	-5.359	-0.693	-5.112
0.15	-0.482	-7.576	-0.471	-7.233	-0.463	-6.902	-0.456	-6.582	-0.450	-6.272
0.10	-0.240	-9.258	-0.238	-8.858	-0.237	-8.473	-0.237	-8.104	-0.238	-7.748
0.05	-0.080	-11.276	-0.082	-10.823	-0.085	-10.392	-0.089	-9.980	-0.093	-9.589
0.00	0.000	-13.939	0.000	-13.661	0.000	-13.430	0.000	-13.243	0.000	-13.096

E

$\ln(\gamma_w)$, $\ln(\gamma_a)$

x_a	190.0 C		200.0 C		210.0 C		220.0 C		230.0 C	
	x^*=0.9401		x^*=0.9400		x^*=0.9399		x^*=0.9397		x^*=0.9394	
1.00	-5.987	-0.002	-5.812	-0.002	-5.649	-0.002	-5.500	-0.002	-5.365	-0.002
0.99	-5.859	0.016	-5.646	0.016	-5.441	0.015	-5.244	0.015	-5.054	0.014
0.98	-6.016	0.029	-5.783	0.029	-5.555	0.028	-5.332	0.027	-5.112	0.026
0.97	-5.993	0.032	-5.756	0.031	-5.523	0.030	-5.293	0.029	-5.066	0.027
0.96	-5.874	0.028	-5.634	0.027	-5.397	0.026	-5.161	0.024	-4.927	0.021
0.95	-5.711	0.023	-5.469	0.022	-5.229	0.020	-4.991	0.018	-4.755	0.015
0.90	-5.006	-0.017	-4.789	-0.016	-4.576	-0.016	-4.365	-0.017	-4.157	-0.018
0.85	-4.473	-0.086	-4.282	-0.081	-4.095	-0.077	-3.913	-0.073	-3.733	-0.070
0.80	-4.087	-0.179	-3.914	-0.170	-3.747	-0.162	-3.584	-0.154	-3.425	-0.146
0.75	-3.879	-0.269	-3.721	-0.256	-3.567	-0.244	-3.418	-0.231	-3.272	-0.219
0.70	-3.742	-0.364	-3.595	-0.346	-3.452	-0.328	-3.311	-0.310	-3.173	-0.293
0.65	-3.621	-0.476	-3.484	-0.453	-3.349	-0.430	-3.216	-0.407	-3.085	-0.384
0.60	-3.450	-0.624	-3.323	-0.595	-3.197	-0.565	-3.073	-0.536	-2.950	-0.507
0.55	-3.194	-0.712	-3.081	-0.673	-2.969	-0.636	-2.858	-0.600	-2.748	-0.565
0.50	-2.663	-0.954	-2.560	-0.909	-2.461	-0.865	-2.366	-0.821	-2.275	-0.779
0.45	-2.291	-1.360	-2.196	-1.306	-2.105	-1.254	-2.019	-1.201	-1.937	-1.149
0.40	-1.921	-1.860	-1.839	-1.788	-1.761	-1.718	-1.687	-1.649	-1.618	-1.580
0.35	-1.565	-2.453	-1.500	-2.352	-1.439	-2.253	-1.382	-2.155	-1.329	-2.059
0.30	-1.261	-3.087	-1.215	-2.948	-1.172	-2.812	-1.132	-2.679	-1.096	-2.549
0.25	-0.969	-3.868	-0.940	-3.683	-0.913	-3.503	-0.889	-3.328	-0.867	-3.158
0.20	-0.676	-4.871	-0.661	-4.638	-0.649	-4.412	-0.638	-4.192	-0.629	-3.977
0.15	-0.445	-5.974	-0.442	-5.685	-0.440	-5.406	-0.440	-5.137	-0.441	-4.878
0.10	-0.240	-7.406	-0.243	-7.077	-0.247	-6.760	-0.251	-6.456	-0.257	-6.164
0.05	-0.097	-9.218	-0.102	-8.866	-0.108	-8.533	-0.113	-8.220	-0.119	-7.926
0.00	0.000	-12.984	0.000	-12.904	0.000	-12.852	0.000	-12.824	0.000	-12.816

F

$\ln(\gamma_w)$, $\ln(\gamma_a)$

x_a	240.0 C		250.0 C		260.0 C		270.0 C		280.0 C	
	x^*=0.9390		x^*=0.9384		x^*=0.9375		x^*=0.9362		x^*=0.9344	
1.00	-5.243	0.002	-5.134	-0.002	-5.038	-0.003	-4.956	-0.003	-4.887	-0.003
0.99	4.871	0.013	-4.695	0.011	-4.526	0.010	-4.362	0.008	-4.205	0.006
0.98	-4.896	0.024	4.683	0.022	-4.473	0.019	-4.265	0.016	-4.059	0.012
0.97	4.841	0.025	4.617	0.022	-4.395	0.019	-4.173	0.015	-3.951	0.011
0.96	-4.694	0.019	-4.461	0.015	-4.228	0.011	-3.994	0.007	-3.759	0.002
0.95	-4.519	0.012	-4.283	0.008	-4.046	0.004	-3.808	-0.001	-3.569	-0.006
0.90	-3.951	0.019	-3.746	-0.022	-3.543	-0.025	-3.339	-0.029	-3.136	-0.033
0.85	-3.557	-0.068	-3.383	-0.065	-3.212	-0.064	-3.043	-0.063	-2.875	-0.063
0.80	-3.270	-0.138	3.119	-0.130	-2.970	-0.123	-2.825	-0.116	-2.682	-0.109
0.75	-3.129	-0.207	-2.988	-0.194	-2.850	-0.182	-2.715	-0.171	-2.581	-0.159
0.70	-3.037	0.275	-2.902	-0.257	-2.769	-0.239	-2.637	-0.221	-2.506	-0.203
0.65	-2.954	-0.360	-2.824	-0.337	-2.694	-0.313	-2.564	-0.289	-2.433	-0.265
0.60	-2.827	-0.477	-2.704	-0.447	-2.580	-0.417	-2.456	-0.387	-2.331	-0.356
0.55	-2.637	0.531	-2.527	-0.499	-2.415	-0.467	-2.302	-0.438	-2.187	-0.409
0.50	-2.188	0.738	-2.104	-0.697	-2.022	-0.656	-1.944	-0.617	-1.868	-0.577
0.45	1.860	1.097	-1.787	-1.045	-1.718	-0.991	-1.654	-0.937	-1.594	-0.881
0.40	-1.552	-1.511	-1.492	-1.441	-1.436	-1.370	-1.384	-1.298	-1.338	-1.223
0.35	-1.280	-1.962	-1.236	-1.866	-1.195	-1.769	-1.159	-1.671	-1.127	-1.572
0.30	-1.062	-2.422	-1.032	-2.296	-1.005	-2.172	-0.981	-2.050	-0.961	-1.928
0.25	-0.848	2.992	-0.830	-2.831	-0.815	-2.673	-0.802	-2.520	-0.792	-2.369
0.20	-0.622	-3.769	-0.617	-3.566	0.614	-3.367	-0.613	-3.174	-0.614	-2.986
0.15	-0.442	-4.627	-0.445	-4.387	-0.449	-4.155	-0.454	-3.932	-0.461	-3.719
0.10	-0.263	-5.883	-0.271	-5.614	-0.279	-5.356	-0.288	-5.108	-0.298	-4.871
0.05	-0.125	-7.652	0.132	-7.397	-0.139	-7.161	-0.145	-6.944	-0.153	-6.747
0.00	0.000	-12.824	0.000	-12.844	0.000	-12.874	0.000	-12.908	0.000	-12.945

G

$\ln(\gamma_w)$, $\ln(\gamma_a)$

x_a	290.0 C		300.0 C		310.0 C		320.0 C		330.0 C	
	x^*=0.9312		x^*=0.9288		x^*=0.9249		x^*=0.9213		x^*=0.9203	
1.00	-4.832	-0.003	-4.789	-0.003	-4.761	-0.003	-4.746	-0.003	-4.744	-0.004
0.99	-4.053	0.004	-3.907	0.002	-3.766	-0.001	-3.630	-0.004	-3.500	-0.007
0.98	-3.854	0.008	-3.651	0.004	-3.449	-0.002	-3.247	-0.007	-3.046	-0.014
0.97	-3.728	0.006	-3.505	0.001	-3.282	-0.005	-3.056	-0.011	-2.829	-0.018
0.96	-3.522	-0.003	-3.283	-0.009	-3.042	0.016	-2.797	-0.023	-2.549	-0.031
0.95	-3.328	-0.013	-3.084	-0.020	-2.838	-0.027	-2.588	-0.035	-2.335	-0.044
0.90	-2.933	-0.038	-2.729	-0.044	-2.524	-0.051	-2.318	-0.059	-2.111	-0.067
0.85	-2.708	-0.063	-2.543	-0.064	-2.378	-0.065	-2.213	-0.067	-2.049	-0.070
0.80	-2.542	-0.102	-2.403	-0.095	-2.267	-0.089	-2.132	-0.082	-1.999	-0.076
0.75	2.449	-0.147	2.318	-0.135	-2.188	-0.124	-2.059	-0.112	-1.931	-0.101
0.70	-2.375	-0.185	-2.244	-0.167	-2.112	-0.149	-1.981	-0.130	-1.849	-0.111
0.65	-2.301	-0.241	-2.169	-0.217	-2.035	-0.192	-1.899	-0.167	-1.761	-0.142
0.60	-2.204	-0.325	-2.075	-0.294	-1.944	-0.262	-1.810	-0.230	-1.674	-0.198
0.55	-2.070	-0.383	-1.950	-0.358	-1.827	-0.334	-1.701	-0.313	-1.571	-0.294
0.50	-1.794	-0.539	-1.723	-0.500	-1.653	-0.463	-1.585	-0.425	-1.518	-0.388
0.45	-1.538	-0.824	-1.486	-0.764	-1.439	-0.703	-1.396	-0.640	-1.357	-0.574
0.40	-1.296	-1.147	1.258	1.068	1.226	-0.986	-1.199	-0.900	-1.177	-0.811
0.35	-1.100	-1.471	-1.078	-1.367	-1.060	-1.261	-1.047	-1.152	-1.038	-1.040
0.30	-0.944	1.807	-0.930	-1.686	-0.920	-1.566	-0.913	-1.445	-0.910	-1.323
0.25	-0.784	-2.222	-0.778	-2.078	-0.774	-1.936	-0.773	-1.798	-0.774	-1.662
0.20	0.617	-2.801	0.622	-2.621	0.629	-2.446	-0.638	-2.274	-0.649	-2.105
0.15	-0.468	3.514	-0.476	-3.318	-0.485	-3.131	-0.495	-2.953	-0.506	-2.784
0.10	-0.308	-4.645	-0.320	-4.429	-0.332	-4.223	-0.345	-4.027	-0.359	-3.840
0.05	0.160	6.570	-0.167	-6.413	-0.174	-6.276	-0.182	-6.159	-0.189	-6.062
0.00	0.000	-12.980	0.000	-13.010	0.000	-13.033	0.000	-13.044	0.000	-13.042

Table VIII. Calculated Vapor Pressure of H_2O over Hypoazeotropic H_2O–H_2SO_4 Solutions

A-1

log (P_{H_2O} / bar)

X_a	T = 0.0°C	10.0°C	20.0°C	25.0°C	30.0°C	40.0°C	50.0°C
	X^* = 0.9402	0.9402	0.9402	0.9402	0.9402	0.9402	0.9402
1.00	-9.738	-9.131	-8.574	-8.311	-8.057	-7.578	-7.128
0.99	-9.333	-8.781	-8.266	-8.021	-7.784	-7.334	-6.909
0.98	-9.216	-8.664	-8.151	-7.908	-7.672	-7.224	-6.802
0.97	-9.040	-8.508	-8.011	-7.775	-7.547	-7.112	-6.702
0.96	-8.890	-8.360	-7.867	-7.633	-7.406	-6.975	-6.570
0.95	-8.726	-8.203	-7.716	-7.485	-7.262	-6.837	-6.437
0.90	-7.997	-7.483	-7.006	-6.781	-6.563	-6.149	-5.761
0.85	-7.438	-6.923	-6.446	-6.220	-6.002	-5.589	-5.203
0.80	-6.984	-6.480	-6.014	-5.794	-5.581	-5.178	-4.802
0.75	-6.657	-6.152	-5.686	-5.466	-5.254	-4.852	-4.477
0.70	-6.346	-5.859	-5.410	-5.199	-4.994	-4.608	-4.249
0.65	-6.096	-5.613	-5.167	-4.957	-4.755	-4.371	-4.015
0.60	-5.831	-5.357	-4.920	-4.714	-4.515	-4.138	-3.788
0.55	-5.507	-5.057	-4.640	-4.443	-4.253	-3.892	-3.556
0.50	-5.120	-4.700	-4.309	-4.124	-3.945	-3.606	-3.288
0.45	-4.700	-4.304	-3.937	-3.762	-3.594	-3.273	-2.973
0.40	-4.300	-3.922	-3.571	-3.404	-3.244	-2.938	-2.651
0.35	-3.917	-3.553	-3.215	-3.054	-2.900	-2.606	-2.331
0.30	-3.550	-3.199	-2.873	-2.720	-2.571	-2.289	-2.026
0.25	-3.208	-2.869	-2.555	-2.407	-2.264	-1.993	-1.740
0.20	-2.902	-2.573	-2.269	-2.126	-1.988	-1.726	-1.483
0.15	-2.639	-2.319	-2.024	-1.885	-1.751	-1.497	-1.262
0.10	-2.427	-2.115	-1.828	-1.693	-1.563	-1.316	-1.087
0.05	-2.280	-1.975	-1.694	-1.561	-1.433	-1.192	-0.967
0.00	-2.214	-1.911	-1.631	-1.499	-1.372	-1.132	-0.909

A-2

log (P_{H_2O} / bar)

X_a	T = 60.0°C	70.0°C	80.0°C	90.0°C	100.0°C	110.0°C	120.0°C
	X^* = 0.9402	0.9402	0.9402	0.9402	0.9402	0.9402	0.9402
1.00	-6.707	-6.311	-5.938	-5.586	-5.253	-4.938	-4.640
0.99	-6.510	-6.132	-5.775	-5.437	-5.117	-4.813	-4.524
0.98	-6.405	-6.030	-5.676	-5.341	-5.023	-4.721	-4.434
0.97	-6.317	-5.952	-5.607	-5.280	-4.969	-4.674	-4.393
0.96	-6.188	-5.828	-5.487	-5.164	-4.857	-4.566	-4.288
0.95	-6.061	-5.707	-5.371	-5.053	-4.751	-4.464	-4.191
0.90	-5.398	-5.056	-4.734	-4.429	-4.141	-3.868	-3.608
0.85	-4.842	-4.503	-4.184	-3.884	-3.600	-3.331	-3.076
0.80	-4.450	-4.121	-3.811	-3.519	-3.243	-2.983	-2.736
0.75	-4.127	-3.800	-3.492	-3.203	-2.930	-2.672	-2.428
0.70	-3.913	-3.599	-3.304	-3.028	-2.767	-2.521	-2.289
0.65	-3.682	-3.371	-3.080	-2.806	-2.548	-2.305	-2.075
0.60	-3.461	-3.155	-2.869	-2.599	-2.346	-2.107	-1.882
0.55	-3.243	-2.949	-2.674	-2.416	-2.173	-1.944	-1.729
0.50	-2.990	-2.710	-2.448	-2.200	-1.967	-1.748	-1.540
0.45	-2.690	-2.425	-2.175	-1.939	-1.715	-1.504	-1.304
0.40	-2.382	-2.129	-1.890	-1.665	-1.452	-1.250	-1.058
0.35	-2.073	-1.831	-1.603	-1.387	-1.184	-0.992	-0.810
0.30	-1.779	-1.548	-1.331	-1.127	-0.934	-0.752	-0.580
0.25	-1.504	-1.283	-1.076	-0.882	-0.699	-0.526	-0.364
0.20	-1.255	-1.043	-0.844	-0.657	-0.482	-0.317	-0.162
0.15	-1.042	-0.837	-0.646	-0.467	-0.299	-0.141	0.007
0.10	-0.874	-0.675	-0.489	-0.315	-0.152	0.001	0.145
0.05	-0.758	-0.563	-0.380	-0.209	-0.049	0.101	0.242
0.00	-0.701	-0.506	-0.325	-0.154	0.006	0.156	0.298

A-3

log (P_{H_2O} / bar)

X_a	T = 130.0°C	140.0°C	150.0°C	160.0°C	170.0°C	180.0°C	190.0 °
	X^* = 0.9402	0.9402	0.9402	0.9402	0.9401	0.9401	0.9401
1.00	-4.356	-4.085	-3.828	-3.582	-3.345	-3.119	-2.900
0.99	-4.249	-3.985	-3.735	-3.495	-3.265	-3.043	-2.830
0.98	-4.161	-3.899	-3.650	-3.411	-3.182	-2.961	-2.749
0.97	-4.124	-3.867	-3.622	-3.386	-3.160	-2.942	-2.731
0.96	-4.023	-3.769	-3.527	-3.293	-3.069	-2.853	-2.644
0.95	-3.929	-3.679	-3.439	-3.208	-2.987	-2.772	-2.565
0.90	-3.360	-3.123	-2.896	-2.679	-2.470	-2.268	-2.074
0.85	-2.834	-2.603	-2.383	-2.172	-1.971	-1.777	-1.591
0.80	-2.502	-2.280	-2.068	-1.866	-1.672	-1.487	-1.309
0.75	-2.197	-1.978	-1.769	-1.569	-1.379	-1.196	-1.021
0.70	-2.068	-1.859	-1.659	-1.469	-1.287	-1.113	-0.946
0.65	-1.857	-1.650	-1.453	-1.265	-1.085	-0.913	-0.747
0.60	-1.668	-1.464	-1.271	-1.087	-0.910	-0.741	-0.578
0.55	-1.524	-1.331	-1.147	-0.971	-0.804	-0.644	-0.490
0.50	-1.344	-1.158	-0.981	-0.814	-0.655	-0.503	-0.359
0.45	-1.114	-0.934	-0.763	-0.600	-0.445	-0.297	-0.156
0.40	-0.876	-0.704	-0.540	-0.383	-0.234	-0.093	0.042
0.35	-0.637	-0.473	-0.318	-0.170	-0.029	0.105	0.232
0.30	-0.418	-0.264	-0.118	0.021	0.152	0.277	0.396
0.25	-0.210	-0.065	0.072	0.202	0.325	0.442	0.553
0.20	-0.016	0.122	0.253	0.376	0.493	0.603	0.708
0.15	0.147	0.278	0.402	0.519	0.630	0.735	0.835
0.10	0.280	0.408	0.529	0.642	0.750	0.852	0.949
0.05	0.376	0.501	0.620	0.732	0.838	0.939	1.034
0.00	0.432	0.558	0.678	0.791	0.899	1.001	1.099

A-4

log (P_{H_2O} / bar)

X_a	T = 200.0°C	210.0°C	220.0°C	230.0°C	240.0°C	250.0°C	260.0°C
	X^* = 0.9400	0.9399	0.9397	0.9394	0.9390	0.9384	0.9375
1.00	-2.690	-2.486	-2.288	-2.096	-1.908	-1.725	-1.545
0.99	-2.625	-2.426	-2.232	-2.045	-1.862	-1.683	-1.508
0.98	-2.544	-2.346	-2.153	-1.966	-1.783	-1.605	-1.431
0.97	-2.529	-2.332	-2.141	-1.955	-1.773	-1.596	-1.422
0.96	-2.443	-2.246	-2.056	-1.870	-1.689	-1.511	-1.337
0.95	-2.365	-2.170	-1.981	-1.796	-1.615	-1.438	-1.264
0.90	-1.886	-1.703	-1.525	-1.352	-1.184	-1.019	-0.857
0.85	-1.411	-1.238	-1.070	-0.908	-0.750	-0.596	-0.446
0.80	-1.138	-0.974	-0.815	-0.662	-0.514	-0.370	-0.231
0.75	-0.853	-0.692	-0.535	-0.385	-0.239	-0.097	0.040
0.70	-0.785	-0.630	-0.480	-0.334	-0.194	-0.057	0.077
0.65	-0.587	-0.433	-0.284	-0.139	0.002	0.139	0.273
0.60	-0.422	-0.270	-0.123	0.019	0.158	0.293	0.425
0.55	-0.342	-0.199	-0.061	0.073	0.204	0.331	0.456
0.50	-0.221	-0.089	0.037	0.158	0.274	0.386	0.493
0.45	-0.022	0.107	0.229	0.346	0.458	0.564	0.666
0.40	0.171	0.294	0.411	0.522	0.629	0.730	0.826
0.35	0.353	0.468	0.578	0.682	0.781	0.876	0.965
0.30	0.509	0.616	0.719	0.816	0.908	0.996	1.080
0.25	0.658	0.759	0.854	0.945	1.032	1.114	1.192
0.20	0.807	0.902	0.991	1.077	1.158	1.235	1.308
0.15	0.929	1.019	1.104	1.185	1.262	1.335	1.406
0.10	1.040	1.128	1.210	1.289	1.364	1.436	1.504
0.05	1.125	1.211	1.294	1.373	1.448	1.520	1.589
0.00	1.192	1.280	1.365	1.447	1.525	1.599	1.671

A-5

log (P_{H_2O} / bar)

X_a	T = 270.0°C	280.0°C	290.0°C	300.0°C	310.0°C	320.0°C	330.0°C
	X^* = 0.9362	0.9344	0.9312	0.9288	0.9249	0.9213	0.9203
1.00	-1.368	-1.194	-1.022	-0.851	-0.681	-0.512	-0.346
0.99	-1.335	-1.165	-0.998	-0.831	-0.665	-0.500	-0.338
0.98	-1.259	-1.091	-0.925	-0.760	-0.596	-0.434	-0.275
0.97	-1.250	-1.082	-0.916	-0.751	-0.587	-0.424	-0.264
0.96	-1.165	-0.996	-0.829	-0.663	-0.498	-0.334	-0.172
0.95	-1.093	-0.924	-0.757	-0.590	-0.425	-0.260	-0.098
0.90	-0.698	-0.541	-0.387	-0.234	-0.082	0.068	0.217
0.85	-0.300	-0.157	-0.016	0.122	0.258	0.392	0.525
0.80	-0.095	0.036	0.165	0.292	0.415	0.536	0.655
0.75	0.173	0.304	0.431	0.556	0.678	0.797	0.915
0.70	0.207	0.335	0.460	0.583	0.704	0.824	0.942
0.65	0.405	0.534	0.661	0.786	0.910	1.033	1.154
0.60	0.555	0.682	0.808	0.933	1.056	1.178	1.300
0.55	0.579	0.700	0.819	0.938	1.056	1.173	1.290
0.50	0.596	0.696	0.793	0.887	0.978	1.067	1.154
0.45	0.763	0.856	0.945	1.030	1.111	1.189	1.263
0.40	0.918	1.005	1.087	1.166	1.241	1.311	1.378
0.35	1.050	1.131	1.207	1.279	1.347	1.412	1.472
0.30	1.160	1.235	1.307	1.375	1.440	1.502	1.560
0.25	1.267	1.338	1.406	1.471	1.533	1.592	1.648
0.20	1.377	1.444	1.507	1.567	1.624	1.679	1.731
0.15	1.473	1.536	1.598	1.657	1.713	1.767	1.819
0.10	1.570	1.632	1.692	1.749	1.804	1.857	1.908
0.05	1.655	1.719	1.780	1.839	1.896	1.952	2.005
0.00	1.740	1.807	1.872	1.934	1.994	2.053	2.109

B-1

log ($P_{H_2SO_4}$ / bar)

X_a	T = 0.0°C	10.0°C	20.0°C	25.0°C	30.0°C	40.0°C	50.0°C
	X^* = 0.9402	0.9402	0.9402	0.9402	0.9402	0.9402	0.9402
1.00	-8.712	-8.147	-7.626	-7.380	-7.144	-6.697	-6.281
0.99	-8.704	-8.139	-7.617	-7.371	-7.134	-6.686	-6.270
0.98	-8.707	-8.141	-7.618	-7.371	-7.134	-6.685	-6.268
0.97	-8.710	-8.143	-7.621	-7.374	-7.137	-6.688	-6.271
0.96	-8.717	-8.150	-7.626	-7.379	-7.142	-6.692	-6.274
0.95	-8.725	-8.158	-7.634	-7.386	-7.149	-6.699	-6.280
0.90	-8.784	-8.216	-7.692	-7.445	-7.207	-6.755	-6.336
0.85	-8.863	-8.296	-7.772	-7.525	-7.287	-6.836	-6.416
0.80	-8.960	-8.390	-7.863	-7.615	-7.376	-6.922	-6.500
0.75	-9.059	-8.487	-7.959	-7.710	-7.470	-7.015	-6.591
0.70	-9.176	-8.598	-8.064	-7.811	-7.568	-7.107	-6.678
0.65	-9.296	-8.717	-8.180	-7.927	-7.683	-7.221	-6.790
0.60	-9.457	-8.871	-8.330	-8.074	-7.828	-7.361	-6.927
0.55	-9.697	-9.094	-8.538	-8.275	-8.023	-7.544	-7.098
0.50	-10.049	-9.418	-8.838	-8.564	-8.301	-7.804	-7.342
0.45	-10.510	-9.853	-9.247	-8.962	-8.688	-8.169	-7.688
0.40	-11.052	-10.371	-9.743	-9.447	-9.162	-8.624	-8.124
0.35	-11.691	-10.988	-10.338	-10.032	-9.737	-9.178	-8.659
0.30	-12.455	-11.724	-11.048	-10.728	-10.421	-9.837	-9.293
0.25	-13.355	-12.593	-11.887	-11.553	-11.231	-10.619	-10.048
0.20	-14.414	-13.615	-12.873	-12.522	-12.183	-11.539	-10.936
0.15	-15.661	-14.820	-14.038	-13.667	-13.309	-12.626	-11.986
0.10	-17.152	-16.250	-15.410	-15.012	-14.627	-13.894	-13.206
0.05	-18.965	-17.965	-17.084	-16.655	-16.242	-15.447	-14.708
0.00							

Table VIII (Continued)

B-2

log ($P_{H_2SO_4}$ / bar)

X_a	T = 60.0°C	70.0°C	80.0°C	90.0°C	100.0°C	110.0°C	120.0 °
	X^* = 0.9402	0.9402	0.9402	0.9402	0.9402	0.9402	0.9402
1.00	-5.894	-5.534	-5.196	-4.879	-4.582	-4.302	-4.038
0.99	-5.882	-5.522	-5.183	-4.865	-4.567	-4.287	-4.023
0.98	-5.879	-5.517	-5.177	-4.858	-4.559	-4.277	-4.011
0.97	-5.882	-5.520	-5.181	-4.862	-4.563	-4.281	-4.017
0.96	-5.884	-5.521	-5.181	-4.861	-4.561	-4.278	-4.013
0.95	-5.890	-5.526	-5.185	-4.865	-4.564	-4.281	-4.015
0.90	-5.944	-5.579	-5.236	-4.913	-4.610	-4.325	-4.055
0.85	-6.024	-5.659	-5.316	-4.992	-4.689	-4.402	-4.131
0.80	-6.106	-5.739	-5.393	-5.068	-4.762	-4.473	-4.201
0.75	-6.195	-5.826	-5.478	-5.151	-4.844	-4.553	-4.279
0.70	-6.276	-5.902	-5.550	-5.218	-4.905	-4.610	-4.331
0.65	-6.387	-6.011	-5.658	-5.324	-5.010	-4.713	-4.433
0.60	-6.521	-6.141	-5.785	-5.448	-5.132	-4.832	-4.549
0.55	-6.683	-6.294	-5.929	-5.585	-5.260	-4.954	-4.664
0.50	-6.912	-6.511	-6.135	-5.781	-5.448	-5.134	-4.838
0.45	-7.240	-6.824	-6.434	-6.068	-5.724	-5.401	-5.097
0.40	-7.659	-7.226	-6.820	-6.439	-6.083	-5.747	-5.430
0.35	-8.175	-7.724	-7.300	-6.903	-6.529	-6.177	-5.845
0.30	-8.785	-8.311	-7.865	-7.444	-7.049	-6.675	-6.322
0.25	-9.513	-9.012	-8.540	-8.094	-7.673	-7.274	-6.897
0.20	-10.371	-9.840	-9.339	-8.866	-8.418	-7.994	-7.590
0.15	-11.384	-10.817	-10.281	-9.772	-9.290	-8.832	-8.396
0.10	-12.559	-11.951	-11.375	-10.830	-10.314	-9.823	-9.357
0.05	-14.013	-13.3[illegible]0	-12.743	-12.160	-11.608	-11.085	-10.588
0.00							

B-3

log ($P_{H_2SO_4}$ / bar)

XI	T =130.0°C	140.0°C	150.0°C	160.0°C	170.0°C	180.0°C	190.0°C
	X*= 0.9402	0.9402	0.9402	0.9402	0.9401	0.9401	0.9401
1.00	-3.788	-3.552	-3.326	-3.109	-2.903	-2.704	-2.511
0.99	-3.772	-3.535	-3.310	-3.093	-2.886	-2.687	-2.496
0.98	-3.759	-3.521	-3.294	-3.076	-2.868	-2.668	-2.475
0.97	-3.765	-3.527	-3.300	-3.083	-2.876	-2.676	-2.484
0.96	-3.760	-3.521	-3.294	-3.075	-2.867	-2.667	-2.474
0.95	-3.762	-3.522	-3.294	-3.075	-2.866	-2.666	-2.472
0.90	-3.799	-3.557	-3.325	-3.103	-2.891	-2.687	-2.491
0.85	-3.874	-3.630	-3.397	-3.172	-2.959	-2.753	-2.554
0.80	-3.941	-3.695	-3.460	-3.233	-3.017	-2.809	-2.608
0.75	-4.017	-3.769	-3.532	-3.304	-3.085	-2.875	-2.672
0.70	-4.065	-3.813	-3.571	-3.339	-3.116	-2.902	-2.695
0.65	-4.165	-3.911	-3.668	-3.434	-3.209	-2.993	-2.784
0.60	-4.279	-4.023	-3.777	-3.540	-3.313	-3.094	-2.882
0.55	-4.387	-4.124	-3.873	-3.630	-3.398	-3.175	-2.958
0.50	-4.556	-4.289	-4.033	-3.786	-3.551	-3.324	-3.105
0.45	-4.807	-4.534	-4.272	-4.021	-3.781	-3.550	-3.327
0.40	-5.130	-4.846	-4.574	-4.314	-4.065	-3.826	-3.595
0.35	-5.529	-5.230	-4.944	-4.670	-4.407	-4.155	-3.910
0.30	-5.985	-5.666	-5.360	-5.066	-4.785	-4.515	-4.253
0.25	-6.536	-6.194	-5.865	-5.548	-5.246	-4.953	-4.671
0.20	-7.205	-6.838	-6.486	-6.147	-5.821	-5.507	-5.203
0.15	-7.979	-7.581	-7.199	-6.830	-6.477	-6.136	-5.807
0.10	-8.912	-8.487	-8.080	-7.689	-7.314	-6.953	-6.605
0.05	-10.115	-9.665	-9.235	-8.823	-8.430	-8.054	-7.693
0.00							

B-4

log ($P_{H_2SO_4}$ / bar)

X_a	T = 200.0°C	210.0°C	220.0°C	230.0°C	240.0°C	250.0°C	260.0°C
	X_*= 0.9400	0.9399	0.9397	0.9394	0.9390	0.9384	0.9375
1.00	-2.325	-2.142	-1.963	-1.789	-1.615	-1.442	-1.271
0.99	-2.309	-2.127	-1.949	-1.776	-1.604	-1.433	-1.264
0.98	-2.288	-2.105	-1.927	-1.753	-1.580	-1.409	-1.240
0.97	-2.297	-2.115	-1.937	-1.764	-1.592	-1.421	-1.253
0.96	-2.286	-2.104	-1.925	-1.751	-1.579	-1.408	-1.239
0.95	-2.284	-2.101	-1.922	-1.748	-1.575	-1.404	-1.236
0.90	-2.300	-2.114	-1.933	-1.757	-1.583	-1.411	-1.242
0.85	-2.361	-2.172	-1.989	-1.811	-1.634	-1.459	-1.288
0.80	-2.412	-2.221	-2.035	-1.854	-1.674	-1.497	-1.323
0.75	-2.474	-2.281	-2.092	-1.909	-1.727	-1.547	-1.371
0.70	-2.493	-2.296	-2.103	-1.916	-1.730	-1.546	-1.365
0.65	-2.580	-2.381	-2.186	-1.997	-1.808	-1.622	-1.439
0.60	-2.676	-2.474	-2.276	-2.084	-1.893	-1.704	-1.518
0.55	-2.747	-2.542	-2.342	-2.147	-1.954	-1.764	-1.577
0.50	-2.891	-2.683	-2.479	-2.281	-2.085	-1.891	-1.701
0.45	-3.109	-2.897	-2.690	-2.487	-2.286	-2.087	-1.891
0.40	-3.370	-3.150	-2.935	-2.725	-2.517	-2.310	-2.107
0.35	-3.672	-3.440	-3.213	-2.991	-2.771	-2.553	-2.338
0.30	-3.998	-3.750	-3.507	-3.271	-3.037	-2.807	-2.580
0.25	-4.396	-4.129	-3.868	-3.615	-3.364	-3.118	-2.876
0.20	-4.908	-4.620	-4.340	-4.067	-3.798	-3.534	-3.275
0.15	-5.488	-5.177	-4.876	-4.583	-4.296	-4.015	-3.741
0.10	-6.268	-5.941	-5.625	-5.318	-5.017	-4.724	-4.439
0.05	-7.346	-7.012	-6.692	-6.384	-6.087	-5.800	-5.524
0.00							

B-5

log ($P_{H_2SO_4}$ / bar)

X_a	T = 270.0°C	280.0°C	290.0°C	300.0°C	310.0°C	320.0°C	330.0°C
	X^* = 0.9362	0.9344	0.9312	0.9288	0.9249	0.9213	0.9203
1.00	-1.100	-0.929	-0.756	-0.582	-0.406	-0.228	-0.048
0.99	-1.095	-0.925	-0.755	-0.583	-0.410	-0.234	-0.056
0.98	-1.072	-0.903	-0.734	-0.563	-0.392	-0.219	-0.043
0.97	-1.085	-0.916	-0.747	-0.578	-0.407	-0.234	-0.059
0.96	-1.071	-0.902	-0.734	-0.564	-0.393	-0.221	-0.046
0.95	-1.068	-0.900	-0.731	-0.562	-0.392	-0.221	-0.047
0.90	-1.073	-0.906	-0.739	-0.571	-0.403	-0.234	-0.063
0.85	-1.118	-0.948	-0.779	-0.611	-0.441	-0.271	-0.099
0.80	-1.149	-0.976	-0.804	-0.632	-0.459	-0.285	-0.109
0.75	-1.195	-1.019	-0.844	-0.669	-0.494	-0.317	-0.138
0.70	-1.185	-1.006	-0.827	-0.648	-0.468	-0.287	-0.104
0.65	-1.256	-1.074	-0.892	-0.711	-0.528	-0.345	-0.159
0.60	-1.332	-1.147	-0.962	-0.778	-0.592	-0.406	-0.217
0.55	-1.392	-1.208	-1.025	-0.843	-0.661	-0.479	-0.296
0.50	-1.511	-1.323	-1.134	-0.947	-0.759	-0.570	-0.380
0.45	-1.695	-1.499	-1.303	-1.106	-0.908	-0.708	-0.505
0.40	-1.903	-1.699	-1.494	-1.289	-1.081	-0.872	-0.658
0.35	-2.123	-1.908	-1.692	-1.476	-1.259	-1.039	-0.815
0.30	-2.354	-2.129	-1.905	-1.681	-1.457	-1.232	-1.005
0.25	-2.637	-2.400	-2.164	-1.931	-1.697	-1.464	-1.230
0.20	-3.018	-2.764	-2.513	-2.263	-2.015	-1.768	-1.520
0.15	-3.472	-3.208	-2.947	-2.691	-2.438	-2.188	-1.939
0.10	-4.159	-3.884	-3.614	-3.349	-3.088	-2.830	-2.574
0.05	-5.257	-5.000	-4.751	-4.512	-4.280	-4.057	-3.839
0.00							

C-1

log (P_{SO_3} / bar)

X_a	T = 0.0°C	10.0°C	20.0°C	25.0°C	30.0°C	40.0°C	50.0°C
	X^* = 0.9402	0.9402	0.9402	0.9402	0.9402	0.9402	0.9402
1.00	-10.166	-9.539	-8.952	-8.673	-8.404	-7.890	-7.413
0.99	-10.562	-9.881	-9.251	-8.953	-8.667	-8.124	-7.620
0.98	-10.682	-10.000	-9.367	-9.068	-8.780	-8.234	-7.726
0.97	-10.861	-10.159	-9.510	-9.203	-8.908	-8.348	-7.828
0.96	-11.019	-10.313	-9.659	-9.351	-9.053	-8.489	-7.964
0.95	-11.190	-10.478	-9.817	-9.505	-9.205	-8.634	-8.102
0.90	-11.979	-11.257	-10.586	-10.268	-9.961	-9.379	-8.834
0.85	-12.616	-11.896	-11.227	-10.909	-10.602	-10.019	-9.473
0.80	-13.167	-12.433	-11.750	-11.425	-11.112	-10.516	-9.958
0.75	-13.593	-12.858	-12.173	-11.848	-11.534	-10.935	-10.373
0.70	-14.022	-13.262	-12.553	-12.217	-11.891	-11.271	-10.689
0.65	-14.392	-13.627	-12.913	-12.574	-12.247	-11.622	-11.035
0.60	-14.817	-14.037	-13.310	-12.964	-12.631	-11.995	-11.399
0.55	-15.382	-14.561	-13.798	-13.436	-13.088	-12.424	-11.802
0.50	-16.120	-15.242	-14.428	-14.044	-13.674	-12.971	-12.314
0.45	-17.002	-16.072	-15.210	-14.803	-14.411	-13.668	-12.975
0.40	-17.944	-16.973	-16.072	-15.647	-15.236	-14.458	-13.732
0.35	-18.965	-17.959	-17.024	-16.581	-16.155	-15.344	-14.588
0.30	-20.096	-19.048	-18.074	-17.613	-17.167	-16.320	-15.527
0.25	-21.338	-20.247	-19.232	-18.750	-18.285	-17.398	-16.567
0.20	-22.704	-21.565	-20.504	-20.000	-19.513	-18.584	-17.713
0.15	-24.214	-23.025	-21.915	-21.387	-20.876	-19.901	-18.984
0.10	-25.917	-24.658	-23.482	-22.923	-22.382	-21.350	-20.378
0.05	-27.876	-26.513	-25.290	-24.698	-24.127	-23.027	-22.001
0.00							

C-2

log (P_{SO_3} / bar)

X_a	T = 60.0°C	70.0°C	80.0°C	90.0°C	100.0°C	110.0°C	120.0°C
	X^* = 0.9402	0.9402	0.9402	0.9402	0.9402	0.9402	0.9402
1.00	-6.965	-6.547	-6.153	-5.782	-5.434	-5.105	-4.794
0.99	-7.151	-6.713	-6.303	-5.918	-5.556	-5.216	-4.895
0.98	-7.252	-6.810	-6.396	-6.007	-5.641	-5.297	-4.973
0.97	-7.344	-6.892	-6.469	-6.072	-5.700	-5.349	-5.020
0.96	-7.474	-7.017	-6.589	-6.186	-5.809	-5.454	-5.120
0.95	-7.606	-7.143	-6.709	-6.301	-5.919	-5.559	-5.220
0.90	-8.324	-7.847	-7.397	-6.974	-6.575	-6.198	-5.843
0.85	-8.960	-8.480	-8.026	-7.598	-7.195	-6.812	-6.451
0.80	-9.434	-8.942	-8.477	-8.039	-7.624	-7.232	-6.860
0.75	-9.845	-9.350	-8.881	-8.438	-8.020	-7.622	-7.246
0.70	-10.141	-9.627	-9.140	-8.679	-8.244	-7.830	-7.438
0.65	-10.483	-9.964	-9.473	-9.008	-8.568	-8.150	-7.753
0.60	-10.838	-10.310	-9.811	-9.338	-8.891	-8.466	-8.063
0.55	-11.218	-10.669	-10.150	-9.658	-9.193	-8.751	-8.331
0.50	-11.700	-11.124	-10.582	-10.070	-9.587	-9.128	-8.694
0.45	-12.328	-11.723	-11.154	-10.619	-10.115	-9.638	-9.188
0.40	-13.054	-12.420	-11.825	-11.264	-10.737	-10.238	-9.768
0.35	-13.879	-13.216	-12.593	-12.005	-11.451	-10.927	-10.431
0.30	-14.784	-14.086	-13.429	-12.807	-12.221	-11.665	-11.137
0.25	-15.787	-15.053	-14.359	-13.702	-13.080	-12.490	-11.929
0.20	-16.893	-16.121	-15.390	-14.698	-14.042	-13.418	-12.824
0.15	-18.120	-17.304	-16.530	-15.795	-15.097	-14.433	-13.799
0.10	-19.463	-18.599	-17.781	-17.004	-16.267	-15.566	-14.898
0.05	-21.033	-20.121	-19.258	-18.440	-17.664	-16.927	-16.226
0.00							

Table VIII (Continued)

C-3

log (P_{SO_3} / bar)

x_a	T = 130.0°C	140.0°C	150.0°C	160.0°C	170.0°C	180.0°C	190.0°C
	x^* = 0.9402	0.9402	0.9402	0.9402	0.9401	0.9401	0.9401
1.00	-4.499	-4.220	-3.953	-3.698	-3.455	-3.223	-3.001
0.99	-4.591	-4.304	-4.030	-3.768	-3.520	-3.282	-3.055
0.98	-4.665	-4.376	-4.099	-3.835	-3.584	-3.345	-3.116
0.97	-4.708	-4.414	-4.134	-3.867	-3.614	-3.372	-3.141
0.96	-4.804	-4.506	-4.222	-3.952	-3.696	-3.452	-3.219
0.95	-4.899	-4.598	-4.310	-4.037	-3.778	-3.531	-3.296
0.90	-5.506	-5.188	-4.884	-4.594	-4.320	-4.057	-3.806
0.85	-6.107	-5.781	-5.469	-5.170	-4.886	-4.614	-4.352
0.80	-6.506	-6.169	-5.847	-5.538	-5.244	-4.960	-4.688
0.75	-6.887	-6.546	-6.219	-5.905	-5.605	-5.317	-5.039
0.70	-7.064	-6.708	-6.367	-6.040	-5.728	-5.427	-5.138
0.65	-7.375	-7.015	-6.670	-6.339	-6.022	-5.718	-5.426
0.60	-7.678	-7.312	-6.961	-6.624	-6.301	-5.991	-5.693
0.55	-7.930	-7.548	-7.181	6.829	-6.493	-6.169	-5.857
0.50	-8.279	-7.885	-7.506	-7.143	-6.794	-6.459	-6.135
0.45	-8.760	-8.353	-7.965	-7.591	-7.235	-6.891	-6.560
0.40	-9.320	-8.896	-8.490	-8.101	-7.729	-7.371	-7.026
0.35	-9.959	-9.511	-9.082	-8.671	-8.277	-7.897	-7.531
0.30	-10.635	-10.156	-9.698	-9.258	-8.836	-8.430	-8.038
0.25	-11.393	-10.882	-10.392	-9.921	-9.469	-9.033	-8.613
0.20	-12.256	-11.714	-11.194	-10.693	-10.212	-9.749	-9.300
0.15	-13.193	-12.613	-12.056	-11.520	-11.006	-10.510	-10.031
0.10	-14.259	-13.649	-13.064	-12.502	-11.963	-11.443	-10.943
0.05	-15.557	-14.920	-14.310	-13.725	-13.166	-12.630	-12.116
0.00							

C-5

log (P_{SO_3} / bar)

x_a	T = 270.0°C	280.0°C	290.0°C	300.0°C	310.0°C	320.0°C	330.0°C
	x^* = 0.9362	0.9344	0.9312	0.9288	0.9249	0.9213	0.9203
1.00	-1.455	-1.283	-1.114	-0.949	-0.786	-0.625	-0.464
0.99	-1.483	-1.308	-1.137	-0.970	-0.805	-0.643	-0.480
0.98	-1.535	-1.360	-1.189	-1.021	-0.856	-0.694	-0.531
0.97	-1.557	-1.383	-1.212	-1.045	-0.881	-0.719	-0.557
0.96	-1.629	-1.455	-1.285	-1.119	-0.956	-0.796	-0.637
0.95	-1.698	-1.524	-1.355	-1.190	-1.028	-0.869	-0.711
0.90	-2.099	-1.913	-1.732	-1.555	-1.382	-1.211	-1.042
0.85	-2.541	-2.341	-2.144	-1.950	-1.760	-1.573	-1.386
0.80	-2.777	-2.562	-2.350	-2.141	-1.935	-1.730	-1.527
0.75	-3.091	-2.872	-2.655	-2.442	-2.232	-2.023	-1.816
0.70	-3.116	-2.889	-2.667	-2.448	-2.233	-2.020	-1.809
0.65	-3.384	-3.157	-2.934	-2.715	-2.499	-2.286	-2.075
0.60	-3.610	-3.378	-3.151	-2.928	-2.709	-2.493	-2.279
0.55	-3.694	-3.457	-3.225	-2.999	-2.778	-2.561	-2.349
0.50	-3.831	-3.568	-3.308	-3.052	-2.798	-2.547	-2.296
0.45	-4.182	-3.904	-3.628	-3.354	-3.080	-2.806	-2.531
0.40	-4.544	-4.252	-3.962	-3.673	-3.383	-3.092	-2.799
0.35	-4.896	-4.587	-4.280	-3.973	-3.667	-3.359	-3.050
0.30	-5.237	-4.913	-4.592	-4.275	-3.958	-3.643	-3.326
0.25	-5.627	-5.287	-4.951	-4.620	-4.291	-3.965	-3.641
0.20	-6.119	-5.757	-5.400	-5.048	-4.700	-4.355	-4.013
0.15	-6.668	-6.293	-5.925	-5.565	-5.211	-4.864	-4.520
0.10	-7.452	-7.065	-6.686	-6.316	-5.952	-5.596	-5.244
0.05	-8.636	-8.267	-7.912	-7.569	-7.237	-6.917	-6.607
0.00							

D-2

log (P_t / bar)

x_a	T = 60.0°C	70.0°C	80.0°C	90.0°C	100.0°C	110.0°C	120.0°C
	x^* = 0.9402	0.9402	0.9402	0.9402	0.9402	0.9402	0.9402
1.00	-5.801	-5.432	-5.085	-4.758	-4.450	-4.159	-3.884
0.99	-5.772	-5.404	-5.059	-4.733	-4.426	-4.136	-3.862
0.98	-5.752	-5.384	-5.038	-4.712	-4.404	-4.114	-3.839
0.97	-5.735	-5.370	-5.027	-4.702	-4.397	-4.108	-3.835
0.96	-5.702	-5.338	-4.995	-4.672	-4.367	-4.079	-3.806
0.95	-5.661	-5.300	-4.960	-4.638	-4.335	-4.048	-3.777
0.90	-5.289	-4.942	-4.614	-4.305	-4.013	-3.736	-3.473
0.85	-4.814	-4.474	-4.153	-3.851	-3.565	-3.295	-3.039
0.80	-4.441	-4.110	-3.799	-3.507	-3.230	-2.969	-2.722
0.75	-4.124	-3.795	-3.487	-3.198	-2.924	-2.666	-2.422
0.70	-3.911	-3.597	-3.302	-3.025	-2.764	-2.518	-2.285
0.65	-3.681	-3.370	-3.079	-2.805	-2.547	-2.303	-2.073
0.60	-3.460	-3.155	-2.868	-2.599	-2.345	-2.106	-1.881
0.55	-3.242	-2.949	-2.674	-2.416	-2.173	-1.944	-1.728
0.50	-2.990	-2.710	-2.447	-2.200	-1.967	-1.748	-1.540
0.45	-2.690	-2.425	-2.175	-1.938	-1.715	-1.504	-1.304
0.40	-2.382	-2.129	-1.890	-1.665	-1.452	-1.250	-1.058
0.35	-2.073	-1.831	-1.603	-1.387	-1.184	-0.992	-0.810
0.30	-1.779	-1.548	-1.331	-1.127	-0.934	-0.752	-0.580
0.25	-1.504	-1.283	-1.076	-0.882	-0.699	-0.526	-0.364
0.20	-1.255	-1.043	-0.844	-0.657	-0.482	-0.317	-0.162
0.15	-1.042	-0.837	-0.646	-0.467	-0.299	-0.141	0.007
0.10	-0.874	-0.675	-0.489	-0.315	-0.152	0.001	0.145
0.05	-0.758	-0.563	-0.380	-0.209	-0.049	0.101	0.242
0.00	0.701	-0.506	-0.325	-0.154	0.006	0.156	0.298

C-4

log (P_{SO_3} / bar)

x_a	T = 200.0°C	210.0°C	220.0°C	230.0°C	240.0°C	250.0°C	260.0°C
	x^* = 0.940	0.9399	0.9397	0.9394	0.9390	0.9384	0.9375
1.00	-2.785	-2.577	-2.377	-2.183	-1.994	-1.810	-1.631
0.99	-2.835	-2.623	-2.419	-2.222	-2.030	-1.842	-1.661
0.98	-2.894	-2.681	-2.475	-2.278	-2.084	-1.896	-1.714
.97	-2.918	-2.704	-2.498	-2.300	-2.106	-1.918	-1.736
0.96	-2.994	-2.778	-2.571	-2.372	-2.178	-1.989	-1.807
0.95	-3.069	-2.852	-2.643	-2.443	-2.248	-2.058	-1.876
0.90	-3.565	-3.332	-3.109	-2.895	-2.687	-2.484	-2.289
0.85	-4.099	-3.856	-3.620	-3.393	-3.172	-2.956	-2.746
0.80	-4.424	-4.169	-3.921	-3.682	-3.448	-3.219	-2.996
0.75	-4.771	-4.511	-4.259	-4.015	-3.776	-3.542	-3.315
0.70	-4.858	-4.587	-4.325	-4.072	-3.824	-3.582	-3.347
0.65	-5.143	-4.869	-4.604	-4.348	-4.098	-3.854	-3.617
0.60	-5.404	-5.125	-4.855	-4.594	-4.338	-4.089	-3.847
0.55	-5.556	-5.264	-4.982	-4.711	-4.446	-4.188	-3.938
0.50	-5.820	-5.515	-5.218	-4.930	-4.647	-4.369	-4.098
0.45	-6.238	-5.925	-5.620	-5.324	-5.032	-4.744	-4.462
0.40	-6.691	-6.365	-6.047	-5.738	-5.433	-5.133	-4.837
0.35	-7.175	-6.829	-6.492	-6.164	-5.840	-5.521	-5.207
0.30	-7.657	-7.287	-6.927	-6.577	-6.233	-5.895	-5.564
0.25	-8.205	-7.809	-7.424	-7.050	-6.683	-6.324	-5.973
0.20	-8.866	-8.443	-8.033	-7.634	-7.243	-6.861	-6.487
0.15	-9.567	-9.117	-8.681	-8.258	-7.846	-7.443	-7.051
0.10	-10.459	-9.990	-9.537	-9.098	-8.670	-8.253	-7.848
0.05	-11.621	-11.145	-10.687	-10.247	-9.822	-9.412	-9.017
0.00							

D-1

log (P_t / bar)

	x^* = 0.9402	0.9402	0.9402	0.9402	0.9402	0.9402	0.9402
x_a	T = 0.0°C	10.0°C	20.0°C	25.0°C	30.0°C	40.0°C	50.0°C
1.00	-8.659	-8.089	-7.561	-7.312	-7.073	-6.619	-6.196
0.99	-8.608	-8.043	-7.521	-7.274	-7.036	-6.585	-6.165
0.98	-8.587	-8.022	-7.500	-7.254	-7.016	-6.565	-6.145
0.97	-8.541	-7.984	-7.469	-7.224	-6.989	-6.543	-6.125
0.96	-8.493	-7.939	-7.427	-7.184	-6.950	-6.505	-6.090
0.95	-8.424	-7.878	-7.370	-7.130	-6.899	-6.458	-6.047
0.90	-7.931	-7.409	-6.925	-6.695	-6.474	-6.053	-5.658
0.85	-7.422	-6.905	-6.426	-6.199	-5.980	-5.565	-5.177
0.80	-6.979	-6.475	-6.008	-5.787	-5.574	-5.170	-4.794
0.75	-6.655	-6.150	-5.684	-5.464	-5.251	-4.849	-4.474
0.70	-6.345	-5.858	-5.409	-5.197	-4.993	-4.607	-4.247
0.65	-6.096	-5.613	-5.167	-4.957	-4.754	-4.371	-4.014
0.60	-5.831	-5.357	-4.920	-4.713	-4.515	-4.138	-3.788
0.55	-5.507	-5.057	-4.640	-4.443	-4.253	-3.892	-3.556
0.50	-5.120	-4.700	-4.309	-4.124	-3.945	-3.606	-3.288
0.45	-4.700	-4.304	-3.937	-3.762	-3.594	-3.273	-2.973
0.40	-4.300	-3.922	-3.571	-3.404	-3.244	-2.938	-2.651
0.35	-3.917	-3.553	-3.215	-3.054	-2.900	-2.606	-2.331
0.30	-3.550	-3.199	-2.873	-2.720	-2.571	-2.289	-2.026
0.25	-3.208	-2.869	-2.555	-2.407	-2.264	-1.993	-1.740
0.20	-2.902	-2.573	-2.269	-2.126	-1.988	-1.726	-1.483
0.15	-2.639	-2.319	-2.024	-1.885	-1.751	-1.497	-1.262
0.10	-2.427	-2.115	-1.828	-1.693	-1.563	-1.316	-1.087
0.05	-2.280	-1.975	-1.694	-1.561	-1.433	-1.192	-0.967
0.00	-2.214	-1.911	-1.631	-1.499	-1.372	-1.132	-0.909

D-3

log (P_t / bar)

	x^* = 0.9402	0.9402	0.9402	0.9402	0.9401	0.9401	0.9401
x_a	T = 130.0°C	140.0°C	150.0°C	160.0°C	170.0°C	180.0°C	190.0°C
1.00	-3.622	-3.373	-3.135	-2.906	-2.688	-2.477	-2.273
0.99	-3.600	-3.352	-3.115	-2.887	-2.668	-2.458	-2.255
0.98	-3.577	-3.329	-3.091	-2.862	-2.643	-2.433	-2.229
0.97	-3.574	-3.327	-3.090	-2.862	-2.645	-2.435	-2.232
0.96	-3.546	-3.299	-3.063	-2.835	-2.618	-2.408	-2.205
0.95	-3.518	-3.271	-3.036	-2.809	-2.592	-2.383	-2.181
0.90	-3.223	-2.984	-2.756	-2.536	-2.326	-2.123	-1.927
0.85	-2.796	-2.564	-2.343	-2.131	-1.928	-1.733	-1.545
0.80	-2.487	-2.263	-2.051	-1.847	-1.653	-1.466	-1.288
0.75	-2.191	-1.971	-1.761	-1.561	-1.370	-1.187	-1.012
0.70	-2.064	-1.854	-1.654	-1.463	-1.281	-1.106	-0.938
0.65	-1.855	-1.648	-1.451	-1.262	-1.082	-0.909	-0.743
0.60	-1.667	-1.463	-1.270	-1.085	-0.908	-0.739	-0.576
0.55	-1.524	-1.330	-1.146	-0.970	-0.803	-0.642	-0.489
0.50	-1.344	-1.157	-0.981	-0.814	-0.654	-0.503	-0.358
0.45	-1.114	-0.934	-0.762	-0.600	-0.444	-0.297	-0.156
0.40	-0.876	-0.704	-0.540	-0.383	-0.234	-0.093	0.042
0.35	-0.637	-0.473	-0.318	-0.170	-0.029	0.105	0.232
0.30	-0.418	-0.264	-0.118	0.021	0.152	0.277	0.396
0.25	-0.210	-0.065	0.072	0.202	0.325	0.442	0.553
0.20	-0.016	0.122	0.253	0.376	0.493	0.603	0.708
0.15	0.147	0.278	0.402	0.519	0.630	0.735	0.835
0.10	0.280	0.408	0.529	0.642	0.750	0.852	0.949
0.05	0.376	0.501	0.620	0.732	0.838	0.939	1.034
0.00	0.432	0.558	0.678	0.791	0.899	1.001	1.099

Table VIII (Continued)

D-4

log (P_t / bar)

X_a	T = 200.0°C	210.0°C	220.0°C	230.0°C	240.0°C	250.0°C	260.0°C
	X^* = 0.9400	0.9399	0.9397	0.9394	0.9390	0.9384	0.9375
1.00	-2.075	-1.882	-1.694	-1.511	-1.330	-1.152	-0.977
0.99	-2.058	-1.867	-1.680	-1.498	-1.319	-1.142	-0.969
0.98	-2.032	-1.840	-1.653	-1.472	-1.292	-1.116	-0.943
0.97	-2.036	-1.844	-1.658	-1.477	-1.298	-1.123	-0.950
0.96	-2.009	-1.818	-1.631	-1.450	-1.272	-1.096	-0.923
0.95	-1.985	-1.794	-1.608	-1.427	-1.248	-1.073	-0.900
0.90	-1.738	-1.553	-1.374	-1.199	-1.028	-0.860	-0.696
0.85	-1.364	-1.189	-1.020	-0.855	-0.695	-0.539	-0.386
0.80	-1.116	-0.950	-0.790	-0.635	-0.484	-0.338	-0.196
0.75	-0.843	-0.680	-0.524	-0.372	-0.225	-0.082	0.057
0.70	-0.776	-0.620	-0.469	-0.323	-0.181	-0.043	0.093
0.65	-0.583	-0.428	-0.278	-0.133	0.009	0.147	0.282
0.60	-0.419	-0.267	-0.120	0.022	0.161	0.297	0.430
0.55	-0.340	-0.197	-0.059	0.076	0.207	0.335	0.460
0.50	-0.220	-0.088	0.038	0.160	0.276	0.388	0.496
0.45	-0.021	0.107	0.230	0.347	0.458	0.565	0.667
0.40	0.171	0.294	0.411	0.523	0.629	0.730	0.827
0.35	0.353	0.468	0.578	0.682	0.782	0.876	0.965
0.30	0.509	0.616	0.719	0.816	0.908	0.996	1.080
0.25	0.658	0.759	0.854	0.945	1.032	1.114	1.192
0.20	0.807	0.902	0.991	1.077	1.158	1.235	1.308
0.15	0.929	1.019	1.104	1.185	1.262	1.335	1.406
0.10	1.040	1.128	1.210	1.289	1.364	1.436	1.504
0.05	1.125	1.211	1.294	1.373	1.448	1.520	1.589
0.00	1.192	1.280	1.365	1.447	1.525	1.599	1.671

D-5

log (P_t / bar)

X_a	T = 270.0°C	280.0°C	290.0°C	300.0°C	310.0°C	320.0°C	330.0°C
	X^* = 0.9362	0.9344	0.9312	0.9288	0.9249	0.9213	0.9203
1.00	-0.803	-0.631	-0.459	-0.288	-0.116	0.055	0.228
0.99	-0.797	-0.626	-0.457	-0.287	-0.118	0.052	0.222
0.98	-0.772	-0.602	-0.434	-0.266	-0.098	0.070	0.238
0.97	-0.779	-0.610	-0.442	-0.274	-0.106	0.061	0.229
0.96	-0.752	-0.583	-0.415	-0.247	-0.079	0.088	0.256
0.95	-0.730	-0.561	-0.392	-0.225	-0.058	0.109	0.277
0.90	-0.533	-0.373	-0.214	-0.056	0.102	0.258	0.415
0.85	-0.236	-0.089	0.056	0.199	0.341	0.482	0.622
0.80	-0.058	0.078	0.211	0.342	0.471	0.599	0.727
0.75	0.192	0.324	0.454	0.581	0.706	0.830	0.953
0.70	0.225	0.354	0.482	0.608	0.733	0.857	0.980
0.65	0.414	0.544	0.673	0.800	0.926	1.051	1.175
0.60	0.561	0.689	0.816	0.941	1.066	1.190	1.313
0.55	0.584	0.705	0.826	0.945	1.064	1.183	1.302
0.50	0.600	0.701	0.798	0.894	0.986	1.077	1.166
0.45	0.765	0.858	0.947	1.033	1.116	1.195	1.271
0.40	0.918	1.006	1.089	1.168	1.243	1.314	1.382
0.35	1.050	1.131	1.207	1.280	1.348	1.413	1.474
0.30	1.160	1.235	1.307	1.376	1.441	1.502	1.561
0.25	1.267	1.338	1.406	1.471	1.533	1.592	1.649
0.20	1.377	1.444	1.507	1.567	1.624	1.679	1.731
0.15	1.473	1.537	1.598	1.657	1.713	1.767	1.819
0.10	1.570	1.632	1.692	1.749	1.804	1.857	1.908
0.05	1.655	1.719	1.780	1.839	1.896	1.952	2.005
0.00	1.740	1.807	1.872	1.934	1.994	2.053	2.109

Table IX. Literature Values for the Vapor Pressure of Sulfuric Acid and Azeotropic Compositions of H_2O–H_2SO_4 Solutions

(A) Vapor Pressures

reference	T/°C	X	P_t/bar	$P_{H_2SO_4}$/bar	P_{SO_3}/bar	P_{H_2O}/bar
Abel (*1*)	25	0.997	3.1×10^{-7}	1.9×10^{-7}	9.3×10^{-8}	5.3×10^{-10}
	25	0.948	2.6×10^{-7}	1.7×10^{-7}	8.0×10^{-8}	5.3×10^{-9}
Ayers et al. (*2*)	25	0.901		1.6×10^{-8}		
Gmitro and Vermeulen (*13*)	25	1.000	1.8×10^{-6}	5.3×10^{-7}	1.3×10^{-6}	1.0×10^{-10}
LaMer et al. (*30*)	25	0.948		1.3×10^{-9}		
Luchinskij (*32*)	25	0.914	7.6×10^{-7}	4.7×10^{-7}	2.9×10^{-7}	4.0×10^{-10}
Vermeulen et al. (*44*)	25	1.000	7.8×10^{-8}	4.8×10^{-8}	2.7×10^{-8}	3.4×10^{-9}
	25	0.968	6.7×10^{-8}	4.5×10^{-8}	5.1×10^{-9}	1.8×10^{-8}
present calc	25	0.940	4.9×10^{-8}	4.3×10^{-8}	2.1×10^{-9}	4.9×10^{-9}

(B) Azeotrope

reference	T/°C	composition
Luchinskij (*32*)	338.8	X = 0.915 (98.33 wt %)
Kunzler (*28*)	n.b.p.	X = 0.9222 (98.45 wt %)
Knietsch (*27*)	317	X = 0.925 (98.54 wt %)
Lewis and Randall (*30b*)	326	X = 0.918 (98.38 wt %)
Gmitro and Vermeulen (*13*)	326	X = 0.9225 (98.48 wt %)
Giazitzouglou and Wuster (*12*)	315	X = 0.900 (98.00 wt %)

line for the data points at X = 0.256 suggests some anomaly in the data.

The numerical difference between the present calculations and the correlation formulated by Vermeulen et al. can be traced to the selection of properties at the reference states. Vermeulen's correlation is based on Luchinskij's parameters for the normal azeotropic boiling point and a much higher value for the azeotropic composition at 25 °C (X^* = 0.968, as compared to 0.940 for the present calculation). The resulting differences in calculated vapor pressures near the azeotrope (310 °C) are illustrated in Figure 11.

(7) Summary and Conclusions

It has been found that reported high-temperature P–T–X data together with ambient-temperature thermodynamic data and a relatively simple interpolation procedure allow the calculation of values of thermodynamic parameters for hypoazeotropic aqueous sulfuric acid solutions that appear self-consistent and reasonably accurate when compared to available experimental data. The calculated values should prove useful in estimating thermodynamic parameters in the temperature and concentration ranges where no experimental data are available. The hypoazeotropic composition range is of primary interest for the phenomena relating to precipitation of sulfuric acid in flue

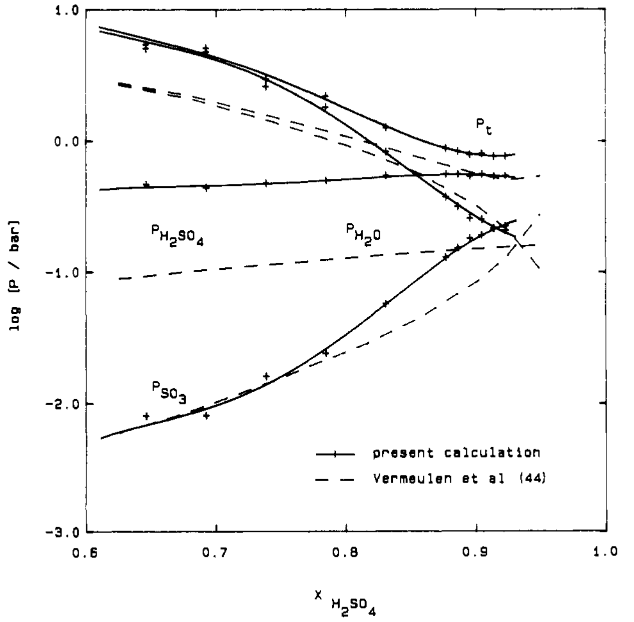

Figure 11. Vapor pressures at 310 °C: comparison of present calculations with the correlation by Vermeulen et al. (*44*).

gases or from the atmosphere. As is illustrated in Figure 5 and in Table VIII, the azeotropic concentration is nearly constant up to temperatures above 200 °C. The value of $X^* = 0.940$ at 25 °C used in the present calculations was obtained by extrapolation of Kunzler's data (*28*) and is subject to some uncertainty. The accuracy of the results is related, of course, to that of the reference values utilized as well as to some implicit assumptions in the calculations. Such are, for example, the three-parameter approximation for the temperature dependence of the partial molar specific heats, the omission of any pressure effects on the liquid-phase activities, and the assumption that the partial pressures are satisfactory approximations of the fugacities over the temperature and pressure ranges under consideration. However, the errors introduced by these approximations are probably small when compared to the prevailing uncertainty in some of the reference parameters, especially the high-temperature azeotrope.

List of Symbols

a_i	activity of species "*i*"
A_i	$i = 0, ..., 4$; empirical constants in equations for free energy (eq 1 and 2)
a, b, c	empirical constants in equations for molar heat capacities (eq 14)
A_i, B_i, C_i	i = w, a; empirical constants in equations for partial molar heat capacities of water and azeotrope, respectively (eq 27)
$\bar{C}^{l}_{p}$	molar heat capacity of liquid phase
$\bar{C}^{v}_{p}$	molar heat capacity of vapor phase
$\bar{C}^{v}_{p,i}$	partial molar heat capacity of species *i*
f_i	fugacity of species *i*
f_i°	fugacity of species *i* in the reference state
$\bar{G}_i$	partial molar free energy of species *i*
$\bar{G}_i^{\circ}$	partial molar free energy of species *i* in the reference state
$\bar{G}_1, \bar{G}_2$	partial molar free energies of H_2O and H_2SO_4, respectively, in H_2O–H_2SO_4 binary system
$\bar{G}_w, \bar{G}_a$	partial molar free energies of H_2O and azeotrope, respectively, in H_2O–azeotrope binary system
$\Delta\bar{G}^*$	molar free energy of mixing for azeotropic composition
$\Delta\bar{H}^{v}$	molar enthalpy of vaporization
$\bar{H}_i$	partial molar enthalpy of species i
$\bar{H}_i^{\circ}$	partial molar enthalpy of species *i* in the reference state
$\Delta\bar{H}^{v,\circ}$	molar enthalpy of vaporization at reference temperature (298 K)
$\Delta\bar{H}_w^{v,\circ}$	molar enthalpy of vaporization of water at reference temperature (298 K)
$\Delta\bar{H}_a^{v,\circ}$	molar enthalpy of vaporization of azeotropic solution at reference temperature (298 K)
K_p	equilibrium constant for the decomposition of H_2SO_4
P_i	partial pressure of species *i*
P_t	total vapor pressure
P_w°	vapor pressure of H_2O in its reference state ($X_a = 0$)
P_a°	vapor pressure of azeotrope in its reference state ($X_a = 1$)
P_w^{a}	partial pressure of water at $X_a = 1$
$\bar{Q}_i$	i = w, a; partial molar heat capacity or temperature derivative of partial molar heat capacity for water or azeotrope (eq 19 and 20)
R	gas constant
T	temperature
X	mole fraction of H_2SO_4 in liquid H_2O–H_2SO_4 solutions
X_w, X_a	mole fractions of water and azeotrope, respectively, in H_2O–azeotrope binary system
X'	mole fraction of H_2SO_4 in liquid H_2O–H_2SO_4 solutions in P–T–X data of ref 12
X^*	azeotropic composition of H_2O–H_2SO_4 solutions (mole fraction of H_2SO_4)
y	fraction of H_2SO_4 decomposed in vapor phase
y^*	fraction of H_2SO_4 decomposed in vapor phase equilibrated with a solution of azeotropic composition
Y	mole fraction of H_2SO_4 in vapor phase
γ_i	activity coefficient of species i
Ω	empirical constant for the integration of the Gibbs–Duhem relation (eq 21a)

Registry No. H_2SO_4, 7664-93-9.

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Vapor–Liquid Equilibria at 100 kPa for Propionic Acid + Carbon Tetrachloride or 2-Butanone

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Vapor–liquid equilibria were measured for the two binary systems made of propionic acid + carbon tetrachloride or 2-butanone at 100 kPa of pressure by the dew-point–bubble-point temperature method. Vapor–liquid equilibrium diagrams were obtained without using any analytical instrument by combining the experimental dew-point and bubble-point temperature curves. The experimental data were correlated with the Wilson equation, accounting for the dimerization effect of propionic acid in the vapor phase.

Introduction

In the present study, vapor–liquid equilibria (VLE) were measured for the two binary systems made of propionic acid with carbon tetrachloride or 2-butanone at 100 kPa of pressure by the dew-point–bubble-point apparatus recently modified by M.K. (*1*), without using any analytical instrument. For carbon tetrachloride + propionic acid, two sets of data are available in the literature (*2*, *3*), but large differences are seen between them. New reliable data seem, therefore, to be required for this system. For 2-butanone + propionic acid system, isothermal data are available in literature but no isobaric data.

Table I. Densities ρ and Normal Boiling Points T_b of the Materials Used

	ρ(298.15 K)/(g cm^{-3})		T_b/K	
material	exptl	lit. (*9*)	exptl	lit. (*9*)
carbon tetrachloride	1.5845	1.58462	349.84	349.788
2-butanone	0.7995	0.7997	352.72	352.79
propionic acid	0.9879	0.98806	414.01	414.315

Table II. Experimental Dew-Point T_d and Bubble-Point T_b Data for the Carbon Tetrachloride (1) + Propionic Acid (2) System at 100 kPa as a Function of the Mole Fraction x_1 of Carbon Tetrachloride

x_1	T_d/K	T_b/K	x_1	T_d/K	T_b/K
0.000		413.59	0.500	389.64	360.34
0.050		401.24	0.600	384.05	357.26
0.100	409.55	391.28	0.700	377.63	354.55
0.200	404.82	377.78	0.800	369.84	352.56
0.300	400.07	370.04	0.900	360.50	350.78
0.400	395.18	364.16	1.000		349.41

Table III. Experimental Dew-Point T_d and Bubble-Point T_b Data for the 2-Butanone (1) + Propionic Acid (2) System at 100 kPa as a Function of the Mole Fraction x_1 of 2-Butanone

x_1	T_d/K	T_b/K	x_1	T_d/K	T_b/K
0.000		413.59	0.500	393.92	370.83
0.050		407.57	0.600	388.68	366.15
0.100	411.10	402.39	0.700	382.70	361.98
0.200	407.30	392.64	0.800	375.71	358.34
0.300	403.26	384.14	0.900	367.04	355.21
0.400	398.89	377.25	1.000		352.30

Experimental Section

The experimental apparatus and procedures were as described in our previous paper (*1*). Temperature was measured by means of a Hewlett-Packard Model 2804A quartz thermometer with an accuracy of 0.01 K. The solutions of desired composition were prepared with an accuracy of 0.001 in mole

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