state is not certain. The adiabatic third IP of the ferrocene agrees best with the electronic spectrum, being almost exactly 2 eV above the ground state of the ion; however the contour of the 9.4-eV band makes the estimation of the ionization potential difficult. On the basis of the pes we would assign the first five levels in ferrocene to be $e_{2g} > a_{1g} > e_{1u} > e_{1g} > e_{1u}$.

(d) **Chlorine Dioxide and the Chloryl Cation.**—The ClO_2^+ cation has been identified by Carter, Johnson, and Aubke.[10] They reported an electronic spectrum consisting of two bands and a shoulder at 270, 220, and 330 nm, respectively, the two low-energy bands being assigned to $^1A_1 \rightarrow ^1B_1$ and $^1A_1 \rightarrow ^1B_2$ transitions. The photoelectron spectrum of ClO_2 has been observed by Cornford, *et al.*,[11] who reported adiabatic (vertical) ionization potentials at 10.36 (10.48), 12.32 (12.94), 15.27 (15.45), 16.25 (17.50), and 17.69 (17.95) eV. The pe spectrum of a free radical is complicated by the occurrence of a multiplet (singlet–triplet) splitting of all bands after the first with the triplet bands being roughly 3 times more intense than the singlet. Thus in a comparison of the electronic spectrum with the pe

(10) H. A. Carter, W. M. Johnson, and F. Aubke, *Can. J. Chem.*, **47**, 4619 (1969).

(11) A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *Chem. Phys. Lett.*, **10**, 345 (1971).

spectrum care must be exercised to distinguish the singlet and triplet states. The intensity of the third band in the pe spectrum of ClO_2 is such as to identify it as most likely belonging to the $^1B_1$ state and the IP's quoted by Cornford, *et al.*, give a transition energy of 39,600 cm^{-1} (250 nm) which is however closer to the $^1A_1 \rightarrow ^1B_2$ transition assigned by Carter, *et al.* As indicated earlier, estimates of electronic transitions from pes are likely to be to too long wavelengths; thus in this case it would appear that solvent interactions have depressed the $^1B_1$ state of ClO_2^+ some 80 nm relative to the gas phase. It can be noted here that Carter, *et al.*, are careful to point out that the ClO_2^+ is solvent stabilized. If we assume that the $^1B_2$ state is stabilized roughly by the same amount as the $^1B_1$ state, then this state would correspond to the state at 17.7 eV in the pe spectrum. This would imply that the orbital configuration of ClO_2^+ is in fact $\ldots b_2^2 - a_2^2 a_1^2$ with the lowest unoccupied orbital being the b_1.

Thermodynamic Properties of Oxygenated Sulfur Complex Ions. Heat Capacity from 5 to 300°K for K₂S₄O₆(c) and from 273 to 373°K for S₄O₆²⁻(aq). Revised Thermodynamic Functions for HSO₃⁻(aq), SO₃²⁻(aq), S₂O₃²⁻(aq), and S₄O₆²⁻(aq) at 298°K. Revised Potential of the Thiosulfate–Tetrathionate Electrode[1]

BY J. W. COBBLE,*[2] H. P. STEPHENS,[2,3] I. R. McKINNON,[4] AND E. F. WESTRUM, JR.[4]

The heat capacity and thermodynamic functions for crystalline potassium tetrathionate, K₂S₄O₆(c), have been determined by adiabatic calorimetry from 5 to 330°K. The values of the standard thermodynamic functions C_p, $S°$, $-(F° - H°_0)/T$ at 298.15°K are 55.16, 74.01, and 38.91 cal mol^{-1} °K^{-1}, respectively. The heats of solution of K₂S₄O₆(c) in water have been determined at various concentrations between 20 and 95° and extrapolated to infinite dilution to give the standard enthalpies of solution. At 25°, $\Delta H°_s$ = 12,403 cal mol^{-1}. The partial molal heat capacities of K₂S₄O₆(aq) have been evaluated from the heats of solution. The free energy of solution of K₂S₄O₆(c) at 25° was determined to be 1510 cal mol^{-1}; the resulting entropy of K₂S₄O₆(aq) was 110.5 cal mol^{-1} °K^{-1}. Recalculation of previous data in the literature by third-law methods has resulted in revised thermodynamic functions for HSO₃⁻(aq), SO₃²⁻(aq), and S₂O₃²⁻(aq). The standard potential of the S₄O₆²⁻–S₂O₃²⁻ electrode was calculated as 0.169 V at 25°.

I. Introduction

The thermodynamic functions for large complex oxygenated anions are of continuing interest in inorganic chemistry. The tetrathionate ion, $S_4O_6^{2-}$, is a representative of these complex species, the salts of which can be obtained in high purity. Moreover, the potential of the thiosulfate–tetrathionate electrode is of analytical importance. Although thiosulfate can

be titrated quantitatively by iodine or triiodide, the great variation in reported potentials for the couple suggests that the electrode itself is not reversible.[5] Consequently, the potential of this electrode will have to be fixed from thermal measurements. Little data exist on the partial molal heat capacities for any complex electrolyte, and this communication provides the first data for such an anion.

II. Experimental Section

Apparatus.—The heat capacity measurements were made at the University of Michigan by the adiabatic intermittent-heating

(5) B. V. Pmetzen and V. A. Kozlon, *Zh. Anal. Khim.*, **2**, 259 (1947).

technique in a copper calorimeter (laboratory designation W-49), fitted with vanes to aid thermal conduction and a platinum resistance thermometer (laboratory designation A-5) in the Mark II cryostat.[6] The sealed calorimeter contained 82.713 g (*in vacuo*) of sample together with helium gas (45 Torr at 300°K) to hasten thermal equilibrium. Buoyancy corrections were made for a sample density of 2.296 g cm^{-3}. All determinations of mass, time, temperature, resistance, and potential were related to calibrations or standardizations made by the National Bureau of Standards.

A submarine type of heat-of-solution calorimeter (laboratory designation SC-1) described previously[7] was used for the endothermic heat-of-solution measurements at the various temperatures. As the salt dissolved, approximately equivalent amounts of energy were added electrically to the calorimeter through the standard heater and calibration circuit. This nearly isothermal method considerably increases the accuracy of the measurements.

Materials.—Distilled water was purified further using an anion–cation exchange column. Potassium tetrathionate was prepared by a method suggested by Stamm and Goehring[8] and purified by recrystallization from aqueous ethanol solutions. The purity of the salt was established by a combination of gravimetric, polarographic, chromatographic, and thermal measurements. $K_2S_4O_6$ was oxidized in alkaline hypobromite solutions and sulfur determined by precipitation as $BaSO_4$ (S: calcd, 42.40; found, 42.20). Potassium was determined gravimetrically as the sulfate (K: calcd, 25.86; found, 25.84). A polarographic half-wave potential of a 10^{-4} N solution of $K_2S_4O_6$ with 0.5% Seignette salt, 0.1 N $BaCl_2$, and 0.01% gelatin was −0.149 V *vs.* sce, to be compared to the value of −0.15 V reported elsewhere.[9] A paper chromatogram determined by the method of Bighi and Trabanelli[10] showed that the salt contained only one anion. Finally, the thermal data indicated the presence of 0.04% by weight of water and 0.013% by weight of ethanol from a local maximum in the heat capacity at 258°K, presumably caused by melting of recrystallization solvent entrapped in the matrix. The defined thermochemical calorie is taken as 4.184 J, ice point as 273.15°K, and 1 mol of the salt as 302.46 g. Temperatures refer to degrees centigrade, except when absolute temperatures in degrees Kelvin are so indicated.

III. Results

Cryogenic Data.—The experimental heat capacity values for $K_2S_4O_6$(c) are given in chronological order in Table I at the mean temperature of the determination. These data have been corrected for the heat capacities of the empty calorimeter, the Apiezon grease (used to promote thermal contact of the calorimeter with the heater, thermometer, and thermocouples), and the helium gas. Correction has also been made for the curvature occasioned by the finite size of the experimental temperature increments. The smoothed heat capacities and thermodynamic functions derived from the above results are given in Table II. All the values in this table (but not those in Table I) have been corrected for the ethanol and water contamination.

The small maximum in the heat capacity at 258°K is attributed to the presence of the ethanol–water solution used as final recrystallization solvent. The temperature of the maximum indicates that the solvent present is 25% by weight ethanol. The total anomalous enthalpy (10.8 cal) corresponds to the fusion of 0.168 g of solvent mixture per mole of sample. The quantities in Table II were obtained (a) below 230°K by subtracting the heat capacities of the solid solvents

(6) E. F. Westrum, Jr., G. T. Furukawa, and J. P. McCullough, in "Experimental Thermodynamics," J. P. McCullough and D. W. Scott, Ed., Butterworths, London, 1968, p 133.

(7) R. E. Mitchell and J. W. Cobble, *J. Amer. Chem. Soc.,* **86,** 5401 (1964).

(8) H. Stamm and M. Goehring, *Z. Anorg. Allg. Chem.,* **250,** 226 (1942).

(9) L. Cavallaro, C. Bighi, G. Pancaldi, and G. Trabanelli, *Ann. Chim. (Rome),* **48,** 466 (1958).

(10) C. Bighi and G. Trabanelli, *ibid.,* **45,** 1186 (1955).

TABLE I
HEAT CAPACITY OF CRYSTALLINE POTASSIUM TETRATHIONATE[a]

T, °K	C$_p$	T, °K	C$_p$	T, °K	C$_p$
Series I		237.50	50.01	25.52	6.634
92.44	29.20	247.02	51.15	28.01	7.778
98.33	30.38	256.37	52.36	30.86	9.093
105.68	31.80	265.58	52.70	33.95	10.539
112.69	33.14	274.69	53.32	37.31	12.058
120.23	34.51	283.69	54.08	41.11	13.687
128.30	35.93	290.81	54.70	45.37	15.44
136.06	37.21	296.09	55.12	50.04	17.25
143.96	38.44			55.09	19.05
152.02	39.64			60.50	20.88
159.86	40.76	Series III		66.46	22.71
168.38	41.93	5.35	0.1332	71.36	24.04
177.56	43.11	5.77	0.1980	77.69	25.71
186.52	44.19	6.39	0.2610	84.51	27.47
195.28	45.22	6.98	0.3356	91.88	29.09
		7.62	0.4326	100.64	30.84
		8.48	0.5866	110.00	32.63
		9.56	0.8282	118.86	34.23
Series II		10.72	1.0713		
160.18	40.78	11.93	1.336	Series IV	
169.60	42.06	13.21	1.708	271.87	53.06
178.76	43.24	14.60	2.155	281.60	53.89
187.70	44.33	16.15	2.700	291.19	54.68
197.36	45.49	17.85	3.351	300.64	55.48
207.73	46.68	19.61	4.061	309.97	56.27
217.85	47.82	21.43	4.815	319.17	57.02
227.78	48.89	23.37	5.660	326.46	57.62

[a] In cal mol^{-1} °K^{-1}.

from the values in Table I, (b) above 270°K by subtracting the heat capacities of the liquid solvents from the values in Table I, and (c) between these temperatures by interpolation. These adjustments were less than 0.2% of the heat capacity over most of the range.

The probable error of the heat capacity values are about 5% at 10°K, about 0.4% at 20°K, and 0.1% at higher temperatures. The derived thermodynamic functions have a probable error less than 0.1% above 100°K. The free energy and the entropy have not been adjusted for nuclear degrees of freedom and are hence suitable for thermochemical calculations.

Heat of Solution Data.—The heats of solution of crystalline $K_2S_4O_6$ in water at various concentrations and temperatures have been summarized in Table III. Extrapolation of the integral heats to infinite dilution was carried out by means of a two-term Debye–Hückel type of expression. By this method[11] a function, ρ, is defined as

$$\rho = \Delta H_s - (\nu/2)|Z_+Z_-|A_H I^{1/2}\alpha =$$
$$\Delta H°_s - 2.303RT^2(dB/dT)\nu_+\nu_- m \quad (1)$$

where A_H is the Debye–Hückel limiting thermal slope,[12] I is the ionic strength, α is a numerical function tabulated elsewhere,[13] ΔH_s is the integral enthalpy of solution, and ν is the number of ions formed ($\nu_+ + \nu_-$). A plot of ρ *vs.* m is linear, and the extrapolated value of ρ at infinite dilution is simply the standard enthalpy of solution, $\Delta H°_s$, at that temperature. The values for the function are also listed in Table III.

The standard heat capacities of solution, $(\Delta C_p°)_s$, can be evaluated from the integral enthalpies at two temperatures,[11] and these data are listed in Table IV.

(11) C. M. Criss and J. W. Cobble, *J. Amer. Chem. Soc.,* **83,** 3223 (1961).

(12) G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed, revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, N. Y., 1961, p 640.

(13) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1959, Table 5-2-6.

TABLE II
THERMODYNAMIC FUNCTIONS OF CRYSTALLINE
POTASSIUM TETRATHIONATE[a,b]

T, °K	C_p	$S°$	$H°$	$-(F° - H°_0)/T$
5	0.127	0.042	0.159	0.011
10	0.879	0.321	2.378	0.083
15	2.288	0.923	10.038	0.253
20	4.212	1.835	26.13	0.529
25	6.396	3.007	52.58	0.903
30	8.687	4.374	90.26	1.366
35	11.027	5.889	139.53	1.902
40	13.211	7.503	200.11	2.500
45	15.289	9.181	271.4	3.149
50	17.220	10.893	352.8	3.838
60	20.68	14.346	542.7	5.301
70	23.69	17.765	764.9	6.838
80	26.33	21.105	1,015.3	8.414
90	28.64	24.342	1,290.3	10.005
100	30.71	27.468	1,587.3	11.596
110	32.62	30.486	1,904	13.177
120	34.44	33.403	2,239	14.741
130	36.16	36.23	2,592	16.29
140	37.80	38.97	2,962	17.81
150	39.33	41.63	3,348	19.31
160	40.76	44.21	3,749	20.78
170	42.09	46.73	4,163	22.24
180	43.36	49.17	4,590	23.67
190	44.58	51.55	5,030	25.07
200	45.77	53.86	5,482	26.45
210	46.92	56.12	5,945	27.81
220	48.03	58.33	6,420	29.15
230	49.08	60.49	6,906	30.47
240	50.07	62.60	7,401	31.76
250	51.02	64.66	7,907	33.04
260	51.93	66.68	8,422	34.29
270	52.81	68.66	8,945	35.53
280	53.65	70.59	9,478	36.75
290	54.48	72.49	10,018	37.95
300	55.32	74.35	10,567	39.13
310	56.17	76.18	11,125	40.29
320	56.98	77.98	11,691	41.44
330	57.79	79.74	12,264	42.58
273.15	53.08	69.27	9,112	35.91
298.15	55.16	74.01	10,465	38.91

[a] In contrast to the data of Table I, these values have been corrected for the presence of traces of water and ethanol. [b] In cal mol⁻¹ °K⁻¹.

From the heat capacities of the crystalline salt determined in this research up to 330°K, values of $\overline{C}_{p_2}°$, the standard partial molal heat capacity, of $K_2S_4O_6$(aq) can be calculated. Above 330°K, reliable estimates of the heat capacity of the solid salt, C_{p_2}, can be made from extrapolation of lower temperature data, so that it was also possible to evaluate $\overline{C}_{p_2}°$ for $K_2S_4O_6$(aq) up to 361°K. Finally, a plot of $\overline{C}_{p_2}°$ *vs.* T was used to obtain smoothed values of the heat capacities at integral temperatures between 15 and 100°. These are summarized in Table V. The probable error in these values is approximately 1 cal mol⁻¹ °K⁻¹, except at the lowest and highest temperatures.

IV. Calculations and Discussion

The Entropy of $S_4O_6^{2-}$(aq).—The standard free energy of solution for potassium tetrathionate can be calculated from the known solubilities and an estimated activity coefficient. Results of three determinations gave an average solubility of 1.21 *m* at 25°, as compared to a reported value[14] at 20° of 1.00 *m*.

(14) W. F. Linke and A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. II, American Chemical Society, Washington, D. C., 1965, p 330.

TABLE III
INTEGRAL ENTHALPIES OF SOLUTION FOR
POTASSIUM TETRATHIONATE[a]

Molality × 10³[b]	ΔH_s, cal mol⁻¹	$3A_H I^{1/2}\alpha$, cal mol⁻¹	ρ, cal mol⁻¹
	292.90°K		
1.04 (3)	12,813	68	12,745
1.84 (3)	12,847	90	12,757
2.34 (3)	12,847	101	12,746
5.13 (1)	12,879	144	12,735
10.56 (1)	12,904	200	12,704
	$\Delta H°_s = 12,758 \pm 4$ cal mol⁻¹		
	297.86°K		
1.02 (2)	12,516	73	12,443
1.85 (2)	12,523	97	12,426
2.36 (2)	12,542	109	12,433
3.02 (3)	12,551	122	12,429
4.29 (4)	12,566	144	12,422
8.49 (1)	12,649	196	12,453
10.06 (1)	12,687	211	12,476
	$\Delta H°_s = 12,421 \pm 7$ cal mol⁻¹		
	[at 298.15° $\Delta H°_s = 12,403 \pm 10$ cal mol⁻¹]		
	302.88°K		
1.30 (4)	12,224	88	12,136
2.32 (3)	12,266	116	12,150
3.67 (5)	12,297	144	12,153
9.19 (3)	12,380	218	12,162
	$\Delta H°_s = 12,139 \pm 4$ cal mol⁻¹		
	317.88°K		
1.29 (2)	11,454	110	11,344
3.13 (2)	11,543	171	11,372
7.51 (1)	11,580	247	11,333
9.71 (1)	11,621	277	11,344
	$\Delta H_s = 11,359 \pm 13$ cal mol⁻¹		
	333.23°K		
1.19 (1)	10,696	128	10,568
2.01 (1)	10,757	165	10,592
3.05 (1)	10,795	201	10,594
4.14 (1)	10,843	231	10,612
7.57 (1)	10,876	305	10,571
9.80 (1)	10,900	341	10,559
	$\Delta H°_s = 10,596 \pm 12$ cal mol⁻¹		
	353.10°K		
1.30 (1)	9,785	172	9,613
2.91 (1)	9,908	253	9,655
5.60 (1)	9,951	342	9,609
9.66 (1)	10,057	438	9,619
	$\Delta H°_s = 9,630 \pm 16$ cal mol⁻¹		
	368.28°K		
1.97 (2)	9,037	256	8,781
3.65 (1)	9,132	342	8,790
7.17 (1)	9,228	466	8,762
8.97 (1)	9,288	515	8,773
	$\Delta H°_s = 8,791 \pm 8$ cal mol⁻¹		

[a] In cal mol⁻¹. [b] Parenthetical values refer to the number of replicate determinations at each concentration.

TABLE IV
HEAT CAPACITY DATA FOR AQUEOUS
POTASSIUM TETRATHIONATE[a,b]

T_{av}, °K	$(\Delta C_p°)_s$	C_{p_2}	$\overline{C}_{p_2}°$
295.38	−67.8	55.0	−12.8
300.37	−56.2	55.4	−0.8
310.38	−52.0	56.3	4.3
325.56	−49.7	57.5	7.8
343.17	−48.6	(59.0)[c]	10.4
360.69	−55.3	(60.4)[c]	5.1

[a] In cal mol⁻¹ °K⁻¹. [b] The error in this function is between 1 and 2 cal mol⁻¹ °K⁻¹. [c] Extrapolated.

The mean molal activity coefficient of $K_2S_4O_6$ in a saturated solution can be reliably estimated from the corresponding values in $K_2S_2O_3$ ($\gamma_\pm = 0.23$) and K_2SO_4

TABLE V
THERMODYNAMIC FUNCTIONS FOR AQUEOUS
POTASSIUM TETRATHIONATE[a]

T, °K	$\bar{C}_{p_2}°$	$\bar{S}_2°$	$-(\bar{F}° - H°_{298})/T$
288.15	-29.5[b]	111.1[b]	111.9[b]
293.15	-17.1	110.7	110.9
298.15	-5.8	110.5	110.5
303.15	0.2	110.4	110.5
308.15	3.5	110.5	110.5
313.15	5.6	110.6	110.5
318.15	7.2	110.7	110.5
323.15	8.3	110.8	110.5
328.15	9.2	110.9	110.5
333.15	9.6	111.1	110.6
338.15	9.6	111.2	110.6
343.15	9.4	111.3	110.6
348.15	8.7	111.5	110.7
353.15	7.8	111.6	110.7
358.15	6.1	111.7	110.7
363.15	4.0	111.8	110.7
368.15	1.5	111.8	110.7
373.15	-1.9[b]	111.8[b]	110.7[b]

[a] In cal mol^{-1} °K^{-1}. [b] Extrapolated values.

($\gamma_{\pm} = 0.21$) solutions of the same ionic strength. The value of $\gamma_{\pm} = 0.23$ for saturated $K_2S_4O_6$ solutions will be adopted. The standard free energy and entropy of solution then become $\Delta F°_s = 1510 \pm 130$ cal mol^{-1} and $\Delta S°_s = 36.5 \pm 0.4$ cal mol^{-1} °K^{-1}. From the value of the entropy of the solid salt at 25° given in Table II, 74.01 cal mol^{-1} °K^{-1}, the entropy of $K_2S_4O_6$-(aq) is calculated to be 110.5 ± 0.4 cal mol^{-1} °K^{-1}. Taking the value[15] of the entropy of K^+(aq) as 24.5 cal mol^{-1} °K^{-1}, the entropy for $S_4O_6{}^{2-}$(aq) becomes 61.5 ± 0.4 cal mol^{-1} °K^{-1} at 25°. This value may be compared with the experimental value for the closely similar $S_2O_3{}^{2-}$(aq) ion of 59.5 cal mol^{-1} °K^{-1} reported elsewhere[16] at the same temperature.

Values of the standard partial molal entropies at other temperatures were obtained by graphical integration of the partial molal heat capacities and are listed in Table V. Because of the small positive values of $\bar{C}_{p_2}°$ for this electrolyte above 30°, the standard partial molal entropy of $K_2S_4O_6$(aq) does not change very much with temperature.

Although the temperature dependence of the heat capacity of $K_2S_4O_6$(aq) is very similar to that of a similar electrolyte Na_2SO_4(aq)[17] (Figure 1), the quantitative difference is striking. The contribution from the internal degrees of freedom can be estimated by noting the difference in C_{p_2} between $K_2S_4O_6$(c) and K_2SO_4(c),[18] which is 23.4 cal mol^{-1} °K^{-1} at 25°. The difference in $\bar{C}_{p_2}°$ between $K_2S_4O_6$(aq) and K_2SO_4(aq) at 25° is 52.1 cal mol^{-1} °K^{-1}, allowing for the 5.9 cal mol^{-1} °K^{-1} difference between $\bar{C}_{p_2}°$ for Na^+(aq) and K^+(aq).[15] Consequently the heat capacity of $S_4O_6{}^{2-}$-(aq) is approximately 29 cal mol^{-1} °K^{-1} more positive than that of $SO_4{}^{2-}$(aq) as far as effects on the solvent are concerned. This value may mean that the charge density of the $S_4O_6{}^{2-}$ ion is so low that it cannot effectively build any substantial primary hydration shell. Alternatively, it might be concluded that the ion breaks up some of the water structure at 25° in the

(15) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand. (U. S.), Tech. Note*, **No. 270-3** (1968).
(16) T. Hu and L. G. Hepler, *J. Chem. Eng. Data*, **7**, 59 (1962).
(17) W. L. Gardner, E. C. Jekel, and J. W. Cobble, *J. Phys. Chem.*, **73**, 2017 (1969).
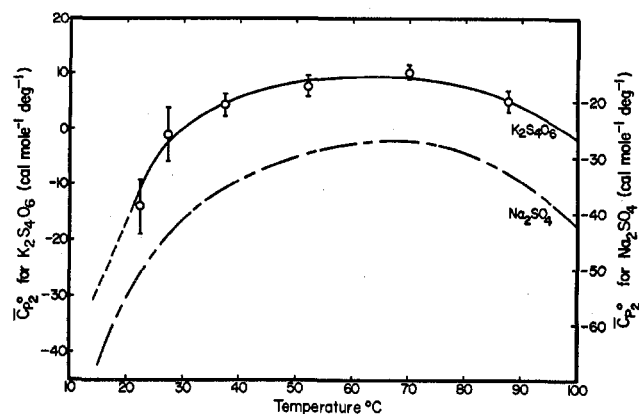(18) K. K. Kelley, *U. S. Bur. Mines, Bull.*, **No. 584** (1960).

Figure 1.—The standard partial molal heat capacities of aqueous $K_2S_4O_6$ (left scale) and Na_2SO_4 (right scale). The sulfate data are from ref 17.

neighborhood of the ion. This latter argument is weakened by the observation that simple low charge density ions such as Cs^+ and I^- have large negative heat capacities.[17]

The Thermodynamic Functions for HSO₃⁻(aq).— Since the bisulfite ion is involved in various equilibria and calculations concerning $S_2O_3{}^{2-}$(aq) and $S_4O_6{}^{2-}$(aq), it is important to have accurate data on $HSO_3{}^-$(aq). The thermodynamic functions for this species can be obtained from the solubility of SO_2(g) and the ionization constant of H_2SO_3(aq).

$$H_2O + SO_2(g) = H_2SO_3(aq) \qquad (2)$$

$$H_2SO_3(aq) = H^+(aq) + HSO_3{}^-(aq) \qquad (3)$$
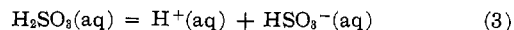
From an analysis of the extensive solubility data on SO_2(g),[19] the Bureau of Standards has adopted[15] -128.56 and 145.51 kcal mol^{-1} for the standard free energy and enthalpy of formation, respectively, of H_2SO_3(aq). A further analysis of the same data indicates that ΔC_p for the solubility equilibria (eq 2) is 20 cal mol^{-1} °K^{-1}, from which $\bar{C}_{p_2}°$ for H_2SO_3(aq) is calculated to be 47 cal mol^{-1} °K^{-1} and constant between 0 and 50°.

Reliable values for the free energy and enthalpy of dissociation of H_2SO_3(aq) can be obtained from third-law calculations on the dissociation constant measurements[20] between 0 and 150°, using estimated values for the heat capacities of H^+(aq) and $HSO_3{}^-$(aq).[21] Assuming the heat capacity of H_2SO_3(aq) to be the same as before, $\Delta C_p°$ of ionization (eq 3) is estimated to be -40 cal mol^{-1} °K^{-1} and constant between 0 and 150°. The free energy of dissociation at any temperature, T_2, is given to a good approximation by the relationship[22]

$$\Delta F°_{T_2} = \Delta F°_{25} - \Delta S°_{25}(t_2 - 25) + A_{(t)}\Delta C_p]_{25}{}^{t_2} \qquad (4)$$

where $A_{(t)} = (t_2 - 25) - T_2 \ln (T_2/298)$. Consequently a plot of $\Delta F°_{T_2} - a(t)\Delta C_p]_{25}{}^{t_2}$ vs. T must be linear with a slope equal to $\Delta S°_{25}$. Such an analysis of the H_2SO_3(aq) dissociation equilibrium gives $\Delta S_3° = -26.9$ cal mol^{-1} °K^{-1}. Using the Bureau of Standards values for the standard free energies, $\Delta F_3°$ for

(19) As summarized by L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17**, 229 (1964).
(20) L. G. Sillen and A. E. Martell, ref 19, quoted references 54I, 51K, 38B/55R.
(21) C. M. Criss and J. W. Cobble, *J. Amer. Chem. Soc.*, **86**, 5390 (1964).
(22) J. W. Cobble, *ibid.*, **86**, 5394 (1964).

the dissociation process is 2410 cal mol^{-1}, from which the standard entropy and enthalpy of HSO$_3$$^-$(aq) at 25° can be calculated as 28.6 cal mol^{-1} °K^{-1} and -151.12 kcal mol^{-1}, respectively. It is believed that the entropy and enthalpy for HSO$_3$$^-$(aq) from this third-law analysis are more accurate than those recently adopted.[15]

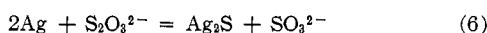**The Thermodynamic Functions for SO$_3$$^{2-}$(aq).**—While the standard free energy of SO$_3$$^{2-}$(aq) can be fixed accurately from the second dissociation constant for H$_2$SO$_3$(aq), the presently accepted[15] enthalpy for the dissociation is based on older data.[23,24] Therefore, the more recent calorimetric value[25] for the heat of dissociation of HSO$_3$$^-$(aq) of -1.25 kcal mol^{-1} will be adopted. Using the Bureau of Standards[15] free energies and the enthalpy and entropy of HSO$_3$$^-$(aq) given above, the standard enthalpy and free energy of formation and the entropy of SO$_3$$^{2-}$(aq) become -152.4 kcal mol^{-1}, -116.3 kcal mol^{-1}, and -8.3 cal mol^{-1} °K^{-1}, respectively.

The Thermodynamic Functions for S$_2$O$_3$$^{2-}$(aq).—There are three separate sources for recalculation of the thermodynamic functions for S$_2$O$_3$$^{2-}$(aq). The first of these are calorimetric studies on the heat of oxidation of S$_2$O$_3$$^{2-}$(aq) by bromine

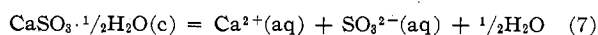$$5H_2O + S_2O_3{}^{2-} + 4Br_2 = 2SO_4{}^{2-} = 10H^+ + 8Br^- \quad (5)$$

for which $\Delta H_5 = -167.1$ kcal mol^{-1}.[26] Using the latest auxiliary values[15] for the other species in eq 5, the enthalpy of formation of S$_2$O$_3$$^{2-}$(aq) becomes -158.3 kcal mol^{-1}.

A second source of data on thiosulfate is the studies on the solubility of Ag$_2$S in sulfite solutions[23] between 25 and 195°.

$$2Ag + S_2O_3{}^{2-} = Ag_2S + SO_3{}^{2-} \quad (6)$$

K_6° was measured at 25.0, 122.5, and 195.0° and found to be 73.1, 16.3, and 8.16, respectively. At the time of the measurements, there was no reliable method to estimate heat capacity data for the aqueous species, and the authors were unable to analyze their data properly. From methods given elsewhere for estimating the heat capacities for S$_2$O$_3$$^{2-}$ and SO$_3$$^{2-}$ on these temperature ranges, and taking values for the heat capacities of the solids from Kelley,[18] $\Delta C_p]_{25}^{t_2}$ for eq 6 is estimated to be constant at -15 cal deg^{-1} mol^{-1} between 25 and 200°. A third-law analysis indicates ΔS_6° for reaction 6 to be 0 $\pm$ 1 cal mol^{-1} °K^{-1} and ΔF_6° and ΔH_6° equal to 2500 $\pm$ 600 cal mol^{-1}. Using the enthalpy of formation of Ag$_2$S(c) as -7.79 kcal mol^{-1} [27] and the revised standard enthalpy of formation given above for SO$_3$$^{2-}$(aq) of -152.4 kcal mol^{-1}, the standard enthalpy of formation of S$_2$O$_3$$^{2-}$(aq) becomes -157.7 kcal mol^{-1} at 25°. From a similar calculation the entropy is found to be 5.7 cal mol^{-1} °K^{-1}.

The third source of data on thiosulfate is the studies by Bichowsky,[28] who measured the low-temperature solubility of hydrated calcium sulfite.

$$CaSO_3 \cdot {}^1\!/_2H_2O(c) = Ca^{2+}(aq) + SO_3{}^{2-}(aq) + {}^1\!/_2H_2O \quad (7)$$

Bichowsky believed the equilibrium solid phase to be the dihydrate, but more recent work[29] has indicated it to be the hemihydrate, which form will be assumed in these calculations. The solubility data give ΔF_7° as 9870 $\pm$ 300 cal mol^{-1} at 25°, assuming $\gamma_\pm$ for saturated (2.4 $\times$ 10^{-4} m) CaSO$_3$(aq) to be 0.97 by analogy to other 2:2 electrolytes.[30] Sillen, et al.,[31] estimate ΔF_7° = 8900 cal mol^{-1} for the same solubility. The average, 9390 $\pm$ 500 cal mol^{-1}, will be adopted.

Bichowsky also measured the high temperature (80–141°) aqueous equilibrium of calcium sulfite hemihydrate in the presence of sulfur.

$$CaSO_3 \cdot {}^1\!/_2H_2O(c) + S(c) =$$
$$Ca^{2+}(aq) + S_2O_3{}^{2-}(aq) + {}^1\!/_2H_2O \quad (8)$$

A third-law analysis[18] of these data was made, estimating the ionic heat capacities as before.[21] Using heat capacity data for CaSO$_4$·^{1}/$_2$H$_2$O(c)[18] in lieu of experimental data for CaSO$_3$·^{1}/$_2$H$_2$O(c)[32] and the heat capacity of rhombic sulfur,[18,33] ΔF_8° and ΔS_8° for reaction 8 were found to be 1450 $\pm$ 200 cal mol^{-1} and -32 $\pm$ 2.0 cal mol^{-1} °K^{-1}, respectively, at 25° from which the standard enthalpy of reaction 8 is calculated as ΔH_8° = -8090 $\pm$ 300 cal mol^{-1}.

Combining eq 7 and 8

$$SO_3{}^{2-}(aq) + S = S_2O_3{}^{2-}(aq) \quad (9)$$

the standard free energy for the conversion of sulfite to thiosulfate becomes ΔF_9° = -7940 $\pm$ 700 cal mol^{-1} at 25°. ΔS_9° for this reaction can be calculated to be 9 cal mol^{-1} °K^{-1} from which it follows that ΔH_9° for the reaction of sulfur with sulfite to give thiosulfate becomes -5260 $\pm$ 1000 cal mol^{-1}. Since the enthalpy of formation of SO$_3$$^{2-}$(aq) is -152.4 kcal mol^{-1}, the standard enthalpy of formation of S$_2$O$_3$$^{2-}$(aq) becomes -157.7 kcal mol^{-1} at 25°.

Bichowsky also obtained thermal data related to eq 9 from heats of precipitation of sulfur from acid sulfite solutions, but we have not been able to reconcile these results with those from other sources of data. In these calculations the high-temperature activity coefficients for CaS$_2$O$_3$(aq) were assumed to be approximated by corresponding data on CaSO$_4$(aq) determined over the same temperature range by Marshall, et al.[34,35]

It is also necessary to obtain a value for the standard entropy of S$_2$O$_3$$^{2-}$(aq) at this point in the calculations. The entropy of CaSO$_3$·^{1}/$_2$H$_2$O(c) will be estimated at 29.3 cal mol^{-1} °K^{-1} at 25° from the known value of 31.2 cal mol^{-1} °K^{-1} for CaSO$_4$·^{1}/$_2$H$_2$O(c). From ΔS_8° = 9 for eq 8, the entropy of S$_2$O$_3$$^{2-}$(aq) becomes 10 cal mol^{-1} °K^{-1}. Alternatively, from the third-law value of ΔS_6° = 0 for eq 6, and the adopted value for the entropy of SO$_3$$^{2-}$(aq) of -8.3 cal mol^{-1} °K^{-1} given above, the entropy of S$_2$O$_3$$^{2-}$(aq) becomes 6 cal mol^{-1} °K^{-1}.

(23) J. Lindner, *Monatsh. Chem.*, **33**, 613 (1912).

(24) W. A. Roth and H. Zeumer, *Z. Elektrochem.*, **38**, 164 (1932).

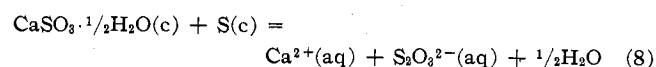(25) P. G. Zambonin and I. Jordan, *Anal. Chem.*, **41**, 427 (1969).

(26) H. C. Mehl, Z. Z. Hugus, and W. M. Latimer, *J. Amer. Chem. Soc.*, **78**, 1822 (1956).

(27) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand. (U. S.), Tech. Note*, **No. 270-4** (1969).

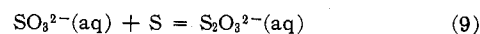(28) F. R. Bichowsky, *J. Amer. Chem. Soc.*, **45**, 2225 (1923).

(29) F. W. Matthews and A. O. McIntosh, *Can. J. Res., Sect. B*, **26**, 747 (1948).

(30) W. M. Latimer, "Oxidation-Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952.

(31) T. Rengemo, U. Brume, and L. G. Sillen, *Acta Chem. Scand.*, **12**, 873 (1958).

(32) Although Bichowsky's measured value[28] for C_p of calcium sulfite "dihydrate" is not unreasonable, the evidence still seems to favor the hemihydrate as the stable phase.[22]

(33) In reaction 8 studied by Bichowsky, the equilibrium form of sulfur varied with temperature. However, within the experimental errors involved, the known free energies of transition are small enough to ignore.

(34) W. L. Marshall and Ruth Slusher, *J. Phys. Chem.*, **70**, 4015 (1966).

(35) W. L. Marshall and E. V. Jones, *ibid.*, **70**, 4028 (1966).

The average value, 8 ± 2 cal mol^{-1} °K^{-1}, will be adopted at 25°. This new value is consistent with the known entropy of the smaller sulfate ion, 4.8 cal mol^{-1} °K^{-1}.

The average of the three separate values for the standard enthalpy of formation of thiosulfate is -157.7 ± 0.2 kcal mol^{-1}. It is believed that this value is superior to the presently adopted[15] one of -155.9 kcal mol^{-1}. The calculated standard free energy of formation for $S_2O_3^{2-}$(aq) is -130.1 ± 1.8 kcal mol^{-1}.

Thermodynamic Functions for $S_4O_6^{2-}$(aq).—The standard enthalpy of formation of $S_4O_6^{2-}$(aq) is based on the calorimetric studies by Zimmermann and Latimer[36] on the heat of oxidation of $S_2O_3^{2-}$ by I_3^-, which was observed to be -8580 ± 250 cal mol^{-1}. Using a new[37] value for the enthalpy of formation of I$^-$(aq), $-13,550$ cal mol^{-1}, and the most recent

value[42] for the heat of reaction of I$^-$(aq) with I$_2$ to give I$_3^-$(aq), 1.074 ± 0.012 kcal mol^{-1}, the standard enthalpy of formation of $S_4O_6^{2-}$ becomes -298.2 ± 1.2 kcal mol^{-1}. From the previously determined entropy given earlier in this communication of 61.5 ± 0.4 cal mol^{-1} deg^{-1}, the standard free energy of formation of $S_4O_6^{2-}$ becomes -252.4 ± 1.2 kcal mol^{-1}.

Potential of the $S_4O_6^{2-}$–$S_2O_3^{2-}$ Electrode.—The potential for the electrode reaction

$$S_4O_6^{2-} + 2e^- = 2S_2O_3^{2-} \quad E°_{25°} = 0.169 \pm 0.010$$
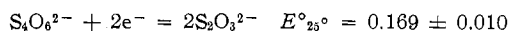
can be calculated from the free energies determined above for $S_4O_6^{2-}$(aq) and $S_2O_3^{2-}$(aq). This potential differs somewhat from the one adopted by Latimer[30] of 0.08 V from less complete and less accurate data.

V. Summary of Data

The new thermodynamic data obtained in this research are summarized in Table VI.

TABLE VI
SUMMARY OF THERMODYNAMIC FUNCTIONS[a]

Species	$\Delta H_f°$ [b]	$\Delta F_f°$ [b]	$S°$ [c]
H_2SO_3(aq)	-145.51	-128.56	55.5
HSO_3^-(aq)	-151.12	-126.15	28.6
SO_3^{2-}(aq)	-152.4	-116.3	-8.3
$S_2O_3^{2-}$(aq)	-157.7	-130.1	8
$S_4O_6^{2-}$(aq)	-298.2	-252.4	61.5
$CaSO_3 \cdot 1/2H_2O$(c)	-313.0	-286.2	(31)
$K_2S_4O_6$(c)	-429.36	-389.31	74.01
I$^-$(aq)	-13.55	-12.330	25.4

[a] Italicized and auxiliary thermodynamic functions are from ref 15. [b] In kcal mol^{-1}. [c] In kcal mol^{-1} °K^{-1}.

(36) H. W. Zimmermann and W. M. Latimer, *J. Amer. Chem. Soc.*, **61**, 1554 (1939).

(37) Unfortunately there are a variety of values for the standard enthalpy of formation of I$^-$(aq). The recently adopted value by the Bureau of Standards[15] is $-13,190$ cal mol^{-1}. Howard and Skinner[38] have obtained data for HI · 50H$_2$O which, when corrected to infinite dilution, give $-13,790$ cal mol^{-1}. Actually the thermodynamic functions for I$^-$(aq) can probably best be fixed from the extensive cell data. The standard free energy of formation of I$^-$(aq) is accurately known to be $-12,330$[15] cal mol^{-1} from cell data on the iodine–iodide electrode. The standard entropy of I$^-$(aq) can be obtained from a third law analysis[22] of the silver–silver iodide electrode in HI solutions. Measurements on this electrode[39,40] have extended over 50°, and can be combined with heat capacities of the pure substances[15,18] and the estimated heat capacities for HI(aq)[21] for a third law analysis.[22] $\Delta S°$ for the silver–silver iodide cell reaction was found to be 7.6 ± 0.2 cal mol^{-1} deg^{-1}, from which the standard entropy of I$^-$(aq) becomes 25.4 ± 0.2 cal mol^{-1} deg^{-1} at 25°, using available auxiliary data.[15] The free energy and entropy combine to give standard enthalpy of formation of $-13,550$ cal mol^{-1} for I$^-$(aq), which value will be adopted. This value is near the mean of the other proposed values and is essentially the same as that tentatively adopted by a recent international committee,[41] -13.60 ± 0.20 kcal mol^{-1}.

(38) P. B. Howard and H. A. Skinner, *J. Chem. Soc. A*, 1536 (1966).

(39) B. B. Owen, *J. Amer. Chem. Soc.*, **57**, 1526 (1935), corrected to absolute volts.[40]

(40) H. B. Hetzer, R. A. Robinson, and R. G. Bates, *J. Phys. Chem.*, **68**, 1929 (1964).

(41) CODATA Task Group, *J. Chem. Thermodyn.*, **3**, 1 (1971).

(42) E. E. Mercer and D. T. Farrar, *Can. J. Chem.*, **46**, 2679 (1968).

Polyatomic Cations of Sulfur. III. Solutions of Sulfur in Oleum

BY R. J. GILLESPIE* AND P. K. UMMAT

It is shown by absorption spectra, esr spectra, and cryoscopic measurements that solutions of sulfur in oleum are, with time and with increasing SO_3 concentration, successively oxidized to S_{16}^{2+}, S_8^{2+}, S_4^{2+}, and SO_2. Esr measurements show that S_{16}^{2+} is in equilibrium with the radical ion S_8^+ and that S_8^{2+} is in equilibrium with the radical ion S_4^+.

Introduction

Colored solutions of sulfur in oleum have been known for a considerable time, the first report of such solutions apparently being by Bucholz in 1804.[1] Brown, green, and blue solutions have been described. Weber[2] and later Masson and Argument[3] attributed the blue color

to the supposed compound S_2O_3 which had been found to have a greenish blue color and to dissolve in oleum to give a blue solution. Auerbach[4] made cryoscopic measurements on solutions of sulfur in oleum and concluded that it was dissolved as S_2 molecules but later Brayford and Wyatt[5] came to the tentative conclusion from their cryoscopic measurements that sulfur is present in 45%

(1) C. F. Bucholz, *Gehlen's Neues J. Chem.*, **3**, 7 (1804); "Gmelin's Handuch der anorganischen Chemie," Vol. 9, Part B1, 1953, p 179.

(2) R. Weber, *J. Prakt. Chem.*, **133**, 218 (1882); *Ann Phys. Chem.*, [2] **156**, 531 (1875).

(3) I. Masson and C. Argument, *J. Chem. Soc.*, 1705 (1938).

(4) R. Auerbach, *Z. Phys. Chem. (Leipzig)*, **121**, 337 (1926).

(5) J. R. Brayford and P. A. H. Wyatt, *Trans. Faraday Soc.*, **52**, 642 (1956).