$$\Delta H^0{}_{298.16°\text{K.}} = \Delta F^0{}_T + T \,\Delta S^0{}_{298.16°\text{K.}} -$$

$$\int_{298.16}^{T} \Delta C_p \, dT + T \int_{298.16}^{T} \Delta C_p \, d \ln T$$

The free energy of reaction 1 may be calculated from data of Carpenter and Jette,[10] and Ishikawa and Murooka.[11] Carpenter and Jette measured the dissociation pressure over $CdSO_4 \cdot H_2O(s)$ — $CdSO_4 \cdot 8/3H_2O(s)$. Ishikawa and Murooka measured the pressure of water vapor over saturated solutions of cadmium sulfate hydrates. At $316.76°\text{K.}$, $CdSO_4 \cdot 8/3H_2O$ undergoes a transition to $\alpha\text{-}CdSO_4 \cdot H_2O$, thus we may use I. and M.'s value at the transition temperature.

The free energy of formation of $CdSO_4 \cdot 8/3H_2O$ from liquid water and $CdSO_4 \cdot H_2O$ is given by the expression $\Delta F^0 = 5/3 \, RT \ln P_{H_2O}(\text{atm.})$.

The heat capacity and entropy of water were based on spectroscopic data.[12] $H_2O(g)$, $S^0{}_{298.16} = 45.106$. This was combined with the heat of vaporization of Osborne, Stimson and Ginnings[8] and

TABLE VIII

HEAT OF THE REACTION $CdSO_4 \cdot H_2O(s) + 5/3H_2O(g) =$ $CdSO_4 \cdot 8/3H_2O(s)$ FROM THE THIRD LAW OF THERMODYNAMICS

Units are cal. mole^{-1}

T, °K.	ΔF_T	Ref.	$T\Delta S_{298.16}$	$-\int_{298.16}^{T}\Delta C_p dT$	$T\int_{298.16}^{T}\Delta C_p d\ln T$	$\Delta H_{298.17}$
298.15	−3719	C. and J.	−17027	0	0	−20746
298.16	−3708	C. and J.	−17028	0	0	−20736
303.33	−3411	C. and J.	−17323	−31	38	−20727
308.33	−3144	C. and J.	−17609	−62	79	−20736
313.28	−2871	C. and J.	−17891	−94	115	−20740
313.41	−2852	C. and J.	−17899	−95	116	−20740
316.76	−2674	I. and M.	−18090	−118	144	−20738

Av. from third law = −20738

Isothermal calorimetric measurement = −20729

(10) C. D. Carpenter and E. R. Jette, THIS JOURNAL, **45**, 578 (1923).

(11) F. Ishikawa and H. Murooka, *Bull. Inst. Phys. Chem. Res.* (*Tokyo*), **9**, 781 (1933).

(12) "Selected Values of Chemical Thermodynamic Properties," Series III National Bureau of Standards, June 30, 1948.

the vapor pressure and gas imperfection equations of Keyes[9] to give $H_2O(1)$, $S^0{}_{298.16} = 16.71$.

$CdSO_4 \cdot 8/3H_2O$, $S_{298.16} = 54.89$ cal. deg.$^{-1}$ mole^{-1}

$CdSO_4 \cdot H_2O$, $S_{298.16} = 36.82$ cal. deg.$^{-1}$ mole^{-1}

$CdSO_4$, $S_{298.16} = 29.41$ cal. deg.$^{-1}$ mole^{-1}

The results are summarized in Table VIII.

The lack of trend in the values of $\Delta H_{298.16}$ in Table VIII supports the accuracy of the third law values although the individual values deviate appreciably from the average due to the limitations of the dissociation pressure data. However, the agreement of the calorimetric and third law values of the heat of reaction within 9 cal. mole^{-1} shows a consistency in terms of entropy of 0.03 cal. deg.$^{-1}$ mole^{-1}

For the reaction
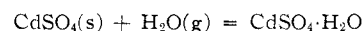
$$CdSO_4(s) + H_2O(g) = CdSO_4 \cdot H_2O$$
$$\Delta F^0 = RT \ln P_{H_2O}(\text{atm.})$$

there is only one observation due to Ishikawa and Murooka[13] who give

$$P_{H_2O} = 0.62 \text{ mm. at } 25°, \Delta H^0 = \Delta F^0 + T\Delta S^0$$
$$\Delta H_{298.16} = -4210 + 298.16 \,(36.82 - 29.41 - 45.11)$$
$$= -15451 \text{ cal. mole}^{-1}.$$

This is in satisfactory agreement with the more reliable calorimetric value, −15,402 cal. mole^{-1}, especially considering that each 0.01 mm. error in p_{H_2O} represents 10 cal. mole^{-1}.

The two third law agreements presented above indicate that $CdSO_4$, $CdSO_4 \cdot H_2O$ and $CdSO_4 \cdot 8/3H_2O$ all approach zero entropy at limiting low temperatures.

We thank E. W. Hornung, W. P. Cox and R. H. Sherman for assistance with the low temperature measurements.

(13) F. Ishikawa and H. Murooka, *Sci. Repts. Tohoku Imp. Univ.*, **22**, 138 (1933).

BERKELEY, CALIFORNIA

The Vapor Pressure of Water Over Aqueous Sulfuric Acid at 25°[1]

BY E. W. HORNUNG AND W. F. GIAUQUE

Direct observations of the vapor pressure of water over $H_2SO_4 \cdot 4H_2O$, $H_2SO_4 \cdot 3H_2O$ and $H_2SO_4 \cdot 2H_2O$ have been made over a range of temperatures above 25°. These results with available partial molal heat content and heat capacity data have been used to calculate accurate values of the partial pressure of water at 25°. These results confirm the accuracy of the direct pressure observations of Shankman and Gordon, and of Stokes, and reinforce the earlier conclusion of Stokes that the cells H_2, H_2SO_4, $PbSO_4$, PbO_2, Pt and H_2, H_2SO_4, Hg_2SO_4, Hg have not given accurate activities of water or of sulfuric acid in the more concentrated range.

In connection with our series of investigations on the thermodynamics of the sulfuric acid–water system, from 15 to 300°K., accurate data on the free energy of dilution at 25° are essential. In much of the range below 20 molal H_2SO_4 the most effective methods appear to be either the direct measurement of the vapor pressure of water over the solu-

tions, or measurements with some cell involving sulfuric acid, e.g.

$$Hg_2SO_4 + H_2 = H_2SO_{4(xm)} + 2Hg$$
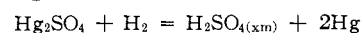
Both types of measurement have been made by several observers. Results calculated from cell measurements by means of the Duhem equation fail to agree with the direct measurements within the expected limits of error. Our problem was to extend the data to a somewhat higher concentra-

tion of sulfuric acid and to make some independent checks on the discrepancies between the cell data and the direct observations.

Cell measurements involve uncertainties as to whether the reactions are as clean cut as they are usually written but it is difficult to imagine anything very obscure about a direct measurement of the vapor pressure of water over a sulfuric acid solution. In the latter case errors are almost certain to be of a very direct kind, such as erroneous observation of pressure including contributions from gaseous impurities. The pressure to be measured in the more concentrated part of the range considered is rather small at 25° and small amounts of dissolved gaseous impurities could make a substantial percentage error.

Since recent work in this Laboratory has made available accurate values of the partial molal heat contents, heat capacities and some information concerning the temperature coefficient of the partial molal heat capacities,[2] it seemed desirable to make measurements at higher temperatures, where the pressure is larger, and then calculate values for 25°. The purpose of this procedure was not entirely to have larger measured pressures, but also to check for the presence of gases other than water. If no gas except water contributes to the pressure, a series of measurements over a temperature range, all calculated to 25°, should give agreement. We found this to be an effective method of disclosing the presence of gaseous impurities, and we also found that such gases were not easily eliminated.

Experimental Procedure

The measurements were made by means of a Société Génévoise cathetometer and a mercury manometer, 16 mm. in diam., attached to a vacuum jacketed gold calorimeter[3] ordinarily used for heat capacity measurements. Pressure observations were usually made in the order of increasing temperature and sufficient stirring could be obtained by heating with the lower half of the gold resistance thermometer–heater. The calorimeter contained some 100 cc. of solution and the amount of water required to fill the manometer volume had a relatively unimportant effect on the acid concentration. Several measurements made after cooling the sample checked those after heating to 0.01 mm. We believe that measurements made after cooling are probably not as reliable because the cooling was slower and more uniform. This produced less convection than the addition of heat to the lower portion of the calorimeter.

The acid was solidified and pumped by means of a mercury diffusion pump to remove foreign gases. In addition to air, a probable gaseous impurity was helium, since this gas had been used to ensure thermal conductivity in the calorimeter. A series of vapor pressure measurements showed that the values calculated for 25° became progressively lower as the temperature increased. It was evident that even long continued pumping of the solid, and the cooled liquid, had not removed all gaseous impurities. Five or six successive cooling and pumping operations brought values at all temperatures into good agreement. However, even after this treatment, a very small residual amount of gaseous impurity was determined by condensing the gas in the manometer space by means of liquid nitrogen.

The sodium sulfate decahydrate point, taken as 32.380°, was used as a temperature reference so that temperatures were known to about 0.005° with respect to this reference.

The Experimental Data.

—The observations are given in Table I. Measurements at $A = 2.999$

(2) J. E. Kunzler and W. F. Giauque, This Journal, 74, 3472 (1952).

(3) W. F. Giauque and C. J. Egan. J. Chem. Phys., 5, 45 (1937).

and 3.999, where A is the number of moles of water per mole of sulfuric acid, agreed well with the direct vapor pressure measurements of Shankman and Gordon[4] at 25°. A series of measurements was made at $A = 2.001$, to extend the results to the region where the freezing point data of Kunzler and Giauque[5] enable the calculation of the activity of water to be extended to more concentrated regions.

TABLE I

Vapor Pressure of Water Over $H_2SO_4 \cdot A H_2O$

P in international mm.

	Obsd.		Calcd.	
t, °C.	P_t	f_t	$f_{25°}$	$P_{25°}$
		$A = 3.999$		
23.17	4.252	4.251	4.789	4.790
24.53	4.627	4.626	4.770	4.771
25.00	4.795	4.794	4.794	4.795
34.47	8.686	8.682	4.782	4.783
47.56	18.528	18.513	4.771	4.772
Accepted			4.778	4.779
S. and G.[4] interpolated				4.790
		$A = 2.999$		
27.67	2.821	2.821	2.361	2.361
29.18	3.102	3.101	2.348	2.348
34.72	4.443	4.442	2.355	2.355
44.51	8.061	8.058	2.353	2.353
54.07	13.895	13.887	2.353	2.353
Accepted			2.353	2.353
S. and G.[4] interpolated				2.358
		$A = 2.001$		
25.00	0.618	0.618	0.618	0.618
42.05	1.980	1.980	.618	.618
52.78	3.878	3.877	.621	.621
63.09	7.027	7.025	.616	.616
71.84	11.316	11.312	.615	.615
Accepted			.617	.617

Each of the observations in Table I is the average of a series of measurements. The accepted values for 25° were obtained by averaging each of the several values weighted in accordance with the total pressure measured, thus the values actually measured near 25° had little weight. Harned and Hamer[6] carried out careful investigations of the two cells

$$H_2, \ H_2SO_{4(xm)}, \ PbSO_4, \ PbO_2, \ Pt \qquad (1)$$

and

$$H_2, \ H_2SO_{4(xm)}, \ Hg_2SO_4, \ Hg \qquad (2)$$
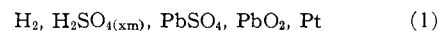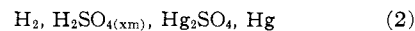
Cell 1 was investigated up to 7 molal and cell 2 to 17.5 molal. Both were studied over a range of temperature and all of the results were in good agreement with respect to the changing activity of sulfuric acid over the common range of concentration. Thus both cells were also in agreement with respect to the activity of water. Shankman and Gordon[4] called attention to the discrepancy between their direct observations and those of Harned and Hamer.[6] Stokes[7] brought NaOH solutions at

(4) F. Shankman and A. R. Gordon, This Journal, 61, 2370 (1939).

(5) J. E. Kunzler and W. F. Giauque, ibid., 72, 5271 (1952).

(6) H. S. Harned and W. J. Hamer, ibid., 57, 27 (1935).

(7) R. H. Stokes, ibid., 69, 1291 (1947).

25° into equilibrium with water vapor from water thermostated at lower temperatures. He compared the NaOH solutions with aqueous H_2SO_4 by accurate isopiestic observations and then calculated values for the latter solutions. His Fig. 2 gives an excellent comparison of his results with those of earlier experimenters. Stokes' vapor pressure data, which extend from about 3 to 11 molal, closely parallel a curve through the results of Shankman and Gordon, and are about 0.25% higher. On the basis of more recent values[8] for the vapor pressure of water, Stokes' results should be lowered by about 0.1% above 5 M, thus bringing him into closer agreement with Shankman and Gordon. Accepting the more extensive range of S. and G. as a reference the results of H. and H. are 3% high at 12 M, agree at 9 M, and are about 1% low at 6 M. The results of the present work at $A = 3.999$ (13.88 M) and $A = 2.999$ (18.51 M) are about 0.2% below those of Shankman and Gordon.

Stokes felt forced to conclude that the results of cells 1 and 2 were not giving the correct activities of water which also implies that they do not give the correct activities of sulfuric acid. We feel obliged to reach a similar conclusion. The manner in which the activity of water obtained from the cell data crosses over the other data at 9M eliminates integration of the Duhem equation from the reference state of pure water as a possible explanation. Stokes points out that the Hg_2SO_4 and Pb-SO_4, PbO_2 electrodes would have to produce identical effects with varying H_2SO_4 concentration over their common range if these electrodes are to be held responsible; thus he considers this source unlikely. The hydrogen electrode occurs in common and thus is more open to suspicion.

Randall and Cushman[9] who investigated cell 2 wondered concerning the reduction of H_2SO_4 by means of H_2 on the platinum surface. They passed exit hydrogen through 0.01 M I_2 solution but found no evidence of SO_2. Harned and Hamer state that they confirmed this test. This still leaves some question as to whether the tests were sensitive enough to disclose all effects resulting from such a possible reduction on the electrode surface.

The small differences between the present results and those of Shankman and Gordon are believed to be within the limitations of their analytical accuracy. The various researches on sulfuric acid solutions in progress in this laboratory have included a very necessary advance in the accuracy of sulfuric

acid standardization.[10] This can now be done with an accuracy of several thousandths of a per cent. and the accuracy in connection with the present results should be well within 0.01% as an upper limit in an absolute sense.

Shankman and Gordon state that their internal consistency with a Na_2CO_3 (from $NaHCO_3$) reference was 0.03%. Even if the Na_2CO_3 standard could be accepted, the 0.03% in their analyses could explain the difference between their values and the present results. The effect of 0.03% leads to S. and G. (interpolated) 4.790 ± 0.013 as against the present value 4.779 at $A = 3.999$. The corresponding values for $A = 2.999$ are S. and G. (interpolated) 2.358 ± 0.012 as against the present result of 2.353. Although the deviation between the present results and those of Shankman and Gordon can be explained by their analytical limitations we cannot claim an accuracy better than the observed difference. Possible errors in the partial molal heat data plus lack of stirring could produce the observed 0.2% difference in the partial pressures. Stokes does not discuss the absolute accuracy of his acid analyses even though accuracy to some hundredths of a per cent. is unusual, and in this case important.

In determining the activity of water in aqueous H_2SO_4 we accept the present result at $A = 2$, the average between the present results and Shankman and Gordon at $A = 3$ to $A = 4$. At values of A greater than 4, where the analytical accuracy becomes of less importance the average of Shankman and Gordon and the corrected values of Stokes seems to be the best choice to 2 molal.

It should be remarked that the above conclusions reached with respect to the cell data are restricted to the region of relatively concentrated sulfuric acid. Harned and Hamer[6] state that activities calculated from freezing point lowering data in more dilute sulfuric acid solutions agree well with the cell data.

The extension of the activity of water to $A = 2$ will be used as a connecting link to the freezing point data at high concentrations of H_2SO_4. These data will permit the determination of the activity of water in concentrations up to anhydrous sulfuric acid.

Smoothed data over the range to anhydrous sulfuric acid will be given in a later paper summarizing the various thermodynamic properties of aqueous sulfuric acid.

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(8) F. G. Keyes, J. Chem. Phys., **15**, 602 (1947).

(9) M. Randall and O. E. Cushman, THIS JOURNAL, **40**, 393 (1918).

(10) J. E. Kunzler, Anal. Chem., **25**, 93 (1953).