x = $(r/a_i)^2$
y_{Ki} = fraction of cavities of type i occupied by a gas molecule K
Z_i = structural constant

Greek Letters

α_i = $(a_i/\sigma)^3/\sqrt{2}$
λ,γ = constants in Equation (26)
ϵ,σ = energy and distance parameters in the Lennard-Jones-Devonshire potential
ν_i = number of cavities of the type i per mole of water
μ = chemical potential
$\phi_K(T)$ = molecular partition function of a solute molecule K with the volume factor removed
$\omega(r)$ = Lennard-Jones-Devonshire potential

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Vapor-Liquid Equilibria for Aqueous Sulfuric Acid

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Because the precise composition of the vapor phase over aqueous sulfuric acid is not accessible experimentally a method is described for calculating the partial pressures of water, sulfuric acid, and sulfur trioxide starting from liquid-phase partial molal thermodynamic quantities. Graphs and tables are provided which give the partial pressures from —50° to 400°C., between 10 and 100 wt. % acid.

The vapor phase over sulfuric acid solutions is composed of water and sulfuric acid, together with sulfur trioxide from the dissociation of the acid:

$$H_2SO_4(g) = H_2O(g) + SO_3(g) \qquad (1)$$

In principle the distribution of these three components at various temperatures and acid concentrations can be determined by either experimental partial-pressure measurements or calculation of partial pressures from liquid-phase thermodynamic data.

The first method, although more direct, is not fully applicable to the sulfuric acid system because of the low volatility of sulfuric acid. Experimental difficulties notwithstanding, the total vapor pressure of sulfuric acid, which in most cases is due entirely to the partial pressure of water, was the subject of numerous investigations between 1845 and 1923. Greenewalt (*8*), who in 1925 assembled the available data, reviewed nineteen separate vapor-pressure determinations. His final result, based essentially on the measurements of Burt (*4*) and of Daudt (*5*), is the accepted standard that appears in today's reference works.

The second method, the calculational approach to partial pressures, requires two types of thermodynamic data: pure-component data for two liquids and three gases (H°_{298}, S°_{298}, and C°_p) and partial molal data for binary solutions ($\overline{H}_{298}$, $\overline{S}_{298}$ or $\overline{F}_{298}$, and $\overline{C}_p$). This approach was first used by Abel (*1*) in 1946, based in part on work by Bodenstein and Katayama (*3*) who had measured K_p for Equation (1) at 300° to 500°C. with 85 to 100 wt. % acid. The calorimetric data available at that time were incomplete, necessitating cross correlations from various sources in order to determine partial molal quantities. More important, values of C°_p, H°_{298}, and S°_{298} for $H_2SO_4(g)$ were not available. This lack necessitated the use of K_p for Equation (1) in the calculation of $p_{H_2SO_4}$, which in turn required an extrapolation of Bodenstein and Katayama's high-temperature equilibrium measurements down to 25°C. The experimental K_p data are shown in Figure 1.

Since 1946 additional data have become available which make the calculation of partial pressures by the second method considerably more reliable. Extremely complete tables of partial molal quantities at 25°C., tested for internal consistency, have been published by Giauque et al. (*6*), who give free energies, enthalpies, entropies, and heat capacities at 109 different sulfuric acid concentrations from 8.93 to 100 wt. %. In addition Giguère (*7*)

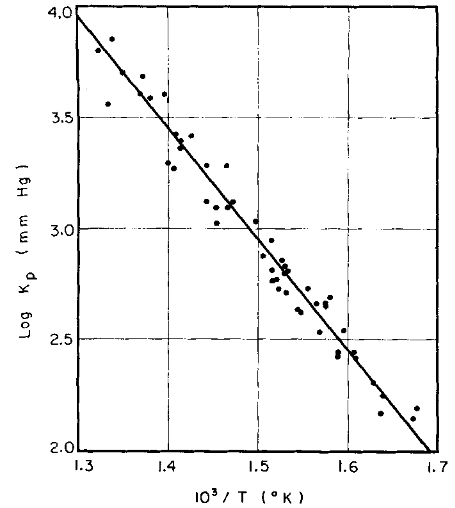

Fig. 1. The fit of Equation (17) to Bodenstein and Katayama's data.

has obtained $C°_p$, $S°$, $(F° - H°_0)/T$, and $(H° - H°_0)/T$ for $H_2SO_4(g)$ from spectroscopic data. The later data, when coupled with Bodenstein and Katayama's K_p, provide a third-law $H°_{298}$ for $H_2SO_4(g)$ and an equation giving the temperature dependence of K_p from 25° to 500°C.

Based upon these new data this paper presents a method for calculating the partial pressures of water, sulfuric acid, and sulfur trioxide as functions of temperature and acid concentration. Partial molal heat-capacity values have had to be estimated by smoothing techniques, so that some inaccuracy still remains. Because of this no correction has been made for nonideal gas behavior, and 10,000 mm. is viewed as the upper limit of applicability of the results.

DERIVATION OF EQUATIONS

Partial Pressure Equation

For any component in a multicomponent mixture at equilibrium the partial molal free energies of the vapor and of the liquid are equal:

$$F°(g) + RT \ln f(g) = F°(l) + RT \ln a(l) \qquad (2)$$

If the pressure is low enough so that the vapor acts as a perfect gas

$$\ln p = -\frac{\Delta F°}{RT} + \ln a \qquad (3)$$

Here the pure-component term $-\Delta F°/RT$ is a function of temperature only, and the activity term is a function of both temperature and composition. In order to evaluate the pressure each term must be related to its standard state value.

The pure-component term is evaluated by use of the Van't Hoff equation to give

$$-\frac{\Delta F°}{RT} = -\left(\frac{\Delta H° - T\Delta S°}{RT}\right)_{298} + \frac{\Delta H°_{298}}{R}\left(\frac{1}{298} - \frac{1}{T}\right) + \frac{1}{R}\int_{298}^{T} \frac{1}{T^2} \left\{\int_{298}^{T} [C°_p(g) - C°_p(l)]dT\right\} dT \qquad (4)$$

where any coefficient or subscript shown as 298 is actually computed as 298.15°K. (25°C.). The activity term is evaluated in a similar manner:

$$\ln a = \left(\frac{\overline{F} - F°}{RT}\right)_{298} - \frac{\overline{L}_{298}}{R}\left(\frac{1}{298} - \frac{1}{T}\right) - \frac{1}{R}\int_{298}^{T} \frac{1}{T^2} \left\{\int_{298}^{T} [\overline{C}_p - C°_p(l)]\, dT\right\} dT \qquad (5)$$

The C_p integrals of Equations (4) and (5) are evaluated by using heat capacity functions in a form given in the literature. For the gas

$$C°_p(g) = a + bT + cT^2 \qquad (6)$$

and for the liquid

$$\overline{C}_p = \overline{C}_{p,\,298} + \alpha\,(T - 298) \qquad (7)$$

This gives, when one combines Equations (3), (4), (5), (6), and (7)

$$\ln p = A \ln\left(\frac{298}{T}\right) + \frac{B}{T} + C + DT + ET^2 \qquad (8)$$

where

$$A = \frac{1}{R}\,(-a + \overline{C}_{p,\,298} - 298\alpha) \qquad (8a)$$

$$B = \frac{1}{R}\left(-\Delta H°_{298} + 298a + \frac{298^2}{2} b + \frac{298^3}{3} c + \overline{L}_{298} - 298\overline{C}_{p,\,298} + \frac{298^2}{2}\alpha\right) \qquad (8b)$$

$$C = \frac{1}{R}\left(\Delta S°_{298} - a - 298b - \frac{298^2}{2} c + \overline{C}_{p,\,298} + [(\overline{F} - F°)_{298} - \overline{L}_{298}]\frac{1}{298}\right) \qquad (8c)$$

$$D = \frac{1}{2R}\,(b - \alpha) \qquad (8d)$$

$$E = \frac{1}{6R}\,c \qquad (8e)$$

For the sulfuric acid system partial molal quantities are available for water and for sulfuric acid. Equation (8) was therefore used to calculate p_{H_2O} and $p_{H_2SO_4}$, and the partial pressure of sulfur trioxide was calculated from

$$p_{SO_3} = K_p\, p_{H_2SO_4}/p_{H_2O} \qquad (9)$$

Dissociation Constant of $H_2SO_4(g)$

The equilibrium for Equation (1), the dissociation of $H_2SO_4(g)$, is given by

$$\ln K_p = -\Delta F°_{(1)}/RT = \frac{[\Delta S°_{(1)}]_{298}}{R} - \frac{[\Delta H°_{(1)}]_{298}}{RT} + \frac{1}{R}\int_{298}^{T} \frac{1}{T^2}\left[\int_{298}^{T} \Delta C°_{p(1)}\, dT\right] dT \qquad (10)$$

Heat capacity data available in the literature give the following function for $\Delta C°_{p(1)}$:

$$\Delta C°_{p(1)} = a' + b'T + c'T^2 + d'T^{-2} \qquad (11)$$

Use of this to evaluate the heat capacity integral in Equation (10) results in the following equation for K_p:

$$\ln K_p = J \ln(298/T) + K/T^2 + L/T + M + NT + QT^2 \qquad (12)$$

where

$J = -a'/R$
$K = d'/2R$
$L = \frac{1}{R}\left[-(\Delta H°_{(1)})_{298} + 298a' + \frac{298^2}{2} b' + \frac{298^3}{3} c' - \frac{d'}{298}\right]$

TABLE 1. VALUE OF THERMODYNAMIC PROPERTIES AT 298.15°K.

Component	Property	State	Value	Units	Reference
SO_3	H^o	g	-94.45	kcal./mole	(8)
	S^o	g	61.24	cal./mole-deg.	(8)
	Cp^{o*}	g	$a = 13.90$	cal./mole-deg.	(9)
			$b = 6.10 \times 10^{-3}$	cal./mole-deg.^{2}	
			$d = -3.22 \times 10^5$	cal.-deg./mole	
H_2O	H^o	l	-68.32	kcal./mole	(8)
		g	-57.80	kcal./mole	(8)
	S^o	l	16.72	cal./mole-deg.	(8)
		g	45.11	cal./mole-deg.	(8)
	Cp^{o*}	g	$a = 7.30$	cal./mole-deg.	(9)
			$b = 2.46 \times 10^{-3}$	cal./mole-deg.^{2}	
Vaporization	ΔH^o		10.52	kcal./mole	
	ΔS^o		28.39	cal./mole-deg.	
H_2SO_4	H^o	l	-193.91	kcal./mole	(8)
		g	-175.01	kcal./mole	See text
	S^o	l	37.50	cal./mole-deg.	(6)
		g	71.93	cal./mole-deg.	(7)
	Cp^{o*}	g	$a = 7.86$	cal./mole-deg.	See text
			$b = 46.15 \times 10^{-3}$	cal./mole-deg.^{2}	
			$c = -2.612 \times 10^{-5}$	cal./mole-deg.^{3}	
Vaporization	ΔH^o		18.90	kcal./mole	From $H^o(l,g)$
	ΔS^o		34.43	cal./mole-deg.	From $S^o(l,g)$
Dissociation	$\Delta H^o_{(1)}$		22.76	kcal./mole	See text
	$\Delta S^o_{(1)}$		34.42	cal./mole-deg.	See text
	$\Delta Cp^o_{(1)}$		$a = 13.34$	cal./mole-deg.	See text
			$b = -37.59 \times 10^{-3}$	cal./mole-deg.^{2}	
			$c = 2.612 \times 10^{-5}$	cal./mole-deg.^{3}	
			$d = 3.22 \times 10^5$	cal.-deg./mole	

* $C_p^* = a + bT + cT^2 + dT^{-2}$.

$$M = \frac{1}{R}\left[(\Delta S^\circ_{(1)})_{298} - a' - 298b' - \frac{298^2}{2}c' + \frac{1}{2}d'/298^2 \right]$$

$$N = b'/2R$$

$$Q = c'/6R$$

THERMODYNAMIC DATA

Pure-Component Properties

The pure-component data required in Equations (8) and (12), listed in Table 1, have been assembled from the following sources.

H°_{298} for $H_2SO_4(g)$. The value of H°_{298} listed in Table 1 for $H_2SO_4(g)$ was calculated as follows. Kelley (9) has tabulated values of $(H^\circ - H^\circ_{298})$ and $(S^\circ - S^\circ_{298})$ at 100°C. intervals for $H_2O(g)$ and $SO_3(g)$. These were used to calculate the free-energy function:

$$\frac{F^\circ - H^\circ_{298}}{T} = \frac{H^\circ - H^\circ_{298}}{T} - (S^\circ - S^\circ_{298}) - S^\circ_{298} \quad (13)$$

Giguère's tables (7) of $(F^\circ - H^\circ_0)/T$ and $(H^\circ - H^\circ_0)/T$ for $H_2SO_4(g)$ were also converted to the same form:

$$\frac{F^\circ - H^\circ_{298}}{T} = \frac{F^\circ - H^\circ_0}{T} - \frac{298.15}{T}\left(\frac{H^\circ - H^\circ_0}{T}\right)_{298} \quad (14)$$

This procedure gave the following results, which were plotted to permit interpolation:

T, °K.	$-(F^\circ - H^\circ_{298})/T$ $H_2O(g)$	$H_2SO_4(g)$	$SO_3(g)$
500	46.03	74.32	62.73
600	46.72	76.22	63.93
700	47.41	78.17	65.19
800	48.10	80.11	66.46

These values allow the calculation of $\Delta(F^\circ - H^\circ_{298})/T$ for the dissociation of $H_2SO_4(g)$, Equation (1). Each of Bodenstein and Katayama's K_p determinations (3) represents an individual measurement of $\Delta F^\circ_{(1)}/T$ and hence of $[\Delta H^\circ_{(1)}]_{298}$ as indicated by the relation

$$[\Delta H^\circ_{(1)}]_{298} = \frac{1}{T}\left[\frac{\Delta F^\circ_{(1)}}{T} - \Delta\left(\frac{F^\circ - H^\circ_{298}}{T}\right)\right] \quad (15)$$

Averaging the results for each data point gave a value of 22,760 ± 285 cal./mole for $[\Delta H^\circ_{(1)}]_{298}$; H°_{298} is then $(-57.80 - 94.45 - 22.76) = -175.01$ kcal./mole.

C°_p for $H_2SO_4(g)$. The C°_p equation for $H_2SO_4(g)$ listed in Table 1 was selected as an empirical fit, accurate to ± 0.3%, to the C°_p data given in tabular form by Giguère (7). His values were calculated from spectroscopic data, both with and without provision for torsional oscillations of the OH groups included. The values used here include the torsional contribution and give a probable uncertainty in the $H_2SO_4(g)$ functions of only 0.25 cal./mole-deg.

Constants in Equations. For calculation it is desirable to separate out the pure-component terms in Equation (8), which are constant for all acid compositions. Upon evaluating these terms from the data in Table 1 one obtains the following equation for calculating p_{H_2O} and $p_{H_2SO_4}$:

$$\ln p = A \ln(298/T) + B/T + C + DT + ET^2 \quad (16)$$

where

$$A = A' + \frac{1}{R}(\bar{C}_{p,298} - 298\,\alpha)$$

$$B = B' + \frac{1}{R}\left(\bar{L}_{298} - 298\,\bar{C}_{p,298} + \frac{298^2}{2}\alpha\right)$$

$$C = C' + \frac{1}{R}\left\{C_{p,298} + [(\bar{F} - F^\circ)_{298} - L_{298}]\frac{1}{298}\right\}$$

$D = D' - \alpha/2R$

$E = \text{constant}$

Term	Units	H_2O value	H_2SO_4 value
A'	Dimensionless	—3.67340	—3.95519
B'	°K.	—4143.5	—7413.3
C'	Dimensionless	10.24353	7.03045
D'	$(°K.)^{-1}$	0.618943×10^{-3}	11.61146×10^{-3}
E	$(°K.)^{-2}$	0	-2.19062×10^{-6}

The constants in the K_p relation, Equation (12), may be evaluated immediately, since they are all pure-component terms. Substitution of the data in Table 1 yields the following K_p equation for calculation of p_{SO_3}:

$$\ln K_p = J \ln(298/T) + K/T^2 + L/T + M + NT + QT^2 \tag{17}$$

where

$J = -6.71464$ $\quad M = 14.74965$

$K = -8.10161 \times 10^4$ $\quad N = -9.4577 \times 10^{-3}$

$L = -9643.04$ $\quad Q = 2.19062 \times 10^{-6}$

The fit of this equation to Bodenstein and Katayama's data is shown in Figure 1. The constants shown for Equations (16) and (17) give pressures in units of atmospheres, for results in millimeters Hg, ln 760 is added to C' and to M.

Partial Molar Properties

The partial molal properties required in Equation (16) for the calculation of p_{H_2O} and $p_{H_2SO_4}$ are listed in Table 3[*] and are interpolated from the data of Giauque et al. (*6*). As described in the next section adjustment of some of the properties in some concentration regions was necessary; the values as finally used are listed in Table 4.[*]

CALCULATION OF PARTIAL PRESSURES

In the present work it was realized early that the thermodynamic properties collected in Table 1 would not give a perfect a priori calculation of partial pressures. Results to temperatures near 200°C. were satisfactory, but at higher temperatures the calculated partial pressures became progressively more erratic.

To correct the observed inconsistencies it was decided to adjust α, the temperature coefficient of the partial molal heat capacity. By determining a suitable average α for the range of 25° to 400°C. one can significantly alter high-temperature partial pressures without affecting the already satisfactory low-temperature values. Partial pressures in the 200° to 400°C. range were thus made consistent with the low-temperature results and with the sulfuric acid azeotrope and boiling point data. Smoothed partial pressures were checked on activity-coefficient plots and finally were examined for consistency by using the Gibbs-Duhem equation.

Sulfuric Acid Azeotrope

Figure 2 shows the partial pressure behavior at 25°C., calculated from Equations (16) and (17) by use of the smoothed constants eventually deduced, in the vicinity of the sulfuric acid azeotrope. An abscissa scale of —log [100—(wt. %)] is used in Figure 2 in order to expand the azeotrope region. The partial pressure behavior shown —$p_{H_2SO_4}$ nearly constant, p_{H_2O} decreasing rapidly, and p_{SO_3} increasing rapidly—continues at higher temperatures and pressures. The concentration at which the azeotrope occurs decreases somewhat as the pressure increases, as shown by Kunzler (*11*). At 100 mm. Hg the composition is 98.790 wt. %. Interpolation of Kunzler's data to 760 mm. gives an azeotrope of 98.479 wt. % which was adopted for the present study.

The available data on the temperature and concentration for the atmospheric-pressure azeotrope are as follows:

t, °C.	H_2SO_4, wt.%	Investigator
317	98.33	Knietsch (*10*)
326	98.39	Lewis and Randall (*13*)
331.7	—	Beckmann (*2*)
338	98.5	Marignac (*16*), Lunge (*15*)
338.8	98.32	Luchinskii (*14*)

In the present calculations it was decided to base high-temperature partial pressures on a temperature of 326°C. for the 1.0-atm. azeotrope, as was done by Abel. Although this temperature is rated as the most probable value, it is subject to an uncertainty of at least ± 5°C.

At an azeotrope the composition of the liquid is equal to the composition of the vapor. When one refers to w as the weight fraction of sulfuric acid at the azeotrope, and uses the subscripts 1, 2, and 3 to indicate water, sulfuric acid, and sulfuric trioxide, respectively, the analytical sulfuric acid mole fraction is

$$\frac{18.016w}{98.082 - 80.066w} = \epsilon = \frac{p_2 + p_3}{(p_1 - p_3) + p_2 + p_3} \tag{18}$$

For the 1.0-atm. azeotrope ϵ is 0.92246. At this azeotrope one also has

$$760 = p_1 + p_2 + p_3 \tag{19}$$

$$K_p = p_1 \, p_3/p_2 \tag{20}$$

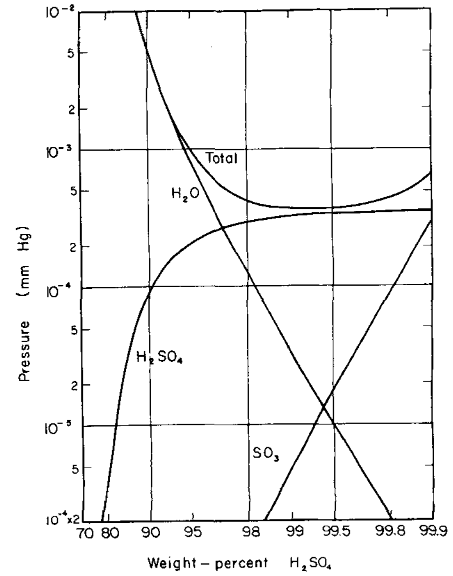

Fig. 2. The sulfuric acid azeotrope at 25°C.

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[*] Tabular material has been deposited as document 8041 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $6.25 for photoprints or $2.50 for 35-mm. microfilm

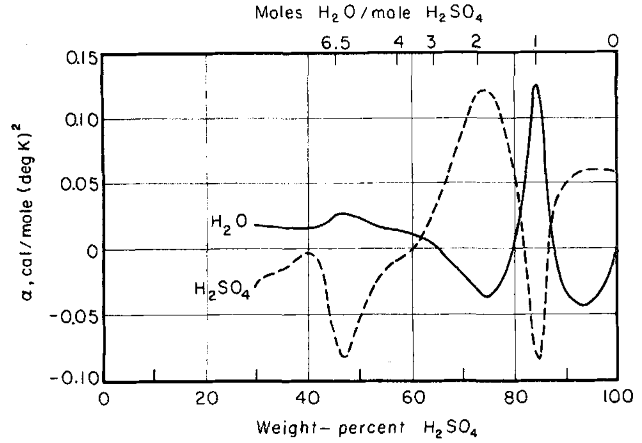

Fig. 3. Temperature coefficient of partial molal heat capacities measured at 25°C. from Giauque et al. (*6*).

The value of K_p at 326°C. from Equation (17) is 130.2 mm. The partial pressures at the azeotrope can now be determined by combining Equations (18), (19), and (20) to give

$$(p_1)^2 + p_1 [K_p (1 + \epsilon) - 760 (1 - \epsilon)] - 760 K_p = 0 \qquad (21)$$

and

$$p_2 = \frac{760 - p_1}{1 + (K_p/p_1)} \qquad (22)$$

The α values required to give the correct azeotrope p_1 and p_2 can then be calculated from Equation (16). This procedure gave the following results for the sulfuric acid azeotrope:

Input	Results
$t = 326$°C.	$p_1 = 233.1$ mm., $\alpha_1 = 0.0160$
$P = 760$ mm.	$p_2 = 338.1$ mm., $\alpha_2 = 0.1249$
$w = 0.9848$	$p_3 = 188.8$ mm.

Adjustment of Alpha, 10 to 98.5 wt.%

The variations in room temperature α values with concentration (*6*) in Figure 3 reflect the differences in heat capacity behavior of the various hydrated forms of sulfuric acid (*21*).

Values of α determined in this study are given in Figure 4. The calculational procedure used for both water and sulfuric acid was as follows.

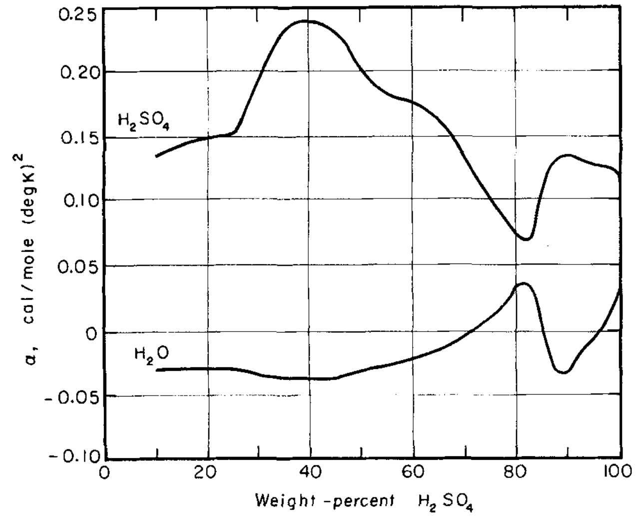

Fig. 4. Average temperature coefficient of partial molal heat capacities between 25° and 400°C.

Partial pressures from 25° to 400°C. were calculated by Equation (8) at temperature intervals of 25°C. with $\alpha = 0$ at all concentrations. These pressures were plotted on log p vs. concentration and log p vs. $1/T$ coordinates. At each 25°C. interval pressures were also calculated with an α equal to the azeotrope value. At 150°C. the difference between the pressures calculated with $\alpha = 0$ and α equal to the azeotrope value was noticeable, the latter producing a lower but parallel curve. By 200°C. irregularities occurred in the pressure curves at acid concentrations where α reaches a maximum or a minimum: 90, 82, and 40 wt. %. Irregularities were smoothed visually, and the α required to give the smoothed pressure was calculated. These new α values were used for the next higher temperature interval. This procedure was repeated over each 25°C. interval up to 400°C. for both α_{H_2O} and $\alpha_{H_2SO_4}$.

98.5 to 100 wt.% Region

In the region between the azeotrope and 100% acid a check of the activity coefficients showed that α adjustments alone would not give consistent results over the complete temperature range. This was especially true in the case of $p_{H_2SO_4}$, which changes very little in the high weight per cent region. Therefore attention was turned next to the heat capacity behavior.

Figure 5 shows specific heat capacity values between 96 and 101 wt. %. The data points are those of Kunzler and Giauque (*12*), which Giauque's smoothed values (*6*) (dashed curve) do not follow exactly. (The cusp in the dashed curve at 100% sulfuric acid, makes the partial molal heat capacity of water indeterminate at that point.) The solid curve, determined as described below, coincides with the dashed curve below 98.5 wt. % and near 101 wt. %. Results between these weight per cents were calculated as follows.

For sulfuric acid, values of $(\overline{F} - F^\circ)$ were adjusted at 99, 99.5, 99.8, and 99.9 wt. %, so that $p_{H_2SO_4}$ gave Raoult law behavior at 25°C [based on two ions formed per molecule of sulfuric acid added, as indicated by Young and Walrafen (*21*)]. Then $\overline{L}$, $\overline{C}_p$, and α were adjusted to give consistent $p_{H_2SO_4}$ behavior at high temperatures; at the same time $\overline{C}_p$ and α at 100% were varied to give smooth activity cefficient behavior between 98.5 and 100 wt. %.

Values of p_{H_2O} between 98.5 and 100 wt. % were then calculated by assuming various heat capacity curves through this region. Partial molal heat capacities for water were calculated from the slopes of the assumed heat capacity curve; then p_{H_2O} was calculated by assuming values

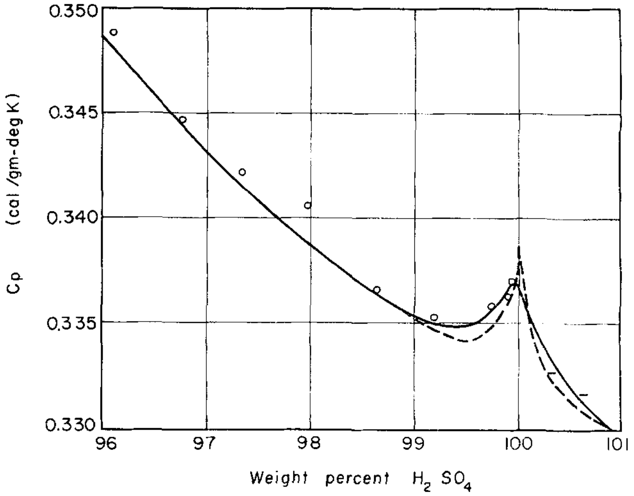

Fig. 5. The heat capacity of aqueous sulfuric acid near 100% sulfuric acid.

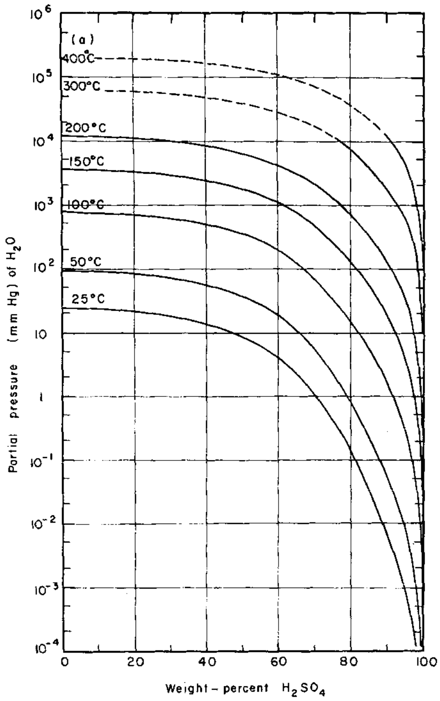

Fig. 6. The partial pressure of water over aqueous sulfuric acid.

of α. New heat capacity curves (with the 100% intercepts kept constant) and alphas were assumed, until consistent values of p_{H_2O} were obtained between 99.0 and 99.9 wt. %. The heat capacity curve was chosen so that these pressures, when extrapolated, gave a satisfactory boiling point for the 100% acid [272°C which lies within the accepted 270° to 280°C. range (*14, 17, 22*)]. Then $\bar{C}_p$ and α for water were fitted to the resulting 100% pressures.

This procedure resulted in a large positive value of $(C_p)_{H_2O}$ for 100% acid, indicating that the peak in the heat capacity curve occurs below 100% (as redrawn in Figure 5). The curve between 99 and 101 wt. % was drawn by assuming a Gaussian variation around the 100% value, added to the wider range downward trend with decreasing water content.

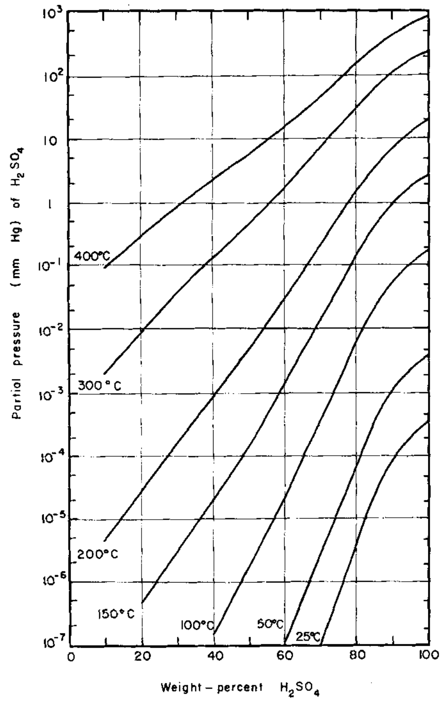

Fig. 7. The partial pressure of sulfuric acid over aqueous sulfuric acid.

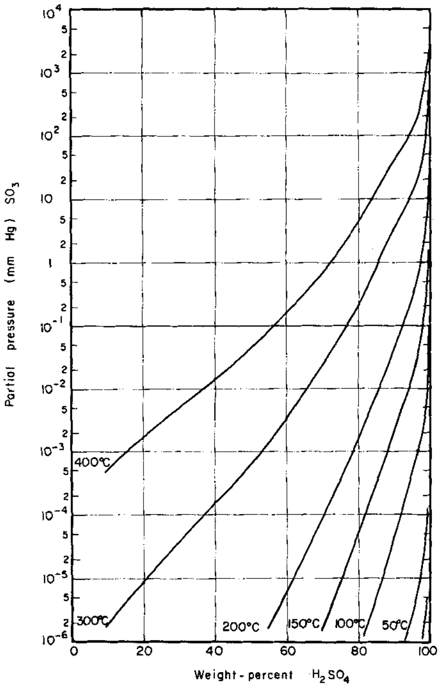

Fig. 8. The partial pressure of sulfur trioxide over aqueous sulfuric acid.

Partial pressures, calculated from Equations (16) and (17) and the thermodynamic properties in Table 4, are shown in Figures 6, 7, and 8. Complete tables of partial and total pressures appear in the Appendix,* for the temperature range −50° to 400°C., together with the Fortran program used. The constants used for the calculation are given in Table A-IV and K_p values in Table A-V.* Single page abridged tables for water, sulfuric acid, and sulfur trioxide, particularly convenient for rapid reference, are provided in Tables A-IIIA, A-IIIB, and A-IIIC.*

DISCUSSION AND CONCLUSIONS

The partial pressures presented above agree in form with those reported by Greenewalt (*8*) and Abel (*1*). In both cases the closest agreement occurs at low temperatures and low acid concentrations, where the observable vapor pressure is predominantly due to p_{H_2O}. At higher temperatures Greenewalt's total pressure correlations gave slightly higher pressures than those reported here. Abel used a K_p equation and an azeotrope composition different from those used in this work. His results show the same trends in vapor pressure behavior as do Figures 6, 7, and 8, but his calculated pressures at 25°C., especially for sulfuric acid, are not in full agreement with the thermodynamic data now available. Moreover Greenewalt carried the correlation only to 95 wt. % and Abel to 98.3 wt. %.

The total pressures calculated for 100 wt. % are appreciably higher than the values reported by Luchinskii (*14*), owing primarily to the contribution from p_{SO_3}; the calculated values for 99.8 wt. % are relatively close to his values for 100 wt. %. Since this discrepancy disappears in the neighborhood of the atmospheric boiling point, the reason for it is not known.

Of the calculated vapor pressures p_{H_2O} is the most accurate. For this calculation the authors have the pure com-

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* See footnote on page 743.

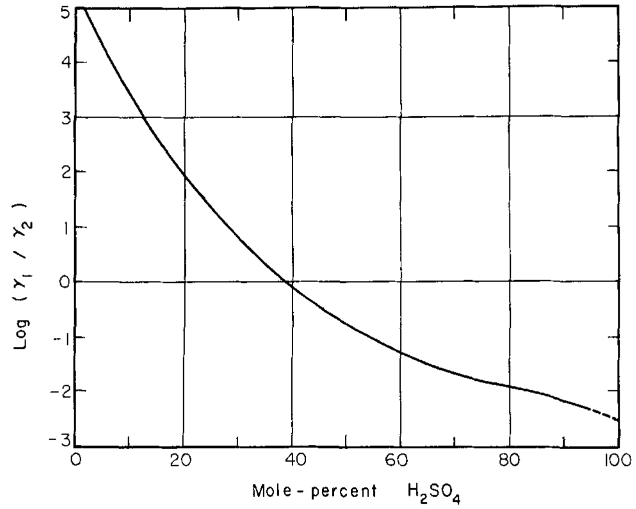

Fig. 9. Thermodynamic-consistency test at 200°C.

ponent vapor pressure data to aid in adjusting α in the low weight per cent range, with the azeotrope data for calculating α in the high weight per cent region.

To test the reliability of $p_{H_2SO_4}$, for which the authors have only azeotrope data, the Gibbs-Duhem equation was applied in the form suggested by Redlich and Kister (*18*), on the assumption that the sulfuric acid system acts as a water/sulfuric acid binary. This assumption appears satisfactory except above 99 mole %, where its failure would have a negligible effect. Figure 9 shows the result of this test at 200°C.; the positive (left-hand) area is 86.5 units and the negative (right-hand) area is 87.5 units, which indicates that $p_{H_2SO_4}$ may be a trifle high in the low weight per cent region. This uncertainty appears to lie within the accuracy of the present calculations and has not been further adjusted.

Regardless of the calculational method used for α pressures calculated at low temperatures (where α is not a significant variable) are as accurate as the available thermodynamic data allow. Changes in α, to correct the high-temperature pressures, affected the results up to 100°C. by no more than 2%. The relative accuracy of the partial pressures calculated in different temperature and composition regions, estimated qualitatively from the foregoing considerations, is shown in Table 2; the correction for nonideal gas behavior, which has not been applied, is estimated to be less than 10% even at 400°C.

It is felt that the utility of the results presented here depends not only upon their absolute accuracy but also upon their internal consistency and upon the versatility of the calculational method. When additional data become available, particularly in the 1.0-atm. azeotrope region, they may be incorporated into the general framework of the calculation and the effect upon calculated results determined.

Table. 2. Estimated mean uncertainty in partial pressure values

Temperature range	0 to 150°C.		150° to 300°C.		300° to 400°C.	
Composition range, wt.-%	10 to 80	80 to 100	10 to 80	80 to 100	10 to 80	80 to 100
Water	± 4%	8	8	16	12	24
Sulfuric acid	±10%	4	20	8	30	12
Sulfur trioxide	±12%	9	22	18	32	27

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NOTATION

a = activity
C_p = heat capacity, cal./g.-°K. or cal./mole-°K.
f = fugacity
F = free energy
g = gas
H = enthalpy
K_p = equilibrium constant
l = liquid
L = partial enthalpy
m = mole fraction
p = partial pressure, mm. Hg or atm.
P = total pressure, mm. Hg or atm.
R = gas constant, 1.98726 cal./mole-°K.
S = entropy
t = temperature, °C.
T = temperature, °K.
w = mass fraction
α = temperature coefficient of $\overline{C}_p$, cal./mole (°K.)^2

Superscripts

o = standard state value
— = (overscore) partial molal quantity

Subscripts

1 = water
2 = sulfuric acid
3 = sulfur trioxide
298 = property at 298.15°K.
0 = property at 0°K.
(1) = property for Equation (1)

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