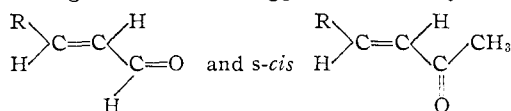


TABLE II
ULTRAVIOLET ABSORPTION CHARACTERISTICS

		$\lambda_{\max},$ m μ	$\epsilon \times 10^{-2}$	$\lambda'_{\max},$ m μ	$\epsilon \times 10^{-2}$
Cinnamic acid	<i>cis</i>	264	9.5	214	10.5
	<i>trans</i>	273	20.0	215	15.0
Benzalacetophenone	<i>cis</i>	290	9.0	248	14.0
	<i>trans</i>	298	23.6	227	12.0
<i>p</i> -Aminocinnamo- nitrile	<i>cis</i>	344	20.1	238	9.0
	<i>trans</i>	344	24.3	235	9.1
<i>p</i> -Dimethylamino- cinnamonnitrile	<i>cis</i>	364	28.6	244	10.3
	<i>trans</i>	364	31.0	243	10.6

This large difference suggests not only *s-trans*



conformations for the aldehyde and ketone but also that there is less resonance interaction between the electron releasing and electron withdrawing groups in the ketone. This latter conclusion is supported by the large interaction polarizability,¹⁵ 10.6 ml., for the aldehyde compared to the value 8.8 ml. for the ketone.

The insertion of the vinyl group between the benzene ring and the electron withdrawing group in *para* disubstituted benzenes has the following effects on the electric moments in benzene solution:

1. The moments of the *p*-dimethylamino ester,¹⁸ nitrile,¹⁹ aldehyde⁵ and nitro compound²⁰ are in-

(18) J. J. Downs, M.S. Thesis, University of Notre Dame, 1952.

(19) E. Hertel and F. Dumont, *Z. physik. Chem.*, **B30**, 139 (1935); value recalculated.

creased by 0.40, 0.78, 0.85 and 0.80 unit, respectively.

2. The moments of the *p*-amino⁵ ester, nitrile and ketone are increased by 0.42, 0.34 and 0.46 units, respectively. These results suggest about equal contributions of highly polar structures to the corresponding benzene and styrene derivatives, the greater charge separation in the latter structures accounting for the greater moments.

The insertion of the vinyl group also brings about a greater change in dipole moment, $\Delta\mu$, from benzene to dioxane solution for the *p*-amino derivatives. The values of $\Delta\mu$ for the ester, nitrile and ketone in the benzene series⁵ are 0.39, 0.50 and 0.46 Debye and in the styrene series 0.53, 0.67 and 0.65, respectively. This suggests that the increased stabilization of highly polar resonance structures in dioxane by O---H---N hydrogen bonding is about the same for the corresponding members of the two series, the greater charge separation in the styrene derivatives accounting for the larger values of $\Delta\mu$.

These data offer conclusive evidence that the vinyl group does not impede resonance between an electron-releasing group on the benzene ring and a beta electron withdrawing substituent. Such impedance might be inferred from the predominantly *ortho*, *para* substitution in alkyl cinnamates by electrophilic groups, which has led some authors to propose electron migration from the vinyl group to the ring in the activated state. It may well be that the vinyl group in reacting molecules is significantly affected by a constituent of the reaction mixture before substitution occurs.

(20) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 599 (1936).

[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

The Heat Capacity and Thermodynamic Functions of Mercurous Sulfate Between 4 and 20°K.¹

BY T. E. BRACKETT, E. W. HORNUNG AND T. E. HOPKINS

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The heat capacity of mercurous sulfate has been measured from 4 to 20°K. The results, together with available heat capacity data at higher temperatures, have been used to calculate the entropy at 298.15°K., which is found to be 47.96 gibbs mole⁻¹.² This value along with the third law values of other compounds is used to compute the change in entropy of two reactions. The change in entropy computed in this way is then compared with the results of cell measurements on these reactions. The comparisons indicate that the cell measurements are in error.

This paper reports the results of an investigation of the heat capacity of mercurous sulfate in the temperature region 4 to 20°K. Measurements of its heat capacity between 15 and 300°K. have been made by Papadopoulos and Giauque.³ The combined results establish accurate values of the thermodynamic properties of mercurous sulfate from 4 to 300°K.

For substances with a very small heat capacity

(1) This work was supported in part by the National Science Foundation Grant G-3014 and the Office of Naval Research, N6ori211, IV; NR-016-405.

(2) 1 gbs. (gibbs) = 1 defined cal./defined deg. K. See, W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, *THIS JOURNAL*, **82**, 62 (1960).

(3) M. N. Papadopoulos and W. F. Giauque (to be published).

at 15°K., or substances which obey a Debye T^3 expression near that temperature, it is usually sufficient to extrapolate the heat capacity *vs.* temperature graph to 0°K. and still retain a high accuracy for the thermodynamic functions of the compound. Mercurous sulfate, however, has the high heat capacity of 3.308 gibbs mole⁻¹ at 15°K. and it departs considerably from a T^3 function; therefore it was considered desirable to extend the measurements on this salt to lower temperatures, thereby obtaining as accurate values as possible for its thermodynamic functions.

Apparatus.—The apparatus was a calorimeter designed to operate in the region from 4 to 20°K. In general the apparatus was not dissimilar to those used in this Laboratory at higher temperatures. A few differences are noted below.

The sample was contained in a copper cylinder having a carbon thermometer-heater cemented to its outer surface. The carbon used for making the thermometer was Binney and Smith Co. "Statex."⁴ Surrounding the sample container was a second cylinder which protected the carbon thermometer and contained conducting gas. Leads to the carbon thermometer were made through Kovar glass seals.⁵

Soldered to the outer wall of the calorimeter were two chambers, one 33.53 cm.³, which served as a gas thermometer bulb; the other 1.36 cm.³, which served as a compensator. The latter was filled with copper wire to have the same surface area as the former. The compensator was used to correct for the effects of obnoxious volume and surface adsorption.⁶

A mechanical thermal switch was incorporated into the design for cooling the calorimeter and a surrounding shield to temperatures below 20°K. However the switch proved ineffective because the pressure which could be applied to the junction was small and because the heat capacity of the thermal shield was high. For these reasons the method of cooling was modified to one in which the heat was dissipated by helium gas or liquid circulating through tubes soldered to the thermal shield. (The calorimeter was cooled from room temperature to 20°K. with liquid hydrogen, using helium exchange gas for breaking the insulating vacuum. This gas was pumped out at 20°K. and at no time was any helium gas readmitted to the insulating vacuum below this temperature.)

For temperature stability of the thermal shield, the high heat of adsorption of helium gas on charcoal at low temperatures was employed. A chamber containing 78 g. of gas mask charcoal was made an integral part of the shield. A stainless steel tube connected the chamber with a 35 liter helium reservoir outside the apparatus. Any heat leaking to the shield would thus cause a desorption of helium (with its large heat requirement) without an appreciable increase in the pressure or temperature.

Sample.—The sample was some of the same material used by Papadopoulos and Giauque.³ It was prepared by precipitation from Hg₂(NO₃)₂ with 0.5 M H₂SO₄. Their analysis of the sample gave a ratio of SO₄²⁻/Hg₂SO₄ equal to 0.19318, 0.19312 and 0.19317, compared with the theoretical 96.06/497.28 = 0.19317. The sample when not in use was stored in a glass container placed inside a metal can to prevent any decomposition resulting from light. An estimate of the particle size of the sample was made by placing a portion of it upon a ruled grating and observing the particles with a microscope. The particle size varied between 0.01 and 0.2 μm. diameter and the total surface was estimated to be about 100,000 cm.².

Measurement of Heat Capacity.—Since the electrical properties of a carbon resistance thermometer, such as the one used here, are not sufficiently reproducible, when warmed to ordinary temperatures and recooled, it cannot be used for the primary measurement of temperature. Therefore the gas thermometer system mentioned above was incorporated into the system. The thermometers were filled and calibrated at the boiling point, 20.273°K., of equilibrium hydrogen as measured with a hydrogen vapor pressure thermometer filled with a chromic oxide catalyst. This calibration was compared with a helium boiling point, 4.216°K., calibration in order to evaluate the accuracy of the gas thermometer over the temperature range from 4 to 20°K. The agreement was to within 0.01°. The resistance thermometer was compared with the gas thermometer before and after each heat capacity determination in order to insure a good knowledge of the temperature at every point in the range of the investigation. The deviation of the gas thermometer temperatures from a smooth curve did not exceed 0.01°. The high precision of the carbon thermometer enabled accurate determination of heat exchange with the surroundings and insured that equilibrium had been obtained.

One defined cal. was taken as 4.1840 absolute joules and 1 gbs. (gibbs) = 1 defined cal./1 defined deg. K.²

The molecular weight of Hg₂SO₄ was taken as 497.28 and the weight of the sample was 549.81 g. = 1.10563 moles.

Correction was made for the cooling effect of work and the variable amount of helium, resulting from the expansion of helium gas, in the thermometer system by measuring the heat capacity of the empty sample container in exactly the same way as the full sample container, thereby including the term as part of the heat capacity of the empty calorimeter.

During the course of the experiments we became concerned with the adsorption of helium gas by the sample itself. This could result in poor internal equilibrium at low temperatures, and the resulting heat of desorption could also affect the results. In order to evaluate the magnitude of this effect in the present investigation, an adsorption isotherm of helium on the sample was determined at approximately 4.2°K. It was established that 1.17 × 10⁻⁴ mole of helium adsorbed on the sample surface under an equilibrium pressure of 10⁻⁴ mm. This gas pressure was considered sufficient for relatively rapid heat exchange. At 8°K. essentially all of the gas was desorbed. The total entropy accompanying this desorption should not exceed the value of the entropy of the gas as given by the Sackur-Tetrode equation at that temperature and pressure—assuming an entropy of zero for the adsorbed helium film at 4.2°K. This estimate gives ΔS = 0.004 gibbs mole⁻¹. Although the correction to the total entropy is very small, the correction to the heat capacity can be relatively much larger. By use of the Clausius-Clapeyron equation, along with an estimate of the heat of desorption given by the Sackur-Tetrode equation, it is possible to estimate the number of moles of gas desorbed and the total heat of this process during any given heat capacity run. The total correction varied from 0.0002 to 0.01 gibbs mole⁻¹.

Results

The corrected experimental data appear in Table I. The deviation of the experimental points from a smooth curve does not exceed 0.1%. The heat capacity of mercurous sulfate obtained from this investigation agrees with that of Papadopoulos and Giauque³ within several tenths of a per cent. in the region in which they can be compared.

TABLE I
EXPERIMENTAL HEAT CAPACITIES OF MERCUROUS SULFATE
549.81 g. in calorimeter; C_p in gibbs mole⁻¹

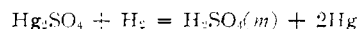
Series I			Series II		
T, °K.	C _p	ΔT	T, °K.	C _p	ΔT
11.156	1.786	1.401	4.851	0.0907	0.7833
12.412	2.286	1.116	5.523	.1573	.5480
13.624	2.774	1.313	6.063	.2324	.5276
15.089	3.327	1.617	6.637	.3361	.6249
16.869	3.996	1.952	7.291	.4767	.6827
19.016	4.695	2.353	8.016	.6773	.7705
21.485	5.633	2.599	8.840	.9407	.8768
			9.967	1.351	1.380

Table II gives the smoothed heat capacities and other thermodynamic functions of mercurous sulfate to 20°K.

TABLE II
THERMODYNAMIC PROPERTIES OF MERCUROUS SULFATE

T, °K.	C _p	S	$-\left(\frac{F^0 - H^0}{T}\right)$	$\frac{H^0 - H^0_0}{T}$
5.0	0.1020	0.0272	0.0061	0.0211
7.5	0.5291	.1350	.0277	.1073
10.0	1.358	.3946	.1143	.2803
12.5	2.319	.800	.209	.591
15.0	3.308	1.311	.349	.962
17.5	4.207	1.890	.527	1.363
20.0	5.072	2.507	.736	1.771

Comparison of the Results with Cell Data.—The reaction



is readily adaptable to cell measurements and

(4) T. H. Geballe, D. N. Lyon, J. M. Whelan and W. F. Giauque, *Rev. Sci. Instr.*, **23**, 489 (1952).

(5) Stupakoff Ceramics and Manufacturing Co., Latrobe, Penn.

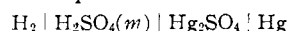
(6) Natl. Bur. Standards Report No. 2 for O.N.R., 12-48.

affords a convenient method of determining the thermodynamic properties of the sulfuric acid-water system. All the pertinent data have now been obtained by other measurements, and they will allow a test of the internal consistency and thus validity of the cell data.

The partial molal heats, free energies, entropies and heat capacities of the sulfuric acid-water system have been measured by numerous methods and various authors. These data have been shown to be internally consistent and in accurate agreement with the results of third law determinations of the thermodynamic properties of all the various hydrates of the sulfuric acid-water system. A comprehensive tabulation of these properties is available.²

The values 31.21⁷ and 18.171 gibbs/mole^{8,9} are taken as the entropies at 298.15°K. of H₂ and Hg, respectively. The results of this work combined with the investigations of Papadopoulos and Giauque³ give the value 47.96 gibbs mole⁻¹ for the entropy of Hg₂SO₄ at 298.15°K.

The most comprehensive data for the cell



are given by Harned and Hamer.¹⁰ The actual data obtained were not published. Instead, the results were presented as an equation of the form,

$$E = E_{250} + a(t - 25) + b(t - 25)^2 \text{ int. volts}$$

The empirical constants "a" and "b" were derived from a least square analysis of the data over the temperature range 0 to 60° for each concentration. The cell was studied over the concentration range 0.05*m* to 17.5*m* and values of E_{250} , "a" and "b" were tabulated for selected values of *m*.

A comparison of the ΔS for the reaction as obtained by application of the third law of thermodynamics along with the sulfuric acid data with the ΔS for the same reaction given by the cell data is presented in Table III.

TABLE III
COMPARISON OF THIRD LAW ENTROPIES WITH THE dE/dt
OF THE CELL AT 25°, GIBBS MOLE⁻¹

<i>m</i>	$\Delta S_{(\text{cell})}$	$\Delta S_{(\text{third law})}$	$\Delta S_{(\text{third law})} - \Delta S_{(\text{cell})}$
1	8.57	9.73	1.16
5	10.81	11.76	0.95
10	9.68	9.99	0.31
15	8.18	9.88	1.70
17	7.51	9.85	2.34

The entropy values are not consistent to within about 2 gibbs mole⁻¹. This corresponds to an error of approximately 0.05 mv./°C., or over a range of 25 degrees, the error could be as large as ± 1.3 mv. A direct calculation of three cell voltages at 17*m* for 0, 25 and 50° shows disagreement to approximately this same value, ± 1.3 mv. The reproducibility of the cells was given as ± 0.1 mv.

It also should be pointed out that Hamer¹¹ measured the cell

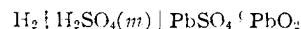
(7) H. W. Woolley, R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379 (1948).

(8) R. H. Busey and W. F. Giauque, *THIS JOURNAL*, **75**, 806 (1953).

(9) P. L. Smith and N. M. Wolcott, *Phil. Mag.*, [8], **1**, 854 (1956).

(10) H. S. Harned and W. J. Hamer, *THIS JOURNAL*, **57**, 27 (1935).

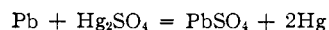
(11) W. J. Hamer, *ibid.*, **57**, 9 (1935).



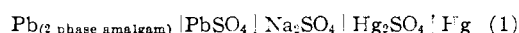
This was also found to be in disagreement of the same order of magnitude with the thermodynamic properties of the sulfuric acid-water system at 25° as pointed out by Shankman and Gordon¹² and later confirmed by Stokes,¹³ both of whose results make up part of the compilation of the sulfuric acid-water system.²

However, the above cell recently was measured by Beck, Singh and Wynne-Jones¹⁴ and found to agree with the vapor pressure measurements of Shankman and Gordon and of Stokes at 25°, thereby showing Hamer to be in error on the lead sulfate cell, at least at that temperature.

It is also interesting to compare the results of cell measurements with the results of heat capacity measurements on the reaction



Harned and Hamer¹⁵ have measured the cell

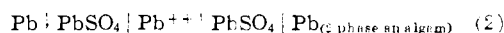


The electromotive force agrees with their equation

$$E_1 = 0.96051 + 0.000155t + 0.0000038t^2 \text{ int. volts}$$

to ± 0.02 mv.

This result combined with the results of Gerke¹⁶ on the cell



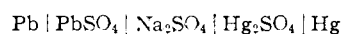
whose electromotive force can be expressed by the equation

$$E_2 = 0.00540 + 0.000016t \text{ int. volts}$$

give

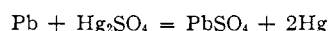
$$E_1 + E_2 = 0.965911 + 0.000171t + 0.0000038t^2 \text{ int. volts}$$

for the electromotive force of the cell



The values 15.51¹⁷ and 35.51 gibbs/mole¹⁸ are taken as the entropies at 298.15°K. of Pb and PbSO₄, respectively.

A comparison of the entropies at three selected temperatures of the reaction



as calculated from third law measurements and cell measurements, appears in Table IV. It is

TABLE IV
A COMPARISON OF THIRD LAW ENTROPIES WITH THE dE/dt
OF THE CELL

<i>t</i> , °C.	$\Delta S_{(\text{third law})}$	$\Delta S_{(\text{cell})}$	$\Delta S_{(\text{third law})} - \Delta S_{(\text{cell})}$
0	8.33	7.89	+0.44
25	8.38	8.76	+0.38
50	8.33	9.64	-1.31

again clear that the cell data are in error of the order of 1 mv.

(12) F. Shankman and A. R. Gordon, *ibid.*, **61**, 2370 (1939).

(13) R. H. Stokes, *ibid.*, **69**, 1291 (1947).

(14) W. H. Beck, K. P. Singh and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **55**, 331 (1959).

(15) H. S. Harned and W. J. Hamer, *THIS JOURNAL*, **57**, 33 (1935).

(16) R. H. Gerke, *ibid.*, **44**, 1684 (1922).

(17) P. F. Meads, W. R. Forsythe and W. F. Giauque, *ibid.*, **63**, 1902 (1941).

(18) K. Gallagher, G. E. Brodale and T. E. Hopkins *Jour. Phys. Chem.*, **64**, 687 (1960).